# Understanding of chemical potential: Kittel Masatsugu Sei Suzuki Department of Physics, SUNY at Binghamton (Date: October 19, 2017)

The chemical potential is equivalent to a true potential energy: the difference in chemical potential between two systems is equal to the potential barrier that will bring the two systems into diffusive equilibrium.

When external potential steps are present, we xan express the total chemical potential of a system as the sum of two parts;

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

where  $\mu_{ext}$  is the potential energy per particle in the external potential, and  $\mu_{int}$  is the internal chemical potential such as  $\mu = k_B T \ln(\frac{n}{n_Q})$ .

((Note))

The chemical potential is very useful in discussing the equilibrium distribution of particles in external electric, magnetic, or gravitational fields. Note that the temperatures of the different parts must be always equal in thermal equilibrium.

For a perfect gas we have

$$\mu = k_B T \ln(\frac{n}{n_Q})$$
$$= k_B T \ln(\frac{P}{k_B T n_Q(T)})$$
$$= k_B T \ln P + f(T)$$

with

$$n = \frac{N}{V},$$

and

$$n_{Q}(T) = \frac{1}{\lambda_{T}^{3}} = \left(\frac{2\pi m k_{B}T}{h^{2}}\right)^{3/2} = \left(\frac{m k_{B}T}{2\pi \hbar^{2}}\right)^{3/2}$$

$$f(T) = -k_B T \ln[k_B T n_O(T)]$$

Here the concept of the chemical potential is discussed using several examples (mainly from Kittel, Thermal Physics, Chapter 5).

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

C. Kittel, Elementary Statistical Physics (Dover, 1986).

### 1. Chemical potential due to the gravitational field

Consider a system at temperature T, with N atoms of mass M in volume V. Let  $\mu(0)$  denote the value of the chemical potential at the surface of the Earth. Prove carefully and honestly that the value of the total chemical potential for the identical system when translated to altitude h is

$$\mu(h) = \mu(0) + Mgh$$

where g is the acceleration of gravity.

((**Solution 1**)) In a gravitational field, we have

$$\mu = \mu_{tot} = \mu_{int} + \mu_{ext} = k_B T \ln(\frac{n(h)}{n_Q}) + Mgh = k_B T \ln(\frac{n(0)}{n_Q})$$

or

$$k_B T \ln[\frac{n(h)}{n(0)}] = -Mgh$$

or

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

Since  $P = nk_BT$ 

and

$$P(h) = P(0) \exp(-\frac{Mgh}{k_{B}T}) = P(0) \exp[-\frac{\rho(0)gh}{P(0)}]$$

which is the isothermal barometric pressure equation.

$$\frac{M}{k_B T} = \frac{Nm}{Nk_B T} = \frac{M}{PV} = \frac{\rho}{P} = \frac{M}{P_0 V_0} = \frac{\rho_0}{P_0}$$

$$\frac{\rho(0)g}{P(0)} = \frac{1.1929 \text{ kg/m}^3 \times 9.8 \text{ m/s}^2}{1.013 \times 10^5 \text{ Pa}} = \frac{1}{8660 \text{ m}}$$

((Note-1))

The canonical partition function is

$$Z_{CN}(h) = Z_{CN}(h=0)\exp(-\beta NMgh)$$

The Helmholtz free energy is

 $F(h) = -k_B T \ln Z_{CN}$ = F(h=0) + NMgh

The chemical potential is obtained as

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = Mgh + \left(\frac{\partial F(h=0)}{\partial N}\right)_{T,V} = Mgh + \mu_{int}.$$

under the gravity field.

((Note-2))

The grand canonical partition function is

$$Z_G(h) = Z_G(h=0) \exp[\beta(\mu N - NMgh)]$$
$$= Z_G(h=0) \exp[\beta N(\mu - Mgh)]$$

The grand thermodynamic potential

$$\Phi_G = -k_B T \ln Z_G = -k_B T \ln Z_G (h=0) - N(\mu - Mgh)$$

The Helmholtz free energy:

$$F = \Phi_G + \mu N = NMgh - k_BT \ln Z_G(h=0) = NMgh + F(h=0)$$

The chemical potential is obtained as

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = Mgh + \mu_{\text{int}}.$$

under the gravity field.

# 2. Example: Kittel, Thermal Physics Chapter 5 Problem 5-1 Centrifuge

A circular cylinder of radius R rotates about the long axis with angular velocity  $\omega$ . The cylinder contains an ideal gas of atoms of mass M at temperature T. Find an expression for the dependence of the concentration n(r) on the radial distance r from the axis, in terms of n(0) on the axis. Take  $\mu$  as for an ideal gas.

## ((Solution))



Fig. Centrifugal force on rating water container. https://www.youtube.com/watch?v=Zip9ft1PgV0 The total chemical potential is given by

$$\mu = \mu_{tot} = \mu_{int} + \mu_{ext} = k_B T \ln(\frac{n(r)}{n_Q}) + V(r) = k_B T \ln(\frac{n(r)}{n_Q}) - \frac{1}{2}M\omega^2 r^2$$

Here we note that the centrifugal force is related to the corresponding potential as

$$F(r) = -\frac{dV}{dr} = Mr\omega^2$$

or

$$V(r) = -\frac{1}{2}M\omega^2 r^2$$

In equilibrium, this must be independent of the radial distance from the axis r. Thus

$$k_{B}T\ln(\frac{n(r)}{n_{Q}}) - \frac{1}{2}M\omega^{2}r^{2} = k_{B}T\ln[\frac{n(0)}{n_{Q}}]$$
$$\ln[\frac{n(r)}{n(0)}] = \frac{M\omega^{2}r^{2}}{2k_{B}T}$$
$$\frac{n(r)}{n(0)} = \exp[\frac{M\omega^{2}r^{2}}{2k_{B}T}]$$

# ((Note-1)) Coriolis force and centrifugal force The centrifugal force is given by

8 8

$$\boldsymbol{F}_{cf} = -m\boldsymbol{\Omega} \times (\boldsymbol{\Omega} \times \boldsymbol{r}_{R})$$

is called the centrifugal force.

$$-2m(\boldsymbol{\omega} \times \boldsymbol{v}_{R}) = 2m\omega \dot{y}_{R}\boldsymbol{e}_{Rx} - 2m\omega \dot{x}_{R}\boldsymbol{e}_{Ry}$$
$$-m\boldsymbol{\omega} \times (\boldsymbol{\omega} \times \boldsymbol{v}_{R}) = m\omega^{2}x_{R}\boldsymbol{e}_{Rx} + m\omega^{2}y_{R}\boldsymbol{e}_{Ry}$$



**Fig.** The centrifugal force in the  $(x_R, y_R, z_R)$  space.



Fig. The centrifugal force  $\mathbf{F}_{cf} = m[(\mathbf{\Omega} \times \mathbf{r}_R) \times \mathbf{\Omega}] = m(\Omega_0^2 r_R \sin \lambda) \mathbf{e}_{\rho}$ .  $\mathbf{\Omega} \times \mathbf{r}_R = (\Omega_0 r_R \sin \lambda) \mathbf{e}_{\phi}$ . The unit vector  $\mathbf{e}_{\rho}$  which points radially outward from the axis of the rotation. The unit vector  $\mathbf{e}_{\phi}$  which is directed tangentially along the circle with radius  $\rho$ .

((Note-2))



**Fig.** Parabolic surface of a spinning pail of water.  $m\omega^2\rho$  is the centrifugal force. (from V. Barger and M. Olsson, Classical Mechanics, A Modern Perspective).

We use  $\rho = r$ .

$$F'\cos\theta = mg$$
,  $F'\sin\theta = m\omega^2 r$ 

$$\tan\theta = \frac{dy}{dr} = \frac{m\omega^2 r}{mg} = \frac{\omega^2 r}{g}$$

Thus we have

$$y = \frac{\omega^2 r^2}{2g}$$

## 2. Example: Kittel, Thermal Physics Chapter 5 Problem 5-2 Molecules in the Earth's atmosphere.

If n is the concentration of molecules at the surface of the Earth, M the mass of a molecule, and g the gravitational acceleration at the surface, show that at constant temperature the total number of molecules in the atmosphere is

$$N = 4\pi n(R_E) \exp(-\beta m g R_E) \int_{R_E}^{\infty} r^2 dr \exp(\frac{\beta m g R_E^2}{r}),$$

where r measured from the center of the Earth: here  $R_E$  is the radius of the Earth. The integral diverges at the upper limit, so that N cannot be bounded and the atmosphere cannot be in equilibrium. Molecules, particularly light molecules, are always escaping from the atmosphere.

#### ((Solution))

The chemical potential:

$$\mu(r) = k_B T \ln[\frac{n(r)}{n_Q}] - \frac{GM_E m}{r} = \mu(R) = k_B T \ln[\frac{n(R)}{n_Q}] - \frac{GM_E m}{R}$$

Noting that

$$mg = \frac{GM_Em}{R_E^2}$$
 or  $GM_E = gR_E^2$ 

we have

$$k_{B}T\ln[\frac{n(r)}{n(R_{E})}] = -mgR_{E}^{2}(\frac{r-R_{E}}{rR_{E}}) = -mgR_{E}(\frac{r-R_{E}}{r})$$

or

$$\ln\left[\frac{n(r)}{n(R_E)}\right] = -\frac{mgR_E}{k_BT} + \frac{mgR_E^2}{k_BTr}$$

or

$$\frac{n(r)}{n(R_E)} = \exp(-\frac{mgR_E}{k_BT})\exp(\frac{mgR_E^2}{k_BTr}) = \exp(-\beta mgR_E)\exp(\frac{\beta mgR_E^2}{r})$$

At constant temperature, the total number of molecules in the atmosphere is

$$N = 4\pi \int_{R_E}^{\infty} r^2 dr \, n(r)$$
  
=  $4\pi n(R_E) \exp(-\beta mg R_E) \int_{R_E}^{\infty} r^2 dr \exp(\frac{\beta mg R_E^2}{r})$ 

Suppose that  $\frac{r}{\beta mg R_E^2} = x$ ,  $x_0 = \frac{1}{\beta mg R_E}$ . we have

$$\frac{N}{4\pi n(R_E)\exp(-\beta mgR_E)(\beta mgR_E^2)} = \int_{x_0}^{\infty} x^2 dx \exp(\frac{1}{x})$$

# 3. Example: Kittel, Thermal Physics Chapter 5 Problem 5-3 Potential energy of gas in gravitational field

Consider a column of atoms each of mass M at temperature T in a uniform gravitational field g. Find the thermal average potential energy per atom. The thermal average kinetic energy density is independent of height. Find the total heat capacity per atom. The total heat capacity is the sum of contributions from the kinetic energy and from the potential energy. Take the zero of the gravitational energy at the bottom h = 0 of the column. Integrate from h = 0 to  $h = \infty$ .

## ((Solution))

$$n(h) = n(0) \exp(-\beta Mgh)$$

The total number of atoms is

$$\int_{0}^{\infty} n(h)dh = n(0)\int_{0}^{\infty} \exp(-\beta Mgh)dh$$

The total potential energy is

$$\int_{0}^{\infty} n(h)dhMgh = Mgn(0)\int_{0}^{\infty} \exp(-\beta Mgh)hdh$$

The potential energy per atom is

$$V = Mg \frac{n(0)\int_{0}^{\infty} \exp(-\beta Mgh)hdh}{\int_{0}^{\infty} n(h)dh}$$
$$= Mg \frac{\int_{0}^{\infty} \exp(-\beta Mgh)hdh}{\int_{0}^{\infty} \exp(-\beta Mgh)dh}$$
$$= Mg \frac{(k_{B}T / Mg)^{2}}{k_{B}T / Mg}$$
$$= k_{B}T$$

The total heat capacity is

$$C = k_B + \frac{3}{2}k_B = \frac{5}{2}k_B$$

where  $\frac{3}{2}k_B$  is the heat capacity of free particle.

# 4. Example: Kittel, Thermal Physics Chapter 5 Problem 5-4 Active transport

The concentration of potassium  $K^+$  ions in the internal sap of sap of a plant cell (for example, a fresh water alga) may exceed by a factor of  $10^4$  the concentration of  $K^+$  ions in the pond water in which cell is growing. The chemical potential of the  $K^+$  ions is higher in the sap because their concentration *n* is higher there. Estimate the difference in chemical potential at 300 K and show that it is equivalent to a voltage of 0.24V across the cell wall. Take  $\mu$  as for an ideal gas. Because the values of the chemical potentials are different, the ions in the cell and in the pond are not in diffusive equilibrium. The plant cell membrane is highly impermeable to the passive leakage of ions through it. Important questions in cell physics include these: How is the high concentration of ions built up within the cell? How is metabolic energy applied to energize the active ion transport?

#### ((Solution))

We take  $\mu$  as for an ideal gas.

$$\mu = k_B T \ln(\frac{n}{n_Q})$$

The difference of  $\mu$  is given by

$$\Delta \mu = k_B T [\ln(\frac{n_2}{n_Q}) - \ln(\frac{n_1}{n_Q})] = k_B T \ln(\frac{n_2}{n_1})$$

For T = 300 K,  $\frac{n_2}{n_1} = 10^4$ . Then we have

$$\Delta \mu = 0.238 \text{ eV}$$

((Mathematica))

Clear["Global`\*"];  
rule1 = {kB 
$$\rightarrow$$
 1.3806504 × 10<sup>-16</sup>, eV  $\rightarrow$  1.602176487 × 10<sup>-12</sup>};  
T = 300;  $\Delta \mu = \frac{\text{kB T Log}[10^4]}{\text{eV}}$  //. rule1  
0.238106

## 5. Example: Kittel, Thermal Physics Chapter 5 Problem 5-12 Ascent of sap in tree

Find the maximum height to which water may rise in a tree under the assumption that the roots stand in a pool of water and the uppermost leaves are in air containing water vapor at a relative humidity r = 0.9. The temperature is 25 C. If the relative humidity is r, the actual concentration of water vapor in the air at the uppermost leaves is  $rn_0$ , where  $n_0$  is the concentration in the saturated air that stands immediately above the pool of water.

((Solution))

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

where  $n = n_0 r$ .

$$\mu(0) = k_B T \ln(\frac{n_0}{n_Q})$$

From the thermal equilibrium condition, we have

$$\mu(h) = k_{B}T\ln(\frac{n}{n_{Q}}) + Mgh = \mu(0) = k_{B}T\ln(\frac{n_{0}}{n_{Q}})$$

or

$$h = \frac{k_B T}{Mg} \ln(\frac{n_0}{n}) = \frac{k_B T}{Mg} \ln(\frac{1}{r})$$

with

$$\frac{n}{n_0} = 0.9$$

where M is the mass of water and is given by 18 gram/N<sub>A</sub>. Using the Mathematica we have

*h* = 1479.9 m.

#### ((Note))

In practice, trees rarely get over 100 m in height, 110 m is about the maximum. This is an over-estimate because the tree does not grow in water, and there is often a temperature gradient between the roots and top. Other mechanical limitations may come into play as trees grow taller.

#### ((Note)) Highest trees in the world

The tallest trees in the world are **redwoods** (Sequoia sempervirens), which tower above the ground in California. These trees can easily reach heights of 300 feet (91 m). Among the **redwoods**, a tree named Hyperion dwarfs them all. The tree was discovered in 2006, and is 379.7 feet (115.7 m) tall, Apr 15, 2013.

((Mathematica))

Clear["Global`\*"];

$$\begin{split} \texttt{rule1} &= \left\{ \texttt{kB} \rightarrow \texttt{1.3806504} \times \texttt{10}^{-\texttt{16}} \;,\; \texttt{NA} \rightarrow \texttt{6.02214179} \times \texttt{10}^{\texttt{23}} \;, \\ &\texttt{eV} \rightarrow \texttt{1.602176487} \times \texttt{10}^{-\texttt{12}} \;,\; \texttt{g} \rightarrow \texttt{980} \;,\; \texttt{m} \rightarrow \texttt{100} \right\}; \end{split}$$

T = 298; M = 18 / NA / . rule1;

$$h = \frac{1}{Mg} \frac{kBT}{m} Log\left[\frac{1}{0.9}\right] / /. rule1$$

1479.89

## REFERENCES

C. Kittel and H. Kroemer, Thermal Physics, second edition (W.H. Freeman and Company, 1980). V. Barger and M. Olsson, Classical Mechanics, A Modern Perspective (McGraw-Hill, 1973).