

Chapter 5. Chemical potential and Gibbs distribution

1 Chemical potential

So far we have only considered systems in contact that are allowed to exchange “heat”, *i.e.* systems in thermal contact with one another. In this chapter we consider systems that can also exchange particles with one another, *i.e.* systems that are in *diffusive* contact.

Consider 2 systems \mathcal{S}_1 and \mathcal{S}_2 that are in diffusive contact with one another and in thermal contact with a 3rd system, a reservoir at temperature τ . We have shown that the Helmholtz free energy for the combined system $\mathcal{S}_1 + \mathcal{S}_2$ will be a minimum when it is in equilibrium with the reservoir. We must therefore minimise

$$F = F_1 + F_2$$

with respect to the distribution of the particles between \mathcal{S}_1 and \mathcal{S}_2 to find the equilibrium state of this combined system. The total number of particles in the system is fixed, so that

$$dF = \left(\frac{\partial F_1}{\partial N_1} \right)_{\tau} dN_1 - \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau} dN_1 = 0$$

in equilibrium, *i.e.*

$$\left(\frac{\partial F_1}{\partial N_1} \right)_{\tau} = \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau}.$$

The quantity

$$\mu(\tau, V, N) = \left(\frac{\partial F}{\partial N} \right)_{\tau, V}$$

is known as the *chemical potential*, so that our equilibrium condition is that

$$\mu_1 = \mu_2.$$

Inspecting the expression for dF , we see that when $\mu_1 > \mu_2$ moving particles from \mathcal{S}_1 to \mathcal{S}_2 decreases F , taking the system closer to equilibrium. Thus, particles tend to flow from systems of high chemical potential to systems of lower chemical potential. μ is the (Helmholtz) free energy “per particle” in a system.

If several chemical species are present within a system, then there is chemical potential associated with each distinct species, *e.g.*

$$\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{\tau, V, N_1, N_2, \dots}$$

is the chemical potential for species j .

1.1 Example: the ideal gas

In chapter 3 we showed that the Helmholtz free energy of an ideal monatomic gas is

$$F = -N\tau \ln(n_Q V) + N\tau \ln N - N\tau,$$

so that

$$\mu = -\tau \ln(n_Q V) + \tau \ln N = \tau \ln \left(\frac{n}{n_Q} \right).$$

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Camilla Rothe



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