# ME346A Introduction to Statistical Mechanics – Wei Cai – Stanford University – Win 2011 Handout 9. NPT and Grand Canonical Ensembles

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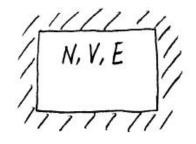
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Reading Assignment: Reif §6.9.

## **1** Summary of *NVE* and *NVT* ensembles

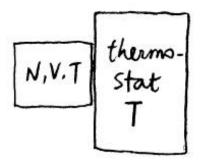
Let us start with a quick summary of the microcanonical (NVE) ensemble. It describes isolated systems with fixed number of particles N, volume V and energy E.



- The microcanonical ensemble is described by a uniform distribution with two constant energy shells.
- The connection with thermodynamics is made through Boltzmann's entropy formula:  $S = k_B \ln \Omega$ , where  $\Omega$  is the number of microscopic states consistent with thermodynamic (macroscopic) variables N, V, E.
- Inverting S(N, V, E) we can obtain E(S, V, N). The other thermodynamic quantities are defined through partial derivatives.

temperature  $T \equiv \left(\frac{\partial E}{\partial S}\right)_{V,N}$ , pressure  $p \equiv -\left(\frac{\partial E}{\partial V}\right)_{S,N}$ , chemical potential  $\mu \equiv \left(\frac{\partial E}{\partial N}\right)_{S,V}$ 

Next, a quick summary of the canonical (NVT) ensemble. It describes systems in contact with a thermostat at temperature T. As a result, the energy of the system no longer remain constant. The number of particles N and volume V remain fixed.



• The canonical ensemble is described by Boltzmann's distribution.

$$\rho(\{q_i\}, \{p_i\}) = \frac{1}{\tilde{Z}} e^{-\beta H(\{p_i\}, \{q_i\})}$$
(1)

$$\tilde{Z} = \int \prod_{i=1}^{3N} dq_i \, dp_i \, \mathrm{e}^{-\beta H(\{p_i\}, \{q_i\})}$$
(2)

• The connection with thermodynamics is made through the expression of Helmholtz free energy A(N, V, T) through the partition function Z,

$$A = -k_B T \ln Z , \qquad Z = \frac{1}{N! h^{3N}} \int \prod_{i=1}^{3N} dq_i \, dp_i \, \mathrm{e}^{-\beta H(\{p_i\}, \{q_i\})} \tag{3}$$

- The other thermodynamic quantities are defined through partial derivatives. entropy  $S \equiv \left(\frac{\partial A}{\partial T}\right)_{V,N}$ , pressure  $p \equiv -\left(\frac{\partial A}{\partial V}\right)_{T,N}$ , chemical potential  $\mu \equiv \left(\frac{\partial A}{\partial N}\right)_{T,V}$
- The energy (Hamiltonian) of system is no longer conserved, but fluctuate around its average value.

$$E \equiv \langle H \rangle = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z$$
(4)

$$(\Delta E)^2 \equiv \langle H^2 \rangle - \langle H \rangle^2 = -\frac{\partial E}{\partial \beta} = k_B T^2 C_v = N k_B T^2 c_v \tag{5}$$

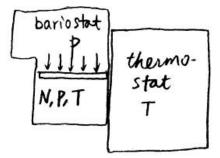
Hence in the thermodynamic limit  $N \to \infty$ ,

$$\Delta E = \sqrt{Nk_B T^2 c_v} \quad \frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}} \to 0 \tag{6}$$

The difference between microcanonical (NVE) ensemble and canonical (NVT) ensemble vanishes.

## 2 NPT ensemble

The NPT ensemble is also called the **isothermal-isobaric** ensemble. It describes systems in contact with a thermostat at temperature T and a bariostat at pressure p. The system not only exchanges heat with the thermostat, it also exchange volume (and work) with the bariostat. The total number of particles N remains fixed. But the total energy E and volume V fluctuate at thermal equilibrium.



- Q: What is the statistical distribution  $\rho(\{q_i\}, \{p_i\})$  at thermal equilibrium?
- Q: What is the microscopic expression for the thermodynamic potential?
- Approach: Consider system of interest + thermostat + bariostat all together as a closed system, which can be described using the microcanonical ensemble.

#### 2.1 Equilibrium distribution

Notice that in the (NPT) ensemble, the probability distribution function must also include V as its variable, because the volume can (in principle) take any value at thermal equilibrium.

 $\rho(\{q_i\}, \{p_i\}, V) \propto \text{number of ways } (\tilde{\Omega})$  the thermostat and the bariostat can rearrange themselves to allow the system to have energy  $E = H(\{q_i\}, \{p_i\})$  and volume V.

Let  $\tilde{S}$  be the entropy of the thermostat + bariostat, then

$$\tilde{\Omega} = \exp\left(\frac{\tilde{S}}{k_B}\right) \tag{7}$$

Let  $V_0$  and  $E_0$  be the total volume and total energy of the thermostat + bariostat + system of interest. Let V and E be the volume and energy of the system of interest. Then the volume and energy left for the thermostat + bariostat are,  $V_0 - V$  and  $E_0 - E$ , respectively.

$$\tilde{S}(\tilde{N}, V_0 - V, E_0 - E) = \tilde{S}(\tilde{N}, V_0, E_0) - \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_{N, E} V - \left(\frac{\partial \tilde{S}}{\partial \tilde{E}}\right)_{N, V} E$$
(8)

We recognize  $\left(\frac{\partial \tilde{S}}{\partial \tilde{E}}\right)_{N,V} \equiv \frac{1}{T}$  where *T* is the temperature of the thermostat. But what is  $\left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_{N,E}$ ?

This is the time to use the second type of Maxwell's relationship.

$$\left(\frac{\partial \tilde{S}}{\partial \tilde{E}}\right)_{V,N} \cdot \left(\frac{\partial \tilde{E}}{\partial \tilde{V}}\right)_{S,N} \cdot \left(\frac{\partial \tilde{V}}{\partial \tilde{S}}\right)_{E,N} = -1 \tag{9}$$

$$\frac{1}{T} \cdot (-p) \cdot \left(\frac{\partial \tilde{V}}{\partial \tilde{S}}\right)_{E,N} = -1 \tag{10}$$

$$\implies \qquad \left(\frac{\partial \tilde{S}}{\partial \tilde{V}}\right)_{N,E} = \frac{p}{T} \tag{11}$$

where p is the pressure of the bariostat. Therefore,

$$\tilde{S}(\tilde{N}, \tilde{V}, \tilde{E}) = \tilde{S}(\tilde{N}, V_0, E_0) - \frac{p}{T}V - \frac{1}{T}E$$
(12)

$$\tilde{\Omega} = \text{const} \cdot \exp\left(-\frac{E + pV}{k_B T}\right) \tag{13}$$

Therefore, the equilibrium distribution of the isothermal-isobaric (NPT) ensemble is,

$$\rho(\{q_i\},\{p_i\},V) = \frac{1}{\Xi} e^{-\beta[H(\{q_i\},\{p_i\})+pV]}$$
(14)

$$\Xi = \int_0^\infty dV \int \prod_{i=1}^{3N} dq_i \, dp_i \, \mathrm{e}^{-\beta [H(\{q_i\}, \{p_i\}) + pV]}$$
(15)

#### 2.2 Thermodynamic potential

By now, we would expect the normalization factor  $\Xi$  should be interpreted as a kind of partition function that will reveal us the fundamental equation of state.

To find out the precise expression, we start with the Shanon entropy expression. (Notice here that V is an internal degree of freedom to be integrated over and p is an external variable.)

$$S = -k_B \sum_{i} p_i \ln p_i$$

$$= -k_B \int_0^\infty dV \int \prod_{i=1}^{3N} dq_i dp_i \rho(\{q_i\}, \{p_i\}, V) \cdot \left[\frac{H(\{q_i\}, \{p_i\}) + pV}{-k_B T} - \ln \tilde{\Xi}\right]$$

$$= \frac{1}{T} (\langle H \rangle + p \langle V \rangle) + k_B \ln \tilde{\Xi}$$
(16)

$$= \frac{1}{T}(E + pV_{\text{avg}}) + k_B \ln \tilde{\Xi}$$
(17)

Hence

$$-k_B T \ln \tilde{\Xi} = E - TS + p V_{avg} \equiv G(N, T, P)$$
(18)

This is the Gibbs free energy, which is the appropriate thermodynamic potential as a function of N, T, P! So everything falls into the right places nicely. We just need to careful that the volume in thermodynamics is the ensemble average  $V_{\text{avg}} \equiv \langle V \rangle$ , because in (N, T, P)ensemble, V is not a constant.

Of course, we still need to put in the quantum corrections  $1/(N!h^{3N})$ , just as before. So the final expression for the Gibbs free energy and chemical potential  $\mu$  is,

$$\mu N = G(T, p, N) = -k_B T \ln \Xi$$
<sup>(19)</sup>

$$\Xi(T, p, N) = \frac{1}{N! h^{3N}} \int_0^\infty dV \int \prod_{i=1}^{3N} dq_i \, dp_i \, p_i \mathrm{e}^{-\beta[H(\{q_i\}, \{p_i\}) + pV]}$$
(20)

$$\Xi(T, p, N) = \int_0^\infty dV Z(T, V, N) e^{-\beta pV}$$
(21)

Therefore,  $\Xi(T, p, N)$  is the **Laplace transform** of the partition function Z(T, V, N) of the canonical ensemble!

#### 2.3 Volume fluctuations

To obtain the average of volume V and its higher moments, we can use the same trick as in the canonical ensemble and take derivatives of  $\Xi$  with respect to p.

$$\langle V \rangle = -k_B T \frac{1}{\Xi} \frac{\partial \Xi}{\partial p} \langle V^2 \rangle = (k_B T)^2 \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial p^2} - \frac{\partial V}{\partial p} = k_B T \frac{\partial}{\partial p} \left( \frac{1}{\Xi} \frac{\partial \Xi}{\partial p} \right) = k_B T \left[ \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial p^2} - \frac{1}{\Xi^2} \left( \frac{\partial \Xi}{\partial p} \right)^2 \right] = \frac{1}{k_B T} \left[ (k_B T)^2 \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial p^2} - \left( k_B T \frac{1}{\Xi} \frac{\partial \Xi}{\partial p} \right)^2 \right] = \frac{1}{k_B T} (\langle V^2 \rangle - \langle V \rangle^2) = \frac{1}{k_B T} (\Delta V)^2$$

$$(22)$$

Define compressibility<sup>1</sup>

$$\beta_c \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_{T,N} = \frac{(\Delta V)^2}{k_B T V} \tag{23}$$

Then we have,

$$(\Delta V)^2 = k_B T \beta_c V \tag{24}$$

$$\Delta V = \sqrt{k_B T \beta_c V} \tag{25}$$

$$\frac{\Delta V}{V} \propto \frac{1}{\sqrt{V}} \to 0 \qquad \text{as V} \to \infty$$
(26)

In other words, in the thermodynamic limit  $(V \to \infty)$ , the relative fluctuation of volume is negligible and the difference between (NPT) ensemble and (NVT) ensemble vanishes.

#### 2.4 Ideal gas example

To describe ideal gas in the (NPT) ensemble, in which the volume V can fluctuate, we introduce a potential function  $U(\mathbf{r}, V)$ , which confines the partial position r within the volume V. Specifically,  $U(\mathbf{r}, V) = 0$  if **r** lies inside volume V and  $U(\mathbf{r}, V) = +\infty$  if **r** lies outside volume V.

The Hamiltonian of the ideal gas can be written as,

$$H(\{q_i\},\{p_i\}) = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + \sum_{j=1}^{N} U(\mathbf{r}_i, V)$$
(27)

<sup>&</sup>lt;sup>1</sup>Not to be confused with  $\beta \equiv 1/(k_B T)$ .

Recall the ideal gas partition function in the (NVT) ensemble.

$$Z(T, V, N) = \frac{V^N}{N! h^{3N}} (2\pi m k_B T)^{3N/2} = \frac{V^N}{N! \Lambda^{3N}}$$
(28)

where  $\Lambda \equiv h/\sqrt{2\pi m k_B T}$  is the thermal **de Broglie wavelength**.

$$\Xi(T, p, N) = \int_{0}^{\infty} dV \cdot Z(T, V, N) \cdot e^{-\beta p V}$$

$$= \frac{1}{N! \lambda^{3N}} \int_{0}^{\infty} dV \cdot V^{N} \cdot e^{-\beta p V}$$

$$= \frac{1}{N! \lambda^{3N}} \frac{1}{(\beta p)^{N+1}} \int_{0}^{\infty} dx \cdot x^{N} \cdot e^{-x}$$

$$= \frac{1}{N! \lambda^{3N}} \frac{1}{(\beta p)^{N+1}} N!$$

$$= \left(\frac{k_{B}T}{p}\right)^{N+1} \frac{1}{\Lambda^{3N}}$$
(29)

In the limit of  $N \to \infty$ ,

$$\Xi(T, p, N) \approx \left(\frac{k_B T}{p}\right)^N \cdot \frac{(2\pi m k_B T)^{3N/2}}{h^{3N}}$$
(30)

The Gibbs free energy is

$$G(T, p, N) = -k_B \ln \Xi = -Nk_B T \ln \left[ \left( \frac{k_B T}{p} \right) \cdot \frac{(2\pi m k_B T)^{3/2}}{h^3} \right]$$
(31)

This is consistent with Lecture Notes 6 Thermodynamics §3.2,

$$\mu = \frac{G}{N} = -k_B T \ln\left[\left(\frac{k_B T}{p}\right) \cdot \frac{(2\pi m k_B T)^{3/2}}{h^3}\right]$$
(32)

## 3 Grand canonical ensemble

The grand canonical ensemble is also called the  $\mu VT$  ensemble. It describes systems in contact with a thermostat at temperature T and a particle reservoir that maintains the chemical potential  $\mu$ . The system not only exchanges heat with the thermostat, it also exchange particles with the reservoir. The volume V remains fixed.<sup>2</sup> But the number of particles N and energy E fluctuate at thermal equilibrium.

<sup>&</sup>lt;sup>2</sup>Remember the Gibbs-Duhem relation. We cannot specify all three variables  $T, p, \mu$  simultaneously.

resevoir	thermo-
4 1	stat
. <i>µ.</i> v.T	Т

- Q: What is the statistical distribution  $\rho(\{q_i\}, \{p_i\})$  at thermal equilibrium?
- Q: What is the microscopic expression for the thermodynamic potential?
- Approach: Consider system of interest + thermostat + particle reservoir all together as a closed system, which can be described using the microcanonical ensemble.

#### 3.1 Equilibrium distribution

Notice that int the grand canonical  $(\mu VT)$  ensemble, the probability distribution function must also include N as its variable, because the number of particle can (in principle) be any non-negative integer at thermal equilibrium.

Following the same approach as in the (NPT) ensemble, we obtain the equilibrium distribution of the grand canonical  $(\mu VT)$  ensemble as the following.

$$\rho(\{q_i\}, \{p_i\}, N) = \frac{1}{\tilde{\mathcal{Z}}} e^{-\beta(H(\{q_i\}, \{p_i\}) - \mu N)}$$
(33)

where

$$\tilde{\mathcal{Z}} = \sum_{N=0}^{\infty} \int \prod_{i=1}^{3N} dq_i \, dp_i \, \mathrm{e}^{-\beta(H(\{q_i\},\{p_i\})-\mu N)}$$
(34)

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} \tilde{Z}(N, V, T)$$
(35)

 $\rho$  is grand canonical distribution and  $\tilde{Z}(N, V, T)$  is the normalization factor in the canonical ensemble for N particles.

### 3.2 Thermodynamic potential

Again, we should expect the normalization factor to give us the thermodynamic potential for  $\mu, V, T$ , which is the **Grand potential**, or Landau potential,<sup>3</sup>

$$\Phi(\mu, V, T) = E - TS - \mu N = -pV \tag{36}$$

<sup>&</sup>lt;sup>3</sup>We called it K in Lecture Notes 6 Thermodynamics.

Starting from Shanon's entropy expression, we can show that

$$\Phi(\mu, V, T) = -k_B T \ln \mathcal{Z} , \quad pV = k_B T \ln \mathcal{Z}$$
(37)

where  $\mathcal{Z}$  is the grand partition function,

$$\mathcal{Z} = \sum_{N=0}^{\infty} \int \prod_{i=1}^{3N} dq_i \, dp_i \, \mathrm{e}^{-\beta(H(\{q_i\},\{p_i\})-\mu N)}$$
(38)

$$= \sum_{N=0}^{\infty} e^{\beta \mu N} Z(N, V, T)$$
(39)

where Z(N, V, T) is the partition function of the canonical ensemble. Notice that we have removed the  $\tilde{s}$  sign, meaning that we have applied the quantum correction  $1/(N!h^{3N})$ .

Define **fugacity**  $z \equiv e^{\beta\mu}$  (so that  $\mu = k_B T \ln z$ ) we can write,

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z(N, V, T)$$
(40)

Therefore, the grand partition function  $\mathcal{Z}(\mu, V, T)$  is the **unilateral Z-transform** of the partition function Z(N, V, T) of the canonical ensemble.<sup>4</sup>

#### 3.3 Number of particles fluctuations

Average number of particles

$$\langle N \rangle = k_B T \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = k_B T \frac{\partial}{\partial \mu} (\ln \mathcal{Z}) = z \frac{\partial}{\partial z} (\ln \mathcal{Z})$$
(41)

$$\langle N^2 \rangle = (k_B T)^2 \frac{1}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2}$$
 (42)

$$\frac{\partial \langle N \rangle}{\partial \mu} = \frac{1}{k_B T} (\langle N^2 \rangle - \langle N \rangle^2) = \frac{(\Delta N)^2}{k_B T}$$
(43)

Define density  $\rho \equiv \frac{\langle N \rangle}{V}, \langle N \rangle = \rho V$ 

$$V \cdot \frac{\partial \rho}{\partial \mu} = \frac{(\Delta N)^2}{k_B T} \tag{44}$$

$$(\Delta N)^2 = k_B T (\partial \rho / \partial \mu) V \tag{45}$$

$$\Delta N = \sqrt{k_B T (\partial \rho / \partial \mu) V} \tag{46}$$

$$\frac{\Delta N}{\langle N \rangle} = \frac{\sqrt{k_B T (\partial \rho / \partial \mu) V}}{\rho V} \propto \frac{1}{\sqrt{V}} \to 0 \quad (\text{as } V \to \infty)$$
(47)

 $^4$ No wonder it is called the Z-transform. See http://en.wikipedia.org/wiki/Z-transform for properties of the Z-transform.

### 3.4 Ideal gas example

Recall the ideal partition function in the canonical ensemble,

$$Z(N,V,T) = \frac{V^N}{N!h^{3N}} (2\pi m k_B T)^{3N/2} = \frac{V^N}{N!\Lambda^{3N}}$$
(48)

(49)

From this we obtain the grand partition function,

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N \frac{V^N}{N! \Lambda^{3N}} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{zV}{\Lambda^3}\right)^N$$
(50)

$$\mathcal{Z} = \exp\left(\frac{zV}{\Lambda^3}\right) \tag{51}$$

Next the grand potential  $\Phi = -pV$ ,

$$pV = k_B T \ln \mathcal{Z} = k_B T \frac{zV}{\Lambda^3}$$
(52)

$$p = k_B T \frac{z}{\Lambda^3}, \quad z = \frac{p}{k_B T} \Lambda^3 \tag{53}$$

$$e^{\beta\mu} = \frac{p}{k_B T} \left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}$$
(54)

$$\mu = k_B T \ln\left[\left(\frac{p}{k_B T}\right) \cdot \left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\right]$$
(55)

This is consistent with the results from the NPT ensemble, as it should!

We now can obtain an explicit expression of the **density fluctuation** of the ideal gas.

$$\langle N \rangle = z \frac{\partial}{\partial z} \ln \mathcal{Z} = z \frac{\partial}{\partial z} \left( \frac{zV}{\Lambda^3} \right) = \frac{zV}{\Lambda^3} = \ln Z = \frac{pV}{k_B T}$$
(56)

$$\langle N \rangle = \frac{e^{\beta \mu} V}{\Lambda^3} \tag{57}$$

$$\frac{\partial \langle N \rangle}{\partial \mu} = \frac{e^{\beta \mu} \beta V}{\Lambda^3} = \beta \cdot \langle N \rangle = \frac{pV}{(k_B T)^2}$$
(58)

$$(\Delta N)^2 = k_B T \frac{\partial \langle N \rangle}{\partial \mu} = \frac{pV}{k_B T} = \langle N \rangle$$
(59)

(60)

Hence the variance of N equals the expectation value of N. The standard deviation of N is

$$\Delta N = \sqrt{\langle N \rangle} \tag{61}$$

The relative fluctuation of N is

$$\frac{\Delta N}{N} = \frac{1}{\sqrt{\langle N \rangle}} \tag{62}$$

From the above we also obtain how density  $\rho = N/V$  changes with the chemical potential,

$$\frac{\partial \rho}{\partial \mu} = \frac{1}{V} \frac{\partial \langle N \rangle}{\partial \mu} = \frac{p}{(k_B T)^2} \tag{63}$$

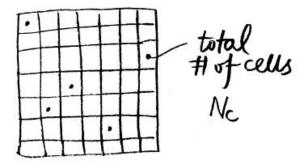
#### 3.5 Lattice gas model

From the previous sections, we see

$$\Delta N = \langle N \rangle \tag{64}$$

Q: Is this result reasonable?

Ideal gas means no correlation between molecules. Hence we can build a lattice gas model as a further simplification to the ideal gas model.



Imagine we divide the volume V into  $N_c$  cells. Each cell can have either 1 molecule or 0 molecule.

Assume  $N_c \gg \langle N \rangle$ , so that we can ignore the possibility that two molecules occupy the same cell.

Define a random variable for each cell,

$$n_i = \begin{cases} 1 & \text{cell } i \text{ contains 1 molecule, probability } p \\ 0 & \text{cell } i \text{ contains 0 molecule, probability } (1-p) \end{cases}$$
(65)

 $n_i$  and  $n_j$  are independent of each other (for  $i \neq j)$ 

The total number of molecules in volume V is

$$N = \sum_{i=1}^{N_c} n_i,\tag{66}$$

The average number of molecules is

$$\langle N \rangle = \sum_{i=1}^{N_c} \langle n_i \rangle = \langle n_i \rangle \cdot N_c \tag{67}$$

Notice that

$$\langle n_i \rangle = p \tag{68}$$

$$\langle n_i^2 \rangle = p \tag{69}$$

$$\langle n_i^2 \rangle - \langle n_i \rangle^2 = p - p^2 = p (1 - p)$$
(70)

Hence

$$\langle N \rangle = N_c p \tag{71}$$

$$\langle N^2 \rangle - \langle N \rangle^2 = N_c p \left(1 - p\right) = \langle N \rangle \left(1 - \frac{\langle N \rangle}{N_c}\right)$$
(72)

In the limit of  $N_c \gg \langle N \rangle$ ,<sup>5</sup>

$$(\Delta N)^2 = \langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle \tag{73}$$

This is consistent with the prediction from the grand canonical ensemble.

 $<sup>{}^{5}</sup>N_{c}$  can be arbitrarily large and hence much larger than N.