Exercises on Thermodynamics and Statistical Mechanics

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1. (Thermodynamics)
(a) Recall the condition that a differential of the form $df = g(u,v)du + h(u,v)dv$ is exact if $\partial g/\partial v = \partial h/\partial u$. The first law tells us that dU is exact. Now, U may be considered a function of any two of the three variables P, V, T, the third being obtained from the equation of state. With $U = U(P,V)$ we obtain

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV.$$

The exactness of dU leads immediately to

$$\frac{\partial}{\partial V}\left[\left(\frac{\partial U}{\partial P}\right)_V\right]_P = \frac{\partial}{\partial P}\left[\left(\frac{\partial U}{\partial V}\right)_P\right]_V.$$

In an infinitesimal, reversible transformation, $dW = pdV$, so the first law becomes $dQ = dU + PdV$. By considering, in turn, $U = U(P,V)$, $U = U(P,T)$, $U = U(V,T)$, derive three different equations for dQ.
(b) The specific heat at constant volume $C_V \equiv \left(\frac{\Delta Q}{\Delta T}\right)_V$. Show, from the dQ equations that $C_V = \left(\frac{\partial U}{\partial T}\right)_V$. A quantity H called the *enthalpy* is defined by $H = U + PV$. The specific heat at constant pressure is $C_V \equiv \left(\frac{\Delta Q}{\Delta T}\right)_P$. Obtain an expression for this in terms of the derivative of the enthalpy.

2. (Entropy).
(a) Give Boltzmann's statistical definition of entropy and describe its physical meaning.
(b) A two level system of $N = n_1 + n_2$ particles is distributed among two states 1 and 2 with corresponding energies E_1 and E_2. The system is in contact with a heat reservoir T. If a single quantum emission into the reservoir occurs, population changes $n_2 \rightarrow n_2 - 1$ and $n_1 \rightarrow n_1 + 1$ take place. Assuming both $n_1 >> 1$ and $n_2 >> 1$, calculate the entropy change of
(a) the two level system,
(b) the reservoir
(c) finally, from the above, find the ratio $\frac{n_2}{n_1}$.
Hint: How many configurations are there of the original system? The final system? What is the entropy change? For part (b), remember the second law. What is the energy change of the reservoir?

3. (Ergodic hypothesis)
Consider a harmonic oscillator with Hamiltonian

$$\mathcal{H}(p, q) = \frac{p^2}{2} + \frac{q^2}{2}.$$

Show that the phase space trajectory with energy E will, on average, spend equal time in all regions of the constant energy surface $\Gamma(E)$. (Hint: Write $p = r\cos\phi;\ q = r\sin\phi$).

4. (Ensembles)
A classical harmonic oscillator

$$\mathcal{H}(p, q) = \frac{p^2}{2m} + \frac{Kq^2}{2}$$

is in thermal equilibrium with a heat bath at temperature T. Calculate the partition function for the oscillator in the canonical ensemble, and show that

$$\langle E \rangle = kT;\ \langle (E - \langle E \rangle)^2 \rangle = kT^2.$$

5. (One-dimensional Ising model)
For the 1-dimensional Ising model,
(a) the transfer matrix is

$$P = \begin{pmatrix} e^{\beta(J+H)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-H)} \end{pmatrix}$$

Show that

$$\lambda_{1,2} = e^{\beta J}[\cosh(\beta H) \pm \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}].$$

(b) The Helmholtz free energy per spin is

$$-\beta A(T) = \lim_{N\to\infty} 1/N \log Z_N =$$
$$\beta J + \log[\cosh(\beta H) + \sqrt{\cosh^2(\beta H) - 2e^{-2\beta J}\sinh^2(2\beta J)}].$$

The magnetisation per spin is

$$M(H,T) = \frac{\sinh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}},$$

and so the spontaneous magnetisation, $M(0,T)$ vanishes for all $T > 0$.
Calculate the susceptibility, $\chi = \frac{\partial M}{\partial H}$, and show that, in zero-field ($H = 0$) there is no singularity for $T > 0$.

6. (Two-dimensional Ising model)
For the two-dimensional Ising model, calculate the internal energy

$$U = -kT^2 \frac{\partial}{\partial T}\frac{\psi}{kT}$$

and hence show that it diverges logarithmically at the origin $\theta_1 = \theta_2 = 0$. Hence show that the specific heat $C_V = \frac{\partial U}{\partial T}$ has a logarithmic divergence.

7. (Enumeration)
Let $n(r)$ be the number of graphs embedable on a lattice such that (a) no bond can occur more than once, and (b) only an even number of bonds can meet at a vertex (thus 2 or 4 for the square lattice). Derive the zero-field partition function for the one-dimensional Ising model on (a) a periodic (closed) chain and (b) an open chain, from the combinatorial formula derived in lectures, viz:

$$Z_N(T) = 2^N (\cosh K)^{Nq/2} \sum_{r=0}^{\infty} n(r)(\tanh K)^r,$$

where q is the co-ordination number of the lattice.

8. (More enumeration)
Generalise the argument given in lectures to show that the partition function of the two-dimensional Ising model in a magnetic field H can be written

$$Z_N(T) = \exp(NKq/2 + N\beta H) \sum_{r,s=1}^{\infty} n_D(r,s)\exp(-2Kr)\exp(-s\beta H),$$

where $n_D(r,s)$ is the number of closed graphs of r bonds on the dual lattice enclosing s points of the original lattice.