11. Systems with varying particle number

See Mandl 8.1

So far we have developed the Boltzmann distribution where the number of particles N is fixed and the energy is a free macroscopic variable. In this chapter, we consider systems where the particle number is also free to fluctuate.

11.1 Motivations

There are two reasons for allowing the particle number to fluctuate:

1. We may wish to consider systems free to exchange particles. An important example is phase co-existence whereby, e.g., a liquid and its vapor are in equilibrium, and a molecule may either be part of the liquid phase or of the gas phase.

2. The second motivation is that since the particle number is a macroscopic variable, for a large system it is sharply defined at some mean value. Thus, a large system with varying particle number is expected to have the same behavior as a system of fixed particle number.

We then use the system with varying particle number as 'a means to an end,' the end being the study of quantum gases for which the calculations turn out to be easier when the particle number is not fixed.

11.2 The chemical potential

Consider first a system as in Figure 1, where two halves (at equilibrium at the same temperature) are free to exchange particles. Since the total number $N = N_1 + N_2$ of particles is conserved:

$$dN_1 = -dN_2$$

As the free energy is extensive, it can be written as a sum of contributions from each half of the system:

$$F = F_1(N_1) + F_2(N_2)$$

$$dF = \frac{\partial F_1(N_1)}{\partial N_1} dN_1 + \frac{\partial F_2(N_2)}{\partial N_2} dN_2 = \left[\frac{\partial F_1(N_1)}{\partial N_1} - \frac{\partial F_2(N_2)}{\partial N_2} \right] dN_1$$
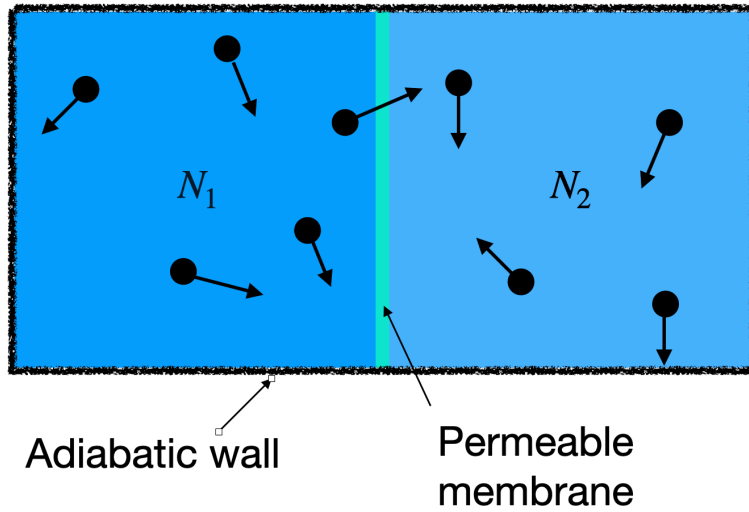
Figure 1: System at equilibrium comprising two subsystems free to exchange particles

At equilibrium, the free energy should be minimized, and $dF = 0$, therefore we must have:

$$\frac{\partial F_1(N_1)}{\partial N_1} = \frac{\partial F_2(N_2)}{\partial N_2}$$

> 💡 Definition
>
> $$\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

is the chemical potential which is a quantity which is common to two systems that can exchange particles.

A statement that is often made is: "the chemical potential is like a temperature for particle number". If a system is not in equilibrium so that there is a chemical potential gradient, then particles will diffuse down then gradient. This is similar to heat diffusing down a temperature gradient (Figure 2).

11.3 Example

A specific example may be helpful. Consider an ideal gas confined to two connected equal volumes V (see Figure 3) separated by height H in a gravitational field g. In the semi-classical
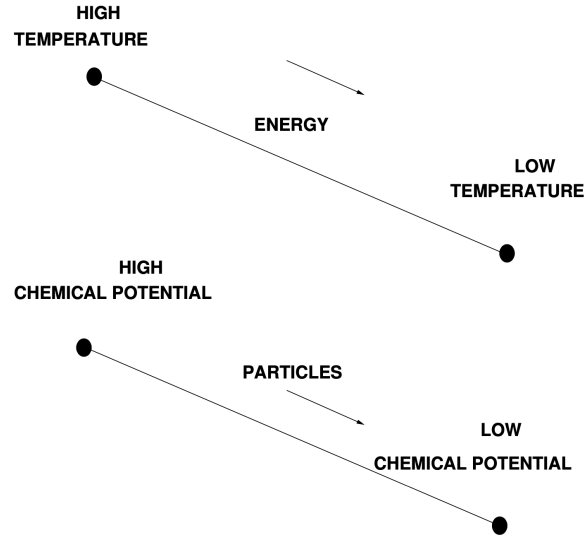
Figure 2: How gradients of temperature and chemical potential effect heat and mass flow respectively
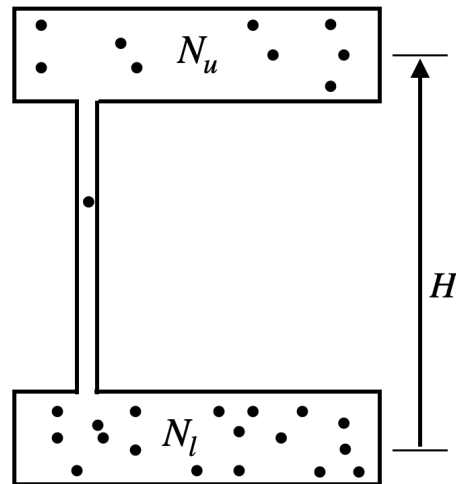

Figure 3: Simple example of two systems free to exchange particles (Baierlein Figure 7.1)

treatment, the partition function factorizes into the contribution from the upper volume Z_u and from the lower volume Z_l :

$$Z(N_l, N_u) = Z_l(N_l) \times Z_u(N_u) = \left(\frac{V}{\lambda^3}\right)^{N_l} \frac{1}{N_l!} \times \left(\frac{V}{\lambda^3}\right)^{N_u} e^{-\beta mgHN_u} \frac{1}{N_u!}$$

where $\lambda = \frac{h}{\sqrt{2\pi MkT}}$. Using semi-classical results from 10.3:

$$F_l = -kT \ln Z_l = N_l kT \left[\ln\left(\frac{N_l \lambda^3}{V}\right) - 1\right]$$

$$F_u = N_u kT \left[\ln\left(\frac{N_u \lambda^3}{V}\right) - 1\right] + N_u MgH$$

$$\mu_l = \frac{\partial F_l}{\partial N_l} = kT \ln\left(\frac{N_l}{V\lambda^3}\right)$$

$$\mu_u = \frac{\partial F_u}{\partial N_u} = kT \ln\left(\frac{N_u}{V\lambda^3}\right) + MgH$$

Equating the chemical potentials $\mu_l = \mu_u$ yields:

$$kT \ln\left(\frac{N_l}{N_u}\right) = MgH \Rightarrow N_u = N_l e^{-MgH/kT}$$

This gives the density dependence on height in the isothermal atmosphere. Note that μ increases with density, and μ_u increases with H , which supports the claim that the chemical potential measures the tendency for particles to diffuse.

> 🔥 Expand to read about an equivalent definition of μ
>
> Consider the scenario of Figure 1, where a system isolated from the rest of the universe comprises two subsystems free to exchange energy and particles. Since the total system is isolated, we must maximize the entropy (see chapter 4, Tutorial 3.1):
>
> $$S = S_1(E_1, N_1) + S_2(E_2, N_2)$$
>
> $$dS = \left[\left(\frac{\partial S_1}{\partial E_1}\right) - \left(\frac{\partial S_2}{\partial E_2}\right)\right] dE_1 + \left[\left(\frac{\partial S_1}{\partial N_1}\right) - \left(\frac{\partial S_2}{\partial N_2}\right)\right] dN_1$$
>
> Since dE_1 and dN_1 are independent, to have $dS = 0$, we must have common values of:

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}$$

where we have used the fact that E and N are functionally independent (knowing N does not specify E and vice-versa) so

$$\mu \equiv \frac{\partial F}{\partial N} = \frac{\partial(E - TS)}{\partial N} = -T\frac{\partial S}{\partial N}.$$

Hence, we identify:

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

This definition is equivalent to the previous boxed definition of μ.

11.4 Grand canonical distribution

Consider the scenario of Figure 4, where, in analogy with chapter 4, the 'composite' comprises the system and the bath, which this time serves as a reservoir of energy and particles at constant T and μ .
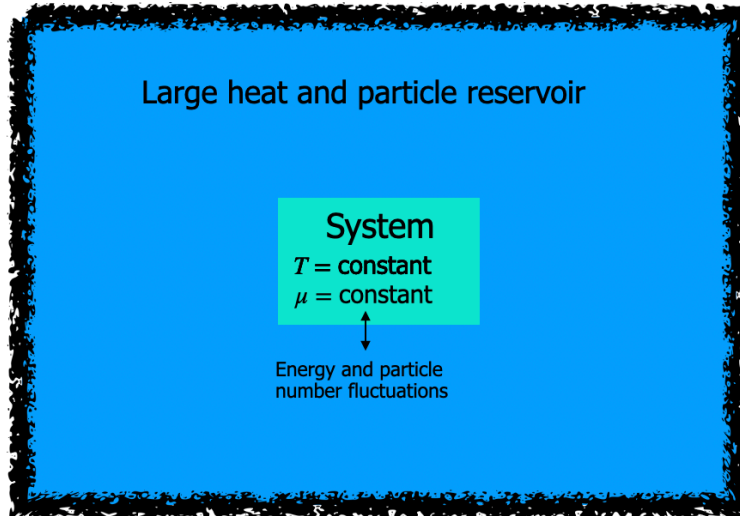

Figure 4: Composite of system + heat and particle reservoir

A microstate r of the system has energy E and N particles. In analogy with chapter 4, using the principle of equal a priori probabilities, the probability of microstate r obeys:

$$P_r \propto \Omega_b(E_{tot} - E, N_{tot} - N) = \exp\left(\frac{S_b(E_{tot} - E, N_{tot} - N)}{k}\right)$$

where the Planck relation has been used. We proceed as in chapter 4 and Taylor expand the entropy (since $N, E \ll N_{TOT}, E_{TOT}$), keeping only the first few terms:

$$S_b(E_{TOT} - E, N_{TOT} - N) = S_b(E_{TOT}, N_{TOT}) - E\frac{\partial S_b(E_{TOT}, N_{TOT})}{\partial E} - N\frac{\partial S_b(E_{TOT}, N_{TOT})}{\partial N} + ...$$

$$= \text{const} - \frac{E}{T} + \frac{N\mu}{T}.$$

Thus

$$P_r \propto \exp\left(\frac{1}{kT}(N\mu - E)\right)$$

We have now derived the 'grand canonical distribution' or Gibbs-Boltzmann distribution (as opposed to the canonical distribution, which is the Boltzmann distribution). The probability that a system in equilibrium with a reservoir of energy and particles at temperature T and chemical potential μ is in microstate r , which has energy E_r and particle number N_r , is:

> 💡 Key Point 15:
>
> $$P_r = \frac{1}{Z}\exp(-\beta E_r + \beta\mu N_r), \quad Z = \sum_j \exp(-\beta E_j + \beta\mu N_j), \quad \beta = \frac{1}{kT}$$