

# General Physics II: Tutorial Material

## Lecture 4 on Chapter 5 (Statistical thermodynamics)

1) The rms speed of molecules in a gas at  $20.0^{\circ}C$  is to be increased by 2.0%. To what temperature must it be raised?

**Solution:**

The rms speed of molecule in a gas is given by

$$v_{rms} = \sqrt{\frac{3kT}{m}} \quad (1)$$

The ratio at two different temperature is then given by

$$\frac{v'_{rms}}{v_{rms}} = \sqrt{\frac{3kT'}{m}} / \sqrt{\frac{3kT}{m}} = \sqrt{\frac{T'}{T}} \quad (2)$$

We have  $T = 20 + 273 = 293K$  and  $\frac{v'_{rms}}{v_{rms}} = 1.02$ , makes

$$T' = \left( \frac{v'_{rms}}{v_{rms}} \right)^2 T = 1.02^2 \times 293 = 305K \quad (3)$$

i.e. the temperature must be increased by  $12^{\circ}C$ .

2) If you double the mass of the molecules in a gas, is it possible to change the temperature to keep the velocity distribution from changing? If so, how much change do you need to make to the temperature?

**Solution:**

The velocity distribution is given by the Maxwell distribution

$$F(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{3/2} v^2 \exp\left(-\frac{m}{2kT}v^2\right) \quad (4)$$

In order to keep the velocity distribution unchanged,  $m/T$  must remain the same. Therefore, when the mass is doubled, the temperature of the gas must be doubled to keep the same velocity distribution.

3) There are four coins with two faces, head and tail. Each coin has 50% probability to show head and 50% probability to show tail, when tossed individually. When we toss the four coins together:

1. How many head-tail configurations are there if we can distinguish individual coins? What are the probabilities for those configurations?
2. How many head-tail configurations are there if we cannot distinguish individual coins? Which configuration has the highest probability to be realized?

**Solution :**

- Possible number of configurations for the case 1) are

All coins are head	1 configuration	
Three coins are head and one coin tail	4 configuration	
Two coins are head and two coins tail	6 configuration	
One coin is head and three coins tail	4 configuration	
All coins are tail	1 configuration	

(5)

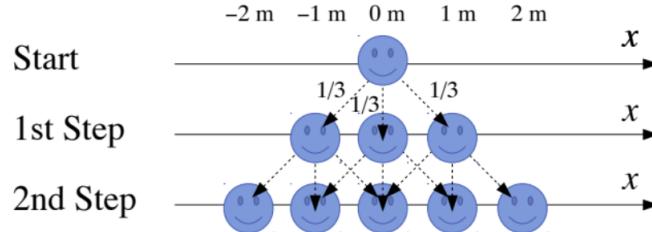
i.e. 16 configurations and each configuration as a probability of  $0.5^4 = 0.0625$ .

- there are only 5 configurations.

- All coins are head
- Three coins are head and one coin tail
- Two coins are head and two coins tail
- One coin is head and three coins tail
- All coins are tail

and the third configuration, i.e. two heads and two tails, has the highest probability of  $0.0625 \times 6 = 0.375$ .

4) A drunken person is standing at  $x = 0\text{ m}$ . When the drunken person makes one step, the person may go to the left (negative direction in  $x$  by 1 m), remain at the same position or to the right (positive direction in  $x$  by 1 m) with a same probability ( $1/3$  for each).



- What is the probability for the drunken person to be at  $x = -8\text{ m}, -7\text{ m}, -6\text{ m}, -5\text{ m}, -4\text{ m}, -3\text{ m}, -2\text{ m}, -1\text{ m}, -0\text{ m}, 1\text{ m}, 2\text{ m}, 3\text{ m}, 4\text{ m}, 5\text{ m}, 6\text{ m}, 7\text{ m}$  and  $8\text{ m}$  after 1, 2, 4 and 7 steps?

- What are the mean values,  $\langle x \rangle$ , and the rms,  $x_{rms}$ , for  $x$  after 1, 2, 4 and 7 steps? Figure 1 below show four probability distributions in  $x$  following the Gauss distribution,  $G(x)$ , given by

$$G(x) = \frac{1}{\sqrt{2\pi x_{rms}^2}} \exp \left[ -\frac{(x - \langle x \rangle)^2}{2x_{rms}^2} \right] \quad (6)$$

with  $x_{rms}$  equal to those obtained for 1, 2, 4 and 7 steps above, but not necessarily in this order.

- Find out which Gauss distributions of Fig. 1 belong to which steps.
- Superimpose the probability distributions of the  $x$  position of the drunken person on the Gauss distribution of corresponding steps. What kind of conclusion can you draw from comparing the distributions?

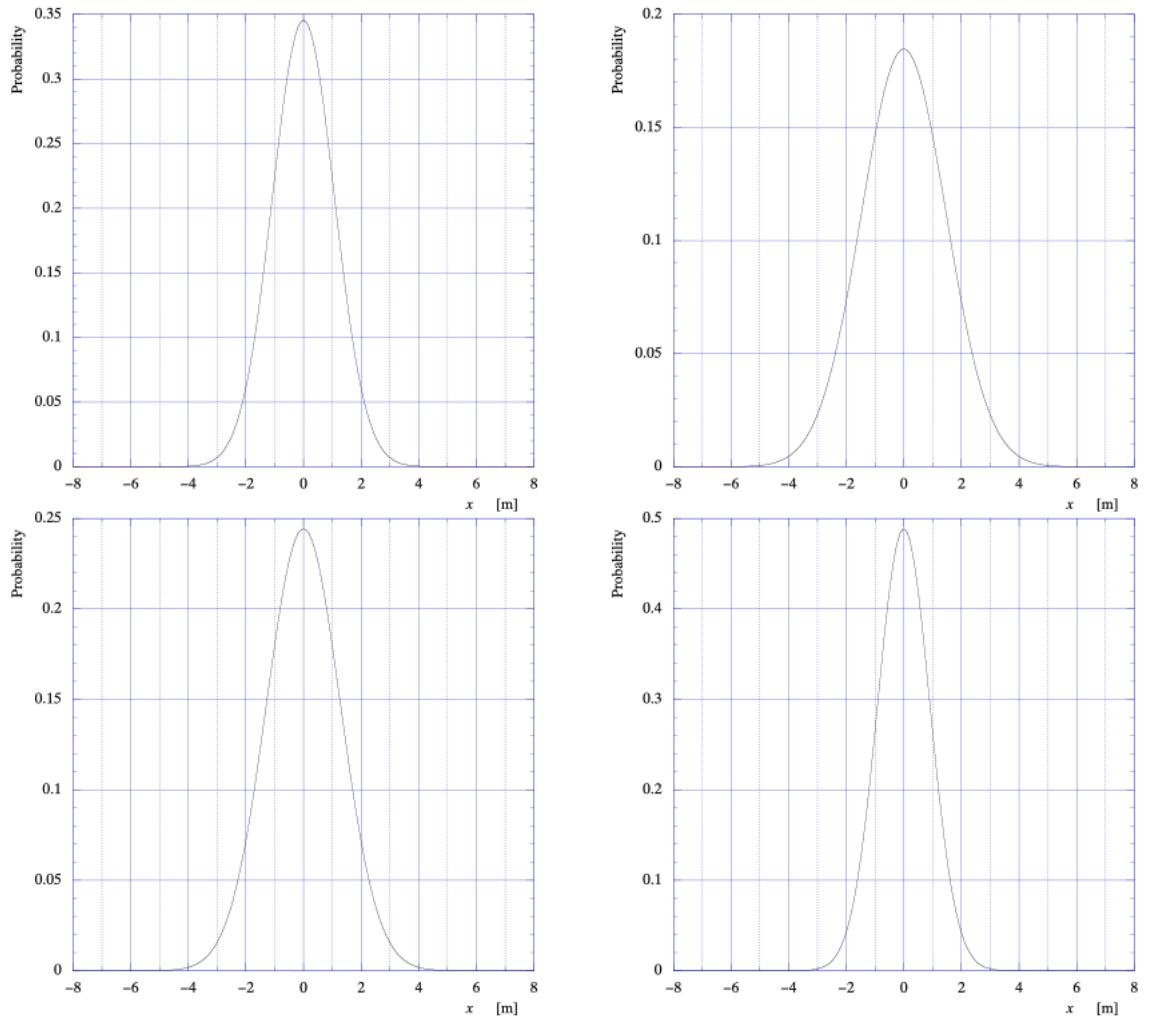


Figure 1: Gauss distributions of task 4-3.

**Solution:**

1. Since the drunken person moves to the left and right with a same probability, the probability distribution in  $x$  is symmetric at around  $x = 0m$ . After  $n$ -steps, the farthest the person can reach is  $x \pm n m$  with a probability  $(1/3)^n$ , and there are in total  $2n+1$   $x$  positions with non-zero probabilities. Furthermore, there are, in total,  $3^n$  different paths the person can take. Now we consider two approaches to obtain the solutions:

- Step by step approach

- (a) After 1st step, the person arrives at  $x = -1m$ ,  $0 m$  or  $1 m$  with  $1/3$ ,  $1/3$  and  $1/3$  probabilities respectively.
- (b) –After 2nd step, the person can reach  $x = -2m$  from  $x = -1m$  of the 1st step with a probability of  $1/3 \times 1/3 = 1/9$ .  
–The position,  $x = -1m$ , after the 2nd step can be reached from  $x = -1m$  and  $0 m$  of the first step with probabilities,  $1/9$  and  $1/9$ , respectively, thus the total probability is  $2/9$ .  
–The  $x = 0m$  after the 2nd step can be reached from three positions in the 1st step,  $x = -1m$ ,  $0 m$  or  $1 m$ , with probabilities  $1/9$ ,  $1/9$  and  $1/9$ , respectively, thus the total probability is  $1/3$ .  
–For the remaining positions,  $x = 1m$  and  $2 m$ , the symmetry around  $x = 0m$  can be used.
- (c) After 3rd step, the person can reach  $x = -3m$  from  $x = -2m$  of the 2nd step with a probability of  $1/9 \times 1/3 = 1/27$ .  
–The position,  $x = -2m$ , after the 3rd step can be reached from  $x = -2m$  and  $x = -1m$  of the first step with probabilities,  $1/27$  and  $2/9 \times 1/3 = 2/27$ , respectively, thus the total probability is  $1/9$ .  
–The  $x = -1m$  after the 3rd step can be reached from the three positions in the 2nd step,  $x = -2m$ ,  $x = -1m$  or  $x = 0m$ , with probabilities  $1/27$ ,  $2/9 \times 1/3 = 2/27$  and  $1/3 \times 1/3 = 1/9$ , respectively, thus the total probability is  $2/9$ .  
–Finally, the  $x = 0m$  after the 3rd step can be reached from the three positions in the 2nd step,  $x = -1m$ ,  $0 m$  or  $1 m$ , with probabilities  $2/9 \times 1/3 = 2/27$ ,  $1/3 \times 1/3 = 1/9$  and  $2/9 \times 1/3 = 2/27$  respectively, thus the total probability is  $7/27$ .  
–For the remaining positions, the symmetry around  $x = 0m$  can be used.
- (d) Continue for the further steps.

- More general approach

The total number of steps,  $n$ , can be written as

$$n = n_L + n_R + n_C \quad (7)$$

where  $n_L$ ,  $n_R$  and  $n_C$  are the numbers of steps moving to the left, right and remaining at the place, respectively. By denoting the position of the person after  $n$  steps to be  $x = -mm$ ,  $m$  is given by

$$m = n_L - n_R \quad (8)$$

From the two equations, we obtain

$$n = m + 2n_R + n_C \quad (9)$$

- (a) If  $m = n$ , i.e. arriving at the furthest negative position in  $x$ , from the equation above, it follows that

$$2n_r + n_c = 0 \quad (10)$$

leading to

$$n_R = 0, n_C = 0, n_L = n \quad (11)$$

The total number of paths to this point is given by a trinomial combination

$$N_{n_R n_C}^n \equiv \frac{n!}{(n - n_R - n_C)! n_R! n_C!} \quad (12)$$

as

$$N_{00}^n = \frac{n!}{n! 0! 0!} = 1 \quad (13)$$

and the probability for this to happen by

$$\frac{N_{00}^n}{3^n} = \left(\frac{1}{3}\right)^n \quad (14)$$

(b) If  $m = n - 1$ , i.e. arriving at the position  $x = -(n - 1)m$  after  $n$ -steps, we obtain

$$2n_R + n_C = 1 \quad (15)$$

which leads to

$$n_R = 0, n_C = 1, n_L = n - 1 \quad (16)$$

and the number of possible paths to reach this point is

$$N_{01}^n = \frac{n!}{(n - 1)! 0! 1!} = n \quad (17)$$

The probability to arrive here after  $n$ -steps is then

$$\frac{N_{01}^n}{3^n} = \frac{n}{3^n} \quad (18)$$

(c) If  $m = n - 2m$ , i.e. arriving at the position  $x = -(n - 2)m$  after  $n$ -steps, we obtain

$$2n_R + n_C = 2 \quad (19)$$

which leads to

$$n_R = 0, n_C = 2, n_L = n - 2 \text{ or } n_R = 1, n_C = 0, n_L = n - 1 \quad (20)$$

and the number of possible paths to reach this point is

$$N_{02}^n + N_{10}^n = \frac{n!}{(n - 2)! 0! 2!} + \frac{n!}{(n - 1)! 1! 0!} \quad (21)$$

The probability to arrive here after  $n$ -steps is

$$\frac{N_{02}^n + N_{10}^n}{3^n} \quad (22)$$

(d) For  $m = n - 3$ ,

$$2n_R + n_C = 3 \quad (23)$$

which leads to

$$n_R = 0, n_C = 3, n_L = n - 3 \text{ or } n_R = 1, n_C = 1, n_L = n - 2 \quad (24)$$

and the number of possible paths to reach this point is

$$N_{03}^n + N_{11}^n = \frac{n!}{(n - 3)! 0! 3!} + \frac{n!}{(n - 2)! 1! 1!} \quad (25)$$

The probability to arrive here after  $n$ -steps is

$$\frac{N_{03}^n + N_{11}^n}{3^n} \quad (26)$$

(e) Continue till  $m = 0$ , and the rest can be obtained by the symmetry at around  $x = 0$ .

To check, we calculate the case for  $n = 3$  and  $m = 0$ , i.e. the person arrives  $x = 0$  after taking three steps, which corresponds to 4) giving the probability to be

$$\frac{N_{03}^3 + N_{11}^3}{3^3} = \frac{1+6}{27} = \frac{7}{27} \quad (27)$$

agreeing with the result given in 3) above.

Table below shows the probabilities for the drunken person to be at different x positions after 1, 2, 3, 4 and 7 steps which can be obtained in two ways described above.

$x$ [m]	Step 1	Step 2	Step 3	Step 4	Step 7
-8	0	0	0	0	0
-7	0	0	0	0	$1/2187$
-6	0	0	0	0	$7/2187$
-5	0	0	0	0	$28/2187$
-4	0	0	0	$1/81$	$77/2187$
-3	0	0	$1/27$	$4/81$	$161/2187$
-2	0	$1/9$	$1/9$	$10/81$	$266/2187$
-1	$1/3$	$2/9$	$2/9$	$16/81$	$119/729$
0	$1/3$	$1/3$	$7/27$	$19/81$	$131/729$
1	$1/3$	$2/9$	$2/9$	$16/81$	$119/729$
2	0	$1/9$	$1/9$	$10/81$	$266/2187$
3	0	0	$1/27$	$4/81$	$161/2187$
4	0	0	0	$1/81$	$77/2187$
5	0	0	0	0	$28/2187$
6	0	0	0	0	$7/2187$
7	0	0	0	0	$1/2187$
8	0	0	0	0	0

Table 1: Table of values for different steps.

#### Note on the trinomial combination:

The formula for the trinomial combination can easily be found using the binomial combination formula. As denoted before, there are  $n = n_L + n_C + n_R$  steps done in total, where  $n_L, n_C$  and  $n_R$  are the number of steps on the left, "on the centre" (not moving) and on the right respectively. The number of possible paths with  $n_L$  steps on the left,  $n_C$  steps "on the centre" and  $n_R$  steps on the right is given by

$$N_{n_R n_C}^n = \frac{n!}{(n - n_R - n_C)! n_R! n_C!} \quad (28)$$

Note that it doesn't depend on  $n_L$  as the number of steps on the left is fixed when the total number of steps, the number of steps on the right and the number of steps "on the center" are known ( $n_L, n - R$  and  $n_C$  respectively). Furthermore, note that all the paths with  $n_L, n_C$  and  $n_R$  are leading to the same final position.

First, let's choose the  $n_R$  steps on the right among the  $n$  total steps. The number of possibilities to make this choice is given by a simple binomial combination:

$$\binom{n}{n_R} = \frac{n!}{(n - n_R)! n_R!} \quad (29)$$

Now, there are  $n - n_R$  steps left to choose. Among these, let's choose  $n_C$  steps "in the center", as before it is given by a binomial combination:

$$\binom{n - n_R}{n_C} = \frac{(n - n_R)!}{(n - n_R - n_C)!n_C!} \quad (30)$$

The rest of the steps are necessarily on the left, so no choice has to be made. Thus,  $N_{n_R n_C}^n$  is given by the product of the number of possibilities of steps on the right and number of steps "on the center"

$$\begin{aligned} N_{n_R n_C}^n &= \binom{n}{n_R} \binom{n - n_R}{n_C} = \frac{n!}{(n - n_R)!n_R!} \frac{(n - n_R)!}{(n - n_R - n_C)!n_C!} \\ &= \frac{n!}{(n - n_R - n_C)!n_R!n_C!} \end{aligned} \quad (31)$$

Note that as  $n = n_L + n_C + n_R$ ,  $n_L = n - n_R - n_C$  and  $N_{n_R n_C}^n = \frac{n!}{n_L!n_R!n_C!}$ .

2. The mean position and rms in x,  $\langle x \rangle$  and  $x_{rms}$  respectively, are given by

	Step 1	Step 2	Step 4	Step 7
$\langle x \rangle [m]$	0	0	0	0
$x_{rms} [m]$	0.8165	1.1547	1.6330	2.1602

Reminder:  $\langle x \rangle = \sum_{m=-n}^n mP(m)$  and  $x_{rms} = \sqrt{\langle x^2 \rangle} = \sqrt{\sum_{m=-n}^n m^2 P(m)}$ .

3. + 4. Finally, Fig. 2 shows the probabilities given in the table compared with the Gauss distribution taking and as the mean and standard deviation for 1, 2, 4 and 7 steps. After 2 steps, the Gauss distribution already describes the probability distribution of the position of the drunken person rather well and the agreement gets better with increasing number of steps. This is a demonstration that by repeating a random process, which itself does not follow the Gauss distribution, resulting in a distribution follows the Gauss distribution. This is why in physics distributions of variables resulting from random processes are often taken as Gaussian form.

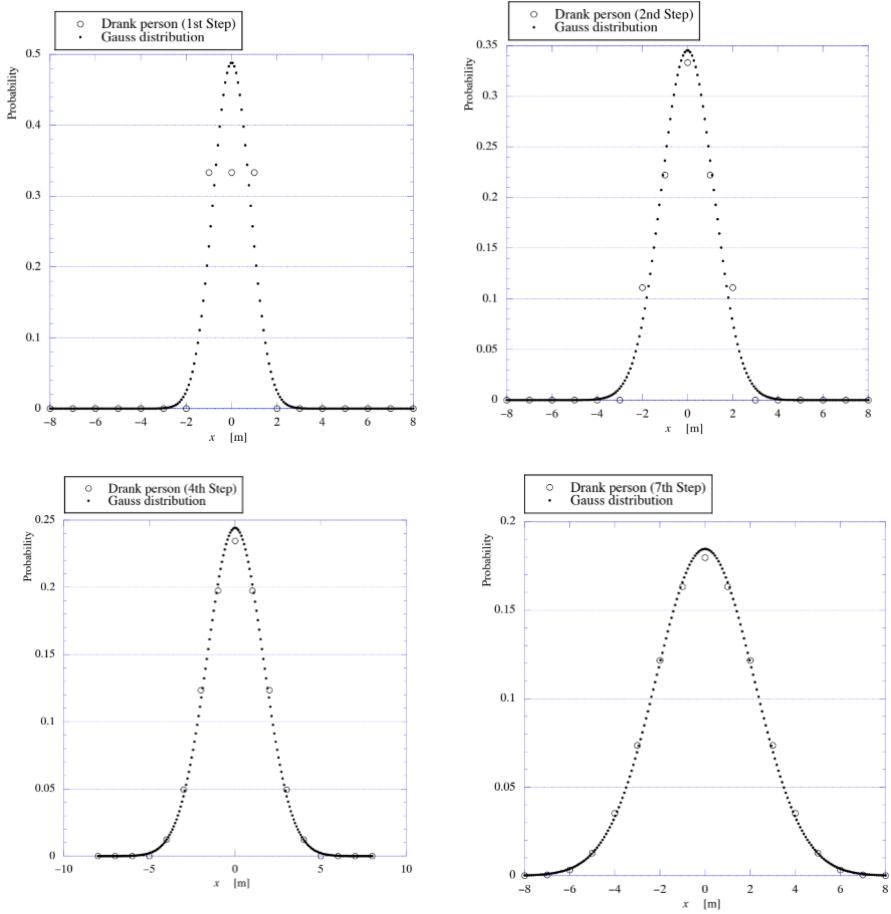


Figure 2: Probabilities given in the table compared with the Gauss distribution taking and as the mean and standard deviation for 1, 2, 4 and 7 steps.

5) There are  $N$  indistinguishable gas molecules uniformly distributed in a box with a volume  $V$ . Consider a small region in the box with a volume  $V_1$ .

1. What is the probability to find any but only one molecule in this region?
2. What is the probability to find any  $n$  molecules in this region?
3. What is the average number of molecules,  $\langle n \rangle$ , and its standard deviation  $\Delta n \equiv \sqrt{\langle n^2 \rangle - \langle n \rangle^2}$ , where  $\langle n^2 \rangle$  is the average of  $n^2$ , in this region?
4. If  $N$  is of the order of the Avogadro number, i.e. about  $10^{24}$ , and the volume of the considered region is about 1% of the total volume, how large is  $\Delta n/\langle n \rangle$ ? What does it mean?

**NB:** The following formula might be useful:

$$\begin{aligned}
 (p+q)^M &= \sum_{m=0}^M \frac{M!}{m!(M-m)!} p^m q^{M-m} \\
 \sum_{m=0}^M m \frac{M!}{m!(M-m)!} p^m q^{M-m} &= M p (p+q)^{M-1} \\
 \sum_{m=0}^M m^2 \frac{M!}{m!(M-m)!} p^m q^{M-m} &= M p (p+q)^{M-1} + M(M-1)p^2 (p+q)^{M-2}
 \end{aligned} \tag{32}$$

**Solution :**

1. Since molecules are uniformly distributed in a volume  $V$ , the probability to find **one particular** molecule in a volume  $V_1$ ,  $p$ , must be proportional to  $V_1$ . When  $V_1 = V$ , this probability must be  $p = 1$ . By combining the two facts, we get

$$p = \frac{V_1}{V} \quad (33)$$

and equally for the probability to find it outside of the volume  $V$ ,  $q$ , is

$$q = \frac{V - V_1}{V} = 1 - \frac{V_1}{V} = 1 - p \quad (34)$$

thus

$$p + q = 1 \quad (35)$$

i.e. the probability to find one particular molecule inside or outside of the volume is one, which is logical. The probability for out of  $N$  molecules to have **one particular molecule** in the volume and **all the other  $N-1$  molecules** outside of the volume is given by

$$pq^{N-1} = \left(\frac{V_1}{V}\right) \left(1 - \frac{V_1}{V}\right)^{N-1} \quad (36)$$

The probability for out of  $N$  molecules to have **any one but only one** molecule in the volume,  $P(1)$ , is then given by

$$P(1) = N \left(\frac{V_1}{V}\right) \left(1 - \frac{V_1}{V}\right)^{N-1} \quad (37)$$

since the one particle in the volume can be any of the  $N$  molecules.

2. By generalizing 1) and using the number of combinations to select  $n$  molecules out of  $N$  molecules, the probability to find  $n$  indistinguishable molecules in the region,  $P(n)$ , is given by

$$P(n) = \frac{N!}{n!(N-n)!} \left(\frac{V_1}{V}\right)^n \left(1 - \frac{V_1}{V}\right)^{N-n} \quad (38)$$

3. The average,  $\langle n \rangle$ , and squared average,  $\langle n^2 \rangle$ , are given by

$$\langle n \rangle = \sum_{n=0}^N n P(n) = \sum_{n=0}^N n \frac{N!}{n!(N-n)!} \left(\frac{V_1}{V}\right)^n \left(1 - \frac{V_1}{V}\right)^{N-n} = N \left(\frac{V_1}{V}\right) \quad (39)$$

and

$$\langle n^2 \rangle = \sum_{n=0}^N n^2 P(n) = \sum_{n=0}^N n^2 \frac{N!}{n!(N-n)!} \left(\frac{V_1}{V}\right)^n \left(1 - \frac{V_1}{V}\right)^{N-n} = N \left(\frac{V_1}{V}\right) + N(N-1) \left(\frac{V_1}{V}\right)^2 \quad (40)$$

respectively. It follows

$$\langle n^2 \rangle - \langle n \rangle^2 = N \left(\frac{V_1}{V}\right) + N(N-1) \left(\frac{V_1}{V}\right)^2 - N^2 \left(\frac{V_1}{V}\right)^2 = N \left(\frac{V_1}{V}\right) \left(1 - \frac{V_1}{V}\right) \quad (41)$$

and the standard deviation is given by

$$\Delta n = \sqrt{N \left(\frac{V_1}{V}\right) \left(1 - \frac{V_1}{V}\right)} \quad (42)$$

4. The ratio,  $\Delta n / \langle n \rangle$ , is given by

$$\frac{\Delta n}{\langle n \rangle} = \frac{1}{\sqrt{N}} \sqrt{\frac{V}{V_1} - 1} \quad (43)$$

and for  $N \approx 10^{24}$  and  $\frac{V_1}{V} = 10^{-2}$ , we have

$$\frac{\Delta n}{\langle n \rangle} \approx 10^{-11} \quad (44)$$

i.e. the relative statistical fluctuations of the number of molecules from the average number is very small.