

# Handout 9. NPT and Grand Canonical Ensembles

January 26, 2011

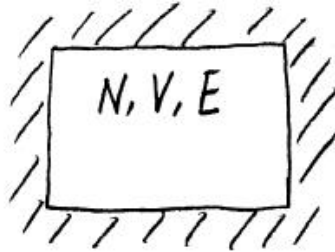
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Reading Assignment: Reif §6.9.

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

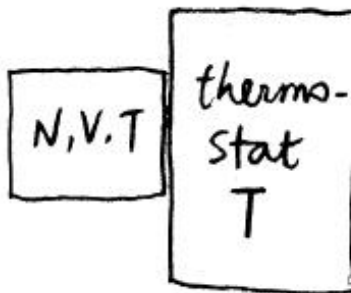
Let us start with a quick summary of the microcanonical ( $NVE$ ) ensemble. It describes isolated systems with fixed number of particles  $N$ , volume  $V$  and energy  $E$ .



- 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.

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

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

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

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

- 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.

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

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

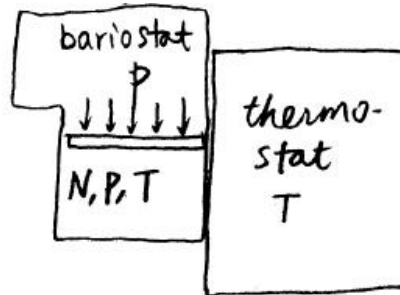
Hence in the thermodynamic limit  $N \rightarrow \infty$ ,

$$\Delta E = \sqrt{N k_B T^2 c_v} \quad \frac{\Delta E}{E} \propto \frac{1}{\sqrt{N}} \rightarrow 0 \quad (6)$$

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 barostat at pressure  $p$ . The system not only exchanges heat with the thermostat, it also exchange volume (and work) with the barostat. 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 + barostat 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.

$\rho(\{q_i\}, \{p_i\}, V) \propto$  number of ways ( $\tilde{\Omega}$ ) the thermostat and the barostat 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 + barostat, then

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

Let  $V_0$  and  $E_0$  be the total volume and total energy of the thermostat + barostat + 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 + barostat are,  $V_0 - V$  and  $E_0 - E$ , respectively.

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

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.

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

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

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

where  $p$  is the pressure of the barostat. Therefore,

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

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

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

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

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

## 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 Shannon entropy expression. (Notice here that  $V$  is an internal degree of freedom to be integrated over and  $p$  is an external variable.)

$$\begin{aligned}
 S &= -k_B \sum_i p_i \ln p_i \\
 &= -k_B \int_0^\infty dV \int \prod_{i=1}^{3N} dq_i dp_i \rho(\{q_i\}, \{p_i\}, V) \cdot \left[ \frac{H(\{q_i\}, \{p_i\}) + pV}{-k_B T} - \ln \tilde{\Xi} \right] \\
 &= \frac{1}{T} (\langle H \rangle + p \langle V \rangle) + k_B \ln \tilde{\Xi} \tag{16}
 \end{aligned}$$

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

Hence

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

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 be 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,

$$\mu N = G(T, p, N) = -k_B T \ln \Xi \tag{19}$$

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

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

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  $p$ .

$$\begin{aligned}
\langle V \rangle &= -k_B T \frac{1}{\Xi} \frac{\partial \Xi}{\partial p} \\
\langle V^2 \rangle &= (k_B T)^2 \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial p^2} \\
-\frac{\partial V}{\partial p} &= k_B T \frac{\partial}{\partial p} \left( \frac{1}{\Xi} \frac{\partial \Xi}{\partial p} \right) = k_B T \left[ \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial p^2} - \frac{1}{\Xi^2} \left( \frac{\partial \Xi}{\partial p} \right)^2 \right] \\
&= \frac{1}{k_B T} \left[ (k_B T)^2 \frac{1}{\Xi} \frac{\partial^2 \Xi}{\partial p^2} - \left( k_B T \frac{1}{\Xi} \frac{\partial \Xi}{\partial p} \right)^2 \right] \\
&= \frac{1}{k_B T} (\langle V^2 \rangle - \langle V \rangle^2) \\
&\equiv \frac{1}{k_B T} (\Delta V)^2
\end{aligned} \tag{22}$$

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,

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

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

$$\frac{\Delta V}{V} \propto \frac{1}{\sqrt{V}} \rightarrow 0 \quad \text{as } V \rightarrow \infty \tag{26}$$

In other words, in the thermodynamic limit ( $V \rightarrow \infty$ ), 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  $\mathbf{r}$  lies inside volume  $V$  and  $U(\mathbf{r}, V) = +\infty$  if  $\mathbf{r}$  lies outside volume  $V$ .

The Hamiltonian of the ideal gas can be written as,

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

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

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

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

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

$$\begin{aligned} \Xi(T, p, N) &= \int_0^\infty dV \cdot Z(T, V, N) \cdot e^{-\beta p V} \\ &= \frac{1}{N! \Lambda^{3N}} \int_0^\infty dV \cdot V^N \cdot e^{-\beta p V} \\ &= \frac{1}{N! \Lambda^{3N}} \frac{1}{(\beta p)^{N+1}} \int_0^\infty dx \cdot x^N \cdot e^{-x} \\ &= \frac{1}{N! \Lambda^{3N}} \frac{1}{(\beta p)^{N+1}} N! \\ &= \left( \frac{k_B T}{p} \right)^{N+1} \frac{1}{\Lambda^{3N}} \end{aligned} \quad (29)$$

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

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

The Gibbs free energy is

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

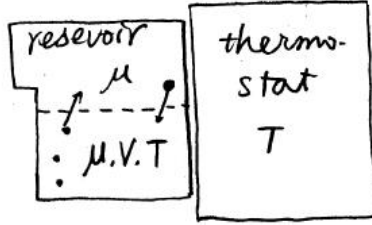
This is consistent with Lecture Notes 6 Thermodynamics §3.2,

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

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



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 in the grand canonical ( $\mu VT$ ) ensemble, the probability distribution function must also include  $N$  as its variable, because the number of particles 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.

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

where

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

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

$\rho$  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>

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

<sup>3</sup>We called it  $K$  in Lecture Notes 6 Thermodynamics.



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

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

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

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

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

where  $Z(N, V, T)$  is the partition function of the canonical ensemble. Notice that we have removed the  $\tilde{\phantom{x}}$  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,

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

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

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

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

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

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

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

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

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

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

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<sup>4</sup>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,

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

$$(49)$$

From this we obtain the grand partition function,

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

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

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

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

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

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

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

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.

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

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

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

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

$$(60)$$

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

$$\Delta N = \sqrt{\langle N \rangle} \quad (61)$$

The relative fluctuation of  $N$  is

$$\frac{\Delta N}{N} = \frac{1}{\sqrt{\langle N \rangle}} \quad (62)$$

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

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

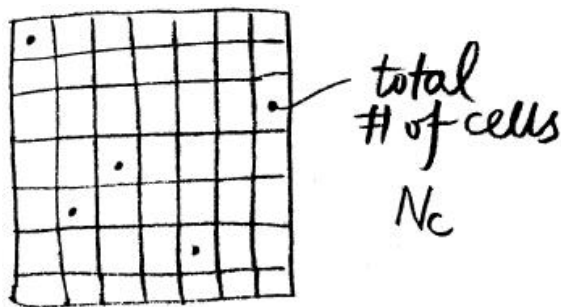
### 3.5 Lattice gas model

From the previous sections, we see

$$\Delta N = \langle N \rangle \quad (64)$$

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,

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

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

The total number of molecules in volume  $V$  is

$$N = \sum_{i=1}^{N_c} n_i, \quad (66)$$

The average number of molecules is

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

Notice that

$$\langle n_i \rangle = p \quad (68)$$

$$\langle n_i^2 \rangle = p \quad (69)$$

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

Hence

$$\langle N \rangle = N_c p \quad (71)$$

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

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

$$(\Delta N)^2 = \langle N^2 \rangle - \langle N \rangle^2 = \langle N \rangle \quad (73)$$

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

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<sup>5</sup> $N_c$  can be arbitrarily large and hence much larger than  $N$ .