

## Recitation: 9

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#### Canonical Ensemble

Consider an ensemble of systems with  $N, V$  and  $T$  constant. Each of the systems is closed to the flow of matter and has the same volume,  $V$  but it allows heat to fluctuate through its walls. Because of this, all the systems are at the same temperature,  $T$ , but their energy  $E$  can fluctuate. Note that the ensemble itself is an *isolated* system, and therefore  $\mathbf{A}$  and  $\mathbf{A}N, \mathbf{A}V$  remain constant.

Because of fluctuations in  $E$ , we have to consider the spectrum of energy  $E_1(N, V), E_2(N, V) \dots$  for *each* system. Each of the systems has access to the same spectrum of energy and therefore each energy value  $E_j$  can be repeated many times (degeneracy).

In the canonical ensemble, the following conditions must be satisfied:

$$\sum_j a_j = A$$

$$\sum_i a_i E_i = E_T$$

where  $E_T$  is the *total* energy of the ensemble. If we use Lagrange multipliers for the total number of systems and energy in the ensemble, we finally obtain:

$$P_j = \frac{a_j^*}{A} = \frac{\exp(-\beta E_j)}{\sum_j \exp(-\beta E_j)}$$

for  $N, V, T$  fixed.

If we use  $Q = \sum_j \exp(-\beta E_j)$ , we can find the *macroscopic* mechanical properties of this ensemble (no  $T, S$ ):

$$U = \bar{E} = \sum_j P_j E_j = \frac{\sum_j E_j \exp(-\beta E_j)}{Q} = -\frac{\partial \ln Q}{\partial \beta}$$

$Q$  is the partition function for this ensemble and it is the most important property. From it, everything else can be derived:

$$p = \bar{p} = \sum_j p_j P_j = -\frac{\sum_j \left( \frac{\partial E_j}{\partial V} \right) e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

#### Finding $T, S$

To find  $S$ , we can use the approach by Hill,

We can take the differential of  $\bar{E} = \sum_j E_j P_j$ :

$$d\bar{E} = \sum_j E_j dP_j + P_j dE_j \quad (1)$$

From:

$$P_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_j}}{Q}$$

We obtain

$$E_j = -\frac{1}{\beta} (\ln P_j + \ln Q)$$

Substituting in Eq. 1, we have:

$$d\bar{E} = -\frac{1}{\beta} \sum_j (\ln P_j + \ln Q) dP_j + \sum_j P_j \left( \frac{\partial E_j}{\partial V} \right)_N dV$$

Note that  $E_j$  are only function of  $N$  and  $V$ .

Using the properties of  $P_j$ :

$$\begin{aligned} \sum_j P_j &= 1 \\ \sum_j dP_j &= 0 \\ d \left( \sum_j P_j \ln P_j \right) &= \sum_j P_j \frac{1}{P_j} dP_j + \sum_j \ln P_j dP_j = \sum_j \ln P_j dP_j \end{aligned}$$

we have:

$$-\frac{1}{\beta} d(P_j \ln P_j) = d\bar{E} + \bar{p} dV$$

From Thermodynamics, we know that

$$TdS = dU + pdV$$

And we therefore can establish the following relations:

$$\begin{aligned} U &\leftrightarrow \bar{E} \\ p &\leftrightarrow \bar{p} \\ TdS &\leftrightarrow -\frac{1}{\beta} d(P_j \ln P_j) \end{aligned}$$

We finally have:

$$S = -k \sum_j P_j \ln P_j$$

If we substitute the expression for  $P_j$ :

$$S = -k \sum_j \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} \left( -\frac{1}{kT} E_j - \ln Q \right)$$

$$S = \frac{\bar{E}}{T} + k \ln Q = \frac{U}{T} - \frac{F}{T}$$

$F$  is the Helmholtz free energy and is the *characteristic potential* for systems with  $N$ ,  $V$  and  $T$  as independent variables. Note that these are the same *boundary conditions* stated for the *Canonical* ensemble.

Once we have  $F(N, V, T) = -kT \ln Q(N, V, T)$ , we can define all the thermodynamic properties related to this potential:

$$dF = -SdT - PdV + \sum_i \mu_i dn_i$$

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N} = kT \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} + k \ln Q$$

$$p = - \left( \frac{\partial F}{\partial V} \right)_{T,N} = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N}$$

$$\mu = \left( \frac{\partial F}{\partial n_i} \right)_{T,V,n_{i \neq j}} = -kT \left( \frac{\partial \ln Q}{\partial n_i} \right)_{T,V,n_{i \neq j}}$$

$$U = E = -T^2 \left( \frac{\partial \frac{F}{T}}{\partial T} \right) = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

The last expression comes from:

$$U = F + TS = F - T \left( \frac{\partial F}{\partial T} \right)_{V,N} = \left( \frac{\partial \frac{F}{T}}{\partial \frac{1}{T}} \right)$$

If you have the partition function  $Q$  you can obtain every thermodynamic property of a system.

### General Structure for any set of Boundary Conditions

For any set of boundary conditions, the probability for the system to be in any microstate  $\nu$  is given by:

$$P_\nu = \frac{e^{\mathcal{O}_\nu}}{\sum_\eta e^{\mathcal{O}_\eta}}$$

The partition function, for this probability distribution, is given by:

$$Z = \sum_{\eta} e^{\Omega_{\eta}}$$

Each ensemble has its characteristic function,  $\Lambda$ :

$$\Lambda = -\frac{1}{\beta} \ln Z$$

For any set of thermodynamic boundary conditions, the main problem is to find  $\Omega$ . This can be done using the following procedure:

i) Write down the Euler relation in the entropy representation and divide by  $k$ :

$$\frac{S}{k} = \beta E + \beta PV - \beta \mu N + \dots$$

ii) Identify the *independent variables* in the ensemble. These variables are the Thermodynamic Boundary Conditions. For the canonical ensemble, the independent variables are  $(T, V, N)$

iii) Compare the *boundary conditions* to the natural variables for the entropy  $S(E, V, N)$ .

iv) Legendre transform the Euler expression in the entropy representation, with respect to the independent intensive variables that appear in the ensemble. For the *Canonical Ensemble*, we have:

$$\Phi = \frac{S}{k} - \beta E$$

v)  $\Omega$  is given by:

$$\Omega = \Phi - \frac{S}{k}$$

For the *Canonical Ensemble*, we have:

$$\Omega = \Phi - \frac{S}{k} = -\beta E$$

vi) The characteristic function  $\Lambda$  is:

$$\Lambda = -\frac{1}{\beta} \Phi$$

For the *Canonical Ensemble* we have:

$$\Lambda = F = E - TS$$

vii) Using the general structure for Stat Mech we have, for the *Canonical Ensemble*:

$$P_{\nu} = \frac{e^{-\beta E_{\nu}}}{\sum_{\eta} e^{-\beta E_{\eta}}}$$

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

$$-\beta F = \frac{S}{k} - \beta E = \ln Q$$

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

**Example: Ensemble with  $N$ ,  $P$  and  $T$  as independent variables:**

1. Euler Relation:

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

2. The independent variables are  $(T, P, N)$

3. We need to do the Legendre Transform:

$$\Phi = \frac{S}{k} - \beta E - \beta PV$$

4. By inspection,

$$G = -\frac{\Phi}{\beta}$$

5. Using the general structure, we finally have:

$$P_\nu = \frac{e^{-\beta E_\nu - \beta p V_\nu}}{\sum_\eta e^{-\beta E_\eta - \beta p V_\eta}}$$
$$Z = \sum_\eta e^{-\beta E_\eta - \beta p V_\eta}$$
$$-\beta G = \frac{S}{k} - \beta E - \beta p V - \beta \mu N = \ln Z$$

Once you have the partition function and you have identified the characteristic function, everything else can be readily obtained:

From Classical Thermodynamics, we have:

$$dG = -SdT + VdP + \mu dN$$

And therefore,

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} = +\left(\frac{\partial kT \ln Z}{\partial T}\right)_{P,N} = kT \left(\frac{\partial \ln Z}{\partial T}\right)_{P,N} + k \ln Z = \frac{kT}{Z} \frac{\partial Z}{\partial T} + k \ln Z$$
$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} = -kT \left(\frac{\partial \ln Z}{\partial P}\right)_{T,N}$$
$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = -kT \left(\frac{\partial \ln Z}{\partial N}\right)_{T,P}$$

**Problem 1**

Lagrange Multipliers:

Show that  $-\sum_{j=1}^N P_j \ln P_j$ , subject to the condition  $\sum_{j=1}^N P_j = 1$  is a maximum when  $P_j$  is a constant.

**Solution 1**

Here we use Lagrange multipliers again with the constraint  $\sum_j P_j = 1$ .

$$M = -\sum_{j=1}^N P_j \ln P_j - \alpha \left( \sum_{j=1}^N P_j - 1 \right)$$

Maximize

$$\left( \frac{\partial M}{\partial P_j} \right) = -\ln P_j - 1 - \alpha = 0$$

$$P_j = \exp [-(1 + \alpha)]$$

Determine  $\alpha$

$$\sum_{j=1}^N P_j = N \exp [-(1 + \alpha)] = 1$$

$$\exp [-(1 + \alpha)] = \frac{1}{N}$$

Thus

$$\boxed{P_j = \frac{1}{N}}$$

**Problem 2**

The partition function of a monatomic ideal gas is:

$$Q(N, V, T) = \frac{1}{N!} \left( \frac{2\pi mkT}{h^2} \right)^{3N/2} V^N$$

Derive an expression for the pressure and the energy from this partition function.

**Solution 2**

For  $\bar{p}$ ,

$$\begin{aligned}\bar{p} &= kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T,N} \\ \ln Q &= \ln \left( \frac{1}{N!} \right) + \frac{3N}{2} \ln \left( \frac{2\pi mkT}{h^2} \right) + N \ln V \\ \bar{p} &= \frac{kTN}{V}\end{aligned}$$

For  $\bar{E}$

$$\begin{aligned}\bar{E} &= kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} = kT^2 \left( \frac{3N}{2} \frac{\frac{2\pi mk}{h^2}}{\frac{2\pi mkT}{h^2}} \right) \\ \bar{E} &= \frac{3N}{2} kT\end{aligned}$$