

## LECTURE 10

### Simple Applications of Statistical Mechanics

We have seen that if we can calculate the partition function

$$Z = \sum_r e^{-\beta E_r} \quad (1)$$

then we can derive just about anything we want to know from the partition function such as the mean internal energy, the entropy, the pressure, the Helmholtz free energy, the specific heat, etc. Let's give some examples of how this works.

#### Paramagnetism

You may remember from E&M that the magnetic behavior of materials usually arises from the angular momentum of the electrons. The electrons have 2 forms of angular momentum: spin and orbital. Classically their orbital angular momentum is associated with their orbital motion around the nucleus. Quantum mechanically the orbital angular momentum is associated with their spatial wavefunction. Even if an electron has zero orbital angular momentum, it still has acts like a tiny magnet and has a magnetic moment  $\approx \vec{\mu}_B$ . Associated with this magnetic moment is the spin angular momentum  $\hbar\vec{S}$  of the electron. Protons and neutrons also have angular momentum  $\hbar\vec{J}$  and magnetic moments  $\vec{\mu}$ . This gives rise to nuclear magnetic moments which are involved in NMR and MRI. The magnetic moment of an atom, ion or single elementary particle such as an electron or proton in free space is proportional to its angular momentum:

$$\vec{\mu} = g\mu_B\vec{J} = -\gamma\hbar\vec{J} \quad (2)$$

where the proportionality factor  $g$  is the "spectroscopic splitting" factor or just the  $g$  factor,  $\mu_B$  the Bohr magneton,  $\gamma$  the gyromagnetic ratio, and  $\hbar\vec{J}$  the total angular momentum. Rather than considering the case of arbitrary  $\vec{J}$  (see Reif 7.8, pages 257-262), let us begin by considering the simple case of spin-1/2 where  $J = 1/2$  and  $g = 2$ . Then the allowed quantum energy states are

$$\begin{aligned} E &= -\vec{\mu} \cdot \vec{H} \\ &= -g\mu_B\vec{J} \cdot \vec{H} \\ &= -g\mu_B J_z H \quad (\text{since } \vec{H} \parallel \hat{z}) \\ &= -2\mu_B(\pm\frac{1}{2})H \\ &= \pm\mu_B H \end{aligned} \quad (3)$$

where  $H$  is the external magnetic field. Let us also assume that we have  $N$  such independent ions or atoms all in contact with a heat reservoir at temperature  $T$ . A physical system that approximates this model is a metal with magnetic impurities like  $\text{Mn}^{2+}$ .

If we consider only one atom or ion, the partition function  $\zeta$  of that one atom or ion becomes

$$\zeta = \sum_{\text{all states } r} e^{-\beta E_r} = e^{\beta\mu_B H} + e^{-\beta\mu_B H} \quad (4)$$

and

$$Z = \zeta^N = \left( e^{\beta\mu_B H} + e^{-\beta\mu_B H} \right)^N \quad (5)$$

The mean energy can be calculated from

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial \ln \zeta}{\partial \beta} = -\frac{N}{\zeta} \mu_B H \left( e^{\beta\mu_B H} - e^{-\beta\mu_B H} \right) \quad (6)$$

$$\bar{E} = -N \mu_B H \frac{e^{\beta\mu_B H} - e^{-\beta\mu_B H}}{e^{\beta\mu_B H} + e^{-\beta\mu_B H}} \quad (7)$$

$$\bar{E} = -N \mu_B H \tanh \left( \frac{\mu_B H}{k_B T} \right) \quad (8)$$

The total magnetic moment or magnetization can be calculated from

$$\begin{aligned} \bar{M} &= N \bar{\mu} \\ &= N (P_{\uparrow} \mu_{\uparrow} + P_{\downarrow} \mu_{\downarrow}) \\ &= N \mu_B \frac{e^{\beta\mu_B H} - e^{-\beta\mu_B H}}{e^{\beta\mu_B H} + e^{-\beta\mu_B H}} \end{aligned} \quad (9)$$

where we used  $\mu_{\uparrow} = -\mu_{\downarrow} = \mu_B$ ,  $P_{\uparrow} = \exp(\beta\mu_B H)/\zeta$ , and  $P_{\downarrow} = \exp(-\beta\mu_B H)/\zeta$ . Thus

$$\bar{M} = N \mu_B \tanh \left( \frac{\mu_B H}{k_B T} \right) \quad (10)$$

Alternatively we can calculate the generalized force associated with the magnetic field. Recall that

$$dW = \bar{X} dx \quad (11)$$

and

$$\bar{X} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x} \quad (12)$$

From Reif 11.1 we find that magnetic work done *by* the sample is

$$dW = \vec{M} \cdot d\vec{H} \quad (13)$$

where  $\vec{M}$  is the magnetization. Suppose  $\vec{H}$  is pointing along the  $\hat{z}$  axis. We can identify  $H$  with the external parameter  $x$ , and  $M$ , the z-component of  $\vec{M}$ , with the generalized force. Then the generalized force is

$$\begin{aligned} M &= \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} \\ &= \frac{N}{\beta} \frac{\partial \ln \zeta}{\partial H} \\ &= N \mu_B \frac{e^{\beta\mu_B H} - e^{-\beta\mu_B H}}{e^{\beta\mu_B H} + e^{-\beta\mu_B H}} \\ &= N \mu_B \tanh \left( \frac{\mu_B H}{k_B T} \right) \\ &= -\frac{\bar{E}}{H} \end{aligned} \quad (14)$$

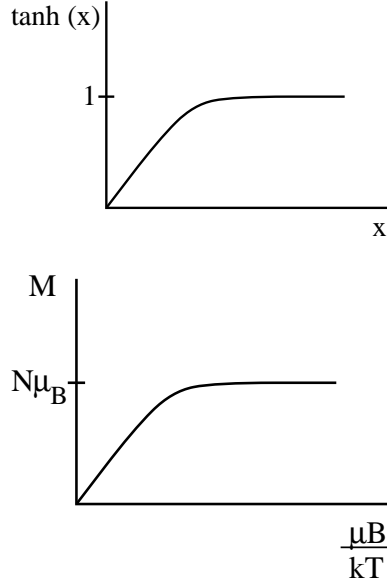
We see that

$$\bar{E} = -\bar{M}H \quad (15)$$

We can examine  $\bar{M}$  in the limit of high and low temperature.

$$\text{If } T \rightarrow 0 \left( \text{or } \frac{\mu_B H}{k_B T} \rightarrow \infty \right) \quad \tanh\left(\frac{\mu_B H}{k_B T}\right) \rightarrow 1 \quad \text{and} \quad \bar{M} \rightarrow N\mu_B \quad (16)$$

Physically at low temperatures all the magnetic moments are aligned with the magnetic field.



At high temperatures,  $\mu_B H/k_B T \rightarrow 0$  and  $T \rightarrow \infty$ . Since  $\tanh(x) \rightarrow x$  as  $x \rightarrow 0$ , we obtain

$$\bar{M} \cong N\mu_B \left( \frac{\mu_B H}{k_B T} \right) = \frac{N\mu_B^2 H}{k_B} \frac{1}{T} \quad (17)$$

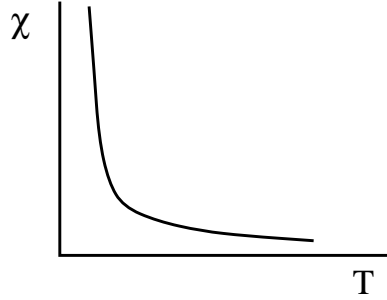
We expect the magnetization to be proportional to the magnetic field  $H$ . This is what characterizes a paramagnet. How easy or hard it is to magnetize the system is reflected in the magnetic susceptibility  $\chi$ :

$$M = \chi H \quad (18)$$

From eq. (17) we can read off the susceptibility:

$$\chi = \frac{\bar{M}}{H} = \frac{N\mu_B^2}{k_B} \frac{1}{T} \quad T \rightarrow \infty \quad (\text{high temperature limit}) \quad (19)$$

The fact that  $\chi$  varies as  $1/T$  is known as the Curie law.  $\chi$  is called the Curie susceptibility and it goes as  $1/T$ .



We can also calculate the Helmholtz free energy using eqns. (5) and (4):

$$F = -k_B T \ln Z = -k_B T \ln(\zeta^N) = -N k_B T \ln \zeta \quad (20)$$

where

$$\zeta = e^{\beta \mu_B H} + e^{-\beta \mu_B H} = 2 \cosh(\beta \mu_B H) = 2 \cosh\left(\frac{\mu_B H}{k_B T}\right) \quad (21)$$

So

$$F = -N k_B T \ln\left(2 \cosh\left(\frac{\mu_B H}{k_B T}\right)\right) \quad (22)$$

We can also calculate the heat capacity. Recall from lecture 9 that

$$C_V = -T \left. \frac{\partial^2 F}{\partial T^2} \right|_V \quad (23)$$

Taking two derivatives of (22) yields

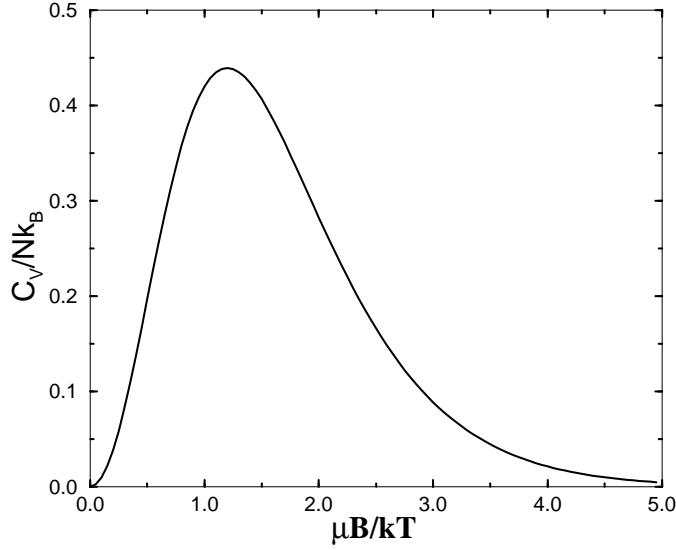
$$C_V = N k_B \left(\frac{\mu_B H}{k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\mu_B H}{k_B T}\right) \quad (24)$$

The specific heat per spin is

$$c_V = \frac{C_V}{N} = k_B \left(\frac{\mu_B H}{k_B T}\right)^2 \operatorname{sech}^2\left(\frac{\mu_B H}{k_B T}\right) \quad (25)$$

This is called the Schottky specific heat. It is the specific heat characteristic of two state systems. A two state system has only 2 states available to it. For example a spin-1/2 object has spin-up and spin-down states. Another example is an object that can only access the lowest states in a double well potential. In considering such discrete states, we are thinking quantum mechanically.

## Schottky Specific Heat



### Classical Harmonic Oscillator

Consider a classical harmonic oscillator with a spring constant  $\kappa$ . The typical example is a mass on a spring. The energy is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}\kappa x^2 \quad (26)$$

Assume the harmonic oscillator is in contact with a thermal reservoir at temperature  $T$ . The partition function is

$$\begin{aligned} Z &= \frac{1}{h_o} \int e^{-\beta E} dx dp \\ &= \frac{1}{h_o} \int_{-\infty}^{\infty} dp \exp\left(-\frac{\beta p^2}{2m}\right) \int_{-\infty}^{\infty} dx \exp\left(-\frac{\beta \kappa x^2}{2}\right) \end{aligned} \quad (27)$$

Recall from Reif Appendix A4 that

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \left(\frac{\pi}{\alpha}\right)^{1/2} \quad (28)$$

Using this (27) becomes

$$Z = \frac{1}{h_o} \left(\frac{2\pi}{\beta\kappa}\right)^{1/2} \left(\frac{2\pi m}{\beta}\right)^{1/2} = \frac{1}{\beta} \frac{2\pi}{h_o} \left(\frac{m}{\kappa}\right)^{1/2} \quad (29)$$

Or

$$\ln Z = -\ln \beta + \ln \left(\frac{2\pi}{h_o} \left(\frac{m}{\kappa}\right)^{1/2}\right) \quad (30)$$

and

$$\overline{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial \ln \beta}{\partial \beta} = \frac{1}{\beta} = k_B T \quad (31)$$

This makes sense; we expect the mean energy to be of order  $k_B T$ . It turns out that  $\overline{E} = k_B T$  has equal contributions from the kinetic energy and from the potential energy. Each contributes  $k_B T/2$ . One can show this explicitly. The mean kinetic energy is

$$\overline{KE} = \frac{\int_{-\infty}^{\infty} \frac{p^2}{2m} e^{-\beta p^2/2m} dp}{\int_{-\infty}^{\infty} dp e^{-\beta p^2/2m}} \quad (32)$$

Use Reif Appendix A4 to evaluate the numerator and denominator:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \left(\frac{\pi}{\alpha}\right)^{1/2} \quad (33)$$

and

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} x^2 dx = \frac{\sqrt{\pi}}{2} \alpha^{-3/2} \quad (34)$$

So

$$\begin{aligned} \overline{KE} &= \frac{\frac{1}{2m} \frac{\sqrt{\pi}}{2} \left(\frac{2m}{\beta}\right)^{3/2}}{\sqrt{\pi} \left(\frac{2m}{\beta}\right)^{1/2}} \\ &= \frac{k_B T}{2} \end{aligned} \quad (35)$$

Similarly the mean potential energy is given by

$$\begin{aligned} \overline{PE} &= \frac{\int_{-\infty}^{\infty} dx \frac{1}{2} \kappa x^2 e^{-\beta \kappa x^2/2}}{\int_{-\infty}^{\infty} dx e^{-\beta \kappa x^2/2}} \\ &= \frac{\frac{\kappa}{2} \frac{\sqrt{\pi}}{2} \left(\frac{2}{\beta \kappa}\right)^{3/2}}{\sqrt{\pi} \left(\frac{2}{\beta \kappa}\right)^{1/2}} \\ &= \frac{k_B T}{2} \end{aligned} \quad (36)$$

The fact that the mean kinetic and potential energies of a harmonic oscillator equals  $k_B T/2$  is an example of the classical equipartition theorem.

#### Classical Equipartition Theorem

Let the energy of a system with  $f$  degrees of freedom be  $E = E(q_1 \dots q_f, p_1 \dots p_f)$  and assume

1. the total energy splits additively into the form

$$E = \epsilon_i(p_i) + E'(q_1, \dots, p_f) \quad (37)$$

where  $\epsilon_i$  involves only  $p_i$  and  $E'$  is independent of  $p_i$ .

2.

$$\epsilon_i(p_i) = bp_i^2 \quad (38)$$

where  $b$  is a constant.

If we replaced  $p_i$  by  $q_i$ , the theorem is still true. We just want  $\epsilon_i$  to be a quadratic function of one component of  $q$  or  $p$ .

Assume that the system is in equilibrium at temperature  $T$ . Then

$$\begin{aligned} \bar{\epsilon}_i &= \frac{\int_{-\infty}^{\infty} \epsilon_i e^{-\beta E} dq_1 \dots dp_f}{\int_{-\infty}^{\infty} e^{-\beta E} dq_1 \dots dp_f} \\ &= \frac{\int_{-\infty}^{\infty} \epsilon_i e^{-\beta(\epsilon_i + E')} dq_1 \dots dp_f}{\int_{-\infty}^{\infty} e^{-\beta(\epsilon_i + E')} dq_1 \dots dp_f} \\ &= \frac{\int_{-\infty}^{\infty} \epsilon_i e^{-\beta \epsilon_i} dp_i \int_{-\infty}^{\infty} e^{-\beta E'} dq_1 \dots dp_f}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \int_{-\infty}^{\infty} e^{-\beta E'} dq_1 \dots dp_f} \end{aligned} \quad (39)$$

where the last integrals in the numerator and denominator do not involve  $dp_i$ . These integrals cancel leaving

$$\begin{aligned} \bar{\epsilon}_i &= \frac{\int_{-\infty}^{\infty} \epsilon_i e^{-\beta \epsilon_i} dp_i}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i} \\ &= \frac{-\frac{\partial}{\partial \beta} \int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i} \\ &= -\frac{\partial}{\partial \beta} \ln \left( \int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \right) \end{aligned} \quad (40)$$

Now use the second assumption:

$$\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i = \int_{-\infty}^{\infty} e^{-\beta b p_i^2} dp_i = \beta^{-1/2} \int_{-\infty}^{\infty} e^{-by^2} dy \quad (41)$$

where  $y \equiv \beta^{1/2} p_i$ . Thus

$$\ln \left( \int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \right) = -\frac{1}{2} \ln \beta + \ln \int_{-\infty}^{\infty} e^{-by^2} dy \quad (42)$$

Notice that the integral does not involve  $\beta$ . So when we take the derivative in (40), only the first term is involved.

$$\bar{\epsilon}_i = -\frac{\partial}{\partial \beta} \left( -\frac{1}{2} \ln \beta \right) = \frac{1}{2\beta} \quad (43)$$

or

$$\bar{\epsilon}_i = \frac{1}{2} k_B T \quad (44)$$

This is the classical equipartition theorem. It says that each additive quadratic term in the energy (i.e., each degree of freedom) contributes  $k_B T/2$  to the mean energy of the system.

Note that this theorem is true only in classical statistical mechanics as opposed to quantum mechanics. In quantum mechanics the energy of a system is discretized into energy levels. At low energies the levels are rather far apart. As the energy increases, the energy levels become more closely spaced. The equipartition theorem holds when the mean energy is such that the levels near it have an energy level spacing  $\Delta E \ll k_B T$ .

Mean kinetic energy of a gas molecule

Let's consider the simple example of a molecule in a gas (not necessarily an ideal gas) at temperature  $T$ . Its kinetic energy is given by

$$K = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) \quad (45)$$

The kinetic energy of the other molecules do not involve the momentum  $\vec{p}$  of this particular molecule. The potential energy of interaction between the gas molecules also is independent of  $\vec{p}$ . So the equipartition theorem tells us that

$$\overline{K} = \frac{3}{2} k_B T \quad (46)$$

Notice that if we write

$$\overline{K} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T \quad (47)$$

then the root-mean-square velocity  $v_{\text{rms}}$  is given by

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} \quad (48)$$

For an ideal monatomic gas the energy is solely kinetic energy, so

$$\overline{E} = N \left( \frac{3}{2} k_B T \right) = \frac{3}{2} \nu R T \quad (49)$$

where  $N$  is the number of gas particles,  $R = N_a k_B$  is the gas constant, and  $\nu$  is the number of moles. The molar specific heat at constant volume is

$$c_V = \frac{C_V}{\nu} = \frac{1}{\nu} \left( \frac{\partial \overline{E}}{\partial T} \right)_V = \frac{3}{2} R \quad (50)$$

The equipartition theorem works for rotational and vibrational degrees of freedom as well. Suppose we have a diatomic molecule lying along the x axis. It can rotate about the y axis and about the z axis. So the average rotational kinetic energy from both these degrees of freedom is  $2 \times k_B T/2$ . (We ignore rotations about the x axis because the moment of inertia is too small.) In this case

$$\overline{E} = N \left( \frac{5}{2} k_B T \right) = \frac{5}{2} \nu R T \quad (51)$$



and

$$c_V = \frac{5}{2}R \quad (52)$$

We can also have vibrations along the axis of the molecule. Think of the 2 atoms as being connected by a spring. The average vibrational kinetic energy contributes  $k_B T/2$  and the average vibrational potential energy also contributes  $k_B T/2$ . So if we add the translational, rotational and vibrational degrees of freedom of a diatomic molecule, we obtain 7 degrees of freedom and

$$\bar{E} = N \left( \frac{7}{2} k_B T \right) = \frac{7}{2} \nu R T \quad (53)$$

and

$$c_V = \frac{7}{2}R \quad (54)$$

### Brownian Motion

Brownian motion was discovered by Brown, a botanist, in the 1800's and was explained by Einstein in 1905. If you put a small macroscopic particle in a liquid and watch it in a microscope, it jiggles around because the molecules in the liquid keep bumping into it. This is called Brownian motion. The molecules in the liquid are moving around because of thermal fluctuations. To see this, let the small macroscopic particle have a mass  $m$  and be immersed in a liquid at temperature  $T$ . Consider the  $x$ -component of the velocity  $v_x$ .

$$\bar{v}_x = 0 \quad (55)$$

Even though the mean value of the velocity vanishes, this does not mean that  $v_x = 0$ . There are velocity fluctuations so that  $\overline{v_x^2} \neq 0$ . From the equipartition theorem we have

$$\overline{\frac{1}{2} m v_x^2} = \frac{1}{2} k_B T \quad (56)$$

or

$$\overline{v_x^2} = \frac{k_B T}{m} \quad (57)$$

The factor of  $1/m$  means that the fluctuations are negligible for large  $m$  like a golf ball. But when  $m$  is small (e.g., when the particle is micron sized), then the velocity fluctuations become appreciable and can be observed under a microscope. Notice that the size of the fluctuations are proportional to temperature. The higher the temperature, the larger the fluctuations. This is what we expect of thermal fluctuations.