Quantum concentration Masatsugu Sei Suzuki Department of Physics, SUNY at Binghamton (Date: September 25, 2017)

Here we discuss the quantum concentration for the ideal gas. The quantum concentration n_Q is the particle concentration (i.e. the number of particles per unit volume) of a system where the interparticle distance is equal to the thermal de Broglie wavelength. The quantum effects become appreciable when the particle concentration is greater than or equal to the quantum concentration.

1. Canonical ensemble

$$\begin{split} Z_{C} &= \sum_{i} \exp(-\beta E_{i}) \\ E_{i} &= \sum_{j} \varepsilon_{j}(i) = \varepsilon_{1}(i) + \varepsilon_{2}(i) + \ldots + \varepsilon_{N}(i) \\ Z_{C} &= \sum_{i} \exp\{-\beta[\varepsilon_{1}(i) + \varepsilon_{2}(i) + \ldots + \varepsilon_{N}(i)\} \\ &= \sum_{i} \exp[-\beta \varepsilon_{1}(i) - \beta \varepsilon_{2}(i) - \ldots - \beta \varepsilon_{N}(i)] \\ &= (\sum_{i} \exp[-\beta \varepsilon_{1}(i)])(\sum_{i} \exp[-\beta \varepsilon_{2}(i)]) \dots (\sum_{i} \exp[-\beta \varepsilon_{N}(i)]) \\ &= (Z_{C\Gamma})^{N} \end{split}$$

for distinguishable particles. When we consider the more common problem of N identical particles in one box, we have to correct the partition function, because it over-counts the distinct states. For different three particles these six states are different. However, for identical (non-distinguishable) particles, these states are actually equivalent to one states. Thus $(Z_{C\Gamma})^N$ over-counts the states by N! and the correct one is

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

We consider the ideal gas in the canonical ensemble, whose Hamiltonian is given by

$$H = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m}$$

We calculate the partition function

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

 $Z_{\rm C1}$ is the partition function of the one particle system.

$$Z_{C1} = \frac{V}{(2\pi\hbar)^3} \int d^3 \boldsymbol{p} \exp\left[-\frac{\beta \boldsymbol{p}^2}{2m}\right]$$
$$= \frac{V}{(2\pi\hbar)^3} \int_0^\infty d\boldsymbol{p} 4\pi \boldsymbol{p}^2 \exp\left[-\frac{\beta \boldsymbol{p}^2}{2m}\right]$$
$$= \frac{V 4\pi}{(2\pi\hbar)^3} \sqrt{\frac{\pi}{2}} \left(\frac{m}{\beta}\right)^{3/2}$$
$$= \frac{V}{\hbar^3} \left(\frac{mk_BT}{2\pi}\right)^{3/2}$$
$$= \frac{V}{\hbar^3} \left(\sqrt{2\pi mk_BT}\right)^3$$
$$= V \left(\frac{\sqrt{2\pi mk_BT}}{\hbar}\right)^3$$
$$= \frac{V}{\lambda_T^3}$$

We define the thermal wavelength λ_T as

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} = \frac{\hbar}{\sqrt{\frac{m k_B T}{2\pi}}} = \sqrt{\frac{2\pi \hbar^2}{m k_B T}}$$

and quantum concentration as

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

Then we have

$$Z_{CN} = \frac{(Z_{C1})^{N}}{N!} = \frac{V^{N}}{N!\lambda_{T}^{3N}} = \frac{1}{N!} \left(\frac{V}{\lambda_{T}^{3}}\right)^{N} = \frac{1}{N!} (n_{Q}V)^{N}.$$

((Note)) Physical meaning of quantum concentration Quantum concentration

$$n_Q = \frac{1}{\lambda^3}$$

which is a concentration associated with one atom in a cube of side equal to the thermal average de Broglie wave λ .

$$p=m\langle v\rangle=\frac{h}{\lambda}=\frac{2\pi\hbar}{\lambda}$$
.

or

$$\lambda = \frac{2\pi\hbar}{m\langle v \rangle}$$

We note that

$$\frac{1}{2}m\langle v \rangle^2 = \frac{3}{2}k_BT$$
 or $\langle v \rangle = \sqrt{\frac{3k_BT}{m}}$

Then we have

$$\lambda = \frac{2\pi\hbar}{m\langle v \rangle} = \frac{2\pi\hbar}{m\sqrt{\frac{3k_BT}{m}}} = \sqrt{\frac{2\pi}{3}} \frac{h}{\sqrt{2\pi mk_BT}} = 1.447\lambda_T$$

The quantum concentration is

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

((Example))

He at 1 atm (T = 300 K)





((Definition))



Fig. The geometry for assessing whether semi-classical analysis is valid (R. Baierlein, Thermal Physics, Cambridge, 1999).



Fig. Cubic cell with the distance L. Suppose that the particles form a 3D cubic lattice with the average distance L. There is one particle per cubic cell. The number density n is $n = \frac{1}{L^3}$. So the average distance L is equal to $L = n^{-1/3}$. The quantum concentration n_Q is defined as $L_Q = n_Q^{-1/3} = \lambda$.

$$\frac{n}{n_o} \ll 1$$
 (Classical region)

An ideal gas is defined as a gas of non-interacting atoms in the classical limit.

The Helmholtz free energy *F*:

$$F = -k_B T \ln Z_{CN}$$

$$= -k_B T \ln \frac{(n_Q V)^N}{N!}$$

$$= -Nk_B T \ln(n_Q V) + k_B T \ln N!$$

$$= -Nk_B T \ln(\frac{V}{\lambda^3}) + k_B T \ln N!$$

$$= -Nk_B T [\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln(\frac{mk_B}{2\pi\hbar^2}) + 1]$$

$$= -Nk_B T [\ln \frac{n_Q}{n} + 1]$$

$$= Nk_B T (\ln \frac{n_Q}{n_Q} - 1)$$

using the Stirling's law, where

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

The entropy S:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V}$$
$$= Nk_{B}\left(\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma\right)$$
$$= Nk_{B}\left(\ln\frac{n_{Q}}{n} + \frac{5}{2}\right)$$

(Sackur-Tetrode equation)

where

$$\sigma = \frac{5}{2} + \frac{3}{2} \ln \left(\frac{mk_B}{2\pi\hbar^2} \right)$$

The energy is

$$\langle E \rangle = E = k_B T^2 \frac{\partial}{\partial T} \ln Z_{CN} = k_B T^2 \frac{3}{2} \frac{N}{T} = \frac{3}{2} N k_B T$$

The pressure P is

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V}, \qquad PV = Nk_BT.$$

The chemical potential is

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

= $-k_B T \left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \frac{3}{2} \ln \left(\frac{mk_B}{2\pi\hbar^2}\right)\right]$
= $-k_B T \ln \frac{n_Q}{n}$
= $k_B T \ln \frac{n}{n_Q}$

The heat capacity (molar)

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{3}{2}N_A k_B = \frac{3}{2}R$$

Using the Mayer relation

$$C_P = C_V + R = \frac{5}{2}R.$$

APPENDIX

Plane wave solution with a periodic boundary condition A. Energy level in 1D system

We consider a free electron gas in 1D system. The Schrödinger equation is given by

$$H\psi_k(x) = \frac{p^2}{2m}\psi_k(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi_k(x)}{dx^2} = \varepsilon_k\psi_k(x), \qquad (1)$$

where

$$p = \frac{\hbar}{i} \frac{d}{dx},$$

and ε_k is the energy of the electron in the orbital.

The orbital is defined as a solution of the wave equation for a system of only one electron: $\langle one-electron problem \rangle \rangle$.

Using a periodic boundary condition: $\psi_k(x+L) = \psi_k(x)$, we have the plane-wave solution

$$\psi_k(x) \sim e^{ikx} \,, \tag{2}$$

with

$$\varepsilon_k = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m} \left(\frac{2\pi}{L}n\right)^2,$$
$$e^{ikL} = 1 \text{ or } k = \frac{2\pi}{L}n,$$

where $n = 0, \pm 1, \pm 2, ...,$ and *L* is the size of the system.

B. Energy level in 3D system

We consider the Schrödinger equation of an electron confined to a cube of edge L.

$$H\psi_{k} = \frac{\boldsymbol{p}^{2}}{2m}\psi_{k} = -\frac{\hbar^{2}}{2m}\nabla^{2}\psi_{k} = \varepsilon_{k}\psi_{k}.$$
(3)

It is convenient to introduce wavefunctions that satisfy periodic boundary conditions. Boundary condition (Born-von Karman boundary conditions).

$$\begin{split} \psi_{\mathbf{k}}(x+L,y,z) &= \psi_{\mathbf{k}}(x,y,z) ,\\ \psi_{\mathbf{k}}(x,y+L,z) &= \psi_{\mathbf{k}}(x,y,z) ,\\ \psi_{\mathbf{k}}(x,y,z+L) &= \psi_{\mathbf{k}}(x,y,z) . \end{split}$$

The wavefunctions are of the form of a traveling plane wave.

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}},\tag{4}$$

with

$$k_{x} = (2\pi/L) n_{x}, (n_{x} = 0, \pm 1, \pm 2, \pm 3,), k_{y} = (2\pi/L) n_{y}, (n_{y} = 0, \pm 1, \pm 2, \pm 3,), k_{z} = (2\pi/L) n_{z}, (n_{z} = 0, \pm 1, \pm 2, \pm 3,).$$

or

$$p_{\rm x} = (2\pi\hbar/L)n_{\rm x}, (n_{\rm x} = 0, \pm 1, \pm 2, \pm 3,....),$$

$$p_{y} = (2\pi\hbar/L)n_{y}, (n_{y} = 0, \pm 1, \pm 2, \pm 3,....),$$

$$p_{z} = (2\pi\hbar/L)n_{z}, (n_{z} = 0, \pm 1, \pm 2, \pm 3,....).$$

where

$$p = \hbar k$$
.

The components of the wavevector k are the quantum numbers, along with the quantum number m_s of the spin direction. The energy eigenvalue is

$$\varepsilon(\mathbf{k}) = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m} \mathbf{k}^2 = \frac{1}{2m} \mathbf{p}^2.$$
(5)

Here

$$\boldsymbol{p}\boldsymbol{\psi}_{k}(\boldsymbol{r}) = \frac{\hbar}{i} \nabla_{k} \boldsymbol{\psi}_{k}(\boldsymbol{r}) = \hbar \boldsymbol{k} \boldsymbol{\psi}_{k}(\boldsymbol{r}) \,. \tag{6}$$

So that the plane wave function $\psi_k(\mathbf{r})$ is an eigenfunction of p with the eigenvalue $\hbar \mathbf{k}$. The ground state of a system of N electrons, the occupied orbitals are represented as a point inside a sphere in k-space.

(c) Density of states

In the *p*-space, there is one state per the volume element $\left(\frac{2\pi\hbar}{L}\right)^3$. So the number of states over the volume element $4\pi p^2 dp$ are obtained as

$$4\pi p^2 dp \left(\frac{L}{2\pi\hbar}\right)^3 = \frac{V}{\left(2\pi\hbar\right)^3} 4\pi p^2 dp \,.$$

In this case we need to use the replacement such as

$$\sum_{p} \rightarrow \frac{V}{\left(2\pi\hbar\right)^{3}} \int 4\pi p^{2} dp$$

where V is a volume; $V = L^3$.