Physics 467/667: Thermal Physics **Spring 2019**

Lecture 7: The Second Law and Entropy

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7.1 Calculate Ω for an Einstein Solid

Remember we have done some computer programming for two-state systems. A general trend is that it approaches a large number N, $\Omega(N)$ tends to be localized. If we treat the histogram of $\Omega(N)$ as a continues function (true when N is very large), it looks like a very smooth curve and $\Omega(N)$ follows some kind of distribution.

Now let's try to figure out what it is, by taking a Einstein solid as an example.

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} \tag{7.1}$$

In reality, there are always many more energy units (q) than oscillators (N), so we assume $q \gg N$.

To make it easier, let's just remove *-1* in eq. 7.1,

$$\begin{aligned} \ln\Omega &= \ln\left(\frac{(q+N)!}{q!N!}\right) \\ &= \ln(q+N)! - \ln q! - \ln N! \\ &\approx (q+N)\ln(q+N) - (q+N) - q\ln q + q - N\ln N + N \\ &= (q+N)\ln(q+N) - q\ln q - N\ln N \end{aligned} \tag{7.2}$$

Remember we have the assumption of $q \gg N$, namely $(N/q \to 0)$

$$\ln(q+N) = \ln\left(q(1+\frac{N}{q})\right) \approx \ln q + \frac{N}{q} \tag{7.3}$$

Therefore, we have

$$\ln\Omega \approx N\ln\frac{q}{N} + N + \frac{N^2}{q} \approx N\ln\frac{q}{N} + N \tag{7.4}$$

If we remove the logarithm sign,

$$\Omega(N,q) \approx (\frac{eq}{N})^N \tag{7.5}$$

7.2 Calculate Ω for two Einstein Solids

Naturally, we now know the general form of *two Einstein Solids* model,

$$\Omega(N_A, q_A, N_B, q_B) = (\frac{eq_A}{N_A})^{N_A}(\frac{eq_B}{N_B})^{N_B} \tag{7.6}$$

For simplicity, let make $N_A = N_B = N$, then

$$\Omega(N, q_A, q_B) = (\frac{e}{N})^{2N}(q_A q_B)^N \tag{7.7}$$

Based on what we plot in the homework, we know that Ω reaches its maximum value at $q_A = q_B = q/2$,

$$\Omega_{\text{max}} = (\frac{e}{N})^{2N}(q/2)^{2N} \tag{7.8}$$

Now let's try to calculate the points near $q/2$, say,

$$q_A = q/2 + x, \qquad q_B = q/2 - x. \tag{7.9}$$

Using eq. 7.7,

$$\Omega(N, q, x) = (\frac{e}{N})^{2N}\left[(\frac{q}{2})^2 - x^2\right]^N. \tag{7.10}$$

To simplify it, we get

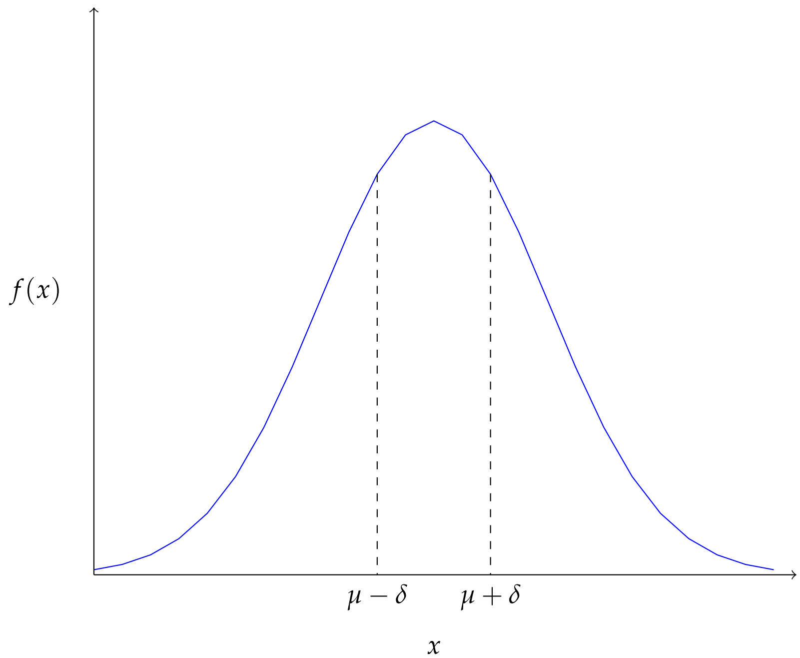
$$\begin{aligned} \ln\left[\left(\frac{q}{2}\right)^2 - x^2\right]^N &= N\ln\left[\left(\frac{q}{2}\right)^2 - x^2\right] \\ &= N\ln\left[\left(\frac{q}{2}\right)^2(1 - \left(\frac{2x}{q}\right)^2)\right] \\ &= N\left[\ln\left(\frac{q}{2}\right)^2 + \ln\left(1 - \left(\frac{2x}{q}\right)^2\right)\right] \\ &\approx N\left[\ln\left(\frac{q}{2}\right)^2 - \left(\frac{2x}{q}\right)^2\right] \end{aligned} \tag{7.11}$$

hence we have

$$\Omega = \Omega_{\text{max}} \cdot e^{-N(2x/q)^2} \tag{7.12}$$

This is a typical Gaussian function. A standard version is as follows,

$$f(x|\mu, \delta^2) = \frac{1}{\sqrt{2\delta^2\pi}} e^{\frac{-(x-\mu)^2}{2\delta^2}}. \tag{7.13}$$



1. symmetric
2. Gaussian width

The multiplicity falls off to 1/e of its maximum when

$$N(\frac{2x}{q})^2 = 1 \quad or \quad x = \frac{q}{2\sqrt{N}} \tag{7.14}$$

Let's plug in some number, say N=10^{20}. This results tell us, when two Einstein solids are in thermodynamical equilibrium, any random fluctuation will be not measurable. The most-likely macrostates are very localized.
Exercises

1. Problem 2.20.
2. Problem 2.23

7.3 Ideal Gas

Suppose we have a single gas atom (Ar), with a kinetic energy U in a container of volume V, what is its corresponding Ω? Obviously, the possible microstate is proportional to V. In principle, the atom can stay at any place of V. Also, each microstate can be represented as a vector, since it has velocity (more precisely Momentum). Therefore

$$\Omega \approx V \cdot V_p \tag{7.15}$$

It appears that both V and V_p somehow relate to very large numbers, but would their product go to infinity? Fortunately, we have the famous **Heisenberg uncertainty principle**:

$$\Delta x \Delta p_x = h. \tag{7.16}$$

For a one-dimensional chain, we define L as the length in real space, L_p as the length in momentum space,

$$\Omega_{1D} = \frac{L}{\Delta x}\frac{L_p}{\Delta p_x} = \frac{LL_p}{h}. \tag{7.17}$$

Therefore, its 3D version is,

$$\Omega_1 = \frac{VV_p}{h^3}. \tag{7.18}$$

Accordingly, the multiplicity function for an ideal gas of two molecules should be

$$\Omega_2 = \frac{1}{2}\frac{V^2}{h^6} \times \text{area of } P \text{ hypersphere} \tag{7.19}$$

if the two molecules are indistinguishable. The general form for N should be

$$\Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}} \times \text{area of } P \text{ hypersphere.} \tag{7.20}$$

For N=1, how to calculate the area? Since U depends on the momentum by

$$U = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) \tag{7.21}$$

$$p_x^2 + p_y^2 + p_z^2 = 2mU \tag{7.22}$$

So the momentum space is the surface of a sphere with radius $\sqrt{2mU}$, namely,

$$\begin{aligned} \text{area} &= 2 && (d{=}1) \\ &= 2\pi r && (d{=}2) \\ &= 4\pi r^2 && (d{=}3) \\ &= .... \\ &= .... \\ &= \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1} && (d \text{ in general}) \end{aligned} \tag{7.23}$$

Therefore, the general Ω is

$$\Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{2\pi^{3N/2}}{(3N/2-1)!}\sqrt{2mU}^{3N-1}. \tag{7.24}$$

$$\Omega(U,V,N) = f(N)V^N U^{3N/2} \tag{7.25}$$

where $f(N)$ is a complicated function of N.

For two interacting gases,

$$\Omega(U,V,N) = [f(N)]^2 (V_A V_B)^N (U_A U_B)^{3N/2} \tag{7.26}$$

7.4 Appendix: Area of high-dimensional Hypersphere

For a d-dimensional hypersphere with a radius of r, we can solve it iteratively. When d=1, $A(r)$=2, d=2, $A(r) = 2\pi r$

$$A_3(r) = \int_0^\pi A_2(r\sin\theta) r d\theta = 2\pi r^2 \int_0^\pi d\theta = 4\pi r^2. \tag{7.27}$$

Consequently, we can keep doing this

$$\begin{aligned} A_d(r) &= \int_0^\pi A_{d-1}(r\sin(\theta)) r d\theta \\ &= \int_0^\pi \frac{2\pi^{(d-1)/2}}{\Gamma(\frac{d-1}{2})} (r\sin\theta)^{d-2} r d\theta \\ &= \frac{2\pi^{(d-1)/2}}{\Gamma(\frac{d-1}{2})} r^{d-1} \int_0^\pi (\sin\theta)^{d-2} d\theta \end{aligned} \tag{7.28}$$

$$\int_0^\pi (\sin\theta)^n d\theta = \frac{\sqrt{\pi}\,\Gamma(\frac{n+2}{2})}{\Gamma(\frac{n+1}{2})} \tag{7.29}$$

so

$$A_d(r) = \frac{2\pi^{d/2}}{\Gamma(d/2)} r^{d-1} \tag{7.30}$$