Lecture 12 - Ensembles

What's Important:
• ensembles
• spin - 1/2 particles in a magnetic field
Text: Reif
Demonstrations:
• magnet and compasses on an overhead projector
• magnetization and temperature - use Monel (Ni+Cu) at near a single compass; no effect at room temperature, but magnetized at liquid nitrogen temperatures.

Review

• Skip Chap. 4
• Skip Chap. 5, except Sec. 5.2, which was covered in Lec. 9
• Carry on to Chap. 6 - applications and results.

Ensembles

The previous lectures have investigated systems under a variety of conditions. Listed below are a few of the more commonly used conditions, and the names of the corresponding ensembles.

1. Completely isolated system or *microcanonical ensemble*
• particle number, volume and energy are all fixed, hence *NVE*
• system is in some small energy range E to $E + \Delta E$, with all states r in the range equally accessible
Defining P_r as the probability of finding the system in state r, one finds

$$P_r = 0 \qquad\qquad E_r > E + \Delta E$$
$$P_r = \text{constant} \qquad E \leq E_r \leq E + \Delta E$$
$$P_r = 0 \qquad\qquad E_r < E$$

2. System in thermal contact with a heat reservoir or *canonical ensemble*
• particle number, volume and temperature are all fixed, hence *NVT*
• energy of the system fluctuates
• all states are accessible, with varying probability.
The probability of occupying state r is then

$$P_r \propto \exp(-\beta E_r)$$
or

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

A variation of this ensemble has fixed pressure, rather than fixed volume, hence *isobaric-isothermal ensemble* or *NPT*

3. System can exchange energy and particles or *grand canonical ensemble*
-   chemical potential, volume and temperature are all fixed, hence *µVT*
-   particle number and energy of the system fluctuates
-   all states are accessible, with varying probability.
    $$P_r \quad \exp(-ßE_r + ßµN_r)$$

We treat the canonical ensemble in some detail in this lecture, and defer the grand canonical ensemble for two lectures.

Canonical ensemble (*NVT*)

The *NVT* ensemble is one which is free to exchange energy (but nothing else) with a heat reservoir, assume to be sufficiently large that any transfer of energy does not change its temperature. Hence, at equilibrium, the temperature of the system is determined by the temperature of the heat reservoir:
$$ß = \frac{\partial \ln \Omega'}{\partial E'} \tag{12.1}$$

What is the probability of finding the small system *A* in a state with energy E_r? For every state *r*, there are 1 x $\Omega'(E^o - E_r)$ states of the combined system *A + A'*, where
    $$E' = E^o - E_r.$$

Thus, the probability of *A+A'* having system *A* in state *r* is
    $$P_r = C \, \Omega'(E^o - E_r). \tag{12.2}$$

Since $E_r << E^o$, then $\ln\Omega'$ can be expanded in a Taylor series:
    $$\ln\Omega'(E^o - E_r) = \ln \Omega'(E^o) + \frac{\partial \ln \Omega'}{\partial E'}\bigg|_{E^o} (-E_r) + ...$$
which becomes, after using Eq. (12.1) for the temperature

    $$\Omega'(E^o - E_r) = \Omega'(E^o)e^{-ßE_r}. \tag{12.3}$$

Now, the first term on the right-hand side can be absorbed into the constant *C* of Eq. (12.2) to yield
    $$P_r = Ce^{-ßE_r}, \tag{12.4}$$

where $\exp(-ßE_r)$ is the Boltzmann factor. The normalization constant in Eq. (12.4) is simply determined by summing over the accessible states, to give:
    $$P_r = \frac{e^{-ßE_r}}{\sum_r e^{-ßE_r}} \tag{12.5}$$

For an observable y, the mean value can be determined from P_r through

$$\bar{y} = \sum_r y_r P_r = \frac{y_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$ (12.6)

where y_r is the value of y in the state r.

Example   Spin - 1/2 particle in a magnetic field

This system is treated earlier in Reif through Problems 2.4 and 3.3 using a Gaussian approximation to Ω. Here, the calculation is repeated using the Boltzmann factor.

Consider a single spin (nuclear, atomic, ...) which can have orientations   or   with respect to a magnetic field H. With energies
          $E_+ = -\mu H$ $E_- = +\mu H$

the probabilities of occurrence are
          $P_+ = $ [*prob. of spin up*] $\exp(+\beta\mu H)$
          $P_- = $ [*prob. of spin down*] $\exp(-\beta\mu H)$.

Defining
          $y = \beta\mu H$,
the sum of the probabilities becomes
          $P_+ + P_-$ $e^{+y} + e^{-y}$.

The mean value of the magnetic moment μ is thus

$$\bar{\mu} = \frac{\mu P_+ + (-\mu) P_-}{P_+ + P_-} = \mu \frac{e^y - e^{-y}}{e^y + e^{-y}} = \mu \tanh y$$ (12.7)

Clearly, $\bar{\mu}$ depends upon βH:

At low temperatures, βH is large, so that $\tanh y$ 1. Eq. (12.7) then says that $\bar{\mu}$ μ, and the spins are aligned: .

At high temperatures, βH is small, so that $\tanh y$ 0 (*i.e.*, $\tanh y$ y). Eq. (12.7) then says that $\bar{\mu}$ 0, and the spins are random: .

The magnetization $\overline{M}$ is the mean magnetic moment per unit volume
          $$\overline{M} = \frac{N\bar{\mu}}{V}.$$
Apart from a universal scaling factor, $\overline{M}$ just follows $\bar{\mu}$ as a function of temperature. At high temperatures or small y, we predict

$$\overline{\mu} = \mu \tanh y \qquad \mu y = \mu \frac{\mu H}{k_B T} = \frac{\mu^2 H}{k_B T}$$

This last relationship is called the Curie Law.

$$\overline{\mu} = \mu \tanh y \qquad \mu y = \mu \frac{\mu H}{k_B T} = \frac{\mu^2 H}{k_B T}$$