**Ideal gas system: canonical and grand canonical ensembles**

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We discuss the thermodynamic properties of ideal gas system using two approaches (canonical and grand canonical ensembles). The quantum mechanics of the ideal gas is also discussed.

## 1. Canonical ensemble

We consider a calculation of the partition function of Maxwell-Boltzmann system (ideal M-B particles). The system consists of *N* particles (distinguishable).

The energy of the system is given by

$$E_i = \varepsilon_1 n_1 + \varepsilon_2 n_2 + ... + n_s \varepsilon_s$$

where $\varepsilon_1, \varepsilon_2, ..., \varepsilon_s$ are the energy levels (quantized, discrete). The total number of particles is

$$N = n_1 + n_2 + n_3 + ... + n_s ,$$

State $|\varepsilon_1\rangle$ with energy $\varepsilon_1$ level $n_1$ particles

State $|\varepsilon_2\rangle$ with energy $\varepsilon_2$ level $n_2$ particles

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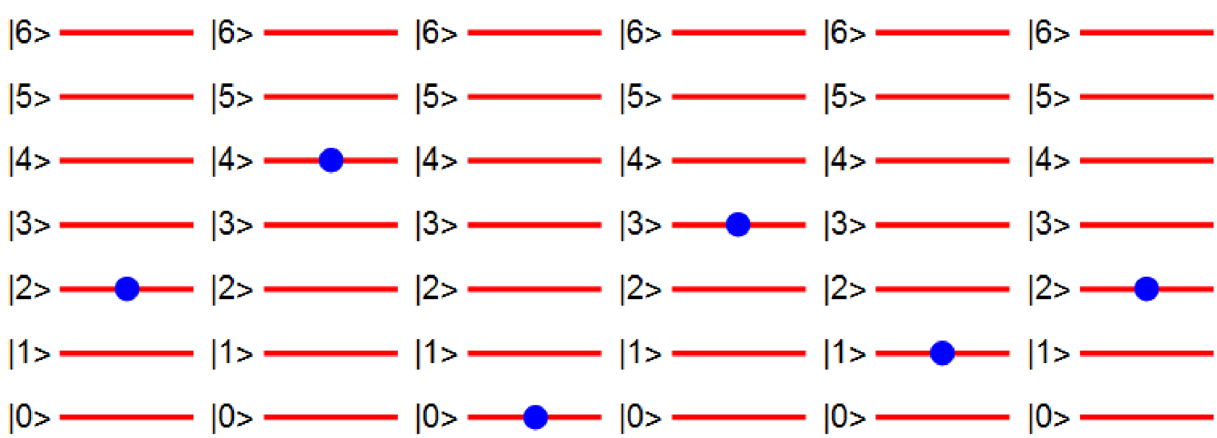
State $|\varepsilon_s\rangle$ with energy $\varepsilon_s$ level $n_s$ particles



The way to choose $n_1$ particles with the state $\left|\varepsilon_1\right\rangle$, $n_2$ particles with the state $\left|\varepsilon_2\right\rangle$, …, and $n_s$ particles with the state $\left|\varepsilon_s\right\rangle$ from $N$ particles is evaluated as

$$\frac{N!}{n_1!n_2!...n_s!}$$

where these particles are distinguishable. Then the partition function for the M-B particles (particle number is $N$) based on the canonical ensemble

$$\begin{aligned}
Z_C(\beta) &= \sum_{n_1}\sum_{n_2}...\sum_{n_s}\frac{N!}{n_1!n_2!...n_s!}\exp[-\beta(\varepsilon_1 n_1+\varepsilon_2 n_2+...+n_s\varepsilon_s)]\delta_{n_1+n_2+...+n_s,\,N} \\
&= \sum_{n_1}\sum_{n_2}...\sum_{n_s}\frac{N!}{n_1!n_2!...n_s!}\left(e^{-\beta\varepsilon_1}\right)^{n_1}\left(e^{-\beta\varepsilon_2}\right)^{n_2}...\left(e^{-\beta\varepsilon_s}\right)^{n_s}\delta_{n_1+n_2+...+n_s,\,N} \\
&= \left(e^{-\beta\varepsilon_1}+e^{-\beta\varepsilon_2}+...+e^{-\beta\varepsilon_s}\right)^N \\
&= \left[Z_{C1}(\beta)\right]^N
\end{aligned}$$

where $\delta_{n_1+n_2+...+n_s,\,N}$ means the condition of total particle number kept constant. We note that $Z_{C1}(\beta)$ is the partition function for the one particle system.

$$Z_{C1}(\beta) = \sum_i e^{-\beta\varepsilon_i} = e^{-\beta\varepsilon_1}+e^{-\beta\varepsilon_2}+...+e^{-\beta\varepsilon_s}$$

In general, when each energy eigenstate has the $g_i$ degeneracy, the partition function is given by

$$Z_{C1}(\beta) = \sum_i g_i e^{-\beta\varepsilon_i}$$

Suppose that $\left|\varepsilon_i\right\rangle = \left|\boldsymbol{k}\right\rangle$,

$$\varepsilon_{\boldsymbol{k}} = \frac{\hbar^2\boldsymbol{k}^2}{2m}$$

instead of $\varepsilon_i$.

$$\hat{H}\left|\boldsymbol{k}\right\rangle = \varepsilon_{\boldsymbol{k}}\left|\boldsymbol{k}\right\rangle$$

## 2. Calculation of $Z_{C1}(\beta)$

Now we calculate the partition function (canonical ensemble) using the density of state for the one particle system

$$
\begin{aligned}
Z_{C1}(\beta) &= \sum_{\boldsymbol{k}} \exp(-\beta\varepsilon_{\boldsymbol{k}}) \\
&= \frac{V}{(2\pi)^3}\int d\boldsymbol{k} \exp(-\beta\varepsilon_{\boldsymbol{k}}) \\
&= \frac{V}{(2\pi)^3}\int_0^\infty 4\pi k^2 dk \exp(-\frac{\beta\hbar^2 k^2}{2m}) \\
&= \frac{V}{2\pi^2}\sqrt{\frac{\pi}{2}}\frac{1}{\hbar^3}\left(\frac{m}{\beta}\right)^{3/2} \\
&= V\left(\frac{mk_B T}{2\pi\hbar^2}\right)
\end{aligned}
$$

## 3. *N* particle system (identical case)

$$
\begin{aligned}
Z_C(\beta) &= \frac{1}{N!}\left[Z_{C1}(\beta)\right]^N \\
&= \frac{V^N}{N!}\left[\frac{1}{2\pi^2}\sqrt{\frac{\pi}{2}}\left(\frac{m}{\hbar^2\beta}\right)^{3/2}\right]^N \\
&= \frac{V^N}{N!}\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3N/2} \\
&= \frac{V^N}{N!}\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3N/2} \\
&= \frac{V^N}{N!}\left(\frac{2\pi mk_B T}{h^2}\right)^{3N/2}
\end{aligned}
$$

Note that

$$
\frac{1}{2\pi^2}\sqrt{\frac{\pi}{2}} = \sqrt{\frac{1}{8\pi^3}} = \frac{1}{(2\pi)^{3/2}}, \qquad \hbar = \frac{h}{2\pi}
$$

The Helmholtz free energy:

$$
\begin{aligned}
F &= -k_B T \ln Z_C(\beta, T, V) \\
&= -k_B T[N \ln V - \ln N! + \frac{3N}{2} \ln T + \frac{3N}{2} \ln(\frac{2\pi m k_B}{h^2})] \\
&= -k_B T[N \ln V - N \ln N + N + \frac{3N}{2} \ln T + \frac{3N}{2} \ln(\frac{2\pi m k_B}{h^2})] \\
&= -N k_B T[\ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln T + 1 + \frac{3}{2} \ln(\frac{2\pi m k_B}{h^2})]
\end{aligned}
$$

or

$$
\boxed{F = -N k_B T[\ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln T + 1 + \frac{3}{2} \ln(\frac{2\pi m k_B}{h^2})]}
$$

$\ln Z_C(\beta, T, V)$ is obtained as

$$
\ln Z_C(\beta, T, V) = N[\ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln T + 1 + \frac{3}{2} \ln(\frac{2\pi m k_B}{h^2})]
$$

The average energy

$$
\begin{aligned}
U &= -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)_V \\
&= k_B T^2 \left(\frac{\partial}{\partial T} \ln Z\right)_V \\
&= -\left(\frac{\partial}{\partial \beta} \ln Z\right)_V \\
&= \frac{3}{2} N k_B T
\end{aligned}
$$

or

$$
\boxed{U = \frac{3}{2} N k_B T}
$$

The heat capacity at constant volume:

$$
\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N k_B}
$$

For $N = N_A$, we have $C_V = \frac{3}{2}R$ , where $R$ is the gas constant. The heat capacity at constant pressure is

$$C_P = Cv + R = \frac{5}{2}R, \qquad \text{(Mayer's relation)}$$

The entropy $S$ is

$$\begin{aligned} S &= \frac{U-F}{T} \\ &= \frac{3}{2}Nk_B + Nk_B[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln T + 1 + \frac{3}{2}\ln(\frac{2\pi mk_B}{h^2})] \\ &= Nk_B[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln(\frac{2\pi mk_B T}{h^2}) + \frac{5}{2}] \end{aligned}$$

or

$$S = Nk_B[\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln(\frac{2\pi mk_B T}{h^2}) + \frac{5}{2}] \qquad \text{(Sackur-Tetrode equation)}$$

The pressure $P$ is

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_B T}{V}$$

or

$$PV = Nk_B T$$

## 4. Partition function in the phase space

We calculate the one-particle partition function in the phase space,

$$
\begin{aligned}
Z_{C1} &= \frac{V}{h^3}\int d\boldsymbol{p}\exp(-\frac{\beta\,\boldsymbol{p}^2}{2m}) \\
&= \frac{V}{h^3}\int_0^\infty 4\pi p^2 dp\exp(-\frac{\beta\,p^2}{2m}) \\
&= \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2} \\
&= \frac{V}{\lambda_T{}^3}
\end{aligned}
$$

$\lambda_T$ is the thermal de Broglie wavelength.

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

Thus we have

$$
Z_C(\beta) = \frac{1}{N!}\left[Z_{C1}(\beta)\right]^N = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2}
$$

## 5. Grand canonical ensemble

When the number of particles is not constant and the particles are identical, we need to calculate the partition function in the Grand canonical ensemble. In this case the calculation becomes much simpler.

$$
Z_G(\beta,\mu) = \sum_{N=0}^{\infty}\frac{1}{N!}(\lambda Z_{C1})^N = \exp(\lambda Z_{C1})
$$

from the definition of the Taylor expansion. Then we get

$$
\ln Z_G(\beta,\mu) = \lambda Z_{C1}
$$

Thermodynamic potential (grand partition function)

$$
\Phi = -PV = -k_B T\ln Z_G = -k_B T\lambda Z_{C1}
$$

The average occupation number

$$N = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V} = k_B T\left(\frac{\partial \ln Z_G}{\partial \mu}\right) = \lambda \frac{\partial}{\partial \lambda}\ln Z_G = \lambda \frac{\partial}{\partial \lambda}(\lambda Z_{C1}) = \lambda Z_{C1}$$

The equation of state,

$$PV = k_B T \ln Z_G(\beta) = k_B T \lambda Z_{C1} = N k_B T$$

The chemical potential:

$$N = \lambda Z_{C1} = e^{\beta\mu}\frac{V}{\lambda_T{}^3}$$

or

$$\frac{N\lambda_T{}^3}{V} = e^{\beta\mu}$$

or

$$\mu = k_B T \ln\left(\frac{N\lambda_T{}^3}{V}\right) = k_B T \ln\left(\frac{P\lambda_T{}^3}{k_B T}\right)$$

Then the chemical potential is expressed as a simple form such that

$$\mu = k_B T \ln(P) + k_B T \ln\left(\frac{\lambda_T{}^3}{k_B T}\right) = k_B T \ln(P) + f(T)$$

where

$$\begin{aligned} f(T) &= k_B T \ln\left(\frac{\lambda_T{}^3}{k_B T}\right) \\ &= k_B T[3\ln\frac{h}{\sqrt{2\pi m k_B T}} - \ln(k_B T)] \\ &= k_B T\{3\ln\left(\frac{h}{\sqrt{2\pi m}}\right) - \frac{5}{2}\ln(k_B T)] \end{aligned}$$

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**APPENDIX**

We show that

$$\sum_{n_1}\sum_{n_2}\ldots\sum_{n_s}\frac{N!}{n_1!n_2!\ldots n_s!}(x_1{}^{n_1}x_2{}^{n_2}\ldots x_s{}^{n_s})\delta_{n_1+n_2+\ldots+n_s,N}=(x_1+x_2+\ldots+x_s)^N$$

by using Mathematica.

((**Mathematica**))

```
Clear["Global`*"]; N1 = 10;
g[n1_, n2_, n3_, n4_, n5_] :=
  N1!/(n1! n2! n3! n4! n5!) x1^n1 x2^n2 x3^n3 x4^n4 x5^n5
   KroneckerDelta[n1 + n2 + n3 + n4 + n5 - N1];
f1 = Sum[g[n1, n2, n3, n4, n5], {n1, 0, N1},
   {n2, 0, N1}, {n3, 0, N1}, {n4, 0, N1},
   {n5, 0, N1}];
f1 // FullSimplify
```

$(x1 + x2 + x3 + x4 + x5)^{10}$