Chemical potential: Baierlein's idea

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1. Introduction

Figure 1 sets the scene. Two volumes, vertically thin in comparison with their horizontal extent, are separated in height by a distance *H.* A narrow tube connects the upper volume V_u to the lower volume V_l. A total number of helium atoms are in thermal equilibrium at temperature *T;* we treat them as a semi-classical ideal gas What value should we anticipate for the number N_u of atoms in the upper volume, especially in comparison with the number N_l in the lower volume? We need the probability $P(N_i, N_u)$ that there are N_l atoms in the lower volume and N_u in the upper.

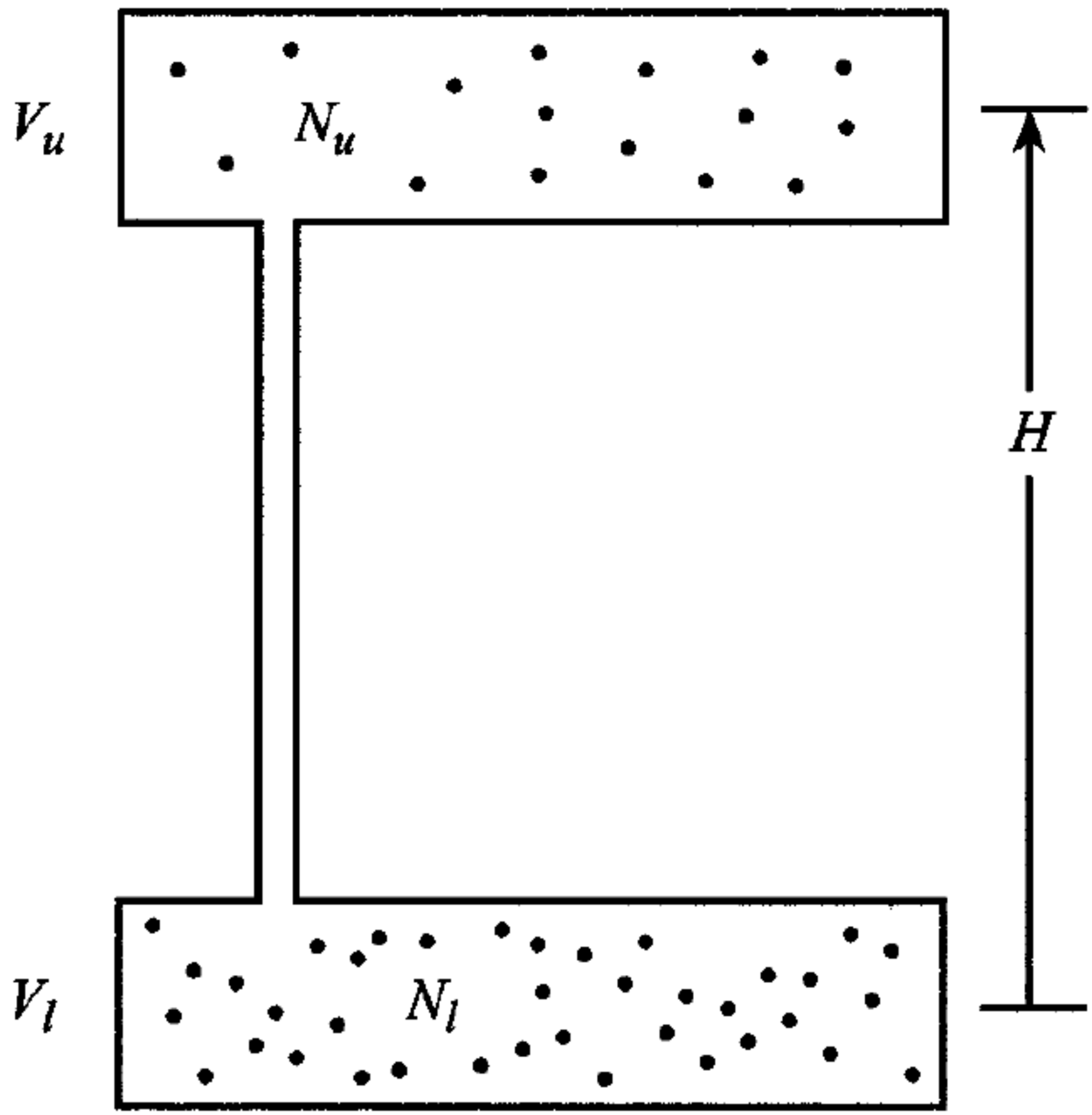


Fig. A model of the variation of atmosphere pressure with altitude: two volumes of gas at different heights in a uniform gravitational field, in thermal and diffusive contact.

The one-particle partition function:

$$Z_l(1) = \frac{V_l}{\lambda_{th}^{\ 3}}, \qquad Z_u(1) = Z_{atom} Z_{trans} = e^{-\beta mgH}\left(\frac{V_u}{\lambda_{th}^{\ 3}}\right)$$

where $\lambda_{th} = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{1/2}$ is the thermal de Broglie length. The N-particle partition function for two different heights

$$Z_l(N_i) = \frac{[Z_l(1)]^{N_l}}{N_l!} = \frac{1}{N_l!} \left(\frac{V_l}{\lambda_{th}^3} \right)^{N_l}$$

or

$$\ln Z_l(N_i) = N_l \ln\left(\frac{V_l}{\lambda_{th}^3} \right) - N_l \ln N_l + N_l$$

and

$$Z_u(N_u) = \frac{[Z_u(1)]^{N_u}}{N_u!} = \frac{1}{N_u!} \left(\frac{V_u}{\lambda_{th}^3} e^{-\beta mgH} \right)^{N_u}$$

or

$$\ln Z_u(N_u) = N_u \ln\left(\frac{V_u}{\lambda_{th}^3} e^{-\beta mgH} \right) - N_u \ln N_u + N_u$$

The partition function of the total system:

$$\begin{aligned} Z(N_l, N_u) &= Z_l(N_i) Z_u(N_u) \\ &= \frac{[Z_l(1)]^{N_l}}{N_l!} \frac{[Z_u(1)]^{N_u}}{N_u!} \\ &= \frac{1}{N_l!} \left(\frac{V_l}{\lambda_{th}^3} \right)^{N_l} \frac{1}{N_u!} \left(\frac{V_u}{\lambda_{th}^3} e^{-\beta mgH} \right)^{N_u} \end{aligned}$$

or

$$\begin{aligned}\ln Z(N_l, N_u) &= \ln Z_l(N_i) + \ln Z_u(N_u) \\ &= N_l \ln\left(\frac{V_l}{\lambda_{th}{}^3}\right) - N_l \ln N_l + N_l \\ &\quad + N_u[\ln\left(\frac{V_u}{\lambda_{th}{}^3}\right) - \beta mgH] - N_u \ln N_u + N_u\end{aligned}$$

where

$$N_{total} = N_u + N_l = \text{constant}$$

We now take a derivative of $\ln Z(N_l, N_u)$ with respect to N_l

$$\begin{aligned}\frac{\partial \ln Z(N_l, N_u)}{\partial N_l} &= \frac{\partial \ln Z_l(N_i)}{\partial N_l} + \frac{\partial \ln Z_u(N_{total} - N_l)}{\partial N_l} \\ &= \frac{\partial \ln Z_l(N_i)}{\partial N_l} - \frac{\partial \ln Z_u(N_u)}{\partial N_u}\end{aligned}$$

or

$$\frac{\partial \ln Z_l(N_i)}{\partial N_l} = \frac{\partial \ln Z_u(N_u)}{\partial N_u}$$

We note that

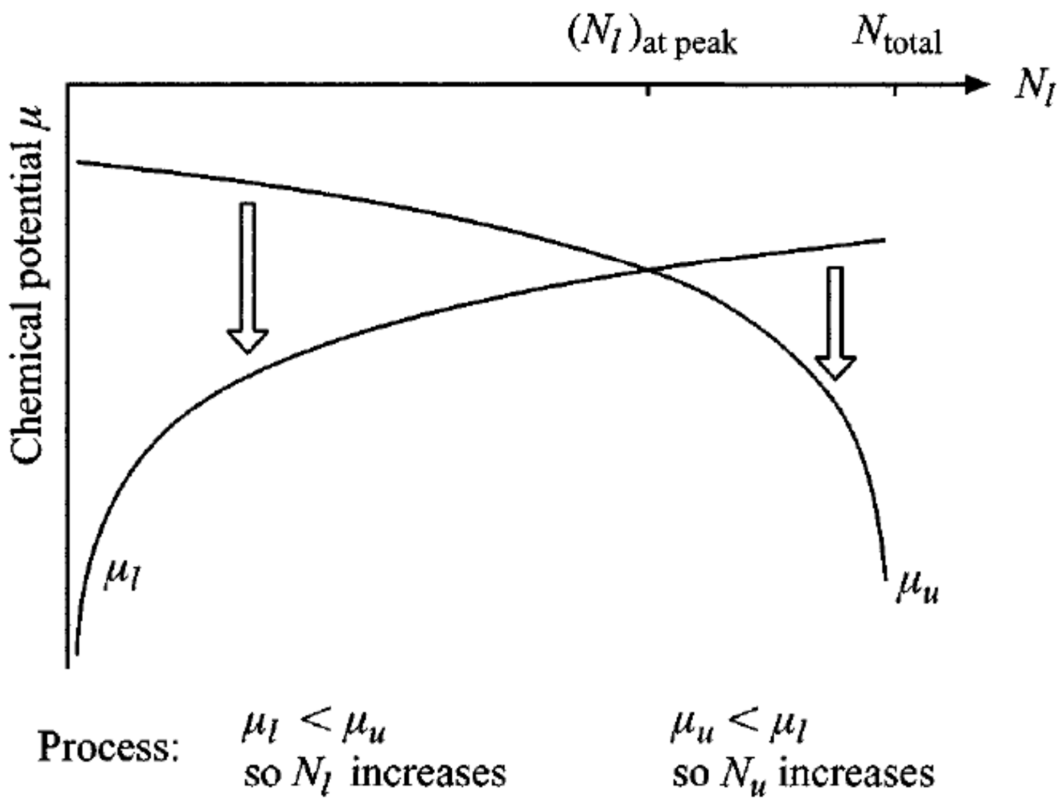
$$\begin{aligned}\frac{\partial \ln Z_l(N_i)}{\partial N_l} &= \ln\left(\frac{V_l}{\lambda_{th}{}^3}\right) - \ln N_l \\ &= \ln\left(\frac{V_l}{\lambda_{th}{}^3 N_l}\right)\end{aligned}$$

and

$$\begin{aligned}\frac{\partial \ln Z_u(N_u)}{\partial N_u} &= \ln\left(\frac{V_u}{\lambda_{th}{}^3}\right) - \beta mgH - \ln N_u \\ &= \ln\left(\frac{V_u}{\lambda_{th}{}^3 N_u}\right) - \beta mgH\end{aligned}$$

Thus we have

$$\frac{N_u}{N_l} = \frac{V_u}{V_l} e^{-\beta mgH}$$



2. Reformulation and generalization

The Helmholtz free energy:

$$F = U - ST = -k_B T \ln Z$$

with

$$F_l(N_l) = -k_B T \ln Z_l(N_l)$$

$$F_u(N_u) = -k_B T \ln Z_u(N_u)$$

Since

$$\frac{\partial \ln Z_l(N_i)}{\partial N_l} = \frac{\partial \ln Z_u(N_u)}{\partial N_u} \qquad \text{(in thermal equilibrium)}$$

The chemical potential is defined as

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

and the pressure is defined as

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

where

$$\begin{aligned} dF &= d(U - ST) \\ &= TdS - pdV + \mu dN - SdT - TdS \\ &= -SdT - pdV + \mu dN \end{aligned}$$

Using this definition of the chemical potential, we get

$$\begin{aligned} \mu_l &= \frac{\partial F_l(N_i)}{\partial N_l} \\ &= -k_B T \frac{\partial \ln Z_l(N_i)}{\partial N_l} \\ &= -k_B T \ln\left(\frac{V_l}{\lambda_{th}{}^3 N_l}\right) \\ &= k_B T \ln\left(\frac{\lambda_{th}{}^3 N_l}{V_l}\right) \\ &= \mu_l^{(0)} \end{aligned}$$

and

$$\begin{aligned}
\mu_u &= \frac{\partial F_u(N_u)}{\partial N_u} \\
&= -k_B T \frac{\partial \ln Z_u(N_u)}{\partial N_u} \\
&= -k_B T \ln\left(\frac{V_u}{\lambda_{th}{}^3 N_u} e^{-\beta mgH} \right) \\
&= mgH - k_B T \ln\left(\frac{V_u}{\lambda_{th}{}^3 N_u} \right) \\
&= mgH + k_B T \ln\left(\frac{\lambda_{th}{}^3 N_u}{V_u} \right) \\
&= mgH + \mu_u^{(0)}
\end{aligned}$$

In thermal equilibrium, we get the condition

$$\mu_u = \mu_l$$

or

$$\mu_u{}^{(0)} + mgH = \mu_l{}^{(0)}$$

Note

$$\mu_u^{(0)} = k_B T \ln\left(\frac{n_u}{n_Q} \right), \qquad \mu_l^{(0)} = k_B T \ln\left(\frac{n_l}{n_Q} \right)$$

and

$$\ln\left(\frac{n_u}{n_Q} \right) + \beta mgH = \ln\left(\frac{n_l}{n_Q} \right)$$

or

$$\ln\left(\frac{n_u}{n_l} \right) = -\beta mgH$$

or

$$n_u = e^{-\beta mgH} n_l$$

where $n_Q = \frac{1}{\lambda_{th}^3} = \left(\frac{mk_B T}{2\pi\hbar^3}\right)^{3/2}$ is the quantum concentration.

We note that

$$\begin{aligned} P_l &= -\left(\frac{\partial F_l(N_i)}{\partial V_l}\right)_{T,N} \\ &= k_B T \frac{\partial \ln Z_l(N_i)}{\partial V_l} \\ &= k_B T \frac{N_l}{V_l} \\ &= k_B T n_l \end{aligned}$$

$$\begin{aligned} P_u &= -\left(\frac{\partial F_u(N_u)}{\partial V_u}\right)_{T,N} \\ &= k_B T \frac{\partial \ln Z_u(N_u)}{\partial V_u} \\ &= k_B T \frac{N_u}{V_u} \\ &= k_B T n_u \end{aligned}$$

Using the expression of the pressure, we have

$$\frac{P_u}{P_i} = e^{-\beta mgH}$$

((**Example**))
We consider an isothermal atmosphere composed of nitrogen molecules.

$$m = m(N_2) = \frac{28\times 10^{-3}}{N_A} = 4.64885\times 10^{-26} \text{ (kg)}$$

$$T = 290 \text{ K}$$

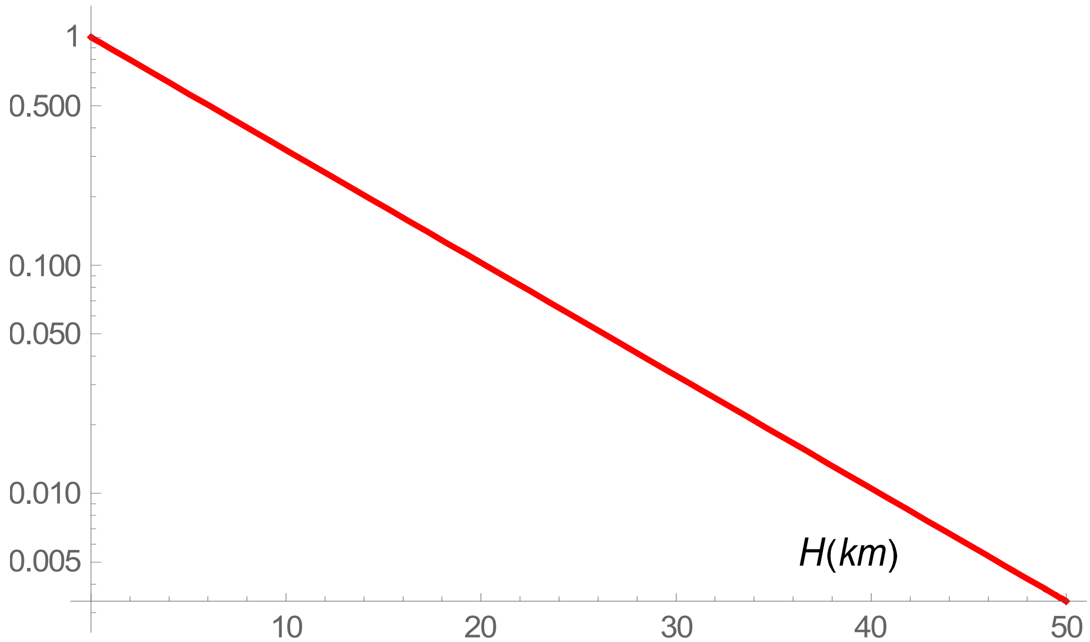


Fig. Decrease of atmospheric pressure with altitude. $T = 290$ K.

3. Isothermal adsorption (Langmuir)

We consider the adsorption of atoms on the substrate (Langmuir).

The one-particle partition function for the adsorbed atom is

$$
\begin{aligned}
Z_{adsorbed}(1) &= Z_{atom}(1) Z_{translate}(1) \\
&= e^{\beta\varepsilon_0} \frac{A}{\lambda_{th}{}^2}
\end{aligned}
$$

where

$$Z_{atom}(1) = e^{\beta\varepsilon_0}$$

and

$$Z_{translate}(1) = \sum_{\boldsymbol{k}(2D)} e^{-\frac{\beta\hbar^2\boldsymbol{k}^2}{2m}}$$

$$= \frac{A}{(2\pi)^2}\int_0^\infty 2\pi k dk e^{-\frac{\beta\hbar^2\boldsymbol{k}^2}{2m}}$$

$$= \frac{A}{2\pi}\int_0^\infty k dk e^{-\frac{\beta\hbar^2 k^2}{2m}}$$

$$= A\frac{mk_B T}{2\pi\hbar^2}$$

$$= \frac{A}{\lambda_{th}{}^2}$$

The partition function of the adsorbed atoms ($N_{adsorbed}$) is

$$Z_{adsorbed}(N_{adsorbed}) = \frac{[Z_{adsorbed}(1)]^{N_{adsorbed}}}{(N_{adsorbed})!}$$

The chemical potential of the adsorbed atoms is

$$\mu_{adsorped} = -k_B T\ln[\frac{Z_{adsorbed}(1)}{N_{adsorped}}]$$

$$= -k_B T\ln(\frac{Ae^{\beta\varepsilon_0}}{\lambda_{th}{}^2 N_{adsorped}})$$

$$= -k_B T\ln(\frac{A}{\lambda_{th}{}^2 N_{adsorped}}) - \varepsilon_0$$

or

$$\mu_{adsorped} = \mu_{adsorped}{}^{(0)} - \varepsilon_0$$

with

$$\mu_{adsorped}{}^{(0)} = -k_B T\ln(\frac{A}{\lambda_{th}{}^2 N_{adsorped}})$$

On the other hand, the chemical potential of the gas is given by

$$\mu_g = -k_B T \ln[\frac{Z_{gas}(1)}{N_{gas}}] = -k_B T \ln[\frac{V}{\lambda_{th}{}^3 N_{gas}}]$$

The pressure of the gas is

$$P_{gas} = \frac{N_{gas}}{V} k_B T$$

In thermal equilibrium, we have

$$\mu_g = \mu_{adsorbed}$$

or

$$-k_B T \ln(\frac{Ae^{\beta\varepsilon_0}}{\lambda_{th}{}^2 N_{adsorped}}) = -k_B T \ln[\frac{V}{\lambda_{th}{}^3 N_{gas}}]$$

or

$$\frac{Ae^{\beta\varepsilon_0}}{\lambda_{th}{}^2 N_{adsorped}} = \frac{V}{\lambda_{th}{}^3 N_{gas}}$$

or

$$\frac{N_{gas}}{V} = \frac{N_{adsorped}}{A\lambda_{th}} e^{-\beta\varepsilon_0}$$

where

$$N_{total} = N_{gas} + N_{adsorbed}, \qquad P_{gas} = \frac{N_{gas}}{V} k_B T$$

Thus we get

$$P_{gas} = \frac{N_{adsorped}}{A} \frac{k_B T}{\lambda_{th}} e^{-\beta\varepsilon_0}$$

Then the coverage is

$$\theta = \frac{N_{adsorbed}}{N_{total}} = \frac{N_{adsorbed}}{N_{gas} + N_{adsorbed}}$$

In summary we have

$$\mu_g = \mu_{adsorbed} = \mu_{adsorped}{}^{(0)} - \varepsilon_0$$

REFERENCES

R. Baierlein, Thermal Physics (Cambridge, 1990).

C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman, 1980).