Problem Set 1

Advanced Statistical Mechanics

Deadline: Tuesday, 19 Esfand, 23:59

1 Classical Thermodynamics

1.1 Entropy of Mixing

Calculate the entropy of mixing of two volumes V_A and V_B of an ideal gas of species A and B, respectively, both initially at the same temperature T and pressure P and, with a final volume $V = V_A + V_B$

1.2 Photon Gas Carnot Cycle

The aim of this problem is to obtain the black-body radiation relation, $E(T, V) \propto VT^4$, starting from the equation of state, by performing an infinitesimal Carnot cycle on the photon gas.

Figure 1: PV Diagram
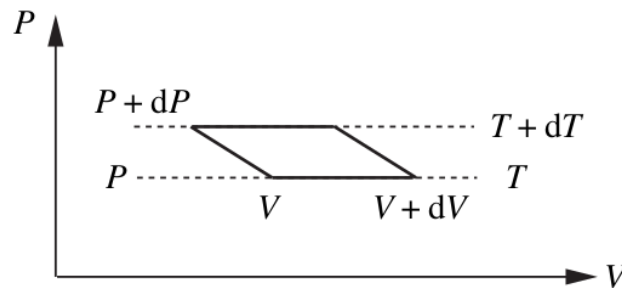
(a) Express the work done, W, in the above cycle, in terms of $\mathrm{d}V$ and $\mathrm{d}P$.

(b) Express the heat absorbed, Q, in expanding the gas along an isotherm, in terms of $P, \mathrm{d}V$, and an appropriate derivative of $E(T, V)$.

(c) Using the efficiency of the Carnot cycle, relate the above expression for W and W to T and $\mathrm{d}T$.

(d) Observations indicates that the pressure of the photon gas is given by $P = AT^4$, where $A = \pi^2 k_B^2 / 45 (\hbar c)^3$ is a constant. Use this information to obtain $E(T, V)$, assuming

$E(0, V) = 0$.
(e) Find the relation describing the adiabatic paths in the above cycle.

1.3 Maximum Entropy Principle

Entropy has the maximum value it can have consistent with constraints on the system, an extremum principle characterizing equilibrium. Because of the randomness of molecular motions, fluctuation in state variables occur about their equilibrium values. Equilibrium must be stable against fluctuation.

To do so, we make use of an oft-used theoretical device in thermodynamics, that of the composite system which consists of subsystem A and B, in contact with each other, surrounded by rigid adiabatic walls. Let A and B be separated by a partition that is moveable, permeable, and diathermic.

(a) The subsystems can exchange volume, particle and energy. they're also assumed to contain the same type of particles. Show the relation between δV_A, δV_B, δN_A, δN_B, δU_A and δU_B.

We consider the change in total system entropy ΔS under these variations to first and second order in small quantities, what we denote by $\Delta S = \delta S + \frac{1}{2}\delta^2 S$, where $S = S_A + S_B$

(b) In the equilibrium state, we know that $\delta S = 0$, write the first order variation δS in terms of δU_A, δV_A, and δN_A and some thermodynamic parameters and show that

$$T_A = T_B \qquad P_A = P_B \qquad \mu_A = \mu_B \tag{1}$$

(c) The change in system entropy up to second order in small quantities is given by the Taylor expansion of a multi-variable function. Calculate ΔS and then $\delta^2 S$.

(d) We require that second-order variations be negative for each subsystem. The key step is that, we can write

$$\delta\left(\frac{\partial S}{\partial U}\right) = \frac{\partial^2 S}{\partial U^2}\delta U + \frac{\partial^2 S}{\partial U \partial V}\delta V + \frac{\partial^2 S}{\partial U \partial N}\delta N \tag{2}$$

and the other parameters are the same. Show that

$$\delta^2 S = \delta U \delta\left(\frac{1}{T}\right) + \delta V \delta\left(\frac{P}{T}\right) - \delta N \delta\left(\frac{\mu}{T}\right) \tag{3}$$

By differentiating and recognizing that $T\delta S = \delta U + P\delta V - \mu\delta N$, we find

$$\delta^2 S = -\frac{1}{T}(\delta T\delta S - \delta P\delta V + \delta\mu\delta N) \tag{4}$$

The criterion for stability of the equilibrium state against fluctuations is thus

$$\delta T\delta S - \delta P\delta V + \delta\mu\delta N > 0 \tag{5}$$

2 Ensemble Theory

2.1 Classical Harmonic Oscillator

Consider N harmonic oscillators with coordinates and momenta $\{q_i, p_i\}$, and subject to a Hamiltonian

$$\mathcal{H}(\{q_i, p_i\}) = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m} + \frac{m\omega^2 q_i^2}{2} \right) \tag{6}$$

(a) Calculate the entropy S, as a function of the total energy E.

(b) Calculate the energy E, and heat capacity C, as a function of temperature T, and N.

(c) Find the joint probability density $P(p, q)$ for a single oscillator. Hence calculate the mean kinetic energy, and mean potential energy for each oscillator.

2.2 Quantum Harmonic Oscillator

Consider N independent quantum oscillators subject to a Hamiltonian

$$\mathcal{H}(n_i) = \sum_{i=1}^{N} \hbar\omega \left(n_i + \frac{1}{2} \right) \tag{7}$$

where $n_i = 0, 1, 2, \cdots$ is the quantum occupation number for the ith oscillator. (a) Calculate the entropy S, as a function of the total energy E.

(b) Calculate the energy E, and heat capacity C as function of temperature T, and N.

(c) Find the probability $p(n)$ that a particular oscillator is in its nth quantum level.

(d) Comment on the difference between heat capacities for classical and quantum oscillators.

2.3 Curie Susceptibility

Consider N non-interacting quantized spins in a magnetic field $\mathbf{B} = B\hat{z}$ and at a temperature T. The work done by the field is given by BM_z, with a magnetization $M_z = \mu \sum_{i=1}^{N} m_i$. For each spin, m_i takes only the $2s + 1$ values $-s, -s+1, \cdots, s-1, s$.

(a) Calculate the Gibbs partition function $\mathcal{Z}(T, B)$.

(b) Calculate the Gibbs free energy $G(T, B)$, and show that for small B,

$$G(B) = G(0) - \frac{N\mu^2 s(s+1)B^2}{6k_B T} + \mathcal{O}(B^4) \tag{8}$$

(c) Calculate the zero field susceptibility $\chi = \frac{\partial M_z}{\partial B}|_{B=0}$ and show that it satisfies Curie's law

$$\chi = c/T \tag{9}$$

(d) Show that $C_B - C_M = cB^2/T^2$, where C_B and C_M are heat capacities at constant B and M, respectively.

2.4 Equipartition

Consider a system of particles in which the force between the particles is derivable from a potential which is a generalized homogeneous function of degree γ, that is

$$U(\lambda \mathbf{r}_1, \lambda \mathbf{r}_2, \cdots, \lambda \mathbf{r}_N) = \lambda^\gamma U(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) \tag{10}$$

Show that the equation of state for this system is of the form

$$PT^{-1+3/\gamma} = f\left(\frac{V}{N} T^{-3/\gamma}\right) \tag{11}$$

where $f(x)$ can be calculated (at least in principle) once U is specified.

2.5 Helmholtz Extensiveness

Making use of the fact that the Helmholtz free energy $F(N, V, T)$ of a thermodynamic system is an extensive property of the system, show that

$$N\left(\frac{\partial F}{\partial N}\right)_{V,T} + V\left(\frac{\partial F}{\partial V}\right)_{N,T} = F \tag{12}$$