Monoatomic ideal gas in grand canonical ensemble

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
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Here we derive the chemical potential of monoatomic ideal gas using the grand canonical ensemble.

1. Grand canonical ensemble

The partition function for the canonical ensemble is given by

$$Z_{CN} = \frac{1}{N!}(Z_{C1})^N$$

Using this, the grand partition function is obtained as

$$\begin{aligned} Z_G &= \sum_{N=0}^{\infty} z^N Z_{CN} \\ &= \sum_{N=0}^{\infty} \frac{1}{N!}(zZ_{C1})^N \\ &= e^{zZ_{C1}} \end{aligned}$$

The average number;

$$\langle N \rangle = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln Z_G = \frac{1}{\beta}\frac{\partial}{\partial \mu}(zZ_{C1}) = \frac{1}{\beta}\frac{\partial z}{\partial \mu}\frac{\partial}{\partial z}(zZ_{C1}) = zZ_{C1}$$

since $z = e^{\beta\mu}$ and $\frac{\partial}{\partial \mu} = \frac{\partial z}{\partial \mu}\frac{\partial}{\partial z} = \beta z \frac{\partial}{\partial z}$. We note that

$$PV = k_B T \ln Z_G = k_B T (zZ_{C1}) = k_B T \langle N \rangle$$

The grand potential is

$$\Phi_G = -k_B T \ln Z_G = -PV .$$

2. Chemical potential

$$Z_{C1} = n_Q V$$

with

$$n_Q = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} = \left(\frac{2\pi mk_BT}{h^2}\right)^{3/2} \qquad \text{(quantum concentration)}$$

Since

$$\langle N \rangle = zZ_{C1} = n_Q V e^{\beta\mu}$$

we have

$$\frac{\langle N \rangle}{V} = n = n_Q e^{\beta\mu}, \qquad \mu = k_BT \ln\left(\frac{n}{n_Q}\right)$$

We also have

$$PV = \langle N \rangle k_BT, \qquad \text{or} \qquad \frac{\langle N \rangle}{V} = n = \frac{P}{k_BT}$$

Then we have a chemical potential

$$\boxed{\mu = k_BT \ln\left(\frac{P}{k_BTn_Q}\right)}$$

The chemical potential is equivalent to a true potential energy. Only difference of chemical potential has a physical meaning. When external potential steps are present, we can express the total chemical potential of the system as

$$\mu = \mu_{tot} = \mu_{ext} + \mu_{\text{int}}.$$

where μ_{ext} is the potential energy per particle in the external potential, and μ_{int} is the internal chemical potential. In the equilibrium condition one get

$$\Delta\mu = 0.$$

or

$$\Delta\mu_{ext} = -\Delta\mu_{\text{int}}$$

((**Example**)) **Evaluatiuon of the chemical potential of He gas**

For T = 300 K and P=1 atm = 101.325 kPa

m(He) = 4.002602 u = 6.64648 x 10^{-27} kg

$$n_Q = \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} = 7.81982 \times 10^{30}\ /\text{m}^3$$

$$n = \frac{P}{k_BT} = 2.44571 \times 10^{25}/\text{m}^3$$

The chemical potential

$$\mu = k_BT\ln\left(\frac{n}{n_Q}\right) = k_BT\ln\left(\frac{P}{k_BTn_Q}\right) = -0.3276\ \text{eV}$$

If the concentration is increased while holding the temperature fixed, μ becomes less negative, indicating that the gas becomes more willing to give up particles to other nearby systems.

3. Example-1

Variation of barometric pressure with altitude (isothermal).

$$\mu = k_BT\ln\left(\frac{n}{n_Q}\right) + Mgh$$

The first term is μ_{int}, and the second term is the potential energy per molecule at the height h. M is the particle mass.

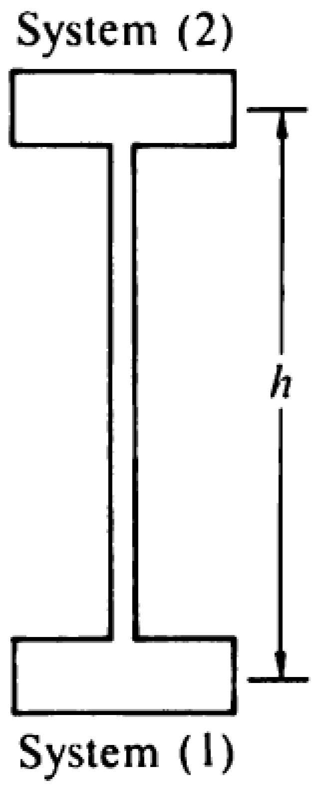


Fig. A model of the variation of atmospheric pressure with altitude: two volumes of gas at different heights in a uniform gravitational field, in thermal and diffusive contact. (Kittel, Thermal Physics).

In equilibrium, $\mu(0) = \mu(h)$,

or the chemical potential at $h = 0$ is equal to that at h. Thus we have

$$\mu(h) = k_B T \ln\left(\frac{n(h)}{n_Q}\right) + Mgh = \mu(0) = k_B T \ln\left(\frac{n(0)}{n_Q}\right)$$

or

$$n(h) = n(0)\exp(-\frac{Mgh}{k_B T})$$

The pressure of an ideal gas is given by

$$PV = Nk_B T\,, \qquad \text{or} \qquad P = \frac{N}{V} k_B T = nk_B T \qquad \text{(equation of states).}$$

Therefore the pressure $P(h)$ at altitude h is

$$P(h) = P(0)\exp(-\frac{Mgh}{k_B T}) = P(0)\exp(-\frac{h}{h_c})$$

where $P(h)$ is the characteristic height,

$$h_c = \frac{k_B T}{Mg}$$

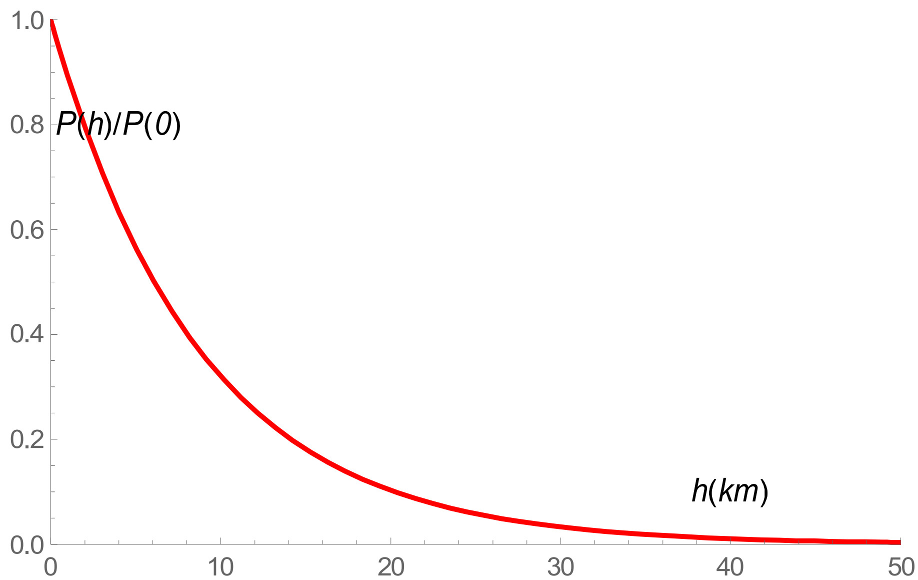
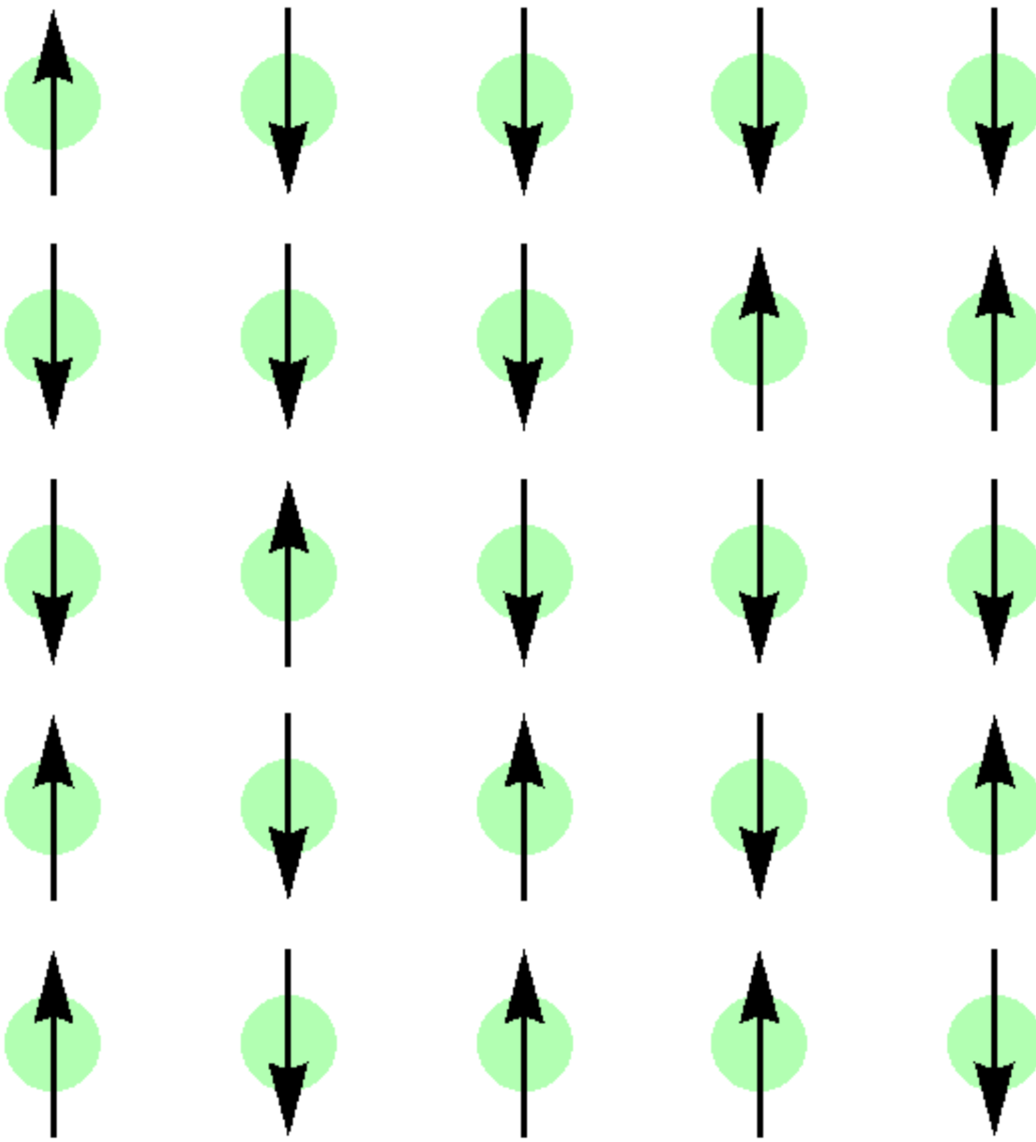


Fig. The plot of $P(h)/P(0)$ vs height h (km) for N_2 gas and T = 290 K.

4. Example-2
Chemical potential of mobile magnetic particles in a magnetic field

We consider a system of N identical particles each with a magnetic moment m. For simplicity suppose that each moment is directed either parallel ($\uparrow$) or antiparallel ($\downarrow$) to an applied magnetic field ***B***. Then the potential energy of a $\uparrow$ particle is mB, and the potential energy of a $\downarrow$ particle is $+mB$.



$$\begin{aligned}\mu_{tot}(\uparrow) &= \mu_{\text{int}}\left(\uparrow\right) + \mu_{ext}\left(\uparrow\right) \\ &= \mu_{\text{int}}\left(\uparrow\right) - mB \\ &= k_B T \ln\left(\frac{n_\uparrow}{n_Q}\right) - mB\end{aligned} \quad ,$$

$$\begin{aligned}\mu_{tot}(\downarrow) &= \mu_{\text{int}}\left(\downarrow\right) + \mu_{ext}\left(\downarrow\right) \\ &= \mu_{\text{int}}\left(\downarrow\right) + mB \\ &= k_B T \ln\left(\frac{n_\downarrow}{n_Q}\right) + mB\end{aligned}$$

with

$$n = n_{\uparrow} + n_{\downarrow}$$

In equilibrium,

$$\mu_{tot}(\uparrow) = \mu_{tot}(\downarrow) .$$

The solution is given by

$$k_B T \ln(\frac{n_{\uparrow}}{n_Q}) - mB = k_B T \ln(\frac{n_{\downarrow}}{n_Q}) + mB = \text{constant}$$

where

$$n_{\uparrow} = \frac{1}{2} n(0) \exp(\frac{mB}{k_B T})$$

$$n_{\downarrow} = \frac{1}{2} n(0) \exp(-\frac{mB}{k_B T})$$

$$n(0) = n_{\uparrow} + n_{\downarrow}$$

$$\begin{aligned} n(B) &= n_{\uparrow}(B) + n_{\downarrow}(B) \\ &= n(0) \cosh(\frac{mB}{k_B T}) \end{aligned}$$