6 Interacting Classical Systems : Worked Examples

(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 3×3 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 σ_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 3×3 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 $P(\lambda) = \det\big(\lambda\mathbb{I} - R\big) = 0$, and the cubic polynomial $P(\lambda)$ factors into the product of λ 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 λ_+, hence, in the thermodynamic limit,

$$F = -k_{\rm B}T \ln Z = -Nk_{\rm B}T \ln\!\bigg(e^{-W/k_{\rm B}T} + \tfrac{1}{2} + \sqrt{e^{-2W/k_{\rm B}T} - e^{-W/k_{\rm B}T} + \tfrac{9}{4}}\bigg) \quad .$$

The entropy is $S = -\frac{\partial F}{\partial T}$. In the limit $T \to 0$ with $W < 0$, we have

$$\lambda_+(T \to 0\,,\,W < 0) = 2\,e^{|W|/k_{\rm B}T} + e^{-|W|/k_{\rm B}T} + \mathcal{O}\big(e^{-2|W|/k_{\rm B}T}\big) \quad .$$

Thus

$$\begin{aligned} F(T \to 0\,,\,W < 0) &= -N\,|W| - Nk_{\rm B}T \ln 2 + \ldots \\ S(T \to 0\,,\,W < 0) &= N \ln 2 \quad . \end{aligned}$$

When $W > 0$, we have

$$\lambda_+(T \to 0\,,\,W > 0) = 2 + \tfrac{2}{3}\,e^{-W/k_{\rm B}T} + \mathcal{O}\big(e^{-2W/k_{\rm B}T}\big) \quad .$$

Then

$$\begin{aligned} F(T \to 0\,,\,W > 0) &= -Nk_{\rm B}T \ln 2 - \tfrac{1}{3}Nk_{\rm B}T\,e^{-W/k_{\rm B}T} + \ldots \\ S(T \to 0\,,\,W > 0) &= N \ln 2 \quad . \end{aligned}$$

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 ${}^4\mathrm{He} - {}^3\mathrm{He}$ mixtures ($S = 0$ for a ^{4}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 Δ.

(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

$$R_{SS'} = e^{\beta J S S'} \, e^{\beta \Delta (S^2 + S'^2)/2} = \begin{pmatrix} e^{\beta(\Delta+J)} & e^{\beta\Delta/2} & e^{\beta(\Delta-J)} \\ e^{\beta\Delta/2} & 1 & e^{\beta\Delta/2} \\ e^{\beta(\Delta-J)} & e^{\beta\Delta/2} & e^{\beta(\Delta+J)} \end{pmatrix} \quad .$$

(b) For an N-site ring, we have

$$Z = \mathrm{Tr}\, e^{-\beta H} = \mathrm{Tr}\left(R^N\right) = \lambda_+^N + \lambda_0^N + \lambda_-^N \quad ,$$

where λ_+, λ_0, and λ_- 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 ψ_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

$$\begin{aligned} \lambda &= 2\, e^{\beta\Delta} \cosh(\beta J) + x\, e^{\beta\Delta/2} \\ \lambda x &= 2 e^{\beta\Delta/2} + x \quad . \end{aligned}$$

Eliminating x, one obtains a quadratic equation for λ. The solutions are

$$\lambda_\pm = \Big(e^{\beta\Delta}\cosh(\beta J) + \tfrac{1}{2}\Big) \pm \sqrt{\Big(e^{\beta\Delta}\cosh(\beta J) + \tfrac{1}{2}\Big)^2 + 2\,e^{\beta\Delta}}$$

$$x_\pm = e^{-\beta\Delta/2}\bigg\{\Big(\tfrac{1}{2} - e^{\beta\Delta}\cosh(\beta J)\Big) \pm \sqrt{\Big(\tfrac{1}{2} - e^{\beta\Delta}\cosh(\beta J)\Big)^2 + 2\,e^{\beta\Delta}}\bigg\} \quad .$$

Note $\lambda_+ > \lambda_0 > 0 > \lambda_-$ and that λ_+ 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

$$F(T, \Delta, N) = -N k_{\rm B} T \ln \lambda_+ \quad .$$

(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

$$\nu_0 = 1 - \frac{r - \frac{1}{2}}{\sqrt{r^2 + 2\,e^{\beta\Delta}}} \quad ,$$

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

$$C(n) = \langle\, S_j\, S_{j+n} \,\rangle = \frac{\mathsf{Tr}\,\big(\,\Sigma\, R^n\, \Sigma\, R^{N-n}\,\big)}{\mathsf{Tr}\,\big(R^N\big)} \quad ,$$

where $\Sigma_{SS'} = S\,\delta_{SS'}$. We work in the thermodynamic limit. Note that $\langle +\,|\,\Sigma\,|\,+\,\rangle = 0$, therefore we must write

$$R = \lambda_+\,|\,+\,\rangle\langle\,+\,| + \lambda_0\,|\,0\,\rangle\langle\,0\,| + \lambda_-\,|\,-\,\rangle\langle\,-\,| \quad ,$$

and we are forced to choose the middle term for the n instances of R between the two Σ matrices. Thus,

$$C(n) = \bigg(\frac{\lambda_0}{\lambda_+}\bigg)^n\,\big|\langle\,+\,|\,\Sigma\,|\,0\,\rangle\big|^2 \quad .$$

We define the correlation length ξ by

$$\xi = \frac{1}{\ln\big(\lambda_+/\lambda_0\big)} \quad ,$$

in which case

$$C(n) = A\,e^{-|n|/\xi} \quad ,$$

where now we generalize to positive and negative values of n, and where

$$A = \big|\langle\,+\,|\,\Sigma\,|\,0\,\rangle\big|^2 = \frac{1}{1 + \frac{1}{2}x_+^2} \quad .$$

(6.3) DC Comics superhero Connected Clusterman and his naughty dog Henry are shown in Fig. 1. Connected 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_γ for Connected 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 Connected Clusterman contributes?

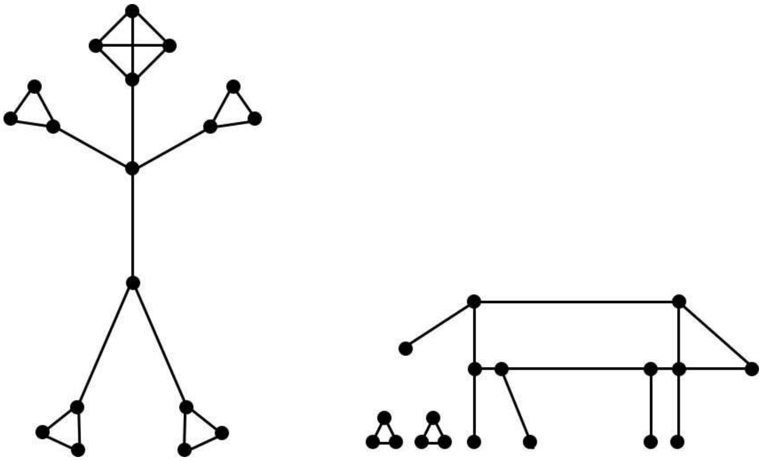

Figure 1: Mayer expansion diagrams for Connected Clusterman and his dog.

Solution :

First of all, this is really disgusting and you should all be ashamed that you had anything to do with this problem.

(a) Connected 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 π about its corresponding arm. The arms themselves can be interchanged, by rotating his shoulders by π about his body axis (Connected 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 Connected Clusterman's torso are not equivalent. Plus, that would be a really mean thing to do to Connected 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 Connected Clusterman, hence one might presume that he will first appear in B_{18}. But in fact he does not contribute to *any* $B_k(T)$ because Connected Clusterman is 1-particle reducible. Trick question!

(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 $Z_{\rm ring} = 2^N (\cosh \beta J)^{N-1}$ since the number of links is $N_{\rm L} = N - 1$ (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 $Z_{\rm chain} = 2^N (\cosh \beta J)^N \big(1 + x^N\big)$, where $x = \tanh \beta J$. As for the numerator Y_{kl}, on the chain there is only one possible string, shown in Fig. 2, which extends between sites k and l. Thus $Y^{\rm chain}_{kl} = 2^N (\cosh \beta J)^{N-1} x^{|k-l|}$. On the ring there are two possible strings, since the ring is multiply connected. Thus $Y^{\rm ring}_{kl} = 2^N (\cosh \beta J)^N \big(x^{|k-l|} + x^{N-|k-l|}\big)$. Therefore,

$$C^{\rm chain}_{kl} = x^{|k-l|} \qquad , \qquad C^{\rm ring}_{kl} = \frac{x^{|k-l|} + x^{N-|k-l|}}{1 + x^N} \quad .$$

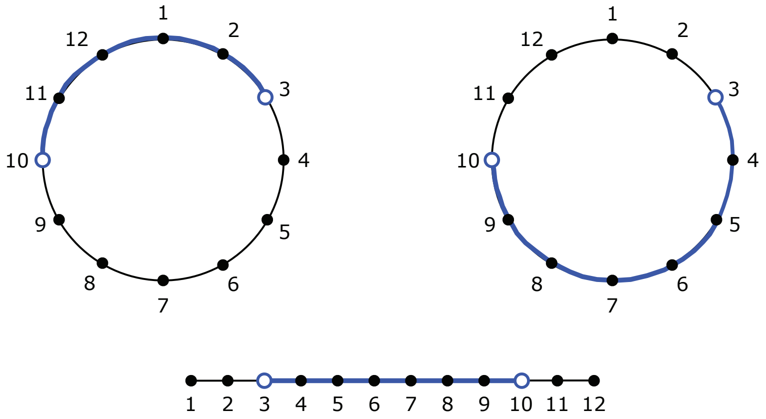

Figure 2: Diagrams for the numerator of the high temperature expansion of the spin-spin correlation function on an Ising ring and chain.

(6.5) An ionic solution of dielectric constant ϵ 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 $Q/r \ll k_{\rm B}T$.

Solution:

Debye-Hückel theory tells us that

$$n_\pm(\boldsymbol{r}) = \tfrac{1}{2}\, n\, e^{\mp e\phi(\boldsymbol{r})/k_{\rm B}T}$$

and

$$\nabla^2\phi = -\frac{4\pi e}{\epsilon}\,(n_+ - n_-) - \frac{4\pi}{\epsilon}\,\rho_{\rm ext}\ ,$$

where ϵ is the dielectric constant. Assuming $\phi \ll k_{\rm B}T$, we have $\nabla^2\phi = \kappa_{\rm D}^2\,\phi - 4\pi\rho_{\rm ext}/e$, with

$$\kappa_{\rm D} = \sqrt{\frac{4\pi n e^2}{\epsilon\, k_{\rm B}T}}\ .$$

Assuming a spherically symmetric solution, with a point charge Q at the origin, we solve

$$\bigg(-\frac{1}{r^2}\,\frac{\partial}{\partial r}\,r^2\,\frac{\partial}{\partial r} + \kappa_{\rm D}^2\bigg)\phi = \frac{4\pi Q}{\epsilon}\,\delta(\boldsymbol{r})\ .$$

The solution is then of the form $\phi(r) = \frac{1}{r}\,u(r)$, with $u'' = \kappa_{\rm D}^2\,u$ for $r > 0$. Thus,

$$\phi(r) = A\,\frac{\cosh(\kappa_{\rm D} r)}{r} + B\,\frac{\sinh(\kappa_{\rm D} r)}{r}\ .$$

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 $B = -A\,{\rm ctnh}\,(\kappa_{\rm D} R)$. Thus,

$$\phi(\boldsymbol{r}) = \frac{Q\cosh(\kappa_{\rm D} r)}{\epsilon\, r}\cdot\bigg(1 - \frac{\tanh(\kappa_{\rm D} r)}{\tanh(\kappa_{\rm D} R)}\bigg)\ .$$

We stress that this solution is valid only where $e\,\phi(\boldsymbol{r}) \ll k_{\rm B}T$.

What happens if we integrate the total charge density? We find

$$\rho(\boldsymbol{r}) = Q\delta(\boldsymbol{r}) - \frac{\epsilon\kappa_{\rm D}^2}{4\pi}\,\phi(\boldsymbol{r}) \quad ,$$

from which we obtain

$$Q_{\rm tot} = Q - \epsilon\kappa_{\rm D}^2\int\limits_0^R\! dr\; r^2\,\phi(r) = \frac{Q\,\kappa_{\rm D} R}{\sinh(\kappa_{\rm D} R)} \quad .$$

Note that at zero temperature, where $\kappa_{\rm D} \to \infty$, we have $Q_{\rm tot} = 0$, which means that the charge Q is completely screened. What happened to our ionic solution which was initially equally constituted of positive and negative charges? Why isn't $Q_{\rm tot} = Q$? The answer lies in the assumption that the sphere is *grounded*. This means there is a wire which connects it to ground, which is an infinite capacity reservoir of charge. As $T \to 0$, the point charge Q is perfectly screened, and a net charge Q will flow from the ionic solution to ground (this should require electron transfer from the electrolyte to the conducting wire). For $T > 0$ the screening is imperfect and $Q_{\rm tot} > 0$. When $T \to \infty$ we have $\kappa_{\rm D} = 0$ and $Q_{\rm tot} = Q$ because thermal fluctuations overwhelm the electrostatic energies.

(6.6) Consider a three-dimensional gas of point particles interacting according to the potential

$$u(r) = \begin{cases} +\Delta_0 & \text{if } r \le a \\ -\Delta_1 & \text{if } a < r \le b \\ 0 & \text{if } b < r \quad , \end{cases}$$

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.

Solution :

The Mayer function is

$$f(r) = \begin{cases} e^{-\Delta_0/k_{\rm B}T} - 1 & \text{if } r \le 0 \\ e^{\Delta_1/k_{\rm B}T} - 1 & \text{if } a < r \le b \\ 0 & \text{if } b < r \quad . \end{cases}$$

The second virial coefficient is

$$\begin{aligned} B_2(T) &= -\tfrac{1}{2}\int\! d^3\!r \; f(r) \\ &= \frac{2\pi a^3}{3} \cdot \Big[\big(1 - e^{-\Delta_0/k_{\rm B}T}\big) + (s^3 - 1)\,\big(1 - e^{\Delta_1/k_{\rm B}T}\big) \Big] \quad , \end{aligned}$$

where $s = b/a$. The inversion temperature is a solution of the equation $B_2(T) = T B_2'(T)$, which gives

$$s^3 - 1 = \frac{1 + \left(\frac{\Delta_0}{k_{\rm B}T} - 1\right) e^{-\Delta_0/k_{\rm B}T}}{1 + \left(\frac{\Delta_1}{k_{\rm B}T} + 1\right) e^{\Delta_1/k_{\rm B}T}} \quad .$$

(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. 3. The electron density outside the metal is very low and Maxwell-Boltzmann statistics are appropriate.

(a) Consider a flat metallic surface, normal to $\hat{\boldsymbol{x}}$, located at $x = 0$. Assume for $x > 0$ an electronic distribution $n(x) = n_0 \exp(e\phi/k_{\text{B}}T)$, where ϕ 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 ϕ 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 $n(x = 0) = n_0$.

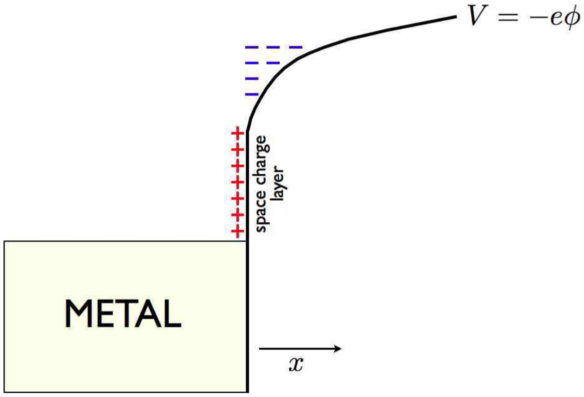

Figure 3: Electron distribution in the vicinity of the surface of a metal.

(c) Find $n(x)$.

Solution :

(a) The self-consistent equation is Poisson's equation,

$$\nabla^2 \phi = -4\pi\rho = 4\pi e n_0 \, e^{e\phi/k_{\text{B}}T} \quad .$$

Since the only variation is along x, we have $\phi'' = 4\pi e n_0 \, e^{e\phi/k_{\text{B}}T}$. Multiplying each side by $\frac{d\phi}{dx}$, we have

$$\frac{d}{dx}\big(\tfrac{1}{2}\phi'^2\big) = \frac{d}{dx}\Big(4\pi n_0 \, k_{\text{B}}T \, e^{e\phi/k_{\text{B}}T}\Big) \quad ,$$

and integrating this equation from x to ∞ we obtain

$$\frac{d\phi}{dx} = -(8\pi n_0 \, k_{\text{B}}T)^{1/2} \, e^{e\phi/2k_{\text{B}}T} \quad .$$

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 $e^{e\phi(\infty)/k_{\text{B}}T} = 0$.

(b) Integrating once more, we have

$$e^{-e\phi(x)/2k_{\text{B}}T} = \left(\frac{2\pi n_0 \, e^2}{k_{\text{B}}T}\right)^{1/2} (x + a) \quad ,$$

where a is a constant of integration. Since $n(x = 0) \equiv n_0$, we must have $\phi(0) = 0$, and hence

$$a = \left(\frac{k_{\text{B}}T}{2\pi n_0 \, e^2}\right)^{1/2} \quad .$$

Thus,

$$\phi(x) = -\frac{2k_{\text{B}}T}{e} \ln\!\left(\frac{x + a}{a}\right) \quad .$$

(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 σ and σ' are the species labels.

(b) For a plasma, show from Debye-Hückel theory that the pair correlation function is $g_{\sigma\sigma'} \propto \exp\big(-\sigma\sigma' q^2 \phi(r)/k_{\rm B}T\big)$, where σ and σ' 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 $\sigma_i = \pm 1$ 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

$$g_{\mu\nu}(\boldsymbol{r}) \equiv \frac{1}{n_\mu n_\nu} \Big\langle \sum_{i\neq j} \delta(\boldsymbol{r} - \boldsymbol{x}_i)\, \delta(\boldsymbol{x}_j)\, \delta_{\sigma_i,\mu}\, \delta_{\sigma_j,\nu} \Big\rangle \quad ,$$

where n_μ is the density of particles of species μ, with $\mu = \pm 1$. As defined, $g_{\mu\nu}(\boldsymbol{r}) \to 1$ as $r \to \infty$. If instead we normalize $g_{\mu\nu}$ by dividing by $n_{\rm tot}^2 = (n_+ + n_-)^2$, then we would have $g_{\mu\nu}(r \to \infty) = \frac{1}{4}$. We next work on the virial equation of state,

$$\frac{p}{k_{\rm B}T} = \frac{N_+ + N_-}{V} - \frac{1}{3Vk_{\rm B}T} \sum_{i=1}^{N_+ + N_-} \big\langle \boldsymbol{x}_i \cdot \boldsymbol{\nabla}_i W \big\rangle \quad .$$

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

$$\frac{p}{k_{\rm B}T} = n_+ + n_- - \frac{2\pi}{3k_{\rm B}T} \sum_{\sigma,\sigma'} n_\sigma n_{\sigma'} \int_0^\infty \!\! dr\, r^3\, u'_{\sigma\sigma'}(r)\, g_{\sigma\sigma'}(r)$$

(b) According to Debye-Hückel theory,

$$g_{\sigma\sigma'}(r) = \exp\bigg(-\frac{\sigma\sigma' q\, \phi(r)}{k_{\rm B}T}\bigg) \quad ,$$

where $\phi(r)$ is the screened potential at r due to a point charge q at the origin, which satisfies

$$\nabla^2 \phi = 4\pi n q \sinh\big(q\phi/k_{\rm B}T\big) - 4\pi q\, \delta(\boldsymbol{r}) \quad ,$$

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

$$\phi(r) = \frac{q}{r}\, e^{-\kappa_{\rm D} r} \quad ,$$

where

$$\kappa_{\rm D} = \bigg(\frac{4\pi n q^2}{k_{\rm B}T}\bigg)^{1/2}$$

is the Debye screening wavevector. Thus, we have

$$
\begin{aligned}
\frac{p}{k_{\mathrm{B}}T} &= n - \frac{\pi n^2}{6k_{\mathrm{B}}T}\int\limits_0^\infty \! dr\; r^3 \left(-\frac{q^2}{r^2}\right)\sum_{\sigma,\sigma'} \sigma\sigma'\; g_{\sigma\sigma'}(r) \\
&= n - \frac{2\pi n^2 q^3}{3(k_{\mathrm{B}}T)^2}\int\limits_0^\infty \! dr\; r\,\phi(r) = n - \frac{2\pi n^2 q^4}{3(k_{\mathrm{B}}T)^2 \kappa_{\mathrm{D}}} \\
&= n\left(1 - \frac{\sqrt{\pi}\, n^{1/2}\, q^3}{3\,(k_{\mathrm{B}}T)^{3/2}}\right) \quad .
\end{aligned}
$$

(6.9) Consider a liquid where the interaction potential is $u(r) = \Delta_0 \, (a/r)^k$, where Δ_0 and a are energy and length scales, respectively. Assume that the pair distribution function is given by $g(r) \approx e^{-u(r)/k_B T}$. 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,

$$p = nk_B T - \tfrac{2}{3}\pi n^2 \int_0^\infty dr \, r^3 \, g(r) \, u'(r) \quad .$$

Substituting for $u(r)$ and $g(r)$ as in the statement of the problem, we change variables to

$$s \equiv \frac{u(r)}{k_B T} \quad \Rightarrow \quad ds = \frac{u'(r)}{k_B T} \, dr \quad ,$$

so

$$r = a \left(\frac{\Delta_0}{k_B T} \right)^{1/k} s^{-1/k}$$

and

$$r^3 \, g(r) \, u'(r) \, dr = k_B T \, a^3 \left(\frac{\Delta_0}{k_B T} \right)^{3/k} s^{-3/k} \, e^{-s} \, ds \quad .$$

We then have

$$\begin{aligned} p &= nk_B T + \tfrac{2}{3}\pi n^3 a^3 k_B T \left(\frac{\Delta_0}{k_B T} \right)^{3/k} \int_0^\infty ds \, s^{-3/k} \, e^{-s} \\ &= nk_B T \left\{ 1 + \tfrac{2}{3}\pi \Gamma\big(1 - \tfrac{3}{k}\big) \, na^3 \left(\frac{\Delta_0}{k_B T} \right)^{3/k} \right\} \quad . \end{aligned}$$

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 $\boldsymbol{r} = (\boldsymbol{\rho}, z)$ 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

$$\hat{\phi}(\boldsymbol{k}, q) = \frac{4\pi Q}{\boldsymbol{k}^2 + q^2} - \frac{4\pi n_0 e^2}{\varepsilon_{\rm F}}\,\frac{\hat{\chi}(\boldsymbol{k})}{\boldsymbol{k}^2 + q^2} \quad ,$$

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 $\varrho(\boldsymbol{\rho}) = en_0 - en(\boldsymbol{\rho})$. Show that $\varrho(\boldsymbol{\rho}) = \frac{Q}{2\pi\lambda^2}\,f(\rho/\lambda)$, where λ 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

$$n = 2\!\int\!\frac{d^2k}{(2\pi)^2}\,\Theta(k_{\rm F} - k) = \frac{k_{\rm F}^2}{2\pi} = \frac{m\varepsilon_{\rm F}}{\pi\hbar^2} \quad ,$$

where we have used $\varepsilon_{\rm F} = \hbar^2 k_{\rm F}^2/2m$. In the presence of a potential, the energy levels are shifted and it is the electrochemical potential $\varepsilon_{\rm F}^\infty = \varepsilon_{\rm F} - e\phi$ which is constant throughout the system. Thus, the local electron density is

$$n(\boldsymbol{\rho}) = \frac{m}{\pi\hbar^2}\Big[\varepsilon_{\rm F}^\infty + e\,\phi(\boldsymbol{\rho}, 0)\Big] = n_0 + \frac{me}{\pi\hbar^2}\,\phi(\boldsymbol{\rho}, 0) \quad .$$

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

$$\nabla^2\phi = \frac{4}{a_{\rm B}}\,\phi(\boldsymbol{\rho}, 0)\,\delta(z) - 4\pi Q\,\delta(\boldsymbol{\rho})\,\delta(z) \quad ,$$

where $a_{\rm B} = \hbar^2/me^2$ 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

$$-(\boldsymbol{k}^2 + q^2)\hat{\phi}(\boldsymbol{k}, q) = \frac{4}{a_{\rm B}}\,\overbrace{\int\limits_{-\infty}^{\infty}\!\frac{dq}{2\pi}\,\hat{\phi}(\boldsymbol{k}, q)}^{\hat{\chi}(\boldsymbol{k})} - 4\pi Q \quad ,$$

```
Integrate[BesselJ[0, u a] / (1 + u), {u, 0, Infinity}, Assumptions → Re[a] > 0 && Abs[Im[a]] == 0]

1
─ π (-BesselY[0, a] + StruveH[0, a])
2

                      1
F[x_] := 1 / x +  ─ π (BesselY[0, x] - StruveH[0, x])
                      2

Plot[F[x], {x, 0, 10}, AxesLabel → {σ, F[σ, 0]}, PlotStyle → Thick]
```

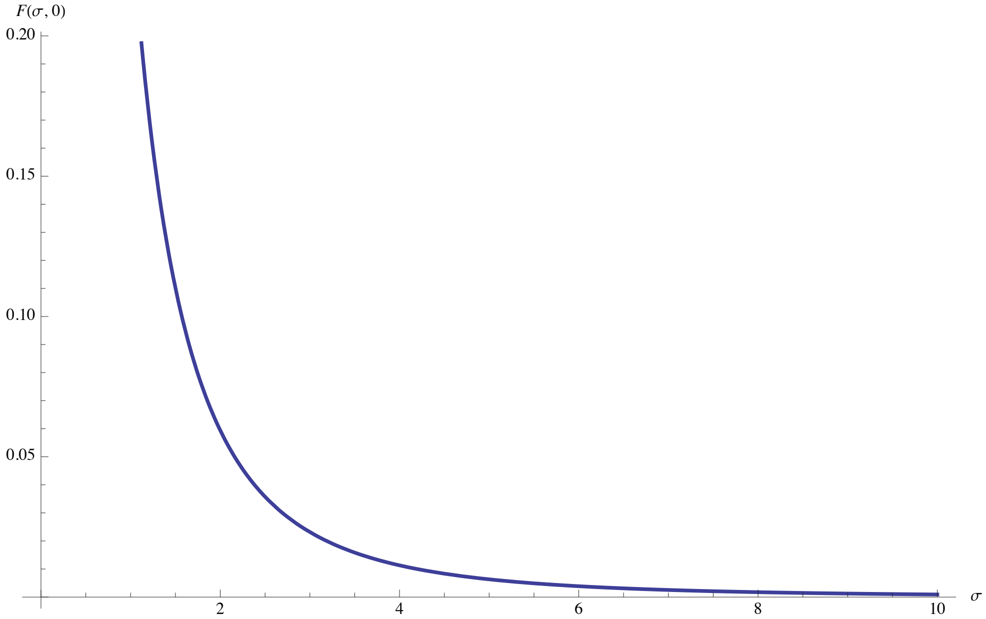

Figure 4: Plot of the screening charge density in units of $-Q/2\pi\lambda^2$ for problem (10).

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

$$\int\limits_{-\infty}^{\infty}\frac{dq}{2\pi}\,\frac{e^{iqz}}{\boldsymbol{k}^2+q^2} = \frac{e^{-|\boldsymbol{k}z|}}{2\,|\boldsymbol{k}|} \quad .$$

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

$$\hat{\phi}(\boldsymbol{k},q) = \frac{4\pi Q\cdot|\boldsymbol{k}\lambda|}{\big(\boldsymbol{k}^2+q^2\big)\big(1+|\boldsymbol{k}\lambda|\big)} \quad .$$

(d) Now we Fourier transform back to real space:

$$\begin{aligned}\phi(\boldsymbol{\rho}, z) &= \int \frac{d^2\!k}{(2\pi)^2} \int\limits_{-\infty}^{\infty} \frac{dq}{2\pi}\, \hat{\phi}(\boldsymbol{k}, q)\, e^{i\boldsymbol{k}\cdot\boldsymbol{\rho}}\, e^{iqz} \\ &= \int \frac{d^2\!k}{(2\pi)^2}\, \frac{e^{-|\boldsymbol{k}z|}}{2\,|\boldsymbol{k}|} \cdot \frac{4\pi Q\,|\boldsymbol{k}\lambda|}{1+|\boldsymbol{k}\lambda|} \cdot e^{i\boldsymbol{k}\cdot\boldsymbol{\rho}} \\ &= \frac{Q}{\lambda}\, F\big(\rho/\lambda, |z|/\lambda\big) \quad ,\end{aligned}$$

where

$$F(\sigma,\zeta) = \int\limits_0^\infty \!du\, \frac{u}{1+u}\, J_0(\sigma u)\, e^{-\zeta u} \quad ,$$

where $J_0(s)$ is the Bessel function of order zero.

(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

$$\begin{aligned}F(\rho/\lambda, 0) = \int\limits_0^\infty \!du\, \frac{u\, J_0(u\rho/\lambda)}{1+u} &= \frac{\lambda}{\rho} - \int\limits_0^\infty \!du\, \frac{J_0(u\rho/\lambda)}{1+u} \\ &= \frac{\lambda}{\rho} + \tfrac{1}{2}\pi\, Y_0(\rho/\lambda) - \tfrac{1}{2}\pi\, \mathbf{H}_0(\rho/\lambda) \quad ,\end{aligned}$$

where $Y_0(s)$ is a Bessel function of the second kind and $\mathbf{H}_0(s)$ is the Struve function. Asymptotically[1] we obtain

$$\varrho(\boldsymbol{\rho}) = \frac{Q}{2\pi\lambda^2} \left\{ \sum_{n=1}^{p-1} (-1)^n\, \Gamma^2\big(\tfrac{1}{2}+n\big) \left(\frac{2\lambda}{\rho}\right)^{(2n+1)} + \quad \mathcal{O}\big(2\lambda/\rho\big)^{2p+1} \right\} \quad .$$

Note that $\varrho(\rho) \propto \rho^{-3}$ at large distances. In the above formula, p is arbitrary. Since $\Gamma(z+\frac{1}{2}) \sim z \ln z - z$, the optimal value of p to minimize the remainder in the sum is $p \approx \rho/2\lambda$. See Fig. 4 for a sketch.

---

[1] 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

$$\Xi = (1+z)^{V/v_0}\big(1+z^{\alpha V/v_0}\big) \quad ,$$

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

$$\Omega(T,z) = -k_B T \ln \Xi = -\frac{k_B T\, V}{v_0}\,\ln(1+z) - k_B T \ln\big(1+z^{\alpha V/v_0}\big) \quad .$$

Now take the thermodynamic limit $V/v_0 \to \infty$. One then has

$$\Omega(T,z) = -\frac{k_B T\, V}{v_0}\,\ln(1+z) - \begin{cases} 0 & \text{if} \quad |z| < 1 \\ \frac{\alpha k_B T\, V}{v_0}\,\ln z & \text{if} \quad |z| > 1 \end{cases} \quad .$$

From this we compute the pressure,

$$\begin{aligned} p = -\bigg(\frac{\partial \Omega}{\partial V}\bigg)_{T,\mu} &= \frac{k_B T}{v_0}\,\ln(1+z) + \frac{\alpha k_B T}{v_0} \cdot \frac{z^{\alpha V/v_0}\,\ln z}{1+z^{\alpha V/v_0}} \\ &= \frac{k_B T}{v_0}\,\ln(1+z) + \begin{cases} 0 & \text{if} \quad |z| < 1 \\ \frac{\alpha k_B T}{v_0}\,\ln z & \text{if} \quad |z| > 1 \end{cases} \quad . \end{aligned}$$

(b) For the density, we have

$$\begin{aligned} n = -\frac{z}{V k_B T}\bigg(\frac{\partial \Omega}{\partial z}\bigg)_{T,V} &= \frac{1}{v_0} \cdot \frac{z}{1+z} + \frac{\alpha}{v_0} \cdot \frac{z^{\alpha V/v_0}}{1+z^{\alpha V/v_0}} \\ &= \frac{1}{v_0} \cdot \frac{z}{1+z} + \begin{cases} 0 & \text{if} \quad |z| < 1 \\ \alpha/v_0 & \text{if} \quad |z| > 1 \end{cases} \quad . \end{aligned}$$

(c) We eliminate z from the above equations, and we write $v = 1/n$ as the volume per particle. The fugacity $z(v)$ satisfies

$$z(v) = \begin{cases} \frac{v_0}{v-v_0} & \text{if} \quad v > 2v_0 \\ \\ 1 & \text{if} \quad \frac{2v_0}{1+2\alpha} < v < 2v_0 \\ \\ \frac{v_0-\alpha v}{(1+\alpha)v-v_0} & \text{if} \quad \frac{v_0}{1+\alpha} < v < \frac{2v_0}{1+2\alpha} \\ \\ \infty & \text{if} \quad v < \frac{v_0}{1+\alpha} \end{cases}$$

We then have

$$\frac{pv_0}{k_B T} = \begin{cases} \ln\left(\frac{v}{v-v_0}\right) & v > 2v_0 \\ \ln 2 & \frac{2v_0}{1+2\alpha} < v < 2v_0 \\ \ln\left[\left(\frac{v}{(1+\alpha)v-v_0}\right)\left(\frac{v_0-\alpha v}{(1+\alpha)v-v_0}\right)^{\alpha}\right] & \frac{v_0}{1+\alpha} < v < \frac{2v_0}{1+2\alpha} \\ \infty & v < \frac{v_0}{1+\alpha} \end{cases}$$

Sample plots of $z(v)$ and $p(v)$ are shown in Fig. 5.

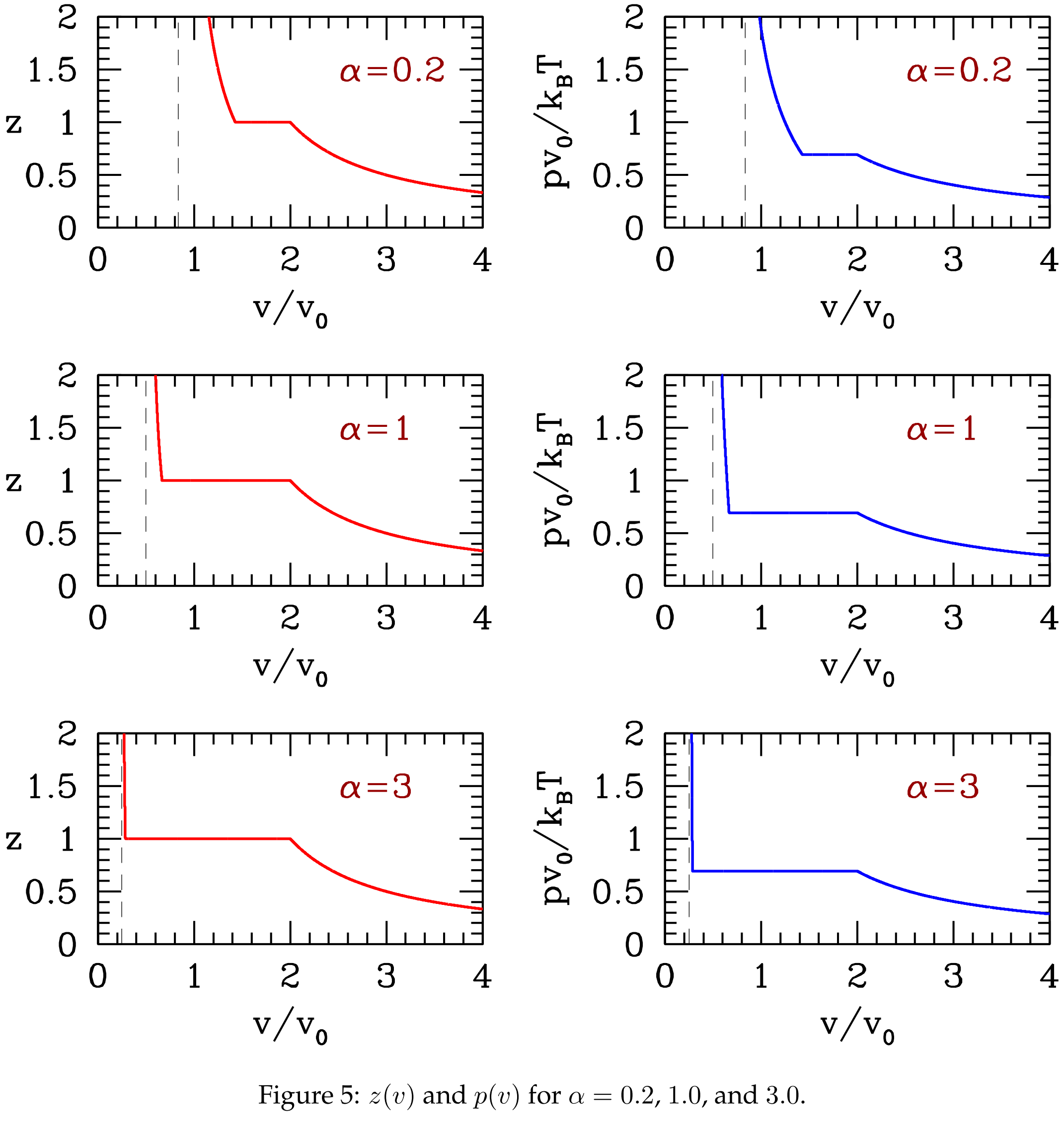

Figure 5: $z(v)$ and $p(v)$ for $\alpha = 0.2$, 1.0, and 3.0.

(6.12) In problem 11, you considered the thermodynamic properties associated with the grand partition function $\Xi(V,z) = (1+z)^{V/v_0}\big(1+z^{\alpha V/v_0}\big)$. Consider now the following partition function:

$$\Xi(V,z) = (1+z)^{V/v_0} \prod_{j=1}^{K} \left\{ 1 + \left(\frac{z}{\sigma_j}\right)^{\alpha V/K v_0} \right\} \quad .$$

Consider the thermodynamic limit where α is a number on the order of unity, $V/v_0 \to \infty$, and $K \to \infty$ but with $K v_0/V \to 0$. For example, we might have $K \propto (V/v_0)^{1/2}$.

(a) Show that the number density is

$$n(T,z) = \frac{1}{v_0}\,\frac{z}{1+z} + \frac{\alpha}{v_0}\int\limits_0^{|z|} \!d\sigma\; g(\sigma) \quad ,$$

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 σ_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[2]: α, r, and w. Solve for $z(v)$. You will have to take cases, and you should find there are three regimes to consider[3].

(d) Plot $pv_0/k_{\rm B}T$ *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 $n = V^{-1} z\,\partial \ln\Xi/\partial z$,

$$\begin{aligned} n &= \frac{1}{v_0}\,\frac{z}{1+z} + \frac{\alpha}{K v_0}\sum_{i=1}^{K} \Theta\big(|z| - \sigma_i\big) \\ &= \frac{1}{v_0}\,\frac{z}{1+z} + \frac{\alpha}{v_0}\int\limits_0^{|z|} \!d\sigma\; g(\sigma) \quad . \end{aligned}$$

---

[2] The quantity v_0 has dimensions of volume and disappears from the problem if one defines $\tilde{v} = v/v_0$.

[3] You should find that a fourth regime, $v < (1 + r^{-1})v_0$, is not permitted.

(b) The pressure is $p = V^{-1} k_{\mathrm{B}} T \ln \Xi$:

$$
\begin{aligned}
p &= \frac{k_{\mathrm{B}} T}{v_0} \ln(1+z) + \frac{\alpha k_{\mathrm{B}} T}{K v_0} \sum_{i=1}^{K} \ln(z/\sigma_i)\,\Theta\big(|z| - \sigma_i\big) \\
&= \frac{k_{\mathrm{B}} T}{v_0} \ln(1+z) + \frac{\alpha k_{\mathrm{B}} T}{v_0} \int\limits_0^{|z|} \! d\sigma\, g(\sigma) \ln\big(z/\sigma\big) \quad .
\end{aligned}
$$

(c) We now consider the given form for $g(\sigma)$. From our equation for $n(z)$, we have

$$
n v_0 = \frac{v_0}{v} = \begin{cases} \frac{z}{1+z} & \text{if } |z| \le r \\ \frac{z}{1+z} + \frac{\alpha}{w}\,(z-r) & \text{if } r \le |z| \le r+w \\ \frac{z}{1+z} + \alpha & \text{if } r+w \le |z| \quad . \end{cases}
$$

We need to invert this result. We assume $z \in \mathbb{R}^+$. In the first regime, we have

$$
z \in [\,0\,,\,r\,] \quad \Rightarrow \quad z = \frac{v_0}{v - v_0} \quad \text{with} \quad \frac{v}{v_0} \in \big[1 + r^{-1}\,,\,\infty\big] \quad .
$$

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, $v_{\text{min}} = v_0/(1+\alpha)$, hence a maximum possible density $n_{\text{max}} = 1/v_{\text{min}}$. 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

$$
z = \frac{-\Big[\frac{\alpha}{w}(1-r) + 1 - \frac{v_0}{v}\Big] + \sqrt{\Big[\frac{\alpha}{w}(1-r) + 1 - \frac{v_0}{v}\Big]^2 + \frac{4\alpha}{w}\Big(\frac{\alpha r}{w} + \frac{v_0}{v}\Big)}}{2\alpha/w} \quad ,
$$

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 $\pi = p v_0 / k_{\mathrm{B}} T$ is given by

$$
z \in [\,0\,,\,r\,] \quad \Rightarrow \quad \pi = \ln(1+z) \quad \text{with} \quad \frac{v}{v_0} \in \big[1 + r^{-1}\,,\,\infty\big] \quad .
$$

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

$$z \in [\,r\,,\,r+w\,] \quad \Rightarrow \quad \frac{v}{v_0} \in \bigg[\frac{1+r+w}{(1+\alpha)(r+w)+\alpha}\,,\,1+r^{-1}\bigg] \quad .$$

(d) The results are plotted in Fig. 4. Note that v is a continuous function of π, 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 ϵ. 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 ϵ, we have

$$\nu < \nu_c \qquad \Rightarrow \qquad \pi = \ln(1+r) + (1+r)(\nu - \nu_c) + \ldots \quad ,$$

where $\nu_c = r/(1+r)$ is the critical dimensionless density. Now investigate the high density side of the transition, where $\epsilon > 0$. Integrating over the region $[\,r\,,\,r+\epsilon\,]$, we find

$$\nu = \frac{z}{1+z} + \frac{\alpha}{w}\,(z-r) = \frac{r}{1+r} + \bigg[\frac{1}{(1+r)^2} + \frac{\alpha}{w}\bigg]\epsilon + \mathcal{O}(\epsilon^2)$$

$$\pi = \ln(1+z) + \frac{\alpha}{w}\Big[z + r\ln(r/z) - r\Big] = \ln(1+r) + \frac{\epsilon}{1+r} + \mathcal{O}(\epsilon^2) \quad .$$

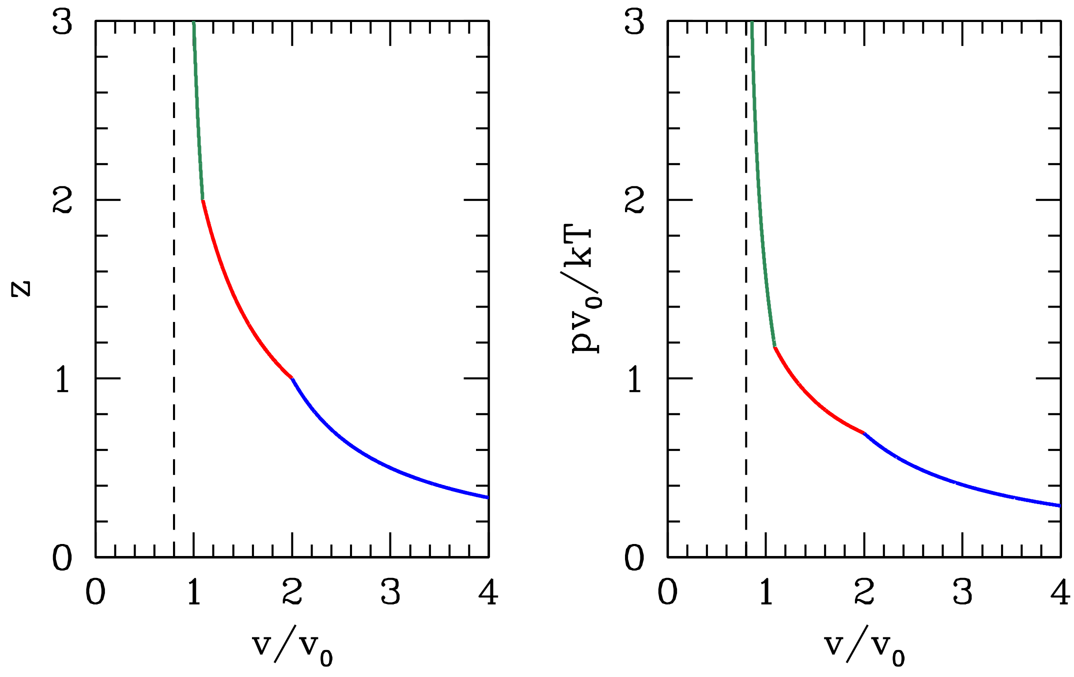

Figure 6: Fugacity z and dimensionless pressure $pv_0/k_B T$ *versus* dimensionless volume per particle v/v_0 for problem (2), with $\alpha = \frac{1}{4}$ and $r = w = 1$. Different portions of the curves are shown in different colors. The dashed line denotes the minimum possible volume $v_{\rm min} = v_0/(1+\alpha)$.

Note that $\partial\pi/\partial z$ is continuous through the transition. As we are about to discover, $\partial\pi/\partial\nu$ is discontinuous. Eliminating ϵ, we have

$$\nu > \nu_{\rm c} \qquad \Rightarrow \qquad \pi = \ln(1+r) + \frac{1+r}{1+(1+r)^2\,(\alpha/w)}\,(\nu-\nu_{\rm c}) + \ldots \quad .$$

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. 6.

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

$$\begin{aligned}\nu &= \frac{r}{1+r} + \frac{\epsilon}{(1+r)^2} + \frac{\alpha A\,\epsilon^{q+1}}{q+1} + \ldots \\ \pi &= \ln(1+r) + \frac{\epsilon}{1+r} + \frac{\alpha A\,\epsilon^{q+2}}{(q+1)(q+2)r} + \ldots \quad .\end{aligned}$$

If $q > 0$, then to order ϵ the expansion is the same for $\epsilon < 0$, and both π 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 ϵ^{q+1} dominates over ϵ in the first of these equations, and we have

$$\epsilon = \left(\frac{(q+1)(\nu-\nu_{\rm c})}{\alpha A}\right)^{\frac{1}{q+1}}$$

and

$$\pi = \ln(1+r) + \frac{1}{1+r}\left(\frac{q+1}{\alpha A}\right)^{\frac{1}{q+1}}(\nu-\nu_{\rm c})^{\frac{1}{q+1}} \quad ,$$

which has a nontrivial power law behavior typical of second order critical phenomena.