

Handout 9. NPT and Grand Canonical Ensembles

January 26, 2011

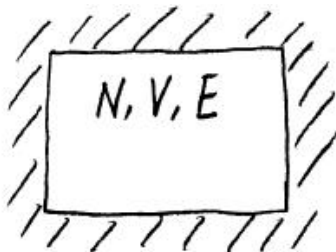
Contents

1	Summary of NVE and NVT ensembles	2
2	NPT ensemble	3
2.1	Equilibrium distribution	4
2.2	Thermodynamic potential	5
2.3	Volume fluctuations	5
2.4	Ideal gas example	6
3	Grand canonical ensemble	7
3.1	Equilibrium distribution	8
3.2	Thermodynamic potential	8
3.3	Number of particles fluctuations	9
3.4	Ideal gas example	10
3.5	Lattice gas model	11

Reading Assignment: Reif §6.9.

1 Summary of NVE and NVT ensembles

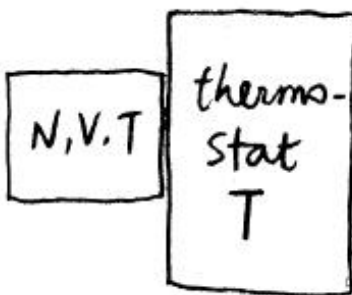
Let us start with a quick summary of the microcanonical (NVE) ensemble. It describes isolated systems with fixed number of particles N , volume V and energy E .



- 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 Ω 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.

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

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

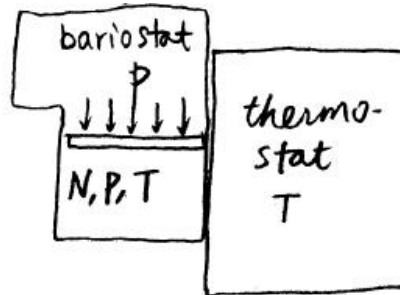
Hence in the thermodynamic limit $N \rightarrow \infty$,

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

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 Ξ 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.)

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

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

Hence

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

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 μ 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 Ξ 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 compressibility¹

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

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,

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

¹Not 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

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

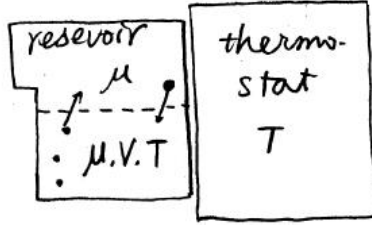
This is consistent with Lecture Notes 6 Thermodynamics §3.2,

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

3 Grand canonical ensemble

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

²Remember the Gibbs-Duhem relation. We cannot specify all three variables T, p, μ 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 (μVT) 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 (μVT) 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

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

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

ρ 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 μ, V, T , which is the **Grand potential**, or Landau potential,³

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

³We 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 $\tilde{}$ 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.⁴

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

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

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

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

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

⁴No 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,

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

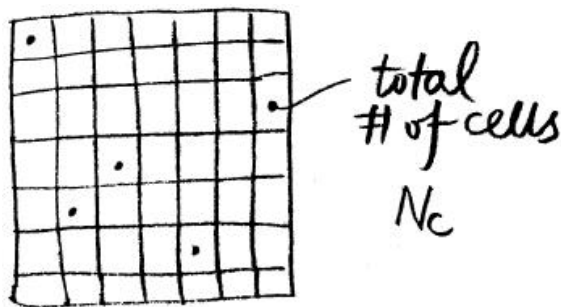
3.5 Lattice gas model

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 $N_c \gg \langle N \rangle$,⁵

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

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

⁵ N_c can be arbitrarily large and hence much larger than N .