# Thermodynamics and Statistical Mechanics
# Example Problems and Solutions

Daniel Arovas
Department of Physics
University of California, San Diego

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## 0.1 Probability

**(1.1)** The *information entropy* of a distribution $\{p_n\}$ is defined as $S = -\sum_n p_n \log_2 p_n$, where $n$ ranges over all possible configurations of a given physical system and $p_n$ is the probability of the state $|n\rangle$. If there are $\Omega$ possible states and each state is equally likely, then $S = \log_2 \Omega$, which is the usual dimensionless entropy in units of $\ln 2$.

Consider a normal deck of 52 distinct playing cards. A new deck always is prepared in the same order (A♠ 2♠ ⋯ K♣).

(a) What is the information entropy of the distribution of new decks?

(b) What is the information entropy of a distribution of completely randomized decks?

Now consider what it means to shuffle the cards. In an ideal *riffle shuffle*, the deck is split and divided into two equal halves of 26 cards each. One then chooses at random whether to take a card from either half, until one runs through all the cards and a new order is established (see figure).



(c) What is the increase in information entropy for a distribution of new decks that each have been shuffled once?

Figure 1: The riffle shuffle.

(d) Assuming each subsequent shuffle results in the same entropy increase (*i.e.* neglecting redundancies), how many shuffles are necessary in order to completely randomize a deck?

<span style="color:red">Solution :</span>

<span style="color:blue">(a) Since each new deck arrives in the same order, we have $p_1 = 1$ while $p_{2,\ldots,52!} = 0$, so $S = 0$.</span>

<span style="color:blue">(b) For completely randomized decks, $p_n = 1/\Omega$ with $n \in \{1, \ldots, \Omega\}$ and $\Omega = 52!$, the total number of possible configurations. Thus, $S_{\text{random}} = \log_2 52! = 225.581$.</span>

<span style="color:blue">(c) After one riffle shuffle, there are $\Omega = \binom{52}{26}$ possible configurations. If all such configurations were equally likely, we would have $(\Delta S)_{\text{riffle}} = \log_2 \binom{52}{26} = 48.817$. However, they are not all equally likely. For example, the probability that we drop the entire left-half deck and then the entire right half-deck is $2^{-26}$. After the last card from the left half-deck is dropped, we have no more choices to make. On the other hand, the probability for the sequence LRLR $\cdots$ is $2^{-51}$, because it is only after the $51^{\text{st}}$ card is dropped that we have no more choices. We can derive an exact expression for the entropy of the riffle shuffle in the following manner. Consider a deck of $N = 2K$ cards. The probability that we run out of choices after $K$ cards is the probability of the first $K$ cards dropped being all from one particular half-deck, which is $2 \cdot 2^{-K}$. Now let's ask what is the probability that we run out of choices after $(K+1)$</span>

| $K$ | $\Omega_K$ | $S_K$ | $\log_2\binom{2K}{K}$ |
|---|---|---|---|
| 2 | 6 | 2.500 | 2.585 |
| 12 | 2704156 | 20.132 | 20.367 |
| 26 | $4.96 \times 10^{14}$ | 46.274 | 48.817 |
| 100 | $9.05 \times 10^{58}$ | 188.730 | 195.851 |

Table 1: Riffle shuffle results.

cards are dropped. If all the remaining $(K-1)$ cards are from the right half-deck, this means that we must have one of the R cards among the first $K$ dropped. Note that this R card cannot be the $(K+1)^{\text{th}}$ card dropped, since then all of the first $K$ cards are L, which we have already considered. Thus, there are $\binom{K}{1} = K$ such configurations, each with a probability $2^{-K-1}$. Next, suppose we run out of choices after $(K+2)$ cards are dropped. If the remaining $(K-2)$ cards are R, this means we must have 2 of the R cards among the first $(K+1)$ dropped, which means $\binom{K+1}{2}$ possibilities. Note that the $(K+2)^{\text{th}}$ card must be L, since if it were R this would mean that the last $(K-1)$ cards are R, which we have already considered. Continuing in this manner, we conclude

$$\Omega_K = 2\sum_{n=0}^{K}\binom{K+n-1}{n} = \binom{2K}{K}$$

and

$$S_K = -\sum_{a=1}^{\Omega_K} p_a \log_2 p_a = \sum_{n=0}^{K-1}\binom{K+n-1}{n} \cdot 2^{-(K+n)} \cdot (K+n) \quad.$$

The results are tabulated below in Table 1. For a deck of 52 cards, the actual entropy per riffle shuffle is $S_{26} = 46.274$.

(d) Ignoring redundancies, we require $k = S_{\text{random}}/(\Delta S)_{\text{riffle}} = 4.62$ shuffles if we assume all riffle outcomes are equally likely, and $4.88$ if we use the exact result for the riffle entropy. Since there are no fractional shuffles, we round up to $k = 5$ in both cases. In fact, computer experiments show that the answer is $k = 9$. The reason we are so far off is that we have ignored redundancies, *i.e.* we have assumed that all the states produced by two consecutive riffle shuffles are distinct. They are not! For decks with asymptotically large numbers of cards $N \gg 1$, the number of riffle shuffles required is $k \simeq \frac{3}{2}\log_2 N$. See D. Bayer and P. Diaconis, *Annals of Applied Probability* **2**, 294 (1992).

**(1.2)** A six-sided die is loaded so that the probability to throw a three is twice that of throwing a two, and the probability of throwing a four is twice that of throwing a five.

  (a) Find the distribution $\{p_n\}$ consistent with maximum entropy, given these constraints.

  (b) Assuming the maximum entropy distribution, given two such identical dice, what is the probability to roll a total of seven if both are thrown simultaneously?

Solution :

(a) We have the following constraints:

$$X^0(\boldsymbol{p}) = p_1 + p_2 + p_3 + p_4 + p_5 + p_6 - 1 = 0$$
$$X^1(\boldsymbol{p}) = p_3 - 2p_2 = 0$$
$$X^2(\boldsymbol{p}) = p_4 - 2p_5 = 0 \quad .$$

We define

$$S^*(\boldsymbol{p}, \boldsymbol{\lambda}) \equiv -\sum_n p_n \ln p_n - \sum_{a=0}^{2} \lambda_a \, X^{(a)}(\boldsymbol{p}) \quad ,$$

and freely extremize over the probabilities $\{p_1, \ldots, p_6\}$ and the undetermined Lagrange multipliers $\{\lambda_0, \lambda_1, \lambda_2\}$. We obtain

$$\frac{\partial S^*}{\partial p_1} = -1 - \ln p_1 - \lambda_0 \qquad\qquad \frac{\partial S^*}{\partial p_4} = -1 - \ln p_4 - \lambda_0 - \lambda_2$$

$$\frac{\partial S^*}{\partial p_2} = -1 - \ln p_2 - \lambda_0 + 2\lambda_1 \qquad\qquad \frac{\partial S^*}{\partial p_5} = -1 - \ln p_5 - \lambda_0 + 2\lambda_2$$

$$\frac{\partial S^*}{\partial p_3} = -1 - \ln p_3 - \lambda_0 - \lambda_1 \qquad\qquad \frac{\partial S^*}{\partial p_6} = -1 - \ln p_6 - \lambda_0 \quad .$$

Extremizing with respect to the undetermined multipliers generates the three constraint equations. We therefore have

$$p_1 = e^{-\lambda_0 - 1} \qquad\qquad p_4 = e^{-\lambda_0 - 1} \, e^{-\lambda_2}$$
$$p_2 = e^{-\lambda_0 - 1} \, e^{2\lambda_1} \qquad\qquad p_5 = e^{-\lambda_0 - 1} \, e^{2\lambda_2}$$
$$p_3 = e^{-\lambda_0 - 1} \, e^{-\lambda_1} \qquad\qquad p_6 = e^{-\lambda_0 - 1} \quad .$$

We solve for $\{\lambda_0, \lambda_1, \lambda_2\}$ by imposing the three constraints. Let $x \equiv p_1 = p_6 = e^{-\lambda_0 - 1}$. Then $p_2 = x \, e^{2\lambda_1}$, $p_3 = x \, e^{-\lambda_1}$, $p_4 = x \, e^{-\lambda_2}$, and $p_5 = x \, e^{2\lambda_2}$. We then have

$$p_3 = 2p_2 \quad \Rightarrow \quad e^{-3\lambda_1} = 2$$
$$p_4 = 2p_5 \quad \Rightarrow \quad e^{-3\lambda_2} = 2 \quad .$$

We may now solve for $x$:

$$\sum_{n=1}^{6} p_n = \left(2 + 2^{1/3} + 2^{4/3}\right) x = 1 \quad \Rightarrow \quad x = \frac{1}{2 + 3 \cdot 2^{1/3}} \quad .$$

We now have all the probabilities:

$$p_1 = x = 0.1730 \qquad\qquad\qquad p_4 = 2^{1/3} x = 0.2180$$
$$p_2 = 2^{-2/3} x = 0.1090 \qquad\qquad p_5 = 2^{-2/3} x = 0.1090$$
$$p_3 = 2^{1/3} x = 0.2180 \qquad\qquad p_6 = x = 0.1730 \quad .$$

(b) The probability to roll a seven with two of these dice is

$$P(7) = 2\, p_1\, p_6 + 2\, p_2\, p_5 + 2\, p_3\, p_4$$
$$= 2\left(1 + 2^{-4/3} + 2^{2/3}\right) x^2 = 0.1787 \quad .$$

**(1.3)** Consider the contraption in Fig. 2. At each of $k$ steps, a particle can fork to either the left ($n_j = 1$) or to the right ($n_j = 0$). The final location is then a $k$-digit binary number.

(a) Assume the probability for moving to the left is $p$ and the probability for moving to the right is $q \equiv 1 - p$ at each fork, independent of what happens at any of the other forks. *I.e.* all the forks are uncorrelated. Compute $\langle X_k \rangle$. *Hint: $X_k$ can be represented as a $k$-digit binary number, i.e.* $X_k = n_{k-1} n_{k-2} \cdots n_1 n_0 = \sum_{j=0}^{k-1} 2^j n_j$.

(b) Compute $\langle X_k^2 \rangle$ and the variance $\langle X_k^2 \rangle - \langle X_k \rangle^2$.

(c) $X_k$ may be written as the sum of $k$ random numbers. Does $X_k$ satisfy the central limit theorem as $k \to \infty$? Why or why not?
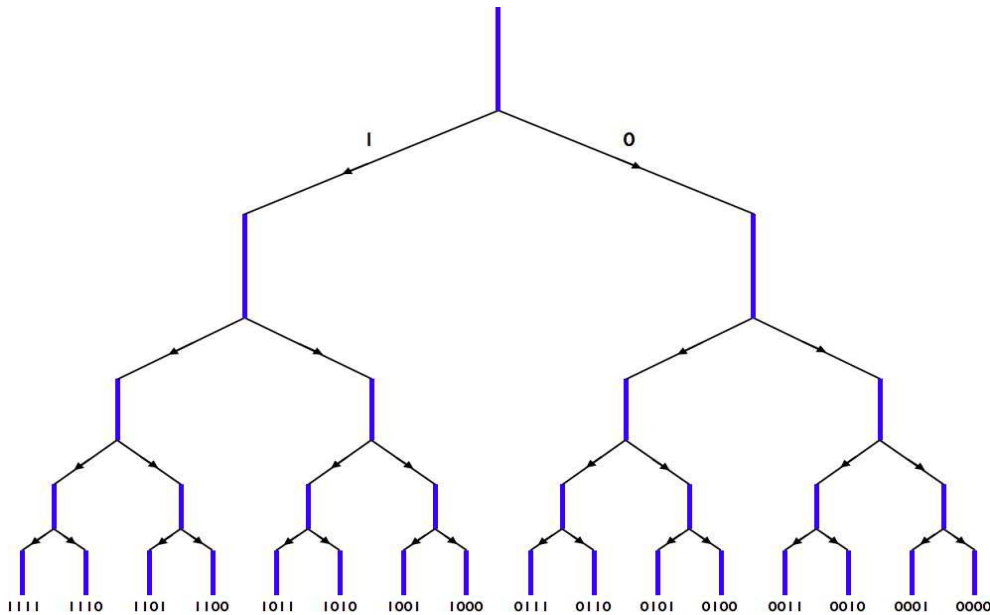


Figure 2: Generator for a $k$-digit random binary number ($k = 4$ shown).

Solution :

(a) The position after $k$ forks can be written as a $k$-digit binary number: $n_{k-1} n_{k-2} \cdots n_1 n_0$. Thus,

$$X_k = \sum_{j=0}^{k-1} 2^j n_j \quad ,$$

where $n_j = 0$ or $1$ according to $P_n = p\, \delta_{n,1} + q\, \delta_{n,0}$. Now it is clear that $\langle n_j \rangle = p$, and therefore

$$\langle X_k \rangle = p \sum_{j=0}^{k-1} 2^j = p \cdot \left(2^k - 1\right) \quad .$$

(b) The variance in $X_k$ is

$$\text{Var}(X_k) = \langle X_k^2 \rangle - \langle X_k \rangle^2 = \sum_{j=0}^{k-1}\sum_{j'=0}^{k-1} 2^{j+j'}\Big(\langle n_j n_{j'}\rangle - \langle n_j\rangle\langle n_{j'}\rangle\Big)$$

$$= p(1-p)\sum_{j=0}^{k-1} 4^j = p(1-p)\cdot\tfrac{1}{3}\big(4^k - 1\big) \quad,$$

since $\langle n_j n_{j'}\rangle - \langle n_j\rangle\langle n_{j'}\rangle = p(1-p)\,\delta_{jj'}$.

(c) Clearly the distribution of $X_k$ does not obey the CLT, since $\langle X_k\rangle$ scales exponentially with $k$. Also note

$$\lim_{k\to\infty} \frac{\sqrt{\text{Var}(X_k)}}{\langle X_k\rangle} = \sqrt{\frac{1-p}{3p}} \quad,$$

which is a constant. For distributions obeying the CLT, the ratio of the rms fluctuations to the mean scales as the inverse square root of the number of trials. The reason that this distribution does not obey the CLT is that the variance of the individual terms is increasing with $j$.

**(1.4)** The binomial distribution,

$$B_N(n, p) = \binom{N}{n} p^n (1 - p)^{N-n} \quad ,$$

tells us the probability for $n$ successes in $N$ trials if the individual trial success probability is $p$. The average number of successes is $\nu = \sum_{n=0}^{N} n \, B_N(n, p) = Np$. Consider the limit $N \to \infty$ with $\nu$ finite.

(a) Show that the probability of $n$ successes becomes a function of $n$ and $\nu$ alone. That is, evaluate

$$P_\nu(n) = \lim_{N \to \infty} B_N(n, \nu/N) \quad .$$

This is the *Poisson distribution*.

(b) Show that the moments of the Poisson distribution are given by

$$\langle n^k \rangle = e^{-\nu} \left( \nu \frac{\partial}{\partial \nu} \right)^k e^\nu \quad .$$

(c) Evaluate the mean and variance of the Poisson distribution.

The Poisson distribution is also known as the *law of rare events* since $p = \nu/N \to 0$ in the $N \to \infty$ limit. See http://en.wikipedia.org/wiki/Poisson_distribution#Occurrence for some amusing applications of the Poisson distribution.

Solution :

(a) We have

$$P_\nu(n) = \lim_{N \to \infty} \frac{N!}{n! \, (N - n)!} \left( \frac{\nu}{N} \right)^n \left( 1 - \frac{\nu}{N} \right)^{N-n} \quad .$$

Note that

$$(N - n)! \simeq (N - n)^{N-n} \, e^{n-N} = N^{N-n} \left( 1 - \frac{n}{N} \right)^N e^{n-N} \to N^{N-n} \, e^N \quad ,$$

where we have used the result $\lim_{N \to \infty} \left( 1 + \frac{x}{N} \right)^N = e^x$. Thus, we find

$$P_\nu(n) = \frac{1}{n!} \nu^n \, e^{-\nu} \quad ,$$

the Poisson distribution. Note that $\sum_{n=0}^{\infty} P_n(\nu) = 1$ for any $\nu$.

(b) We have

$$\langle n^k \rangle = \sum_{n=0}^{\infty} P_\nu(n) \, n^k = \sum_{n=0}^{\infty} \frac{1}{n!} n^k \nu^n \, e^{-\nu}$$

$$= e^{-\nu} \left( \nu \frac{d}{d\nu} \right)^k \sum_{n=0}^{\infty} \frac{\nu^n}{n!} = e^{-\nu} \left( \nu \frac{\partial}{\partial \nu} \right)^k e^\nu \quad .$$

(c) Using the result from (b), we have $\langle n \rangle = \nu$ and $\langle n^2 \rangle = \nu + \nu^2$, hence $\text{Var}(n) = \nu$.

**(1.5)** You should be familiar with Stirling's approximation,

$$\ln K! \sim K \ln K - K + \tfrac{1}{2}\ln(2\pi K) + \mathcal{O}(K^{-1}) \quad,$$

for large $K$. In this exercise, you will derive this expansion.

(a) Start by writing

$$K! = \int\limits_0^\infty dx \, x^K \, e^{-x} \quad,$$

and define $x \equiv K(t+1)$ so that $K! = K^{K+1} \, e^{-K} \, F(K)$, where

$$F(K) = \int\limits_{-1}^\infty dt \, e^{Kf(t)} \quad.$$

Find the function $f(t)$.

(b) Expand $f(t) = \sum_{n=0}^\infty f_n \, t^n$ in a Taylor series and find a general formula for the expansion coefficients $f_n$. In particular, show that $f_0 = f_1 = 0$ and that $f_2 = -\tfrac{1}{2}$.

(c) If one ignores all the terms but the lowest order (quadratic) in the expansion of $f(t)$, show that

$$\int\limits_{-1}^\infty dt \, e^{-Kt^2/2} = \sqrt{\frac{2\pi}{K}} - R(K) \quad,$$

and show that the remainder $R(K) > 0$ is bounded from above by a function which decreases faster than any polynomial in $1/K$.

(d) *For the brave only!* – Find the $\mathcal{O}(K^{-1})$ term in the expansion for $\ln K!$.

Solution :

(a) Setting $x = K(t+1)$, we have

$$K! = K^{K+1} \, e^{-K} \int\limits_{-1}^\infty dt \, (t+1)^K \, e^{-t} \quad,$$

hence $f(t) = \ln(t+1) - t$.

(b) The Taylor expansion of $f(t)$ is

$$f(t) = -\tfrac{1}{2}t^2 + \tfrac{1}{3}t^3 - \tfrac{1}{4}t^4 + \ldots \quad.$$

(c) Retaining only the leading term in the Taylor expansion of $f(t)$, we have

$$F(K) \simeq \int_{-1}^{\infty} dt \, e^{-Kt^2/2}$$

$$= \sqrt{\frac{2\pi}{K}} - \int_{1}^{\infty} dt \, e^{-Kt^2/2} \quad .$$

Writing $t \equiv s + 1$, the remainder is found to be

$$R(K) = e^{-K/2} \int_{0}^{\infty} ds \, e^{-Ks^2/2} \, e^{-Ks} < \sqrt{\frac{\pi}{2K}} \, e^{-K/2} \quad ,$$

which decreases exponentially with $K$, faster than any power.

(d) We have

$$F(K) = \int_{-1}^{\infty} dt \, e^{-\frac{1}{2}Kt^2} e^{\frac{1}{3}Kt^3 - \frac{1}{4}Kt^4 + \cdots}$$

$$= \int_{-1}^{\infty} dt \, e^{-\frac{1}{2}Kt^2} \left\{ 1 + \tfrac{1}{3}Kt^3 - \tfrac{1}{4}Kt^4 + \tfrac{1}{18}K^2 t^6 + \ldots \right\}$$

$$= \sqrt{\frac{2\pi}{K}} \cdot \left\{ 1 - \tfrac{3}{4}K^{-1} + \tfrac{5}{6}K^{-1} + \mathcal{O}(K^{-2}) \right\}$$

Thus,

$$\ln K! = K \ln K - K + \tfrac{1}{2} \ln K + \tfrac{1}{2} \ln(2\pi) + \tfrac{1}{12} K^{-1} + \mathcal{O}(K^{-2}) \quad .$$

**(1.6)** The probability density for a random variable $x$ is given by the Lorentzian,

$$P(x) = \frac{\gamma}{\pi} \cdot \frac{1}{x^2 + \gamma^2} \quad .$$

Consider the sum $X_N = \sum_{i=1}^{N} x_i$, where each $x_i$ is independently distributed according to $P(x_i)$. Find the probability $\Pi_N(Y)$ that $|X_N| < Y$, where $Y > 0$ is arbitrary.

Solution :

The distribution of a sum of identically distributed random variables, $X = \sum_{i=1}^{N} x_i$, is given by

$$P_N(X) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} \left[\hat{P}(k)\right]^N e^{ikX} \quad ,$$

where $\hat{P}(k)$ is the Fourier transform of the probability distribution $P(x_i)$ for each of the $x_i$. The Fourier transform of a Lorentzian is an exponential:

$$\int_{-\infty}^{\infty} dx\, P(x)\, e^{-ikx} = e^{-\gamma|k|} \quad .$$

Thus,

$$P_N(X) = \int_{-\infty}^{\infty} \frac{dk}{2\pi} e^{-N\gamma|k|} e^{ikX}$$

$$= \frac{N\gamma}{\pi} \cdot \frac{1}{X^2 + N^2\gamma^2} \quad .$$

The probability for $X$ to lie in the interval $X \in [-Y, Y]$, where $Y > 0$, is

$$\Pi_N(Y) = \int_{-Y}^{Y} dX\, P_N(X) = \frac{2}{\pi} \tan^{-1}\left(\frac{Y}{N\gamma}\right) \quad .$$

The integral is easily performed with the substitution $X = N\gamma \tan\theta$. Note that $\Pi_N(0) = 0$ and $\Pi_N(\infty) = 1$.

**(1.7)** Let $P(x) = (2\pi\sigma^2)^{-1/2} e^{-(x-\mu)^2/2\sigma^2}$. Compute the following integrals:

(a) $I = \int\limits_{-\infty}^{\infty} dx \, P(x) \, x^3$.

(b) $I = \int\limits_{-\infty}^{\infty} dx \, P(x) \, \cos(Qx)$.

(c) $I = \int\limits_{-\infty}^{\infty} dx \int\limits_{-\infty}^{\infty} dy \, P(x) \, P(y) \, e^{xy}$. You may set $\mu = 0$ to make this somewhat simpler. Under what conditions does this expression converge?

Solution :

(a) Write
$$x^3 = (x - \mu + \mu)^3 = (x - \mu)^3 + 3(x - \mu)^2 \mu + 3(x - \mu)\mu^2 + \mu^3 \quad,$$

so that
$$\langle x^3 \rangle = \frac{1}{\sqrt{2\pi\sigma^2}} \int\limits_{-\infty}^{\infty} dt \, e^{-t^2/2\sigma^2} \left\{ t^3 + 3t^2\mu + 3t\mu^2 + \mu^3 \right\} \quad.$$

Since $\exp(-t^2/2\sigma^2)$ is an even function of $t$, odd powers of $t$ integrate to zero. We have $\langle t^2 \rangle = \sigma^2$, so
$$\langle x^3 \rangle = \mu^3 + 3\mu\sigma^2 \quad.$$

A nice trick for evaluating $\langle t^{2k} \rangle$:
$$\langle t^{2k} \rangle = \frac{\int\limits_{-\infty}^{\infty} dt \, e^{-\lambda t^2} t^{2k}}{\int\limits_{-\infty}^{\infty} dt \, e^{-\lambda t^2}} = \frac{(-1)^k \frac{d^k}{d\lambda^k} \int\limits_{-\infty}^{\infty} dt \, e^{-\lambda t^2}}{\int\limits_{-\infty}^{\infty} dt \, e^{-\lambda t^2}} = \frac{(-1)^k}{\sqrt{\lambda}} \left. \frac{d^k \sqrt{\lambda}}{d\lambda^k} \right|_{\lambda=1/2\sigma^2}$$

$$= \left. \tfrac{1}{2} \cdot \tfrac{3}{2} \cdots \tfrac{(2k-1)}{2} \lambda^{-k} \right|_{\lambda=1/2\sigma^2} = \frac{(2k)!}{2^k \, k!} \sigma^{2k} \quad.$$

(b) We have
$$\langle \cos(Qx) \rangle = \mathsf{Re} \, \langle e^{iQx} \rangle = \mathsf{Re} \left[ \frac{e^{iQ\mu}}{\sqrt{2\pi\sigma^2}} \int\limits_{-\infty}^{\infty} dt \, e^{-t^2/2\sigma^2} \, e^{iQt} \right]$$

$$= \mathsf{Re} \left[ e^{iQ\mu} e^{-Q^2\sigma^2/2} \right] = \cos(Q\mu) \, e^{-Q^2\sigma^2/2} \quad.$$

Here we have used the result
$$\frac{1}{\sqrt{2\pi\sigma^2}} \int\limits_{-\infty}^{\infty} dt \, e^{-\alpha t^2 - \beta t} = \sqrt{\frac{\pi}{\alpha}} \, e^{\beta^2/4\alpha}$$

with $\alpha = 1/2\sigma^2$ and $\beta = -iQ$. Another way to do it is to use the general result derive above in part (a) for $\langle t^{2k} \rangle$ and do the sum:

$$
\langle \cos(Qx) \rangle = \mathsf{Re} \, \langle e^{iQx} \rangle = \mathsf{Re} \left[ \frac{e^{iQ\mu}}{\sqrt{2\pi\sigma^2}} \int\limits_{-\infty}^{\infty} dt \, e^{-t^2/2\sigma^2} \, e^{iQt} \right]
$$

$$
= \cos(Q\mu) \sum_{k=0}^{\infty} \frac{(-Q^2)^k}{(2k)!} \, \langle t^{2k} \rangle = \cos(Q\mu) \sum_{k=0}^{\infty} \frac{1}{k!} \left( -\tfrac{1}{2} Q^2 \sigma^2 \right)^k
$$

$$
= \cos(Q\mu) \, e^{-Q^2 \sigma^2/2} \quad .
$$

(c) We have

$$
I = \int\limits_{-\infty}^{\infty} dx \int\limits_{-\infty}^{\infty} dy \, P(x) \, P(y) \, e^{\kappa^2 xy} = \frac{e^{-\mu^2/2\sigma^2}}{2\pi\sigma^2} \int d^2x \, e^{-\frac{1}{2} A_{ij} x_i x_j} \, e^{b_i x_i} \quad ,
$$

where $\boldsymbol{x} = (x, y)$,

$$
A = \begin{pmatrix} \sigma^2 & -\kappa^2 \\ -\kappa^2 & \sigma^2 \end{pmatrix} \quad , \quad \boldsymbol{b} = \begin{pmatrix} \mu/\sigma^2 \\ \mu/\sigma^2 \end{pmatrix} \quad .
$$

Using the general formula for the Gaussian integral,

$$
\int d^n x \, e^{-\frac{1}{2} A_{ij} x_i x_j} \, e^{b_i x_i} = \frac{(2\pi)^{n/2}}{\sqrt{\det(A)}} \, \exp \left( \tfrac{1}{2} A_{ij}^{-1} b_i b_j \right) \quad ,
$$

we obtain

$$
I = \frac{1}{\sqrt{1 - \kappa^4 \sigma^4}} \, \exp \left( \frac{\mu^2 \kappa^2}{1 - \kappa^2 \sigma^2} \right) \quad .
$$

Convergence requires $\kappa^2 \sigma^2 < 1$.

**(1.8)** Consider a $D$-dimensional *random walk* on a hypercubic lattice. The position of a particle after $N$ steps is

$$\boldsymbol{R}_N = \sum_{j=1}^{N} \hat{\boldsymbol{n}}_j \quad,$$

where $\hat{\boldsymbol{n}}_j$ can take on one of $2D$ possible values: $\hat{\boldsymbol{n}}_j \in \{\pm\hat{\mathbf{e}}_1, \ldots, \pm\hat{\mathbf{e}}_D\}$, where $\hat{\mathbf{e}}_\mu$ is the unit vector along the positive $x_\mu$ axis. Each of these possible values occurs with probability $1/2D$, and each step is statistically independent from all other steps.

(a) Consider the *generating function* $S_N(\boldsymbol{k}) = \langle e^{i\boldsymbol{k}\cdot\boldsymbol{R}_N} \rangle$. Show that

$$\langle R_N^{\alpha_1} \cdots R_N^{\alpha_J} \rangle = \frac{1}{i}\frac{\partial}{\partial k_{\alpha_1}} \cdots \frac{1}{i}\frac{\partial}{\partial k_{\alpha_J}}\bigg|_{\boldsymbol{k}=0} S_N(\boldsymbol{k}) \quad.$$

For example, $\langle R_N^\alpha R_N^\beta \rangle = -\big(\partial^2 S_N(\boldsymbol{k})/\partial k_\alpha \partial k_\beta\big)_{\boldsymbol{k}=0}$.

(b) Evaluate $S_N(\boldsymbol{k})$ for the case $D = 3$ and compute the quantities $\langle X_N^4 \rangle$ and $\langle X_N^2 Y_N^2 \rangle$.

Solution :

(a) The result follows immediately from

$$\frac{1}{i}\frac{\partial}{\partial k_\alpha} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = R_\alpha \, e^{i\boldsymbol{k}\cdot\boldsymbol{R}}$$

$$\frac{1}{i}\frac{\partial}{\partial k_\alpha}\frac{1}{i}\frac{\partial}{\partial k_\beta} e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = R_\alpha \, R_\beta \, e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \quad,$$

*et cetera*. Keep differentiating with respect to the various components of $\boldsymbol{k}$.

(b) For $D = 3$, there are six possibilities for $\hat{\boldsymbol{n}}_j$ : $\pm\hat{x}$, $\pm\hat{y}$, and $\pm\hat{z}$. Each occurs with a probability $\frac{1}{6}$, independent of all the other $\hat{\boldsymbol{n}}_{j'}$ with $j' \neq j$. Thus,

$$S_N(\boldsymbol{k}) = \prod_{j=1}^{N} \langle e^{i\boldsymbol{k}\cdot\hat{\boldsymbol{n}}_j} \rangle = \left[\frac{1}{6}\Big(e^{ik_x} + e^{-ik_x} + e^{ik_y} + e^{-ik_y} + e^{ik_z} + e^{-ik_z}\Big)\right]^N$$

$$= \left(\frac{\cos k_x + \cos k_y + \cos k_z}{3}\right)^N \quad.$$

We have

$$\langle X_N^4 \rangle = \frac{\partial^4 S(\boldsymbol{k})}{\partial k_x^4}\bigg|_{\boldsymbol{k}=0} = \frac{\partial^4}{\partial k_x^4}\bigg|_{k_x=0} \big(1 - \tfrac{1}{6}k_x^2 + \tfrac{1}{72}k_x^4 + \ldots\big)^N$$

$$= \frac{\partial^4}{\partial k_x^4}\bigg|_{k_x=0} \left[1 + N\big(-\tfrac{1}{6}k_x^2 + \tfrac{1}{72}k_x^4 + \ldots\big) + \tfrac{1}{2}N(N-1)\big(-\tfrac{1}{6}k_x^2 + \tfrac{1}{72}k_x^4 + \ldots\big)^2 + \ldots\right]$$

$$= \frac{\partial^4}{\partial k_x^4}\bigg|_{k_x=0} \left[1 - \tfrac{1}{6}Nk_x^2 + \tfrac{1}{72}N^2 k_x^4 + \ldots\right] = \tfrac{1}{3}N^2 \quad.$$

Similarly, we have

$$
\begin{aligned}
\langle X_N^2 \, Y_N^2 \rangle &= \frac{\partial^4 S(\boldsymbol{k})}{\partial k_x^2 \, \partial k_y^2}\bigg|_{\boldsymbol{k}=0} = \frac{\partial^4}{\partial k_x^2 \, \partial k_y^2}\bigg|_{k_x=0} \left(1 - \tfrac{1}{6}\left(k_x^2 + k_y^2\right) + \tfrac{1}{72}\left(k_x^4 + k_y^4\right) + \dots\right)^N \\
&= \frac{\partial^4}{\partial k_x^2 \, \partial k_y^2}\bigg|_{k_x=k_y=0} \left[1 + N\left(-\tfrac{1}{6}\left(k_x^2 + k_y^2\right) + \tfrac{1}{72}\left(k_x^4 + k_y^4\right) + \dots\right) + \tfrac{1}{2}N(N-1)\left(-\tfrac{1}{6}\left(k_x^2 + k_y^2\right) + \dots\right)^2 + \dots\right] \\
&= \frac{\partial^4}{\partial k_x^2 \, \partial k_y^2}\bigg|_{k_x=k_y=0} \left[1 - \tfrac{1}{6}N(k_x^2 + k_y^2) + \tfrac{1}{72}N^2(k_x^4 + k + y^4) + \tfrac{1}{36}k_x^2 \, k_y^2 + \dots\right] = \tfrac{1}{9}N(N-1) \quad .
\end{aligned}
$$

**(1.9)** A rare disease is known to occur in $f = 0.02\%$ of the general population. Doctors have designed a test for the disease with $\nu = 99.90\%$ sensitivity and $\rho = 99.95\%$ specificity.

(a) What is the probability that someone who tests positive for the disease is actually sick?

(b) Suppose the test is administered twice, and the results of the two tests are independent. If a random individual tests positive both times, what are the chances he or she actually has the disease?

(c) For a binary partition of events, find an expression for $P(X|A \cap B)$ in terms of $P(A|X)$, $P(B|X)$, $P(A|\neg X)$, $P(B|\neg X)$, and the priors $P(X)$ and $P(\neg X) = 1 - P(X)$. You should assume $A$ and $B$ are independent, so $P(A \cap B|X) = P(A|X) \cdot P(B|X)$.

Solution :

(a) Let $X$ indicate that a person is infected, and $A$ indicate that a person has tested positive. We then have $\nu = P(A|X) = 0.9990$ is the sensitivity and $\rho = P(\neg A|\neg X) = 0.9995$ is the specificity. From Bayes' theorem, we have

$$P(X|A) = \frac{P(A|X) \cdot P(X)}{P(A|X) \cdot P(X) + P(A|\neg X) \cdot P(\neg X)} = \frac{\nu f}{\nu f + (1 - \rho)(1 - f)} \;,$$

where $P(A|\neg X) = 1 - P(\neg A|\neg X) = 1 - \rho$ and $P(X) = f$ is the fraction of infected individuals in the general population. With $f = 0.0002$, we find $P(X|A) = 0.2856$.

(b) We now need

$$P(X|A^2) = \frac{P(A^2|X) \cdot P(X)}{P(A^2|X) \cdot P(X) + P(A^2|\neg X) \cdot P(\neg X)} = \frac{\nu^2 f}{\nu^2 f + (1 - \rho)^2(1 - f)} \;,$$

where $A^2$ indicates two successive, independent tests. We find $P(X|A^2) = 0.9987$.

(c) Assuming $A$ and $B$ are independent, we have

$$P(X|A \cap B) = \frac{P(A \cap B|X) \cdot P(X)}{P(A \cap B|X) \cdot P(X) + P(A \cap B|\neg X) \cdot P(\neg X)}$$
$$= \frac{P(A|X) \cdot P(B|X) \cdot P(X)}{P(A|X) \cdot P(B|X) \cdot P(X) + P(A|\neg X) \cdot P(B|\neg X) \cdot P(\neg X)} \;.$$

This is exactly the formula used in part (b).

**(1.10)** Let $p(x) = \text{Pr}[X = x]$ where $X$ is a discrete random variable and both $X$ and $x$ are taken from an 'alphabet' $\mathcal{X}$. Let $p(x,y)$ be a normalized joint probability distribution on two random variables $X \in \mathcal{X}$ and $Y \in \mathcal{Y}$. The entropy of the joint distribution is $S(X,Y) = -\sum_{x,y} p(x,y) \log p(x,y)$. The conditional probability $p(y|x)$ for $y$ given $x$ is defined as $p(y|x) = p(x,y)/p(x)$, where $p(x) = \sum_y p(x,y)$.

(a) Show that the conditional entropy $S(Y|X) = -\sum_{x,y} p(x,y) \log p(y|x)$ satisfies

$$S(Y|X) = S(X,Y) - S(X) \quad .$$

Thus, conditioning reduces the entropy, and the entropy of a pair of random variables is the sum of the entropy of one plus the conditional entropy of the other.

(b) The mutual information $I(X,Y)$ is

$$I(X,Y) = \sum_{x,y} p(x,y) \log \left( \frac{p(x,y)}{p(x)\,p(y)} \right) \quad .$$

Show that

$$I(X,Y) = S(X) + S(Y) - S(X,Y) \quad .$$

(c) Show that $S(Y|X) \leq S(Y)$ and that the equality holds only when $X$ and $Y$ are independently distributed.

**Solution :**

**(a) We have**

$$S(Y|X) = -\sum_{x,y} p(x,y) \log \left( \frac{p(x,y)}{p(x)} \right)$$

$$= -\sum_{x,y} p(x,y) \log p(x,y) + \sum_{x,y} p(x,y) \log p(x)$$

$$= S(X,Y) - S(X) \quad ,$$

since $\sum_y p(x,y) = p(x)$.

**(b) Clearly**

$$I(X,Y) = \sum_{x,y} p(x,y) \Big( \log p(x,y) - \log p(x) - \log p(y) \Big)$$

$$= \sum_{x,y} p(x,y) \log p(x,y) - \sum_x p(x) \log p(x) - \sum_y p(y) \log p(y)$$

$$= S(X) + S(Y) - S(X,Y) \quad .$$

(c) Let's introduce some standard notation[1]. Denote the average of a function of a random variable as

$$\mathbb{E}f(X) = \sum_{x \in \mathcal{X}} p(x)f(x) \quad .$$

Equivalently, we could use the familiar angular bracket notation for averages and write $\mathbb{E}f(X)$ as $\langle f(X) \rangle$. For averages over several random variables, we have

$$\mathbb{E}f(X,Y) = \sum_{x \in \mathcal{X}} \sum_{y \in \mathcal{Y}} p(x,y)\, f(x,y) \quad ,$$

*et cetera*. Now here's a useful fact. If $f(x)$ is a convex function, then

$$\mathbb{E}f(X) \geq f(\mathbb{E}X) \quad .$$

For continuous functions, $f(x)$ is convex if $f''(x) \geq 0$ everywhere[2]. If $f(x)$ is convex on some interval $[a,b]$, then for $x_{1,2} \in [a,b]$ we must have

$$f\left(\lambda\, x_1 + (1-\lambda)\, x_2\right) \leq \lambda\, f(x_1) + (1-\lambda)\, f(x_2) \quad .$$

This is easily generalized to

$$f\left(\sum_n p_n\, x_n\right) \leq \sum_n p_n\, f(x_n) \quad ,$$

where $\sum_n p_n = 1$, which proves our claim - a result known as *Jensen's theorem*.

Now $\log x$ is concave, hence the function $f(x) = -\log x$ is convex, and therefore

$$I(X,Y) = -\sum_{x,y} p(x,y) \log\left(\frac{p(x)\, p(y)}{p(x,y)}\right) = -\mathbb{E}\log\left(\frac{p(X)\, p(Y)}{p(X,Y)}\right)$$

$$\geq -\log\mathbb{E}\left(\frac{p(X)\, p(Y)}{p(X,Y)}\right) = -\log\left(\sum_{x,y} p(x,y) \cdot \frac{p(x)\, p(y)}{p(x,y)}\right)$$

$$= -\log\left(\sum_x p(x) \cdot \sum_y p(y)\right) = -\log(1) = 0 \quad .$$

So $I(X,Y) \geq 0$. Clearly $I(X,Y) = 0$ when $X$ and $Y$ are independently distributed, *i.e.* when $p(x,y) = p(x)\, p(y)$. Using the results from part (b), we then have

$$I(X,Y) = S(X) + S(Y) - S(X,Y)$$
$$= S(Y) - S(Y|X) \geq 0 \quad .$$

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[1] See *e.g.* T. M. Cover and J. A. Thomas, *Elements of Information Theory*, 2nd edition (Wiley, 2006).
[2] A *concave* function $g(x)$ is one for which $f(x) = -g(x)$ is convex.

**(1.11)** The $n^{\text{th}}$ moment of the normalized Gaussian distribution $P(x) = (2\pi)^{-1/2} \exp\left(-\frac{1}{2}x^2\right)$ is defined by

$$\langle x^n \rangle = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{\infty} dx\, x^n\, \exp\left(-\frac{1}{2}x^2\right)$$

Clearly $\langle x^n \rangle = 0$ if $n$ is a nonnegative odd integer. Next consider the *generating function*

$$Z(j) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{\infty} dx\, \exp\left(-\frac{1}{2}x^2\right) \exp(jx) = \exp\left(\frac{1}{2}j^2\right) \quad .$$

(a) Show that
$$\langle x^n \rangle = \frac{d^n Z}{dj^n}\bigg|_{j=0}$$

and provide an explicit result for $\langle x^{2k} \rangle$ where $k \in \mathbb{N}$.

(b) Now consider the following integral:

$$F(\lambda) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{\infty} dx\, \exp\left(-\frac{1}{2}x^2 - \frac{\lambda}{4!}x^4\right) \quad .$$

The integral has no known analytic form[3], but we may express the result as a power series in the parameter $\lambda$ by Taylor expanding $\exp\left(-\frac{\lambda}{4!}x^4\right)$ and then using the result of part (a) for the moments $\langle x^{4k} \rangle$. Find the coefficients in the perturbation expansion,

$$F(\lambda) = \sum_{k=0}^{\infty} C_k \lambda^k \quad .$$

(c) Define the *remainder after $N$ terms* as

$$R_N(\lambda) = F(\lambda) - \sum_{k=0}^{N} C_k \lambda^k \quad .$$

Compute $R_N(\lambda)$ by evaluating numerically the integral for $F(\lambda)$ (using `Mathematica` or some other numerical package) and subtracting the finite sum. Then define the ratio $S_N(\lambda) = R_N(\lambda)/F(\lambda)$, which is the relative error from the $N$ term approximation and plot the absolute relative error $|S_N(\lambda)|$ *versus* $N$ for several values of $\lambda$.(I suggest you plot the error on a log scale.) What do you find?? Try a few values of $\lambda$ including $\lambda = 0.01$, $\lambda = 0.05$, $\lambda = 0.2$, $\lambda = 0.5$, $\lambda = 1$, $\lambda = 2$.

---

[3]In fact, it does. According to `Mathematica`, $F(\lambda) = \sqrt{\frac{2u}{\pi}}\, \exp(u)\, K_{1/4}(u)$, where $u = 3/4\lambda$ and $K_\nu(z)$ is the modified Bessel function. I am grateful to Prof. John McGreevy for pointing this out.

(d) Repeat the calculation for the integral

$$G(\lambda) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{\infty} dx \ \exp\left(-\frac{1}{2} x^2 - \frac{\lambda}{6!} x^6\right) \quad .$$

(e) Reflect meaningfully on the consequences for weakly and strongly coupled quantum field theories.

Solution :

(a) Clearly

$$\frac{d^n}{dj^n}\bigg|_{j=0} e^{jx} = x^n \quad,$$

so $\langle x^n \rangle = \left(d^n Z / dj^n\right)_{j=0}$ . With $Z(j) = \exp\left(\frac{1}{2}j^2\right)$, only the $k^{\text{th}}$ order term in $j^2$ in the Taylor series for $Z(j)$ contributes, and we obtain

$$\langle x^{2k} \rangle = \frac{d^{2k}}{dj^{2k}}\left(\frac{j^{2k}}{2^k\,k!}\right) = \frac{(2k)!}{2^k\,k!} \quad.$$

(b) We have

$$F(\lambda) = \sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{\lambda}{4!}\right)^n \langle x^{4n} \rangle = \sum_{n=0}^{\infty} \frac{(4n)!}{4^n\,(4!)^n\,n!\,(2n)!}\,(-\lambda)^n \quad.$$

This series is *asymptotic*. It has the properties

$$\lim_{\lambda \to 0} \frac{R_N(\lambda)}{\lambda^N} = 0 \quad \text{(fixed } N) \quad, \qquad \lim_{N \to \infty} \frac{R_N(\lambda)}{\lambda^N} = \infty \quad \text{(fixed } \lambda) \quad,$$

where $R_N(\lambda)$ is the remainder after $N$ terms, defined in part (c). The radius of convergence is zero. To see this, note that if we reverse the sign of $\lambda$, then the integrand of $F(\lambda)$ diverges badly as $x \to \pm\infty$. So $F(\lambda)$ is infinite for $\lambda < 0$, which means that there is no disk of any finite radius of convergence which encloses the point $\lambda = 0$. Note that by Stirling's rule,

$$(-1)^n\,C_n \equiv \frac{(4n)!}{4^n\,(4!)^n\,n!\,(2n)!} \sim n^n \cdot \left(\tfrac{2}{3}\right)^n e^{-n} \cdot (\pi n)^{-1/2} \quad,$$

and we conclude that the magnitude of the summand reaches a minimum value when $n = n^*(\lambda)$, with

$$n^*(\lambda) \approx \frac{3}{2\lambda}$$

for small values of $\lambda$. For large $n$, the magnitude of the coefficient $C_n$ grows as $|C_n| \sim e^{n\ln n + \mathcal{O}(n)}$, which dominates the $\lambda^n$ term, no matter how small $\lambda$ is.

(c) Results are plotted in fig. 3.

It is worth pointing out that the series for $F(\lambda)$ and for $\ln F(\lambda)$ have diagrammatic interpretations. For a Gaussian integral, one has

$$\langle x^{2k} \rangle = \langle x^2 \rangle^k \cdot A_{2k}$$

where $A_{2k}$ is the *number of contractions*. For a proof, see the lecture notes. For our integral, $\langle x^2 \rangle = 1$. The number of contractions $A_{2k}$ is computed in the following way. For each of the $2k$ powers of $x$, we assign an index running from $1$ to $2k$. The indices are *contracted*, *i.e.* paired, with each other. How many pairings are there? Suppose we start with any from among the $2k$ indices. Then there are $(2k-1)$
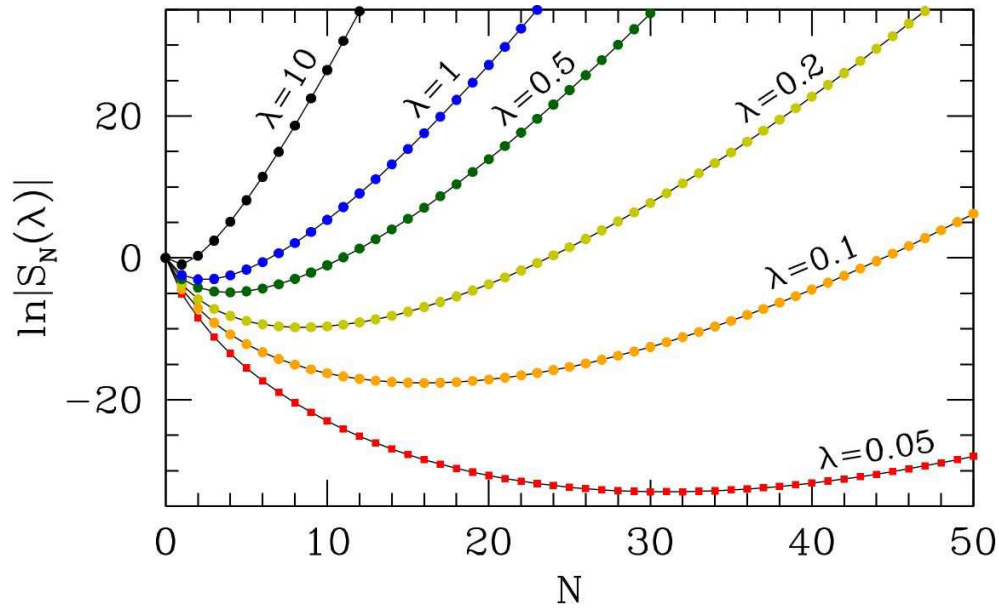
Figure 3: Relative error *versus* number of terms kept for the asymptotic series for $F(\lambda)$. Note that the optimal number of terms to sum is $N^*(\lambda) \approx \frac{3}{2\lambda}$.

choices for its mate. We then choose another index arbitrarily. There are now $(2k - 3)$ choices for *its* mate. Carrying this out to its completion, we find that the number of contractions is

$$A_{2k} = (2k - 1)(2k - 3) \cdots 3 \cdot 1 = \frac{(2k)!}{2^k \, k!} \quad,$$

exactly as we found in part (a). Now consider the integral $F(\lambda)$. If we expand the quartic term in a power series, then each power of $\lambda$ brings an additional four powers of $x$. It is therefore convenient to represent each such quartet with the symbol $\times$. At order $N$ of the series expansion, we have $N$ $\times$'s and $4N$ indices to contract. Each full contraction of the indices may be represented as a labeled diagram, which is in general composed of several disjoint connected subdiagrams. Let us label these subdiagrams, which we will call clusters, by an index $\gamma$. Now suppose we have a diagram consisting of $m_\gamma$ subdiagrams of type $\gamma$, for each $\gamma$. If the cluster $\gamma$ contains $n_\gamma$ vertices ($\times$), then we must have

$$N = \sum_\gamma m_\gamma \, n_\gamma \quad.$$

How many ways are there of assigning the labels to such a diagram? One might think $(4!)^N \cdot N!$, since for each vertex $\times$ there are 4! permutations of its four labels, and there are $N!$ ways to permute all the vertices. However, this overcounts diagrams which are *invariant* under one or more of these permutations. We define the *symmetry factor* $s_\gamma$ of the (unlabeled) cluster $\gamma$ as the number of permutations of the indices of a corresponding labeled cluster which result in the same contraction. We can also permute the $m_\gamma$ identical disjoint clusters of type $\gamma$.

Examples of clusters and their corresponding symmetry factors are provided in fig. 4, for all diagrams with $n_\gamma \leq 3$. There is only one diagram with $n_\gamma = 1$, resembling $\infty$. To obtain $s_\gamma = 8$, note that each of
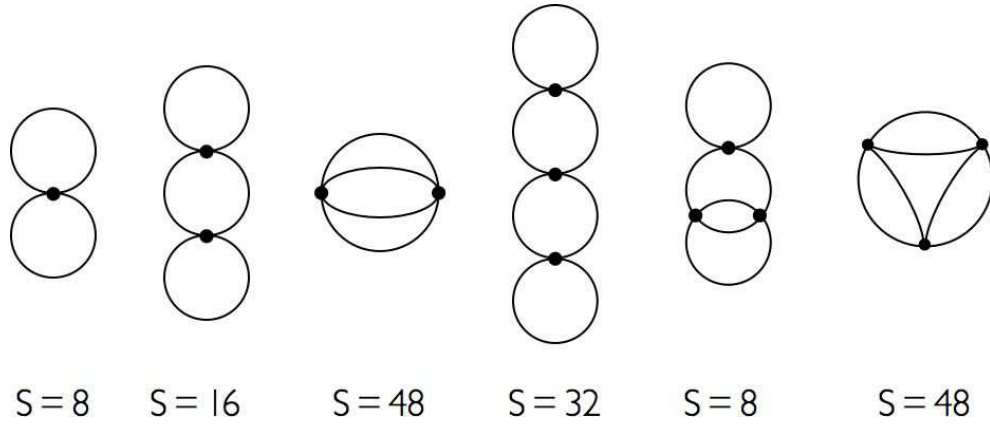
Figure 4: Cluster symmetry factors. A vertex is represented as a black dot (
•) with four 'legs'.

the circles can be separately rotated by an angle $\pi$ about the long symmetry axis. In addition, the figure can undergo a planar rotation by $\pi$ about an axis which runs through the sole vertex and is normal to the plane of the diagram. This results in $s_\gamma = 2 \cdot 2 \cdot 2 = 8$. For the cluster ⊙•⊙, there is one extra circle, so $s_\gamma = 2^4 = 16$. The third diagram in figure shows two vertices connected by four lines. Any of the $4!$ permutations of these lines results in the same diagram. In addition, we may reflect about the vertical symmetry axis, interchanging the vertices, to obtain another symmetry operation. Thus $s_\gamma = 2 \cdot 4! = 48$. One might ask why we don't also count the planar rotation by $\pi$ as a symmetry operation. The answer is that it is equivalent to a combination of a reflection and a permutation, so it is not in fact a distinct symmetry operation. (If it were distinct, then $s_\gamma$ would be $96$.) Finally, consider the last diagram in the figure, which resembles a sausage with three links joined at the ends into a circle. If we keep the vertices fixed, there are $8$ symmetry operations associated with the freedom to exchange the two lines associated with each of the three sausages. There are an additional $6$ symmetry operations associated with permuting the three vertices, which can be classified as three in-plane rotations by $0$, $\frac{2\pi}{3}$ and $\frac{4\pi}{3}$, each of which can also be combined with a reflection about the $y$-axis (this is known as the group $C_{3v}$). Thus, $s_\gamma = 8 \cdot 6 = 48$.

Now let us compute an expression for $F(\gamma)$ in terms of the clusters. We sum over all possible numbers of clusters at each order:

$$F(\gamma) = \sum_{N=0}^{\infty} \frac{1}{N!} \sum_{\{m_\gamma\}} \frac{(4!)^N N!}{\prod_\gamma s_\gamma^{m_\gamma} m_\gamma!} \left( -\frac{\lambda}{4!} \right)^N \delta_{N,\sum_\gamma m_\gamma n_\gamma}$$

$$= \exp\left( \sum_\gamma \frac{(-\lambda)^{n_\gamma}}{s_\gamma} \right) \quad .$$

Thus,

$$\ln F(\gamma) = \sum_\gamma \frac{(-\lambda)^{n_\gamma}}{s_\gamma} \quad ,$$

and *the logarithm of the sum over all diagrams is a sum over connected clusters*. It is instructive to work this

out to order $\lambda^2$. We have, from the results of part (b),

$$F(\lambda) = 1 - \tfrac{1}{8}\lambda + \tfrac{35}{384}\lambda^2 + \mathcal{O}(\lambda^3) \quad \Longrightarrow \quad \ln F(\lambda) = -\tfrac{1}{8}\lambda + \tfrac{1}{12}\lambda^2 + \mathcal{O}(\lambda^3) \quad .$$

Note that there is one diagram with $N = 1$ vertex, with symmetry factor $s = 8$. For $N = 2$ vertices, there are two diagrams, one with $s = 16$ and one with $s = 48$ (see fig. 4). Since $\tfrac{1}{16} + \tfrac{1}{48} = \tfrac{1}{12}$, the diagrammatic expansion is verified to order $\lambda^2$.

(d) We now have[4]

$$G(\lambda) = \frac{1}{\sqrt{2\pi}} \int\limits_{-\infty}^{\infty} dx \, \exp\left(-\frac{1}{2}x^2 - \frac{\lambda}{6!}x^6\right)$$

$$= \sum_{n=0}^{\infty} \frac{1}{n!}\left(-\frac{\lambda}{6!}\right)^n \langle x^{6n}\rangle = \sum_{n=0}^{\infty} C_n\,\lambda^n \quad ,$$

where

$$C_n = \frac{(-1)^n\,(6n)!}{(6!)^n\,n!\,2^{3n}\,(3n)!} \quad .$$

Invoking Stirling's approximation, we find

$$\ln|C_n| \sim 2n\,\ln n - \left(2 + \ln\tfrac{5}{3}\right)n \quad .$$

From the above expression for $C_n$, we see that the magnitude of the contribution of the $n^{\text{th}}$ term in the perturbation series is

$$C_n\,\lambda^n = (-1)^n\,\exp\left(2n\,\ln n - \left(2 + \ln\tfrac{10}{3}\right)n + n\ln\lambda\right) \quad .$$

Differentiating, we find that this contribution is minimized for $n = n^*(\lambda)$, where

$$n^*(\lambda) = \sqrt{\frac{10}{3\lambda}} \quad .$$

Via numerical integration using FORTRAN subroutines from QUADPACK, one obtains the results in Fig. 5 and Tab. **??**.

The series for $G(\lambda)$ and for $\ln G(\lambda)$ again have diagrammatic interpretations. If we expand the sextic term in a power series, each power of $\lambda$ brings an additional six powers of $x$. It is natural to represent each such sextet with as a vertex with six legs. At order $N$ of the series expansion, we have $N$ such vertices and $6N$ legs to contract. As before, each full contraction of the leg indices may be represented as

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[4]According to `Mathematica`, the $G(\lambda)$ has the analytic form $G(\lambda) = \pi\sqrt{u}\left[\text{Ai}^2(u) + \text{Bi}^2(u)\right]$, where $u = (15/2\lambda)^{1/3}$ and $\text{Ai}(z)$ and $\text{Bi}(z)$ are Airy functions. The definitions and properties of the Airy functions are discussed in §9.2 of the NIST *Handbook of Mathematical Functions*.
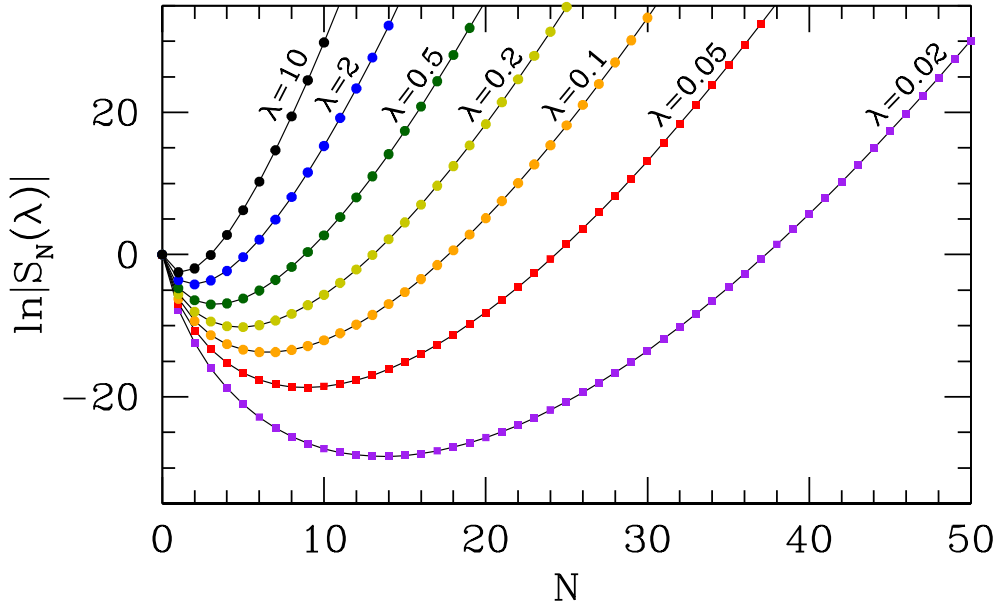
Figure 5: Logarithm of ratio of remainder after $N$ terms $R_N(\lambda)$ to the value of the integral $G(\lambda)$, for various values of $\lambda$.

| $\lambda$ | 10 | 2 | 0.5 | 0.2 | 0.1 | 0.05 | 0.02 |
|---|---|---|---|---|---|---|---|
| $F$ | 0.92344230 | 0.97298847 | 0.99119383 | 0.996153156 | 0.99800488 | 0.99898172 | 0.99958723 |
| $n^*$ | 0.68 | 1.3 | 2.6 | 4.1 | 5.8 | 8.2 | 13 |

Table 2: $F(\lambda)$ and $n^*(\lambda)$ for problem 8d.

a labeled diagram, which is in general composed of several disjoint connected clusters. If the cluster $\gamma$ contains $n_\gamma$ vertices, then for any diagram we again must have $N = \sum_\gamma m_\gamma n_\gamma$, where $m_\gamma$ is the number of times the cluster $\gamma$ appears. As with the quartic example, the number of ways of assigning labels to a given diagram is given by the total number of possible permutations $(6!)^N \cdot N!$ divided by a correction factor $\prod_\gamma s_\gamma^{m_\gamma} m_\gamma!$, where $s_\gamma$ is the symmetry factor of the cluster $\gamma$, and the $m_\gamma!$ term accounts for the possibility of permuting among different labeled clusters of the same type $\gamma$.

Examples of clusters and their corresponding symmetry factors are provided in Fig. 6. There is only one diagram with $n_\gamma = 1$, shown panel (a), resembling a three-petaled flower. To obtain $s_\gamma = 48$, note that each of the petals can be rotated by $180°$ about an axis bisecting the petal, yielding a factor of $2^3$. The three petals can then be permuted, yielding an additional factor of 3!. Hence the total symmetry factor is $s_\gamma = 2^3 \cdot 3! = 48$. Now we can see how dividing by the symmetry factor saves us from overcounting. In this case, we get $6!/s_\gamma = 720/48 = 15 = 5 \cdot 3 \cdot 1$, which is the correct number of contractions. For the diagram in panel (b), the four petals and the central loop can each be rotated about a symmetry axis, yielding a factor $2^5$. The two left petals can be permuted, as can the two right petals. Finally, the two vertices can themselves be permuted. Thus, the symmetry factor is $s_\gamma = 2^5 \cdot 2^2 \cdot 2 = 2^8 = 256$. In panel (c), the six lines can be permuted (6!) and the vertices can be exchanged (2), hence $s_\gamma = 6! \cdot 2 = 1440$. In panel (d), the two outer loops each can be twisted by $180°$, the central four lines can be permuted,
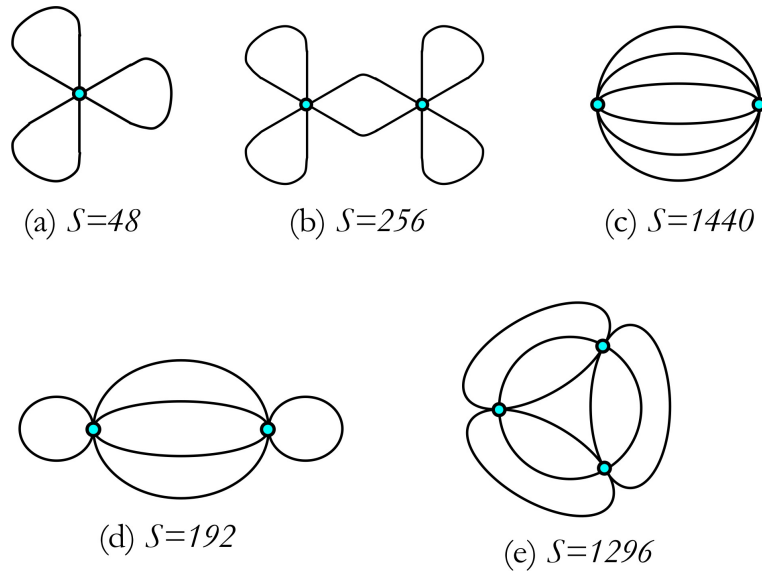
Figure 6: Diagrams and their symmetry factors for the $\frac{1}{6!}\lambda\,x^6$ zero-dimensional field theory

and the vertices can be permuted, hence $s_\gamma = 2^2 \cdot 4! \cdot 2 = 192$. Finally, in panel (e), each pair of vertices is connected by three lines which can be permuted, and the vertices themselves can be permuted, so $s_\gamma = (3!)^3 \cdot 3! = 1296$.

Now let us compute an expression for $F(\gamma)$ in terms of the clusters. We sum over all possible numbers of clusters at each order:

$$G(\gamma) = \sum_{N=0}^{\infty} \frac{1}{N!} \sum_{\{m_\gamma\}} \frac{(6!)^N N!}{\prod_\gamma s_\gamma^{m_\gamma} m_\gamma!} \left(-\frac{\lambda}{6!}\right)^N \delta_{N,\sum_\gamma m_\gamma n_\gamma}$$

$$= \exp\left(\sum_\gamma \frac{(-\lambda)^{n_\gamma}}{s_\gamma}\right) \quad .$$

Thus,

$$\ln G(\gamma) = \sum_\gamma \frac{(-\lambda)^{n_\gamma}}{s_\gamma} \quad ,$$

and *the logarithm of the sum over all diagrams is a sum over connected clusters.* It is instructive to work this out to order $\lambda^2$. We have, from the results of part (a),

$$G(\lambda) = 1 - \frac{\lambda}{2^6 \cdot 3} + \frac{7 \cdot 11 \cdot \lambda^2}{2^9 \cdot 3 \cdot 5} + \mathcal{O}(\lambda^3) \quad \Longrightarrow \quad \ln G(\lambda) = -\frac{\lambda}{2^6 \cdot 3} + \frac{113 \cdot \lambda^2}{2^8 \cdot 3^2 \cdot 5} + \mathcal{O}(\lambda^3) \quad .$$

Note that there is one diagram with $N = 1$ vertex, with symmetry factor $s = 48$. For $N = 2$ vertices, there are three diagrams, one with $s = 256$, one with $s = 1440$, and one with $s = 192$ (see Fig. 6). Since $\frac{1}{256} + \frac{1}{1440} + \frac{1}{192} = \frac{113}{2^8 3^2 5}$, the diagrammatic expansion is verified to order $\lambda^2$.

(e) In quantum field theory (QFT), the vertices themselves carry space-time labels, and the contractions, *i.e.* the lines connecting the legs of the vertices, are *propagators* $G(x_i^\mu - x_j^\mu)$, where $x_i^\mu$ is the space-time

label associated with vertex $i$. It is convenient to work in momentum-frequency space, in which case we work with the Fourier transform $\hat{G}(p^\mu)$ of the space-time propagators. Integrating over the space-time coordinates of each vertex then enforces total 4-momentum conservation at each vertex. We then must integrate over all the internal 4-momenta to obtain the numerical value for a given diagram. The diagrams, as you know, are associated with Feynman's approach to QFT and are known as Feynman diagrams. Our example here is equivalent to a $(0+0)$-dimensional field theory, *i.e.* zero space dimensions and zero time dimensions. There are then no internal 4-momenta to integrate over, and each propagator is simply a number rather than a function. The discussion above of symmetry factors $s_\gamma$ carries over to the more general QFT case.

There is an important lesson to be learned here about the behavior of asymptotic series. As we have seen, if $\lambda$ is sufficiently small, summing more and more terms in the perturbation series results in better and better results, until one reaches an optimal order when the error is minimized. Beyond this point, summing additional terms makes the result *worse*, and indeed the perturbation series diverges badly as $N \to \infty$. Typically the optimal order of perturbation theory is inversely proportional to the coupling constant. For quantum electrodynamics (QED), where the coupling constant is the fine structure constant $\alpha = e^2/\hbar c \approx \frac{1}{137}$, we lose the ability to calculate in a reasonable time long before we get to 137 loops, so practically speaking no problems arise from the lack of convergence. In quantum chromodynamics (QCD), however, the effective coupling constant is about two orders of magnitude larger, and perturbation theory is a much more subtle affair.

## 0.2  Thermodynamics

**(2.1)** $\nu$ moles of an ideal diatomic gas are driven along the cycle depicted in Fig. 7. Section AB is an adiabatic free expansion; section BC is an isotherm at temperature $T_A = T_B = T_C$; CD is an isobar, and DA is an isochore. The volume at B is given by $V_B = (1 - x) V_A + x V_C$, where $0 \leq x \leq 1$.

   (a) Find an expression for the total work $W_{\text{cycle}}$ in terms of $\nu$, $T_A$, $V_A$, $V_C$, and $x$.

   (b) Suppose $V_A = 1.0\,\text{L}$, $V_C = 5.0\,\text{L}$, $T_A = 500\,\text{K}$, and $\nu = 5$. What is the volume $V_B$ such that $W_{\text{cycle}} = 0$?

Solution :

(a) We have $W_{AB} = W_{DA} = 0$, and

$$W_{BC} = \int_B^C p\,dV = \nu R T_A \int_B^C \frac{dV}{V} = \nu R T_A \ln\left(\frac{V_C}{V_B}\right)$$

$$W_{CD} = \int_C^D p\,dV = p_C(V_D - V_C) = -\nu R T_A \left(1 - \frac{V_A}{V_C}\right) \quad.$$

Thus,

$$W_{\text{CYC}} = \nu R T_A \left[ \ln\left(\frac{V_C}{V_B}\right) - 1 + \frac{V_A}{V_C} \right] \quad.$$



Figure 7: Engine cycle for problem 1, consisting of adiabatic free expansion (AB), isotherm (BC), isobar (CD), and isochore (DA).

(b) Setting $V_B = (1 - x) V_A + x V_C$, and defining $r \equiv V_A/V_C$, we have

$$W_{\text{CYC}} = \nu R T_A \Big( - \ln \big(x + (1 - x) r\big) + 1 - r \Big) \quad,$$

and setting $W_{\text{CYC}} = 0$ we obtain $x = x^*$, with

$$x^* = \frac{e^{r-1} - r}{1 - r} \quad.$$

For $V_A = 1.0\,\text{L}$ and $V_C = 5.0\,\text{L}$, we have $r = \frac{1}{5}$ and $x^* = 0.31$, corresponding to $V_B = 2.2\,\text{L}$.

**(2.2)** A strange material obeys the equation of state $E(S, V, N) = a\, S^7/V^4 N^2$, where $a$ is a dimensionful constant.

- (a) What are the SI dimensions of $a$?

- (b) Find the equation of state relating $p$, $T$, and $n = N/V$.

- (c) Find the coefficient of thermal expansion $\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and the isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$. Express your answers in terms of $p$ and $T$.

- (d) $\nu$ moles of this material execute a Carnot cycle between reservoirs at temperatures $T_1$ and $T_2$. Find the heat $Q$ and work $W$ for each leg of the cycle, and find the cycle efficiency $\eta$.

<p style="text-align:center;">Solution :</p>

(a) Clearly $[a] = \mathrm{K}^7\,\mathrm{m}^{12}/\mathrm{J}^6$ where K are Kelvins, m are meters, and J are Joules.

(b) We have

$$T = +\left(\frac{\partial E}{\partial S}\right)_{V,N} = \frac{7aS^6}{N^2V^4}$$

$$p = -\left(\frac{\partial E}{\partial V}\right)_{S,N} = \frac{4aS^7}{N^2V^5} \quad .$$

We must eliminate $S$. Dividing the second of these equations by the first, we find $S = 7pV/4T$, and substituting this into either equation, we obtain the equation of state,
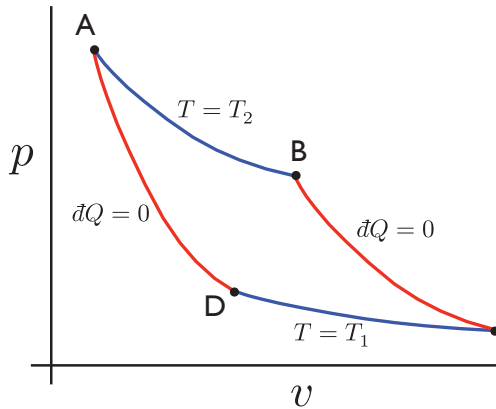
$$p = c \cdot \left(\frac{N}{V}\right)^{1/3} T^{7/6} \quad ,$$

Figure 8: The Carnot cycle.

with $c = \frac{6}{7^{7/6}} a^{-1/6}$.

(c) Taking the logarithm and then the differential of the above equation of state, we have

$$\frac{dp}{p} + \frac{dV}{3V} - \frac{7\,dT}{6T} - \frac{dN}{3N} = 0 \quad .$$

Thus,

$$\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{7}{2T} \quad , \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{3}{p} \quad .$$

(d) From the results of part (b), we have that $dS = 0$ means $d(N^2V^4T) = 0$, so with $N$ constant the equation for adiabats is $d(TV^4) = 0$. Thus, for the Carnot cycle of Fig. 38, we have

$$T_2\, V_{\mathsf{A}}^4 = T_1\, V_{\mathsf{D}}^4 \quad , \qquad T_2\, V_{\mathsf{B}}^4 = T_1\, V_{\mathsf{C}}^4 \quad .$$

We shall use this relation in due time. Another relation we shall use is obtained by dividing out the $S^7$ factor common in the expressions for $E$ and for $p$, then substituting for $p$ using the equation of state:

$$E = \tfrac{1}{4}pV = \tfrac{1}{4}c\,N^{1/3}\,V^{2/3}\,T^{7/6} \quad .$$

AB: Consider the AB leg of the Carnot cycle. We use the equation of state along the isotherm to find

$$W_{AB} = \int_{V_A}^{V_B} dV\, p = \tfrac{3}{2}c\,N^{1/3}\,T_2^{7/6}\big(V_B^{2/3} - V_A^{2/3}\big) \quad .$$

Since $E$ depends on volume, unlike the case of the ideal gas, there is a change in energy along this leg:

$$(\Delta E)_{AB} = E_B - E_A = \tfrac{1}{4}c\,N^{1/3}\,T_2^{7/6}\big(V_B^{2/3} - V_A^{2/3}\big) \quad .$$

Finally, the heat absorbed by the engine material during this leg is

$$Q_{AB} = (\Delta E)_{AB} + W_{AB} = \tfrac{7}{4}c\,N^{1/3}\,T_2^{7/6}\big(V_B^{2/3} - V_A^{2/3}\big) \quad .$$

BC: Next, consider the BC leg. Clearly $Q_{BC} = 0$ since BC is an adiabat. Thus,

$$W_{BC} = -(\Delta E)_{BC} = E_B - E_C = \tfrac{1}{4}c\,N^{1/3}\big(T_2^{7/6}\,V_B^{2/3} - T_1^{7/6}\,V_C^{2/3}\big) \quad .$$

But the fact that BC is an adiabat guarantees $V_C^{2/3} = (T_2/T_1)^{1/6}\,V_B^{2/3}$, hence

$$W_{BC} = \tfrac{1}{4}c\,N^{1/3}\,V_B^{2/3}\,T_2^{1/6}(T_2 - T_1) \quad .$$

CD: For the CD leg, we can apply the results from AB, *mutatis mutandis*. Thus,

$$W_{CD} = \tfrac{3}{2}c\,N^{1/3}\,T_2^{7/6}\big(V_D^{2/3} - V_C^{2/3}\big) \quad .$$

We now use the adiabat conditions $V_C^{2/3} = (T_2/T_1)^{1/6}\,V_B^{2/3}$ and $V_D^{2/3} = (T_2/T_1)^{1/6}\,V_A^{2/3}$ to write $W_{CD}$ as

$$W_{CD} = \tfrac{3}{2}c\,N^{1/3}\,T_1\,T_2^{1/6}\big(V_A^{2/3} - V_B^{2/3}\big) \quad .$$

We therefore have

$$Q_{CD} = \tfrac{7}{4}c\,N^{1/3}\,T_1\,T_2^{1/6}\big(V_A^{2/3} - V_B^{2/3}\big) \quad .$$

Note that both $W_{CD}$ and $Q_{CD}$ are negative.

DA: We apply the results from the BC leg, *mutatis mutandis*, and invoke the adiabat conditions. We find $Q_{DA} = 0$ and

$$W_{DA} = \tfrac{1}{4}c\,N^{1/3}\,V_A^{2/3}\,T_2^{1/6}(T_2 - T_1) \quad .$$

For the cycle, we therefore have

$$W_{\text{cyc}} = W_{\text{AB}} + W_{\text{BC}} + W_{\text{CD}} + W_{\text{DA}} = \tfrac{7}{4} c \, N^{1/3} \, T_2^{1/6} (T_2 - T_1) \big( V_{\text{B}}^{2/3} - V_{\text{A}}^{2/3} \big) \quad .$$

and thus

$$\eta = \frac{W_{\text{cyc}}}{Q_{\text{AB}}} = 1 - \frac{T_1}{T_2} \quad .$$

This is the same result as for an ideal gas, as must be the case as per the Second Law of Thermodynamics.

**(2.3)** For each of the following situations, explain clearly and fully why it is or is not thermodynamically possible.

(a) Energy function $E(S, V, N) = a\,S\,V\,N$ with $a$ constant.

(b) Equation of state $V = a\,N\,p\,T$ with $a$ constant.

(c) A system where $\left(\frac{\partial V}{\partial T}\right)_{p,N} < 0$ over some range of $T$ and $p$.

(d) The phase diagram for a single component system depicted in Fig. 9 (left panel). (You only need know that a superfluid is a distinct thermodynamic phase.)

(e) The phase diagram for a single component system in Fig. 9 (right panel). (You only need know that BCC, HCP, and FCC solids are distinct phases.)

(f) $E(S, V, N) = a\,N^2\,V^{-1}\,\exp(S/Nb)$ with $a$ and $b$ constant.

(g) 15 Joules of heat energy are required to raise the temperature of a system by $\Delta T = 1°\mathrm{C}$ at constant volume. 10 Joules of heat energy are required to raise the temperature of the same system by $\Delta T = 1°\mathrm{F}$ at constant pressure.

(h) A heat engine operating between reservoirs at temperatures $T_1 = 400\,\mathrm{K}$ and $T_2 = 600\,\mathrm{K}$. During each cycle, the engine does work $W = 300\,\mathrm{J}$ and the entropy of the upper reservoir decreases by $2.00\,\mathrm{J/K}$.
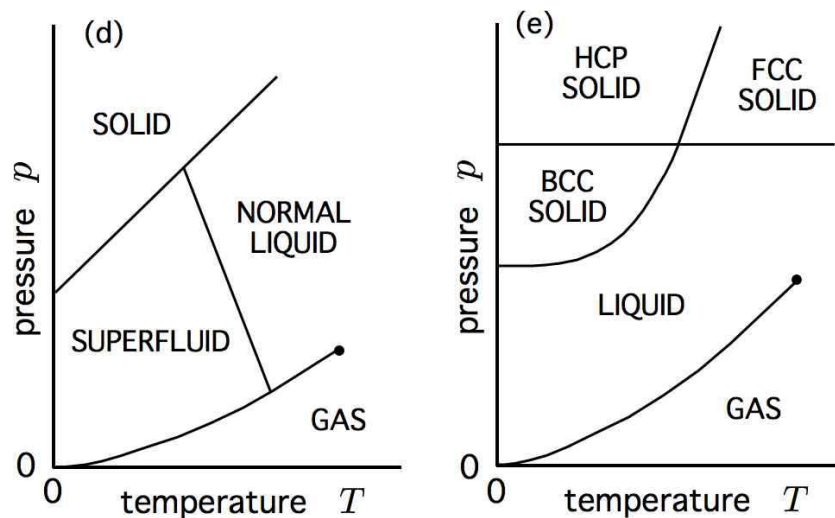


Figure 9: Phase diagrams for parts (d) and (e) of problem 3.

Solution :

(a) No! $E(\lambda S, \lambda V, \lambda N) = \lambda^3 E(S, V, N)$ is homogeneous of degree 3 – not extensive.

(b) No! The isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -1/p$ is negative, which violates $\kappa_T > \kappa_S > 0$.

(c) Yes! Many systems, such as water, contract upon a temperature increase over some range of temperature.

(d) No! This one is tricky. From the Clapeyron equation, we have $\left(\frac{dp}{dT}\right)_{\text{coex}} = \frac{\Delta s}{\Delta v}$. Nernst's law says that the entropy of both the solid and superfluid phases must vanish at $T = 0$. Therefore all coexistence curves which intersect the pressure axis at $T = 0$ must do so with zero slope.

(e) No! The Gibbs phase rule $d = 2 + \sigma - \varphi$ gives the dimension of thermodynamic space over which $\varphi$ distinct phases among $\sigma$ species can coexist. For $\sigma = 1$ we have $\varphi \leq 3$, since $d \geq 0$. So four phase coexistence with a single component is impossible.

(f) Yes! $E$ is properly extensive and convex. One can derive $E = pV = NbT$, which is the ideal gas law with $k_{\text{B}}$ replaced by $b$.

(d) Yes! The heat capacity at constant volume is $C_V = \left(\frac{dQ}{dT}\right)_V = 15\,\text{J/K}$. The heat capacity at constant pressure is $C_p = \left(\frac{dQ}{dT}\right)_p = 10\,\text{J}/\frac{5}{9}\text{K} = 18\,\text{J/K}$. Stability requires $C_p > C_V$, which is satisfied.

(h) Yes! The only possible obstacle here is whether the engine's efficiency is greater than that of the corresponding Carnot cycle, for which $\eta_{\text{C}} = 1 - \frac{T_1}{T_2} = \frac{1}{3}$. We have $\eta = \frac{W}{Q_2}$ and $\Delta S_2 = -\frac{Q_2}{T_2}$. Thus, $\eta = W/\left[T_2(-\Delta S_2)\right] = 300\,\text{J}/\left[(600\,\text{K})(2.00\,\text{J/K})\right] = \frac{1}{4} < \eta_{\text{C}}$.

**(2.4)** Using the chain rule from multivariable calculus (see the lecture notes), solve the following:

(a) Find $(\partial N/\partial T)_{S,p}$ in terms of $T$, $N$, $S$, and $C_{p,N}$.

(b) Experimentalists can measure $C_{V,N}$ but for many problems it is theoretically easier to work in the grand canonical ensemble, whose natural variables are $(T, V, \mu)$. Show that

$$C_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,z} - \left(\frac{\partial E}{\partial z}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{V,z} \Big/ \left(\frac{\partial N}{\partial z}\right)_{T,V} \quad,$$

where $z = \exp(\mu/k_{\mathrm{B}}T)$ is the fugacity.

Solution :

(a) We have

$$\left(\frac{\partial N}{\partial T}\right)_{S,p} = \frac{\partial(N,S,p)}{\partial(T,S,p)} = \frac{\partial(N,S,p)}{\partial(N,T,p)} \cdot \frac{\partial(N,T,p)}{\partial(T,S,p)} = -\frac{NC_{p,N}}{TS} \quad.$$

(b) Using the chain rule,

$$
\begin{aligned}
C_{V,N} = \frac{\partial(E,V,N)}{\partial(T,V,N)} &= \frac{\partial(E,V,N)}{\partial(T,V,z)} \cdot \frac{\partial(T,V,z)}{\partial(T,V,N)} \\
&= \left[ \left(\frac{\partial E}{\partial T}\right)_{V,z} \left(\frac{\partial N}{\partial z}\right)_{T,V} - \left(\frac{\partial E}{\partial z}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{V,z} \right] \cdot \left(\frac{\partial z}{\partial N}\right)_{T,V} \\
&= \left(\frac{\partial E}{\partial T}\right)_{V,z} - \left(\frac{\partial E}{\partial z}\right)_{T,V} \left(\frac{\partial N}{\partial T}\right)_{V,z} \Big/ \left(\frac{\partial N}{\partial z}\right)_{T,V} \quad.
\end{aligned}
$$

**(2.5)** The entropy of a thermodynamic system $S(E, V, N)$ is given by

$$S(E, V, N) = r\, E^\alpha\, V^\beta\, N^\gamma \quad ,$$

where $r$ is a dimensionful constant.

    (a) Extensivity of $S$ imposes a condition on $(\alpha, \beta, \gamma)$. Find this constraint.

    (b) Even with the extensivity condition satisfied, the system may violate one or more stability criteria. Find the general conditions on $(\alpha, \beta, \gamma)$ which are thermodynamically permissible.

Solution :

(a) Clearly we must have $\alpha + \beta + \gamma = 1$ in order for $S$ to be extensive.

(b) The Hessian is

$$Q = \frac{\partial^2 S}{\partial X_i\, \partial X_j} = \begin{pmatrix} \alpha(\alpha - 1)\, S/E^2 & \alpha\beta\, S/EV & \alpha\gamma\, S/EN \\ \alpha\beta\, S/EV & \beta(\beta - 1)\, S/V^2 & \beta\gamma\, S/VN \\ \alpha\gamma\, S/EN & \beta\gamma\, S/VN & \gamma(\gamma - 1)\, S/N^2 \end{pmatrix} \quad .$$

As shown in the notes, for any $2 \times 2$ submatrix of $Q$, obtained by eliminating a single row and its corresponding column, and written $\begin{pmatrix} a & b \\ b & c \end{pmatrix}$, we must have $a < 0$, $c < 0$, and $ac > b^2$. For example, if we take the upper left $2 \times 2$ submatrix, obtained by eliminating the third row and third column of $Q$, we have $a = \alpha(\alpha - 1)S/E^2$, $b = \alpha\beta\, S/EV$, and $c = \beta(\beta - 1)S/V^2$. The condition $a < 0$ requires $\alpha \in (0, 1)$. Similarly, $b < 0$ requires $\beta \in (0, 1)$. Finally, $ac > b^2$ requires $\alpha + \beta < 1$. Since $\alpha + \beta + \gamma = 1$, this last condition requires $\gamma > 0$. Obviously we must have $\gamma < 1$ as well, else either $\alpha$ or $\beta$ would have to be negative. An examination of either of the other two submatrices yields the same conclusions. Thus,

$$\alpha \in (0, 1) \qquad , \qquad \beta \in (0, 1) \qquad , \qquad \gamma \in (0, 1) \quad .$$

**(2.6)** Consider the equation of state,

$$p = \frac{R^2 T^2}{a + vRT} \quad ,$$

where $v = N_A V/N$ is the molar volume and $a$ is a constant.

- (a) Find an expression for the molar energy $\varepsilon(T, v)$. Assume that in the limit $v \to \infty$, where the ideal gas law $pv = RT$ holds, that the gas is ideal with $\varepsilon(v \to \infty, T) = \frac{1}{2} f RT$.

- (b) Find the molar specific heat $c_{V,N}$.

Solution :

(a) We fix $N$ throughout the analysis. As shown in the lecture notes,

$$\left( \frac{\partial E}{\partial V} \right)_{T,N} = T \left( \frac{\partial p}{\partial T} \right)_{V,N} - p \quad .$$

Defining the molar energy $\varepsilon = E/\nu = N_A E/N$ and the molar volume $v = V/\nu = N_A V/N$, we can write the above equation as

$$\left( \frac{\partial \varepsilon}{\partial v} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_v - p = p \left[ \left( \frac{\partial \ln p}{\partial \ln T} \right)_v - 1 \right] \quad .$$

Now from the equation of state, we have

$$\ln p = 2 \ln T - \ln(a + vRT) + 2 \ln R \quad ,$$

hence

$$\left( \frac{\partial \ln p}{\partial \ln T} \right)_v = 2 - \frac{vRT}{a + vRT} \quad .$$

Plugging this into our formula for $\left( \frac{\partial \varepsilon}{\partial v} \right)_T$, we have

$$\left( \frac{\partial \varepsilon}{\partial v} \right)_T = \frac{a \, p}{a + vRT} = \frac{aR^2 T^2}{(a + vRT)^2} \quad .$$

Now we integrate with respect to $v$ at fixed $T$, using the method of partial fractions. After some grinding, we arrive at

$$\varepsilon(T, v) = \omega(T) - \frac{aRT}{(a + vRT)} \quad .$$

In the limit $v \to \infty$, the second term on the RHS tends to zero. This is the ideal gas limit, hence we must have $\omega(T) = \frac{1}{2} f RT$, where $f = 3$ for a monatomic gas, $f = 5$ for diatomic, *etc.* Thus,

$$\varepsilon(T, v) = \frac{1}{2} f RT - \frac{aRT}{a + vRT} = \frac{1}{2} f RT - \frac{a}{v} + \frac{a^2}{v(a + vRT)} \quad .$$

(b) To find the molar specific heat, we compute

$$c_{V,N} = \left( \frac{\partial \varepsilon}{\partial T} \right)_v = \frac{1}{2} f R - \frac{a^2 R}{(a + vRT)^2} \quad .$$

**(2.7)** A diatomic gas obeys the equation of state

$$p = \frac{RT}{v-b} - \frac{a}{v^2} + \frac{cRT}{v^3} \quad,$$

where $a$, $b$, and $c$ are constants.

(a) Find the adiabatic equation of state relating temperature $T$ and molar volume $v$.

(b) What is the internal energy per mole, $\varepsilon(T, v)$?

(c) What is the Helmholtz free energy per mole, $f(T, v)$?

Solution :

(a) Let $\varepsilon$ be the molar internal energy and $v$ the molar volume. We have already shown in the lecture notes

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \quad.$$

Thus, for our system,

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_T = \frac{a}{v^2} \quad \Rightarrow \quad \varepsilon(T,v) = \tfrac{5}{2}RT - \frac{a}{v} \quad,$$

where the first term is the result for the rarefied limit $v \to \infty$, where the gas presumably becomes ideal. Now if $s = S/\nu$ is the molar entropy ($\nu = N/N_A$ is the number of moles), then

$$T\,ds = d\varepsilon + p\,dv = \tfrac{5}{2}R\,dT + RT\,\frac{dv}{v-b} + cRT\,\frac{dv}{v^3} \quad.$$

Dividing by $T$ and then integrating, we have

$$s(T,v) = R\ln\left[T^{5/2}(v-b)\,e^{-c/2v^2}\right] + \text{const.} \quad.$$

Thus, the equation of the adiabat is

$$T^{5/2}(v-b)\,e^{-c/2v^2} = \text{const.}$$

(b) We have already obtained the result

$$\varepsilon(T,v) = \tfrac{5}{2}RT - \frac{a}{v} \quad.$$

(c) From $f = \varepsilon - Ts$, where $f = F/\nu$ is the Helmholtz free energy per mole, we have

$$f(T,v) = \tfrac{5}{2}RT - \frac{a}{v} - \tfrac{5}{2}RT\ln\left(\frac{bRT}{a}\right) - RT\ln\left(\frac{v-b}{b}\right) + \frac{cRT}{2v^2} - Ts_0 \quad.$$

Here we have inserted constants with the proper dimensions in order to render our expression for $f$ with the appropriate dimensions. Thus, the constant $s_0$ has dimensions of $\mathrm{J/mol\cdot K}$, the same as the gas constant $R$. Since $c/b^2$ is dimensionless, there is more than one way to do this. Any resulting differences will show up in a different expression for $s_0$.

**(2.8)** A van der Waals gas undergoes an adiabatic free expansion from initial volume $V_i$ to final volume $V_f$. The equation of state is given in the lecture notes. The number of particles $N$ is held constant.

(a) If the initial temperature is $T_i$, what is the final temperature $T_f$?

(b) Find an expression for the change in entropy $\Delta S$ of the gas.

Solution :

(a) This part is done for you in the lecture notes. One finds

$$\Delta T = T_f - T_i = \frac{2a}{fR}\left(\frac{1}{v_f} - \frac{1}{v_i}\right) \quad .$$

(b) Consider a two-legged thermodynamic path, consisting first of a straight leg from $(T_i, V_i)$ to $(T_i, V_f)$, and second of a straight leg from $(T_i, V_f)$ to $(T_f, V_f)$. We then have

$$\Delta S = \overbrace{\int_{V_i}^{V_f} dV \left(\frac{\partial S}{\partial V}\right)_{T_i,N}}^{\Delta S_1} + \overbrace{\int_{T_i}^{T_f} dT \left(\frac{\partial S}{\partial T}\right)_{V_f,N}}^{\Delta S_2} \quad .$$

Along the first leg we use

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{R}{v - b}$$

and we then find

$$\Delta S_1 = R\ln\left(\frac{v_f - b}{v_i - b}\right) \quad .$$

Along the second leg, we have

$$\Delta S_2 = \int_{T_i}^{T_f} dT \left(\frac{\partial S}{\partial T}\right)_{V_f,N} = \int_{T_i}^{T_f} dT \frac{C_{V_f,N}}{T} = \tfrac{1}{2}fR\int_{T_i}^{T_f}\frac{dT}{T} = \tfrac{1}{2}fR\ln\left(\frac{T_f}{T_i}\right) \quad .$$

Thus,

$$\Delta S = R\ln\left(\frac{v_f - b}{v_i - b}\right) + \tfrac{1}{2}fR\ln\left[1 + \frac{2a}{fRT_i}\left(\frac{1}{v_f} - \frac{1}{v_i}\right)\right] \quad .$$

**(2.9)** Recall that a van der Waals gas obeys the equation of state

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad,$$

where $v$ is the molar volume. We showed that the energy per mole of such a gas is given by

$$\varepsilon(T, v) = \tfrac{1}{2}fRT - \frac{a}{v} \quad,$$

where $T$ is temperature and $f$ is the number of degrees of freedom per particle.

(a) For an ideal gas, the adiabatic equation of state is $v\,T^{f/2} = \mathrm{const}$. Find the adiabatic equation of state (at fixed particle number) for the van der Waals gas.

(b) One mole of a van der Waals gas is used as the working substance in a Carnot engine (see Fig. 1). Find the molar volume at $v_{\mathsf{C}}$ in terms of $v_{\mathsf{B}}$, $T_1$, $T_2$, and constants.

(c) Find the heat $Q_{\mathsf{AB}}$ absorbed by the gas from the upper reservoir.

(d) Find the work done per cycle, $W_{\mathsf{cyc}}$. *Hint: you only need to know $Q_{\mathsf{AB}}$ and the cycle efficiency $\eta$.*

Solution :

(a) We have

$$\begin{aligned}
0 = T\,ds &= d\varepsilon + p\,dv \\
&= \tfrac{1}{2}fR\,dT + \left(p + \frac{a}{v^2}\right)dv \\
&= \tfrac{1}{2}fR\,dT + \frac{RT\,dv}{v - b} = \tfrac{1}{2}fRT\,d\ln\!\left[(v - b)\,T^{f/2}\right] \quad,
\end{aligned}$$

where $s = N_{\mathrm{A}}S/N$ is the molar entropy. Thus, the adiabatic equation of state for the van der Waals gas is

$$ds = 0 \quad \Rightarrow \quad (v - b)\,T^{f/2} = \mathrm{const.}$$

Setting $b = 0$, we recover the ideal gas result.

(b) Since BC is an adiabat, we have

$$(v_{\mathsf{B}} - b)\,T_2^{f/2} = (v_{\mathsf{C}} - b)\,T_1^{f/2} \quad \Rightarrow \quad v_{\mathsf{C}} = b + (v_{\mathsf{B}} - b)\left(\frac{T_2}{T_1}\right)^{f/2}$$

(c) We have, from the First Law,

$$Q_{AB} = E_B - E_A + W_{AB}$$

$$= \nu \left( \frac{a}{v_A} - \frac{a}{v_B} \right) + \nu \int_{v_A}^{v_B} dv \, p$$

$$= \nu \left( \frac{a}{v_A} - \frac{a}{v_B} \right) + \nu \int_{v_A}^{v_B} dv \left[ \frac{RT_2}{v - b} - \frac{a}{v^2} \right] \quad ,$$

hence

$$Q_{AB} = \nu RT_2 \ln \left( \frac{v_B - b}{v_A - b} \right)$$

with $\nu = 1$.

(d) Since the cycle is reversible, we must have

$$\eta = \frac{W_{cyc}}{Q_{AB}} \quad \Rightarrow \quad W_{cyc} = \nu R(T_2 - T_1) \ln \left( \frac{v_B - b}{v_A - b} \right)$$

**(2.10)** The *triple point* of a single component thermodynamic system is an isolated point $(T_t, p_t)$ in the $(T, p)$ plane where there is three phase coexistence between solid, liquid, and vapor. Consider three phase coexistence between a pure solid, a pure vapor, and a solution where the solute fraction is $x$. Find the shift $(\Delta T_t, \Delta p_t)$ as a function of $x$, $T_t$, and the quantities $s_{\mathrm{S,L,V}}$ and $v_{\mathrm{S,L,V}}$, *i.e.* the molar entropies and volumes of the three respective phases.

Solution :

At the triple point, we have $\mu_{\mathrm{S}}(T_t, p_t) = \mu_{\mathrm{L}}(T_t, p_t) = \mu_{\mathrm{V}}(T_t, p_t)$, which gives two equations for the two unknowns $T_t$ and $p_t$. We write $T_t = T_t^0 + \Delta T$ and $p_t = p_t^0 + \Delta p$, and we solve

$$\mu_{\mathrm{L}}^0(T_t^0 + \Delta T, p_t^0 + \Delta p) - x k_{\mathrm{B}}(T_t^0 + \Delta T) = \mu_{\mathrm{V}}^0(T_t^0 + \Delta T, p_t^0 + \Delta p)$$
$$\mu_{\mathrm{V}}^0(T_t^0 + \Delta T, p_t^0 + \Delta p) = \mu_{\mathrm{S}}^0(T_t^0 + \Delta T, p_t^0 + \Delta p) \quad,$$

where the $0$ superscript indicates the value for a pure phase. We now expand in the notionally small quantities $\Delta T$ and $\Delta p$, and we use

$$\left(\frac{\partial \mu}{\partial T}\right)_{p,N} = -\left(\frac{\partial S}{\partial N}\right)_{p,T} = -\frac{s}{N_{\mathrm{A}}} \quad , \qquad \left(\frac{\partial \mu}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial N}\right)_{p,T} = \frac{v}{N_{\mathrm{A}}} \quad ,$$

where $s$ and $v$ are the molar entropy and molar volume, respectively. This yields the linear system,

$$\begin{pmatrix} s_{\mathrm{V}} - s_{\mathrm{L}} & v_{\mathrm{L}} - v_{\mathrm{V}} \\ s_{\mathrm{S}} - s_{\mathrm{V}} & v_{\mathrm{V}} - v_{\mathrm{S}} \end{pmatrix} \begin{pmatrix} \Delta T \\ \Delta p \end{pmatrix} = \begin{pmatrix} x R T_t^0 \\ 0 \end{pmatrix} \quad .$$

This yields

$$\Delta T = \frac{(v_{\mathrm{V}} - v_{\mathrm{S}}) \cdot x R T_t^0}{s_{\mathrm{V}}(v_{\mathrm{L}} - v_{\mathrm{S}}) + s_{\mathrm{L}}(v_{\mathrm{S}} - v_{\mathrm{V}}) + s_{\mathrm{S}}(v_{\mathrm{V}} - v_{\mathrm{L}})}$$

$$\Delta p = \frac{(s_{\mathrm{V}} - s_{\mathrm{S}}) \cdot x R T_t^0}{s_{\mathrm{V}}(v_{\mathrm{L}} - v_{\mathrm{S}}) + s_{\mathrm{L}}(v_{\mathrm{S}} - v_{\mathrm{V}}) + s_{\mathrm{S}}(v_{\mathrm{V}} - v_{\mathrm{L}})} \quad .$$

Note that we do not retain terms of order $x \Delta T$, because we have assumed $x$ is small, *i.e.* a weak solution.

**(2.11)** A grocer starts his day with 4 boxes of pears, 5 boxes of oranges, and 6 boxes of apples. Each box contains 24 fruit and is initially completely filled.

(a) At some time, the grocer notes that exactly half the pears, a third of the oranges, and a quarter of the apples have been sold. Assuming that customers take fruit from random positions in each of the boxes, find the dimensionless entropy $\ln W$ of the fruit distribution.

(b) A clumsy customer then topples the table on which the fruit boxes rest, and all the fruit fall to the ground. The customer cleans up the mess, putting all the fruit back into the boxes, but into random locations. What is the entropy of the final state?

Solution :

(a) The grocer starts with 96 pears, 120 oranges, and 144 apples. By the time the grocer checks, 48 pears, 40 oranges, and 36 apples have been removed. The number of ways of doing this is

$$W = \binom{96}{48}\binom{120}{40}\binom{144}{36} = 8.303 \times 10^{93} \quad .$$

Thus, $\ln W = 216.3$.

(b) There are a total of $96 + 120 + 144 = 360$ slots for the fruit, which contain the remaining 48 pears, 120 oranges, and 108 apples. The rest of the slots, which amount to $360 - 48 - 120 - 108 = 84$ in total, are empty. Therefore,

$$W' = \frac{360!}{84! \cdot 48! \cdot 120! \cdot 108!} = 1.093 \times 10^{205} \quad ,$$

and the dimensionless entropy is $\ln W' = 472.1$.

**(2.12)** In a chemical reaction among $\sigma$ species,

$$\zeta_1\, A_1 + \zeta_2\, A_2 + \cdots + \zeta_\sigma\, A_\sigma = 0 \quad ,$$

where $A_a$ is a chemical formula and $\zeta_a$ is a stoichiometric coefficient. When $\zeta_a > 0$, the corresponding $A_a$ is a *product*; when $\zeta_a < 0$, $A_a$ is a *reactant*. (See the lecture notes.) The condition for equilibrium is

$$\sum_{a=1}^{\sigma} \zeta_a\, \mu_a = 0 \quad ,$$

where $\mu_a$ is the chemical potential of the $a^{\text{th}}$ species. The *equilibrium constant* for the reaction is defined as

$$\kappa(T,p) = \prod_{a=1}^{\sigma} x_a^{\zeta_a} \quad ,$$

where $x_a = n_a / \sum_{b=1}^{\sigma} n_b$ is the fraction of species $a$.

(a) Working in the grand canonical ensemble, show that

$$\kappa(T,p) = \prod_{a=1}^{\sigma} \left( \frac{k_{\mathrm{B}} T\, \xi_a(T)}{p \lambda_a^3} \right)^{\zeta_a} \quad .$$

Note that the above expression does not involve any of the chemical potentials $\mu_a$.

(b) Compute the equilibrium constant $\kappa(T,p)$ for the dissociative reaction $N_2 \rightleftharpoons 2\,N$ at $T = 5000\,\mathrm{K}$, assuming the following: the characteristic temperature of rotation and that of vibration of the $N_2$ molecule are $\Theta_{\mathrm{rot}} = 2.84\,\mathrm{K}$ and $\Theta_{\mathrm{vib}} = 3350\,\mathrm{K}$. The dissociation energy, including zero point contributions, is $\Delta = 169.3\,\mathrm{kcal\,mol^{-1}}$. The electronic ground state of $N_2$ has no degeneracy, but that of the N atom is $4$ due to electronic spin.

<span style="color:red">Solution :</span>

<span style="color:blue">(a) In the GCE, we have</span>

$$\Omega\big(T,V,\{\mu_a\}\big) = -k_{\mathrm{B}} T V \sum_{a=1}^{\sigma} \lambda_a^{-3}\, e^{\mu_a/k_{\mathrm{B}}T}\, \xi_a \quad ,$$

<span style="color:blue">where $\lambda_a = (2\pi\hbar^2/m_a k_{\mathrm{B}} T)^{1/2}$ the thermal wavelength for species $a$ and $\xi_a(T)$ is the internal coordinate partition function for species $a$. We then have</span>

$$n_a = -\frac{1}{V} \left( \frac{\partial \Omega}{\partial \mu_a} \right)_{T,V,\mu_{b\neq a}} = z_a\, \lambda_a^{-3}\, \xi_a \quad ,$$

<span style="color:blue">where $z_a = e^{\mu_a/k_{\mathrm{B}}T}$. OK, so we now define</span>

$$x_a = \frac{n_a}{\sum_{b=1}^{\sigma} n_b} = \frac{z_a \lambda_a^{-3} \xi_a}{p/k_{\mathrm{B}}T} = \frac{k_{\mathrm{B}} T\, \xi_a\, z_a}{p\, \lambda_a^3} \quad ,$$

since $\sum_b n_b = -\Omega/V k_{\mathrm{B}}T = p/k_{\mathrm{B}}T$. (Remember $\Omega = -pV$). Therefore

$$\kappa(T,p) \equiv \prod_{a=1}^{\sigma} x_a^{\zeta_a}$$
$$= \prod_{a=1}^{\sigma} \left(\frac{k_{\mathrm{B}}T\,\xi_a}{p\lambda_a^3}\right)^{\zeta_a} \cdot \prod_{a=1}^{\sigma} z_a^{\zeta_a} \quad .$$

However,

$$\prod_{a=1}^{\sigma} z_a^{\zeta_a} = \prod_{a=1}^{\sigma} e^{\zeta_a \mu_a / k_{\mathrm{B}}T} = \exp\left(\frac{1}{k_{\mathrm{B}}T}\sum_{a=1}^{\sigma} \zeta_a\,\mu_a\right) = 1 \quad ,$$

since $\sum_{a=1}^{\sigma} \zeta_a\,\mu_a = 0$.

(b) The internal partition function for N is just $\xi_{\mathrm{N}} = (2S+1)(2I+1)$, where $S = \frac{3}{2}$ is the total electronic spin from Hund's rules, and $I = 1$ is the nuclear spin. It turns out that we will never need to know the value of $I$. For $\mathrm{N}_2$ the internal partition function is

$$\xi_{\mathrm{N}_2} = (2I+1)^2 \cdot \frac{T}{2\Theta_{\mathrm{rot}}} \cdot \frac{e^{\Delta/T}}{1 - e^{-\Theta_{\mathrm{vib}}/T}} \quad .$$

This formula requires some explanation. (See ch. 4 of the lecture notes.) Since $T \gg \Theta_{\mathrm{rot}}$, we have

$$\zeta_g \approx \zeta_u \approx \tfrac{1}{2}\int_0^{\infty} du\, e^{-u\Theta_{\mathrm{rot}}/T} = \frac{T}{2\Theta_{\mathrm{rot}}} \quad ,$$

where the factor of $\frac{1}{2}$ comes from summing only over half the allowed $L$ values, *i.e.* either all even or all odd, and where $u = L(L+1)$ so $du = (2L+1)\,dL$. We then have $\xi_{\mathrm{rot}} = (2I+1)^2 T/2\Theta_{\mathrm{rot}}$ because $g_g + g_u = (2I+1)^2$. The vibrational partition function was derived to be $\xi_{\mathrm{vib}} = \frac{1}{2}\operatorname{csch}(\Theta_{\mathrm{vib}}/2T)$, however since we are including the zero point vibrational energy $\frac{1}{2}\hbar\omega_{\mathrm{vib}} = \frac{1}{2}k_{\mathrm{B}}\Theta_{\mathrm{vib}}$ in the dissociation energy, we get the above expression for $\xi_{\mathrm{N}_2}$. According to our result from part (a), we have

$$\kappa(T,p) = 32 k_{\mathrm{B}}\Theta_{\mathrm{rot}} \cdot e^{-\Delta/T} \cdot \left(1 - e^{-\Theta_{\mathrm{vib}}/T}\right) \cdot \frac{\lambda_{\mathrm{N}_2}^3}{p\lambda_{\mathrm{N}}^6}$$
$$= 16\sqrt{2} \cdot \frac{k_{\mathrm{B}}\Theta_{\mathrm{rot}}}{p\lambda_{\mathrm{N}}^3} \cdot e^{-\Delta/T} \cdot \left(1 - e^{-\Theta_{\mathrm{vib}}/T}\right) \quad .$$

Now we need to evaluate some quantities. The gas constant is

$$R = N_{\mathrm{A}}k_{\mathrm{B}} = 8.314\,\mathrm{J/mol \cdot K} = 1.986 \times 10^{-3}\,\mathrm{kcal/mol \cdot K} \quad ,$$

hence at $T = 5000\,\mathrm{K}$, we have

$$\frac{\Delta}{k_{\mathrm{B}}T} = \frac{(169.3\,\mathrm{kcal/mol})(4184\,\mathrm{J/kcal})}{(8.314\,\mathrm{J/mol \cdot K})(5000\,\mathrm{K})} = 17.0 \quad .$$

Furthermore, $\Theta_{\mathrm{vib}}/T = 0.670$. The thermal wavelength of N at this temperature is found to be

$$\lambda_{\mathrm{N}} = \left(\frac{2\pi \cdot (1.055 \times 10^{-27}\,\mathrm{g\,cm^2/s})^2}{(14\,\mathrm{g}/6.02 \times 10^{23}) \cdot (1.38 \times 10^{-16}\,\mathrm{erg/K}) \cdot 5000\,\mathrm{K}}\right)^{1/2} = 6.60\,\text{Å} \quad .$$

We also have

$$\frac{k_{\mathrm{B}}\Theta_{\mathrm{rot}}}{p\lambda_{\mathrm{N}}^{3}} = \frac{(1.38 \times 10^{-16}\,\mathrm{erg/K}) \cdot (2.84\,\mathrm{K})}{(1.013 \times 10^{6}\,\mathrm{g/cm} \cdot \mathrm{s}^{2})(6.60 \times 10^{-8}\,\mathrm{cm})^{3}} \cdot \frac{p_0}{p} = \frac{1.35\,p_0}{p} \quad ,$$

where $p_0 = 1.013 \times 10^5\,\mathrm{Pa}$ is atmospheric pressure. Putting it all together, we obtain

$$\kappa(T = 5000\,\mathrm{K}, p) = 6.2 \times 10^{-7} \cdot \frac{p_0}{p} \quad .$$

**(2.13)** The phase diagram for a binary *eutectic* system is depicted in Fig. 10. The liquid phase is completely miscible, but the solid phase separates into A-rich $\alpha$ and B-rich $\beta$ phases over a broad range of temperatures and compositions. There is a single chemical composition which solidifies at a temperature lower than any other for this system - the eutectic composition. You are invited to model such a system using the Gibbs free energy densities

$$g_L(T,p,x) = (1-x)\,\mu_L^A(T,p) + x\,\mu_L^B(T,p) + k_B T\Big[x\ln x + (1-x)\ln(1-x)\Big] + \lambda_L\,x(1-x)$$

$$g_S(T,p,x) = (1-x)\,\mu_S^A(T,p) + x\,\mu_S^B(T,p) + k_B T\Big[x\ln x + (1-x)\ln(1-x)\Big] + \lambda_S\,x(1-x) \quad,$$

where $\lambda_L < 0$ and $\lambda_S > 0$. For simplicity, you may assume

$$\mu_L^A(T,p) \approx \mu_L^B(T,p) \equiv \mu_L(T,p)$$
$$\mu_S^A(T,p) \approx \mu_S^B(T,p) \equiv \mu_S(T,p) \quad,$$

with $\mu_S(T,p) = \mu_L(T,p) + r k_B(T-T_0)$, where $r > 0$.



Figure 10: Eutectic phase diagram (from *Wikipedia*). $L$ denotes the liquid phase, and $\alpha$ and $\beta$ are two solid phases.

(a) By sketching the free energies, show that the phase diagram is as shown in Fig. 10.

(b) Solve numerically for the eutectic temperature assuming $\lambda_L = -1$, $\lambda_S = +1$, and $k_B T_0 = 1$, and $r = 0.8$.

**Solution** :

(a) A set of curves illustrating the phenomenon is shown in Fig. 11. We have taken the valus in part (b) of the problem and varied the quantity $k_B T$ (in dimensionless units). For our system, both the liquid and solid free energies are symmetric in $x$ about the point $x = \frac{1}{2}$. At high temperatures, $g_L < g_S$ for all $x$, as shown in the upper left panel of Fig. 11. As the temperature is lowered, $g_S$ starts to dip below $g_L$ at the endpoints $x = 0,1$. For our model and parameters, this happens for $k_B T = k_B T_0 = 1$. Because $\lambda_L > \lambda_S$, the curvature of $g_L(x)$ is greater than that of $g_S(x)$, which means that initially there will be two intersections where $g_L(x) = g_S(x)$, at $x = x^* < \frac{1}{2}$ and $x = 1 - x^* > \frac{1}{2}$. To guarantee thermodynamics stability, one must invoke the Maxwell construction which connects the solid curve at some point $x_1 < x^*$ to the liquid curve at point $x_2 > x^*$, with $x_2 < \frac{1}{2}$. A similar construction follows on the second half of the curve, between $g_L(1 - x_2)$ and $g_S(1 - x_1)$. These two phase regions represent mixtures of the liquid at intermediate concentration and a low or high concentration solid phase. Furthering lower the temperature, the solid curve develops a negative curvature at $x = \frac{1}{2}$ for $k_B T < \frac{1}{2}\lambda_S$. Eventually, the temperature gets
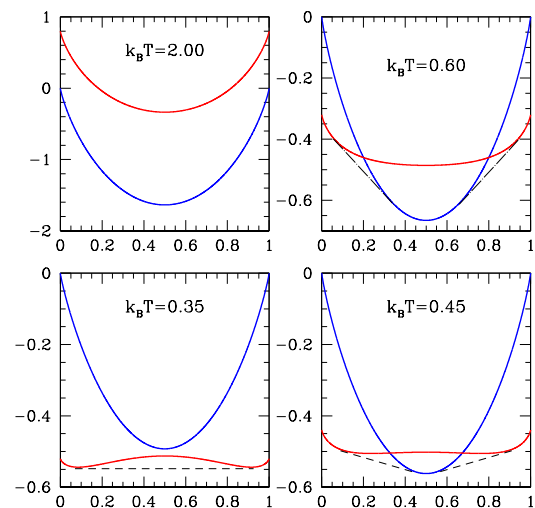


Figure 11: Gibbs free energies for liquid (blue) and solid (red) phases at different temperatures, with Maxwell constructions shown.

so low that $g_S(x)$ lies below $g_L(x)$ for all $x \in [0, 1]$. The system is then in the solid phase, but one must nevertheless invoke a Maxwell construction, as shown in the lower left panel in Fig. 11, between a low-concentration solid at $x = x_3 < \frac{1}{2}$ and a high-concentration solid at $x = 1 - x_3 > \frac{1}{2}$. At such temperatures, the solid is in a homogeneous phase for $x < x_3$ or $x > 1 - x_3$, and in a mixed phase for $x_3 < x < 1 - x_3$.
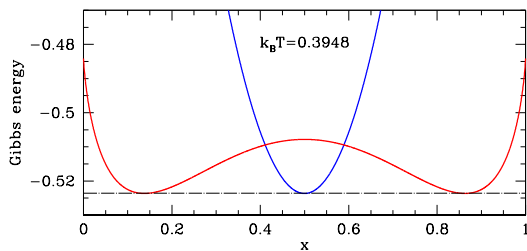


Figure 12: Gibbs free energies for the liquid (blue) and solid (red) phases at the eutectic temperature.

(b) A crude numerical experiment is performed by successively lowering $k_B T$ until the minima of the $g_L(x)$ and $g_S(x)$ curves cross, and then iterating to find the temperature where the minima coincide. In this manner, I find a eutectic temperature $k_B T_e = 0.3948$, as shown in Fig. 12.

## 0.3 Approach to Equilibrium : Worked Examples

**(3.1)** Consider the matrix

$$M = \begin{pmatrix} 4 & 4 \\ -1 & 9 \end{pmatrix} \quad .$$

(a) Find the characteristic polynomial $P(\lambda) = \det(\lambda \mathbb{I} - M)$ and the eigenvalues.

(b) For each eigenvalue $\lambda_\alpha$, find the associated right eigenvector $R_i^\alpha$ and left eigenvector $L_i^\alpha$. Normalize your eigenvectors so that $\langle L^\alpha | R^\beta \rangle = \delta_{\alpha\beta}$.

(c) Show explicitly that $M_{ij} = \sum_\alpha \lambda_\alpha R_i^\alpha L_j^\alpha$.

*Solution :*

(a) The characteristic polynomial is

$$P(\lambda) = \det \begin{pmatrix} \lambda - 4 & -4 \\ 1 & \lambda - 9 \end{pmatrix} = \lambda^2 - 13\lambda + 40 = (\lambda - 5)(\lambda - 8) \quad ,$$

so the two eigenvalues are $\lambda_1 = 5$ and $\lambda_2 = 8$.

(b) Let us write the right eigenvectors as $\vec{R}^\alpha = \begin{pmatrix} R_1^\alpha \\ R_2^\alpha \end{pmatrix}$ and the left eigenvectors as $\vec{L}^\alpha = \begin{pmatrix} L_1^\alpha & L_2^\alpha \end{pmatrix}$. Having found the eigenvalues, we only need to solve four equations:

$$4R_1^1 + 4R_2^1 = 5R_1^1 \quad , \quad 4R_1^2 + 4R_2^2 = 8R_1^2 \quad , \quad 4L_1^1 - L_2^1 = 5L_1^1 \quad , \quad 4L_1^2 - L_2^2 = 8L_1^2 \quad .$$

We are free to choose $R_1^\alpha = 1$ when possible. We must also satisfy the normalizations $\langle L^\alpha | R^\beta \rangle = L_i^\alpha R_i^\beta = \delta^{\alpha\beta}$. We then find

$$\vec{R}^1 = \begin{pmatrix} 1 \\ \frac{1}{4} \end{pmatrix} \quad , \quad \vec{R}^2 = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad , \quad \vec{L}^1 = \begin{pmatrix} \frac{4}{3} & -\frac{4}{3} \end{pmatrix} \quad , \quad \vec{L}^2 = \begin{pmatrix} -\frac{1}{3} & \frac{4}{3} \end{pmatrix} \quad .$$

(c) The projectors onto the two eigendirections are

$$P_1 = |R^1\rangle\langle L^1| = \begin{pmatrix} \frac{4}{3} & -\frac{4}{3} \\ \frac{1}{3} & -\frac{1}{3} \end{pmatrix} \quad , \quad P_2 = |R^2\rangle\langle L^2| = \begin{pmatrix} -\frac{1}{3} & \frac{4}{3} \\ -\frac{1}{3} & \frac{4}{3} \end{pmatrix} \quad .$$

Note that $P_1 + P_2 = \mathbb{I}$. Now construct

$$\lambda_1 P_1 + \lambda_2 P_2 = \begin{pmatrix} 4 & 4 \\ -1 & 9 \end{pmatrix} \quad ,$$

as expected.

**(3.2)** Consider a three-state system with the following transition rates:

$$W_{12} = 0 \quad , \quad W_{21} = \gamma \quad , \quad W_{23} = 0 \quad , \quad W_{32} = 3\gamma \quad , \quad W_{13} = \gamma \quad , \quad W_{31} = \gamma \quad .$$

(a) Find the matrix $\Gamma$ such that $\dot{P}_i = -\Gamma_{ij} P_j$.

(b) Find the equilibrium distribution $P_i^{\text{eq}}$.

(c) Does this system satisfy detailed balance? Why or why not?

Solution :

(a) Following the prescription in the lecture notes, we have

$$\Gamma = \gamma \begin{pmatrix} 2 & 0 & -1 \\ -1 & 3 & 0 \\ -1 & -3 & 1 \end{pmatrix} \quad .$$

(b) Note that summing on the row index yields $\sum_i \Gamma_{ij} = 0$ for any $j$, hence $(1,1,1)$ is a left eigenvector of $\Gamma$ with eigenvalue zero. It is quite simple to find the corresponding right eigenvector. Writing $\vec{\psi}^{\,t} = (a, b, c)$, we obtain the equations $c = 2a$, $a = 3b$, and $a + 3b = c$, the solution of which, with $a + b + c = 1$ for normalization, is $a = \frac{3}{10}$, $b = \frac{1}{10}$, and $c = \frac{6}{10}$. Thus,

$$P^{\text{eq}} = \begin{pmatrix} 0.3 \\ 0.1 \\ 0.6 \end{pmatrix} \quad .$$

(c) The equilibrium distribution does not satisfy detailed balance. Consider for example the ratio $P_1^{\text{eq}}/P_2^{\text{eq}} = 3$. According to detailed balance, this should be the same as $W_{12}/W_{21}$, which is zero for the given set of transition rates.

**(3.3)** A *Markov chain* is a process which describes transitions of a discrete stochastic variable occurring at discrete times. Let $P_i(t)$ be the probability that the system is in state $i$ at time $t$. The evolution equation is

$$P_i(t+1) = \sum_j Q_{ij}\, P_j(t) \quad .$$

The *transition matrix* $Q_{ij}$ satisfies $\sum_i Q_{ij} = 1$ so that the total probability $\sum_i P_i(t)$ is conserved. The element $Q_{ij}$ is the *conditional probability* that for the system to evolve to state $i$ at time $t+1$ given that it was in state $j$ at time $t$. Now consider a group of Physics graduate students consisting of three theorists and four experimentalists. Within each group, the students are to be regarded as indistinguishable. Together, the students rent two apartments, A and B. Initially the three theorists live in A and the four experimentalists live in B. Each month, a random occupant of A and a random occupant of B exchange domiciles. Compute the transition matrix $Q_{ij}$ for this Markov chain, and compute the average fraction of the time that B contains two theorists and two experimentalists, averaged over the effectively infinite time it takes the students to get their degrees. *Hint: $Q$ is a $4 \times 4$ matrix.*

<span style="color:red">Solution:</span>

There are four states available, and they are listed together with their degeneracies in Table 2.

| $\lvert j\rangle$ | room A | room B | $g_j^{\mathrm{A}}$ | $g_j^{\mathrm{B}}$ | $g_j^{\mathrm{TOT}}$ |
|---|---|---|---|---|---|
| $\lvert 1\rangle$ | TTT | EEEE | 1 | 1 | 1 |
| $\lvert 2\rangle$ | TTE | EEET | 3 | 4 | 12 |
| $\lvert 3\rangle$ | TEE | EETT | 3 | 6 | 18 |
| $\lvert 4\rangle$ | EEE | ETTT | 1 | 4 | 4 |

Table 3: States and their degeneracies.

Let's compute the transition probabilities. First, we compute the transition probabilities out of state $\lvert 1\rangle$, *i.e.* the matrix elements $Q_{j1}$. Clearly $Q_{21} = 1$ since we must exchange a theorist (T) for an experimentalist (E). All the other probabilities are zero: $Q_{11} = Q_{31} = Q_{41} = 0$. For transitions out of state $\lvert 2\rangle$, the nonzero elements are

$$Q_{12} = \tfrac{1}{4} \times \tfrac{1}{3} = \tfrac{1}{12} \quad , \quad Q_{22} = \tfrac{3}{4} \times \tfrac{1}{3} + \tfrac{1}{4} \times \tfrac{2}{3} = \tfrac{5}{12} \quad , \quad Q_{32} = \tfrac{1}{2} \quad .$$

To compute $Q_{12}$, we must choose the experimentalist from room A (probability $\tfrac{1}{3}$) with the theorist from room B (probability $\tfrac{1}{4}$). For $Q_{22}$, we can either choose E from A and one of the E's from B, or one of the T's from A and the T from B. This explains the intermediate steps written above. For transitions out of state $\lvert 3\rangle$, the nonzero elements are then

$$Q_{23} = \tfrac{1}{3} \quad , \quad Q_{33} = \tfrac{1}{2} \quad , \quad Q_{43} = \tfrac{1}{6} \quad .$$

Finally, for transitions out of state $\lvert 4\rangle$, the nonzero elements are

$$Q_{34} = \tfrac{3}{4} \quad , \quad Q_{44} = \tfrac{1}{4} \quad .$$

The full transition matrix is then

$$Q = \begin{pmatrix} 0 & \frac{1}{12} & 0 & 0 \\ 1 & \frac{5}{12} & \frac{1}{3} & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} & \frac{3}{4} \\ 0 & 0 & \frac{1}{6} & \frac{1}{4} \end{pmatrix} \quad .$$

Note that $\sum_i Q_{ij} = 1$ for all $j = 1, 2, 3, 4$. This guarantees that $\phi^{(1)} = (1, 1, 1, 1)$ is a left eigenvector of $Q$ with eigenvalue 1. The corresponding right eigenvector is obtained by setting $Q_{ij} \psi_j^{(1)} = \psi_i^{(1)}$. Simultaneously solving these four equations and normalizing so that $\sum_j \psi_j^{(1)} = 1$, we easily obtain

$$\psi^{(1)} = \frac{1}{35} \begin{pmatrix} 1 \\ 12 \\ 18 \\ 4 \end{pmatrix} \quad .$$

This is the state we converge to after repeated application of the transition matrix $Q$. If we decompose $Q = \sum_{\alpha=1}^{4} \lambda_\alpha | \psi^{(\alpha)} \rangle \langle \phi^{(\alpha)} |$, then in the limit $t \to \infty$ we have $Q^t \approx | \psi^{(1)} \rangle \langle \phi^{(1)} |$, where $\lambda_1 = 1$, since the remaining eigenvalues are all less than 1 in magnitude[5]. Thus, $Q^t$ acts as a *projector* onto the state $| \psi^{(1)} \rangle$. Whatever the initial set of probabilities $P_j(t = 0)$, we must have $\langle \phi^{(1)} | P(0) \rangle = \sum_j P_j(0) = 1$. Therefore, $\lim_{t \to \infty} P_j(t) = \psi_j^{(1)}$, and we find $P_3(\infty) = \frac{18}{35}$. Note that the equilibrium distribution satisfies detailed balance:

$$\psi_j^{(1)} = \frac{g_j^{\text{TOT}}}{\sum_l g_l^{\text{TOT}}} \quad .$$

---

[5]One can check that $\lambda_1 = 1$, $\lambda_2 = \frac{5}{12}$, $\lambda_3 = -\frac{1}{4}$. and $\lambda_4 = 0$.

**(3.4)** Suppose I have three bags containing among them four coins. Initially, bag #1 contains a quarter, bag #2 contains a dime, and bag #3 contains two nickels. At each time step, I choose two bags randomly and randomly exchange one coin from each bag. The time evolution satisfies $P_i(t+1) = \sum_j Q_{ij}\, P_j(t)$, where $Q_{ij}$ is the conditional probability $Q_{ij} = P(i\,,\,t+1\,|\,j\,,\,t)$ that the system is in state $i$ at time $t+1$ given that it was in state $j$ at time $t$.

(a) How many configurations are there for this system?

(b) Construct the transition matrix $Q_{ij}$ and verify that $\sum_i Q_{ij} = 1$.

(c) Find the eigenvalues of $Q$ (you may want to use something like `Mathematica`).

(d) Find the equilibrium distribution $P_i^{\mathrm{eq}}$.

Solution :

(a) There are seven possible configurations for this system, shown in Table 4 below.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| bag 1 | Q | Q | D | D | N | N | N |
| bag 2 | D | N | Q | N | Q | D | N |
| bag 3 | NN | DN | NN | QN | DN | QN | DQ |
| $g$ | 1 | 2 | 1 | 2 | 2 | 2 | 2 |

Table 4: Configurations and their degeneracies for problem 3.

(b) The transition matrix is

$$
Q = \begin{pmatrix}
0 & \frac{1}{6} & \frac{1}{3} & 0 & 0 & \frac{1}{6} & 0 \\[4pt]
\frac{1}{3} & \frac{1}{6} & 0 & \frac{1}{6} & \frac{1}{3} & 0 & \frac{1}{6} \\[4pt]
\frac{1}{3} & 0 & 0 & \frac{1}{6} & \frac{1}{6} & 0 & 0 \\[4pt]
0 & \frac{1}{6} & \frac{1}{3} & \frac{1}{6} & 0 & \frac{1}{3} & \frac{1}{6} \\[4pt]
0 & \frac{1}{3} & \frac{1}{3} & 0 & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} \\[4pt]
\frac{1}{3} & 0 & 0 & \frac{1}{3} & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} \\[4pt]
0 & \frac{1}{6} & 0 & \frac{1}{6} & \frac{1}{6} & \frac{1}{6} & \frac{1}{3}
\end{pmatrix}
$$

(c) Interrogating `Mathematica`, I find the eigenvalues are

$$\lambda_1 = 1 \quad,\quad \lambda_2 = -\tfrac{2}{3} \quad,\quad \lambda_3 = \tfrac{1}{3} \quad,\quad \lambda_4 = \tfrac{1}{3} \quad,\quad \lambda_5 = \lambda_6 = \lambda_7 = 0 \quad.$$

(d) We may decompose $Q$ into its left and right eigenvectors, writing

$$Q = \sum_{a=1}^{7} \lambda_a \,|\, R^a \,\rangle\langle\, L^a \,|$$

$$Q_{ij} = \sum_{a=1}^{7} \lambda_a \, R_i^a \, L_j^a$$

The full matrix of left (row) eigenvectors is

$$L = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ -2 & 1 & 2 & -1 & -1 & 1 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 1 \\ 0 & -1 & 0 & 1 & -1 & 1 & 0 \\ 1 & -1 & 1 & -1 & 0 & 0 & 1 \\ 1 & 0 & -1 & -1 & 0 & 1 & 0 \\ -1 & -1 & 1 & 0 & 1 & 0 & 0 \end{pmatrix}$$

The corresponding matrix of right (column) eigenvectors is

$$R = \frac{1}{24} \begin{pmatrix} 2 & -3 & -6 & 0 & 4 & 1 & -5 \\ 4 & 3 & 0 & -6 & -4 & -1 & -7 \\ 2 & 3 & -6 & 0 & 4 & -5 & 1 \\ 4 & -3 & 0 & 6 & -4 & -7 & -1 \\ 4 & -3 & 0 & -6 & -4 & 5 & 11 \\ 4 & 3 & 0 & 6 & -4 & 11 & 5 \\ 4 & 0 & 12 & 0 & 8 & -4 & -4 \end{pmatrix}$$

Thus, we have $RL = LR = \mathbb{I}$, *i.e.* $R = L^{-1}$, and

$$Q = R\,\Lambda\,L \quad,$$

with $\Lambda = \mathrm{diag}\big(1\,,\,-\tfrac{2}{3}\,,\,\tfrac{1}{3}\,,\,\tfrac{1}{3}\,,\,0\,,\,0\,,\,0\big)$.

The right eigenvector corresponding to the $\lambda = 1$ eigenvalue is the equilibrium distribution. We therefore read off the first column of the $R$ matrix:

$$(P^{\mathrm{eq}})^{\mathrm{t}} = \big(\tfrac{1}{12} \quad \tfrac{1}{6} \quad \tfrac{1}{12} \quad \tfrac{1}{6} \quad \tfrac{1}{6} \quad \tfrac{1}{6} \quad \tfrac{1}{6}\big) \quad .$$

Note that

$$P_i^{\mathrm{eq}} = \frac{g_i}{\sum_j g_j} \quad,$$

where $g_j$ is the degeneracy of state $j$ (see Tab. 2). Why is this so? It is because our random choices guarantee that $Q_{ij}\, g_j = Q_{ji}\, g_i$ for each $i$ and $j$ (*i.e.* no sum on repeated indices). Now sum this equation on $j$, and use $\sum_j Q_{ji} = 1$. We obtain $\sum_j Q_{ij}\, g_j = g_i$, which says that the $|\, g \,\rangle$ is a right eigenvector of $Q$ with eigenvalue 1. To obtain the equilibrium probability distribution, we just have to normalize by dividing by $\sum_j g_j$.

**(3.5)** A ball of mass $m$ executes perfect one-dimensional motion along the symmetry axis of a piston. Above the ball lies a mobile piston head of mass $M$ which slides frictionlessly inside the piston. Both the ball and piston head execute ballistic motion, with two types of collision possible: (i) the ball may bounce off the floor, which is assumed to be infinitely massive and fixed in space, and (ii) the ball and piston head may engage in a one-dimensional elastic collision. The Hamiltonian is

$$H = \frac{P^2}{2M} + \frac{p^2}{2m} + MgX + mgx \quad ,$$

where $X$ is the height of the piston head and $x$ the height of the ball. Another quantity is conserved by the dynamics: $\Theta(X - x)$. I.e., the ball always is below the piston head.

(a) Choose an arbitrary length scale $L$, and then energy scale $E_0 = MgL$, momentum scale $P_0 = M\sqrt{gL}$, and time scale $\tau_0 = \sqrt{L/g}$. Show that the dimensionless Hamiltonian becomes

$$\bar{H} = \tfrac{1}{2}\bar{P}^2 + \bar{X} + \frac{\bar{p}^2}{2r} + r\bar{x} \quad ,$$

with $r = m/M$, and with equations of motion $dX/dt = \partial\bar{H}/\partial\bar{P}$, etc. (Here the bar indicates dimensionless variables: $\bar{P} = P/P_0$, $\bar{t} = t/\tau_0$, etc.) What special dynamical consequences hold for $r = 1$?

(b) Compute the microcanonical average piston height $\langle X \rangle$. The analogous dynamical average is

$$\langle X \rangle_T = \lim_{T\to\infty} \frac{1}{T} \int\limits_0^T dt\, X(t) \quad .$$

When computing microcanonical averages, it is helpful to use the Laplace transform, discussed in ch. 3 of the lecture notes. (It is possible to compute the microcanonical average by more brute force methods as well.)

(c) Compute the microcanonical average of the rate of collisions between the ball and the floor. Show that this is given by

$$\left\langle \sum_i \delta(t - t_i) \right\rangle = \left\langle \Theta(v)\, v\, \delta(x - 0^+) \right\rangle \quad .$$

The analogous dynamical average is

$$\langle \gamma \rangle_T = \lim_{T\to\infty} \frac{1}{T} \int\limits_0^T dt \sum_i \delta(t - t_i) \quad ,$$

where $\{t_i\}$ is the set of times at which the ball hits the floor.

(d) How do your results change if you do not enforce the dynamical constraint $X \geq x$?

(e) Write a computer program to simulate this system. The only input should be the mass ratio $r$ (set $\bar{E} = 10$ to fix the energy). You also may wish to input the initial conditions, or perhaps to choose the initial conditions randomly (all satisfying energy conservation, of course!). Have your program compute the microcanonical as well as dynamical averages in parts (b) and (c). Plot out the Poincaré section of $P$ *vs.* $X$ for those times when the ball hits the floor. Investigate this for several values of $r$. Just to show you that this is interesting, I've plotted some of my own numerical results in fig. 13.

Solution:

(a) Once we choose a length scale $L$ (arbitrary), we may define $E_0 = MgL$, $P_0 = M\sqrt{gL}$, $V_0 = \sqrt{gL}$, and $\tau_0 = \sqrt{L/g}$ as energy, momentum, velocity, and time scales, respectively, the result follows directly. Rather than write $\bar{P} = P/P_0$ *etc.*, we will drop the bar notation and write

$$ H = \tfrac{1}{2}P^2 + X + \frac{p^2}{2r} + rx \quad . $$

(b) What is missing from the Hamiltonian of course is the interaction potential between the ball and the piston head. We assume that both objects are impenetrable, so the potential energy is infinite when the two overlap. We further assume that the ball is a point particle (otherwise reset ground level to minus the diameter of the ball). We can eliminate the interaction potential from $H$ if we enforce that each time $X = x$ the ball and the piston head undergo an elastic collision. From energy and momentum conservation, it is easy to derive the elastic collision formulae

$$ P' = \frac{1-r}{1+r} P + \frac{2}{1+r} p $$

$$ p' = \frac{2r}{1+r} P - \frac{1-r}{1+r} p \quad . $$

We can now answer the last question from part (a). When $r = 1$, we have that $P' = p$ and $p' = P$, *i.e.* the ball and piston simply exchange momenta. The problem is then equivalent to two identical particles elastically bouncing off the bottom of the piston, and moving through each other as if they were completely transparent. When the trajectories cross, however, the particles exchange identities.

Averages within the microcanonical ensemble are normally performed with respect to the phase space distribution

$$ \varrho(\varphi) = \frac{\delta\big(E - H(\varphi)\big)}{\text{Tr } \delta\big(E - H(\varphi)\big)} \quad , $$

where $\varphi = (P, X, p, x)$, and

$$ \text{Tr } F(\varphi) = \int\limits_{-\infty}^{\infty} dP \int\limits_{0}^{\infty} dX \int\limits_{-\infty}^{\infty} dp \int\limits_{0}^{\infty} dx \, F(P, X, p, x) \quad . $$

Since $X \geq x$ is a dynamical constraint, we should define an appropriately restricted microcanonical average:

$$ \big\langle F(\varphi) \big\rangle_{\mu\text{ce}} \equiv \widetilde{\text{Tr}} \left[ F(\varphi) \, \delta\big(E - H(\varphi)\big) \right] \Big/ \widetilde{\text{Tr}} \, \delta\big(E - H(\varphi)\big) $$

where

$$ \widetilde{\text{Tr}} \, F(\varphi) \equiv \int\limits_{-\infty}^{\infty} dP \int\limits_{0}^{\infty} dX \int\limits_{-\infty}^{\infty} dp \int\limits_{0}^{X} dx \, F(P, X, p, x) $$
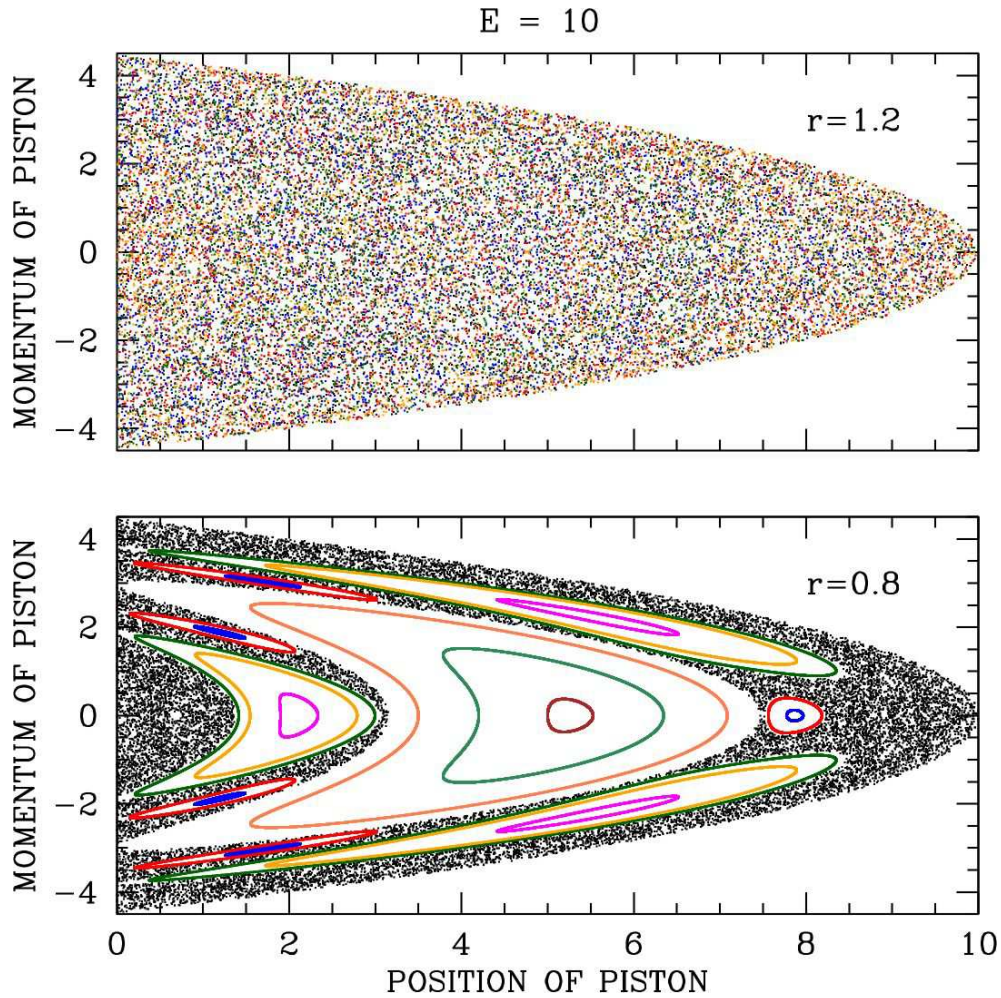
Figure 13: Poincaré sections for the ball and piston head problem. Each color corresponds to a different initial condition. When the mass ratio $r = m/M$ exceeds unity, the system apparently becomes ergodic.

is the modified trace. Note that the integral over $x$ has an upper limit of $X$ rather than $\infty$, since the region of phase space with $x > X$ is *dynamically inaccessible*.

When computing the traces, we shall make use of the following result from the theory of Laplace transforms. The Laplace transform of a function $K(E)$ is

$$\widehat{K}(\beta) = \int_0^\infty dE \, K(E) \, e^{-\beta E} \quad .$$

The inverse Laplace transform is given by

$$K(E) = \int_{c-i\infty}^{c+i\infty} \frac{d\beta}{2\pi i} \, \widehat{K}(\beta) \, e^{\beta E} \quad ,$$

where the integration contour, which is a line extending from $\beta = c - i\infty$ to $\beta = c + i\infty$, lies to the right of any singularities of $\widehat{K}(\beta)$ in the complex $\beta$-plane. For this problem, all we shall need is the following:

$$K(E) = \frac{E^{t-1}}{\Gamma(t)} \quad \Longleftrightarrow \quad \widehat{K}(\beta) = \beta^{-t} \quad .$$

For a proof, see ch. 4 of the lecture notes.

We're now ready to compute the microcanonical average of $X$. We have

$$\langle X \rangle = \frac{N(E)}{D(E)} \quad ,$$

where

$$N(E) = \widetilde{\text{Tr}} \left[ X \, \delta(E - H) \right]$$
$$D(E) = \widetilde{\text{Tr}} \, \delta(E - H) \quad .$$

Let's first compute $D(E)$. To do this, we compute the Laplace transform $\widehat{D}(\beta)$:

$$\widehat{D}(\beta) = \widetilde{\text{Tr}} \, e^{-\beta H}$$

$$= \int_{-\infty}^{\infty} dP \, e^{-\beta P^2/2} \int_{-\infty}^{\infty} dp \, e^{-\beta p^2/2r} \int_{0}^{\infty} dX \, e^{-\beta X} \int_{0}^{X} dx \, e^{-\beta r x}$$

$$= \frac{2\pi\sqrt{r}}{\beta} \int_{0}^{\infty} dX \, e^{-\beta X} \left( \frac{1 - e^{-\beta r X}}{\beta r} \right) = \frac{\sqrt{r}}{1+r} \cdot \frac{2\pi}{\beta^3} \quad .$$

Similarly for $\widehat{N}(\beta)$ we have

$$\widehat{N}(\beta) = \widetilde{\text{Tr}} \, X \, e^{-\beta H}$$

$$= \int_{-\infty}^{\infty} dP \, e^{-\beta P^2/2} \int_{-\infty}^{\infty} dp \, e^{-\beta p^2/2r} \int_{0}^{\infty} dX \, X \, e^{-\beta X} \int_{0}^{X} dx \, e^{-\beta r x}$$

$$= \frac{2\pi\sqrt{r}}{\beta} \int_{0}^{\infty} dX \, X \, e^{-\beta X} \left( \frac{1 - e^{-\beta r X}}{\beta r} \right) = \frac{(2+r) \, r^{3/2}}{(1+r)^2} \cdot \frac{2\pi}{\beta^4} \quad .$$

Taking the inverse Laplace transform, we then have

$$D(E) = \frac{\sqrt{r}}{1+r} \cdot \pi E^2 \quad , \qquad N(E) = \frac{(2+r) \, \sqrt{r}}{(1+r)^2} \cdot \tfrac{1}{3}\pi E^3 \quad .$$

We then have

$$\langle X \rangle = \frac{N(E)}{D(E)} = \left( \frac{2+r}{1+r} \right) \cdot \tfrac{1}{3} E \quad .$$

The 'brute force' evaluation of the integrals isn't so bad either. We have

$$D(E) = \int\limits_{-\infty}^{\infty} dP \int\limits_{0}^{\infty} dX \int\limits_{-\infty}^{\infty} dp \int\limits_{0}^{X} dx \; \delta\big(\tfrac{1}{2}P^2 + \tfrac{1}{2r}p^2 + X + rx - E\big) \quad.$$

To evaluate, define $P = \sqrt{2}\,u_x$ and $p = \sqrt{2r}\,u_y$. Then we have $dP\,dp = 2\sqrt{r}\,du_x\,du_y$ and $\tfrac{1}{2}P^2 + \tfrac{1}{2r}p^2 = u_x^2 + u_y^2$. Now convert to 2D polar coordinates with $w \equiv u_x^2 + u_y^2$. Thus,

$$\begin{aligned}
D(E) &= 2\pi\sqrt{r} \int\limits_{0}^{\infty} dw \int\limits_{0}^{\infty} dX \int\limits_{0}^{X} dx \; \delta\big(w + X + rx - E\big) \\
&= \frac{2\pi}{\sqrt{r}} \int\limits_{0}^{\infty} dw \int\limits_{0}^{\infty} dX \int\limits_{0}^{X} dx \; \Theta(E - w - X)\,\Theta(X + rX - E + w) \\
&= \frac{2\pi}{\sqrt{r}} \int\limits_{0}^{E} dw \int\limits_{\frac{E-w}{1+r}}^{E-w} dX = \frac{2\pi\sqrt{r}}{1+r} \int\limits_{0}^{E} dq\, q = \frac{\sqrt{r}}{1+r}\cdot\pi E^2 \quad,
\end{aligned}$$

with $q = E - w$. Similarly,

$$\begin{aligned}
N(E) &= 2\pi\sqrt{r} \int\limits_{0}^{\infty} dw \int\limits_{0}^{\infty} dX\, X \int\limits_{0}^{X} dx \; \delta\big(w + X + rx - E\big) \\
&= \frac{2\pi}{\sqrt{r}} \int\limits_{0}^{\infty} dw \int\limits_{0}^{\infty} dX\, X \int\limits_{0}^{X} dx \; \Theta(E - w - X)\,\Theta(X + rX - E + w) \\
&= \frac{2\pi}{\sqrt{r}} \int\limits_{0}^{E} dw \int\limits_{\frac{E-w}{1+r}}^{E-w} dX\, X = \frac{2\pi}{\sqrt{r}} \int\limits_{0}^{E} dq \left(1 - \frac{1}{(1+r)^2}\right)\cdot\tfrac{1}{2}q^2 = \left(\frac{2+r}{1+r}\right)\cdot\frac{\sqrt{r}}{1+r}\cdot\tfrac{1}{3}\pi E^3 \quad.
\end{aligned}$$

(c) Using the general result

$$\delta\big(F(x) - A\big) = \sum_i \frac{\delta(x - x_i)}{|F'(x_i)|} \quad,$$

where $F(x_i) = A$, we recover the desired expression. We should be careful not to double count, so to avoid this difficulty we can evaluate $\delta(t - t_i^+)$, where $t_i^+ = t_i + 0^+$ is infinitesimally later than $t_i$. The point here is that when $t = t_i^+$ we have $p = r\,v > 0$ (*i.e.* just after hitting the bottom). Similarly, at times $t = t_i^-$ we have $p < 0$ (*i.e.* just prior to hitting the bottom). Note $v = p/r$. Again we write $\gamma(E) = N(E)/D(E)$, this time with

$$N(E) = \widetilde{\mathrm{Tr}}\left[\Theta(p)\,r^{-1}p\,\delta(x - 0^+)\,\delta(E - H)\right] \quad.$$

The Laplace transform is

$$\widehat{N}(\beta) = \int_{-\infty}^{\infty} dP \, e^{-\beta P^2/2} \int_0^{\infty} dp \, r^{-1} \, p \, e^{-\beta p^2/2r} \int_0^{\infty} dX \, e^{-\beta X}$$

$$= \sqrt{\frac{2\pi}{\beta}} \cdot \frac{1}{\beta} \cdot \frac{1}{\beta} = \sqrt{2\pi} \, \beta^{-5/2} \quad .$$

Thus,

$$N(E) = \tfrac{4\sqrt{2}}{3} \, E^{3/2}$$

and

$$\langle \gamma \rangle = \frac{N(E)}{D(E)} = \tfrac{4\sqrt{2}}{3\pi} \left( \frac{1+r}{\sqrt{r}} \right) E^{-1/2} \quad .$$

(d) When the constraint $X \geq x$ is removed, we integrate over all phase space. We then have

$$\widehat{D}(\beta) = \mathsf{Tr} \, e^{-\beta H}$$

$$= \int_{-\infty}^{\infty} dP \, e^{-\beta P^2/2} \int_{-\infty}^{\infty} dp \, e^{-\beta p^2/2r} \int_0^{\infty} dX \, e^{-\beta X} \int_0^{\infty} dx \, e^{-\beta rx} = \frac{2\pi\sqrt{r}}{\beta^3} \quad .$$

For part (b) we would then have

$$\widehat{N}(\beta) = \mathsf{Tr} \, X \, e^{-\beta H}$$

$$= \int_{-\infty}^{\infty} dP \, e^{-\beta P^2/2} \int_{-\infty}^{\infty} dp \, e^{-\beta p^2/2r} \int_0^{\infty} dX \, X \, e^{-\beta X} \int_0^{\infty} dx \, e^{-\beta rx} = \frac{2\pi\sqrt{r}}{\beta^4} \quad .$$

The respective inverse Laplace transforms are $D(E) = \pi\sqrt{r} \, E^2$ and $N(E) = \frac{1}{3}\pi\sqrt{r} \, E^3$. The microcanonical average of $X$ would then be

$$\langle X \rangle = \tfrac{1}{3} E \quad .$$

Using the restricted phase space, we obtained a value which is greater than this by a factor of $(2+r)/(1+r)$. That the restricted average gives a larger value makes good sense, since $X$ is not allowed to descend below $x$ in that case. For part (c), we would obtain the same result for $N(E)$ since $x = 0$ in the average. We would then obtain

$$\langle \gamma \rangle = \tfrac{4\sqrt{2}}{3\pi} \, r^{-1/2} E^{-1/2} \quad .$$

The restricted microcanonical average yields a rate which is larger by a factor $1 + r$. Again, it makes good sense that the restricted average should yield a higher rate, since the ball is not allowed to attain a height greater than the instantaneous value of $X$.

(e) It is straightforward to simulate the dynamics. So long as $0 < x(t) < X(t)$, we have

$$\dot{X} = P \quad , \quad \dot{P} = -1 \quad , \quad \dot{x} = \frac{p}{r} \quad , \quad \dot{p} = -r \quad .$$

Starting at an arbitrary time $t_0$, these equations are integrated to yield

$$X(t) = X(t_0) + P(t_0)(t - t_0) - \tfrac{1}{2}(t - t_0)^2$$
$$P(t) = P(t_0) - (t - t_0)$$
$$x(t) = x(t_0) + \frac{p(t_0)}{r}(t - t_0) - \tfrac{1}{2}(t - t_0)^2$$
$$p(t) = p(t_0) - r(t - t_0) \quad .$$

We must stop the evolution when one of two things happens. The first possibility is a bounce at $t = t_{\rm b}$, meaning $x(t_{\rm b}) = 0$. The momentum $p(t)$ changes discontinuously at the bounce, with $p(t_{\rm b}^+) = -p(t_{\rm b}^-)$, and where $p(t_{\rm b}^-) < 0$ necessarily. The second possibility is a collision at $t = t_{\rm c}$, meaning $X(t_{\rm c}) = x(t_{\rm c})$. Integrating across the collision, we must conserve both energy and momentum. This means

$$P(t_{\rm c}^+) = \frac{1-r}{1+r}P(t_{\rm c}^-) + \frac{2}{1+r}p(t_{\rm c}^-)$$

$$p(t_{\rm c}^+) = \frac{2r}{1+r}P(t_{\rm c}^-) - \frac{1-r}{1+r}p(t_{\rm c}^-) \quad .$$

| $r$ | $X(0)$ | $\langle X(t)\rangle$ | $\langle X\rangle_{\mu\mathrm{ce}}$ | $\langle\gamma(t)\rangle$ | $\langle\gamma\rangle_{\mu\mathrm{ce}}$ | $r$ | $X(0)$ | $\langle X(t)\rangle$ | $\langle X\rangle_{\mu\mathrm{ce}}$ | $\langle\gamma(t)\rangle$ | $\langle\gamma\rangle_{\mu\mathrm{ce}}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.3 | 0.1 | 6.1743 | 5.8974 | 0.5283 | 0.4505 | 1.2 | 0.1 | 4.8509 | 4.8545 | 0.3816 | 0.3812 |
| 0.3 | 1.0 | 5.7303 | 5.8974 | 0.4170 | 0.4505 | 1.2 | 1.0 | 4.8479 | 4.8545 | 0.3811 | 0.3812 |
| 0.3 | 3.0 | 5.7876 | 5.8974 | 0.4217 | 0.4505 | 1.2 | 3.0 | 4.8493 | 4.8545 | 0.3813 | 0.3812 |
| 0.3 | 5.0 | 5.8231 | 5.8974 | 0.4228 | 0.4505 | 1.2 | 5.0 | 4.8482 | 4.8545 | 0.3813 | 0.3812 |
| 0.3 | 7.0 | 5.8227 | 5.8974 | 0.4228 | 0.4505 | 1.2 | 7.0 | 4.8472 | 4.8545 | 0.3808 | 0.3812 |
| 0.3 | 9.0 | 5.8016 | 5.8974 | 0.4234 | 0.4505 | 1.2 | 9.0 | 4.8466 | 4.8545 | 0.3808 | 0.3812 |
| 0.3 | 9.9 | 6.1539 | 5.8974 | 0.5249 | 0.4505 | 1.2 | 9.9 | 4.8444 | 4.8545 | 0.3807 | 0.3812 |

Table 5: Comparison of time averages and microcanonical ensemble averages for $r = 0.3$ and $r = 1.2$. Initial conditions are $P(0) = x(0) = 0$, with $X(0)$ given in the table and $E = 10$. Averages were performed over a period extending for $N_{\rm b} = 10^7$ bounces.

In the following tables I report on the results of numerical simulations, comparing dynamical averages with (restricted) phase space averages within the microcanonical ensemble. For $r = 0.3$ the microcanonical averages poorly approximate the dynamical averages, and the dynamical averages are dependent on the initial conditions, indicating that the system is not ergodic. For $r = 1.2$, the agreement between dynamical and microcanonical averages generally improves with averaging time. Indeed, it has been shown by N. I. Chernov, *Physica D* **53**, 233 (1991), building on the work of M. P. Wojtkowski, *Comm. Math. Phys.* **126**, 507 (1990) that this system is ergodic for $r > 1$. Wojtkowski also showed that this system is equivalent to the *wedge billiard*, in which a single point particle of mass $m$ bounces inside a two-dimensional wedge-shaped region $\{(x, y) \,|\, x \geq 0 \,,\, y \geq x\,\mathrm{ctn}\,\phi\}$ for some fixed angle $\phi = \tan^{-1}\sqrt{\frac{m}{M}}$.

To see this, pass to relative ($\mathcal{X}$) and center-of-mass ($\mathcal{Y}$) coordinates,

$$\mathcal{X} = X - x \qquad\qquad \mathcal{P}_x = \frac{mP - Mp}{M + m}$$

$$\mathcal{Y} = \frac{MX + mx}{M + m} \qquad\qquad \mathcal{P}_y = P + p \quad .$$

Then

$$H = \frac{(M+m)\,\mathcal{P}_x^2}{2Mm} + \frac{\mathcal{P}_y^2}{2(M+m)} + (M+m)\,g\mathcal{Y} \quad .$$

There are two constraints. One requires $X \geq x$, *i.e.* $\mathcal{X} \geq 0$. The second requires $x > 0$, *i.e.*

$$x = \mathcal{Y} - \frac{M}{M+m}\,\mathcal{X} \geq 0 \quad .$$
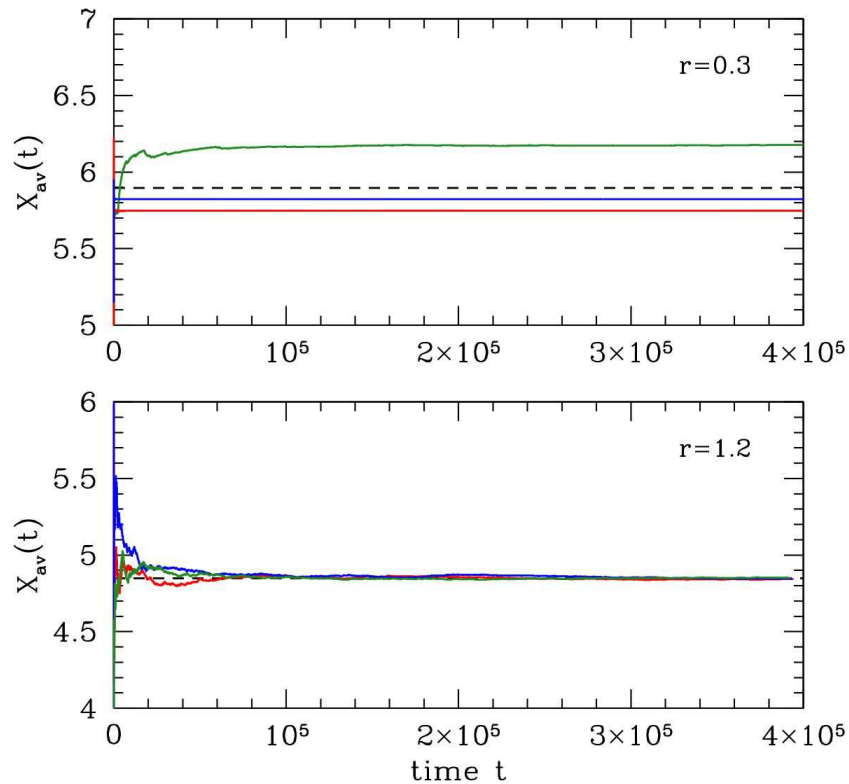


Figure 14: Long time running numerical averages $X_{\mathrm{av}}(t) \equiv t^{-1}\int_0^t dt'\, X(t')$ for $r = 0.3$ (top) and $r = 1.2$ (bottom), each for three different initial conditions, with $E = 10$ in all cases. Note how in the $r = 0.3$ case the long time average is dependent on the initial condition, while the $r = 1.2$ case is ergodic and hence independent of initial conditions. The dashed black line shows the restricted microcanonical average, $\langle X \rangle_{\mu\mathrm{ce}} = \frac{(2+r)}{(1+r)} \cdot \frac{1}{3}E$.

Now define $\mathsf{x} \equiv \mathcal{X}$, $\mathsf{p}_x \equiv \mathcal{P}_x$, and rescale $\mathsf{y} \equiv \frac{M+m}{\sqrt{Mm}} \, \mathcal{Y}$ and $\mathsf{p}_y \equiv \frac{\sqrt{Mm}}{M+m} \, \mathcal{P}_y$ to obtain

$$H = \frac{1}{2\mu} \left( \mathsf{p}_x^2 + \mathsf{p}_y^2 \right) + \mathsf{M} \, g \, \mathsf{y}$$

with $\mu = \frac{Mm}{M+m}$ the familiar reduced mass and $\mathsf{M} = \sqrt{Mm}$. The constraints are then $\mathsf{x} \geq 0$ and $\mathsf{y} \geq \sqrt{\frac{M}{m}}\mathsf{x}$.

| $r$ | $X(0)$ | $N_{\mathrm{b}}$ | $\langle X(t) \rangle$ | $\langle X \rangle_{\mu\mathrm{ce}}$ | $\langle \gamma(t) \rangle$ | $\langle \gamma \rangle_{\mu\mathrm{ce}}$ |
|---|---|---|---|---|---|---|
| 1.2 | 7.0 | $10^4$ | 4.8054892 | 4.8484848 | 0.37560388 | 0.38118510 |
| 1.2 | 7.0 | $10^5$ | 4.8436969 | 4.8484848 | 0.38120356 | 0.38118510 |
| 1.2 | 7.0 | $10^6$ | 4.8479414 | 4.8484848 | 0.38122778 | 0.38118510 |
| 1.2 | 7.0 | $10^7$ | 4.8471686 | 4.8484848 | 0.38083749 | 0.38118510 |
| 1.2 | 7.0 | $10^8$ | 4.8485825 | 4.8484848 | 0.38116282 | 0.38118510 |
| 1.2 | 7.0 | $10^9$ | 4.8486682 | 4.8484848 | 0.38120259 | 0.38118510 |
| 1.2 | 1.0 | $10^9$ | 4.8485381 | 4.8484848 | 0.38118069 | 0.38118510 |
| 1.2 | 9.9 | $10^9$ | 4.8484886 | 4.8484848 | 0.38116295 | 0.38118510 |

Table 6: Comparison of time averages and microcanonical ensemble averages for $r = 1.2$, with $N_{\mathrm{b}}$ ranging from $10^4$ to $10^9$.

**(3.6)** Consider a toroidal phase space $(x, p) \in \mathbb{T}^2$. You can describe the torus as a square $[0, 1] \times [0, 1]$ with opposite sides identified. Design your own modified Arnold cat map acting on this phase space, *i.e.* a $2 \times 2$ matrix with integer coefficients and determinant 1.

(a) Start with an initial distribution localized around the center – say a disc centered at $(\frac{1}{2}, \frac{1}{2})$. Show how these initial conditions evolve under your map. Can you tell whether your dynamics are mixing?

(b) Now take a pixelated image. For reasons discussed in the lecture notes, this image should exhibit Poincaré recurrence. Can you see this happening?

Solution :

(a) Any map

$$
\begin{pmatrix} x' \\ p' \end{pmatrix} = \overbrace{\begin{pmatrix} a & b \\ c & d \end{pmatrix}}^{M} \begin{pmatrix} x \\ p \end{pmatrix} \quad ,
$$

will do, provided $a, b, c, d \in \mathbb{Z}$ and $\det M = ad - bc = 1$. Such matrices are said to be elements of the *modular group*: $M \in \mathsf{SL}(2, \mathbb{Z})$. Arnold's cat map $M = \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}$ and its generalizations $M = \begin{pmatrix} 1 & 1 \\ p & p+1 \end{pmatrix}$ are modular transformations. Starting from an initial square distribution, we iterate the map up to three times and show the results in Fig. 15. The numerical results are consistent with a mixing flow. (With just a few further interations, almost the entire torus is covered.)

(c) A pixelated image exhibits Poincaré recurrence, as we see in Fig. 16.

**(3.7)** Consider a modified version of the Kac ring model where each spin exists in one of three states: A, B, or C. The flippers rotate the internal states cyclically: A→B→C→A.

(a) What is the Poincaré recurrence time for this system? *Hint:* the answer depends on whether or not the total number of flippers is a multiple of 3.

(b) Simulate the system numerically. Choose a ring size on the order of $N = 10,000$ and investigate a few flipper densities: $x = 0.001$, $x = 0.01$, $x = 0.1$, $x = 0.99$. Remember that the flippers are located randomly at the start, but do not move as the spins evolve. Starting from a configuration where all the spins are in the A state, plot the probabilities $p_A(t)$, $p_B(t)$, and $p_C(t)$ *versus* the discrete time coordinate $t$, with $t$ ranging from 0 to the recurrence time. If you can, for each value of $x$, plot the three probabilities in different colors or line characteristics (*e.g.* solid, dotted, dashed) on the same graph.

(c) Let's call $a_t = p_A(t)$, *etc.* Explain in words why the *Stosszahlansatz* results in the equations

$$a_{t+1} = (1-x)\,a_t + x\,c_t$$
$$b_{t+1} = (1-x)\,b_t + x\,a_t$$
$$c_{t+1} = (1-x)\,c_t + x\,b_t \quad .$$

This describes what is known as a *Markov process*, which is governed by coupled equations of the
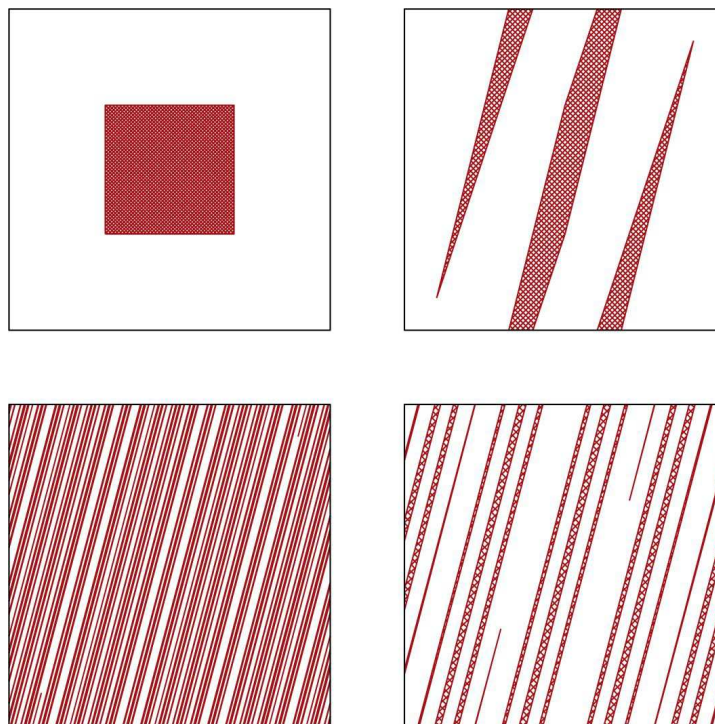


Figure 15:  Zeroth, first, second, and third iterates of the generalized cat map with $p = 2$, acting on an initial square distribution (clockwise from upper left).
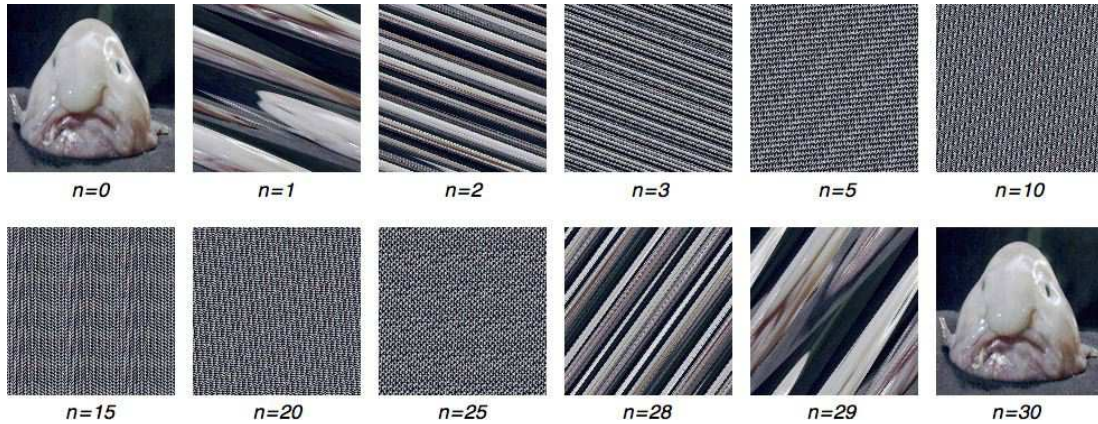
Figure 16: Evolution of a pixelated blobfish under the $p = 2$ generalized cat map.

form $P_i(t + 1) = \sum_j Q_{ij} P_j(t)$, where $Q$ is the *transition matrix*. Find the $3 \times 3$ transition matrix for this Markov process.

(d) Show that the total probability is conserved by a Markov process if $\sum_i Q_{ij} = 1$ and verify this is the case for the equations in (c).

(e) One can then eliminate $c_t = 1 - a_t - b_t$ and write these as two coupled equations. Show that if we define

$$\tilde{a}_t \equiv a_t - \tfrac{1}{3} \quad , \quad \tilde{b}_t \equiv b_t - \tfrac{1}{3} \quad , \quad \tilde{c}_t \equiv c_t - \tfrac{1}{3}$$

that we can write

$$\begin{pmatrix} \tilde{a}_{t+1} \\ \tilde{b}_{t+1} \end{pmatrix} = R \begin{pmatrix} \tilde{a}_t \\ \tilde{b}_t \end{pmatrix} \quad ,$$

and find the $2 \times 2$ matrix $R$. Note that this is *not* a Markov process in A and B, since total probability for the A and B states is not itself conserved. Show that the eigenvalues of $R$ form a complex conjugate pair. Find the amplitude and phase of these eigenvalues. Show that the amplitude never exceeds unity.

(f) The fact that the eigenvalues of $R$ are complex means that the probabilities should *oscillate* as they decay to their equilibrium values $p_A = p_B = p_C = \tfrac{1}{3}$. Can you see this in your simulations?

**Solution :**

(a) If the number of flippers $N_f$ is a multiple of 3, then each spin will have made an integer number of complete cyclic changes A→B→C→A after one complete passage around the ring. The recurrence time is then $N$, where $N$ is the number of sites. If the number of flippers $N_f$ is not a multiple of 3, then the recurrence time is simply $3N$.

(b) See figs. 17, 18, 19.

(c) According to the *Stosszahlansatz*, the probability $a_{t+1}$ that a given spin will be in state A at time $(t+1)$ is the probability $a_t$ it was in A at time $t$ times the probability $(1 - x)$ that it did not encounter a flipper,
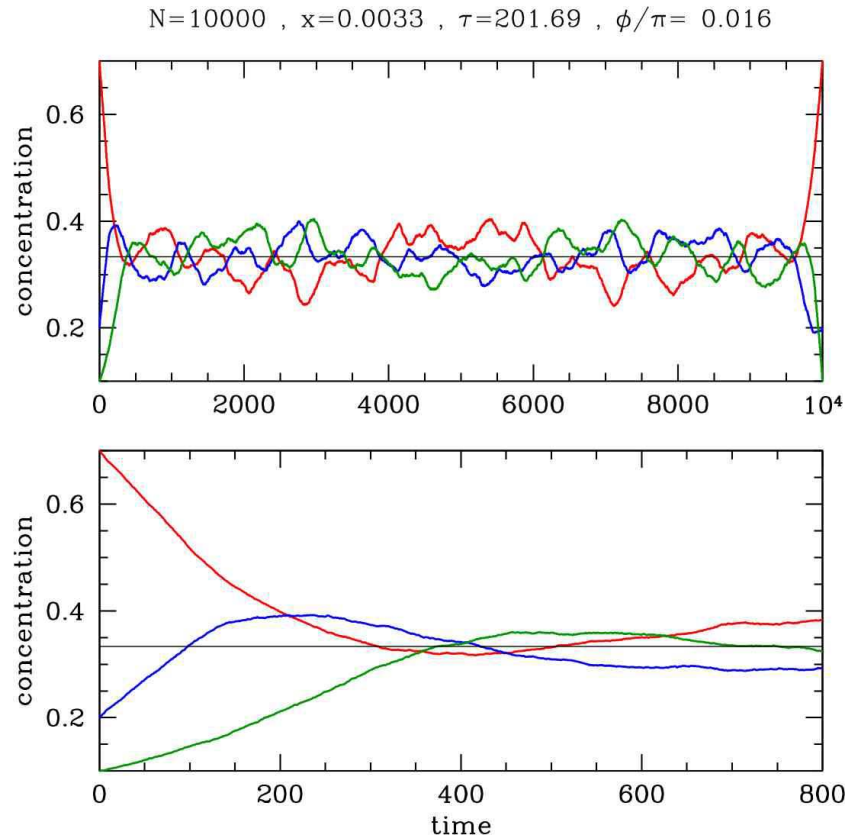
Figure 17:   Simulation of three state Kac ring model with initial conditions $a_{t=0} = 0.7$, $b_{t=0} = 0.2$, $c_{t=0} = 0.1$. Note the oscillations as equilibrium is approached.

plus the probability $c_t$ it was in state C at time $t$ times the probability $x$ that it did encounter a flipper. This explains the first equation. The others follow by cyclic permutation. The transition matrix is

$$Q = \begin{pmatrix} 1-x & 0 & x \\ x & 1-x & 0 \\ 0 & x & 1-x \end{pmatrix} \quad .$$

(d) The total probability is $\sum_i P_i$. Assuming $\sum_i Q_{ij} = 1$, we have

$$\sum_i P_i(t+1) = \sum_i \sum_j Q_{ij} P_j(t) = \sum_j \left( \sum_i Q_{ij} \right) P_j(t) = \sum_j P_j(t)$$

and the total probability is conserved. That's a Good Thing.

(e) Substituting $a_t = \tilde{a}_t + \frac{1}{3}$, etc. into the Markov process and eliminating $\tilde{c}_t = -(\tilde{a}_t + \tilde{b}_t)$, we obtain

$$R = \begin{pmatrix} 1-2x & -x \\ x & 1-x \end{pmatrix} \quad .$$
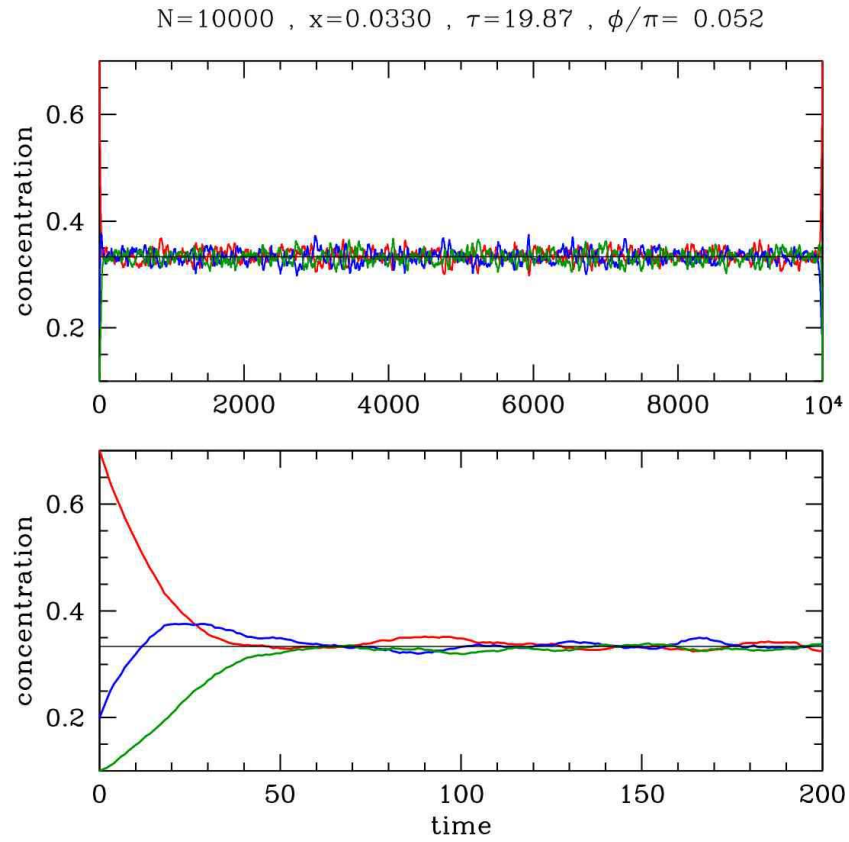
Figure 18: Simulation of three state Kac ring model with initial conditions $a_{t=0} = 0.7$, $b_{t=0} = 0.2$, $c_{t=0} = 0.1$.

The characteristic polynomial for $R$ is

$$P(\lambda) = \det\left(\lambda \cdot 1 - R\right) = (\lambda - 1 + 2x)(\lambda - 1 + x) + x^2$$
$$= \lambda^2 - (2 - 3x)\,\lambda + (1 - 3x + 3x^2) \quad .$$

The eigenvalues are the two roots of $P(\lambda)$:

$$\lambda_\pm = 1 - \tfrac{3}{2}x \pm i\tfrac{\sqrt{3}}{2}x \quad .$$

Note that we can write

$$\lambda_\pm(x) = e^{-1/\tau(x)}\,e^{\pm i\phi(x)}$$

where

$$\tau(x) = -\frac{2}{\ln\left(1 - 3x + 3x^2\right)} \quad , \qquad \phi(x) = \tan^{-1}\left(\frac{\sqrt{3}\,x}{2 - 3x}\right) \quad .$$

Since $x(1 - x)$ achieves its maximum volume on the unit interval $x \in [0, 1]$ at $x = \tfrac{1}{2}$, where $x(1 - x) = \tfrac{1}{4}$, we see that $\tfrac{1}{2} \leq |\lambda(x)| \leq 1$, hence $0 \leq \tau(x) \leq \ln 2$. We plot $\tau(x)$ and $\phi(x)$ in fig. 19.

If you managed to get this far, then you've done all that was asked. However, one can go farther and analytically solve the equations for the Markov chain. In so doing, we will discuss the linear algebraic aspects of the problem.

The matrix $R$ is real but not symmetric. For such a matrix, the characteristic polynomial satisfies $\left[P(\lambda)\right]^* = P(\lambda^*)$, hence if $\lambda$ is a root of $P(\lambda = 0)$, which is to say $\lambda$ is an eigenvalue, then so is $\lambda^*$. Accordingly, the eigenvalues of a real asymmetric matrix are either real or come in complex conjugate pairs. We can decompose such a matrix $R$ as a sum over its eigenvectors,

$$R_{ij} = \sum_\alpha \lambda_\alpha \, \psi_i^\alpha \, \phi_j^\alpha \quad,$$

where

$$\sum_j R_{ij} \, \psi_j^\alpha = \lambda_\alpha \, \psi_i^\alpha$$

$$\sum_i \phi_i^\alpha \, R_{ij} = \lambda_\alpha \, \phi_j^\alpha \quad.$$

Thus, $\psi_j^\alpha$ is the $j^{\text{th}}$ component of the $\alpha^{\text{th}}$ *right eigenvector* of $R$, while $\phi_i^\alpha$ is the $i^{\text{th}}$ component of the $\alpha^{\text{th}}$ *left eigenvector* of $R$. Note that $\phi^\alpha$ is a right eigenvector for the transposed matrix $R^{\text{t}}$. We can further impose the normalization condition,

$$\left\langle \phi^\alpha \,\middle|\, \psi^\beta \right\rangle = \sum_i \psi_i^\alpha \, \phi_i^\beta = \delta^{\alpha\beta} \quad.$$



Figure 19: Phase angle and relaxation time for the three state Kac ring model with *Stosszahlansatz.*
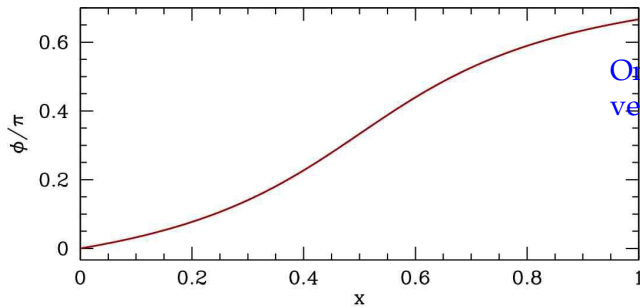
One can check that the following assignment of eigenvectors is valid for our $R(x)$ matrix:

$$\vec{\psi}_+ = \begin{pmatrix} 1 \\ -e^{i\pi/3} \end{pmatrix}$$
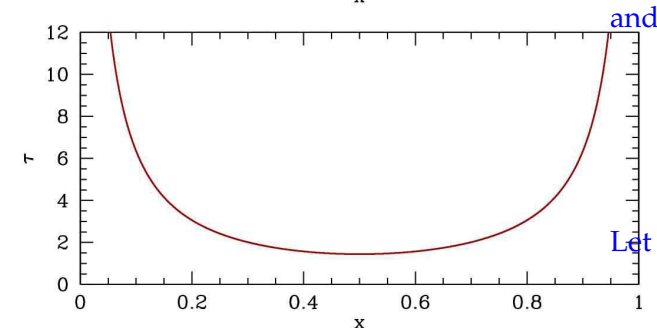
$$\vec{\phi}_+ = \tfrac{1}{\sqrt{3}} \, e^{i\pi/6} \begin{pmatrix} 1 & e^{i\pi/3} \end{pmatrix} \quad.$$

and

$$\vec{\psi}_- = \begin{pmatrix} 1 \\ -e^{-i\pi/3} \end{pmatrix}$$

$$\vec{\phi}_+ = \tfrac{1}{\sqrt{3}} \, e^{-i\pi/6} \begin{pmatrix} 1 & e^{-i\pi/3} \end{pmatrix} \quad.$$

Let us write the vector

$$\vec{\eta}_t = \begin{pmatrix} \tilde{a}_t \\ \tilde{b}_t \end{pmatrix} \quad.$$

We then may expand $\vec{\eta}_t$ in the right eigenvectors of $R$, writing

$$\vec{\eta}_t = \sum_\alpha C_\alpha \, \lambda_\alpha^t \, \vec{\psi}^\alpha \quad.$$

Suppose we begin in a state where $a_{t=0} = 1$ and $b_{t=0} = c_{t=0} = 0$. Then we have $\tilde{a}_{t=0} = \frac{2}{3}$ and $\tilde{b}_{t=0} = -\frac{1}{3}$, hence

$$C_\alpha = \langle \vec{\phi}^\alpha \mid \begin{pmatrix} +2/3 \\ -1/3 \end{pmatrix} \rangle \quad .$$

We thereby find $C_+ = C_- = \frac{1}{3}$, and

$$\tilde{a}_t = \tfrac{2}{3} \, e^{-t/\tau} \, \cos\left(t\,\phi\right)$$
$$\tilde{b}_t = \tfrac{2}{3} \, e^{-t/\tau} \, \sin\left(t\,\phi - \tfrac{\pi}{6}\right) \quad ,$$

with $\tilde{c}_t = -\left(\tilde{a}_t + \tilde{b}_t\right)$.

(f) Yes! The oscillation is particularly clear in the lower panel of fig. 17.

**(3.8)** Consider a spin singlet formed by two $S = \frac{1}{2}$ particles, $|\Psi\rangle = \frac{1}{\sqrt{2}}(|\uparrow_A \downarrow_B\rangle - |\downarrow_A \uparrow_B\rangle)$. Find the reduced density matrix, $\rho_A = \text{Tr}_B |\Psi\rangle\langle\Psi|$.

Solution :

We have

$$|\Psi\rangle\langle\Psi| = \tfrac{1}{2}|\uparrow_A \downarrow_B\rangle\langle\uparrow_A \downarrow_B| + \tfrac{1}{2}|\downarrow_A \uparrow_B\rangle\langle\downarrow_A \uparrow_B| - \tfrac{1}{2}|\uparrow_A \downarrow_B\rangle\langle\downarrow_A \uparrow_B| - \tfrac{1}{2}|\downarrow_A \uparrow_B\rangle\langle\uparrow_A \downarrow_B| \quad .$$

Now take the trace over the spin degrees of freedom on site B. Only the first two terms contribute, resulting in the reduced density matrix

$$\rho_A = \text{Tr}_B |\Psi\rangle\langle\Psi| = \tfrac{1}{2}|\uparrow_A\rangle\langle\uparrow_A| + \tfrac{1}{2}|\downarrow_A\rangle\langle\downarrow_A| \quad .$$

Note that $\text{Tr}\,\rho_A = 1$, but whereas the full density matrix $\rho = \text{Tr}_B |\Psi\rangle\langle\Psi|$ had one eigenvalue of $1$, corresponding to eigenvector $|\Psi\rangle$, and three eigenvalues of $0$, corresponding to any state orthogonal to $|\Psi\rangle$, the reduced density matrix $\rho_A$ does not correspond to a 'pure state' in that it is not a projector. It has two degenerate eigenvalues at $\lambda = \frac{1}{2}$. The quantity $S_A = -\text{Tr}\,\rho_A \ln \rho_A = \ln 2$ is the *quantum entanglement entropy* for the spin singlet.

## 0.4 Statistical Ensembles

**(4.1)** Consider a system of $N$ identical but distinguishable particles, each of which has a nondegenerate ground state with energy zero, and a $g$-fold degenerate excited state with energy $\varepsilon > 0$.

(a) Let the total energy of the system be fixed at $E = M\varepsilon$, where $M$ is the number of particles in an excited state. What is the total number of states $\Omega(E, N)$?

(b) What is the entropy $S(E, N)$? Assume the system is thermodynamically large. You may find it convenient to define $\nu \equiv M/N$, which is the fraction of particles in an excited state.

(c) Find the temperature $T(\nu)$. Invert this relation to find $\nu(T)$.

(d) Show that there is a region where the temperature is negative.

(e) What happens when a system at negative temperature is placed in thermal contact with a heat bath at positive temperature?

Solution :

(a) Since each excited particle can be in any of $g$ degenerate energy states, we have

$$\Omega(E, N) = \binom{N}{M} g^M = \frac{N! \, g^M}{M! \, (N - M)!} \quad .$$

(b) Using Stirling's approximation, we have

$$S(E, N) = k_{\mathrm{B}} \ln \Omega(E, N) = -N k_{\mathrm{B}} \Big\{ \nu \ln \nu + (1 - \nu) \ln(1 - \nu) - \nu \ln g \Big\} \quad ,$$

where $\nu = M/N = E/N\varepsilon$.

(c) The inverse temperature is

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_N = \frac{1}{N\varepsilon} \left( \frac{\partial S}{\partial \nu} \right)_N = \frac{k_{\mathrm{B}}}{\varepsilon} \cdot \left\{ \ln \left( \frac{1 - \nu}{\nu} \right) + \ln g \right\} \quad ,$$

hence

$$k_{\mathrm{B}} T = \frac{\varepsilon}{\ln \left( \frac{1-\nu}{\nu} \right) + \ln g} \quad .$$

Inverting,

$$\nu(T) = \frac{g \, e^{-\varepsilon/k_{\mathrm{B}}T}}{1 + g \, e^{-\varepsilon/k_{\mathrm{B}}T}} \quad .$$

(d) The temperature diverges when the denominator in the above expression for $T(\nu)$ vanishes. This occurs at $\nu = \nu^* \equiv g/(g + 1)$. For $\nu \in (\nu^*, 1)$, the temperature is negative! This is technically correct,

and a consequence of the fact that the energy is bounded for this system: $E \in [0, N\varepsilon]$. The entropy as a function of $\nu$ therefore has a maximum at $\nu = \nu^*$. The model is unphysical though in that it neglects various excitations such as kinetic energy (*e.g.* lattice vibrations) for which the energy can be arbitrarily large.

(e) When a system at negative temperature is placed in contact with a heat bath at positive temperature, heat flows from the system to the bath. The energy of the system therefore decreases, and since $\frac{\partial S}{\partial E} < 0$, this results in a net entropy increase, which is what is demanded by the Second Law of Thermodynamics. More precisely, let $đQ$ be the heat added *to* the system from the bath. The first law then says $dE = đQ$. The total entropy change due to such a differential heat transfer is

$$dS_{\text{tot}} = dS + dS_{\text{b}} = \left( \frac{1}{T} - \frac{1}{T_{\text{b}}} \right) dE \quad ,$$

where $dS = dS_{\text{sys}}$ is the entropy change of the system and $T$ is the system temperature; $T_{\text{b}} > 0$ is the temperature of the bath. We see that the Second Law, $dS_{\text{tot}} \geq 0$, requires that $dE \leq 0$. For $đQ = dE < 0$, the total entropy increases. Note that the heat capacity of the system is

$$C = \frac{\partial E}{\partial T} = N\varepsilon \frac{\partial \nu}{\partial T} = \frac{N\varepsilon^2}{k_{\text{B}} T^2} \frac{g\, e^{-\varepsilon/k_{\text{B}}T}}{\left( 1 + g\, e^{-\varepsilon/k_{\text{B}}T} \right)^2}$$

and that $C \geq 0$. Even though the temperature $T$ can be negative, we always have $C(T) \geq 0$; this is necessary for thermodynamic stability. We conclude that the system's temperature changes by $dT = dE/C$, so if $dE < 0$ we have $dT < 0$ and the system cools.

All should be clear upon examination of Fig. 38. When $\nu > \nu^*$, the system temperature is negative. Placing the system in contact with a bath at temperature $T_{\text{b}} > 0$ will cause heat to flow from the system to the bath: $đQ = dE < 0$. This means $d\nu = dE/N\varepsilon < 0$, hence $\nu$ decreases and approaches $\nu^*$ from above, at which point $T = -\infty$. At this point, a further differential transfer $-đQ > 0$ from the system to the bath continues to result in an increase of total entropy, with $dS_{\text{tot}} = -đQ/T_{\text{b}}$ at $\nu = \nu^*$. Thus, $\nu$ crosses $\nu^*$, and the temperature flips from $T = -\infty$ to $T = +\infty$. At this point, we can appeal to our normal intuition. The system is much hotter than the bath, and heat continues to flow to the bath. This has the (familiar) effect of lowering the system temperature, which will then approach $T_{\text{b}}$ from above. Ultimately, both system and bath will be at temperature $T_{\text{b}}$, as required for thermodynamic equilibrium.
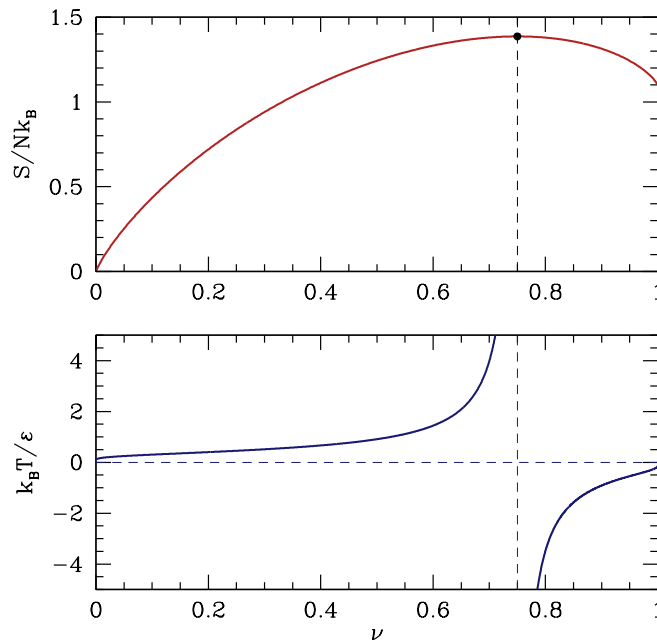
Figure 20: Bottom: dimensionless temperature $\theta(\nu) \equiv k_\mathrm{B}T/\varepsilon$ *versus* dimensionless energy density $\nu = E/N\varepsilon$ for problem 1, shown here for $g = 3$. Note that $T \to \mp\infty$ for $\nu \to \nu^* \pm 0^+$, where $\nu^* = g/(g+1)$ is the energy density at which the entropy is maximum. Top: dimensionless entropy $s(\nu) \equiv S/Nk_\mathrm{B}$ *versus* dimensionless energy density $\nu$. Note the maximum at $\nu^* = g/(g+1)$, where $g$ is the degeneracy of the excited level.

**(4.2)** Solve for the model in problem 1 using the ordinary canonical ensemble. The Hamiltonian is

$$\hat{H} = \varepsilon \sum_{i=1}^{N} \left(1 - \delta_{\sigma_i,1}\right) \quad ,$$

where $\sigma_i \in \{1, \ldots, g+1\}$.

   (a) Find the partition function $Z(T, N)$ and the Helmholtz free energy $F(T, N)$.

   (b) Show that $\hat{M} = \frac{\partial \hat{H}}{\partial \varepsilon}$ counts the number of particles in an excited state. Evaluate the thermodynamic average $\nu(T) = \langle \hat{M} \rangle / N$.

   (c) Show that the entropy $S = -\left(\frac{\partial F}{\partial T}\right)_N$ agrees with your result from problem 1.

Solution :

(a) We have

$$Z(T, N) = \mathrm{Tr}\ e^{-\beta\hat{H}} = \left(1 + g\,e^{-\varepsilon/k_\mathrm{B}T}\right)^N \quad .$$

The free energy is

$$F(T,N) = -k_\mathrm{B}T \ln F(T,N) = -Nk_\mathrm{B}T \ln\left(1 + g\,e^{-\varepsilon/k_\mathrm{B}T}\right) \quad .$$

(b) We have

$$\hat{M} = \frac{\partial \hat{H}}{\partial \varepsilon} = \sum_{i=1}^{N} \left(1 - \delta_{\sigma_i,1}\right) \quad .$$

Clearly this counts all the excited particles, since the expression $1 - \delta_{\sigma_i,1}$ vanishes if $i = 1$, which is the ground state, and yields $1$ if $i \neq 1$, *i.e.* if particle $i$ is in any of the $g$ excited states. The thermodynamic average of $\hat{M}$ is $\langle \hat{M} \rangle = \left(\frac{\partial F}{\partial \varepsilon}\right)_{T,N}$, hence

$$\nu = \frac{\langle \hat{M} \rangle}{N} = \frac{g\,e^{-\varepsilon/k_\mathrm{B}T}}{1 + g\,e^{-\varepsilon/k_\mathrm{B}T}} \quad ,$$

which agrees with the result in problem 1c.

(c) The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_N = Nk_\mathrm{B} \ln\left(1 + g\,e^{-\varepsilon/k_\mathrm{B}T}\right) + \frac{N\varepsilon}{T}\frac{g\,e^{-\varepsilon/k_\mathrm{B}T}}{1 + g\,e^{-\varepsilon/k_\mathrm{B}T}} \quad .$$

Working with our result for $\nu(T)$, we derive

$$1 + g\,e^{-\varepsilon/k_\mathrm{B}T} = \frac{1}{1 - \nu}$$

$$\frac{\varepsilon}{k_\mathrm{B}T} = \ln\left(\frac{g(1 - \nu)}{\nu}\right) \quad .$$

Inserting these results into the above expression for $S$, we verify

$$S = -Nk_\mathrm{B} \ln(1 - \nu) + Nk_\mathrm{B}\,\nu \ln\left(\frac{g(1 - \nu)}{\nu}\right)$$

$$= -Nk_\mathrm{B}\Big\{\nu \ln \nu + (1 - \nu)\ln(1 - \nu) - \nu \ln g\Big\} \quad ,$$

as we found in problem 1b.

**(4.3)** Consider a system of noninteracting spin trimers, each of which is described by the Hamiltonian

$$\hat{H} = -J(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_3\sigma_1) - \mu_0 H(\sigma_1 + \sigma_2 + \sigma_3) \quad .$$

The individual spin polarizations $\sigma_i$ are two-state Ising variables, with $\sigma_i = \pm 1$.

(a) Find the single trimer partition function $\zeta$.

(b) Find the magnetization per trimer $m = \mu_0 \langle \sigma_1 + \sigma_2 + \sigma_3 \rangle$.

(c) Suppose there are $N_\triangle$ trimers in a volume $V$. The magnetization density is $M = N_\triangle m/V$. Find the zero field susceptibility $\chi(T) = (\partial M/\partial H)_{H=0}$.

(d) Find the entropy $S(T, H, N_\triangle)$.

(e) Interpret your results for parts (b), (c), and (d) physically for the limits $J \to +\infty$, $J \to 0$, and $J \to -\infty$.

Solution :

The eight trimer configurations and their corresponding energies are listed in the table below.

| $\vert \sigma_1\sigma_2\sigma_3 \rangle$ | $E$ | $\vert \sigma_1\sigma_2\sigma_3 \rangle$ | $E$ |
|---|---|---|---|
| $\vert\uparrow\uparrow\uparrow\rangle$ | $-3J - 3\mu_0 H$ | $\vert\downarrow\downarrow\downarrow\rangle$ | $-3J + 3\mu_0 H$ |
| $\vert\uparrow\uparrow\downarrow\rangle$ | $+J - \mu_0 H$ | $\vert\downarrow\downarrow\uparrow\rangle$ | $+J + \mu_0 H$ |
| $\vert\uparrow\downarrow\uparrow\rangle$ | $+J - \mu_0 H$ | $\vert\downarrow\uparrow\downarrow\rangle$ | $+J + \mu_0 H$ |
| $\vert\downarrow\uparrow\uparrow\rangle$ | $+J - \mu_0 H$ | $\vert\uparrow\downarrow\downarrow\rangle$ | $+J + \mu_0 H$ |

Table 7: Spin configurations and their corresponding energies.

(a) The single trimer partition function is then

$$\zeta = \sum_\alpha e^{-\beta E_\alpha} = 2\, e^{3\beta J} \cosh(3\beta\mu_0 H) + 6\, e^{-\beta J} \cosh(\beta\mu_0 H) \quad .$$

(b) The magnetization is

$$m = \frac{1}{\beta\zeta}\frac{\partial\zeta}{\partial H} = 3\mu_0 \cdot \left( \frac{e^{3\beta J}\sinh(3\beta\mu_0 H) + e^{-\beta J}\sinh(\beta\mu_0 H)}{e^{3\beta J}\cosh(3\beta\mu_0 J) + 3\, e^{-\beta J}\cosh(\beta\mu_0 H)} \right)$$

(c) Expanding $m(T, H)$ to lowest order in $H$, we have

$$m = 3\beta\mu_0^2\, H \cdot \left( \frac{3\, e^{3\beta J} + e^{-\beta J}}{e^{3\beta J} + 3\, e^{-\beta J}} \right) + \mathcal{O}(H^3) \quad .$$

Thus,

$$\chi(T) = \frac{N_\triangle}{V} \cdot \frac{3\mu_0^2}{k_{\mathrm{B}}T} \cdot \left( \frac{3\,e^{3J/k_{\mathrm{B}}T} + e^{-J/k_{\mathrm{B}}T}}{e^{3J/k_{\mathrm{B}}T} + 3\,e^{-J/k_{\mathrm{B}}T}} \right) \quad .$$

(d) Note that

$$F = \frac{1}{\beta}\ln Z \quad , \quad E = \frac{\partial \ln Z}{\partial \beta} \quad .$$

Thus,

$$S = \frac{E - F}{T} = k_{\mathrm{B}}\left( \ln Z - \beta\,\frac{\partial \ln Z}{\partial \beta} \right) = N_\triangle k_{\mathrm{B}}\left( \ln \zeta - \beta\,\frac{\partial \ln \zeta}{\partial \beta} \right) \quad .$$

So the entropy is

$$S(T, H, N_\triangle) = N_\triangle k_{\mathrm{B}} \ln\left( 2\,e^{3\beta J} \cosh(3\beta\mu_0 H) + 6\,e^{-\beta J} \cosh(\beta\mu_0 H) \right)$$

$$- 6N_\triangle \beta J k_{\mathrm{B}} \cdot \left( \frac{e^{3\beta J} \cosh(3\beta\mu_0 H) - e^{-\beta J} \cosh(\beta\mu_0 H)}{2\,e^{3\beta J} \cosh(3\beta\mu_0 H) + 6\,e^{-\beta J} \cosh(\beta\mu_0 H)} \right)$$

$$- 6N_\triangle \beta\mu_0 H k_{\mathrm{B}} \cdot \left( \frac{e^{3\beta J} \sinh(3\beta\mu_0 H) + e^{-\beta J} \sinh(\beta\mu_0 H)}{2\,e^{3\beta J} \cosh(3\beta\mu_0 H) + 6\,e^{-\beta J} \cosh(\beta\mu_0 H)} \right) \quad .$$

Setting $H = 0$ we have

$$S(T, H = 0, N_\triangle) = N_\triangle k_{\mathrm{B}} \ln 2 + N_\triangle k_{\mathrm{B}} \ln\left( 1 + 3\,e^{-4J/k_{\mathrm{B}}T} \right) + \frac{N_\triangle J}{T} \cdot \left( \frac{12\,e^{-4J/k_{\mathrm{B}}T}}{1 + 3\,e^{-4J/k_{\mathrm{B}}T}} \right)$$

$$= N_\triangle k_{\mathrm{B}} \ln 6 + N_\triangle k_{\mathrm{B}} \ln\left( 1 + \tfrac{1}{3}\,e^{4J/k_{\mathrm{B}}T} \right) - \frac{N_\triangle J}{T} \cdot \left( \frac{4\,e^{4J/k_{\mathrm{B}}T}}{3 + e^{4J/k_{\mathrm{B}}T}} \right) \quad .$$

(e) Note that for $J = 0$ we have $m = 3\mu_0^2 H/k_{\mathrm{B}}T$, corresponding to three independent Ising spins. The $H = 0$ entropy is then $N_\triangle k_{\mathrm{B}} \ln 8 = 3N_\triangle k_{\mathrm{B}} \ln 2$, as expected. As $J \to +\infty$ we have $m = 9\mu_0^2 H/k_{\mathrm{B}}T = (3\mu_0)^2 H/k_{\mathrm{B}}T$, and each trimer acts as a single $\mathbb{Z}_2$ Ising spin, but with moment $3\mu_0$. The zero field entropy in this limit tends to $N_\triangle k_{\mathrm{B}} \ln 2$, again corresponding to a single $\mathbb{Z}_2$ Ising degree of freedom per trimer. For $J \to -\infty$, we have $m = \mu_0^2 H/k_{\mathrm{B}}T$ and $S = N_\triangle k_{\mathrm{B}} \ln 6$. This is because the only allowed (*i.e.* finite energy) states of each trimer are the three states with magnetization $+\mu_0$ and the three states with magnetization $-\mu_0$, all of which are degenerate at $H = 0$.

**(4.4)** In chapter 4 of the lecture notes, we considered a simple model for the elasticity of wool in which each of $N$ monomers was in one of two states A or B, with energies $\varepsilon_{A,B}$ and lengths $\ell_{A,B}$. Consider now the case where the A state is doubly degenerate due to a magnetic degree of freedom which does not affect the energy or the length of the $A^{\pm}$ monomers.

(a) Generalize the results from this section of the lecture notes and show that you can write the Hamiltonian $\hat{H}$ and chain length $\hat{L}$ in terms of spin variables $S_j \in \{-1, 0, 1\}$, where $S_j = \pm 1$ if monomer $j$ is in state $A^{\pm}$, and $S_j = 0$ if it is in state B. Construct the appropriate generalization of $\hat{K} - \hat{H} - \tau\hat{L}$.

(b) Find the equilibrium length $L(T, \tau, N)$ as a function of the temperature, tension, and number of monomers.

(c) Now suppose an external magnetic field is present, so the energies of the $A^{\pm}$ states are split, with $\varepsilon_{A^{\pm}} = \varepsilon_A \mp \mu_0 H$. Find an expression for $L(T, \tau, H, N)$.

<span style="color:red">Solution :</span>

<span style="color:blue">(a) Take</span>

$$\hat{H} = \sum_{j=1}^{N} \left[ \varepsilon_B + (\varepsilon_A - \varepsilon_B) S_j^2 \right] \quad , \quad \hat{L} = \sum_{j=1}^{N} \left[ \ell_B + (\ell_A - \ell_B) S_j^2 \right] \quad ,$$

<span style="color:blue">resulting in</span>

$$\hat{K} = \hat{H} - \tau\hat{L} = N(\varepsilon_B - \tau\ell_B) + \Delta \sum_{j=1}^{N} S_j^2 \quad ,$$

<span style="color:blue">where</span>

$$\Delta = (\varepsilon_A - \varepsilon_B) - \tau(\ell_A - \ell_B) \quad .$$

<span style="color:blue">(b) The partition function is</span>

$$Y(T, \tau, N) = e^{-G/k_B T} = \mathsf{Tr}\, e^{-\hat{K}/k_B T}$$
$$= e^{-N(\varepsilon_B - \tau\ell_B)/k_B T} \left(1 + 2\, e^{-\Delta/k_B T}\right)^N \quad .$$

<span style="color:blue">Thus, the Gibbs free energy is</span>

$$G(T, \tau, N) = -k_B T \ln Y(T, \tau, N) = N(\varepsilon_B - \tau\ell_B) - Nk_B T \ln\left(1 + 2\, e^{-\Delta/k_B T}\right) \quad .$$

<span style="color:blue">The equilibrium length is</span>

$$L = -\frac{\partial G}{\partial \tau} = N\ell_B + N(\ell_A - \ell_B) \cdot \frac{2\, e^{-\Delta/k_B T}}{1 + 2\, e^{-\Delta/k_B T}} \quad .$$

<span style="color:blue">Note that $L = N\ell_A$ for $\Delta \to -\infty$ and $L = N\ell_B$ for $\Delta \to +\infty$.</span>

<span style="color:blue">(c) Accounting for the splitting of the two A states,</span>

$$L = N\ell_B + N(\ell_A - \ell_B) \cdot \frac{2\, e^{-\Delta/k_B T} \cosh(\mu_0 H/k_B T)}{1 + 2\, e^{-\Delta/k_B T} \cosh(\mu_0 H/k_B T)} \quad .$$

**(4.5)** Consider a generalization of the situation in ch. 4 of the notes where now three reservoirs are in thermal contact, with any pair of systems able to exchange energy.

(a) Assuming interface energies are negligible, what is the total density of states $D(E)$? Your answer should be expressed in terms of the densities of states functions $D_{1,2,3}$ for the three individual systems.

(b) Find an expression for $P(E_1, E_2)$, which is the joint probability distribution for system 1 to have energy $E_1$ while system 2 has energy $E_2$ and the total energy of all three systems is $E_1 + E_2 + E_3 = E$.

(c) Extremize $P(E_1, E_2)$ with respect to $E_{1,2}$. Show that this requires the temperatures for all three systems must be equal: $T_1 = T_2 = T_3$. Writing $E_j = E_j^* + \delta E_j$, where $E_j^*$ is the extremal solution ($j = 1, 2$), expand $\ln P(E_1^* + \delta E_1, E_2^* + \delta E_2)$ to second order in the variations $\delta E_j$. Remember that

$$S = k_{\mathrm{B}} \ln D \quad, \quad \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} \quad, \quad \left(\frac{\partial^2 S}{\partial E^2}\right)_{V,N} = -\frac{1}{T^2 C_V} \quad.$$

(d) Assuming a Gaussian form for $P(E_1, E_2)$ as derived in part (c), find the variance of the energy of system 1,
$$\mathsf{Var}(E_1) = \left\langle (E_1 - E_1^*)^2 \right\rangle \quad.$$

Solution :

(a) The total density of states is a convolution:

$$D(E) = \int\limits_{-\infty}^{\infty} dE_1 \int\limits_{-\infty}^{\infty} dE_2 \int\limits_{-\infty}^{\infty} dE_3 \, D_1(E_1) \, D_2(E_2) \, D_3(E_3) \, \delta(E - E_1 - E_2 - E_3) \quad.$$

(b) The joint probability density $P(E_1, E_2)$ is given by

$$P(E_1, E_2) = \frac{D_1(E_2) \, D_2(E_2) \, D_3(E - E_1 - E_2)}{D(E)} \quad.$$

(c) We set the derivatives $\partial \ln P/\partial E_{1,2} = 0$, which gives

$$\frac{\partial \ln P}{\partial E_1} = \frac{\partial \ln D_1}{\partial E_1} - \frac{\partial D_3}{\partial E_3} = 0 \quad, \quad \frac{\partial \ln P}{\partial E_2} = \frac{\partial \ln D_3}{\partial E_2} - \frac{\partial D_3}{\partial E_3} = 0 \quad,$$

where $E_3 = E - E_1 - E_2$ in the argument of $D_3(E_3)$. Thus, we have

$$\frac{\partial \ln D_1}{\partial E_1} = \frac{\partial \ln D_2}{\partial E_2} = \frac{\partial \ln D_3}{\partial E_3} \equiv \frac{1}{T} \quad.$$

Expanding $\ln P(E_1^* + \delta E_1 \,,\, E_2^* + \delta E_2)$ to second order in the variations $\delta E_j$, we find the first order terms cancel, leaving

$$\ln P(E_1^* + \delta E_1 \,,\, E_2^* + \delta E_2) = \ln P(E_1^* \,,\, E_2^*) - \frac{(\delta E_1)^2}{2k_{\rm B}T^2 C_1} - \frac{(\delta E_2)^2}{2k_{\rm B}T^2 C_2} - \frac{(\delta E_1 + \delta E_2)^2}{2k_{\rm B}T^2 C_3} + \cdots \quad,$$

where $\partial^2 \ln D_j / \partial E_j^2 = -1/2k_{\rm B}T^2 C_j$, with $C_j$ the heat capacity at constant volume and particle number. Thus,

$$P(E_1, E_2) = \frac{\sqrt{\det(\mathcal{C}^{-1})}}{2\pi k_{\rm B}T^2} \exp\left( - \frac{1}{2k_{\rm B}T^2}\, \mathcal{C}_{ij}^{-1}\, \delta E_i\, \delta E_j \right) \quad,$$

where the matrix $\mathcal{C}^{-1}$ is defined as

$$\mathcal{C}^{-1} = \begin{pmatrix} C_1^{-1} + C_3^{-1} & C_3^{-1} \\ C_3^{-1} & C_2^{-1} + C_3^{-1} \end{pmatrix} \quad.$$

One finds

$$\det(\mathcal{C}^{-1}) = C_1^{-1}\, C_2^{-1} + C_1^{-1}\, C_3^{-1} + C_2^{-1}\, C_3^{-1} \quad.$$

The prefactor in the above expression for $P(E_1, E_2)$ has been fixed by the normalization condition $\int dE_1 \int dE_2\, P(E_1, E_2) = 1$.

(d) Integrating over $E_2$, we obtain $P(E_1)$:

$$P(E_1) = \int\limits_{-\infty}^{\infty} dE_2\, P(E_1, E_2) = \frac{1}{\sqrt{2\pi k_{\rm B}\widetilde{C}_1 T^2}} e^{-(\delta E_1)^2/2k_{\rm B}\widetilde{C}_1 T^2} \quad,$$

where

$$\widetilde{C}_1 = \frac{C_2^{-1} + C_3^{-1}}{C_1^{-1}\, C_2^{-1} + C_1^{-1}\, C_3^{-1} + C_2^{-1}\, C_3^{-1}} \quad.$$

Thus,

$$\langle (\delta E_1)^2 \rangle = \int\limits_{-\infty}^{\infty} dE_1\, (\delta E_1)^2 = k_{\rm B}\widetilde{C}_1 T^2 \quad.$$

**(4.6)** Show that the Boltzmann entropy $S = -k_{\mathrm{B}} \sum_n P_n \ln P_n$ agrees with the statistical entropy $S(E) = k_{\mathrm{B}} \ln D(E, V, N)$ in the thermodynamic limit.

Solution :

Let's first examine the canonical partition function, $Z = \int\limits_0^\infty dE\, D(E)\, e^{-\beta E}$. We compute this integral via the saddle point method, extremizing the exponent, $\ln D(E) - \beta E$, with respect to $E$. The resulting maximum lies at $\bar{E}$ such that $\frac{1}{T} = \frac{\partial S}{\partial E}\big|_{\bar{E}}$, where $S(E) = k_{\mathrm{B}} \ln D(E)$ is the statistical entropy computed in the microcanonical ensemble. The ordinary canonical partition function is then

$$Z \approx D(\bar{E})\, e^{-\beta \bar{E}} \int\limits_{-\infty}^{\infty} d\,\delta E\; e^{-(\delta E)^2/2k_{\mathrm{B}}T^2 C_V}$$

$$= (2\pi k_{\mathrm{B}} T^2 C_V)^{1/2}\, D(\bar{E})\, e^{-\beta \bar{E}} \quad .$$

Taking the logarithm, we obtain the Helmholtz free energy,

$$F = -k_{\mathrm{B}} T \ln Z = -k_{\mathrm{B}} \ln D(\bar{E}) + \bar{E} - \tfrac{1}{2} k_{\mathrm{B}} T \ln\big(2\pi k_{\mathrm{B}} T^2 C_V\big) \quad .$$

Now $S_{\mathrm{OCE}} = -k_{\mathrm{B}} \sum_n P_n \ln P_n$, with $P_n = \frac{1}{Z} e^{-\beta E_n}$. Therefore

$$S_{\mathrm{OCE}}(T) = \frac{k_{\mathrm{B}}}{Z} \int\limits_0^\infty dE\, D(E)\, e^{-\beta E} \big( \ln Z + \beta E \big)$$

$$= k_{\mathrm{B}} \ln Z + \frac{1}{T} \cdot \frac{\int_0^\infty dE\, E\, D(E)\, e^{-\beta E}}{\int_0^\infty dE\, D(E)\, e^{-\beta E}} \quad .$$

The denominator of the second term is $Z$, which we have already evaluated. We evaluate the numerator using the same expansion about $\bar{E}$. The only difference is the additional factor of $E = \bar{E} + \delta E$ in the integrand. The $\delta E$ term integrates to zero, since the remaining factors in the integrand yield $D(\bar{E})\, e^{-\beta \bar{E}}\, e^{-(\delta E)^2/2k_{\mathrm{B}}T^2 C_V}$, which is even in $\delta E$. Thus, the second term in the above equation is simply $\bar{E}/T$, and we obtain

$$S_{\mathrm{OCE}} = k_{\mathrm{B}} \ln D(\bar{E}) + \tfrac{1}{2} k_{\mathrm{B}} \ln\big(2\pi k_{\mathrm{B}} T^2 C_V\big) \quad .$$

The RHS here is dominated by the first term, which is extensive, whereas the second term is of order $\ln V$. Thus, we conclude that $S_{\mathrm{OCE}}(T, V, N) = S_{\mu\mathrm{CE}}(\bar{E}, V, N)$, where $\bar{E}$ and $T$ are related by $\frac{1}{T} = \frac{\partial S}{\partial E}\big|_{\bar{E}}$.

**(4.7)** Consider rod-shaped molecules with moment of inertia $I$, and a dipole moment $\mu$. The contribution of the rotational degrees of freedom to the Hamiltonian is

$$\hat{H}_{\rm rot} = \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta} - \mu E\cos\theta \quad,$$

where $E$ is the external electric field, and $(\theta, \phi)$ are polar and azimuthal angles describing the molecular orientation[6].

(a) Calculate the contribution of the rotational degrees of freedom of each dipole to the classical partition function.

(b) Obtain the mean polarization $P = \langle \mu\cos\theta \rangle$ of each dipole.

(c) Find the zero-field isothermal polarizability, $\chi(T) = \left(\frac{\partial P}{\partial E}\right)_{E=0}$.

(d) Calculate the rotational energy per particle at finite field $E$, and comment on its high and low-temperature limits.

(e) Sketch the rotational heat capacity per dipole as a function of temperature.

Solution :

(a) The rotational contribution to the single particle partition function is

$$\xi_{\rm rot} = \int\limits_{-\infty}^{\infty} dp_\theta \int\limits_{-\infty}^{\infty} dp_\phi \int\limits_{0}^{\pi} d\theta \int\limits_{0}^{2\pi} d\phi \, e^{-p_\theta^2/2Ik_{\rm B}T} \, e^{-p_\phi^2/2Ik_{\rm B}T\sin^2\theta} \, e^{\mu E\cos\theta/k_{\rm B}T}$$

$$= 2\pi \cdot (2\pi Ik_{\rm B}T)^{1/2} \int\limits_{0}^{\pi} d\theta \, e^{\mu E\cos\theta/k_{\rm B}T} \int\limits_{-\infty}^{\infty} dp_\theta \, e^{-p_\phi^2/2Ik_{\rm B}T\sin^2\theta}$$

$$= 4\pi^2 Ik_{\rm B}T \int\limits_{0}^{\pi} d\theta \, \sin\theta \, e^{\mu E\cos\theta/k_{\rm B}T} = \frac{8\pi^2 I(k_{\rm B}T)^2}{\mu E} \sinh\left(\frac{\mu E}{k_{\rm B}T}\right) \quad.$$

The translational contribution is $\xi_{\rm tr} = V\lambda_T^{-3}$. The single particle free energy is then

$$f = -k_{\rm B}T\ln\left(8\pi^2 Ik_{\rm B}^2 T^2\right) + k_{\rm B}T\ln(\mu E) - k_{\rm B}T\ln\sinh\left(\frac{\mu E}{k_{\rm B}T}\right) - k_{\rm B}T\ln\left(V/\lambda_T^3\right) \quad.$$

(b) The mean polarization of each dipole is

$$P = -\frac{\partial f}{\partial E} = -\frac{k_{\rm B}T}{E} + \mu\,{\rm ctnh}\left(\frac{\mu E}{k_{\rm B}T}\right) \quad.$$

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[6]This is problem 4.12 from vol. 1 of M. Kardar.

(c) We expand $\mathrm{ctnh}\,(x) = \frac{1}{x} + \frac{x}{3} + \mathcal{O}(x^3)$ in a Laurent series, whence $P = \mu^2 E/3k_{\mathrm{B}}T + \mathcal{O}(E^3)$. Then $\chi(T) = \mu^2/3k_{\mathrm{B}}T$, which is of the Curie form familiar from magnetic systems.

(d) We have $\xi_{\mathrm{rot}} = \mathsf{Tr}\,e^{-\beta\hat{h}_{\mathrm{rot}}}$, hence

$$\varepsilon_{\mathrm{rot}} = \langle\hat{h}_{\mathrm{rot}}\rangle = -\frac{\partial\ln\xi_{\mathrm{rot}}}{\partial\beta} = -\frac{\partial}{\partial\beta}\Big\{-2\ln\beta + \ln\sinh(\beta\mu E)\Big\}$$

$$= 2k_{\mathrm{B}}T - \mu E\,\mathrm{ctnh}\Big(\frac{\mu E}{k_{\mathrm{B}}T}\Big) \quad.$$

At high temperatures $T \gg \mu E/k_{\mathrm{B}}$, the argument of $\mathrm{ctnh}\,x$ is very small, and using the Laurent expansion we find $\varepsilon_{\mathrm{rot}} = k_{\mathrm{B}}T$. This comports with our understanding from equipartition, since there are only two quadratic degrees of freedom present ($p_\theta$ and $p_\phi$). The orientational degree of freedom $\theta$ does not enter because $\mu E\cos\theta \ll k_{\mathrm{B}}T$ in this regime. Unlike the rotational kinetic energy, the rotational potential energy is bounded. In the limit $T \ll \mu E/k_{\mathrm{B}}$, we have that the argument of $\mathrm{ctnh}\,x$ is very large, hence $\varepsilon_{\mathrm{rot}} \approx 2k_{\mathrm{B}}T - \mu E$. This can be understood as follows. If we change variables to $\tilde{p}_\phi \equiv p_\phi/\sin\theta$, then we have

$$\xi_{\mathrm{rot}} = \int\limits_{-\infty}^{\infty}dp_\theta \int\limits_{-\infty}^{\infty}d\tilde{p}_\phi \int\limits_{0}^{\pi}d\theta\,\sin\theta \int\limits_{0}^{2\pi}d\phi\,e^{-p_\theta^2/2Ik_{\mathrm{B}}T}\,e^{-\tilde{p}_\phi^2/2Ik_{\mathrm{B}}T}\,e^{\mu E\cos\theta/k_{\mathrm{B}}T}$$

$$= \int\limits_{-\infty}^{\infty}dp_\theta \int\limits_{-\infty}^{\infty}d\tilde{p}_\phi \int\limits_{-1}^{1}dx \int\limits_{0}^{2\pi}d\phi\,e^{-p_\theta^2/2Ik_{\mathrm{B}}T}\,e^{-\tilde{p}_\phi^2/2Ik_{\mathrm{B}}T}\,e^{\mu Ex/k_{\mathrm{B}}T} \quad,$$

where $x = \cos\theta$. We see that $x$ appears *linearly* in the energy, and simple dimensional analysis reveals that any degree of freedom $\zeta$ which appears homogeneously as $U(\zeta) \propto \zeta^r$ contributes $k_{\mathrm{B}}T/r$ to the average energy. In our case, we have quadratic contributions to the Hamiltonian from $p_\theta$ and $\tilde{p}_\phi$, a linear contribution from $x = \cos\theta$, and $\phi$ itself does not appear. Hence $\varepsilon = -\mu E + 2\times\frac{1}{2}k_{\mathrm{B}}T + k_{\mathrm{B}}T = -\mu E + 2k_{\mathrm{B}}T$. The $-\mu E$ term is the minimum value of the potential energy.

(e) The rotational heat capacity per molecule, sketched in Fig. 36, is given by

$$c_{\mathrm{rot}} = \frac{\partial\varepsilon_{\mathrm{rot}}}{\partial T} = 2k_{\mathrm{B}} - k_{\mathrm{B}}\Big(\frac{\mu E/k_{\mathrm{B}}T}{\sinh(\mu E/k_{\mathrm{B}}T)}\Big)^2 \quad.$$
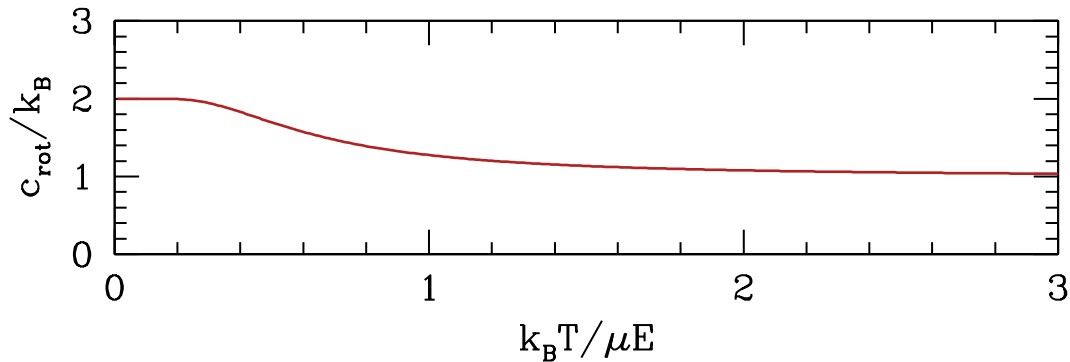
Figure 21: Rotational heat capacity $c_{\rm rot}(T)$ for problem 7.

**(4.8)** Consider a surface containing $N_s$ adsorption sites which is in equilibrium with a two-component nonrelativistic ideal gas containing atoms of types A and B . (Their respective masses are $m_A$ and $m_B$). Each adsorption site can be in one of three possible states: (i) vacant, (ii) occupied by an A atom, with energy $-\Delta_A$, and (ii) occupied with a B atom, with energy $-\Delta_B$.

(a) Find the grand partition function for the surface, $\Xi_{\rm surf}(T, \mu_A, \mu_B, N_s)$.

(b) Suppose the number densities of the gas atoms are $n_A$ and $n_B$. Find the fraction $f_A(n_A, n_B, T)$ of adsorption sites with A atoms, and the fraction $f_0(n_A, n_B, T)$ of adsorption sites which are vacant.

Solution :

(a) The surface grand partition function is

$$\Xi_{\rm surf}(T, \mu_A, \mu_B, N_s) = \left(1 + e^{(\Delta_A + \mu_A)/k_B T} + e^{(\Delta_B + \mu_B)/k_B T}\right)^{N_s} \quad .$$

(b) From the grand partition function of the gas, we have

$$n_A = \lambda_{T,A}^{-3}\, e^{\mu_A/k_B T} \qquad , \qquad n_B = \lambda_{T,B}^{-3}\, e^{\mu_B/k_B T} \quad ,$$

with

$$\lambda_{T,A} = \sqrt{\frac{2\pi \hbar^2}{m_A k_B T}} \qquad , \qquad \lambda_{T,B} = \sqrt{\frac{2\pi \hbar^2}{m_B k_B T}} \quad .$$

Thus,

$$f_0 = \frac{1}{1 + n_A\, \lambda_{T,A}^3\, e^{\Delta_A/k_B T} + n_B\, \lambda_{T,B}^3\, e^{\Delta_B/k_B T}}$$

$$f_A = \frac{n_A\, \lambda_{T,A}^3\, e^{\Delta_A/k_B T}}{1 + n_A\, \lambda_{T,A}^3\, e^{\Delta_A/k_B T} + n_B\, \lambda_{T,B}^3\, e^{\Delta_B/k_B T}}$$

$$f_B = \frac{n_B\, \lambda_{T,B}^3\, e^{\Delta_B/k_B T}}{1 + n_A\, \lambda_{T,A}^3\, e^{\Delta_A/k_B T} + n_B\, \lambda_{T,B}^3\, e^{\Delta_B/k_B T}} \quad .$$

Note that $f_0 + f_A + f_B = 1$.

**(4.9)** Consider a two-dimensional gas of identical classical, noninteracting, massive relativistic particles with dispersion $\varepsilon(\boldsymbol{p}) = \sqrt{\boldsymbol{p}^2 c^2 + m^2 c^4}$.

    (a) Compute the free energy $F(T, V, N)$.

    (b) Find the entropy $S(T, V, N)$.

    (c) Find an equation of state relating the fugacity $z = e^{\mu/k_{\mathrm{B}}T}$ to the temperature $T$ and the pressure $p$.

Solution :

(a) We have $Z = \zeta^N/N!$ where $A$ is the area and

$$\zeta(T) = \int \frac{d^2x\, d^2p}{h^2}\, e^{-\beta\sqrt{p^2 c^2 + m^2 c^4}} = \frac{2\pi A}{(\beta h c)^2}\left(1 + \beta m c^2\right) e^{-\beta m c^2} \quad .$$

To obtain this result it is convenient to change variables to $u = \beta\sqrt{p^2 c^2 + m^2 c^4}$, in which case $p\, dp = u\, du/\beta^2 c^2$, and the lower limit on $u$ is $mc^2$. The free energy is then

$$F = -k_{\mathrm{B}}T\,\ln Z = N k_{\mathrm{B}}T\,\ln\left(\frac{2\pi\hbar^2 c^2 N}{(k_{\mathrm{B}}T)^2 A}\right) - N k_{\mathrm{B}}T\,\ln\left(1 + \frac{mc^2}{k_{\mathrm{B}}T}\right) - N k_{\mathrm{B}}T + N mc^2 \quad .$$

where we are taking the thermodynamic limit with $N \to \infty$.

(b) We have

$$S = -\frac{\partial F}{\partial T} = -N k_{\mathrm{B}}\ln\left(\frac{2\pi\hbar^2 c^2 N}{(k_{\mathrm{B}}T)^2 A}\right) + N k_{\mathrm{B}}\ln\left(1 + \frac{mc^2}{k_{\mathrm{B}}T}\right) + \frac{N k_{\mathrm{B}}^2 T}{mc^2 + k_{\mathrm{B}}T} + 2N k_{\mathrm{B}} \quad .$$

(c) The grand partition function is

$$\Xi(T, V, \mu) = e^{-\beta\Omega} = e^{\beta p V} = \sum_{N=0}^{\infty} Z_N(T, V, N)\, e^{\beta\mu N} \quad .$$

We then find $\Xi = \exp\left(\zeta A\, e^{\beta\mu}\right)$, and

$$p = \frac{(k_{\mathrm{B}}T)^3}{2\pi(\hbar c)^2}\left(1 + \frac{mc^2}{k_{\mathrm{B}}T}\right) e^{(\mu - mc^2)/k_{\mathrm{B}}T} \quad .$$

Note that

$$n = \frac{\partial(\beta p)}{\partial\mu} = \frac{p}{k_{\mathrm{B}}T} \quad\Longrightarrow\quad p = n k_{\mathrm{B}}T \quad .$$

**(4.10)** A nonrelativistic gas of spin-$\frac{1}{2}$ particles of mass $m$ at temperature $T$ and pressure $p$ is in equilibrium with a surface. There is no magnetic field in the bulk, but the surface itself is magnetic, so the energy of an adsorbed particle is $-\Delta - \mu_0 H \sigma$, where $\sigma = \pm 1$ is the spin polarization and $H$ is the surface magnetic field. The surface has $N_S$ adsorption sites.

(a) Compute the Landau free energy of the gas $\Omega_{\text{gas}}(T, V, \mu)$. Remember that each particle has two spin polarization states.

(b) Compute the Landau free energy of the surface $\Omega_{\text{surf}}(T, H, N_S)$. Remember that each adsorption site can be in one of three possible states: empty, occupied with $\sigma = +1$, and occupied with $\sigma = -1$.

(c) Find an expression for the fraction $f(p, T, \Delta, H)$ of occupied adsorption sites.

(d) Find the surface magnetization, $M = \mu_0 (N_{\text{surf},\uparrow} - N_{\text{surf},\downarrow})$.

Solution :

(a) We have

$$\Xi_{\text{gas}}(T, V, \mu) = \sum_{N=0}^{\infty} e^{N\mu/k_B T} \, Z(T, V, N) = \sum_{N=0}^{\infty} \frac{V^N}{N!} \, e^{N\mu/k_B T} \, 2^N \, \lambda_T^{-3N}$$

$$= \exp\left( 2V k_B T \lambda_T^{-3} \, e^{\mu/k_B T} \right) \quad ,$$

where $\lambda_T = \sqrt{2\pi\hbar^2/mk_B T}$ is the thermal wavelength. Thus,

$$\Omega_{\text{gas}} = -k_B T \ln \Xi_{\text{gas}} = -2V k_B T \lambda_T^{-3} \, e^{\mu/k_B T} \quad .$$

(b) Each site on the surface is independent, with three possible energy states: $E = 0$ (vacant), $E = -\Delta - \mu_0 H$ (occupied with $\sigma = +1$), and $E = -\Delta + \mu_0 H$ (occupied with $\sigma = -1$). Thus,

$$\Xi_{\text{surf}}(T, H, N_S) = \left( 1 + e^{(\mu+\Delta+\mu_0 H)/k_B T} + e^{(\mu+\Delta-\mu_0 H)/k_B T} \right)^{N_S} \quad .$$

The surface free energy is

$$\Omega_{\text{surf}}(T, H, N_S) = -k_B T \ln \Xi_{\text{surf}} = -N_S k_B T \ln\left( 1 + 2\, e^{(\mu+\Delta)/k_B T} \cosh(\mu_0 H/k_B T) \right) \quad .$$

(c) The fraction of occupied surface sites is $f = \langle N_{\text{surf}}/N_S \rangle$. Thus,

$$f = -\frac{1}{N_S} \frac{\partial \Omega_{\text{surf}}}{\partial \mu} = \frac{2\, e^{(\mu+\Delta)/k_B T} \cosh(\mu_0 H/k_B T)}{1 + 2\, e^{(\mu+\Delta)/k_B T} \cosh(\mu_0 H/k_B T)} = \frac{2}{2 + e^{-(\mu+\Delta)/k_B T} \text{sech}(\mu_0 H/k_B T)} \quad .$$

To find $f(p, T, \Delta, H)$, we must eliminate $\mu$ in favor of $p$, the pressure in the gas. This is easy! From $\Omega_{\text{gas}} = -pV$, we have $p = 2k_{\text{B}}T\lambda_T^{-3} e^{\mu/k_{\text{B}}T}$, hence

$$e^{-\mu/k_{\text{B}}T} = \frac{2k_{\text{B}}T}{p\,\lambda_T^3} \quad.$$

Thus,

$$f(p, T, \Delta, H) = \frac{p\,\lambda_T^3}{p\,\lambda_T^3 + k_{\text{B}}T\,e^{-\Delta/k_{\text{B}}T}\,\text{sech}(\mu_0 H/k_{\text{B}}T)} \quad.$$

Note that $f \to 1$ when $\Delta \to \infty$, when $T \to 0$, when $p \to \infty$, or when $H \to \infty$.

(d) The surface magnetization is

$$M = -\frac{\partial \Omega_{\text{surf}}}{\partial H} = N_{\text{S}}\,\mu_0 \cdot \frac{2\,e^{(\mu+\Delta)/k_{\text{B}}T}\,\sinh(\mu_0 H/k_{\text{B}}T)}{1 + 2\,e^{(\mu+\Delta)/k_{\text{B}}T}\,\cosh(\mu_0 H/k_{\text{B}}T)}$$

$$= \frac{N_{\text{S}}\,\mu_0\,p\,\lambda_T^3\,\tanh(\mu_0 H/k_{\text{B}}T)}{p\,\lambda_T^3 + k_{\text{B}}T\,e^{-\Delta/k_{\text{B}}T}\,\text{sech}(\mu_0 H/k_{\text{B}}T)} \quad.$$

**(4.11)** A classical gas consists of particles of two species: A and B. The dispersions for these species are

$$\varepsilon_{\mathrm{A}}(\boldsymbol{p}) = \frac{\boldsymbol{p}^2}{2m} \quad , \quad \varepsilon_{\mathrm{B}}(\boldsymbol{p}) = \frac{\boldsymbol{p}^2}{4m} - \Delta \quad .$$

In other words, $m_{\mathrm{A}} = m$ and $m_{\mathrm{B}} = 2m$, and there is an additional energy offset $-\Delta$ associated with the B species.

(a) Find the grand potential $\Omega(T, V, \mu_{\mathrm{A}}, \mu_{\mathrm{B}})$.

(b) Find the number densities $n_{\mathrm{A}}(T, \mu_{\mathrm{A}}, \mu_{\mathrm{B}})$ and $n_{\mathrm{B}}(T, \mu_{\mathrm{A}}, \mu_{\mathrm{B}})$.

(c) If $2\mathrm{A} \rightleftharpoons \mathrm{B}$ is an allowed reaction, what is the relation between $n_{\mathrm{A}}$ and $n_{\mathrm{B}}$?
 (*Hint : What is the relation between $\mu_{\mathrm{A}}$ and $\mu_{\mathrm{B}}$?*)

(d) Suppose initially that $n_{\mathrm{A}} = n$ and $n_{\mathrm{B}} = 0$. Find $n_{\mathrm{A}}$ in equilibrium, as a function of $T$ and $n$ and constants.

Solution :

(a) The grand partition function $\Xi$ is a product of contributions from the A and B species, and the grand potential is a sum:

$$\Omega = -V k_{\mathrm{B}} T \, \lambda_T^{-3} \, e^{\mu_{\mathrm{A}}/k_{\mathrm{B}}T} - 2^{3/2} \, V k_{\mathrm{B}} T \, \lambda_T^{-3} \, e^{(\mu_{\mathrm{B}}+\Delta)/k_{\mathrm{B}}T}$$

Here, we have defined the thermal wavelength for the A species as $\lambda_T \equiv \lambda_{T,\mathrm{A}} = \sqrt{2\pi\hbar^2/mk_{\mathrm{B}}T}$. For the B species, since the mass is twice as great, we have $\lambda_{T,\mathrm{B}} = 2^{-1/2}\,\lambda_{T,\mathrm{A}}$.

(b) The number densities are

$$n_{\mathrm{A}} = -\frac{1}{V} \cdot \frac{\partial\Omega}{\partial\mu_{\mathrm{A}}} = V \lambda_T^{-3} \, e^{\mu_{\mathrm{A}}/k_{\mathrm{B}}T}$$

$$n_{\mathrm{B}} = -\frac{1}{V} \cdot \frac{\partial\Omega}{\partial\mu_{\mathrm{B}}} = 2^{3/2} \, V \lambda_T^{-3} \, e^{(\mu_{\mathrm{B}}+\Delta)/k_{\mathrm{B}}T} \quad .$$

If the reaction $2\mathrm{A} \rightleftharpoons \mathrm{B}$ is allowed, then the chemical potentials of the A and B species are related by $\mu_{\mathrm{B}} = 2\mu_{\mathrm{A}} \equiv 2\mu$. We then have

$$n_{\mathrm{A}}\lambda_T^3 = e^{\mu/k_{\mathrm{B}}T} \quad , \quad n_{\mathrm{B}}\lambda_T^3 = 2^{3/2} \, e^{(2\mu+\Delta)/k_{\mathrm{B}}T} \quad .$$

(c) The relation we seek is therefore

$$n_{\mathrm{B}} = 2^{3/2} \, n_{\mathrm{A}}^2 \lambda_T^3 \, e^{\Delta/k_{\mathrm{B}}T} \quad .$$

(d) If we initially have $n_{\rm A} = n$ and $n_{\rm B} = 0$, then in general we must have

$$n_{\rm A} + 2n_{\rm B} = n \qquad \Longrightarrow \qquad n_{\rm B} = \tfrac{1}{2}\big(n - n_{\rm A}\big) \quad .$$

Thus, eliminating $n_{\rm B}$, we have a quadratic equation,

$$2^{3/2}\, \lambda_T^3\, e^{\Delta/k_{\rm B}T}\, n_{\rm A}^2 = \tfrac{1}{2}(n - n_{\rm A}) \quad ,$$

the solution of which is

$$n_{\rm A} = \frac{-1 + \sqrt{1 + 16\sqrt{2}\, n\lambda_T^3\, e^{\Delta/k_{\rm B}T}}}{8\sqrt{2}\, \lambda_T^3\, e^{\Delta/k_{\rm B}T}} \quad .$$

**(4.12)** The potential energy density for an isotropic elastic solid is given by

$$\mathcal{U}(\boldsymbol{x}) = \mu \, \text{Tr} \, \varepsilon^2 + \tfrac{1}{2}\lambda \, (\text{Tr} \, \varepsilon)^2$$

$$= \mu \sum_{\alpha,\beta} \varepsilon_{\alpha\beta}^2(\boldsymbol{x}) + \tfrac{1}{2}\lambda \left( \sum_{\alpha} \varepsilon_{\alpha\alpha}(\boldsymbol{x}) \right)^2 \quad,$$

where $\mu$ and $\lambda$ are the Lamé parameters and

$$\varepsilon_{\alpha\beta} = \frac{1}{2}\left( \frac{\partial u^\alpha}{\partial x^\beta} + \frac{\partial u^\beta}{\partial x^\alpha} \right) \quad,$$

with $\boldsymbol{u}(\boldsymbol{x})$ the local displacement field, is the *strain tensor*. The Cartesian indices $\alpha$ and $\beta$ run over $x, y, z$. The kinetic energy density is

$$\mathcal{T}(\boldsymbol{x}) = \tfrac{1}{2}\rho \, \dot{\boldsymbol{u}}^2(\boldsymbol{x}) \quad.$$

(a) Assume periodic boundary conditions, and Fourier transform to wavevector space,

$$u^\alpha(\boldsymbol{x},t) = \tfrac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \hat{u}_{\boldsymbol{k}}^\alpha(t) \, e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$$

$$\hat{u}_{\boldsymbol{k}}^\alpha(t) = \tfrac{1}{\sqrt{V}} \int d^3x \, u^\alpha(\boldsymbol{x},t) \, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}} \quad.$$

Write the Lagrangian $L = \int d^3x \, (\mathcal{T} - \mathcal{U})$ in terms of the generalized coordinates $\hat{u}_{\boldsymbol{k}}^\alpha(t)$ and generalized velocities $\dot{\hat{u}}_{\boldsymbol{k}}^\alpha(t)$.

(b) Find the Hamiltonian $H$ in terms of the generalized coordinates $\hat{u}_{\boldsymbol{k}}^\alpha(t)$ and generalized momenta $\hat{\pi}_{\boldsymbol{k}}^\alpha(t)$.

(c) Find the thermodynamic average $\langle \boldsymbol{u}(0) \cdot \boldsymbol{u}(\boldsymbol{x}) \rangle$.

(d) Suppose we add in a nonlocal interaction of the strain field of the form

$$\Delta U = \tfrac{1}{2} \int d^3x \int d^3x' \, \text{Tr} \, \varepsilon(\boldsymbol{x}) \, \text{Tr} \, \varepsilon(\boldsymbol{x}') \, v(\boldsymbol{x} - \boldsymbol{x}') \quad.$$

Repeat parts (b) and (c).

<span style="color:red">Solution :</span>

<span style="color:blue">To do the mode counting we are placing the system in a box of dimensions $L_x \times L_y \times L_z$ and imposing periodic boundary conditions. The allowed wavevectors $\boldsymbol{k}$ are of the form</span>

$$\boldsymbol{k} = \left( \frac{2\pi n_x}{L_x}, \frac{2\pi n_y}{L_y}, \frac{2\pi n_z}{L_z} \right) \quad.$$

<span style="color:blue">We shall repeatedly invoke the orthogonality of the plane waves:</span>

$$\int_0^{L_x} dx \int_0^{L_y} dy \int_0^{L_z} dz \, e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}} = V \delta_{\boldsymbol{k},\boldsymbol{k}'} \quad,$$

where $V = L_x L_y L_z$ is the volume. When we Fourier decompose the displacement field, we must take care to note that $\hat{u}_{\boldsymbol{k}}^\alpha$ is complex, and furthermore that $\hat{u}_{-\boldsymbol{k}}^\alpha = \left(\hat{u}_{\boldsymbol{k}}^\alpha\right)^*$, since $u^\alpha(\boldsymbol{x})$ is a real function.

(a) We then have

$$T = \int\limits_{-\infty}^{\infty} dx \, \tfrac{1}{2}\rho \, \dot{\boldsymbol{u}}^2(\boldsymbol{x}, t) = \tfrac{1}{2}\rho \sum_{\boldsymbol{k}} \left|\dot{\hat{u}}_{\boldsymbol{k}}^\alpha(t)\right|^2$$

and

$$U = \int\limits_{-\infty}^{\infty} dx \, \left[ \tfrac{1}{2}\mu \, \frac{\partial u^\alpha}{\partial x^\beta} \, \frac{\partial u^\alpha}{\partial x^\beta} + \tfrac{1}{2}(\lambda + \mu)\left(\boldsymbol{\nabla}\cdot\boldsymbol{u}\right)^2 \right]$$

$$= \tfrac{1}{2}\sum_{\boldsymbol{k}} \left( \mu \, \delta^{\alpha\beta} + (\lambda + \mu)\, \hat{k}^\alpha \, \hat{k}^\beta \right) \boldsymbol{k}^2 \, \hat{u}_{\boldsymbol{k}}^\alpha(t) \, \hat{u}_{-\boldsymbol{k}}^\beta(t) \quad .$$

The Lagrangian is of course $L = T - U$.

(b) The momentum $\hat{\pi}_{\boldsymbol{k}}^\alpha$ conjugate to the generalized coordinate $\hat{u}_{\boldsymbol{k}}^\alpha$ is

$$\hat{\pi}_{\boldsymbol{k}}^\alpha = \frac{\partial L}{\partial \dot{\hat{u}}_{\boldsymbol{k}}^\alpha} = \rho \, \dot{\hat{u}}_{-\boldsymbol{k}}^\alpha \quad ,$$

and the Hamiltonian is

$$H = \sum_{\boldsymbol{k}} \hat{\pi}_{\boldsymbol{k}}^\alpha \, \dot{\hat{u}}_{\boldsymbol{k}}^\alpha - L$$

$$= \sum_{\boldsymbol{k}} \left\{ \frac{\left|\hat{\pi}_{\boldsymbol{k}}^\alpha\right|^2}{2\rho} + \tfrac{1}{2}\left[\mu\left(\delta^{\alpha\beta} - \hat{k}^\alpha\,\hat{k}^\beta\right) + (\lambda + 2\mu)\,\hat{k}^\alpha\,\hat{k}^\beta\right]\boldsymbol{k}^2 \, \hat{u}_{\boldsymbol{k}}^\alpha \, \hat{u}_{-\boldsymbol{k}}^\beta \right\} \quad .$$

Note that we have added and subtracted a term $\mu\,\hat{k}^\alpha\,\hat{k}^\beta$ within the expression for the potential energy. This is because $\mathbb{P}_{\alpha\beta} = \hat{k}^\alpha\,\hat{k}^\beta$ and $\mathbb{Q}_{\alpha\beta} = \delta^{\alpha\beta} - \hat{k}^\alpha\,\hat{k}^\beta$ are *projection operators* satisfying $\mathbb{P}^2 = \mathbb{P}$ and $\mathbb{Q}^2 = \mathbb{Q}$, with $\mathbb{P} + \mathbb{Q} = \mathbb{I}$, the identity. $\mathbb{P}$ projects any vector onto the direction $\hat{\boldsymbol{k}}$, and $\mathbb{Q}$ is the projector onto the (two-dimensional) subspace orthogonal to $\hat{\boldsymbol{k}}$.

(c) We can decompose $\hat{\boldsymbol{u}}_{\boldsymbol{k}}$ into a *longitudinal* component parallel to $\hat{\boldsymbol{k}}$ and a *transverse* component perpendicular to $\hat{\boldsymbol{k}}$, writing

$$\hat{\boldsymbol{u}}_{\boldsymbol{k}} = i\hat{\boldsymbol{k}}\,\hat{u}_{\boldsymbol{k}}^{\|} + i\hat{\mathbf{e}}_{k,1}\,\hat{u}_{\boldsymbol{k}}^{\perp,1} + i\hat{\mathbf{e}}_{k,2}\,\hat{u}_{\boldsymbol{k}}^{\perp,2} \quad ,$$

where $\{\hat{\mathbf{e}}_{k,1}\,,\,\hat{\mathbf{e}}_{k,2}\,,\,\hat{\boldsymbol{k}}\}$ is a right-handed orthonormal triad for each direction $\hat{\boldsymbol{k}}$. A factor of $i$ is included so that $\hat{u}_{-\boldsymbol{k}}^{\|} = \left(\hat{u}_{\boldsymbol{k}}^{\|}\right)^*$, *etc.* With this decomposition, the potential energy takes the form

$$U = \tfrac{1}{2}\sum_{\boldsymbol{k}} \left[ \mu\,\boldsymbol{k}^2 \left( \left|\hat{u}_{\boldsymbol{k}}^{\perp,1}\right|^2 + \left|\hat{u}_{\boldsymbol{k}}^{\perp,2}\right|^2 \right) + (\lambda + 2\mu)\,\boldsymbol{k}^2 \left|\hat{u}_{\boldsymbol{k}}^{\|}\right|^2 \right] \quad .$$

Equipartition then means each independent degree of freedom which is quadratic in the potential contributes an average of $\tfrac{1}{2}k_{\mathrm{B}}T$ to the total energy. Recalling that $u_{\boldsymbol{k}}^{\|}$ and $u_{\boldsymbol{k}}^{\perp,j}$ ($j = 1, 2$) are complex functions, and that they are each the Fourier transform of a real function (so that $\boldsymbol{k}$ and $-\boldsymbol{k}$ terms in the sum

for $U$ are equal), we have

$$\left\langle \mu\, \boldsymbol{k}^2 \left|\hat{u}_{\boldsymbol{k}}^{\perp,1}\right|^2 \right\rangle = \left\langle \mu\, \boldsymbol{k}^2 \left|\hat{u}_{\boldsymbol{k}}^{\perp,2}\right|^2 \right\rangle = 2 \times \tfrac{1}{2} k_{\mathrm{B}} T$$

$$\left\langle (\lambda + 2\mu)\, \boldsymbol{k}^2 \left|\hat{u}_{\boldsymbol{k}}^{\|}\right|^2 \right\rangle = 2 \times \tfrac{1}{2} k_{\mathrm{B}} T \quad .$$

Thus,

$$\left\langle |\hat{\boldsymbol{u}}_{\boldsymbol{k}}|^2 \right\rangle = 4 \times \tfrac{1}{2} k_{\mathrm{B}} T \times \frac{1}{\mu \boldsymbol{k}^2} + 2 \times \tfrac{1}{2} k_{\mathrm{B}} T \times \frac{1}{(\lambda + 2\mu)\, \boldsymbol{k}^2}$$

$$= \left( \frac{2}{\mu} + \frac{1}{\lambda + 2\mu} \right) \frac{k_{\mathrm{B}} T}{\boldsymbol{k}^2} \quad .$$

Then

$$\left\langle \boldsymbol{u}(0) \cdot \boldsymbol{u}(\boldsymbol{x}) \right\rangle = \frac{1}{V} \sum_{\boldsymbol{k}} \left\langle |\hat{\boldsymbol{u}}_{\boldsymbol{k}}|^2 \right\rangle e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$$

$$= \int \frac{d^3k}{(2\pi)^3} \left( \frac{2}{\mu} + \frac{1}{\lambda + 2\mu} \right) \frac{k_{\mathrm{B}} T}{\boldsymbol{k}^2} e^{i\boldsymbol{k}\cdot\boldsymbol{x}}$$

$$= \left( \frac{2}{\mu} + \frac{1}{\lambda + 2\mu} \right) \frac{k_{\mathrm{B}} T}{4\pi |\boldsymbol{x}|} \quad .$$

Recall that in three space dimensions the Fourier transform of $4\pi/\boldsymbol{k}^2$ is $1/|\boldsymbol{x}|$.

(d) The $\boldsymbol{k}$-space representation of $\Delta U$ is

$$\Delta U = \tfrac{1}{2} \sum_{\boldsymbol{k}} \boldsymbol{k}^2\, \hat{v}(\boldsymbol{k})\, \hat{k}^\alpha\, \hat{k}^\beta\, \hat{u}_{\boldsymbol{k}}^\alpha\, \hat{u}_{-\boldsymbol{k}}^\beta \quad ,$$

where $\hat{v}(\boldsymbol{k})$ is the Fourier transform of the interaction $v(\boldsymbol{x} - \boldsymbol{x}')$:

$$\hat{v}(\boldsymbol{k}) = \int d^3r\, v(\boldsymbol{r})\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \quad .$$

We see then that the effect of $\Delta U$ is to replace the Lamé parameter $\lambda$ with the $\boldsymbol{k}$-dependent quantity,

$$\lambda \to \lambda(\boldsymbol{k}) \equiv \lambda + \hat{v}(\boldsymbol{k}) \quad .$$

With this simple replacement, the results of parts (b) and (c) retain their original forms, *mutatis mutandis*.

**(4.13)** For polyatomic molecules, the full internal partition function is written as the product

$$\xi(T) = \frac{g_{\text{el}} \cdot g_{\text{nuc}}}{g_{\text{sym}}} \cdot \xi_{\text{vib}}(T) \cdot \xi_{\text{rot}}(T) \quad ,$$

where $g_{\text{el}}$ is the degeneracy of the lowest electronic state[7], $g_{\text{nuc}} = \prod_j (2I_j + 1)$ is the total nuclear spin degeneracy, $\xi_{\text{vib}}(T)$ is the vibrational partition function, and $\xi_{\text{rot}}(T)$ is the rotational partition function[8]. The integer $g_{\text{sym}}$ is the *symmetry factor* of the molecule, which is defined to be the number of identical configurations of a given molecule which are realized by rotations when the molecule contains identical nuclei. Evaluate $g_{\text{nuc}}$ and $g_{\text{sym}}$ for the molecules $CH_4$ (methane), $CH_3D$, $CH_2D_2$, $CHD_3$, and $CD_4$. Discuss how the successive deuteration of methane will affect the vibrational and rotational partition functions. For the vibrations your discussion can be qualitative, but for the rotations note that all one needs, as we derived in problem (6), is the product $I_1 I_2 I_3$ of the moments of inertia, which is the determinant of the inertia tensor $I_{\alpha\beta}$ *in a body-fixed center-of-mass frame*. Using the parallel axis theorem, one has

$$I_{\alpha\beta} = \sum_j m_j \left( r_j^2 \, \delta_{\alpha\beta} - r_j^\alpha \, r_j^\beta \right) + M \left( \boldsymbol{R}^2 \, \delta_{\alpha\beta} - R^\alpha R^\beta \right)$$

where $M = \sum_j m_j$ and $\boldsymbol{R} = M^{-1} \sum_j m_j \boldsymbol{r}_j$. Recall that methane is structurally a tetrahedron of hydrogen atoms with a carbon atom at the center, so we can take $r_1 = (0,0,0)$ to be the location of the carbon atom and $r_{2,3,4,5} = (1,1,1)$, $(1,-1,-1)$, $(-1,1,-1)$, $(-1,-1,1)$ to be the location of the hydrogen atoms, with all distances in units of $\frac{1}{\sqrt{3}}$ times the $C - H$ separation.

Solution :

The total partition function is given by

$$Z(T,V,N) = \frac{V^N}{N!} \left( \frac{2\pi\hbar^2}{Mk_{\text{B}}T} \right)^{3N/2} \xi_{\text{int}}^N(T) \quad ,$$

The Gibbs free energy per particle is

$$\mu(T,p) = \frac{G(T,p,N)}{N} = k_{\text{B}}T \ln\left( \frac{p\,\lambda_T^d}{k_{\text{B}}T} \right) - k_{\text{B}}T \ln\xi(T)$$

$$= k_{\text{B}}T \ln\left( \frac{p\,\lambda_T^d}{k_{\text{B}}T} \right) - k_{\text{B}}T \ln\left( \frac{g_{\text{el}} \cdot g_{\text{nuc}}}{g_{\text{sym}}} \right)$$

$$+ k_{\text{B}}T \sum_a \ln\left( 2\sinh(\Theta_a/2T) \right) - k_{\text{B}}T \ln\left[ \left( \frac{2k_{\text{B}}T}{\hbar^2} \right)^{3/2} \sqrt{\pi I_1 I_2 I_3} \right] \quad .$$

The electronic degeneracy is $g_{\text{el}} = 1$ for all stages of deuteration. The nuclear spin of the proton is $I = \frac{1}{2}$ and that of the deuteron is $I = 1$. Thus there is a nuclear degeneracy of $2I_{\text{p}} + 1 = 2$ for each hydrogen

---

[7] We assume the temperature is low enough that we can ignore electronic excitations.

[8] Note that for linear polyatomic molecules such as $CO_2$ and HCN, we must treat the molecule as a rotor, which is discussed in the lecture notes.

nucleus and $2I_{\mathrm{d}} + 1 = 3$ for each deuterium nucleus. The symmetry factor is analyzed as follows. For methane $CH_4$, there are four threefold symmetry axes, resulting in $g_{\mathrm{sym}} = 12$. The same result holds for $CD_4$. For $CH_3D$ or $CHD_3$, there is a single threefold axis, hence $g_{\mathrm{sym}} = 3$. For $CH_2D_2$, the two hydrogen nuclei lie in a plane together with the carbon, and the two deuterium nuclei lie in a second plane together with the carbon. The intersection of these two planes provides a twofold symmetry axis, about which a $180°$ rotation will rotate one hydrogen into the other and one deuterium into the other. Thus $g_{\mathrm{sym}} = 2$.

To analyze the rotational partition function, we need the product $I_1 I_2 I_3$ of the principal moments of inertia, which is to say the determinant of the inertia tensor $\det I$. We work here in units of amu for mass and $\frac{1}{\sqrt{3}}$ times the $C - H$ separation for distance. The inertia tensor is

$$I_{\alpha\beta} = \sum_j m_j \left( r_j^2 \, \delta_{\alpha\beta} - r_j^\alpha \, r_j^\beta \right) + M \left( \boldsymbol{R}^2 \, \delta_{\alpha\beta} - R^\alpha R^\beta \right)$$

where

$$M = \sum_j m_j$$

$$\boldsymbol{R} = M^{-1} \sum_j m_j \boldsymbol{r}_j \quad .$$

The locations of the four hydrogen/deuterium ions are:

$$L1 : (+1, +1, +1)$$
$$L2 : (+1, -1, -1)$$
$$L3 : (-1, +1, -1)$$
$$L4 : (-1, -1, +1) \quad .$$

For $CH_4$ we have $M = 16$ and $\boldsymbol{R} = 0$. The inertia tensor is

$$I_{CH_4} = \begin{pmatrix} 8 & 0 & 0 \\ 0 & 8 & 0 \\ 0 & 0 & 8 \end{pmatrix} \quad .$$

Similarly, for $CD_4$ we have

$$I_{CD_4} = \begin{pmatrix} 16 & 0 & 0 \\ 0 & 16 & 0 \\ 0 & 0 & 16 \end{pmatrix} \quad .$$

For $CH_3D$, there is an extra mass unit located at L1 relative to methane, so $M = 17$. The CM is at $\boldsymbol{R} = \frac{1}{17}(+1, +1, +1)$. According to the general formula above for $I_{\alpha\beta}$, thie results in two changes to the inertia tensor, relative to $I_{CH_4}$. We find

$$\Delta I = \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} + \frac{1}{17} \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} \quad ,$$

| molecule | mass $M$ (amu) | degeneracy factor $g_{\text{nuc}}$ | symmetry factor $g_{\text{sym}}$ | $\det I$ (amu) $\cdot a^2/3$ |
|----------|----------------|-----------------------------------|----------------------------------|------------------------------|
| $CH_4$ | 16 | $2^4 = 16$ | $4 \times 3 = 12$ | $8^3$ |
| $CH_3D$ | 17 | $2^3 \cdot 3 = 24$ | $1 \times 3 = 3$ | $8 \cdot \left(11 + \frac{3}{17}\right)^2$ |
| $CH_2D_2$ | 18 | $2^2 \cdot 3^2 = 36$ | $1 \times 2 = 2$ | $12 \cdot \left(8 + \frac{2}{9}\right) \cdot \left(16 + \frac{2}{9}\right)$ |
| $CHD_3$ | 19 | $2 \cdot 3^3 = 54$ | $1 \times 3 = 3$ | $16 \cdot \left(13 + \frac{3}{19}\right)^2$ |
| $CD_4$ | 20 | $3^4 = 81$ | $4 \times 3 = 12$ | $16^3$ |

Table 8: Nuclear degeneracy, symmetry factor, and $I_1 I_2 I_3$ product for successively deuterated methane.

where the first term accounts for changes in $I$ in the frame centered at the carbon atom, and the second term shifts to the center-of-mass frame. Thus,

$$
I_{CH_3D} = \begin{pmatrix} 10 + \frac{2}{17} & -\frac{18}{17} & -\frac{18}{17} \\ -\frac{18}{17} & 10 + \frac{2}{17} & -\frac{18}{17} \\ -\frac{18}{17} & -\frac{18}{17} & 10 + \frac{2}{17} \end{pmatrix} .
$$

For $CHD_3$, we regard the system as $CD_4$ with a missing mass unit at L1, hence $M = 19$. The CM is now at $\boldsymbol{R} = \frac{1}{17}(-1, -1, -1)$. The change in the inertia tensor relative to $I_{CD_4}$ is then

$$
\Delta I = - \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} + \frac{1}{19} \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} .
$$

Thus,

$$
I_{CHD_3} = \begin{pmatrix} 14 + \frac{2}{19} & \frac{18}{19} & \frac{18}{19} \\ \frac{18}{19} & 14 + \frac{2}{19} & \frac{18}{19} \\ \frac{18}{19} & \frac{18}{19} & 14 + \frac{2}{19} \end{pmatrix} .
$$

Finally, for $CH_2D_2$. we start with methane and put extra masses at L1 and L2, so $M = 18$ and $\boldsymbol{R} =$

$\frac{1}{9}(+1, 0, 0)$. Then

$$\Delta I = - \begin{pmatrix} 4 & 0 & 0 \\ 0 & 4 & -2 \\ 0 & -2 & 4 \end{pmatrix} + \frac{2}{9} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and

$$I_{CH_2D_2} = \begin{pmatrix} 12 & 0 & 0 \\ 0 & 12 + \frac{2}{9} & -2 \\ 0 & -2 & 12 + \frac{2}{9} \end{pmatrix}.$$

For the vibrations, absent a specific model for the small oscillations problem the best we can do is to say that adding mass tends to lower the normal mode frequencies since $\omega \sim \sqrt{k/M}$.

## 0.5  Quantum Statistics

**(5.1)** For a system of noninteracting $S = 0$ bosons obeying the dispersion $\varepsilon(\boldsymbol{k}) = \hbar v |\boldsymbol{k}|$.

  (a) Find the density of states per unit volume $g(\varepsilon)$.

  (b) Determine the critical temperature for Bose-Einstein condensation in three dimensions.

  (c) Find the condensate fraction $n_0/n$ for $T < T_{\mathrm{c}}$.

  (d) For this dispersion, is there a finite transition temperature in $d = 2$ dimensions? If not, explain why. If so, compute $T_{\mathrm{c}}^{(d=2)}$.

Solution :

(a) The density of states in $d$ dimensions is

$$g(\varepsilon) = \int \frac{d^d k}{(2\pi)^d} \, \delta(\varepsilon - \hbar v k) = \frac{\Omega_d}{(2\pi)^d} \frac{\varepsilon^{d-1}}{(\hbar v)^d} \quad .$$

(b) The condition for $T = T_{\mathrm{c}}$ is to write $n = n(T_{\mathrm{c}}, \mu = 0)$:

$$n = \int\limits_0^\infty d\varepsilon \, \frac{g(\varepsilon)}{e^{\varepsilon/k_{\mathrm{B}}T_{\mathrm{c}}} - 1} = \frac{1}{2\pi^2(\hbar v)^3} \int\limits_0^\infty d\varepsilon \, \frac{\varepsilon^2}{e^{\varepsilon/k_{\mathrm{B}}T_{\mathrm{c}}} - 1} = \frac{\zeta(3)}{\pi^2} \left( \frac{k_{\mathrm{B}}T_{\mathrm{c}}}{\hbar v} \right)^3 \quad .$$

Thus,

$$k_{\mathrm{B}}T_{\mathrm{c}} = \left( \frac{\pi^2}{\zeta(3)} \right)^{1/3} \hbar v \, n^{1/3} \quad .$$

(c) For $T < T_{\mathrm{c}}$, we have

$$n = n_0 + \frac{\zeta(3)}{\pi^2} \left( \frac{k_{\mathrm{B}}T}{\hbar v} \right)^3 \qquad \Rightarrow \qquad \frac{n_0}{n} = 1 - \left( \frac{T}{T_{\mathrm{c}}(n)} \right)^3 \quad .$$

(d) In $d = 2$ we have

$$n = \frac{1}{2\pi(\hbar v)^2} \int\limits_0^\infty d\varepsilon \, \frac{\varepsilon}{e^{\varepsilon/k_{\mathrm{B}}T_{\mathrm{c}}} - 1} = \frac{\zeta(2)}{2\pi} \left( \frac{k_{\mathrm{B}}T_{\mathrm{c}}}{\hbar v} \right)^2 \qquad \Rightarrow \qquad k_{\mathrm{B}}T_{\mathrm{c}}^{(d=2)} = \hbar v \sqrt{\frac{2\pi n}{\zeta(2)}} \quad .$$

**(5.2)** Consider a three-dimensional Fermi gas of $S = \frac{1}{2}$ particles obeying the dispersion relation $\varepsilon(\boldsymbol{k}) = A \, |\boldsymbol{k}|^4$.

- (a) Compute the density of states $g(\varepsilon)$.

- (b) Compute the molar heat capacity at low temperatures.

- (c) Compute the lowest order nontrivial temperature dependence for $\mu(T)$ at low temperatures. *I.e.* compute the $\mathcal{O}(T^2)$ term in $\mu(T)$.

Solution :

(a) The density of states in $d = 3$, with $\mathrm{g} = 2S + 1 = 2$, is given by

$$g(\varepsilon) = \frac{1}{\pi^2} \int\limits_0^\infty dk \, k^2 \, \delta\big(\varepsilon - \varepsilon(k)\big) = \frac{1}{\pi^2} \, k^2(\varepsilon) \, \frac{dk}{d\varepsilon}\bigg|_{k=(\varepsilon/A)^{1/4}} = \frac{\varepsilon^{-1/4}}{4\pi^2 A^{3/4}} \quad .$$

(b) The molar heat capacity is

$$c_V = \frac{\pi^2}{3n} \, R \, g(\varepsilon_{\mathrm{F}}) \, k_{\mathrm{B}} T = \frac{\pi^2 R}{4} \cdot \frac{k_{\mathrm{B}} T}{\varepsilon_{\mathrm{F}}} \quad ,$$

where $\varepsilon_{\mathrm{F}} = \hbar^2 k_{\mathrm{F}}^2/2m$ can be expressed in terms of the density using $k_{\mathrm{F}} = (3\pi^2 n)^{1/3}$, which is valid for any isotropic dispersion in $d = 3$. In deriving this formula we had to express the density $n$, which enters in the denominator in the above expression, in terms of $\varepsilon_{\mathrm{F}}$. But this is easy:

$$n = \int\limits_0^{\varepsilon_{\mathrm{F}}} d\varepsilon \, g(\varepsilon) = \frac{1}{3\pi^2} \left(\frac{\varepsilon_{\mathrm{F}}}{A}\right)^{3/4} \quad .$$

(c) We have (lecture notes, ch. 5)

$$\delta\mu = -\frac{\pi^2}{6} \, (k_{\mathrm{B}} T)^2 \, \frac{g'(\varepsilon_{\mathrm{F}})}{g(\varepsilon_{\mathrm{F}})} = \frac{\pi^2}{24} \cdot \frac{(k_{\mathrm{B}} T)^2}{\varepsilon_{\mathrm{F}}} \quad .$$

Thus,

$$\mu(n, T) = \varepsilon_{\mathrm{F}}(n) + \frac{\pi^2}{24} \cdot \frac{(k_{\mathrm{B}} T)^2}{\varepsilon_{\mathrm{F}}(n)} + \mathcal{O}(T^4) \quad ,$$

where $\varepsilon_{\mathrm{F}}(n) = A \, (3\pi^2 n)^{4/3}$.

**(5.3)** A bosonic gas is known to have a power law density of states $g(\varepsilon) = A\,\varepsilon^{\sigma}$ per unit volume, where $\sigma$ is a real number.

(a) Experimentalists measure $T_{\rm c}$ as a function of the number density $n$ and make a log-log plot of their results. They find a beautiful straight line with slope $\frac{3}{7}$. That is, $T_{\rm c}(n) \propto n^{3/7}$. Assuming the phase transition they observe is an ideal Bose-Einstein condensation, find the value of $\sigma$.

(b) For $T < T_{\rm c}$, find the heat capacity $C_V$.

(c) For $T > T_{\rm c}$, find an expression for $p(T, z)$, where $z = e^{\beta\mu}$ is the fugacity. Recall the definition of the polylogarithm (or generalized Riemann zeta function)[9],

$$\mathrm{Li}_q(z) \equiv \frac{1}{\Gamma(q)} \int\limits_0^\infty dt\, \frac{t^{q-1}}{z^{-1}e^t - 1} = \sum_{n=1}^{\infty} \frac{z^n}{n^q} \quad,$$

where $\Gamma(q) = \int\limits_0^\infty dt\, t^{q-1}\, e^{-t}$ is the Gamma function.

(d) If these particles were fermions rather than bosons, find (i) the Fermi energy $\varepsilon_{\rm F}(n)$ and (ii) the pressure $p(n)$ as functions of the density $n$ at $T = 0$.

<span style="color:red">Solution :</span>

<span style="color:red">(a) At $T = T_{\rm c}$, we have $\mu = 0$ and $n_0 = 0$, hence</span>

$$n = \int\limits_{-\infty}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{e^{\varepsilon/k_{\rm B}T_{\rm c}} - 1} = \Gamma(1+\sigma)\,\zeta(1+\sigma)\,A\,(k_{\rm B}T_{\rm c})^{1+\sigma} \quad.$$

<span style="color:blue">Thus, $T_{\rm c} \propto n^{\frac{1}{1+\sigma}} = n^{3/7}$ which means $\sigma = \frac{4}{3}$.</span>

<span style="color:blue">(b) For $T < T_{\rm c}$ we have $\mu = 0$, but the condensate carries no energy. Thus,</span>

$$E = V \int\limits_{-\infty}^{\infty} d\varepsilon\, \frac{\varepsilon\,g(\varepsilon)}{e^{\varepsilon/k_{\rm B}T} - 1} = \Gamma(2+\sigma)\,\zeta(2+\sigma)\,A\,(k_{\rm B}T)^{2+\sigma}$$

$$= \Gamma\!\left(\tfrac{10}{3}\right) \zeta\!\left(\tfrac{10}{3}\right) A\,(k_{\rm B}T)^{10/3} \quad.$$

<span style="color:blue">Thus,</span>

$$C_V = \Gamma\!\left(\tfrac{13}{3}\right) \zeta\!\left(\tfrac{10}{3}\right) A\,(k_{\rm B}T)^{7/3} \quad,$$

<span style="color:blue">where we have used $z\,\Gamma(z) = \Gamma(z+1)$.</span>

---

[9]Some sources use the notation $\zeta_q(z)$ for the polylogarithm, but for those of you who have yet to master the scribal complexities of the Greek $\zeta$, you can use the notation $\mathrm{Li}_q(z)$ instead.

(c) The pressure is $p = -\Omega/V$, which is

$$p(T, z) = -k_{\rm B}T \int\limits_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) \, \ln\!\big(1 - z\, e^{-\varepsilon/k_{\rm B}T}\big) = -A\, k_{\rm B}T \int\limits_{0}^{\infty} d\varepsilon \, \varepsilon^{\sigma} \, \ln\!\big(1 - z\, e^{-\varepsilon/k_{\rm B}T}\big)$$

$$= \frac{A}{1+\sigma} \int\limits_{0}^{\infty} d\varepsilon \, \frac{\varepsilon^{1+\sigma}}{z^{-1}\, e^{\varepsilon/k_{\rm B}T} - 1} = \Gamma(1+\sigma)\, A\, (k_{\rm B}T)^{2+\sigma} \, \mathrm{Li}_{2+\sigma}(z)$$

$$= \Gamma\!\big(\tfrac{7}{3}\big)\, A\, (k_{\rm B}T)^{10/3} \, \mathrm{Li}_{10/3}(z) \quad .$$

(d) The Fermi energy is obtained from

$$n = \int\limits_{0}^{\varepsilon_{\rm F}} d\varepsilon \, g(\varepsilon) = \frac{A\, \varepsilon_{\rm F}^{1+\sigma}}{1+\sigma} \qquad \Rightarrow \qquad \varepsilon_{\rm F}(n) = \left(\frac{(1+\sigma)\, n}{A}\right)^{\frac{1}{1+\sigma}} = \left(\frac{7n}{3A}\right)^{3/7} \quad .$$

We obtain the pressure from $p = -\big(\frac{\partial E}{\partial V}\big)_{N}$. The energy is

$$E = V \int\limits_{0}^{\varepsilon_{\rm F}} d\varepsilon \, g(\varepsilon)\, \varepsilon = V \cdot \frac{A\, \varepsilon_{\rm F}^{2+\sigma}}{2+\sigma} \propto V^{-\frac{1}{1+\sigma}} \quad .$$

Thus, $p = \frac{1}{1+\sigma} \cdot \frac{E}{V}$, i.e.

$$p(n) = \frac{A\, \varepsilon_{\rm F}^{2+\sigma}}{(1+\sigma)(2+\sigma)} = \tfrac{3}{10}\big(\tfrac{7}{3}\big)^{3/7} A^{-3/7} n^{10/7} \quad .$$

**(5.4)** At low energies, the conduction electron states in graphene can be described as fourfold degenerate fermions with dispersion $\varepsilon(\mathbf{k}) = \hbar v_{\mathrm{F}} |\mathbf{k}|$. Graphene is a two-dimensional sheet of carbon. Using the Sommerfeld expension,

   (a) Find the density of single particle states $g(\varepsilon)$.

   (b) Find the chemical potential $\mu(T, n)$ up to terms of order $T^4$.

   (c) Find the energy density $\mathcal{E}(T, n) = E/V$ up to terms of order $T^4$.

Solution :

(a) The DOS per unit volume is

$$g(\varepsilon) = 4 \int \frac{d^2 k}{(2\pi)^2} \, \delta(\varepsilon - \hbar v_{\mathrm{F}} k) = \frac{2\varepsilon}{\pi (\hbar v_{\mathrm{F}})^2} \quad .$$

(b) The Sommerfeld expansion is

$$\int\limits_{-\infty}^{\infty} d\varepsilon \, f(\varepsilon - \mu) \, \phi(\varepsilon) = \int\limits_{-\infty}^{\mu} d\varepsilon \, \phi(\varepsilon) + \frac{\pi^2}{6} \, (kT)^2 \, \phi'(\mu) + \frac{7\pi^4}{360} \, (k_{\mathrm{B}} T)^4 \, \phi'''(\mu) + \dots \quad .$$

For the particle density, set $\phi(\varepsilon) = g(\varepsilon)$, in which case

$$n = \frac{1}{\pi} \left( \frac{\mu}{\hbar v_{\mathrm{F}}} \right)^2 + \frac{\pi}{3} \left( \frac{k_{\mathrm{B}} T}{\hbar v_{\mathrm{F}}} \right)^2 \quad .$$

The expansion terminates after the $\mathcal{O}(T^2)$ term. Solving for $\mu$,

$$\mu(T, n) = \hbar v_{\mathrm{F}} (\pi n)^{1/2} \left[ 1 - \frac{\pi}{3n} \left( \frac{k_{\mathrm{B}} T}{\hbar v_{\mathrm{F}}} \right)^2 \right]^{1/2}$$

$$= \hbar v_{\mathrm{F}} (\pi n)^{1/2} \left\{ 1 - \frac{\pi}{6n} \left( \frac{k_{\mathrm{B}} T}{\hbar v_{\mathrm{F}}} \right)^2 - \frac{\pi^2}{72n^2} \left( \frac{k_{\mathrm{B}} T}{\hbar v_{\mathrm{F}}} \right)^4 + \dots \right\}$$

(c) For the energy density $\mathcal{E}$, we take $\phi(\varepsilon) = \varepsilon \, g(\varepsilon)$, whence

$$\mathcal{E}(T, n) = \frac{2\mu}{3\pi} \left[ \left( \frac{\mu}{\hbar v_{\mathrm{F}}} \right)^2 + \left( \frac{\pi k_{\mathrm{B}} T}{\hbar v_{\mathrm{F}}} \right)^2 \right]$$

$$= \tfrac{2}{3} \sqrt{\pi} \, \hbar v_{\mathrm{F}} n^{3/2} \left\{ 1 + \frac{\pi}{2n} \left( \frac{k_{\mathrm{B}} T}{\hbar v_{\mathrm{F}}} \right)^2 - \frac{\pi^2}{8n^2} \left( \frac{k_{\mathrm{B}} T}{\hbar v_{\mathrm{F}}} \right)^4 + \dots \right\}$$

**(5.5)** Consider a system of $N$ spin-$\frac{1}{2}$ particles occupying a volume $V$ at temperature $T$. Opposite spin fermions may bind in a singlet state to form a boson:

$$\mathrm{f}\!\uparrow + \mathrm{f}\!\downarrow \;\rightleftharpoons\; \mathrm{b}$$
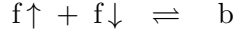
with a binding energy $-\Delta < 0$. Assume that all the particles are nonrelativistic; the fermion mass is $m$ and the boson mass is $2m$. Assume further that spin-flip processes exist, so that the $\uparrow$ and $\downarrow$ fermion species have identical chemical potential $\mu_{\mathrm{f}}$.

(a) What is the equilibrium value of the boson chemical potential, $\mu_{\mathrm{b}}$? *Hint*: the answer is $\mu_{\mathrm{b}} = 2\mu_{\mathrm{f}}$.

(b) Let the total mass density be $\rho$. Derive the equation of state $\rho = \rho(\mu_{\mathrm{f}}, T)$, assuming the bosons have not condensed. You may wish to abbreviate

$$\mathrm{Li}_p(z) \equiv \sum_{n=1}^{\infty} \frac{z^n}{n^p} \quad .$$

(c) At what value of $\mu_{\mathrm{f}}$ do the bosons condense?

(d) Derive an equation for the Bose condensation temperature $T_{\mathrm{c}}$. Solve this equation for $T_{\mathrm{c}}$ in the limits $\varepsilon_0 \ll \Delta$ and $\varepsilon_0 \gg \Delta$, respectively, where

$$\varepsilon_0 \equiv \frac{\pi\hbar^2}{m}\left(\frac{\rho/2m}{\zeta\!\left(\frac{3}{2}\right)}\right)^{2/3} \quad .$$

(e) What is the equation for the condensate fraction $\rho_0(T, \rho)/\rho$ when $T < T_{\mathrm{c}}$?

<span style="color:red">Solution :</span>

<span style="color:red">(a) The chemical potential is the Gibbs free energy per particle. If the fermion and boson species are to coexist at the same $T$ and $p$, the reaction $\mathrm{f}\!\uparrow + \mathrm{f}\!\downarrow \rightleftharpoons \mathrm{b}$ must result in $\Delta G = \mu_{\mathrm{b}} - 2\mu_{\mathrm{f}} = 0$.</span>

<span style="color:red">(b) For $T > T_{\mathrm{c}}$,</span>

$$\rho = -2m\,\lambda_T^{-3}\,\mathrm{Li}_{3/2}\!\left(-e^{\mu_{\mathrm{f}}/k_{\mathrm{B}}T}\right) + 2\sqrt{8}\,m\,\lambda_T^{-3}\,\mathrm{Li}_{3/2}\!\left(e^{(2\mu_{\mathrm{f}}+\Delta)/k_{\mathrm{B}}T}\right) \quad ,$$

<span style="color:red">where $\lambda_T = \sqrt{2\pi\hbar^2/mk_{\mathrm{B}}T}$ is the thermal wavelength for particles of mass $m$. This formula accounts for both fermion spin polarizations, each with number density $n_{\mathrm{f}\uparrow} = n_{\mathrm{f}\downarrow} = -\lambda_T^{-3}\,\mathrm{Li}_{3/2}(-z_{\mathrm{f}})$ and the bosons with number density $\sqrt{8}\,\lambda_T^{-3}\,\mathrm{Li}_{3/2}(z_{\mathrm{b}}\,e^{\beta\Delta})$, with $z_{\mathrm{b}} = z_{\mathrm{f}}^2$ due to chemical equilibrium among the species. The factor of $2^{3/2} = \sqrt{8}$ arises from the fact that the boson mass is $2m$, hence the boson thermal wavelength is $\lambda_T/\sqrt{2}$.</span>

<span style="color:red">(c) The bosons condense when $\mu_{\mathrm{b}} = -\Delta$, the minimum single particle energy. This means $\mu_{\mathrm{f}} = -\frac{1}{2}\Delta$. The equation of state for $T < T_{\mathrm{c}}$ is then</span>

$$\rho = -2m\,\lambda_T^{-3}\,\mathrm{Li}_{3/2}\!\left(-e^{-\Delta/2k_{\mathrm{B}}T}\right) + 4\sqrt{2}\,\zeta\!\left(\tfrac{3}{2}\right) m\,\lambda_T^{-3} + \rho_0 \quad ,$$

where $\rho_0$ is the condensate mass density.

(d) At $T = T_c$ we have $\rho_0 = 0$, hence

$$\frac{\rho}{2m} \left( \frac{2\pi\hbar^2}{mk_B T_c} \right)^{3/2} = \sqrt{8}\, \zeta\left(\tfrac{3}{2}\right) - \mathrm{Li}_{3/2}\left( - e^{-\Delta/2k_B T_c} \right) \quad,$$

which is a transcendental equation. Om. In the limit where $\Delta$ is very large, we have

$$T_c(\Delta \gg \varepsilon_0) = \frac{\pi\hbar^2}{mk_B} \left( \frac{\rho/2m}{\zeta\left(\tfrac{3}{2}\right)} \right)^{2/3} = \frac{\varepsilon_0}{k_B} \quad.$$

In the opposite limit, we have $\Delta \to 0^+$ and $-\mathrm{Li}_{3/2}(-1) = \eta(3/2)$, where $\eta(s)$ is the Dirichlet $\eta$-function,

$$\eta(s) = \sum_{j=1}^{\infty} (-1)^{j-1} j^{-s} = \left( 1 - 2^{1-s} \right) \zeta(s) \quad.$$

Then

$$T_c(\Delta \ll \varepsilon_0) = \frac{2\varepsilon_0/k_B}{\left( 1 + \tfrac{3}{2}\sqrt{2} \right)^{2/3}} \quad.$$

(e) The condensate fraction is

$$\nu = \frac{\rho_0}{\rho} = 1 - \left( \frac{T}{T_c} \right)^{3/2} \cdot \frac{\sqrt{8}\, \zeta\left(\tfrac{3}{2}\right) - \mathrm{Li}_{3/2}\left( - e^{-\Delta/2k_B T} \right)}{\sqrt{8}\, \zeta\left(\tfrac{3}{2}\right) - \mathrm{Li}_{3/2}\left( - e^{-\Delta/2k_B T_c} \right)} \quad.$$

Note that as $\Delta \to -\infty$ we have $-\mathrm{Li}_{3/2}\left( - e^{-\Delta/2k_B T} \right) \to 0$ and the condensate fraction approaches the free boson result, $\nu = 1 - (T/T_c)^{3/2}$. In this limit there are no fermions present.

**(5.6)** A three-dimensional system of spin-0 bosonic particles obeys a dispersion relation $\varepsilon(\boldsymbol{k})$ with lowest energy $\varepsilon_0 = 0$. The Hamiltonian is given by

$$\hat{H} = \sum_{\boldsymbol{k}} \varepsilon(\boldsymbol{k})\, \hat{n}_{\boldsymbol{k}} + \frac{U}{2V}\, \hat{N}^2 \quad ,$$

where $\hat{n}_{\boldsymbol{k}}$ is the number operator for particles with wavevector $\boldsymbol{k}$, $\hat{N} = \sum_{\boldsymbol{k}} \hat{n}_{\boldsymbol{k}}$ is the total number of particles, $V$ is the volume of the system, and $U$ is an interaction parameter with dimensions of $\mathrm{E} \cdot \mathrm{L}^3$.

(a) Treat the interaction term within mean field theory. That is, define $\hat{N} = \langle \hat{N} \rangle + \delta \hat{N}$, where $\langle \hat{N} \rangle$ is the thermodynamic average of $\hat{N}$, and derive the mean field self-consistency equation for the number density $n = \langle \hat{N} \rangle / V$ by neglecting terms quadratic in the fluctuations $\delta \hat{N}$. Show that the mean field Hamiltonian is

$$\hat{H}_{\mathrm{MF}} = -\tfrac{1}{2} V U n^2 + \sum_{\boldsymbol{k}} \left[ \varepsilon(\boldsymbol{k}) + U n \right] \hat{n}_{\boldsymbol{k}} \quad ,$$

(b) Derive the criterion for Bose condensation. Examine the cases $T < T_{\mathrm{c}}(n)$ and $T > T_{\mathrm{c}}(n)$. For $T > T_{\mathrm{c}}(n)$, what is the relation between $T$, $n$, and $\mu$?

Solution :
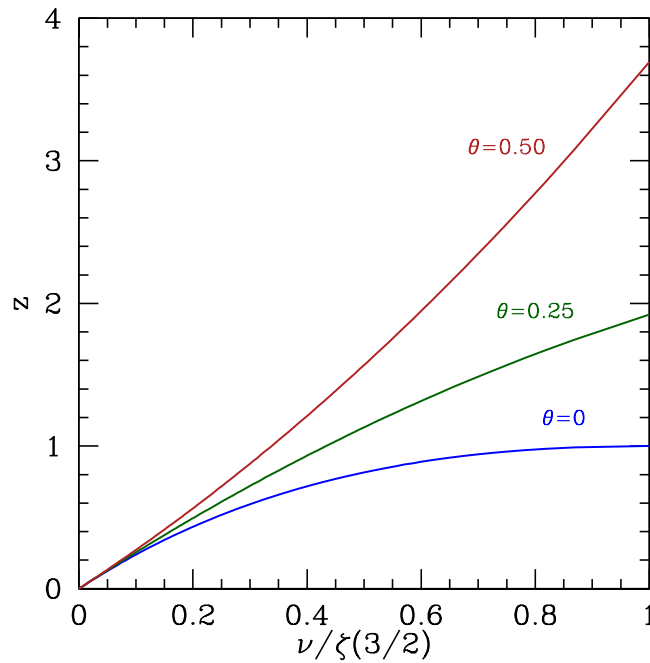


Figure 22: Fugacity $z$ *versus* dimensionless density $\nu = n\lambda_T^3$.

(a) We write

$$
\begin{aligned}
\hat{N}^2 &= \left( \langle \hat{N} \rangle + \delta \hat{N} \right)^2 \\
&= \langle \hat{N} \rangle^2 + 2 \langle \hat{N} \rangle \, \delta \hat{N} + (\delta \hat{N})^2 \\
&= -\langle \hat{N} \rangle^2 + 2 \langle \hat{N} \rangle \, \hat{N} + (\delta \hat{N})^2 \quad .
\end{aligned}
$$

We drop the last term, $(\delta \hat{N})^2$, because it is quadratic in the fluctuations. This is the mean field assumption. The Hamiltonian now becomes

$$
\mathcal{H}_{\mathrm{MF}} = -\tfrac{1}{2} V U n^2 + \sum_{\boldsymbol{k}} \left[ \varepsilon(\boldsymbol{k}) + U n \right] \hat{n}_{\boldsymbol{k}} \quad ,
$$

where $n = \langle \hat{N} \rangle / V$ is the number density. This, the dispersion is effectively changed, to

$$
\tilde{\varepsilon}(\boldsymbol{k}) = \frac{\hbar^2 \boldsymbol{k}^2}{2m} + U n \quad .
$$

The average number of particles in state $\big| \, \boldsymbol{k} \, \big\rangle$ is given by the Bose function,

$$
\langle \hat{n}_{\boldsymbol{k}} \rangle = \frac{1}{\exp \left[ \tilde{\varepsilon}(\boldsymbol{k}) / k_{\mathrm{B}} T \right] - 1} \quad .
$$

(b) At criticality, we must have $\mu = \min_{\boldsymbol{k}} \tilde{\varepsilon}(\boldsymbol{k}) = U n$, and the critical number density $n_{\mathrm{c}}(T)$ is given by

$$
n_{\mathrm{c}}(T) = \int\limits_0^\infty d\varepsilon \, \frac{g(\varepsilon)}{e^{\varepsilon / k_{\mathrm{B}} T} - 1} \quad ,
$$

which may be inverted to yield $T_{\mathrm{c}}(n)$.

$$
\begin{aligned}
T < T_{\mathrm{c}}(n) \quad &: \quad n(T, n_0) = n_0 + n_{\mathrm{c}}(T) \qquad (n_0 > 0, \mu = U n) \\
T > T_{\mathrm{c}}(n) \quad &: \quad n(T, \mu) = n_{\mathrm{c}}(T) = \int\limits_0^\infty d\varepsilon \, \frac{g(\varepsilon)}{e^{(\varepsilon + U n - \mu)/k_{\mathrm{B}} T} - 1} \quad (n_0 = 0, \mu < U n) \quad ,
\end{aligned}
$$

For ballistic particles we define $\nu \equiv n \lambda_T^3$, where $\lambda_T = \sqrt{2 \pi \hbar^2 / m k_{\mathrm{B}} T}$ is the thermal wavelength. We then have for $T > T_{\mathrm{c}}(n)$

$$
\nu = \mathsf{Li}_{3/2}(z \, e^{-\theta \nu})
$$

with $\theta \equiv U / k_{\mathrm{B}} T \lambda_T^3 \propto U T^{1/2}$ a dimensionless parameter formed from $U$ and $T$. This may be considered an equation of state relating the three intensive quantities $(\theta, z, \nu)$, or, equivalently, $(T, \mu, n)$. In Fig. 22 we show $z(\nu)$ for three different values of $\theta$.

**(5.7)** A three-dimensional gas of particles obeys the dispersion $\varepsilon(\boldsymbol{k}) = A\,k^{5/2}$. There are no internal degrees of freedom (*i.e.* the degeneracy factor is $g = 1$). The number density is $n$.[10]

    (a) Compute the single particle density of states $g(\varepsilon)$.

    (b) For bosons, compute the condensation temperature $T_{\mathrm{BEC}}(n)$.

    (c) For fermions, compute the ground state energy density $e_0(n)$.

    (d) For photon statistics, compute the temperature $T(n)$.

    (e) For photon statistics, compute the entropy density $s(n) = S/V$.

    (f) For bosons and fermions, compute the second virial coefficient $B_2(T)$.

Solution :

(a) With $\varepsilon = A\,k^\sigma$ we have $k(\varepsilon) = (\varepsilon/A)^{1/\sigma}$, and

$$g(\varepsilon) = \frac{1}{2\pi^2}\,\frac{k^2}{\varepsilon'(k)}\bigg|_{k=k(\varepsilon)} = \frac{\varepsilon^{\frac{3}{\sigma}-1}}{2\pi^2\sigma A^{3/\sigma}} = \frac{\varepsilon^{1/5}}{5\pi^2 A^{6/5}} \quad.$$

(b) The number density $n(T, z, n_0)$ for bosons, in the grand canonical ensemble, is

$$n(T, z, n_0) = \int\limits_0^\infty d\varepsilon\,\frac{g(\varepsilon)}{z^{-1}e^{\varepsilon/k_{\mathrm{B}}T} - 1} + n_0 \quad,$$

where $n_0$ is the condensate density. For $T < T_{\mathrm{BEC}}$, we have $z = 1$ and $n_0 > 0$. For $T > T_{\mathrm{BEC}}$, we have $z < 1$ and $n_0 = 0$. Precisely at $T = T_{\mathrm{BEC}}$, both conditions apply: $z = 1$ and $n_0 = 0$. Thus,

$$n = \int\limits_0^\infty d\varepsilon\,\frac{g(\varepsilon)}{e^{\varepsilon/k_{\mathrm{B}}T_{\mathrm{c}}} - 1} = \frac{\Gamma\!\left(\frac{3}{\sigma}\right)\zeta\!\left(\frac{3}{\sigma}\right)}{2\pi^2\sigma}\left(\frac{k_{\mathrm{B}}T_{\mathrm{c}}}{A}\right)^{3/\sigma} = \frac{\Gamma\!\left(\frac{6}{5}\right)\zeta\!\left(\frac{6}{5}\right)}{5\pi^2}\left(\frac{k_{\mathrm{B}}T_{\mathrm{c}}}{A}\right)^{6/5} \quad.$$

Thus,

$$T_{\mathrm{BEC}}(n) = \left(\frac{2\pi^2\sigma\,n}{\Gamma\!\left(\frac{3}{\sigma}\right)\zeta\!\left(\frac{3}{\sigma}\right)}\right)^{\!\sigma/3}\cdot\frac{A}{k_{\mathrm{B}}} = \left(\frac{5\pi^2 n}{\Gamma\!\left(\frac{6}{5}\right)\zeta\!\left(\frac{6}{5}\right)}\right)^{\!5/6}\cdot\frac{A}{k_{\mathrm{B}}} \quad.$$

(c) The ground state energy density for spinless (*i.e.* $g = 1$) fermions is

$$\varepsilon_0 = \frac{E_0}{V} = \int\frac{d^3k}{(2\pi)^3}\,A\,k^\sigma\,\Theta(k_{\mathrm{F}} - k) = \frac{A}{2\pi^2}\,\frac{k_{\mathrm{F}}^{3+\sigma}}{3+\sigma} \quad.$$

---

[10]We will solve the problem for the more general dispersion $\varepsilon(k) = A\,k^\sigma$ and then indicate the result for $\sigma = \frac{5}{2}$.

The number density is

$$n = \frac{N}{V} = \int \frac{d^3k}{(2\pi)^3}\, \Theta(k_{\mathrm{F}} - k) = \frac{k_{\mathrm{F}}^3}{6\pi^2} \quad \Longrightarrow \quad k_{\mathrm{F}} = \left(6\pi^2 n\right)^{1/3} \quad .$$

Thus,

$$\varepsilon_0(n) = \frac{\left(6\pi^2\right)^{\sigma/3}}{1 + \frac{\sigma}{3}} \cdot A\, n^{1 + \frac{\sigma}{3}} = \tfrac{6}{11}\left(6\pi^2\right)^{5/6} \cdot A\, n^{11/6} \quad .$$

(d) The photon density is

$$n = \int\limits_0^\infty d\varepsilon\, \frac{g(\varepsilon)}{e^{\varepsilon/k_{\mathrm{B}}T} - 1} \quad ,$$

which is the same expression as in part (b) above! Thus,

$$T(n) = \left(\frac{2\pi^2 \sigma\, n}{\Gamma\!\left(\frac{3}{\sigma}\right) \zeta\!\left(\frac{3}{\sigma}\right)}\right)^{\sigma/3} \cdot \frac{A}{k_{\mathrm{B}}} = \left(\frac{5\pi^2 n}{\Gamma\!\left(\frac{6}{5}\right) \zeta\!\left(\frac{6}{5}\right)}\right)^{5/6} \cdot \frac{A}{k_{\mathrm{B}}} \quad .$$

(e) The grand potential is

$$\Omega(T,V) = V k_{\mathrm{B}} T \int\limits_0^\infty d\varepsilon\, g(\varepsilon)\, \ln\!\left(1 - e^{-\varepsilon/k_{\mathrm{B}}T}\right) = -V \int\limits_0^\infty d\varepsilon\, \frac{H(\varepsilon)}{e^{\varepsilon/k_{\mathrm{B}}T} - 1} \quad ,$$

where $g(\varepsilon) = H'(\varepsilon)$. Integrating $g(\varepsilon)$ to obtain $H(\varepsilon)$, we have

$$\Omega(T,V) = -\frac{V}{6\pi^2 A^{3/\sigma}} \int\limits_0^\infty d\varepsilon\, \frac{\varepsilon^{3/\sigma}}{e^{\varepsilon/k_{\mathrm{B}}T} - 1} = -\frac{\Gamma\!\left(\frac{3}{\sigma} + 1\right) \zeta\!\left(\frac{3}{\sigma}\right)}{6\pi^2 A^{3/\sigma}}\, V \left(k_{\mathrm{B}} T\right)^{1 + \frac{3}{\sigma}}$$

The entropy density is then

$$s(T) = -\frac{1}{V}\, \frac{\partial \Omega}{\partial T} = \frac{\Gamma\!\left(\frac{3}{\sigma} + 2\right) \zeta\!\left(\frac{3}{\sigma} + 1\right)}{6\pi^2} \left(\frac{k_{\mathrm{B}} T}{A}\right)^{3/\sigma} k_{\mathrm{B}} \quad ,$$

The number density, as we have seen, is

$$n(T) = \frac{\Gamma\!\left(\frac{3}{\sigma}\right) \zeta\!\left(\frac{3}{\sigma}\right)}{2\pi^2 \sigma} \left(\frac{k_{\mathrm{B}} T}{A}\right)^{3/\sigma} \quad ,$$

hence

$$s(n) = \frac{\zeta\!\left(\frac{3}{\sigma} + 1\right)}{\zeta\!\left(\frac{3}{\sigma}\right)} \cdot \left(\tfrac{3}{\sigma} + 1\right) n k_{\mathrm{B}} = \frac{\zeta\!\left(\frac{11}{5}\right)}{\zeta\!\left(\frac{6}{5}\right)} \cdot \tfrac{11}{5}\, n k_{\mathrm{B}} \quad .$$

On dimensionful grounds, we knew *a priori* that $s(n) \propto n k_{\mathrm{B}}$.

(f) We have

$$
n = \int\limits_0^\infty d\varepsilon \, \frac{g(\varepsilon)}{z^{-1} e^{\varepsilon/k_{\mathrm{B}}T} - 1} = \pm \frac{\Gamma\!\left(\frac{3}{\sigma}\right)}{2\pi^2 \sigma} \left(\frac{k_{\mathrm{B}}T}{A}\right)^{3/\sigma} \mathsf{Li}_{\frac{3}{\sigma}}(\pm z)
$$

$$
\frac{p}{k_{\mathrm{B}}T} = \int\limits_0^\infty d\varepsilon \, \frac{H(\varepsilon)}{z^{-1} e^{\varepsilon/k_{\mathrm{B}}T} - 1} = \pm \frac{\Gamma\!\left(\frac{3}{\sigma}\right)}{2\pi^2 \sigma} \left(\frac{k_{\mathrm{B}}T}{A}\right)^{3/\sigma} \mathsf{Li}_{\frac{3}{\sigma}+1}(\pm z) \quad ,
$$

where the top sign is for bosons and the bottom for fermions. It helps to define the thermal wavelength

$$
\lambda_T \equiv \left(\frac{2\pi^2 \sigma}{\Gamma\!\left(\frac{3}{\sigma}\right)}\right)^{1/3} \cdot \left(\frac{k_{\mathrm{B}}T}{A}\right)^{1/\sigma} = \left(\frac{5\pi^2}{\Gamma\!\left(\frac{6}{5}\right)}\right)^{1/3} \left(\frac{A}{k_{\mathrm{B}}T}\right)^{2/5} \quad ,
$$

so

$$
n\lambda_T^3 = \pm \mathsf{Li}_{\frac{3}{\sigma}}(\pm z) = z \pm 2^{-3/\sigma} z^2 + \mathcal{O}\!\left(z^3\right)
$$

$$
\frac{p\lambda_T^3}{k_{\mathrm{B}}T} = \pm \mathsf{Li}_{\frac{3}{\sigma}+1}(\pm z) = z \pm 2^{-1-(3/\sigma)} z^2 + \mathcal{O}\!\left(z^3\right) \quad .
$$

From the first of these, we have

$$
z = n\lambda_T^3 \mp 2^{-3/\sigma} n^2 \lambda_T^6 + \mathcal{O}\!\left(n^3 \lambda_T^9\right) \quad .
$$

Substituting this into the second equation, we obtain the lowest nontrivial term in the virial expansion of the equation of state:

$$
\frac{p}{k_{\mathrm{B}}T} = n \mp 2^{-1-(3/\sigma)} \, n^2 \lambda_T^3 + \mathcal{O}\!\left(n^3 \lambda_T^6\right) \quad .
$$

The second virial coefficient is then

$$
B_2(T) = \mp 2^{-1-(3/\sigma)} \, \lambda_T^3 = \mp \frac{5\pi^2}{2^{11/5}\,\Gamma\!\left(\frac{6}{5}\right)} \left(\frac{A}{k_{\mathrm{B}}T}\right)^{6/5} \quad .
$$

**(5.8)** Consider a three-dimensional gas of noninteracting quantum particles with dispersion $\varepsilon(\boldsymbol{k}) = A\,|\boldsymbol{k}|^{3/2}$.

(a) Find the single particle density of states per unit volume $g(\varepsilon)$.

(b) Find expressions for $n(T, z)$ and $p(T, z)$, each expressed as power series in the fugacity $z$, for both Bose-Einstein and Fermi-Dirac statistics.

(c) Find the virial expansion for the equation of state up to terms of order $n^3$, for both bosons and fermions.

<span style="color:red">Solution :</span>

<span style="color:blue">(a) The density of states for dispersion $\varepsilon(\boldsymbol{k}) = A\,|\boldsymbol{k}|^{\sigma}$ is</span>

$$
\begin{aligned}
g(\varepsilon) &= \mathrm{g}\int \frac{d^d\!k}{(2\pi)^d}\,\delta\!\left(\varepsilon - Ak^{\sigma}\right)\\
&= \frac{\mathrm{g}\Omega_d}{(2\pi)^d}\int\limits_0^{\infty} dk\, k^{d-1}\,\frac{\delta\!\left(k - (\varepsilon/A)^{1/\sigma}\right)}{\sigma A k^{\sigma-1}} = D\,\varepsilon^{\frac{d}{\sigma}-1}\quad,
\end{aligned}
$$

<span style="color:blue">with</span>

$$
D = \frac{2\mathrm{g}}{(2\sqrt{\pi})^d\,\sigma\Gamma(d/2)}\,A^{-d/\sigma}\quad.
$$

<span style="color:blue">(b) We have</span>

$$
n(T, z) = \sum_{j=1}^{\infty}(\pm 1)^{j-1}\,C_j(T)\,z^j
$$

$$
p(T, z) = k_{\mathrm{B}}T\sum_{j=1}^{\infty}(\pm 1)^{j-1}\,z^j\,j^{-1}\,C_j(T)\,z^j\quad,
$$

<span style="color:blue">where</span>

$$
C_j(T) = \int\limits_0^{\infty} d\varepsilon\, g(\varepsilon)\,e^{-j\varepsilon/k_{\mathrm{B}}T} = D\,\Gamma(d/\sigma)\left(\frac{k_{\mathrm{B}}T}{j}\right)^{d/\sigma}\quad.
$$

<span style="color:blue">Thus, we have</span>

$$
\pm n v_T = \sum_{j=1}^{\infty} j^{-r}\,(\pm z)^j
$$

$$
\pm p v_T/k_{\mathrm{B}}T = \sum_{j=1}^{\infty} j^{-(r+1)}\,(\pm z)^j\quad,
$$

where $r = d/\sigma$ and

$$v_T = \frac{1}{D\,\Gamma(d/\sigma)\,(k_{\mathrm{B}}T)^{d/\sigma}} = \frac{(2\sqrt{\pi})^d\,\sigma\,\Gamma(d/2)}{2\mathrm{g}\,D\,\Gamma(d/\sigma)}\left(\frac{A}{k_{\mathrm{B}}T}\right)^{d/\sigma}\quad.$$

has dimensions of volume.

(c) We now let $x = \pm z$, and interrogate `Mathematica`:

```
In[1]=  y = InverseSeries[x + x^2/2^r + x^3/3^r + x^4/4^r + O[x]^5]
```

```
In[2]=  w = y + y^2/2^(r+1) + y^3/3^(r+1) + y^4/4^(r+1) + O[y]^5  .
```

The result is
$$p = nk_{\mathrm{B}}T\Big[1 + B_2(T)\,n + B_3(T)\,n^2 + \ldots\Big]\quad,$$

where

$$B_2(T) = \mp 2^{-(r+1)}\,v_T$$

$$B_3(T) = \left(2^{-2r} - 2\cdot 3^{-(r+1)}\right)v_T^2$$

$$B_4(T) = \pm 2^{-(3r+1)}\,3^{1-r}\left(2^{2r+1} - 5\cdot 3^{r-1} - 2^{r-1}\,3^r\right)v_T^3\quad.$$

Substitute $\sigma = \frac{3}{2}$ to find the solution for the conditions given.

**(5.9)** You know that at most one fermion may occupy any given single-particle state. A *parafermion* is a particle for which the maximum occupancy of any given single-particle state is $k$, where $k$ is an integer greater than zero. (For $k = 1$, parafermions are regular everyday fermions; for $k = \infty$, parafermions are regular everyday bosons.) Consider a system with one single-particle level whose energy is $\varepsilon$, *i.e.* the Hamiltonian is simply $\mathcal{H} = \varepsilon n$, where $n$ is the particle number.

(a) Compute the partition function $\Xi(\mu, T)$ in the grand canonical ensemble for parafermions.

(b) Compute the occupation function $n(\mu, T)$. What is $n$ when $\mu = -\infty$? When $\mu = \varepsilon$? When $\mu = +\infty$? Does this make sense? Show that $n(\mu, T)$ reduces to the Fermi and Bose distributions in the appropriate limits.

(c) Sketch $n(\mu, T)$ as a function of $\mu$ for both $T = 0$ and $T > 0$.

Solution:

The general expression for $\Xi$ is

$$\Xi = \prod_\alpha \sum_{n_\alpha} \left( z\, e^{-\beta \varepsilon_\alpha} \right)^{n_\alpha} \quad .$$

Now the sum on $n$ runs from 0 to $k$, and

$$\sum_{n=0}^{k} x^n = \frac{1 - x^{k+1}}{1 - x} \quad .$$

(a) Thus,

$$\Xi = \frac{1 - e^{(k+1)\beta(\mu - \varepsilon)}}{1 - e^{\beta(\mu - \varepsilon)}} \quad .$$
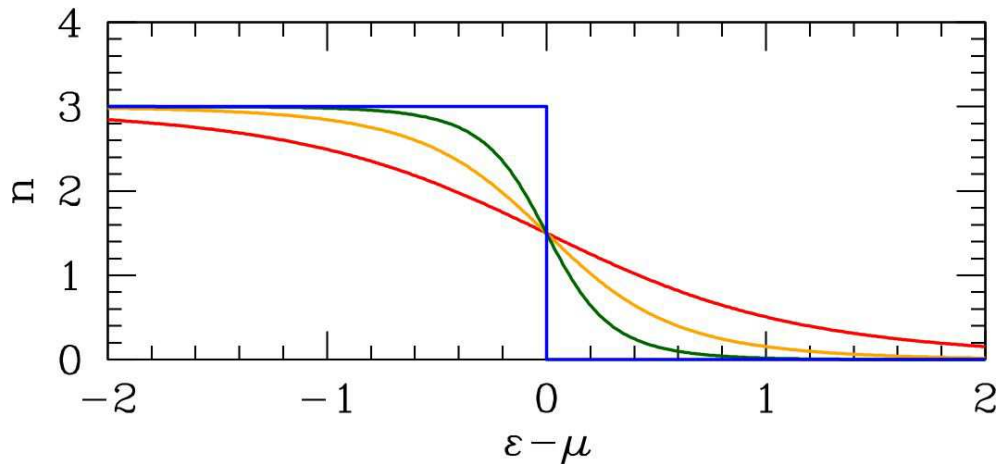


Figure 23: labelpara $k = 3$ parafermion occupation number *versus* $\varepsilon - \mu$ for $k_{\mathrm{B}}T = 0$, $k_{\mathrm{B}}T = 0.25$, $k_{\mathrm{B}}T = 0.5$, and $k_{\mathrm{B}}T = 1$.

(b) We then have

$$
\begin{aligned}
n &= -\frac{\partial \Omega}{\partial \mu} = \frac{1}{\beta}\frac{\partial \ln \Xi}{\partial \mu} \\
&= \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} - \frac{k+1}{e^{(k+1)\beta(\varepsilon-\mu)} - 1}
\end{aligned}
$$

(c) A plot of $n(\varepsilon, T, \mu)$ for $k = 3$ is shown in Fig. **??**. Qualitatively the shape is that of the Fermi function $f(\varepsilon - \mu)$. At $T = 0$, the occupation function is $n(\varepsilon, T = 0, \mu) = k\,\Theta(\mu - \varepsilon)$. This step function smooths out for $T$ finite.

(d) For each $k < \infty$, the occupation number $n(z, T)$ is a finite order polynomial in $z$, and hence an analytic function of $z$. Therefore, there is no possibility for Bose condensation except for $k = \infty$.

**(5.10)** A gas of quantum particles with photon statistics has dispersion $\varepsilon(\boldsymbol{k}) = A\,|\boldsymbol{k}|^4$.

   (a) Find the single particle density of states per unit volume $g(\varepsilon)$.

   (b) Repeat the arguments in ch. 5 of the lecture notes for this dispersion.

   (c) Assuming our known values for the surface temperature of the sun, the radius of the earth-sun orbit, and the radius of the earth, what would you expect the surface temperature of the earth to be if the sun radiated particles with this dispersion instead of photons?

Solution :

(a) See the solution to part (a) of problem 8 above. For $d = 3$ and $\sigma = 4$ we have

$$g(\varepsilon) = \frac{\mathsf{g}}{2\pi^2}\, A^{-3/4}\, \varepsilon^{-1/4} \quad.$$

(b) Scaling volume by $\lambda$ scales the lengths by $\lambda^{1/3}$, the quantized wavevectors by $\lambda^{-1/3}$, and the energy eigenvalues by $\lambda^{-4/3}$, since $\varepsilon \propto k^4$. Thus,

$$p = -\left(\frac{\partial E}{\partial V}\right)_S = \frac{4E}{3V} \quad,$$

which says

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \tfrac{3}{4}\,p \quad \Rightarrow \quad p(T) = B\,T^{7/4} \quad.$$

Indeed,

$$p(T) = -k_{\mathrm{B}}T \int\limits_{-\infty}^{\infty} g(\varepsilon)\,\ln\!\left(1 - e^{-\varepsilon/k_{\mathrm{B}}T}\right)$$

$$= -\frac{\mathsf{g}}{2\pi^2\,A^{3/4}}\,(k_{\mathrm{B}}T)^{7/4}\int\limits_{-\infty}^{\infty} du\; u^{-1/4}\,\ln(1 - e^{-u}) \quad.$$

(c) See ch. 5 of the lecture notes. Assume a dispersion of the form $\varepsilon(k)$ for the (nonconserved) bosons. Then the energy current incident on a differential area $dA$ of surface normal to $\hat{\boldsymbol{z}}$ is

$$dP = dA \cdot \int \frac{d^3k}{(2\pi)^3}\,\Theta(\cos\theta)\cdot\varepsilon(k)\cdot\frac{1}{\hbar}\frac{\partial\varepsilon(k)}{\partial k_z}\cdot\frac{1}{e^{\varepsilon(k)/k_{\mathrm{B}}T}-1} \quad.$$

Note that

$$\frac{\partial\varepsilon(k)}{\partial k_z} = \frac{k_z}{k}\frac{\partial\varepsilon}{\partial k} = \cos\theta\,\varepsilon'(k) \quad.$$

Now let us assume a power law dispersion $\varepsilon(k) = Ak^\alpha$. Changing variables to $t = Ak^\alpha/k_{\mathrm{B}}T$, we find

$$\frac{dP}{dA} = \sigma\, T^{2+\frac{2}{\alpha}} \quad,$$

where

$$\sigma = \zeta\left(2+\tfrac{2}{\alpha}\right)\Gamma\left(2+\tfrac{2}{\alpha}\right)\cdot\frac{\mathrm{g}\, k_{\mathrm{B}}^{2+\frac{2}{\alpha}}\, A^{-\frac{2}{\alpha}}}{8\pi^2\hbar} \quad.$$

One can check that for $\mathrm{g} = 2$, $A = \hbar c$, and $\alpha = 1$ that this result reduces to Stefan's Law. Equating the power incident on the earth to that radiated by the earth,

$$4\pi R_{\odot}^2 \cdot \sigma T_{\odot}^{2(1+\alpha^{-1})} \cdot \frac{\pi R_{\mathrm{e}}^2}{4\pi a_{\mathrm{e}}^2} = 4\pi R_{\mathrm{e}}^2 \cdot \sigma T_{\mathrm{e}}^{2(1+\alpha^{-1})} \quad,$$

which yields

$$T_{\mathrm{e}} = \left(\frac{R_{\odot}}{2a_{\mathrm{e}}}\right)^{\frac{\alpha}{\alpha+1}} T_{\odot} \quad.$$

Plugging in the appropriate constants and setting $\alpha = 4$, we obtain $T_{\mathrm{e}} = 45.2\,\mathrm{K}$. Brrr!

**(5.11)** Consider a three-dimensional ultrarelativistic gas, with dispersion $\varepsilon = \hbar c |\mathbf{k}|$. Find the viral expansion of the equation of state $p = p(n, T)$ to order $n^3$ for both bosons and fermions.

Solution : We have

$$\beta p = \mp \mathbf{g} \int \frac{d^3k}{(2\pi)^3} \, \ln\left(1 \mp z \, e^{-\beta\varepsilon(\mathbf{k})}\right)$$

$$z = \mathbf{g} \int \frac{d^3k}{(2\pi)^3} \frac{1}{z^{-1} e^{\beta\varepsilon(\mathbf{k})} \mp 1} \quad ,$$

where g is the degeneracy of each $\mathbf{k}$ mode. WIth $\varepsilon(\mathbf{k}) = \hbar c k$, we change variables to $t = \beta \hbar c k$ and find

$$\beta p = \frac{\mathbf{g}}{6\pi^2} \left(\frac{k_{\mathrm{B}} T}{\hbar c}\right)^3 \int\limits_{-\infty}^{\infty} dt \, \frac{t^3}{z^{-1} e^t \mp 1} = \frac{\mathbf{g}}{\pi^2} \left(\frac{k_{\mathrm{B}} T}{\hbar c}\right)^3 \sum_{j=1}^{\infty} (\pm 1)^{j-1} \frac{z^j}{j^4}$$

$$n = \frac{\mathbf{g}}{2\pi^2} \left(\frac{k_{\mathrm{B}} T}{\hbar c}\right)^3 \int\limits_{-\infty}^{\infty} dt \, \frac{t^2}{z^{-1} e^t \mp 1} = \frac{\mathbf{g}}{\pi^2} \left(\frac{k_{\mathrm{B}} T}{\hbar c}\right)^3 \sum_{j=1}^{\infty} (\pm 1)^{j-1} \frac{z^j}{j^3} \quad ,$$

where we have integrated by parts in the first of these equations. Now it's time to ask `Mathematica`:

```
In[1] =  y = InverseSeries[x + x^2/2^3 + x^3/3^3 + x^4/4^3 + x^5/5^3 + O[x]^6]
```

$$\mathtt{Out[1] =} \quad \mathtt{x} - \frac{\mathtt{x^2}}{8} - \frac{5\,\mathtt{x^3}}{864} - \frac{31\,\mathtt{x^4}}{13\,824} - \frac{56\,039\,\mathtt{x^5}}{62\,208\,000} + \mathtt{O[x]^6}$$

```
In[2] =  w = y + y^2/2^4 + y^3/3^4 + y^4/4^4 + y^5/5^4
```

$$\mathtt{Out[2] =} \quad \mathtt{x} - \frac{\mathtt{x^2}}{16} - \frac{47\,\mathtt{x^3}}{5184} - \frac{25\,\mathtt{x^4}}{9216} - \frac{2\,014\,561\,\mathtt{x^5}}{1\,866\,240\,000} + \mathtt{O[x]^6}$$

So with the definition

$$\lambda_T = \pi^{2/3} \, \mathbf{g}^{-1/3} \, \frac{\hbar c}{k_{\mathrm{B}} T} \quad ,$$

we have

$$p = n k_{\mathrm{B}} T \left(1 + B_2 \, n + B_3 \, n^2 + \dots\right) \quad ,$$

where

$$B_2 = \mp \tfrac{1}{16} \, \lambda_T^3 \quad , \quad B_3 = -\tfrac{47}{5184} \, \lambda_T^6 \quad , \quad B_4 = \mp \tfrac{25}{9216} \, \lambda_T^9 \quad , \quad B_5 = -\tfrac{2014561}{1866240000} \, \lambda_T^{12} \quad .$$

**(5.11)** Almost all elements freeze into solids well before they can undergo Bose condensation. Setting the Lindemann temperature equal to the Bose condensation temperature, show that this implies a specific ratio of $k_\mathrm{B}\Theta_\mathrm{D}$ to $\hbar^2/Ma^2$, where $M$ is the atomic mass and $a$ is the lattice spacing. Evaluate this ratio for the noble gases He, Ne, Ar, Kr, and Xe. (You will have to look up some numbers.)

Solution : The Lindemann melting temperature $T_\mathrm{M}$ and the Bose condensation temperature $T_\mathrm{c}$ for monatomic solids are given by

$$T_\mathrm{M} = x^2 \cdot \frac{Mk_\mathrm{B}\Theta_\mathrm{D}^2 \, a^2}{9\hbar^2} \quad , \quad T_\mathrm{c} = \frac{2\pi\hbar^2}{Mk_\mathrm{B}} \left(\frac{n}{\zeta(3/2)}\right)^{2/3} \quad ,$$

where $a$ is the lattice constant, $M$ the atomic mass, and $\Theta_\mathrm{D}$ the Debye temperature. For a simple cubic lattice, the number density is $n = a^{-3}$. Helium solidifies into a hexagonal close packed (HCP) structure, while Neon, Argon, Krypton, and Xenon solidify into a face-centered cubic (FCC) structure. The unit cell volume for both HCP and FCC is $a^3/\sqrt{2}$, where $a$ is the lattice spacing, so $n = \sqrt{2}\,a^{-3}$ for the rare gas solids. Thus, we find

$$\frac{T_\mathrm{M}}{T_\mathrm{c}} = \frac{x}{\alpha} \cdot \left(\frac{k_\mathrm{B}\Theta_\mathrm{D}}{\hbar^2/Ma^2}\right)^2 \quad .$$

where

$$\alpha = 18\pi \left(\frac{\sqrt{2}}{\zeta(3/2)}\right)^{2/3} \approx 40 \quad .$$

If we set $x = 0.1$ we find $\frac{x}{\alpha} \approx \frac{1}{400}$. Now we need some data for $\Theta_\mathrm{D}$ and $a$. The most convenient table of data I've found is from H. Glyde's article on solid helium in the *Encyclopedia of Physics*. The table entry for ${}^4$He is for the BCC structure at a pressure $p = 25$ bar. For a BCC structure the unit cell volume is $4a^3/3\sqrt{3}$. Define the ratio $R \equiv k_\mathrm{B}\Theta_\mathrm{D}/(\hbar^2/Ma^2)$.

As one can see from Tab. 9 and from the above equation for $T_\mathrm{M}/T_\mathrm{c}$. the $R$ values are such that the melting temperature is predicted to be several orders of magnitude higher than the ideal Bose condensation temperature in every case except ${}^4$He, where the ratio is on the order of unity (and is less than unity if the actual melting temperature is used). The reason that ${}^4$He under high pressure is a solid rather than a Bose condensate at low temperatures is because the ${}^4$He atoms are not free particles.

| crystal | $a$ (Å) | $M$ (amu) | $\Theta_\mathrm{D}$ (K) | $T_\mathrm{M}^\mathrm{actual}$ (K) | $T_\mathrm{c}$ | $\hbar^2/Ma^2 k_\mathrm{B}$ (K) | $R$ |
|---------|---------|-----------|------------------|-------------------------|-------|------------------------|------|
| ${}^4$He | 3.57 | 4.00 | 25 | 1.6 | 3.9 | 0.985 | 25 |
| Ne | 4.46 | 20.2 | 66 | 24.6 | 0.50 | 0.125 | 530 |
| Ar | 5.31 | 39.9 | 84 | 83.8 | 0.18 | 0.0446 | 1900 |
| Kr | 5.65 | 83.8 | 64 | 161.4 | 0.076 | 0.0188 | 3400 |
| Xe | 6.13 | 131 | 55 | 202.0 | 0.041 | 0.0102 | 20000 |

Table 9: Lattice constants for Ne, Ar, Kr, and Xe from F. W. de Wette and R. M. J. Cotterill, *Solid State Comm.* **6**, 227 (1968). Debye temperatures and melting temperatures from H. Glyde, *Solid Helium* in *Encyclopedia of Physics*. ${}^4$He data are for $p = 25$ bar, in the bcc phase (from Glyde).

**(5.13)** A nonrelativistic Bose gas consists of particles of spin $S = 1$. Each boson has mass $m$ and magnetic moment $\mu_0$. A gas of these particles is placed in an external field $H$.

(a) What is the relationship of the Bose condensation temperature $T_c(H)$ to $T_c(H = 0)$ when $\mu_0 H \gg k_B T$?

(b) Find the magnetization $M$ for $T < T_c$ when $\mu_0 H \gg k_B T$. Calculate through order $\exp(-\mu_0 H/k_B T)$.

Solution :

The number density of bosons is given by

$$n(T, z) = \lambda_T^{-3} \left\{ \text{Li}_{3/2}\left(z\, e^{\mu_0 H/k_B T}\right) + \text{Li}_{3/2}(z) + \text{Li}_{3/2}\left(z\, e^{-\mu_0 H/k_B T}\right) \right\} \quad .$$

The argument of $\text{Li}_z(z)$ cannot exceed unity, thus Bose condensation occurs for $z = \exp(-\mu_0 H/k_B T)$ (assuming $H > 0$). Thus, the condition for Bose condensation is given by

$$n\lambda_{T_c}^3 = \zeta(3/2) + \text{Li}_{3/2}\left(e^{-\mu_0 H/k_B T_c}\right) + \text{Li}_{3/2}\left(e^{-2\mu_0 H/k_B T_c}\right) \quad .$$

This is a transcendental equation for $T = T_c(n, H)$. In the limit $\mu_0 H \gg k_B T_c$, the second two terms become negligible, since

$$\text{Li}_s(z) = \sum_{j=1}^{\infty} \frac{z^j}{j^s} \quad .$$

Thus,

$$T_c(H \to \infty) = \frac{2\pi\hbar^2}{m} \left(\frac{n}{\zeta(3/2)}\right)^{2/3} \quad .$$

When $H = 0$, we have Thus,

$$T_c(H \to 0) = \frac{2\pi\hbar^2}{m} \left(\frac{n}{3\,\zeta(3/2)}\right)^{2/3} \quad .$$

Thus,

$$\frac{T_c(H \to \infty)}{T_c(H \to 0)} = 3^{2/3} = 2.08008\ldots$$

The magnetization density is

$$M = \mu_0\, \lambda_T^{-3} \left\{ \text{Li}_{3/2}\left(z\, e^{\mu_0 H/k_B T}\right) - \text{Li}_{3/2}\left(z\, e^{-\mu_0 H/k_B T}\right) \right\} \quad .$$

For $T < T_c$, we have $z = \exp(-\mu_0 H/k_B T)$ and therefore

$$M = \mu_0\, \lambda_T^{-3} \left\{ \zeta(3/2) - \sum_{j=1}^{\infty} j^{-3/2}\, e^{-2j\mu_0 H/k_B T} \right\}$$

$$= n\mu_0 \left\{ 1 - \frac{e^{-2\mu_0 H/k_B T}}{\zeta(3/2)} + \mathcal{O}\left(e^{-4\mu_0 H/k_B T}\right) \right\}$$

**(5.14)** Consider a set of $N$ noninteracting $S = \frac{1}{2}$ fermions in a one-dimensional harmonic oscillator potential. The oscillator frequency is $\omega$. For $k_{\mathrm{B}}T \ll \hbar\omega$, find the lowest order nontrivial contribution to the heat capacity $C(T)$, using the ordinary canonical ensemble. The calculation depends on whether $N$ is even or odd, so be careful! Then repeat your calculation for $S = \frac{3}{2}$.

Solution :

The partition function is given by

$$Z = g_0 \, e^{-\beta E_0} + g_1 \, E^{-\beta E_1} + \dots \quad ,$$

where $g_j$ and $E_j$ are the degeneracy and energy of the $j^{\mathrm{th}}$ energy level, respectively. From this, we have

$$F = -k_{\mathrm{B}}T \ln Z = E_0 - k_{\mathrm{B}}T \ln\left(g_0 + g_1 \, e^{-\Delta_1/k_{\mathrm{B}}T} + \dots\right) \quad ,$$

where $\Delta_j \equiv E_j - E_0$ is the excitation energy for energy level $j > 1$. Suppose that the spacings between consecutive energy levels are much larger than the temperature, *i.e.* $E_{j+1} - E_j \gg k_{\mathrm{B}}T$. This is the case for any harmonic oscillator system so long as $\hbar\omega \gg k_{\mathrm{B}}T$, where $\omega$ is the oscillator frequency. We then have

$$F = E_0 - k_{\mathrm{B}}T \ln g_0 - \frac{g_1}{g_0} k_{\mathrm{B}}T \, e^{-\Delta_1/k_{\mathrm{B}}T} + \dots$$

The entropy is

$$S = -\frac{\partial F}{\partial T} = \ln g_0 + \frac{g_1}{g_0} \, e^{-\Delta_1/k_{\mathrm{B}}T} + \frac{g_1}{g_0} \frac{\Delta_1}{T} \, e^{-\Delta_1/k_{\mathrm{B}}T} + \dots$$

and thus the heat capacity is

$$C(T) = T \frac{\partial S}{\partial T} = \frac{g_1}{g_0} \frac{\Delta_1^2}{k_{\mathrm{B}}T^2} \, e^{-\Delta_1/k_{\mathrm{B}}T} + \dots$$

With $g_0 = g_1 = 1$, this recovers what we found in ch. 4 of the lecture notes for the low temperature behavior of the Schottky two level system.

OK, so now let us consider the problem at hand, which is the one-dimensional harmonic oscillator, whose energy levels lie at $E_j = (j + \frac{1}{2})\hbar\omega$, hence $\Delta_j = j\hbar\omega$ is the $j^{\mathrm{th}}$ excitation energy. For $S = \frac{1}{2}$, each level is twofold degenerate. When $N$ is even, the ground state is unique, and we occupy states $|j, \uparrow\rangle$ and $|j, \downarrow\rangle$ for $j \in \{0, \dots, \frac{N}{2} - 1\}$. Thus, the ground state is nondegenerate and $g_0 = 1$. The lowest energy excited states are then made, at fixed total particle number $N$, by promoting either of the $|j = \frac{N}{2} - 1, \sigma\rangle$ levels ($\sigma = \uparrow$ or $\downarrow$) to $j = \frac{N}{2}$. There are $g_1 = 2$ ways to do this, each of which increases the energy by $\Delta_1 = \hbar\omega$. When $N$ is odd, we fill one of the spin species up to level $j = \frac{N-1}{2}$ and the other up to level $j = \frac{N+1}{2}$. In this case $g_0 = 2$. What about the excited states? It turns out that $g_1 = 4$, as can be seen from the diagrams in Fig. 36. For $N$ odd, in either of the two ground states, the highest occupied oscillator level is $j = \frac{N+1}{2}$, which is only half-occupied with one of the two spin species. To make an excited state, one can either *(i)* promote the occupied state to the next oscillator level $j = \frac{N+3}{2}$, or *(ii)* fill the unoccupied state by promoting the occupied state from the $j = \frac{N-1}{2}$ level. So $g_1 = 2 \cdot 2 = 4$. Thus, for either possibility regarding the parity of $N$, we have $g_1/g_0 = 2$, which means

$$C(T) = \frac{2(\hbar\omega)^2}{k_{\mathrm{B}}T^2} \, e^{-\hbar\omega/k_{\mathrm{B}}T} + \dots$$

This result is valid for $N > 1$.

An exception occurs when $N = 1$, where the lone particle is in the $n = 0$ oscillator level. Since there is no $n = -1$ level, the excited state degeneracy is then $g_1 = 2$, and the heat capacity is half the above value. Of course, for $N = 0$ we have $C = 0$.

What happens for general spin $S$? Now each oscillator level has a $K \equiv 2S+1$ spin degeneracy. We may write $N = rK + s$, where $r$ and $s$ are integers and $s \in \{0, 1, \ldots, K-1\}$. The ground states are formed by fully occupying all $|j, m\rangle$ states, with $m \in \{1, \ldots, K\}$, from $j = 0$ to $j = r-1$. The remaining $s$ particles must all be placed in the $K$ degenerate levels at $j = r$, and there are $\binom{K}{s}$ ways of achieving this. Thus, $g_0 = \binom{K}{s}$.

Now consider the excited states. We first assume $r > 0$. There are then two ways to make an excited state. If $s > 0$, we can promote one of the $s$ occupied states with $j = r$ to the next oscillator level $j = r+1$. One then has $s-1$ of the $K$ states with $j = r$ occupied, and one of the $K$ states with $j = r+1$ occupied. The degeneracy for this configuration is $g = \binom{K}{1}\binom{K}{s-1} = K\binom{K}{s-1}$. Another possibility is to promote one of the filled $j = r-1$ levels to the $j = r$ level, resulting in $K - 1$ occupied states with $j = r-1$ and $s+1$ occupied states with $j = r$. This is possible for any allowed value of $s$. The degeneracy of this configuration is $g = \binom{K}{K-1}\binom{K}{s+1} = K\binom{K}{s+1}$. Thus,

$$g_1 = K\binom{K}{s+1} + K\binom{K}{s-1} \quad,$$
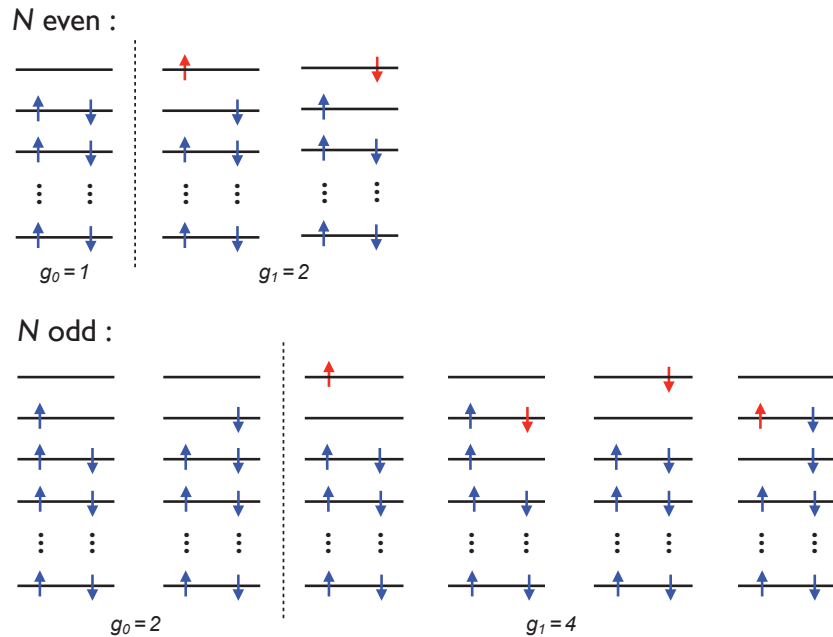


Figure 24: Ground states and first excited states for the $S = \frac{1}{2}$ one-dimensional simple harmonic oscillator.
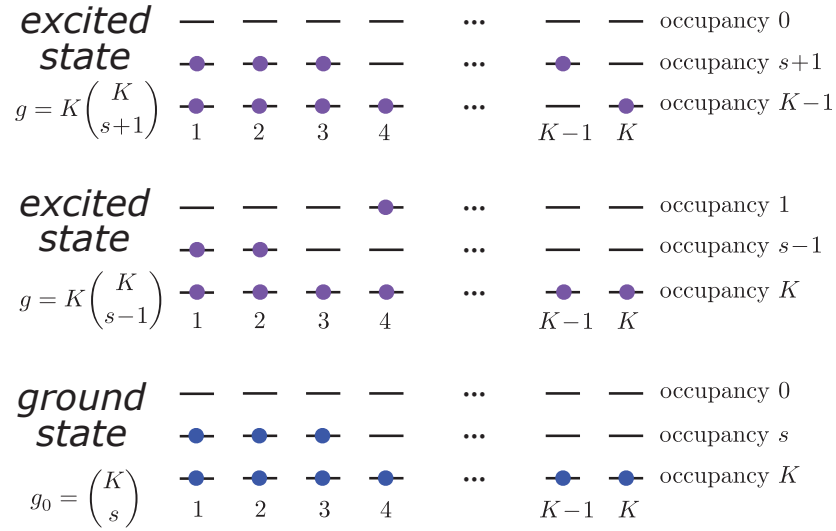
Figure 25: Ground states and first excited states for the general $S$ case, with $K = 2S+1$.

and thus for $r > 0$ and $s > 0$ we have

$$
C(T) = \frac{g_1}{g_0} \, k_{\mathrm{B}} \left( \frac{\hbar\omega}{k_{\mathrm{B}}T} \right)^2 e^{-\hbar\omega/k_{\mathrm{B}}T} + \dots
$$

$$
= K \cdot \left\{ \frac{K-s}{s+1} + \frac{s}{K-s+1} \right\} \cdot k_{\mathrm{B}} \left( \frac{\hbar\omega}{k_{\mathrm{B}}T} \right)^2 e^{-\hbar\omega/k_{\mathrm{B}}T} + \dots
$$

The situation is depicted in Fig. 37. Upon reflection, it becomes clear that this expression is also valid for $s = 0$, since the second term in the curly brackets in the above equation, which should be absent, yields zero anyway.

The exceptional cases occur when $r = 0$, in which case there is no $j = r-1$ level to depopulate. In this case, $g_1 = K\binom{K}{s-1}$ and $g_1/g_0 = Ks/(K - s + 1)$. Note that all our results are consistent with the $K = 2$ case studied earlier.

**(5.15)** A noninteracting Bose gas in $d = 3$ dimensions has dispersion $\varepsilon(\mathbf{k}) = \hbar c |\mathbf{k}|$.

(a) Find $T_{\mathrm{c}}(n)$.

(b) For $T < T_{\mathrm{c}}$, find $n(T, n_0)$ and $p(T)$.

(c) For $T > T_{\mathrm{c}}$, find $n(T, z)$ and $p(T, z)$.

(d) Find and plot the molar heat capacity at constant volume as a function of $T/T_{\mathrm{c}}$. Comment on its noteworthy features.

Solution :

(a) The density of states is obtained from $g(\varepsilon)\, d\varepsilon = \frac{d^3k}{(2\pi)^3}$, which yields

$$g(\varepsilon) = \frac{\varepsilon^2}{2\pi^2 (\hbar c)^3} \quad .$$

The critical temperature is then determined by

$$n = \int\limits_0^\infty d\varepsilon \; \frac{g(\varepsilon)}{e^{\varepsilon/k_{\mathrm{B}}T_{\mathrm{c}}} - 1} = \frac{\zeta(3)}{\pi^2} \left( \frac{k_{\mathrm{B}}T_{\mathrm{c}}}{\hbar c} \right)^3 \quad,$$

hence

$$T_{\mathrm{c}}(n) = \frac{\hbar c}{k_{\mathrm{B}}} \left( \frac{\pi^2 n}{\zeta(3)} \right)^{1/3} \quad .$$

One has $\zeta(3) \approx 1.2020569$.

(b) For $T < T_{\mathrm{c}}$, we have

$$n(T, n_0) = n_0 + \frac{\zeta(3)}{\pi^2} \left( \frac{k_{\mathrm{B}}T}{\hbar c} \right)^3$$

$$p(T) = \frac{\zeta(4)}{\pi^2} \frac{(k_{\mathrm{B}}T)^4}{(\hbar c)^3} \quad .$$

One has $\zeta(4) = \frac{\pi^4}{90} \approx 1.0823232$.

(c) For $T > T_{\mathrm{c}}$, we have

$$n(T, z) = \frac{1}{\pi^2} \left( \frac{k_{\mathrm{B}}T}{\hbar c} \right)^3 \mathrm{Li}_3(z)$$

$$p(T, z) = \frac{1}{\pi^2} \frac{(k_{\mathrm{B}}T)^4}{(\hbar c)^3} \mathrm{Li}_4(z) \quad .$$

(d) The energy is given by $E - \mu N = -\frac{\partial}{\partial \beta} \ln \Xi$. With $\ln \Xi = -\beta \Omega = \beta p V$, the energy for $T > T_{\mathrm{c}}$ is

$$E(T, V, z) = \mu N - V \frac{\partial}{\partial \beta} (\beta p)$$

$$= \frac{3V}{\pi^3} \frac{(k_{\mathrm{B}} T)^4}{(\hbar c)^3} \operatorname{Li}_4(z) \quad .$$

The particle number for $T > T_{\mathrm{c}}$ is

$$N(T, V, z) = \frac{V}{\pi^2} \left( \frac{k_{\mathrm{B}} T}{\hbar c} \right)^3 \operatorname{Li}_3(z) \quad .$$

When $T < T_{\mathrm{c}}$, we have

$$E(T, V) = \frac{3 \zeta(4) V}{\pi^3} \frac{(k_{\mathrm{B}} T)^4}{(\hbar c)^3} \quad , \qquad N(T, V, n_0) = V n_0 + \frac{\zeta(3) V}{\pi^2} \left( \frac{k_{\mathrm{B}} T}{\hbar c} \right)^3 \quad .$$

We may now compute $c_{V,N}$, the molar heat capacity at constant volume. For $T < T_{\mathrm{c}}$,

$$c_{V,N}(T, z) = \frac{N_{\mathrm{A}}}{N} \left( \frac{\partial E}{\partial T} \right)_{V,N} = \frac{12 \zeta(4)}{\zeta(3)} \left( \frac{T}{T_{\mathrm{c}}(n)} \right)^3 R \quad .$$

For $T > T_{\mathrm{c}}$, we write

$$dN\big|_V = \frac{3 V}{\pi^2} \left( \frac{k_{\mathrm{B}} T}{\hbar c} \right)^3 \operatorname{Li}_3(z) \frac{dT}{T} + \frac{V}{\pi^2} \left( \frac{k_{\mathrm{B}} T}{\hbar c} \right)^3 \operatorname{Li}_2(z) \frac{dz}{z} \quad ,$$

so setting $dN\big|_V = 0$ requires a relation between $dz$ and $dT$, *viz.*

$$\frac{dz}{z} = -\frac{dT}{T} \cdot \frac{3 \operatorname{Li}_3(z)}{\operatorname{Li}_2(z)} \quad .$$

We next differentiate the energy $E$, obtaining

$$dE\big|_V = \frac{12 k_{\mathrm{B}}}{\pi^2} V \left( \frac{k_{\mathrm{B}} T}{\hbar c} \right)^3 \operatorname{Li}_4(z) \, dT + \frac{3}{\pi^2} \frac{(k_{\mathrm{B}} T)^4}{(\hbar c)^3} \operatorname{Li}_2(z) \frac{dz}{z}$$

$$= \frac{3 k_{\mathrm{B}}}{\pi^2} V \left( \frac{k_{\mathrm{B}} T}{\hbar c} \right)^3 \left\{ 4 \operatorname{Li}_4(z) - \frac{3 \operatorname{Li}_3^2(z)}{\operatorname{Li}_2(z)} \right\} dT \quad .$$

Thus, dividing through by $dT$ and then by $N/N_{\mathrm{A}}$,

$$c_{V,N}(T, z) = 3R \left[ \frac{4 \operatorname{Li}_4(z)}{\operatorname{Li}_3(z)} - \frac{3 \operatorname{Li}_3(z)}{\operatorname{Li}_2(z)} \right] \quad ,$$

along with

$$n(T, z) = \frac{1}{\pi^2} \left( \frac{k_{\mathrm{B}} T}{\hbar c} \right)^3 \operatorname{Li}_3(z) \quad \Rightarrow \quad \operatorname{Li}_3(z) = \zeta(3) \left( \frac{T_{\mathrm{c}}(n)}{T} \right)^3 \quad .$$

Note that $z \to 0$ as $T \to \infty$, in which case $c_{V,N} \to 3R$, which is the appropriate Dulong-Petit result for the case of a linear dispersion in $d = 3$ dimensions.

One remarkable aspect to our result is that

$$\lim_{T \to T_c^-(n)} c_{V,N}(T) = \frac{12\,\zeta(4)}{\zeta(3)}\,R \approx 10.80471\,R$$

$$\lim_{T \to T_c^+(n)} c_{V,N}(T) = \left[\frac{12\,\zeta(4)}{\zeta(3)} - \frac{9\,\zeta(3)}{\zeta(2)}\right] R \approx 4.227845\,R \quad ,$$

which says that $c_{V,N}(T)$ exhibits a *discontinuous drop* at the critical temperature $T_c(n)$.

**(5.16)** Consider free fermions with density of states $g(\varepsilon) = A\,\varepsilon^\alpha$ and number density $n$.

    (a) Find the Fermi energy $\varepsilon_{\mathrm{F}}(n)$.

    (b) Find the chemical potential shift at finite temperature up to terms of order $T^4$.

    (c) Find the heat capacity at constant volume $C_{V,N}$ to first order in $T$.

Solution :

(a) We have

$$n = \int_0^{\varepsilon_{\mathrm{F}}} d\varepsilon\, g(\varepsilon) = \frac{A\,\varepsilon_{\mathrm{F}}^{\alpha+1}}{\alpha+1} \quad \Rightarrow \quad \varepsilon_{\mathrm{F}} = \left(\frac{(\alpha+1)\,n}{A}\right)^{\frac{1}{\alpha+1}} \quad .$$

(b) Invoking the Sommerfeld expansion,

$$n = \int_0^{\varepsilon_{\mathrm{F}}} d\varepsilon\, g(\varepsilon) + \tfrac{\pi^2}{6}\, g'(\varepsilon_{\mathrm{F}})\,(k_{\mathrm{B}}T)^2 + \tfrac{7\pi^4}{360}\, g'''(\varepsilon_{\mathrm{F}})\,(k_{\mathrm{B}}T)^4 + \ldots$$

We now write $\mu = \varepsilon_{\mathrm{F}} + \delta\mu$ and solve for $\delta\mu(\varepsilon_{\mathrm{F}}, T)$, using $n = \int_0^{\varepsilon_{\mathrm{F}}} d\varepsilon\, g(\varepsilon)$. We write the double power series expansion of the above result, up to orders $(k_{\mathrm{B}}T)^4$ and $(k_{\mathrm{B}}T)^2\,\delta\mu$:

$$0 = g(\varepsilon_{\mathrm{F}})\,\delta\mu + \tfrac{1}{2}g'(\varepsilon_{\mathrm{F}})\,(\delta\mu)^2 + \tfrac{\pi^2}{6}g'(\varepsilon_{\mathrm{F}})\,(k_{\mathrm{B}}T)^2 + \tfrac{\pi^2}{6}g''(\varepsilon_{\mathrm{F}})\,(k_{\mathrm{B}}T)^2\,\delta\mu + \tfrac{7\pi^4}{360}\,g'''(\varepsilon_{\mathrm{F}})\,(k_{\mathrm{B}}T)^4 + \ldots$$

We now solve for the coefficients of the order $(k_{\mathrm{B}}T)^2$ and $(k_{\mathrm{B}}T)^4$ terms in $\delta\mu(T)$, yielding

$$\delta\mu(T) = -\frac{\pi^2}{6}\frac{g'(\varepsilon_{\mathrm{F}})}{g(\varepsilon_{\mathrm{F}})}\,(k_{\mathrm{B}}T)^2 - \frac{\pi^4}{360}\left\{\frac{7\,g'''(\varepsilon_{\mathrm{F}})}{g(\varepsilon_{\mathrm{F}})} - \frac{10\,g'(\varepsilon_{\mathrm{F}})\,g''(\varepsilon_{\mathrm{F}})}{g^2(\varepsilon_{\mathrm{F}})} + \frac{5\,g'^3(\varepsilon_{\mathrm{F}})}{g^3(\varepsilon_{\mathrm{F}})}\right\}(k_{\mathrm{B}}T)^4 + \ldots$$

Substituting $g(\varepsilon) = A\,\varepsilon^\alpha$ into the above expression, we find

$$\delta\mu(T) = -\frac{\alpha\pi^2}{6}\frac{(k_{\mathrm{B}}T)^2}{\varepsilon_{\mathrm{F}}} - \frac{\alpha(\alpha-2)(2\alpha-7)\pi^4}{360}\frac{(k_{\mathrm{B}}T)^4}{\varepsilon_{\mathrm{F}}^3} + \ldots$$

(c) The heat capacity is

$$C_{V,N} = \tfrac{\pi^2}{3}\,V g(\varepsilon_{\mathrm{F}})\,k_{\mathrm{B}}^2 T = \tfrac{\pi^2}{3}\,V A\,\varepsilon_{\mathrm{F}}^\alpha\,k_{\mathrm{B}}^2 T \quad ,$$

where $\varepsilon_{\mathrm{F}}(n)$ is given in the solution to part (a).

**(5.17)** In an $n$-type semiconductor, the donor levels lie a distance $\Delta$ below the bottom of the conduction band. Suppose there are $M$ such donor levels. Due to the fact that such donor levels are spatially localized, one can ignore the possibility of double occupancy. Thus, each donor level can be occupied by at most one electron, but of either spin polarization. Assume the conduction band dispersion is isotropic, given by $\varepsilon_{\boldsymbol{k}} = \hbar^2 \boldsymbol{k}^2/2m^*$. You may set the conduction band minimum to $\varepsilon_c(0) \equiv 0$.

(a) Assuming that the conduction band is very sparsely populated, find an expression for the conduction electron density $n_c(T, \mu)$.

(b) Suppose there are $N_d$ electrons sitting on the donor sites, *i.e.* $N_d$ of the $M$ donor levels are singly occupied. Find the entropy of these electrons.

(c) Find the chemical potential of the donor electrons.

(d) Use the fact that the donor electrons and the conduction band electrons are in thermal equilibrium to eliminate $\mu$ from the problem, and find the conduction electron density $n_c(T)$ and the fraction $\nu_d(T)$ of occupied donor sites. Assume that the donor concentration is $\rho_d$, and that all conduction electrons are due to singly ionized donors.

Solution :

(a) We have
$$n_c = 2 \int \frac{d^3k}{(2\pi)^d} \frac{1}{e^{\beta(\varepsilon_{\boldsymbol{k}} - \mu_c)} + 1} \approx 2\lambda_c^{-3}\, e^{\mu_c/k_{\mathrm{B}}T} \quad,$$
where $\mu_c$ is the chemical potential and $\lambda_c = (2\pi\hbar^2/m^* k_{\mathrm{B}}T)^{1/2}$ thermal de Broglie wavelength for the conduction electrons.

(b) We assume that each donor site can either be empty, or else occupied by an electron in one of two possible polarization states. We forbid double occupancy of the donors, due to the large Coulomb energy associated with such a state. The number of configurations for $N_d$ occupied donor sites is then
$$\Omega(N_d, M) = 2^{N_d} \binom{M}{N_d} \quad,$$
and therefore
$$S_d = k_{\mathrm{B}} \ln\left(\frac{2^{N_d}\, M!}{N_d!\,(M - N_d)!}\right) \quad.$$
The free energy of the donor system is then
$$F(T, N_d, M) = -N_d\,\Delta - k_{\mathrm{B}}T \ln\left(\frac{2^{N_d}\, M!}{N_d!\,(M - N_d)!}\right)$$
$$\approx -N_d\,\Delta - N_d\, k_{\mathrm{B}}T \ln 2 + Mk_{\mathrm{B}}T \left\{ \frac{N_d}{M} \ln\left(\frac{N_d}{M}\right) + \left(\frac{M - N_d}{M}\right) \ln\left(\frac{M - N_d}{M}\right) \right\} \quad,$$

where we have invoked Stirling's approximation. The chemical potential for the donor level electrons, which we will need later, is then

$$\mu_{\mathrm{d}} = \left(\frac{\partial F}{\partial N_{\mathrm{d}}}\right)_{T,M} = -\Delta - k_{\mathrm{B}}T\ln 2 + k_{\mathrm{B}}T\ln\left(\frac{f_{\mathrm{d}}}{1-f_{\mathrm{d}}}\right) \quad,$$

where $f_{\mathrm{d}} = N_{\mathrm{d}}/M$ is the fraction of donor sites which are occupied.

(c) Invoking our results from part (a) and (b), and setting $\mu_{\mathrm{c}} = \mu_{\mathrm{d}} \equiv \mu$, we have

$$e^{\mu/k_{\mathrm{B}}T} = \tfrac{1}{2}\,n_{\mathrm{c}}\lambda_{\mathrm{c}}^3 = \tfrac{1}{2}\,e^{-\Delta/k_{\mathrm{B}}T}\,\frac{f_{\mathrm{d}}}{1-f_{\mathrm{d}}} \quad,$$

Thus,

$$\left(f_{\mathrm{d}}^{-1} - 1\right)n_{\mathrm{c}} = \lambda_{\mathrm{c}}^{-3}\,e^{-\Delta/k_{\mathrm{B}}T} \quad.$$

Now suppose the donor site density is $\rho_{\mathrm{d}}$. All the conduction electrons must come from ionized donor sites. The fraction of such sites is $1 - f_{\mathrm{d}}$, hence $n_{\mathrm{c}} = (1 - f_{\mathrm{d}})\,\rho_{\mathrm{d}}$. Therefore, we have

$$\frac{(1-f_{\mathrm{d}})^2}{f_{\mathrm{d}}} = \frac{e^{-\Delta/k_{\mathrm{B}}T}}{\rho_{\mathrm{d}}\lambda_{\mathrm{c}}^3} \equiv b(T) \quad.$$

This yields a quadratic equation for $1 - f_{\mathrm{d}}$, whose solution is

$$1 - f_{\mathrm{d}} = -\tfrac{1}{2}b + \sqrt{\tfrac{1}{4}b^2 + b} \qquad \Rightarrow \qquad n_{\mathrm{c}} = \left\{-\tfrac{1}{2}b + \sqrt{\tfrac{1}{4}b^2 + b}\right\}\rho_{\mathrm{d}} \quad.$$

Note that $f_{\mathrm{d}} \to 1$ as $b \to 0$. In this limit, which is achieved when $k_{\mathrm{B}}T \ll \Delta$, or when $\rho_{\mathrm{d}}\lambda_{\mathrm{c}}^3 \gg 1$, or by some combination of these two conditions, all the donor sites are occupied, and the conduction electron density is zero. It is energetically/entropically two costly for the donors to donate an electron to the conduction band. In the $T \to 0$ limit, we have $1 - f_{\mathrm{d}} \simeq \sqrt{b}$, hence the chemical potential becomes

$$\mu(T \to 0) = -\tfrac{1}{2}\Delta + k_{\mathrm{B}}T\ln\left[\tfrac{1}{2}\rho_{\mathrm{d}}\left(\frac{2\pi\hbar^2}{m^*k_{\mathrm{B}}T}\right)^{3/2}\right] \quad,$$

which ultimately ends up exactly halfway between the donor levels and the bottom of the conduction band.

This problem is very similar to the adsorption model considered in ch. 4 of the lecture notes. There, we considered a surface of adsorption sites in equilibrium with a classical gas. The only difference here is that the adsorbate particles can exist in one of two energetically degenerate polarization states. One can also solve for the donor density in the grand canonical ensemble. The donors are independent, hence the partition function for the donor electrons is

$$\Xi_{\mathrm{d}} = \left(1 + 2\,e^{\mu/k_{\mathrm{B}}T}\,e^{\Delta/k_{\mathrm{B}}T}\right)^M \quad.$$

Note the factor of two, due to the degeneracy of the spin polarization states. If we were to include the possibility of doubly occupied donors, we would have instead

$$\Xi_{\mathrm{d}} = \left(1 + 2\,e^{\mu/k_{\mathrm{B}}T}\,e^{\Delta/k_{\mathrm{B}}T} + e^{2\mu/k_{\mathrm{B}}T}\,e^{(2\Delta-U)/k_{\mathrm{B}}T}\right)^M \quad,$$

where the energy of the doubly occupied level is $-2\Delta + U$, with $U$ being the Coulomb repulsion energy for two electrons to sit on the same localized donor site. Again, we have assumed $U$ is much larger than every other energy scale in this problem, meaning we can ignore the possibility of double occupancy. The grand potential for the donor electrons is then $\Omega_{\mathrm{d}} = -k_{\mathrm{B}}T \ln \Xi_{\mathrm{d}}$, and so

$$f_{\mathrm{d}} = -\frac{1}{M} \left( \frac{\partial \Omega_{\mathrm{d}}}{\partial \mu} \right)_{T,M} = \frac{1}{\frac{1}{2} e^{-(\mu+\Delta)/k_{\mathrm{B}}T} + 1} \quad ,$$

which recovers the result previously obtained in part (a).

## 0.6   Interacting Classical Systems

**(6.1)** Consider a model in which there are three possible states per site, which we can denote by A, B, and V. The states A and B are for our purposes identical. The energies of A-A, A-B, and B-B links are all identical and equal to $W$. The state V represents a vacancy, and any link containing a vacancy, meaning A-V, B-V, or V-V, has energy $0$.

(a) Suppose we write $\sigma = +1$ for A, $\sigma = -1$ for B, and $\sigma = 0$ for V. How would you write a Hamiltonian for this system? Your result should be of the form

$$\hat{H} = \sum_{\langle ij \rangle} E(\sigma_i, \sigma_j) \quad .$$

Find a simple and explicit function $E(\sigma, \sigma')$ which yields the correct energy for each possible bond configuration.

(b) Consider a triangle of three sites. Find the average total energy at temperature $T$. *There are $3^3 = 27$ states for the triangle. You can just enumerate them all and find the energies.*

(c) For a one-dimensional ring of $N$ sites, find the $3 \times 3$ transfer matrix $R$. Find the free energy per site $F(T, N)/N$ and the ground state entropy per site $S(T, N)/N$ in the $N \to \infty$ limit for the cases $W < 0$ and $W > 0$. Interpret your results. *The eigenvalue equation for $R$ factorizes, so you only have to solve a quadratic equation.*

Solution :

(a) The quantity $\sigma_i^2$ is $1$ if site $i$ is in state A or B and is $0$ in state V. Therefore we have

$$\hat{H} = W \sum_{\langle ij \rangle} \sigma_i^2 \sigma_j^2 \quad .$$

(b) Of the 27 states, eight have zero vacancies – each site has two possible states A and B – with energy $E = 3W$. There are 12 states with one vacancy, since there are three possible locations for the vacancy and then four possibilities for the remaining two sites (each can be either A or B). Each of these 12 single vacancy states has energy $E = W$. There are 6 states with two vacancies and 1 state with three vacancies, all of which have energy $E = 0$. The partition function is therefore

$$Z = 8\,e^{-3\beta W} + 12\,e^{-\beta W} + 7 \quad .$$

Note that $Z(\beta = 0) = \text{Tr } 1 = 27$ is the total number of 'microstates'. The average energy is then

$$E = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \left( \frac{24\,e^{-3\beta W} + 12\,e^{-\beta W}}{8\,e^{-3\beta W} + 12\,e^{-\beta W} + 7} \right) W$$

(c) The transfer matrix is

$$R_{\sigma\sigma'} = e^{-\beta W \sigma^2 \sigma'^2} = \begin{pmatrix} e^{-\beta W} & e^{-\beta W} & 1 \\ e^{-\beta W} & e^{-\beta W} & 1 \\ 1 & 1 & 1 \end{pmatrix} \quad ,$$

where the row and column indices are A (1), B (2), and V (3), respectively. The partition function on a ring of $N$ sites is

$$Z = \lambda_1^N + \lambda_2^N + \lambda_3^N \quad ,$$

where $\lambda_{1,2,3}$ are the three eigenvalues of $R$. Generally the eigenvalue equation for a $3 \times 3$ matrix is cubic, but we can see immediately that $\det R = 0$ because the first two rows are identical. Thus, $\lambda = 0$ is a solution to the characteristic equation $P(\lambda) = \det(\lambda \mathbb{I} - R) = 0$, and the cubic polynomial $P(\lambda)$ factors into the product of $\lambda$ and a quadratic. The latter is easily solved. One finds

$$P(\lambda) = \lambda^3 - (2x + 1)\,\lambda^2 + (2x - 2)\,\lambda \quad ,$$

where $x = e^{-\beta W}$. The roots are $\lambda = 0$ and

$$\lambda_\pm = x + \tfrac{1}{2} \pm \sqrt{x^2 - x + \tfrac{9}{4}} \quad .$$

The largest of the three eigenvalues is $\lambda_+$, hence, in the thermodynamic limit,

$$F = -k_{\mathrm{B}} T \ln Z = -N k_{\mathrm{B}} T \ln\left( e^{-W/k_{\mathrm{B}}T} + \tfrac{1}{2} + \sqrt{e^{-2W/k_{\mathrm{B}}T} - e^{-W/k_{\mathrm{B}}T} + \tfrac{9}{4}} \right) \quad .$$

The entropy is $S = -\frac{\partial F}{\partial T}$. In the limit $T \to 0$ with $W < 0$, we have

$$\lambda_+(T \to 0\,,\, W < 0) = 2\, e^{|W|/k_{\mathrm{B}}T} + e^{-|W|/k_{\mathrm{B}}T} + \mathcal{O}(e^{-2|W|/k_{\mathrm{B}}T}) \quad .$$

Thus

$$F(T \to 0\,,\, W < 0) = -N\,|W| - N k_{\mathrm{B}} T \ln 2 + \dots$$
$$S(T \to 0\,,\, W < 0) = N \ln 2 \quad .$$

When $W > 0$, we have

$$\lambda_+(T \to 0\,,\, W > 0) = 2 + \tfrac{2}{3}\, e^{-W/k_{\mathrm{B}}T} + \mathcal{O}(e^{-2W/k_{\mathrm{B}}T}) \quad .$$

Then

$$F(T \to 0\,,\, W > 0) = -N k_{\mathrm{B}} T \ln 2 - \tfrac{1}{3} N k_{\mathrm{B}} T\, e^{-W/k_{\mathrm{B}}T} + \dots$$
$$S(T \to 0\,,\, W > 0) = N \ln 2 \quad .$$

Thus, the ground state entropies are the same, even though the allowed microstates are very different. For $W < 0$, there are no vacancies. For $W > 0$, every link must contain at least one vacancy.

**(6.2)** The Blume-Capel model is a spin-1 version of the Ising model, with Hamiltonian

$$H = -J \sum_{\langle ij \rangle} S_i \, S_j - \Delta \sum_i S_i^2 \quad ,$$

where $S_i \in \{-1, \, 0, \, +1\}$ and where the first sum is over all links of a lattice and the second sum is over all sites. It has been used to describe magnetic solids containing vacancies ($S = 0$ for a vacancy) as well as phase separation in ${}^4\text{He} - {}^3\text{He}$ mixtures ($S = 0$ for a ${}^4\text{He}$ atom). For parts (b), (c), and (d) you should work in the thermodynamic limit. The eigenvalues and eigenvectors are such that it would shorten your effort considerably to use a program like `Mathematica` to obtain them.

- (a) Find the transfer matrix for the $d = 1$ Blume-Capel model.

- (b) Find the free energy $F(T, \Delta, N)$.

- (c) Find the density of $S = 0$ sites as a function of $T$ and $\Delta$.

- (d) *Exciting!* Find the correlation function $\langle \, S_j \, S_{j+n} \, \rangle$ .

Solution :

(a) The transfer matrix $R$ can be written in a number of ways, but it is aesthetically pleasing to choose it to be symmetric. In this case we have

$$R_{SS'} = e^{\beta JSS'} e^{\beta \Delta (S^2 + S'^2)/2} = \begin{pmatrix} e^{\beta(\Delta+J)} & e^{\beta\Delta/2} & e^{\beta(\Delta-J)} \\ e^{\beta\Delta/2} & 1 & e^{\beta\Delta/2} \\ e^{\beta(\Delta-J)} & e^{\beta\Delta/2} & e^{\beta(\Delta+J)} \end{pmatrix} \quad .$$

(b) For an $N$-site ring, we have

$$Z = \text{Tr}\, e^{-\beta H} = \text{Tr}\,(R^N) = \lambda_+^N + \lambda_0^N + \lambda_-^N \quad ,$$

where $\lambda_+$, $\lambda_0$, and $\lambda_-$ are the eigenvalues of the transfer matrix $R$. To find the eigenvalues, note that

$$\vec{\psi}_0 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

is an eigenvector with eigenvalue $\lambda_0 = 2 \, e^{\beta\Delta} \sinh(\beta J)$. The remaining eigenvectors must be orthogonal to $\psi_0$, and hence are of the form

$$\vec{\psi}_\pm = \frac{1}{\sqrt{2 + x_\pm^2}} \begin{pmatrix} 1 \\ x_\pm \\ 1 \end{pmatrix} \quad .$$

We now demand

$$R \begin{pmatrix} 1 \\ x \\ 1 \end{pmatrix} = \begin{pmatrix} 2 \, e^{\beta\Delta} \cosh(\beta J) + x \, e^{\beta\Delta/2} \\ 2 \, e^{\beta\Delta/2} + x \\ 2 \, e^{\beta\Delta} \cosh(\beta J) + x \, e^{\beta\Delta/2} \end{pmatrix} = \begin{pmatrix} \lambda \\ \lambda x \\ \lambda \end{pmatrix} \quad ,$$

resulting in the coupled equations

$$\lambda = 2\,e^{\beta\Delta}\cosh(\beta J) + x\,e^{\beta\Delta/2}$$
$$\lambda x = 2e^{\beta\Delta/2} + x \quad.$$

Eliminating $x$, one obtains a quadratic equation for $\lambda$. The solutions are

$$\lambda_{\pm} = \left(e^{\beta\Delta}\cosh(\beta J) + \tfrac{1}{2}\right) \pm \sqrt{\left(e^{\beta\Delta}\cosh(\beta J) + \tfrac{1}{2}\right)^2 + 2\,e^{\beta\Delta}}$$
$$x_{\pm} = e^{-\beta\Delta/2}\left\{\left(\tfrac{1}{2} - e^{\beta\Delta}\cosh(\beta J)\right) \pm \sqrt{\left(\tfrac{1}{2} - e^{\beta\Delta}\cosh(\beta J)\right)^2 + 2\,e^{\beta\Delta}}\right\} \quad.$$

Note $\lambda_{+} > \lambda_0 > 0 > \lambda_{-}$ and that $\lambda_{+}$ is the eigenvalue of the largest magnitude. This is in fact guaranteed by the *Perron-Frobenius theorem*, which states that for any positive matrix $R$ (*i.e.* a matrix whose elements are all positive) there exists a positive real number $p$ such that $p$ is an eigenvalue of $R$ and any other (possibly complex) eigenvalue of $R$ is smaller than $p$ in absolute value. Furthermore the associated eigenvector $\vec{\psi}$ is such that all its components are of the same sign. In the thermodynamic limit $N \to \infty$ we then have

$$F(T, \Delta, N) = -Nk_{\mathrm{B}}T \ln \lambda_{+} \quad.$$

(c) Note that, at any site,

$$\langle S^2 \rangle = -\frac{1}{N}\frac{\partial F}{\partial \Delta} = \frac{1}{\beta}\frac{\partial \ln \lambda_{+}}{\partial \Delta} \quad,$$

and furthermore that

$$\delta_{S,0} = 1 - S^2 \quad.$$

Thus,

$$\nu_0 \equiv \frac{N_0}{N} = 1 - \frac{1}{\beta}\frac{\partial \ln \lambda_{+}}{\partial \Delta} \quad.$$

After some algebra, find

$$\nu_0 = 1 - \frac{r - \tfrac{1}{2}}{\sqrt{r^2 + 2\,e^{\beta\Delta}}} \quad,$$

where

$$r = e^{\beta\Delta}\cosh(\beta J) + \tfrac{1}{2} \quad.$$

It is now easy to explore the limiting cases $\Delta \to -\infty$, where we find $\nu_0 = 1$, and $\Delta \to +\infty$, where we find $\nu_0 = 0$. Both these limits make physical sense.

(d) We have

$$C(n) = \langle S_j\,S_{j+n}\rangle = \frac{\mathsf{Tr}\left(\Sigma\,R^n\,\Sigma\,R^{N-n}\right)}{\mathsf{Tr}\left(R^N\right)} \quad,$$

where $\Sigma_{SS'} = S\,\delta_{SS'}$. We work in the thermodynamic limit. Note that $\langle + | \Sigma | + \rangle = 0$, therefore we must write

$$R = \lambda_{+}\,|+\rangle\langle+| + \lambda_0\,|0\rangle\langle0| + \lambda_{-}\,|-\rangle\langle-| \quad,$$

and we are forced to choose the middle term for the $n$ instances of $R$ between the two $\Sigma$ matrices. Thus,

$$C(n) = \left(\frac{\lambda_0}{\lambda_+}\right)^n |\langle + | \Sigma | 0 \rangle|^2 \quad .$$

We define the correlation length $\xi$ by

$$\xi = \frac{1}{\ln\left(\lambda_+/\lambda_0\right)} \quad ,$$

in which case

$$C(n) = A \, e^{-|n|/\xi} \quad ,$$

where now we generalize to positive and negative values of $n$, and where

$$A = |\langle + | \Sigma | 0 \rangle|^2 = \frac{1}{1 + \frac{1}{2}x_+^2} \quad .$$

**(6.3)** DC Comics superhero Clusterman and his naughty dog Henry are shown in Fig. 26. Clusterman, as his name connotes, is a connected diagram, but the diagram for Henry contains some disconnected pieces.

(a) Interpreting the diagrams as arising from the Mayer cluster expansion, compute the symmetry factor $s_\gamma$ for Clusterman.

(b) What is the *total* symmetry factor for Henry and his disconnected pieces? What would the answer be if, unfortunately, another disconnected piece of the same composition were to be found?

(c) What is the lowest order virial coefficient to which Clusterman contributes?
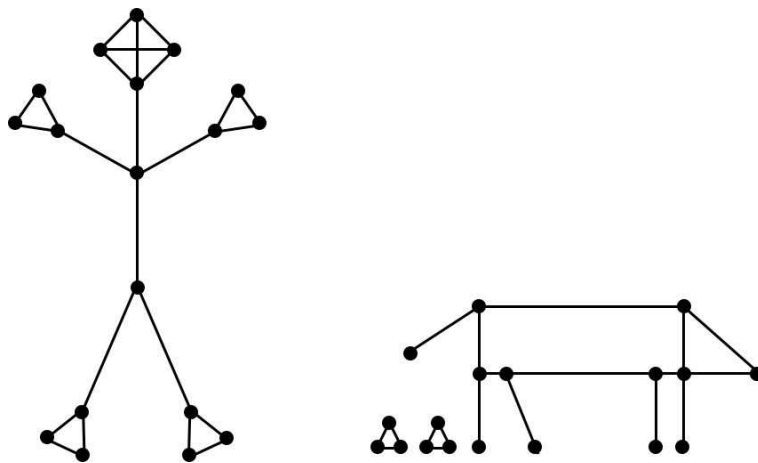


Figure 26: Mayer expansion diagrams for Clusterman and his dog.

Solution :

First of all, this is really disgusting and you should all be ashamed that you had anything to do with this problem.

(a) Clusterman's head gives a factor of 6 because the upper three vertices can be permuted among themselves in any of $3! = 6$ ways. Each of his hands gives a factor of 2 because each hand can be rotated by $\pi$ about its corresponding arm. The arms themselves can be interchanged, by rotating his shoulders by $\pi$ about his body axis (Clusterman finds this invigorating). Finally, the analysis for the hands and arms applies just as well to the feet and legs, so we conclude

$$s_\gamma = 6 \cdot \left(2^2 \cdot 2\right)^2 = 3 \cdot 2^7 = 384 \quad .$$

Note that an arm cannot be exchanged with a leg, because the two lower vertices on Clusterman's torso are not equivalent. Plus, that would be a really mean thing to do to Clusterman.

(b) Henry himself has no symmetries. The little pieces each have $s_\triangle = 3!$, and moreover they can be exchanged, yielding another factor of 2. So the total symmetry factor for Henry plus disconnected

pieces is $s_{\triangle\triangle} = 2! \cdot (3!)^2 = 72$. Were another little piece of the same... er... consistency to be found, the symmetry factor would be $s_{\triangle\triangle\triangle} = 3! \cdot (3!)^3 = 2^4 \cdot 3^4 = 1296$, since we get a factor of $3!$ from each of the $\triangle$ pieces, and a fourth factor of $3!$ from the permutations among the $\triangle$s.

(c) There are $18$ vertices in Clusterman, hence he will first appear in $B_{18}$.

**(6.4)** Use the high temperature expansion to derive the spin-spin correlation functions for a spin-$\frac{1}{2}$ ($\sigma_n = \pm 1$) Ising chain and Ising ring. Compare with the results in chapter 6 of the lecture notes.

**Solution :**

The spin-spin correlation function $C_{kl} = \langle \sigma_k \sigma_l \rangle$ is expressed as a ratio $Y_{kl}/Z$ as in ch. 6 of the lecture notes. For the chain, the only diagram which contributes to $Z$ is $\Gamma = \{\emptyset\}$, *i.e.* the trivial empty lattice. This is because there is no way to form closed loops on a chain. Thus $Z_{\text{ring}} = 2^N (\cosh \beta J)^{N-1}$ since the number of links is $N_{\text{L}} = N - 1$ (see LN eqn. 6.45). For the chain, in addition to the empty lattice, there is one closed loop that can be formed which includes every link of the chain. Thus $Z_{\text{chain}} = 2^N (\cosh \beta J)^N (1 + x^N)$, where $x = \tanh \beta J$. As for the numerator $Y_{kl}$, on the chain there is only one possible string, shown in Fig. 38, which extends between sites $k$ and $l$. Thus $Y_{kl}^{\text{chain}} = 2^N (\cosh \beta J)^{N-1} x^{|k-l|}$. On the ring there are two possible strings, since the ring is multiply connected. Thus $Y_{kl}^{\text{ring}} = 2^N (\cosh \beta J)^N (x^{|k-l|} + x^{N-|k-l|})$. Therefore,

$$C_{kl}^{\text{chain}} = x^{|k-l|} \qquad , \qquad C_{kl}^{\text{ring}} = \frac{x^{|k-l|} + x^{N-|k-l|}}{1 + x^N} \qquad .$$
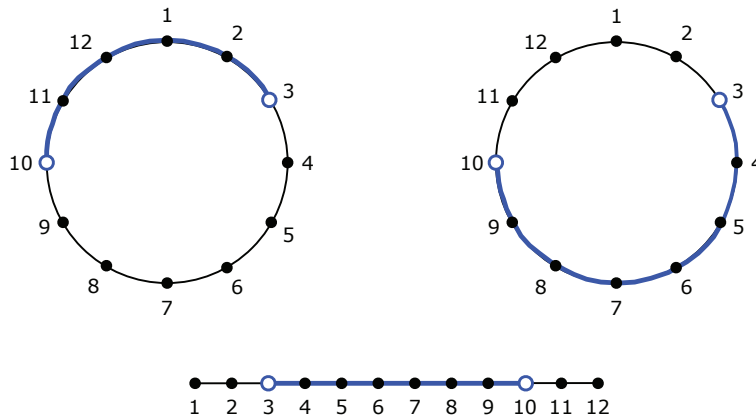


Figure 27: Diagrams for the numerator of the high temperature expansion of the spin-spin correlation function on an Ising ring and chain.

**(6.5)** An ionic solution of dielectric constant $\epsilon$ and mean ionic density $n$ fills a grounded conducting sphere of radius $R$. A charge $Q$ lies at the center of the sphere. Calculate the ionic charge density as a function of the radial coordinate $r$, assuming $Q/r \ll k_{\mathrm{B}}T$.

Solution :

Debye-Hückel theory tells us that

$$n_{\pm}(\boldsymbol{r}) = \tfrac{1}{2}n_{\infty}\, e^{\mp e\phi(\boldsymbol{r})/k_{\mathrm{B}}T}$$

and

$$\nabla^2\phi = -\frac{4\pi e}{\epsilon}\left(n_+ - n_-\right) - \frac{4\pi}{\epsilon}\,\rho_{\mathrm{ext}} \quad,$$

where $\epsilon$ is the dielectric constant. Assuming $\phi \ll k_{\mathrm{B}}T$, we have $\nabla^2\phi = \kappa_{\mathrm{D}}^2\,\phi - 4\pi\epsilon^{-1}\rho_{\mathrm{ext}}$, with

$$\kappa_{\mathrm{D}} = \sqrt{\frac{4\pi n_{\infty}e^2}{\epsilon\, k_{\mathrm{B}}T}} \quad.$$

Assuming a spherically symmetric solution, with a point charge $Q$ at the origin, we solve

$$\left(-\frac{1}{r}\frac{\partial^2}{\partial r^2}\,r + \kappa_{\mathrm{D}}^2\right)\phi = \frac{4\pi Q}{\epsilon}\,\delta(\boldsymbol{r}) \quad.$$

The solution is then of the form $\phi(r) = \frac{1}{r}\,u(r)$, with $u'' = \kappa_{\mathrm{D}}^2\,u$ for $r > 0$. Thus,

$$\phi(r) = A\,\frac{\cosh(\kappa_{\mathrm{D}}r)}{r} + B\,\frac{\sinh(\kappa_{\mathrm{D}}r)}{r} \quad.$$

As $r \to 0$ we must have an unscreened charge $Q$, hence $A = Q/\epsilon$. The boundary condition on the conducting sphere is $\phi(R) = 0$, hence $B = -A\,\mathrm{ctnh}\,(\kappa_{\mathrm{D}}R)$. Thus,

$$\phi(\boldsymbol{r}) = \frac{Q\cosh(\kappa_{\mathrm{D}}r)}{\epsilon\,r}\cdot\left(1 - \frac{\tanh(\kappa_{\mathrm{D}}r)}{\tanh(\kappa_{\mathrm{D}}R)}\right) \quad.$$

We stress that this solution is valid only where $e\,\phi(\boldsymbol{r}) \ll k_{\mathrm{B}}T$.

**(6.6)** Consider a three-dimensional gas of point particles interacting according to the potential

$$u(r) = \begin{cases} +\Delta_0 & \text{if } r \leq a \\ -\Delta_1 & \text{if } a < r \leq b \\ 0 & \text{if } b < r \end{cases} \quad ,$$

where $\Delta_{0,1}$ are both positive. Compute the second virial coefficient $B_2(T)$ and find a relation which determines the inversion temperature in a throttling process.

<span style="color:red">Solution :</span>

<span style="color:blue">The Mayer function is</span>

$$f(r) = \begin{cases} e^{-\Delta_0/k_B T} - 1 & \text{if } r \leq 0 \\ e^{\Delta_1/k_B T} - 1 & \text{if } a < r \leq b \\ 0 & \text{if } b < r \end{cases} \quad .$$

<span style="color:blue">The second virial coefficient is</span>

$$B_2(T) = -\tfrac{1}{2} \int d^3r \, f(r)$$

$$= \frac{2\pi a^3}{3} \cdot \left[ \left(1 - e^{-\Delta_0/k_B T}\right) + (s^3 - 1)\left(1 - e^{\Delta_1/k_B T}\right) \right] \quad ,$$

<span style="color:blue">where $s = b/a$. The inversion temperature is a solution of the equation $B_2(T) = T B_2'(T)$, which gives</span>

$$s^3 - 1 = \frac{1 + \left(\frac{\Delta_0}{k_B T} - 1\right) e^{-\Delta_0/k_B T}}{1 + \left(\frac{\Delta_1}{k_B T} + 1\right) e^{\Delta_1/k_B T}} \quad .$$

**(6.7)** At the surface of every metal a dipolar layer develops which lowers the potential energy for electrons inside the metal. Some electrons near the surface escape to the outside, leaving a positively charged layer behind, while overall there is charge neutrality. The situation is depicted in Fig. 28. The electron density outside the metal is very low and Maxwell-Boltzmann statistics are appropriate.
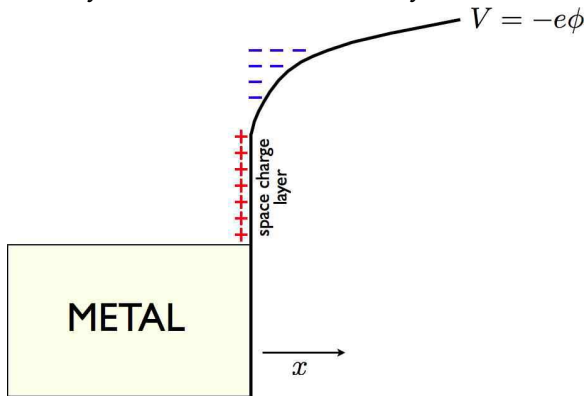


Figure 28: Electron distribution in the vicinity of the surface of a metal.

(a) Consider a flat metallic surface, normal to $\hat{x}$, located at $x = 0$. Assume for $x > 0$ an electronic distribution $n(x) = n_0 \exp(e\phi/k_{\mathrm{B}}T)$, where $\phi$ is the electric potential. For $x > 0$ there are only electrons; all the positive charges are located within the metal. Write down the self-consistent equation for the potential $\phi(x)$.

(b) Having found the self-consistent equation for $\phi(x)$, show that, multiplying by $\phi'(x)$, the equation can be integrated once, analogous to the conservation of energy for mechanical systems (with $\phi$ playing the role of the coordinate and $x$ playing the role of time). Show that the equation can be integrated once again to yield $\phi(x)$, with the constant determined by the requirement that $n(x = 0) = n_0$.

(c) Find $n(x)$.

Solution :

(a) The self-consistent equation is Poisson's equation,

$$\nabla^2 \phi = -4\pi\rho = 4\pi e n_0 \, e^{e\phi/k_{\mathrm{B}}T} \quad .$$

Since the only variation is along $x$, we have $\phi'' = 4\pi e n_0 \, e^{e\phi/k_{\mathrm{B}}T}$. Multiplying each side by $\frac{d\phi}{dx}$, we have

$$\frac{d}{dx}\left(\tfrac{1}{2}\phi'^2\right) = \frac{d}{dx}\left(4\pi n_0 \, k_{\mathrm{B}}T \, e^{e\phi/k_{\mathrm{B}}T}\right) \quad ,$$

and integrating this equation from $x$ to $\infty$ we obtain

$$\frac{d\phi}{dx} = -(8\pi n_0 \, k_{\mathrm{B}}T)^{1/2} \, e^{e\phi/2k_{\mathrm{B}}T} \quad .$$

Note also the choice of sign here, due to the fact that the potential $-e\phi$ for electrons must increase with $x$. The boundary term at $x = \infty$ must vanish since $n(\infty) = 0$, which requires $e^{e\phi(\infty)/k_{\mathrm{B}}T} = 0$.

(b) Integrating once more, we have

$$e^{-e\phi(x)/2k_{\mathrm{B}}T} = \left(\frac{2\pi n_0 \, e^2}{k_{\mathrm{B}}T}\right)^{1/2} (x + a) \quad ,$$

where $a$ is a constant of integration. Since $n(x = 0) \equiv n_0$, we must have $\phi(0) = 0$, and hence

$$a = \left(\frac{k_{\mathrm{B}}T}{2\pi n_0 \, e^2}\right)^{1/2} \quad .$$

Thus,

$$\phi(x) = -\frac{2k_{\mathrm{B}}T}{e} \ln\left(\frac{x+a}{a}\right) \quad .$$

(c) The electron number distribution is then

$$n(x) = n_0 \left(\frac{a}{x+a}\right)^2 \quad .$$

**(6.8)** In ch. 6 of the lecture notes, the virial equation of state is derived for a single species of particle.

(a) Generalize eqn. 5.160 to the case of two species interacting by $u_{\sigma\sigma'}(r)$, where $\sigma$ and $\sigma'$ are the species labels.

(b) For a plasma, show from Debye-Hückel theory that the pair correlation function is $g_{\sigma\sigma'} \propto \exp\left(-\sigma\sigma'q^2\phi(r)/k_BT\right)$, where $\sigma$ and $\sigma'$ are the signs of the charges (magnitude $q$), and $\phi(r)$ is the screened potential due to a unit positive test charge.

(c) Find the equation of state for a three-dimensional two-component plasma, in the limit where $T$ is large.

Solution :

(a) Let $i = 1, \ldots, N_+ + N_-$ index all the particles, and let $\sigma_i = \pm1$ denote the sign of the charge of particle $i$, with $\sigma_i = +1$ for $1 \le i \le N_+$ and $\sigma_i = -1$ for $(N_+ + 1) \le i \le (N_+ + N_-)$. In a globally neutral system, $N_+ = N_- \equiv \frac{1}{2}N$. We define

$$g_{\mu\nu}(\boldsymbol{r}) \equiv \frac{1}{n_\mu n_\nu} \Big\langle \sum_{i \ne j} \delta(\boldsymbol{r} - \boldsymbol{x}_i)\,\delta(\boldsymbol{x}_j)\,\delta_{\sigma_i,\mu}\,\delta_{\sigma_j,\nu} \Big\rangle \quad,$$

where $n_\mu$ is the density of particles of species $\mu$, with $\mu = \pm1$. As defined, $g_{\mu\nu}(\boldsymbol{r}) \to 1$ as $r \to \infty$. If instead we normalize $g_{\mu\nu}$ by dividing by $n_{\text{tot}}^2 = (n_+ + n_-)^2$, then we would have $g_{\mu\nu}(r \to \infty) = \frac{1}{4}$. We next work on the virial equation of state,

$$\frac{p}{k_BT} = \frac{N_+ + N_-}{V} - \frac{1}{3Vk_BT} \sum_{i=1}^{N_+ + N_-} \langle \boldsymbol{x}_i \cdot \boldsymbol{\nabla}_i W \rangle \quad.$$

The potential is

$$W = \sum_{i<j} \frac{\sigma_i\sigma_j\,q^2}{|\boldsymbol{x}_i - \boldsymbol{x}_j|} \equiv \sum_{i<j} u_{\sigma_i\sigma_j}\big(|\boldsymbol{x}_i - \boldsymbol{x}_j|\big) \quad,$$

with $u_{\sigma\sigma'}(r) = \sigma\sigma'q^2/r$. Then using translational invariance one has

$$\frac{p}{k_BT} = n_+ + n_- - \frac{2\pi}{3k_BT} \sum_{\sigma,\sigma'} n_\sigma n_{\sigma'} \int_0^\infty dr\, r^3\, u'_{\sigma\sigma'}(r)\, g_{\sigma\sigma'}(r)$$

(b) According to Debye-Hückel theory,

$$g_{\sigma\sigma'}(r) = \exp\left(-\frac{\sigma\sigma'q\,\phi(r)}{k_BT}\right) \quad,$$

where $\phi(r)$ is the screened potential at $r$ due to a point charge $q$ at the origin, which satisfies

$$\nabla^2\phi = 4\pi nq\,\sinh\big(q\phi/k_BT\big) - 4\pi q\,\delta(\boldsymbol{r}) \quad,$$

where $n_+ = n_- \equiv \frac{1}{2}n$. In the high temperature limit, we can expand the sinh function and we obtain the Yukawa potential

$$\phi(r) = \frac{q}{r}\, e^{-\kappa_{\mathrm{D}} r} \quad,$$

where

$$\kappa_{\mathrm{D}} = \left( \frac{4\pi n q^2}{k_{\mathrm{B}} T} \right)^{1/2}$$

is the Debye screening wavevector. Thus, we have

$$\frac{p}{k_{\mathrm{B}}T} = n - \frac{\pi n^2}{6 k_{\mathrm{B}} T} \int\limits_0^\infty dr\, r^3 \left( -\frac{q^2}{r^2} \right) \sum_{\sigma,\sigma'} \sigma\sigma'\, g_{\sigma\sigma'}(r)$$

$$= n - \frac{2\pi n^2 q^3}{3(k_{\mathrm{B}}T)^2} \int\limits_0^\infty dr\, r\, \phi(r) = n - \frac{2\pi n^2 q^4}{3(k_{\mathrm{B}}T)^2 \kappa_{\mathrm{D}}}$$

$$= n \left( 1 - \frac{\sqrt{\pi}\, n^{1/2}\, q^3}{3\, (k_{\mathrm{B}}T)^{3/2}} \right) \quad.$$

**(6.9)** Consider a liquid where the interaction potential is $u(r) = \Delta_0\,(a/r)^k$, where $\Delta_0$ and $a$ are energy and length scales, respectively. Assume that the pair distribution function is given by $g(r) \approx e^{-u(r)/k_{\mathrm B}T}$. Compute the equation of state. For what values of $k$ do your expressions converge?

Solution:

According to the virial equation of state in ch. 6 of the lecture notes,

$$p = nk_{\mathrm B}T - \tfrac{2}{3}\pi n^2 \int\limits_0^\infty dr\; r^3\, g(r)\, u'(r) \quad.$$

Substituting for $u(r)$ and $g(r)$ as in the statement of the problem, we change variables to

$$s \equiv \frac{u(r)}{k_{\mathrm B}T} \quad\Rightarrow\quad ds = \frac{u'(r)}{k_{\mathrm B}T}\, dr \quad,$$

so

$$r = a\left(\frac{\Delta_0}{k_{\mathrm B}T}\right)^{1/k} s^{-1/k}$$

and

$$r^3\, g(r)\, u'(r)\, dr = k_{\mathrm B}T\, a^3 \left(\frac{\Delta_0}{k_{\mathrm B}T}\right)^{3/k} s^{-3/k}\, e^{-s}\, ds \quad.$$

We then have

$$p = nk_{\mathrm B}T + \tfrac{2}{3}\pi n^3 a^3 k_{\mathrm B}T \left(\frac{\Delta_0}{k_{\mathrm B}T}\right)^{3/k} \int\limits_0^\infty ds\; s^{-3/k}\, e^{-s}$$

$$= nk_{\mathrm B}T\left\{1 + \tfrac{2}{3}\pi\Gamma\left(1 - \tfrac{3}{k}\right) na^3 \left(\frac{\Delta_0}{k_{\mathrm B}T}\right)^{3/k}\right\} \quad.$$

Note that a minus sign appears because we must switch the upper and lower limits on the $s$ integral. This expression converges provided $k < 0$ or $k > 3$.

**(6.10)** Consider a charge $Q$ impurity located at the origin of a two-dimensional metallic plane. You may model the plane initially as a noninteracting Fermi gas in the presence of a neutralizing background. Poisson's equation is

$$\nabla^2 \phi = 4\pi e \big[ n(\boldsymbol{\rho}) - n_0 \big] \delta(z) - 4\pi Q \, \delta(\boldsymbol{\rho}) \, \delta(z) \quad ,$$

where $r = (\boldsymbol{\rho}, z)$ is decomposed into a two-dimensional vector $\boldsymbol{\rho}$ and the scalar $z$, and where $n_0$ is the number density of electrons at $|\boldsymbol{\rho}| = \infty$.

- (a) Using the Thomas-Fermi approach, find the two-dimensional electron number density $n(\boldsymbol{\rho})$ in terms of the local potential $\phi(\boldsymbol{\rho}, 0)$.

- (b) By Fourier transformation, show that

$$\hat{\phi}(\boldsymbol{k}, q) = \frac{4\pi Q}{k^2 + q^2} - \frac{4\pi n_0 e^2}{\varepsilon_{\mathrm{F}}} \frac{\hat{\chi}(\boldsymbol{k})}{k^2 + q^2} \quad ,$$

  where $\boldsymbol{k}$ is a two-dimensional wavevector, and

$$\hat{\chi}(\boldsymbol{k}) = \int\limits_{-\infty}^{\infty} \frac{dq}{2\pi} \, \hat{\phi}(\boldsymbol{k}, q) \quad .$$

- (c) Solve for $\hat{\chi}(\boldsymbol{k})$ and then for $\hat{\phi}(\boldsymbol{k}, q)$.

- (d) Derive an expression for the potential $\phi(\boldsymbol{\rho}, z)$.

- (e) Derive an expression for the local charge density $\varrho(\boldsymbol{\rho}) = e n_0 - e n(\boldsymbol{\rho})$. Show that $\varrho(\boldsymbol{\rho}) = \frac{Q}{2\pi\lambda^2} f(\rho/\lambda)$, where $\lambda$ is a screening length and $f(s)$ is some function, and expression for which you should derive. Sketch $f(s)$.

Solution:

(a) In two dimensions we have

$$n = 2 \int \frac{d^2k}{(2\pi)^2} \, \Theta(k_{\mathrm{F}} - k) = \frac{k_{\mathrm{F}}^2}{2\pi} = \frac{m\varepsilon_{\mathrm{F}}}{\pi\hbar^2} \quad ,$$

where we have used $\varepsilon_{\mathrm{F}} = \hbar^2 k_{\mathrm{F}}^2 / 2m$. In the presence of a potential, the energy levels are shifted and it is the electrochemical potential $\varepsilon_{\mathrm{F}}^\infty = \varepsilon_{\mathrm{F}} - e\phi$ which is constant throughout the system. Thus, the local electron density is

$$n(\boldsymbol{\rho}) = \frac{m}{\pi\hbar^2} \Big[ \varepsilon_{\mathrm{F}}^\infty + e\,\phi(\boldsymbol{\rho}, 0) \Big] = n_0 + \frac{me}{\pi\hbar^2} \, \phi(\boldsymbol{\rho}, 0) \quad .$$

Here, $\phi(\boldsymbol{r}) = \phi(\boldsymbol{\rho}, z)$ is the electrostatic potential in three-dimensional space. When we restrict to the $z = 0$ plane we write $\phi(\boldsymbol{\rho}, 0)$.

(b) We now have

$$\nabla^2 \phi = \frac{4}{a_{\mathrm{B}}} \, \phi(\boldsymbol{\rho}, 0) \, \delta(z) - 4\pi Q \, \delta(\boldsymbol{\rho}) \, \delta(z) \quad ,$$

where $a_{\mathrm{B}} = \hbar^2/me^2$ is the Bohr radius. Now we take the Fourier transform by multiplying the above equation by $e^{i\boldsymbol{k}\cdot\boldsymbol{\rho}}e^{iqz}$ and then integrating over all $\boldsymbol{\rho}$ and $z$. This gives

$$-(\boldsymbol{k}^2 + q^2)\hat{\phi}(\boldsymbol{k}, q) = \frac{4}{a_{\mathrm{B}}} \overbrace{\int_{-\infty}^{\infty} \frac{dq}{2\pi} \, \hat{\phi}(\boldsymbol{k}, q)}^{\hat{\chi}(\boldsymbol{k})} - 4\pi Q \quad ,$$

hence

$$\hat{\phi}(\boldsymbol{k}, q) = \frac{4\pi Q}{\boldsymbol{k}^2 + q^2} - \frac{4}{a_{\mathrm{B}}} \frac{\hat{\chi}(\boldsymbol{k})}{\boldsymbol{k}^2 + q^2} \quad .$$

(c) To solve for $\hat{\chi}(\boldsymbol{k})$ we integrate the above equation over $q$ and use the fact that

$$\int_{-\infty}^{\infty} \frac{dq}{2\pi} \frac{e^{iqz}}{\boldsymbol{k}^2 + q^2} = \frac{e^{-|\boldsymbol{k}z|}}{2\,|\boldsymbol{k}|} \quad .$$

Thus,

$$\hat{\chi}(\boldsymbol{k}) = \frac{2\pi Q}{|\boldsymbol{k}|} - \frac{2}{|\boldsymbol{k}a_{\mathrm{B}}|} \hat{\chi}(\boldsymbol{k})$$

Thus,

$$\hat{\chi}(\boldsymbol{k}) = \frac{2\pi Q}{|\boldsymbol{k}| + \lambda^{-1}} \quad ,$$

where $\lambda = \frac{1}{2}a_{\mathrm{B}}$. Plugging this back into our equation for $\hat{\phi}(\boldsymbol{k}, q)$, we obtain

$$\hat{\phi}(\boldsymbol{k}, q) = \frac{4\pi Q \cdot |\boldsymbol{k}\lambda|}{\left(\boldsymbol{k}^2 + q^2\right)\left(1 + |\boldsymbol{k}\lambda|\right)} \quad .$$

(d) Now we Fourier transform back to real space:

$$\begin{aligned}
\phi(\boldsymbol{\rho}, z) &= \int \frac{d^2k}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{dq}{2\pi} \, \hat{\phi}(\boldsymbol{k}, q) \, e^{i\boldsymbol{k}\cdot\boldsymbol{\rho}} \, e^{iqz} \\
&= \int \frac{d^2k}{(2\pi)^2} \frac{e^{-|\boldsymbol{k}z|}}{2\,|\boldsymbol{k}|} \cdot \frac{4\pi Q\,|\boldsymbol{k}\lambda|}{1 + |\boldsymbol{k}\lambda|} \cdot e^{i\boldsymbol{k}\cdot\boldsymbol{\rho}} \\
&= \frac{Q}{\lambda} \, F\big(\rho/\lambda, |z|/\lambda\big) \quad ,
\end{aligned}$$

where

$$F(\sigma, \zeta) = \int_0^{\infty} du \, \frac{u}{1 + u} \, J_0(\sigma u) \, e^{-\zeta u} \quad ,$$

where $J_0(s)$ is the Bessel function of order zero.

```
Integrate[BesselJ[0, u a] / (1 + u), {u, 0, Infinity}, Assumptions → Re[a] > 0 && Abs[Im[a]] == 0]
```

$$\frac{1}{2}\pi\,(-\text{BesselY}[0, a] + \text{StruveH}[0, a])$$

```
F[x_] := 1 / x + 1/2 π (BesselY[0, x] - StruveH[0, x])
```

```
Plot[F[x], {x, 0, 10}, AxesLabel → {σ, F[σ, 0]}, PlotStyle → Thick]
```
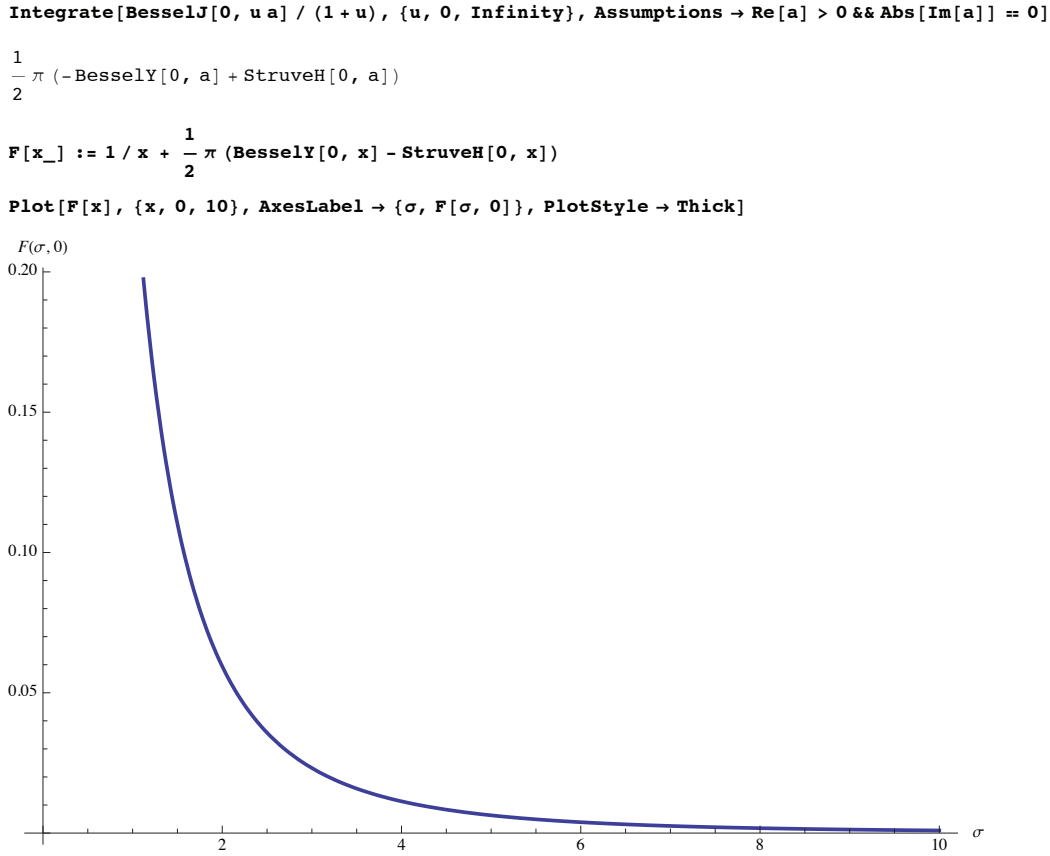


Figure 29: Plot of the screening charge density in units of $-Q/2\pi\lambda^2$ for problem (10).

(e) We have

$$\varrho(\boldsymbol{\rho}) = e\big[n_0 - n(\boldsymbol{\rho})\big] = -\frac{Q}{2\pi\lambda^2}\,F(\rho/\lambda, 0) \quad.$$

Note

$$F(\rho/\lambda, 0) = \int_0^\infty du\,\frac{u\,J_0(u\rho/\lambda)}{1 + u} = \frac{\lambda}{\rho} - \int_0^\infty du\,\frac{J_0(u\rho/\lambda)}{1 + u}$$

$$= \frac{\lambda}{\rho} + \tfrac{1}{2}\pi\,Y_0(\rho/\lambda) - \tfrac{1}{2}\pi\,\mathbf{H}_0(\rho/\lambda) \quad,$$

where $Y_0(s)$ is a Bessel function of the second kind and $\mathbf{H}_0(s)$ is the Struve function. Asymptotically[11] we obtain

$$\varrho(\boldsymbol{\rho}) = \frac{Q}{2\pi\lambda^2}\left\{\sum_{n=1}^{p-1}(-1)^n\,\Gamma^2\big(\tfrac{1}{2} + n\big)\left(\frac{2\lambda}{\rho}\right)^{(2n+1)} + \mathcal{O}\big(2\lambda/\rho\big)^{2p+1}\right\} \quad.$$

Note that $\varrho(\rho) \propto \rho^{-3}$ at large distances. In the above formula, $p$ is arbitrary. Since $\Gamma(z + \tfrac{1}{2}) \sim z\ln z - z$, the optimal value of $p$ to minimize the remainder in the sum is $p \approx \rho/2\lambda$. See Fig. 37 for a sketch.

---

[11]See Gradshteyn and Ryzhik §8.554, then use $\Gamma(z)\,\Gamma(1 - z) = \pi\csc(\pi z)$.

(**11**) The grand partition function for a system is given by the expression

$$\Xi = (1+z)^{V/v_0}\left(1 + z^{\alpha V/v_0}\right) \quad,$$

where $\alpha > 0$. In this problem, you are to work in the thermodynamic limit. You will also need to be careful to distinguish the cases $|z| < 1$ and $|z| > 1$.

(a) Find an expression for the pressure $p(T, z)$.

(b) Find an expression for the number density $n(T, z)$.

(c) Plot $v(p, T)$ as a function of $p$ for different temperatures and show there is a first order phase transition, *i.e.* a discontinuity in $v(p)$, which occurs for $|z| = 1$. What is the change in volume at the transition? .

Solution :

(a) The grand potential is

$$\Omega(T, z) = -k_{\rm B}T \ln \Xi = -\frac{k_{\rm B}TV}{v_0}\ln(1+z) - k_{\rm B}T\ln\left(1 + z^{\alpha V/v_0}\right) \quad.$$

Now take the thermodynamic limit $V/v_0 \to \infty$. One then has

$$\Omega(T, z) = -\frac{k_{\rm B}TV}{v_0}\ln(1+z) - \begin{cases} 0 & \text{if} \quad |z| < 1 \\ \frac{\alpha k_{\rm B}TV}{v_0}\ln z & \text{if} \quad |z| > 1 \end{cases} \quad.$$

From this we compute the pressure,

$$p = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = \frac{k_{\rm B}T}{v_0}\ln(1+z) + \frac{\alpha k_{\rm B}T}{v_0}\cdot\frac{z^{\alpha V/v_0}\ln z}{1 + z^{\alpha V/v_0}}$$

$$= \frac{k_{\rm B}T}{v_0}\ln(1+z) + \begin{cases} 0 & \text{if} \quad |z| < 1 \\ \frac{\alpha k_{\rm B}T}{v_0}\ln z & \text{if} \quad |z| > 1 \end{cases} \quad.$$

(b) For the density, we have

$$n = -\frac{z}{Vk_{\rm B}T}\left(\frac{\partial\Omega}{\partial z}\right)_{T,V} = \frac{1}{v_0}\cdot\frac{z}{1+z} + \frac{\alpha}{v_0}\cdot\frac{z^{\alpha V/v_0}}{1 + z^{\alpha V/v_0}}$$

$$= \frac{1}{v_0}\cdot\frac{z}{1+z} + \begin{cases} 0 & \text{if} \quad |z| < 1 \\ \alpha/v_0 & \text{if} \quad |z| > 1 \end{cases} \quad.$$

(c) We eliminate $z$ from the above equations, and we write $v = 1/n$ as the volume per particle. The fugacity $z(v)$ satisfies

$$
z(v) = \begin{cases}
\frac{v_0}{v-v_0} & \text{if} \quad v > 2v_0 \\[2ex]
1 & \text{if} \quad \frac{2v_0}{1+2\alpha} < v < 2v_0 \\[2ex]
\frac{v_0-\alpha v}{(1+\alpha)v-v_0} & \text{if} \quad \frac{v_0}{1+\alpha} < v < \frac{2v_0}{1+2\alpha} \\[2ex]
\infty & \text{if} \quad v < \frac{v_0}{1+\alpha}
\end{cases}
$$

We then have

$$
\frac{pv_0}{k_{\mathrm{B}}T} = \begin{cases}
\ln\left(\frac{v}{v-v_0}\right) & v > 2v_0 \\[2ex]
\ln 2 & \frac{2v_0}{1+2\alpha} < v < 2v_0 \\[2ex]
\ln\left[\left(\frac{v}{(1+\alpha)v-v_0}\right)\left(\frac{v_0-\alpha v}{(1+\alpha)v-v_0}\right)^{\alpha}\right] & \frac{v_0}{1+\alpha} < v < \frac{2v_0}{1+2\alpha} \\[2ex]
\infty & v < \frac{v_0}{1+\alpha}
\end{cases}
$$

Sample plots of $z(v)$ and $p(v)$ are shown in Fig. 30.
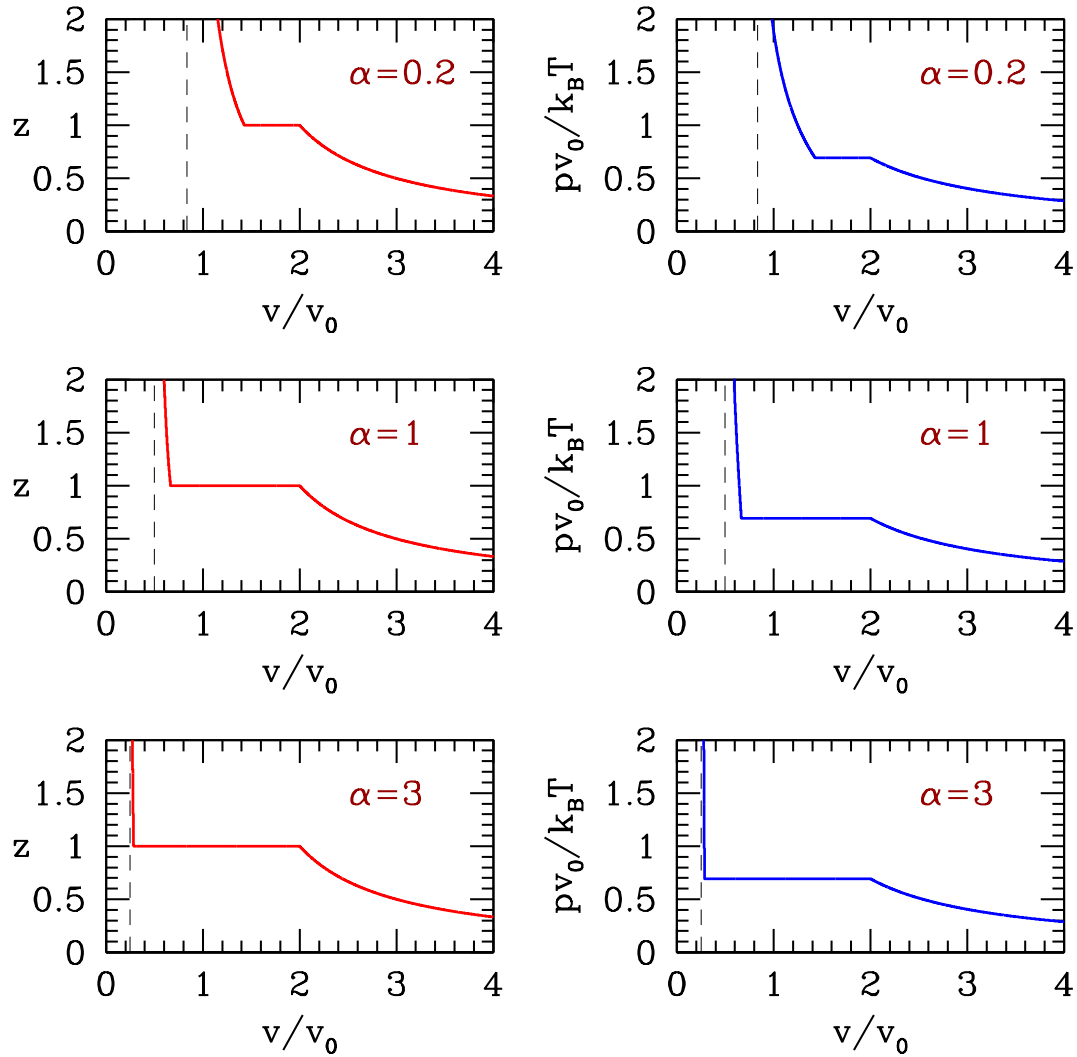
Figure 30: $z(v)$ and $p(v)$ for $\alpha = 0.2$, 1.0, and 3.0.

**(6.12)** In problem 11, you considered the thermodynamic properties associated with the grand partition function $\Xi(V,z) = (1+z)^{V/v_0}\left(1 + z^{\alpha V/v_0}\right)$. Consider now the following partition function:

$$\Xi(V,z) = (1+z)^{V/v_0} \prod_{j=1}^{K} \left\{ 1 + \left(\frac{z}{\sigma_j}\right)^{\alpha V/Kv_0} \right\} \quad .$$

Consider the thermodynamic limit where $\alpha$ is a number on the order of unity, $V/v_0 \to \infty$, and $K \to \infty$ but with $Kv_0/V \to 0$. For example, we might have $K \propto (V/v_0)^{1/2}$.

(a) Show that the number density is

$$n(T,z) = \frac{1}{v_0}\frac{z}{1+z} + \frac{\alpha}{v_0}\int_0^{|z|} d\sigma\, g(\sigma) \quad ,$$

where

$$g(\sigma) = \frac{1}{K} \sum_{j=1}^{K} \delta(\sigma - \sigma_j) \quad .$$

(b) Derive the corresponding expression for $p(T, z)$.

(c) In the thermodynamic limit, the spacing between consecutive $\sigma_j$ values becomes infinitesimal. In this case, $g(\sigma)$ approaches a continuous distribution. Consider the flat distribution,

$$g(\sigma) = \frac{1}{w} \, \Theta(\sigma - r) \, \Theta(r + w - \sigma) = \begin{cases} w^{-1} & \text{if } r < \sigma < r + w \\ 0 & \text{otherwise.} \end{cases}$$

The model now involves three dimensionless parameters[12]: $\alpha$, $r$, and $w$. Solve for $z(v)$. You will have to take cases, and you should find there are three regimes to consider[13].

(d) Plot $pv_0/k_{\mathrm{B}}T$ *versus* $v/v_0$ for the case $\alpha = \frac{1}{4}$ and $r = w = 1$.

(e) Comment on the critical properties (*i.e.* the singularities) of the equation of state.

Solution :

(a) We have

$$\frac{1}{V} \ln \Xi = \frac{1}{v_0} \ln(1 + z) + \frac{\alpha}{K v_0} \sum_{i=1}^{K} \ln(z/\sigma_i) \, \Theta\big(|z| - \sigma_i\big) \quad ,$$

so from $n = V^{-1} z \, \partial \ln \Xi / \partial z$,

$$n = \frac{1}{v_0} \frac{z}{1 + z} + \frac{\alpha}{K v_0} \sum_{i=1}^{K} \Theta\big(|z| - \sigma_i\big)$$

$$= \frac{1}{v_0} \frac{z}{1 + z} + \frac{\alpha}{v_0} \int_0^{|z|} d\sigma \, g(\sigma) \quad .$$

(b) The pressure is $p = V^{-1} k_{\mathrm{B}} T \ln \Xi$:

$$p = \frac{k_{\mathrm{B}} T}{v_0} \ln(1 + z) + \frac{\alpha k_{\mathrm{B}} T}{K v_0} \sum_{i=1}^{K} \ln(z/\sigma_i) \, \Theta\big(|z| - \sigma_i\big)$$

$$= \frac{k_{\mathrm{B}} T}{v_0} \ln(1 + z) + \frac{\alpha k_{\mathrm{B}} T}{v_0} \int_0^{|z|} d\sigma \, g(\sigma) \ln\big(z/\sigma\big) \quad .$$

---

[12] The quantity $v_0$ has dimensions of volume and disappears from the problem if one defines $\tilde{v} = v/v_0$.
[13] You should find that a fourth regime, $v < (1 + r^{-1})v_0$, is not permitted.

(c) We now consider the given form for $g(\sigma)$. From our equation for $n(z)$, we have

$$
nv_0 = \frac{v_0}{v} = \begin{cases} \frac{z}{1+z} & \text{if } |z| \leq r \\ \frac{z}{1+z} + \frac{\alpha}{w}(z-r) & \text{if } r \leq |z| \leq r+w \\ \frac{z}{1+z} + \alpha & \text{if } r+w \leq |z| \end{cases} .
$$

We need to invert this result. We assume $z \in \mathbb{R}^+$. In the first regime, we have

$$
z \in [\,0\,,\,r\,] \quad \Rightarrow \quad z = \frac{v_0}{v-v_0} \quad \text{with} \quad \frac{v}{v_0} \in \left[1+r^{-1},\,\infty\right] \quad .
$$

In the third regime,

$$
z \in [\,r+w\,,\,\infty\,] \quad \Rightarrow \quad z = \frac{v_0 - \alpha v}{(1+\alpha)\,v - v_0} \quad \text{with} \quad \frac{v}{v_0} \in \left[\frac{1}{1+\alpha}\,,\,\frac{1+r+w}{(1+\alpha)(r+w)+\alpha}\right] \quad .
$$

Note that there is a minimum possible volume per particle, $v_{\min} = v_0/(1+\alpha)$, hence a maximum possible density $n_{\max} = 1/v_{\min}$. This leaves us with the second regime, where $z \in [\,r\,,\,r+w\,]$. We must invert the relation

$$
\frac{v_0}{v} = \frac{z}{1+z} + \frac{\alpha}{w}(z-r) \quad \Rightarrow \quad \frac{\alpha}{w}z^2 + \left(\frac{\alpha}{w}(1-r)+1-\frac{v_0}{v}\right)z - \left(\frac{\alpha r}{w}+\frac{v_0}{v}\right) = 0 \quad .
$$

obtaining

$$
z = \frac{-\left[\frac{\alpha}{w}(1-r)+1-\frac{v_0}{v}\right] + \sqrt{\left[\frac{\alpha}{w}(1-r)+1-\frac{v_0}{v}\right]^2 + \frac{4\alpha}{w}\left(\frac{\alpha r}{w}+\frac{v_0}{v}\right)}}{2\alpha/w} \quad ,
$$

which holds for

$$
a \in [\,r\,,\,r+w\,] \quad \Rightarrow \quad \frac{v}{v_0} \in \left[\frac{1+r+w}{(1+\alpha)(r+w)+\alpha}\,,\,1+r^{-1}\right] \quad .
$$

The dimensionless pressure $\pi = pv_0/k_{\mathrm{B}}T$ is given by

$$
z \in [\,0\,,\,r\,] \quad \Rightarrow \quad \pi = \ln(1+z) \quad \text{with} \quad \frac{v}{v_0} \in \left[1+r^{-1},\,\infty\right] \quad .
$$

and

$$
z \in [\,r+w\,,\,\infty\,] \quad \Rightarrow \quad \pi = \ln(1+z) + \alpha \ln z - \frac{\alpha}{w}\Big[(r+w)\ln(r+w) - r\ln r - w\Big]
$$

in the large volume region and

$$
\frac{v}{v_0} \in \left[\frac{1}{1+\alpha}\,,\,\frac{1+r+w}{(1+\alpha)(r+w)+\alpha}\right]
$$

in the small volume region. In the intermediate volume region, we have

$$
\pi = \ln(1+z) + \frac{\alpha}{w}(z-r)\ln z - \frac{\alpha}{w}\Big(z\ln z - r\ln r - z + r\Big) \quad ,
$$

which holds for

$$
z \in [\,r\,,\,r+w\,] \quad \Rightarrow \quad \frac{v}{v_0} \in \left[\frac{1+r+w}{(1+\alpha)(r+w)+\alpha}\,,\,1+r^{-1}\right] \quad .
$$

(d) The results are plotted in Fig. 37. Note that $v$ is a continuous function of $\pi$, indicating a second order transition.

(e) Consider the thermodynamic behavior in the vicinity of $z = r$, *i.e.* near $v = (1 + r^{-1})v_0$. Let's write $z = r + \epsilon$ and work to lowest nontrivial order in $\epsilon$. On the low density side of this transition, *i.e.* for $\epsilon < 0$, we have, with $\nu = nv_0 = v_0/v$,

$$\nu = \frac{z}{1+z} = \frac{r}{1+r} + \frac{\epsilon}{(1+r)^2} + \mathcal{O}(\epsilon^2)$$

$$\pi = \ln(1+z) = \ln(1+r) + \frac{\epsilon}{1+r} + \mathcal{O}(\epsilon^2) \quad .$$

Eliminating $\epsilon$, we have

$$\nu < \nu_{\rm c} \qquad \Rightarrow \qquad \pi = \ln(1+r) + (1+r)(\nu - \nu_{\rm c}) + \ldots \quad ,$$

where $\nu_{\rm c} = r/(1+r)$ is the critical dimensionless density. Now investigate the high density side of the
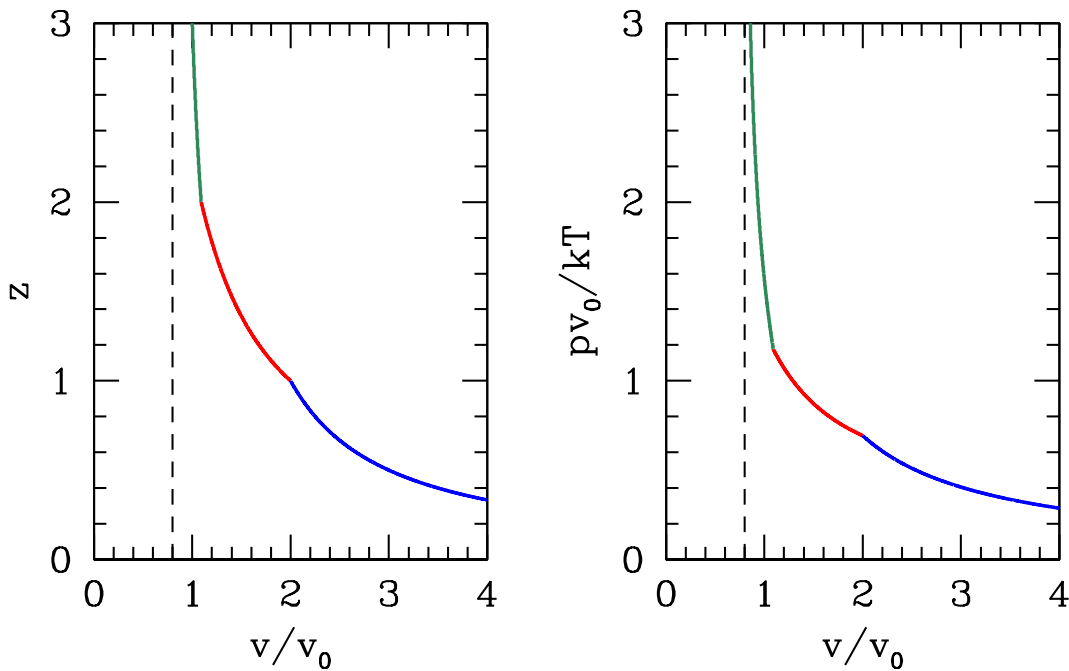


Figure 31:  Fugacity $z$ and dimensionless pressure $pv_0/k_{\rm B}T$ *versus* dimensionless volume per particle $v/v_0$ for problem (2), with $\alpha = \frac{1}{4}$ and $r = w = 1$. Different portions of the curves are shown in different colors. The dashed line denotes the minimum possible volume $v_{\rm min} = v_0/(1+\alpha)$.

transition, where $\epsilon > 0$. Integrating over the region $[\,r\,,\,r+\epsilon\,]$, we find

$$\nu = \frac{z}{1+z} + \frac{\alpha}{w}\,(z-r) = \frac{r}{1+r} + \left[\frac{1}{(1+r)^2} + \frac{\alpha}{w}\right]\epsilon + \mathcal{O}(\epsilon^2)$$

$$\pi = \ln(1+z) + \frac{\alpha}{w}\Big[z + r\ln(r/z) - r\Big] = \ln(1+r) + \frac{\epsilon}{1+r} + \mathcal{O}(\epsilon^2) \quad .$$

Note that $\partial\pi/\partial z$ is continuous through the transition. As we are about to discover, $\partial\pi/\partial\nu$ is discontinuous. Eliminating $\epsilon$, we have

$$\nu > \nu_{\mathrm{c}} \qquad \Rightarrow \qquad \pi = \ln(1+r) + \frac{1+r}{1+(1+r)^2\,(\alpha/w)}\,(\nu - \nu_{\mathrm{c}}) + \ldots \quad .$$

Thus, the isothermal compressibility $\kappa_T = -\frac{1}{v}\big(\frac{\partial v}{\partial p}\big)_T$ is discontinuous at the transition. This can be seen clearly as a kink in Fig. 31.

Suppose the density of states $g(\sigma)$ behaves as a power law in the vicinity of $\sigma = r$, with $g(\sigma) \simeq A\,(\sigma-r)^q$. Normalization of the integral of $g(\sigma)$ then requires $t > -1$ for convergence at this lower limit. For $z = r + \epsilon$ with $\epsilon > 0$, one now has

$$\nu = \frac{r}{1+r} + \frac{\epsilon}{(1+r)^2} + \frac{\alpha A\,\epsilon^{q+1}}{q+1} + \ldots$$

$$\pi = \ln(1+r) + \frac{\epsilon}{1+r} + \frac{\alpha A\,\epsilon^{q+2}}{(q+1)(q+2)r} + \ldots \quad .$$

If $q > 0$, then to order $\epsilon$ the expansion is the same for $\epsilon < 0$, and both $\pi$ and its derivative $\frac{\partial\pi}{\partial\nu}$ are continuous across the transition. (Higher order derivatives, however, may be discontinuous or diverge.) If $-1 < q < 0$, then $\epsilon^{q+1}$ dominates over $\epsilon$ in the first of these equations, and we have

$$\epsilon = \left(\frac{(q+1)(\nu - \nu_{\mathrm{c}})}{\alpha A}\right)^{\frac{1}{q+1}}$$

and

$$\pi = \ln(1+r) + \frac{1}{1+r}\left(\frac{q+1}{\alpha A}\right)^{\frac{1}{q+1}}(\nu - \nu_{\mathrm{c}})^{\frac{1}{q+1}} \quad ,$$

which has a nontrivial power law behavior typical of second order critical phenomena.

## 0.7  Mean Field Theory of Phase Transitions

**(7.1)** Find $v_{\rm c}$, $T_{\rm c}$, and $p_{\rm c}$ for the equation of state,

$$p = \frac{RT}{v-b} - \frac{\alpha}{v^3} \quad .$$

Solution :

We find $p'(v)$:

$$\frac{\partial p}{\partial v} = -\frac{RT}{(v-b)^2} + \frac{3\alpha}{v^4} \quad .$$

Setting this to zero yields the equation

$$f(u) \equiv \frac{u^4}{(u-1)^2} = \frac{3\alpha}{RTb^2} \quad ,$$

where $u \equiv v/b$ is dimensionless. The function $f(u)$ on the interval $[1, \infty]$ has a minimum at $u = 2$, where $f_{\rm min} = f(2) = 16$. This determines the critical temperature, by setting the RHS of the above equation to $f_{\rm min}$. Then evaluate $p_{\rm c} = p(v_{\rm c}, T_{\rm c})$. One finds

$$v_{\rm c} = 2b \quad , \qquad T_{\rm c} = \frac{3\alpha}{16Rb^2} \quad , \qquad p_{\rm c} = \frac{\alpha}{16b^3} \quad .$$

**(7.2)** The Dieterici equation of state is

$$p\,(v-b) = RT\,\exp\!\left(-\frac{a}{vRT}\right) \quad .$$

(a) Find the critical point $(p_{\rm c}, v_{\rm c}, T_{\rm c})$ for this equation of state

(b) Writing $\bar{p} = p/p_{\rm c}$, $\bar{v} = v/v_{\rm c}$, and $\bar{T} = T/T_{\rm c}$, rewrite the equation of state in the form $\bar{p} = \bar{p}(\bar{v}, \bar{T})$.

(c) *For the brave only!* Writing $\bar{p} = 1 + \pi$, $\bar{T} = 1 + t$, and $\bar{v} = 1 + \epsilon$, find $\epsilon_{\rm liq}(t)$ and $\epsilon_{\rm gas}(t)$ for $0 < (-t) \ll 1$, working to lowest nontrivial order in $(-t)$.

Solution :

(a) We have

$$p = \frac{RT}{v-b}\,e^{-a/vRT} \quad ,$$

hence

$$\left(\frac{\partial p}{\partial v}\right)_T = p \cdot \left\{ -\frac{1}{v-b} + \frac{a}{v^2 RT} \right\} \quad .$$

Setting the LHS of the above equation to zero, we then have

$$\frac{v^2}{v-b} = \frac{a}{RT} \quad \Rightarrow \quad f(u) \equiv \frac{u^2}{u-1} = \frac{a}{bRT} \quad ,$$

where $u = v/b$ is dimensionless. Setting $f'(u^*) = 0$ yields $u^* = 2$, hence $f(u)$ on the interval $u \in (1, \infty)$ has a unique global minimum at $u = 2$, where $f(2) = 4$. Thus,

$$v_{\rm c} = 2b \quad , \quad T_{\rm c} = \frac{a}{4bR} \quad , \quad p_{\rm c} = \frac{a}{4b^2}\,e^{-2} \quad .$$

(b) In terms of the dimensionless variables $\bar{p}$, $\bar{v}$, and $\bar{T}$, the equation of state takes the form

$$\bar{p} = \frac{\bar{T}}{2\bar{v} - 1}\,\exp\!\left(2 - \frac{2}{\bar{v}\bar{T}}\right) \quad .$$

When written in terms of the dimensionless deviations $\pi$, $\epsilon$, and $t$, this becomes

$$\pi = \left(\frac{1+t}{1+2\epsilon}\right)\exp\!\left(\frac{2(\epsilon + t + \epsilon t)}{1 + \epsilon + t + \epsilon t}\right) - 1 \quad .$$

Expanding via Taylor's theorem, one finds

$$\pi(\epsilon, t) = 3t - 2t\epsilon + 2t^2 - \tfrac{2}{3}\epsilon^3 + 2\epsilon^2 t - 4\epsilon t^2 - \tfrac{2}{3}t^3 + \dots \quad .$$

Thus,

$$\pi_{\epsilon t} \equiv \frac{\partial^2 \pi}{\partial \epsilon \, \partial t} = -2 \quad , \quad \pi_{\epsilon\epsilon\epsilon} \equiv \frac{\partial^3 \pi}{\partial \epsilon^3} = -4 \quad ,$$

and according to the results in ch. 7 of the lecture notes, we have

$$\epsilon_{\rm L,G} = \mp\left(\frac{6\,\pi_{\epsilon t}}{\pi_{\epsilon\epsilon\epsilon}}\right)^{1/2} = \mp\big(-3t\big)^{1/2} \quad .$$

**(7.3)** Consider a ferromagnetic spin-1 triangular lattice Ising model . The Hamiltonian is

$$\hat{H} = -J \sum_{\langle ij \rangle} S_i^z \, S_j^z - H \sum_i S_i^z \quad ,$$

where $S_i^z \in \{-1\, , 0\, , +1\}$ on each site $i$, $H$ is a uniform magnetic field, and where the first sum is over all links of the lattice.

(a) Derive the mean field Hamiltonian $\hat{H}_{\mathrm{MF}}$ for this model.

(b) Derive the free energy per site $F/N$ within the mean field approach.

(c) Derive the self consistent equation for the local moment $m = \langle S_i^z \rangle$.

(d) Find the critical temperature $T_{\mathrm{c}}(H = 0)$.

(e) Assuming $|H| \ll k_{\mathrm{B}}|T - T_{\mathrm{c}}| \ll J$, expand the dimensionless free energy $f = F/6NJ$ in terms of $\theta = T/T_{\mathrm{c}}$, $h = H/k_{\mathrm{B}}T_{\mathrm{c}}$, and $m$. Minimizing with respect to $m$, find an expression for the dimensionless magnetic susceptibility $\chi = \partial m/\partial h$ close to the critical point.

<span style="color:red">Solution :</span>

<span style="color:blue">(a) Writing $S_i^z = m + \delta S_i^z$, where $m = \langle S_i^z \rangle$ and expanding $\hat{H}$ to linear order in the fluctuations $\delta S_i^z$, we find</span>

$$\hat{H}_{\mathrm{MF}} = \tfrac{1}{2}NzJm^2 - (H + zJm) \sum_i S_i^z \quad ,$$

<span style="color:blue">where $z = 6$ for the triangular lattice.</span>

<span style="color:blue">(b) The free energy per site is</span>

$$F/N = \tfrac{1}{2}zJm^2 - k_{\mathrm{B}}T \ln \mathrm{Tr}\; e^{(H+zJm)S^z}$$

$$= \tfrac{1}{2}zJm^2 - k_{\mathrm{B}}T \ln\left\{ 1 + 2\cosh\left( \frac{H + zJm}{k_{\mathrm{B}}T} \right) \right\} \quad .$$

<span style="color:blue">(c) The mean field equation is $\partial F/\partial m = 0$, which is equivalent to $m = \langle S_i^z \rangle$. We obtain</span>

$$m = \frac{2 \sinh\left( \frac{H+zJm}{k_{\mathrm{B}}T} \right)}{1 + 2\cosh\left( \frac{H+zJm}{k_{\mathrm{B}}T} \right)} \quad .$$

<span style="color:blue">(d) To find $T_{\mathrm{c}}$, we set $H = 0$ in the mean field equation:</span>

$$m = \frac{2\sinh(\beta zJm)}{1 + 2\cosh(\beta zJm)}$$

$$= \tfrac{2}{3}\beta zJm + \mathcal{O}(m^3) \quad .$$

The critical temperature is obtained by setting the slope on the RHS of the above equation to unity. Thus,

$$T_{\mathrm{c}} = \frac{2zJ}{3k_{\mathrm{B}}} \quad .$$

So for the triangular lattice, where $z = 6$, one has $T_{\mathrm{c}} = 4J/k_{\mathrm{B}}$.

(e) Scaling $T$ and $H$ as indicated, the mean field equation becomes

$$m = \frac{2\sinh\big((m+h)/\theta\big)}{1 + 2\cosh\big((m+h)/\theta\big)} = \frac{m+h}{\theta/\theta_{\mathrm{c}}} + \ldots \quad ,$$

where $\theta_{\mathrm{c}} = \frac{2}{3}$, and where we assume $\theta > \theta_{\mathrm{c}}$. Solving for $m(h)$, we have

$$m = \frac{h}{1 - \frac{\theta_{\mathrm{c}}}{\theta}} = \frac{\theta_{\mathrm{c}}\,h}{\theta - \theta_{\mathrm{c}}} + \mathcal{O}\big((\theta - \theta_{\mathrm{c}})^2\big) \quad .$$

Thus, $\chi = \theta_{\mathrm{c}}/(\theta - \theta_{\mathrm{c}})$, which reflects the usual mean field susceptibility exponent $\gamma = 1$.

**(7.4)** Consider a ferromagnetic spin-$S$ Ising model on a lattice of coordination number $z$. The Hamiltonian is

$$\hat{H} = -J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j - \mu_0 H \sum_i \sigma_i \quad ,$$

where $\sigma \in \{-S, -S+1, \ldots, +S\}$ with $2S \in \mathbb{Z}$.

(a) Find the mean field Hamiltonian $\hat{H}_{\mathrm{MF}}$.

(b) Adimensionalize by setting $\theta \equiv k_{\mathrm{B}} T / zJ$, $h \equiv \mu_0 H / zJ$, and $f \equiv F / NzJ$. Find the dimensionless free energy per site $f(m, h)$ for arbitrary $S$.

(c) Expand the free energy as

$$f(m, h) = f_0 + \tfrac{1}{2} a m^2 + \tfrac{1}{4} b m^4 - c h m + \mathcal{O}(h^2, h m^3, m^6)$$

and find the coefficients $f_0$, $a$, $b$, and $c$ as functions of $\theta$ and $S$.

(d) Find the critical point $(\theta_{\mathrm{c}}, h_{\mathrm{c}})$.

(e) Find $m(\theta_{\mathrm{c}}, h)$ to leading order in $h$.

**Solution :**

(a) Writing $\sigma_i = m + \delta \sigma_i$, we find

$$\hat{H}_{\mathrm{MF}} = \tfrac{1}{2} N z J m^2 - (\mu_0 H + zJ) \sum_i \sigma_i \quad .$$

(b) Using the result

$$\sum_{\sigma=-S}^{S} e^{\beta \mu_0 H_{\mathrm{eff}} \sigma} = \frac{\sinh\big((S + \tfrac{1}{2}) \beta \mu_0 H\big)}{\sinh\big(\tfrac{1}{2} \beta \mu_0 H\big)} \quad ,$$

we have

$$f = \tfrac{1}{2} m^2 - \theta \ln \sinh\big((2S + 1)(m + h)/2\theta\big) + \theta \ln \sinh\big((m + h)/2\theta\big) \quad .$$

(c) Expanding the free energy, we obtain

$$f = f_0 + \tfrac{1}{2} a m^2 + \tfrac{1}{4} b m^4 - c h m + \mathcal{O}(h^2, h m^3, m^6)$$
$$= -\theta \ln(2S + 1) + \left(\frac{3\theta - S(S+1)}{6\theta}\right) m^2 + \frac{S(S+1)(2S^2 + 2S + 1)}{360 \, \theta^3} m^4 - \tfrac{2}{3} S(S+1) \, h m + \ldots \quad .$$

Thus,

$$f_0 = -\theta \ln(2S + 1) \quad , \quad a = 1 - \tfrac{1}{3} S(S+1) \theta^{-1} \quad , \quad b = \frac{S(S+1)(2S^2 + 2S + 1)}{90 \, \theta^3} \quad , \quad c = \tfrac{2}{3} S(S+1) \quad .$$

(d) Set $a = 0$ and $h = 0$ to find the critical point: $\theta_{\mathrm{c}} = \frac{1}{3}S(S+1)$ and $h_{\mathrm{c}} = 0$.

(e) At $\theta = \theta_{\mathrm{c}}$, we have $f = f_0 + \frac{1}{4}bm^4 - chm + \mathcal{O}(m^6)$. Extremizing with respect to $m$, we obtain $m = (ch/b)^{1/3}$. Thus,

$$m(\theta_{\mathrm{c}}, h) = \left(\frac{60}{2S^2 + 2S + 1}\right)^{1/3} \theta \, h^{1/3} \quad .$$

**(7.5)** Consider the $O(2)$ model,

$$\hat{H} = -\tfrac{1}{2} \sum_{i,j} J_{ij}\,\hat{\mathbf{n}}_i\cdot\hat{\mathbf{n}}_j - \mathbf{H}\cdot\sum_i \hat{\mathbf{n}}_i \quad,$$

where $\hat{\mathbf{n}}_i = \cos\phi_i\,\hat{\mathbf{x}} + \sin\phi_i\,\hat{\mathbf{y}}$. Consider the case of infinite range interactions, where $J_{ij} = J/N$ for all $i, j$, where $N$ is the total number of sites.

  (a) Show that

$$\exp\left[\frac{\beta J}{2N}\sum_{i,j}\hat{\mathbf{n}}_i\cdot\hat{\mathbf{n}}_j\right] = \frac{N\beta J}{2\pi}\int d^2m\, e^{-N\beta J\mathbf{m}^2/2}\, e^{\beta J\mathbf{m}\cdot\sum_i\hat{\mathbf{n}}_i} \quad.$$

  (b) Using the definition of the modified Bessel function $I_0(z)$,

$$I_0(z) = \int\limits_0^{2\pi} \frac{d\phi}{2\pi}\, e^{z\cos\phi} \quad,$$

    show that

$$Z = \mathsf{Tr}\, e^{-\beta\hat{H}} = \int d^2m\, e^{-NA(\mathbf{m},\mathbf{h})/\theta} \quad,$$

    where $\theta = k_{\mathrm{B}}T/J$ and $\mathbf{h} = \mathbf{H}/J$. Find an expression for $A(\mathbf{m},\mathbf{h})$.

  (c) Find the equation which extremizes $A(\mathbf{m},\mathbf{h})$ as a function of $\mathbf{m}$.

  (d) Look up the properties of $I_0(z)$ and write down the first few terms in the Taylor expansion of $A(\mathbf{m},\mathbf{h})$ for small $m$ and $h$. Solve for $\theta_{\mathrm{c}}$.

<span style="color:red">Solution :</span>

<span style="color:blue">(a) We have</span>

$$\frac{\hat{H}}{k_{\mathrm{B}}T} = -\frac{J}{2Nk_{\mathrm{B}}T}\left(\sum_i\hat{\mathbf{n}}_i\right)^2 - \frac{\mathbf{H}}{k_{\mathrm{B}}T}\cdot\sum_i\hat{\mathbf{n}}_i \quad.$$

<span style="color:blue">Therefore</span>

$$e^{-\hat{H}/k_{\mathrm{B}}T} = \exp\left[\frac{1}{2N\theta}\left(\sum_i\hat{\mathbf{n}}_i\right)^2 + \frac{\mathbf{h}}{\theta}\cdot\sum_i\hat{\mathbf{n}}_i\right]$$

$$= \frac{N}{2\pi\theta}\int d^2m\,\exp\left[-\frac{N\mathbf{m}^2}{2\theta} + \left(\frac{\mathbf{m}+\mathbf{h}}{\theta}\right)\cdot\sum_i\hat{\mathbf{n}}_i\right] \quad.$$

<span style="color:blue">(b) Integrating the previous expression, we have</span>

$$Z = \mathsf{Tr}\, e^{-\hat{H}/k_{\mathrm{B}}T} = \prod_i\int\frac{d\hat{\mathbf{n}}_i}{2\pi}\, e^{-\hat{H}[\{\hat{\mathbf{n}}_i\}]/k_{\mathrm{B}}T}$$

$$= \frac{N}{2\pi\theta}\int d^2m\, e^{-N\mathbf{m}^2/2\theta}\left[I_0\big(|\mathbf{m}+\mathbf{h}|/\theta\big)\right]^N \quad.$$

Thus, we identify

$$A(\mathbf{m}, \mathbf{h}) = \tfrac{1}{2}\mathbf{m}^2 - \theta \ln I_0\big(|\mathbf{m} + \mathbf{h}|/\theta\big) - \frac{\theta}{N}\ln(N/2\pi\theta) \quad .$$

(c) Extremizing with respect to the vector $\mathbf{m}$, we have

$$\frac{\partial A}{\partial \mathbf{m}} = \mathbf{m} - \frac{\mathbf{m} + \mathbf{h}}{|\mathbf{m} + \mathbf{h}|} \cdot \frac{I_1\big(|\mathbf{m} + \mathbf{h}|/\theta\big)}{I_0\big(|\mathbf{m} + \mathbf{h}|/\theta\big)} = 0 \quad ,$$

where $I_1(z) = I_0'(z)$. Clearly any solution requires that $\mathbf{m}$ and $\mathbf{h}$ be colinear, hence

$$m = \frac{I_1\big((m + h)/\theta\big)}{I_0\big((m + h)/\theta\big)} \quad .$$

(d) To find $\theta_{\mathrm{c}}$, we first set $h = 0$. We then must solve

$$m = \frac{I_1(m/\theta)}{I_0(m/\theta)} \quad .$$

The modified Bessel function $I_\nu(z)$ has the expansion

$$I_\nu(z) = \big(\tfrac{1}{2}z\big)^\nu \sum_{k=0}^\infty \frac{\big(\tfrac{1}{4}z^2\big)^k}{k!\,\Gamma(k + \nu + 1)} \quad .$$

Thus,

$$I_0(z) = 1 + \tfrac{1}{4}z^2 + \ldots$$
$$I_1(z) = \tfrac{1}{2}z + \tfrac{1}{16}z^3 + \ldots \quad ,$$

and therefore $I_1(z)/I_0(z) = \tfrac{1}{2}z - \tfrac{1}{16}z^3 + \mathcal{O}(z^5)$, and we read off $\theta_{\mathrm{c}} = \tfrac{1}{2}$.

**(7.6)** Consider the O$(3)$ model,

$$\hat{H} = -J \sum_{\langle ij \rangle} \hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j - \mathbf{H} \cdot \sum_i \hat{\mathbf{n}}_i \quad,$$

where each $\hat{\mathbf{n}}_i$ is a three-dimensional unit vector.

(a) Writing

$$\hat{\mathbf{n}}_i = \mathbf{m} + \delta\hat{\mathbf{n}}_i \quad,$$

with $\mathbf{m} = \langle \hat{\mathbf{n}}_i \rangle$ and $\delta\hat{\mathbf{n}}_i = \hat{\mathbf{n}}_i - \mathbf{m}$, derive the mean field Hamiltonian.

(b) Compute the mean field free energy $f(m, \theta, \mathbf{h})$, where $\theta = k_{\mathrm{B}}T/zJ$ and $\mathbf{h} = \mathbf{H}/zJ$, with $f = F/NzJ$. Here $z$ is the lattice coordination number and $N$ the total number of lattice sites, as usual. You may assume that $\mathbf{m} \parallel \mathbf{h}$. Note that the trace over the local degree of freedom at each site $i$ is given by

$$\mathop{\mathrm{Tr}}_i \to \int \frac{d\hat{\mathbf{n}}_i}{4\pi} \quad,$$

where the integral is over all solid angle.

(c) Find the critical point $(\theta_{\mathrm{c}}, h_{\mathrm{c}})$.

(d) Find the behavior of the magnetic susceptibility $\chi = \partial m/\partial h$ as a function of temperature $\theta$ just above $\theta_{\mathrm{c}}$.

*Solution :*

(a) Making the mean field *Ansatz*, one obtains the effective field $\mathbf{H}_{\mathrm{eff}} = \mathbf{H} + zJ\mathbf{m}$, and the mean field Hamiltonian

$$\hat{H}_{\mathrm{MF}} = \tfrac{1}{2}NzJ\mathbf{m}^2 - (\mathbf{H} + zJ\mathbf{m}) \cdot \sum_i \hat{\mathbf{n}}_i \quad.$$

(b) We assume that $\mathbf{m} \parallel \mathbf{h}$, in which case

$$f(m, \theta, h) = \tfrac{1}{2}m^2 - \theta \ln \int \frac{d\hat{\mathbf{n}}}{4\pi} \, e^{(m+h)\hat{\mathbf{z}}\cdot\hat{\mathbf{n}}/\theta}$$

$$= \tfrac{1}{2}m^2 - \theta \ln \left( \frac{\sinh\big((m+h)/\theta\big)}{(m+h)/\theta} \right) \quad.$$

Here we have without loss of generality taken $\mathbf{h}$ to lie in the $\hat{\mathbf{z}}$ direction.

(c) We expand $f(m, \theta, h)$ for small $m$ and $\theta$, obtaining

$$f(m, \theta, h) = \tfrac{1}{2}m^2 - \frac{(m+h)^2}{6\,\theta} + \frac{(m+h)^4}{180\,\theta^3} + \cdots$$

$$= \tfrac{1}{2}\left(1 - \frac{1}{3\theta}\right)m^2 - \frac{hm}{3\,\theta} + \frac{m^4}{180\,\theta^4} + \cdots$$

We now read off $h_{\mathrm{c}} = 0$ and $\theta_{\mathrm{c}} = \frac{1}{3}$.

(d) Setting $\partial f / \partial m = 0$, we obtain

$$\left(1 - \frac{\theta_{\mathrm{c}}}{\theta}\right) m = \frac{\theta_{\mathrm{c}}}{\theta} \, hm + \mathcal{O}(m^3) \quad .$$

We therefore have

$$m(h, \theta > \theta_{\mathrm{c}}) = \frac{\theta_{\mathrm{c}} \, h}{\theta - \theta_{\mathrm{c}}} + \mathcal{O}(h^3) \qquad , \qquad \chi(\theta > \theta_{\mathrm{c}}) = \left. \frac{\partial m}{\partial h} \right|_{h=0} = \frac{\theta_{\mathrm{c}}}{\theta - \theta_{\mathrm{c}}} \quad .$$

**(7.7)** Consider an Ising model on a square lattice with Hamiltonian

$$\hat{H} = -J \sum_{i \in A} {\sum_{j \in B}}' S_i \, \sigma_j \quad ,$$

where the sum is over all nearest-neighbor pairs, such that $i$ is on the A sublattice and j is on the B sublattice (this is the meaning of the prime on the $j$ sum), as depicted in Fig. 32. The A sublattice spins take values $S_i \in \{-1, 0, +1\}$, while the B sublattice spins take values $\sigma_j \in \{-1, +1\}$.

(a) Make the mean field assumptions $\langle S_i \rangle = m_A$ for $i \in A$ and $\langle \sigma_j \rangle = m_B$ for $j \in B$. Find the mean field free energy $F(T, N, m_A, m_B)$. Adimensionalize as usual, writing $\theta \equiv k_B T / zJ$ (with $z = 4$ for the square lattice) and $f = F/zJN$. Then write $f(\theta, m_A, m_B)$.

(b) Write down the two mean field equations (one for $m_A$ and one for $m_B$).

(c) Expand the free energy $f(\theta, m_A, m_B)$ up to fourth order in the order parameters $m_A$ and $m_B$.

(d) Show that the part of $f(\theta, m_A, m_B)$ which is quadratic in $m_A$ and $m_B$ may be written as a quadratic form, *i.e.*

$$f(\theta, m_A, m_B) = f_0 + \tfrac{1}{2} \begin{pmatrix} m_A & m_B \end{pmatrix} \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} m_A \\ m_B \end{pmatrix} + \mathcal{O}(m_A^4, m_B^4) \quad ,$$

where the matrix $M$ is symmetric, with components $M_{aa'}$ which depend on $\theta$. The critical temperature $\theta_c$ is identified as the largest value of $\theta$ for which $\det M(\theta) = 0$. Find $\theta_c$ and explain why this is the correct protocol to determine it.

<span style="color:red">Solution :</span>

<span style="color:blue">(a) Writing $S_i = m_A + \delta S_i$ and $\sigma_j = m_B + \delta \sigma_j$ and dropping the terms proportional to $\delta S_i \, \delta \sigma_j$, which are quadratic in fluctuations, one obtains the mean field Hamiltonian</span>

$$\hat{H}_{MF} = \tfrac{1}{2} N z J m_A m_B - z J m_B \sum_{i \in A} S_i - z J m_A \sum_{j \in B} \sigma_j \quad ,$$

<span style="color:blue">with $z = 4$ for the square lattice. Thus, the internal field on each A site is $H_{int,A} = z J m_B$, and the internal field on each B site is $H_{int,B} = z J m_A$. The mean field free energy, $F_{MF} = -k_B T \ln Z_{MF}$, is then</span>

$$F_{MF} = \tfrac{1}{2} N z J m_A m_B - \tfrac{1}{2} N k_B T \ln\left[1 + 2 \cosh(z J m_B / k_B T)\right] - \tfrac{1}{2} N k_B T \ln\left[2 \cosh(z J m_A / k_B T)\right] \quad .$$

<span style="color:blue">Adimensionalizing,</span>

$$f(\theta, m_A, m_B) = \tfrac{1}{2} m_A m_B - \tfrac{1}{2} \theta \ln\left[1 + 2 \cosh(m_B / \theta)\right] - \tfrac{1}{2} \theta \ln\left[2 \cosh(m_A / \theta)\right] \quad .$$
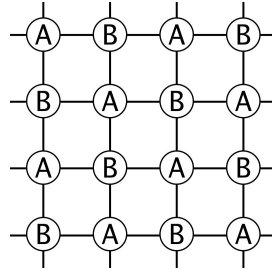
Figure 32:  The square lattice and its A and B sublattices.

(b) The mean field equations are obtained from $\partial f / \partial m_{\mathrm{A}} = 0$ and $\partial f / \partial m_{\mathrm{B}} = 0$. Thus,

$$m_{\mathrm{A}} = \frac{2 \sinh(m_{\mathrm{B}}/\theta)}{1 + 2 \cosh(m_{\mathrm{B}}/\theta)}$$

$$m_{\mathrm{B}} = \tanh(m_{\mathrm{A}}/\theta) \quad .$$

(c) Using

$$\ln\big(2 \cosh x\big) = \ln 2 + \frac{x^2}{2} - \frac{x^4}{12} + \mathcal{O}(x^6) \quad , \quad \ln\big(1 + 2 \cosh x\big) = \ln 3 + \frac{x^2}{3} - \frac{x^4}{36} + \mathcal{O}(x^6) \quad ,$$

we have

$$f(\theta, m_{\mathrm{A}}, m_{\mathrm{B}}) = f_0 + \tfrac{1}{2} m_{\mathrm{A}} m_{\mathrm{B}} - \frac{m_{\mathrm{A}}^2}{4\,\theta} - \frac{m_{\mathrm{B}}^2}{6\,\theta} + \frac{m_{\mathrm{A}}^4}{24\,\theta^3} + \frac{m_{\mathrm{B}}^4}{72\,\theta^3} + \cdots \quad ,$$

with $f_0 = -\tfrac{1}{2}\theta \ln 6$.

(d) From the answer to part (c), we read off

$$M(\theta) = \begin{pmatrix} -\frac{1}{2\theta} & \frac{1}{2} \\[2mm] \frac{1}{2} & -\frac{1}{3\theta} \end{pmatrix} \quad ,$$

from which we obtain $\det M = \frac{1}{6}\theta^{-2} - \frac{1}{4}$. Setting $\det M = 0$ we obtain $\theta_{\mathrm{c}} = \sqrt{\frac{2}{3}} \quad .$

**(7.8)** The spin lattice Hamiltonian for the three state ($\mathbb{Z}_3$) clock model is written

$$\hat{H} = -J\sum_{\langle ij\rangle} \hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j \quad ,$$

where each local unit vector $\hat{\mathbf{n}}_i$ is a planar spin which can take one of three possible values:

$$\hat{\mathbf{n}} = \hat{\mathbf{e}}_1 \quad , \quad \hat{\mathbf{n}} = -\tfrac{1}{2}\hat{\mathbf{e}}_1 + \tfrac{\sqrt{3}}{2}\hat{\mathbf{e}}_2 \quad , \quad \hat{\mathbf{n}} = -\tfrac{1}{2}\hat{\mathbf{e}}_1 - \tfrac{\sqrt{3}}{2}\hat{\mathbf{e}}_2 \quad .$$

Note that the *internal space* in which each unit vector $\hat{\mathbf{n}}_i$ exists is distinct from the physical Euclidean space in which the lattice points reside.

(a) Consider the clock model on a lattice of coordination number $z$. Make the mean field assumption $\langle \hat{\mathbf{n}}_i \rangle = m\,\hat{\mathbf{e}}_1$. Expanding the Hamiltonian to linear order in the fluctuations, derive the mean field Hamiltonian for this model $\hat{H}_{\mathrm{MF}}$.

(b) Rescaling $\theta = k_{\mathrm{B}}T/zJ$ and $f = F/NzJ$, where $F$ is the Helmholtz free energy and $N$ is the number of sites, find $f(m,\theta)$.

(c) Is the transition second order or first order? Why?

(d) Find the equations which determine the critical temperature $\theta_{\mathrm{c}}$.

(e) Show that this model is equivalent to the three state Potts model. Is the $\mathbb{Z}_4$ clock model equivalent to the four state Potts model? Why or why not?

<span style="color:red">Solution :</span>

<span style="color:blue">(a) We can solve the mean field theory on a general lattice of coordination number $z$. The mean field Hamiltonian is</span>

$$\hat{H}_{\mathrm{MF}} = \tfrac{1}{2}NzJm^2 - zJm\,\hat{\mathbf{e}}_1 \cdot \sum_i \hat{\mathbf{n}}_i \quad .$$

<span style="color:blue">(b) We have</span>

$$
\begin{aligned}
f(m,\theta) &= \tfrac{1}{2}m^2 - \theta\ln \mathop{\mathrm{Tr}}_{\hat{\mathbf{n}}} \exp\!\big(m\,\hat{\mathbf{e}}_1\cdot\hat{\mathbf{n}}/\theta\big)\\[4pt]
&= \tfrac{1}{2}m^2 - \theta\ln\!\Big(\tfrac{1}{3}e^{m/\theta} + \tfrac{2}{3}e^{-m/2\theta}\Big)\\[4pt]
&= \frac{1}{2}\left(1 - \frac{1}{2\theta}\right)m^2 - \frac{m^3}{24\,\theta^2} + \frac{m^4}{64\,\theta^3} + \mathcal{O}(m^5) \quad .
\end{aligned}
$$

<span style="color:blue">Here we have defined $\mathrm{Tr}_{\hat{\mathbf{n}}} = \tfrac{1}{3}\sum_{\hat{\mathbf{n}}}$ as the normalized trace. The last line is somewhat tedious to obtain, but is not necessary for this problem.</span>

<span style="color:blue">(c) Since $f(m,\theta) \neq f(-m,\theta)$, the Landau expansion of the free energy (other than constants) should include terms of all orders starting with $\mathcal{O}(m^2)$. This means that there will in general be a cubic term, hence we expect a first order transition.</span>

(d) At the critical point, the magnetization $m = m_{\rm c}$ is finite. We then have to solve two equations to determine $m_{\rm c}$ and $\theta_{\rm c}$. The first condition is that the free energy have degenerate minima at the transition, *i.e.* $f(m=0, \theta = \theta_{\rm c}) = f(m = m_{\rm c}, \theta = \theta_{\rm c})$. Thus,

$$\tfrac{1}{2}m^2 = \theta \ln\left(\tfrac{1}{3}e^{m/\theta} + \tfrac{2}{3}e^{-m/2\theta}\right) \quad .$$

The second is the mean field equation itself, *i.e.*

$$\frac{\partial f}{\partial m} = 0 \quad \Rightarrow \quad m = \frac{e^{m/\theta} - e^{-m/2\theta}}{e^{m/\theta} + 2\,e^{-m/2\theta}} \quad .$$

These equations for $(m, \theta) = (m_{\rm c}, \theta_{\rm c})$ are nonlinear and hence we cannot expect to solve them analytically.

If, however, the transition were *very weakly* first order, then $m_{\rm c}$ is by assumption small, which means we should be able to get away with the fourth order Landau expansion of the free energy. For a free energy $f(m) = \tfrac{1}{2}am^2 - \tfrac{1}{3}ym^3 + \tfrac{1}{4}bm^4$, setting $f(m) = f'(m) = 0$ we obtain $m = 3a/y$ and $y^2 = 9ab$. For our system, $a = 1 - \tfrac{1}{2\theta}$, $y = \tfrac{1}{8\theta^2}$, and $b = \tfrac{1}{16\theta^3}$. We then obtain $\theta_{\rm c} = \tfrac{5}{9}$. Note that the second order term in $f(m)$ changes sign at $\theta^* = \tfrac{1}{2}$, so $\theta_{\rm c} > \theta^*$ is consistent with the fact that the second order transition is preempted by the first order one. Now we may ask, just how good was our assumption that the transition *is* weakly first order. To find out, we compute $m_{\rm c} = 3a/y = 24\,\theta_{\rm c}(\theta_{\rm c} - \tfrac{1}{2}) = \tfrac{20}{27}$ which is not particularly small compared to unity. Hence the assumption that our transition is weakly first order is not justified.

(e) Let $\varepsilon(\hat{\mathbf{n}}, \hat{\mathbf{n}}') = -J\hat{\mathbf{n}} \cdot \hat{\mathbf{n}}'$ be the energy for a given link. The unit vectors $\hat{\mathbf{n}}$ and $\hat{\mathbf{n}}'$ can each point in any of three directions, which we can label as $0°$, $120°$, and $240°$. The matrix of possible bond energies is shown in Tab. 10.

| $\varepsilon_{\sigma\sigma'}^{\rm clock}$ | $0°$ | $120°$ | $240°$ |
|:---:|:---:|:---:|:---:|
| $0°$ | $-J$ | $\tfrac{1}{2}J$ | $\tfrac{1}{2}J$ |
| $120°$ | $\tfrac{1}{2}J$ | $-J$ | $\tfrac{1}{2}J$ |
| $240°$ | $\tfrac{1}{2}J$ | $\tfrac{1}{2}J$ | $-J$ |

Table 10: $\mathbb{Z}_3$ clock model energy matrix.

Now consider the $q = 3$ Potts model, where the local states are labeled $|\,{\rm A}\,\rangle$, $|\,{\rm B}\,\rangle$, and $|\,{\rm C}\,\rangle$. The Hamiltonian is

$$\hat{H} = -\tilde{J}\sum_{\langle ij \rangle} \delta_{\sigma_i, \sigma_j} \quad .$$

The interaction energy matrix for the Potts model is given in Tab. 11.

We can in each case label the three states by a local variable $\sigma \in \{1, 2, 3\}$, corresponding, respectively, to $0°$, $120°$, and $240°$ for the clock model and to A, B, and C for the Potts model. We then observe

$$\varepsilon_{\sigma\sigma'}^{\rm clock}(J) = \varepsilon_{\sigma\sigma'}^{\rm Potts}(\tfrac{3}{2}J) + \tfrac{1}{2}J \quad .$$

Thus, the free energies satisfy

$$F^{\text{clock}}(J) = \tfrac{1}{4}NzJ + F^{\text{Potts}}(\tfrac{3}{2}J) \quad ,$$

and the models are equivalent. However, the $\mathbb{Z}_q$ clock model and $q$-state Potts model are *not* equivalent for $q > 3$. Can you see why? *Hint: construct the corresponding energy matrices for $q = 4$.*

| $\varepsilon_{\sigma\sigma'}^{\text{Potts}}$ | A | B | C |
|:---:|:---:|:---:|:---:|
| A | $-\tilde{J}$ | 0 | 0 |
| B | 0 | $-\tilde{J}$ | 0 |
| C | 0 | 0 | $-\tilde{J}$ |

Table 11: $q = 3$ Potts model energy matrix.

**(7.9)** Consider the $\mathsf{U}(1)$ Ginsburg-Landau theory with

$$F = \int d^d\mathbf{r} \left[ \tfrac{1}{2} a \, |\Psi|^2 + \tfrac{1}{4} b \, |\Psi|^4 + \tfrac{1}{2}\kappa \, |\boldsymbol{\nabla}\Psi|^2 \right] \quad.$$

Here $\Psi(\mathbf{r})$ is a complex-valued field, and both $b$ and $\kappa$ are positive. This theory is appropriate for describing the transition to superfluidity. The order parameter is $\langle\Psi(\mathbf{r})\rangle$. Note that the free energy is a functional of the two independent fields $\Psi(\mathbf{r})$ and $\Psi^*(\mathbf{r})$, where $\Psi^*$ is the complex conjugate of $\Psi$. Alternatively, one can consider $F$ a functional of the real and imaginary parts of $\Psi$.

(a) Show that one can rescale the field $\Psi$ and the coordinates $\mathbf{r}$ so that the free energy can be written in the form

$$F = \varepsilon_0 \int d^d x \left[ \pm \tfrac{1}{2} |\psi|^2 + \tfrac{1}{4} |\psi|^4 + \tfrac{1}{2} |\boldsymbol{\nabla}\psi|^2 \right] \quad,$$

where $\psi$ and $\mathbf{x}$ are dimensionless, $\varepsilon_0$ has dimensions of energy, and where the sign on the first term on the RHS is $\mathsf{sgn}(a)$. Find $\varepsilon_0$ and the relations between $\Psi$ and $\psi$ and between $\mathbf{r}$ and $\mathbf{x}$.

(b) By extremizing the functional $F[\psi, \psi^*]$ with respect to $\psi^*$, find a partial differential equation describing the behavior of the order parameter field $\psi(\mathbf{x})$.

(c) Consider a two-dimensional system ($d = 2$) and let $a < 0$ (*i.e.* $T < T_c$). Consider the case where $\psi(\mathbf{x})$ describe a *vortex* configuration: $\psi(\mathbf{x}) = f(r) \, e^{i\phi}$, where $(r, \phi)$ are two-dimensional polar coordinates. Find the ordinary differential equation for $f(r)$ which extremizes $F$.

(d) Show that the free energy, up to a constant, may be written as

$$F = 2\pi\varepsilon_0 \int\limits_0^R dr \, r \left[ \tfrac{1}{2}(f')^2 + \frac{f^2}{2r^2} + \tfrac{1}{4}(1 - f^2)^2 \right] \quad,$$

where $R$ is the radius of the system, which we presume is confined to a disk. Consider a *trial solution* for $f(r)$ of the form

$$f(r) = \frac{r}{\sqrt{r^2 + a^2}} \quad,$$

where $a$ is the variational parameter. Compute $F(a, R)$ in the limit $R \to \infty$ and extremize with respect to $a$ to find the optimum value of $a$ within this variational class of functions.

<span style="color:red">Solution :</span>

<span style="color:red">(a) Taking the ratio of the second and first terms in the free energy density, we learn that $\Psi$ has units of $A \equiv (|a|/b)^{1/2}$. Taking the ratio of the third to the first terms yields a length scale $\xi = (\kappa/|a|)^{1/2}$. We therefore write $\Psi = A\,\psi$ and $\tilde{\mathbf{x}} = \xi x$ to obtain the desired form of the free energy, with</span>

$$\varepsilon_0 = A^2 \, \xi^d \, |a| = |a|^{2 - \frac{1}{2}d} \, b^{-1} \, \kappa^{\frac{1}{2}d} \quad.$$

(b) We extremize with respect to the field $\psi^*$. Writing $F = \varepsilon_0 \int d^3x \, \mathcal{F}$, with $\mathcal{F} = \pm \frac{1}{2} |\psi|^2 + \frac{1}{4} |\psi|^4 + \frac{1}{2} |\boldsymbol{\nabla}\psi|^2$,

$$\frac{\delta(F/\varepsilon_0)}{\delta\psi^*(\mathbf{x})} = \frac{\partial \mathcal{F}}{\partial\psi^*} - \boldsymbol{\nabla}\cdot\frac{\partial \mathcal{F}}{\partial \boldsymbol{\nabla}\psi^*} = \pm \tfrac{1}{2}\,\psi + \tfrac{1}{2}\,|\psi|^2\,\psi - \tfrac{1}{2}\,\nabla^2\psi \quad .$$

Thus, the desired PDE is

$$-\nabla^2\psi \pm \psi + |\psi|^2\,\psi = 0 \quad ,$$

which is known as the time-independent nonlinear Schrödinger equation.

(c) In two dimensions,

$$\boldsymbol{\nabla}^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\phi^2} \quad .$$

Plugging in $\psi = f(r)\,e^{i\phi}$ into $\nabla^2\psi + \psi - |\psi|^2\psi = 0$, we obtain

$$\frac{d^2f}{dr^2} + \frac{1}{r}\frac{df}{dr} - \frac{f}{r^2} + f - f^3 = 0 \quad .$$

(d) Plugging $\boldsymbol{\nabla}\psi = \hat{\mathbf{r}}\,f'(r) + \frac{i}{r}\,f(r)\,\hat{\boldsymbol{\phi}}$ into our expression for $F$, we have

$$\mathcal{F} = \tfrac{1}{2}\,|\boldsymbol{\nabla}\psi|^2 - \tfrac{1}{2}\,|\psi|^2 + \tfrac{1}{4}\,|\psi|^4$$
$$= \tfrac{1}{2}\big(f'\big)^2 + \frac{f^2}{2r^2} + \tfrac{1}{4}\big(1 - f^2\big)^2 - \tfrac{1}{4} \quad ,$$

which, up to a constant, is the desired form of the free energy. It is a good exercise to show that the Euler-Lagrange equations,

$$\frac{\partial\,(r\mathcal{F})}{\partial f} - \frac{d}{dr}\left(\frac{\partial\,(r\mathcal{F})}{\partial f'}\right) = 0$$

results in the same ODE we obtained for $f$ in part (c). We now insert the trial form for $f(r)$ into $F$. The resulting integrals are elementary, and we obtain

$$F(a, R) = \tfrac{1}{4}\pi\varepsilon_0\left\{1 - \frac{a^4}{(R^2 + a^2)^2} + 2\ln\left(\frac{R^2}{a^2} + 1\right) + \frac{R^2\,a^2}{R^2 + a^2}\right\} \quad .$$

Taking the limit $R \to \infty$, we have

$$F(a, R \to \infty) = 2\ln\left(\frac{R^2}{a^2}\right) + a^2 \quad .$$

We now extremize with respect to $a$, which yields $a = \sqrt{2}$. Note that the energy in the vortex state is logarithmically infinite. In order to have a finite total free energy (relative to the ground state), we need to introduce an *antivortex* somewhere in the system. An antivortex has a phase winding which is opposite to that of the vortex, *i.e.* $\psi = f\,e^{-i\phi}$. If the vortex and antivortex separation is $r$, the energy is

$$V(r) = \tfrac{1}{2}\pi\varepsilon_0 \ln\left(\frac{r^2}{a^2} + 1\right) \quad .$$

This tends to $V(r) = \pi \varepsilon_0 \ln(d/a)$ for $d \gg a$ and smoothly approaches $V(0) = 0$, since when $r = 0$ the vortex and antivortex annihilate leaving the ground state condensate. Recall that two-dimensional point charges also interact via a logarithmic potential, according to Maxwell's equations. Indeed, there is a rather extensive analogy between the physics of two-dimensional models with $O(2)$ symmetry and $(2+1)$-dimensional electrodynamics.

**(7.10)** Consider a two-state Ising model, with an added dash of quantum flavor. You are invited to investigate the *transverse Ising model*, whose Hamiltonian is written

$$\hat{H} = -\tfrac{1}{2} \sum_{i,j} J_{ij} \sigma_i^x \sigma_j^x - H \sum_i \sigma_i^z \quad,$$

where the $\sigma_i^\alpha$ are Pauli matrices:

$$\sigma_i^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_i \quad , \qquad \sigma_i^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_i \quad .$$

(a) Using the trial density matrix,

$$\varrho_i = \tfrac{1}{2} + \tfrac{1}{2}\, m_x\, \sigma_i^x + \tfrac{1}{2}\, m_z\, \sigma_i^z$$

compute the mean field free energy $F/N\hat{J}(0) \equiv f(\theta, h, m_x, m_z)$, where $\theta = k_{\mathrm{B}} T/\hat{J}(0)$, and $h = H/\hat{J}(0)$. *Hint: Work in an eigenbasis when computing* $\mathrm{Tr}\, (\varrho \ln \varrho)$.

(b) Derive the mean field equations for $m_x$ and $m_z$.

(c) Show that there is always a solution with $m_x = 0$, although it may not be the solution with the lowest free energy. What is $m_z(\theta, h)$ when $m_x = 0$?

(d) Show that $m_z = h$ for all solutions with $m_x \neq 0$.

(e) Show that for $\theta \leq 1$ there is a curve $h = h^*(\theta)$ below which $m_x \neq 0$, and along which $m_x$ vanishes. That is, sketch the mean field phase diagram in the $(\theta, h)$ plane. Is the mean field transition at $h = h^*(\theta)$ first order or second order?

(f) Sketch, on the same plot, the behavior of $m_x(\theta, h)$ and $m_z(\theta, h)$ as functions of the field $h$ for fixed $\theta$. Do this for $\theta = 0$, $\theta = \tfrac{1}{2}$, and $\theta = 1$.

Solution :

(a) We have $\mathrm{Tr}\, (\varrho \sigma^x) = m_x$ and $\mathrm{Tr}\, (\varrho \sigma^z) = m_z$. The eigenvalues of $\varrho$ are $\tfrac{1}{2}(1 \pm m)$, where $m = (m_x^2 + m_z^2)^{1/2}$. Thus,

$$f(\theta, h, m_x, m_z) = -\tfrac{1}{2} m_x^2 - h m_z + \theta \left[ \frac{1+m}{2} \ln\!\left( \frac{1+m}{2} \right) + \frac{1-m}{2} \ln\!\left( \frac{1-m}{2} \right) \right] \quad.$$

(b) Differentiating with respect to $m_x$ and $m_z$ yields

$$\frac{\partial f}{\partial m_x} = 0 = -m_x + \frac{\theta}{2} \ln\!\left( \frac{1+m}{1-m} \right) \cdot \frac{m_x}{m}$$

$$\frac{\partial f}{\partial m_z} = 0 = -h + \frac{\theta}{2} \ln\!\left( \frac{1+m}{1-m} \right) \cdot \frac{m_z}{m} \quad.$$

Note that we have used the result

$$\frac{\partial m}{\partial m_\mu} = \frac{m_\mu}{m}$$

where $m_\alpha$ is any component of the vector $\mathbf{m}$.

(c) If we set $m_x = 0$, the first mean field equation is satisfied. We then have $m_z = m\,\mathrm{sgn}(h)$, and the second mean field equation yields $m_z = \tanh(h/\theta)$. Thus, in this phase we have

$$m_x = 0 \quad , \quad m_z = \tanh(h/\theta) \quad .$$

(d) When $m_x \neq 0$, we divide the first mean field equation by $m_x$ to obtain the result

$$m = \frac{\theta}{2}\,\ln\!\left(\frac{1+m}{1-m}\right) \quad ,$$

which is equivalent to $m = \tanh(m/\theta)$. Plugging this into the second mean field equation, we find $m_z = h$. Thus, when $m_x \neq 0$,

$$m_z = h \quad , \quad m_x = \sqrt{m^2 - h^2} \quad , \quad m = \tanh(m/\theta) \quad .$$

Note that the length of the magnetization vector, $m$, is purely a function of the temperature $\theta$ in this phase and thus does not change as $h$ is varied when $\theta$ is kept fixed. What does change is the canting angle of $\mathbf{m}$, which is $\alpha = \tan^{-1}(h/m)$ with respect to the $\hat{\mathbf{z}}$ axis.

(e) The two solutions coincide when $m = h$, hence

$$h = \tanh(h/\theta) \quad \Longrightarrow \quad \theta^*(h) = \frac{2h}{\ln\!\left(\frac{1+h}{1-h}\right)} \quad .$$

Inverting the above transcendental equation yields $h^*(\theta)$. The component $m_x$, which serves as the order parameter for this system, vanishes smoothly at $\theta = \theta_\mathrm{c}(h)$. The transition is therefore second order.

(f) See fig. 33.
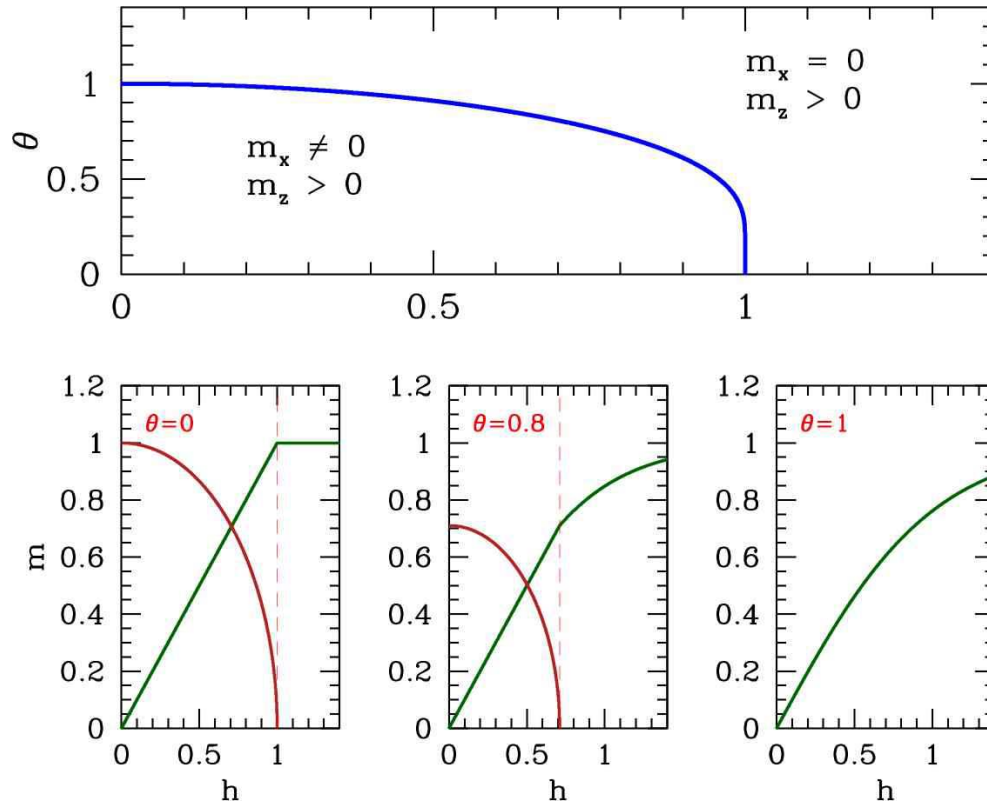
Figure 33: Solution to the mean field equations for problem 2. Top panel: phase diagram. The region within the thick blue line is a canted phase, where $m_x \neq 0$ and $m_z = h > 0$; outside this region the moment is aligned along $\hat{z}$ and $m_x = 0$ with $m_z = \tanh(h/\theta)$.

**(7.11)** The Landau free energy of a crystalline magnet is given by the expression

$$f = \tfrac{1}{2}\alpha t \left(m_x^2 + m_y^2\right) + \tfrac{1}{4}b_1\left(m_x^4 + m_y^4\right) + \tfrac{1}{2}b_2\, m_x^2\, m_y^2 \quad,$$

where the constants $\alpha$ and $b_1$ are both positive, and where $t$ is the dimensionless reduced temperature, $t = (T - T_c)/T_c$.

(a) Rescale, so that $f$ is of the form

$$f = \varepsilon_0\left\{\tfrac{1}{2}t\left(\phi_x^2 + \phi_y^2\right) + \tfrac{1}{4}\left(\phi_x^4 + \phi_y^4 + 2\lambda\,\phi_x^2\,\phi_y^2\right)\right\} \quad,$$

where $m_{x,y} = s\,\phi_{x,y}$, where $s$ is a scale factor. Find the appropriate scale factor and find expressions for the energy scale $\varepsilon_0$ and the dimensionless parameter $\lambda$ in terms of $\alpha$, $b_1$, and $b_2$.

(b) For what values of $\lambda$ is the free energy unbounded from below?

(c) Find the equations which minimize $f$ as a function of $\phi_{x,y}$.

(d) Show that there are three distinct phases: one in which $\phi_x = \phi_y = 0$ (phase I), another in which one of $\phi_{x,y}$ vanishes but the other is finite (phase II) and one in which both of $\phi_{x,y}$ are finite (phase III). Find $f$ in each of these phases, and be clear to identify any constraints on the parameters $t$ and $\lambda$.

(e) Sketch the phase diagram for this theory in the $(t, \lambda)$ plane, clearly identifying the unphysical region where $f$ is unbounded, and indicating the phase boundaries for all phase transitions. Make sure to label the phase transitions according to whether they are first or second order.

Solution :

(a) It is a simple matter to find

$$m_{x,y} = \sqrt{\frac{\alpha}{b_1}}\, \phi_{x,y} \quad , \quad \varepsilon_0 = \frac{\alpha^2}{b_1} \quad , \quad \lambda = \frac{b_2}{b_1} \quad .$$

(b) Note that

$$f = \tfrac{1}{4}\,\varepsilon_0 \begin{pmatrix} \phi_x^2 & \phi_y^2 \end{pmatrix} \begin{pmatrix} 1 & \lambda \\ \lambda & 1 \end{pmatrix} \begin{pmatrix} \phi_x^2 \\ \phi_y^2 \end{pmatrix} + \tfrac{1}{2}\,\varepsilon_0 \begin{pmatrix} \phi_x^2 & \phi_y^2 \end{pmatrix} \begin{pmatrix} t \\ t \end{pmatrix} \tag{1}$$

We need to make sure that the quartic term goes to positive infinity when the fields $\phi_{x,y}$ tend to infinity. Else the free energy will not be bounded from below and the model is unphysical. Clearly the matrix in the first term on the RHS has eigenvalues $1 \pm \lambda$ and corresponding (unnormalized) eigenvectors $\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}$. Since $\phi_{x,y}^2$ cannot be negative, we only need worry about the eigenvalue $1 + \lambda$. This is negative for $\lambda < -1$. Thus, $\lambda \le -1$ is unphysical.

(c) Differentiating with respect to $\phi_{x,y}$ yields the equations

$$\frac{\partial f}{\partial \phi_x} = \left( t + \phi_x^2 + \lambda\,\phi_y^2 \right) \phi_x = 0 \quad , \quad \frac{\partial f}{\partial \phi_y} = \left( t + \phi_y^2 + \lambda\,\phi_x^2 \right) \phi_y = 0 \quad .$$

(d) Clearly phase I with $\phi_x = \phi_y = 0$ is a solution to these equations. In phase II, we set one of the fields to zero, $\phi_y = 0$ and solve for $\phi_x = \sqrt{-t}$, which requires $t < 0$. A corresponding solution exists if we exchange $\phi_x \leftrightarrow \phi_y$. In phase III, we solve

$$\begin{pmatrix} 1 & \lambda \\ \lambda & 1 \end{pmatrix} \begin{pmatrix} \phi_x^2 \\ \phi_y^2 \end{pmatrix} = -\begin{pmatrix} t \\ t \end{pmatrix} \quad \Rightarrow \quad \phi_x^2 = \phi_y^2 = -\frac{t}{1+\lambda} \quad .$$

This phase also exists only for $t < 0$, and $\lambda > -1$ as well, which is required if the free energy is to be bounded from below. Thus, we find

$$(\phi_{x,\mathrm{I}}\,,\,\phi_{y,\mathrm{I}}) = (0,0) \quad , \quad f_\mathrm{I} = 0$$

and

$$(\phi_{x,\mathrm{II}}\,,\,\phi_{y,\mathrm{II}}) = (\pm\sqrt{-t}\,,\,0) \text{ or } (0\,,\,\pm\sqrt{-t}) \quad , \quad f_\mathrm{II} = -\tfrac{1}{4}\varepsilon_0\,t^2$$
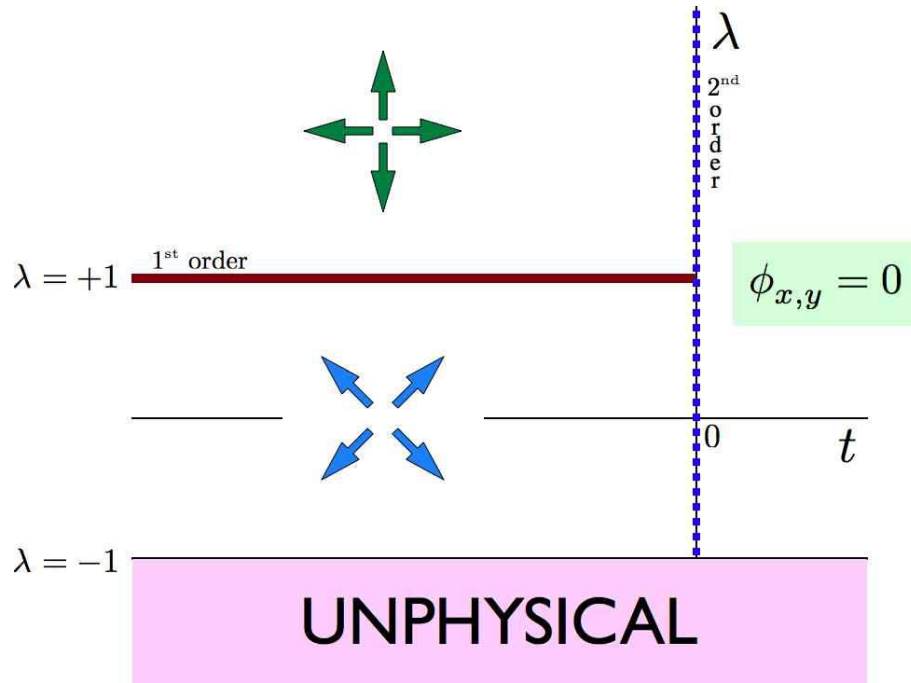
Figure 34: Phase diagram for problem (2e).

and

$$(\phi_{x,\mathrm{III}} , \phi_{y,\mathrm{III}}) = \pm\sqrt{\tfrac{-t}{1+\lambda}} \, (1 , 1) \text{ or } \pm \sqrt{\tfrac{-t}{1+\lambda}} \, (1 , -1) \quad , \quad f_{\mathrm{III}} = -\frac{\varepsilon_0 \, t^2}{2 \, (1+\lambda)} \quad .$$

(e) To find the phase diagram, we note that phase I has the lowest free energy for $t > 0$. For $t < 0$ we find

$$f_{\mathrm{III}} - f_{\mathrm{II}} = \tfrac{1}{4} \, \varepsilon_0 \, t^2 \, \frac{\lambda - 1}{\lambda + 1} \quad , \tag{2}$$

which is negative for $|\lambda| < 1$. Thus, the phase diagram is as depicted in fig. 34.

**(7.12)** A system is described by the Hamiltonian

$$\hat{H} = -J \sum_{\langle ij \rangle} \varepsilon(\mu_i, \mu_j) - H \sum_i \delta_{\mu_i, \mathrm{A}} \quad , \tag{3}$$

where on each site $i$ there are four possible choices for $\mu_i$: $\mu_i \in \{\mathrm{A, B, C, D}\}$. The interaction matrix $\varepsilon(\mu, \mu')$ is given in the following table:

| $\varepsilon$ | A | B | C | D |
|---|---|---|---|---|
| A | $+1$ | $-1$ | $-1$ | $0$ |
| B | $-1$ | $+1$ | $0$ | $-1$ |
| C | $-1$ | $0$ | $+1$ | $-1$ |
| D | $0$ | $-1$ | $-1$ | $+1$ |

(a) Write a trial density matrix

$$\varrho(\mu_1, \ldots, \mu_N) = \prod_{i=1}^{N} \varrho_1(\mu_i)$$

$$\varrho_1(\mu) = x \, \delta_{\mu, \mathrm{A}} + y(\delta_{\mu, \mathrm{B}} + \delta_{\mu, \mathrm{C}} + \delta_{\mu, \mathrm{D}}) \quad .$$

What is the relationship between $x$ and $y$? Henceforth use this relationship to eliminate $y$ in terms of $x$.

(b) What is the variational energy per site, $E(x, T, H)/N$?

(c) What is the variational entropy per site, $S(x, T, H)/N$?

(d) What is the mean field equation for $x$?

(e) What value $x^*$ does $x$ take when the system is disordered?

(f) Write $x = x^* + \frac{3}{4}\varepsilon$ and expand the free energy to fourth order in $\varepsilon$. (The factor $\frac{3}{4}$ should generate manageable coefficients in the Taylor series expansion.)

(g) Sketch $\varepsilon$ as a function of $T$ for $H = 0$ and find $T_\mathrm{c}$. Is the transition first order or second order?

Solution :

(a) Clearly we must have $y = \frac{1}{3}(1 - x)$ in order that $\mathrm{Tr}(\varrho_1) = x + 3y = 1$.

(b) We have

$$\frac{E}{N} = -\tfrac{1}{2}zJ\left(x^2 - 4\,xy + 3\,y^2 - 4\,y^2\right) - Hx \quad ,$$

The first term in the bracket corresponds to AA links, which occur with probability $x^2$ and have energy $-J$. The second term arises from the four possibilities AB, AC, BA, CA, each of which occurs with probability $xy$ and with energy $+J$. The third term is from the BB, CC, and DD configurations, each

with probability $y^2$ and energy $-J$. The last term is from the BD, CD, DB, and DC configurations, each with probability $y^2$ and energy $+J$. Finally, there is the field term. Eliminating $y = \frac{1}{3}(1-x)$ from this expression we have

$$\frac{E}{N} = \tfrac{1}{18}zJ\big(1 + 10\,x - 20\,x^2\big) - Hx$$

Note that with $x = 1$ we recover $E = -\frac{1}{2}NzJ - H$, *i.e.* an interaction energy of $-J$ per link and a field energy of $-H$ per site.

(c) The variational entropy per site is

$$s(x) = -k_{\mathrm{B}}\,\mathsf{Tr}\,\big(\varrho_1 \ln \varrho_1\big)$$

$$= -k_{\mathrm{B}}\Big(x\ln x + 3y \ln y\Big)$$

$$= -k_{\mathrm{B}}\left[x\ln x + (1-x)\ln\left(\frac{1-x}{3}\right)\right] \quad.$$

(d) It is convenient to adimensionalize, writing $f = F/N\varepsilon_0$, $\theta = k_{\mathrm{B}}T/\varepsilon_0$, and $h = H/\varepsilon_0$, with $\varepsilon_0 = \frac{5}{9}zJ$. Then

$$f(x,\theta,h) = \tfrac{1}{10} + x - 2x^2 - hx + \theta\left[x\ln x + (1-x)\ln\left(\frac{1-x}{3}\right)\right] \quad.$$

Differentiating with respect to $x$, we obtain the mean field equation

$$\frac{\partial f}{\partial x} = 0 \quad\Longrightarrow\quad 1 - 4x - h + \theta\ln\left(\frac{3x}{1-x}\right) = 0 \quad.$$

(e) When the system is disordered, there is no distinction between the different polarizations of $\mu_0$. Thus, $x^* = \frac{1}{4}$. Note that $x = \frac{1}{4}$ is a solution of the mean field equation from part (d) when $h = 0$.

(f) Find

$$f\big(x = \tfrac{1}{4} + \tfrac{3}{4}\,\varepsilon, \theta, h\big) = f_0 + \tfrac{3}{2}\big(\theta - \tfrac{3}{4}\big)\,\varepsilon^2 - \theta\,\varepsilon^3 + \tfrac{7}{4}\,\theta\,\varepsilon^4 - \tfrac{3}{4}\,h\,\varepsilon$$

with $f_0 = \frac{9}{40} - \frac{1}{4}h - \theta\ln 4$.

(g) For $h = 0$, the cubic term in the mean field free energy leads to a first order transition which preempts the second order one which would occur at $\theta^* = \frac{3}{4}$, where the coefficient of the quadratic term vanishes. We learned in ch. 7 of the lecture notes that for a free energy $f = \frac{1}{2}am^2 - \frac{1}{3}ym^3 + \frac{1}{4}bm^4$ that the first order transition occurs for $a = \frac{2}{9}\,b^{-1}y^2$, where the magnetization changes discontinuously from $m = 0$ at $a = a_{\mathrm{c}}^+$ to $m_0 = \frac{2}{3}\,b^{-1}y$ at $a = a_{\mathrm{c}}^-$. For our problem here, we have $a = 3\big(\theta - \frac{3}{4}\big)$, $y = 3\theta$, and $b = 7\theta$. This gives

$$\theta_{\mathrm{c}} = \tfrac{63}{76} \approx 0.829 \qquad,\qquad \varepsilon_0 = \tfrac{2}{7} \quad.$$

As $\theta$ decreases further below $\theta_{\mathrm{c}}$ to $\theta = 0$, $\varepsilon$ increases to $\varepsilon(\theta = 0) = 1$. No sketch needed!

**(7.13)** Consider a $q$-state Potts model on the body-centered cubic (BCC) lattice. The Hamiltonian is given by

$$\hat{H} = -J \sum_{\langle ij \rangle} \delta_{\sigma_i, \sigma_j} \quad ,$$

where $\sigma_i \in \{1, \ldots, q\}$ on each site.

(a) Following the mean field treatment in ch. 7 of the lecture notes, write $x = \langle \delta_{\sigma_i, 1} \rangle = q^{-1} + s$, and expand the free energy in powers of $s$ up through terms of order $s^4$. Neglecting all higher order terms in the free energy, find the critical temperature $\theta_c$, where $\theta = k_B T / zJ$ as usual. Indicate whether the transition is first order or second order (this will depend on $q$).

(b) For second order transitions, the truncated Landau expansion is sufficient, since we care only about the sign of the quadratic term in the free energy. First order transitions involve a discontinuity in the order parameter, so any truncation of the free energy as a power series in the order parameter involves an approximation. Find a way to numerically determine $\theta_c(q)$ based on the full mean field (*i.e.* variational density matrix) free energy. Compare your results with what you found in part (a), and sketch both sets of results for several values of $q$.

Solution :

(a) The expansion of the free energy $f(s, \theta)$ is given in ch. 7 of the lecture notes (set $h = 0$). We have

$$f = f_0 + \tfrac{1}{2} a\, s^2 - \tfrac{1}{3} y\, s^3 + \tfrac{1}{4} b\, s^4 + \mathcal{O}(s^5) \quad ,$$

with

$$a = \frac{q(q\theta - 1)}{q - 1} \quad , \qquad y = \frac{(q-2)\, q^3 \theta}{2(q-1)^2} \quad , \qquad b = \tfrac{1}{3} q^3 \theta \left[ 1 + (q-1)^{-3} \right] \quad .$$

For $q = 2$ we have $y = 0$, and there is a second order phase transition when $a = 0$, *i.e.* $\theta = q^{-1}$. For $q > 2$, there is a cubic term in the Landau expansion, and this portends a first order transition. Restricting to the quartic free energy above, a first order at $a > 0$ transition preempts what would have been a second order transition at $a = 0$. The transition occurs for $y^2 = \tfrac{9}{2} ab$. Solving for $\theta$, we obtain

$$\theta_c^L = \frac{6(q^2 - 3q + 3)}{(5q^2 - 14q + 14)\, q} \quad .$$

The value of the order parameter $s$ just below the first order transition temperature is

$$s(\theta_c^-) = \sqrt{2a/b} \quad ,$$

where $a$ and $b$ are evaluated at $\theta = \theta_c$

(b) The full variational free energy, neglecting constants, is

$$f(x, \theta) = -\tfrac{1}{2} x^2 - \frac{(1-x)^2}{2(q-1)} + \theta\, x \ln x + \theta\, (1-x) \ln \left( \frac{1-x}{q-1} \right) \quad .$$
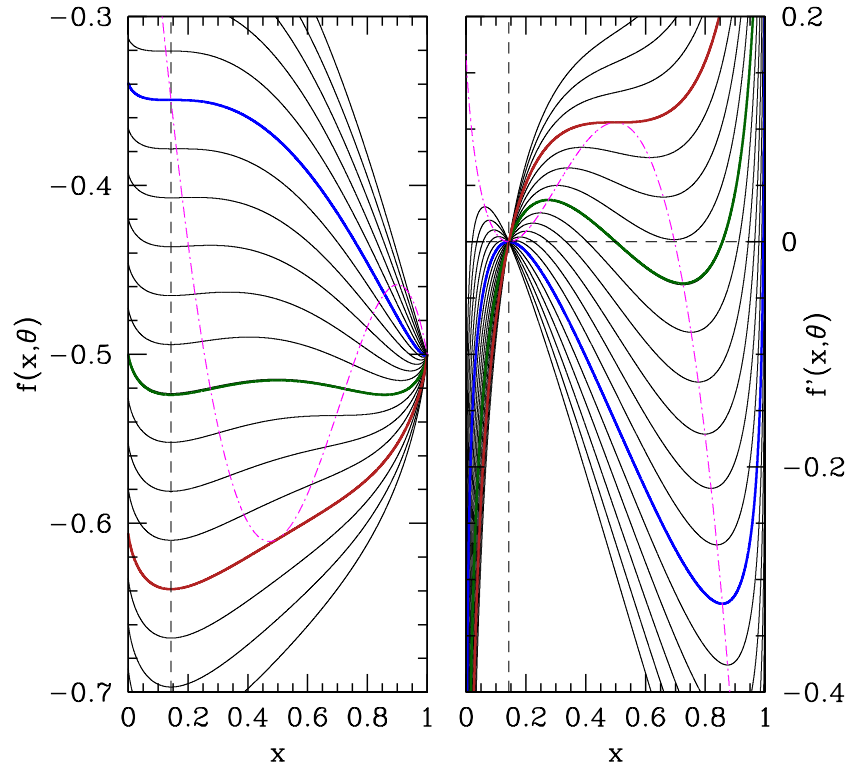
Figure 35: Variational free energy of the $q = 7$ Potts model *versus* variational parameter $x$. Left: free energy $f(x, \theta)$. Right: derivative $f'(x, \theta)$ with respect to the $x$. The dot-dash magenta curve in both cases is the locus of points for which the second derivative $f''(x, \theta)$ with respect to $x$ vanishes. Three characteristic temperatures are marked $\theta = q^{-1}$ (blue), where the coefficient of the quadratic term in the Landau expansion changes sign; $\theta = \theta_0$ (red), where there is a saddle-node bifurcation and above which the free energy has only one minimum at $x = q^{-1}$ (symmetric phase); and $\theta = \theta_c$ (green), where the first order transition occurs.

Therefore

$$\frac{\partial f}{\partial x} = -x + \frac{1-x}{q-1} + \theta \ln x - \theta \ln\left(\frac{1-x}{q-1}\right)$$

$$\frac{\partial^2 f}{\partial x^2} = -\frac{q}{q-1} + \frac{\theta}{x(1-x)} \quad .$$

Solving for $\frac{\partial^2 f}{\partial x^2} = 0$, we obtain

$$x_\pm = \frac{1}{2} \pm \frac{1}{2}\sqrt{1 - \frac{\theta}{\theta_0}} \quad ,$$

where

$$\theta_0 = \frac{q}{4(q-1)} \quad .$$
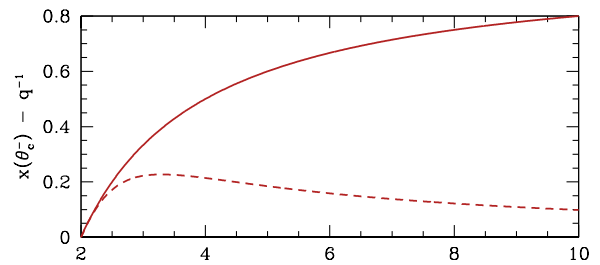
For temperatures below $\theta_0$, the function $f(x, \theta)$ has three extrema: two local minima and one local maximum. The points $x_\pm$ lie between either minimum and the maximum. The situation is depicted in fig. 35 for the case $q = 7$. To locate the first order transition, we must find the temperature $\theta_c$ for which the two minima are degenerate. This can be done numerically, but there is an analytic solution:

$$\theta_c^{\mathrm{MF}} = \frac{q - 2}{2(q - 1) \ln(q - 1)} \qquad , \qquad s(\theta_c^-) = \frac{q - 2}{q} \quad .$$

A comparison of with results from part (a) is shown in fig. 36. Note that the truncated free energy is sufficient to obtain the mean field solution for $q = 2$. This is because the transition for $q = 2$ is continuous (*i.e.* second order), and we only need to know $f(\theta, m)$ in the vicinity of $m = 0$.

**(7.14)** The Blume-Capel model is a $S = 1$ Ising model described by the Hamiltonian

$$\hat{H} = -\tfrac{1}{2} \sum_{i,j} J_{ij}\, S_i\, S_j + \Delta \sum_i S_i^2 \quad ,$$

where $J_{ij} = J(\mathbf{R}_i - \mathbf{R}_j)$ and $S_i \in \{-1, 0, +1\}$. The mean field theory for this model is discussed in ch. 7 of the lecture notes, using the 'neglect of fluctuations' method. Consider instead a variational density matrix approach. Take $\varrho(S_1, \ldots, S_N) = \prod_i \tilde{\varrho}(S_i)$, where

$$\tilde{\varrho}(S) = \left(\frac{n+m}{2}\right)\delta_{S,+1} + (1-n)\,\delta_{S,0} + \left(\frac{n-m}{2}\right)\delta_{S,-1} \quad .$$

(a) Find $\langle 1 \rangle$, $\langle S_i \rangle$, and $\langle S_i^2 \rangle$.

(b) Find $E = \mathrm{Tr}\,(\varrho H)$.

(c) Find $S = -k_{\mathrm{B}}\,\mathrm{Tr}\,(\varrho \ln \varrho)$.

(d) Adimensionalizing by writing $\theta = k_{\mathrm{B}}T/\hat{J}(0)$, $\delta = \Delta/\hat{J}(0)$, and $f = F/N\hat{J}(0)$, find the dimensionless free energy per site $f(m, n, \theta, \delta)$.

(e) Write down the mean field equations.

(f) Show that $m = 0$ always permits a solution to the mean field equations, and find $n(\theta, \delta)$ when $m = 0$.

(g) To find $\theta_{\mathrm{c}}$, set $m = 0$ but use both mean field equations. You should recover the result in ch. 7 of the lecture notes.

(h) Show that the equation for $\theta_{\mathrm{c}}$ has two solutions for $\delta < \delta_*$ and no solutions for $\delta > \delta_*$. Find the value of $\delta_*$.[14]

(i) Assume $m^2 \ll 1$ and solve for $n(m, \theta, \delta)$ using one of the mean field equations. Plug this into your result for part (d) and obtain an expansion of $f$ in terms of powers of $m^2$ alone. Find the first order line. You may find it convenient to use `Mathematica` here.

Solution :

(a) From the given expression for $\tilde{\varrho}$, we have

$$\langle 1 \rangle = 1 \quad , \qquad \langle S \rangle = m \quad , \qquad \langle S^2 \rangle = n \quad ,$$

where $\langle A \rangle = \mathrm{Tr}(\tilde{\varrho}\, A)$.

(b) From the results of part (a), we have

$$E = \mathrm{Tr}(\tilde{\varrho}\,\hat{H})$$
$$= -\tfrac{1}{2}N\hat{J}(0)\,m^2 + N\Delta\,n \quad ,$$

---

[14]*Nota bene :* $(\theta_*, \delta_*)$ is not the tricritical point.

assuming $J_{ii} = 0$ for al $i$.

(c) The entropy is

$$S = -k_{\rm B}\,{\rm Tr}\,(\varrho\ln\varrho)$$

$$= -Nk_{\rm B}\left\{\left(\frac{n-m}{2}\right)\ln\left(\frac{n-m}{2}\right) + (1-n)\ln(1-n) + \left(\frac{n+m}{2}\right)\ln\left(\frac{n+m}{2}\right)\right\}\quad.$$

(d) The dimensionless free energy is given by

$$f(m,n,\theta,\delta) = -\tfrac{1}{2}m^2 + \delta n + \theta\left\{\left(\frac{n-m}{2}\right)\ln\left(\frac{n-m}{2}\right) + (1-n)\ln(1-n) + \left(\frac{n+m}{2}\right)\ln\left(\frac{n+m}{2}\right)\right\}\quad.$$

(e) The mean field equations are

$$0 = \frac{\partial f}{\partial m} = -m + \tfrac{1}{2}\theta\,\ln\left(\frac{n-m}{n+m}\right)$$

$$0 = \frac{\partial f}{\partial n} = \delta + \tfrac{1}{2}\theta\,\ln\left(\frac{n^2-m^2}{4\,(1-n)^2}\right)\quad.$$

These can be rewritten as

$$m = n\tanh(m/\theta)$$

$$n^2 = m^2 + 4\,(1-n)^2\,e^{-2\delta/\theta}\quad.$$

(f) Setting $m = 0$ solves the first mean field equation always. Plugging this into the second equation, we find

$$n = \frac{2}{2 + \exp(\delta/\theta)}\quad.$$

(g) If we set $m \to 0$ in the first equation, we obtain $n = \theta$, hence

$$\theta_{\rm c} = \frac{2}{2 + \exp(\delta/\theta_{\rm c})}\quad.$$

(h) The above equation may be recast as

$$\delta = \theta\ln\left(\frac{2}{\theta} - 2\right)$$

with $\theta = \theta_{\rm c}$. Differentiating, we obtain

$$\frac{\partial\delta}{\partial\theta} = \ln\left(\frac{2}{\theta} - 2\right) - \frac{1}{1-\theta}\qquad\Longrightarrow\qquad \theta = \frac{\delta}{\delta + 1}\quad.$$

Plugging this into the result for part (g), we obtain the relation $\delta\, e^{\delta+1} = 2$, and numerical solution yields the maximum of $\delta(\theta)$ as

$$\theta_* = 0.3164989\ldots \qquad , \qquad \delta = 0.46305551\ldots \quad .$$

This is *not* the tricritical point.

(i) Plugging in $n = m/\tanh(m/\theta)$ into $f(n,m,\theta,\delta)$, we obtain an expression for $f(m,\theta,\delta)$, which we then expand in powers of $m$, obtaining

$$f(m,\theta,\delta) = f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 + \tfrac{1}{6}cm^6 + \mathcal{O}(m^8) \quad .$$

We find

$$a = \frac{2}{3\theta}\left\{\delta - \theta\ln\left(\frac{2(1-\theta)}{\theta}\right)\right\}$$

$$b = \frac{1}{45\,\theta^3}\left\{4(1-\theta)\,\theta\ln\left(\frac{2(1-\theta)}{\theta}\right) + 15\theta^2 - 5\theta + 4\delta(\theta-1)\right\}$$

$$c = \frac{1}{1890\,\theta^5(1-\theta)^2}\left\{24\,(1-\theta)^2\,\theta\ln\left(\frac{2(1-\theta)}{\theta}\right) + 24\delta(1-\theta)^2 + \theta\left(35 - 154\,\theta + 189\,\theta^2\right)\right\} \quad .$$

The tricritical point occurs for $a = b = 0$, which yields

$$\theta_{\mathrm{t}} = \tfrac{1}{3} \qquad , \qquad \delta_{\mathrm{t}} = \tfrac{2}{3}\ln 2 \quad .$$

If, following Landau, we consider terms only up through order $m^6$, we predict a first order line given by the solution to the equation

$$b = -\tfrac{4}{\sqrt{3}}\sqrt{ac} \quad .$$

The actual first order line is obtained by solving for the locus of points $(\theta,\delta)$ such that $f(m,\theta,\delta)$ has a degenerate minimum, with one of the minima at $m = 0$ and the other at $m = \pm m_0$. The results from Landau theory will coincide with the exact mean field solution at the tricritical point, where the $m_0 = 0$, but in general the first order lines obtained by the exact mean field theory solution and by a truncated sixth order Landau expansion of the free energy will differ.

**(7.15)** Consider the following model Hamiltonian,

$$\hat{H} = \sum_{\langle ij \rangle} E(\sigma_i, \sigma_j) \quad ,$$

where each $\sigma_i$ may take on one of three possible values, and

$$E(\sigma, \sigma') = \begin{pmatrix} -J & +J & 0 \\ +J & -J & 0 \\ 0 & 0 & +K \end{pmatrix} \quad ,$$

with $J > 0$ and $K > 0$. Consider a variational density matrix $\varrho_v(\sigma_1, \ldots, \sigma_N) = \prod_i \tilde{\varrho}(\sigma_i)$, where the normalized single site density matrix has diagonal elements

$$\tilde{\varrho}(\sigma) = \left( \frac{n+m}{2} \right) \delta_{\sigma,1} + \left( \frac{n-m}{2} \right) \delta_{\sigma,2} + (1-n) \, \delta_{\sigma,3} \quad .$$

(a) What is the global symmetry group for this Hamiltonian?

(b) Evaluate $E = \text{Tr}\,(\varrho_v \, \hat{H})$.

(c) Evaluate $S = -k_B \, \text{Tr}\,(\varrho_v \ln \varrho_v)$.

(d) Adimensionalize by writing $\theta = k_B T / zJ$ and $c = K/J$, where $z$ is the lattice coordination number. Find $f(n, m, \theta, c) = F/NzJ$.

(e) Find all the mean field equations.

(f) Find an equation for the critical temperature $\theta_c$, and show graphically that it has a unique solution.

<span style="color:red">Solution :</span>

<span style="color:blue">(a) The global symmetry group is $\mathbb{Z}_2$. If we label the spin values as $\sigma \in \{1, 2, 3\}$, then the group elements can be written as permutations, $1 = \binom{123}{123}$ and $\mathcal{J} = \binom{123}{213}$, with $\mathcal{J}^2 = 1$.</span>

<span style="color:blue">(b) For each nearest neighbor pair $(ij)$, the distribution of $\{\sigma, \sigma_j\}$ is according to the product $\tilde{\varrho}(\sigma_i) \, \tilde{\varrho}(\sigma_j)$. Thus, we have</span>

<span style="color:blue">$$E = \tfrac{1}{2} NzJ \sum_{\sigma, \sigma'} \tilde{\varrho}(\sigma) \, \tilde{\varrho}(\sigma') \, \varepsilon(\sigma, \sigma')$$</span>

<span style="color:blue">$$= \tfrac{1}{2} NzJ \cdot \left\{ \overbrace{\left( \frac{n+m}{2} \right)^2}^{\tilde{\varrho}^2(1)} (-J) + \overbrace{\left( \frac{n-m}{2} \right)^2}^{\tilde{\varrho}^2(2)} (-J) + \overbrace{2 \left( \frac{n+m}{2} \right) \left( \frac{n-m}{2} \right)}^{2\,\tilde{\varrho}(1)\,\tilde{\varrho}(2)} (+J) + \overbrace{(1-n)^2}^{\tilde{\varrho}^2(3)} (+K) \right\}$$</span>

<span style="color:blue">$$= -\tfrac{1}{2} Nz \Big[ Jm^2 - K(1-n)^2 \Big] \quad .$$</span>

(c) The entropy is

$$S = -Nk_{\rm B} \, {\sf Tr}\left(\tilde{\varrho}\ln\tilde{\varrho}\right)$$

$$= -Nk_{\rm B}\left\{\left(\frac{n+m}{2}\right)\ln\left(\frac{n+m}{2}\right) + \left(\frac{n-m}{2}\right)\ln\left(\frac{n-m}{2}\right) + (1-n)\ln(1-n)\right\} \quad .$$

(d) This can be solved by inspection from the results of parts (b) and (c):

$$f = -\tfrac{1}{2}m^2 + \tfrac{1}{2}c\left(1-n\right)^2 + \theta\left[\left(\frac{n+m}{2}\right)\ln\left(\frac{n+m}{2}\right) + \left(\frac{n-m}{2}\right)\ln\left(\frac{n-m}{2}\right) + (1-n)\ln(1-n)\right] \quad .$$

(e) There are two mean field equations, obtained by extremizing with respect to $n$ and to $m$, respectively:

$$\frac{\partial f}{\partial n} = 0 = c\left(n-1\right) + \tfrac{1}{2}\theta\,\ln\left(\frac{n^2 - m^2}{4\left(1-n\right)^2}\right)$$

$$\frac{\partial f}{\partial m} = 0 = -m + \tfrac{1}{2}\theta\,\ln\left(\frac{n-m}{n+m}\right) \quad .$$

These may be recast as

$$n^2 = m^2 + 4\left(1-n\right)^2 e^{-2c(n-1)/\theta}$$

$$m = n\tanh(m/\theta) \quad .$$

(f) To find $\theta_{\rm c}$, we take the limit $m \to 0$. The second mean field equation then gives $n = \theta$. Substituting this into the first mean field equation yields

$$\theta = 2\left(1-\theta\right)e^{-2c(\theta-1)/\theta} \quad .$$

If we define $u \equiv \theta^{-1} - 1$, this equation becomes

$$2u = e^{-cu} \quad .$$

It is clear that for $c > 0$ this equation has a unique solution, since the LHS is monotonically increasing and the RHS is monotonically decreasing, and the difference changes sign for some $u > 0$. The low temperature phase is the ordered phase, which spontaneously breaks the aforementioned $\mathbb{Z}_2$ symmetry. In the high temperature phase, the $\mathbb{Z}_2$ symmetry is unbroken.

**(7.16)** Consider a set of magnetic moments on a cubic lattice ($z = 6$). Due to the cubic anisotropy, the system is modeled by the Hamiltonian

$$\hat{H} = -J \sum_{\langle ij \rangle} \hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j - \mathbf{H} \cdot \sum_i \hat{\mathbf{n}}_i \quad ,$$

where at each site $\hat{\mathbf{n}}_i$ can take one of six possible values: $\hat{\mathbf{n}}_i \in \{\pm\hat{\mathbf{x}}, \pm\hat{\mathbf{y}}, \pm\hat{\mathbf{z}}\}$.

(a) Find the mean field free energy $f(\theta, \mathbf{m}, \mathbf{h})$, where $\theta = k_{\mathrm{B}}T/6J$ and $\mathbf{h} = \mathbf{H}/6J$.

(b) Find the self-consistent mean field equation for $\mathbf{m}$, and determine the critical temperature $\theta_{\mathrm{c}}(\mathbf{h} = 0)$. How does $\mathbf{m}$ behave just below $\theta_{\mathrm{c}}$? *Hint: you will have to go beyond $\mathcal{O}(\mathbf{m}^2)$ to answer this.*

(c) Find the phase diagram as a function of $\theta$ and $h$ when $\mathbf{H} = h\,\hat{\mathbf{x}}$.

Solution :

(a) The effective mean field is $\mathbf{H}_{\mathrm{eff}} = zJ\mathbf{m} + \mathbf{H}$, where $\mathbf{m} = \langle\hat{\mathbf{n}}_i\rangle$. The mean field Hamiltonian is

$$\hat{H}_{\mathrm{MF}} = \tfrac{1}{2}NzJ\mathbf{m}^2 - \mathbf{H}_{\mathrm{eff}} \cdot \sum_i \hat{\mathbf{n}}_i \quad .$$

With $\mathbf{h} = \mathbf{H}/zJ$ and $\theta = k_{\mathrm{B}}T/zJ$, we then have

$$f(\theta, \mathbf{h}, \mathbf{m}) = -\frac{k_{\mathrm{B}}T}{NzJ} \ln \mathsf{Tr}\, e^{-\hat{H}_{\mathrm{eff}}/k_{\mathrm{B}}T}$$

$$= \tfrac{1}{2}(m_x^2 + m_y^2 + m_z^2) - \theta \ln\left[2\cosh\left(\frac{m_x + h_x}{\theta}\right) + 2\cosh\left(\frac{m_y + h_y}{\theta}\right) + 2\cosh\left(\frac{m_z + h_z}{\theta}\right)\right] \quad .$$

(b) The mean field equation is obtained by setting $\frac{\partial f}{\partial m_\alpha} = 0$ for each Cartesian component $\alpha \in \{x, y, z\}$ of the order parameter $\mathbf{m}$. Thus,

$$m_x = \frac{\sinh\left(\frac{m_x + h_x}{\theta}\right)}{\cosh\left(\frac{m_x + h_x}{\theta}\right) + \cosh\left(\frac{m_y + h_y}{\theta}\right) + \cosh\left(\frac{m_z + h_z}{\theta}\right)} \quad ,$$

with corresponding equations for $m_y$ and $m_z$. We now set $\mathbf{h} = 0$ and expand in powers of $\mathbf{m}$, using $\cosh u = 1 + \tfrac{1}{2}u^2 + \tfrac{1}{24}u^4 + \mathcal{O}(u^6)$ and $\ln(1 + u) = u - \tfrac{1}{2}u^2 + \mathcal{O}(u^3)$. We have

$$f(\theta, \mathbf{h} = 0, \mathbf{m}) = \tfrac{1}{2}(m_x^2 + m_y^2 + m_z^2) - \theta \ln\left(6 + \frac{m_x^2 + m_y^2 + m_z^2}{\theta^2} + \frac{m_x^4 + m_y^4 + m_z^4}{12\,\theta^4} + \mathcal{O}(\mathbf{m}^6)\right)$$

$$= -\theta \ln 6 + \tfrac{1}{2}\left(1 - \tfrac{1}{3\theta}\right)(m_x^2 + m_y^2 + m_z^2) + \frac{m_x^2\,m_y^2 + m_y^2\,m_z^2 + m_z^2\,m_x^2}{36\,\theta^3} + \mathcal{O}(\mathbf{m}^6) \quad .$$

We see that the quadratic term is negative for $\theta < \theta_{\mathrm{c}} = \tfrac{1}{3}$. Furthermore, the quadratic term depends only on the magnitude of $\mathbf{m}$ and not its direction. How do we decide upon the direction, then? We must turn

to the quartic term. Note that the quartic term is minimized when **m** lies along one of the three cubic axes, in which case the term vanishes. So we know that in the ordered phase **m** prefers to lie along $\pm\hat{\mathbf{x}}$, $\pm\hat{\mathbf{y}}$, or $\pm\hat{\mathbf{z}}$. How can we determine its magnitude? We must turn to the *sextic* term in the expansion:

$$f(\theta, h = 0, m) = -\theta \ln 6 + \tfrac{1}{2}\left(1 - \tfrac{1}{3\theta}\right)m^2 + \frac{m^6}{3240\,\theta^5} + \mathcal{O}(m^8) \quad,$$

which is valid provided $\mathbf{m} = m\hat{\mathbf{n}}$ lies along a cubic axis. Extremizing, we obtain

$$m(\theta) = \pm\left[540\,\theta^4\,(\theta_{\mathrm{c}} - \theta)\right]^{1/4} \simeq \left(\tfrac{20}{3}\right)^{1/4}(\theta_{\mathrm{c}} - \theta)^{1/4} \quad,$$

where $\theta_{\mathrm{c}} = \tfrac{1}{3}$. So due to an accidental cancellation of the quartic term, we obtain a nonstandard mean field order parameter exponent of $\beta = \tfrac{1}{4}$.

(c) When $\mathbf{h} = h\,\hat{\mathbf{x}}$, the magnetization will choose to lie along the $\hat{\mathbf{x}}$ axis in order to minimize the free energy. One then has

$$f(\theta, h, m) = -\theta \ln 6 + \tfrac{1}{2}m^2 - \theta \ln\left[\tfrac{2}{3} + \tfrac{1}{3}\cosh\left(\frac{m + h}{\theta}\right)\right]$$

$$= -\theta \ln 6 + \tfrac{3}{2}(\theta - \theta_{\mathrm{c}})\,m^2 + \tfrac{3}{40}\,m^6 - hm + \ldots \quad,$$

where in the second line we have assumed $\theta \approx \theta_{\mathrm{c}}$, and we have expanded for small $m$ and $h$. The phase diagram resembles that of other Ising systems. The $h$ field breaks the $m \to -m$ symmetry, and there is a first order line extending along the $\theta$ axis (*i.e.* for $h = 0$) from $\theta = 0$ and terminating in a critical point at $\theta = \theta_{\mathrm{c}}$. As we have seen, the order parameter exponent is nonstandard, with $\beta = \tfrac{1}{4}$. What of the other critical exponents? Minimizing $f$ with respect to $m$, we have

$$3(\theta - \theta_{\mathrm{c}})\,m + \tfrac{9}{20}\,m^5 - h = 0 \quad.$$

For $\theta > \theta_{\mathrm{c}}$ and $m$ small, we can neglect the $\mathcal{O}(m^5)$ term and we find $m(\theta, h) = \frac{h}{3(\theta - \theta_{\mathrm{c}})}$, corresponding to the familiar susceptibility exponent $\gamma = 1$.

Consider next the heat capacity. For $\theta > \theta_{\mathrm{c}}$ the free energy is $f = -\theta \ln 6$, arising from the entropy term alone, whereas for $\theta < \theta_{\mathrm{c}}$ we have $m^2 = \sqrt{\tfrac{20}{3}}\,(\theta_{\mathrm{c}} - \theta)^{1/2}$, which yields

$$f(\theta < \theta_{\mathrm{c}}, h = 0) = -\theta \ln 6 - \sqrt{\tfrac{20}{3}}\,(\theta_{\mathrm{c}} - \theta)^{3/2} \quad.$$

Thus, the heat capacity, which is $c = -\theta\,\frac{\partial^2 f}{\partial \theta^2}$, behaves as $c(\theta) \propto (\theta_{\mathrm{c}} - \theta)^{-1/2}$, corresponding to $\alpha = \tfrac{1}{2}$, rather than the familiar $\alpha = 0$.

Finally, we examine the behavior of $m(\theta_{\mathrm{c}}, h)$. Setting $\theta = \theta_{\mathrm{c}}$, we have

$$f(\theta_{\mathrm{c}}, h, m) = -hm + \tfrac{9}{40}\,m^6 + \mathcal{O}(m^8) \quad.$$

Setting $\frac{\partial f}{\partial m} = 0$, we find $m \propto h^{1/\delta}$ with $\delta = 5$, which is also nonstandard.

**(7.17)** A magnet consists of a collection of local moments which can each take the values $S_i = -1$ or $S_i = +3$. The Hamiltonian is

$$\hat{H} = -\tfrac{1}{2}\sum_{i,j} J_{ij}\, S_i S_j - H\sum_i S_i \quad .$$

(a) Define $m = \langle S_i\rangle$, $h = H/\hat{J}(0)$, $\theta = k_{\mathrm{B}}T/\hat{J}(0)$. Find the dimensionless mean field free energy per site, $f = F/N\hat{J}(0)$ as a function of $\theta$, $h$, and $m$.

(b) Write down the self-consistent mean field equation for $m$.

(c) At $\theta = 0$, there is a first order transition as a function of field between the $m = +3$ state and the $m = -1$ state. Find the critical field $h_{\mathrm{c}}(\theta = 0)$.

(d) Find the critical point $(\theta_{\mathrm{c}},\, h_{\mathrm{c}})$ and plot the phase diagram for this system.

(e) Solve the problem using the variational density matrix approach.

Solution :

(a) We invoke the usual mean field treatment of dropping terms quadratic in fluctuations, resulting in an effective field $H_{\mathrm{eff}} = \hat{J}(0)\, m + H$ and a mean field Hamiltonian

$$\hat{H}_{\mathrm{MF}} = \tfrac{1}{2}N\hat{J}(0)\, m^2 - H_{\mathrm{eff}}\sum_{i=1}^{N} S_i \quad .$$

The free energy is then found to be

$$f(\theta, h, m) = \tfrac{1}{2}m^2 - \theta\,\ln\!\left(e^{3(m+h)/\theta} + e^{-(m+h)/\theta}\right)$$

$$= \tfrac{1}{2}m^2 - m - h - \theta\ln\cosh\!\left(\frac{2(m+h)}{\theta}\right) - \theta\ln 2 \quad .$$

(b) We extremize $f$ with respect to the order parameter $m$ and obtain

$$m = 1 + 2\tanh\!\left(\frac{2(m+h)}{\theta}\right) \quad .$$

(c) When $T = 0$ there are no fluctuations, and since the interactions are ferromagnetic we may examine the two uniform states. In the state where $S_i = +3$ for each $i$, the energy is $E_1 = \tfrac{9}{2}N\hat{J}(0) - 3NH$. In the state where $S_i = -1\ \forall\ i$, the energy is $E_2 = \tfrac{1}{2}N\hat{J}(0) + NH$. Equating these energies gives $H = -\hat{J}(0)$, *i.e.* $h = -1$.

(d) The first order transition at $h = -1$ and $\theta = 0$ continues in a curve emanating from this point into the finite $\theta$ region of the phase diagram. This phase boundary is determined by the requirement that
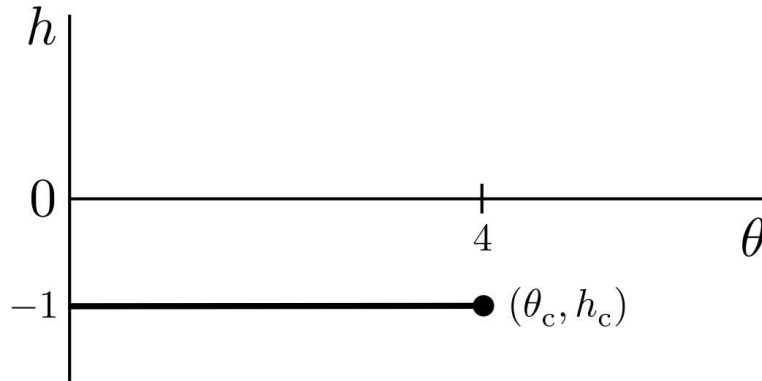
Figure 37: Phase diagram for problem 17.

$f(\theta, h, m)$ have a degenerate double minimum as a function of $m$ for fixed $\theta$ and $h$. This provides us with two conditions on the three quantities $(\theta, h, m)$, which in principle allows the determination of the curve $h = h_c(\theta)$. The first order line terminates in a critical point where these two local minima annihilate with a local maximum, which requires that $\frac{\partial f}{\partial m} = \frac{\partial^2 f}{\partial m^2} = \frac{\partial^3 f}{\partial m^3} = 0$, which provides the three conditions necessary to determine $(\theta_c, h_c, m_c)$. Now from our expression for $f(\theta, h, m)$, we have

$$\frac{\partial f}{\partial m} = m - 1 - 2\tanh\left(\frac{2(m+h)}{\theta}\right)$$

$$\frac{\partial^2 f}{\partial m^2} = 1 - \frac{4}{\theta}\operatorname{sech}^2\left(\frac{2(m+h)}{\theta}\right)$$

$$\frac{\partial^3 f}{\partial m^3} = \frac{16}{\theta^2}\tanh\left(\frac{2(m+h)}{\theta}\right)\operatorname{sech}^2\left(\frac{2(m+h)}{\theta}\right) \quad .$$

Now set all three of these quantities to zero. From the third of these, we get $m + h = 0$, which upon insertion into the second gives $\theta = 4$. From the first we then get $m = 1$, hence $h = -1$.

For a slicker derivation, note that the free energy may be written

$$f(\theta, h, m) = \tfrac{1}{2}(m+h)^2 - \theta \ln\cosh\left(\frac{2(m+h)}{\theta}\right) - (1+h)(m+h) + \tfrac{1}{2}h^2 - \theta \ln 2 \quad .$$

Thus, when $h = -1$, we have that $f$ is an even function of $m - 1$. Expanding then in powers of $m + h$, we have

$$f(\theta, h = -1, m) = f_0 + \tfrac{1}{2}\left(1 - \tfrac{4}{\theta}\right)(m-1)^2 + \tfrac{4}{3\theta^3}(m-1)^4 + \ldots \quad ,$$

whence we conclude $\theta_c = 4$ and $h_c = -1$.

(e) The most general single site variational density matrix is

$$\varrho(S) = x\,\delta_{S,-1} + (1-x)\,\delta_{S,+3} \quad .$$

This is normalized by construction. The average magnetization is

$$m = \operatorname{Tr}(S\varrho) = (-1) \cdot x + (+3) \cdot (1-x) = 3 - 4x \quad \Rightarrow \quad x = \frac{3-m}{4} \quad .$$

Thus we have

$$\varrho(S) = \frac{3-m}{4}\,\delta_{S,-1} + \frac{1+m}{4}\,\delta_{S,+3} \quad .$$

The variational free energy is then

$$F = \mathsf{Tr}\,(\hat{H}\hat{\varrho}) + k_{\mathrm{B}}T\,\mathsf{Tr}\,(\hat{\varrho}\ln\hat{\varrho})$$

$$= -\tfrac{1}{2}N\hat{J}(0)\,m^2 - NHm + k_{\mathrm{B}}T\left[\left(\frac{3-m}{4}\right)\ln\left(\frac{3-m}{4}\right) + \left(\frac{1+m}{4}\right)\ln\left(\frac{1+m}{4}\right)\right] \quad ,$$

where we assume all the diagonal elements vanish, *i.e.* $J_{ii} = 0$ for all $i$. Dividing by $N\hat{J}(0)$, we have

$$f(\theta, h, m) = -\tfrac{1}{2}m^2 - hm - \theta\left[\left(\frac{3-m}{4}\right)\ln\left(\frac{3-m}{4}\right) + \left(\frac{1+m}{4}\right)\ln\left(\frac{1+m}{4}\right)\right] \quad .$$

Minimizing with respect to the variational parameter $m$ yields

$$\frac{\partial f}{\partial m} = -m - h + \tfrac{1}{4}\theta\,\ln\left(\frac{1+m}{3-m}\right) \quad ,$$

which is equivalent to our earlier result $m = 1 + 2\tanh\big[2(m+h)/\theta\big]$.

If we once again expand in powers of $(m-1)$, we have

$$f(\theta, h, m) = -\big(\tfrac{1}{2} + h + \theta\ln 2\big) - (h+1)(m-1) + \tfrac{1}{8}(\theta-4)(m-1)^2 + \tfrac{1}{48}(m-1)^4 + \ldots \quad .$$

Again, we see $(\theta_{\mathrm{c}}, h_{\mathrm{c}}) = (4, -1)$.

## 0.8 Boltzmann Equation

**(8.1)** Consider a monatomic ideal gas in the presence of a temperature gradient $\boldsymbol{\nabla} T$. Answer the following questions within the framework of the relaxation time approximation to the Boltzmann equation.

(a) Compute the particle current $\mathbf{j}$ and show that it vanishes.

(b) Compute the 'energy squared' current,

$$\mathbf{j}_{\varepsilon^2} = \int d^3p \, \varepsilon^2 \mathbf{v} \, f(\mathbf{r}, \mathbf{p}, t) \quad .$$

(c) Suppose the gas is diatomic, so $c_p = \frac{7}{2} k_{\mathrm{B}}$. Show explicitly that the particle current $\mathbf{j}$ is zero. *Hint: To do this, you will have to understand the derivation of ch. 8 of the lecture notes and how this changes when the gas is diatomic. You may assume $\mathcal{Q}_{\alpha\beta} = \mathbf{F} = 0$.*

Solution :

(a) Under steady state conditions, the solution to the Boltzmann equation is $f = f^0 + \delta f$, where $f^0$ is the equilibrium distribution and

$$\delta f = -\frac{\tau f^0}{k_{\mathrm{B}} T} \cdot \frac{\varepsilon - c_p T}{T} \, \mathbf{v} \cdot \boldsymbol{\nabla} T \quad .$$

For the monatomic ideal gas, $c_p = \frac{5}{2} k_{\mathrm{B}}$. The particle current is

$$
\begin{aligned}
j^\alpha &= \int d^3p \, v^\alpha \, \delta f \\
&= -\frac{\tau}{k_{\mathrm{B}} T^2} \int d^3p \, f^0(\mathbf{p}) \, v^\alpha \, v^\beta \left( \varepsilon - \tfrac{5}{2} k_{\mathrm{B}} T \right) \frac{\partial T}{\partial x^\beta} \\
&= -\frac{2n\tau}{3mk_{\mathrm{B}} T^2} \frac{\partial T}{\partial x^\alpha} \left\langle \varepsilon \left( \varepsilon - \tfrac{5}{2} k_{\mathrm{B}} T \right) \right\rangle \quad ,
\end{aligned}
$$

where the average over momentum/velocity is converted into an average over the energy distribution,

$$\tilde{P}(\varepsilon) = 4\pi v^2 \frac{dv}{d\varepsilon} \, P_{\mathrm{M}}(v) = \tfrac{2}{\sqrt{\pi}} (k_{\mathrm{B}} T)^{-3/2} \, \varepsilon^{1/2} \, \phi(\varepsilon) \, e^{-\varepsilon/k_{\mathrm{B}} T} \quad .$$

As discussed in the lecture notes, the average of a homogeneous function of $\varepsilon$ under this distribution is given by

$$\left\langle \varepsilon^\alpha \right\rangle = \tfrac{2}{\sqrt{\pi}} \Gamma\left( \alpha + \tfrac{3}{2} \right) (k_{\mathrm{B}} T)^\alpha \quad .$$

Thus,

$$\left\langle \varepsilon \left( \varepsilon - \tfrac{5}{2} k_{\mathrm{B}} T \right) \right\rangle = \tfrac{2}{\sqrt{\pi}} (k_{\mathrm{B}} T)^2 \left\{ \Gamma\left( \tfrac{7}{2} \right) - \tfrac{5}{2} \Gamma\left( \tfrac{5}{2} \right) \right\} = 0 \quad .$$

(b) Now we must compute

$$j_{\varepsilon^2}^\alpha = \int d^3p\, v^\alpha\, \varepsilon^2\, \delta f$$

$$= -\frac{2n\tau}{3mk_{\mathrm{B}}T^2}\frac{\partial T}{\partial x^\alpha}\left\langle \varepsilon^3\big(\varepsilon - \tfrac{5}{2}k_{\mathrm{B}}T\big)\right\rangle \quad.$$

We then have

$$\left\langle \varepsilon^3\big(\varepsilon - \tfrac{5}{2}k_{\mathrm{B}}T\big)\right\rangle = \tfrac{2}{\sqrt{\pi}}\,(k_{\mathrm{B}}T)^4\left\{\Gamma\big(\tfrac{11}{2}\big) - \tfrac{5}{2}\,\Gamma\big(\tfrac{9}{2}\big)\right\} = \tfrac{105}{2}\,(k_{\mathrm{B}}T)^4$$

and so

$$\mathbf{j}_{\varepsilon^2} = -\frac{35\,n\tau k_{\mathrm{B}}}{m}\,(k_{\mathrm{B}}T)^2\,\boldsymbol{\nabla}T \quad.$$

(c) For diatomic gases in the presence of a temperature gradient, the solution to the linearized Boltzmann equation in the relaxation time approximation is

$$\delta f = -\frac{\tau\, f^0}{k_{\mathrm{B}}T}\cdot\frac{\varepsilon(\Gamma) - c_p T}{T}\,\mathbf{v}\cdot\boldsymbol{\nabla}T \quad,$$

where

$$\varepsilon(\Gamma) = \varepsilon_{\mathrm{tr}} + \varepsilon_{\mathrm{rot}} = \tfrac{1}{2}m\mathbf{v}^2 + \frac{\mathsf{L}_1^2 + \mathsf{L}_2^2}{2I} \quad,$$

where $\mathsf{L}_{1,2}$ are components of the angular momentum about the instantaneous body-fixed axes, with $I \equiv I_1 = I_2 \gg I_3$. We assume the rotations about axes 1 and 2 are effectively classical, so equipartition gives $\langle \varepsilon_{\mathrm{rot}}\rangle = 2 \times \tfrac{1}{2}k_{\mathrm{B}} = k_{\mathrm{B}}$. We still have $\langle \varepsilon_{\mathrm{tr}}\rangle = \tfrac{3}{2}k_{\mathrm{B}}$. Now in the derivation of the factor $\varepsilon(\varepsilon - c_p T)$ above, the first factor of $\varepsilon$ came from the $v^\alpha v^\beta$ term, so this is translational kinetic energy. Therefore, with $c_p = \tfrac{7}{2}k_{\mathrm{B}}$ now, we must compute

$$\left\langle \varepsilon_{\mathrm{tr}}\big(\varepsilon_{\mathrm{tr}} + \varepsilon_{\mathrm{rot}} - \tfrac{7}{2}k_{\mathrm{B}}T\big)\right\rangle = \left\langle \varepsilon_{\mathrm{tr}}\big(\varepsilon_{\mathrm{tr}} - \tfrac{5}{2}k_{\mathrm{B}}T\big)\right\rangle = 0 \quad.$$

So again the particle current vanishes.

Note added :

It is interesting to note that there is no particle current flowing in response to a temperature gradient when $\tau$ is energy-independent. This is a consequence of the fact that the pressure gradient $\boldsymbol{\nabla}p$ vanishes. Newton's Second Law for the fluid says that $nm\dot{\mathbf{V}} + \boldsymbol{\nabla}p = 0$, to lowest relevant order. With $\boldsymbol{\nabla}p \neq 0$, the fluid will accelerate. In a pipe, for example, eventually a steady state is reached where the flow is determined by the fluid viscosity, which is one of the terms we just dropped. (This is called *Poiseuille flow*.) When $p$ is constant, the local equilibrium distribution is

$$f^0(\mathbf{r}, \mathbf{p}) = \frac{p/k_{\mathrm{B}}T}{(2\pi m k_{\mathrm{B}}T)^{3/2}}\,e^{-\mathbf{p}^2/2mk_{\mathrm{B}}T} \quad,$$

where $T = T(\mathbf{r})$. We then have

$$f(\mathbf{r}, \mathbf{p}) = f^0(\mathbf{r} - \mathbf{v}\tau, \mathbf{p}) \quad,$$

which says that no new collisions happen for a time $\tau$ after a given particle thermalizes. *I.e.* we evolve the streaming terms for a time $\tau$. Expanding, we have

$$
\begin{aligned}
f &= f^0 - \frac{\tau \mathbf{p}}{m} \cdot \frac{\partial f^0}{\partial \mathbf{r}} + \dots \\
&= \left\{ 1 - \frac{\tau}{2 k_{\mathrm{B}} T^2} \left( \varepsilon(\mathbf{p}) - \tfrac{5}{2} k_{\mathrm{B}} T \right) \frac{\mathbf{p}}{m} \cdot \boldsymbol{\nabla} T + \dots \right\} f^0(\mathbf{r}, \mathbf{p}) \quad,
\end{aligned}
$$

which leads to $\mathbf{j} = 0$, assuming the relaxation time $\tau$ is energy-independent.

When the flow takes place in a restricted geometry, a dimensionless figure of merit known as the *Knudsen number*, $\mathsf{Kn} = \ell / L$, where $\ell$ is the mean free path and $L$ is the characteristic linear dimension associated with the geometry. For $\mathsf{Kn} \ll 1$, our Boltzmann transport calculations of quantities like $\kappa$, $\eta$, and $\zeta$ hold, and we may apply the Navier-Stokes equations[15]. In the opposite limit $\mathsf{Kn} \gg 1$, the boundary conditions on the distribution are crucial. Consider, for example, the case $\ell = \infty$. Suppose we have ideal gas flow in a cylinder whose symmetry axis is $\hat{\mathbf{x}}$. Particles with $v_x > 0$ enter from the left, and particles with $v_x < 0$ enter from the right. Their respective velocity distributions are

$$
P_j(\mathbf{v}) = n_j \left( \frac{m}{2\pi k_{\mathrm{B}} T_j} \right)^{3/2} e^{-m\mathbf{v}^2/2 k_{\mathrm{B}} T_j} \quad,
$$

where $j = \mathrm{L}$ or $\mathrm{R}$. The average current is then

$$
\begin{aligned}
j_x &= \int d^3v \, \left\{ n_{\mathrm{L}} \, v_x \, P_{\mathrm{L}}(\mathbf{v}) \, \Theta(v_x) + n_{\mathrm{R}} \, v_x \, P_{\mathrm{R}}(\mathbf{v}) \, \Theta(-v_x) \right\} \\
&= n_{\mathrm{L}} \sqrt{\frac{2 k_{\mathrm{B}} T_{\mathrm{L}}}{m}} - n_{\mathrm{R}} \sqrt{\frac{2 k_{\mathrm{B}} T_{\mathrm{R}}}{m}} \quad.
\end{aligned}
$$

---

[15]These equations may need to be supplemented by certain conditions which apply in the vicinity of solid boundaries.

**(8.2)** Consider a classical gas of charged particles in the presence of a magnetic field $\mathbf{B}$. The Boltzmann equation is then given by

$$\frac{\varepsilon - h}{k_{\mathrm{B}} T^2} f^0 \, \mathbf{v} \cdot \boldsymbol{\nabla} T - \frac{e}{mc} \mathbf{v} \times \mathbf{B} \cdot \frac{\partial \, \delta f}{d \mathbf{v}} = \left( \frac{df}{dt} \right)_{\mathrm{coll}} \quad .$$

Consider the case where $T = T(x)$ and $\mathbf{B} = B \hat{\mathbf{z}}$. Making the relaxation time approximation, show that a solution to the above equation exists in the form $\delta f = \mathbf{v} \cdot \mathbf{A}(\varepsilon)$, where $\mathbf{A}(\varepsilon)$ is a vector-valued function of $\varepsilon(\mathbf{v}) = \frac{1}{2} m \mathbf{v}^2$ which lies in the $(x, y)$ plane. Find the energy current $\mathbf{j}_\varepsilon$. Interpret your result physically.

<span style="color:red">Solution</span> : We'll use index notation and the Einstein summation convention for ease of presentation. Recall that the curl is given by $(\mathbf{A} \times \mathbf{B})_\mu = \epsilon_{\mu\nu\lambda} A_\nu B_\lambda$. We write $\delta f = v_\mu A_\mu(\varepsilon)$, and compute

$$\frac{\partial \, \delta f}{\partial v_\lambda} = A_\lambda + v_\alpha \frac{\partial A_\alpha}{\partial v_\lambda}$$

$$= A_\lambda + m v_\lambda v_\alpha \frac{\partial A_\alpha}{\partial \varepsilon} \quad .$$

Thus,

$$\mathbf{v} \times \mathbf{B} \cdot \frac{\partial \, \delta f}{\partial \mathbf{v}} = \epsilon_{\mu\nu\lambda} v_\mu B_\nu \frac{\partial \, \delta f}{\partial v_\lambda}$$

$$= \epsilon_{\mu\nu\lambda} v_\mu B_\nu \left( A_\lambda + m v_\lambda v_\alpha \frac{\partial A_\alpha}{\partial \varepsilon} \right)$$

$$= \epsilon_{\mu\nu\lambda} v_\mu B_\nu A_\lambda \quad .$$

We then have

$$\frac{\varepsilon - h}{k_{\mathrm{B}} T^2} f^0 \, v_\mu \, \partial_\mu T = \frac{e}{mc} \epsilon_{\mu\nu\lambda} v_\mu B_\nu A_\lambda - \frac{v_\mu A_\mu}{\tau} \quad .$$

Since this must be true for all $\mathbf{v}$, we have

$$A_\mu - \frac{eB\tau}{mc} \epsilon_{\mu\nu\lambda} n_\nu A_\lambda = -\frac{(\varepsilon - h) \, \tau}{k_{\mathrm{B}} T^2} f^0 \, \partial_\mu T \quad ,$$

where $\mathbf{B} \equiv B \, \hat{\mathbf{n}}$. It is conventional to define the *cyclotron frequency*, $\omega_{\mathrm{c}} = eB/mc$, in which case

$$\left( \delta_{\mu\nu} + \omega_{\mathrm{c}} \tau \, \epsilon_{\mu\nu\lambda} \, n_\lambda \right) A_\nu = X_\mu \quad ,$$

where $\mathbf{X} = -(\varepsilon - h) \, \tau f^0 \, \boldsymbol{\nabla} T / k_{\mathrm{B}} T^2$. So we must invert the matrix

$$M_{\mu\nu} = \delta_{\mu\nu} + \omega_{\mathrm{c}} \tau \, \epsilon_{\mu\nu\lambda} \, n_\lambda \quad .$$

To do so, we make the *Ansatz*,

$$M_{\nu\sigma}^{-1} = A \, \delta_{\nu\sigma} + B \, n_\nu \, n_\sigma + C \, \epsilon_{\nu\sigma\rho} \, n_\rho \quad ,$$

and we determine the constants $A$, $B$, and $C$ by demanding

$$M_{\mu\nu} M_{\nu\sigma}^{-1} = \left( \delta_{\mu\nu} + \omega_{\mathrm{c}} \tau \, \epsilon_{\mu\nu\lambda} \, n_\lambda \right) \left( A \, \delta_{\nu\sigma} + B \, n_\nu \, n_\sigma + C \, \epsilon_{\nu\sigma\rho} \, n_\rho \right)$$

$$= \left( A - C \, \omega_{\mathrm{c}} \, \tau \right) \delta_{\mu\sigma} + \left( B + C \, \omega_{\mathrm{c}} \, \tau \right) n_\mu \, n_\sigma + \left( C + A \, \omega_{\mathrm{c}} \, \tau \right) \epsilon_{\mu\sigma\rho} \, n_\rho \equiv \delta_{\mu\sigma} \quad .$$

Here we have used the result

$$\epsilon_{\mu\nu\lambda}\,\epsilon_{\nu\sigma\rho} = \epsilon_{\nu\lambda\mu}\,\epsilon_{\nu\sigma\rho} = \delta_{\lambda\sigma}\,\delta_{\mu\rho} - \delta_{\lambda\rho}\,\delta_{\mu\sigma} \quad ,$$

as well as the fact that $\hat{\mathbf{n}}$ is a unit vector: $n_\mu\,n_\mu = 1$. We can now read off the results:

$$A - C\,\omega_{\mathrm{c}}\tau = 1 \quad , \quad B + C\,\omega_{\mathrm{c}}\tau = 0 \quad , \quad C + A\,\omega_{\mathrm{c}}\tau = 0 \quad ,$$

which entail

$$A = \frac{1}{1 + \omega_{\mathrm{c}}^2\tau^2} \quad , \quad B = \frac{\omega_{\mathrm{c}}^2\tau^2}{1 + \omega_{\mathrm{c}}^2\tau^2} \quad , \quad C = -\frac{\omega_{\mathrm{c}}\tau}{1 + \omega_{\mathrm{c}}^2\tau^2} \quad .$$

So we can now write

$$A_\mu = M_{\mu\nu}^{-1}\,X_\nu = \frac{\delta_{\mu\nu} + \omega_{\mathrm{c}}^2\tau^2\,n_\mu\,n_\nu - \omega_{\mathrm{c}}\tau\,\epsilon_{\mu\nu\lambda}\,n_\lambda}{1 + \omega_{\mathrm{c}}^2\tau^2}\,X_\nu \quad .$$

The $\alpha$-component of the energy current is

$$j_\varepsilon^\alpha = \int \frac{d^3p}{h^3}\,v_\alpha\,v_\mu\,\varepsilon\,A_\mu(\varepsilon) = \frac{2}{3m}\int \frac{d^3p}{h^3}\,\varepsilon^2\,A_\alpha(\varepsilon) \quad ,$$

where we have replaced $v_\alpha\,v_\mu \to \frac{2}{3m}\,\varepsilon\,\delta_{\alpha\mu}$. Next, we use

$$\frac{2}{3m}\int \frac{d^3p}{h^3}\,\varepsilon^2\,X_\nu = -\frac{5\tau}{3m}\,k_{\mathrm{B}}^2 T\,\frac{\partial T}{\partial x_\nu} \quad ,$$

hence

$$\mathbf{j}_\varepsilon = -\frac{5\tau}{3m}\,\frac{k_{\mathrm{B}}^2 T}{1 + \omega_{\mathrm{c}}^2\tau^2}\,\Big(\boldsymbol{\nabla}T + \omega_{\mathrm{c}}^2\tau^2\,\hat{\mathbf{n}}\,(\hat{\mathbf{n}}\cdot\boldsymbol{\nabla}T) + \omega_{\mathrm{c}}\tau\,\hat{\mathbf{n}}\times\boldsymbol{\nabla}T\Big) \quad .$$

We are given that $\hat{\mathbf{n}} = \hat{\mathbf{z}}$ and $\boldsymbol{\nabla}T = T'(x)\,\hat{\mathbf{x}}$. We see that the energy current $\mathbf{j}_\varepsilon$ is flowing both along $-\hat{\mathbf{x}}$ and along $-\hat{\mathbf{y}}$. Why does heat flow along $\hat{\mathbf{y}}$? It is because the particles are charged, and as they individually flow along $-\hat{\mathbf{x}}$, there is a Lorentz force in the $-\hat{\mathbf{y}}$ direction, so the energy flows along $-\hat{\mathbf{y}}$ as well.

**(8.3)** Consider one dimensional motion according to the equation

$$\dot{p} + \gamma p = \eta(t) \quad ,$$

and compute the average $\langle p^4(t) \rangle$. You should assume that

$$\langle \eta(s_1)\,\eta(s_2)\,\eta(s_3)\,\eta(s_4) \rangle = \phi(s_1 - s_2)\,\phi(s_3 - s_4) + \phi(s_1 - s_3)\,\phi(s_2 - s_4) + \phi(s_1 - s_4)\,\phi(s_2 - s_3)$$

where $\phi(s) = \Gamma\,\delta(s)$. You may further assume that $p(0) = 0$.

Solution :

Integrating the Langevin equation, we have

$$p(t) = \int_0^t dt_1\, e^{-\gamma(t-t_1)}\,\eta(t_1) \quad .$$

Raising this to the fourth power and taking the average, we have

$$\langle p^4(t) \rangle = \int_0^t dt_1\, e^{-\gamma(t-t_1)} \int_0^t dt_2\, e^{-\gamma(t-t_2)} \int_0^t dt_3\, e^{-\gamma(t-t_3)} \int_0^t dt_4\, e^{-\gamma(t-t_4)} \, \langle \eta(t_1)\,\eta(t_2)\,\eta(t_3)\,\eta(t_4) \rangle$$

$$= 3\Gamma^2 \int_0^t dt_1\, e^{-2\gamma(t-t_1)} \int_0^t dt_2\, e^{-2\gamma(t-t_2)} = \frac{3\,\Gamma^2}{4\,\gamma^2}\,\left(1 - e^{-2\gamma t}\right)^2 \quad .$$

We have here used the fact that the three contributions to the average of the product of the four $\eta$'s each contribute the same amount to $\langle p^4(t) \rangle$. Recall $\Gamma = 2M\gamma k_{\mathrm{B}}T$, where $M$ is the mass of the particle. Note that

$$\langle p^4(t) \rangle = 3 \left\langle p^2(t) \right\rangle^2 \quad .$$

**(8.4)** A photon gas in equilibrium is described by the distribution function

$$f^0(\mathbf{p}) = \frac{2}{e^{cp/k_{\mathrm{B}}T} - 1} \quad ,$$

where the factor of 2 comes from summing over the two independent polarization states.

(a) Consider a photon gas (in three dimensions) slightly out of equilibrium, but in steady state under the influence of a temperature gradient $\boldsymbol{\nabla}T$. Write $f = f^0 + \delta f$ and write the Boltzmann equation in the relaxation time approximation. Remember that $\varepsilon(\mathbf{p}) = cp$ and $\mathbf{v} = \frac{\partial \varepsilon}{\partial \mathbf{p}} = c\hat{\mathbf{p}}$, so the speed is always $c$.

(b) What is the formal expression for the energy current, expressed as an integral of something times the distribution $f$?

(c) Compute the thermal conductivity $\kappa$. It is OK for your expression to involve *dimensionless* integrals.

Solution :

(a) We have

$$df^0 = -\frac{2cp\,e^{\beta cp}}{(e^{\beta cp} - 1)^2}\,d\beta = \frac{2cp\,e^{\beta cp}}{(e^{\beta cp} - 1)^2}\,\frac{dT}{k_{\mathrm{B}}T^2} \quad .$$

The steady state Boltzmann equation is $\mathbf{v} \cdot \frac{\partial f^0}{\partial \mathbf{r}} = \left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}}$, hence with $\mathbf{v} = c\hat{\mathbf{p}}$,

$$\frac{2\,c^2\,e^{cp/k_{\mathrm{B}}T}}{(e^{cp/k_{\mathrm{B}}T} - 1)^2}\,\frac{1}{k_{\mathrm{B}}T^2}\,\mathbf{p} \cdot \boldsymbol{\nabla}T = -\frac{\delta f}{\tau} \quad .$$

(b) The energy current is given by

$$\mathbf{j}_\varepsilon(\mathbf{r}) = \int \frac{d^3p}{h^3}\,c^2\mathbf{p}\,f(\mathbf{p}, \mathbf{r}) \quad .$$

(c) Integrating, we find

$$\kappa = \frac{2c^4\tau}{3h^3 k_{\mathrm{B}}T^2}\int d^3p\,\frac{p^2\,e^{cp/k_{\mathrm{B}}T}}{(e^{cp/k_{\mathrm{B}}T} - 1)^2}$$

$$= \frac{8\pi k_{\mathrm{B}}\tau}{3c}\left(\frac{k_{\mathrm{B}}T}{hc}\right)^3\int\limits_0^\infty ds\,\frac{s^4\,e^s}{(e^s - 1)^2}$$

$$= \frac{4k_{\mathrm{B}}\tau}{3\pi^2 c}\left(\frac{k_{\mathrm{B}}T}{hc}\right)^3\int\limits_0^\infty ds\,\frac{s^3}{e^s - 1} \quad ,$$

where we simplified the integrand somewhat using integration by parts. The integral may be computed in closed form:

$$\mathcal{I}_n = \int\limits_0^\infty ds \, \frac{s^n}{e^s - 1} = \Gamma(n+1)\,\zeta(n+1) \quad \Rightarrow \quad \mathcal{I}_3 = \frac{\pi^4}{15} \quad ,$$

and therefore

$$\kappa = \frac{\pi^2 k_{\mathrm{B}} \tau}{45\,c} \left( \frac{k_{\mathrm{B}} T}{hc} \right)^3 \quad .$$

**(8.5)** Suppose the relaxation time is energy-dependent, with $\tau(\varepsilon) = \tau_0 \, e^{-\varepsilon/\varepsilon_0}$. Compute the particle current $\mathbf{j}$ and energy current $\mathbf{j}_\varepsilon$ flowing in response to a temperature gradient $\boldsymbol{\nabla} T$.

Solution :

Now we must compute

$$
\left\{ \begin{matrix} j^\alpha \\ j_\varepsilon^\alpha \end{matrix} \right\} = \int d^3p \left\{ \begin{matrix} v^\alpha \\ \varepsilon \, v^\alpha \end{matrix} \right\} \delta f
$$

$$
= -\frac{2n}{3mk_{\mathrm{B}}T^2} \frac{\partial T}{\partial x^\alpha} \left\langle \tau(\varepsilon) \left\{ \begin{matrix} \varepsilon \\ \varepsilon^2 \end{matrix} \right\} \left( \varepsilon - \tfrac{5}{2}k_{\mathrm{B}}T \right) \right\rangle \quad ,
$$

where $\tau(\varepsilon) = \tau_0 \, e^{-\varepsilon/\varepsilon_0}$. We find

$$
\left\langle e^{-\varepsilon/\varepsilon_0} \, \varepsilon^\alpha \right\rangle = \tfrac{2}{\sqrt{\pi}} \, (k_{\mathrm{B}}T)^{-3/2} \int\limits_0^\infty d\varepsilon \, \varepsilon^{\alpha+\frac{1}{2}} e^{-\varepsilon/k_{\mathrm{B}}T} \, e^{-\varepsilon/\varepsilon_0}
$$

$$
= \tfrac{2}{\sqrt{\pi}} \, \Gamma\!\left(\alpha + \tfrac{3}{2}\right) (k_{\mathrm{B}}T)^\alpha \left( \frac{\varepsilon_0}{\varepsilon_0 + k_{\mathrm{B}}T} \right)^{\alpha+\frac{3}{2}} \quad .
$$

Therefore,

$$
\left\langle e^{-\varepsilon/\varepsilon_0} \, \varepsilon \right\rangle = \tfrac{3}{2} \, k_{\mathrm{B}}T \left( \frac{\varepsilon_0}{\varepsilon_0 + k_{\mathrm{B}}T} \right)^{5/2}
$$

$$
\left\langle e^{-\varepsilon/\varepsilon_0} \, \varepsilon^2 \right\rangle = \tfrac{15}{4} \, (k_{\mathrm{B}}T)^2 \left( \frac{\varepsilon_0}{\varepsilon_0 + k_{\mathrm{B}}T} \right)^{7/2}
$$

$$
\left\langle e^{-\varepsilon/\varepsilon_0} \, \varepsilon^3 \right\rangle = \tfrac{105}{8} \, (k_{\mathrm{B}}T)^3 \left( \frac{\varepsilon_0}{\varepsilon_0 + k_{\mathrm{B}}T} \right)^{9/2}
$$

and

$$
\mathbf{j} = \frac{5n\tau_0 k_{\mathrm{B}}^2 T}{2m} \frac{\varepsilon_0^{5/2}}{(\varepsilon_0 + k_{\mathrm{B}}T)^{7/2}} \boldsymbol{\nabla} T
$$

$$
\mathbf{j}_\varepsilon = -\frac{5n\tau_0 k_{\mathrm{B}}^2 T}{4m} \left( \frac{\varepsilon_0}{\varepsilon_0 + k_{\mathrm{B}}T} \right)^{7/2} \left( \frac{2\varepsilon_0 - 5k_{\mathrm{B}}T}{\varepsilon_0 + k_{\mathrm{B}}T} \right) \boldsymbol{\nabla} T \quad .
$$

The previous results are obtained by setting $\varepsilon_0 = \infty$ and $\tau_0 = 1/\sqrt{2}\,n\bar{v}\sigma$. Note the strange result that $\kappa$ becomes negative for $k_{\mathrm{B}}T > \tfrac{2}{5}\varepsilon_0$.

**(8.6)** Use the linearized Boltzmann equation to compute the bulk viscosity $\zeta$ of an ideal gas.

- (a) Consider first the case of a monatomic ideal gas. Show that $\zeta = 0$ within this approximation. Will your result change if the scattering time is energy-dependent?

- (b) Compute $\zeta$ for a diatomic ideal gas.

Solution :

According to the lecture notes, the solution to the linearized Boltzmann equation in the relaxation time approximation is

$$\delta f = -\frac{\tau f^0}{k_{\mathrm{B}} T} \left\{ m v^\alpha v^\beta \frac{\partial V_\alpha}{\partial x^\beta} - (\varepsilon_{\mathrm{tr}} + \varepsilon_{\mathrm{rot}}) \frac{k_{\mathrm{B}}}{c_V} \boldsymbol{\nabla} \cdot \mathbf{V} \right\} \quad .$$

We also have

$$\mathrm{Tr}\ \Pi = nm \langle \mathbf{v}^2 \rangle = 2n \langle \varepsilon_{\mathrm{tr}} \rangle = 3p - 3\zeta \boldsymbol{\nabla} \cdot \mathbf{V} \quad .$$

We then compute $\mathrm{Tr}\ \Pi$:

$$\mathrm{Tr}\ \Pi = 2n \langle \varepsilon_{\mathrm{tr}} \rangle = 3p - 3\zeta \boldsymbol{\nabla} \cdot \mathbf{V}$$

$$= 2n \int d\Gamma \, (f^0 + \delta f) \, \varepsilon_{\mathrm{tr}}$$

The $f^0$ term yields a contribution $3nk_{\mathrm{B}} T = 3p$ in all cases, which agrees with the first term on the RHS of the equation for $\mathrm{Tr}\ \Pi$. Therefore

$$\zeta \boldsymbol{\nabla} \cdot \mathbf{V} = -\tfrac{2}{3} n \int d\Gamma \, \delta f \, \varepsilon_{\mathrm{tr}} \quad .$$

(a) For the monatomic gas, $\Gamma = \{p_x, p_y, p_z\}$. We then have

$$\zeta \boldsymbol{\nabla} \cdot \mathbf{V} = \frac{2n\tau}{3k_{\mathrm{B}} T} \int d^3p \, f^0(\mathbf{p}) \, \varepsilon \left\{ m v^\alpha v^\beta \frac{\partial V_\alpha}{\partial x^\beta} - \frac{\varepsilon}{c_V / k_{\mathrm{B}}} \boldsymbol{\nabla} \cdot \mathbf{V} \right\}$$

$$= \frac{2n\tau}{3k_{\mathrm{B}} T} \left\langle \left( \tfrac{2}{3} - \tfrac{k_{\mathrm{B}}}{c_V} \right) \varepsilon \right\rangle \boldsymbol{\nabla} \cdot \mathbf{V} = 0 \quad .$$

Here we have replaced $m v^\alpha v^\beta \to \tfrac{1}{3} m \mathbf{v}^2 = \tfrac{2}{3} \varepsilon_{\mathrm{tr}}$ under the integral. If the scattering time is energy dependent, then we put $\tau(\varepsilon)$ inside the energy integral when computing the average, but this does not affect the final result: $\zeta = 0$.

(b) Now we must include the rotational kinetic energy in the expression for $\delta f$, and we have $c_V = \tfrac{5}{2} k_{\mathrm{B}}$. Thus,

$$\zeta \boldsymbol{\nabla} \cdot \mathbf{V} = \frac{2n\tau}{3k_{\mathrm{B}} T} \int d\Gamma \, f^0(\Gamma) \, \varepsilon_{\mathrm{tr}} \left\{ m v^\alpha v^\beta \frac{\partial V_\alpha}{\partial x^\beta} - (\varepsilon_{\mathrm{tr}} + \varepsilon_{\mathrm{rot}}) \frac{k_{\mathrm{B}}}{c_V} \boldsymbol{\nabla} \cdot \mathbf{V} \right\}$$

$$= \frac{2n\tau}{3k_{\mathrm{B}} T} \left\langle \tfrac{2}{3} \varepsilon_{\mathrm{tr}}^2 - \tfrac{k_{\mathrm{B}}}{c_V} (\varepsilon_{\mathrm{tr}} + \varepsilon_{\mathrm{rot}}) \varepsilon_{\mathrm{tr}} \right\rangle \boldsymbol{\nabla} \cdot \mathbf{V} \quad ,$$

and therefore

$$\zeta = \frac{2n\tau}{3k_{\mathrm{B}}T} \left\langle \tfrac{4}{15}\, \varepsilon_{\mathrm{tr}}^2 - \tfrac{2}{5}k_{\mathrm{B}}T\, \varepsilon_{\mathrm{tr}} \right\rangle = \tfrac{4}{15}n\tau k_{\mathrm{B}}T \quad .$$

**(8.7)** Consider a two-dimensional gas of particles with dispersion $\varepsilon(\mathbf{k}) = J\mathbf{k}^2$, where $\mathbf{k}$ is the wavevector. The particles obey photon statistics, so $\mu = 0$ and the equilibrium distribution is given by

$$f^0(\mathbf{k}) = \frac{1}{e^{\varepsilon(\mathbf{k})/k_{\mathrm{B}}T} - 1} \quad .$$

(a) Writing $f = f^0 + \delta f$, solve for $\delta f(\mathbf{k})$ using the steady state Boltzmann equation in the relaxation time approximation,

$$\mathbf{v} \cdot \frac{\partial f^0}{\partial \mathbf{r}} = -\frac{\delta f}{\tau} \quad .$$

Work to lowest order in $\boldsymbol{\nabla} T$. Remember that $\mathbf{v} = \frac{1}{\hbar} \frac{\partial \varepsilon}{\partial \mathbf{k}}$ is the velocity.

(b) Show that $\mathbf{j} = -\lambda \, \boldsymbol{\nabla} T$, and find an expression for $\lambda$. Represent any integrals you cannot evaluate as dimensionless expressions.

(c) Show that $\mathbf{j}_\varepsilon = -\kappa \, \boldsymbol{\nabla} T$, and find an expression for $\kappa$. Represent any integrals you cannot evaluate as dimensionless expressions.

Solution :

(a) We have

$$\delta f = -\tau \, \mathbf{v} \cdot \frac{\partial f^0}{\partial \mathbf{r}} = -\tau \, \mathbf{v} \cdot \boldsymbol{\nabla} T \, \frac{\partial f^0}{\partial T}$$

$$= -\frac{2\tau}{\hbar} \frac{J^2 k^2}{k_{\mathrm{B}} T^2} \frac{e^{\varepsilon(\mathbf{k})/k_{\mathrm{B}}T}}{\left(e^{\varepsilon(\mathbf{k})/k_{\mathrm{B}}T} - 1\right)^2} \, \mathbf{k} \cdot \boldsymbol{\nabla} T$$

(b) The particle current is

$$j^\mu = \frac{2J}{\hbar} \int \frac{d^2k}{(2\pi)^2} \, k^\mu \, \delta f(\mathbf{k}) = -\lambda \frac{\partial T}{\partial x^\mu}$$

$$= -\frac{4\tau}{\hbar^2} \frac{J^3}{k_{\mathrm{B}} T^2} \frac{\partial T}{\partial x^\nu} \int \frac{d^2k}{(2\pi)^2} \, k^2 \, k^\mu \, k^\nu \, \frac{e^{Jk^2/k_{\mathrm{B}}T}}{\left(e^{Jk^2/k_{\mathrm{B}}T} - 1\right)^2}$$

We may now send $k^\mu k^\nu \to \frac{1}{2} k^2 \delta^{\mu\nu}$ under the integral. We then read off

$$\lambda = \frac{2\tau}{\hbar^2} \frac{J^3}{k_{\mathrm{B}} T^2} \int \frac{d^2k}{(2\pi)^2} \, k^4 \, \frac{e^{Jk^2/k_{\mathrm{B}}T}}{\left(e^{Jk^2/k_{\mathrm{B}}T} - 1\right)^2}$$

$$= \frac{\tau k_{\mathrm{B}}^2 T}{\pi \hbar^2} \int\limits_0^\infty ds \, \frac{s^2 \, e^s}{\left(e^s - 1\right)^2} = \frac{\zeta(2)}{\pi} \frac{\tau k_{\mathrm{B}}^2 T}{\hbar^2} \quad .$$

Here we have used

$$\int\limits_0^\infty ds\, \frac{s^\alpha\, e^s}{\left(e^s - 1\right)^2} = \int\limits_0^\infty ds\, \frac{\alpha\, s^{\alpha-1}}{e^s - 1} = \Gamma(\alpha + 1)\, \zeta(\alpha) \quad .$$

(c) The energy current is

$$j_\varepsilon^\mu = \frac{2J}{\hbar} \int \frac{d^2k}{(2\pi)^2}\, Jk^2\, k^\mu\, \delta f(\mathbf{k}) = -\kappa\, \frac{\partial T}{\partial x^\mu} \quad .$$

We therefore repeat the calculation from part (c), including an extra factor of $Jk^2$ inside the integral. Thus,

$$\kappa = \frac{2\tau}{\hbar^2}\, \frac{J^4}{k_\mathrm{B} T^2} \int \frac{d^2k}{(2\pi)^2}\, k^6\, \frac{e^{Jk^2/k_\mathrm{B} T}}{\left(e^{Jk^2/k_\mathrm{B} T} - 1\right)^2}$$

$$= \frac{\tau k_\mathrm{B}^3 T^2}{\pi \hbar^2} \int\limits_0^\infty ds\, \frac{s^3\, e^s}{\left(e^s - 1\right)^2} = \frac{6\, \zeta(3)}{\pi}\, \frac{\tau k_\mathrm{B}^3 T^2}{\hbar^2} \quad .$$

**(8.8)** Consider the collisionless Boltzmann equation for the Hamiltonian $\hat{H}(p) = \frac{1}{4}Ap^4$ in one space dimension. Suppose the initial distribution is given by

$$f(x, p, t = 0) = C\, e^{-x^2/2\sigma^2}\, e^{-p^2/2\kappa^2} \quad .$$

(a) Find $f(x, p, t)$ for all $t > 0$.

(b) Find the equation for the locus of points $(x, p)$ for which $f(x, p, t) = \exp(-\alpha^2/2)$.

(c) Express your result in (b) in dimensionless form and plot it for various values of the dimensionless time.

Solution :

(a) The velocity is $v(p) = \partial\varepsilon/\partial p = Ap^3$ and thus

$$f(x, p, t) = f\big(x - v(p)t, p, 0\big) = C\, e^{-(x - Ap^3 t)^2/2\sigma^2}\, e^{-p^2/2\kappa^2} \quad .$$

(b) Clearly we have

$$\frac{(x - Ap^3 t)^2}{\sigma^2} + \frac{p^2}{\kappa^2} = \alpha^2 \quad \Rightarrow \quad x(p, t; \alpha) = Ap^3 t \pm \sigma\sqrt{\alpha^2 - \frac{p^2}{\kappa^2}} \quad .$$
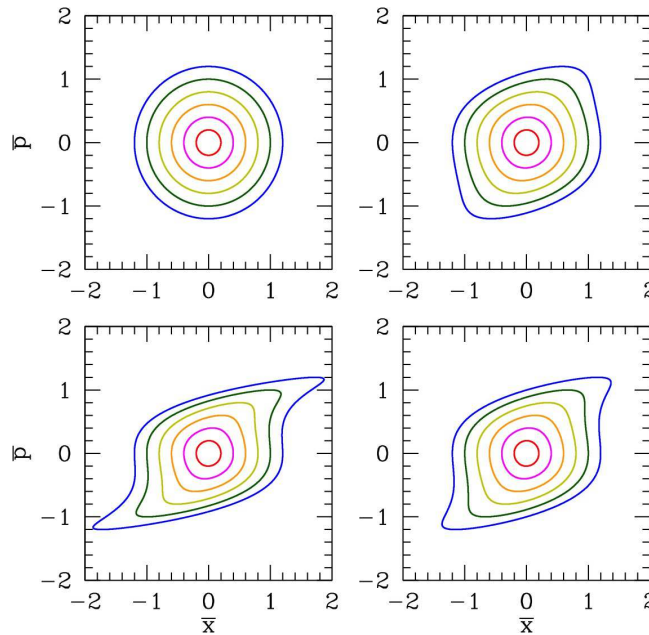


Figure 38: Level sets $\bar{x}(\bar{p}, s; \alpha) = \bar{p}^3 s \pm \sqrt{\alpha^2 - \bar{p}^2}$ for $\alpha = 0.2$ (red) to $\alpha = 1.2$ (blue) and $s = 0$ (upper left), $s = \frac{1}{3}$ (upper right), $s = \frac{2}{3}$ (lower right), and $s = 1$ (lower left). Compare with fig. 8.1 of the lecture notes.

If we write

$$\bar{x} \equiv \frac{x}{\sigma} \quad , \quad \bar{p} \equiv \frac{p}{\kappa} \quad , \quad s \equiv \frac{A\kappa^3 t}{\sigma} \quad ,$$

then in dimensionless form we have

$$\bar{x}(\bar{p}, s; \alpha) = \bar{p}^3 s \pm \sqrt{\alpha^2 - \bar{p}^2} \quad .$$

(c) See fig. 1.

**(8.9)** Consider an ideal gas of point particles in $d = 3$ dimensions with isotropic dispersion $\varepsilon(p) = Ap^\sigma$.

(a) Find the enthalpy per particle $h = \mu + Ts$, where $\mu$ is the chemical potential and $s$ is the entropy per particle. (You may find it useful to review some of the material in chapter 4 of the notes.)

(b) Find the thermal conductivity $\kappa$ within the relaxation time approximation.

Solution :

(a) For the dispersion $\varepsilon(p) = Ap^\sigma$, in $d$ dimensions, one obtains the density of states $g(\varepsilon) = C\varepsilon^{r-1}$ where $r = d/\sigma$ and $C$ is a constant. One then obtains the Helmholtz free energy

$$F = -Nk_{\mathrm{B}}T\log(V/N) - Nk_{\mathrm{B}}T - Nk_{\mathrm{B}}T\log\int\limits_0^\infty d\varepsilon\, g(\varepsilon)\,\exp(-\varepsilon/k_{\mathrm{B}}T)$$

$$= -Nk_{\mathrm{B}}T\log(V/N) - Nk_{\mathrm{B}}T\log\big[eA\,\Gamma(r)\big] - rNk_{\mathrm{B}}T\log(k_{\mathrm{B}}T) \quad.$$

We then have

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_{\mathrm{B}}T\log(V/N) - k_{\mathrm{B}}T\log\big[A\,\Gamma(r)\big] - rk_{\mathrm{B}}T\log(k_{\mathrm{B}}T)$$

$$s = -\frac{1}{N}\left(\frac{\partial F}{\partial T}\right)_{V,N} = k_{\mathrm{B}}\log(V/N) + k_{\mathrm{B}}\log\big[eA\,\Gamma(r)\big] + rk_{\mathrm{B}}\log(ek_{\mathrm{B}}T) \quad,$$

and thus

$$h = \mu + Ts = (r+1)\,k_{\mathrm{B}} \quad.$$

The thermal conductivity is obtained from the energy current $\mathbf{j}_\varepsilon = -\kappa\,\boldsymbol{\nabla}T$, where

$$j_\varepsilon^\alpha = \int d^d p\,\varepsilon\,v^\alpha\,\delta f = -\frac{n\tau}{k_{\mathrm{B}}T^2}\big\langle v^\alpha v^\beta\,\varepsilon\,(\varepsilon - h)\big\rangle\,\frac{\partial T}{\partial x^\beta} \quad,$$

where we have used the result (see eqn. 8.71 of the lecture notes)

$$\delta f = -\frac{\tau}{k_{\mathrm{B}}T^2}\,(\varepsilon - h)(\mathbf{v}\cdot\boldsymbol{\nabla}T)\,f^0$$

and $h = c_p T$ for our ideal gas. Thus from isotropy we can replace $\langle v^\alpha v^\beta \to d^{-1}\mathbf{v}^2\,\delta^{\alpha\beta}$, in which case

$$\kappa = \frac{n\tau}{dk_{\mathrm{B}}T^2}\big\langle\mathbf{v}^2\,\varepsilon\,(\varepsilon - h)\big\rangle \quad.$$

With $\varepsilon(p) = Ap^\sigma$ we have $\mathbf{v}(\mathbf{p}) = \sigma A p^{\sigma-1}\hat{\mathbf{p}}$ and thus $\mathbf{v}^2 = \sigma^2 A^{2/\sigma}\,\varepsilon^{2-2\sigma^{-1}}$. We then have

$$\kappa = \frac{n\tau}{dk_{\mathrm{B}}T^2}\,\sigma^2 A^{2/\sigma}\big\langle\varepsilon^{3-2\sigma^{-1}}\big(\varepsilon - (r+1)\,k_{\mathrm{B}}T\big)\big\rangle$$

Now with the density of states $g(\varepsilon)\propto\varepsilon^{r-1}$ we have

$$\langle\varepsilon^s\rangle = \int\limits_0^\infty d\varepsilon\,\varepsilon^{r-1+s}\,e^{-\beta\varepsilon}\,\bigg/\int\limits_0^\infty d\varepsilon\,\varepsilon^{r-1}\,e^{-\beta\varepsilon} = \frac{\Gamma(r+s)}{\Gamma(r)}\,(k_{\mathrm{B}}T)^s \quad.$$

Working out the remaining details, we arrive at the expression

$$\kappa = \frac{2\sigma(\sigma-1)\,\Gamma(r+3-2\sigma^{-1})}{d\,\Gamma(r)}\,A^{2/\sigma}\cdot n\tau k_{\mathrm{B}}\cdot (k_{\mathrm{B}}T)^{2(1-\sigma^{-1})}\quad.$$

As a check, if we set $\sigma = 2$ and $A = 1/2m$ (ballistic dispersion), then for $d = 3$ we have $r = \frac{3}{2}$ and find $\kappa = \frac{5}{2}\,n\tau k_{\mathrm{B}}^2 T$, which is identical to the result in §8.4.4 of the lecture notes.

## 0.9   Stochastic Processes

**(9.1)** Due to quantum coherence effects in the backscattering from impurities, one-dimensional wires don't obey Ohm's law (in the limit where the 'inelastic mean free path' is greater than the sample dimensions, which you may assume). Rather, let $\mathcal{R}(L) = R(L)/(h/e^2)$ be the dimensionless resistance of a quantum wire of length $L$, in units of $h/e^2 = 25.813\,\mathrm{k\Omega}$. Then the dimensionless resistance of a quantum wire of length $L + \delta L$ is given by

$$\mathcal{R}(L + \delta L) = \mathcal{R}(L) + \mathcal{R}(\delta L) + 2\,\mathcal{R}(L)\,\mathcal{R}(\delta L) + 2\cos\alpha\,\sqrt{\mathcal{R}(L)\left[1 + \mathcal{R}(L)\right]\mathcal{R}(\delta L)\left[1 + \mathcal{R}(\delta L)\right]}\quad,$$

where $\alpha$ is a *random phase* uniformly distributed over the interval $[0, 2\pi)$. Here,

$$\mathcal{R}(\delta L) = \frac{\delta L}{2\ell}\quad,$$

is the dimensionless resistance of a small segment of wire, of length $\delta L \lesssim \ell$, where $\ell$ is the 'elastic mean free path'. (Using the Boltzmann equation, we would obtain $\ell = 2\pi\hbar n\tau/m$.)

Show that the distribution function $P(\mathcal{R}, L)$ for resistances of a quantum wire obeys the equation

$$\frac{\partial P}{\partial L} = \frac{1}{2\ell}\frac{\partial}{\partial \mathcal{R}}\left\{\mathcal{R}\,(1 + \mathcal{R})\,\frac{\partial P}{\partial \mathcal{R}}\right\}\quad.$$

Show that this equation* may be solved in the limits $\mathcal{R} \ll 1$ and $\mathcal{R} \gg 1$, with

$$P(\mathcal{R}, z) = \frac{1}{z}\,e^{-\mathcal{R}/z}$$

for $\mathcal{R} \ll 1$, and

$$P(\mathcal{R}, z) = (4\pi z)^{-1/2}\,\frac{1}{\mathcal{R}}\,e^{-(\ln\mathcal{R} - z)^2/4z}$$

for $\mathcal{R} \gg 1$, where $z = L/2\ell$ is the dimensionless length of the wire. Compute $\langle\mathcal{R}\rangle$ in the former case, and $\langle\ln\mathcal{R}\rangle$ in the latter case.

**Solution :**

From the composition rule for series quantum resistances, we derive the phase averages

$$\langle\delta\mathcal{R}\rangle = \left(1 + 2\,\mathcal{R}(L)\right)\frac{\delta L}{2\ell}$$

$$\langle(\delta\mathcal{R})^2\rangle = \left(1 + 2\,\mathcal{R}(L)\right)^2\left(\frac{\delta L}{2\ell}\right)^2 + 2\,\mathcal{R}(L)\left(1 + \mathcal{R}(L)\right)\frac{\delta L}{2\ell}\left(1 + \frac{\delta L}{2\ell}\right)$$

$$= 2\,\mathcal{R}(L)\left(1 + \mathcal{R}(L)\right)\frac{\delta L}{2\ell} + \mathcal{O}\!\left((\delta L)^2\right)\quad,$$

whence we obtain the drift and diffusion terms

$$F_1(\mathcal{R}) = \frac{2\,\mathcal{R} + 1}{2\ell}\quad,\qquad F_2(\mathcal{R}) = \frac{2\mathcal{R}(1 + \mathcal{R})}{2\ell}\quad.$$

Note that $2F_1(\mathcal{R}) = dF_2/d\mathcal{R}$, which allows us to write the Fokker-Planck equation as

$$\frac{\partial P}{\partial L} = \frac{\partial}{\partial \mathcal{R}}\left\{\frac{\mathcal{R}\,(1+\mathcal{R})}{2\ell}\,\frac{\partial P}{\partial \mathcal{R}}\right\} \quad .$$

Defining the dimensionless length $z = L/2\ell$, we have

$$\frac{\partial P}{\partial z} = \frac{\partial}{\partial \mathcal{R}}\left\{\mathcal{R}\,(1+\mathcal{R})\,\frac{\partial P}{\partial \mathcal{R}}\right\} \quad .$$

In the limit $\mathcal{R} \ll 1$, this reduces to

$$\frac{\partial P}{\partial z} = \mathcal{R}\,\frac{\partial^2 P}{\partial \mathcal{R}^2} + \frac{\partial P}{\partial \mathcal{R}} \quad ,$$

which is satisfied by $P(\mathcal{R}, z) = z^{-1} \exp(-\mathcal{R}/z)$. For this distribution one has $\langle \mathcal{R}\rangle = z$.

In the opposite limit, $\mathcal{R} \gg 1$, we have

$$\frac{\partial P}{\partial z} = \frac{\partial}{\partial \mathcal{R}}\left(\mathcal{R}^2\frac{\partial}{\partial \mathcal{R}}\right) = \frac{\partial^2 P}{\partial \nu^2} + \frac{\partial P}{\partial \nu} \quad ,$$

where $\nu \equiv \ln \mathcal{R}$. This is solved by the log-normal distribution,

$$P(\mathcal{R}, z) = (4\pi z)^{-1/2}\, e^{-(\nu + z)^2/4z} \quad .$$

Note that

$$P(\mathcal{R}, z)\, d\mathcal{R} = \widetilde{P}(\nu, z)\, d\nu = \frac{1}{\sqrt{4\pi z}}\, e^{-(\nu - z)^2/4z}\, d\nu \quad ,$$

One then obtains $\langle \nu\rangle = \langle \ln \mathcal{R}\rangle = z$. Furthermore,

$$\langle \mathcal{R}^n\rangle = \langle e^{n\nu}\rangle = \frac{1}{\sqrt{4\pi z}}\int\limits_{-\infty}^{\infty} d\nu\, e^{-(\nu - z)^2/4z}\, e^{n\nu} = e^{k(k+1)z}$$

Note then that $\langle \mathcal{R}\rangle = \exp(2z)$, so the mean resistance grows *exponentially* with length. However, note also that $\langle \mathcal{R}^2\rangle = \exp(6z)$, so

$$\langle (\Delta \mathcal{R})^2\rangle = \langle \mathcal{R}^2\rangle - \langle \mathcal{R}\rangle^2 = e^{6z} - e^{4z} \quad ,$$

and so the standard deviation grows as $\sqrt{\langle \mathcal{R}^2\rangle} \sim \exp(3z)$ which grows faster than $\langle \mathcal{R}\rangle$. In other words, the resistance $\mathcal{R}$ itself is not a *self-averaging* quantity, meaning the ratio of its standard deviation to its mean doesn't vanish in the thermodynamic limit – indeed it diverges. However, $\nu = \ln \mathcal{R}$ *is* a self-averaging quantity, with $\langle \nu\rangle = z$ and $\sqrt{\langle \nu^2\rangle} = \sqrt{2z}$.

**(9.2)** Show that for time scales sufficiently greater than $\gamma^{-1}$ that the solution $x(t)$ to the Langevin equation $\ddot{x} + \gamma\dot{x} = \eta(t)$ describes a Markov process. You will have to construct the matrix $M$ defined in ch. 9 of the lecture notes. You should assume that the random force $\eta(t)$ is distributed as a Gaussian, with $\langle\eta(s)\rangle = 0$ and $\langle\eta(s)\,\eta(s')\rangle = \Gamma\,\delta(s-s')$.

Solution:

The probability distribution is

$$
P(x_1, t_1\,;\,\ldots\,;\,x_N, t_N) = \det^{-1/2}(2\pi M)\,\exp\left\{-\tfrac{1}{2}\sum_{j,j'=1}^{N} M_{jj'}^{-1}\,x_j\,x_{j'}\right\}\quad,
$$

where

$$
M(t, t') = \int\limits_0^t ds \int\limits_0^{t'} ds'\, G(s-s')\,K(t-s)\,K(t'-s')\quad,
$$

and $K(s) = (1 - e^{-\gamma s})/\gamma$. Thus,

$$
M(t, t') = \frac{\Gamma}{\gamma^2}\int\limits_0^{t_{\min}} ds\,(1 - e^{-\gamma(t-s)})(1 - e^{-\gamma(t'-s)})
$$

$$
= \frac{\Gamma}{\gamma^2}\left\{t_{\min} - \frac{1}{\gamma} + \frac{1}{\gamma}\left(e^{-\gamma t} + e^{-\gamma t'}\right) - \frac{1}{2\gamma}\left(e^{-\gamma|t-t'|} + e^{-\gamma(t+t')}\right)\right\}\quad.
$$

In the limit where $t$ and $t'$ are both large compared to $\gamma^{-1}$, we have $M(t, t') = 2D\min(t, t')$, where the diffusions constant is $D = \Gamma/2\gamma^2$. Thus,

$$
M = 2D\begin{pmatrix}
t_1 & t_2 & t_3 & t_4 & t_5 & \cdots & t_N \\
t_2 & t_2 & t_3 & t_4 & t_5 & \cdots & t_N \\
t_3 & t_3 & t_3 & t_4 & t_5 & \cdots & t_N \\
t_4 & t_4 & t_4 & t_4 & t_5 & \cdots & t_N \\
t_5 & t_5 & t_5 & t_5 & t_5 & \cdots & t_N \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
t_N & t_N & t_N & t_N & t_N & \cdots & t_N
\end{pmatrix}\quad.
$$

To find the determinant of $M$, subtract row 2 from row 1, then subtract row 3 from row 2, *etc.*The result is

$$
\widetilde{M} = 2D\begin{pmatrix}
t_1 - t_2 & 0 & 0 & 0 & 0 & \cdots & 0 \\
t_2 - t_3 & t_2 - t_3 & 0 & 0 & 0 & \cdots & 0 \\
t_3 - t_4 & t_3 - t_4 & t_3 - t_4 & 0 & 0 & \cdots & 0 \\
t_4 - t_5 & t_4 - t_5 & t_4 - t_5 & t_4 - t_5 & 0 & \cdots & 0 \\
t_5 - t_6 & t_5 - t_6 & t_5 - t_6 & t_5 - t_6 & t_5 - t_6 & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
t_N & t_N & t_N & t_N & t_N & \cdots & t_N
\end{pmatrix}\quad.
$$

Note that the last row is unchanged, since there is no row $N+1$ to subtract from it Since $\widetilde{M}$ is obtained from $M$ by consecutive row additions, we have

$$\det M = \det \widetilde{M} = (2D)^N (t_1 - t_2)(t_2 - t_3) \cdots (t_{N-1} - t_N)\, t_N \quad .$$

The inverse is

$$M^{-1} = \frac{1}{2D} \begin{pmatrix} \frac{1}{t_1-t_2} & -\frac{1}{t_1-t_2} & 0 & \cdots & & & \\ -\frac{1}{t_1-t_2} & \frac{t_1-t_3}{(t_1-t_2)(t_2-t_3)} & -\frac{1}{t_2-t_3} & 0 & \cdots & & \\ \vdots & \vdots & \ddots & & & & \\ \cdots & 0 & -\frac{1}{t_{n-1}-t_n} & \frac{t_{n-1}-t_{n+1}}{(t_{n-1}-t_n)(t_n-t_{n+1})} & -\frac{1}{t_n-t_{n+1}} & 0 & \cdots \\ & & & \ddots & & & \\ & & & \cdots & 0 & -\frac{1}{t_{N-1}-t_N} & \frac{t_{N-1}}{t_N}\frac{1}{t_{N-1}-t_N} \end{pmatrix} \;.$$

This yields the general result

$$\sum_{j,j'=1}^{N} M_{j,j'}^{-1}(t_1,\ldots,t_N)\, x_j\, x_{j'} = \sum_{j=1}^{N} \left( \frac{1}{t_{j-1}-t_j} + \frac{1}{t_j - t_{j+1}} \right) x_j^2 - \frac{2}{t_j - t_{j+1}}\, x_j\, x_{j+1} \quad ,$$

where $t_0 \equiv \infty$ and $t_{N+1} \equiv 0$. Now consider the conditional probability density

$$\begin{aligned} P(x_1,t_1\,|\,x_2,t_2\,;\,\ldots\,;\,x_N,t_N) &= \frac{P(x_1,t_1\,;\,\ldots\,;\,x_N,t_N)}{P(x_2,t_2\,;\,\ldots\,;\,x_N,t_N)} \\ &= \frac{\det^{1/2} 2\pi M(t_2,\ldots,t_N)}{\det^{1/2} 2\pi M(t_1,\ldots,t_N)} \, \frac{\exp\left\{ -\frac{1}{2}\sum_{j,j'=1}^{N} M_{jj'}^{-1}(t_1,\ldots,t_N)\, x_j\, x_{j'} \right\}}{\exp\left\{ -\frac{1}{2}\sum_{k,k'=2}^{N} M_{kk'}^{-1}(t_2,\ldots,t_N)\, x_k\, x_{k'} \right\}} \end{aligned}$$

We have

$$\sum_{j,j'=1}^{N} M_{jj'}^{-1}(t_1,\ldots,t_N)\, x_j\, x_{j'} = \left( \frac{1}{t_0-t_1} + \frac{1}{t_1-t_2} \right) x_1^2 - \frac{2}{t_1-t_2}\, x_1\, x_2 + \left( \frac{1}{t_1-t_2} + \frac{1}{t_2-t_3} \right) x_2^2 + \ldots$$

$$\sum_{k,k'=2}^{N} M_{kk'}^{-1}(t_2,\ldots,t_N)\, x_k\, x_{k'} = \left( \frac{1}{t_0-t_2} + \frac{1}{t_2-t_3} \right) x_2^2 + \ldots$$

Subtracting, and evaluating the ratio to get the conditional probability density, we find

$$P(x_1,t_1\,|\,x_2,t_2\,;\,\ldots\,;\,x_N,t_N) = \frac{1}{\sqrt{4\pi D(t_1-t_2)}}\, e^{-(x_1-x_2)^2/4D(t_1-t_2)} \quad ,$$

which depends only on $\{x_1, t_1, x_2, t_2\}$, *i.e.* on the current and most recent data, and not on any data before the time $t_2$. Note the normalization:

$$\int\limits_{-\infty}^{\infty} dx_1 \; P(x_1, t_1 \,|\, x_2, t_2 \,;\, \ldots \,;\, x_N, t_N) = 1 \quad .$$

**(9.3)** Consider a discrete one-dimensional random walk where the probability to take a step of length 1 in either direction is $\frac{1}{2}p$ and the probability to take a step of length 2 in either direction is $\frac{1}{2}(1-p)$. Define the generating function

$$\hat{P}(k,t) = \sum_{n=-\infty}^{\infty} P_n(t) e^{-ikn} \quad ,$$

where $P_n(t)$ is the probability to be at position $n$ at time $t$. Solve for $\hat{P}(k,t)$ and provide an expression for $P_n(t)$. Evaluate $\sum_n n^2 P_n(t)$.

Solution:

We have the master equation

$$\frac{dP_n}{dt} = \tfrac{1}{2}(1-p)\,P_{n+2} + \tfrac{1}{2}p\,P_{n+1} + \tfrac{1}{2}p\,P_{n-1} + \tfrac{1}{2}(1-p)\,P_{n-2} - P_n \quad .$$

Upon Fourier transforming,

$$\frac{d\hat{P}(k,t)}{dt} = \Big[(1-p)\cos(2k) + p\cos(k) - 1\Big]\hat{P}(k,t) \quad ,$$

with the solution

$$\hat{P}(k,t) = e^{-\lambda(k)\,t}\,\hat{P}(k,0) \quad ,$$

where

$$\lambda(k) = 1 - p\cos(k) - (1-p)\cos(2k) \quad .$$

One then has

$$P_n(t) = \int_{-\pi}^{\pi} \frac{dk}{2\pi}\, e^{ikn}\,\hat{P}(k,t) \quad .$$

The average of $n^2$ is given by

$$\langle n^2 \rangle_t = -\frac{\partial^2 \hat{P}(k,t)}{\partial k^2}\bigg|_{k=0} = \Big[\lambda''(0)\,t - \lambda'(0)^2\,t^2\Big] = \big(4 - 3p\big)\,t \quad .$$

Note that $\hat{P}(0,t) = 1$ for all $t$ by normalization.

**(9.4)** Numerically simulate the one-dimensional Wiener and Cauchy processes discussed in ch. 9 of the lecture notes, and produce a figure similar.

Solution:

Most computing languages come with a random number generating function which produces uniform deviates on the interval $x \in [0, 1]$. Suppose we have a prescribed function $y(x)$. If $x$ is distributed uniformly on $[0, 1]$, how is $y$ distributed? Clearly

$$\left| p(y)\, dy \right| = \left| p(x)\, dx \right| \qquad \Rightarrow \qquad p(y) = \left| \frac{dx}{dy} \right| p(x) \quad ,$$

where for the uniform distribution on the unit interval we have $p(x) = \Theta(x)\, \Theta(1 - x)$. For example, if $y = -\ln x$, then $y \in [0, \infty]$ and $p(y) = e^{-y}$ which is to say $y$ is exponentially distributed. Now suppose we want to specify $p(y)$. We have

$$\frac{dx}{dy} = p(y) \qquad \Rightarrow \qquad x = F(y) = \int_{y_0}^{y} d\tilde{y}\, p(\tilde{y}) \quad ,$$

where $y_0$ is the minimum value that $y$ takes. Therefore, $y = F^{-1}(x)$, where $F^{-1}$ is the inverse function.

To generate normal (Gaussian) deviates with a distribution $p(y) = (4\pi D\varepsilon)^{-1/2} \exp(-y^2/4D\varepsilon)$, we have

$$F(y) = \frac{1}{\sqrt{4\pi D\varepsilon}} \int_{-\infty}^{y} d\tilde{y}\, e^{-\tilde{y}^2/4D\varepsilon} = \tfrac{1}{2} + \tfrac{1}{2}\, \mathsf{erf}\!\left( \frac{y}{\sqrt{4D\varepsilon}} \right) \quad .$$

We now have to invert the error function, which is slightly unpleasant.

A slicker approach is to use the *Box-Muller* method, which used a two-dimensional version of the above transformation,

$$p(y_1, y_2) = p(x_1, x_2) \left| \frac{\partial(x_1, x_2)}{\partial(y_1, y_2)} \right| \quad .$$

This has an obvious generalization to higher dimensions. The transformation factor is the Jacobian determinant. Now let $x_1$ and $x_2$ each be uniformly distributed on $[0, 1]$, and let

$$x_1 = \exp\left( -\frac{y_1^2 + y_2^2}{4D\varepsilon} \right) \qquad\qquad y_1 = \sqrt{-4D\varepsilon \ln x_1}\; \cos(2\pi x_2)$$

$$x_2 = \frac{1}{2\pi}\, \tan^{-1}(y_2/y_1) \qquad\qquad y_2 = \sqrt{-4D\varepsilon \ln x_1}\; \sin(2\pi x_2)$$

Then

$$\frac{\partial x_1}{\partial y_1} = -\frac{y_1\, x_1}{2D\varepsilon} \qquad\qquad\qquad \frac{\partial x_2}{\partial y_1} = -\frac{1}{2\pi}\, \frac{y_2}{y_1^2 + y_2^2}$$

$$\frac{\partial x_1}{\partial y_2} = -\frac{y_2\, x_1}{2D\varepsilon} \qquad\qquad\qquad \frac{\partial x_2}{\partial y_2} = \frac{1}{2\pi}\, \frac{y_1}{y_1^2 + y_2^2}$$
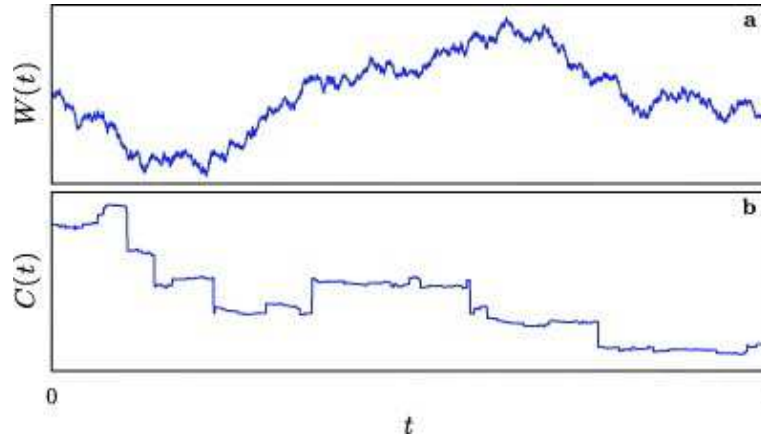
Figure 39: (a) Wiener process sample path $W(t)$. (b) Cauchy process sample path $C(t)$. From K. Jacobs and D. A. Steck, *New J. Phys.* **13**, 013016 (2011).

and therefore the Jacobian determinant is

$$J = \left| \frac{\partial(x_1, x_2)}{\partial(y_1, y_2)} \right| = \frac{1}{4\pi D\varepsilon} e^{-(y_1^2 + y_2^2)/4D\varepsilon} = \frac{e^{-y_1^2/4D\varepsilon}}{\sqrt{4\pi D\varepsilon}} \cdot \frac{e^{-y_2^2/4D\varepsilon}}{\sqrt{4\pi D\varepsilon}} \quad ,$$

which says that $y_1$ and $y_2$ are each independently distributed according to the normal distribution, which is $p(y) = (4\pi D\varepsilon)^{-1/2} \exp(-y^2/4D\varepsilon)$. Nifty!

For the Cauchy distribution, with

$$p(y) = \frac{1}{\pi} \frac{\varepsilon}{y^2 + \varepsilon^2} \quad ,$$

we have

$$F(y) = \frac{1}{\pi} \int_{-\infty}^{y} d\tilde{y} \, \frac{\varepsilon}{\tilde{y}^2 + \varepsilon^2} = \tfrac{1}{2} + \tfrac{1}{\pi} \tan^{-1}(y/\varepsilon) \quad ,$$

and therefore

$$y = F^{-1}(x) = \varepsilon \tan \left( \pi x - \tfrac{\pi}{2} \right) \quad .$$

**(9.5)** A *Markov chain* is a probabilistic process which describes the transitions of discrete stochastic variables in time. Let $P_i(t)$ be the probability that the system is in state $i$ at time $t$. The time evolution equation for the probabilities is

$$P_i(t+1) = \sum_j Y_{ij} P_j(t) \quad .$$

Thus, we can think of $Y_{ij} = P(i, t+1 \,|\, j, t)$ as the *conditional probability* that the system is in state $i$ at time $t+1$ given that it was in state $j$ at time $t$. $Y$ is called the *transition matrix*. It must satisfy $\sum_i Y_{ij} = 1$ so that the total probability $\sum_i P_i(t)$ is conserved.

Suppose I have two bags of coins. Initially bag A contains two quarters and bag B contains five dimes. Now I do an experiment. Every minute I exchange a random coin chosen from each of the bags. Thus the number of coins in each bag does not fluctuate, but their values do fluctuate.

(a) Label all possible states of this system, consistent with the initial conditions. (*I.e.* there are always two quarters and five dimes shared among the two bags.)

(b) Construct the transition matrix $Y_{ij}$.

(c) Show that the total probability is conserved is $\sum_i Y_{ij} = 1$, and verify this is the case for your transition matrix $Y$. This establishes that $(1, 1, \ldots, 1)$ is a left eigenvector of $Y$ corresponding to eigenvalue $\lambda = 1$.

(d) Find the eigenvalues of $Y$.

(e) Show that as $t \to \infty$, the probability $P_i(t)$ converges to an equilibrium distribution $P_i^{\mathrm{eq}}$ which is given by the right eigenvector of $i$ corresponding to eigenvalue $\lambda = 1$. Find $P_i^{\mathrm{eq}}$, and find the long time averages for the value of the coins in each of the bags.

Solution :

(a) There are three possible states consistent with the initial conditions. In state $|1\rangle$, bag A contains two quarters and bag B contains five dimes. In state $|2\rangle$, bag A contains a quarter and a dime while bag B contains a quarter and five dimes. In state $|3\rangle$, bag A contains two dimes while bag B contains three dimes and two quarters. We list these states in the table below, along with their degeneracies. The degeneracy of a state is the number of configurations consistent with the state label. Thus, in state $|2\rangle$ the first coin in bag A could be a quarter and the second a dime, or the first could be a dime and the second a quarter. For bag B, any of the five coins could be the quarter.

(b) To construct $Y_{ij}$, note that transitions out of state $|1\rangle$, *i.e.* the elements $Y_{i1}$, are particularly simple. With probability 1, state $|1\rangle$ always evolves to state $|2\rangle$. Thus, $Y_{21} = 1$ and $Y_{11} = Y_{31} = 0$. Now consider transitions out of state $|2\rangle$. To get to state $|1\rangle$, we need to choose the D from bag A (probability $\frac{1}{2}$) and the Q from bag B (probability $\frac{1}{5}$). Thus, $Y_{12} = \frac{1}{2} \times \frac{1}{5} = \frac{1}{10}$. For transitions back to state $|2\rangle$, we could choose the Q from bag A (probability $\frac{1}{2}$) if we also chose the Q from bag B (probability $\frac{1}{5}$). Or we could choose the $D$ from bag A (probability $\frac{1}{2}$) and one of the D's from bag B (probability $\frac{4}{5}$). Thus,

$Y_{22} = \frac{1}{2} \times \frac{1}{5} + \frac{1}{2} \times \frac{4}{5} = \frac{1}{2}$. Reasoning thusly, one obtains the transition matrix,

$$Y = \begin{pmatrix} 0 & \frac{1}{10} & 0 \\ 1 & \frac{1}{2} & \frac{2}{5} \\ 0 & \frac{2}{5} & \frac{3}{5} \end{pmatrix} \quad .$$

Note that $\sum_i Y_{ij} = 1$.

| $\lvert j \rangle$ | bag A | bag B | $g_j^{\mathrm{A}}$ | $g_j^{\mathrm{B}}$ | $g_j^{\mathrm{TOT}}$ |
|---|---|---|---|---|---|
| $\lvert 1 \rangle$ | QQ | DDDDD | 1 | 1 | 1 |
| $\lvert 2 \rangle$ | QD | DDDDQ | 2 | 5 | 10 |
| $\lvert 3 \rangle$ | DD | DDDQQ | 1 | 10 | 10 |

Table 12: States and their degeneracies.

(c) Our explicit form for $Y$ confirms the sum rule $\sum_i Y_{ij} = 1$ for all $j$. Thus, $\vec{L}^1 = (1\ 1\ 1)$ is a left eigenvector of $Y$ with eigenvalue $\lambda = 1$.

(d) To find the other eigenvalues, we compute the characteristic polynomial of $Y$ and find, easily,

$$P(\lambda) = \det(\lambda \mathbb{I} - Y) = \lambda^3 - \tfrac{11}{10}\lambda^2 + \tfrac{1}{25}\lambda + \tfrac{3}{50} \quad .$$

This is a cubic, however we already know a root, *i.e.* $\lambda = 1$, and we can explicitly verify $P(\lambda = 1) = 0$. Thus, we can divide $P(\lambda)$ by the monomial $\lambda - 1$ to get a quadratic function, which we can factor. One finds after a small bit of work,

$$\frac{P(\lambda)}{\lambda - 1} = \lambda^2 - \tfrac{3}{10}\lambda - \tfrac{3}{50} = \left(\lambda - \tfrac{3}{10}\right)\left(\lambda + \tfrac{1}{5}\right) \quad .$$

Thus, the eigenspectrum of $Y$ is $\lambda_1 = 1$, $\lambda_2 = \frac{3}{10}$, and $\lambda_3 = -\frac{1}{5}$.

(e) We can decompose $Y$ into its eigenvalues and eigenvectors, like we did in problem (1). Write

$$Y_{ij} = \sum_{\alpha=1}^{3} \lambda_\alpha R_i^\alpha L_j^\alpha \quad .$$

Now let us start with initial conditions $P_i(0)$ for the three configurations. We can always decompose this vector in the right eigenbasis for $Y$, *viz.*

$$P_i(t) = \sum_{\alpha=1}^{3} C_\alpha(t) R_i^\alpha \quad ,$$

The initial conditions are $C_\alpha(0) = \sum_i L_i^\alpha P_i(0)$. But now using our eigendecomposition of $Y$, we find that the equations for the discrete time evolution for each of the $C_\alpha$ decouple:

$$C_\alpha(t+1) = \lambda_\alpha C_\alpha(t) \quad .$$

Clearly as $t \to \infty$, the contributions from $\alpha = 2$ and $\alpha = 3$ get smaller and smaller, since $C_\alpha(t) = \lambda_\alpha^t C_\alpha(0)$, and both $\lambda_2$ and $\lambda_3$ are smaller than unity in magnitude. Thus, as $t \to \infty$ we have $C_1(t) \to C_1(0)$, and $C_{2,3}(t) \to 0$. Note $C_1(0) = \sum_i L_i^1 P_i(0) = \sum_i P_i(0) = 1$, since $\vec{L}^1 = (1\ 1\ 1)$. Thus, we obtain $P_i(t \to \infty) \to R_i^1$, the components of the eigenvector $\vec{R}^1$. It is not too hard to explicitly compute the eigenvectors:

$$\vec{L}^1 = \begin{pmatrix} 1 & 1 & 1 \end{pmatrix} \qquad \vec{L}^2 = \begin{pmatrix} 10 & 3 & -4 \end{pmatrix} \qquad \vec{L}^3 = \begin{pmatrix} 10 & -2 & 1 \end{pmatrix}$$

$$\vec{R}^1 = \tfrac{1}{21} \begin{pmatrix} 1 \\ 10 \\ 10 \end{pmatrix} \qquad \vec{R}^2 = \tfrac{1}{35} \begin{pmatrix} 1 \\ 3 \\ -4 \end{pmatrix} \qquad \vec{R}^3 = \tfrac{1}{15} \begin{pmatrix} 1 \\ -2 \\ 1 \end{pmatrix} \quad .$$

Thus, the equilibrium distribution $P_i^{\mathrm{eq}} = \lim_{t \to \infty} P_i(t)$ satisfies detailed balance:

$$P_j^{\mathrm{eq}} = \frac{g_j^{\mathrm{TOT}}}{\sum_l g_l^{\mathrm{TOT}}} \quad .$$

Working out the average coin value in bags A and B under equilibrium conditions, one finds $A = \frac{200}{7}$ and $B = \frac{500}{7}$ (cents), and $B/A$ is simply the ratio of the number of coins in bag B to the number in bag A. Note $A + B = 100$ cents, as the total coin value is conserved.