11. Systems with varying particle number

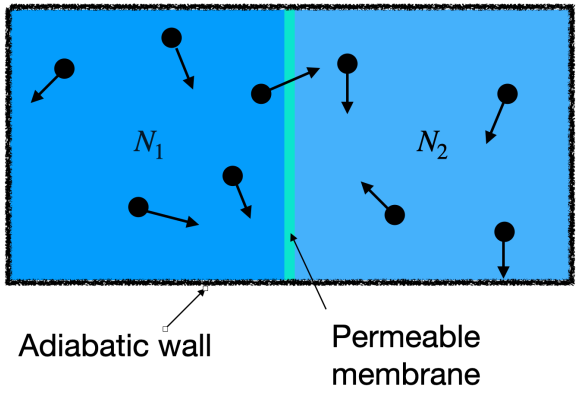
Motivation

- We developed the Boltzmann distribution assuming N is fixed and E is a free macroscopic variable.
- Now consider case where both N and E fluctuate.

- Why?

1. Some systems are free to exchange particles eg. coexisting gas and liquid phases where a molecule may either be part of the liquid phase or of the gas phase.
2. If N is a free, for a large system it is sharply defined at some mean value and thus we get the same behavior as a system of fixed particle number.
3. Useful means to an end for simplifying study of quantum gases

The chemical potential



- Consider a system where two halves are free to exchange particles.
- Since $N = N_1 + N_2$ is conserved, $dN = 0$ and hence:

$$dN_1 = -\,dN_2$$

- Now free energy is extensive ie. $F = F_1(N_1) + F_2(N_2)$

$$dF = \frac{\partial F_1(N_1)}{\partial N_1} dN_1 + \frac{\partial F_2(N_2)}{\partial N_2} dN_2 = \left[\frac{\partial F_1(N_1)}{\partial N_1} - \frac{\partial F_2(N_2)}{\partial N_2}\right] dN_1$$

- As system at equilibrium, free energy is at a minimum $dF = 0$

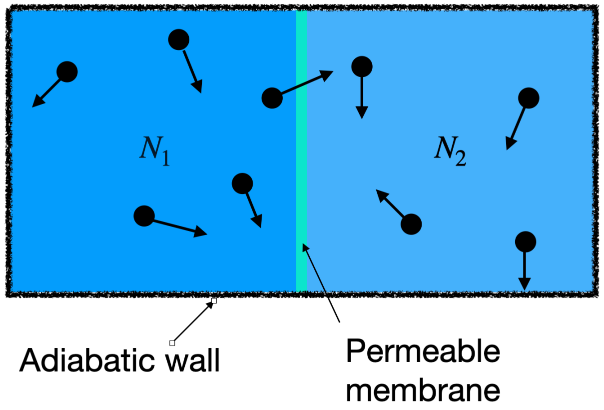
$$\Rightarrow \frac{\partial F_1(N_1)}{\partial N_1} = \frac{\partial F_2(N_2)}{\partial N_2}$$

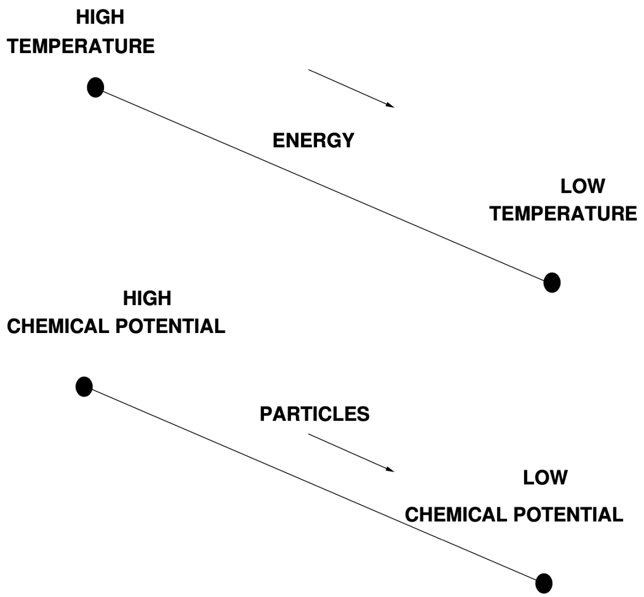
The chemical potential

Statistical Mechanics

- Thus the quantity $\mu \equiv \left(\frac{\partial F}{\partial N}\right)_{T,V}$

is common to both systems that can exchange particles.
We call μ the **chemical potential**.

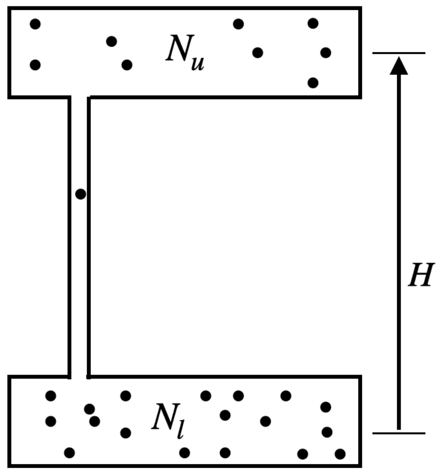




- If a system is not in equilibrium so that there is a chemical potential gradient, then particles will diffuse down then gradient
- Similar to heat diffusing down a temperature gradient

Example

- Two connected volumes of gas at different heights in a gravitational field



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

$$F_l = -kT \ln Z_l = N_l kT \left[\ln(N_l \lambda^3/V) - 1\right] \qquad F_u = N_u kT \left[\ln(N_u \lambda^3/V) - 1\right] + N_u MgH$$

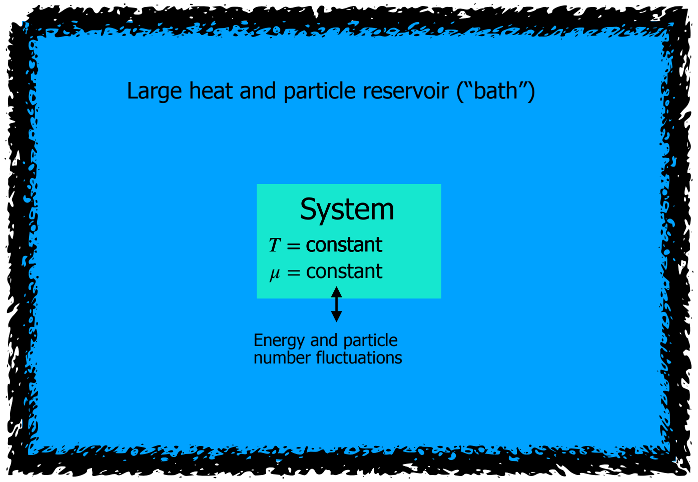
$$\mu_l = \frac{\partial F_l}{\partial N_l} = kT \ln\left(\frac{N_l}{V\lambda^3}\right) \qquad \mu_u = \frac{\partial F_u}{\partial N_u} = kT \ln\left(\frac{N_u}{V\lambda^3}\right) + MgH$$

$$\mu_l = \mu_u \Rightarrow \quad kT \ln\left(\frac{N_l}{N_u}\right) = MgH$$

$$\Rightarrow N_u = N_l e^{-MgH/kT}$$

- Consistent with the Boltzmann distribution

The grand canonical distribution



- A microstate r has energy E and N particles.

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

$$S_b(E_{TOT} - E, N_{TOT} - N) = S_b(E_{TOT}, N_{TOT}) - E\frac{\partial S_b(E_{TOT}, N_{TOT})}{\partial E} - N\frac{\partial S_b(E_{TOT}, N_{TOT})}{\partial N} + \ldots$$
$$= \text{const} - \frac{E}{T} + \frac{N\mu}{T}$$

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

- Key point 15: $P_r = \dfrac{1}{Z}\exp(-\beta E_r + \beta\mu N_r), \quad Z = \sum_i \exp(-\beta E_j + \beta\mu N_j), \quad \beta = \dfrac{1}{kT}$