Problem Set 8

8.1 Chemical Equilibrium

Reif §8.12

8.2 Partial Pressure

Reif §8.14

8.3 Paramagnet

As a model of a paramagnet, one can consider a system of $N \gg 1$ localized particles with spin 1/2. We neglect magnetic interactions between the spins. The only contribution to the energy of is the Zeeman energy in an applied magnetic field,

$$E = -2\sum_{i=1}^{N} s_i \mu_B H,$$

where H is the magnetic field strength, μ_B is the Bohr magneton, and s_i takes the values $\pm 1/2$, and $i = 1, 2, \ldots, N$.

(a) Calculate the number of microstates $\Omega(E)$ in which the total energy of the N spins is between E and $E + \delta E$. Use the fact that the number of spins, N is large and take the Energy uncertainty δE large in comparison to the microscopic energy scale $\mu_B H$ but small in comparison to $N \mu_B H$.

(b) Use your answer to (a) to calculate the temperature T of the system of spins.

(c) Express the energy E, the entropy S, and the Helmholtz free energy F in terms of T.

(d) Calculate the canonical partition function $Z(T)$ for the same system of spins.

(e) Use your answer to (d) to calculate the energy E, the entropy S, and the Helmhotz free energy F.

8.4 Quantum Harmonic Oscillator

The energy levels of a quantum mechanical harmonic oscillator at a frequency ω are

$$\epsilon_n = \hbar\omega\left(\frac{1}{2} + n\right) \quad ,n = 0, 1, 2, \ldots$$

The canonical partition function $Z(T)$ of this harmonic oscillator is

$$Z(T) = \frac{1}{2\sinh(\hbar\omega/2kT)} \; .$$

In this exercise we'll take a different look at this calculation: We view each oscillation quantum as a "particle". The total energy of the system is given by the first equation above, but now "n" is interpreted as the number of particles.

(a) Calculate the "canonical partition function" $Z_n(T)$ for a harmonic oscillator with n oscillation quanta.

(b) Calculate the "grand canonical partition function" $\Xi(T, \mu)$, where μ is the "chemical potential" for the oscillation quanta. [You'll fix the value of μ in part (d) below.]

(c) Use your answer to (b) to calculate the average energy $\bar{E}(T, \mu)$ and the entropy $S(T, \mu)$ of the harmonic oscillator.

(d) Calculate the average energy and the entropy from the canonical parition function $Z(T)$. How do your answers compare to those of part (c)? What chemical potential should one choose for the oscillation quanta?

8.5 Equilibrium Fluctuations

The grand canonical ensemble describes a system for which the temperature T, the volume V, and the chemical potential μ are fixed. In the grand canonical ensemble the number of particles N is allowed to fluctuate.

(a) Express var N in terms of T, V, μ, and derivatives of the average particle $\bar{N}$ to T, V, and μ.

(b) Use thermodynamic relations to rewrite your answer in terms of the isothermal compressibility $\kappa = -(1/V)(\partial V/\partial p)_{T,N}$.

8.6 Grand Canonical Ensemble

Consider an ideal gas in a container of vlume V and at temperature T.

(a) Calculate the grand canonical partition function $\Xi(\mu, V, T)$ for this system.

(b) Make use of the relation $pV = kT \ln \Xi$ to express the chemical potential μ in terms of pressure p and the temperature T.

8.8: Email Questions

Email three questions