Advanced Statistical Mechanics 171.703

Homework Assignment 4

Due date Friday, February 27

Reading. Chapters 24, 35, 36 in Landau; Chapter 6.5 in Pathria. R. Peierls, Phys. Rev. **54**, 918 (1938).

1. Grand canonical ensemble. The appropriate thermodynamic potential for a variable number of particles N is

$$\Omega = \Omega(T, V, \mu) = E - TS - \mu N.$$

The system has energy levels $\{E_{nN}\}$, which may (and does) depend on N.

(a) Show that maximization of entropy $S = -\sum_{nN} w_{nN} \log w_{nN}$, subject to constraints

$$\begin{array}{ll} \sum_{nN} w_{nN} = 1 & \text{(total probability)}, \\ \sum_{nN} w_{nN} E_{nN} = \bar{E} & \text{(mean energy)}, \\ \sum_{nN} w_{nN} N = \bar{N} & \text{(mean particle number)}, \end{array}$$

yields the probability distribution

$$w_{nN} = \frac{1}{\mathcal{Z}} \mathrm{e}^{-(E_{nN} - \mu N)/T}.$$

The normalization constant

$$\mathcal{Z}(T, V, \mu) = \sum_{nN} \mathrm{e}^{-(E_{nN} - \mu N)/T} = \sum_N Z_N \mathrm{e}^{\mu N/T}$$

is also known as the grand partition function.

(b) Show that the ensemble average $\bar{\Omega} = \bar{E} - T\bar{S} - \mu\bar{N}$ can be obtained directly from the normalization constant: $\bar{\Omega} = -T \log \mathcal{Z}$.

2. Chemical potential of a paramagnet. Consider a collection of N spins $S = 1/2$ in magnetic field H. (See Prob. 2 in Assignment 3.)

(a) Show that the chemical potential μ equals the Helmholtz free energy $F(T, H, N) = E - TS$ per particle. Thus determine μ at given T and H.

(b) Check that your answer makes sense in the limits $T \to +0$ and $T \to \infty$. Use the original definition of μ as the energy cost of inserting a particle *adiabatically*: $\mu = (\partial E/\partial N)_{S,H}$.

3. Specific heat of carbon dioxide. Prob. 6.27 in Pathria.