

## Recitation: 10

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#### Ensembles and Relation to T.D.

It is possible to expand both sides of the equation

$$F = -kT \ln Q$$

with

$$Q = \sum_i e^{-\beta E_i}$$

If we expand both sides of this equation, we *apparently* obtain:

$$F = E - TS = E$$

According to the expression above, the  $TS$  term has disappeared!!

To resolve this discrepancy, remember that **the summation in  $Q$  is over all the microstates available to the system and not over the energy levels**. Each energy level is highly degenerate, and  $Q$  can be expressed as:

$$Q = \sum_{E \text{ levels}} \Omega(N, V, E) e^{-\beta E_{E \text{ levels}}}$$

Now, we can perform the expansion:

$$F = E - TS = E - kT \ln \sum_{E \text{ levels}} \Omega(N, V, E)$$

By inspection, it can be seen that

$$S = k \sum_{E \text{ levels}} \ln \Omega(N, V, E)$$

This expression is the classical expression for the entropy of an isolated system (microcanonical ensemble).

Note that the *Canonical* ensemble is basically a collection of *microcanonical* ensembles.

In general, we can write down the partition function for any ensemble as:

$$Z = \sum_{X_1, X_2, \dots} \Omega(N, V, E) e^{-\beta X_1} e^{-\beta X_2}$$

In this general expression, the degeneracy of each energy level has been taken into account by  $\Omega(N, V, E)$ . The sum in this case is not over all the microstates but over the different values that the extensive properties (such as energy, volume,  $N$ , magnetization, etc. can take).

For more details, see Hill, p. 30

### Fluctuations

In Statistical Mechanics, the mechanical variables (those variables that can be explicitly defined for each of the microstates accessible to the system) fluctuate around their average (or most probable) value with a characteristic spread, which is a function of the actual boundary conditions of the system under study.

Depending on the boundary conditions (i.e. ensemble) used, different mechanical properties fluctuate.

It is important to answer to these two questions:

- How big are fluctuations of mechanical properties?
- Does the relative size of the fluctuations offer new information?

In general, the spread of the distribution for the values of the *instantaneous* mechanical properties around their *average* values is given by:

$$\sigma_M^2 = \overline{(M - \bar{M})^2} = \overline{M^2} - \bar{M}^2$$

In class, we saw a three-step procedure to obtain the fluctuation of a mechanical variable:

Given the explicit equation for the average value for a mechanical property  $M$ :

$$\bar{M} = \sum_{\nu} M_{\nu} P_{\nu}$$

1) Multiply both sides by the partition function of the ensemble:

$$\bar{M}Z = \sum_{\nu} M_{\nu} P_{\nu} Z$$

- 2) Take the derivative of the equality with respect to the conjugate variable of the fluctuating mechanical variable.
- 3) Divide both sides by the partition function and re-arrange.

In general, the spread for extensive mechanical variables is very small for large systems ( $N \sim 10^{23}$ ):

$$\frac{\sigma_M}{\bar{M}} \sim \frac{1}{\sqrt{N}}$$

There are some cases, however, when fluctuations are not negligible:

- Small Systems

- Critical Points

### Applications of Statistical Mechanics to Specific Systems

In general, the partition function for a statistical mechanical ensemble (in this case the Canonical Ensemble) is given by:

$$Q = \sum_{\nu} e^{-\beta E_{\nu}}$$

For systems of *non-interacting* particles, it is possible to write their partition function in an explicit manner.

Examples of these systems:

- Ideal Gas
- Electrons in a periodic crystal
- Photon Gas
- Lattice Vibrations

### Distinguishable Particles

For non interacting particles, we saw in class that the total energy of the system can be expressed as:

$$E_T = \varepsilon_l^a + \varepsilon_m^b + \varepsilon_n^c + \dots$$

where  $\varepsilon_l^a$  is the energy of particle  $a$  in microstate  $l$ .

If the particles are non-distinguishable, the partition function is very easy to evaluate:

$$\begin{aligned} Q &= \sum_{\nu} e^{-\beta E_{\nu}} = \sum_l \sum_m \sum_n \dots e^{-\beta(\varepsilon_l^a + \varepsilon_m^b + \varepsilon_n^c + \dots)} \\ Q &= \left( \sum_l e^{-\beta \varepsilon_l^a} \right) \cdot \left( \sum_m e^{-\beta \varepsilon_m^b} \right) \cdot \left( \sum_n e^{-\beta \varepsilon_n^c} \right) \dots \\ Q &= q_a \cdot q_b \cdot q_c \dots \end{aligned}$$

If all the particles are identical,  $q_a = q_b = q_c \dots$ :

$$Q = q^N$$

where

$$q = \sum_l e^{-\beta \varepsilon_l}$$

where  $l$  is the subindex corresponding to each of the microstates accessible to each of the particles comprising the system.

### Non-distinguishable Particles

When the system is composed of non-interacting, non-distinguishable particles, the unrestricted sum:

$$Q = \sum_{\nu} e^{-\beta E_{\nu}} = \sum_l \sum_m \sum_n \dots e^{-\beta(\epsilon_l^a + \epsilon_m^b + \epsilon_n^c + \dots)}$$

has to be corrected.

For **fermions**, there cannot be two particles in the same microstate:

$$\epsilon_l^a + \epsilon_l^b + \epsilon_n^c + \dots \rightarrow \text{violates Pauli}$$

For **bosons**:

$$\epsilon_l^a + \epsilon_m^b + \epsilon_m^c + \epsilon_m^d \leftrightarrow \epsilon_m^a + \epsilon_l^b + \epsilon_m^c + \epsilon_m^d \quad \text{Over counting } N \text{ times}$$

$$\epsilon_l^a + \epsilon_l^b + \epsilon_m^c + \epsilon_m^d \leftrightarrow \epsilon_m^a + \epsilon_m^b + \epsilon_l^c + \epsilon_l^d \quad \text{Over counting } \frac{N(N-1)}{2} \text{ times}$$

$$\epsilon_l^a + \epsilon_m^b + \epsilon_n^c + \epsilon_o^d \leftrightarrow \epsilon_o^a + \epsilon_l^b + \epsilon_m^c + \epsilon_n^d \quad \text{Over counting } N! \text{ times}$$

When the number of states available is much greater than the number of particles in the system  $\Phi(E) \gg N$ , the last term dominates the sum, and the partition function can be **approximated** as:

$$Q = \frac{q^N}{N!}$$

This is usually the case for:

- High Temperatures
- Low Density
- Large Mass

### Problem 1

Consider the isothermal-isobaric ensemble, for which the partition function is

$$\Delta = \sum_{i,j} e^{-\beta E_i - \beta p V_j}$$

For this ensemble, calculate the standard deviation  $\sigma_V$  of the volume, as a fraction of the total volume of the system.

### Solution 1

We know that

$$\sigma_V^2 = \overline{V^2} - \bar{V}^2$$

In order to calculate the fluctuation for the volume in this ensemble, we follow the procedure seen in class:

First, we write the explicit equation for the average volume in this ensemble:

$$\bar{V} = \frac{\sum_{i,j} V_j e^{-\beta E_i - \beta p V_j}}{\Delta}$$

1) Multiply both sides of the equality by the partition function  $\Delta$ :

$$\bar{V} \cdot \Delta = \sum_{i,j} V_j e^{-\beta E_i - \beta p V_j}$$

2) Take the derivative of both sides with respect to the conjugate variable for  $V$ , in this case, we define the conjugate variable as  $\gamma = \beta p$ :

$$\begin{aligned} \frac{\partial (\bar{V} \cdot \Delta)}{\partial \gamma} &= \frac{\partial \left( \sum_{i,j} V_j e^{-\beta E_i - \gamma V_j} \right)}{\partial \gamma} \\ \frac{\partial \bar{V}}{\partial \gamma} \Delta + \bar{V} \frac{\partial \Delta}{\partial \gamma} &= - \sum_{i,j} V_j^2 e^{-\beta E_i - \gamma V_j} \\ \frac{\partial \bar{V}}{\partial \gamma} \Delta + \bar{V} \frac{\partial \left( \sum_{i,j} e^{-\beta E_i - \gamma V_j} \right)}{\partial \gamma} &= - \sum_{i,j} V_j^2 e^{-\beta E_i - \gamma V_j} \\ \frac{\partial \bar{V}}{\partial \gamma} \Delta - \bar{V} \cdot \sum_{i,j} V_j e^{-\beta E_i - \gamma V_j} &= - \sum_{i,j} V_j^2 e^{-\beta E_i - \gamma V_j} \end{aligned}$$

3) Divide both sides by the partition function:

$$\frac{\partial \bar{V}}{\partial \gamma} - \bar{V}^2 = -\bar{V}^2$$

From this we finally obtain (here we have expanded  $\gamma = \frac{p}{kT}$ ):

$$\sigma_V^2 = \overline{V^2} - \bar{V}^2 = -kT \left( \frac{\partial \bar{V}}{\partial p} \right)_{T,N}$$

Using the definition for the isothermal compressibility, we have:

$$\sigma_V^2 = kTV \kappa_T$$

The *normalized* standard deviation of the volume is given by:

$$\frac{\sigma_V}{\bar{V}} = \frac{(kTV \kappa_T)^{1/2}}{\bar{V}} = \sqrt{\frac{kT \kappa_T}{\bar{V}}}$$

For an ideal gas,  $\kappa_T = \frac{1}{p}$  and we have:

$$\frac{\sigma_V}{V} = \sqrt{\frac{kT}{PV}} = \sqrt{\frac{kT}{NkT}} = \frac{1}{\sqrt{N}}$$

### Problem 2

Consider a system of  $N$  distinguishable non-interacting spins in a magnetic field  $H$ . Each spin has a magnetic moment of size  $\mu$ , and each can point either parallel or anti-parallel to the field. The magnetic moment is given by  $n_i\mu$  where  $n_i = +/ - 1$ . Note that since the system is made of non-interacting particles, the total energy of the system does not depend on the arrangements of the spins, i.e. the energy is constant.

- Determine the internal energy of this system as a function of  $\beta$ ,  $H$ , and  $N$  by employing an ensemble characterized by these variables.
- Determine the entropy of this system as a function of  $\beta$ ,  $H$ , and  $N$ .
- Determine the behavior of the energy and entropy for this system as  $T \rightarrow 0$ .

### Solution 2

The magnetization is given as

$$M = \sum_{i=1}^N n_i \mu_o$$

- This is basically saying that we have atoms localized in a crystal and the magnetic moment at each site can be either up or down. The problem asks us to determine the thermodynamic properties as a function of  $T$ ,  $N$ ,  $H$ . Let us also assume for simplicity that we can work at constant volume. Therefore, our controlling variables are  $T$ ,  $N$ ,  $V$ ,  $H$ .

- We need to make the appropriate Legendre transform to the entropy. Remember the entropy can be written starting from  $E$ :

$$E = TS - pV + HM + \mu N$$

rearranging to get things in terms of  $S$  and  $\beta$  we get

$$\frac{S}{k} = \beta E + \beta pV - \beta HM - \beta \mu N$$

Legendre transform such that our controlling variables are  $V$ ,  $N$ ,  $T$ ,  $H$

$$\frac{S}{k} - \beta E + \beta HM = \beta(TS - E + HM) = -\beta\psi = \ln \Gamma$$

where  $\psi$  is the characteristic potential for this ensemble with  $V$ ,  $N$ ,  $T$ ,  $H$  constant and  $\Gamma$  is the partition function.  $\Gamma$  can be written as

$$\Gamma = \sum_{states} \exp[-\beta(E_{state} - M_{state}H)]$$

where we sum over all possible energy states and magnetizations  $M_{state}$ .

• Since the particles are non-interacting, the energy at  $N, \beta = \text{constant}$  and  $H = 0$  is constant.  $E$  is independent of the number or arrangement of up versus down spins. Since the absolute scale of energy is not important for thermodynamics, we can arbitrarily set the constant energy equal to zero giving us

$$\Gamma = \sum_{states} \exp[\beta M_{state} H] = \sum_{n_1, n_2, \dots, n_N} \exp \left[ \beta \sum_{i=1}^N n_i \mu_o H \right] = \sum_{n_1, n_2, \dots, n_N} \prod_{i=1}^N \exp[\beta n_i \mu_o H]$$

$$\Gamma = \sum_{n_1, n_2, \dots, n_N} \prod_{i=1}^N \exp[\beta n_i \mu_o H] = \prod_{i=1}^N \sum_{n_i=-1}^{+1} \exp[\beta n_i \mu_o H]$$

We can evaluate the sum since  $n_i = \pm 1$  so,

$$\Gamma = (\exp[\beta \mu_o H] + \exp[-\beta \mu_o H])^N$$

We know the characteristic potential of an ensemble is related to the partition function for that ensemble according to

$$-\beta \psi = \ln \Gamma \rightarrow \psi = -kT \ln \Gamma$$

Furthermore, we know from thermo that

$$d\psi = -SdT - pdV + \mu dN - MdH$$

which gives us the following relationships for the properties of the system:

$$S = - \left( \frac{\partial \psi}{\partial T} \right)_{V, N, H}$$

$$M = - \left( \frac{\partial \psi}{\partial H} \right)_{V, N, T}$$

$$\mu = \left( \frac{\partial \psi}{\partial N} \right)_{V, T, H}$$

$$p = - \left( \frac{\partial \psi}{\partial V} \right)_{T, N, H}$$

and from stat mech we have from above

$$\psi = -kTN \ln [\exp[\beta \mu_o H] + \exp[-\beta \mu_o H]]$$

• Lets get the entropy,  $S$

$$S = - \left( \frac{\partial \psi}{\partial T} \right)_{V, N, H}$$

$$S = kN \ln (\exp [\beta \mu_o H] + \exp [-\beta \mu_o H]) + kTN \frac{\left( -\frac{\mu_o H}{kT^2} \right) (\exp [\beta \mu_o H] - \exp [-\beta \mu_o H])}{\exp [\beta \mu_o H] + \exp [-\beta \mu_o H]}$$

$$\boxed{S = kN \{ \ln (\exp [\beta \mu_o H] + \exp [-\beta \mu_o H]) - \beta \mu_o \tanh (\beta \mu_o H) \}}$$

• Now for the magnetization

$$M = - \left( \frac{\partial \psi}{\partial H} \right)_{V, N, T} = kTN \beta \mu_o \left\{ \frac{\exp [\beta \mu_o H] - \exp [-\beta \mu_o H]}{\exp [\beta \mu_o H] + \exp [-\beta \mu_o H]} \right\} = N \mu_o \tanh (\beta \mu_o H)$$

$$\boxed{M = N \mu_o \tanh (\beta \mu_o H)}$$

• The energy  $E$

$$\psi = E - TS - HM$$

$$E = \psi + TS + HM = 0$$

• However if you define a quantity called the internal magnetic energy (which is a quantity analogous to the enthalpy in the  $T, p, N$  ensemble)

$$E_H = E - HM$$

you can get

$$E_H = -N \mu_o H \tanh (\beta \mu_o H)$$

• The last part of this problem asks you to determine the behavior of the energy and entropy as  $T \rightarrow 0$ .

$$E_H (T \rightarrow 0) = -N \mu_o H$$

$$\lim_{\beta \rightarrow \infty} S = \lim_{\beta \rightarrow \infty} kN \{ \ln (\exp [\beta \mu_o H] + \exp [-\beta \mu_o H]) - \beta \mu_o \tanh (\beta \mu_o H) \} = 0$$

$S(T \rightarrow 0) = 0$  is in accordance with the third law of thermodynamics.