

HH0066 Chemical Potential

The chemical potential μ governs the particle flows, just as the temperature τ governs the energy flows.

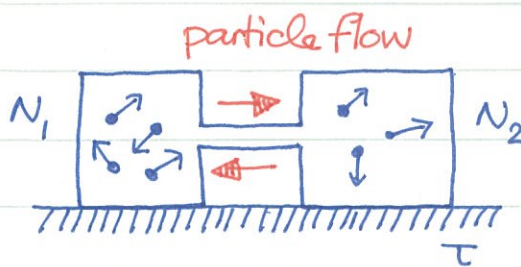
$$\mu(\tau, V, N) \equiv \left(\frac{\partial F}{\partial N} \right)_{\tau, V}$$

The chemical potential is defined by the derivative of free energy F .

⊙ Diffusive equilibrium

Consider two systems in thermal equilibrium of the same temp. τ .

Set up diffusive contact between them and the Helmholtz free energy $F = F_1 + F_2$ should be a minimum with the constraint $N_1 + N_2 = N$.



$$dF = \left(\frac{\partial F_1}{\partial N_1} \right)_{\tau} dN_1 + \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau} dN_2 = 0 \quad \leftarrow \text{Making use of } dN_1 = -dN_2 \dots$$

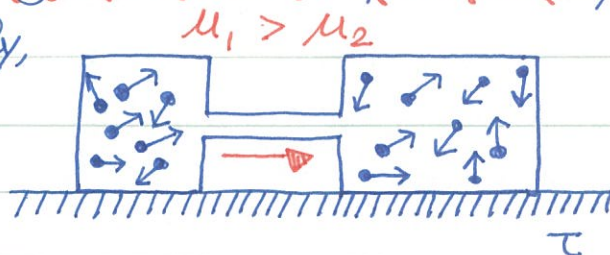
$$\left(\frac{\partial F_1}{\partial N_1} \right)_{\tau} = \left(\frac{\partial F_2}{\partial N_2} \right)_{\tau}$$

This is the criterion for diffusive equilibrium. Now, you should not be surprised why μ is defined this way,

way, $\mu \equiv \left(\frac{\partial F}{\partial N} \right)_{\tau, V}$. Rewrite the criterion $\rightarrow \mu_1 = \mu_2$

Note that $dF = \mu_1 dN_1 + \mu_2 dN_2 = (\mu_1 - \mu_2) dN_1$. For $\mu_1 > \mu_2$, to minimize the free energy ($dF < 0$) implies $dN_1 < 0$. That is to say, particles flow from higher chemical potential (μ_1) to lower one (μ_2). Similarly,

for $\mu_1 < \mu_2$, particles flow from higher μ_2 to lower μ_1 .



Let's compute the chemical potential for the ideal gas.

$$Z_N = \frac{1}{N!} (Z_1)^N = \frac{1}{N!} (n_{\phi} V)^N \quad \text{and} \quad F = -\tau \log Z_N$$

With the Stirling approximation, the free energy is

$$F = -\tau N \log(n_0 V) + \tau N \log N - \tau N \approx N \log N - N$$

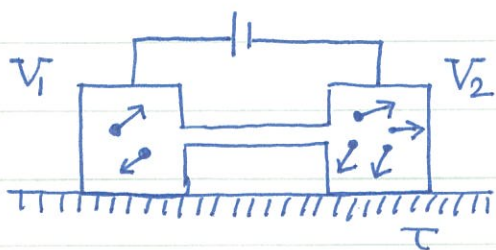
log N!
≈ N log N - N

Take derivative to obtain the chemical potential,

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{\tau, V} = -\tau \log(n_0 V) + \tau \log N + \tau - \tau$$

→ $\mu = \tau \log(n/n_0)$ OR, $n = n_0 e^{\mu/\tau}$ μ < 0 because n << n₀ for the ideal gas.

⊙ Internal and total chemical potentials



Consider charged particles in diffusive contact held at different voltages.

The average energy can be separated into two parts: $U = U_{int} + N \cdot qV$

Thus, the free energy is $F = U - \tau \sigma = F_{int} + NqV$. The applied voltage gives simple correction to the free energy.

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{\tau} = \left(\frac{\partial F_{int}}{\partial N} \right)_{\tau} + qV \rightarrow \mu = \mu_{int} + qV$$

↑ total ↑ internal.

The equilibrium condition

$\mu_1 = \mu_2$ can be expressed as

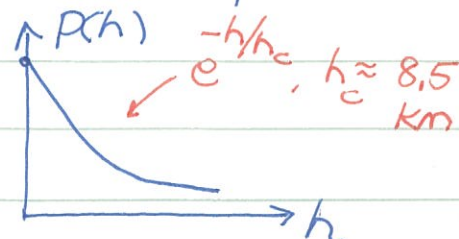
$$\mu_{int,1} + qV_1 = \mu_{int,2} + qV_2$$

That is to say, the criterion

$\Delta \mu_{int} = -q \Delta V \neq 0$ implies the internal chemical potentials are NOT the same anymore for $\Delta V \neq 0$ ☹

Let's apply the above criterion to derive barometric pressure equation

$$P(h) = p(0) e^{-Mgh/\tau}$$



$p(h)$: pressure at height h .
 M : molecular mass.

Following the same argument, the total chemical potential is

$$\mu = \mu_{\text{int}} + Mgh = \tau \log(\gamma/n_0) + Mgh$$

For simplicity, assume the temperature is constant,

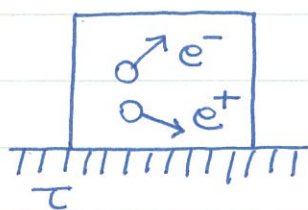
$$\tau \log(\gamma/n_0) + Mgh = \tau \log[n(h)/n_0] \rightarrow n(h) = n_0 e^{-Mgh/\tau}$$

Apply the ideal gas law $p = n\tau$. The pressure decays as

$$p(h) = p_0 e^{-Mgh/\tau} \leftarrow \text{barometric equation.}$$

Pair creation.

Consider pair creation for matter and antimatter due to thermal fluctuations at temperature τ .



We need both N_+ and N_- to characterize the system. The pair

creation/annihilation processes ensure that

$\Delta N_+ = \Delta N_-$ so that $N_- - N_+$ is conserved,

$$N_- - N_+ = N_0$$

Derive the equilibrium criterion from $dF = 0$,

$$\frac{\partial F_+}{\partial N_+} dN_+ + \frac{\partial F_-}{\partial N_-} dN_- = 0, \text{ with the constraint } dN_+ = dN_-$$

$$\rightarrow \mu_+ + \mu_- = 0 \leftarrow \text{The sum of chemical potentials is zero.}$$

The kinetic energy for e^- and e^+ is described by

$$E = \sqrt{p^2 c^2 + m_0^2 c^4} \approx \underbrace{m_0 c^2}_{\text{rest energy}} + \frac{p^2}{2m_0} + \dots$$

rest energy.

We will see that $m_0 c^2$ would be important and cannot be shifted away.....

Suppose the particle density is dilute.

$$\mu = \tau \log(n/n_0) + m_0 c^2 \quad \leftarrow e^-, e^+ \text{ can be viewed as the ideal gases.}$$

The equilibrium condition requires

$$\tau \log(n_+/n_0) + m_0 c^2 + \tau \log(n_-/n_0) + m_0 c^2 = 0$$

$$\log\left(\frac{n_+ n_-}{n_0^2}\right) = -\frac{2m_0 c^2}{\tau} \quad \rightarrow \quad n_+ n_- = n_0^2 e^{-2m_0 c^2/\tau}$$

Suppose we don't have any e^+ in the $\tau \rightarrow 0$ limit. The particle densities can be written this way:

$$\begin{cases} n_+ = n_0(0+x) \\ n_- = n_0(1+x) \end{cases} \quad \text{where } x \ll 1 \quad \rightarrow \quad n_0^2 x(1+x) = n_0^2 e^{-2m_0 c^2/\tau}$$

Solve for the pair creation fraction x .

The density for position due to thermal

fluctuations is

$$\frac{n_+}{n_0} \approx \left(\frac{n_0}{n_0}\right)^2 e^{-2m_0 c^2/\tau} \quad \rightarrow \quad \approx e^{-40000000}$$

The exponential

suppression is caused by the minimal energy

$\Delta = 2m_0 c^2$ for pair creation in vacuum.



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