

Lecture 11: Entropy and Chemical Potential

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11.1 Chemical Potential

When we talk a system of ideal gas, it is described by the following fundamental parameters, T, P, N ,

1. uneven $T \rightarrow$ heat flow ($S \uparrow$), we call it *thermal equilibrium*
2. uneven $P \rightarrow$ pressure flow ($S \uparrow$), we call it *mechanical equilibrium*
3. uneven $N \rightarrow$ particle flow ($S \uparrow$), we call it ?

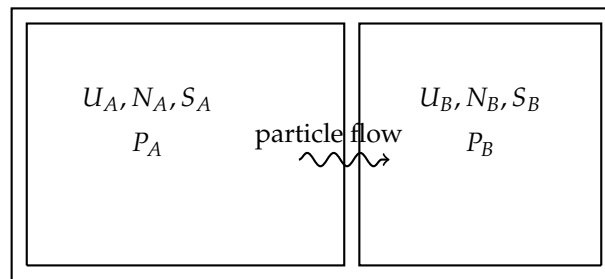


Figure 11.1: A schematic particle flow between two gases.

Such a process due to an exchange of particles is called *diffusion*. Since diffusion is also a spontaneous process, it must lead to the increase of entropy (recall we have learned the mixing entropy). This indicates that S is also a function of N (as we learned in Chapter 2). Therefore, we can also derive the equilibrium condition for a diffusion (analogous to P).

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \quad (11.1)$$

What's the physical meaning of $\partial S_A / \partial N_A$?

If we dig into the units, we will find $\partial S_A / \partial N_A$ has a unit of J/K. Not a very pleasant quantity. Let's multiply it by $-T$ so that it has the dimension of energy.

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V} \quad (11.2)$$

So it means the equilibrium condition for diffusive process is $\mu_A = \mu_B$.

Now let us generalize the processes which was shown in the beginning.

1. uneven $T \left(\frac{\partial S}{\partial U} = 1/T \right) \rightarrow$ heat flow ($S \uparrow$), we call it *thermal equilibrium*.

- uneven $P(\frac{\partial S}{\partial V} = P/T) \rightarrow$ pressure flow ($S \uparrow$), we call it *mechanical equilibrium*.
- uneven $N(\frac{\partial S}{\partial N} = \mu/T) \rightarrow$ particle flow ($S \uparrow$), we call it *diffusive equilibrium*.

11.2 The Generalized Thermodynamic Identity

$$dS = \left(\frac{\partial S}{\partial U}\right)dU + \left(\frac{\partial S}{\partial V}\right)dV + \left(\frac{\partial S}{\partial N}\right)dN \quad (11.3)$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN \quad (11.4)$$

$$dU = TdS - PdV + \mu dN \quad (11.5)$$

- $\Delta U = 0, \Delta V=0, \mu=$
- $\Delta S = 0, \Delta V=0, \mu=$

μ is the system's energy change when you add one particle while S and V is fixed. Normally, μ is negative.

$$dU = TdS - PdV + \sum_i \mu_i dN_i \quad (11.6)$$

11.3 Chemical potential for Einstein Solid



For an Einstein solid, $\mu=-\epsilon$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \quad (11.7)$$

11.4 Chemical potential for ideal gas

For a more realistic example, let us look at an ideal gas

$$S = Nk \left[\ln \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{5}{2} \right] \quad (11.8)$$

Differentiating with respect to N gives

$$\begin{aligned}\mu &= -Tk\left[\ln\left(V\left(\frac{4\pi mU}{3h^2}\right)^{3/2}\right) - \ln N^{5/2} + \frac{5}{2}\right] - Nk\frac{5}{2}\frac{1}{N} \\ &= -kT\ln\left[\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right] \\ &= -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]\end{aligned}\tag{11.9}$$

Note that here $U = 3/2NkT$ was used in the last step.

He (0.32 eV, how to calculate?) Ar (0.42 eV, how to calculate?)

1. Mixing 1 mol He with 1 mol He (both at standard conditions)
2. Mixing 1 mol He with 1 mol Ar (both at standard conditions)

11.5 Exercise

Problem 3.37. Consider a monoatomic ideal gas that lives at a height z above sea level, so each molecule has potential energy mgz in addition to its kinetic energy.

(a) Show that the chemical potential is the same as if the gas were at sea level plus mgz

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + mgz\tag{11.10}$$

(b) Suppose you have two chunks of He gas, one at sea level, and one at height z , each having the same temperature and volume. Assuming that they are in diffusive equilibrium, show that the number of molecules in the higher chunk is

$$N(z) = N(0)e^{-mgz/kT}\tag{11.11}$$

11.6 Homework

Problem 3.36, 3.37, 3.38