1 Probability Distributions : Summary

• *Discrete distributions*: Let n label the distinct possible outcomes of a discrete random process, and let p_n be the probability for outcome n. Let A be a quantity which takes values which depend on n, with A_n being the value of A under the outcome n. Then the expected value of A is $\langle A\rangle = \sum_n p_n\, A_n$, where the sum is over all possible allowed values of n. We must have that the distribution is normalized, *i.e.* $\langle 1\rangle = \sum_n p_n = 1$.

• *Continuous distributions*: When the random variable $\boldsymbol{\varphi}$ takes a continuum of values, we define the *probability density* $P(\boldsymbol{\varphi})$ to be such that $P(\boldsymbol{\varphi})\, d\mu$ is the probability for the outcome to lie within a differential volume $d\mu$ of $\boldsymbol{\varphi}$, where $d\mu = W(\boldsymbol{\varphi}) \prod_{i=1}^{n} d\varphi_i$, were $\boldsymbol{\varphi}$ is an n-component vector in the configuration space Ω, and where the function $W(\boldsymbol{\varphi})$ accounts for the possibility of different configuration space measures. Then if $A(\boldsymbol{\varphi})$ is any function on Ω, the expected value of A is $\langle A\rangle = \int\limits_{\Omega} d\mu\, P(\boldsymbol{\varphi})\, A(\boldsymbol{\varphi})$.

• *Central limit theorem*: If $\{x_1, \ldots, x_N\}$ are each independently distributed according to $P(x)$, then the distribution of the sum $X = \sum_{i=1}^{N} x_i$ is

$$\mathcal{P}_N(X) = \int\limits_{-\infty}^{\infty} \! dx_1 \cdots \int\limits_{-\infty}^{\infty} \! dx_N\, P(x_1) \cdots P(x_N)\, \delta\Big(X - \sum_{i=1}^{N} x_i\Big) = \int\limits_{-\infty}^{\infty} \frac{dk}{2\pi} \, \Big[\hat{P}(k)\Big]^N e^{ikX} \quad ,$$

where $\hat{P}(k) = \int dx\, P(x)\, e^{-ikx}$ is the Fourier transform of $P(x)$. Assuming that the lowest moments of $P(x)$ exist, $\ln\big[\hat{P}(k)\big] = -i\mu k - \frac{1}{2}\sigma^2 k^2 + \mathcal{O}(k^3)$, where $\mu = \langle x\rangle$ and $\sigma^2 = \langle x^2\rangle - \langle x\rangle^2$ are the mean and standard deviation. Then for $N \to \infty$,

$$P_N(X) = (2\pi N\sigma^2)^{-1/2}\, e^{-(X-N\mu)^2/2N\sigma^2} \quad ,$$

which is a Gaussian with mean $\langle X\rangle = N\mu$ and standard deviation $\sqrt{\langle X^2\rangle - \langle X\rangle^2} = \sqrt{N}\,\sigma$. Thus, X is distributed as a Gaussian, even if $P(x)$ is not a Gaussian itself.

• *Entropy*: The entropy of a statistical distribution is $\{p_n\}$ is $S = -\sum_n p_n \ln p_n$. (Sometimes the base 2 logarithm is used, in which case the entropy is measured in *bits*.) This has the interpretation of the *information content* per element of a random sequence.

• *Distributions from maximum entropy*: Given a distribution $\{p_n\}$ subject to $(K+1)$ constraints of the form $\mathcal{X}^a = \sum_n X_n^a\, p_n$ with $a \in \{0, \ldots, K\}$, where $\mathcal{X}^0 = X_n^0 = 1$ (normalization), the distribution consistent with these constraints which maximizes the entropy function is obtained by extremizing the multivariable function

$$S^*\big(\{p_n\}, \{\lambda_a\}\big) = -\sum_n p_n \ln p_n - \sum_{a=0}^{K} \lambda_a \Big(\sum_n X_n^a\, p_n - \mathcal{X}^a\Big) \quad ,$$

with respect to the probabilities $\{p_n\}$ and the Lagrange multipliers $\{\lambda_a\}$. This results in a Gibbs distribution,

$$p_n = \frac{1}{Z} \exp\bigg\{ -\sum_{a=1}^{K} \lambda_a X_n^a \bigg\} \quad ,$$

where $Z = e^{1+\lambda_0}$ is determined by normalization, *i.e.* $\sum_n p_n = 1$ (*i.e.* the $a = 0$ constraint) and the K remaining multipliers determined by the K additional constraints.

• *Multidimensional Gaussian integral*:

$$\int\limits_{-\infty}^{\infty} dx_1 \cdots \int\limits_{-\infty}^{\infty} dx_n \, \exp\Big(-\tfrac{1}{2}\, x_i\, A_{ij}\, x_j + b_i\, x_i\Big) = \bigg(\frac{(2\pi)^n}{\mathsf{det}A}\bigg)^{1/2} \exp\Big(\tfrac{1}{2}\, b_i\, A^{-1}_{ij}\, b_j\Big) \quad .$$

• *Bayes' theorem*: Let the *conditional probability* for B given A be $P(B|A)$. Then Bayes' theorem says $P(A|B) = P(A) \cdot P(B|A) \,/\, P(B)$. If the 'event space' is partitioned as $\{A_i\}$, then we have the extended form,

$$P(A_i|B) = \frac{P(B|A_i) \cdot P(A_i)}{\sum_j P(B|A_j) \cdot P(A_j)} \quad .$$

When the event space is a 'binary partition' $\{A, \neg A\}$, as is often the case in fields like epidemiology (*i.e.* test positive or test negative), we have

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

Note that $P(A|B) + P(\neg A|B) = 1$ (which follows from $\neg\neg A = A$).

• *Updating Bayesian priors*: Given data in the form of observed values $\boldsymbol{x} = \{x_1, \ldots, x_N\} \in \mathcal{X}$ and a hypothesis in the form of parameters $\boldsymbol{\theta} = \{\theta_1, \ldots, \theta_K\} \in \mathit{\Theta}$, we write the conditional probability (density) for observing $\boldsymbol{x}$ given $\boldsymbol{\theta}$ as $f(\boldsymbol{x}|\boldsymbol{\theta})$. Bayes' theorem says that the corresponding distribution $\pi(\boldsymbol{\theta}|\boldsymbol{x})$ for $\boldsymbol{\theta}$ conditioned on $\boldsymbol{x}$ is

$$\pi(\boldsymbol{\theta}|\boldsymbol{x}) = \frac{f(\boldsymbol{x}|\boldsymbol{\theta})\, \pi(\boldsymbol{\theta})}{\int\limits_{\mathit{\Theta}} d\boldsymbol{\theta}'\, f(\boldsymbol{x}|\boldsymbol{\theta}')\, \pi(\boldsymbol{\theta}')} \quad ,$$

We call $\pi(\boldsymbol{\theta})$ the *prior* for $\boldsymbol{\theta}$, $f(\boldsymbol{x}|\boldsymbol{\theta})$ the *likelihood* of $\boldsymbol{x}$ given $\boldsymbol{\theta}$, and $\pi(\boldsymbol{\theta}|\boldsymbol{x})$ the *posterior* for $\boldsymbol{\theta}$ given $\boldsymbol{x}$. We can use the posterior to find the distribution of new data points $\boldsymbol{y}$, called the *posterior predictive distribution*, $f(\boldsymbol{y}|\boldsymbol{x}) = \int\limits_{\mathit{\Theta}} d\boldsymbol{\theta}\, f(\boldsymbol{y}|\boldsymbol{\theta})\, \pi(\boldsymbol{\theta}|\boldsymbol{x})$. This is the update of the *prior predictive distribution*, $f(\boldsymbol{x}) = \int\limits_{\mathit{\Theta}} d\boldsymbol{\theta}\, f(\boldsymbol{x}|\boldsymbol{\theta})\, \pi(\boldsymbol{\theta})$. As an example, consider coin flipping with $f(\boldsymbol{x}|\boldsymbol{\theta}) = \theta^X\, (1-\theta)^{N-X}$, where N is the number of flips, and $X = \sum_{j=1}^N x_j$ with x_j a discrete variable which is 0 for tails and 1 for heads. The parameter $\theta \in [0,1]$ is the probability to flip heads. We choose a prior $\pi(\theta) = \theta^{\alpha-1}\, (1-\theta)^{\beta-1} / \mathsf{B}(\alpha, \beta)$ where $\mathsf{B}(\alpha, \beta) = \Gamma(\alpha)\, \Gamma(\beta) / \Gamma(\alpha + \beta)$ is the Beta distribution. This results in a normalized prior $\int\limits_0^1 d\theta\, \pi(\theta) = 1$. The posterior distribution for θ is then

$$\pi(\theta|x_1, \ldots, x_N) = \frac{f(x_1, \ldots, x_N|\theta)\, \pi(\theta)}{\int_0^1 d\theta'\, f(x_1, \ldots, x_N|\theta')\, \pi(\theta')} = \frac{\theta^{X+\alpha-1}(1-\theta)^{N-X+\beta-1}}{\mathsf{B}(X+\alpha, N-X+\beta)} \quad .$$

The prior predictive is $f(\boldsymbol{x}) = \int_0^1 d\theta f(\boldsymbol{x}|\theta)\,\pi(\theta) = \mathsf{B}(X+\alpha, N-X+\beta)/\mathsf{B}(\alpha,\beta)$, and the posterior predictive for the total number of heads Y in M flips is

$$f(\boldsymbol{y}|\boldsymbol{x}) = \int_0^1 d\theta\, f(\boldsymbol{y}|\theta)\,\pi(\theta|\boldsymbol{x}) = \frac{\mathsf{B}(X+Y+\alpha, N-X+M-Y+\beta)}{\mathsf{B}(X+\alpha, N-X+\beta)} \quad .$$

2 Thermodynamics : Summary

• *Extensive and intensive variables*: The equilibrium state of a thermodynamic system is characterized by specifying a number of *state variables* which can be either *extensive* (scaling linearly with system size), or *intensive* (scaling as the zeroth power of system size). Extensive quantities include: energy E, entropy S, particle number N, magnetization $\boldsymbol{M}$, *etc.* Intensive quantities include temperature T, pressure p, number density n, magnetic field $\boldsymbol{H}$, *etc.* The ratio of two extensive quantities is intensive, *e.g.* $n = N/V$. In the *thermodynamic limit*, all extensive state variables tend to infinity (in whatever units are appropriate), while their various ratios are all finite. A full description of the state of any thermodynamic system must involve at least one extensive variable (but may or may not include intensive variables).

• *Work*: The internal energy of a thermodynamic system can change as a result of a *generalized displacement* dX_i, as a result of work W done *by* the system. We write the differential form of W as

$$đW = -\sum_i y_i \, dX_i - \sum_a \mu_a \, dN_a \quad ,$$

where $-y_i$ is the *generalized force* conjugate to the generalized displacement X_i, and μ_a is the *chemical potential* of species a, which is conjugate to the number of particles of that species, N_a. Think of chemical work as the work required to assemble particles out of infinitely remote constituents. The slash through the differential symbol indicates that $đW$ is an *inexact differential*, *i.e.* there is no function $W(T, p, V, \ldots)$.

• *Heat*: Aside from work done by or on the system, there is another way of changing the system's internal energy, which is by transferring *heat*, Q. Heat is a form of energy contained in the random microscopic motions of the constituent particles. Like $đW$, the differential $đQ$ is also inexact, and there is no heat function $Q(T, p, V, \ldots)$. Transfer of heat under conditions of constant volume or pressure and constant particle number results in a change of the the thermodynamic state via a change in temperature: $dT = đQ/C$, where C is the *heat capacity* of the system at fixed volume/pressure and particle number.

• *First Law*: The First Law of Thermodynamics is a statement of energy conservation which accounts for both types of energies: $\Delta E = Q - W$, or in differential form $dE = đQ - đW$.

• *Single component systems*: A single component system is completely specified by three state variables, which can be taken to be E, V, and N, and writing $đW = p \, dV - \mu \, dN$, we have

$$đQ = dE + p \, dV - \mu \, dN \quad .$$

If, for example, we want to use variables (T, V, N), we write

$$dE = \left(\frac{\partial E}{\partial T}\right)_{V,N} dT + \left(\frac{\partial E}{\partial V}\right)_{T,N} dV + \left(\frac{\partial E}{\partial N}\right)_{T,V} dN \quad .$$

Proceeding in this way, one can derive expressions like

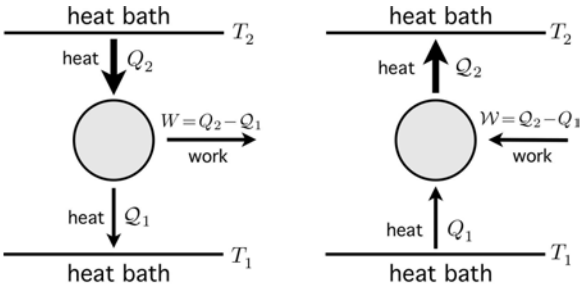
$$C_{V,N} = \left(\frac{đQ}{dT}\right)_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,N} \quad , \quad C_{p,N} = \left(\frac{đQ}{dT}\right)_{p,N} = \left(\frac{\partial E}{\partial T}\right)_{p,N} + p \left(\frac{\partial V}{\partial T}\right)_{p,N} \quad .$$

• *Equations of state*: An equation of state is a relation among state variables. Examples include the familiar ideal gas law, $pV = Nk_{\rm B}T$, and the van der Waals equation of state, $\big(p + \frac{aN^2}{V^2}\big)(V - Nb) = Nk_{\rm B}T$.

• *Ideal gases*: For ideal gases, one has $pV = Nk_{\rm B}T$ and $E = \frac{1}{2}fNk_{\rm B}T$, where f is the number of kinetic degrees of freedom ($f = 3$ for monatomic, $f = 5$ for diatomic, and $f = 6$ for polyatomic gases, assuming only translational and rotational freedoms are excited).

• *Special thermodynamic processes*: Remember adiabatic ($\text{đ}Q = 0$), isothermal ($dT = 0$), isobaric ($dp = 0$), and isochoric ($dV = 0$). A *quasistatic* process is one which follows a continuous path is a space of state variables infinitely slowly, so that the system is in equilibrium at any instant. A *reversible* process is necessarily quasistatic, and moreover is nondissipative (*i.e.* no friction), so that its thermodynamic path may be followed in reverse.

• *Heat engines and the Second Law*: A heat engine takes a thermodynamic system through a repeated cycle of equilibrium states A $\to$ B $\to$ C $\to \cdots \to$ A, the net result of which is to convert heat into mechanical work, or *vice versa*. A perfect engine, which would extract heat Q from a large thermal reservoir[1], such as the ocean, and convert it into work $W = Q$ each cycle, is not possible, according to the Second Law of Thermodynamics. Real engines extract heat Q_2 from an upper reservoir at temperature T_2, dump heat $\mathcal{Q}_1$ into a lower reservoir at temperature T_1, and transform the difference into useful mechanical work $W = Q_2 - \mathcal{Q}_1$. A refrigerator is simply an engine operating in reverse: work is done in order to extract heat Q_1 from the lower reservoir, and $\mathcal{Q}_2 = W + Q_1$ is dumped into the upper reservoir in each cycle. The *efficiency* of the engine cycle is defined to be $\eta = 1 - \frac{\mathcal{Q}_1}{Q_2}$. The engine efficiency is bounded from above by the efficiency of a reversible cycle operating between those two reservoirs, such as the Carnot cycle (two adiabats and two isotherms). Thus, $\eta \le \eta_{\rm C} = 1 - \frac{T_1}{T_2}$.



(a) engine (b) refrigerator

Figure 1: An engine (left) extracts heat Q_2 from a reservoir at temperature T_2 and deposits a smaller amount of heat $\mathcal{Q}_1$ into a reservoir at a lower temperature T_1, during each cycle. The difference $W = Q_2 - \mathcal{Q}_1$ is transformed into mechanical work. A refrigerator (right) performs the inverse process, drawing heat Q_1 from a low temperature reservoir and depositing heat $\mathcal{Q}_2 = Q_1 + \mathcal{W}$ into a high temperature reservoir, where $\mathcal{W}$ is the work done per cycle.

• *Entropy*: The Second Law guarantees that an engine operating between two reservoirs must satisfy $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \le 0$, with the equality holding for reversible cycles. Here $Q_1 = -\mathcal{Q}_1$ is the (negative) heat transferred *to* the engine from reservoir #1. Since an arbitrary curve in the p-V plane (at fixed N) can be composed of a combination of Carnot cycles, one

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[1] A thermal reservoir, or *heat bath*, is any very large object with a fixed temperature. Because it is so large, the change in temperature $\Delta T = Q/C$ which results from a heat transfer Q is negligible, since the heat capacity C is an extensive quantity.

concludes $\oint \frac{đQ}{T} \leq 0$, again with equality holding for reversible cycles. Clausius, in 1865, realized that one could thereby define a new state function, the *entropy*, S, with $dS = \frac{đQ}{T}$. Thus, $đQ \leq T\,dS$, with equality holding for reversible processes. The entropy is extensive, with units $[S] = \mathrm{J/K}$.

• *Gibbs-Duhem relation*: For reversible processes, we now have

$$dE = T\,dS + \sum_i y_i\,dX_i + \sum_a \mu_a\,dN_a \quad ,$$

which says $E = E\big(S, \{X_i\}, \{N_a\}\big)$, which is to say E is a function of all the extensive variables. It therefore must be homogeneous of degree one, *i.e.* $\lambda E = E\big(\lambda S, \{\lambda X_i\}, \{\lambda N_a\}\big)$, and from Euler's theorem it then follows that

$$\begin{aligned} E &= TS + \sum_i y_i\,X_i + \sum_a \mu_a\,N_a \\ 0 &= S\,dT + \sum_i X_i\,dy_i + \sum_a N_a\,d\mu_a \quad . \end{aligned}$$

This means that there is one equation of state which can be written as a function of all the 'proper' intensive variables.

• *Thermodynamic potentials*: Under equilibrium conditions, one can make Legendre transforms to an appropriate or convenient system of thermodynamic variables. Some common examples:

$$\begin{aligned} E(S,V,N) &= E & dE &= T\,dS - p\,dV + \mu\,dN \\ F(T,V,N) &= E - TS & dF &= -S\,dT - p\,dV + \mu\,dN \\ \mathsf{H}(S,p,N) &= E + pV & d\mathsf{H} &= T\,dS + V\,dp + \mu\,dN \\ G(T,p,N) &= E - TS + pV & dG &= -S\,dT + V\,dp + \mu\,dN \\ \varOmega(T,V,\mu) &= E - TS - \mu N & d\varOmega &= -S\,dT - p\,dV - N\,d\mu \quad . \end{aligned}$$

Under general nonequilibrium conditions, the Second Law says that each of the equalities on the right is replaced by an inequality, *i.e.* $dG \leq -S\,dT + V\,dp + \mu\,dN$. Thus, under conditions of constant temperature, pressure, and particle number, the Gibbs free energy G will achieve its minimum possible value via spontaneous processes. Note that Gibbs-Duhem says that $G = \mu N$ and $\varOmega = -pV$.

• *Maxwell relations*: Since the various thermodynamic potentials are state variables, we have that the mixed second derivatives can each be expressed in two ways. This leads to relations of the form

$$\frac{\partial^2 G}{\partial T\,\partial p} = -\bigg(\frac{\partial S}{\partial p}\bigg)_{T,N} = \bigg(\frac{\partial V}{\partial T}\bigg)_{p,N} \quad .$$

• *Thermodynamic stability*: Suppose T, p, and N are fixed. Then

$$\Delta G = \frac{1}{2}\bigg[\frac{\partial E}{\partial S^2}\,(\Delta S)^2 + \frac{\partial^2 E}{\partial S\,\partial V}\,\Delta S\,\Delta V + \frac{\partial^2 E}{\partial V^2}\,(\Delta V)^2\bigg] + \ldots \quad ,$$

and since in equilibrium G is at a minimum, $\Delta G > 0$ requires that the corresponding Hessian matrix of second derivatives be positive definite:

$$\frac{\partial^2 E}{\partial S^2} = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0$$

$$\frac{\partial^2 E}{\partial V^2} = -\left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V\kappa_S} > 0$$

$$\frac{\partial^2 E}{\partial S^2}\cdot\frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S\,\partial V}\right)^2 = \frac{T}{V\kappa_S\,C_V} - \left(\frac{\partial T}{\partial V}\right)_S^2 > 0 \quad .$$

• *Response coefficients*: In addition to heat capacities $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$ and $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$ one defines the isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ and the adiabatic compressibility $\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$, as well as the thermal expansion coefficient $\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$. Invoking the Maxwell relations, one derives certain identities, such as

$$C_p - C_V = \frac{VT\alpha_p^2}{\kappa_T} \qquad , \qquad \kappa_T - \kappa_S = \frac{VT\alpha_p^2}{C_p} \quad .$$

• *Entropy of mixing*: The entropy of any substance obeying the ideal gas law is given by the expression $S(T,V,N) = Nk_{\rm B}\ln(V/N) + N\phi(T)$. If different ideal gases at the same p and T were separated via physical barriers, and the barriers were then removed, the change in entropy would be $\Delta S = -Nk_{\rm B}\sum_a x_a \ln x_a$, where $x_a = N_a/N$ with $N = \sum_a N_a$ being the total number of particles over all species. This is called the *entropy of mixing*.

• *Weak solutions and osmotic pressure*: If one species is much more plentiful than the others, we give it a particle label $a = 0$ and call it the *solvent*. The Gibbs free energy of a weak solution is then

$$G\big(T,p,N_0,\{N_a\}\big) = N_0\,g_0(T,p) + \sum_a N_a\left\{k_{\rm B}T\ln\!\left(\frac{N_a}{eN_0}\right) + \psi_a(T,p)\right\} + \frac{1}{2N_0}\sum_{a,b} A_{ab}(T,p)\,N_a\,N_b \quad .$$

Assuming $x_a = N_a/N_0 \ll 1$ for $a > 0$, we have $\mu_0 = g_0 - xk_{\rm B}T$ and $\mu_a = k_{\rm B}T\ln x_a + \psi_a$. If $x > 0$ on the right side of a semipermeable membrane and $x = 0$ on the left, then assuming the membrane is permeable to the solvent, we must have $\mu_0 = g_0(T,p_{\rm L}) = g_0(T,p_{\rm R}) - xk_{\rm B}T$. This leads to a pressure difference, π, called the *osmotic pressure*, given by $\pi = p_{\rm R} - p_{\rm L} = xk_{\rm B}T/\left(\frac{\partial\mu_0}{\partial p}\right)_{T,N}$. Since a Maxwell relation guarantees $\left(\frac{\partial\mu_0}{\partial p}\right)_{T,N} = \left(\frac{\partial V_0}{\partial N}\right)_{T,p}$, we have the equation of state $\pi v = xRT$, where v is the molar volume of the solvent.

• *Binary solutions*: In a mixture of A and B species, let $x = N_{\sf B}/(N_{\sf A} + N_{\sf B})$. The Gibbs free energy per particle is

$$g(T,p,x) = (1-x)\,\mu^0_{\sf A}(T,p) + x\,\mu^0_{\sf B}(T,p) + k_{\rm B}T\Big[x\ln x + (1-x)\ln(1-x)\Big] + \lambda_{\sf AB}x(1-x) \quad .$$

If $\lambda_{\mathsf{AB}} > 0$, the A and B components repel, and the mixture becomes unstable. There is a local instability, corresponding to *spinodal decomposition*, when $g''(x) = 0$. This occurs at a temperature $k_{\mathrm{B}}T^* = 2\lambda_{\mathsf{AB}}\, x(1-x)$. But for a given x, an instability toward phase separation survives to even higher temperature, and is described by the Maxwell construction. The coexistence boundary is obtained from $\big[g(x_2) - g(x_1)\big]/(x_2 - x_1) = g'(x_1) = g'(x_2)$, and from the symmetry under $x \leftrightarrow 1-x$, one finds $k_{\mathrm{B}}T_{\mathrm{coex}} = \lambda_{\mathsf{AB}}(1-2x)/\ln\big(x^{-1}-1\big)$, where *nucleation* of the minority phase sets in.

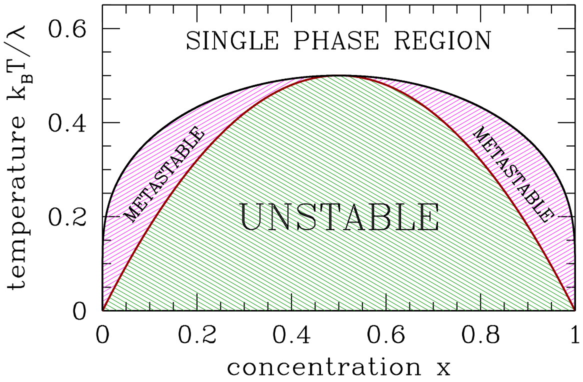

Figure 2: Phase diagram for the binary system. The black curve is the coexistence curve, and the dark red curve is the spinodal. A-rich material is to the left and B-rich to the right.

• *Miscible fluids and liquid-vapor coexistence*: If $\lambda_{\mathsf{AB}} < 0$, there is no instability toward phase separation, and the A and B fluids are said to be *completely miscible*. Example: benzene C_6H_6 and toluene $C_6H_5CH_3$. At higher temperatures, near the liquid gas transition, there is an instability toward phase separation. In the vapor phase, $\lambda^{\mathsf{V}}_{\mathsf{AB}} \approx 0$, while for the liquid $\lambda^{\mathsf{L}}_{\mathsf{AB}} < 0$. The free energy curves $g_{\mathsf{L}}(T,p,x)$ and $g_{\mathsf{V}}(T,p,x)$ are then both convex as a function of x, but choosing the minimum $g(x) = \min\big(g_{\mathsf{L}}(x), g_{\mathsf{V}}(x)\big)$, one is forced toward a Maxwell construction, hence phase coexistence. In the case of 'ideal liquids' with different boiling points, we can even take $\lambda^{\mathsf{L}}_{\mathsf{AB}} \approx 0$. By successively boiling and then separating and condensing the resulting vapor, the mixture may be *distilled* (see Fig. 3). When $\lambda^{\mathsf{L}}_{\mathsf{AB}} \neq 0$, the mixture may be *azeotropic* in which case the extremum of the boiling point occurs at an intermediate concentration (see Fig. 4).

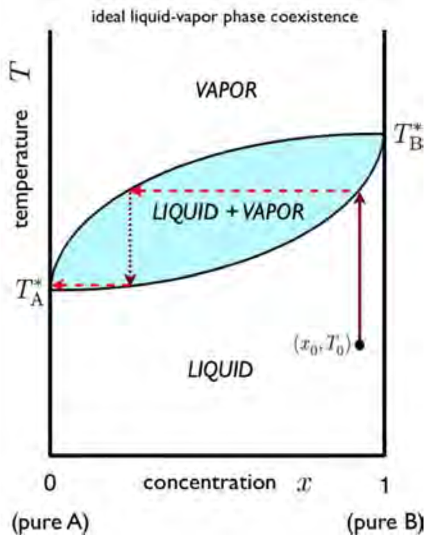

Figure 3: Phase diagram and distillation sequence for an ideal mixture.

• *Thermochemistry*: A chemical reaction among σ species may be represented

$$\zeta_1\, \mathsf{A}_1 + \zeta_2\, \mathsf{A}_2 + \cdots + \zeta_\sigma\, \mathsf{A}_\sigma = 0 \quad ,$$

where A_a is a chemical formula, and ζ_a is a *stoichiometric coefficient*. If $\zeta_a > 0$, then A_a is a *product*, while for $\zeta_a < 0$, A_a is a *reactant*. Chemical equilibrium requires $\sum_{a=1}^{\sigma} \zeta_a\, \mu_a = 0$. For a mixture of ideal gases, one has the *law of mass action*,

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

where $\xi_a(T)$ is the internal coordinate partition function for molecular species a. $\kappa(T,p)$ is the *equilibrium constant* of the reaction. When κ is large, products are favored over reactants. When κ is small, reactants are favored over products. One may further show

$$\left(\frac{\partial \ln \kappa}{\partial T}\right)_{p} = \frac{\Delta \mathsf{h}}{k_{\mathrm{B}} T^2} \quad ,$$

where Δh is the enthalpy of the reaction. When $\Delta\mathsf{h} < 0$, the reaction is *exothermic*. At finite pressure, this means that heat is transferred to the environment: $Q = \Delta E + p\,\Delta V = \Delta\mathsf{H} < 0$, where $\mathsf{H} = E + pV$. When $\Delta\mathsf{h} > 0$, the reaction is *endothermic*, and requires heat be transferred from the environment.

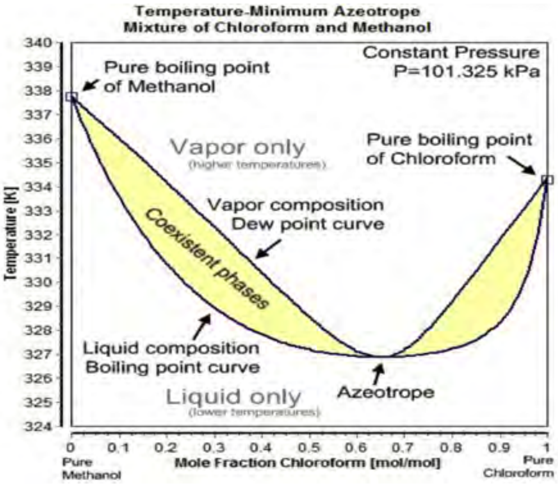

Figure 4: Phase diagram for the positive azeotrope chloroform plus methanol.

• *Clapeyron relation*: Across a *coexistence curve* $p(T)$ separating two phases, the chemical potential μ is continuous. This says $dg_1 = -s_1\,dT + v_1\,dp = -s_2\,dT + v_2\,dp = dg_2$, where g, s, and v are the Gibbs free energy, entropy, and volume per mole, respectively. Then

$$\left(\frac{\partial p}{\partial t}\right)_{\mathrm{coex}} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T\,\Delta v} \quad ,$$

where $\ell = T\,\Delta s = T(s_2 - s_1)$ is the *molar latent heat of transition* which must be supplied in order to change from phase #1 to phase #2, even without changing T or p.

• *Gibbs phase rule*: For a system with σ species, Gibbs-Duhem says $\mu_\sigma = \mu_\sigma(T, p, \mu_1, \ldots, \mu_{\sigma-1})$, so a maximum of $\sigma + 1$ intensive quantities may be specified. If a system with σ species has equilibrium among φ phases, then there are $\sigma(\varphi - 1)$ independent equilibrium conditions $\mu_a^{(j)} = \mu_a^{(j')}$, where a labels species and j labels phases, among the $2 + \varphi(\sigma - 1)$ intensive variables, and so φ-phase equilibrium can exist over a space of dimension $d = 2 + \sigma - \varphi$. Since this cannot be negative, we have $\varphi \leq 2 + \sigma$. Thus, for a single species, we can at most have three phase coexistence, which would then occur on a set of dimension zero, as is the case for the triple point of water, for example.

3 Approach to Equilibrium : Summary

• *Distributions*: Equilibrium statistical mechanics describes systems of particles in terms of time-independent statistical distributions. Where do these distributions come from? How does a system with a given set of initial conditions come to have time-independent properties which can be described in this way?

• *Master equation*: Let $P_i(t)$ be the probability that a system is in state $|\, i\,\rangle$ at time t. The evolution of the $P_i(t)$ is given by $\frac{dP_i}{dt} = \sum_j (W_{ij} P_j - W_{ji} P_i) = -\sum_j \varGamma_{ij}\, P_j$, where the rates $W_{ij} \geq 0$ are nonnegative. Conservation of probability means $\sum_i \varGamma_{ij} = 0$ for all j, hence $\boldsymbol{\psi}^{\rm t} = (1, 1, \ldots, 1)$ is a left eigenvector with eigenvalue zero. The corresponding right eigenvector is the equilibrium distribution: $\varGamma_{ij}\, P^{\rm eq}_j = 0$. Detailed balance, $W_{ij}\, P^{\rm eq}_j = W_{ji}\, P^{\rm eq}_i$, is a more stringent condition than the requirement of a stationary distribution alone. Boltzmann's H-theorem: $\dot{\mathsf{H}} \leq 0$, where $\mathsf{H} = \sum_i P_i \ln(P_i/P^{\rm eq}_i)$. Thus, the ME dynamics are *irreversible*. But the underlying microscopic laws are reversible!

• *Hamiltonian evolution*: $\dot{\varphi}_i = J_{ij}\, \frac{\partial H}{\partial \varphi_j}$, where $\boldsymbol{\varphi} = (q_1, \ldots, q_r, p_1, \ldots, p_r)$ is a point in $2r$-dimensional phase space, and $J = \begin{pmatrix} 0 & \mathbb{I} \\ -\mathbb{I} & 0 \end{pmatrix}$. Phase space flow is then incompressible: $\boldsymbol{\nabla} \cdot \dot{\boldsymbol{\varphi}} = 0$, hence phase space densities $\varrho(\boldsymbol{\varphi}, t)$ obey Liouville's equation, $\partial_t\, \varrho + \dot{\boldsymbol{\varphi}} \cdot \boldsymbol{\nabla}\varrho = 0$ (follows from continuity and incompressibility). Any function $\varrho(\varLambda_1, \ldots, \varLambda_k)$, where each $\varLambda_i$ is conserved by the phase space dynamics, will be a stationary solution to Liouville's equation. In particular, the microcanonical distribution, $\varrho_E(\boldsymbol{\varphi}) = \delta\big(E - H(\boldsymbol{\varphi})\big)/D(E)$ is such a solution, where $D(E) = \mathsf{Tr}\, \delta\big(E - H(\boldsymbol{\varphi})\big)$ is the *density of states*.

• *Poincaré Recurrence*: Let $g_\tau \boldsymbol{\varphi}(t) = \boldsymbol{\varphi}(t + \tau)$ be the τ-advance mapping for a dynamical system $\dot{\boldsymbol{\varphi}} = \boldsymbol{V}(\boldsymbol{\varphi})$. If (i) g_τ is invertible, (ii) g_τ preserves phase space volumes, and (iii) the volume of phase accessible given the dynamics and initial conditions is finite, then in any finite neighborhood $\mathcal{R}_0$ of phase space there exists a point $\boldsymbol{\varphi}_0 \in \mathcal{R}_0$ such that $g^n_\tau \boldsymbol{\varphi}_0 \in \mathcal{R}_0$ with n finite. This means all the perfume molecules eventually go back inside the bottle (if it is opened in a sealed room).

• *Kac ring model*: Normally the recurrence time is orders of magnitude greater than the age of the Universe, but for the Kac ring model, one can simulate the recurrence phenomenon easily. The model consists of a ring of N sites, and a quenched (*i.e.* fixed) random distribution of flippers on F of the links ($F \leq N$). On each site lies a discrete spin variable which is polarized either up or down. The system evolves discretely by all spins advancing clockwise by one site during a given time step. All spins which pass through a flipper reverse their polarization. Viewed probabilistically, if p_n is the probability any given spin is up at time n, then under the assumptions of the *Stosszahlansatz* $p_{n+1} = (1 - x)p_n + x(1 - p_n)$, where $x = F/N$ is the flipper density. This leads to exponential relaxation with a time scale $\tau = -1/\ln|1 - 2x|$, but the recurrence time is clearly N (if F is even) or $2N$ (if F is odd).

• *Ergodicity and mixing*: A dynamical system is *ergodic* if

$$\big\langle f(\boldsymbol{\varphi})\big\rangle_T = \lim_{T\to\infty} \frac{1}{T}\int\limits_0^T\! dt\, f\big(\boldsymbol{\varphi}(t)\big) = \frac{\mathsf{Tr}\, f(\boldsymbol{\varphi})\,\delta\big(E-H(\boldsymbol{\varphi})\big)}{\mathsf{Tr}\;\delta\big(E-H(\boldsymbol{\varphi})\big)} = \big\langle f(\boldsymbol{\varphi})\big\rangle_S \quad .$$

This means long time averages are equal to phase space averages. This does not necessarily mean that the phase space distribution will converge to the microcanonical distribution. A stronger condition, known as *mixing*, means that the distribution spreads out 'evenly' over the phase space hypersurface consistent with all conservation laws. Thus, if g is a phase space map, and if $\nu(A) \equiv D_A(E)/D(E)$ is the fraction of the energy hypersurface (assume no conserved quantities other than $H = E$) contained in A, then g is mixing if $\lim_{n\to\infty} \nu\,(g^n A \cap B) = \nu(A)\,\nu(B)$. An example of a mixing map on a two-dimensional torus is the Arnold 'cat map',

$$\begin{pmatrix} q' \\ p' \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} q \\ p \end{pmatrix} \ \mathsf{mod}\ \mathbb{Z}^2 \quad .$$

• *Thermalization of quantum systems*: This is a current research topic. One proposal, due to Deutsch (1991) and Srednicki (1994) is the *eigenstate thermalization hypothesis* (ETH). This says that thermal information is encoded in each eigenstate, such that if $E_\alpha \in [E, E + \Delta E]$, then

$$\langle\, \Psi_\alpha \,|\, \mathcal{A} \,|\, \Psi_\alpha \,\rangle = \langle \mathcal{A} \rangle_{E_\alpha} \quad ,$$

i.e. the expectation value of some local, translationally-invariant, few-body operator $\mathcal{A}$ in the state $|\,\Psi_\alpha\,\rangle$, is given by its average over a small energy window containing E_α. If this is the case, then so long as we prepare an initial state such that the spread of energies is within ΔE of some value E, where $\Delta E \ll E - E_0$ with E_0 the ground state energy, then $\langle\mathcal{A}\rangle_T = \langle\mathcal{A}\rangle_E$, and time averages become energy averages. Equivalently, the *reduced density matrix* ρ_S corresponding to a system S which is a subset of a universe U, with $W \cup S = U$ (W is the 'world'), is a thermal density matrix: $\rho_S = Z_S^{-1} e^{-\beta \hat{H}_S}$, where $\hat{H}_S$ is the Hamiltonian restricted to S, and with temperature fixed by the requirement $\mathsf{Tr}(\rho_S \hat{H}_S) = E \cdot (V_S/V_U)$, where the last factor is a ratio of volumes. ETH does not hold for so-called *integrable models* with an extensive number of independent conserved quantities. But it has been shown, both perturbatively as well as numerically, to hold for certain model nonintegrable systems. An interesting distinction between classical and quantum thermalization: in the quantum case, time evolution does not create the thermal state. Rather, it *reveals* the thermal distribution which is *encoded in each eigenstate* after sufficient time that dephasing has occurred and all correlations between the different wavefunction expansion coefficients is lost.

4 Statistical Ensembles : Summary

• *Distributions*: Let $\varrho(\boldsymbol{\varphi})$ be a normalized distribution on phase space. Then

$$\big\langle f(\boldsymbol{\varphi})\big\rangle = \mathsf{Tr}\left[\varrho(\boldsymbol{\varphi})\, f(\boldsymbol{\varphi})\right] = \int \! d\mu\; \varrho(\boldsymbol{\varphi})\, f(\boldsymbol{\varphi}) \quad ,$$

where $d\mu = W(\boldsymbol{\varphi}) \prod_i d\varphi_i$ is the phase space measure. For a Hamiltonian system of N identical indistinguishable point particles in d space dimensions, we have

$$d\mu = \frac{1}{N!} \prod_{i=1}^{N} \frac{d^d\!p_i \, d^d\!q_i}{(2\pi\hbar)^d} \quad .$$

The $\frac{1}{N!}$ prefactor accounts for indistinguishability. Normalization means $\mathsf{Tr}\,\varrho = 1$.

• *Microcanonical ensemble* (μCE): $\varrho(\boldsymbol{\varphi}) = \delta\big(E - \hat{H}(\boldsymbol{\varphi})\big)/D(E)$, where $D(E) = \mathsf{Tr}\;\delta\big(E - \hat{H}(\boldsymbol{\varphi})\big)$ is the density of states and $\hat{H}(\boldsymbol{\varphi}) = \hat{H}(\boldsymbol{q},\boldsymbol{p})$ is the Hamiltonian. The energy E, volume V, and particle number N are held fixed. Thus, the density of states $D(E,V,N)$ is a function of all three variables. The statistical entropy is $S(E,V,N) = k_{\rm B} \ln D(E,V,N)$, where $k_{\rm B}$ is Boltzmann's constant. Since D has dimensions of E^{-1}, an arbitrary energy scale is necessary to convert D to a dimensionless quantity before taking the log. In the thermodynamic limit, one has

$$S(E,V,N) = N k_{\rm B}\, \phi\bigg(\frac{E}{N},\frac{V}{N}\bigg) \quad .$$

The differential of E is defined to be $dE = T\,dS - p\,dV + \mu\,dN$, thus $T = \big(\frac{\partial E}{\partial S}\big)_{V,N}$ is the temperature, $p = -\big(\frac{\partial E}{\partial V}\big)_{S,N}$ is the pressure, and $\mu = \big(\frac{\partial E}{\partial N}\big)_{S,V}$ is the chemical potential. Note that E, S, V, and N are all extensive quantities, *i.e.* they are halved when the system itself is halved.

• *Ordinary canonical ensemble* (OCE): In the OCE, energy fluctuates, while V, N, and the temperature T are fixed. The distribution is $\varrho = Z^{-1}\, e^{-\beta \hat{H}}$, where $\beta = 1/k_{\rm B}T$ and $Z = \mathsf{Tr}\; e^{-\beta\hat{H}}$ is the partition function. Note that Z is the Laplace transform of the density of states: $Z = \int \! dE\; D(E)\, e^{-\beta E}$. The Boltzmann entropy is $S = -k_{\rm B}\, \mathsf{Tr}\,(\varrho \ln \varrho)$. This entails $F = E - TS$, where $F = -k_{\rm B}T \ln Z$ is the Helmholtz free energy, a Legendre transform of the energy E. From this we derive $dF = -S\,dT - p\,dV + \mu\,dN$.

• *Grand canonical ensemble* (GCE): In the GCE, both E and N fluctuate, while T, V, and chemical potential μ remain fixed. Then $\varrho = \Xi^{-1}\, e^{-\beta(\hat{H}-\mu\hat{N})}$, where $\Xi = \mathsf{Tr}\; e^{-\beta(\hat{H}-\mu\hat{N})}$ is the grand partition function and $\Omega = -k_{\rm B}T \ln \Xi$ is the grand potential. Assuming $[\hat{H},\hat{N}] = 0$, we can label states $|\, n\,\rangle$ by both energy and particle number. Then $P_n = \Xi^{-1}\, e^{-\beta(E_n - \mu N_n)}$. We also have $\Omega = E - TS - \mu N$, hence $d\Omega = -S\,dT - p\,dV - N\,d\mu$.

• *Thermodynamics*: From $E = \mathsf{Tr}\,(\varrho\,\hat{H})$, we have $dE = \mathsf{Tr}\,(\hat{H}\,d\varrho) + \mathsf{Tr}\,(\varrho\,d\hat{H}) = đQ - đW$, where $đQ = T\,dS$ and

$$đW = -\,\mathsf{Tr}\,(\varrho\, d\hat{H}) = -\sum_n P_n \sum_i \frac{\partial E_n}{\partial X_i}\, dX_i = \sum_i F_i\, dX_i \quad ,$$

with $P_n = Z^{-1} e^{-E_n/k_{\rm B}T}$. Here $F_i = -\big\langle \frac{\partial \hat{H}}{\partial X_i} \big\rangle$ is the generalized force conjugate to the generalized displacement X_i.

• *Thermal contact*: In equilibrium, two systems which can exchange energy satisfy $T_1 = T_2$. Two systems which can exchange volume satisfy $p_1/T_1 = p_2/T_2$. Two systems which can exchange particle number satisfy $\mu_1/T_1 = \mu_2/T_2$.

• *Gibbs-Duhem relation*: Since $E(S,V,N)$ is extensive, Euler's theorem for homogeneous functions guarantees that $E = TS - pV + \mu N$. Taking the differential, we obtain the equation $S\,dT - V\,dp + N\,d\mu = 0$, so there must be a relation among any two of the intensive quantities T, p, and μ.

• *Generalized susceptibilities*: Within the OCE[1], let $\hat{H}(\boldsymbol{\lambda}) = \hat{H}_0 - \sum_i \lambda_i \, \hat{Q}_i$, where $\hat{Q}_i$ are observables with $[\hat{Q}_i, \hat{Q}_j] = 0$. Then

$$Q_k(T,V,N;\boldsymbol{\lambda}) = \langle \hat{Q}_k \rangle = -\frac{\partial F}{\partial \lambda_k} \qquad , \qquad \chi_{kl}(T,V,N;\boldsymbol{\lambda}) = \frac{1}{V}\,\frac{\partial Q_k}{\partial \lambda_l} = -\frac{1}{V}\,\frac{\partial^2 F}{\partial \lambda_k \, \partial \lambda_l} \quad .$$

The quantities χ_{kl} are the generalized susceptibilities.

• *Ideal gases*: For $\hat{H} = \sum_{i=1}^N \frac{\boldsymbol{p}_i^2}{2m}$, one finds $Z(T,V,N) = \frac{1}{N!}\big(\frac{V}{\lambda_T^d}\big)^N$, where $\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_{\rm B}T}}$ is the thermal wavelength. Thus $F = Nk_{\rm B}T \ln(N/V) - \frac{1}{2} d N k_{\rm B} T \ln T + Na$, where a is a constant. From this one finds $p = -\big(\frac{\partial F}{\partial V}\big)_{T,N} = n k_{\rm B} T$, which is the ideal gas law, with $n = \frac{N}{V}$ the number density. The distribution of velocities in $d=3$ dimensions is given by

$$f(\boldsymbol{v}) = \bigg\langle \frac{1}{N} \sum_{i=1}^N \delta(\boldsymbol{v} - \boldsymbol{v}_i) \bigg\rangle = \bigg(\frac{m}{2\pi k_{\rm B} T}\bigg)^{3/2} e^{-m\boldsymbol{v}^2/2k_{\rm B}T} \quad ,$$

and this leads to a speed distribution $\bar{f}(v) = 4\pi v^2 f(v)$.

• *Example*: For N noninteracting spins in an external magnetic field H, the Hamiltonian is $\hat{H} = -\mu_0 H \sum_{i=1}^N \sigma_i$, where $\sigma_i = \pm 1$. The spins, if on a lattice, are regarded as distinguishable. Then $Z = \zeta^N$, where $\zeta = \sum_{\sigma=\pm 1} e^{\beta \mu_0 H \sigma} = 2\cosh(\beta \mu_0 H)$. The magnetization and magnetic susceptibility are then

$$M = -\bigg(\frac{\partial F}{\partial H}\bigg)_{T,N} = N\mu_0 \tanh\bigg(\frac{\mu_0 H}{k_{\rm B} T}\bigg) \qquad , \qquad \chi = \frac{\partial M}{\partial H} = \frac{N\mu_0^2}{k_{\rm B}T}\,{\rm sech}^2\bigg(\frac{\mu_0 H}{k_{\rm B} T}\bigg) \quad .$$

• *Example*: For noninteracting particles with kinetic energy $\frac{\boldsymbol{p}^2}{2m}$ and internal degrees of freedom, $Z_N = \frac{1}{N!}\big(\frac{V}{\lambda_T^d}\big)^N \xi^N(T)$, where $\xi(T) = {\sf Tr}\; e^{-\beta \hat{h}_{\rm int}}$ is the partition function for the internal degrees of freedom, which include rotational, vibrational, and electronic excitations. One still has $pV = Nk_{\rm B}T$, but the heat capacities at constant V and p are

$$C_V = T\bigg(\frac{\partial S}{\partial T}\bigg)_{V,N} = \tfrac{1}{2} d N k_{\rm B} - NT\varphi''(T) \qquad , \qquad C_p = T\bigg(\frac{\partial S}{\partial T}\bigg)_{p,N} = C_V + Nk_{\rm B} \quad ,$$

where $\varphi(T) = -k_{\rm B} T \ln \xi(T)$.

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[1] The generalization to the GCE is straightforward.

5 Quantum Statistics : Summary

• *Second-quantized Hamiltonians*: A noninteracting quantum system is described by a Hamiltonian $\hat{H} = \sum_\alpha \varepsilon_\alpha \, \hat{n}_\alpha$, where ε_α is the energy eigenvalue for the single particle state ψ_α (possibly degenerate), and $\hat{n}_\alpha$ is the number operator. Many-body eigenstates $|\vec{n}\rangle$ are labeled by the set of occupancies $\vec{n} = \{n_\alpha\}$, with $\hat{n}_\alpha \, |\vec{n}\rangle = n_\alpha |\vec{n}\rangle$. Thus, $\hat{H} \, |\vec{n}\rangle = E_{\vec{n}} \, |\vec{n}\rangle$, where $E_{\vec{n}} = \sum_\alpha n_\alpha \, \varepsilon_\alpha$.

• *Bosons and fermions*: The allowed values for n_α are $n_\alpha \in \{0, 1, 2, \ldots, \infty\}$ for bosons and $n_\alpha \in \{0, 1\}$ for fermions.

• *Grand canonical ensemble*: Because of the constraint $\sum_\alpha n_\alpha = N$, the ordinary canonical ensemble is inconvenient. Rather, we use the grand canonical ensemble, in which case

$$\Omega(T, V, \mu) = \pm k_{\rm B} T \sum_\alpha \ln\!\Big(1 \mp e^{-(\varepsilon_\alpha - \mu)/k_{\rm B}T}\Big) \quad ,$$

where the upper sign corresponds to bosons and the lower sign to fermions. The average number of particles occupying the single particle state ψ_α is then

$$\langle \hat{n}_\alpha \rangle = \frac{\partial \Omega}{\partial \varepsilon_\alpha} = \frac{1}{e^{(\varepsilon_\alpha - \mu)/k_{\rm B}T} \mp 1} \quad .$$

In the Maxwell-Boltzmann limit, $\mu \ll -k_{\rm B}T$ and $\langle n_\alpha \rangle = z \, e^{-\varepsilon_\alpha / k_{\rm B}T}$, where $z = e^{\mu/k_{\rm B}T}$ is the fugacity. Note that this low-density limit is common to both bosons and fermions.

• *Single particle density of states*: The single particle density of states per unit volume is defined to be

$$g(\varepsilon) = \frac{1}{V} \, \mathsf{Tr} \;\, \delta(\varepsilon - \hat{h}) = \frac{1}{V} \sum_\alpha \delta(\varepsilon - \varepsilon_\alpha) \quad ,$$

where $\hat{h}$ is the one-body Hamiltonian. If $\hat{h}$ is isotropic, then $\varepsilon = \varepsilon(k)$, where $k = |\boldsymbol{k}|$ is the magnitude of the wavevector, and

$$g(\varepsilon) = \frac{\mathsf{g} \, \Omega_d}{(2\pi)^d} \, \frac{k^{d-1}}{d\varepsilon / dk} \quad ,$$

where g is the degeneracy of each single particle energy state (due to spin, for example).

• *Quantum virial expansion*: From $\Omega = -pV$, we have

$$\begin{aligned} n(T, z) &= \int\limits_{-\infty}^{\infty} \! d\varepsilon \; \frac{g(\varepsilon)}{z^{-1} \, e^{\varepsilon / k_{\rm B}T} \mp 1} = \sum_{j=1}^{\infty} z^j \, C_j(T) \\ \frac{p(T, z)}{k_{\rm B}T} &= \mp \int\limits_{-\infty}^{\infty} \! d\varepsilon \; g(\varepsilon) \; \ln\!\big(1 \mp z \, e^{-\varepsilon / k_{\rm B}T}\big) = \sum_{j=1}^{\infty} j^{-1} \, C_j(T) \, z^j \quad , \end{aligned}$$

where

$$C_j(T) = (\pm 1)^{j-1} \int\limits_{-\infty}^{\infty} \! d\varepsilon \, g(\varepsilon) \, e^{-j\varepsilon/k_{\rm B}T} \quad .$$

One now inverts $n = n(T, z)$ to obtain $z = z(T, n)$, then substitutes this into $p = p(T, z)$ to obtain a series expansion for the equation of state,

$$p(T, n) = n k_{\rm B} T \Big(1 + B_2(T)\, n + B_3(T)\, n^2 + \ldots \Big) \quad .$$

The coefficients $B_j(T)$ are the *virial coefficients*. One finds

$$B_2 = \mp \frac{C_2}{2C_1^2} \qquad , \qquad B_3 = \frac{C_2^2}{C_1^4} - \frac{2\, C_3}{3\, C_1^3} \quad .$$

• *Photon statistics*: Photons are bosonic excitations whose number is not conserved, hence $\mu = 0$. The number distribution for photon statistics is then $n(\varepsilon) = 1/(e^{\beta\varepsilon} - 1)$. Examples of particles obeying photon statistics include phonons (lattice vibrations), magnons (spin waves), and of course photons themselves, for which $\varepsilon(k) = \hbar c k$ with $\mathsf{g} = 2$. The pressure and number density for the photon gas obey $p(T) = A_d \, T^{d+1}$ and $n(T) = A'_d \, T^d$, where d is the dimension of space and A_d and A'_d are constants.

• *Blackbody radiation*: The energy density per unit frequency of a three-dimensional blackbody is givenP by

$$\varepsilon(\nu, T) = \frac{8\pi h}{c^3} \cdot \frac{\nu^3}{e^{h\nu/k_{\rm B}T} - 1} \quad .$$

The total power emitted per unit area of a blackbody is $\frac{dP}{dA} = \sigma T^4$, where $\sigma = \pi^2 k_{\rm B}^4 / 60 \hbar^3 c^2 = 5.67 \times 10^{-8}\ {\rm W/m^2\,K^4}$ is Stefan's constant.

• *Ideal Bose gas*: For Bose systems, we must have $\varepsilon_\alpha > \mu$ for all single particle states. The number density is

$$n(T, \mu) = \int\limits_{-\infty}^{\infty} \! d\varepsilon \, \frac{g(\varepsilon)}{e^{\beta(\varepsilon - \mu)} - 1} \quad .$$

This is an increasing function of μ and an increasing function of T. For fixed T, the largest value $n(T, \mu)$ can attain is $n(T, \varepsilon_0)$, where ε_0 is the lowest possible single particle energy, for which $g(\varepsilon) = 0$ for $\varepsilon < \varepsilon_0$. If $n_{\rm c}(T) \equiv n(T, \varepsilon_0) < \infty$, this establishes a *critical density* above which there is *Bose condensation* into the energy ε_0 state. Conversely, for a given density n there is a *critical temperature* $T_{\rm c}(n)$ such that n_0 is finite for $T < T_{\rm c}$. For $T < T_{\rm c}$, $n = n_0 + n_{\rm c}(T)$, with $\mu = \varepsilon_0$. For $T > T_{\rm c}$, $n(T, \mu)$ is given by the integral formula above, with $n_0 = 0$. For a ballistic dispersion $\varepsilon(\boldsymbol{k}) = \hbar^2 \boldsymbol{k}^2 / 2m$, one finds $n \lambda^d_{T_{\rm c}} = \mathsf{g}\, \zeta(d/2)$, *i.e.* $k_{\rm B} T_{\rm c} = \frac{2\pi\hbar^2}{m} \big(n / \mathsf{g}\, \zeta(d/2) \big)^{2/d}$. For $T < T_{\rm c}(n)$, one has $n_0 = n - \mathsf{g}\, \zeta(\frac{1}{2}d)\, \lambda_T^{-d} = n \left(1 - (T/T_{\rm c})^{d/2} \right)$ and $p = \mathsf{g}\, \zeta(1 + \frac{1}{2}d)\, k_{\rm B} T \, \lambda_T^{-d}$. For $T > T_{\rm c}(n)$, one has $n = \mathsf{g}\, {\rm Li}_{\frac{d}{2}}(z)\, \lambda_T^{-d}$ and $p = \mathsf{g}\, {\rm Li}_{\frac{d}{2}+1}(z)\, k_{\rm B} T \, \lambda_T^{-d}$, where

$${\rm Li}_q(z) \equiv \sum_{n=1}^{\infty} \frac{z^n}{n^q} .$$

- *Ideal Fermi gas*: The Fermi distribution is $n(\varepsilon) = f(\varepsilon - \mu) = 1\big/\big(e^{(\varepsilon-\mu)/k_{\mathrm{B}}T} + 1\big)$. At $T = 0$, this is a step function: $n(\varepsilon) = \Theta(\mu - \varepsilon)$, and $n = \int\limits_{-\infty}^{\mu} d\varepsilon\, g(\varepsilon)$. The chemical potential at $T = 0$ is called the *Fermi energy*: $\mu(T = 0, n) = \varepsilon_{\mathrm{F}}(n)$. If the dispersion is $\varepsilon(\boldsymbol{k})$, the locus of $\boldsymbol{k}$ values satisfying $\varepsilon(\boldsymbol{k}) = \varepsilon_{\mathrm{F}}$ is called the *Fermi surface*. For an isotropic and monotonic dispersion $\varepsilon(k)$, the Fermi surface is a sphere of radius k_{F}, the *Fermi wavevector*. For isotropic three-dimensional systems, $k_{\mathrm{F}} = (6\pi^2 n/\mathsf{g})^{1/3}$.

- *Sommerfeld expansion*: Let $\phi(\varepsilon) = \varPhi'(\varepsilon)$. Then

$$\int\limits_{-\infty}^{\infty} d\varepsilon\, f(\varepsilon - \mu)\, \phi(\varepsilon) = \pi D \csc(\pi D)\, \varPhi(\mu)$$

$$= \left\{ 1 + \frac{\pi^2}{6}\, (k_{\mathrm{B}}T)^2\, \frac{d^2}{d\mu^2} + \frac{7\pi^4}{360}\, (k_{\mathrm{B}}T)^4\, \frac{d^4}{d\mu^4} + \ldots \right\} \varPhi(\mu) \quad ,$$

where $D = k_{\mathrm{B}}T\, \frac{d}{d\mu}$. One then finds, for example, $C_V = \gamma V T$ with $\gamma = \frac{1}{3}\pi^2 k_{\mathrm{B}}^2\, g(\varepsilon_{\mathrm{F}})$. Note that nonanalytic terms proportional to $\exp(-\mu/k_{\mathrm{B}}T)$ are invisible in the Sommerfeld expansion.

6 Interacting Classical Systems : Summary

- *Lattice-based models*: Amongst the many lattice-based models of physical interest are

$$\begin{aligned}
\hat{H}_{\text{Ising}} &= -J\sum_{\langle ij\rangle}\sigma_i\,\sigma_j - H\sum_i \sigma_i &&;\qquad \sigma_i \in \{-1,+1\}\\
\hat{H}_{\text{Potts}} &= -J\sum_{\langle ij\rangle}\delta_{\sigma_i,\sigma_j} - H\sum_i \delta_{\sigma,1} &&;\qquad \sigma_i \in \{1,\ldots,q\}\\
\hat{H}_{\mathsf{O}(n)} &= -J\sum_{\langle ij\rangle}\hat{\boldsymbol{n}}_i\cdot\hat{\boldsymbol{n}}_j - \boldsymbol{H}\cdot\sum_i \hat{\boldsymbol{n}}_i &&;\qquad \hat{\boldsymbol{n}}_i \in S^{n-1}\quad .
\end{aligned}$$

Here J is the coupling between neighboring sites and H (or $\boldsymbol{H}$) is a polarizing field which breaks a global symmetry (groups $\mathbb{Z}_2$, $\mathcal{S}_q$, and $\mathsf{O}(n)$, respectively). $J > 0$ describes a ferromagnet and $J < 0$ an antiferromagnet. One can generalize to include further neighbor interactions, described by a matrix of couplings J_{ij}. When $J = 0$, the degrees of freedom at each site are independent, and $Z(T, N, J = 0, H) = \zeta^N$, where $\zeta(T, H)$ is the single site partition function. When $J \neq 0$ it is in general impossible to compute the partition function analytically, except in certain special cases.

- *Transfer matrix solution in $d = 1$*: One such special case is that of one-dimensional systems. In that case, one can write $Z = \mathsf{Tr}(R^N)$, where R is the *transfer matrix*. Consider a general one-dimensional model with nearest-neighbor interactions and Hamiltonian

$$\hat{H} = -\sum_n U(\alpha_n, \alpha_{n+1}) - \sum_n W(\alpha_n) \quad ,$$

where α_n describes the local degree of freedom, which could be discrete or continuous, single component or multi-component. Then

$$R_{\alpha\alpha'} = e^{U(\alpha,\alpha')/k_{\text{B}}T}\, e^{W(\alpha')/k_{\text{B}}T} \quad .$$

The form of the transfer matrix is not unique, although its eigenvalues are. We could have taken $R_{\alpha\alpha'} = e^{W(\alpha)/2k_{\text{B}}T}\, e^{U(\alpha,\alpha')/k_{\text{B}}T}\, e^{W(\alpha')/2k_{\text{B}}T}$, for example. The interaction matrix $U(\alpha, \alpha')$ may or may not be symmetric itself. On a ring of N sites, one has $Z = \sum_{i=1}^{K} \lambda_i^N$, where $\{\lambda_i\}$ are the eigenvalues and K the rank of R. In the thermodynamic limit, the partition function is dominated by the eigenvalue with the largest magnitude.

- *Higher dimensions*: For one-dimensional classical systems with finite range interactions, the thermodynamic properties vary smoothly with temperature for all $T > 0$. The *lower critical dimension* d_ℓ of a model is the dimension at or below which there is no finite temperature phase transition. For models with discrete global symmetry groups, $d_\ell = 1$, while for continuous global symmetries $d_\ell = 2$. In zero external field the ($d = 2$) square lattice Ising model has a critical temperature $T_{\text{c}} = 2.269\,J$. On the honeycomb lattice, $T_{\text{c}} = 1.519\,J$. For the $\mathsf{O}(3)$ model on the cubic lattice, $T_{\text{c}} = 4.515\,J$. In general, for unfrustrated systems, one expects for $d > d_\ell$ that $T_{\text{c}} \propto z$, where z is the *lattice coordination number* (*i.e.* number of nearest neighbors).

- *Nonideal classical gases*: For $\hat{H} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j} u\big(|\boldsymbol{x}_i - \boldsymbol{x}_j|\big)$, one has $Z(T,V,N) = \lambda_T^{-Nd}\, Q_N(T,V)$, where

$$Q_N(T,V) = \frac{1}{N!} \int \! d^d\!x_1 \cdots \int \! d^d\!x_N \prod_{i<j} e^{-u(r_{ij})/k_{\rm B}T}$$

is the *configuration integral*. For the one-dimensional *Tonks gas* of N hard rods of length a confined to the region $x \in [0, L]$, one finds $Q_N(T,L) = (L - Na)^N$, whence the equation of state $p = nk_{\rm B}T/(1 - na)$. For more complicated interactions, or in higher dimensions, the configuration integral is analytically intractable.

- *Mayer cluster expansion*: Writing the *Mayer function* $f_{ij} \equiv e^{-u_{ij}/k_{\rm B}T} - 1$, and assuming $\int \! d^d\!r\, f(r)$ is finite, one can expand the pressure $p(T,z)$ and $n(T,z)$ as power series in the fugacity $z = \exp(\mu/k_{\rm B}T)$, *viz.*

$$\begin{aligned} p/k_{\rm B}T &= \lambda_T^{-d} \sum_\gamma z^{n_\gamma}\, b_\gamma \\ n &= \lambda_T^{-d} \sum_\gamma n_\gamma\, z^{n_\gamma}\, b_\gamma \quad . \end{aligned}$$

The sum is over *unlabeled connected clusters* γ, and n_γ is the number of vertices in γ. The *dimensionless cluster integral* $b_\gamma(T)$ is obtained by assigning labels $\{1, \ldots n_\gamma\}$ to all the vertices, and computing

$$b_\gamma(T) \equiv \frac{1}{s_\gamma} \int \frac{d^d\!x_1}{\lambda_T^d} \cdots \int \frac{d^d\!x_{n_\gamma - 1}}{\lambda_T^d} \prod_{i<j}^{\gamma} f_{ij} \quad ,$$

where f_{ij} appears in the product if there is a link between vertices i and j. s_γ is the *symmetry factor* of the cluster, defined to be the number of elements from the symmetric group $\mathcal{S}_{n_\gamma}$ which, acting on the labels, would leave the product $\prod_{i<j}^{\gamma} f_{ij}$ invariant. By definition, a cluster consisting of a single site has $b_\bullet = 1$. Translational invariance implies $b_\gamma(T) \propto V^0$. One then inverts $n(T,z)$ to obtain $z(T,n)$, and inserting the result into the equation for $p(T,z)$ one obtains the *virial expansion* of the equation of state,

$$p = nk_{\rm B}T \Big\{ 1 + B_2(T)\, n + B_3(T)\, n^2 + \ldots \Big\} \quad .$$

where

$$B_k(T) = -(k-1)\, \lambda_T^{(k-1)d} \sum_{\gamma \in \varGamma_k} b_\gamma(T)$$

is the $k^{\rm th}$ *virial coefficient* and the sum over γ is limited to the set $\varGamma_k$ of all *one-particle irreducible k-site* clusters. A one-particle irreducible cluster is a connected cluster which does not break apart into more than one piece if any of its sites and all of that site's connecting links are removed from the graph. Any site whose removal, along with all its connecting links, would result in a disconnected graph is called an *articulation point*. Irreducible clusters have no articulation points.

• *Liquids*: In the ordinary canonical ensemble,

$$P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) = Q_N^{-1}\cdot\frac{1}{N!}\,e^{-\beta W(\boldsymbol{x}_1,\,\ldots\,,\boldsymbol{x}_N)} \quad ,$$

where W is the total potential energy, and Q_N is the configuration integral,

$$Q_N(T,V) = \frac{1}{N!}\int\! d^dx_1\cdots\int\! d^dx_N\; e^{-\beta W(\boldsymbol{x}_1,\,\ldots\,,\boldsymbol{x}_N)} \quad .$$

We can use P, or its grand canonical generalization, to compute thermal averages, such as the average local density

$$\begin{aligned} n_1(\boldsymbol{r}) &= \Big\langle \sum_i \delta(\boldsymbol{r}-\boldsymbol{x}_i)\Big\rangle \\ &= N\!\int\! d^dx_2\cdots\int\! d^dx_N\; P(\boldsymbol{r},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N) \end{aligned}$$

and the two particle density matrix, two-particle density matrix $n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is defined by

$$\begin{aligned} n_2(\boldsymbol{r}_1,\boldsymbol{r}_2) &= \Big\langle \sum_{i\neq j} \delta(\boldsymbol{r}_1-\boldsymbol{x}_i)\,\delta(\boldsymbol{r}_2-\boldsymbol{x}_j)\Big\rangle \\ &= N(N-1)\!\int\! d^dx_3\cdots\int\! d^dx_N\; P(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{x}_3,\ldots,\boldsymbol{x}_N) \quad . \end{aligned}$$

• *Pair distribution function*: For translationally invariant simple fluids consisting of identical point particles interacting by a two-body central potential $u(r)$, the thermodynamic properties follow from the behavior of the *pair distribution function* (pdf),

$$g(r) = \frac{1}{Vn^2}\,\Big\langle \sum_{i\neq j} \delta(\boldsymbol{r}-\boldsymbol{x}_i+\boldsymbol{x}_j)\Big\rangle \,,$$

where V is the total volume and $n = N/V$ the average density. The average energy per particle is then

$$\varepsilon(n,T) = \frac{\langle E\rangle}{N} = \tfrac{3}{2}\,k_{\rm B}T + 2\pi n\!\int\limits_0^\infty\! dr\; r^2\, g(r)\, u(r) \quad .$$

Here $g(r)$ is implicitly dependent on n and T as well In the grand canonical ensemble, the pdf satisfies the *compressibility sum rule*, $\int\! d^3\!r\,\big[g(r)-1\big] = k_{\rm B}T\,\kappa_T - n^{-1}$, where κ_T is the isothermal compressibility. Note $g(\infty)=1$. The pdf also implies the *virial equation of state*,

$$p = nk_{\rm B}T - \tfrac{2}{3}\pi n^2\!\int\limits_0^\infty\! dr\; r^3\, g(r)\, u'(r) \quad .$$

• *Scattering*: Scattering experiments are sensitive to momentum transfer $\hbar\boldsymbol{q}$ and energy transfer $\hbar\omega$, and allow determination of the *dynamic structure factor*

$$\begin{aligned}
S(\boldsymbol{q},\omega) &= \frac{1}{N}\int\limits_{-\infty}^{\infty}\!dt\, e^{i\omega t}\,\big\langle \sum_{l,l'} e^{i\boldsymbol{q}\cdot\boldsymbol{x}_l(0)}\, e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_{l'}(t)}\big\rangle_T \\
&= \frac{2\pi\hbar}{N}\sum_i P_i\,\sum_j \big|\langle\, j\,|\sum_{l=1}^{N} e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_l}\,|\, i\,\rangle\big|^2\,\delta(E_j - E_i + \hbar\omega) \quad ,
\end{aligned}$$

where $|\, i\,\rangle$ and $|\, j\,\rangle$ are (quantum) states of the system being studied, and P_i is the equilibrium probability for state i.[1] Integrating over all frequency, one obtains the *static structure factor*,

$$\begin{aligned}
S(\boldsymbol{q}) &= \int\limits_{-\infty}^{\infty}\!\frac{d\omega}{2\pi}\,S(\boldsymbol{q},\omega) = \frac{1}{N}\sum_{l,l'}\big\langle e^{i\boldsymbol{q}\cdot(\boldsymbol{x}_l-\boldsymbol{x}_{l'})}\big\rangle \\
&= N\,\delta_{\boldsymbol{q},0} + 1 + n\!\int\!d^d\!r\, e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\,\big[g(r)-1\big] \quad .
\end{aligned}$$

• *Theories of fluid structure* – The BBGKY hierarchy is set of coupled integrodifferential equations relating k- and $(k+1)$-particle distribution functions. In order to make progress, a truncation must be performed, expressing higher order distributions in terms of lower order ones. This results in various theories of fluids, known by their defining equations for the pdf $g(r)$. Examples include the Born-Green-Yvon equation, the Percus-Yevick equation, the hypernetted chains equation, the Ornstein-Zernike approximation, *etc.* Except in the simplest cases (such as the OZ approximation), these equations must be solved numerically. OZ approximation deserves special mention. There we write $S(\boldsymbol{q}) \approx \frac{1}{(R/\xi)^2+R^2\boldsymbol{q}^2}$ for small q, where $\xi(T)$ is the *correlation length* and $R(T)$ is related to the range of interactions.

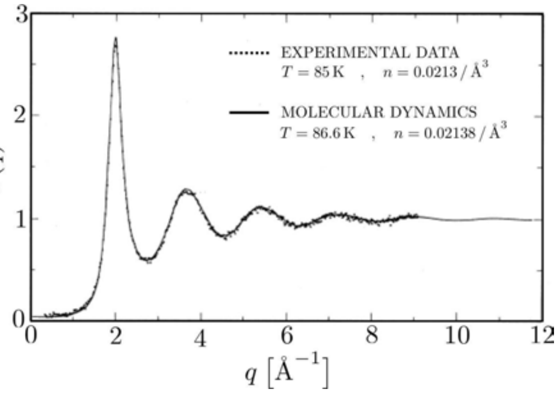

Figure 1: Comparison of the static structure factor as determined by neutron scattering work of J. L. Yarnell *et al.*, *Phys. Rev. A* **7**, 2130 (1973) with molecular dynamics calculations by Verlet (1967) for a Lennard-Jones fluid.

• *Debye-Hückel theory* – Due to the long-ranged nature of the Coulomb interaction, the Mayer function decays so slowly as $r \to \infty$ that it is not integrable, so the virial expansion is problematic. Progress can be made by a self-consistent mean field approach. For a system consisting of charges $\pm e$, one assumes a local electrostatic potential $\phi(\boldsymbol{r})$. Boltzmann

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[1] In practice, what is measured is $S(q,\omega)$ convolved with spatial and energy resolution filters appropriate to the measuring apparatus.

statistics then gives a charge density

$$\rho(\boldsymbol{r}) = e\lambda_+^{-d} z_+ \, e^{-e\,\phi(\boldsymbol{r})/k_B T} - e\lambda_-^{-d} z_- \, e^{e\,\phi(\boldsymbol{r})/k_B T} \quad ,$$

where $\lambda_\pm$ and $z_\pm$ are the thermal de Broglie wavelengths and fugacities for the $+$ and $-$ species. Assuming overall charge neutrality at infinity, one has $\lambda_+^{-d} z_+ = \lambda_-^{-d} z_- = n_\infty$, and we have $\rho(\boldsymbol{r}) = -2en_\infty \, \sinh\big(e\,\phi(\boldsymbol{r})/k_B T\big)$. The local potential is then determined self-consistently, using Poisson's equation:

$$\nabla^2\phi = 8\pi e n_\infty \, \sinh(e\phi/k_B T) - 4\pi\rho_{\text{ext}} \quad .$$

If $e\phi \ll k_B T$, we can expand the sinh function to obtain $\nabla^2\phi = \kappa_D^2\,\phi - 4\pi\rho_{\text{ext}}$, where the *Debye screening wavevector* is $\kappa_D = (8\pi n_\infty e^2/k_B T)^{1/2}$. The self-consistent potential arising from a point charge $\rho_{\text{ext}}(\boldsymbol{r}) = Q\,\delta(\boldsymbol{r})$ is then of the Yukawa form $\phi(\boldsymbol{r}) = Q\exp(-\kappa_D r)/r$ in three space dimensions.

- *Thomas-Fermi screening* – In an electron gas with $k_B T \ll \varepsilon_F$, we may take $T = 0$. If the Fermi energy is constant, we write $\varepsilon_F = \frac{\hbar^2 k_F^2(\boldsymbol{r})}{2m} - e\,\phi(\boldsymbol{r})$, and local electron number density is $n(\boldsymbol{r}) = k_F^3(\boldsymbol{r})/3\pi^2$. Assuming a compensating smeared positive charge background $\rho_+ = e\,n_\infty$, Poisson's equation takes the form

$$\nabla^2\phi = 4\pi e\, n_\infty \cdot \left\{ \left(1 + \frac{e\phi(\boldsymbol{r})}{\varepsilon_F}\right)^{3/2} - 1 \right\} - 4\pi\rho_{\text{ext}}(\boldsymbol{r}) \quad .$$

If $e\phi \ll \varepsilon_F$, we expand in the presence of external sources to obtain $\nabla^2\phi = \kappa_{TF}^2\,\phi - 4\pi\rho_{\text{ext}}$, where $\kappa_{TF} = (6\pi n_\infty e^2/\varepsilon_F)^{1/2}$ is the *Thomas-Fermi screening wavevector*. In metals, where the electron dispersion is a more general function of crystal momentum, the density response to a local potential $\phi(\boldsymbol{r})$ is $\delta n(\boldsymbol{r}) = e\,\phi(\boldsymbol{r})\,g(\varepsilon_F)$ to lowest order, where $g(\varepsilon_F)$ is the density of states at the Fermi energy. One then finds $\kappa_{TF} = \sqrt{4\pi e^2 g(\varepsilon_F)}$.

7 Mean Field Theory of Phase Transitions : Summary

• *van der Waals system*: The van der Waals equation of state may be written $p = \frac{RT}{v-b} - \frac{a}{v^2}$, where v is the molar volume. Comparing with the ideal gas law $p = RT/v$, the vdW equation accounts for (i) an excluded volume effect due to finite molecular size, and (ii) a long-distance attraction between molecules. The energy per mole is $\varepsilon(T,v) = \frac{1}{2}\mathrm{f}RT - \frac{a}{v}$, where f is the number of independent quadratic terms in the individual molecular Hamiltonian. At fixed T, $p(v)$ is monotonic and decreasing for sufficiently large T, *i.e.* $T > T_{\mathrm{c}}$. For $T < T_{\mathrm{c}}$, the pressure is no longer monotonic, and $p'(v)$ vanishes at two points $v_{\pm}(T)$. For $v \in [v_-, v_+]$, the isothermal compressibility $\kappa_T = -v^{-1}(\partial v/\partial p)_T$ is negative, indicating an absolute thermodynamic instability. From $p(v,T)$ and $\varepsilon(v,T)$, one can derive the molar free energy

$$f(T,v) = -RT\ln\big(T^{\mathrm{f}/2}(v-b)\big) - \frac{a}{v} - Ts_0$$

where s_0 is a constant. Analyzing $f(T,v)$, one finds an even wider range of instability applies, with $v_\ell < v_- < v_+ < v_g$, where the extremal liquid and gas volumes are determined by the coupled equations

$$p(T,v_\ell) = p(T,v_g) \qquad , \qquad \int\limits_{v_\ell}^{v_g} dv\, p(T,v) = \big(v_g - v_\ell\big)\, p(T,v_\ell) \quad .$$

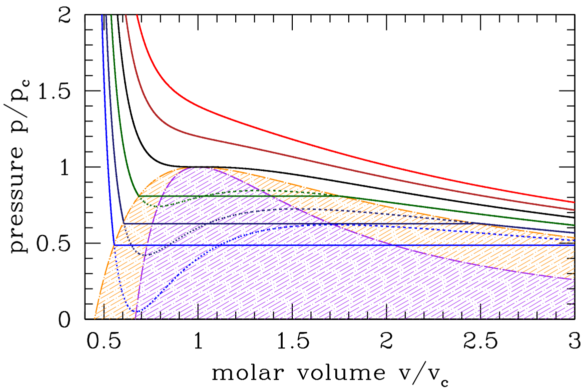

Figure 1: Pressure-volume isotherms for the van der Waals system, corrected to account for the Maxwell construction. Orange region: nucleation. Purple region: spinodal decomposition.

The *Maxwell construction* extends $f(T,v)$ by a straight line connecting $f(T,v_\ell)$ and $f(T,v_g)$, resulting in the isotherms in Fig. 1. This corresponds to a *two phase region* in which the homogeneous phase is unstable, either to *nucleation*, which requires surmounting an energy barrier, or *spinodal composition*, which is a spontaneous process. The *critical point* $(v_{\mathrm{c}}, T_{\mathrm{c}})$ is given by the simultaneous solution to the equations $\partial p/\partial v = 0$ and $\partial^2 p/\partial v^2 = 0$, which defines a saddle-node bifurcation in the extrema of $p(v)$ at fixed T. This yields $T_{\mathrm{c}} = 8a/27bR$ and $v_{\mathrm{c}} = 3b$. Plugging these into the vdW equation of state, we find $p_{\mathrm{c}} = a/27b^2$.

• *Lattice gas model*: For interactions consisting of a hard core and a weakly attractive tail, such as the Lennard-Jones potential, one can imagine discretizing space into unit cells on the scale of the core size a. Each cell i can then accommodate either zero or one particle. The resulting Hamiltonian is an Ising ferromagnet,

$$\hat{H} = -\sum_{i<j} J_{ij}\, \sigma_i \sigma_j - H \sum_i \sigma_i \quad ,$$

with $\sigma_i = \pm 1$, $J_{ij} = -\frac{1}{4}V(\boldsymbol{R}_i - \boldsymbol{R}_j)$, and $H = \frac{1}{2}k_{\mathrm{B}}T\ln\big(e^{\mu/k_{\mathrm{B}}T}\lambda_T^{-d}a^d\big)$. The correspondences between the ferromagnet and the liquid-gas system are then v (or n) $\leftrightarrow$ m, with $m =$

M/N the magnetization per site, and p (or μ) $\leftrightarrow$ H. The isothermal compressibility κ_T is analogous to the isothermal magnetic susceptibility $\chi_T = \big(\frac{\partial m}{\partial H}\big)_T$. At the critical point, $\kappa_T(T_c, p_c) = \infty \leftrightarrow \chi_T(T_c, H_c) = \infty$. See Fig. 2.

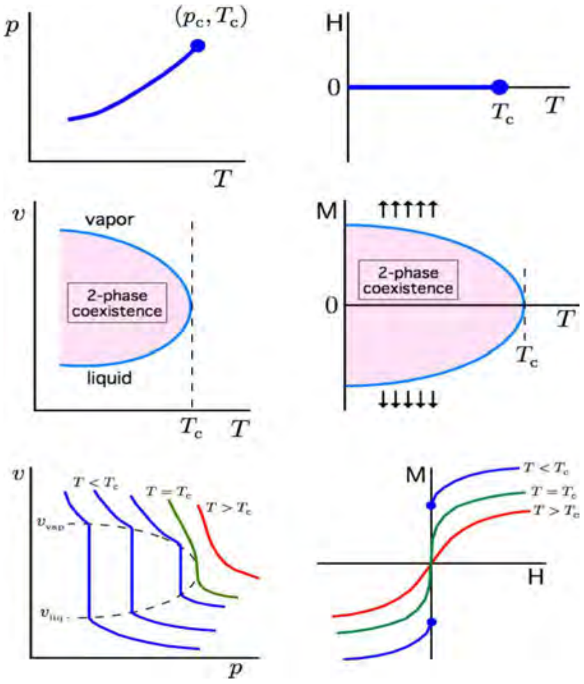

Figure 2: Comparison of the liquid-gas phase diagram with that of the Ising ferromagnet.

- *Mean field theory*: Consider the Ising model, $\hat{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i$. On each site i, write $\sigma_i = m + \delta\sigma_i$, where $m = \langle \sigma_i \rangle$. Then $\sigma_i \sigma_j = -m^2 + m\,(\sigma_i + \sigma_j) + \delta\sigma_i\,\delta\sigma_j$, and neglecting the term quadratic in the fluctuations, we arrive at the *mean field Hamiltonian*,

$$\hat{H}_{\rm MF} = \tfrac{1}{2} N z J\, m^2 - \big(H + zJm\big) \sum_i \sigma_i \quad ,$$

where z is the lattice coordination number. This corresponds to independent spins in an effective field $H_{\rm eff} = H + zJm$. For non-interacting spins in an external field, we have $m = \tanh(H_{\rm eff}/k_{\rm B}T)$, *i.e.*

$$m = \tanh\!\bigg(\frac{H + zJm}{k_{\rm B}T}\bigg) \quad ,$$

which is a self-consistent equation for $m(T, H)$. This equation also follows from extremizing the mean field free energy, given by $F = -k_{\rm B}T \ln {\sf Tr}\, e^{-\hat{H}_{\rm MF}/k_{\rm B}T}$. It is convenient to dimensionalize by writing $f = F/zJN$, $h = H/zJ$, and $\theta = k_{\rm B}T/zJ$. Then

$$\begin{aligned} f(m, T, h) &= \tfrac{1}{2} m^2 - \theta \ln\cosh\!\bigg(\frac{m+h}{\theta}\bigg) - \theta \ln 2 \\ &= f_0 + \tfrac{1}{2}\,(\theta - 1)\, m^2 + \tfrac{1}{12} m^4 - hm + \ldots \quad , \end{aligned}$$

where the second line is an expansion for small m and h. The dimensionless mean field equation is $m = \tanh\big((m+h)/\theta\big)$. When $h = 0$, we have $m = \tanh(m/\theta)$, and for $\theta > \theta_c$, where $\theta_c = 1$ (*i.e.* $T_c = zJ/k_{\rm B}$), there is only one solution at $m = 0$. For $\theta < \theta_c$, there are two additional *broken symmetry solutions* at $m = \pm m_0$, and one can check that they correspond to minima in the free energy, whereas $m = 0$ is a local maximum. Just below θ_c, one finds $m(\theta) = \sqrt{3(1-\theta)} \propto (\theta_c - \theta)^\beta$, where $\beta = \frac{1}{2}$ is the mean field order parameter exponent.

An *order parameter* is a quantity which vanishes throughout a disordered phase, usually at high temperature, but which *spontaneously* breaks a global symmetry to take a finite value in the ordered phase. For the Ising ferromagnet, the order parameter is m, the local magnetization. The global symmetry of the Ising model in zero external field is the $\mathbb{Z}_2$ symmetry associated with flipping all the spins: $\sigma_i \to -\sigma_i$ for all i. An external field

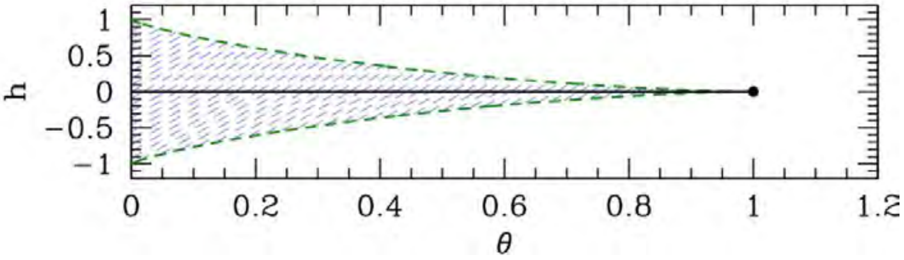

Figure 3: Phase diagram for the Ising ferromagnet. In the hatched blue region, the mean field equations have three solutions. Along the boundary dashed green line, where is a saddle-node bifurcation so that there is a unique solution to the MF equations in the white region. The thermodynamic properties are singular, with discontinuous magnetization, along the solid black line, which terminates in the critical point at $(\theta, h) = (1, 0)$.

explicitly breaks this symmetry. For a given system, there may be several distinct ordered phases and a cascade of symmetry-breaking transitions as temperature is lowered.

Again setting $h = 0$, we see that $f(\theta > \theta_c) = f_0$, while $f(\theta < \theta_c) = f_0 - \frac{3}{4}(\theta_c - \theta)^2$ just below the transition. Thus, there is a jump in the specific heat $c = -\theta\,\frac{\partial^2 f}{\partial\theta^2}$ at the transition, with $\Delta c = -\frac{3}{2}$. Very close to the transition, we therefore have $c(T) \propto |\theta - \theta_c|^{-\alpha}$, where the mean field value of the exponent is $\alpha = 0$.

As we increase $|h|$ from zero, two of the solutions merge and eventually annihilate at $h^*(\theta)$, leaving a unique solution for $h > h^*(\theta)$, as depicted in Fig. 3. For small m and h,, setting $\frac{\partial f}{\partial m} = 0$, we obtain $\frac{1}{3}m^3 + (\theta - 1)\,m - h = 0$. Thus, when θ is just above $\theta_c = 1$, we have $m = h/(\theta - 1)$, hence the susceptibility is $\chi = \frac{\partial m}{\partial h} \propto |\theta - \theta_c|^{-\gamma}$, where $\gamma = 1$ is the mean field susceptibility exponent. The same power law behavior is found for $\theta < \theta_c$; one finds $m(\theta) = m_0(\theta) + \frac{h}{2(1-\theta)}$. Finally, if we fix $\theta = \theta_c$, we have $m(\theta_c, h) \propto h^{1/\delta}$ with $\delta = 3$. The quantities α, β, γ, and δ are *critical exponents* for the Ising transition. Mean field theory becomes exact when the number of neighbors is infinite, which arises in two hypothetical settings: (i) infinite range interactions, or (ii) infinite spatial dimension.

A phenomenological model for magnetization dynamics takes $\frac{\partial m}{\partial t} = -\frac{\partial f}{\partial m}$, so m is dissipatively driven to a local minimum of the free energy. This is a simple dynamical system with control parameters (θ, h). For $h = 0$, the point $\theta = \theta_c$ corresponds to a supercritical pitchfork bifurcation, and more generally there is an imperfect bifurcation everywhere along the curve $h = h^*(\theta)$, defined by the simultaneous vanishing of both $\partial f/\partial m$ and $\partial^2 f/\partial m^2$, corresponding to the dashed green curve in Fig. 3. This leads to the phenomenon of *hysteresis*: a protocol in which the control parameters cross both branches of this curve is *irreversible*.

• *Variational density matrix*: The free energy is given by $F = \mathsf{Tr}\,(\varrho\hat{H}) + k_B T\,\mathsf{Tr}\,(\varrho \ln \varrho)$. Extremizing F with respect to ϱ subject to the normalization condition $\mathsf{Tr}\;\varrho = 1$ yields the equilibrium Gibbs distribution $\varrho = Z^{-1}e^{-\beta\hat{H}}$. Any distribution other than that of Gibbs will yield a larger value of F. Therefore, we can construct a variational *Ansatz* for ϱ and minimize F with respect to its variational parameters. For example, in the case of the Ising model $\hat{H} = -\sum_{i<j} J_{ij}\, \sigma_i\, \sigma_j - H \sum_i \sigma_i$, then assuming translational invariance $J_{ij} = J\big(|\boldsymbol{R}_i - \boldsymbol{R}_j|\big)$, we write $\varrho_{\rm var}(\sigma_1, \ldots, \sigma_N) = \prod_{i=1}^N \tilde{\varrho}(\sigma_i)$, with

$$\tilde{\varrho}(\sigma) = \bigg(\frac{1+m}{2}\bigg)\, \delta_{\sigma,1} + \bigg(\frac{1-m}{2}\bigg)\, \delta_{\sigma,-1} \quad .$$

Adimensionalizing by writing $\theta = k_{\rm B}T/\hat{J}(0)$ and $h = H/\hat{J}(0)$ with $\hat{J}(0) = \sum_j J_{ij}$, one finds the variational free energy is

$$\begin{aligned} f(m, \theta, h) &= -\tfrac{1}{2}\, m^2 - hm + \theta\, \bigg\{ \bigg(\frac{1+m}{2}\bigg) \ln \bigg(\frac{1+m}{2}\bigg) + \bigg(\frac{1-m}{2}\bigg) \ln \bigg(\frac{1-m}{2}\bigg) \bigg\} \\ &= -\theta\, \ln 2 - hm + \tfrac{1}{2}\, (\theta - 1)\, m^2 + \tfrac{\theta}{12}\, m^4 + \tfrac{\theta}{30}\, m^6 + \ldots \end{aligned}$$

Extremizing with respect to m yields the same equation as before: $m = \tanh\big((m+h)/\theta\big)$. One can prove that this variational density matrix formulation of mean field theory yields identical results to the ”neglect of fluctuations” method described above.

• *Landau theory of phase transitions*: The basic idea is to write a phenomenological expansion of the free energy in powers of the order parameter(s) of a system, with coefficients depending on quantities such as temperature and field, and keeping terms only up to some low order. On then analyzes how the minima of the resulting finite degree polynomial behave as a function of these coefficients. The simplest case is that of a model with Ising symmetry, where the order parameter is a real scalar quantity m. One writes

$$f = f_0 + \tfrac{1}{2} a m^2 + \tfrac{1}{4} b m^4 - hm \quad ,$$

with $b > 0$ for stability. Extremizing with respect to m yields $am + bm^3 - h = 0$. For $a > 0$ there is a unique solution to this equation for $m(h)$, but for $a < 0$ there are three roots when $|h| < h^*(a)$, with $h^*(a) = \frac{2}{3^{3/2}}\, b^{-1/2}\, (-a)^{3/2}$. For $h = 0$, one has $m(a > 0) = 0$ and $m(a < 0) = \pm\sqrt{-a/b}$. Thus, $a_{\rm c} = 0$ is the critical point in zero field.

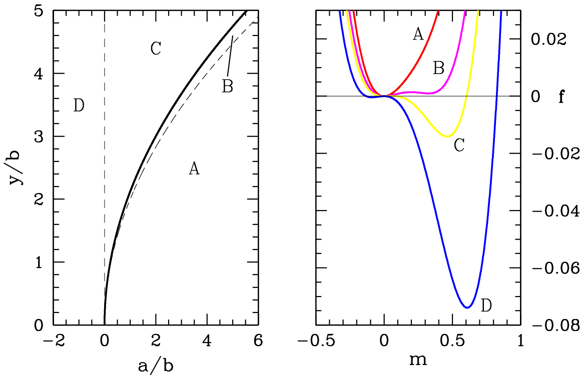

Figure 4: Behavior of the quartic free energy $f(m) = \frac{1}{2}am^2 - \frac{1}{3}ym^3 + \frac{1}{4}bm^4$. A: $y^2 < 4ab$; B: $4ab < y^2 < \frac{9}{2}ab$; C and D: $y^2 > \frac{9}{2}ab$. The thick black line denotes a line of first order transitions, where the order parameter is discontinuous.

For certain systems, such as the liquid-gas transition, there is no true Ising symmetry between the two homogeneous phases. The order parameter, which can taken to be proportional to the density relative to that at the critical point, is again a real scalar. With no $\mathbb{Z}_2$ symmetry, we write

$$f = f_0 + \tfrac{1}{2} a m^2 - \tfrac{1}{3} y m^3 + \tfrac{1}{4} b m^4 \quad ,$$

with $b > 0$ and $y > 0$. Extremizing yields $(a - ym + bm^2)\, m = 0$, which has three roots, one at $m = 0$ and the other two at $m = m_\pm \equiv \frac{y}{2b} \pm \sqrt{\big(\frac{y}{2b}\big)^2 - \frac{a}{b}}$. The situation is as depicted in Fig. 4. For $y^2 > 4ab$ only

the $m=0$ root is real. For $4ab < y^2 < \frac{9}{2}ab$,
all three roots are real, but the minimum of f remains at $m=0$. For $y^2 > \frac{9}{2}ab$, all three roots are real, with a global minimum at $m = m_+$ and a local one at $m = m_-$. Thus, along the curve $y^2 = \frac{9}{2}ab$, there is a discontinuous change in the order parameter, between $m=0$ and $m = 3a/y$, which is the hallmark of a *first order phase transition*. Note that this occurs for $a > 0$, before the coefficient of the quadratic term in $f(m)$ has changed sign. One says in this case that the first order transition *preempts* the second order one.

• *Mean field theory of fluctuations*: For the Ising model, $\hat{H} = -\sum_{i<j} J_{ij}\,\sigma_i\,\sigma_j - \sum_i H_i\,\sigma_i$, now with local fields H_i, the local magnetization is $m_i = \langle\sigma_i\rangle = -\frac{\partial F}{\partial H_i}$. The susceptibility, given by $\chi_{ij} = \frac{\partial m_i}{\partial H_j}$, is an example of a thermodynamic *response function*. In equilibrium, it is related to the *correlation function*,

$$C_{ij} \equiv \langle\sigma_i\,\sigma_j\rangle - \langle\sigma_i\rangle\,\langle\sigma_j\rangle \quad ,$$

with $C_{ij} = k_{\rm B}T\,\chi_{ij}$. Within mean field theory, this relation no longer applies, and it is the response functions which are more accurately represented: the usual MF description treats each site as independent, hence $C^{\rm MF}_{ij} = 0$ (!) To compute $\chi^{\rm MF}_{ij}$, take a variational density matrix which is a product of single-site ones, as above, where the local magnetization is m_i. Extremizing the resulting free energy with respect to each m_i yields a set of coupled nonlinear equations,

$$m_i = \tanh\!\left(\frac{\sum_j J_{ij}\,m_j + H_i}{k_{\rm B}T}\right) \quad .$$

Expanding for small fields and magnetizations, one obtains $\sum_j \big(k_{\rm B}T\,\delta_{ij} - J_{ij}\big)\,m_j = H_i$, hence $\chi_{ij} = \frac{\partial m_i}{\partial H_j} = \big(k_{\rm B}T\cdot\mathbb{I} - \mathbb{J}\big)^{-1}_{ij}$. For translationally invariant systems, the eigenvectors of the matrix J_{ij} are plane waves $\psi_{\boldsymbol{q},i} = e^{i\boldsymbol{q}\cdot\boldsymbol{R}_i}$, and one has

$$\hat{m}(\boldsymbol{q}) = \frac{\hat{H}(\boldsymbol{q})}{k_{\rm B}T - \hat{J}(\boldsymbol{q})} \qquad \Rightarrow \qquad \hat{\chi}(\boldsymbol{q}) = \frac{\partial\hat{m}(\boldsymbol{q})}{\partial\hat{H}(\boldsymbol{q})} = \frac{1}{k_{\rm B}T - \hat{J}(\boldsymbol{q})} \quad ,$$

where $\hat{J}(\boldsymbol{q}) = \sum_{\boldsymbol{R}} J(\boldsymbol{R})\,e^{-i\boldsymbol{q}\cdot\boldsymbol{R}}$. The mean field value of $T_{\rm c}$ is then $\hat{J}(\boldsymbol{Q})$, where $\boldsymbol{q} = \boldsymbol{Q}$ is the *ordering wavevector* which maximizes $\hat{J}(\boldsymbol{q})$. For a ferromagnet, which is dominated by positive values of J_{ij}, one has $\boldsymbol{Q} = 0$, and expanding about this point one may write $\hat{J}(\boldsymbol{q}) = k_{\rm B}T_{\rm c} - C\boldsymbol{q}^2 + \ldots$, in which case $\chi(\boldsymbol{q}) \propto (\xi^{-2} + \boldsymbol{q}^2)^{-1}$ at long wavelengths, which is of the *Ornstein-Zernike (OZ) form*.

• *Global symmetries*: A global symmetry is an operation carried out equally at every point in space (continuous systems) or in every unit cell of the lattice (discrete systems) such that the Hamiltonian is left invariant. The symmetry operations comprise a group G. In the absence of a symmetry-breaking external field, Ising systems have symmetry group $\mathbb{Z}_2$. The p-state clock model has symmetry group $\mathbb{Z}_p$. The q-state Potts model has symmetry group $\mathcal{S}_q$ (the permutation group on q elements). In each of these cases, the group G is *discrete*. Examples of models with *continuous* symmetries include the XY model ($G = \mathsf{O}(2)$), the Heisenberg model ($G = \mathsf{O}(3)$ or $\mathsf{O}(n)$), the Standard Model of particle physics ($G = \mathsf{SU}(3) \times \mathsf{SU}(2) \times \mathsf{U}(1)$), *etc.* Depending on whether G is discrete or continuous, and on the dimension of space, there may be no ordered phase possible. The *lower critical dimension* d_ℓ of a model is the dimension at or below which there is no spontaneous symmetry breaking at any finite temperature. For systems with discrete global symmetries, $d_\ell = 1$. For systems with continuous global symmetries, $d_\ell = 2$. The *upper critical dimension* d_u is the dimension above which mean field exponents are exact. This depends on structure of the model itself, and not all models have a finite upper critical dimension.

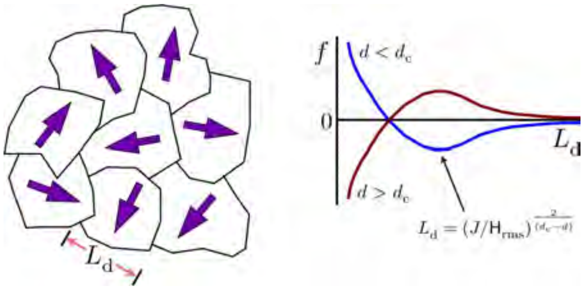

Figure 5: Left panel : Imry-Ma domains for an $\mathsf{O}(2)$ model. The arrows point in the direction of the local order parameter field $\langle \hat{\boldsymbol{\Omega}}(\boldsymbol{r}) \rangle$. Right panel : free energy density as a function of domain size L_d. Note $L_\mathrm{d} > a$ always.

- *Random systems*: A system with quenched randomness orders in a different way than a pure one. Typically the randomness may be modeled as a weak symmetry breaking field that is spatially varying, but averages to zero on large scales. Imry and Ma (1975) reasoned that such a system could try to lower its energy by forming *domains* in which the order parameter takes advantage of local fluctuations in the random field. If the size of these domains is L_d, then the rms fluctuations of the random field integrated over a single domain are proportional to $L_\mathrm{d}^{d/2}$, where d is the dimension of space. By aligning the order parameter in each domain with the direction of the average field therein, one lowers the energy by $E_\mathrm{bulk} \approx -H_\mathrm{rms}\,(L_\mathrm{d}/a)^{d/2}$ per domain, where a is a microscopic length. The surface energy of a single domain is $E_\mathrm{surf} \approx J(L_\mathrm{d}/a)^{d-\sigma}$, where $\sigma = 1$ if the global symmetry is discrete and $\sigma = 2$ if it is continuous. This follows from a simple calculation of the associated *domain wall* energy. Dividing by the number of atoms (or unit cells) in a domain $(L_\mathrm{d}/a)^d$, one obtains the energy density,

$$f \approx J\left(\frac{a}{L_\mathrm{d}}\right)^{\sigma} - H_\mathrm{rms}\left(\frac{a}{L_\mathrm{d}}\right)^{\frac{d}{2}} \quad .$$

For $d < 2\sigma$ the surface term ($\propto J$) dominates for small L_d and the bulk term for large L_d. The energy has a minimum at $L_\mathrm{d} \approx a\,(2\sigma J/dH_\mathrm{rms})^{2/(2\sigma-d)}$. *Thus, for $d < 2\sigma$ the ordered state is always unstable to domain formation in the presence of a random field.* For $d > 2\sigma$, the relevant dominance of the two terms is reversed, and the minimum becomes a maximum. There are then two possibilities, depending on the relative size of J and H_rms. The smallest allowed value for L_d is the lattice scale a, in which case $f(L_\mathrm{d} = a) \approx J - H_\mathrm{rms}$. Comparing with $f(L_\mathrm{d} = \infty) = 0$, we see that if the random field is weak, so $J > H_\mathrm{rms}$, the minimum energy state occurs for $L_\mathrm{d} = \infty$, *i.e.* the system has an ordered ground state. We then expect a finite critical temperature $T_\mathrm{c} > 0$ for a transition to a high T disordered state. If on the other hand the random field is strong and $J < H_\mathrm{rms}$, then the energy is minimized for $L_\mathrm{d} = a$, meaning the ground state of the system is disordered down to the scale of the lattice spacing. In this case there is no longer any finite temperature phase transition, because there is no ordered phase.

- *Ginzburg-Landau theory*: Allow the order parameter to vary in space. The free energy is then a *functional* of $m(\boldsymbol{x})$:

$$F\big[m(\boldsymbol{x})\,,\,h(\boldsymbol{x})\big] = \int\! d^d\!x \left\{ f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 \; - hm + \tfrac{1}{2}\kappa\,(\boldsymbol{\nabla} m)^2 + \ldots \right\} \quad .$$

Extremize F by setting the functional derivative $\delta F/\delta m(\boldsymbol{x})$ to zero, resulting in

$$am + bm^3 - hm - \kappa\,\nabla^2 m = 0 \quad .$$

For $a > 0$ and small h (take $b, c > 0$) then m is small, and one has $(a - \kappa\nabla^2)m = h$, hence $\hat{m}(\boldsymbol{q}) = \hat{h}(\boldsymbol{q})/(a + \kappa\boldsymbol{q}^2)$, which is of the OZ form. If $a < 0$, write $m(\boldsymbol{x}) = m_0 + \delta m(\boldsymbol{x})$, and for small $|a|$ find $m_0^2 = -a/3b$ and $\delta\hat{m}(\boldsymbol{q}) = \hat{h}(\boldsymbol{q})/(-2a + \kappa\boldsymbol{q}^2)$. Deeper in the ordered ($a < 0$) phase, and for $h = 0$, one can envisage a situation where $m(\boldsymbol{x})$ interpolates between the two degenerate values $\pm m_0$. Assuming the variation occurs only along one direction, one can solve $am + bm^3 - \kappa\, d^2\!m/dx^2 = 0$ to obtain $m(x) = m_0 \tanh(x/\sqrt{2}\,\xi)$, where the *coherence length* is $\xi = (\kappa/|a|)^{1/2}$.

• *Ginzburg criterion*: The actual Helmholtz free energy, which we will here call $A(T, H, V, N)$, is obtained by performing a functional integral over the order parameter field. The partition function is $Z = e^{-\beta A} = \int\! Dm\, e^{-\beta F[m(\boldsymbol{x})]}$. Near T_c, we are licensed to keep only up to quadratic terms in m and its gradients in $F[m]$, resulting in

$$A = \tfrac{1}{2}k_{\rm B}T \sum_{\boldsymbol{q}} \ln\!\left(\frac{a + \kappa\,\boldsymbol{q}^2}{\pi k_{\rm B}T}\right) \quad .$$

Let $a(t) = \alpha t$ with $t \equiv (T - T_c)/T_c$, and let Λ^{-1} be the microscopic (lattice) cutoff. The specific heat is then (for $t > 0$):

$$c = -\frac{1}{V\Lambda^d}\,T\frac{\partial^2 A}{\partial T^2} = \frac{\alpha^2\Lambda^{-d}}{2\kappa^2}\int^{\Lambda}\!\frac{d^dq}{(2\pi)^d}\;\frac{1}{(\xi^{-2} + \boldsymbol{q}^2)^2} \sim \begin{cases} \text{const.} & \text{if } d > 4 \\ -\ln t & \text{if } d = 4 \\ t^{\frac{d}{2}-2} & \text{if } d < 4 \end{cases} \quad ,$$

with $\xi = \big(\kappa/\alpha|t|\big)^{1/2} \propto |t|^{-1/2}$.

The upper critical dimension is $d_\ell = 4$. For $d > 4$, mean field theory is qualitatively accurate, with finite corrections. In dimensions $d \le 4$, the mean field result is overwhelmed by fluctuation contributions as $t \to 0^+$ (*i.e.* as $T \to T_c^+$). We see that MFT is sensible provided the fluctuation contributions are small, *i.e.* provided

$$R^{-4}\,\mathsf{a}^d\,\xi^{4-d} \ll 1 \quad , \tag{1}$$

with $R = (\kappa/\alpha)^{1/2}$, which entails $t \gg t_{\rm G}$, where

$$t_{\rm G} = \left(\frac{\mathsf{a}}{R}\right)^{\frac{2d}{4-d}} \tag{2}$$

is the *Ginzburg reduced temperature*. The criterion for the sufficiency of mean field theory, namely $t \gg t_{\rm G}$, is known as the *Ginzburg criterion*. The region $|t| < t_{\rm G}$ is known as the *critical region*. In a lattice ferromagnet, $R \sim \mathsf{a}$ is on the scale of the lattice spacing itself, hence $t_{\rm G} \sim 1$ and the critical regime is very large. Mean field theory then fails quickly as $T \to T_{\rm c}$. In a (conventional) three-dimensional superconductor, R is on the order of the Cooper pair size, and $R/\mathsf{a} \sim 10^2 - 10^3$, hence $t_{\rm G} = (a/R)^6 \sim 10^{-18} - 10^{-12}$ is negligibly narrow. The mean field theory of the superconducting transition – BCS theory – is then valid essentially all the way to $T = T_{\rm c}$.

8 Nonequilibrium and Transport Phenomena : Summary

• *Boltzmann equation*: The full phase space distribution for a Hamiltonian system, $\varrho(\boldsymbol{\varphi},t)$, where $\boldsymbol{\varphi} = \big(\{q_\sigma\},\{p_\sigma\}\big)$, satisfies $\dot{\varrho} + \dot{\boldsymbol{\varphi}} \cdot \boldsymbol{\nabla}\varrho = 0$. This is not true, however, for the one-particle distribution $\boldsymbol{f}(\boldsymbol{q},\boldsymbol{p},t)$. Rather, $\dot{f}$ is related to two-, three-, and higher order particle number distributions in a chain of integrodifferential equations known as the BBGKY hierarchy. We can lump our ignorance of these other terms into a *collision integral* and write

$$\frac{\partial f}{\partial t} = \overbrace{-\,\dot{\boldsymbol{r}} \cdot \frac{\partial f}{\partial \boldsymbol{r}} - \dot{\boldsymbol{p}} \cdot \frac{\partial f}{\partial \boldsymbol{p}}}^{\text{streaming}} + \overbrace{\bigg(\frac{df}{dt}\bigg)_{\text{coll}}}^{\text{collision}} \quad .$$

In the absence of collisions, the distribution evolves solely due to the streaming term with $\dot{\boldsymbol{r}} = \boldsymbol{p}/m$ and $\dot{\boldsymbol{p}} = -\boldsymbol{\nabla} U_{\text{ext}}$. If $\dot{\boldsymbol{p}} = \boldsymbol{F}_{\text{ext}}$ is constant, we have the general solution

$$f(\boldsymbol{r},\boldsymbol{p},t) = \phi\bigg(\boldsymbol{r} - \frac{\boldsymbol{p}\,t}{m} + \frac{\boldsymbol{F}_{\text{ext}} t^2}{2m}\,,\,\boldsymbol{p} - \frac{\boldsymbol{F}_{\text{ext}} t}{m}\bigg) \quad ,$$

valid for any initial condition $f(\boldsymbol{r},\boldsymbol{p},t=0) = \phi(\boldsymbol{r},\boldsymbol{p})$. We write the *convective derivative* as $\frac{D}{Dt} = \frac{\partial}{\partial t} + \dot{\boldsymbol{r}} \cdot \frac{\partial}{\partial \boldsymbol{r}} + \dot{\boldsymbol{p}} \cdot \frac{\partial}{\partial \boldsymbol{p}}$. Then the Boltzmann equation may be written $\frac{Df}{Dt} = \big(\frac{\partial f}{\partial t}\big)_{\text{coll}}$.

• *Collisions*: We are concerned with two types of collision processes: single-particle scattering, due to a local potential, and two-particle scattering, due to interparticle forces. Let $\varGamma$ denote the set of single particle kinematic variables, *e.g.* $\varGamma = (p_x, p_y, p_z)$ for point particles and $\varGamma = (\boldsymbol{p}, \boldsymbol{L})$ for diatomic molecules. Then

$$\bigg(\frac{df}{dt}\bigg)_{\text{coll}} = \int\! d\varGamma' \,\Big\{ w(\varGamma \,|\, \varGamma')\, f(\boldsymbol{r},\varGamma';t) - w(\varGamma' \,|\, \varGamma)\, f(\boldsymbol{r},\varGamma;t) \Big\}$$

for single particle scattering, and

$$\begin{aligned}\bigg(\frac{df}{dt}\bigg)_{\text{coll}} &= \int\! d\varGamma_1 \!\int\! d\varGamma' \!\int\! d\varGamma'_1 \,\Big\{ w\big(\varGamma\varGamma_1 \,|\, \varGamma'\varGamma'_1\big)\, f_2(\boldsymbol{r},\varGamma';\boldsymbol{r},\varGamma'_1;t) - w\big(\varGamma'\varGamma'_1 \,|\, \varGamma\varGamma_1\big)\, f_2(\boldsymbol{r},\varGamma;\boldsymbol{r},\varGamma_1;t) \Big\} \\ &\approx \int\! d\varGamma_1 \!\int\! d\varGamma' \!\int\! d\varGamma'_1 \,\Big\{ w\big(\varGamma\varGamma_1 \,|\, \varGamma'\varGamma'_1\big)\, f(\boldsymbol{r},\varGamma';t)\, f(\boldsymbol{r},\varGamma'_1;t) \\ &\qquad\qquad\qquad\qquad - w\big(\varGamma'\varGamma'_1 \,|\, \varGamma\varGamma_1\big)\, f(\boldsymbol{r},\varGamma;t)\, f(\boldsymbol{r},\varGamma_1;t) \Big\} \quad .\end{aligned}$$

for two-body scattering, where f_2 is the two-body distribution, and where the approximation $f_2(\boldsymbol{r},\varGamma';\boldsymbol{r}',\varGamma';t) \approx f(\boldsymbol{r},\varGamma;t)\, f(\boldsymbol{r}',\varGamma';t)$ in the second line closes the equation. A quantity $\mathcal{A}(\boldsymbol{r},\varGamma)$ which is preserved by the dynamics between collisions then satisfies

$$\frac{dA}{dt} \equiv \frac{d}{dt} \int\! d^d\!r \, d\varGamma \; \mathcal{A}(\boldsymbol{r},\varGamma)\, f(\boldsymbol{r},\varGamma,t) = \int\! d^d\!r \, d\varGamma \; A(\boldsymbol{r},\varGamma) \bigg(\frac{df}{dt}\bigg)_{\text{coll}} \quad .$$

Quantities which are conserved by collisions satisfy $\dot{A} = 0$ and are called *collisional invariants*. Examples include $\mathcal{A} = 1$ (particle number), $\mathcal{A} = \boldsymbol{p}$ (linear momentum, if translational invariance applies), and $\mathcal{A} = \varepsilon_{\boldsymbol{p}}$ (energy).

- *Time reversal, parity, and detailed balance*: With $\varGamma = (\boldsymbol{p}, \boldsymbol{L})$, we define the actions of time reversal and parity as

$$\varGamma^T = (-\boldsymbol{p}, -\boldsymbol{L}) \qquad , \qquad \varGamma^P = (-\boldsymbol{p}, \boldsymbol{L}) \qquad , \qquad \varGamma^C = (\boldsymbol{p}, -\boldsymbol{L}) \quad ,$$

where $C = PT$ is the combined operation. Time reversal symmetry of the underlying equations of motion requires $w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big) = w\big(\varGamma^T\varGamma_1^T \,|\, \varGamma'^T\varGamma_1'^T\big)$. Under conditions of *detailed balance*, this leads to $f^0(\varGamma)\, f^0(\varGamma_1) = f^0(\varGamma'^T)\, f^0(\varGamma_1'^T)$, where f^0 is the equilibrium distribution. For systems with both P and T symmetries, $w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big) = w\big(\varGamma^C\varGamma_1^C \,|\, \varGamma'^C\varGamma_1'^C\big)$, whence $w(\boldsymbol{p}', \boldsymbol{p}_1' \,|\, \boldsymbol{p}, \boldsymbol{p}_1) = w(\boldsymbol{p}, \boldsymbol{p}_1 \,|\, \boldsymbol{p}', \boldsymbol{p}_1')$ for point particles.

- *Boltzmann's $\mathcal{H}$-theorem*: Let $h(\boldsymbol{r}, t) = \int\! d\varGamma\, f(\boldsymbol{r}, \varGamma, t) \ln f(\boldsymbol{r}, \varGamma, t)$. Invoking the Boltzmann equation, it can be shown that $\frac{\partial h}{\partial t} \leq 0$, which means $\frac{d\mathcal{H}}{dt} \leq 0$, where $\mathcal{H}(t) = \int\! d^d\!r\; h(\boldsymbol{r}, t)$ is Boltzmann's $\mathcal{H}$-function. $h(\boldsymbol{r}, t)$ is everywhere decreasing or constant, due to collisions.

- *Weakly inhomogeneous gas*: Under equilibrium conditions, f^0 can be a function only of collisional invariants, and takes the Gibbs form $f^0(\boldsymbol{r}, \boldsymbol{p}) = C e^{(\mu + \boldsymbol{V}\cdot\boldsymbol{p} - \varepsilon_\varGamma)/k_\text{B}T}$. Assume now that μ, $\boldsymbol{V}$, and T are all weakly dependent on $\boldsymbol{r}$ and t. f^0 then describes a *local equilibrium* and as such is annihilated by the collision term in the Boltzmann equation, but not by the streaming term. Accordingly, we seek a solution $f = f^0 + \delta f$. A lengthy derivation results in

$$\left\{ \frac{\varepsilon_\varGamma - \mathsf{h}}{T}\, \boldsymbol{v} \cdot \boldsymbol{\nabla} T + m\, v_\alpha v_\beta\, \mathcal{Q}_{\alpha\beta} - \frac{\varepsilon_\varGamma - \mathsf{h} + T c_p}{c_V / k_\text{B}}\, \boldsymbol{\nabla}\!\cdot\! \boldsymbol{V} - \boldsymbol{F}^\text{ext} \cdot \boldsymbol{v} \right\} \frac{f^0}{k_\text{B} T} + \frac{\partial\, \delta f}{\partial t} = \left(\frac{df}{dt}\right)_\text{coll} \quad ,$$

where $\boldsymbol{v} = \frac{\partial\varepsilon}{\partial\boldsymbol{p}}$ is the particle velocity, h is the enthalpy per particle, $\mathcal{Q}_{\alpha\beta} = \frac{1}{2}\Big(\frac{\partial V^\alpha}{\partial x^\beta} + \frac{\partial V^\beta}{\partial x^\alpha}\Big)$, and $\boldsymbol{F}^\text{ext}$ is an external force. For an ideal gas, $\mathsf{h} = c_p T$. The RHS is to be evaluated to first order in δf. The simplest model for the collision integral is the *relaxation time approximation*, where $\big(\frac{\partial f}{\partial t}\big)_\text{coll} = -\frac{\delta f}{\tau}$. Note that this form does not preserve any collisional invariants. The scattering time is obtained from the relation $n\bar{v}_\text{rel}\sigma\tau = 1$, where σ is the two particle total scattering cross section and $\bar{v}_\text{rel}$ is the average relative speed of a pair of particles. This says that there is on average one collision within a tube of cross sectional area σ and length $\bar{v}_\text{rel}\tau$. For the Maxwellian distribution, $\bar{v}_\text{rel} = \sqrt{2}\,\bar{v} = \sqrt{\frac{16\, k_\text{B} T}{\pi m}}$, so $\tau(T) \propto T^{-1/2}$. The *mean free path* is defined as $\ell = \bar{v}\tau = \frac{1}{\sqrt{2}\, n\sigma}$.

- *Transport coefficients*: Assuming $F_\alpha^\text{ext} = \mathcal{Q}_{\alpha\beta} = 0$ and steady state, Eq. 8 yields

$$\delta f = -\frac{\tau(\varepsilon - c_p\, T)}{k_\text{B} T^2}\, (\boldsymbol{v} \cdot \boldsymbol{\nabla} T)\, f^0 \quad .$$

The energy current is given by

$$j_\varepsilon^\alpha = \int\! d\varGamma\; \varepsilon_\varGamma\, v^\alpha\, \delta f = -\overbrace{\frac{n\tau}{k_\text{B} T^2}\, \big\langle v^\alpha v^\beta\, \varepsilon_\varGamma (\varepsilon_\varGamma - c_p T) \big\rangle}^{\text{thermal conductivity } \kappa^{\alpha\beta}}\, \frac{\partial T}{\partial x^\beta} \quad .$$

For a monatomic gas, one finds $\kappa^{\alpha\beta} = \kappa\,\delta^{\alpha\beta}$ with $\kappa(T) = \frac{\pi}{8} n\ell\bar{v}c_p \propto T^{1/2}$. A similar result follows by considering any intensive quantity ϕ which is spatially dependent through the temperature $T(\boldsymbol{r})$. The ϕ-current across the surface $z=0$ is

$$\boldsymbol{j}_\phi = n\hat{\boldsymbol{z}} \int\limits_{v_z>0} \! d^3\!v\, P(\boldsymbol{v})\, v_z\, \phi(z - \ell\cos\theta) + n\hat{\boldsymbol{z}} \int\limits_{v_z<0} \! d^3\!v\, P(\boldsymbol{v})\, v_z\, \phi(z + \ell\cos\theta) = -\tfrac{1}{3} n\,\bar{v}\,\ell\, \frac{\partial\phi}{\partial z}\,\hat{\boldsymbol{z}} \quad .$$

Thus, $\boldsymbol{j}_\phi = -K\boldsymbol{\nabla}T$, with $K = \frac{1}{3} n\,\ell\,\bar{v}\,\frac{\partial\phi}{\partial T}$ the associated transport coefficient. If $\phi = \langle \varepsilon_\Gamma \rangle$, then $\frac{\partial\phi}{\partial T} = c_p$, yielding $\kappa = \frac{1}{3} n\ell\bar{v}c_p$. If $\phi = \langle p_x \rangle$, then $j^z_{p_x} = \Pi_{xz} = -\frac{1}{3} nm\ell\bar{v}\frac{\partial V_x}{\partial z} \equiv -\eta\frac{\partial V_x}{\partial z}$, where η is the shear viscosity. Using the Boltzmann equation in the relaxation time approximation, one obtains $\eta = \frac{\pi}{8} nm\ell\bar{v}$. From κ and η, we can form a dimensionless quantity $\mathsf{Pr} = \eta c_p / m\kappa$, known as the *Prandtl number*. Within the relaxation time approximation, $\mathsf{Pr} = 1$. Most monatomic gases have $\mathsf{Pr} \approx \frac{2}{3}$.

• *Linearized Boltzmann equation*: To go beyond the phenomenological relaxation time approximation, one must grapple with the collision integral,

$$\left(\frac{df}{dt}\right)_{\rm coll} = \int\! d^3\!p_1 \!\int\! d^3\!p' \!\int\! d^3\!p_1'\; w(\boldsymbol{p}', \boldsymbol{p}_1' \,|\, \boldsymbol{p}, \boldsymbol{p}_1)\, \Big\{ f(\boldsymbol{p}')\, f(\boldsymbol{p}_1') - f(\boldsymbol{p})\, f(\boldsymbol{p}_1) \Big\} \quad ,$$

which is a nonlinear functional of the distribution $f(\boldsymbol{p},t)$ (we suppress the t index here). Writing $f(\boldsymbol{p}) = f^0(\boldsymbol{p}) + f^0(\boldsymbol{p})\,\psi(\boldsymbol{p})$, we have $\big(\frac{\partial f}{\partial t}\big)_{\rm coll} = f^0(\boldsymbol{p})\,\hat{L}\psi + \mathcal{O}(\psi^2)$, with

$$\hat{L}\psi(\boldsymbol{p}) = \int\! d^3\!p_1 \!\int\! d\Omega\, |\boldsymbol{v} - \boldsymbol{v}_1|\, \frac{\partial\sigma}{\partial\Omega}\, f^0(\boldsymbol{p}_1)\, \Big\{ \psi(\boldsymbol{p}') + \psi(\boldsymbol{p}_1') - \psi(\boldsymbol{p}) - \psi(\boldsymbol{p}_1) \Big\} \quad .$$

The linearized Boltzmann equation (LBE) then takes the form $\big(\hat{L} - \frac{\partial}{\partial t}\big)\psi = Y$, where

$$Y = \frac{1}{k_{\rm B}T} \left\{ \frac{\varepsilon(\boldsymbol{p}) - \frac{5}{2}k_{\rm B}T}{T}\, \boldsymbol{v}\cdot\boldsymbol{\nabla}T + m\, v_\alpha v_\beta\, \mathcal{Q}_{\alpha\beta} - \frac{k_{\rm B}\,\varepsilon(\boldsymbol{p})}{c_V}\, \boldsymbol{\nabla}\!\cdot\!\boldsymbol{V} - \boldsymbol{F}\cdot\boldsymbol{v} \right\} \quad .$$

for point particles. To solve the LBE, we must invert the operator $\hat{L} - \frac{\partial}{\partial t}$. Various useful properties follow from defining the inner product $\langle \psi_1 | \psi_2 \rangle \equiv \int\! d^3\!p\, f^0(\boldsymbol{p})\, \psi_1(\boldsymbol{p})\, \psi_2(\boldsymbol{p})$, such as the self-adjointness of $\hat{L}$: $\langle \psi_1 | \hat{L}\psi_2 \rangle = \langle \hat{L}\psi_1 | \psi_2 \rangle$. We then have $\hat{L}|\phi_n\rangle = -\lambda_n |\,\phi_n\,\rangle$, with $\langle \phi_m | \phi_n \rangle = \delta_{mn}$ and real eigenvalues λ_n. There are five zero eigenvalues corresponding to the collisional invariants:

$$\phi_1(\boldsymbol{p}) = \frac{1}{\sqrt{n}} \qquad , \qquad \phi_{2,3,4}(\boldsymbol{p}) = \frac{p_\alpha}{\sqrt{nmk_{\rm B}T}} \qquad , \qquad \phi_5(\boldsymbol{p}) = \sqrt{\frac{2}{3n}} \left(\frac{\varepsilon(\boldsymbol{p})}{k_{\rm B}T} - \frac{3}{2} \right) \quad .$$

When $Y = 0$, the formal solution to $\frac{\partial\psi}{\partial t} = \hat{L}\psi$ is $\psi(\boldsymbol{p},t) = \sum_n C_n\, \phi_n(\boldsymbol{p})\, e^{-\lambda_n t}$. Aside from the collisional invariants, all the eigenvalues λ_n must be positive, corresponding to relaxation to the equilibrium state. One can check that the particle, energy, and heat currents are given by $\boldsymbol{j} = \langle\, \boldsymbol{v} \,|\, \psi \,\rangle$, $\boldsymbol{j}_\varepsilon = \langle\, \boldsymbol{v}\, \varepsilon \,|\, \psi \,\rangle$, and $\boldsymbol{j}_q = \langle\, \boldsymbol{v}\, (\varepsilon - \mu) \,|\, \psi \,\rangle$.

In steady state, the solution to $\hat{L}\psi = Y$ is $\psi = \hat{L}^{-1}Y$. This is valid provided Y is orthogonal to each of the collisional invariants, in which case

$$\psi(\boldsymbol{p}) = \sum_{n \notin \mathsf{CI}} \lambda_n^{-1} \, \langle\, \phi_n \,|\, Y \,\rangle \, \phi_n(\boldsymbol{p}) \quad .$$

Once we have $|\,\psi\,\rangle$, we may obtain the various transport coefficients by computing the requisite currents. For example, to find the thermal conductivity κ and shear viscosity η,

$$\begin{aligned} \kappa \quad &: \quad Y = \frac{1}{k_{\mathrm{B}} T^2} \frac{\partial T}{\partial x} X_\kappa \quad , \quad X_\kappa \equiv \big(\varepsilon - \tfrac{5}{2} k_{\mathrm{B}}\big)\, v_x \quad \Rightarrow \quad \kappa = -\frac{\langle\, X_\kappa \,|\, \psi \,\rangle}{\partial T/\partial x} \\ \eta \quad &: \quad Y = \frac{m}{k_{\mathrm{B}} T} \frac{\partial V_x}{\partial y} X_\eta \quad , \quad X_\eta \equiv v_x \, v_y \quad \Rightarrow \quad \eta = -\frac{m \, \langle\, X_\eta \,|\, \psi \,\rangle}{\partial V_x/\partial y} \quad . \end{aligned}$$

• *Variational approach*: The Schwarz inequality, $\langle\, \psi \,|\, -\hat{L} \,|\, \psi \,\rangle \cdot \langle\, \phi \,|\, \hat{H} \,|\, \phi \,\rangle \ \geq\ \langle\, \phi \,|\, \hat{H} \,|\, \psi \,\rangle^2$, holds for the positive semidefinite operator $\hat{H} \equiv -\hat{L}$. One therefore has

$$\kappa \geq \frac{1}{k_{\mathrm{B}} T^2} \, \frac{\langle\, \phi \,|\, X_\kappa \,\rangle^2}{\langle\, \phi \,|\, \hat{H} \,|\, \phi \,\rangle} \qquad , \qquad \eta \geq \frac{m^2}{k_{\mathrm{B}} T} \, \frac{\langle\, \phi \,|\, X_\eta \,\rangle^2}{\langle\, \phi \,|\, \hat{H} \,|\, \phi \,\rangle} \quad .$$

Using variational functions $\phi_\kappa = \big(\varepsilon - \frac{5}{2} k_{\mathrm{B}} T\big)\, v_x$ and $\phi_\eta = v_x \, v_y$, one finds, after tedious calculations,

$$\kappa \geq \frac{75\, k_{\mathrm{B}}}{64 \sqrt{\pi}\, d^2} \left(\frac{k_{\mathrm{B}} T}{m}\right)^{1/2} \qquad , \qquad \eta \geq \frac{5\, (m k_{\mathrm{B}} T)^{1/2}}{16 \sqrt{\pi}\, d^2} \quad .$$

Taking the lower limit in each case, we obtain a Prandtl number $\mathsf{Pr} = \frac{\eta\, c_p}{m \kappa} = \frac{2}{3}$, which is close to what is observed for monatomic gases.

• *Quantum transport*: For quantum systems, the local equilibrium distribution is of the Bose-Einstein or Fermi-Dirac form,

$$f^0(\boldsymbol{r}, \boldsymbol{k}, t) = \left\{ \exp\left(\frac{\varepsilon(\boldsymbol{k}) - \mu(\boldsymbol{r}, t)}{k_{\mathrm{B}} T(\boldsymbol{r}, t)} \right) \mp 1 \right\}^{-1} \quad ,$$

with $\boldsymbol{k} = \boldsymbol{p}/\hbar$, and

$$\left(\frac{df}{dt}\right)_{\mathrm{coll}} = \int\!\frac{d^3k_1}{(2\pi)^3} \int\!\frac{d^3k'}{(2\pi)^3} \int\!\frac{d^3k_1'}{(2\pi)^3} \, w \, \Big\{ f' f_1' \, (1 \pm f)\, (1 \pm f_1) - f f_1 \, (1 \pm f')\, (1 \pm f_1') \Big\}$$

where $w = w(\boldsymbol{k}, \boldsymbol{k}_1 \,|\, \boldsymbol{k}', \boldsymbol{k}_1')$, $f = f(\boldsymbol{k})$, $f_1 = f(\boldsymbol{k}_1)$, $f' = f(\boldsymbol{k}')$, and $f_1' = f(\boldsymbol{k}_1')$, and where we have assumed time-reversal and parity symmetry. The most important application is to electron transport in metals and semiconductors, in which case f^0 is the Fermi distribution. With $f = f^0 + \delta f$, one has, within the relaxation time approximation,

$$\frac{\partial\, \delta f}{\partial t} - \frac{e}{\hbar c} \, \boldsymbol{v} \times \boldsymbol{B} \cdot \frac{\partial\, \delta f}{\partial \boldsymbol{k}} - \boldsymbol{v} \cdot \left[e\, \boldsymbol{\mathcal{E}} + \frac{\varepsilon - \mu}{T} \, \boldsymbol{\nabla} T \right] \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f}{\tau} \quad ,$$

where $\boldsymbol{\mathcal{E}} = -\boldsymbol{\nabla}(\phi - \mu/e) = \boldsymbol{E} - e^{-1}\boldsymbol{\nabla}\mu$ is the gradient of the 'electrochemical potential' $\phi - e^{-1}\mu$. For steady state transport with $\boldsymbol{B} = 0$, one has

$$\boldsymbol{j} = -2e\int\limits_{\hat{\Omega}} \frac{d^3\!k}{(2\pi)^3}\, \boldsymbol{v}\,\delta f \equiv L_{11}\,\boldsymbol{\mathcal{E}} - L_{12}\,\boldsymbol{\nabla}\,T$$

$$\boldsymbol{j}_q = 2\int\limits_{\hat{\Omega}} \frac{d^3\!k}{(2\pi)^3}\,(\varepsilon-\mu)\,\boldsymbol{v}\,\delta f \equiv L_{21}\,\boldsymbol{\mathcal{E}} - L_{22}\,\boldsymbol{\nabla}\,T$$

where $L_{11}^{\alpha\beta} = e^2\mathcal{J}_0^{\alpha\beta}$, $L_{21}^{\alpha\beta} = TL_{12}^{\alpha\beta} = -e\,\mathcal{J}_1^{\alpha\beta}$, and $L_{22}^{\alpha\beta} = \frac{1}{T}\,\mathcal{J}_2^{\alpha\beta}$, with

$$\mathcal{J}_n^{\alpha\beta} \equiv \frac{1}{4\pi^3\hbar}\int\! d\varepsilon\,\tau(\varepsilon)\,(\varepsilon-\mu)^n\left(-\frac{\partial f^0}{\partial\varepsilon}\right)\int\! dS_\varepsilon\,\frac{v^\alpha\,v^\beta}{|\boldsymbol{v}|} \quad .$$

These results entail

$$\boldsymbol{\mathcal{E}} = \rho\,\boldsymbol{j} + Q\,\boldsymbol{\nabla}\,T \qquad , \qquad \boldsymbol{j}_q = \sqcap\,\boldsymbol{j} - \kappa\,\boldsymbol{\nabla}\,T \quad ,$$

or, in terms of the $\mathcal{J}_n$,

$$\rho = \frac{1}{e^2}\,\mathcal{J}_0^{-1} \quad , \quad Q = -\frac{1}{e\,T}\,\mathcal{J}_0^{-1}\,\mathcal{J}_1 \quad , \quad \sqcap = -\frac{1}{e}\,\mathcal{J}_1\,\mathcal{J}_0^{-1} \quad , \quad \kappa = \frac{1}{T}\Big(\mathcal{J}_2 - \mathcal{J}_1\,\mathcal{J}_0^{-1}\,\mathcal{J}_1\Big) \quad .$$

These results describe the following physical phenomena:

<u>Electrical resistance</u> ($\boldsymbol{\nabla}T = \boldsymbol{B} = 0$): An electrical current $\boldsymbol{j}$ will generate an electric field $\boldsymbol{\mathcal{E}} = \rho\boldsymbol{j}$, where ρ is the *electrical resistivity*.

<u>Peltier effect</u> ($\boldsymbol{\nabla}T = \boldsymbol{B} = 0$): An electrical current $\boldsymbol{j}$ will generate an heat current $\boldsymbol{j}_q = \sqcap\boldsymbol{j}$, where $\sqcap$ is the *Peltier coefficient*.

<u>Thermal conduction</u> ($\boldsymbol{j} = \boldsymbol{B} = 0$): A temperature gradient $\boldsymbol{\nabla}T$ gives rise to a heat current $\boldsymbol{j}_q = -\kappa\boldsymbol{\nabla}T$, where κ is the *thermal conductivity*.

<u>Seebeck effect</u> ($\boldsymbol{j} = \boldsymbol{B} = 0$): A temperature gradient $\boldsymbol{\nabla}T$ gives rise to an electric field $\boldsymbol{\mathcal{E}} = Q\boldsymbol{\nabla}T$, where Q is the *Seebeck coefficient*.

For a parabolic band with effective electron mass m^*, one finds

$$\rho = \frac{m^*}{ne^2\tau} \quad , \quad Q = -\frac{\pi^2 k_{\mathrm{B}}^2 T}{2e\,\varepsilon_{\mathrm{F}}} \quad , \quad \kappa = \frac{\pi^2 n\tau k_{\mathrm{B}}^2 T}{3m^*}$$

with $\sqcap = TQ$, where ε_{F} is the Fermi energy. The ratio $\kappa/\sigma T = \frac{\pi^2}{3}(k_{\mathrm{B}}/e)^2 = 2.45 \times 10^{-8}\mathrm{V}^2\mathrm{K}^{-2}$ is then predicted to be universal, a result known as the *Wiedemann-Franz law*. This also predicts all metals to have negative thermopower, which is not the case. In the presence of an external magnetic field $\boldsymbol{B}$, additional transport effects arise:

<u>Hall effect</u> ($\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} = j_y = 0$): An electrical current $\boldsymbol{j} = j_x\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an electric field $\boldsymbol{\mathcal{E}}$. The *Hall coefficient* is $R_{\mathrm{H}} = \mathcal{E}_y/j_x\,B_z$.

Ettingshausen effect ($\frac{\partial T}{\partial x} = j_y = j_{q,y} = 0$): An electrical current $\boldsymbol{j} = j_x\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield a temperature gradient $\frac{\partial T}{\partial y}$. The *Ettingshausen coefficient* is $P = \frac{\partial T}{\partial y}\big/ j_x\,B_z$.

Nernst effect ($j_x = j_y = \frac{\partial T}{\partial y} = 0$): A temperature gradient $\boldsymbol{\nabla}\,T = \frac{\partial T}{\partial x}\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an electric field $\boldsymbol{\mathcal{E}}$. The *Nernst coefficient* is $\Lambda = \mathcal{E}_y\big/\frac{\partial T}{\partial x}\,B_z$.

Righi-Leduc effect ($j_x = j_y = \mathcal{E}_y = 0$): A temperature gradient $\boldsymbol{\nabla}\,T = \frac{\partial T}{\partial x}\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an orthogonal gradient $\frac{\partial T}{\partial y}$. The *Righi-Leduc coefficient* is $\mathcal{L} = \frac{\partial T}{\partial y}\big/\frac{\partial T}{\partial x} B_z$.

• *Stochastic processes*: Stochastic processes involve a random element, hence they are not wholly deterministic. The simplest example is the Langevin equation for Brownian motion, $\dot{p} + \gamma p = F + \eta(t)$, where p is a particle's momentum, γ a damping rate due to friction, F an external force, and $\eta(t)$ a *stochastic random force*. We can integrate this first order equation to obtain

$$p(t) = p(0)\,e^{-\gamma t} + \frac{F}{\gamma}\,\big(1 - e^{-\gamma t}\big) + \int\limits_0^t\! ds\;\eta(s)\,e^{\gamma(s-t)} \quad .$$

We assume that the random force $\eta(t)$ has zero mean, and furthermore that

$$\big\langle \eta(s)\,\eta(s')\big\rangle = \phi(s-s') \approx \mathit{\Gamma}\,\delta(s-s') \quad ,$$

in which case one finds $\langle p^2(t)\rangle = \langle p(t)\rangle^2 + \frac{\mathit{\Gamma}}{2\gamma}(1 - e^{-2\gamma t})$. If there is no external force, we expect the particle thermailzes at long times, *i.e.* $\langle \frac{p^2}{2m}\rangle = \frac{1}{2} k_{\rm B} T$. This fixes $\mathit{\Gamma} = 2\gamma m k_{\rm B} T$, where m is the particle's mass. One can integrate again to find the position. At late times $t \gg \gamma^{-1}$, one finds $\langle x(t)\rangle = \text{const.} + \frac{Ft}{\gamma m}$, corresponding to a mean velocity $\langle p/m\rangle = F/\gamma$. The RMS fluctuations in position, however, grow as

$$\langle x^2(t)\rangle - \langle x(t)\rangle^2 = \frac{2k_{\rm B}Tt}{\gamma m} \equiv 2Dt \quad ,$$

where $D = k_{\rm B}T/\gamma m$ is the *diffusion constant*. Thus, after the memory of the initial conditions is lost ($t \gg \gamma^{-1}$), the mean position advances linearly in time due to the external force, and the RMS fluctuations in position also increase linearly.

• *Fokker-Planck equation*: Suppose $x(t)$ is a stochastic variable, and define

$$\delta x(t) \equiv x(t + \delta t) - x(t) \quad .$$

Furthermore, assume $\langle \delta x(t)\rangle = F_1\big(x(t)\big)\delta t$ and $\big\langle [\delta x(t)]^2\big\rangle = F_2\big(x(t)\big)\delta t$, but that $\big\langle [\delta x(t)]^n\big\rangle -$ $\mathcal{O}(\delta t^2)$ for $n > 2$. One can then show that the probability density $P(x,t) = \big\langle \delta\big(x - x(t)\big)\big\rangle$ satisfies the *Fokker-Planck equation*,

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\big[F_1(x)\,P(x,t)\big] + \frac{1}{2}\,\frac{\partial^2}{\partial x^2}\big[F_2(x)\,P(x,t)\big] \quad .$$

For Brownian motion, $F_1(x) = F/\gamma m \equiv u$ and $F_2(x) = 2D$. The resulting Fokker-Planck equation is then $P_t = -uP_x + DP_{xx}$, where $P_t = \frac{\partial P}{\partial t}$, $P_{xx} = \frac{\partial^2 P}{\partial x^2}$, *etc.* The Galilean transformation $x \to x - ut$ then results in $P_t = DP_{xx}$, which is known as the *diffusion equation*, a general solution to which is given by $P(x,t) = \int\limits_{-\infty}^{\infty} dx' \, K(x - x', t - t') \, P(x', t')$, where

$$K(\Delta x, \Delta t) = (4\pi D \Delta t)^{-1/2} e^{-(\Delta x)^2/4D\Delta t}$$

is the *diffusion kernel*. Thus, $\Delta x_{\text{RMS}} = \sqrt{2D\Delta t}$.