Chapter 1

Solution Set #1

(1) Prove that for $x \geq 0$ and $y \geq 0$ that

$$(x-y)\,(\ln x - \ln y) \geq 0 \,.$$

Solution: Trivial. Both $f(x) = x$ and $g(x) = \ln x$ are strictly increasing functions on the interval $(0, \infty)$. Hence $\ln x < \ln y$ if $0 < x < y$, and $\ln y < \ln x$ if $0 < y < x$. Thus, $(x-y)\big(\ln x - \ln y\big) \geq 0$.

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

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

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

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

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

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

Table 1.1: States and their degeneracies.

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

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

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

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

The full transition matrix is then

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

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

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

This is the state we converge to after repeated application of the transition matrix Q. If we decompose $Q = \sum_{\alpha=1}^4 \lambda_\alpha \,\lvert\, \psi^{(\alpha)}\,\rangle\langle\, \phi^{(\alpha)}\,\rvert$, then in the limit $t \to \infty$ we have $Q^t \approx \lvert\, \psi^{(1)}\,\rangle\langle\, \phi^{(1)}\,\rvert$, where $\lambda_1 = 1$, since the remaining eigenvalues are all less than 1 in magnitude[1]. Thus, Q^t acts as a *projector* onto the state $\lvert\, \psi^{(1)}\,\rangle$. Whatever the initial set of probabilities $P_j(t=0)$,

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

we must have $\langle\, \phi^{(1)} \,|\, P(0)\,\rangle = \sum_j P_j(0) = 1$. Therefore, $\lim_{t\to\infty} P_j(t) = \psi_j^{(1)}$, and we find $P_3(\infty) = \frac{18}{35}$. Note that the equilibrium distribution satisfies detailed balance:

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

(3) Consider a q-state generalization of the Kac ring model in which $\mathbb{Z}_q$ spins rotate around an N-site ring which contains a fraction $x = N_{\rm F}/N$ of flippers on its links. Each flipper cyclically rotates the spin values: $1 \to 2 \to 3 \to \cdots \to q \to 1$ (hence the clock model symmetry $\mathbb{Z}_q$).

(a) What is the Poincare recurrence time?

(b) Make the *Stosszahlansatz*, *i.e.* assume the spin flips are stochastic random processes. Then one has

$$P_\sigma(t+1) = (1-x)\, P_\sigma(t) + x\, P_{\sigma-1}(t) \ ,$$

where $P_0 \equiv P_q$. This defines a Markov chain

$$P_\sigma(t+1) = Q_{\sigma\sigma'}\, P_{\sigma'}(t) \ .$$

Decompose the transition matrix Q into its eigenvectors. *Hint:* The matrix may be diagonalized by a simple Fourier transform.

(c) The eigenvalues of Q may be written as $\lambda_\alpha = e^{-1/\tau_\alpha}\, e^{-i\delta_\alpha}$, where τ_α is a relaxation time and δ_α is a phase. Find the spectrum of relaxation times. What is the longest finite relaxation time?

(d) Suppose all the spins are initially in the state $\sigma = q$. Write down an expression for $P_\sigma(t)$ for all subsequent times $t \in \mathbb{Z}^+$. Plot your results for different values of x and q.

Hint: It may be helpful to study carefully the solution to problem 5.1 (*i.e.* problem 1 of assignment 5) from F08 Physics 140A. You can access this through the link to the 140B website on the 210A course web page.

Solution:

(a) The recurrence time is $\tau = qN/\mathsf{gcd}(N_{\rm F}, q)$, where $\mathsf{gcd}(N_{\rm F}, q)$ is the greatest common divisor of $N_{\rm F}$ and q. After τ steps, which is to say $q/\mathsf{gcd}(N_{\rm F}, q)$ cycles around the ring, each spin will have visited $qN_{\rm F}/\mathsf{gcd}(N_{\rm F}, q)$ flippers. This is necessarily an integer multiple of q, which means that each spin will have mate $N_{\rm F}/\mathsf{gcd}(N_{\rm F}, q)$ complete cycles of its internal $\mathbb{Z}_q$ clock.

(b) We have

$$Q_{\sigma\sigma'} = (1-x)\, \widetilde{\delta}_{\sigma,\sigma'} + x\, \widetilde{\delta}_{\sigma,\sigma'+1} \ ,$$

where

$$\widetilde{\delta}_{ij} = \begin{cases} 1 & \text{if } i = j \bmod q \\ 0 & \text{otherwise.} \end{cases}$$

Q is known as a *circulant matrix*, which is to say it satisfies $Q_{\sigma\sigma'} = Q(\sigma - \sigma' \bmod q)$. A circulant matrix of rank q has only q independent entries. Such a matrix may be brought to diagonal form by a unitary transformation: $Q = U\,\widehat{Q}\,U^{\dagger}$,[2] where $U_{\sigma k} = \frac{1}{\sqrt{q}}\,e^{2\pi i k\sigma/q}$ and $\widehat{Q}_{kk'} \equiv \widehat{Q}(k)\,\widetilde{\delta}_{kk'}$ with

$$\widehat{Q}(k) = \sum_{n=1}^{q} Q(\mu)\,e^{-2\pi i k\mu/q} \ . \tag{1.1}$$

Since $Q(\mu) = (1-x)\,\widetilde{\delta}_{\mu,0} + x\,\widetilde{\delta}_{\mu,1}$, we have

$$\widehat{Q}(k) = 1 - x + x\,e^{-2\pi i k/q} \ .$$

(c) In the polar representation, we have $\widehat{Q}(k) = e^{-1/\tau_k(x)}\,e^{-i\delta_k(x)}$, where

$$\tau_k(x) = -\frac{2}{\ln\Big[1 - 2x(1-x)\big(1 - \cos(2\pi k/q)\big)\Big]}$$

and

$$\delta_k(x) = \tan^{-1}\left(\frac{x\,\sin(2\pi k/q)}{1 - x + x\,\cos(2\pi k/q)}\right) \ .$$

Note that $\tau_q = \infty$, because the total probability is conserved by the Markov process. The longest finite relaxation time is $\tau_1 = \tau_{q-1}$.

(d) Given the initial conditions $P_\sigma(0) = \delta_{\sigma,q}$, we have

$$\begin{aligned} P_\sigma(t) &= \big(Q^t\big)_{\sigma\sigma'}\,P_{\sigma'}(0) \\ &= \frac{1}{q}\sum_{k=1}^{q} U_{\sigma k}\,\widehat{Q}^t(k)\,U^*_{\sigma' k}\,P_{\sigma'}(0) \\ &= \frac{1}{q}\sum_{k=1}^{q} e^{-t/\tau_k}\,e^{-it\delta_k}\,e^{2\pi i\sigma k/q} \ . \end{aligned}$$

We can combine the terms in the k sum by pairing k with $q-k$, since $\tau_{q-k} = \tau_k$ and $\delta_{q-k} = -\delta_k$. We should however consider separately the cases $k = q$ and, if q is even, $k = \frac{1}{2}q$, since for those values of k we have $\widehat{Q}(k)$ is real.

If q is even, then $\widehat{Q}\big(k = \frac{1}{2}q\big) = 1 - 2x$. We then have

$$P_\sigma(t) = \frac{1}{q} + \frac{(-1)^\sigma}{q}\,(1-2x)^t + \frac{2}{q}\sum_{k=1}^{\frac{q}{2}-1} e^{-t/\tau_k(x)}\,\cos\!\left(\frac{2\pi\sigma k}{q} - t\,\delta_k(x)\right) \ .$$

If q is odd, then

$$P_\sigma(t) = \frac{1}{q} + \frac{2}{q}\sum_{k=1}^{\frac{q-1}{2}} e^{-t/\tau_k(x)}\,\cos\!\left(\frac{2\pi\sigma k}{q} - t\,\delta_k(x)\right) \ .$$

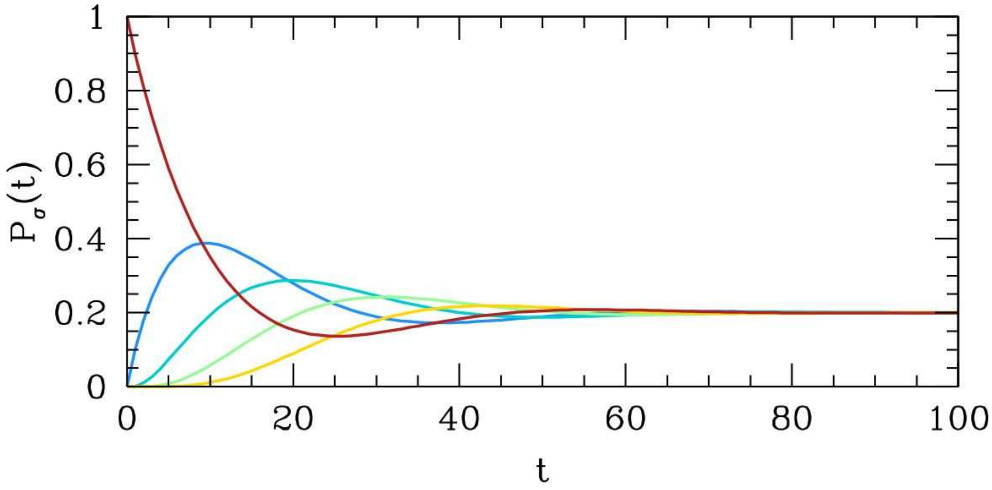

Figure 1.1: Behavior of $P_\sigma(t)$ for $q = 5$ and $x = 0.1$ within the *Stosszahlansatz* with initial conditions $P_\sigma(0) = \delta_{\sigma,q}$. Note that at large times the probabilities all converge to $\lim_{t\to\infty} P_\sigma(t) = q^{-1}$.

(e) See fig. 1.2.

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

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

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

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

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

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

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

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[2] There was some discussion of the details on the web forum pages for Physics 210A this past week.

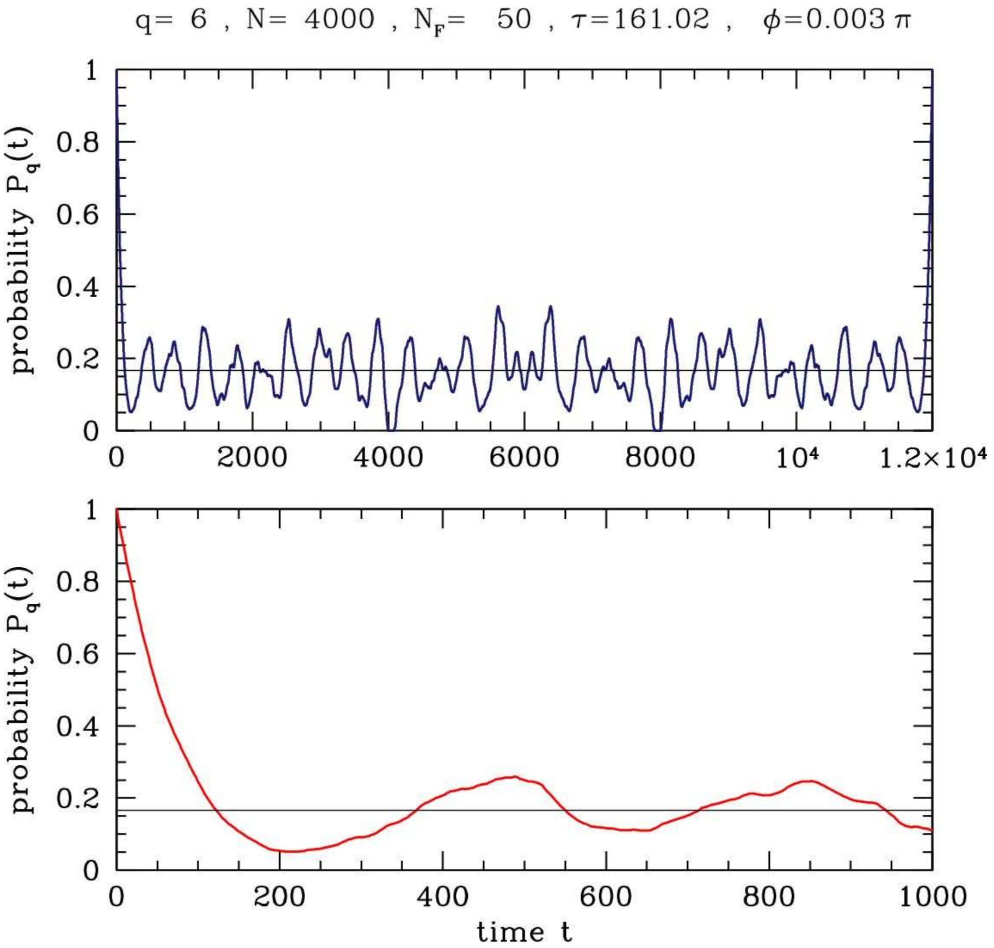

Figure 1.2: Evolution of the initial distribution $P_\sigma(0) = \delta_{\sigma,q}$ for the $\mathbb{Z}_q$ Kac ring model for $q = 6$, from a direct numerical simulation of the model.

average is

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

When computing microcanonical averages, it is helpful to use the Laplace transform, discussed toward the end of §3.3 of the notes. (It is possible to compute the microcanonical average by more brute force methods as well.)

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

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

The analogous dynamical average is

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

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

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

(e) Write a computer program to simulate this system. The only input should be the mass ratio r (set $\bar{E} = 10$ to fix the energy). You also may wish to input the initial conditions, or perhaps to choose the initial conditions randomly (all satisfying energy conservation, of course!). Have your program compute the microcanonical as well as dynamical averages in parts (b) and (c). Plot out the Poincaré section of P *vs.* X for those times when the ball hits the floor. Investigate this for several values of r. Just to show you that this is interesting, I've plotted some of my own numerical results in fig. 1.3.

Solution:

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

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

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

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

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

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

Averages within the microcanonical ensemble are normally performed with respect to the

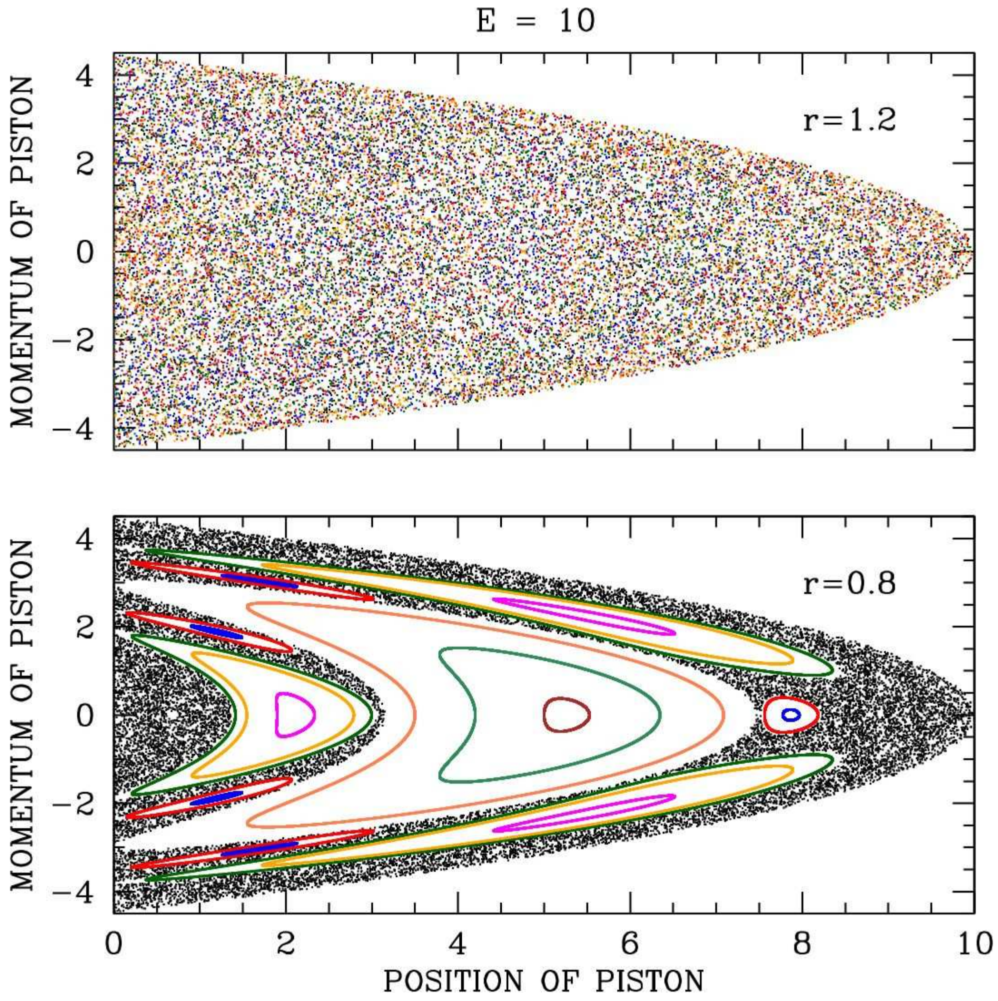

Figure 1.3: Poincaré sections for the ball and piston head problem. Each color corresponds to a different initial condition. When the mass ratio $r = m/M$ exceeds unity, the system apparently becomes ergodic.

phase space distribution

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

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

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

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

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

where

$$\widetilde{\mathsf{Tr}}\,F(\boldsymbol{\varphi}) \equiv \int\limits_{-\infty}^{\infty}\!dP\int\limits_{0}^{\infty}\!dX\int\limits_{-\infty}^{\infty}\!dp\int\limits_{0}^{X}\!dx\;F(P,X,p,x)$$

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

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

$$\widehat{K}(\beta) = \int\limits_{0}^{\infty}\!dE\;K(E)\,e^{-\beta E}\ .$$

The inverse Laplace transform is given by

$$K(E) = \int\limits_{c-i\infty}^{c+i\infty}\!\frac{d\beta}{2\pi i}\;\widehat{K}(\beta)\,e^{\beta E}\ ,$$

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

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

For a proof, see §3.3.1 of the lecture notes.

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

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

where

$$\begin{aligned} N(E) &= \widetilde{\mathsf{Tr}}\,\big[X\,\delta(E-H)\big] \\ D(E) &= \widetilde{\mathsf{Tr}}\,\delta(E-H)\ . \end{aligned}$$

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

$$\begin{aligned} \widehat{D}(\beta) &= \widetilde{\mathsf{Tr}}\,e^{-\beta H} \\ &= \int\limits_{-\infty}^{\infty}\!dP\,e^{-\beta P^2/2}\int\limits_{-\infty}^{\infty}\!dp\,e^{-\beta p^2/2r}\int\limits_{0}^{\infty}\!dX\;e^{-\beta X}\int\limits_{0}^{X}\!dx\,e^{-\beta r x} \\ &= \frac{2\pi\sqrt{r}}{\beta}\int\limits_{0}^{\infty}\!dX\,e^{-\beta X}\left(\frac{1-e^{-\beta r X}}{\beta r}\right) = \frac{\sqrt{r}}{1+r}\cdot\frac{2\pi}{\beta^3}\ . \end{aligned}$$

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

$$\begin{aligned}
\widehat{N}(\beta) &= \widetilde{\mathsf{Tr}}\, X\, e^{-\beta H} \\
&= \int\limits_{-\infty}^{\infty}\!dP\, e^{-\beta P^2/2}\int\limits_{-\infty}^{\infty}\!dp\, e^{-\beta p^2/2r}\int\limits_{0}^{\infty}\!dX\, X\, e^{-\beta X}\int\limits_{0}^{X}\!dx\, e^{-\beta r x} \\
&= \frac{2\pi\sqrt{r}}{\beta}\int\limits_{0}^{\infty}\!dX\, X\, e^{-\beta X}\left(\frac{1-e^{-\beta r X}}{\beta r}\right) = \frac{(2+r)\, r^{3/2}}{(1+r)^2}\cdot\frac{2\pi}{\beta^4}\ .
\end{aligned}$$

Taking the inverse Laplace transform, we then have

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

We then have

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

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

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

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

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

with $q = E - w$. Similarly,

$$\begin{aligned}
N(E) &= 2\pi\sqrt{r}\int\limits_0^\infty \! dw \int\limits_0^\infty \! dX\, X \int\limits_0^X \! dx\, \delta\big(w + X + rx - E\big) \\
&= \frac{2\pi}{\sqrt{r}} \int\limits_0^\infty \! dw \int\limits_0^\infty \! dX\, X \int\limits_0^X \! dx\;\; \Theta(E - w - X)\, \Theta(X + rX - E + w) \\
&= \frac{2\pi}{\sqrt{r}} \int\limits_0^E \! dw \int\limits_{\frac{E-w}{1+r}}^{E-w} \! dX\, X = \frac{2\pi}{\sqrt{r}} \int\limits_0^E \! dq \left(1 - \frac{1}{(1+r)^2}\right) \cdot \tfrac{1}{2} q^2 = \left(\frac{2+r}{1+r}\right) \cdot \frac{\sqrt{r}}{1+r} \cdot \tfrac{1}{3}\pi E^3 \ .
\end{aligned}$$

(c) Using the general result

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

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

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

The Laplace transform is

$$\begin{aligned}
\widehat{N}(\beta) &= \int\limits_{-\infty}^\infty \! dP\, e^{-\beta P^2/2} \int\limits_0^\infty \! dp\, r^{-1}\, p\, e^{-\beta p^2/2r} \int\limits_0^\infty \! dX\, e^{-\beta X} \\
&= \sqrt{\frac{2\pi}{\beta}} \cdot \frac{1}{\beta} \cdot \frac{1}{\beta} = \sqrt{2\pi}\, \beta^{-5/2} \ .
\end{aligned}$$

Thus,

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

and

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

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

$$\begin{aligned}
\widehat{D}(\beta) &= \mathsf{Tr}\; e^{-\beta H} \\
&= \int\limits_{-\infty}^\infty \! dP\, e^{-\beta P^2/2} \int\limits_{-\infty}^\infty \! dp\, e^{-\beta p^2/2r} \int\limits_0^\infty \! dX\, e^{-\beta X} \int\limits_0^\infty \! dx\, e^{-\beta r x} = \frac{2\pi\sqrt{r}}{\beta^3} \ .
\end{aligned}$$

For part (b) we would then have

$$\begin{aligned}\widehat{N}(\beta) &= \mathsf{Tr}\; X\, e^{-\beta H}\\ &= \int\limits_{-\infty}^{\infty}\!dP\, e^{-\beta P^2/2}\int\limits_{-\infty}^{\infty}\!dp\, e^{-\beta p^2/2r}\int\limits_{0}^{\infty}\!dX\; X\, e^{-\beta X}\int\limits_{0}^{\infty}\!dx\, e^{-\beta r x} = \frac{2\pi\sqrt{r}}{\beta^4}\;.\end{aligned}$$

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

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

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

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

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

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

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

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

$$\begin{aligned}X(t) &= X(t_0) + P(t_0)\,(t-t_0) - \tfrac{1}{2}(t-t_0)^2\\ P(t) &= P(t_0) - (t-t_0)\\ x(t) &= x(t_0) + \frac{p(t_0)}{r}\,(t-t_0) - \tfrac{1}{2}(t-t_0)^2\\ p(t) &= p(t_0) - r(t-t_0)\;.\end{aligned}$$

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

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

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

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

$$\begin{aligned}
\mathcal{X} &= X - x & \qquad \mathcal{P}_x &= \frac{mP - Mp}{M+m} \\
\mathcal{Y} &= \frac{MX + mx}{M+m} & \qquad \mathcal{P}_y &= P + p\ .
\end{aligned}$$

Then

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

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

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

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

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

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

Finally, in fig. 8.1, I plot the running averages of $X_{\text{av}}(t) \equiv t^{-1}\int\limits_0^t dt'\,X(t')$ for the cases $r = 0.3$ and $r = 1.2$, each with $E = 10$, and each for three different sets of initial conditions. For $r = 0.3$, the system is not ergodic, and the dynamics will be restricted to a subset of phase space. Accordingly the long time averages vary with the initial conditions. For $r = 1.2$ the system is ergodic and the results converge to the appropriate restricted microcanonical average $\langle X\rangle_{\mu\text{ce}}$ at large times, independent of initial conditions.

r	$X(0)$	$\langle X(t)\rangle$	$\langle X\rangle_{\mu\text{ce}}$	$\langle\gamma(t)\rangle$	$\langle\gamma\rangle_{\mu\text{ce}}$
0.3	0.1	6.1743	5.8974	0.5283	0.4505
0.3	1.0	5.7303	5.8974	0.4170	0.4505
0.3	3.0	5.7876	5.8974	0.4217	0.4505
0.3	5.0	5.8231	5.8974	0.4228	0.4505
0.3	7.0	5.8227	5.8974	0.4228	0.4505
0.3	9.0	5.8016	5.8974	0.4234	0.4505
0.3	9.9	6.1539	5.8974	0.5249	0.4505

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

r	$X(0)$	$\langle X(t)\rangle$	$\langle X\rangle_{\mu\text{ce}}$	$\langle\gamma(t)\rangle$	$\langle\gamma\rangle_{\mu\text{ce}}$
1.2	0.1	4.8509	4.8545	0.3816	0.3812
1.2	1.0	4.8479	4.8545	0.3811	0.3812
1.2	3.0	4.8493	4.8545	0.3813	0.3812
1.2	5.0	4.8482	4.8545	0.3813	0.3812
1.2	7.0	4.8472	4.8545	0.3808	0.3812
1.2	9.0	4.8466	4.8545	0.3808	0.3812
1.2	9.9	4.8444	4.8545	0.3807	0.3812

Table 1.3: Comparison of time averages and microcanonical ensemble averages for $r = 1.2$. Initial conditions are $P(0) = x(0) = 0$, with $X(0)$ given in the table and $E = 10$. Averages were performed over a period extending for $N_\text{b} = 10^7$ bounces.

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

Table 1.4: Comparison of time averages and microcanonical ensemble averages for $r = 1.2$, with N_b ranging from 10^4 to 10^9.

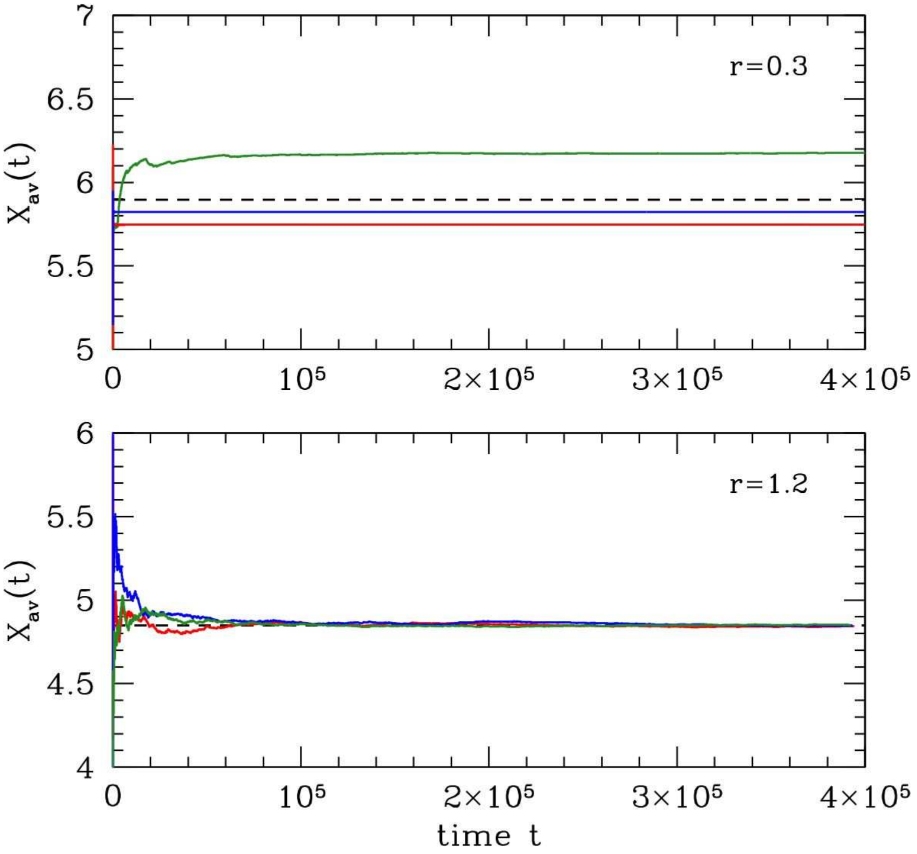

Figure 1.4: Long time running numerical averages $X_{\rm av}(t) \equiv t^{-1} \int\limits_0^t dt'\, X(t')$ for $r = 0.3$ (top) and $r = 1.2$ (bottom), each for three different initial conditions, with $E = 10$ in all cases. Note how in the $r = 0.3$ case the long time average is dependent on the initial condition, while the $r = 1.2$ case is ergodic and hence independent of initial conditions. The dashed black line shows the restricted microcanonical average, $\langle X \rangle_{\mu\rm ce} = \frac{(2+r)}{(1+r)} \cdot \frac{1}{3} E$.

Chapter 2

Solution Set #2

(1) Consider a d-dimensional ideal gas with dispersion $\varepsilon(\boldsymbol{p}) = A|\boldsymbol{p}|^\alpha$, with $\alpha > 0$. Find the density of states $D(E)$, the statistical entropy $S(E)$, the equation of state $p = p(N,V,T)$, the heat capacity at constant volume $C_V(N,V,T)$, and the heat capacity at constant pressure $C_p(N,V,T)$.

Solution: The density of states is

$$D(E,V,N) = \frac{V^N}{N!}\int\!\frac{d^dp_1}{h^d}\cdots\int\!\frac{d^dp_N}{h^d}\,\delta\big(E - Ap_1^\alpha - \ldots - Ap_N^\alpha\big)\ .$$

The Laplace transform is

$$\begin{aligned}
\widehat{D}(\beta,V,N) &= \frac{V^N}{N!}\bigg(\int\!\frac{d^dp}{h^d}\,e^{-\beta A p^\alpha}\bigg)^{\!N} \\
&= \frac{V^N}{N!}\bigg(\frac{\Omega_d}{h^d}\int\limits_0^\infty\!dp\,p^{d-1}\,e^{-\beta A p^\alpha}\bigg)^{\!N} \\
&= \frac{V^N}{N!}\bigg(\frac{\Omega_d\,\Gamma(d/\alpha)}{\alpha h^d A^{d/\alpha}}\bigg)^{\!N}\beta^{-Nd/\alpha}\ .
\end{aligned}$$

Now we inverse transform, recalling

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

We then conclude

$$D(E,V,N) = \frac{V^N}{N!}\bigg(\frac{\Omega_d\,\Gamma(d/\alpha)}{\alpha h^d A^{d/\alpha}}\bigg)^{\!N}\frac{E^{\frac{Nd}{\alpha}-1}}{\Gamma(Nd/\alpha)}$$

and

$$\begin{aligned}
S(E,V,N) &= k_{\rm B}\ln D(E,V,N) \\
&= Nk_{\rm B}\ln\!\bigg(\frac{V}{N}\bigg) + \frac{d}{\alpha}\,Nk_{\rm B}\,\ln\!\bigg(\frac{E}{N}\bigg) + Na_0\ ,
\end{aligned}$$

where a_0 is a constant, and we take the thermodynamic limit $N \to \infty$ with V/N and E/N fixed. From this we obtain the differential relation

$$\begin{aligned} dS &= \frac{Nk_{\rm B}}{V}\, dV + \frac{d}{\alpha}\, \frac{Nk_{\rm B}}{E}\, dE + s_0\, dN \\ &= \frac{p}{T}\, dV + \frac{1}{T}\, dE - \frac{\mu}{T}\, dN \ , \end{aligned}$$

where s_0 is a constant. From the coefficients of dV and dE, we conclude

$$\begin{aligned} pV &= Nk_{\rm B}T \\ E &= \frac{d}{\alpha}\, Nk_{\rm B}T \ . \end{aligned}$$

Setting $dN = 0$, we have

$$\begin{aligned} đQ &= dE + p\, dV \\ &= \frac{d}{\alpha}\, Nk_{\rm B}\, dT + p\, dV \\ &= \frac{d}{\alpha}\, Nk_{\rm B}\, dT + p\, d\bigg(\frac{Nk_{\rm B}T}{p}\bigg) \ . \end{aligned}$$

Thus,

$$C_V = \frac{đQ}{dT}\bigg|_V = \frac{d}{\alpha}\, Nk_{\rm B} \quad , \quad C_p = \frac{đQ}{dT}\bigg|_p = \bigg(1 + \frac{d}{\alpha}\bigg) Nk_{\rm B} \ .$$

(2) Find the velocity distribution $f(\boldsymbol{v})$ for the particles in problem (1). Compute the most probable speed, mean speed, and root-mean-square velocity.

Solution: The momentum distribution is

$$g(\boldsymbol{p}) = C\, e^{-\beta A p^\alpha} \ ,$$

where C is a normalization constant, defined so that $\int d^d\!p\; g(\boldsymbol{p}) = 1$. Changing variables to $t \equiv \beta A p^\alpha$, we find

$$C = \frac{\alpha\, (\beta A)^{\frac{d}{\alpha}}}{\Omega_d\, \Gamma\big(\frac{d}{\alpha}\big)} \ .$$

The velocity $\boldsymbol{v}$ is given by

$$\boldsymbol{v} = \frac{\partial \varepsilon}{\partial \boldsymbol{p}} = \alpha A p^{\alpha - 1}\, \hat{\boldsymbol{p}} \ .$$

Thus, the speed distribution is given by

$$f(v) = C \int \! d^d\!p\; e^{-\beta A p^\alpha}\, \delta\big(v - \alpha A p^{\alpha-1}\big) \ .$$

Thus,

$$\langle v^r \rangle = C \int \! d^d\!p\; e^{-\beta A p^\alpha}\, \big(\alpha A p^{\alpha-1}\big)^r$$

Thus,

$$\|v\|_r = \langle v^r \rangle^{1/r} = \alpha A^{\alpha^{-1}} \, (k_{\rm B}T)^{1-\alpha^{-1}} \left(\frac{\Gamma\big(\frac{d-r}{\alpha} + r\big)}{\Gamma\big(\frac{d}{\alpha}\big)} \right)^{1/\alpha} .$$

To find the most probable speed, we extremize $f(v)$. We write

$$\delta\big(v - \alpha A p^{\alpha-1}\big) = \frac{\delta\big(p - (v/\alpha A)^{1/(\alpha-1)}\big)}{\alpha(\alpha-1)Ap^{\alpha-2}} .$$

We then find

$$f(v) = \frac{C}{\alpha(\alpha-1)A} \, p^{d-\alpha+1} \, e^{-\beta A p^\alpha} \bigg|_{p=(v/\alpha A)^{1/(\alpha-1)}} .$$

Extremizing, we obtain

$$\beta A p^\alpha = \frac{d-\alpha+1}{\alpha} ,$$

which means

$$v = \alpha A \bigg(\frac{d-\alpha+1}{\alpha\beta A} \bigg)^{1-\alpha^{-1}} = (\alpha A)^{\alpha^{-1}} (d-\alpha+1)^{1-\alpha^{-1}} (k_{\rm B}T)^{1-\alpha^{-1}} .$$

(3) A spin-1 Ising magnet is described by the noninteracting Hamiltonian

$$H = -\mu_0 \mathsf{H} \sum_{i=1}^{\mathsf{N}} \sigma_i ,$$

where $\sigma_i = -1, 0, +1$.

(a) Find the entropy $S(\mathsf{H}, T, \mathsf{N})$.

(b) Suppose the system starts off at a temperature $T = 10\,\text{mK}$ and a field $\mathsf{H} = 20\,\text{T}$. The field is then lowered adiabatically to $\mathsf{H} = 1\,\text{T}$. What is the final temperature of the system?

Solution: The partition function for a single spin is

$$\zeta = 1 + 2\cosh(\beta\mu_0\mathsf{H}) .$$

The free energy is therefore

$$F = -\mathsf{N} k_{\rm B} T \ln \Big(1 + 2\cosh\big(\mu_0\mathsf{H}/k_{\rm B}T\big) \Big) .$$

The entropy is

$$S = -\bigg(\frac{\partial F}{\partial T}\bigg)_{VN} = \mathsf{N} k_{\rm B} \ln \Big(1 + 2\cosh\big(\mu_0\mathsf{H}/k_{\rm B}T\big) \Big) - \mathsf{N} \, \frac{\mu_0\mathsf{H}}{T} \, \frac{2\sinh\big(\mu_0\mathsf{H}/k_{\rm B}T\big)}{1 + 2\cosh\big(\mu_0\mathsf{H}/k_{\rm B}T\big)}$$

Note that $S = Ns(\mathsf{H}/T)$. Thus, an adiabatic process is one which takes place at constant H/T. If H is lowered by a factor of 20, then T is lowered by a factor of 20. For this problem, then, the final temperature is $0.5\,$mK.

(4) Consider an adsorption model where each of N sites on a surface can accommodate either one or two adsorbate molecules. When one molecule is present the energy is $\varepsilon = -\Delta$, but when two are present the energy is $\varepsilon = -2\Delta + U$, where U models the local interaction of two adsorbate molecules at the same site. You should think of there being two possible binding locations within each adsorption site, so there are four possible states per site: unoccupied (1 possibility), singly occupied (2 possibilities), and doubly occupied (1 possibility). The surface is in equilibrium with a gas at temperature T and number density n.

(a) Find the surface partition function.

(b) Find the fraction f_j which contain j adsorbate molecules, where $j = 0, 1, 2$.

Solution: The surface partition function is

$$\Xi = \Big(1 + 2\,e^{\beta(\mu+\Delta)} + e^{2\beta(\mu+\Delta)}\,e^{-\beta U}\Big)^{\mathsf{N}} ,$$

hence

$$\Omega = -\mathsf{N}k_{\rm B}T\ln\Big(1 + 2\,e^{(\mu+\Delta)/k_{\rm B}T} + e^{2(\mu+\Delta)/k_{\rm B}T}\,e^{-U/k_{\rm B}T}\Big) .$$

In the gas, we have $e^{\mu/k_{\rm B}T} = n\lambda_T^3$. Therefore

$$\begin{aligned}
f_0 &= \frac{1}{1 + 2\,n\lambda_T^3\,e^{\Delta/k_{\rm B}T} + n^2\lambda_T^6\,e^{2\Delta/k_{\rm B}T}\,e^{-U/k_{\rm B}T}}\\
f_1 &= \frac{2\,n\lambda_T^3\,e^{\Delta/k_{\rm B}T}}{1 + 2\,n\lambda_T^3\,e^{\Delta/k_{\rm B}T} + n^2\lambda_T^6\,e^{2\Delta/k_{\rm B}T}\,e^{-U/k_{\rm B}T}}\\
f_2 &= \frac{(n\lambda_T^3)^2\,e^{2\Delta/k_{\rm B}T}\,e^{-U/k_{\rm B}T}}{1 + 2\,n\lambda_T^3\,e^{\Delta/k_{\rm B}T} + n^2\lambda_T^6\,e^{2\Delta/k_{\rm B}T}\,e^{-U/k_{\rm B}T}} .
\end{aligned}$$

(5) Consider a system of dipoles with the Hamiltonian

$$H = \sum_{i<j} J_{ij}^{\alpha\beta}\,m_i^\alpha\,m_j^\beta - \mu_0\sum_i \mathsf{H}_i^\alpha\,m_i^\alpha ,$$

where

$$J_{ij}^{\alpha\beta} = \frac{J}{R_{ij}^3}\,\big(\delta^{\alpha\beta} - 3\,\hat{R}_{ij}^\alpha\,\hat{R}_{ij}^\beta\big) .$$

Here $\boldsymbol{R}_i$ is the spatial position of the dipole $\boldsymbol{m}_i$, and $\boldsymbol{R}_{ij} = \boldsymbol{R}_i - \boldsymbol{R}_j$ with $\hat{R}_{ij}^\alpha \equiv R_{ij}^\alpha/R_{ij}$ the unit direction vector from j to i. The dipole vectors m_i^α are three-dimensional unit vectors. H_i^α is the local magnetic field.

(a) Find an expression for the free energy $F\big(T, \{\vec{\mathsf{H}}_i\}\big)$ valid to order β^2, where $\beta = 1/k_{\rm B}T$.

(b) Obtain an expression for the uniform field magnetic susceptibility tensor $\chi_{\alpha\beta}$.

(c) An experimentalist plots the quantity $T\chi_{\alpha\beta}$ *versus* T^{-1} for large temperatures. What should the data resemble if the dipoles are arranged in a cubic lattice structure? How about if they are arranged in a square lattice in the (x, y) plane? (You'll need to separately consider the various cases for the indices α and β. You will also need to numerically evaluate certain lattice sums.)

Solution: Since $Z = e^{-\beta F}$, we will need to expand Z to order β^3 in order to obtain F to order β^2. We have

$$\begin{aligned} Z &= \mathsf{Tr}\ e^{-\beta H} \\ &= \mathsf{Tr}\ 1 - \beta\, \mathsf{Tr}\, H + \tfrac{1}{2}\beta^2\, \mathsf{Tr}\, H^2 - \tfrac{1}{6}\beta^3\, \mathsf{Tr}\, H^3 + \mathcal{O}(\beta^4)\ . \end{aligned}$$

Taking the logarithm, and recalling $\ln(1+\varepsilon) = \sum_{k=1}^\infty (-1)^{k-1} \varepsilon^k / k$, we have

$$F = \mathsf{Tr}\, H - \tfrac{1}{2}\beta \Big[\, \mathsf{Tr}\,\big(H^2\big) - (\mathsf{Tr}\, H)^2 \Big] + \tfrac{1}{6}\beta^2 \Big[\, \mathsf{Tr}\,\big(H^3\big) - 3\, \mathsf{Tr}\,\big(H^2\big)\, \mathsf{Tr}\, H + 2\, (\mathsf{Tr}\, H)^3 \Big] + \mathcal{O}(\beta^3)\ .$$

We define the trace as

$$\mathsf{Tr}\, F(\hat{m}_1, \ldots, \hat{m}_N) = \int \prod_{j=1}^N \frac{d\hat{m}_j}{4\pi}\, F(\hat{m}_1, \ldots, \hat{m}_N)\ ,$$

so that $\mathsf{Tr}\, 1 = 1$. Thus,

$$\mathsf{Tr}\,\big(m_i^\mu m_j^\nu\big) = \tfrac{1}{3}\, \delta_{ij}\, \delta^{\mu\nu}\ .$$

Clearly the trace of any product of an odd number of terms m_i^μ with the same i, no matter what the choices of the $\mathsf{O}(3)$ indices (*e.g.* μ), must vanish, since the trace itself is invariant under $\hat{m}_i \to -\hat{m}_i$. It isn't so easy to compute traces of higher order even products, since the unit vector constraint on $\hat{m}_i$ invalidates the application of Wick's theorem, which can be invoked when computing the averages of Gaussianly distributed variables. For example, one finds $\mathsf{Tr}\,\big(\hat{m}^x \hat{m}^x \hat{m}^y \hat{m}^y\big) = \frac{2}{3}$ while $\mathsf{Tr}\,\big(\hat{m}^x \hat{m}^x \hat{m}^x \hat{m}^x\big) = \frac{1}{5}$. No matter; we shall only need $\mathsf{Tr}\,\big(m_i^\mu m_j^\nu\big)$, computed above.

We now write $H = H_0 + H_1$, where $H_0 = \sum_{i<j} J_{ij}^{\alpha\beta}\, m_i^\alpha\, m_j^\beta$ and $H_1 = -\mu_0 \sum_i \mathsf{H}_i^\alpha\, m_i^\alpha$. Eliminating the odd terms whose traces vanish, we have

$$\begin{aligned} \mathsf{Tr}\, H &= \mathsf{Tr}(H_0 + H_1) = 0 \\ \mathsf{Tr}\,\big(H^2\big) &= \mathsf{Tr}\,\big(H_0^2 + 2\, H_0\, H_1 + H_1^2\big) = \mathsf{Tr}\,\big(H_0^2\big) + \mathsf{Tr}\,\big(H_1^2\big) \\ \mathsf{Tr}\,\big(H^3\big) &= \mathsf{Tr}\,\big(H_0^3 + 3\, H_0^2\, H_1 + 3\, H_0\, H_1^2 + H_1^3\big) = \mathsf{Tr}\,\big(H_0^3\big) + \mathsf{Tr}\,\big(H_0\, H_1^2\big)\ . \end{aligned}$$

Note that $\mathsf{Tr}\, H_0 = 0$ since i and j are distinct in the sum. We may now compute

$$\begin{aligned}
\mathsf{Tr}\,\big(H_0^2\big) &= \sum_{i<j} J_{ij}^{\mu\nu}\, J_{ij}^{\mu\nu} \\
\mathsf{Tr}\,\big(H_1^2\big) &= \tfrac{1}{3}\mu_0^2 \sum_i \mathsf{H}_i^\alpha \mathsf{H}_i^\alpha \\
\mathsf{Tr}\,\big(H_0^3\big) &= 3 \sum_{i<j<k} J_{ij}^{\mu\nu}\, J_{jk}^{\nu\lambda} J_{ki}^{\lambda\mu} \\
\mathsf{Tr}\,\big(H_0\, H_1^2\big) &= \tfrac{1}{3}\mu_0^2 \sum_{i<j} J_{ij}^{\mu\nu} \mathsf{H}_i^\mu \mathsf{H}_j^\nu \ .
\end{aligned}$$

Next we must contract the $\mathsf{O}(3)$ indices. We find

$$\begin{aligned}
J_{ij}^{\mu\nu}\, J_{ij}^{\mu\nu} &= \frac{6J^2}{R_{ij}^6} \\
J_{ij}^{\mu\nu}\, J_{jk}^{\nu\lambda}\, J_{ki}^{\lambda\mu} &= \Big[-6 + 9\,(\hat{R}_{ij}\cdot\hat{R}_{jk})^2 + 9\,(\hat{R}_{jk}\cdot\hat{R}_{ki})^2 + 9\,(\hat{R}_{ki}\cdot\hat{R}_{ij})^2 \\
&\qquad\qquad - 27\,(\hat{R}_{ij}\cdot\hat{R}_{jk})(\hat{R}_{jk}\cdot\hat{R}_{ki})(\hat{R}_{ki}\cdot\hat{R}_{ij})\Big] \cdot \frac{J^3}{R_{ij}^3 R_{jk}^3 R_{ki}^3} \ .
\end{aligned}$$

(a) Thus, the free energy is

$$\begin{aligned}
F = -\frac{3J^2}{k_\mathrm{B}T} \sum_{i<j} \frac{1}{R_{ij}^6} - \frac{\mu_0^2}{6\,k_\mathrm{B}T} \sum_i \mathsf{H}_i^\alpha\, \mathsf{H}_i^\alpha + \frac{\mu_0^2 J}{18\,(k_\mathrm{B}T)^2} \sum_{i<j} \left(\frac{\delta^{\mu\nu} - 3\hat{R}_{ij}^\mu \hat{R}_{ij}^\nu}{R_{ij}^3} \right) \mathsf{H}_i^\mu\, \mathsf{H}_j^\nu \\
+ \frac{J^3}{(k_\mathrm{B}T)^2} \sum_{i<j<k} \frac{-2 + 3\,\hat{R}_{ij}\cdot\hat{R}_{jk} + 3\,\hat{R}_{jk}\cdot\hat{R}_{ki} + 3\,\hat{R}_{ki}\cdot\hat{R}_{ij} - 9\,(\hat{R}_{ij}\cdot\hat{R}_{jk})(\hat{R}_{jk}\cdot\hat{R}_{ki})(\hat{R}_{ki}\cdot\hat{R}_{ij})}{R_{ij}^3 R_{jk}^3 R_{ki}^3}
\end{aligned}$$

to order β^2.

(b) We have

$$\begin{aligned}
\chi_{ij}^{\mu\nu} &= \frac{\partial\,\langle \mu_0\, m_i^\mu \rangle}{\partial \mathsf{H}_j^\nu} = -\frac{\partial^2 F}{\partial \mathsf{H}_i^\mu\, \partial \mathsf{H}_j^\nu} \\
&= \frac{\mu_0^2}{3k_\mathrm{B}T}\, \delta^{\mu\nu}\, \delta_{ij} - \frac{\mu_0^2\, J}{9\,(k_\mathrm{B}T)^2} \left(\frac{\delta^{\mu\nu} - 3\hat{R}_{ij}^\mu \hat{R}_{ij}^\nu}{R_{ij}^3} \right) (1-\delta_{ij}) + \mathcal{O}(T^{-3}) \ .
\end{aligned}$$

The second term is here multiplied by $(1-\delta_{ij})$ since i and j must be distinct in the corresponding term from the free energy. $\chi_{ij}^{\mu\nu}$ tells us how the moment at site i changes in response to a change in the magnetic field at site j. To get the uniform magnetic susceptibility, we differentiate the total moment $M^\mu = \mu_0 \sum_i \langle m_i^\mu \rangle$ with respect to a uniform field H^ν, and we then divide by the system volume. Thus,

$$\chi^{\mu\nu} = \frac{1}{V} \sum_{i,j} \chi_{ij}^{\mu\nu} = \frac{N}{V} \cdot \frac{\mu_0^2}{3k_\mathrm{B}T}\, \delta^{\mu\nu} - \frac{\mu_0^2\, J}{9\,(k_\mathrm{B}T)^2} \cdot \frac{1}{V} \sum_{i\neq j} \left(\frac{\delta^{\mu\nu} - 3\hat{R}_{ij}^\mu \hat{R}_{ij}^\nu}{R_{ij}^3} \right) + \mathcal{O}(T^{-3}) \ .$$

The above expression is valid for any spatial arrangement of the dipoles. They don't have to be in a regular lattice, for example.

(c) If the dipoles are located at the sites of a Bravais lattice, then we may write

$$\chi^{\mu\nu} = \frac{1}{V} \sum_{i,j} \chi^{\mu\nu}_{ij} = \frac{N}{V} \cdot \frac{\mu_0^2}{3k_{\rm B}T}\, \delta^{\mu\nu} - \frac{N}{V} \cdot \frac{\mu_0^2\, J}{9\,(k_{\rm B}T)^2} \sum_{\boldsymbol{R}\neq 0} \left(\frac{\delta^{\mu\nu} - 3\hat{R}^\mu \hat{R}^\nu}{R^3} \right) + \mathcal{O}(T^{-3})\ ,$$

where the sum is over all Bravais lattice vectors (*i.e.* all lattice points) other than $\boldsymbol{R} = 0$. Now let's do the lattice sum in the second term for the case of a cubic lattice. We write $\boldsymbol{R} = (l\,\hat{\boldsymbol{x}} + m\,\hat{\boldsymbol{y}} + n\,\hat{\boldsymbol{z}})a$, where a is the lattice constant and (l,m,n) are integers. We sum over all triples of integers (l,m,n) other than $(0,0,0)$. We then have

$$R = \big(l^2 + n^2 + n^2\big)^{1/2}\, a \quad , \quad \hat{R} = \frac{\boldsymbol{R}}{R} = \frac{l\,\hat{\boldsymbol{x}} + m\,\hat{\boldsymbol{y}} + n\,\hat{\boldsymbol{z}}}{(l^2 + m^2 + n^2)^{1/2}}\ .$$

It is clear that the off-diagonal terms in $\chi^{\mu\nu}$ must vanish due to the cubic symmetry. For example, when $\mu = x$ and $\nu = y$ we have to compute

$$\sum_{l,m,n}{}' \frac{lm}{(l^2+m^2+n^2)^{5/2}} = 0\ ,$$

since the summand is odd separately in both l and m. The prime on the sum indicates that the term $(0,0,0)$ is to be excluded.

Next, consider the diagonal elements. For a cubic lattice, we must have $\chi^{xx} = \chi^{yy} = \chi^{zz}$, so we need only compute the xx term:

$$\sum_{\boldsymbol{R}\neq 0} \left(\frac{1 - 3\hat{R}^x \hat{R}^x}{R^3} \right) = \frac{1}{a^3} \sum_{l,m,n}{}' \frac{m^2 + n^2 - 2l^2}{(l^2+m^2+n^2)^{5/2}} = 0\ .$$

To see why this term vanishes, note that any permutation of the triple (l,m,n) is also a Bravais lattice site. Summing over all permutations, we see that the above sum must vanish. We therefore conclude that all components of the $\mathcal{O}(T^{-2})$ term in the susceptibility vanish for a cubic lattice. In fact, it is clear from the outset that

$$\mathsf{Tr}\,\big(\delta^{\mu\nu} - 3\hat{R}^\mu \hat{R}^\nu\big) = 0\ ,$$

so this result coupled with the cubic symmetry immediately tells us that the $\mathcal{O}(T^{-2})$ must vanish for all components.

For a square lattice, we set $n = 0$. The off-diagonal component χ^{xy} still vanishes due to the square symmetry, but now we have $\chi^{xx} = \chi^{yy} = -\frac{1}{2}\chi^{zz}$. The lattice sum for the xx term is

$$-\sum_{l,m}{}' \frac{m^2 - 2l^2}{(l^2+m^2)^{5/2}} = \sum_{l,m}{}' \frac{l^2}{(l^2+m^2)^{5/2}} = \tfrac{1}{2} \sum_{l,m}{}' \frac{1}{(l^2+m^2)^{3/2}} = 1.7302\ ,$$

where the numerical value is obtained by numerical summation. Thus,

$$\chi^{\mu\nu}(\text{SC}) = \frac{N}{V} \cdot \frac{\mu_0^2}{3k_\text{B}T}\,\delta^{\mu\nu} + \mathcal{O}(T^{-3})$$

$$\chi^{\mu\nu}(\text{SQ}) = \frac{N}{V} \cdot \frac{\mu_0^2}{3k_\text{B}T}\,\delta^{\mu\nu} + \frac{N}{V} \cdot \frac{\mu_0^2\,J}{9\,(k_\text{B}T)^2} \cdot \frac{1.7302}{a^3} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} + \mathcal{O}(T^{-3})$$

for simple cubic and square lattices, respectively. Thus, if we plot $T\chi^{\mu\nu}$ *versus* T^{-1} at high temperatures, we should observe a straight line with intercept $n\mu_0^2/3k_\text{B}$, with $n = N/V$. The slope of the line is zero for the case of a cubic lattice, but for a square lattice, we should observe a positive slope of $1.7302\,n\mu_0^2 J/9k_\text{B}^2$ for χ^{xx} and χ^{yy} and a negative slope of twice this magnitude for χ^{zz}.

(6) The general form of the kinetic energy for a rotating body is

$$T = \tfrac{1}{2} I_1 \big(\dot\phi\,\sin\theta\sin\psi + \dot\theta\cos\psi\big)^2 + \tfrac{1}{2} I_2\,\big(\dot\phi\,\sin\theta\cos\psi - \dot\theta\,\sin\psi\big)^2 + \tfrac{1}{2} I_3\,\big(\dot\phi\cos\theta + \dot\psi\big)^2 \ ,$$

where (ϕ, θ, ψ) are the Euler angles.

(a) Find the Hamiltonian $H(p_\phi, p_\theta, p_\psi)$ for a free asymmetric rigid body.

(b) Compute the rotational partition function,

$$\xi_\text{rot}(T) = \frac{1}{h^3} \int\limits_{-\infty}^{\infty}\! dp_\phi \int\limits_{-\infty}^{\infty}\! dp_\theta \int\limits_{-\infty}^{\infty}\! dp_\psi \int\limits_0^{2\pi}\! d\phi \int\limits_0^{\pi}\! d\theta \int\limits_0^{2\pi}\! d\psi\; e^{-H(p_\phi, p_\theta, p_\psi)/k_\text{B}T}$$

and show that you recover the result in §3.13.3 of the notes.

Solution: We define generalized coordinates (ϕ, θ, ψ), in which case we may write $T = \frac{1}{2} \mathsf{T}_{ij}\,\dot q_i\,\dot q_j$, with

$$\mathsf{T}_{ij} = \begin{pmatrix} (I_1\sin^2\!\psi + I_2\cos^2\!\psi)\sin^2\!\theta + I_3\cos^2\!\theta & (I_1 - I_2)\sin\theta\sin\psi\cos\psi & I_3\cos\theta \\ (I_1 - I_2)\sin\theta\sin\psi\cos\psi & I_1\cos^2\!\psi + I_2\sin^2\!\psi & 0 \\ I_3\cos\theta & 0 & I_3 \end{pmatrix}$$

The generalized momenta are $p_i = \partial T/\partial \dot q_i = \mathsf{T}_{ij}\,\dot q_j$, and the Hamiltonian is

$$H = \tfrac{1}{2} \mathsf{T}^{-1}_{ij}\, p_i\, p_j \ .$$

Recall the general formula for a matrix inverse: $M^{-1}_{ij} = (-1)^{i+j} \Delta_{ji} / \det M$, where the *minor* Δ_{ij} is the determinant of the square matrix formed from M by eliminating the i^th row and the j^th column. The matrix T is of the form

$$\mathsf{T} = \begin{pmatrix} a & d & e \\ d & b & 0 \\ e & 0 & c \end{pmatrix} \ ,$$

hence the determinant is $\mathsf{det}\,\mathsf{T} = abc - cd^2 - be^2$ and the inverse is

$$\mathsf{T}^{-1} = \frac{1}{abc - cd^2 - be^2} \begin{pmatrix} bc & -cd & -be \\ -cd & ac - e^2 & de \\ -be & de & ab - d^2 \end{pmatrix} .$$

Taking the determinant of T is straightforward, and one finds $\mathsf{det}\,\mathsf{T} = I_1 I_2 I_3 \sin^2\!\theta$. The rotational partition function is then given by the multidimensional integral

$$\begin{aligned} \xi_{\rm rot}(T) &= \frac{1}{h^3} \int_0^{2\pi}\! d\phi \int_0^{\pi}\! d\theta \int_0^{2\pi}\! d\psi \int_{-\infty}^{\infty}\! dp_\phi \int_{-\infty}^{\infty}\! dp_\theta \int_{-\infty}^{\infty}\! dp_\psi \; e^{-\mathsf{T}^{-1}_{ij}\, p_i p_j / 2 k_{\rm B} T} \\ &= \frac{1}{h^3} \int_0^{2\pi}\! d\phi \int_0^{\pi}\! d\theta \int_0^{2\pi}\! d\psi \; (2\pi k_{\rm B} T)^{3/2} \sqrt{\mathsf{det}\,\mathsf{T}} \\ &= \left(\frac{2 k_{\rm B} T}{\hbar^2} \right)^{3/2} \sqrt{\pi I_1 I_2 I_3} \; , \end{aligned}$$

as in §3.13.3 of the notes.

(7) For polyatomic molecules, the full internal partition function is written as the product

$$\xi(T) = \frac{g_{\rm el} \cdot g_{\rm nuc}}{g_{\rm sym}} \cdot \xi_{\rm vib}(T) \cdot \xi_{\rm rot}(T) \; ,$$

where $g_{\rm el}$ is the degeneracy of the lowest electronic state[1], $g_{\rm nuc} = \prod_j (2 I_j + 1)$ is the total nuclear spin degeneracy, $\xi_{\rm vib}(T)$ is the vibrational partition function, and $\xi_{\rm rot}(T)$ is the rotational partition function[2]. The integer $g_{\rm sym}$ is the *symmetry factor* of the molecule, which is defined to be the number of identical configurations of a given molecule which are realized by rotations when the molecule contains identical nuclei. Evaluate $g_{\rm nuc}$ and $g_{\rm sym}$ for the molecules CH_4 (methane), CH_3D, CH_2D_2, CHD_3, and CD_4. Discuss how the successive deuteration of methane will affect the vibrational and rotational partition functions. For the vibrations your discussion can be qualitative, but for the rotations note that all one needs, as we derived in problem (6), is the product $I_1 I_2 I_3$ of the moments of inertia, which is the determinant of the inertia tensor $I_{\alpha\beta}$ *in a body-fixed center-of-mass frame*. Using the parallel axis theorem, one has

$$I_{\alpha\beta} = \sum_j m_j \big(\boldsymbol{r}_j^2 \, \delta_{\alpha\beta} - r_j^\alpha \, r_j^\beta \big) + M \big(\boldsymbol{R}^2 \, \delta_{\alpha\beta} - R^\alpha R^\beta \big)$$

where $M = \sum_j m_j$ and $\boldsymbol{R} = M^{-1} \sum_j m_j \boldsymbol{r}_j$. Recall that methane is structurally a tetrahedron of hydrogen atoms with a carbon atom at the center, so we can take $\boldsymbol{r}_1 = (0,0,0)$ to be the location of the carbon atom and $\boldsymbol{r}_{2,3,4,5} = (1,1,1) \, , \; (1,-1,-1) \, , \; (-1,1,-1) \, , \; (-1,-1,1)$

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[1] We assume the temperature is low enough that we can ignore electronic excitations.

[2] Note that for linear polyatomic molecules such as CO_2 and HCN, we must treat the molecule as a rotor, *i.e.* we use eqn. 3.278 of the notes.

to be the location of the hydrogen atoms, with all distances in units of $\frac{1}{\sqrt{3}}$ times the $\mathrm{C-H}$ separation.

Solution: The total partition function is given by

$$Z(T,V,N) = \frac{V^N}{N!}\bigg(\frac{2\pi\hbar^2}{Mk_{\rm B}T}\bigg)^{3N/2}\,\xi^N_{\rm int}(T)\ ,$$

The Gibbs free energy per particle is

$$\begin{aligned}\mu(T,p) = \frac{G(T,p,N)}{N} &= k_{\rm B}T\ln\bigg(\frac{p\,\lambda_T^d}{k_{\rm B}T}\bigg) - k_{\rm B}T\ln\xi(T)\\ &= k_{\rm B}T\ln\bigg(\frac{p\,\lambda_T^d}{k_{\rm B}T}\bigg) - k_{\rm B}T\ln\bigg(\frac{g_{\rm el}\cdot g_{\rm nuc}}{g_{\rm sym}}\bigg)\\ &\qquad + k_{\rm B}T\sum_a \ln\Big(2\sinh(\Theta_a/2T)\Big) - k_{\rm B}T\ln\Bigg[\bigg(\frac{2k_{\rm B}T}{\hbar^2}\bigg)^{3/2}\sqrt{\pi I_1 I_2 I_3}\Bigg]\ .\end{aligned}$$

The electronic degeneracy is $g_{\rm el}=1$ for all stages of deuteration. The nuclear spin of the proton is $I=\frac{1}{2}$ and that of the deuteron is $I=1$. Thus there is a nuclear degeneracy of $2I_{\rm p}+1=2$ for each hydrogen nucleus and $2I_{\rm d}+1=3$ for each deuterium nucleus. The symmetry factor is analyzed as follows. For methane $\mathrm{CH_4}$, there are four threefold symmetry axes, resulting in $g_{\rm sym}=12$. The same result holds for $\mathrm{CD_4}$. For $\mathrm{CH_3D}$ or $\mathrm{CHD_3}$, there is a single threefold axis, hence $g_{\rm sym}=3$. For $\mathrm{CH_2D_2}$, the two hydrogen nuclei lie in a plane together with the carbon, and the two deuterium nuclei lie in a second plane together with the carbon. The intersection of these two planes provides a twofold symmetry axis, about which a 180° rotation will rotate one hydrogen into the other and one deuterium into the other. Thus $g_{\rm sym}=2$.

To analyze the rotational partition function, we need the product $I_1I_2I_3$ of the principal moments of inertia, which is to say the determinant of the inertia tensor $\mathsf{det}\ I$. We work here in units of amu for mass and $\frac{1}{\sqrt{3}}$ times the $\mathrm{C-H}$ separation for distance. The inertia tensor is

$$I_{\alpha\beta} = \sum_j m_j\big(\boldsymbol{r}_j^2\,\delta_{\alpha\beta} - r_j^\alpha\,r_j^\beta\big) + M\big(\boldsymbol{R}^2\,\delta_{\alpha\beta} - R^\alpha R^\beta\big)$$

where

$$\begin{aligned}M &= \sum_j m_j\\ \boldsymbol{R} &= M^{-1}\sum_j m_j\boldsymbol{r}_j\ .\end{aligned}$$

The locations of the four hydrogen/deuterium ions are:

$$\begin{aligned}&\mathrm{L1}:(+1,+1,+1)\\ &\mathrm{L2}:(+1,-1,-1)\\ &\mathrm{L3}:(-1,+1,-1)\\ &\mathrm{L4}:(-1,-1,+1)\ .\end{aligned}$$

For CH_4 we have $M = 16$ and $\boldsymbol{R} = 0$. The inertia tensor is

$$I_{\mathrm{CH}_4} = \begin{pmatrix} 8 & 0 & 0 \\ 0 & 8 & 0 \\ 0 & 0 & 8 \end{pmatrix} .$$

Similarly, for CD_4 we have

$$I_{\mathrm{CD}_4} = \begin{pmatrix} 16 & 0 & 0 \\ 0 & 16 & 0 \\ 0 & 0 & 16 \end{pmatrix} .$$

For $\mathrm{CH}_3\mathrm{D}$, there is an extra mass unit located at L1 relative to methane, so $M = 17$. The CM is at $\boldsymbol{R} = \frac{1}{17}(+1, +1, +1)$. According to the general formula above for $I_{\alpha\beta}$, thie results in two changes to the inertia tensor, relative to I_{CH_4}. We find

$$\Delta I = \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} + \frac{1}{17} \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} ,$$

where the first term accounts for changes in I in the frame centered at the carbon atom, and the second term shifts to the center-of-mass frame. Thus,

$$I_{\mathrm{CH}_3\mathrm{D}} = \begin{pmatrix} 10 + \frac{2}{17} & -\frac{18}{17} & -\frac{18}{17} \\ -\frac{18}{17} & 10 + \frac{2}{17} & -\frac{18}{17} \\ -\frac{18}{17} & -\frac{18}{17} & 10 + \frac{2}{17} \end{pmatrix} .$$

For CHD_3, we regard the system as CD_4 with a missing mass unit at L1, hence $M = 19$. The CM is now at $\boldsymbol{R} = \frac{1}{17}(-1, -1, -1)$. The change in the inertia tensor relative to I_{CD_4} is then

$$\Delta I = -\begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} + \frac{1}{19} \begin{pmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix} .$$

Thus,

$$I_{\mathrm{CHD}_3} = \begin{pmatrix} 14 + \frac{2}{19} & \frac{18}{19} & \frac{18}{19} \\ \frac{18}{19} & 14 + \frac{2}{19} & \frac{18}{19} \\ \frac{18}{19} & \frac{18}{19} & 14 + \frac{2}{19} \end{pmatrix} .$$

Finally, for $\mathrm{CH}_2\mathrm{D}_2$. we start with methane and put extra masses at L1 and L2, so $M = 18$ and $\boldsymbol{R} = \frac{1}{9}(+1, 0, 0)$. Then

$$\Delta I = -\begin{pmatrix} 4 & 0 & 0 \\ 0 & 4 & -2 \\ 0 & -2 & 4 \end{pmatrix} + \frac{2}{9} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and

$$I_{\mathrm{CH_2D_2}} = \begin{pmatrix} 12 & 0 & 0 \\ 0 & 12+\frac{2}{9} & -2 \\ 0 & -2 & 12+\frac{2}{9} \end{pmatrix} .$$

For the vibrations, absent a specific model for the small oscillations problem the best we can do is to say that adding mass tends to lower the normal mode frequencies since $\omega \sim \sqrt{k/M}$.

molecule	mass M (amu)	degeneracy factor g_{nuc}	symmetry factor g_{sym}	det I $(\mathrm{amu}) \cdot a^2/3$
$\mathrm{CH_4}$	16	$2^4 = 16$	$4 \times 3 = 12$	8^3
$\mathrm{CH_3D}$	17	$2^3 \cdot 3 = 24$	$1 \times 3 = 3$	$8 \cdot \big(11 + \frac{3}{17}\big)^2$
$\mathrm{CH_2D_2}$	18	$2^2 \cdot 3^2 = 36$	$1 \times 2 = 2$	$12 \cdot \big(8 + \frac{2}{9}\big) \cdot \big(16 + \frac{2}{9}\big)$
$\mathrm{CHD_3}$	19	$2 \cdot 3^3 = 54$	$1 \times 3 = 3$	$16 \cdot \big(13 + \frac{3}{19}\big)^2$
$\mathrm{CD_4}$	20	$3^4 = 81$	$4 \times 3 = 12$	16^3

Table 2.1: Nuclear degeneracy, symmetry factor, and $I_1 I_2 I_3$ product for successively deuterated methane.

Chapter 3

Solution Set #3

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

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

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

(a) Find the single trimer partition function ζ.

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

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

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

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

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

$\vert\,\sigma_1\sigma_2\sigma_3\,\rangle$	E	$\vert\,\sigma_1\sigma_2\sigma_3\,\rangle$	E
$\vert\uparrow\uparrow\uparrow\,\rangle$	$-3J - 3\mu_0\mathsf{H}$	$\vert\downarrow\downarrow\downarrow\,\rangle$	$-3J + 3\mu_0\mathsf{H}$
$\vert\uparrow\uparrow\downarrow\,\rangle$	$+J - \mu_0\mathsf{H}$	$\vert\downarrow\downarrow\uparrow\,\rangle$	$+J + \mu_0\mathsf{H}$
$\vert\uparrow\downarrow\uparrow\,\rangle$	$+J - \mu_0\mathsf{H}$	$\vert\downarrow\uparrow\downarrow\,\rangle$	$+J + \mu_0\mathsf{H}$
$\vert\downarrow\uparrow\uparrow\,\rangle$	$+J - \mu_0\mathsf{H}$	$\vert\uparrow\downarrow\downarrow\,\rangle$	$+J + \mu_0\mathsf{H}$

Table 3.1: Spin configurations and their corresponding energies.

(a) The single trimer partition function is then

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

(b) The magnetization is

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

(c) Expanding $m(T,\mathsf{H})$ to lowest order in H, we have

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

Thus,

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

(d) Note that

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

Thus,

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

So the entropy is

$$\begin{aligned} S(T,\mathsf{H},N_\triangle) &= N_\triangle k_{\rm B}\ln\Big(2\,e^{3\beta J}\cosh(3\beta\mu_0\mathsf{H}) + 6\,e^{-\beta J}\cosh(\beta\mu_0\mathsf{H})\Big) \\ &\qquad - 6N_\triangle\beta J k_{\rm B}\cdot\left(\frac{e^{3\beta J}\cosh(3\beta\mu_0\mathsf{H}) - e^{-\beta J}\cosh(\beta\mu_0\mathsf{H})}{2\,e^{3\beta J}\cosh(3\beta\mu_0\mathsf{H}) + 6\,e^{-\beta J}\cosh(\beta\mu_0\mathsf{H})}\right) \\ &\qquad\quad - 6N_\triangle\beta\mu_0\mathsf{H}k_{\rm B}\cdot\left(\frac{e^{3\beta J}\sinh(3\beta\mu_0\mathsf{H}) + e^{-\beta J}\sinh(\beta\mu_0\mathsf{H})}{2\,e^{3\beta J}\cosh(3\beta\mu_0\mathsf{H}) + 6\,e^{-\beta J}\cosh(\beta\mu_0\mathsf{H})}\right)\ . \end{aligned}$$

Setting $\mathsf{H}=0$ we have

$$\begin{aligned} S(T,\mathsf{H}=0,N_\triangle) &= N_\triangle k_{\rm B}\ln 2 + N_\triangle k_{\rm B}\ln\left(1 + 3\,e^{-4J/k_{\rm B}T}\right) + \frac{N_\triangle J}{T}\cdot\left(\frac{12\,e^{-4J/k_{\rm B}T}}{1 + 3\,e^{-4J/k_{\rm B}T}}\right) \\ &= N_\triangle k_{\rm B}\ln 6 + N_\triangle k_{\rm B}\ln\left(1 + \tfrac{1}{3}\,e^{4J/k_{\rm B}T}\right) - \frac{N_\triangle J}{T}\cdot\left(\frac{4\,e^{4J/k_{\rm B}T}}{3 + e^{4J/k_{\rm B}T}}\right)\ . \end{aligned}$$

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

(2) The potential energy density for an isotropic elastic solid is given by

$$\begin{aligned}\mathcal{U}(\boldsymbol{x}) &= \mu \,\mathsf{Tr}\,\varepsilon^2 + \tfrac{1}{2}\lambda\,(\mathsf{Tr}\,\varepsilon)^2 \\ &= \mu \sum_{\alpha,\beta} \varepsilon^2_{\alpha\beta}(\boldsymbol{x}) + \tfrac{1}{2}\lambda \Big(\sum_\alpha \varepsilon_{\alpha\alpha}(\boldsymbol{x})\Big)^2 ,\end{aligned}$$

where μ and λ are the Lamé parameters and

$$\varepsilon_{\alpha\beta} = \frac{1}{2}\bigg(\frac{\partial u^\alpha}{\partial x^\beta} + \frac{\partial u^\beta}{\partial x^\alpha}\bigg) ,$$

with $\boldsymbol{u}(\boldsymbol{x})$ the local displacement field, is the *strain tensor*. The Cartesian indices α and β run over x, y, z. The kinetic energy density is

$$\mathcal{T}(\boldsymbol{x}) = \tfrac{1}{2}\rho\,\dot{\boldsymbol{u}}^2(\boldsymbol{x}) \ .$$

(a) Assume periodic boundary conditions, and Fourier transform to wavevector space,

$$\begin{aligned}u^\alpha(\boldsymbol{x},t) &= \tfrac{1}{\sqrt{V}} \sum_{\boldsymbol{k}} \hat{u}^\alpha_{\boldsymbol{k}}(t)\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \\ \hat{u}^\alpha_{\boldsymbol{k}}(t) &= \tfrac{1}{\sqrt{V}} \int\! d^3\!x\; u^\alpha(\boldsymbol{x},t)\, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}} \ .\end{aligned}$$

Write the Lagrangian $L = \int\! d^3\!x\,\big(\mathcal{T} - \mathcal{U}\big)$ in terms of the generalized coordinates $\hat{u}^\alpha_{\boldsymbol{k}}(t)$ and generalized velocities $\dot{\hat{u}}^\alpha_{\boldsymbol{k}}(t)$.

(b) Find the Hamiltonian H in terms of the generalized coordinates $\hat{u}^\alpha_{\boldsymbol{k}}(t)$ and generalized momenta $\hat{\pi}^\alpha_{\boldsymbol{k}}(t)$.

(c) Find the thermodynamic average $\langle \boldsymbol{u}(0)\cdot\boldsymbol{u}(\boldsymbol{x})\rangle$.

(d) Suppose we add in a nonlocal interaction of the strain field of the form

$$\Delta U = \tfrac{1}{2}\!\int\! d^3\!x \!\int\! d^3\!x'\ \mathsf{Tr}\,\varepsilon(\boldsymbol{x})\ \mathsf{Tr}\,\varepsilon(\boldsymbol{x}')\; v(\boldsymbol{x}-\boldsymbol{x}') \ .$$

Repeat parts (b) and (c).

Solution : To do the mode counting we are placing the system in a box of dimensions $L_x \times L_y \times L_z$ and imposing periodic boundary conditions. The allowed wavevectors $\boldsymbol{k}$ are of the form

$$\boldsymbol{k} = \bigg(\frac{2\pi n_x}{L_x}\,,\,\frac{2\pi n_y}{L_y}\,,\,\frac{2\pi n_z}{L_z}\bigg) \ .$$

We shall repeatedly invoke the orthogonality of the plane waves:

$$\int\limits_0^{L_x}\!\!dx \int\limits_0^{L_y}\!\!dy \int\limits_0^{L_z}\!\!dz\; e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}} = V\,\delta_{\boldsymbol{k},\boldsymbol{k}'} \ ,$$

where $V = L_x L_y L_z$ is the volume. When we Fourier decompose the displacement field, we must take care to note that $\hat{u}^\alpha_{\boldsymbol{k}}$ is complex, and furthermore that $\hat{u}^\alpha_{-\boldsymbol{k}} = \big(\hat{u}^\alpha_{\boldsymbol{k}}\big)^*$, since $u^\alpha(\boldsymbol{x})$ is a real function.

(a) We then have

$$T = \int\limits_{-\infty}^{\infty} dx \, \tfrac{1}{2}\rho \, \dot{\boldsymbol{u}}^2(\boldsymbol{x},t) = \tfrac{1}{2}\rho \sum_{\boldsymbol{k}} \big|\dot{\hat{u}}^\alpha_{\boldsymbol{k}}(t)\big|^2$$

and

$$\begin{aligned} U &= \int\limits_{-\infty}^{\infty} dx \left[\tfrac{1}{2}\mu \, \frac{\partial u^\alpha}{\partial x^\beta} \, \frac{\partial u^\alpha}{\partial x^\beta} + \tfrac{1}{2}(\lambda+\mu)\,(\boldsymbol{\nabla}\!\cdot\!\boldsymbol{u})^2 \right] \\ &= \tfrac{1}{2} \sum_{\boldsymbol{k}} \Big(\mu\,\delta^{\alpha\beta} + (\lambda+\mu)\,\hat{k}^\alpha\,\hat{k}^\beta \Big)\, \boldsymbol{k}^2 \, \hat{u}^\alpha_{\boldsymbol{k}}(t)\,\hat{u}^\beta_{-\boldsymbol{k}}(t) \ . \end{aligned}$$

The Lagrangian is of course $L = T - U$.

(b) The momentum $\hat{\pi}^\alpha_{\boldsymbol{k}}$ conjugate to the generalized coordinate $\hat{u}^\alpha_{\boldsymbol{k}}$ is

$$\hat{\pi}^\alpha_{\boldsymbol{k}} = \frac{\partial L}{\partial \dot{\hat{u}}^\alpha_{\boldsymbol{k}}} = \rho\,\dot{\hat{u}}^\alpha_{-\boldsymbol{k}} \ ,$$

and the Hamiltonian is

$$\begin{aligned} H &= \sum_{\boldsymbol{k}} \hat{\pi}^\alpha_{\boldsymbol{k}}\,\dot{\hat{u}}^\alpha_{\boldsymbol{k}} - L \\ &= \sum_{\boldsymbol{k}} \left\{ \frac{\big|\hat{\pi}^\alpha_{\boldsymbol{k}}\big|^2}{2\rho} + \tfrac{1}{2}\Big[\mu\,\big(\delta^{\alpha\beta} - \hat{k}^\alpha\,\hat{k}^\beta\big) + (\lambda+2\mu)\,\hat{k}^\alpha\,\hat{k}^\beta\Big]\boldsymbol{k}^2\,\hat{u}^\alpha_{\boldsymbol{k}}\,\hat{u}^\beta_{-\boldsymbol{k}} \right\} \ . \end{aligned}$$

Note that we have added and subtracted a term $\mu\,\hat{k}^\alpha\,\hat{k}^\beta$ within the expression for the potential energy. This is because $\mathbb{P}_{\alpha\beta} = \hat{k}^\alpha\,\hat{k}^\beta$ and $\mathbb{Q}_{\alpha\beta} = \delta^{\alpha\beta} - \hat{k}^\alpha\,\hat{k}^\beta$ are *projection operators* satisfying $\mathbb{P}^2 = \mathbb{P}$ and $\mathbb{Q}^2 = \mathbb{Q}$, with $\mathbb{P} + \mathbb{Q} = \mathbb{I}$, the identity. $\mathbb{P}$ projects any vector onto the direction $\hat{\boldsymbol{k}}$, and $\mathbb{Q}$ is the projector onto the (two-dimensional) subspace orthogonal to $\hat{\boldsymbol{k}}$.

(c) We can decompose $\hat{\boldsymbol{u}}_{\boldsymbol{k}}$ into a *longitudinal* component parallel to $\hat{\boldsymbol{k}}$ and a *transverse* component perpendicular to $\hat{\boldsymbol{k}}$, writing

$$\hat{\boldsymbol{u}}_{\boldsymbol{k}} = i\hat{\boldsymbol{k}}\,\hat{u}^{\parallel}_{\boldsymbol{k}} + i\hat{\boldsymbol{e}}_{\boldsymbol{k},1}\,\hat{u}^{\perp,1}_{\boldsymbol{k}} + i\hat{\boldsymbol{e}}_{\boldsymbol{k},2}\,\hat{u}^{\perp,2}_{\boldsymbol{k}} \ ,$$

where $\{\hat{\boldsymbol{e}}_{\boldsymbol{k},1}\,,\,\hat{\boldsymbol{e}}_{\boldsymbol{k},2}\,,\,\hat{\boldsymbol{k}}\}$ is a right-handed orthonormal triad for each direction $\hat{\boldsymbol{k}}$. A factor of i is included so that $\hat{u}^{\parallel}_{-\boldsymbol{k}} = \big(\hat{u}^{\parallel}_{\boldsymbol{k}}\big)^*$, *etc.* With this decomposition, the potential energy takes the form

$$U = \tfrac{1}{2}\sum_{\boldsymbol{k}} \Big[\mu\,\boldsymbol{k}^2 \,\Big(\big|\hat{u}^{\perp,1}_{\boldsymbol{k}}\big|^2 + \big|\hat{u}^{\perp,2}_{\boldsymbol{k}}\big|^2 \Big) + (\lambda+2\mu)\,\boldsymbol{k}^2\,\big|\hat{u}^{\parallel}_{\boldsymbol{k}}\big|^2 \Big] \ .$$

Equipartition then means each independent degree of freedom which is quadratic in the potential contributes an average of $\frac{1}{2}k_{\mathrm{B}}T$ to the total energy. Recalling that $u^{\parallel}_{\boldsymbol{k}}$ and $u^{\perp,j}_{\boldsymbol{k}}$

($j\,=\,1,2$) are complex functions, and that they are each the Fourier transform of a real function (so that $\boldsymbol{k}$ and $-\boldsymbol{k}$ terms in the sum for U are equal), we have

$$\begin{aligned}\Big\langle \mu\,\boldsymbol{k}^2\,\big|\hat{u}^{\perp,1}_{\boldsymbol{k}}\big|^2\Big\rangle = \Big\langle \mu\,\boldsymbol{k}^2\,\big|\hat{u}^{\perp,2}_{\boldsymbol{k}}\big|^2\Big\rangle &= 2\times\tfrac{1}{2}k_{\rm B}T\\ \Big\langle (\lambda+2\mu)\,\boldsymbol{k}^2\,\big|\hat{u}^{\parallel}_{\boldsymbol{k}}\big|^2\Big\rangle &= 2\times\tfrac{1}{2}k_{\rm B}T\ .\end{aligned}$$

Thus,

$$\begin{aligned}\big\langle|\hat{\boldsymbol{u}}_{\boldsymbol{k}}|^2\big\rangle &= 4\times\tfrac{1}{2}k_{\rm B}T\times\frac{1}{\mu\boldsymbol{k}^2}+2\times\tfrac{1}{2}k_{\rm B}T\times\frac{1}{(\lambda+2\mu)\,\boldsymbol{k}^2}\\ &=\bigg(\frac{2}{\mu}+\frac{1}{\lambda+2\mu}\bigg)\frac{k_{\rm B}T}{\boldsymbol{k}^2}\ .\end{aligned}$$

Then

$$\begin{aligned}\big\langle\boldsymbol{u}(0)\cdot\boldsymbol{u}(\boldsymbol{x})\big\rangle &= \frac{1}{V}\sum_{\boldsymbol{k}}\big\langle|\hat{\boldsymbol{u}}_{\boldsymbol{k}}|^2\big\rangle\,e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\\ &=\int\!\frac{d^3\!k}{(2\pi)^3}\,\bigg(\frac{2}{\mu}+\frac{1}{\lambda+2\mu}\bigg)\frac{k_{\rm B}T}{\boldsymbol{k}^2}\,e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\\ &=\bigg(\frac{2}{\mu}+\frac{1}{\lambda+2\mu}\bigg)\frac{k_{\rm B}T}{4\pi|\boldsymbol{x}|}\ .\end{aligned}$$

Recall that in three space dimensions the Fourier transform of $4\pi/\boldsymbol{k}^2$ is $1/|\boldsymbol{x}|$.

(d) The $\boldsymbol{k}$-space representation of ΔU is

$$\Delta U = \tfrac{1}{2}\sum_{\boldsymbol{k}}\boldsymbol{k}^2\,\hat{v}(\boldsymbol{k})\,\hat{k}^\alpha\,\hat{k}^\beta\,\hat{u}^\alpha_{\boldsymbol{k}}\,\hat{u}^\beta_{-\boldsymbol{k}}\ ,$$

where $\hat{v}(\boldsymbol{k})$ is the Fourier transform of the interaction $v(\boldsymbol{x}-\boldsymbol{x}')$:

$$\hat{v}(\boldsymbol{k}) = \int\!d^3\!r\;v(\boldsymbol{r})\,e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\ .$$

We see then that the effect of ΔU is to replace the Lamé parameter λ with the $\boldsymbol{k}$-dependent quantity,

$$\lambda\rightarrow\lambda(\boldsymbol{k})\equiv\lambda+\hat{v}(\boldsymbol{k})\ .$$

With this simple replacement, the results of parts (b) and (c) retain their original forms, *mutatis mutandis*.

Chapter 4

Solution Set #4

(1) Consider a three-dimensional ultrarelativistic gas, with dispersion $\varepsilon = \hbar c|\boldsymbol{k}|$. Find the viral expansion of the equation of state $p = p(n,T)$ to order n^3 for both bosons and fermions.

Solution : We have

$$\begin{aligned}\beta p &= \mp \mathsf{g}\!\int\!\frac{d^3\!k}{(2\pi)^3}\;\ln\big(1 \mp z\,e^{-\beta\varepsilon(\boldsymbol{k})}\big)\\ z &= \mathsf{g}\!\int\!\frac{d^3\!k}{(2\pi)^3}\,\frac{1}{z^{-1}\,e^{\beta\varepsilon(\boldsymbol{k})}\mp 1}\ ,\end{aligned}$$

where g is the degeneracy of each $\boldsymbol{k}$ mode. WIth $\varepsilon(\boldsymbol{k}) = \hbar ck$, we change variables to $t = \beta\hbar ck$ and find

$$\begin{aligned}\beta p &= \frac{\mathsf{g}}{6\pi^2}\bigg(\frac{k_{\rm B}T}{\hbar c}\bigg)^{\!3}\int\limits_{-\infty}^{\infty}\!dt\;\frac{t^3}{z^{-1}\,e^t\mp 1} = \frac{\mathsf{g}}{\pi^2}\bigg(\frac{k_{\rm B}T}{\hbar c}\bigg)^{\!3}\;\sum_{j=1}^{\infty}(\pm 1)^{j-1}\,\frac{z^j}{j^4}\\ n &= \frac{\mathsf{g}}{2\pi^2}\bigg(\frac{k_{\rm B}T}{\hbar c}\bigg)^{\!3}\int\limits_{-\infty}^{\infty}\!dt\;\frac{t^2}{z^{-1}\,e^t\mp 1} = \frac{\mathsf{g}}{\pi^2}\bigg(\frac{k_{\rm B}T}{\hbar c}\bigg)^{\!3}\;\sum_{j=1}^{\infty}(\pm 1)^{j-1}\,\frac{z^j}{j^3}\ ,\end{aligned}$$

where we have integrated by parts in the first of these equations. Now it's time to ask

```
Mathematica:

 In[1] =  y = InverseSeries[x + x^2/2^3 + x^3/3^3 + x^4/4^3 + x^5/5^3 + O[x]^6]

              x^2     5 x^3     31 x^4      56 039 x^5
Out[1] =  x - ---  -  -----  -  ------  -  ----------  + O[x]^6
               8       864      13 824     62 208 000

 In[2] =  w = y + y^2/2^4 + y^3/3^4 + y^4/4^4 + y^5/5^4

              x^2     47 x^3     25 x^4     2 014 561 x^5
Out[2] =  x - ---  -  ------  -  ------  -  -------------  + O[x]^6
              16       5184       9216      1 866 240 000
```

So with the definition

$$\lambda_T = \pi^{2/3}\,\mathsf{g}^{-1/3}\,\frac{\hbar c}{k_{\rm B}T}\ ,$$

we have

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

where

$$B_2 = \mp\tfrac{1}{16}\,\lambda_T^3 \quad , \quad B_3 = -\tfrac{47}{5184}\,\lambda_T^6 \quad , \quad B_4 = \mp\tfrac{25}{9216}\,\lambda_T^9 \quad , \quad B_4 = -\tfrac{2014561}{1866240000}\,\lambda_T^{12}\ .$$

(2) Suppose photons had a dispersion $\varepsilon = J\boldsymbol{k}^2$. All other things being equal (surface temperature of the sun, earth-sun distance, earth and solar radii, *etc.*), what would be the surface temperature of the earth? *Hint: Derive the corresponding version of Stefan's law.*

Solution : This material has been added to the notes; see §4.4.4. Assume a dispersion of the form $\varepsilon(k)$ for the (nonconserved) bosons. Then the energy current incident on a differential area dA of surface normal to $\hat{\boldsymbol{z}}$ is

$$dP = dA\cdot\int\!\frac{d^3\!k}{(2\pi)^3}\,\Theta(\cos\theta)\cdot\varepsilon(k)\cdot\frac{1}{\hbar}\frac{\partial\varepsilon(k)}{\partial k_z}\cdot\frac{1}{e^{\varepsilon(k)/k_{\rm B}T}-1}\ .$$

Note that

$$\frac{\partial\varepsilon(k)}{\partial k_z} = \frac{k_z}{k}\,\frac{\partial\varepsilon}{\partial k} = \cos\theta\,\varepsilon'(k)\ .$$

Now let us assume a power law dispersion $\varepsilon(k) = Ak^\alpha$. Changing variables to $t = Ak^\alpha/k_{\rm B}T$, we find

$$\frac{dP}{dA} = \sigma\,T^{2+\frac{2}{\alpha}}\ ,$$

where

$$\sigma = \zeta\big(2+\tfrac{2}{\alpha}\big)\,\Gamma\big(2+\tfrac{2}{\alpha}\big)\cdot\frac{\mathsf{g}\,k_{\rm B}^{2+\frac{2}{\alpha}}\,A^{-\frac{2}{\alpha}}}{8\pi^2\hbar}\ .$$

One can check that for $\mathsf{g}=2$, $A=\hbar c$, and $\alpha=1$ that this result reduces to Stefan's Law.

Equating the power incident on the earth to that radiated by the earth, we obtain

$$T_{\rm e} = \left(\frac{R_\odot}{2\,a_{\rm e}}\right)^{\frac{\alpha}{\alpha+1}} T_\odot \ .$$

Plugging in the appropriate constants and setting $\alpha = 2$, we obtain $T_{\rm e} = 101.3\,{\rm K}$. Brrr!

(3) Almost all elements freeze into solids well before they can undergo Bose condensation. Setting the Lindemann temperature equal to the Bose condensation temperature, show that this implies a specific ratio of $k_{\rm B}\Theta_{\rm D}$ to $\hbar^2/Ma^2$, where M is the atomic mass and a is the lattice spacing. Evaluate this ratio for the noble gases He, Ne, Ar, Kr, and Xe. (You will have to look up some numbers.)

Solution : The Lindemann melting temperature $T_{\rm M}$ and the Bose condensation temperature $T_{\rm c}$ for monatomic solids are given by

$$T_{\rm M} = x^2 \cdot \frac{M k_{\rm B} \Theta_{\rm D}^2\, a^2}{9\hbar^2} \quad , \quad T_{\rm c} = \frac{2\pi\hbar^2}{M k_{\rm B}} \bigg(\frac{n}{\zeta(3/2)}\bigg)^{2/3} \ ,$$

where a is the lattice constant, M the atomic mass, and $\Theta_{\rm D}$ the Debye temperature. For a simple cubic lattice, the number density is $n = a^{-3}$. Helium solidifies into a hexagonal close packed (HCP) structure, while Neon, Argon, Krypton, and Xenon solidify into a face-centered cubic (FCC) structure. The unit cell volume for both HCP and FCC is $a^3/\sqrt{2}$, where a is the lattice spacing, so $n = \sqrt{2}\,a^{-3}$ for the rare gas solids. Thus, we find

$$\frac{T_{\rm M}}{T_{\rm c}} = \frac{x}{\alpha} \cdot \left(\frac{k_{\rm B}\Theta_{\rm D}}{\hbar^2/Ma^2}\right)^2 \ .$$

where

$$\alpha = 18\pi \left(\frac{\sqrt{2}}{\zeta(3/2)}\right)^{2/3} \approx 40 \ .$$

If we set $x = 0.1$ we find $\frac{x}{\alpha} \approx \frac{1}{400}$. Now we need some data for $\Theta_{\rm D}$ and a. The most convenient table of data I've found is from H. Glyde's article on solid helium in the *Encyclopedia of Physics*. The table entry for ^{4}He is for the BCC structure at a pressure $p = 25$ bar. For a BCC structure the unit cell volume is $4a^3/3\sqrt{3}$. Define the ratio $R \equiv k_{\rm B}\Theta_{\rm D}/(\hbar^2/Ma^2)$.

As one can see from the table and from the above equation for $T_{\rm M}/T_{\rm c}$. the R values are such that the melting temperature is predicted to be several orders of magnitude higher than the ideal Bose condensation temperature in every case except ^{4}He, where the ratio is on the order of unity (and is less than unity if the actual melting temperature is used). The reason that ^{4}He under high pressure is a solid rather than a Bose condensate at low temperatures is because the ^{4}He atoms are not free particles.

(4) A nonrelativistic Bose gas consists of particles of spin $S = 1$. Each boson has mass m and magnetic moment μ_0. A gas of these particles is placed in an external field H.

(a) What is the relationship of the Bose condensation temperature $T_{\rm c}(H)$ to $T_{\rm c}(\mathsf{H} = 0)$ when $\mu_0 \mathsf{H} \gg k_{\rm B}T$?

crystal	a (Å)	M (amu)	$\Theta_{\rm D}$ (K)	$T_{\rm M}^{\rm actual}$ (K)	$T_{\rm c}$	$\hbar^2/Ma^2k_{\rm B}$ (K)	R
^{4}He	3.57	4.00	25	1.6	3.9	0.985	25
Ne	4.46	20.2	66	24.6	0.50	0.125	530
Ar	5.31	39.9	84	83.8	0.18	0.0446	1900
Kr	5.65	83.8	64	161.4	0.076	0.0188	3400
Xe	6.13	131	55	202.0	0.041	0.0102	20000

Table 4.1: Lattice constants for Ne, Ar, Kr, and Xe from F. W. de Wette and R. M. J. Cotterill, *Solid State Comm.* **6**, 227 (1968). Debye temperatures and melting temperatures from H. Glyde, *Solid Helium* in *Encyclopedia of Physics*. ^{4}He data are for $p = 25$ bar, in the bcc phase (from Glyde).

(b) Find the magnetization M for $T < T_{\rm c}$ when $\mu_0\mathsf{H} \gg k_{\rm B}T$. Calculate through order $\exp(-\mu_0\mathsf{H}/k_{\rm B}T)$.

Solution : The number density of bosons is given by

$$n(T,z) = \lambda_T^{-3}\Big\{\zeta_{3/2}\big(z\,e^{\mu_0\mathsf{H}/k_{\rm B}T}\big) + \zeta_{3/2}\big(z\big) + \zeta_{3/2}\big(z\,e^{-\mu_0\mathsf{H}/k_{\rm B}T}\big)\Big\} \ .$$

The argument of $\zeta_z(z)$ cannot exceed unity, thus Bose condensation occurs for $z = \exp(-\mu_0\mathsf{H}/k_{\rm B}T)$ (assuming $\mathsf{H} > 0$). Thus, the condition for Bose condensation is given by

$$n\lambda_{T_{\rm c}}^3 = \zeta(3/2) + \zeta_{3/2}\big(e^{-\mu_0\mathsf{H}/k_{\rm B}T_{\rm c}}\big) + \zeta_{3/2}\big(e^{-2\mu_0\mathsf{H}/k_{\rm B}T_{\rm c}}\big) \ .$$

This is a transcendental equation for $T = T_{\rm c}(n,\mathsf{H})$. In the limit $\mu_0\mathsf{H} \gg k_{\rm B}T_{\rm c}$, the second two terms become negligible, since

$$\zeta_s(z) = \sum_{j=1}^{\infty} \frac{z^j}{j^s} \ .$$

Thus,

$$T_{\rm c}(\mathsf{H}\to\infty) = \frac{2\pi\hbar^2}{m}\bigg(\frac{n}{\zeta(3/2)}\bigg)^{2/3} \ .$$

When $\mathsf{H} = 0$, we have Thus,

$$T_{\rm c}(\mathsf{H}\to 0) = \frac{2\pi\hbar^2}{m}\bigg(\frac{n}{3\,\zeta(3/2)}\bigg)^{2/3} \ .$$

Thus,

$$\frac{T_{\rm c}(\mathsf{H}\to\infty)}{T_{\rm c}(\mathsf{H}\to 0)} = 3^{2/3} = 2.08008\ldots$$

The magnetization density is

$$M = \mu_0\,\lambda_T^{-3}\Big\{\zeta_{3/2}\big(z\,e^{\mu_0\mathsf{H}/k_{\rm B}T}\big) - \zeta_{3/2}\big(z\,e^{-\mu_0\mathsf{H}/k_{\rm B}T}\big)\Big\} \ .$$

For $T < T_{\rm c}$, we have $z = \exp(-\mu_0 \mathsf{H}/k_{\rm B}T)$ and therefore

$$\begin{aligned} M &= \mu_0\,\lambda_T^{-3}\left\{\zeta(3/2) - \sum_{j=1}^{\infty} j^{-3/2}\,e^{-2j\mu_0\mathsf{H}/k_{\rm B}T}\right\} \\ &= n\mu_0\left\{1 - \frac{e^{-2\mu_0\mathsf{H}/k_{\rm B}T}}{\zeta(3/2)} + \mathcal{O}\big(e^{-4\mu_0\mathsf{H}/k_{\rm B}T}\big)\right\} \end{aligned}$$

Chapter 5

Solution Set #5

(1) You know that at most one fermion may occupy any given single-particle state. A *parafermion* is a particle for which the maximum occupancy of any given single-particle state is k, where k is an integer greater than zero. (For $k = 1$, parafermions are regular everyday fermions; for $k = \infty$, parafermions are regular everyday bosons.) Consider a system with one single-particle level whose energy is ε, *i.e.* the Hamiltonian is simply $\mathcal{H} = \varepsilon\, n$, where n is the particle number.

(a) Compute the partition function $\Xi(\mu, T)$ in the grand canonical ensemble for parafermions.

(b) Compute the occupation function $n(\mu, T)$. What is n when $\mu = -\infty$? When $\mu = \varepsilon$? When $\mu = +\infty$? Does this make sense? Show that $n(\mu, T)$ reduces to the Fermi and Bose distributions in the appropriate limits.

(c) Sketch $n(\mu, T)$ as a function of μ for both $T = 0$ and $T > 0$.

(d) Can a gas of ideal parafermions condense in the sense of Bose condensation?

Solution : The general expression for Ξ is

$$\Xi = \prod_\alpha \sum_{n_\alpha} \left(z\, e^{-\beta\varepsilon_\alpha}\right)^{n_\alpha} .$$

Now the sum on n runs from 0 to k, and

$$\sum_{n=0}^{k} x^n = \frac{1 - x^{k+1}}{1 - x} .$$

(a) Thus,

$$\Xi = \frac{1 - e^{(k+1)\beta(\mu-\varepsilon)}}{1 - e^{\beta(\mu-\varepsilon)}} .$$

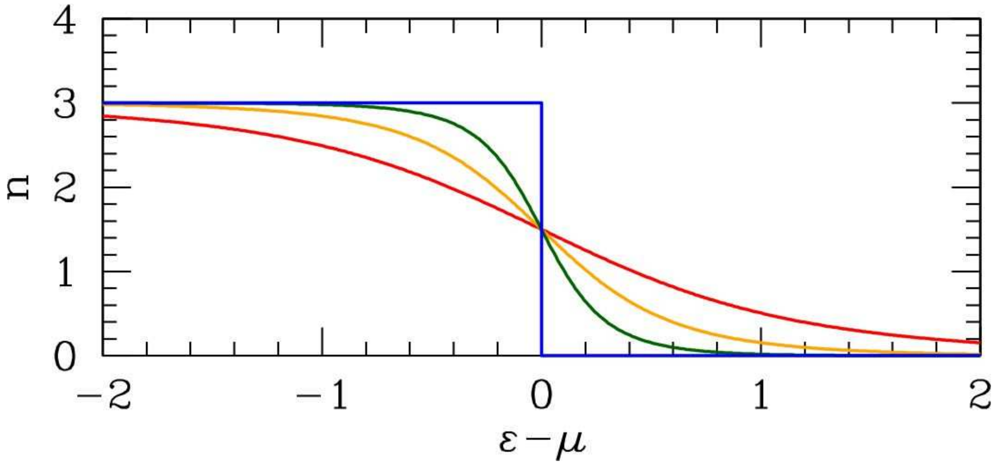

Figure 5.1: (3)(c) $k=3$ parafermion occupation number *versus* $\varepsilon-\mu$ for $k_{\rm B}T=0$, $k_{\rm B}T=0.25$, $k_{\rm B}T=0.5$, and $k_{\rm B}T=1$.

(b) We then have

$$\begin{aligned} n &= -\frac{\partial\Omega}{\partial\mu} = \frac{1}{\beta}\frac{\partial\ln\Xi}{\partial\mu} \\ &= \frac{1}{e^{\beta(\varepsilon-\mu)}-1} - \frac{k+1}{e^{(k+1)\beta(\varepsilon-\mu)}-1} \end{aligned}$$

(c) A plot of $n(\varepsilon,T,\mu)$ for $k=3$ is shown in fig. 5.1. Qualitatively the shape is that of the Fermi function $f(\varepsilon-\mu)$. At $T=0$, the occupation function is $n(\varepsilon,T=0,\mu)=k\,\Theta(\mu-\varepsilon)$. This step function smooths out for T finite.

(d) For each $k<\infty$, the occupation number $n(z,T)$ is a finite order polynomial in z, and hence an analytic function of z. Therefore, there is no possibility for Bose condensation except for $k=\infty$.

(2) Consider a system of N spin-$\frac{1}{2}$ particles occupying a volume V at temperature T. Opposite spin fermions may bind in a singlet state to form a boson:

$$\mathrm{f}{\uparrow} + \mathrm{f}{\downarrow} \quad \rightleftharpoons \quad \mathrm{b}$$

with a binding energy $-\Delta<0$. Assume that all the particles are nonrelativistic; the fermion mass is m and the boson mass is $2m$. Assume further that spin-flip processes exist, so that the ↑ and ↓ fermion species have identical chemical potential $\mu_{\rm f}$.

(a) What is the equilibrium value of the boson chemical potential, $\mu_{\rm b}$? *Hint* : the answer is $\mu_{\rm b}=2\mu_{\rm f}$.

(b) Let the total mass density be ρ. Derive the equation of state $\rho=\rho(\mu_{\rm f},T)$, assuming the bosons have not condensed. You may wish to abbreviate

$$\zeta_p(z) \equiv \sum_{n=1}^{\infty} \frac{z^n}{n^p} \ .$$

(c) At what value of $\mu_{\rm f}$ do the bosons condense?

(d) Derive an equation for the Bose condensation temperature $T_{\rm c}$. Solve for $T_{\rm c}$ in the limits $\varepsilon_0 \ll \Delta$ and $\varepsilon_0 \gg \Delta$, respectively, where

$$\varepsilon_0 \equiv \frac{\pi\hbar^2}{m}\bigg(\frac{\rho/2m}{\zeta\big(\frac{3}{2}\big)}\bigg)^{2/3} .$$

(e) What is the equation for the condensate fraction $\rho_0(T,\rho)/\rho$ when $T < T_{\rm c}$?

Solution :

(a) The chemical potential is the Gibbs free energy per particle. If the fermion and boson species are to coexist at the same T and p, the reaction f$\uparrow$ +f$\downarrow$ $\longrightarrow$ b must result in $\Delta G = \mu_{\rm b} - 2\mu_{\rm f} = 0$.

(b) For $T > T_{\rm c}$,

$$\rho = -2m\,\lambda_T^{-3}\,\zeta_{3/2}\big(-\,e^{\mu_{\rm f}/k_{\rm B}T}\big) + 2\sqrt{8}\,m\,\lambda_T^{-3}\,\zeta_{3/2}\big(e^{(2\mu_{\rm f}+\Delta)/k_{\rm B}T}\big) ,$$

where $\lambda_T = \sqrt{2\pi\hbar^2/mk_{\rm B}T}$ is the thermal wavelength for particles of mass m. This formula accounts for both fermion spin polarizations, each with number density $n_{{\rm f}\uparrow} = n_{{\rm f}\downarrow} = -\lambda_T^{-3}\,\zeta_{3/2}(-z_{\rm f})$ and the bosons with number density $\sqrt{8}\,\lambda_T^{-3}\,\zeta_{3/2}(z_{\rm b}\,e^{\beta\Delta})$, with $z_{\rm b} = z_{\rm f}^2$ due to chemical equilibrium among the species. The factor of $2^{3/2} = \sqrt{8}$ arises from the fact that the boson mass is $2m$, hence the boson thermal wavelength is $\lambda_T/\sqrt{2}$.

(c) The bosons condense when $\mu_{\rm b} = -\Delta$, the minimum single particle energy. This means $\mu_{\rm f} = -\frac{1}{2}\Delta$. The equation of state for $T < T_{\rm c}$ is then

$$\rho = -2m\,\lambda_T^{-3}\,\zeta_{3/2}\big(-\,e^{-\Delta/2k_{\rm B}T}\big) + 4\sqrt{2}\,\zeta\big(\tfrac{3}{2}\big)\,m\,\lambda_T^{-3} + \rho_0 ,$$

where ρ_0 is the condensate mass density.

(d) At $T = T_{\rm c}$ we have $\rho_0 = 0$, hence

$$\frac{\rho}{2m}\bigg(\frac{2\pi\hbar^2}{mk_{\rm B}T_{\rm c}}\bigg)^{3/2} = \sqrt{8}\,\zeta\big(\tfrac{3}{2}\big) - \zeta_{3/2}\big(-\,e^{-\Delta/2k_{\rm B}T_{\rm c}}\big) ,$$

which is a transcendental equation. Om. In the limit where Δ is very large, we have

$$T_{\rm c}(\Delta \gg \varepsilon_0) = \frac{\pi\hbar^2}{mk_{\rm B}}\bigg(\frac{\rho/2m}{\zeta\big(\frac{3}{2}\big)}\bigg)^{2/3} = \frac{\varepsilon_0}{k_{\rm B}} .$$

In the opposite limit, we have $\Delta \to 0^+$ and $-\zeta_{3/2}(-1) = \eta(3/2)$, where $\eta(s)$ is the Dirichlet η-function,

$$\eta(s) = \sum_{j=1}^{\infty}(-1)^{j-1}\,j^{-s} = \big(1 - 2^{1-s}\big)\,\zeta(s) .$$

Then

$$T_{\rm c}(\Delta \ll \varepsilon_0) = \frac{2\varepsilon_0/k_{\rm B}}{\big(1+\frac{3}{2}\sqrt{2}\big)^{2/3}} \ .$$

(e) The condensate fraction is

$$\nu = \frac{\rho_0}{\rho} = 1 - \left(\frac{T}{T_{\rm c}}\right)^{3/2} \cdot \frac{\sqrt{8}\,\zeta\big(\frac{3}{2}\big) - \zeta_{3/2}\big(-\,e^{-\Delta/2k_{\rm B}T}\big)}{\sqrt{8}\,\zeta\big(\frac{3}{2}\big) - \zeta_{3/2}\big(-\,e^{-\Delta/2k_{\rm B}T_{\rm c}}\big)} \ .$$

Note that as $\Delta \to -\infty$ we have $-\zeta_{3/2}\big(-\,e^{-\Delta/2k_{\rm B}T}\big) \to 0$ and the condensate fraction approaches the free boson result, $\nu = 1 - (T/T_{\rm c})^{3/2}$. In this limit there are no fermions present.

(3) A three-dimensional system of spin-0 bosonic particles obeys the dispersion relation

$$\varepsilon(\boldsymbol{k}) = \Delta + \frac{\hbar^2\boldsymbol{k}^2}{2m} \ .$$

The quantity Δ is the formation energy and m the mass of each particle. These particles are not conserved – they may be created and destroyed at the boundaries of their environment. (A possible example: vacancies in a crystalline lattice.) The Hamiltonian for these particles is

$$\mathcal{H} = \sum_{\boldsymbol{k}} \varepsilon(\boldsymbol{k})\,\hat{n}_{\boldsymbol{k}} + \frac{U}{2V}\,\hat{N}^2 \ ,$$

where $\hat{n}_{\boldsymbol{k}}$ is the number operator for particles with wavevector $\boldsymbol{k}$, $\hat{N} = \sum_{\boldsymbol{k}} \hat{n}_{\boldsymbol{k}}$ is the total number of particles, V is the volume of the system, and U is an interaction potential.

(a) Treat the interaction term within mean field theory. That is, define $\hat{N} = \langle\hat{N}\rangle + \delta\hat{N}$, where $\langle\hat{N}\rangle$ is the thermodynamic average of $\hat{N}$, and derive the mean field self-consistency equation for the number density $\rho = \langle\hat{N}\rangle/V$ by neglecting terms quadratic in the fluctuations $\delta\hat{N}$. Show that the mean field Hamiltonian is

$$\mathcal{H}_{\rm MF} = -\tfrac{1}{2}VU\rho^2 + \sum_{\boldsymbol{k}} \Big[\varepsilon(\boldsymbol{k}) + U\rho\Big]\,\hat{n}_{\boldsymbol{k}} \ ,$$

(b) Derive the criterion for Bose condensation. Show that this requires $\Delta < 0$. Find an equation relating $T_{\rm c}$, U, and Δ.

Solution :

(a) We write

$$\begin{aligned}\hat{N}^2 &= \big(\langle\hat{N}\rangle + \delta\hat{N}\big)^2 \\ &= \langle\hat{N}\rangle^2 + 2\langle\hat{N}\rangle\,\delta\hat{N} + (\delta\hat{N})^2 \\ &= -\langle\hat{N}\rangle^2 + 2\langle\hat{N}\rangle\,\hat{N} + (\delta\hat{N})^2 \ .\end{aligned}$$

We drop the last term, $(\delta\hat{N})^2$, because it is quadratic in the fluctuations. This is the mean field assumption. The Hamiltonian now becomes

$$\mathcal{H}_{\rm MF} = -\tfrac{1}{2}VU\rho^2 + \sum_{\boldsymbol{k}} \Big[\varepsilon(\boldsymbol{k}) + U\rho\Big]\,\hat{n}_{\boldsymbol{k}}\ ,$$

where $\rho = \langle\hat{N}\rangle/V$ is the number density. This, the dispersion is effectively changed, to

$$\tilde{\varepsilon}(\boldsymbol{k}) = \frac{\hbar^2\boldsymbol{k}^2}{2m} + \Delta + U\rho\ .$$

The average number of particles in state $\big|\,\boldsymbol{k}\,\big\rangle$ is given by the Bose function,

$$\langle\hat{n}_{\boldsymbol{k}}\rangle = \frac{1}{\exp\big[\tilde{\varepsilon}(\boldsymbol{k})/k_{\rm B}T\big]-1}\ .$$

Summing over all $\boldsymbol{k}$ states, and using

$$\frac{1}{V}\sum_{\boldsymbol{k}} \longrightarrow \int\!\frac{d^3\!k}{(2\pi)^3}\ ,$$

we obtain

$$\begin{aligned}\rho &= \frac{1}{V}\sum_{\boldsymbol{k}}\langle\hat{n}_{\boldsymbol{k}}\rangle\\ &= \rho_0 + \int\!\frac{d^3\!k}{(2\pi)^3}\,\frac{1}{e^{\hbar^2k^2/2mk_{\rm B}T}\,e^{(\Delta+U\rho)/k_{\rm B}T}-1}\\ &= \rho_0 + \int\limits_0^\infty\! d\varepsilon\,\frac{g(\varepsilon)}{e^{(\varepsilon+\Delta+U\rho)/k_{\rm B}T}-1}\end{aligned}$$

where $\rho_0 = \langle\hat{n}_{\boldsymbol{k}=0}\rangle/V$ is the number density of the $\boldsymbol{k}=0$ state alone, *i.e.* the condensate density. When there is no condensate, $\rho_0 = 0$. The above equation is the mean field equation. It is equivalent to demanding $\partial F/\partial\rho = 0$, *i.e.* to extremizing the free energy with respect to the mean field parameter ρ. Though it is not a required part of the solution, we have here written this relation in terms of the density of states $g(\varepsilon)$, defined according to

$$g(\varepsilon) \equiv \int\!\frac{d^3\!k}{(2\pi)^3}\,\delta\bigg(\varepsilon - \frac{\hbar^2\boldsymbol{k}^2}{2m}\bigg) = \frac{m^{3/2}}{\sqrt{2}\,\pi^2\hbar^3}\,\sqrt{\varepsilon}\ .$$

(b) Bose condensation requires

$$\Delta + U\rho = 0\ ,$$

which clearly requires $\Delta < 0$. Writing $\Delta = -|\Delta|$, we have, just at $T = T_{\rm c}$,

$$\rho(T_{\rm c}) = \frac{|\Delta|}{U} = \int\!\frac{d^3\!k}{(2\pi)^3}\,\frac{1}{e^{\hbar^2k^2/2mk_{\rm B}T_{\rm c}}-1}\ ,$$

since $\rho_0(T_c) = 0$. This relation determines T_c. Explicitly, we have

$$\begin{aligned}\frac{|\Delta|}{U} &= \int\limits_0^\infty \! d\varepsilon \, g(\varepsilon) \sum_{j=1}^\infty e^{-j\varepsilon/k_B T_c} \\ &= \zeta\big(\tfrac{3}{2}\big) \left(\frac{m k_B T_c}{2\pi\hbar^2}\right)^{3/2} ,\end{aligned}$$

where $\zeta(\ell) = \sum_{n=1}^\infty n^{-\ell}$ is the Riemann zeta function. Thus,

$$T_c = \frac{2\pi\hbar^2}{m k_B} \left(\frac{|\Delta|}{\zeta\big(\frac{3}{2}\big)\, U}\right)^{2/3} .$$

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

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

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

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

(a) Show that

$$\langle x^n \rangle = \frac{d^n Z}{dj^n}\bigg|_{j=0}$$

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

(b) Now consider the following integral:

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

This has no analytic solution but we may express the result as a power series in the parameter λ by Taylor expanding $\exp\big(-\frac{\lambda}{4!}\, x^4\big)$ and then using the result of part (a) for the moments $\langle x^{4k} \rangle$. Find the coefficients in the perturbation expansion,

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

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

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

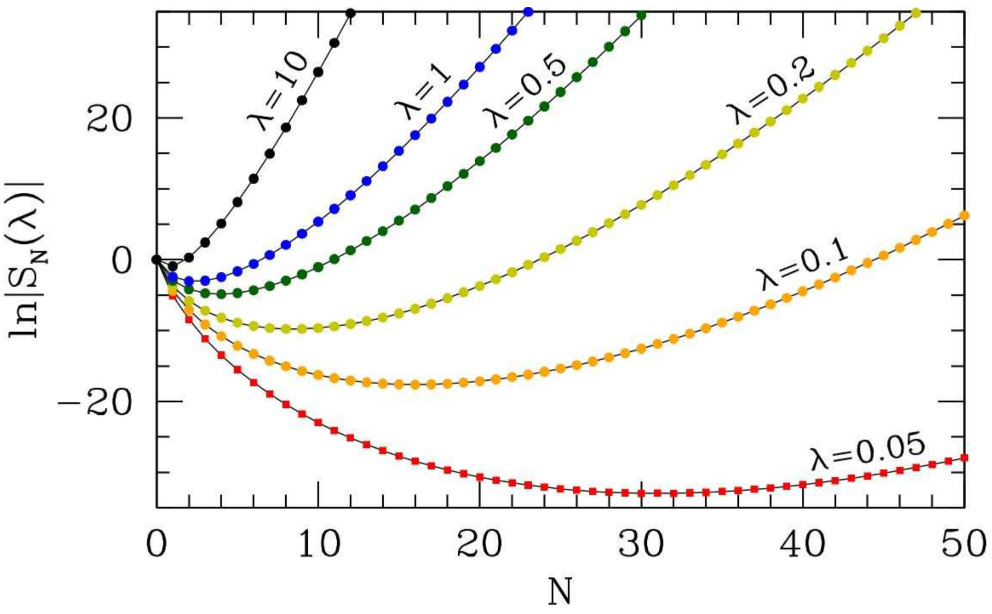

Figure 5.2: (5)(c) Relative error *versus* number of terms kept for the asymptotic series for $F(\lambda)$. Note that the optimal number of terms to sum is $N^*(\lambda) \approx \frac{3}{2\lambda}$.

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

Solution :

(a) Clearly

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

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

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

(b) We have

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

This series is *asymptotic*. It has the properties

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

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

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

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

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

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

(c) Results are plotted in fig. 5.2.

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

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

where A_{2k} is the *number of contractions*. For a proof, see §3.2.2 of the notes. For our integral, $\langle\, x^2 \,\rangle = 1$. The number of contractions A_{2k} is computed in the following way. For each of the $2k$ powers of x, we assign an index running from 1 to $2k$. The indices are *contracted*, *i.e.* paired, with each other. How many pairings are there? Suppose we start with any from among the $2k$ indices. Then there are $(2k-1)$ choices for its mate. We then choose another index arbitrarily. There are now $(2k-3)$ choices for *its* mate. Carrying this out to its completion, we find that the number of contractions is

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

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

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

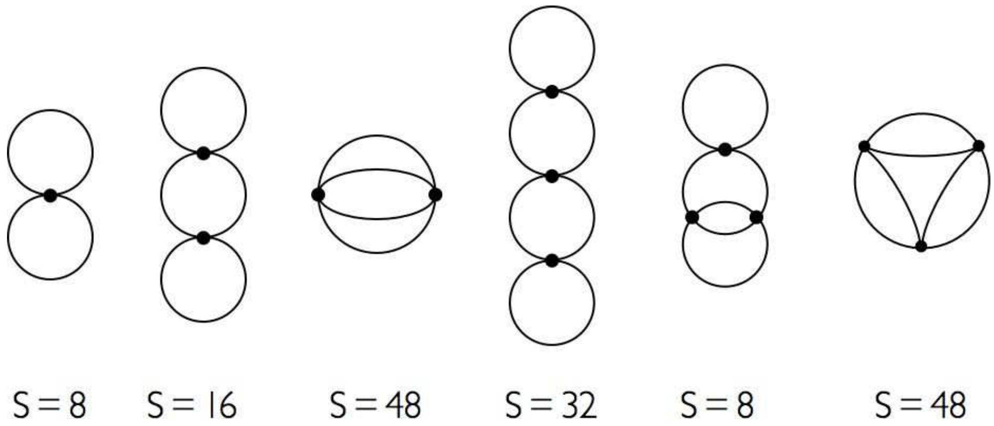

Figure 5.3: (5)(c) Cluster symmetry factors. A vertex is represented as a black dot (•) with four 'legs'.

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

Examples of clusters and their corresponding symmetry factors are provided in fig. 5.3, for all diagrams with $n_\gamma \leq 3$. There is only one diagram with $n_\gamma = 1$, resembling . To obtain $s_\gamma = 8$, note that each of the circles can be separately rotated by an angle π about the long symmetry axis. In addition, the figure can undergo a planar rotation by π about an axis which runs through the sole vertex and is normal to the plane of the diagram. This results in $s_\gamma = 2 \cdot 2 \cdot 2 = 8$. For the cluster , there is one extra circle, so $s_\gamma = 2^4 = 16$. The third diagram in figure shows two vertices connected by four lines. Any of the $4!$ permutations of these lines results in the same diagram. In addition, we may reflect about the vertical symmetry axis, interchanging the vertices, to obtain another symmetry operation. Thus $s_\gamma = 2 \cdot 4! = 48$. One might ask why we don't also count the planar rotation by π as a symmetry operation. The answer is that it is equivalent to a combination of a reflection and a permutation, so it is not in fact a distinct symmetry operation. (If it were distinct, then s_γ would be 96.) Finally, consider the last diagram in the figure, which resembles a sausage with three links joined at the ends into a circle. If we keep the vertices fixed, there are 8 symmetry operations associated with the freedom to exchange the two lines associated with each of the three sausages. There are an additional 6 symmetry operations associated with permuting the three vertices, which can be classified as three in-plane rotations by 0, $\frac{2\pi}{3}$ and $\frac{4\pi}{3}$, each of which can also be combined with a reflection about the y-axis (this is known as the group C_{3v}). Thus, $s_\gamma = 8 \cdot 6 = 48$.

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

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

Thus,

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

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

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

Note that there is one diagram with $N = 1$ vertex, with symmetry factor $s = 8$. For $N = 2$ vertices, there are two diagrams, one with $s = 16$ and one with $s = 48$ (see fig. 5.3). Since $\frac{1}{16} + \frac{1}{48} = \frac{1}{12}$, the diagrammatic expansion is verified to order λ^2.

In quantum field theory (QFT), the vertices themselves carry space-time (or, more commonly, momentum-frequency) labels, and the contractions, *i.e.* the lines connecting legs of the vertices, are *propagators* $G(p_i^\mu - p_j^\mu)$, where p_i^μ is the 4-momentum associated with vertex i. We then must integrate over all the internal 4-momenta to obtain the numerical value for a given diagram. The diagrams, as you know, are associated with Feynman's approach to QFT and are known as Feynman diagrams. Our example here is equivalent to a $(0+0)$-dimensional field theory, *i.e.* zero space dimensions and zero time dimensions. There are then no internal 4-momenta to integrate over, and each propagator is simply a number rather than a function. The discussion above of symmetry factors s_γ carries over to the more general QFT case.

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

Chapter 6

Solution Set #6

(1) The Blume-Capel model is a spin-1 version of the Ising model, with Hamiltonian

$$H = -J \sum_{\langle ij \rangle} S_i \, S_j - \Delta \sum_i S_i^2 \ ,$$

where $S_i \in \{-1\,,\,0\,,\,+1\}$ and where the first sum is over all links of a lattice and the second sum is over all sites. It has been used to describe magnetic solids containing vacancies ($S = 0$ for a vacancy) as well as phase separation in ${}^4\text{He} - {}^3\text{He}$ mixtures ($S = 0$ for a ${}^4\text{He}$ atom). This problem will give you an opportunity to study and learn the material in §§5.2,3 of the notes. For parts (b), (c), and (d) you should work in the thermodynamic limit. The eigenvalues and eigenvectors are such that it would shorten your effort considerably to use a program like `Mathematica` to obtain them.

(a) Find the transfer matrix for the $d = 1$ Blume-Capel model.

(b) Find the free energy $F(T, \Delta, N)$.

(c) Find the density of $S = 0$ sites as a function of T and Δ.

(d) *Exciting!* Find the correlation function $\langle \, S_j \, S_{j+n} \, \rangle$.

Solution :

(a) The transfer matrix R can be written in a number of ways, but it is aesthetically pleasing to choose it to be symmetric. In this case we have

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

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

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

where λ_+, λ_0, and λ_- are the eigenvalues of the transfer matrix R. To find the eigenvalues, note that

$$\vec{\psi}_0 = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$$

is an eigenvector with eigenvalue $\lambda_0 = 2\, e^{\beta\Delta} \sinh(\beta J)$. The remaining eigenvectors must be orthogonal to ψ_0, and hence are of the form

$$\vec{\psi}_\pm = \frac{1}{\sqrt{2 + x_\pm^2}} \begin{pmatrix} 1 \\ x_\pm \\ 1 \end{pmatrix} .$$

We now demand

$$R \begin{pmatrix} 1 \\ x \\ 1 \end{pmatrix} = \begin{pmatrix} 2\, e^{\beta\Delta} \cosh(\beta J) + x\, e^{\beta\Delta/2} \\ 2\, e^{\beta\Delta/2} + x \\ 2\, e^{\beta\Delta} \cosh(\beta J) + x\, e^{\beta\Delta/2} \end{pmatrix} = \begin{pmatrix} \lambda \\ \lambda x \\ \lambda \end{pmatrix} ,$$

resulting in the coupled equations

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

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

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

Note $\lambda_+ > \lambda_0 > 0 > \lambda_-$ and that λ_+ is the eigenvalue of the largest magnitude. This is in fact guaranteed by the *Perron-Frobenius theorem*, which states that for any positive matrix R (*i.e.* a matrix whose elements are all positive) there exists a positive real number p such that p is an eigenvalue of R and any other (possibly complex) eigenvalue of R is smaller than p in absolute value. Furthermore the associated eigenvector $\vec{\psi}$ is such that all its components are of the same sign. In the thermodynamic limit $N \to \infty$ we then have

$$F(T, \Delta, N) = -N k_B T \ln \lambda_+ \, .$$

(c) Note that, at any site,

$$\langle S^2 \rangle = -\frac{1}{N} \frac{\partial F}{\partial \Delta} = \frac{1}{\beta} \frac{\partial \ln \lambda_+}{\partial \Delta} ,$$

and furthermore that

$$\delta_{S,0} = 1 - S^2 \, .$$

Thus,

$$\nu_0 \equiv \frac{N_0}{N} = 1 - \frac{1}{\beta} \frac{\partial \ln \lambda_+}{\partial \Delta} \, .$$

After some algebra, find

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

where

$$r = e^{\beta\Delta} \cosh(\beta J) + \tfrac{1}{2} \ .$$

It is now easy to explore the limiting cases $\Delta \to -\infty$, where we find $\nu_0 = 1$, and $\Delta \to +\infty$, where we find $\nu_0 = 0$. Both these limits make physical sense.

(d) We have

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

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

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

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

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

We define the correlation length ξ by

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

in which case

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

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

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

(2) DC Comics superhero Clusterman and his naughty dog Henry are shown in fig. 6.1. Clusterman, as his name connotes, is a connected diagram, but the diagram for Henry contains some disconnected pieces.

(a) Interpreting the diagrams as arising from the Mayer cluster expansion, compute the symmetry factor s_γ for Clusterman.

(b) What is the *total* symmetry factor for Henry and his disconnected pieces? What would the answer be if, unfortunately, another disconnected piece of the same composition were to be found?

(c) What is the lowest order virial coefficient to which Clusterman contributes?

Solution :

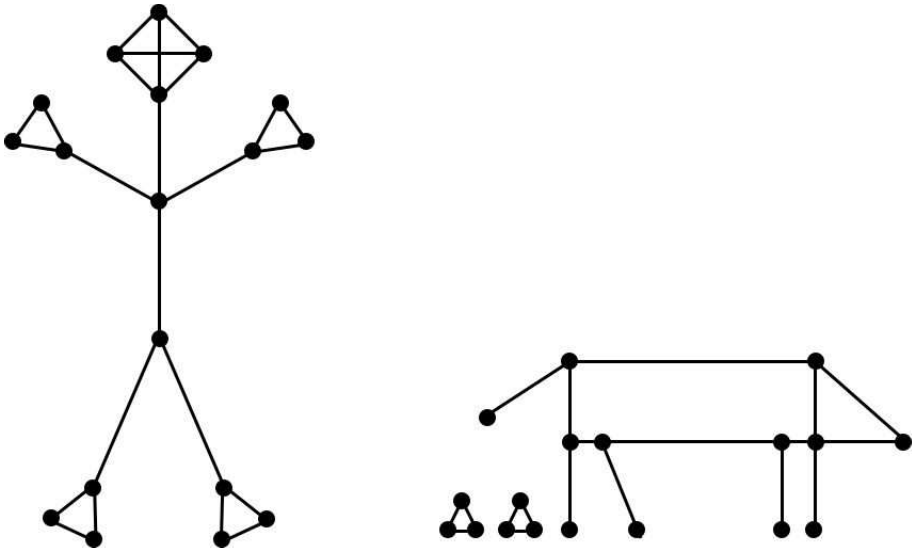

Figure 6.1: Mayer expansion diagrams for Clusterman and his dog.

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

(a) Clusterman's head gives a factor of 6 because the upper three vertices can be permuted among themselves in any of $3! = 6$ ways. Each of his hands gives a factor of 2 because each hand can be rotated by π about its corresponding arm. The arms themselves can be interchanged, by rotating his shoulders by π about his body axis (Clusterman finds this invigorating). Finally, the analysis for the hands and arms applies just as well to the feet and legs, so we conclude

$$s_\gamma = 6 \cdot \left(2^2 \cdot 2\right)^2 = 3 \cdot 2^7 = 384 \ .$$

Note that an arm cannot be exchanged with a leg, because the two lower vertices on Clusterman's torso are not equivalent. Plus, that would be a really mean thing to do to Clusterman.

(b) Henry himself has no symmetries. The little pieces each have $s_\triangle = 3!$, and moreover they can be exchanged, yielding another factor of 2. So the total symmetry factor for Henry plus disconnected pieces is $s_{\triangle\triangle} = 2! \cdot (3!)^2 = 72$. Were another little piece of the same…er…consistency to be found, the symmetry factor would be $s_{\triangle\triangle\triangle} = 3! \cdot (3!)^3 = 2^4 \cdot 3^4 = 1296$, since we get a factor of $3!$ from each of the $\triangle$ pieces, and a fourth factor of $3!$ from the permutations among the $\triangle$s.

(c) There are 18 vertices in Clusterman, hence he will first appear in B_{18}.

(3) The Tonks gas is a one-dimensional generalization of the hard sphere gas. Consider a one-dimensional gas of indistinguishable particles of mass m interacting via the potential

$$u(x-x') = \begin{cases} \infty & \text{if } |x-x'| < a \\ 0 & \text{if } |x-x'| \geq a \ . \end{cases}$$

Let the gas be placed in a finite volume L. The hard sphere nature of the particles means that no particle can get within a distance $\frac{1}{2}a$ of the ends at $x=0$ and $x=L$. That is, there is a one-body potential $v(x)$ acting as well, where

$$v(x) = \begin{cases} \infty & \text{if } x < \frac{1}{2}a \\ 0 & \text{if } \frac{1}{2}a \leq x \leq L - \frac{1}{2}a \\ \infty & \text{if } x > L - \frac{1}{2}a \ . \end{cases}$$

(a) Compute the N particle partition function $Z(T,L,N)$ for the Tonks gas. Present a clear derivation of your result. Please try your best to solve this, either by yourself or in collaboration with classmates. If you get stuck there is an $Sk\log$*Wiki* page on the web on "1-dimensional hard rods" where you can look up the derivation.

(b) Find the equation of state $p = p(T,L,N)$.

(c) Find the grand potential $\Omega(T,L,\mu)$. *Hint : There is a small subtlety you must appreciate in order to obtain the correct answer.*

Solution :

(a) The partition function is

$$Z(T,L,N) = \frac{\lambda_T^N}{N!} \int\limits_0^L \! dx_1 \cdots \int\limits_0^L \! dx_N \ \chi(x_1,\ldots,x_N) \ ,$$

where $\chi = e^{-U/k_\text{B}T}$ is zero if any two 'rods' (of length a) overlap, or if any rod overlaps with either boundary at $x=0$ and $x=L$, and $\chi = 1$ otherwise. Note that χ does not depend on temperature. Without loss of generality, we can integrate over the subspace where $x_1 < x_2 < \cdots < x_N$ and then multiply the result by $N!$. Clearly x_j must lie to the right of $x_{j-1} + a$ and to the left of $Y_j \equiv L - (N-j)a - \frac{1}{2}a$. Thus,

$$\begin{aligned}
Z(T,L,N) &= \lambda_T^N \int\limits_{a/2}^{Y_1} dx_1 \int\limits_{x_1+a}^{Y_2} dx_2 \cdots \int\limits_{x_{N-1}+a}^{Y_N} dx_N \\
&= \lambda_T^N \int\limits_{a/2}^{Y_1} dx_1 \int\limits_{x_1+a}^{Y_2} dx_2 \cdots \int\limits_{x_{N-2}+a}^{Y_{N-1}} dx_{N-1}\, \big(Y_{N-1} - x_{N-1}\big) \\
&= \lambda_T^N \int\limits_{a/2}^{Y_1} dx_1 \int\limits_{x_1+a}^{Y_2} dx_2 \cdots \int\limits_{x_{N-3}+a}^{Y_{N-2}} dx_{N-2}\, \tfrac{1}{2}\big(Y_{N-2} - x_{N-2}\big)^2 \\
&= \cdots = \frac{\lambda_T^N}{N!}\, \big(X_1 - \tfrac{1}{2}a\big)^N = \frac{\lambda_T^N}{N!}\,(L - Na)^N \ .
\end{aligned}$$

The λ_T^N factor comes from integrating over the momenta; recall $\lambda_T = \sqrt{2\pi\hbar^2/mk_B T}$.

(b) The free energy is

$$F = -k_B T \ln Z = -N k_B T \bigg\{ \ln \lambda_T + 1 + \ln\bigg(\frac{L}{N} - a\bigg)\bigg\} \ ,$$

where we have used Stirling's rule to write $\ln N! \approx N \ln N - N$. The pressure is

$$p = -\frac{\partial F}{\partial L} = \frac{k_B T}{\frac{L}{N} - a} = \frac{n k_B T}{1 - na} \ ,$$

where $n = N/L$ is the one-dimensional density. Note that the pressure diverges as n approaches a^{-1} from below, and $n > a^{-1}$ is not allowed.

(c) We have

$$\Xi(T,L,\mu) = \sum_{N=0}^{N_{\rm max}} e^{N\mu/k_B T}\, Z(T,L,N) \ ,$$

where $N_{\rm max} = [L/a]$, where $[x]$ is the greatest integer less than or equal to x. Then $\Omega = -k_B T \ln \Xi$. Not much more we can do with this.

(4) In §5.5.3 of the notes, the virial equation of state is derived for a single species of particle.

(a) Generalize eqn. 5.160 to the case of two species interacting by $u_{\sigma\sigma'}(r)$, where σ and σ' are the species labels.

(b) For a plasma, show from Debye-Hückel theory that the pair correlation function is $g_{\sigma\sigma'} \propto \exp\big(-\sigma\sigma' q^2 \phi(r)/k_B T\big)$, where σ and σ' are the signs of the charges (magnitude q), and $\phi(r)$ is the screened potential due to a unit positive test charge.

(c) Find the equation of state for a three-dimensional two-component plasma, in the limit where T is large.

Solution :

(a) Let $i = 1, \ldots, N_+ + N_-$ index all the particles, and let $\sigma_i = \pm 1$ denote the sign of the charge of particle i, with $\sigma_i = +1$ for $1 \le i \le N_+$ and $\sigma_i = -1$ for $(N_+ {+} 1) \le i \le (N_+ {+} N_-)$. In a globally neutral system, $N_+ = N_- \equiv \frac{1}{2}N$. We define

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

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

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

The potential is

$$W = \sum_{i<j} \frac{\sigma_i\, \sigma_j\, q^2}{|\boldsymbol{x}_i - \boldsymbol{x}_j|} \equiv \sum_{i<j} u_{\sigma_i \sigma_j}\big(|\boldsymbol{x}_i - \boldsymbol{x}_j|\big) \ ,$$

with $u_{\sigma\sigma'}(r) = \sigma\sigma' q^2/r$. Then using translational invariance one has

$$\frac{p}{k_{\rm B}T} = n_+ + n_- - \frac{2\pi}{3k_{\rm B}T} \sum_{\sigma,\sigma'} n_\sigma n_{\,\sigma'} \int\limits_0^\infty \! dr\, r^3\, u'_{\sigma\sigma'}(r)\, g_{\sigma\sigma'}(r)$$

(b) According to Debye-Hückel theory,

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

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

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

where $n_+ = n_- \equiv \frac{1}{2}n$. In the high temperature limit, we can expand the sinh function and we obtain the Yukawa potential

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

where

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

is the Debye screening wavevector. Thus, we have

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

Chapter 7

Solution Set #7

(1) Consider the ferromagnetic XY model, with

$$\hat{H} = -\sum_{i<j} J_{ij}\,\cos(\phi_i - \phi_j) - \mathsf{H}\sum_i \cos\phi_i \ .$$

Defining $z_i \equiv \exp(i\phi_i)$, write $z_i = \langle z_i \rangle + \delta z_i$ with

$$\langle z_i \rangle = m\, e^{i\alpha} \ .$$

(a) Assuming $\mathsf{H} > 0$, what should you take for α?

(b) Making this choice for α, find the mean field free energy using the 'neglect of fluctuations' method. *Hint*: Note that $\cos(\phi_i - \phi_j) = \mathsf{Re}\,(z_i z_j^*)$.

(c) Find the self-consistency equation for m.

(d) Find $T_{\rm c}$.

(e) Find the mean field critical behavior for $m(T, \mathsf{H} = 0)$, $m(T = T_{\rm c}, \mathsf{H})$, $C_V(T, \mathsf{H} = 0)$, and $\chi(T, \mathsf{H} = 0)$, and identify the critical exponents α, β, γ, and δ.

Solution :

(a) To minimize the free energy we clearly must take $\alpha = 0$ so that the mean field is aligned with the external field.

(b) Writing $z_i = m + \delta z_i$ we have

$$\begin{aligned} H &= -\tfrac{1}{2}\sum_{i,j} J_{ij}\,\mathsf{Re}\,\big(m^2 + m\,\delta z_i + m\,\delta z_j + \delta z_i\,\delta z_j\big) - \mathsf{H}\sum_i \mathsf{Re}\,(z_i) \\ &= \tfrac{1}{2}N\hat{J}(0)\,m^2 - \big(\hat{J}(0)\,m + \mathsf{H}\big)\sum_i \cos\phi_i + \mathcal{O}\big(\delta z_i\,\delta z_j\big) \end{aligned}$$

The mean field free energy is then

$$\begin{aligned} F &= \tfrac{1}{2} N \hat{J}(0)\, m^2 - N k_{\rm B} T \ln \Bigg[\int\limits_0^{2\pi} \frac{d\phi}{2\pi}\, e^{(\hat{J}(0) m + \mathsf{H}) \cos\phi / k_{\rm B} T} \Bigg] \\ &= \tfrac{1}{2} N \hat{J}(0)\, m^2 - N k_{\rm B} T \ln I_0 \bigg(\frac{\hat{J}(0)\, m + \mathsf{H}}{k_{\rm B} T} \bigg) \ , \end{aligned}$$

where $I_\alpha(x)$ is the modified Bessel function of order α.

(c) Differentiating, we find

$$\frac{\partial F}{\partial m} = 0 \qquad \Longrightarrow \qquad m = \frac{I_1\Big(\frac{\hat{J}(0) m + \mathsf{H}}{k_{\rm B} T}\Big)}{I_0\Big(\frac{\hat{J}(0) m + \mathsf{H}}{k_{\rm B} T}\Big)} \ ,$$

which is equivalent to eqn. 6.119 of the notes, which was obtained using the variational density matrix method.

(d) It is convenient to define $f = F/N\hat{J}(0)$, $\theta = k_{\rm B}T/\hat{J}(0)$, and $h = \mathsf{H}/\hat{J}(0)$. Then

$$f(\theta, h) = \tfrac{1}{2} m^2 - \theta \ln I_0 \bigg(\frac{m + h}{\theta} \bigg) \ .$$

We now expand in powers of m and h, keeping terms only to first order in the field h. This yields

$$f = \big(\tfrac{1}{2} - \tfrac{1}{4\theta} \big)\, m^2 + \tfrac{1}{64\,\theta^3}\, m^4 - \tfrac{1}{2\,\theta}\, h m + \ldots \ ,$$

from which we read off $\theta_{\rm c} = \frac{1}{2}$, *i.e.* $T_{\rm c} = \hat{J}(0)/2k_{\rm B}$.

(e) The above free energy is of the standard Landau form for an Ising system, therefore $\alpha = 0$, $\beta = \frac{1}{2}$, $\gamma = 1$, and $\delta = 3$. The $\mathsf{O}(2)$ symmetry, which cannot be spontaneously broken in dimensions $d \le 2$, is not reflected in the mean field solution. In $d = 2$, the $\mathsf{O}(2)$ model *does* have a finite temperature phase transition, but one which is *not associated with a spontaneous breaking of the symmetry group*. The $\mathsf{O}(2)$ model in $d = 2$ undergoes a Kosterlitz-Thouless transition, which is associated with the unbinding of vortex-antivortex pairs as T exceeds $T_{\rm c}$. The existence of vortex excitations in the $\mathsf{O}(2)$ model in $d = 2$ is a special feature of the topology of the group.

(2) Consider a nearest neighbor two-state Ising *antiferromagnet* on a triangular lattice. The Hamiltonian is

$$\hat{H} = J \sum_{\langle ij \rangle} \sigma_i \sigma_j - \mathsf{H} \sum_i \sigma_i \ ,$$

with $J > 0$.

(a) Show graphically that the triangular lattice is *tripartite*, *i.e.* that it may be decomposed into three component sublattices A, B, and C such that every neighbor of A is either B or C, *etc.*

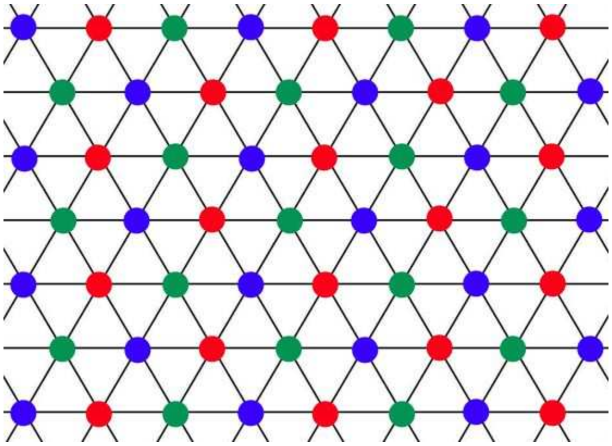

Figure 7.1: **(2)**(a) The three triangular sublattices of the (tripartite) triangular lattice.

(b) Use a variational density matrix which is a product over single site factors, where

$$\begin{aligned}\rho(\sigma_i) &= \frac{1+m}{2}\,\delta_{\sigma_i,+1} + \frac{1-m}{2}\,\delta_{\sigma_i,-1} \qquad \text{if } i \in \text{A or } i \in \text{B} \\ &= \frac{1+m_{\rm C}}{2}\,\delta_{\sigma_i,+1} + \frac{1-m_{\rm C}}{2}\,\delta_{\sigma_i,-1} \qquad \text{if } i \in \text{C} \ .\end{aligned}$$

Compute the variational free energy $F(m, m_{\rm C}, T, \mathsf{H}, N)$.

(c) Find the mean field equations.

(d) Find the mean field phase diagram.

(e) While your mean field analysis predicts the existence of an ordered phase, it turns out that $T_{\rm c} = 0$ for this model because it is so highly frustrated for $h = 0$. The ground state is highly degenerate. Show that for any ground state, no triangle can be completely ferromagnetically aligned. What is the ground state energy? Find a lower bound for the ground state entropy per spin.

Solution :

(a) See fig. 7.1.

(b) Of the $3N$ links of the lattice, N are between A and B sites, N are between A and C sites, and N are between B and C sites. Thus the mean field energy is

$$E = NJm^2 + 2NJmm_{\rm C} - \tfrac{2}{3}N\mathsf{H}m - \tfrac{1}{3}N\mathsf{H}m_{\rm C} \ .$$

The entropy of the A and B sublattices is $S_{\rm A} = S_{\rm B} = \frac{2}{3}Ns(m)$, while that for the C sublattice is $S_{\rm C} = \frac{1}{3}Ns(m_{\rm C})$, where

$$s(m) = -\left[\left(\frac{1+m}{2}\right)\ln\left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right)\ln\left(\frac{1-m}{2}\right)\right] .$$

The free energy is $F = E - TS$. We define $f \equiv F/2JN$, $\theta \equiv k_{\rm B}T/6J$, and $h \equiv \mathsf{H}/6J$. Then

$$f(m, m_{\rm C}, \theta, h) = \tfrac{1}{2}m^2 + m m_{\rm C} - 2hm - hm_{\rm C} - 2\theta s(m) - \theta s(m_{\rm C}) \ .$$

(c) The mean field equations are

$$\frac{\partial f}{\partial m} = 0 = m + m_{\rm C} - 2h + \theta \ln\!\bigg(\frac{1+m}{1-m}\bigg)$$

$$\frac{\partial f}{\partial m_{\rm C}} = 0 = m - h + \tfrac{1}{2}\theta \ln\!\bigg(\frac{1+m_{\rm C}}{1-m_{\rm C}}\bigg) \ .$$

Equivalently,

$$m = \tanh\!\bigg(\frac{2h - m - m_{\rm C}}{2\theta}\bigg) \qquad , \qquad m_{\rm C} = \tanh\!\bigg(\frac{h-m}{\theta}\bigg) \ .$$

(d) The order parameter for our model is the difference in sublattice magnetizations, $\varepsilon \equiv m_{\rm C} - m$. Let us first consider the zero temperature limit, $\theta \to 0$, for which the entropy term makes no contribution in the free energy. We compare two competing states: the ferromagnetic state with $m = m_{\rm C} = 1$, and the antiferromagnetic state with $m = 1$ and $m_{\rm C} = -1$. The energies of these two states are

$$e_0(1,1,h) = \tfrac{3}{2} - 3h$$

$$e_0(1,-1,h) = -\tfrac{1}{2} - h \ .$$

We see that for $h < 1$ the AF configuration wins (*i.e.* has lower energy per site e_0), while for $h > 1$ the F configuration wins. Thus, at $\theta = 0$ there is a first order transition from AF to F at $h_{\rm c} = 1$.

Next, let us examine the behavior with θ when $h = 0$. We can combine the two mean field equations to give

$$m + \theta \, \ln\!\bigg(\frac{1+m}{1-m}\bigg) = \tanh\big(m/\theta\big) \ .$$

Expanding in powers of m, we equate the coefficient of the linear term on either side to identify $\theta_{\rm c}$ and thus we obtain the equation $2\theta^2 + \theta - 1 = (2\theta - 1)(\theta + 1) = 0$, hence $\theta_{\rm c}(h=0) = 1$.

We identify the order parameter as $\varepsilon = m_{\rm C} - m$, the difference in the sublattice magnetizations. We now seek the phase boundary $h(\theta)$ along which the order parameter vanishes in the (θ, h) plane. To this end, we write the two mean field equations in terms of m and ε, rather than m and $m_{\rm C}$. We find

$$m + \tfrac{1}{2}\varepsilon = h - \frac{\theta}{2} \ln\!\bigg(\frac{1+m}{1-m}\bigg)$$

$$m = h - \frac{\theta}{2} \ln\!\bigg(\frac{1+m+\varepsilon}{1-m-\varepsilon}\bigg) \ .$$

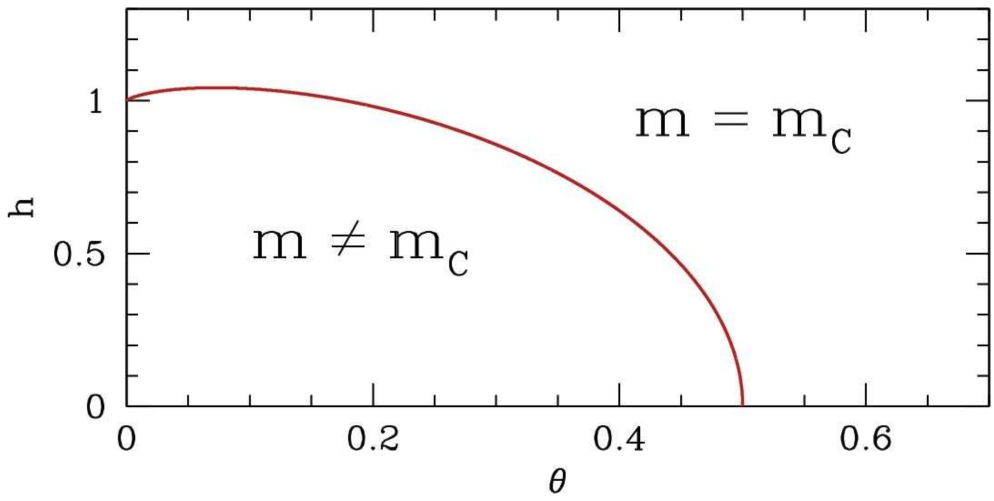

Figure 7.2: **(2)**(d) Phase diagram for the mean field theory of problem 2.

Taking the difference, we obtain

$$\varepsilon = \theta \ln\left(\frac{1+\frac{\varepsilon}{1+m}}{1-\frac{\varepsilon}{1-m}}\right) = \frac{2\varepsilon\theta}{1-m^2} + \mathcal{O}(\varepsilon^2)\ .$$

Along the phase boundary, *i.e.* in the $\varepsilon \to 0$ limit, we therefore have

$$\frac{2\theta}{1-m^2} = 1\ .$$

We also have the mean field equation for m,

$$m = \tanh\left(\frac{h-m}{\theta}\right)\ .$$

Putting these together, we obtain the curve

$$h^*(\theta) = \sqrt{1-2\theta} + \frac{\theta}{2}\ln\left(\frac{1+\sqrt{1-2\theta}}{1-\sqrt{1-2\theta}}\right)\ .$$

The phase boundary is shown in Fig. 7.2.

If we eliminate $m_{\rm C}$ through the second mean field equation, we can generate the Landau expansion

$$\begin{aligned} f(m,\theta,h) = -3\ln(2)\,\theta + \big(\theta - \tfrac{1}{2}\big)\big(\theta^{-1}+1\big)\,m^2 + \tfrac{1}{6}\big(\theta + \tfrac{1}{2}\theta^{-3}\big)\,m^4 \\ - 2\theta^{-1}\big(\theta - \tfrac{1}{2}\big)\,hm - \tfrac{1}{3}\theta^{-3}hm^3 + \mathcal{O}\big(m^6, hm^5, h^3\big) \end{aligned}$$

The full expression $f(m, m_{\rm C}(m), \theta, h)$ is shown as a function of m for various values of θ and h in fig. 7.3. Thus, we obtain a Landau theory with a second order transition at $\theta_{\rm c} = \frac{1}{2}$.

We retain the $\mathcal{O}\big(hm^3\big)$ term because the coefficient of hm vanishes at $\theta=\theta_{\rm c}$. Differentiating with respect to m, we obtain

$$\frac{\partial f}{\partial m}=0=2\theta^{-1}\big(\theta+1\big)\big(\theta-\tfrac{1}{2}\big)\,m+\tfrac{1}{3}\theta^{-3}\big(1+2\theta^4\big)\,m^3-2\theta^{-1}\big(\theta-\tfrac{1}{2}\big)\,h-\theta^{-2}hm^2$$

Thus,

$$\begin{aligned}m\big(\theta,h_{\rm c}\big)&=\sqrt{2}\,\big(\theta_{\rm c}-\theta\big)_{+}^{1/2}+\mathcal{O}\big(|\theta-\theta_{\rm c}|^{3/2}\big)\\ m\big(\theta,h\big)&=\tfrac{2}{3}h+\mathcal{O}\big(h^3\big)\\ m\big(\theta_{\rm c},h\big)&=\tfrac{4}{3}h+\mathcal{O}\big(h^3\big)\ .\end{aligned}$$

Note that $h_{\rm c}=0$. In the second equation, we have $\epsilon\equiv\theta-\theta_{\rm c}\to 0$ with $\epsilon\gg h$, while in the third equation we have $h\to 0$ with $\epsilon\equiv 0$, so the two equations represent two different limits. We obtain the exponents $\alpha=0$, $\beta=\frac{1}{2}$, $\gamma=0$, $\delta=1$. This seemingly violates the Rushbrooke scaling law $\alpha+2\beta+\gamma=2$, but satisfies the Griffiths relation $\beta+\gamma=\beta\delta$. However, this is because we are using the wrong field. Rather than defining the exponents γ and δ with respect to a uniform field h, we should instead consider a *staggered* field $h_{\rm s}$ such that $h_{\rm A}=h_{\rm B}=h_{\rm s}$ but $h_{\rm C}=-h_{\rm s}$.

(e) With antiferromagnetic interactions and $h=0$, it is impossible for every link on an odd-membered ring (*e.g.* a triangle) to be satisfied. This is because on a k-site ring (with $(k+1)\equiv 1$), taking the product of $\sigma_j\sigma_{j+1}$ over all links on the ring gives

$$\big(\sigma_1\sigma_2\big)\big(\sigma_2\sigma_3\big)\cdots\big(\sigma_k\sigma_1\big)=1\ ,$$

If we assume, however, that each link satisfies the antiferromagnetic interaction, then $\sigma_j\sigma_{j+1}=-1$ and the product would be $(-1)^k=-1$ since k is odd. So not all odd-membered rings can be completely satisfied. Clearly the best we can do on any odd-membered ring is to have $k-1$ of the bonds antiferromagnetically aligned and the remaining bond ferromagnetically aligned.

Now let us decompose the triangular lattice into A, B, and C sublattices. If we place all spins on the A and B sublattices are up ($\sigma=+1$) and all spins on the C sublattice are down ($\sigma=-1$), then each elementary triangle has two AF bonds and one F bond, which is the best we can do for the nearest neighbor triangular lattice Ising antiferromagnet. The energy of this configuration is given in part (b) above: $E=NJm^2+2NJmm_{\rm C}=-NJ$, since $m=1$ and $m_{\rm C}=-1$. However, it is clear that at each site of the B sublattice, the choice of σ_i is arbitrary. This is because one third of all the links on the lattice are AC links, and they are already antiferromagnetically aligned. Now there are $\frac{1}{3}N$ sites on each of the sublattices, hence we have identified $2^{N/3}$ degenerate ground states. This set of ground state configurations is not complete, however. We could immediately double it simply by choosing to reverse spins on the A sublattice instead, leaving the B sublattice with $m_{\rm B}=1$. But even this enumeration is not complete – we have simply identified a lower bound to the number of degenerate ground states. The ground state entropy per spin is then

$$\frac{S_0}{N}\geq\tfrac{1}{3}\ln 2\approx 0.23105\ .$$

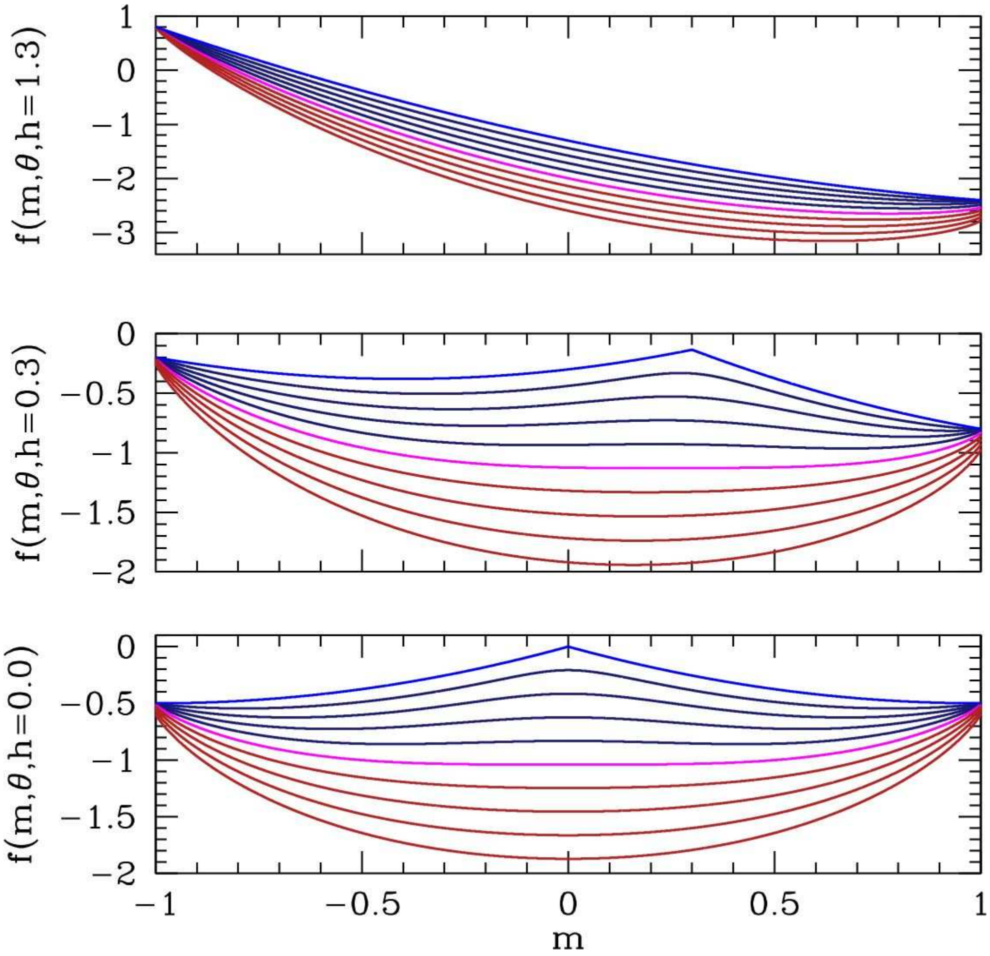

Figure 7.3: **(2)**(d) Free energy for the mean field theory of problem (2) at ten equally spaced dimensionless temperatures between $\theta = 0.0$ and $\theta = 0.9$. Bottom panel: $h = 0$; middle panel: $h = 0.3$; top panel: $h = 1.3$.

The exact value, obtained by Wannier and by Houtappel in 1950, is $s_0 \approx 0.3231$ per spin. So there are exponentially (in the system size!) many more ground states than we have identified here.

(3) A system is described by the Hamiltonian

$$\hat{H} = -J \sum_{\langle ij \rangle} \mathcal{I}(\mu_i, \mu_j) - \mathsf{H} \sum_i \delta_{\mu_i, \mathrm{A}} \ , \tag{7.1}$$

where on each site i there are four possible choices for μ_i: $\mu_i \in \{\mathrm{A}, \mathrm{B}, \mathrm{C}, \mathrm{D}\}$. The interaction matrix $\mathcal{I}(\mu, \mu')$ is given in the following table:

$\mathcal{I}$	A	B	C	D
A	$+1$	-1	-1	0
B	-1	$+1$	0	-1
C	-1	0	$+1$	-1
D	0	-1	-1	$+1$

(a) Write a trial density matrix

$$\varrho(\mu_1,\ldots,\mu_N)=\prod_{i=1}^{N}\varrho_1(\mu_i)$$
$$\varrho_1(\mu)=x\,\delta_{\mu,\mathrm{A}}+y(\delta_{\mu,\mathrm{B}}+\delta_{\mu,\mathrm{C}}+\delta_{\mu,\mathrm{D}})\ .$$

What is the relationship between x and y? Henceforth use this relationship to eliminate y in terms of x.

(b) What is the variational energy per site, $E(x,T,\mathsf{H})/N$?

(c) What is the variational entropy per site, $S(x,T,\mathsf{H})/N$?

(d) What is the mean field equation for x?

(e) What value x^* does x take when the system is disordered?

(f) Write $x=x^*+\frac{3}{4}\varepsilon$ and expand the free energy to fourth order in ε. (The factor $\frac{3}{4}$ should generate manageable coefficients in the Taylor series expansion.)

(g) Sketch ε as a function of T for $\mathsf{H}=0$ and find T_c. Is the transition first order or second order?

Solution :

(a) Clearly we must have $y=\frac{1}{3}(1-x)$ in order that $\mathsf{Tr}(\varrho_1)=x+3y=1$.

(b) We have

$$\frac{E}{N}=-\tfrac{1}{2}zJ\big(x^2-4\,xy+3\,y^2-4\,y^2\big)-\mathsf{H}x\ ,$$

The first term in the bracket corresponds to AA links, which occur with probability x^2 and have energy $-J$. The second term arises from the four possibilities AB, AC, BA, CA, each of which occurs with probability xy and with energy $+J$. The third term is from the BB, CC, and DD configurations, each with probability y^2 and energy $-J$. The last term is from the BD, CD, DB, and DC configurations, each with probability y^2 and energy $+J$. Finally, there is the field term. Eliminating $y=\frac{1}{3}(1-x)$ from this expression we have

$$\frac{E}{N}=\tfrac{1}{18}zJ\big(1+10\,x-20\,x^2\big)-\mathsf{H}x$$

Note that with $x=1$ we recover $E=-\frac{1}{2}NzJ-\mathsf{H}$, *i.e.* an interaction energy of $-J$ per link and a field energy of $-\mathsf{H}$ per site.

(c) The variational entropy per site is

$$\begin{aligned} s(x) &= -k_{\rm B}\, \mathsf{Tr}\,\big(\varrho_1 \ln \varrho_1\big) \\ &= -k_{\rm B}\Big(x \ln x + 3y \ln y\Big) \\ &= -k_{\rm B}\left[x \ln x + (1-x)\ln\!\left(\frac{1-x}{3}\right)\right] . \end{aligned}$$

(d) It is convenient to adimensionalize, writing $f = F/N\varepsilon_0$, $\theta = k_{\rm B}T/\varepsilon_0$, and $h = \mathsf{H}/\varepsilon_0$, with $\varepsilon_0 = \frac{5}{9} zJ$. Then

$$f(x,\theta,h) = \tfrac{1}{10} + x - 2x^2 - hx + \theta\left[x \ln x + (1-x)\ln\!\left(\frac{1-x}{3}\right)\right] .$$

Differentiating with respect to x, we obtain the mean field equation

$$\frac{\partial f}{\partial x} = 0 \qquad \Longrightarrow \qquad 1 - 4x - h + \theta \ln\!\left(\frac{3x}{1-x}\right) = 0 .$$

(e) When the system is disordered, there is no distinction between the different polarizations of μ_0. Thus, $x^* = \frac{1}{4}$. Note that $x = \frac{1}{4}$ is a solution of the mean field equation from part (d) when $h = 0$.

(f) Find

$$f\big(x = \tfrac{1}{4} + \tfrac{3}{4}\,\varepsilon, \theta, h\big) = f_0 + \tfrac{3}{2}\big(\theta - \tfrac{3}{4}\big)\,\varepsilon^2 - \theta\,\varepsilon^3 + \tfrac{7}{4}\,\theta\,\varepsilon^4 - \tfrac{3}{4}\,h\,\varepsilon$$

with $f_0 = \frac{9}{40} - \frac{1}{4}h - \theta \ln 4$.

(g) For $h = 0$, the cubic term in the mean field free energy leads to a first order transition which preempts the second order one which would occur at $\theta^* = \frac{3}{4}$, where the coefficient of the quadratic term vanishes. We learned in §6.7.1,2 of the notes that for a free energy $f = \frac{1}{2}am^2 - \frac{1}{3}ym^3 + \frac{1}{4}bm^4$ that the first order transition occurs for $a = \frac{2}{9}\,b^{-1}y^2$, where the magnetization changes discontinuously from $m = 0$ at $a = a_{\rm c}^+$ to $m_0 = \frac{2}{3}\,b^{-1}y$ at $a = a_{\rm c}^-$. For our problem here, we have $a = 3\big(\theta - \frac{3}{4}\big)$, $y = 3\theta$, and $b = 7\theta$. This gives

$$\theta_{\rm c} = \tfrac{63}{76} \approx 0.829 \qquad , \qquad \varepsilon_0 = \tfrac{2}{7} .$$

As θ decreases further below $\theta_{\rm c}$ to $\theta = 0$, ε increases to $\varepsilon(\theta = 0) = 1$. No sketch needed!

Chapter 8

Final Exam Solutions

(1) Consider a lattice of noninteracting spin dimers, where the dimer Hamiltonian is

$$\hat{H} = -\mathsf{H}^\sigma \sigma - \mathsf{H}^\tau \tau - K\sigma\tau \ ,$$

where H^σ and H^τ are magnetic fields acting on the σ and τ spins, respectively. Each spin is a two-state Ising variable, *i.e.* $\sigma = \pm 1$ and $\tau = \pm 1$.

(a) Compute the partition function ξ for a single dimer. `[5 points]`

The single dimer partition function is

$$\xi = 2\cosh\!\left(\frac{\mathsf{H}^\sigma + \mathsf{H}^\tau}{k_\mathrm{B}T}\right) e^{K/k_\mathrm{B}T} + 2\cosh\!\left(\frac{\mathsf{H}^\sigma - \mathsf{H}^\tau}{k_\mathrm{B}T}\right) e^{-K/k_\mathrm{B}T} \ .$$

(b) Find $m \equiv \langle\sigma\rangle$. `[5 points]`

$$\langle\sigma\rangle = -\frac{\partial F}{\partial \mathsf{H}^\sigma} = \frac{k_\mathrm{B}T}{\xi}\,\frac{\partial \xi}{\partial \mathsf{H}^\sigma} = \frac{\sinh\!\left(\frac{\mathsf{H}^\sigma + \mathsf{H}^\tau}{k_\mathrm{B}T}\right) e^{K/k_\mathrm{B}T} + 2\sinh\!\left(\frac{\mathsf{H}^\sigma - \mathsf{H}^\tau}{k_\mathrm{B}T}\right) e^{-K/k_\mathrm{B}T}}{\cosh\!\left(\frac{\mathsf{H}^\sigma + \mathsf{H}^\tau}{k_\mathrm{B}T}\right) e^{K/k_\mathrm{B}T} + 2\cosh\!\left(\frac{\mathsf{H}^\sigma - \mathsf{H}^\tau}{k_\mathrm{B}T}\right) e^{-K/k_\mathrm{B}T}} \ .$$

Now consider an interacting model,

$$\hat{H} = -\tfrac{1}{2}\sum_{i,j} J^\sigma_{ij}\,\sigma_i\,\sigma_j - \tfrac{1}{2}\sum_{i,j} J^\tau_{ij}\,\tau_i\,\tau_j - K\sum_i \sigma_i\,\tau_i \ .$$

Treat the first two terms by mean field theory, writing $\sigma_i = m + \delta\sigma_i$ and $\tau_i = n + \delta\tau_i$, with $m = \langle\sigma_i\rangle$ and $n = \langle\tau_i\rangle$ are presumed to be independent of i. You may assume that all interactions are ferromagnetic. *Treat the third term exactly and do not make the mean field approximation for this term.*

(c) What is the mean field $\mathsf{H}^\sigma_{\text{eff}}$ for the σ spins? `[5 points]`

The mean fields are

$$\mathsf{H}^\sigma_{\text{eff}} = \hat{J}^\sigma(0)\, m \qquad , \qquad \mathsf{H}^\tau_{\text{eff}} = \hat{J}^\tau(0)\, n \ ,$$

where $\hat{J}^\sigma(0) = \sum_j J^\sigma_{ij}$ and $\hat{J}^\tau(0) = \sum_j J^\tau_{ij}$.

(d) What is the mean field free energy per site F/N? *Hint : Once you have the mean fields* H^σ *and* H^τ*, you can make use of the results of part (a).* `[5 points]`

$$\begin{aligned} F =& \tfrac{1}{2} N \hat{J}^\sigma(0)\, m^2 + \tfrac{1}{2} N \hat{J}^\tau(0)\, n^2 \\ &- N k_{\rm B} T \left\{ 2\cosh\!\left(\frac{\hat{J}^\sigma(0)\, m + \hat{J}^\tau(0)\, n}{k_{\rm B}T}\right) e^{K/k_{\rm B}T} + 2\cosh\!\left(\frac{\hat{J}^\sigma(0)\, m - \hat{J}^\tau(0)\, n}{k_{\rm B}T}\right) e^{-K/k_{\rm B}T} \right\} . \end{aligned}$$

(e) Find the mean field equations. `[5 points]`

Setting the variation of F with respect to m and n to zero, we find

$$m = \frac{\sinh\!\left(\frac{m T_\sigma + n T_\tau}{T}\right) e^{T_K/T} + \sinh\!\left(\frac{m T_\sigma - n T_\tau}{T}\right) e^{-T_K/T}}{\cosh\!\left(\frac{m T_\sigma + n T_\tau}{T}\right) e^{T_K/T} + \cosh\!\left(\frac{m T_\sigma - n T_\tau}{T}\right) e^{-T_K/T}}$$

and

$$n = \frac{\sinh\!\left(\frac{m T_\sigma + n T_\tau}{T}\right) e^{T_K/T} - \sinh\!\left(\frac{m T_\sigma - n T_\tau}{T}\right) e^{-T_K/T}}{\cosh\!\left(\frac{m T_\sigma + n T_\tau}{T}\right) e^{T_K/T} + \cosh\!\left(\frac{m T_\sigma - n T_\tau}{T}\right) e^{-T_K/T}} \ ,$$

where $k_{\rm B} T_\sigma \equiv \hat{J}^\sigma(0)$, $k_{\rm B} T_\tau \equiv \hat{J}^\tau(0)$, and $k_{\rm B} T_K \equiv K$.

(f) The mean field free energy has a Landau expansion of the form

$$f(m,n) = f_0 + \tfrac{1}{2} a_{\sigma\sigma}\, m^2 + \tfrac{1}{2}\, a_{\tau\tau} n^2 + a_{\sigma\tau}\, mn + \mathcal{O}\big(m^4, m^3 n, m^2 n^2, m n^3, n^4\big) \ .$$

Focusing only on the quadratic terms, find an equation for the temperature where the curvature of the free energy first changes sign as T is decreased from infinity. If there is no preempting first order transition, this gives you the critical temperature $T_{\rm c}$. *You will need to first find the coefficients* $a_{\sigma\sigma}$*,* $a_{\tau\tau}$*, and* $a_{\sigma\tau}$*.* `[10 points]`

Expanding $f = F/N$ in powers of m and n, we must go to work on the log, expanding the hyperbolic cosine terms each to fourth order in their arguments, and then using the power series for the logarithm itself. This is tedious, but you were only asked to go to the lowest nontrivial order, which isn't so difficult. Here I will show how to obtain the Landau coefficients up to fourth order. We have

$$f = k_{\rm B} T \,\ln\big[4\cosh(T_K/T)\big] + \tfrac{1}{2} k_{\rm B} T_\sigma m^2 + \tfrac{1}{2} k_{\rm B} T_\tau n^2 + \Delta f$$

where

$$\Delta f = -k_{\rm B} T \,\ln\left[\frac{\cosh\!\left(\frac{m T_\sigma + n T_\tau}{T}\right) e^{T_K/T} + \cosh\!\left(\frac{m T_\sigma - n T_\tau}{T}\right) e^{-T_K/T}}{2\cosh(T_K/T)}\right] .$$

Working on the log term,

$$\Delta f = -k_{\rm B}T\,\ln\Bigg[1 + \frac{m^2\,T_\sigma^2 + n^2\,T_\tau^2 + 2\,m\,n\,T_\sigma\,T_\tau\,\tanh\big(T_K/T\big)}{2\,T^2} + \frac{m^4\,T_\sigma^4 + 6\,m^2\,n^2\,T_\sigma^2\,T_\tau^2 + n^4\,T_\tau^4 + 4\,\big(m^2\,T_\sigma^2 + n^2\,T_\tau^2\big)\,m\,n\,T_\sigma\,T_\tau\,\tanh\big(T_K/T\big)}{24\,T^3} + \ldots\Bigg] \ .$$

To carry out the Landau expansion to quadratic order, as you were asked, one needs only the first nontrivial term inside the big brackets. To go to fourth order, however, we must invoke $\ln(1+\varepsilon) = \varepsilon - \frac{1}{2}\varepsilon^2 + \mathcal{O}(\varepsilon^3)$ and then combine the square of the second term and the third term inside the big brackets. The result to fourth order is

$$f = k_{\rm B}T\,\ln\big[4\cosh(T_K/T)\big] + \tfrac{1}{2}k_{\rm B}T_\sigma\bigg(1-\frac{T_\sigma}{T}\bigg)\,m^2 + \tfrac{1}{2}k_{\rm B}T_\tau\bigg(1-\frac{T_\tau}{T}\bigg)\,n^2 - \frac{k_{\rm B}\,T_\sigma\,T_\tau}{T}\,\tanh\big(T_K/T\big)\,m\,n + \frac{k_{\rm B}\,T_\sigma^4}{12\,T^3}\,m^4 + \frac{k_{\rm B}\,T_\tau^4}{12\,T^3}\,n^4 + \frac{k_{\rm B}\,T_\sigma^2\,T_\tau^2}{4\,T^3}\,\tanh^2\big(T_K/T\big)\,m^4 + \frac{k_{\rm B}\big(m^2\,T_\sigma^2 + n^2\,T_\tau^2\big)\,T_\sigma\,T_\tau\,m\,n}{3\,T^3}\,\tanh\big(T_K/T\big) + \ldots$$

At any rate, the coefficients of the quadratic form are

$$a_{\sigma\sigma} = k_{\rm B}T_\sigma\bigg(1-\frac{T_\sigma}{T}\bigg) \quad , \quad a_{\tau\tau} = k_{\rm B}T_\tau\bigg(1-\frac{T_\tau}{T}\bigg) \quad , \quad a_{\sigma\tau} = -\frac{k_{\rm B}\,T_\sigma\,T_\tau}{T}\,\tanh\big(T_K/T\big) \ .$$

If $K = 0$, the model decomposes into two independent Landau theories, with critical temperatures T_σ and T_τ, respectively. When $K \neq 0$, we need to find the eigenvalues of the matrix

$$M = \begin{pmatrix} a_{\sigma\sigma} & a_{\sigma\tau} \\ a_{\sigma\tau} & a_{\tau\tau} \end{pmatrix} \ ,$$

which are

$$\lambda_\pm = \tfrac{1}{2}\big(a_{\sigma\sigma} + a_{\tau\tau}\big) \pm \sqrt{\tfrac{1}{4}\big(a_{\sigma\sigma} - a_{\tau\tau}\big)^2 + a_{\sigma\tau}^2}$$

Setting the lower of the two eigenvalues to zero, we obtain the equation $a_{\sigma\sigma}\,a_{\tau\tau} = a_{\sigma\tau}^2$. This gives rise to the transcendental equation

$$T^2 - \big(T_\sigma + T_\tau\big)\,T + T_\sigma\,T_\tau\,{\rm sech}^2\big(T_K/T\big) = 0 \ ,$$

the solution of which is the critical temperature $T_{\rm c}$.

This is as far as you were asked to go. Proceeding further, let us adimensionalize by defining $\theta \equiv T/\sqrt{T_\sigma\,T_\tau}$, $\theta_K = T_K/\sqrt{T_\sigma\,T_\tau}$, and $\varepsilon \equiv \sqrt{T_\tau/T_\sigma}$. We may, without loss of generality, assume $0 \le \varepsilon \le 1$. We then have

$$\theta\,\big(\varepsilon + \varepsilon^{-1} - \theta\big) = {\rm sech}^2\big(\theta_K/\theta\big) \ .$$

In the top panel of Fig. 8.1 we plot the left hand side (LHS) of this equation in black and the right hand side in different colors corresponding to three different values of θ_K, all for $\varepsilon = 0.7$. Defining $D(\theta) \equiv \theta^2 - \big(\varepsilon + \varepsilon^{-1}\big)\theta + {\rm sech}^2\big(\theta_K/\theta\big)$, the determinant $\det(M)$ is proportional to $D(\theta)/\theta^2$. For high temperatures, $D(\theta) > 0$ and both eigenvalues $\lambda_\pm$ of M

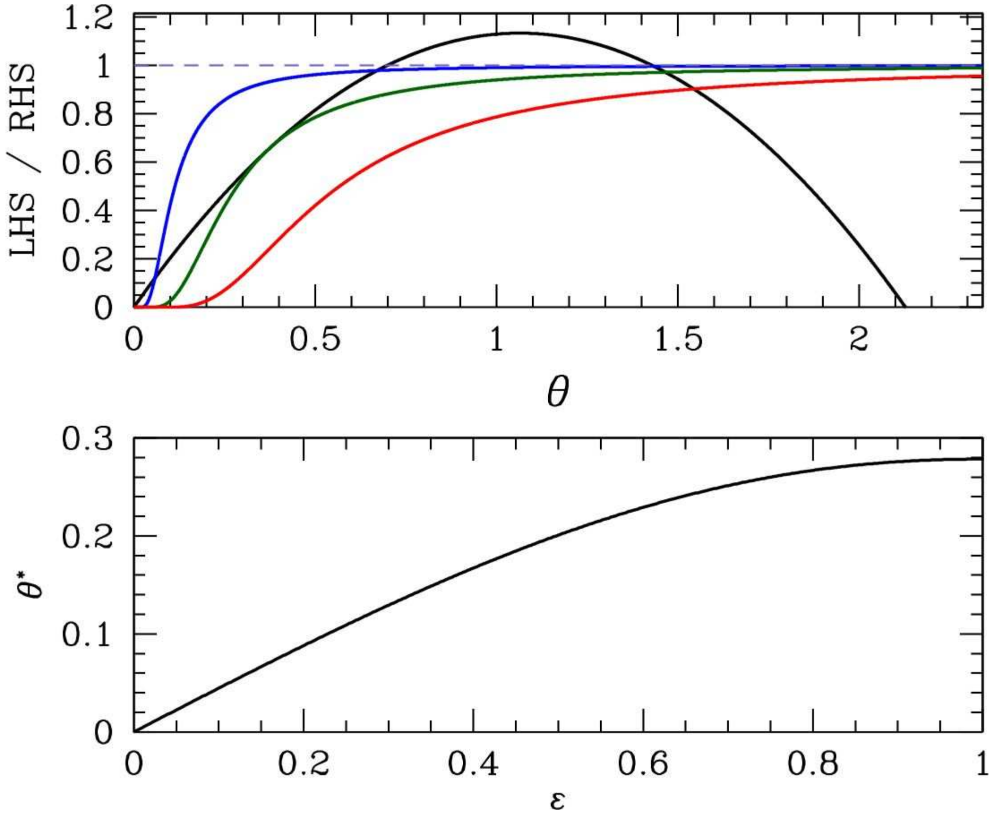

Figure 8.1: Top panel: Graphical solution to the transcendental equation from problem (1)(f) for $\varepsilon = 0.7$. Blue curve: $\theta_K = 0.1$; green curve: $\theta_K = \theta^*(\epsilon) = 0.2514$; red curve: $\theta_K = 0.5$. Bottom panel: Critical value of θ_K below which there are three solutions to $\det(M) = 0$.

are positive. What happens as we lower θ then depends on the value of θ_K. If $\theta_K > \theta^*(\varepsilon)$, then there is a single second order phase transition at the unique root of the equation $D(\theta) = 0$. As we pass through this temperature, the lower eigenvalue λ_- passes through zero and becomes negative. The low temperature phase exhibits a spontaneous moment, where both m and n are nonzero. As θ is further decreased toward $\theta = 0$, we still have $\lambda_- < 0 < \lambda_+$ and no additional transitions are encountered.

If $\theta_K < \theta^*(\varepsilon)$, then $D(\theta) = 0$ has three roots, $\theta_{\rm A} > \theta_{\rm B} > \theta_{\rm C}$. For $\theta > \theta_{\rm A}$, we have $0 < \lambda_- < \lambda_+$. For $\theta_{\rm B} < \theta < \theta_{\rm A}$, we have $\lambda_- < 0 < \lambda_+$. At $\theta = \theta_B$, the upper eigenvalue λ_+ changes sign, and for $\theta_{\rm C} < \theta < \theta_{\rm B}$, we have $\lambda_- < \lambda_+ < 0$, *i.e.* both eigenvalues are negative. Finally, at $\theta = \theta_{\rm C}$, the upper eigenvalue changes sign once again, and for $\theta < \theta_{\rm C}$, we have $\lambda_- < 0 < \lambda_+$ once more. Throughout the entire region $\theta < \theta_{\rm A}$ the system is ordered and there is a spontaneous moment in which both m and n are nonzero.

Despite the additional roots of $D(\theta) = 0$ when $\theta_K < \theta^*(\varepsilon)$, *there are no additional phase transitions*. It is worth emphasizing two things that are *not* happening here. The first thing is a spontaneous breaking of an additional symmetry. For $K \neq 0$, there is only one global symmetry in this problem, which is the $\mathbb{Z}_2$ Ising symmetry under which $\sigma_i \to -\sigma_i$ and $\tau_i \to -\tau_i$ for every spin. Many systems in Nature exhibit a cascade of symmetry breaking transitions. Not this one. As soon as the σ spins develop a spontaneous moment, this acts, through the K term, as an external field which immediately polarizes the τ spins, and there is no phase where $m \neq 0$ and $n = 0$ (and *vice versa*). The second thing which isn't happening is a reentrant transition. If the *lower* eigenvalue λ_- were to change sign at $\theta_{\rm B}$ and $\theta_{\rm C}$, as well as at $\theta_{\rm A}$, then throughout the range $\theta_{\rm C} < \theta < \theta_{\rm B}$ we would have both eigenvalues again positive, and the minimum of $f(m,n)$ would again lie at $m = n = 0$ as it does in the high temperature phase. As θ finally passed through $\theta_{\rm C}$, the moment would spontaneously reappear. The sign change of λ_+ at $\theta = \theta_{\rm B}$ however is inconsequential, since λ_- is negative and the minimum of $f(m,n)$ already lies away from the origin for $\theta < \theta_{\rm A}$.

(2) A three-dimensional gas of particles obeys the dispersion $\varepsilon(\boldsymbol{k}) = A\,k^{5/2}$. There are no internal degrees of freedom (*i.e.* the degeneracy factor is $\mathsf{g} = 1$). The number density is n. We will solve the problem for the more general dispersion $\varepsilon(k) = A\,k^\sigma$ and then indicate the result for $\sigma = \frac{5}{2}$.

(a) Compute the single particle density of states $g(\varepsilon)$. `[5 points]`

WIth $\varepsilon = A\,k^\sigma$ we have $k(\varepsilon) = (\varepsilon/A)^{1/\sigma}$, and

$$g(\varepsilon) = \frac{1}{2\pi^2}\,\frac{k^2}{\varepsilon'(k)}\bigg|_{k=k(\varepsilon)} = \frac{\varepsilon^{\frac{3}{\sigma}-1}}{2\pi^2\sigma A^{3/\sigma}} = \frac{\varepsilon^{1/5}}{5\pi^2 A^{6/5}}\ .$$

(b) For bosons, compute the condensation temperature $T_{\rm BEC}(n)$. `[5 points]`

The number density $n(T,z,n_0)$ for bosons, in the grand canonical ensemble, is

$$n(T,z,n_0) = \int\limits_0^\infty \! d\varepsilon\ \frac{g(\varepsilon)}{z^{-1}e^{\varepsilon/k_{\rm B}T} - 1} + n_0\ ,$$

where n_0 is the condensate density. For $T < T_{\rm BEC}$, we have $z = 1$ and $n_0 > 0$. For $T > T_{\rm BEC}$, we have $z < 1$ and $n_0 = 0$. Precisely at $T = T_{\rm BEC}$, both conditions apply: $z = 1$ and $n_0 = 0$. Thus,

$$n = \int\limits_0^\infty \! d\varepsilon\ \frac{g(\varepsilon)}{e^{\varepsilon/k_{\rm B}T_{\rm c}} - 1} = \frac{\Gamma\big(\frac{3}{\sigma}\big)\,\zeta\big(\frac{3}{\sigma}\big)}{2\pi^2\sigma}\left(\frac{k_{\rm B}T_{\rm c}}{A}\right)^{3/\sigma} = \frac{\Gamma\big(\frac{6}{5}\big)\,\zeta\big(\frac{6}{5}\big)}{5\pi^2}\left(\frac{k_{\rm B}T_{\rm c}}{A}\right)^{6/5}\ .$$

Thus,

$$T_{\rm BEC}(n) = \left(\frac{2\pi^2\sigma\,n}{\Gamma\big(\frac{3}{\sigma}\big)\,\zeta\big(\frac{3}{\sigma}\big)}\right)^{\sigma/3}\cdot\frac{A}{k_{\rm B}} = \left(\frac{5\pi^2 n}{\Gamma\big(\frac{6}{5}\big)\,\zeta\big(\frac{6}{5}\big)}\right)^{5/6}\cdot\frac{A}{k_{\rm B}}\ .$$

(c) For fermions, compute the ground state energy density $e_0(n)$. `[5 points]`

The ground state energy density for spinless (*i.e.* $\mathsf{g}=1$) fermions is

$$\varepsilon_0 = \frac{E_0}{V} = \int\!\frac{d^3\!k}{(2\pi)^3}\,A\,k^\sigma\,\Theta(k_{\rm F}-k) = \frac{A}{2\pi^2}\,\frac{k_{\rm F}^{3+\sigma}}{3+\sigma}\ .$$

The number density is

$$n = \frac{N}{V} = \int\!\frac{d^3\!k}{(2\pi)^3}\,\Theta(k_{\rm F}-k) = \frac{k_{\rm F}^3}{6\pi^2} \qquad \Longrightarrow \qquad k_{\rm F} = \big(6\pi^2 n\big)^{1/3}\ .$$

Thus,

$$\varepsilon_0(n) = \frac{(6\pi^2)^{\sigma/3}}{1+\frac{\sigma}{3}}\cdot A\,n^{1+\frac{\sigma}{3}} = \tfrac{6}{11}\,\big(6\pi^2\big)^{5/6}\cdot A\,n^{11/6}\ .$$

(d) For photon statistics, compute the temperature $T(n)$. `[5 points]`

The photon density is

$$n = \int\limits_0^\infty\! d\varepsilon\,\frac{g(\varepsilon)}{e^{\varepsilon/k_{\rm B}T}-1}\ ,$$

which is the same expression as in part (b) above! Thus,

$$T(n) = \left(\frac{2\pi^2\sigma\,n}{\Gamma\big(\frac{3}{\sigma}\big)\,\zeta\big(\frac{3}{\sigma}\big)}\right)^{\!\sigma/3}\cdot\frac{A}{k_{\rm B}} = \left(\frac{5\pi^2 n}{\Gamma\big(\frac{6}{5}\big)\,\zeta\big(\frac{6}{5}\big)}\right)^{\!5/6}\cdot\frac{A}{k_{\rm B}}\ .$$

(e) For photon statistics, compute the entropy density $s(n)=S/V$. `[5 points]`

The grand potential is

$$\Omega(T,V) = V k_{\rm B}T\int\limits_0^\infty\! d\varepsilon\;g(\varepsilon)\,\ln\!\big(1-e^{-\varepsilon/k_{\rm B}T}\big) = -V\!\int\limits_0^\infty\! d\varepsilon\,\frac{H(\varepsilon)}{e^{\varepsilon/k_{\rm B}T}-1}\ ,$$

where $g(\varepsilon)=H'(\varepsilon)$. Integrating $g(\varepsilon)$ to obtain $H(\varepsilon)$, we have

$$\Omega(T,V) = -\frac{V}{6\pi^2 A^{3/\sigma}}\int\limits_0^\infty\! d\varepsilon\,\frac{\varepsilon^{3/\sigma}}{e^{\varepsilon/k_{\rm B}T}-1} = -\frac{\Gamma\big(\frac{3}{\sigma}+1\big)\,\zeta\big(\frac{3}{\sigma}\big)}{6\pi^2 A^{3/\sigma}}\,V\big(k_{\rm B}T\big)^{1+\frac{3}{\sigma}}$$

The entropy density is then

$$s(T) = -\frac{1}{V}\,\frac{\partial\Omega}{\partial T} = \frac{\Gamma\big(\frac{3}{\sigma}+2\big)\,\zeta\big(\frac{3}{\sigma}+1\big)}{6\pi^2}\,\left(\frac{k_{\rm B}T}{A}\right)^{\!3/\sigma} k_{\rm B}\ ,$$

The number density, as we have seen, is

$$n(T) = \frac{\Gamma\big(\frac{3}{\sigma}\big)\,\zeta\big(\frac{3}{\sigma}\big)}{2\pi^2\sigma}\,\left(\frac{k_{\rm B}T}{A}\right)^{\!3/\sigma}\ ,$$

hence

$$s(n) = \frac{\zeta\big(\frac{3}{\sigma}+1\big)}{\zeta\big(\frac{3}{\sigma}\big)} \cdot \big(\tfrac{3}{\sigma}+1\big)\, n k_{\rm B} = \frac{\zeta\big(\frac{11}{5}\big)}{\zeta\big(\frac{6}{5}\big)} \cdot \tfrac{11}{5}\, n k_{\rm B} \ .$$

On dimensionful grounds, we knew *a priori* that $s(n) \propto n k_{\rm B}$.

(f) For bosons and fermions, compute the second virial coefficient $B_2(T)$. `[5 points]`

We have

$$\begin{aligned} n &= \int\limits_0^\infty \! d\varepsilon \, \frac{g(\varepsilon)}{z^{-1} e^{\varepsilon/k_{\rm B}T} - 1} = \pm \frac{\Gamma\big(\frac{3}{\sigma}\big)}{2\pi^2\sigma} \left(\frac{k_{\rm B}T}{A}\right)^{3/\sigma} \zeta_{\frac{3}{\sigma}}(\pm z) \\ \frac{p}{k_{\rm B}T} &= \int\limits_0^\infty \! d\varepsilon \, \frac{H(\varepsilon)}{z^{-1} e^{\varepsilon/k_{\rm B}T} - 1} = \pm \frac{\Gamma\big(\frac{3}{\sigma}\big)}{2\pi^2\sigma} \left(\frac{k_{\rm B}T}{A}\right)^{3/\sigma} \zeta_{\frac{3}{\sigma}+1}(\pm z) \ , \end{aligned}$$

where the top sign is for bosons and the bottom for fermions. It helps to define the thermal wavelength

$$\lambda_T \equiv \left(\frac{2\pi^2\sigma}{\Gamma\big(\frac{3}{\sigma}\big)}\right)^{1/3} \cdot \left(\frac{k_{\rm B}T}{A}\right)^{1/\sigma} = \left(\frac{5\pi^2}{\Gamma\big(\frac{6}{5}\big)}\right)^{1/3} \left(\frac{A}{k_{\rm B}T}\right)^{2/5} ,$$

so

$$\begin{aligned} n\lambda_T^3 &= \pm \zeta_{\frac{3}{\sigma}}(\pm z) = z \pm 2^{-3/\sigma} z^2 + \mathcal{O}(z^3) \\ \frac{p\lambda_T^3}{k_{\rm B}T} &= \pm \zeta_{\frac{3}{\sigma}+1}(\pm z) = z \pm 2^{-1-(3/\sigma)} z^2 + \mathcal{O}(z^3) \ . \end{aligned}$$

From the first of these, we have

$$z = n\lambda_T^3 \mp 2^{-3/\sigma} n^2 \lambda_T^6 + \mathcal{O}(n^3 \lambda_T^9) \ .$$

Substituting this into the second equation, we obtain the lowest nontrivial term in the virial expansion of the equation of state:

$$\frac{p}{k_{\rm B}T} = n \mp 2^{-1-(3/\sigma)}\, n^2 \lambda_T^3 + \mathcal{O}(n^3 \lambda_T^6) \ .$$

The second virial coefficient is then

$$B_2(T) = \mp 2^{-1-(3/\sigma)}\, \lambda_T^3 = \mp \frac{5\pi^2}{2^{11/5}\, \Gamma\big(\frac{6}{5}\big)} \left(\frac{A}{k_{\rm B}T}\right)^{6/5} .$$

(3) Provide clear, accurate, and brief answers for each of the following:

(a) For the free energy density $f = \frac{1}{2}am^2 - \frac{1}{3}ym^3 + \frac{1}{4}bm^4$, what does it mean to say that 'a first order transition preempts the second order transition'? `[5 points]`

In the absence of a cubic term (*i.e.* when $y = 0$), there is a second order transition at $a = 0$, assuming $b > 0$ for stability. The ordered phase, for $a < 0$, has a spontaneous moment

$m \neq 0$. When the cubic term is present, a *first order* (*i.e.* discontinuous) transition takes place at $a = \frac{2y^2}{9b}$, which is positive. Thus, as a is decreased from large positive values, the first order transition takes place before a reaches $a = 0$, hence we say that the second order transition that *would have* occurred at $a = 0$ is *preempted*. Typically we write $a \propto T - T_c$, where T_c is what the second order transition temperature would be in the case $y = 0$.

(b) A system of noninteracting bosons has a power law dispersion $\varepsilon(\boldsymbol{k}) = A\, k^\sigma$. What is the condition on the power σ and the dimension d of space such that Bose condensation will occur at some finite temperature? `[5 points]`

At $T = T_{\text{BEC}}$, we have the relation

$$n = \int \frac{d^d\!k}{(2\pi)^d}\, \frac{1}{e^{\varepsilon(\boldsymbol{k})/k_B T_{\text{BEC}}} - 1} \ .$$

If the integral fails to converge, then there is no finite temperature solution and no Bose condensation. For small k, we may expand the exponential in the denominator, and we find the occupancy function behaves as $k_B T_{\text{BEC}}/\varepsilon(\boldsymbol{k}) \propto k^{-\sigma}$. From the integration metric, in d-dimensional polar coordinates, we have $d^d\!k = \Omega_d\, k^{d-1}\, dk$, where Ω_d is the surface area of the d-dimensional unit sphere. Thus, the integrand is proportional to $k^{d-\sigma-1}$. For convergence, then, we require $d > \sigma$. This is the condition for finite temperature Bose condensation.

(c) Which has a longer Thomas-Fermi screening length: a metal with a high density of states at the Fermi level, or a metal with a low density of states? Explain why. `[5 points]`

A small electrical potential $\phi(\boldsymbol{r})$ will induce a local density change $\delta n(\boldsymbol{r}) = e\phi(\boldsymbol{r})\, g(\varepsilon_F)$ in a metal, where $g(\varepsilon_F)$ is the density of states at the Fermi energy. We assume $k_B T \ll \varepsilon_F$, which is very much the case for most metals at room temperature. Then from Poisson's equation we derive $\nabla^2\phi = 4\pi e\, \delta n = \lambda_{\text{TF}}^{-2}\, \phi$, where $\lambda_{\text{TF}} = 1/\sqrt{4\pi e^2 g(\varepsilon_F)}$ is the Thomas-Fermi screening length. Thus, high density of states is associated with a shorter screening length – there are more electrons present per unit volume to participate in screening. The metal with the lower density of states has the longer TF screening length.

(d) Sketch what the pair distribution function $g(r)$ should look like for a fluid composed of infinitely hard spheres of diameter a. How does $g(r)$ change with temperature? `[5 points]`

The PDF for a hard sphere gas is shown in Fig. 8.2 below. The main features are $g(r = 0)$ for $r < a$, and a decaying oscillation for $r > a$. Since the potential is either $U = 0$ (no two spheres overlapping), or $U = \infty$ (overlap of at least two spheres), temperature has no effect, because $U/k_B T$ is also either 0 or ∞. The hard sphere gas is a reasonable model for the physics of liquid Argon (see figure).

(e) For the cluster γ shown in Fig. 8.3, identify the symmetry factor s_γ, the lowest order virial coefficient B_j to which this contributes, and write an expression for the cluster integral $b_\gamma(T)$ in terms of the Mayer function. `[5 points]`

The symmetry factor is $2!\cdot 3! = 12$, because, consulting the right panel of Fig. 8.3, vertices

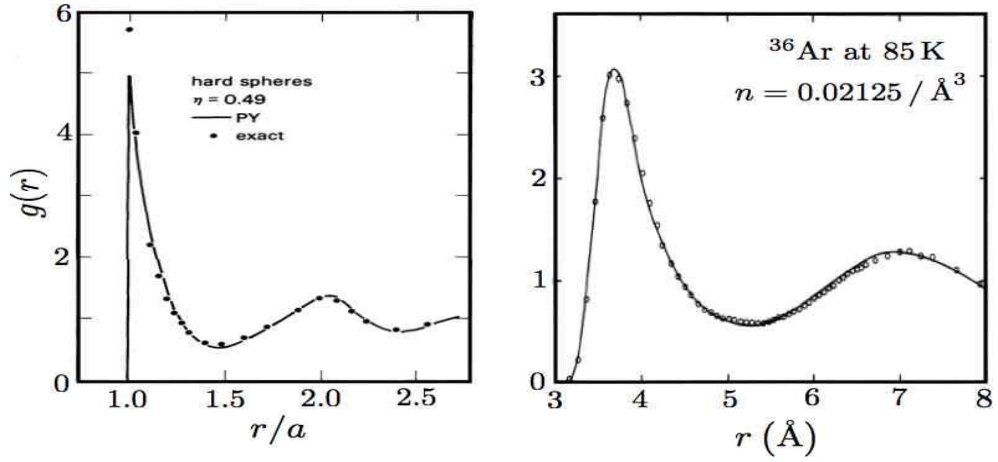

Figure 8.2: (3)(d) Pair distribution functions (PDF) for hard spheres of diameter a at filling fraction $\eta = \frac{\pi}{6}a^3 n = 0.49$ (left) and for liquid Argon at $T = 85\,\text{K}$ (right). Molecular dynamics data for hard spheres (points) is compared with the result of the Percus-Yevick approximation. Experimental data on liquid argon are from the neutron scattering work of Yarnell *et al.* (1973). The data (points) are compared with molecular dynamics calculations by Verlet (1967) for a Lennard-Jones fluid. See fig. 5.8 of the lecture notes.

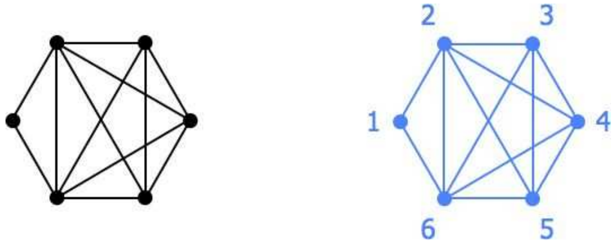

Figure 8.3: Left: the connected cluster γ for problem (3)(e). Right: a labeled version of this cluster used in expressing the cluster integral b_γ.

2 and 6 can be exchanged, and vertices 3, 4, and 5 can be permuted in any way. There are six vertices, hence the lowest order virial coefficient to which this cluster contributes is B_6. The cluster integral is

$$b_\gamma = \frac{1}{12\,V}\int\! d^dx_1 \!\int\! d^dx_2 \!\int\! d^dx_3 \!\int\! d^dx_4 \!\int\! d^dx_5 \!\int\! d^dx_6 \; f_{12}\, f_{16}\, f_{23}\, f_{24}\, f_{25}\, f_{26}\, f_{34}\, f_{35}\, f_{36}\, f_{45}\, f_{46}\, f_{56} \,,$$

where $f_{ij} = e^{-u(r_{ij})/k_B T} - 1$. See Fig. 8.3 for the labels. Whee!

(f) Explain the following terms in the context of dynamical systems: *recurrent*, *ergodic*, and *mixing*. How are these classifications arranged hierarchically? `[5 points]`

A recurrent dynamical system exhibits the property that within any finite region of phase space one can find a point which will return to that region in a finite time. Poincaré recurrence is guaranteed whenever the dynamics are invertible and volume-preserving on a finite phase space. An ergodic system is one where time averages are equal to phase space averages. For the dynamical system $\dot{\boldsymbol{\varphi}} = \boldsymbol{V}(\boldsymbol{\varphi})$, ergodicity means

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

where $f(\boldsymbol{\varphi})$ is any smooth function on phase space. A mixing system is one where any smooth normalized distribution $\varrho(\boldsymbol{\varphi},t)$ satisfies

$$\lim_{t\to\infty} \mathsf{Tr}\, \varrho(\boldsymbol{\varphi},t)\, f(\boldsymbol{\varphi}) = \big\langle f(\boldsymbol{\varphi})\big\rangle_S \,.$$

Thus, the distribution spreads out 'evenly' over the entire energy surface. The hierarchy is

$$\text{mixing} \subset \text{ergodic} \subset \text{recurrent} \,.$$

(g) What is the significance of the Ginzburg criterion? `[5 points]`

The Ginzburg criterion tells how close we can come to a second order phase transition before fluctuation effects start to overwhelm the mean field contribution to the heat capacity. The criterion for the sufficiency of mean field theory is $|t| \gg t_{\mathrm{G}}$, where $t = (T-T_{\mathrm{c}})/T_{\mathrm{c}}$ is the reduced temperature and $t_{\mathrm{G}} = \big(\mathsf{a}/R_*\big)^{\frac{2d}{4-d}}$, where a is the lattice spacing and R_* is a length scale set by the interactions. For most magnetic transitions, R_* is on the order of the lattice spacing, $t_{\mathrm{G}} \sim 1$, and mean field theory breaks down rapidly. For most superconductors, R_* is on the order of the coherence length, which is large on the scale of the lattice spacing, and $t_{\mathrm{G}} \sim 10^{-18} - 10^{-12}$, and mean field exponents are quantitatively accurate essentially all the way up to the transition.

Some useful formulas:

$$\zeta_\alpha(z) = \sum_{k=1}^\infty \frac{z^k}{k^\alpha}$$

$$\int\limits_0^\infty\! d\varepsilon\; \frac{\varepsilon^{\alpha-1}}{z^{-1}e^{\beta\varepsilon}-1} = \Gamma(\alpha)\,\zeta_\alpha(z)\,(k_{\mathrm{B}}T)^\alpha$$

$$\ln(1+x) = x - \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 - \tfrac{1}{4}x^4 + \ldots$$

$$\cosh(x) = 1 + \tfrac{1}{2!}x^2 + \tfrac{1}{4!}x^4 + \ldots$$