

Notes for Lecture 5

I. THE GRAND CANONICAL ENSEMBLE

In the grand canonical ensemble, the control variables are the chemical potential μ , the volume V and the temperature T . The total particle number N is therefore allowed to fluctuate. It is therefore related to the canonical ensemble by a Legendre transformation with respect to the particle number N . Its utility lies in the fact that it closely represents the conditions under which experiments are often performed and, as we shall see, it gives direct access to the equation of state.

A. Thermodynamics

In the canonical ensemble, the Helmholtz free energy $A(N, V, T)$ is a natural function of N , V and T . As usual, we perform a Legendre transformation to eliminate N in favor of $\mu = \partial A / \partial N$:

$$\begin{aligned}\tilde{A}(\mu, V, T) &= A(N(\mu), V, T) - N \left(\frac{\partial A}{\partial N} \right)_{V, T} \\ &= A(N(\mu), V, T) - \mu N\end{aligned}$$

It turns out that the free energy $\tilde{A}(\mu, V, T)$ is the quantity $-PV$. We shall derive this result below in the context of the partition function. Thus,

$$-PV = A(N(\mu), V, T) - \mu N$$

To motivate the fact that PV is the proper free energy of the grand canonical ensemble from thermodynamic considerations, we need to introduce a mathematical theorem, known as Euler's theorem:

Euler's Theorem: Let $f(x_1, \dots, x_N)$ be a function such that

$$f(\lambda x_1, \dots, \lambda x_N) = \lambda^n f(x_1, \dots, x_N)$$

Then f is said to be a *homogeneous function of degree n* . For example, the function $f(x) = 3x^2$ is a homogeneous function of degree 2, $f(x, y, z) = xy^2 + z^3$ is a homogeneous function of degree 3, however, $f(x, y) = e^{xy} - xy$ is not a homogeneous function. *Euler's Theorem* states that, for a homogeneous function f ,

$$nf(x_1, \dots, x_N) = \sum_{i=1}^N x_i \frac{\partial f}{\partial x_i}$$

Proof: To prove Euler's theorem, simply differentiate the the homogeneity condition with respect to lambda:

$$\begin{aligned}\frac{d}{d\lambda} f(\lambda x_1, \dots, \lambda x_N) &= \frac{d}{d\lambda} \lambda^n f(x_1, \dots, x_N) \\ \sum_{i=1}^N x_i \frac{\partial f}{\partial (\lambda x_i)} &= n \lambda^{n-1} f(x_1, \dots, x_N)\end{aligned}$$

Then, setting $\lambda = 1$, we have

$$\sum_{i=1}^N x_i \frac{\partial f}{\partial x_i} = nf(x_1, \dots, x_N)$$

which is exactly Euler's theorem.

Now, in thermodynamics, extensive thermodynamic functions are homogeneous functions of degree 1. Thus, to see how Euler's theorem applies in thermodynamics, consider the familiar example of the Gibbs free energy:

$$G = G(N, P, T)$$

The extensive dependence of G is on N , so, being a homogeneous function of degree 1, it should satisfy

$$G(\lambda N, P, T) = \lambda G(N, P, T)$$

Applying Euler's theorem, we thus have

$$G(N, P, T) = N \frac{\partial G}{\partial N} = \mu N$$

or, for a multicomponent system,

$$G = \sum_j \mu_j N_j$$

But, since

$$G = E - TS + PV$$

it can be seen that $G = \mu N$ is consistent with the first law of thermodynamics.

Now, for the Legendre transformed free energy in the grand canonical ensemble, the thermodynamics are

$$d\tilde{A} = dA - \mu dN - Nd\mu = -PdV - SdT - Nd\mu$$

But, since

$$\begin{aligned} \tilde{A} &= \tilde{A}(\mu, V, T) \\ d\tilde{A} &= \left(\frac{\partial \tilde{A}}{\partial \mu} \right)_{V, T} d\mu + \left(\frac{\partial \tilde{A}}{\partial V} \right)_{\mu, T} dV + \left(\frac{\partial \tilde{A}}{\partial T} \right)_{\mu, V} dT \end{aligned}$$

the thermodynamics will be given by

$$\begin{aligned} N &= - \left(\frac{\partial \tilde{A}}{\partial \mu} \right)_{V, T} \\ P &= - \left(\frac{\partial \tilde{A}}{\partial V} \right)_{\mu, T} \\ S &= - \left(\frac{\partial \tilde{A}}{\partial T} \right)_{V, \mu} \end{aligned}$$

Since, \tilde{A} is a homogeneous function of degree 1, and its extensive argument is V , it should satisfy

$$\tilde{A}(\mu, \lambda V, T) = \lambda \tilde{A}(\mu, V, T)$$

Thus, applying Euler's theorem,

$$\tilde{A}(\mu, V, T) = V \frac{\partial \tilde{A}}{\partial V} = -PV$$

and since

$$\tilde{A} = A - \mu N = E - TS - \mu N$$

the assignment $\tilde{A} = -PV$ is consistent with the first law of thermodynamics. It is customary to work with PV , rather than $-PV$, so PV is the natural free energy in the grand canonical ensemble, and, unlike the other ensembles, it is not given a special name or symbol!

B. Partition function

Consider two canonical systems, 1 and 2, with particle numbers N_1 and N_2 , volumes V_1 and V_2 and at temperature T . The systems are in chemical contact, meaning that they can exchange particles. Furthermore, we assume that $N_2 \gg N_1$ and $V_2 \gg V_1$ so that system 2 is a particle reservoir. The total particle number and volume are

$$\begin{aligned} V &= V_1 + V_2 \\ N &= N_1 + N_2 \end{aligned}$$

The total Hamiltonian $H(\mathbf{x}, N)$ is

$$H(\mathbf{x}, N) = H_1(\mathbf{x}_1, N_1) + H_2(\mathbf{x}_2, N_2)$$

If the systems *could not* exchange particles, then the canonical partition function for the whole system would be

$$\begin{aligned} Q(N, V, T) &= \frac{1}{N! h^{3N}} \int d\mathbf{x} e^{-\beta(H_1(\mathbf{x}_1, N_1) + H_2(\mathbf{x}_2, N_2))} \\ &= \frac{N_1! N_2!}{N!} Q_1(N_1, V_1, T) Q_2(N_2, V_2, T) \end{aligned}$$

where

$$\begin{aligned} Q_1(N_1, V_1, T) &= \frac{1}{N_1! h^{3N_1}} \int d\mathbf{x} e^{-\beta H_1(\mathbf{x}_1, N_1)} \\ Q_2(N_2, V_2, T) &= \frac{1}{N_2! h^{3N_2}} \int d\mathbf{x} e^{-\beta H_2(\mathbf{x}_2, N_2)} \end{aligned}$$

However, N_1 and N_2 are *not* fixed, therefore, in order to sum over all microstates, we need to sum over all values that N_1 can take on subject to the constraint $N = N_1 + N_2$. Thus, we can write the canonical partition function for the whole system as

$$Q(N, V, T) = \sum_{N_1=0}^N f(N_1, N) \frac{N_1! N_2!}{N!} Q_1(N_1, V_1, T) Q_2(N_2, V_2, T)$$

where $f(N_1, N)$ is a function that weights each value of N_1 for a given N . Thus,

$f(0, N)$ is the number of configurations with 0 particles in V_1 and N particles in V_2 .

$f(1, N)$ is the number of configurations with 1 particles in V_1 and $N - 1$ particles in V_2 .

etc.

Determining the values of $f(N_1, N)$ amounts to a problem of counting the number of ways we can put N identical objects into 2 baskets. Thus,

$$f(0, N) = 1$$

$$f(1, N) = N = N!/1!(N-1)!$$

$$f(2, N) = N(N-1)/2 = N!/2!(N-2)!$$

etc.

or generally,

$$f(N_1, N) = \frac{N!}{N_1!(N-N_1)!} = \frac{N!}{N_1! N_2!}$$

which is clearly a classical degeneracy factor. If we were doing a purely classical treatment of the grand canonical ensemble, then this factor would appear in the sum for $Q(N, V, T)$, however, we always include the *ad hoc* quantum

correction $1/N!$ in the expression for the canonical partition function, and we see that these quantum factors will exactly cancel the classical degeneracy factor, leading to the following expression:

$$Q(N, V, T) = \sum_{N_1=0}^N Q_1(N_1, V_1, T) Q_2(N_2, V_2, T)$$

which expresses the fact that, in reality, the various configurations are not distinguishable from each other, and so each one should count with equal weighting. Now, the distribution function $\rho(\mathbf{x})$ is given by

$$\rho(\mathbf{x}, N) = \frac{\frac{1}{N!h^{3N}} e^{-\beta H(\mathbf{x}, N)}}{Q(N, V, T)}$$

which is chosen so that

$$\int d\mathbf{x} \rho(\mathbf{x}, N) = 1$$

However, recognizing that $N_2 \approx N$, we can obtain the distribution for $\rho_1(\mathbf{x}_1, N_1)$ immediately, by integrating over the phase space of system 2:

$$\rho_1(\mathbf{x}_1, N_1) = \frac{1}{Q(N, V, T)} \frac{1}{N_1!h^{3N_1}} e^{-\beta H_1(\mathbf{x}_1, N_1)} \frac{1}{N_2!h^{3N_2}} \int d\mathbf{x}_2 e^{-\beta H_2(\mathbf{x}_2, N_2)}$$

where the $1/N_1!h^{3N_1}$ prefactor has been introduced so that

$$\sum_{N_1=0}^N \int d\mathbf{x}_1 \rho(\mathbf{x}_1, N_1) = 1$$

and amounts to the usual *ad hoc* quantum correction factor that must be multiplied by the distribution function for each ensemble to account for the identical nature of the particles. Thus, we see that the distribution function becomes

$$\rho_1(\mathbf{x}_1, N_1) = \frac{Q_2(N_2, V_2, T)}{Q(N, V, T)} \frac{1}{N_1!h^{3N_1}} e^{-\beta H_1(\mathbf{x}_1, N_1)}$$

Recall that the Hemlholtz free energy is given by

$$A = -\frac{1}{\beta} \ln Q$$

Thus,

$$\begin{aligned} Q(N, V, T) &= e^{-\beta A(N, V, T)} \\ Q_2(N_2, V_2, T) &= e^{-\beta A(N_2, V_2, T)} = e^{-\beta A(N - N_1, V - V_1, T)} \end{aligned}$$

or

$$\frac{Q_2(N_2, V_2, T)}{Q(N, V, T)} = e^{-\beta(A(N - N_1, V - V_1, T) - A(N, V, T))}$$

But since $N \gg N_1$ and $V \gg V_1$, we may expand:

$$\begin{aligned} A(N - N_1, V - V_1, T) &= A(N, V, T) - \frac{\partial A}{\partial N} N_1 - \frac{\partial A}{\partial V} V_1 + \dots \\ &= A(N, V, T) - \mu N_1 + PV_1 + \dots \end{aligned}$$

Therefore the distribution function becomes

$$\begin{aligned} \rho_1(\mathbf{x}_1, N_1) &= \frac{1}{N_1!h^{3N_1}} e^{\beta \mu N_1} e^{-\beta PV_1} e^{-\beta H_1(\mathbf{x}_1, N_1)} \\ &= \frac{1}{N_1!h^{3N_1}} \frac{1}{e^{\beta PV_1}} e^{\beta \mu N_1} e^{-\beta H_1(\mathbf{x}_1, N_1)} \end{aligned}$$

Dropping the “1” subscript, we have

$$\rho(\mathbf{x}, N) = \frac{1}{e^{\beta PV}} \left[\frac{1}{N! h^{3N}} e^{\beta \mu N} e^{-\beta H(\mathbf{x}, N)} \right]$$

We require that $\rho(\mathbf{x}, N)$ be normalized:

$$\sum_{N=0}^{\infty} \int d\mathbf{x} \rho(\mathbf{x}, N) = 1$$

$$\frac{1}{e^{\beta PV}} \left[\sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} e^{\beta \mu N} \int d\mathbf{x} e^{-\beta H(\mathbf{x}, N)} \right] = 1$$

Now, we define the grand canonical partition function

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} e^{\beta \mu N} \int d\mathbf{x} e^{-\beta H(\mathbf{x}, N)}$$

Then, the normalization condition clearly requires that

$$\mathcal{Z}(\mu, V, T) = e^{\beta PV}$$

$$\ln \mathcal{Z}(\mu, V, T) = \frac{PV}{kT}$$

Therefore PV is the free energy of the grand canonical ensemble, and the entropy $S(\mu, V, T)$ is given by

$$S(\mu, V, T) = \left(\frac{\partial(PV)}{\partial T} \right)_{\mu, V} = k \ln \mathcal{Z}(\mu, V, T) - k\beta \left(\frac{\partial}{\partial \beta} \ln \mathcal{Z}(\mu, V, T) \right)_{\mu, V}$$

We now introduce the *fugacity* ζ defined to be

$$\zeta = e^{\beta \mu}$$

Then, the grand canonical partition function can be written as

$$\mathcal{Z}(\zeta, V, T) = \sum_{N=0}^{\infty} \frac{1}{N! h^{3N}} \zeta^N \int d\mathbf{x} e^{-\beta H(\mathbf{x}, N)} = \sum_{N=0}^{\infty} \zeta^N Q(N, V, T)$$

which allows us to view the grand canonical partition function as a function of the thermodynamic variables ζ , V , and T .

Other thermodynamic quantities follow straightforwardly:

Energy:

$$E = \langle H(\mathbf{x}, N) \rangle = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} \frac{\zeta^N}{N! h^{3N}} \int d\mathbf{x} H(\mathbf{x}, N) e^{-\beta H(\mathbf{x}, N)}$$

$$= - \left(\frac{\partial \ln \mathcal{Z}(\zeta, V, T)}{\partial \beta} \right)_{\zeta, V}$$

Average particle number:

$$\langle N \rangle = kT \left(\frac{\partial \ln \mathcal{Z}(\mu, V, T)}{\partial \mu} \right)_{V, T}$$

This can also be expressed using the fugacity by noting that

$$\frac{\partial}{\partial \mu} = \frac{\partial \zeta}{\partial \mu} \frac{\partial}{\partial \zeta} = \beta \zeta \frac{\partial}{\partial \zeta}$$

Thus,

$$\langle N \rangle = \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z}(\zeta, V, T)$$

C. Ideal gas

Recall the canonical partition function expression for the ideal gas:

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

Define the thermal wavelength $\lambda(\beta)$ as

$$\lambda(\beta) = \left(\frac{\beta h^2}{2\pi m} \right)^{1/2}$$

which has a quantum mechanical meaning as the width of the free particle distribution function. Here it serves as a useful parameter, since the canonical partition can be expressed as

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$$

The grand canonical partition function follows directly from $Q(N, V, T)$:

$$\mathcal{Z}(\zeta, V, T) = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{V\zeta}{\lambda^3} \right)^N = e^{V\zeta/\lambda^3}$$

Thus, the free energy is

$$\frac{PV}{kT} = \ln \mathcal{Z} = \frac{V\zeta}{\lambda^3}$$

In order to obtain the equation of state, we first compute the average particle number $\langle N \rangle$

$$\langle N \rangle = \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z} = \frac{V\zeta}{\lambda^3}$$

Thus, eliminating ζ in favor of $\langle N \rangle$ in the equation of state gives

$$PV = \langle N \rangle kT$$

as expected. Similarly, the average energy is given by

$$E = - \left(\frac{\partial \ln \mathcal{Z}}{\partial \beta} \right)_{\zeta V} = \frac{3V\zeta}{\lambda^4} \frac{\partial \lambda}{\partial \beta} = \frac{3}{2} \langle N \rangle kT$$

where the fugacity has been eliminated in favor of the average particle number. Finally, the entropy

$$S(\mu, V, T) = k \ln \mathcal{Z}(\mu, V, T) - k\beta \left(\frac{\partial \ln \mathcal{Z}(\mu, V, T)}{\partial \beta} \right)_{\mu, V} = \frac{5}{2} \langle N \rangle k + \langle N \rangle k \ln \left[\frac{V\lambda^3}{\langle N \rangle} \right]$$

which is the Sackur-Tetrode equation derived in the context of the canonical and microcanonical ensembles.

D. Particle number fluctuations

In the grand canonical ensemble, the particle number N is not constant. It is, therefore, instructive to calculate the fluctuation in this quantity. As usual, this is defined to be

$$\Delta N = \sqrt{\langle N^2 \rangle - \langle N \rangle^2}$$

Note that

$$\begin{aligned}\zeta \frac{\partial}{\partial \zeta} \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z}(\zeta, V, T) &= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} N^2 \zeta^N Q(N, V, T) - \frac{1}{\mathcal{Z}^2} \left[\sum_{N=0}^{\infty} N \zeta^N Q(N, V, T) \right]^2 \\ &= \langle N^2 \rangle - \langle N \rangle^2\end{aligned}$$

Thus,

$$(\Delta N)^2 = \zeta \frac{\partial}{\partial \zeta} \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z}(\zeta, V, T) = (kT)^2 \frac{\partial^2}{\partial \mu^2} \ln \mathcal{Z}(\mu, V, T) = kTV \frac{\partial^2 P}{\partial \mu^2}$$

In order to calculate this derivative, it is useful to introduce the Helmholtz free energy per particle defined as follows:

$$a(v, T) = \frac{1}{N} A(N, V, T)$$

where $v = V/N = 1/\rho$ is the volume per particle.

The chemical potential is defined by

$$\begin{aligned}\mu &= \frac{\partial A}{\partial N} = a(v, T) + N \frac{\partial a}{\partial v} \frac{\partial v}{\partial N} \\ &= a(v, T) - v \frac{\partial a}{\partial v}\end{aligned}$$

Similarly, the pressure is given by

$$P = -\frac{\partial A}{\partial V} = -N \frac{\partial a}{\partial v} \frac{\partial v}{\partial V} = -\frac{\partial a}{\partial v}$$

Also,

$$\frac{\partial \mu}{\partial v} = -v \frac{\partial^2 a}{\partial v^2}$$

Therefore,

$$\frac{\partial P}{\partial \mu} = \frac{\partial P}{\partial v} \frac{\partial v}{\partial \mu} = \frac{\partial^2 a}{\partial v^2} \left[v \frac{\partial^2 a}{\partial v^2} \right]^{-1} = \frac{1}{v}$$

and

$$\frac{\partial^2 P}{\partial \mu^2} = \frac{\partial}{\partial v} \frac{\partial P}{\partial \mu} \frac{\partial v}{\partial \mu} = \frac{1}{v^2} \left[v \frac{\partial^2 a}{\partial v^2} \right]^{-1} = -\frac{1}{v^3 \partial P / \partial v}$$

But recall the definition of the isothermal compressibility:

$$\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P} = -\frac{1}{v \partial p / \partial v}$$

Thus,

$$\frac{\partial^2 P}{\partial \mu^2} = \frac{1}{v^2} \kappa_T$$

and

$$\Delta N = \sqrt{\frac{\langle N \rangle kT \kappa_T}{v}}$$

and the relative fluctuation is given by

$$\frac{\Delta N}{N} = \frac{1}{\langle N \rangle} \sqrt{\frac{\langle N \rangle kT \kappa_T}{v}} \sim \frac{1}{\sqrt{\langle N \rangle}} \rightarrow 0 \text{ as } \langle N \rangle \rightarrow \infty$$

Therefore, in the thermodynamic limit, the particle number fluctuations vanish, and the grand canonical ensemble is equivalent to the canonical ensemble.