Physics 210A, Spring 2012 : Homework Problems and Solutions

Daniel Arovas
Department of Physics
University of California, San Diego

September 13, 2012

Solution Set #1

(1) Consider a system with K possible states $|\,i\,\rangle$, with $i \in \{1, \ldots, K\}$, where the transition rate W_{ij} between any two states is the same, with $W_{ij} = \gamma > 0$.

   (a) Find the matrix Γ_{ij} governing the master equation $\dot{P}_i = -\Gamma_{ij}\, P_j$.

   (b) Find all the eigenvalues and eigenvectors of Γ. What is the equilibrium distribution?

   (c) Now suppose there are $2K$ possible states $|\,i\,\rangle$, with $i \in \{1, \ldots, 2K\}$, and the transition rate matrix is
$$W_{ij} = \begin{cases} \alpha & \text{if} \quad (-1)^{ij} = +1 \\ \beta & \text{if} \quad (-1)^{ij} = -1 \,, \end{cases}$$
with $\alpha, \beta > 0$. Repeat parts (a) and (b) for this system.

Solution :

(a) We have, from Eq. 3.3 of the Lecture Notes,
$$\Gamma_{ij} = \begin{cases} -W_{ij} = -\gamma & \text{if } i \neq j \\ \sum'_k W_{kj} = (K-1)\gamma & \text{if } i = j \,. \end{cases}$$

I.e. Γ is a symmetric $K \times K$ matrix with all off-diagonal entries $-\gamma$ and all diagonal entries $(K-1)\gamma$.

(b) It is convenient to define the unit vector $\vec{\psi} = K^{-1/2}(1, 1, \ldots, 1)$. Then
$$\Gamma = K\gamma \left(\mathbb{I} - |\,\psi\,\rangle\langle\,\psi\,| \right).$$

We now see that $|\,\psi\,\rangle$ is an eigenvector of Γ with eigenvalue $\lambda = 0$, and furthermore that any vector orthogonal to $|\,\psi\,\rangle$ is an eigenvector of Γ with eigenvalue $K\gamma$. This means that there is a degenerate $(K-1)$-dimensional subspace associated with the eigenvalue $K\gamma$. The equilibrium distribution is given by $|\,P^{\text{eq}}\,\rangle = K^{-1/2}|\,\psi\,\rangle$, i.e. $P_i^{\text{eq}} = \frac{1}{K}$.

(c) Define the unit vectors
$$\vec{\psi}_{\mathsf{E}} = \tfrac{1}{\sqrt{K}}\,(0, 1, 0, \ldots, 1)$$
$$\vec{\psi}_{\mathsf{O}} = \tfrac{1}{\sqrt{K}}\,(1, 0, 1, \ldots, 0)\,.$$

Note that $\langle\,\psi_{\mathsf{E}}\,|\,\psi_{\mathsf{O}}\,\rangle=0$. Furthermore, we may write Γ as

$$\Gamma=\tfrac{1}{2}K(3\alpha+\beta)\,\mathbb{I}+\tfrac{1}{2}K(\alpha-\beta)\,\mathbb{J}-K\alpha\left(|\,\psi_{\mathsf{E}}\,\rangle\langle\,\psi_{\mathsf{E}}\,|+|\,\psi_{\mathsf{O}}\,\rangle\langle\,\psi_{\mathsf{E}}\,|+|\,\psi_{\mathsf{E}}\,\rangle\langle\,\psi_{\mathsf{O}}\,|\right)-K\beta\,|\,\psi_{\mathsf{O}}\,\rangle\langle\,\psi_{\mathsf{O}}\,|$$

where $\mathbb{I}$ is the identity matrix and $\mathbb{J}_{nn'}=(-1)^{n}\,\delta_{nn'}$ is a diagonal matrix with alternating -1 and $+1$ entries. Note that $\mathbb{J}\,|\,\psi_{\mathsf{O}}\,\rangle=-|\,\psi_{\mathsf{O}}\,\rangle$ and $\mathbb{J}\,|\,\psi_{\mathsf{E}}\,\rangle=+|\,\psi_{\mathsf{E}}\,\rangle$. The key to deriving the above relation is to notice that

$$\mathbb{M}=K\alpha\left(|\,\psi_{\mathsf{E}}\,\rangle\langle\,\psi_{\mathsf{E}}\,|+|\,\psi_{\mathsf{O}}\,\rangle\langle\,\psi_{\mathsf{E}}\,|+|\,\psi_{\mathsf{E}}\,\rangle\langle\,\psi_{\mathsf{O}}\,|\right)+K\beta\,|\,\psi_{\mathsf{O}}\,\rangle\langle\,\psi_{\mathsf{O}}\,|$$

$$=\begin{pmatrix}\beta&\alpha&\beta&\alpha&\cdots&\beta&\alpha\\\alpha&\alpha&\alpha&\alpha&\cdots&\alpha&\alpha\\\beta&\alpha&\beta&\alpha&\cdots&\beta&\alpha\\\alpha&\alpha&\alpha&\alpha&\cdots&\alpha&\alpha\\\vdots&\vdots&\vdots&\vdots&\ddots&\vdots&\vdots\\\beta&\alpha&\beta&\alpha&\cdots&\beta&\alpha\\\alpha&\alpha&\alpha&\alpha&\cdots&\alpha&\alpha\end{pmatrix}.$$

Now $\mathbb{J}$ has K eigenvalues $+1$ and K eigenvalues -1. There is therefore a $(K-1)$-dimensional degenerate eigenspace of Γ with eigenvalue $2K\alpha$ and a $(K-1)$-dimensional degenerate subspace with eigenvalue $K(\alpha+\beta)$. These subspaces are mutually orthogonal as well as being orthogonal to the vectors $|\,\psi_{\mathsf{E}}\,\rangle$ and $|\,\psi_{\mathsf{O}}\,\rangle$. The remaining two-dimensional subspace spanned by these vectors yields the reduced matrix

$$\Gamma_{\mathrm{red}}=\begin{pmatrix}\langle\,\psi_{\mathsf{E}}\,|\,\Gamma\,|\,\psi_{\mathsf{E}}\,\rangle&\langle\,\psi_{\mathsf{E}}\,|\,\Gamma\,|\,\psi_{\mathsf{O}}\,\rangle\\\langle\,\psi_{\mathsf{O}}\,|\,\Gamma\,|\,\psi_{\mathsf{E}}\,\rangle&\langle\,\psi_{\mathsf{O}}\,|\,\Gamma\,|\,\psi_{\mathsf{O}}\,\rangle\end{pmatrix}=\begin{pmatrix}K\alpha&-K\alpha\\-K\alpha&K\alpha\end{pmatrix}.$$

The eigenvalues in this subspace are therefore 0 and $2K\alpha$. Thus, Γ has the following eigenvalues:

$$\begin{aligned}\lambda&=0 &&\text{(nondegenerate)}\\\lambda&=K(\alpha+\beta) &&\text{(degeneracy }K-1)\\\lambda&=2K\alpha &&\text{(degeneracy }K)\,.\end{aligned}$$

(2) A six-sided die is loaded so that the probability to throw a six is twice that of throwing a one. Find the distribution $\{p_n\}$ consistent with maximum entropy, given this constraint.

Solution :

The constraint may be written as $2p_1-p_6=0$. Thus, $X_n^1=2\delta_{n,1}-\delta_{n,6}$, and

$$p_n=\begin{cases}C\,e^{-2\lambda}&\text{if }n=1\\C&\text{if }n\in\{2,3,4,5\}\\C\,e^{\lambda}&\text{if }n=6\,.\end{cases}$$

We solve for the unknowns C and λ by enforcing the constraints:

$$C e^{-2\lambda} + 4C + C e^{\lambda} = 1$$
$$2C e^{-2\lambda} - C e^{\lambda} = 0 \, .$$

The second equation gives $e^{3\lambda} = 2$, or $\lambda = \frac{1}{3} \ln 2$. Plugging this in the normalization condition, we have

$$C = \frac{1}{4 + 2^{1/3} + 2^{-2/3}} = 0.16798\ldots \, .$$

We then have

$$p_1 = C e^{-2\lambda} = 0.10695\ldots$$
$$p_2 = p_3 = p_4 = p_5 = C = 0.16798\ldots$$
$$p_6 = C e^{\lambda} = 0.21391\ldots \, .$$

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

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

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

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

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

Solution :

(a) Following the prescription in Eq. 3.3 of the Lecture Notes, we have

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

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

$$P^{\mathrm{eq}} = \begin{pmatrix} 0.3 \\ 0.1 \\ 0.6 \end{pmatrix} \, .$$

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

(4) The cumulative grade distributions of six 'old school' (no + or - distinctions) professors from various fields are given in the table below. For each case, compute the entropy of the grade distribution.

Solution :

We compute the probabilities p_n for $n \in \{A, B, C, D, F\}$ and then the statistical entropy of the distribution, $S = -\sum_n p_n \log_2 p_n$ in units of bits. The results are shown in the amended table below. The maximum possible entropy is $S = \log_2 5 \approx 2.3219$.

Professor	A	B	C	D	F	N
	p_A	p_B	p_C	p_D	p_F	S
Landau	1149	2192	1545	718	121	5725
	0.2007	0.3829	0.2699	0.1254	0.0211	1.999
Vermeer	8310	1141	231	56	7	9745
	0.8527	0.1171	0.0237	0.0057	0.0007	0.7365
Keynes	3310	4141	3446	1032	642	12571
	0.2633	0.3294	0.2741	0.0821	0.0511	2.062
Noether	1263	1874	988	355	290	4770
	0.2648	0.3929	0.2071	0.0744	0.0608	2.032
Borges	4002	2121	745	109	57	7034
	0.5690	0.3015	0.1059	0.0155	0.0081	1.477
Salk	3318	3875	2921	1011	404	11529
	0.2878	0.3361	0.2534	0.0877	0.0350	2.025
Turing	2800	3199	2977	1209	562	10747
	0.2605	0.2977	0.2770	0.1125	0.0523	2.116

(5) A generalized two-dimensional cat map can be defined by

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \overbrace{\begin{pmatrix} 1 & p \\ q & pq+1 \end{pmatrix}}^{M} \begin{pmatrix} x \\ y \end{pmatrix} \bmod \mathbb{Z}^2 \ ,$$

where p and q are integers. Here $x, y \in [0, 1]$ are two real numbers on the unit interval, so $(x, y) \in \mathbb{T}^2$ lives on a two-dimensional torus. The inverse map is

$$M^{-1} = \begin{pmatrix} pq+1 & -p \\ -q & q \end{pmatrix} \ .$$

Note that det $M = 1$.

(a) Consider the action of this map on a pixelated image of size $(lK) \times (lK)$, where $l \sim 4 - 10$ and $K \sim 20 - 100$. Starting with an initial state in which all the pixels in the left half of the array are "on" and the others are all "off", iterate the image with the generalized cat map, and compute at each state the entropy $S = -\sum_r p_r \ln p_r$, where the sum is over the K^2 different $l \times l$ subblocks, and p_r is the probability to find an "on" pixel in subblock r. (Take $p = q = 1$ for convenience, though you might want to explore other values).

Now consider a three-dimensional generalization (Chen *et al.*, *Chaos, Solitons, and Fractals* **21**, 749 (2004)), with

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = M \begin{pmatrix} x \\ y \\ z \end{pmatrix} \mod \mathbb{Z}^3 \,,$$

which is a discrete automorphism of $\mathbb{T}^3$, the three-dimensional torus. Again, we require that both M and M^{-1} have integer coefficients. This can be guaranteed by writing

$$M_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & p_x \\ 0 & q_x & p_x q_x + 1 \end{pmatrix} \quad , \quad M_y = \begin{pmatrix} 1 & 0 & p_y \\ 0 & 1 & 0 \\ q_y & 0 & p_y q_y + 1 \end{pmatrix} \quad , \quad M_z = \begin{pmatrix} 1 & p_z & 0 \\ q_z & p_z q_z + 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and taking $M = M_x M_y M_z$, reminiscent of how we build a general $O(3)$ rotation from a product of three $O(2)$ rotations about different axes.

(b) Find M and M^{-1} when $p_x = q_x = p_y = q_y = p_z = q_z = 1$.

(c) Repeat part (a) for this three-dimensional generalized cat map, computing the entropy by summing over the K^3 different $l \times l \times l$ subblocks.

(d) 100 quatloos extra credit if you find a way to show how a three dimensional object (a ball, say) evolves under this map. Is it Poincaré recurrent?

Solution :

(a) See Figs. 7.3 and 7.2.

(b) We have

$$M_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & 2 \end{pmatrix} \quad , \quad M_x^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 2 & -1 \\ 0 & -1 & 1 \end{pmatrix} \,.$$

$$M_y = \begin{pmatrix} 1 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 2 \end{pmatrix} \quad , \quad M_y^{-1} = \begin{pmatrix} 2 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix}$$

$$M_z = \begin{pmatrix} 1 & 1 & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad , \quad M_z^{-1} = \begin{pmatrix} 2 & -1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
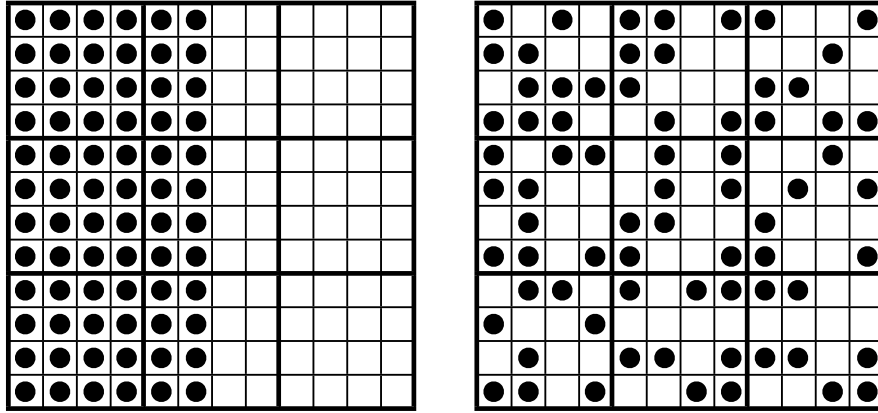
Figure 1: Two-dimensional cat map on a 12×12 square array with $l = 4$ and $K = 3$ shown. Left: initial conditions at $t = 0$. Right: possible conditions at some later time $t > 0$. Within each $l \times l$ cell $\boldsymbol{r}$, the occupation probability $p_{\boldsymbol{r}}$ is computed. The entropy $-p_{\boldsymbol{r}} \log_2 p_{\boldsymbol{r}}$ is then averaged over the K^2 cells.

Thus,

$$M = M_x M_y M_z = \begin{pmatrix} 1 & 1 & 1 \\ 2 & 3 & 2 \\ 3 & 4 & 4 \end{pmatrix}$$

$$M^{-1} = M_z^{-1} M_y^{-1} M_x^{-1} = \begin{pmatrix} 4 & 0 & -1 \\ -2 & 1 & 0 \\ -1 & -1 & 1 \end{pmatrix} .$$

Note that det $M = 1$.

Figure 2: Coarse-grained entropy per unit volume for the iterated two-dimensional cat map ($p = q = 1$) on a 200×200 pixelated torus, with $l = 4$ and $K = 50$. Bottom panel: coarse-grained entropy per unit volume *versus* iteration number. Top panel: power spectrum of entropy *versus* frequency bin. A total of $2^{14} = 16384$ iterations were used.
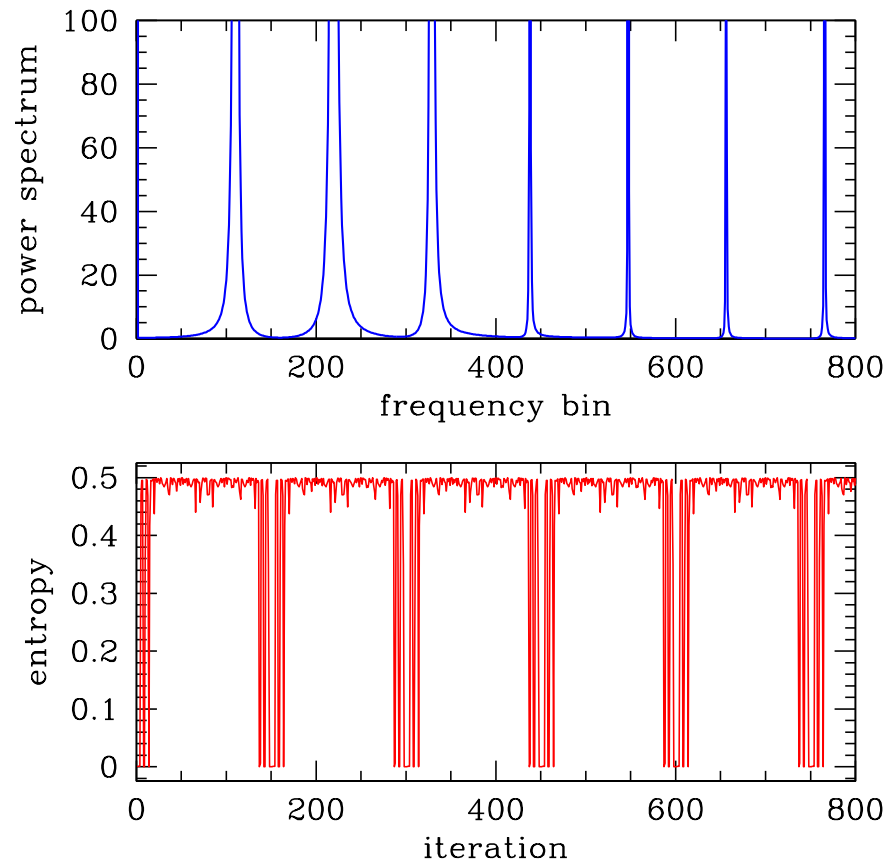
Figure 3: Coarse-grained entropy per unit volume for the iterated two-dimensional cat map ($p = q = 1$) on a 200×200 pixelated torus, with $l = 10$ and $K = 20$. Bottom panel: coarse-grained entropy per unit volume *versus* iteration number. Top panel: power spectrum of entropy *versus* frequency bin. A total of $2^{14} = 16384$ iterations were used.
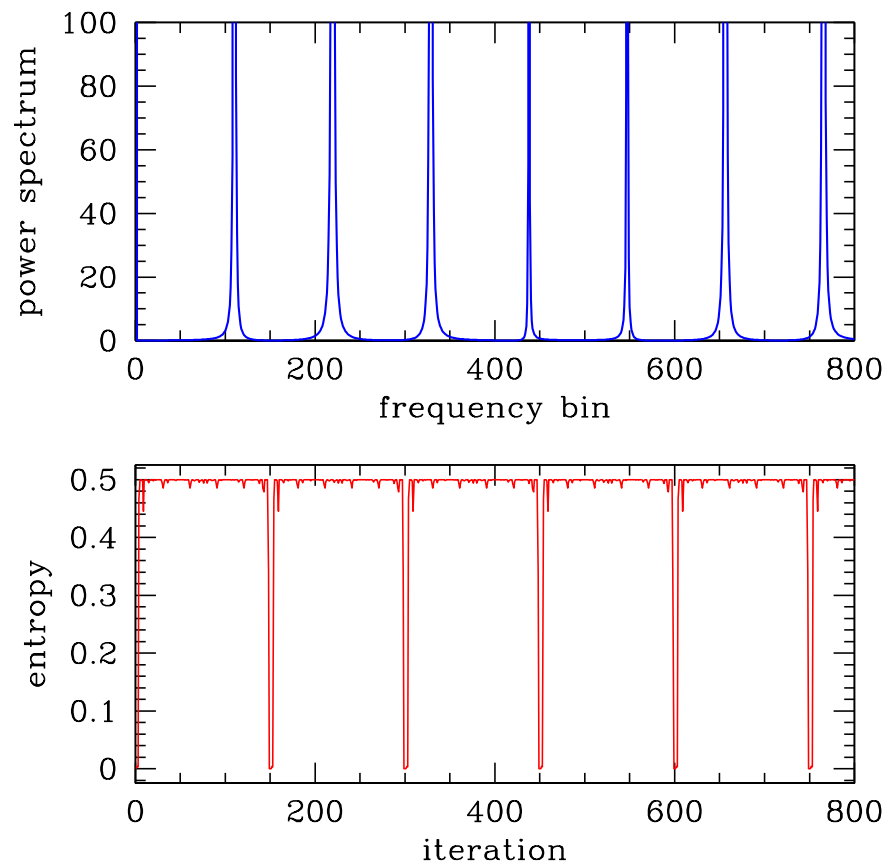
Figure 4: Coarse-grained entropy per unit volume for the iterated three-dimensional cat map ($p_x = q_x = p_y = q_y = p_z = q_z = 1$) on a $40 \times 40 \times 40$ pixelated three-dimensional torus, with $l = 4$ and $K = 10$. Bottom panel: coarse-grained entropy per unit volume *versus* iteration number. Top panel: power spectrum of entropy *versus* frequency bin. A total of $2^{14} = 16384$ iterations were used.
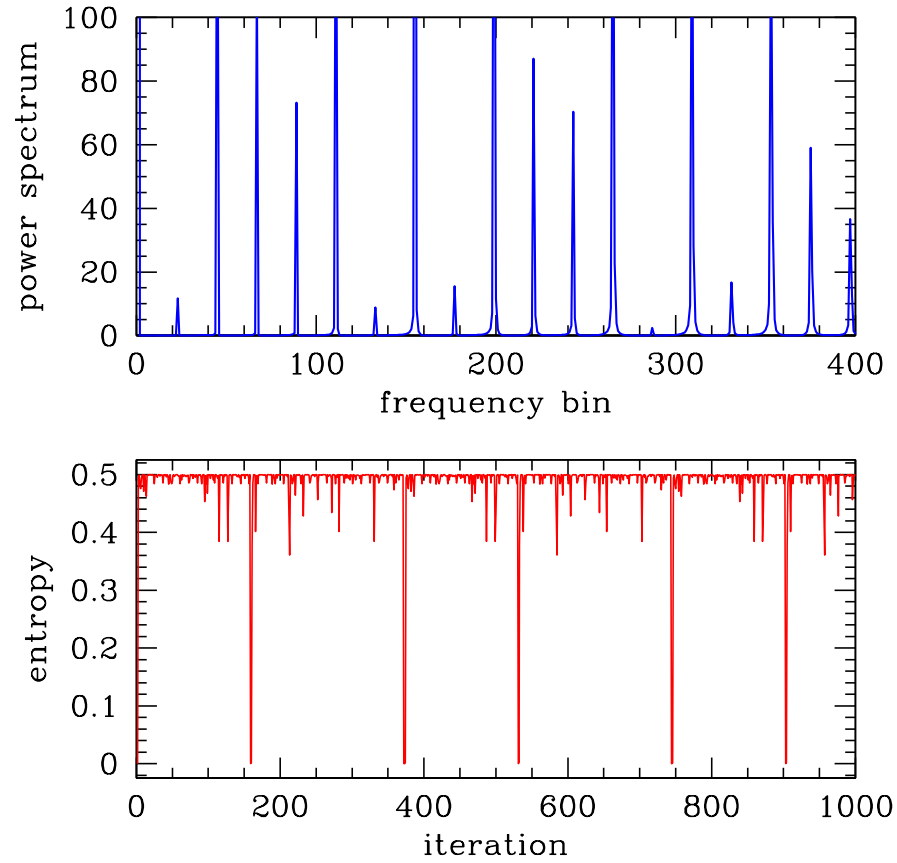
Solution Set #2

(1) Compute the density of states $D(E, V, N)$ for a three-dimensional gas of particles with Hamiltonian $\hat{H} = \sum_{i=1}^{N} A |\boldsymbol{p}_i|^4$, where A is a constant. Find the entropy $S(E, V, N)$, the Helmholtz free energy $F(T, V, N)$, and the chemical potential $\mu(T, p)$.

Solution :

Let's solve the problem for a general dispersion $\varepsilon(\boldsymbol{p}) = A|\boldsymbol{p}|^\alpha$. The density of states is

$$D(E, V, N) = \frac{V^N}{N!} \int \frac{d^d p_1}{h^d} \cdots \int \frac{d^d p_N}{h^d} \, \delta\big(E - A p_1^\alpha - \ldots - A p_N^\alpha\big) .$$

The Laplace transform is

$$
\begin{aligned}
\widehat{D}(\beta, V, N) &= \frac{V^N}{N!} \left(\int \frac{d^d p}{h^d} \, e^{-\beta A p^\alpha} \right)^N \\
&= \frac{V^N}{N!} \left(\frac{\Omega_d}{h^d} \int_0^\infty dp \, p^{d-1} \, e^{-\beta A p^\alpha} \right)^N \\
&= \frac{V^N}{N!} \left(\frac{\Omega_d \, \Gamma(d/\alpha)}{\alpha h^d A^{d/\alpha}} \right)^N \beta^{-Nd/\alpha} .
\end{aligned}
$$

Now we inverse transform, recalling

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

We then conclude

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

and

$$
\begin{aligned}
S(E, V, N) &= k_{\mathrm{B}} \ln D(E, V, N) \\
&= N k_{\mathrm{B}} \ln\left(\frac{V}{N} \right) + \frac{d}{\alpha} N k_{\mathrm{B}} \, \ln\left(\frac{E}{N} \right) + N k_{\mathrm{B}} a_0 ,
\end{aligned}
$$

11

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

$$dS = \frac{N k_{\mathrm{B}}}{V} \, dV + \frac{d}{\alpha} \frac{N k_{\mathrm{B}}}{E} \, dE + s_0 \, dN$$

$$= \frac{p}{T} \, dV + \frac{1}{T} \, dE - \frac{\mu}{T} \, dN \ ,$$

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

$$pV = N k_{\mathrm{B}} T$$

$$E = \frac{d}{\alpha} \, N k_{\mathrm{B}} T \ .$$

Note that we have replaced $E = \frac{d}{\alpha} N k_{\mathrm{B}} T$ in order to express F in terms of its 'natural variables' T, V, and N.

The Helmholtz free energy is

$$F = E - TS = E - N k_{\mathrm{B}} T \ln\left(\frac{V}{N}\right) - \frac{d}{\alpha} N k_{\mathrm{B}} T \ln\left(\frac{E}{N}\right) - N k_{\mathrm{B}} T a_0$$

$$= \frac{d}{\alpha} \, N k_{\mathrm{B}} T - \frac{d}{\alpha} N k_{\mathrm{B}} T \ln\left(\frac{d}{\alpha} k_{\mathrm{B}} T\right) - N k_{\mathrm{B}} T \ln\left(\frac{V}{N}\right) - N k_{\mathrm{B}} T a_0 \ .$$

The chemical potential is

$$\mu = T \left(\frac{\partial F}{\partial N}\right)_{T,V} = -\frac{d}{\alpha} k_{\mathrm{B}} T \ln\left(\frac{d}{\alpha} k_{\mathrm{B}} T\right) + \frac{d}{\alpha} k_{\mathrm{B}} T - k_{\mathrm{B}} T \ln\left(\frac{V}{N}\right) + (1 - a_0) \, k_{\mathrm{B}} T$$

$$= -\frac{d}{\alpha} k_{\mathrm{B}} T \ln\left(\frac{d}{\alpha} k_{\mathrm{B}} T\right) + \frac{d}{\alpha} k_{\mathrm{B}} T - k_{\mathrm{B}} T \ln\left(\frac{k_{\mathrm{B}} T}{p}\right) + (1 - a_0) \, k_{\mathrm{B}} T \ .$$

Suppose we wanted the heat capacities C_V and C_p. Setting $dN = 0$, we have

$$đQ = dE + p \, dV$$

$$= \frac{d}{\alpha} \, N k_{\mathrm{B}} \, dT + p \, dV$$

$$= \frac{d}{\alpha} \, N k_{\mathrm{B}} \, dT + p \, d\left(\frac{N k_{\mathrm{B}} T}{p}\right) \ .$$

Thus,

$$C_V = \frac{đQ}{dT}\bigg|_V = \frac{d}{\alpha} \, N k_{\mathrm{B}} \quad , \quad C_p = \frac{đQ}{dT}\bigg|_p = \left(1 + \frac{d}{\alpha}\right) N k_{\mathrm{B}} \ .$$

(2) Consider a gas of classical spin-$\frac{3}{2}$ particles, with Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} - \mu_0 H \sum_i S_i^z \ ,$$

where $S_i^z \in \left\{ -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2} \right\}$ and H is the external magnetic field. Find the Helmholtz free energy $F(T, V, H, N)$, the entropy $S(T, V, H, N)$, and the magnetic susceptibility $\chi(T, H, n)$, where $n = N/V$ is the number density.

Solution :

The partition function is

$$Z = \mathsf{Tr}\ e^{-\hat{H}/k_{\mathrm{B}}T} = \frac{1}{N!} \frac{V^N}{\lambda_T^{dN}} \Big(2 \cosh(\mu_0 H/2k_{\mathrm{B}}T) + 2 \cosh(3\mu_0 H/2k_{\mathrm{B}}T) \Big)^N ,$$

so

$$F = -Nk_{\mathrm{B}}T \ln\left(\frac{V}{N\lambda_T^d} \right) - Nk_{\mathrm{B}}T - Nk_{\mathrm{B}}T \ln\Big(2 \cosh(\mu_0 H/2k_{\mathrm{B}}T) + 2 \cosh(3\mu_0 H/2k_{\mathrm{B}}T) \Big) ,$$

where $\lambda_T = \sqrt{2\pi\hbar^2/mk_{\mathrm{B}}T}$ is the thermal wavelength. The entropy is

$$S = -\left(\frac{\partial F}{\partial T} \right)_{V,N,H} = Nk_{\mathrm{B}} \ln\left(\frac{V}{N\lambda_T^d} \right) + (\tfrac{1}{2}d+1)Nk_{\mathrm{B}} + N \ln\Big(2 \cosh(\mu_0 H/2k_{\mathrm{B}}T) + 2 \cosh(3\mu_0 H/2k_{\mathrm{B}}T) \Big)$$
$$- \frac{\mu_0 H}{2T} \cdot \frac{\sinh(\mu_0 H/2k_{\mathrm{B}}T) + 3 \sinh(3\mu_0 H/2k_{\mathrm{B}}T)}{\cosh(\mu_0 H/2k_{\mathrm{B}}T) + \cosh(3\mu_0 H/2k_{\mathrm{B}}T)} .$$

The magnetization is

$$M = -\left(\frac{\partial F}{\partial H} \right)_{T,V,N} = \tfrac{1}{2}N\mu_0 \cdot \frac{\sinh(\mu_0 H/2k_{\mathrm{B}}T) + 3 \sinh(3\mu_0 H/2k_{\mathrm{B}}T)}{\cosh(\mu_0 H/2k_{\mathrm{B}}T) + \cosh(3\mu_0 H/2k_{\mathrm{B}}T)} .$$

The magnetic susceptibility is

$$\chi(T, H, n) = \frac{1}{V} \left(\frac{\partial M}{\partial H} \right)_{T,V,N} = \frac{n\mu_0^2}{4k_{\mathrm{B}}T} f(\mu_0 H/2k_{\mathrm{B}}T)$$

where

$$f(x) = \frac{d}{dx} \left(\frac{\sinh x + 3 \sinh(3x)}{\cosh x + \cosh(3x)} \right) .$$

In the limit $H \to 0$, we have $f(0) = 5$, so $\chi = 4n\mu_0^2/4k_{\mathrm{B}}T$ at high temperatures. This is a version of Curie's law.

(3) Compute the RMS volume fluctuations in the $T - p - N$ ensemble.

Solution :

Averages within the $T - p - N$ ensemble are computed by

$$\langle A \rangle = \frac{\mathsf{Tr}\ A\, e^{-\beta(\hat{H}+pV)}}{\mathsf{Tr}\ e^{-\beta(\hat{H}+pV)}} .$$

Let $Y = \text{Tr } ^{-\beta(\hat{H}+pV)} = e^{-\beta G}$. Then

$$\langle V^2 \rangle = \frac{1}{\beta^2 Y} \frac{\partial^2 Y}{\partial p^2} = \beta^{-2} e^{\beta G} \frac{\partial^2}{\partial p^2} e^{-\beta G}$$

$$= -\frac{1}{\beta} \frac{\partial^2 G}{\partial p^2} + \left(\frac{\partial G}{\partial p}\right)^2 ,$$

and since $\frac{\partial G}{\partial p} = V$, we have

$$\langle V^2 \rangle - \langle V \rangle^2 = -k_{\mathrm{B}} T \frac{\partial^2 G}{\partial p^2} .$$

For the case of a nonrelativistic ideal gas, we have

$$\langle V^k \rangle = \int\limits_0^\infty dV\, e^{-\beta p V}\, Z(T,V,N)\, V^k \Bigg/ \int\limits_0^\infty dV\, e^{-\beta p V}\, Z(T,V,N)$$

$$= \int\limits_0^\infty dV\, e^{-\beta p V}\, V^{N+k} \Bigg/ \int\limits_0^\infty dV\, e^{-\beta p V}\, V^N = \frac{(N+k)!}{N!} \left(\frac{k_{\mathrm{B}} T}{p}\right)^k ,$$

since $Z(T,V,N) = \frac{1}{N!}(V/\lambda_T)^N$. Thus,

$$\langle V \rangle = (N+1) \frac{k_{\mathrm{B}} T}{p} \qquad , \qquad \langle V^2 \rangle = (N+1)(N+2)\left(\frac{k_{\mathrm{B}} T}{p}\right)^2$$

and therefore

$$V_{\mathrm{rms}}^2 = \langle V^2 \rangle - \langle V \rangle^2 = (N+1)\left(\frac{k_{\mathrm{B}} T}{p}\right)^2 \quad \Rightarrow \quad V_{\mathrm{rms}} = N^{1/2} \frac{k_{\mathrm{B}} T}{p} .$$

Thus $V_{\mathrm{rms}}/\langle V \rangle = N^{-1/2} \ll 1$. This is, once again, the Central Limit Theorem in action.

(4) For the system described in problem (1), compute the distribution of speeds $\bar{f}(v)$. Find the most probable speed, the mean speed, and the RMS speed.

Solution :

Again, we solve for the general case $\varepsilon(\boldsymbol{p}) = A p^\alpha$. 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

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

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

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

Now

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

We therefore have

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

We can now calculate

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

and so

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

To find the most probable speed, we extremize $\bar{f}(v)$. We obtain

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

which means

$$v = \alpha A \left(\frac{d - \alpha + 1}{\alpha \beta A} \right)^{1-\alpha^{-1}} = (\alpha A)^{\alpha^{-1}} (d - \alpha + 1)^{1-\alpha^{-1}} (k_{\mathrm{B}}T)^{1-\alpha^{-1}} \, .$$

Solution Set #3

(1) Consider an ultrarelativistic ideal gas in three space dimensions. The dispersion is $\varepsilon(\boldsymbol{p}) = pc$.

   (a) Find T, p, and μ within the microcanonical ensemble (variables S, V, N).

   (b) Find F, S, p, and μ within the ordinary canonical ensemble (variables T, V, N).

   (c) Find Ω, S, p, and N within the grand canonical ensemble (variables T, V, μ).

   (d) Find G, S, V, and μ within the Gibbs ensemble (variables T, p, N).

   (e) Find H, T, V, and μ within the S-p-N ensemble. Here $\mathsf{H} = E + pV$ is the enthalpy.

Solution :

(a) The density of states $D(E, V, N)$ is the inverse Laplace transform of the ordinary canonical partition function $Z(\beta, V, N)$. We have

$$Z(\beta, V, N) = \frac{V^N}{N!}\left(\int \frac{d^3p}{h^3}\, e^{-\beta pc}\right)^N = \frac{V^N}{N!}\,\frac{\beta^{-3N}}{\pi^{2N}(\hbar c)^{3N}}\ .$$

Thus,

$$D(E, V, N) = \int\limits_{c-i\infty}^{c+i\infty} \frac{d\beta}{2\pi i}\, Z(\beta, V, N)\, e^{\beta E} = \frac{V^N}{N!}\left(\pi^{2/3}\hbar c\right)^{-3N} \frac{E^{3N-1}}{(3N-1)!}\ .$$

Taking the logarithm, and using $\ln(K!) = K\ln K - K + \mathcal{O}(\ln K)$ for large K,

$$S(E, V, N) = k_{\mathrm{B}}\ln D(E, V, N) = Nk_{\mathrm{B}}\ln\left(\frac{V}{N}\right) + 3Nk_{\mathrm{B}}\ln\left(\frac{E}{N}\right) - 3Nk_{\mathrm{B}}\ln a\ ,$$

where $a = 3\pi^{2/3}e^{-4/3}\hbar c$ is a constant. Inverting to find $E(S, V, N)$, we have

$$E(S, V, N) = \frac{aN^{4/3}}{V^{1/3}}\,\exp\left(\frac{S}{3Nk_{\mathrm{B}}}\right)\ .$$

From the differential relation

$$dE = T\,dS - p\,dV + \mu\,dN$$

we then derive

$$T(S,V,N) = +\left(\frac{\partial E}{\partial S}\right)_{V,N} = \frac{a}{3k_{\mathrm{B}}}\left(\frac{N}{V}\right)^{1/3}\exp\left(\frac{S}{3Nk_{\mathrm{B}}}\right)$$

$$p(S,V,N) = -\left(\frac{\partial E}{\partial V}\right)_{S,N} = \frac{a}{3}\left(\frac{N}{V}\right)^{4/3}\exp\left(\frac{S}{3Nk_{\mathrm{B}}}\right)$$

$$\mu(S,V,N) = +\left(\frac{\partial E}{\partial N}\right)_{S,V} = \frac{a}{3}\left(\frac{N}{V}\right)^{1/3}\left(4 - \frac{S}{Nk_{\mathrm{B}}}\right)\exp\left(\frac{S}{3Nk_{\mathrm{B}}}\right).$$

Note that $pV = Nk_{\mathrm{B}}T$.

(b) The Helmholtz free energy is

$$F(T,V,N) = -k_{\mathrm{B}}T\ln Z$$
$$= 3Nk_{\mathrm{B}}T - Nk_{\mathrm{B}}T\ln\left(\frac{V}{N}\right) - 3Nk_{\mathrm{B}}T\ln(3k_{\mathrm{B}}T) + 3Nk_{\mathrm{B}}T\ln a\ ,$$

and from

$$dF = -S\,dT - p\,dV + \mu\,dN$$

we read off

$$S(T,V,N) = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_{\mathrm{B}}\ln\left(\frac{V}{N}\right) + 3Nk_{\mathrm{B}}\ln(3k_{\mathrm{B}}T) + 3Nk_{\mathrm{B}}\ln a$$

$$p(T,V,N) = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_{\mathrm{B}}T}{V}$$

$$\mu(T,V,N) = +\left(\frac{\partial F}{\partial N}\right)_{T,V} = -k_{\mathrm{B}}T\ln\left(\frac{V}{N}\right) - 3k_{\mathrm{B}}T\ln(3k_{\mathrm{B}}T) + (4 + 3\ln a)\,k_{\mathrm{B}}T\ .$$

(c) The grand potential is $\Omega = F - \mu N = -k_{\mathrm{B}}T\ln\Xi$, where

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N}Z(\beta,V,N) = \exp\left\{Ve^{\mu/k_{\mathrm{B}}T}\left(\frac{k_{\mathrm{B}}T}{\pi^{2/3}\hbar c}\right)^{3}\right\}.$$

Thus,

$$\Omega(T,V,N) = -\frac{V}{\pi^2}\cdot\frac{(k_{\mathrm{B}}T)^4}{(\hbar c)^3}\cdot e^{\mu/k_{\mathrm{B}}T}\ .$$

The differential is

$$d\Omega = -S\,dT - p\,dV - N\,d\mu\ ,$$

and therefore

$$S(T,V,\mu) = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} = \frac{V}{\pi^2}\cdot\frac{(k_{\mathrm{B}}T)^3}{(\hbar c)^3}\cdot e^{\mu/k_{\mathrm{B}}T}\cdot\left(4k_{\mathrm{B}} - \frac{\mu}{T}\right)$$

$$p(T,V,\mu) = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = \frac{(k_{\mathrm{B}}T)^4}{\pi^2(\hbar c)^3}\cdot e^{\mu/k_{\mathrm{B}}T}$$

$$N(T,V,\mu) = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = \frac{V}{\pi^2}\cdot\left(\frac{k_{\mathrm{B}}T}{\hbar c}\right)^3\cdot e^{\mu/k_{\mathrm{B}}T}\ .$$

Note that $p = -\Omega/V$.

(d) The Gibbs free energy is

$$\begin{aligned} G(T,p,N) &= F + pV \\ &= Nk_{\mathrm{B}}T\ln p - 4Nk_{\mathrm{B}}T\ln(k_{\mathrm{B}}T) + Nk_{\mathrm{B}}T\left(4 + 3\ln(\tfrac{1}{3}a)\right) \end{aligned}$$

The differential of G is

$$dG = -S\,dT + V\,dP + \mu\,dN\ ,$$

and therefore

$$S(T,p,N) = -\left(\frac{\partial G}{\partial T}\right)_{p,N} = -Nk_{\mathrm{B}}\ln p + 4Nk_{\mathrm{B}}\ln(k_{\mathrm{B}}T) - Nk_{\mathrm{B}}\ln(\tfrac{1}{3}a)$$

$$V(T,p,N) = +\left(\frac{\partial G}{\partial p}\right)_{T,N} = \frac{Nk_{\mathrm{B}}T}{p}$$

$$\mu(T,p,N) = +\left(\frac{\partial G}{\partial N}\right)_{T,p} = k_{\mathrm{B}}T\ln p - 4k_{\mathrm{B}}T\ln(k_{\mathrm{B}}T) + k_{\mathrm{B}}T\left(4 + 3\ln(\tfrac{1}{3}a)\right)\ .$$

Note that $\mu = G/N$.

(e) The enthalpy is

$$\begin{aligned} \mathsf{H}(S,p,N) &= E + pV \\ &= 4N\left(\tfrac{1}{3}a\right)^{3/4}p^{1/4}\exp\left(\frac{S}{4Nk_{\mathrm{B}}}\right)\ . \end{aligned}$$

From

$$d\mathsf{H} = T\,dS + V\,dp + \mu\,dN\ ,$$

we have

$$T(S,p,N) = +\left(\frac{\partial\mathsf{H}}{\partial S}\right)_{p,N} = \frac{\left(\tfrac{1}{3}a\right)^{3/4}p^{1/4}}{k_{\mathrm{B}}}\exp\left(\frac{S}{4Nk_{\mathrm{B}}}\right)$$

$$V(S,p,N) = +\left(\frac{\partial\mathsf{H}}{\partial p}\right)_{S,N} = N\left(\frac{a}{3p}\right)^{3/4}\exp\left(\frac{S}{4Nk_{\mathrm{B}}}\right)$$

$$\mu(S,p,N) = \left(\frac{\partial\mathsf{H}}{\partial N}\right)_{S,p} = \left(\tfrac{1}{3}a\right)^{3/4}p^{1/4}\left(4 - \frac{S}{Nk_{\mathrm{B}}}\right)\exp\left(\frac{S}{4Nk_{\mathrm{B}}}\right)\ .$$

(2) Consider a surface containing N_s adsorption sites which is in equilibrium with a two-component nonrelativistic ideal gas containing atoms of types A and B . (Their respective masses are m_A and m_B). Each adsorption site can be in one of three possible states: (i) vacant, (ii) occupied by an A atom, with energy $-\Delta_\mathsf{A}$, and (ii) occupied with a B atom, with energy $-\Delta_\mathsf{B}$.

  (a) Find the grand partition function for the surface, $\Xi_\mathrm{surf}(T, \mu_\mathsf{A}, \mu_\mathsf{B}, N_\mathsf{s})$.

  (b) Suppose the number densities of the gas atoms are n_A and n_B. Find the fraction $f_\mathsf{A}(n_\mathsf{A}, n_\mathsf{B}, T)$ of adsorption sites with A atoms, and the fraction $f_0(n_\mathsf{A}, n_\mathsf{B}, T)$ of adsorption sites which are vacant.

Solution :

(a) The surface grand partition function is

$$\Xi_\mathrm{surf}(T, \mu_\mathsf{A}, \mu_\mathsf{B}, N_\mathsf{s}) = \left(1 + e^{(\Delta_\mathsf{A} + \mu_\mathsf{A})/k_\mathrm{B}T} + e^{(\Delta_\mathsf{B} + \mu_\mathsf{B})/k_\mathrm{B}T}\right)^{N_\mathsf{s}} .$$

(b) From the grand partition function of the gas, we have

$$n_\mathsf{A} = \lambda_{T,\mathsf{A}}^{-3}\, e^{\mu_\mathsf{A}/k_\mathrm{B}T} \quad , \qquad n_\mathsf{B} = \lambda_{T,\mathsf{B}}^{-3}\, e^{\mu_\mathsf{B}/k_\mathrm{B}T} \ ,$$

with

$$\lambda_{T,\mathsf{A}} = \sqrt{\frac{2\pi\hbar^2}{m_\mathsf{A} k_\mathrm{B} T}} \quad , \qquad \lambda_{T,\mathsf{B}} = \sqrt{\frac{2\pi\hbar^2}{m_\mathsf{B} k_\mathrm{B} T}} \ .$$

Thus,

$$f_0 = \frac{1}{1 + n_\mathsf{A}\, \lambda_{T,\mathsf{A}}^3\, e^{\Delta_\mathsf{A}/k_\mathrm{B}T} + n_\mathsf{B}\, \lambda_{T,\mathsf{B}}^3\, e^{\Delta_\mathsf{B}/k_\mathrm{B}T}}$$

$$f_\mathsf{A} = \frac{n_\mathsf{A}\, \lambda_{T,\mathsf{A}}^3\, e^{\Delta_\mathsf{A}/k_\mathrm{B}T}}{1 + n_\mathsf{A}\, \lambda_{T,\mathsf{A}}^3\, e^{\Delta_\mathsf{A}/k_\mathrm{B}T} + n_\mathsf{B}\, \lambda_{T,\mathsf{B}}^3\, e^{\Delta_\mathsf{B}/k_\mathrm{B}T}}$$

$$f_\mathsf{B} = \frac{n_\mathsf{B}\, \lambda_{T,\mathsf{B}}^3\, e^{\Delta_\mathsf{B}/k_\mathrm{B}T}}{1 + n_\mathsf{A}\, \lambda_{T,\mathsf{A}}^3\, e^{\Delta_\mathsf{A}/k_\mathrm{B}T} + n_\mathsf{B}\, \lambda_{T,\mathsf{B}}^3\, e^{\Delta_\mathsf{B}/k_\mathrm{B}T}} \ .$$

Note that $f_0 + f_\mathsf{A} + f_\mathsf{B} = 1$.

(3) Consider a system composed of spin tetramers, each of which is described by the Hamiltonian

$$\hat{H} = -J(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_1\sigma_4 + \sigma_2\sigma_3 + \sigma_2\sigma_4 + \sigma_3\sigma_4) - \mu_0 H(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) .$$

The individual tetramers are otherwise noninteracting.

(a) Find the single tetramer partition function ζ.

(b) Find the magnetization per tetramer $m = \mu_0 \langle \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 \rangle$.

(c) Suppose the tetramer number density is n_t. The magnetization density is $M = n_t m$. Find the zero field susceptibility $\chi(T) = (\partial M / \partial H)_{H=0}$.

Solution :

(a) Note that we can write

$$\hat{H} = 2J - \tfrac{1}{2}J(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)^2 - \mu_0 H \left(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4\right).$$

Thus, for each of the $2^4 = 16$ configurations of the spins of any given tetramer, only the sum $\sum_{i=1}^4 \sigma_i$ is necessary in computing the energy. We list the degeneracies of these states in the table below. Thus, according to the table, we have

$\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4$	degeneracy g	energy E
$+4$	1	$-6J - 4\mu_0 H$
$+2$	4	$-2\mu_0 H$
0	6	$-2J$
-2	4	$+2\mu_0 H$
-4	1	$-6J + 4\mu_0 H$

$$\zeta = 6\,e^{-2J/k_B T} + 8\,\cosh\left(\frac{2\mu_0 H}{k_B T}\right) + 2\,e^{6J/k_B T}\,\cosh\left(\frac{4\mu_0 H}{k_B T}\right).$$

(b) The magnetization per tetramer is

$$m = -\frac{\partial f}{\partial H} = k_B T\,\frac{\partial \ln \zeta}{\partial H} = 4\mu_0 \cdot \frac{2\,\sinh(2\beta\mu_0 H) + e^{6\beta J}\,\sinh(4\beta\mu_0 H)}{3\,e^{-2\beta J} + 4\,\cosh(2\beta\mu_0 H) + e^{6\beta J}\,\cosh(4\beta\mu_0 H)}.$$

(c) The zero field susceptibility is

$$\chi(T) = \frac{16\,n_t\,\mu_0^2}{k_B T} \cdot \frac{1 + e^{6\beta J}}{3\,e^{-2\beta J} + 4 + e^{6\beta J}}$$

Note that for $\beta J \to \infty$ we have $\chi(T) = (4\mu_0)^2 n_t / k_B T$, which is the Curie value for a single Ising spin with moment $4\mu_0$. In this limit, all the individual spins are locked together, and there are only two allowed configurations for each tetramer: $|\uparrow\uparrow\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\downarrow\downarrow\rangle$. When $J = 0$, we have $\chi = 4\mu_0^2 n_t / k_B T$, which is to say four times the single spin susceptibility. *I.e.* all the spins in each tetramer are independent when $J = 0$. When $\beta J \to -\infty$, the only allowed configurations are the six ones with $\sum_{i=1}^4 \sigma_i = 0$. In order to exhibit a moment, an energy gap of $2|J|$ must be overcome, hence $\chi \propto \exp(-2\beta|J|)$, which is exponentially suppressed.

Solution Set #4

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

    (a) What are the SI dimensions of a?

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

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

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

Solution :

(a) Clearly $[a] = \mathrm{K}^7\, \mathrm{m}^{12}/\mathrm{J}^2$ where K are Kelvins, m are meters, and J are Joules.

(b) We have

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

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

We must eliminate S. Dividing the second of these equations by the first, we find $S = 7pV/4T$, and substituting this into either equation, we obtain the equation of state,

$$p = c \cdot \left(\frac{N}{V}\right)^{1/3} T^{7/6}\ ,$$

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

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

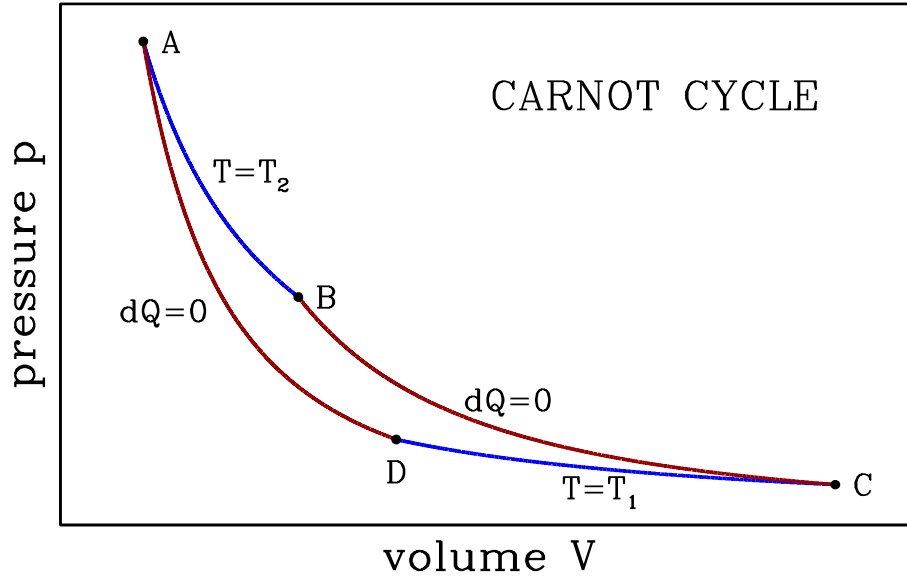$$\frac{dp}{p} + \frac{dV}{3V} - \frac{7\, dT}{6T} - \frac{dN}{3N} = 0\ .$$

23

Figure 3.5: The Carnot cycle.

Thus,

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

(d) From the results of part (b), we have that $dS = 0$ means $d(N^2 V^4 T) = 0$, so with N constant the equation for adiabats is $d(TV^4) = 0$. Thus, for the Carnot cycle of Fig. 7.1, we have

$$T_2\, V_A^4 = T_1\, V_D^4 \qquad , \qquad T_2\, V_B^4 = T_1\, V_C^4 \; .$$

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

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

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

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

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

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

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

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

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

$$W_{\mathsf{BC}} = -(\Delta E)_{\mathsf{BC}} = E_{\mathsf{B}} - E_{\mathsf{C}} = \tfrac{1}{4} c \, N^{1/3} \big(T_2^{7/6} \, V_{\mathsf{B}}^{2/3} - T_1^{7/6} \, V_{\mathsf{C}}^{2/3} \big) \, .$$

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

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

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

$$W_{\mathsf{CD}} = \tfrac{3}{2} c \, N^{1/3} \, T_2^{7/6} \big(V_{\mathsf{D}}^{2/3} - V_{\mathsf{C}}^{2/3} \big) \, .$$

We now use the adiabat conditions $V_{\mathsf{C}}^{2/3} = (T_2/T_1)^{1/6} \, V_{\mathsf{B}}^{2/3}$ and $V_{\mathsf{D}}^{2/3} = (T_2/T_1)^{1/6} \, V_{\mathsf{A}}^{2/3}$ to write W_{CD} as

$$W_{\mathsf{CD}} = \tfrac{3}{2} c \, N^{1/3} \, T_1 \, T_2^{1/6} \big(V_{\mathsf{A}}^{2/3} - V_{\mathsf{B}}^{2/3} \big) \, .$$

We therefore have

$$Q_{\mathsf{CD}} = \tfrac{7}{4} c \, N^{1/3} \, T_1 \, T_2^{1/6} \big(V_{\mathsf{A}}^{2/3} - V_{\mathsf{B}}^{2/3} \big) \, .$$

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

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

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

For the cycle, we therefore have

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

and thus

$$\eta = \frac{W_{\mathrm{cyc}}}{Q_{\mathsf{AB}}} = 1 - \frac{T_1}{T_2} \, .$$

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

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

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

where r is a dimensionful constant.

(a) Extensivity of S imposes a condition on (α, β, γ). Find this constraint.

(b) Even with the extensivity condition satisfied, the system may violate one or more stability criteria. Find the general conditions on (α, β, γ) which are thermodynamically permissible.

Solution :

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

(b) The Hessian is

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

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

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

(3) For an ideal gas, find the difference $C_\varphi - C_V$ for the following functions φ. You are to assume N is fixed in each case.

(a) $\varphi(p, V) = p^3 \, V^2$

(b) $\varphi(p, T) = p \, e^{T/T_0}$

(c) $\varphi(T, V) = V T^{-1}$

Solution :

In general,

$$
C_\varphi = T \left(\frac{\partial S}{\partial T} \right)_\varphi .
$$

Note that

$$
đQ = dE + p \, dV .
$$

We will also appeal to the ideal gas law, $pV = Nk_{\mathrm{B}}T$. Below, we shall abbreviate $\varphi_V = \frac{\partial \varphi}{\partial V}$, $\varphi_T = \frac{\partial \varphi}{\partial T}$, and $\varphi_p = \frac{\partial \varphi}{\partial p}$.

(a) We have

$$dQ = \tfrac{1}{2} f N k_{\mathrm{B}} \, dT + p \, dV \ ,$$

and therefore

$$C_\varphi - C_V = p \left(\frac{\partial V}{\partial T} \right)_\varphi \ .$$

Now for a general function $\varphi(p, V)$, we have

$$d\varphi = \varphi_p \, dp + \varphi_V \, dV$$
$$= \frac{Nk_{\mathrm{B}}}{V} \varphi_p \, dT + \left(\varphi_V - \frac{p}{V} \varphi_p \right) dV \ ,$$

after writing $dp = d(Nk_{\mathrm{B}}T/V)$ in terms of dT and dV. Setting $d\varphi = 0$, we then have

$$C_\varphi - C_V = p \left(\frac{\partial V}{\partial T} \right)_\varphi = \frac{Nk_{\mathrm{B}} \, p \, \varphi_p}{p \, \varphi_p - V \varphi_V} \ .$$

This is the general result. For $\varphi(p, V) = p^3 V^2$, we find

$$C_\varphi - C_V = 3Nk_{\mathrm{B}} \ .$$

(b) We have

$$dQ = \left(\tfrac{1}{2} f + 1 \right) N k_{\mathrm{B}} \, dT - V \, dp \ ,$$

and therefore

$$C_\varphi - C_V = Nk_{\mathrm{B}} - V \left(\frac{\partial p}{\partial T} \right)_\varphi \ .$$

For a general function $\varphi(p, T)$, we have

$$d\varphi = \varphi_p \, dp + \varphi_T \, dT \quad \Longrightarrow \quad \left(\frac{\partial p}{\partial T} \right)_\varphi = -\frac{\varphi_T}{\varphi_p} \ .$$

Therefore,

$$C_\varphi - C_V = Nk_{\mathrm{B}} + V \frac{\varphi_T}{\varphi_p} \ .$$

This is the general result. For $\varphi(p, T) = p \, e^{T/T_0}$, we find

$$C_\varphi - C_V = Nk_{\mathrm{B}} \left(1 + \frac{T}{T_0} \right) \ .$$

(c) We have

$$C_\varphi - C_V = p \left(\frac{\partial V}{\partial T} \right)_\varphi \ ,$$

as in part (a). For a general function $\varphi(T, V)$, we have

$$d\varphi = \varphi_T \, dT + \varphi_V \, dV \quad \Longrightarrow \quad \left(\frac{\partial V}{\partial T} \right)_\varphi = -\frac{\varphi_T}{\varphi_V} \; ,$$

and therefore

$$C_\varphi - C_V = -p \, \frac{\varphi_T}{\varphi_V} \; .$$

This is the general result. For $\varphi(T, V) = V/T$, we find

$$C_\varphi - C_V = N k_{\mathrm{B}} \; .$$

(4) Find an expression for the energy density $\varepsilon = E/V$ for a system obeying the Dieterici equation of state,

$$p(V - Nb) = N k_{\mathrm{B}} T \, e^{-Na/V k_{\mathrm{B}} T} \; ,$$

where a and b are constants. Your expression for $\varepsilon(v, T)$ should involve an integral which can be expressed in terms of the exponential integral,

$$\mathrm{Ei}(x) = \int\limits_{-\infty}^{x} dt \, \frac{e^t}{t} \; .$$

Solution :

We have

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

where we have invoked a Maxwell relation. For the Dieterici equation of state, then,

$$\left(\frac{\partial E}{\partial V} \right)_{T,N} = \frac{N k_{\mathrm{B}} T}{V - Nb} \cdot \frac{Na}{V k_{\mathrm{B}} T} \cdot e^{-Na/V k_{\mathrm{B}} T} \; .$$

Let $n = N/V$ be the density and $\varepsilon = E/N$ be the energy per particle. Then the above result is equivalent to

$$\frac{\partial \varepsilon}{\partial n} = -\frac{a}{1 - bn} \, e^{-na/k_{\mathrm{B}} T} \; .$$

We integrate this between $n = 0$ and n, with $bn < 1$. Define the dimensionless quantity $\lambda = a/b k_{\mathrm{B}} T$ and $t = \lambda(1 - bn)$. Then

$$\varepsilon(n, T) - \varepsilon(0, T) = -\frac{a \, e^{-\lambda}}{b} \int\limits_{(1-bn)\lambda}^{\lambda} \frac{dt}{t} \, e^t = \left\{ \mathrm{Ei}\big((1 - bn)\lambda \big) - \mathrm{Ei}(\lambda) \right\} \frac{a \, e^{-\lambda}}{b}$$

In the zero density limit, the gas must be ideal, in which case $\varepsilon(0, T) = \frac{1}{2} f k_{\mathrm{B}} T$. Thus,

$$\varepsilon(n, T) = \tfrac{1}{2} f k_{\mathrm{B}} T - \left\{ \mathrm{Ei}\left(\frac{(1 - bn)a}{b k_{\mathrm{B}} T} \right) - \mathrm{Ei}\left(\frac{a}{b k_{\mathrm{B}} T} \right) \right\} \cdot \frac{a \, e^{-a/b k_{\mathrm{B}} T}}{b} \; .$$

In terms of the volume per particle, write $v = V/N = 1/n$.

Solution Set #5

(1) For a noninteracting quantum system with single particle density of states $g(\varepsilon) = A\,\varepsilon^r$ (with $\varepsilon \geq 0$), find the first three virial coefficients for bosons and for fermions.

Solution :

We have

$$n(T,z) = \sum_{j=1}^{\infty} (\pm 1)^{j-1}\, C_j(T)\, z^j \qquad , \qquad p(T,z) = k_{\mathrm{B}}T \sum_{j=1}^{\infty} (\pm 1)^{j-1}\, z^j\, j^{-1}\, C_j(T)\, z^j \ ,$$

where

$$C_j(T) = \int_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)\, e^{-j\varepsilon/k_{\mathrm{B}}T} = A\,\Gamma(r+1) \left(\frac{k_{\mathrm{B}}T}{j}\right)^{r+1} \ .$$

Thus, we have

$$\pm n v_T = \sum_{j=1}^{\infty} j^{-(r+1)}\, (\pm z)^j$$

$$\pm p v_T/k_{\mathrm{B}}T = \sum_{j=1}^{\infty} j^{-(r+2)}\, (\pm z)^j \ ,$$

where

$$v_T = \frac{1}{A\,\Gamma(r+1)\,(k_{\mathrm{B}}T)^{r+1}} \ .$$

has dimensions of volume. Thus, we let $x = \pm z$, and interrogate `Mathematica`:

```
In[1]=  y = InverseSeries[x + x^2/2^(r+1) + x^3/3^(r+1) + x^4/4^(r+1) + O[x]^5]
```

```
In[2]=  w = y + y^2/2^(r+2) + y^3/3^(r+2) + y^4/4^(r+2) + O[y]^5 .
```

The result is

$$p = n k_{\mathrm{B}}T \left[1 + B_2(T)\, n + B_3(T)\, n^2 + \ldots \right] \ ,$$

where

$$B_2(T) = \mp 2^{-2-r} \, v_T$$

$$B_3(T) = \left(2^{-2-2r} - 2 \cdot 3^{-2-r} \right) v_T^2$$

$$B_4(T) = \pm 2^{-4-3r} \, 3^{-r} \left(2^{3+2r} - 5 \cdot 3^r - 2^r \, 3^{1+r} \right) v_T^3 \; .$$

(2) How would you formulate the Lindemann melting criterion for Einstein phonons?

Solution :

For a one-dimensional harmonic oscillator, we have

$$\langle u^2 \rangle = \frac{\hbar}{2m\omega_0} \operatorname{ctnh}\!\left(\hbar\omega_0 / 2k_{\mathrm{B}}T \right) ,$$

where ω_0 is the oscillation frequency and m is the mass. For a d-dimensional Einstein solid, then, the Lindemann criterion should take the form

$$\langle \boldsymbol{u}^2 \rangle = \frac{d\hbar}{2m\omega_0} \operatorname{ctnh}\left(\hbar\omega_0 / 2k_{\mathrm{B}}T_{\mathrm{L}} \right) = (fa)^2 ,$$

where $f \approx \frac{1}{10}$, with a the lattice spacing. The Lindemann temperature is then

$$k_{\mathrm{B}}T_{\mathrm{L}} = \frac{\hbar\omega_0}{\ln\!\left(\frac{1+\eta}{1-\eta} \right)} ,$$

where

$$\eta = \frac{d\hbar}{2f^2 m\omega_0 a^2} \; .$$

Plugging in typical numbers, one finds $\eta \ll 1$ for most solids, assuming $\hbar\omega_0/k_{\mathrm{B}} \sim 100\,\mathrm{K}$. This procedure would then predict a melting temperature much higher than that observed for most solids.

(3) Derive the analogue of Stefan's Law for a two-dimensional blackbody. What happens if the photon dispersion is replaced by $\varepsilon(\boldsymbol{k}) = C|\boldsymbol{k}|^\alpha$?

Solution :

The power emitted per unit length of the boundary of such a two-dimensional blackbody

is

$$\frac{dP}{dL} = \int \frac{d^2k}{(2\pi)^2} \; \hat{\boldsymbol{k}} \cdot \frac{\partial \varepsilon}{\partial \boldsymbol{k}} \cdot \frac{\varepsilon(\boldsymbol{k})}{e^{\varepsilon(\boldsymbol{k})/k_{\mathrm{B}}T} - 1} \, \Theta(\hat{\boldsymbol{k}} \cdot \boldsymbol{v})$$

$$= \frac{\alpha C^2}{2\pi^2} \int\limits_0^\infty dk \, \frac{k^{2\alpha}}{e^{\beta C k^\alpha} - 1}$$

$$= \frac{1}{2\pi^2} \, \Gamma(2 + \alpha^{-1}) \, \zeta(2 + \alpha^{-1}) \, C^{-\alpha^{-1}} (k_{\mathrm{B}}T)^{2+\alpha^{-1}}$$

$$\equiv \sigma T^{2+\alpha^{-1}} \; .$$

Thus, for $\alpha = 1$, we have $P/L = \sigma T^3$.

Solution Set #6

(1) In our derivation of the low temperature phase of an ideal Bose condensate, we split off the lowest energy state ε_0 but treated the remainder as a continuum, taking $\mu = 0$ in all expressions relating to the overcondensate. Under what conditions is this justified? *I.e.* why are we not obligated to separately consider the contributions from the first excited state, *etc.*?

Solution :

In the condensed phase, there is an extensive population N_0 of the lowest single particle energy state, and the chemical potential takes the value $\mu = \varepsilon_0 - \frac{k_{\mathrm{B}}T}{\mathsf{g}_0 N_0}$, where g_0 is the degeneracy of the single particle ground state. Let ε_1 be the energy of the first excited state and g_1 its degeneracy Then the number of bosons in the first excited state is

$$N_1 = \frac{\mathsf{g}_1}{e^{(\varepsilon_1 - \mu)/k_{\mathrm{B}}T} - 1} \approx \frac{\mathsf{g}_1 k_{\mathrm{B}}T}{\varepsilon_1 - \mu} \ ,$$

assuming $\varepsilon_1 - \mu \ll k_{\mathrm{B}}T$. Now

$$\varepsilon_1 - \mu = (\varepsilon_0 - \mu) + (\varepsilon_1 - \varepsilon_0) = \frac{k_{\mathrm{B}}T}{\mathsf{g}_0 N_0} + (\varepsilon_1 - \varepsilon_0) \ .$$

So we need to ask about the energy difference $\Delta \varepsilon_1 \equiv \varepsilon_1 - \varepsilon_0$. If $\Delta \varepsilon_1 \propto V^{-r}$, assuming $0 < r < 1$, then the number of particles in the first excited state will be subextensive, and the corresponding density $n_1 = N_1/V \propto V^{r-1}$ will vanish in the thermodynamic limit. In this case, we are justified in singling out only the single particle ground state as having an extensive occupancy. For a ballistic dispersion and periodic boundary conditions, the quantized single particle plane wave energies are given by

$$\varepsilon(l_x, l_y, l_z) = \frac{\hbar^2}{2m} \left\{ \left(\frac{2\pi l_x}{L_x} \right)^2 + \left(\frac{2\pi l_y}{L_y} \right)^2 + \left(\frac{2\pi l_z}{L_z} \right)^2 \right\} \ ,$$

and thus $\varepsilon_1 \propto V^{-2/3}$. Therefore $r = \frac{2}{3}$ and the occupancy of the first excited state is subextensive.

(2) Consider a three-dimensional Bose gas of particles which have two internal polarization states, labeled by $\sigma = \pm 1$. The single particle energies are given by

$$\varepsilon(\boldsymbol{p}, \sigma) = \frac{\boldsymbol{p}^2}{2m} + \sigma \Delta \ ,$$

where $\Delta > 0$.

(a) Find the density of states per unit volume $g(\varepsilon)$.

(b) Find an implicit expression for the condensation temperature $T_c(n, \Delta)$. When $\Delta \to \infty$, your expression should reduce to the familiar one derived in class.

(c) When $\Delta = \infty$, the condensation temperature should agree with the familiar result for three-dimensional Bose condensation. Assuming $\Delta \ll k_B T_c(n, \Delta = \infty)$, find analytically the leading order difference $T_c(n, \Delta) - T_c(n, \Delta = \infty)$.

Solution :

(a) Let $g_0(\varepsilon)$ be the DOS per unit volume for the case $\Delta = 0$. Then

$$g_0(\varepsilon)\,d\varepsilon = \frac{d^3k}{(2\pi)^3} = \frac{k^2\,dk}{2\pi^2} \quad \Rightarrow \quad g_0(\varepsilon) = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\varepsilon^{1/2}\,\Theta(\varepsilon)\ .$$

For finite Δ, the single particle energies are shifted uniformly by $\pm\Delta$ for the $\sigma = \pm 1$ states, hence

$$g(\varepsilon) = g_0(\varepsilon + \Delta) + g_0(\varepsilon - \Delta)\ .$$

(b) For Bose statistics, we have in the uncondensed phase,

$$\begin{aligned}
n &= \int\limits_{-\infty}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{e^{(\varepsilon - \mu)/k_B T} - 1}\\
&= \mathrm{Li}_{3/2}\big(e^{(\mu + \Delta)/k_B T}\big)\,\lambda_T^{-3} + \mathrm{Li}_{3/2}\big(e^{(\mu - \Delta)/k_B T}\big)\,\lambda_T^{-3}\ .
\end{aligned}$$

In the condensed phase, $\mu = -\Delta - \mathcal{O}(N^{-1})$ is pinned just below the lowest single particle energy, which occurs for $\mathbf{k} = \mathbf{p}/\hbar = 0$ and $\sigma = -1$. We then have

$$n = n_0 + \zeta(3/2)\,\lambda_T^{-3} + \mathrm{Li}_{3/2}\big(e^{-2\Delta/k_B T}\big)\,\lambda_T^{-3}\ .$$

To find the critical temperature, set $n_0 = 0$ and $\mu = -\Delta$:

$$n = \zeta(3/2)\,\lambda_{T_c}^{-3} + \mathrm{Li}_{3/2}\big(e^{-2\Delta/k_B T_c}\big)\,\lambda_{T_c}^{-3}\ .$$

This is a nonlinear and implicit equation for $T_c(n, \Delta)$. When $\Delta = \infty$, we have

$$k_B T_c^\infty(n) = \frac{2\pi\hbar^2}{m}\left(\frac{n}{\zeta(3/2)}\right)^{2/3}\ .$$

(c) For finite Δ, we still have the implicit nonlinear equation to solve, but in the limit $\Delta \gg k_B T_c$, we can expand $T_c(\Delta) = T_c^\infty + \Delta T_c(\Delta)$. We may then set $T_c(n, \Delta)$ to $T_c^\infty(n)$ in the second term of our nonlinear implicit equation, move this term to the LHS, whence

$$\zeta(3/2)\,\lambda_{T_c}^{-3} \approx n - \mathrm{Li}_{3/2}\big(e^{-2\Delta/k_B T_c^\infty}\big)\,\lambda_{T_c^\infty}^{-3}\ .$$

which is a simple algebraic equation for $T_c(n, \Delta)$. The second term on the RHS is tiny since $\Delta \gg k_B T_c^\infty$. We then find

$$T_c(n, \Delta) = T_c^\infty(n) \left\{ 1 - \tfrac{3}{2} e^{-2\Delta/k_B T_c^\infty(n)} + \mathcal{O}\left(e^{-4\Delta/k_B T_c^\infty(n)}\right) \right\} .$$

(3) For an ideal Fermi gas in three dimensions,

(a) Find an expression for the isothermal compressibility $\kappa_{T,N}$ as a function of the temperature T and fugacity z.

(b) Find an expression for the adiabatic compressibility $\kappa_{S,N}$ as a function of the temperature T and fugacity z.

(c) Find an expression for the ratio $C_{p,N}/C_{V,N}$ as a function of the temperature T and fugacity z.

Solution :

Recall

$$N = V \int\limits_{-\infty}^{\infty} d\varepsilon \, g \, f$$

$$S = -k_B V \int\limits_{-\infty}^{\infty} d\varepsilon \, g \left\{ f \ln f + (1-f) \ln(1-f) \right\}$$

$$p = -k_B T \int\limits_{-\infty}^{\infty} d\varepsilon \, g \, \ln(1-f) ,$$

where $g = g(\varepsilon)$ and $f = f(\varepsilon - \mu)$ in the above expressions. Note further that the differential of the Fermi function is written in terms of dT and $d\mu$ as follows:

$$df = d\left(\frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1} \right) = \left(-\frac{\partial f}{\partial \varepsilon} \right) \cdot \left\{ (\varepsilon - \mu) \frac{dT}{T} + d\mu \right\} .$$

Thus, we have

$$V^{-1} \, dN = I_1 \, d\ln V + I_2 \, dT + I_3 \, d\mu$$

$$V^{-1} \, dS = J_1 \, d\ln V + J_2 \, dT + J_3 \, d\mu$$

$$dp = K_1 \, dT + K_2 \, d\mu ,$$

where

$$I_1 = \int\limits_{-\infty}^{\infty} d\varepsilon\, g\, f \qquad\qquad J_1 = -k_{\mathrm{B}} \int\limits_{-\infty}^{\infty} d\varepsilon\, g\left\{ f\, \ln f + (1-f)\,\ln(1-f) \right\}$$

$$I_2 = \int\limits_{-\infty}^{\infty} d\varepsilon\, g\left(-\frac{\partial f}{\partial \varepsilon}\right)\left(\frac{\varepsilon-\mu}{k_{\mathrm{B}}T}\right) \qquad J_2 = k_{\mathrm{B}} \int\limits_{-\infty}^{\infty} d\varepsilon\, g\left(-\frac{\partial f}{\partial \varepsilon}\right)\left(\frac{\varepsilon-\mu}{k_{\mathrm{B}}T}\right)^2$$

$$I_3 = \int\limits_{-\infty}^{\infty} d\varepsilon\, g\left(-\frac{\partial f}{\partial \varepsilon}\right) \qquad J_3 = k_{\mathrm{B}} \int\limits_{-\infty}^{\infty} d\varepsilon\, g\left(-\frac{\partial f}{\partial \varepsilon}\right)\left(\frac{\varepsilon-\mu}{k_{\mathrm{B}}T}\right) = k_{\mathrm{B}}\, I_2$$

and

$$K_1 = -k_{\mathrm{B}} \int\limits_{-\infty}^{\infty} d\varepsilon\, g\left\{ \ln(1-f) + \left(-\frac{\partial f}{\partial \varepsilon}\right)(\varepsilon-\mu) \right\}$$

$$K_2 = -k_{\mathrm{B}}T \int\limits_{-\infty}^{\infty} d\varepsilon\, \frac{g}{1-f}\left(-\frac{\partial f}{\partial \varepsilon}\right)$$

(a) Setting $dT = dN = 0$, we obtain $d\mu = -(I_1/I_3)\, d\ln V$, and therefore

$$\kappa_{T,N} = -\left(\frac{\partial \ln V}{\partial p}\right)_{T,N} = \frac{I_3}{I_1 K_2 - I_3 K_1}\ .$$

(b) Setting $dN = dS = 0$, we obtain

$$d\mu = \frac{I_1}{I_3}\, d\ln V + \frac{I_2}{I_3}\, dT = \frac{J_1}{J_3}\, d\ln V + \frac{J_2}{J_3}\, dT\ .$$

This can be used to express dT and $d\mu$ in terms of $d\ln V$ at fixed N and S. The final answer is quite involved and I won't reproduce it here. I regret asking this question!

(c) We set $dN = 0$ to write $d\ln V\big|_N$ in terms of dT and $d\mu$, and set $dp = 0$ to write $d\mu\big|_p = -(K_1/K_2)\, dT$. Thus, we can write both $d\mu$ and $d\ln V$ in terms of dT and compute $C_{p,N}$. For $C_{V,N}$, set $dN = d\ln V = 0$ to find $d\mu = -(I_2/I_3)\, dT$ and substitute into the equation for dS. Again the final result is somewhat tedious.

(4) At low energies, the conduction electron states in graphene can be described as fourfold degenerate fermions with dispersion $\varepsilon(\boldsymbol{k}) = \hbar v_{\mathrm{F}}|\boldsymbol{k}|$. Using the Sommerfeld expension,

(a) Find the density of single particle states $g(\varepsilon)$.

(b) Find the chemical potential $\mu(T, n)$ up to terms of order T^4.

(c) Find the energy density $\mathcal{E}(T,n) = E/V$ up to terms of order T^4.

Solution :

(a) The DOS per unit volume is

$$g(\varepsilon) = 4 \int \frac{d^2k}{(2\pi)^2} \, \delta(\varepsilon - \hbar v_{\mathrm{F}} k) = \frac{2\varepsilon}{\pi(\hbar v_{\mathrm{F}})^2} \ .$$

(b) The Sommerfeld expansion is

$$\int\limits_{-\infty}^{\infty} d\varepsilon \, f(\varepsilon - \mu) \, \phi(\varepsilon) = \int\limits_{-\infty}^{\mu} d\varepsilon \, \phi(\varepsilon) + \frac{\pi^2}{6} \, (kT)^2 \, \phi'(\mu) + \frac{7\pi^4}{360} \, (k_{\mathrm{B}}T)^4 \, \phi'''(\mu) + \dots \ .$$

For the particle density, set $\phi(\varepsilon) = g(\varepsilon)$, in which case

$$n = \frac{1}{\pi} \left(\frac{\mu}{\hbar v_{\mathrm{F}}} \right)^2 + \frac{\pi}{3} \left(\frac{k_{\mathrm{B}}T}{\hbar v_{\mathrm{F}}} \right)^2 \ .$$

The expansion terminates after the $\mathcal{O}(T^2)$ term. Solving for μ,

$$\mu(T,n) = \hbar v_{\mathrm{F}} (\pi n)^{1/2} \left[1 - \frac{\pi}{3n} \left(\frac{k_{\mathrm{B}}T}{\hbar v_{\mathrm{F}}} \right)^2 \right]^{1/2}$$

$$= \hbar v_{\mathrm{F}} (\pi n)^{1/2} \left\{ 1 - \frac{\pi}{6n} \left(\frac{k_{\mathrm{B}}T}{\hbar v_{\mathrm{F}}} \right)^2 - \frac{\pi^2}{72n^2} \left(\frac{k_{\mathrm{B}}T}{\hbar v_{\mathrm{F}}} \right)^4 + \dots \right\}$$

(c) For the energy density $\mathcal{E}$, we take $\phi(\varepsilon) = \varepsilon \, g(\varepsilon)$, whence

$$\mathcal{E}(T,n) = \frac{2\mu}{3\pi} \left[\left(\frac{\mu}{\hbar v_{\mathrm{F}}} \right)^2 + \left(\frac{\pi k_{\mathrm{B}}T}{\hbar v_{\mathrm{F}}} \right)^2 \right]$$

$$= \tfrac{2}{3} \sqrt{\pi} \, \hbar v_{\mathrm{F}} n^{3/2} \left\{ 1 + \frac{\pi}{2n} \left(\frac{k_{\mathrm{B}}T}{\hbar v_{\mathrm{F}}} \right)^2 - \frac{\pi^2}{8n^2} \left(\frac{k_{\mathrm{B}}T}{\hbar v_{\mathrm{F}}} \right)^4 + \dots \right\}$$

Solution Set #7

(1) For each of the two cluster diagrams in Fig. 1, find the symmetry factor s_γ and write an expression for the cluster integral $b_\gamma(T)$.
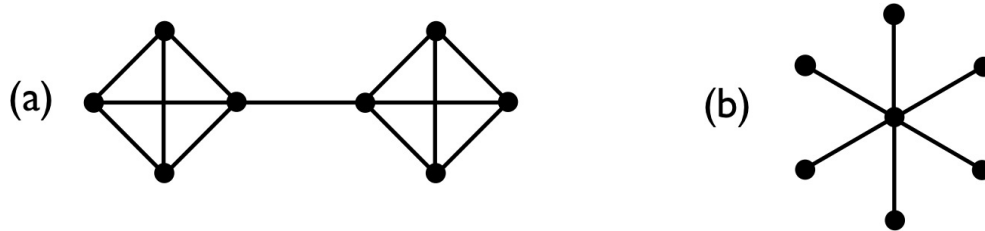

Figure 6.6: Mayer cluster expansion diagrams.

Solution :

The symmetry factors of the diagrams are $s_{\mathsf{a}} = 2 \cdot (3!)^2 = 72$ and $s_{\mathsf{b}} = 6! = 720$. To see this, note that sites 2, 3, and 4 and sites 5, 6, and 7 of figure 1a can be separately permuted in any of $3! = 6$ ways, and finally that the two triples themselves can be swapped to give a final factor of 2. For figure 1b, the sites $\{2, 3, 4, 5, 6, 7\}$ can be permuted in any way. One then has

$$b_{\mathsf{a}} = \frac{1}{72\,V} \int \prod_{i=1}^{8} d^d x_i \, f_{12} \, f_{13} \, f_{14} \, f_{23} \, f_{24} \, f_{34} \cdot f_{78} \, f_{68} \, f_{58} \, f_{67} \, f_{57} \, f_{56} \cdot f_{18}$$

$$b_{\mathsf{b}} = \frac{1}{720\,V} \int \prod_{i=1}^{7} d^d x_i \, f_{12} \, f_{13} \, f_{14} \, f_{15} \, f_{16} \, f_{17} \ .$$

(2) Consider the one-dimensional Ising model with next-nearest neighbor interactions,

$$\hat{H} = -J \sum_n \sigma_n \sigma_{n+1} - K \sum_n \sigma_n \sigma_{n+2} \ ,$$

on a ring with N sites, where N is even. By considering consecutive pairs of sites, show that the partition function may be written in the form $Z = \mathsf{Tr}\,(R^{N/2})$, where R is a 4×4 transfer matrix. Find R. *Hint:* It may be useful to think of the system as a railroad trestle,
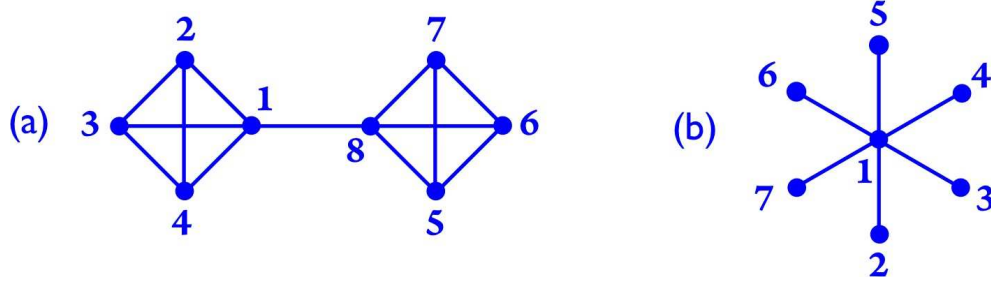
Figure 6.7: Labeled Mayer cluster expansion diagrams.

depicted in Fig. 2, with Hamiltonian

$$\hat{H} = -\sum_j \left[J\sigma_j\mu_j + J\mu_j\sigma_{j+1} + K\sigma_j\sigma_{j+1} + K\mu_j\mu_{j+1} \right] .$$

Then $R = R_{(\sigma_j\mu_j),(\sigma_{j+1}\mu_{j+1})}$, with $(\sigma\mu)$ a composite index which takes one of four possible values $(++)$, $(+-)$, $(-+)$, or $(--)$.
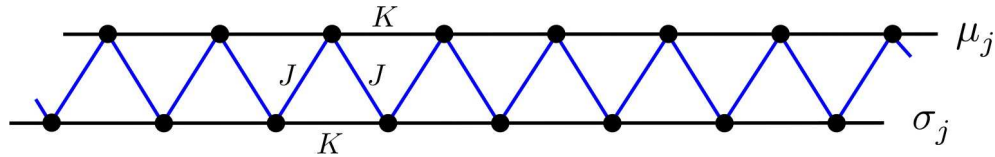

Figure 6.8: Railroad trestle representation of next-nearest neighbor chain.

Solution :

The transfer matrix can be read off from the Hamiltonian:

$$R_{(\sigma\mu),(\sigma'\mu')} = e^{\beta J\mu(\sigma+\sigma')} \, e^{\beta K(\sigma\sigma'+\mu\mu')} .$$

Expressed as a matrix of rank four, with rows and columns corresponding to $\{++, +-, -+, --\}$, we have

$$R = \begin{pmatrix} e^{2\beta(J+K)} & e^{2\beta J} & 1 & e^{-2\beta K} \\ e^{-2\beta J} & e^{-2\beta(J-K)} & e^{-2\beta K} & 1 \\ 1 & e^{-2\beta K} & e^{-2\beta(J-K)} & e^{-2\beta J} \\ e^{-2\beta K} & 1 & e^{2\beta J} & e^{2\beta(J+K)} \end{pmatrix} .$$

Querying WolframAlpha for the eigenvalues, we find

$$\lambda_1 = \tfrac{1}{2}\left[uv - (1+u^{-1})\sqrt{u^2v^2 - 2uv^2 + 4u + v^2} + 2v^{-1} + u^{-1}v \right]$$

$$\lambda_2 = \tfrac{1}{2}\left[uv + (1+u^{-1})\sqrt{u^2v^2 - 2uv^2 + 4u + v^2} + 2v^{-1} + u^{-1}v \right]$$

$$\lambda_3 = \tfrac{1}{2}\left[uv - (1-u^{-1})\sqrt{u^2v^2 + 2uv^2 - 4u + v^2} - 2v^{-1} + u^{-1}v \right]$$

$$\lambda_4 = \tfrac{1}{2}\left[uv + (1-u^{-1})\sqrt{u^2v^2 + 2uv^2 - 4u + v^2} - 2v^{-1} + u^{-1}v \right] ,$$

where $u = e^{2\beta J}$ and $v = e^{2\beta K}$. The partition function on a ring of N sites, with N even, is

$$Z = \mathsf{Tr}\big(R^{N/2}\big) = \lambda_1^{N/2} + \lambda_2^{N/2} + \lambda_3^{N/2} + \lambda_4^{N/2} \ .$$

Solution Set #8

(1) Consider a ferromagnetic spin-S Ising model on a lattice of coordination number z. The Hamiltonian is

$$\hat{H} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - \mu_0 H \sum_i \sigma_i \,,$$

where $\sigma \in \{-S, -S+1, \ldots, +S\}$ with $2S \in \mathbb{Z}$.

    (a) Find the mean field Hamiltonian $\hat{H}_{\mathrm{MF}}$.

    (b) Adimensionalize by setting $\theta \equiv k_{\mathrm{B}} T / zJ$, $h \equiv \mu_0 H / zJ$, and $f \equiv F / NzJ$. Find the dimensionless free energy per site $f(m, h)$ for arbitrary S.

    (c) Expand the free energy as

$$f(m, h) = f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 - chm + \mathcal{O}(h^2, hm^3, m^6)$$

    and find the coefficients f_0, a, b, and c as functions of θ and S.

    (d) Find the critical point $(\theta_{\mathrm{c}}, h_{\mathrm{c}})$.

    (e) Find $m(\theta_{\mathrm{c}}, h)$ to leading order in h.

Solution :

(a) Writing $\sigma_i = m + \delta\sigma_i$, we find

$$\hat{H}_{\mathrm{MF}} = \tfrac{1}{2}NzJm^2 - (\mu_0 H + zJ) \sum_i \sigma_i \,.$$

(b) Using the result

$$\sum_{\sigma=-S}^{S} e^{\beta\mu_0 H_{\mathrm{eff}}\sigma} = \frac{\sinh\big((S + \tfrac{1}{2})\beta\mu_0 H\big)}{\sinh\big(\tfrac{1}{2}\beta\mu_0 H\big)} \,,$$

we have

$$f = \tfrac{1}{2}m^2 - \theta \ln \sinh\big((2S + 1)(m + h)/2\theta\big) + \theta \ln \sinh\big((m + h)/2\theta\big) \,.$$

(c) Expanding the free energy, we obtain

$f = f_0 + \frac{1}{2}am^2 + \frac{1}{4}bm^4 - chm + \mathcal{O}(h^2, hm^3, m^6)$

$= -\theta \ln(2S+1) + \left(\dfrac{3\theta - S(S+1)}{6\theta}\right)m^2 + \dfrac{S(S+1)(2S^2+2S+1)}{360\,\theta^3}\,m^4 - \frac{2}{3}S(S+1)\,hm + \dots .$

Thus,

$f_0 = -\theta \ln(2S+1)$, $a = 1 - \frac{1}{3}S(S+1)\theta^{-1}$, $b = \dfrac{S(S+1)(2S^2+2S+1)}{90\,\theta^3}$, $c = \frac{2}{3}S(S+1)$.

(d) Set $a = 0$ and $h = 0$ to find the critical point: $\theta_{\mathrm{c}} = \frac{1}{3}S(S+1)$ and $h_{\mathrm{c}} = 0$.

(e) At $\theta = \theta_{\mathrm{c}}$, we have $f = f_0 + \frac{1}{4}bm^4 - chm + \mathcal{O}(m^6)$. Extremizing with respect to m, we obtain $m = (ch/b)^{1/3}$. Thus,

$$m(\theta_{\mathrm{c}}, h) = \left(\dfrac{60}{2S^2 + 2S + 1}\right)^{1/3} \theta\, h^{1/3} .$$

(2) The Blume-Capel model is a $S = 1$ Ising model described by the Hamiltonian

$$\hat{H} = -\frac{1}{2}\sum_{i,j} J_{ij}\, S_i\, S_j + \Delta \sum_i S_i^2 ,$$

where $J_{ij} = J(\boldsymbol{R}_i - \boldsymbol{R}_j)$ and $S_i \in \{-1, 0, +1\}$. The mean field theory for this model is discussed in section 7.11 of the Lecture Notes, using the 'neglect of fluctuations' method. Consider instead a variational density matrix approach. Take $\varrho(S_1, \dots, S_N) = \prod_i \tilde{\varrho}(S_i)$, where

$$\tilde{\varrho}(S) = \left(\dfrac{n+m}{2}\right)\delta_{S,+1} + (1-n)\,\delta_{S,0} + \left(\dfrac{n-m}{2}\right)\delta_{S,-1} .$$

   (a) Find $\langle 1 \rangle$, $\langle S_i \rangle$, and $\langle S_i^2 \rangle$.

   (b) Find $E = \mathsf{Tr}\,(\varrho H)$.

   (c) Find $S = -k_{\mathrm{B}}\mathsf{Tr}\,(\varrho \ln \varrho)$.

   (d) Adimensionalizing by writing $\theta = k_{\mathrm{B}}T/\hat{J}(0)$, $\delta = \Delta/\hat{J}(0)$, and $f = F/N\hat{J}(0)$, find the dimensionless free energy per site $f(m, n, \theta, \delta)$.

   (e) Write down the mean field equations.

   (f) Show that $m = 0$ always permits a solution to the mean field equations, and find $n(\theta, \delta)$ when $m = 0$.

(g) To find θ_c, set $m = 0$ but use both mean field equations. You should recover eqn. 7.322 of the Lecture Notes.

(h) Show that the equation for θ_c has two solutions for $\delta < \delta_*$ and no solutions for $\delta > \delta_*$, and find the value of δ_*.[1]

(i) Assume $m^2 \ll 1$ and solve for $n(m, \theta, \delta)$ using one of the mean field equations. Plug this into your result for part (d) and obtain an expansion of f in terms of powers of m^2 alone. Find the first order line. You may find it convenient to use `Mathematica` here.

Solution :

(a) From the given expression for $\tilde{\varrho}$, we have

$$\langle 1 \rangle = 1 \quad , \quad \langle S \rangle = m \quad , \quad \langle S^2 \rangle = n ,$$

where $\langle A \rangle = \mathsf{Tr}(\tilde{\varrho} A)$.

(b) From the results of part (a), we have

$$
\begin{aligned}
E &= \mathsf{Tr}(\tilde{\varrho}\, \hat{H}) \\
&= -\tfrac{1}{2} N \hat{J}(0)\, m^2 + N\Delta\, n ,
\end{aligned}
$$

assuming $J_{ii} = 0$ for al i.

(c) The entropy is

$$
\begin{aligned}
S &= -k_{\mathrm{B}} \mathsf{Tr}\left(\varrho \ln \varrho\right) \\
&= -Nk_{\mathrm{B}}\left\{ \left(\frac{n-m}{2}\right) \ln\left(\frac{n-m}{2}\right) + (1-n)\ln(1-n) + \left(\frac{n+m}{2}\right) \ln\left(\frac{n+m}{2}\right) \right\} .
\end{aligned}
$$

(d) The dimensionless free energy is given by

$$f(m,n,\theta,\delta) = -\tfrac{1}{2}m^2 + \delta n + \theta\left\{ \left(\frac{n-m}{2}\right) \ln\left(\frac{n-m}{2}\right) + (1-n)\ln(1-n) + \left(\frac{n+m}{2}\right) \ln\left(\frac{n+m}{2}\right) \right\} .$$

(e) The mean field equations are

$$
\begin{aligned}
0 &= \frac{\partial f}{\partial m} = -m + \tfrac{1}{2}\theta \ln\left(\frac{n-m}{n+m}\right) \\
0 &= \frac{\partial f}{\partial n} = \delta + \tfrac{1}{2}\theta \ln\left(\frac{n^2 - m^2}{4\,(1-n)^2}\right) .
\end{aligned}
$$

---

[1]This problem has been corrected: (θ_*, δ_*) is not the tricritical point.

These can be rewritten as

$$m = n \tanh(m/\theta)$$
$$n^2 = m^2 + 4(1-n)^2 e^{-2\delta/\theta} .$$

(f) Setting $m = 0$ solves the first mean field equation always. Plugging this into the second equation, we find

$$n = \frac{2}{2 + \exp(\delta/\theta)} .$$

(g) If we set $m \to 0$ in the first equation, we obtain $n = \theta$, hence

$$\theta_c = \frac{2}{2 + \exp(\delta/\theta_c)} .$$

(h) The above equation may be recast as

$$\delta = \theta \ln\left(\frac{2}{\theta} - 2\right)$$

with $\theta = \theta_c$. Differentiating, we obtain

$$\frac{\partial \delta}{\partial \theta} = \ln\left(\frac{2}{\theta} - 2\right) - \frac{1}{1-\theta} \qquad \Longrightarrow \qquad \theta = \frac{\delta}{\delta + 1} .$$

Plugging this into the result for part (g), we obtain the relation $\delta\, e^{\delta + 1} = 2$, and numerical solution yields the maximum of $\delta(\theta)$ as

$$\theta_* = 0.3164989\ldots \qquad , \qquad \delta = 0.46305551\ldots .$$

This is *not* the tricritical point.

(i) Plugging in $n = m/\tanh(m/\theta)$ into $f(n, m, \theta, \delta)$, we obtain an expression for $f(m, \theta, \delta)$, which we then expand in powers of m, obtaining

$$f(m, \theta, \delta) = f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 + \tfrac{1}{6}cm^6 + \mathcal{O}(m^8) .$$

We find

$$a = \frac{2}{3\theta}\left\{\delta - \theta \ln\left(\frac{2(1-\theta)}{\theta}\right)\right\}$$

$$b = \frac{1}{45\,\theta^3}\left\{4(1-\theta)\,\theta \ln\left(\frac{2(1-\theta)}{\theta}\right) + 15\theta^2 - 5\theta + 4\delta(\theta - 1)\right\}$$

$$c = \frac{1}{1890\,\theta^5(1-\theta)^2}\left\{24\,(1-\theta)^2\,\theta \ln\left(\frac{2(1-\theta)}{\theta}\right) + 24\delta(1-\theta)^2 + \theta\left(35 - 154\,\theta + 189\,\theta^2\right)\right\} .$$

The tricritical point occurs for $a = b = 0$, which yields

$$\theta_t = \tfrac{1}{3} \qquad , \qquad \delta_t = \tfrac{2}{3} \ln 2 \ .$$

If, following Landau, we consider terms only up through order m^6, we predict a first order line given by the solution to the equation

$$b = -\tfrac{4}{\sqrt{3}} \sqrt{ac} \ .$$

The actual first order line is obtained by solving for the locus of points (θ, δ) such that $f(m, \theta, \delta)$ has a degenerate minimum, with one of the minima at $m = 0$ and the other at $m = \pm m_0$. The results from Landau theory will coincide with the exact mean field solution at the tricritical point, where the $m_0 = 0$, but in general the first order lines obtained by the exact mean field theory solution and by a truncated sixth order Landau expansion of the free energy will differ.

Solution Set #9

(1) Consider a two-state Ising model, with an added quantum dash of flavor. You are invited to investigate the *transverse Ising model*, whose Hamiltonian is written

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

where the σ_i^α are Pauli matrices:

$$\sigma_i^x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_i \quad , \qquad \sigma_i^z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_i .$$

(a) Using the trial density matrix,

$$\varrho_i = \tfrac{1}{2} + \tfrac{1}{2} m_x \, \sigma_i^x + \tfrac{1}{2} m_z \, \sigma_i^z$$

on each site, compute the mean field free energy $F/N\hat{J}(0) \equiv f(\theta, h, m_x, m_z)$, where $\theta = k_{\mathrm{B}}T/\hat{J}(0)$, and $h = H/\hat{J}(0)$. *Hint: Work in an eigenbasis when computing* $\mathrm{Tr}\,(\varrho \ln \varrho)$.

(b) Derive the mean field equations for m_x and m_z.

(c) Show that there is always a solution with $m_x = 0$, although it may not be the solution with the lowest free energy. What is $m_z(\theta, h)$ when $m_x = 0$?

(d) Show that $m_z = h$ for all solutions with $m_x \neq 0$.

(e) Show that for $\theta \leq 1$ there is a curve $h = h^*(\theta)$ below which $m_x \neq 0$, and along which m_x vanishes. That is, sketch the mean field phase diagram in the (θ, h) plane. Is the transition at $h = h^*(\theta)$ first order or second order?

(f) Sketch, on the same plot, the behavior of $m_x(\theta, h)$ and $m_z(\theta, h)$ as functions of the field h for fixed θ. Do this for $\theta = 0$, $\theta = \tfrac{1}{2}$, and $\theta = 1$.

Solution :

49

(a) We have $\text{Tr}\,(\varrho\,\sigma^x) = m_x$ and $\text{Tr}\,(\varrho\,\sigma^z) = m_z$. The eigenvalues of ϱ are $\frac{1}{2}(1 \pm m)$, where $m = (m_x^2 + m_z^2)^{1/2}$. Thus,

$$f(\theta, h, m_x, m_z) = -\tfrac{1}{2}m_x^2 - hm_z + \theta\left[\frac{1+m}{2}\ln\left(\frac{1+m}{2}\right) + \frac{1-m}{2}\ln\left(\frac{1-m}{2}\right)\right].$$

(b) Differentiating with respect to m_x and m_z yields

$$\frac{\partial f}{\partial m_x} = 0 = -m_x + \frac{\theta}{2}\ln\left(\frac{1+m}{1-m}\right)\cdot\frac{m_x}{m}$$

$$\frac{\partial f}{\partial m_z} = 0 = -h + \frac{\theta}{2}\ln\left(\frac{1+m}{1-m}\right)\cdot\frac{m_z}{m}.$$

Note that we have used the result

$$\frac{\partial m}{\partial m_\mu} = \frac{m_\mu}{m}$$

where m_α is any component of the vector $\boldsymbol{m}$.

(c) If we set $m_x = 0$, the first mean field equation is satisfied. We then have $m_z = m\,\text{sgn}(h)$, and the second mean field equation yields $m_z = \tanh(h/\theta)$. Thus, in this phase we have

$$m_x = 0 \qquad , \qquad m_z = \tanh(h/\theta)\,.$$

(d) When $m_x \neq 0$, we divide the first mean field equation by m_x to obtain the result

$$m = \frac{\theta}{2}\ln\left(\frac{1+m}{1-m}\right),$$

which is equivalent to $m = \tanh(m/\theta)$. Plugging this into the second mean field equation, we find $m_z = h$. Thus, when $m_x \neq 0$,

$$m_z = h \qquad , \qquad m_x = \sqrt{m^2 - h^2} \qquad , \qquad m = \tanh(m/\theta)\,.$$

Note that the length of the magnetization vector, m, is purely a function of the temperature θ in this phase and thus does not change as h is varied when θ is kept fixed. What does change is the canting angle of $\boldsymbol{m}$, which is $\alpha = \tan^{-1}(h/m)$ with respect to the $\hat{z}$ axis.

(e) The two solutions coincide when $m = h$, hence

$$h = \tanh(h/\theta) \qquad \Longrightarrow \qquad \theta^*(h) = \frac{2h}{\ln\left(\frac{1+h}{1-h}\right)}\,.$$

Inverting the above transcendental equation yields $h^*(\theta)$. The component m_x, which serves as the order parameter for this system, vanishes smoothly at $\theta = \theta_c(h)$. The transition is therefore second order.
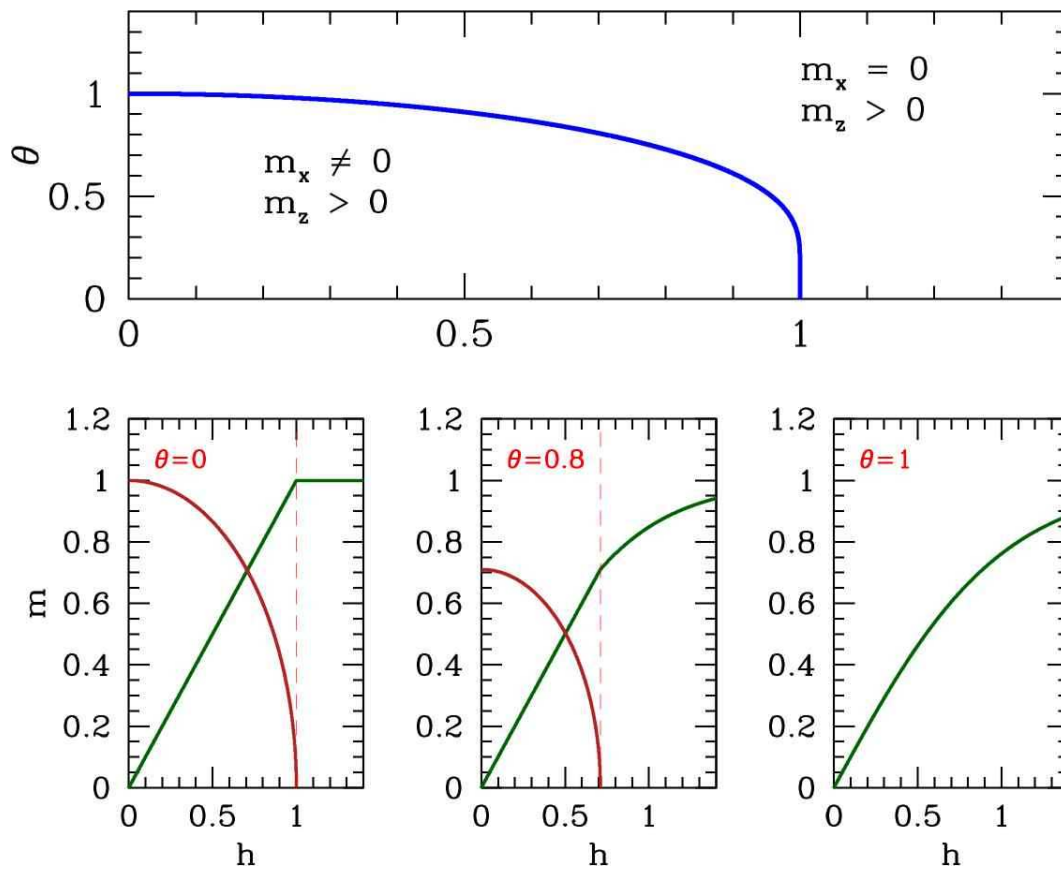
(f) See Fig. 9.1.

Figure 8.9: Solution to the mean field equations for problem 2. Top panel: phase diagram. The region within the thick blue line is a canted phase, where $m_x \neq 0$ and $m_z = h > 0$; outside this region the moment is aligned along $\hat{z}$ and $m_x = 0$ with $m_z = \tanh(h/\theta)$.

Final Examination

(1) [40 points total] Consider a noninteracting gas of bosons in d dimensions. Let the single particle dispersion be $\varepsilon(\boldsymbol{k}) = A\,|\boldsymbol{k}|^\sigma$, where $\sigma > 0$.

(a) Find the single particle density of states per unit volume $g(\varepsilon)$. Show that $g(\varepsilon) = C\,\varepsilon^{p-1}\,\Theta(\varepsilon)$, and find C and p in terms of A, d, and σ. You may abbreviate the total solid angle in d dimensions as $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$.

We have

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

and hence

$$g(\varepsilon) = (2\pi)^{-d}\Omega_d\,k^{d-1}\,\frac{dk}{d\varepsilon} = C\,\varepsilon^{p-1}\;,$$

where $p = d/\sigma$ and

$$C = \frac{\Omega_d\,A^{-d/\sigma}}{\sigma(2\pi)^d} = \frac{A^{-d/\sigma}}{2^{d-1}\pi^{d/2}\,\Gamma(d/2)\,\sigma}\;.$$

(b) Under what conditions will there be a finite temperature T_{c} for Bose condensation?

The number density is

$$n(T,z) = \int\limits_0^\infty d\varepsilon\;\frac{g(\varepsilon)}{z^{-1}\,e^{\beta\varepsilon} - 1} = C\,\Gamma(p)\,\beta^{-p}\,\mathrm{Li}_p(z)\;.$$

The RHS is a monotonically increasing function of the fugacity z. It vanishes for $z = 0$. In the limit $z \to 1^-$, the RHS diverges for $p \le 1$. In this case, we can invert this equation to obtain a unique solution for $z(T, n)$. In this case, there is no Bose condensation. If $p > 1$, the RHS is finite for $z = 1$, which establishes a maximum density $n_{\mathrm{max}}(T)$ at each temperature, above which the system must be in a condensed phase. Thus, the criterion for a finite T_{c} is $p > 1$, *i.e.* $d > \sigma$.

(c) For $T > T_{\mathrm{c}}$, find an expression for the number density $n(T, z)$. You may find the following useful:

$$\int\limits_0^\infty d\varepsilon\, \frac{\varepsilon^{q-1}}{z^{-1}e^{\beta\varepsilon} - 1} = \Gamma(q)\,\beta^{-q}\,\mathsf{Li}_q(z)\,,$$

where $\mathsf{Li}_q(z) = \sum_{j=1}^\infty z^j/j^q$ is the polylogarithm function. Note that $\mathsf{Li}_q(1) = \zeta(q)$.

This has been computed in part (b) above: $n(T, z) = C\,\Gamma(p)\,(k_{\mathrm{B}}T)^p\,\mathsf{Li}_p(z)$.

(d) Assuming $T_{\mathrm{c}} > 0$, find an expression for $T_{\mathrm{c}}(n)$.

Set $z = 1$ and $T = T_{\mathrm{c}}$. We then have

$$k_{\mathrm{B}}T_{\mathrm{c}} = \left(\frac{n}{C\,\Gamma(p)\,\zeta(p)}\right)^{1/p}.$$

(e) For $T < T_{\mathrm{c}}$, find an expression for the condensate number density $n_0(T, n)$.

We set $z = 1$. Then $n_0 = n - n_{\mathrm{max}}(T)$, i.e.

$$n_0(T) = n \cdot \left\{1 - \left(\frac{T}{T_{\mathrm{c}}(n)}\right)^p\right\}.$$

where $T_{\mathrm{c}}(n)$ is given in part (d).

(f) For $T < T_{\mathrm{c}}$, compute the molar heat capacity at constant volume and particle number $c_{V,N}(T, n)$. Recall that $c_{V,N} = \frac{N_{\mathrm{A}}}{N}\left(\frac{\partial E}{\partial T}\right)_{V,N}$.

The energy density is

$$E = V\int\limits_0^\infty d\varepsilon\, \frac{\varepsilon\, g(\varepsilon)}{e^{\beta\varepsilon} - 1} = C\,V\,\Gamma(p+1)\,\zeta(p+1)\,(k_{\mathrm{B}}T)^{p+1}\,.$$

Thus,

$$C_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,N} = C\,k_{\mathrm{B}}\,V\,\Gamma(p+2)\,\zeta(p+1)\,(k_{\mathrm{B}}T)^p\,.$$

As we have derived above, the particle number is related to the critical temperature by

$$N = C\,V\,\Gamma(p)\,\zeta(p)\,(k_{\mathrm{B}}T_{\mathrm{c}})^p\,.$$

Therefore the molar heat capacity is

$$c_{V,N}(T, n) = \frac{N_{\mathrm{A}}}{N}\cdot C_{V,N} = R\cdot\frac{p(p+1)\,\zeta(p+1)}{\zeta(p)}\cdot\left(\frac{T}{T_{\mathrm{c}}(n)}\right)^p\,.$$

where $R = N_{\mathrm{A}}k_{\mathrm{B}}$ is the gas constant.

(g) For $T > T_c$, compute the molar heat capacity at constant volume and particle number $c_{V,N}(T, z)$.

In this regime,

$$N(T, V, z) = V \int_0^\infty d\varepsilon \, \frac{g(\varepsilon)}{z^{-1}e^{\beta\varepsilon} - 1} = C V \Gamma(p) \, (k_{\mathrm{B}}T)^p \, \mathrm{Li}_p(z)$$

$$E(T, V, z) = V \int_0^\infty d\varepsilon \, \frac{\varepsilon \, g(\varepsilon)}{z^{-1} \, e^{\beta\varepsilon} - 1} = C V \Gamma(p+1) \, (k_{\mathrm{B}}T)^{p+1} \, \mathrm{Li}_{p+1}(z) \, .$$

Now take the differentials:

$$dN = C V \Gamma(p) \, (k_{\mathrm{B}}T)^p \cdot \left\{ p \, \mathrm{Li}_p(z) \, \frac{dT}{T} + \mathrm{Li}_{p-1}(z) \, \frac{dz}{z} \right\}$$

$$dE = C V \Gamma(p+1) \, (k_{\mathrm{B}}T)^{p+1} \cdot \left\{ (p+1) \, \mathrm{Li}_{p+1}(z) \, \frac{dT}{T} + \mathrm{Li}_p(z) \, \frac{dz}{z} \right\} \, .$$

Since $dN = 0$, we can use the first of these to solve for dz in terms of dT:

$$\left. \frac{dz}{z} \right|_N = -\frac{p \, \mathrm{Li}_p(z)}{\mathrm{Li}_{p-1}(z)} \cdot \frac{dT}{T}.$$

Inserting this into the equation for dE, we have

$$dE \big|_N = C V \Gamma(p+1) \, (k_{\mathrm{B}}T)^{p+1} \cdot \left\{ (p+1) \, \mathrm{Li}_{p+1}(z) - \frac{p \, \mathrm{Li}_p^2(z)}{\mathrm{Li}_{p-1}(z)} \right\} \cdot \frac{dT}{T}$$

$$= p N k_{\mathrm{B}} T \cdot \left\{ \frac{(p+1) \, \mathrm{Li}_{p+1}(z)}{\mathrm{Li}_p(z)} - \frac{p \, \mathrm{Li}_p(z)}{\mathrm{Li}_{p-1}(z)} \right\} \cdot \frac{dT}{T} \, ,$$

and hence

$$c_{V,N}(T, z) = p R \cdot \left\{ \frac{(p+1) \, \mathrm{Li}_{p+1}(z)}{\mathrm{Li}_p(z)} - \frac{p \, \mathrm{Li}_p(z)}{\mathrm{Li}_{p-1}(z)} \right\} \, .$$

(h) Show that under certain conditions the heat capacity is discontinuous at T_c, and evaluate $c_{V,N}(T_c^\pm)$ just above and just below the transition.

Setting $z = 1$ and $T = T_c$, the results from parts (f) and (g) yield

$$c_{V,N}(T_c^-) = \frac{p(p+1) \, \zeta(p+1) R}{\zeta(p)}$$

$$c_{V,N}(T_c^+) = \frac{p(p+1) \, \zeta(p+1) R}{\zeta(p)} - \frac{p^2 \zeta(p) R}{\zeta(p-1)} \, .$$

Subtracting these values we obtain the discontinuity at the transition,

$$\Delta c \equiv c_{V,N}(T_c^+) - c_{V,N}(T_c^-) = -\frac{p^2\,\zeta(p)\,R}{\zeta(p-1)}\,.$$

For $1 < p < 2$ we have $T_c > 0$ and $\Delta c = 0$, since $\zeta(p-1) = \infty$. For $p > 2$, however, there is a finite discontinuity in the specific heat at the transition.

(2) [30 points total] Consider the following model Hamiltonian,

$$\hat{H} = \sum_{\langle ij \rangle} E(\sigma_i, \sigma_j)\,,$$

where each σ_i may take on one of three possible values, and

$$E(\sigma, \sigma') = \begin{pmatrix} -J & +J & 0 \\ +J & -J & 0 \\ 0 & 0 & +K \end{pmatrix}\,,$$

with $J > 0$ and $K > 0$. Consider a variational density matrix $\varrho_v(\sigma_1, \ldots, \sigma_N) = \prod_i \tilde{\varrho}(\sigma_i)$, where the normalized single site density matrix has diagonal elements

$$\tilde{\varrho}(\sigma) = \left(\frac{n+m}{2}\right)\delta_{\sigma,1} + \left(\frac{n-m}{2}\right)\delta_{\sigma,2} + (1-n)\,\delta_{\sigma,3}\,.$$

(a) What is the global symmetry group for this Hamiltonian?

The global symmetry group is $\mathbb{Z}_2$. If we label the spin values as $\sigma \in \{1, 2, 3\}$, then the group elements can be written as permutations, $1 = \left(\begin{smallmatrix}123\\123\end{smallmatrix}\right)$ and $\mathcal{J} = \left(\begin{smallmatrix}123\\213\end{smallmatrix}\right)$, with $\mathcal{J}^2 = 1$.

(b) Evaluate $E = \text{Tr}\left(\varrho_v\,\hat{H}\right)$.

For each nearest neighbor pair (ij), the distribution of $\{\sigma_i \sigma_j\}$ is according to the product $\tilde{\varrho}(\sigma_i)\,\tilde{\varrho}(\sigma_j)$. Thus, we have

$$E = \tfrac{1}{2}NzJ\sum_{\sigma,\sigma'}\tilde{\varrho}(\sigma)\,\tilde{\varrho}(\sigma')\,\varepsilon(\sigma,\sigma')$$

$$= \tfrac{1}{2}NzJ\cdot\left\{\overbrace{\left(\frac{n+m}{2}\right)^2}^{\tilde{\varrho}^2(1)}(-J)+\overbrace{\left(\frac{n-m}{2}\right)^2}^{\tilde{\varrho}^2(2)}(-J)+\overbrace{2\left(\frac{n+m}{2}\right)\left(\frac{n-m}{2}\right)}^{2\,\tilde{\varrho}(1)\,\tilde{\varrho}(2)}(+J)+\overbrace{(1-n)^2}^{\tilde{\varrho}^2(3)}(+K)\right\}$$

$$= -\tfrac{1}{2}Nz\left[Jm^2 - K(1-n)^2\right]\,.$$

(c) Evaluate $S = -k_{\mathrm{B}} \, \mathsf{Tr} \, (\varrho_{\mathrm{v}} \ln \varrho_{\mathrm{v}})$.

The entropy is

$$S = -Nk_{\mathrm{B}} \, \mathsf{Tr} \, \left(\tilde{\varrho} \ln \tilde{\varrho} \right)$$

$$= -Nk_{\mathrm{B}} \left\{ \left(\frac{n+m}{2} \right) \ln \left(\frac{n+m}{2} \right) + \left(\frac{n-m}{2} \right) \ln \left(\frac{n-m}{2} \right) + (1-n) \ln(1-n) \right\}.$$

(d) Adimensionalize by writing $\theta = k_{\mathrm{B}}T/zJ$ and $c = K/J$, where z is the lattice coordination number. Find $f(n, m, \theta, c) = F/NzJ$.

This can be solved by inspection from the results of parts (b) and (c):

$$f = -\tfrac{1}{2}m^2 + \tfrac{1}{2}c \, (1-n)^2 + \theta \left[\left(\frac{n+m}{2} \right) \ln \left(\frac{n+m}{2} \right) + \left(\frac{n-m}{2} \right) \ln \left(\frac{n-m}{2} \right) + (1-n) \ln(1-n) \right].$$

(e) Find all the mean field equations.

There are two mean field equations, obtained by extremizing with respect to n and to m, respectively:

$$\frac{\partial f}{\partial n} = 0 = c \, (n-1) + \tfrac{1}{2}\theta \, \ln \left(\frac{n^2 - m^2}{4 \, (1-n)^2} \right)$$

$$\frac{\partial f}{\partial m} = 0 = -m + \tfrac{1}{2}\theta \, \ln \left(\frac{n-m}{n+m} \right).$$

These may be recast as

$$n^2 = m^2 + 4 \, (1-n)^2 \, e^{-2c(n-1)/\theta}$$

$$m = n \tanh(m/\theta) \, .$$

(f) Find an equation for the critical temperature θ_{c}, and show graphically that it has a unique solution.

To find θ_{c}, we take the limit $m \to 0$. The second mean field equation then gives $n = \theta$. Substituting this into the first mean field equation yields

$$\theta = 2 \, (1-\theta) \, e^{-2c(\theta-1)/\theta} \, .$$

If we define $u \equiv \theta^{-1} - 1$, this equation becomes

$$2u = e^{-cu} \, .$$

It is clear that for $c > 0$ this equation has a unique solution, since the LHS is monotonically increasing and the RHS is monotonically decreasing, and the difference changes sign for some $u > 0$. The low temperature phase is the ordered phase, which spontaneously breaks the aforementioned $\mathbb{Z}_2$ symmetry. In the high temperature phase, the $\mathbb{Z}_2$ symmetry is unbroken.

(3) [30 points total] Provide clear, accurate, and brief answers for each of the following:

(a) Explain what is meant by (i) recurrent, (ii) ergodic, and (iii) mixing phase flows.

(i) In a recurrent system, for every neighborhood $\mathcal{N}$ of phase space there exists a point $\varphi_0 \in \mathcal{N}$ which will return to $\mathcal{N}$ after a finite number of application of the τ-advance map g_τ, where τ is finite. (ii) An ergodic system is one in which time averages may be replaced by phase space averages. (iii) A mixing system is one for which, as $t \to \infty$, the *instantaneous* time average of a quantity may be replaced by its phase space average.

(b) Why is it more accurate to compute response functions $\chi_{ij} = \partial m_i / \partial H_j$ rather than correlation functions $C_{ij} = \langle \sigma_i \, \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle$ in mean field theory? What is the exact thermodynamic relationship between χ_{ij} and C_{ij}?

Within the conventional mean field theory approach we have discussed, $C_{ij} = 0$ because each site is independent, as the trial density matrix is a direct product of individual single site density matrices. Extremizing the free energy, though yields a set of coupled nonlinear equations for m_i in terms of all the local fields $\{H_j\}$, so χ_{ij} is nonzero. Another way to look at it is that $\chi_{ij} = -\partial^2 F / \partial H_i \, \partial H_j$, and the variational approach assures us that F is accurate up to terms of order $(\delta\rho)^2$, where $\rho = \rho_{\rm v} + \delta\rho$. Using this expression, we see that C_{ij} is only accurate up to terms of order $\delta\rho$. The exact relation between correlation and response functions is $C_{ij} = k_{\rm B} T \chi_{ij}$.

(c) What is a tricritical point?

A critical point $T_{\rm c}$ may be extended to a critical *curve* in an extended parameter space (T, λ), where λ is an additional parameter which does not explicitly break the symmetry group G which is spontaneously broken in the ordered phase. At a specific point $(T_{\rm t}, \lambda_{\rm t})$ along this critical curve, the transition may change from first to second order. The confluence of the first and second order boundaries lies at a *tricritical point*.

(d) Sketch what the radial distribution function $g(r)$ looks like for a simple fluid like liquid Argon. Identify any relevant length scales, as well as the proper limiting value for $g(r \to \infty)$.

See Fig. 6.13 of the Lecture Notes. Note that $g(\infty) = 1$, and $g(r) = 0$ for $r < a$, where a is the hard sphere core diameter.

(e) Discuss the First Law of Thermodynamics from the point of view of statistical mechanics.

The thermodynamic energy is $E = \sum_n P_n E_n$, where $P_n = Z^{-1} e^{-E_n / k_{\rm B} T}$. Thus $dE = \dbar Q = \dbar W$, with $\dbar Q = \sum_n E_n \, dP_n$ and $\dbar W = -\sum_n P_n \, dE_n$. The differential heat is due to changes in the probability distribution P_n, while the differential work is due to changes in the energy eigenvalues E_n.

(f) Explain what is meant by the Dulong-Petit limit of the heat capacity of a solid.

In the high temperature limit (but below the melting point), the ion cores of any solid behave classically. Each of the N ion cores has $2d$ degrees of freedom: d coordinates and d momenta. The potential energy can be modeled as a harmonic potential (in all the coordinates), and the kinetic energy is the usual ballistic expression. Thus, from equipartition, the energy is $N \times 2d \times \frac{1}{2}k_{\mathrm{B}}T = Ndk_{\mathrm{B}}T$, and the heat capacity in this limit is $C_{V,N} = Ndk_{\mathrm{B}}$.