Micro-canonical ensemble I

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We consider a system enclosed by an adiabatic wall. By an adiabatic wall we mean that energy cannot be transferred through this wall. The system can be a gas, liquid, or solid. For this system, the volume V, the number of particles N, and the total energy E are kept constant. These variables represent the only possible constraints for this system. Other than these constraints, we cannot place any restriction on the microscopic motions of the molecules. Therefore, according to the principle of equal probability, each molecule can do anything that is possible under these macroscopic constraints, and various microscopic states should be realized with equal probability in thermal equilibrium. Among these microscopic states, some states may be quite special, such that they will not be realized in reality. However, except for a few such exceptional states, almost all microscopic states will actually be realized as the state of the system changes temporally. Because of the vast number of possible microscopic states, the exceptional states will practically never be realized anyway; this is the conclusion of the previous chapter. We call this situation, where every possible microscopic state is realized with equal probability, the *micro-canonical distribution*. We write the total number of microscopic states allowed under the macroscopic constraints as $W(E, \delta E, V,N)$. Therefore, the probability of each microscopic state being realized is $1/W$. Here we have allowed some uncertainty δE in the total energy, and have counted microscopic states where the total energy is between E and $E + \delta E$. Using this W, we define the *entropy* $S(E, \delta E, V,N)$ as follows:

$$S(E,\delta E,V,N) = k_B \ln W(E,\delta E,V,N)$$

Furthermore, we define the *temperature* of the system as follows: In this equation, the partial differentiation is done keeping δE, N, and V fixed. As we shall see later, the temperature thus defined coincides with the temperature defined by thermodynamics.

1. Approach I: Classical free particles (the number of particles, N)

The total number of states for the energy of the system between 0 and E

$$\Omega(N,.E) = \frac{1}{N!}\frac{V^N}{h^{3N}} \int d\boldsymbol{p}_1 \int d\boldsymbol{p}_2 ......\int d\boldsymbol{p}_N \theta(E - \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^{\,2}}{2m})$$

Suppose that

$$p_i = \sqrt{2m}y_i, \qquad dp_1 = \sqrt{2m}dy_1$$

$$\Omega(N,.E) = (2m)^{3N/2}\frac{1}{N!}\frac{V^N}{h^{3N}}\int dy_1 ... \int dy_{3N}\theta(E - y_1^{\ 2} - y_2^{\ 2} - ... - y_{3N}^{\ 2})$$

The integral part corresponds to the volume of momentum space ($3N$ dimension) with radius $\sqrt{E}$. Using the formula of the volume of the hypersphere with radius $\sqrt{E}$, we get the phase-space volume (see the Appendix for the calculation of the volume of hypersphere)

$$\Omega(N,.E) = (2m)^{3N/2}\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2}+1)}E^{3N/2}$$
$$= (\frac{2\pi mE}{h^2})^{3N/2}\frac{V^N}{N!}\frac{1}{\Gamma(\frac{3N}{2}+1)}$$

where

$$\Gamma(\frac{3}{2}) = \frac{\sqrt{\pi}}{2}$$

The density of states is

$$D(N,E) = \frac{\partial\Omega(N,E)}{\partial E} = (2m)^{3N/2}\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2}+1)}\frac{3N}{2}E^{\frac{3N}{2}}\frac{1}{E}$$

The number of states between E and $E+\delta E$

$$W(N,E,\delta E) = D(N,E)\delta E$$
$$= (2m)^{3N/2}\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2}+1)}\frac{3N}{2}E^{\frac{3N}{2}}\frac{\delta E}{E}$$
$$= \frac{3N}{2}\frac{V^N}{N!}(\frac{2\pi mE}{h^2})^{3N/2}\frac{1}{\Gamma(\frac{3N}{2}+1)}\frac{\delta E}{E}$$

The entropy S is defined by

$$
\begin{aligned}
S &= k_B \ln W(N, E, \delta E) \\
&= k_B \{N \ln(V) + \frac{3N}{2}\ln E - 3N\ln h + \frac{3N}{2}\ln\pi + \frac{3N}{2}\ln(2m) \\
&- \ln N! - \ln\Gamma\left(\frac{3N}{2}+1\right) + \ln(\frac{3N}{2}) + \ln\left(\frac{\delta E}{E}\right)\} \\
&\approx k_B \{N \ln(V) + \frac{3N}{2}\ln E - 3N\ln h + \frac{3N}{2}\ln\pi + \frac{3N}{2}\ln(2m) \\
&- N(\ln N - 1) - \frac{3N}{2}(\ln\frac{3N}{2} - 1) + \ln(\frac{3N}{2}) + \ln\left(\frac{\delta E}{E}\right)\} \\
&= k_B \{N \ln(\frac{V}{N}) + \frac{3N}{2}\ln E - 3N\ln h + \frac{3N}{2}\ln(2m\pi) \\
&+ \frac{5}{2}N - \frac{3N}{2}(\ln N + \ln\frac{3}{2}) + \ln(\frac{3N}{2}) + \ln\left(\frac{\delta E}{E}\right)\} \\
&= k_B N \{\ln(\frac{V}{N}) + \frac{3}{2}\ln(\frac{E}{N}) + \frac{3}{2}\ln\frac{4\pi m}{3h^2} + \frac{5}{2} + \frac{1}{N}\ln(\frac{3N}{2}) + \frac{1}{N}\ln\left(\frac{\delta E}{E}\right)\}
\end{aligned}
$$

or

$$S = k_B N[\ln(\frac{V}{N}) + \frac{3}{2}\ln(\frac{E}{N}) + \frac{3}{2}\ln\frac{4\pi m}{3h^2} + \frac{5}{2}]$$

where we use the Stirling's relation

$$\ln N! = N\ln N - N$$

and

$$\ln\Gamma\left(\frac{3N}{2}+1\right) \approx \ln\left(\frac{3N}{2}\right)! = \frac{3N}{2}(\ln\frac{3N}{2} - 1)$$

In the limit of large N, we pick up only the terms which is proportional to N. The entropy S can be written as

$$S = k_B N[\ln(\frac{V}{N}) + \frac{3}{2}\ln(\frac{E}{N}) + \frac{3}{2}\ln\frac{4m\pi}{3h^2} + \frac{5}{2}]$$

From the relation

$$\frac{1}{T}=\left(\frac{\partial S}{\partial E}\right)_V=\frac{3Nk_B}{2}\frac{1}{E}$$

we have

$$E=\frac{3N}{2}k_BT \qquad \text{(energy partition law)}$$

The Helmholtz free energy:

$$F=E-ST=\frac{3N}{2}k_BT-Nk_BT[\ln(\frac{V}{N})+\frac{3}{2}\ln(\frac{E}{N})+\frac{3}{2}\ln\frac{4m\pi}{3h^2}+\frac{5}{2}]$$

Since $dF=-PdV-SdT$, the pressure is obtained as

$$P=-\left(\frac{\partial F}{\partial V}\right)_T=Nk_BT\frac{1}{V}$$

leading to the Boyle's law

$$PV=Nk_BT.$$

This can be rewritten as

$$PV=\frac{2}{3}E$$

2. From micro-canonical ensemble to canonical ensemble

First we consider the results from the micro-canonical ensemble for classical free particles. We calculate the ratio

$$\frac{\Omega(N,E-\varepsilon)}{\Omega(N,E)} = \frac{\frac{V^N}{N!}[\frac{2\pi m(E-\varepsilon)}{h^2}]^{3N/2}\frac{1}{\Gamma(\frac{3N}{2}+1)}}{\frac{V^N}{N!}(\frac{2\pi mE}{h^2})^{3N/2}\frac{1}{\Gamma(\frac{3N}{2}+1)}}$$

$$= (1-\frac{\varepsilon}{E})^{3N/2}$$

$$= (1-\frac{2}{3N}\frac{\varepsilon}{k_BT})^{3N/2}$$

where

$$E = \frac{3N}{2}k_BT$$

In the limit of $N \to \infty$, we get

$$\lim_{N\to\infty}(1-\frac{2}{3N}\frac{\varepsilon}{k_BT})^{3N/2} = \exp(-\frac{\varepsilon}{k_BT}) = \exp(-\beta\varepsilon)$$

since

$$\lim_{N\to\infty}(1+\frac{1}{N})^N = e.$$

Then we have

$$\frac{\Omega(N,E-\varepsilon)}{\Omega(N,E)} = e^{-\beta\varepsilon}.$$

We assume that the system is in a single state with the energy ε. Then the probability of finding the system in the state with the energy ε isgiven by

$$p(\varepsilon) \propto \frac{1\times\Omega(N,E-\varepsilon)}{\Omega(N,E)} = e^{-\beta\varepsilon},$$

which corresponds to the probability of canonical ensemble.

3. Derivation of Maxwell-Boltzmann distribution function from the micro-canonical ensemble

We start with the number of states given by

$$\Omega\ (N,.E) = \frac{1}{N!}\frac{V^N}{h^{3N}}\int d\boldsymbol{p}\int d\boldsymbol{p}_2......\int d\boldsymbol{p}_{N-1}\theta(E-\frac{\boldsymbol{p}^2}{2m}-\sum_{i=1}^{N-1}\frac{\boldsymbol{p}_i^{\ 2}}{2m})$$
$$= \frac{1}{N!}\frac{V^N}{h^{3N}}\int d\boldsymbol{p}\int d\boldsymbol{p}_2......\int d\boldsymbol{p}_{N-1}\theta(E-\frac{\boldsymbol{p}^2}{2m}-\sum_{i=1}^{N-1}\frac{\boldsymbol{p}_i^{\ 2}}{2m})$$

Suppose that

$$p_i = \sqrt{2m}y_i\,, \qquad dp_i = \sqrt{2m}dy_i$$

$$\Omega_1(N,.E) = (2m)^{(3N-3)/2}\frac{1}{N!}\frac{V^N}{h^{3N}}\int d^3\boldsymbol{p}\int dy_4...\int dy_{3N}\theta(E-\frac{\boldsymbol{p}^2}{2m}-y_4^{\ 2}-...-y_{3N}^{\ 2})$$

The integral part corresponds to the volume of momentum space ($3N-4+1=3N-3$ dimension) with radius $\sqrt{E-\frac{\boldsymbol{p}^2}{2m}}$. Using the formula of the volume of the hypersphere with radius $\sqrt{E}$, we get the phase-space volume (see the Appendix for the calculation of the volume of hypersphere)

$$\Omega_1(N,.E) = d^3\boldsymbol{p}\,(2m)^{\frac{3}{2}(N-1)}\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{\frac{3}{2}(N-1)}}{\Gamma(\frac{3(N-1)}{2}+1)}(E-\frac{\boldsymbol{p}^2}{2m})^{\frac{3}{2}(N-1)}$$

The density of states is

$$\frac{\partial\Omega_1(N,E)}{\partial E} = d^3\boldsymbol{p}\,(2m)^{\frac{3}{2}(N-1)}\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{\frac{3}{2}(N-1)}}{\Gamma(\frac{3(N-1)}{2}+1)}\frac{3(N-1)}{2}(E-\frac{\boldsymbol{p}^2}{2m})^{\frac{3}{2}(N-1)-1}$$

The number of states between E and $E+\delta E$ is

$$W_1(N,E,\delta E) = \frac{\partial \Omega_1(N,E)}{\partial E}\delta E$$

$$= d^3\boldsymbol{p}\,(2m)^{\frac{3}{2}(N-1)}\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{\frac{3}{2}(N-1)}}{\Gamma(\frac{3(N-1)}{2}+1)}\frac{3(N-1)}{2}\delta E(E-\frac{\boldsymbol{p}^2}{2m})^{\frac{3}{2}(N-1)-1}$$

We note that

$$\Omega_0(N,.E) = (\frac{2\pi mE}{h^2})^{\frac{3N}{2}}\frac{V^N}{N!}\frac{1}{\Gamma(\frac{3N}{2}+1)}$$

$$D_0(N,E) = \frac{\partial \Omega_0(N,.E)}{\partial E}$$

$$= (2m)^{\frac{3N}{2}}\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2}+1)}\frac{3N}{2E}E^{\frac{3N}{2}}$$

$$W_0(N,E,\delta E) = D_0(N,.E)\delta E$$

$$= (2m)^{\frac{3N}{2}}\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2}+1)}\frac{3N}{2}E^{\frac{3N}{2}}\frac{\delta E}{E}$$

$$= \frac{3N}{2}\frac{V^N}{N!}(\frac{2\pi mE}{h^2})^{\frac{3N}{2}}\frac{1}{\Gamma(\frac{3N}{2}+1)}\frac{\delta E}{E}$$

Now we calculate the ratio

$$\frac{\Omega_1(N,E)}{\Omega_0(N,E)} = \frac{d^3\boldsymbol{p}\,(2m)^{\frac{3}{2}(N-1)}\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{\frac{3}{2}(N-1)}}{\Gamma(\frac{3(N-1)}{2}+1)}\delta E(E-\frac{\boldsymbol{p}^2}{2m})^{\frac{3}{2}(N-1)}}{(2m)^{\frac{3N}{2}}\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2}+1)}E^{\frac{3N}{2}}}$$

$$= \frac{d^3\boldsymbol{p}\,(2m)^{\frac{3}{2}(N-1)}\frac{\pi^{\frac{3}{2}(N-1)}}{\Gamma(\frac{3(N-1)}{2}+1)}(E-\frac{\boldsymbol{p}^2}{2m})^{\frac{3}{2}(N-1)}}{(2m)^{\frac{3}{2}N}\frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2}+1)}\frac{3N}{2}E^{\frac{3}{2}N}}$$

$$\approx \frac{d^3\boldsymbol{p}}{(2\pi m)^{3/2}}\frac{1}{E^{\frac{3}{2}N}}\frac{\Gamma(\frac{3N}{2}+1)}{\Gamma(\frac{3(N-1)}{2}+1)}(E-\frac{\boldsymbol{p}^2}{2m})^{\frac{3}{2}(N-1)}$$

$$= 1.83712\frac{d^3\boldsymbol{p}}{(2\pi m)^{3/2}}N^{\frac{3}{2}}E^{-\frac{3}{2}}(1-\frac{\boldsymbol{p}^2}{2mE})^{\frac{3}{2}(N-1)}$$

where

$$\frac{\Gamma(\frac{3N}{2}+1)}{\Gamma(\frac{3(N-1)}{2}+1)} = \left(\frac{3}{2}\right)^{3/2}N^{3/2} = 1.83712N^{\frac{3}{2}} \qquad \text{(in the limit of } N\to\infty\text{).}$$

Thus we have

$$\frac{\Omega_1(N,E)}{\Omega_0(N,E)} = \left(\frac{3}{2}\right)^{3/2}\frac{d^3\boldsymbol{p}}{(2\pi m)^{3/2}}\left(\frac{N}{E}\right)^{\frac{3}{2}}(1-\frac{\boldsymbol{p}^2}{2mE})^{\frac{3}{2}N}$$

$$= \left(\frac{3}{2}\right)^{3/2}\frac{d^3\boldsymbol{p}}{(2\pi m)^{3/2}}\left(\frac{2\beta}{3}\right)^{\frac{3}{2}}(1-\frac{\beta\boldsymbol{p}^2}{2m}\frac{2}{3N})^{\frac{3}{2}N}$$

$$= d^3\boldsymbol{p}\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}}(1-\frac{\beta\boldsymbol{p}^2}{2m}\frac{2}{3N})^{\frac{3}{2}N}$$

$$= d^3\boldsymbol{p}\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}}\exp(-\frac{\beta\boldsymbol{p}^2}{2m})$$

where

$$\frac{E}{N} = \frac{3}{2}k_B T = \frac{3}{2\beta},$$

This form is exactly the same as that of the Maxwell-Boltzmann distribution function

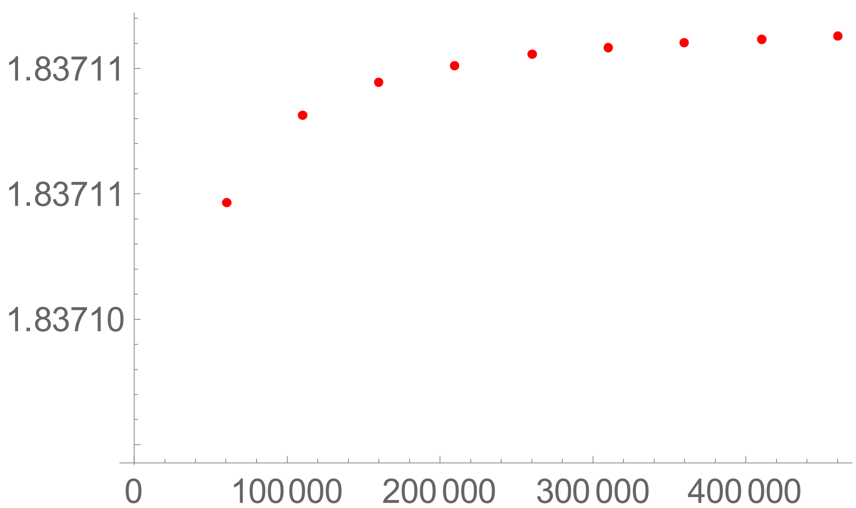
$$\frac{d\boldsymbol{p}\exp(-\frac{\beta p^2}{2m})}{\int_0^\infty 4\pi p^2 \exp(-\frac{\beta p^2}{2m})} = d^3\boldsymbol{p}\left(\frac{\beta}{2\pi m}\right)^{3/2} \exp(-\frac{\beta \boldsymbol{p}^2}{2m})$$

((**Mathematica**))

```
Clear["Global`*"];
f[N1_] := Log[Gamma[3/2 N1 + 1]] -
   Log[Gamma[3/2 N1 - 1/2]] - 3/2 Log[N1];

h1 = Table[{N1, Exp[f[N1]] // N},
    {N1, 10 000, 500 000, 50 000}];

ListPlot[h1, PlotStyle → {Thick, Red}]
```




```
Exp[f[10^6]] // N

1.83712
```

4. Application II: simple harmonics

The total number of states for the energy of the system between 0 and E

$$\Omega_0(N,.E)=\frac{1}{h^{3N}}\int d\boldsymbol{p}_1\int d\boldsymbol{p}_2......\int d\boldsymbol{p}_N\int d\boldsymbol{q}_1\int d\boldsymbol{q}_2......\int d\boldsymbol{p}_N\,\theta[E-\sum_{i=1}^{N}(\frac{\boldsymbol{p}_i^{\ 2}}{2m}+\frac{1}{2}m^2\omega^2\boldsymbol{q}_i^{\ 2})]$$

Suppose that

$$p_i = \sqrt{2m}x_i, \qquad dp_i = \sqrt{2m}dx_i \qquad (i = 1, 2, \ldots, 3N)$$

$$q_j = \sqrt{\frac{2}{m\omega^2}}x_{3N+j}, \qquad dq_i = \sqrt{\frac{2}{m\omega^2}}dx_{3N+j} \qquad (j = 1, 2, \ldots, 3N)$$

$$\Omega(N,.E) = (2m)^{3N/2}(\frac{2}{m\omega^2})^{3N/2}\frac{1}{N!}\frac{1}{h^{3N}}$$
$$\int dx_1 \ldots \int dx_{6N}\theta(E - x_1{}^2 - x_2{}^2 - \ldots - X_{6N}{}^2)$$

The integral part corresponds to the volume of momentum space ($6N$ dimension) with radius $\sqrt{E}$. Using the formula of the volume of the hypersphere with radius $\sqrt{E}$, we get the phase-space volume as

$$\Omega(N,.E) = (\frac{4}{\omega^2})^{3N/2}\frac{1}{N!}\frac{1}{h^{3N}}\frac{\pi^{3N}}{\Gamma(3N+1)}E^{3N}$$

The density of states is

$$D(N,E) = \frac{\partial\Omega(N,E)}{\partial E} = (\frac{4}{\omega^2})^{3N/2}\frac{1}{N!}\frac{1}{h^{3N}}\frac{\pi^{3N}}{\Gamma(3N+1)}3N(E^{3N}\frac{1}{E})$$

The number of states between E and $E + \delta E$

$$W(N,E,\delta E) = D(N,E)\delta E = (\frac{4}{\omega^2})^{3N/2}\frac{1}{h^{3N}}\frac{\pi^{3N}}{\Gamma(3N+1)}3N(E^{3N})\frac{\delta E}{E}$$

The entropy S is

$$
\begin{aligned}
S &= k_B \ln W(N, E, \delta E) \\
&= k_B \{3N \ln E - 3N \ln h + 3N \ln \pi + \frac{3N}{2} \ln(\frac{4}{\omega^2}) \\
&\quad - \ln \Gamma(3N+1) + \ln(3N) + \ln\left(\frac{\delta E}{E}\right)\} \\
&= k_B \{3N \ln E - 3N \ln h + 3N \ln \pi + \frac{3N}{2} \ln(\frac{4}{\omega^2}) \\
&\quad - 3N \ln(3N) + 3N + \ln(3N) + \ln\left(\frac{\delta E}{E}\right)\} \\
&= k_B N[3 \ln \frac{E}{N} - \frac{3}{2} \ln h^2 + \frac{3}{2} \ln \pi^2 + \frac{3}{2} \ln(\frac{4}{\omega^2}) \\
&\quad - \frac{3}{2} \ln 3^2 + 3 + \frac{1}{N} \ln(3N) + \frac{1}{N} \ln\left(\frac{\delta E}{E}\right)]
\end{aligned}
$$

where

$$
\ln \Gamma\left(\frac{3N}{2}+1\right) \approx \ln\left(\frac{3N}{2}\right)! = \frac{3N}{2}(\ln \frac{3N}{2} - 1)
$$

In the limit of large *N*, we pick up only the terms which is proportional to *N*. The entropy *S* can be written as

$$
S = k_B N\{3 \ln \frac{E}{N} + \frac{3}{2} \ln(\frac{4\pi^2}{9h^2\omega^2}) + 3\}
$$

From the relation

$$
\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = 3Nk_B \frac{1}{E}
$$

we have

$$
E = 3Nk_B T = \frac{3}{2} Nk_B T + \frac{3}{2} Nk_B T
$$

We note that the energy contribution from the kinetic energy is $3Nk_B T/2$, while the energy contribution from the potential energy is $3Nk_B T/2$; energy partition relation.

5. Another method: classical simple harmonics

We consider a one-dimensional simple harmonics with mass *m* and angular frequency ω,

$$\varepsilon_1 = \frac{1}{2m} p_1^2 + \frac{1}{2} m\omega^2 q_1^2$$

We introduce new variables

$$P_1 = \frac{1}{\sqrt{2m}} p_1, \qquad Q_1 = \sqrt{\frac{m\omega^2}{2}} q_1$$

So we have

$$\varepsilon_1 = P_1^2 + Q_1^2$$

which means a circle with radius $\sqrt{\varepsilon_1}$. Note that

$$dq_1 dp_1 = \frac{\partial(q_1, p_1)}{\partial(Q_1, P_1)} dQ_1 dP_1$$

with the Jacobian determinant

$$\frac{\partial(q_1, p_1)}{\partial(Q_1, P_1)} = \begin{vmatrix} \frac{\partial q_1}{\partial Q_1} & \frac{\partial q_1}{\partial P_1} \\ \frac{\partial p_1}{\partial Q_1} & \frac{\partial p_1}{\partial P_1} \end{vmatrix} = \begin{vmatrix} \sqrt{\frac{2}{m\omega^2}} & 0 \\ 0 & \sqrt{2m} \end{vmatrix} = \frac{2}{\omega}$$

We now consider the *f* simple harmonics with the same angular frequency ω. The total number of states for the energy of the system between 0 and *E*

$$\begin{aligned} \Omega(f, E) &= \frac{1}{h^f} \int dq_1 dp_1 \int dq_2 dp_2 \cdots \int dq_f dp_f \theta(E - \varepsilon_1 - \varepsilon_2 ... - \varepsilon_n) \\ &= \frac{1}{h^f} (\frac{2}{\omega})^f \int dQ_1 dP_1 \int dQ_2 dP_2 \cdots \int dQ_f dP_f \theta(E - \varepsilon_1 - \varepsilon_2 ... - \varepsilon_n) \\ &= \frac{1}{h^f} (\frac{2}{\omega})^f \pi^f \int d\varepsilon_1 \int d\varepsilon_2 \cdots \int d\varepsilon_f \theta(E - \varepsilon_1 - \varepsilon_2 ... - \varepsilon_n) \end{aligned}$$

where $\theta(x) = 1$ for $x>0$, and 0 otherwise.

$$dQ_1 dP_1 = 2\pi r_1 dr_1 = 2\pi\sqrt{\varepsilon_1}\frac{d\varepsilon_1}{2\sqrt{\varepsilon_1}} = \pi d\varepsilon_1$$

Note that

$$P_1^2 + Q_1^{\ 2} = r_1^{\ 2} = \varepsilon_1$$

$$r_1 = \sqrt{\varepsilon_1}\,, \qquad dr_1 = \frac{d\varepsilon_1}{2\sqrt{\varepsilon_1}}$$

Using the formula (see the note below), we get

$$\Omega(f,E) = \frac{1}{h^f}(\frac{2}{\omega})^f \pi^f \frac{E^f}{f!} = \frac{1}{f!}(\frac{2\pi E}{h\omega})^f = \frac{1}{f!}(\frac{2\pi E}{2\pi\hbar\omega})^f = \frac{1}{f!}(\frac{E}{\hbar\omega})^f$$

The density of states is

$$D(f,E) = \frac{\partial\Omega(f,E)}{\partial E} = \frac{1}{(f-1)!E}(\frac{E}{\hbar\omega})^f$$

The number of states between E and $E+\delta E$

$$W(f,E,\delta E) = D(f,E)\delta E = \frac{1}{(f-1)!}(\frac{E}{\hbar\omega})^f \frac{\delta E}{E} \approx \frac{1}{f!}(\frac{E}{\hbar\omega})^f \frac{\delta E}{E}$$

The entropy S is

$$
\begin{aligned}
S &= k_B \ln W(f, E, \delta E) \\
&= k_B [f \ln\left(\frac{E}{\hbar\omega}\right) - \ln E - \ln f!] \\
&\approx k_B [f \ln\left(\frac{E}{\hbar\omega}\right) - \ln\frac{\delta E}{E} - f \ln f + f] \\
&= k_B [f \ln\left(\frac{E}{\hbar\omega f}\right) - \ln\frac{\delta E}{E} + f] \\
&\approx k_B f [\ln\left(\frac{E}{\hbar\omega f}\right) - \ln\frac{\delta E}{E} + 1]
\end{aligned}
$$

in the limit of large *f*. Using the relation

$$
\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right) = \frac{k_B f}{E}
$$

or

$$
E = f k_B T = \frac{1}{2} f k_B T + \frac{1}{2} f k_B T
$$

We note that the energy contribution from the kinetic energy is $f k_B T / 2$, while the energy contribution from the potential energy is $f k_B T / 2$; energy partition relation.

We note that

$$
\begin{aligned}
\frac{\Omega(f, E-\varepsilon)}{\Omega(f, E)} &= \frac{\frac{1}{f!}(\frac{E-\varepsilon}{\hbar\omega})^f}{\frac{1}{f!}(\frac{E}{\hbar\omega})^f} \\
&= (\frac{E-\varepsilon}{E})^f \\
&= (1 - \frac{\varepsilon}{E})^f \\
&= (1 - \frac{\beta\varepsilon}{f})^f
\end{aligned}
$$

In the limit of $f \to \infty$, we have

$$\frac{\Omega(f,E-\varepsilon)}{\Omega(f,E)} = e^{-\beta\varepsilon}$$

((**Note**))

We show the proof of the formula.

$$\int d\varepsilon_1 \int d\varepsilon_2 \cdots \int d\varepsilon_f \theta(E-\varepsilon_1-\varepsilon_2 ... -\varepsilon_n) = \frac{1}{f!}E^f$$

First we calculate the simple case ($f = 2$)

$$\begin{aligned}\int_0^\infty d\varepsilon_1 \int_0^\infty d\varepsilon_2 \theta(E-\varepsilon_1-\varepsilon_2) &= \int_0^E d\varepsilon_1 \theta(E-\varepsilon_1) \int_0^{E-\varepsilon_1} d\varepsilon_2 \\ &= \int_0^E d\varepsilon_1 (E-\varepsilon_1)\theta(E-\varepsilon_1) \\ &= \frac{1}{2!}E^2\end{aligned}$$

$$\begin{aligned}\int_0^\infty d\varepsilon_1 \int_0^\infty d\varepsilon_2 \int_0^\infty d\varepsilon_3 \theta(E-\varepsilon_1-\varepsilon_2-\varepsilon_2) &= \int_0^\infty d\varepsilon_1 \int_0^\infty d\varepsilon_2 \theta(E-\varepsilon_1-\varepsilon_2) \int_0^{E-\varepsilon_1-\varepsilon_2} d\varepsilon_3 \\ &= \int_0^\infty d\varepsilon_1 \theta(E-\varepsilon_1) \int_0^{E-\varepsilon_1} d\varepsilon_2 (E-\varepsilon_1-\varepsilon_2)\theta(E-\varepsilon_1-\varepsilon_2) \\ &= \int_0^\infty d\varepsilon_1 \theta(E-\varepsilon_1)\frac{1}{2}(E-\varepsilon_1)^2 \\ &= \int_0^E d\varepsilon_1 \frac{1}{2}(E-\varepsilon_1)^2 \\ &= \frac{1}{3!}E^3\end{aligned}$$

((**Mathematica**))

```
Clear["Global`*"]; f1 = UnitStep[E1 - x1 - x2];
Integrate[Integrate[f1, {x2, 0, ∞}], {x1, 0, ∞}] //
 Simplify
```

$\frac{1}{2}$ E1^2 UnitStep[E1]

```
f2 = UnitStep[E1 - x1 - x2 - x3];

Integrate[Integrate[Integrate[f2, {x3, 0, ∞}],
   {x2, 0, ∞}], {x1, 0, ∞}] // Simplify
```

$\frac{1}{6}$ E1^3 UnitStep[E1]

```
f3 = UnitStep[E1 - x1 - x2 - x3 - x4];

Integrate[
  Integrate[Integrate[Integrate[f3, {x4, 0, ∞}],
    {x3, 0, ∞}], {x2, 0, ∞}], {x1, 0, ∞}] //
 Simplify
```

$\frac{1}{24}$ E1^4 UnitStep[E1]

---

6. Photon

We consider the case when the energy dispersion of photons is given by

$$\varepsilon(\boldsymbol{p}) = c|\boldsymbol{p}| = cp$$

where $\boldsymbol{p}$ is the momentum of photon, and c is the velocity of light.

The total number of states for the energy of the system between 0 and E

$$\Omega(f,.E) = \frac{1}{N!}\frac{V^N}{h^{3N}}\int d\boldsymbol{p}_1\int d\boldsymbol{p}_2......\int d\boldsymbol{p}_N\theta(E - \sum_{i=1}^{N}\varepsilon_i)$$

Note that the energy of one particle is given by

$$\varepsilon_1 = cp_1, \qquad dp_1 = \frac{1}{c} d\varepsilon_1$$

$$d\boldsymbol{p}_1 = 4\pi p_1^{\ 2} dp_1 = 4\pi (\frac{\varepsilon_1}{c})^2 \frac{1}{c} d\varepsilon_1 = \frac{4\pi}{c^3} \varepsilon_1^{\ 2} d\varepsilon_1$$

Then we have

$$\begin{aligned}\Omega(N,.E) &= \frac{1}{N!} \frac{V^N}{h^{3N}} \left(\frac{4\pi}{c^3}\right)^N \int \varepsilon_1^{\ 2} d\varepsilon_1 \int \varepsilon_2^{\ 2} d\varepsilon_2 ......\int \varepsilon_N^{\ 2} d\varepsilon_N \theta(E - \varepsilon_1 - \varepsilon_2 - ... - \varepsilon_N) \\ &= \frac{1}{N!} \frac{V^N}{h^{3N}} \left(\frac{4\pi}{c^3}\right)^N \frac{2^N E^{3N}}{(3N)!} \\ &= \frac{1}{N!} \frac{(8\pi V)^N}{(3N)!} \left(\frac{E}{hc}\right)^{3N}\end{aligned}$$

where we use the formula

$$\int \varepsilon_1^{\ 2} d\varepsilon_1 \int \varepsilon_2^{\ 2} d\varepsilon_2 ......\int \varepsilon_N^{\ 2} d\varepsilon_N \theta(E - \varepsilon_1 - \varepsilon_2 - ... - \varepsilon_N) = \frac{[\Gamma(3)]^N E^{3N}}{\Gamma(3N+1)} = \frac{2^N E^{3N}}{(3N)!}$$

The density of states is

$$\begin{aligned}D(N,E) &= \frac{\partial \Omega(N,E)}{\partial E} \\ &= \frac{1}{N!} \frac{(8\pi V)^N}{(3N-1)!} \left(\frac{E}{hc}\right)^{3N} \frac{1}{E}\end{aligned}$$

The number of states between E and $E + \delta E$

$$W(N,E,\delta E) = D(N,E)\delta E = \frac{1}{N!} \frac{(8\pi V)^N}{(3N-1)!} \left(\frac{E}{hc}\right)^{3N} \frac{\delta E}{E}$$

The entropy S is

$$S = k_B \ln W(N, E, \delta E)$$
$$= k_B\{-\ln N! + N\ln(8\pi V) - \ln(3N-1)! + 3N\ln\left(\frac{E}{hc}\right) + \ln(\frac{\delta E}{E})\}$$
$$= k_B\{-N\ln N + N + N\ln(8\pi V) - (3N-1)\ln(3N-1)$$
$$+ 3N - 1 + 3N\ln\left(\frac{E}{hc}\right) + \ln(\frac{\delta E}{E})\}$$
$$= k_B N\{-\ln N + 1 + \ln(8\pi V) - (3 - \frac{1}{N})\ln(3N-1)$$
$$+ 3 - \frac{1}{N} + 3\ln\left(\frac{E}{hc}\right) + \frac{1}{N}\ln(\frac{\delta E}{E})\}$$
$$\approx k_B N[3\ln\left(\frac{E}{3Nhc}\right) + \ln(8\pi\frac{V}{N}) + 4]$$

or

$$S = 3k_B N\ln E + k_B N\ln(V) + \text{const}$$

Thus we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right) = \frac{3k_B N}{E}$$

The energy E is obtained as

$$E = 3Nk_B T$$

The Helmholtz free energy:

$$F = E - ST = 3Nk_B T - Nk_B T\{3\ln\left(\frac{k_B T}{hc}\right) + \ln(8\pi\frac{V}{N}) + 4\}$$

Since $dF = -PdV - SdT$, the pressure is obtained as

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = Nk_B T\frac{1}{V}$$

or

$$PV = Nk_BT = \frac{1}{3}E$$

which is different from the expression from the classical free particles.

APPENDIX-I Volume of *n*-dimensional supersphere

An n-dimensional hypersphere of radius R consists of the locus of points such that the distance from the origin is less than or equal to R. A point in an n-dimensional Euclidean space is designated by $(x_1, x_2, ..., x_n)$. In equation form, the hypersphere corresponds to the set of points such that

$$x_1^{\ 2} + x_2^{\ 2} + ... + x_n^{\ 2} = R^2 \qquad (1)$$

To compute the volume of this hypersphere, we simply integrate the infinitesimal volume element

$$dV = dx_1 dx_2 ... dx_n$$

over the region of n-dimensional (D) space indicated by Eq.(1). We need to calculate the volume

$$dV = dx_1 dx_2 ... dx_n$$

over the region of n-dimensional space indicated. We wish to compute this volume $V_n(R)$. Explicitly,

$$V_n(R) = \int ... \int dx_1 dx_2 ... dx_n \theta(R^2 - x_1^{\ 2} - x_2^{\ 2} - ... - x_n^{\ 2}) = C_n R^n, \qquad (2)$$

The factor of R^n is a consequence of dimensional analysis. The surface "area" of the n-dimensional hypersphere defined by eq. (1) will be denoted by

$$S_{n-1}(R).$$

The surface of the hypersphere corresponds to the locus of points such that

$$x_1^{\ 2} + x_2^{\ 2} + ... + x_n^{\ 2} = R^2.$$

We can construct the volume $V_n(R)$ by adding infinitely thin spherical shells of radius . $0 \le r \le R$. In equation form, this reads:

$$V_n(R) = \int_0^R S_{n-1}(r)dr\,. \tag{3}$$

It follows from the fundamental theorem of calculus that

$$S_{n-1}(R) = \frac{dV_n(R)}{dR} = nC_n R^{n-1}, \tag{4}$$

where we have used eq. (2). Thus, the only remaining task is to compute C_n. In order to obtain a better intuition on the meaning of C_n, let us equate the two expressions we have for $V_n(R)$, namely eq. (2) and eq. (3). In the latter, $S_{n-1}(r)$ is
determined by eq. (4). Thus,

$$\begin{aligned} V_n(R) &= \int \ldots \int dx_1 dx_2 \ldots dx_n \theta(R^2 - x_1{}^2 - x_2{}^2 - \ldots - x_n{}^2) \\ &= nC_n \int_0^R r^{n-1} dr \end{aligned} \tag{5}$$

In *n*-dimensions, using the relation

$$dx_1 dx_2 \ldots dx_n = r^{n-1} dr d\Omega_{n-1}$$

we get

$$V_n(R) = C_n R^n = \int \theta(R-r) r^{n-1} dr \int \ldots \int d\Omega_{n-1}$$

or

$$nC_n = \int \ldots \int d\Omega_{n-1}$$

In order to get the value of C_n, we consider a special function

$$f(x_1, x_2, \ldots, x_n) = \exp(-x_1{}^2 - x_2{}^2 - \ldots - x_n{}^2) = \exp(-r^2)$$

Then we have

$$\int ... \int dx_1 dx_2 ... dx_n \exp(-x_1{}^2 - x_2{}^2 - ... - x_n{}^2) = \int e^{-r^2} r^{n-1} dr \int ... \int d\Omega_{n-1}$$

Using the integral

$$\int dx e^{-x^2} = \sqrt{\pi}\,, \qquad \int e^{-x^2} x^{n-1} dx = \frac{1}{2}\Gamma\left(\frac{n}{2}\right)$$

we have

$$\pi^{n/2} = C_n \frac{n}{2}\Gamma\left(\frac{n}{2}\right) = C_n \Gamma(1+\frac{n}{2})$$

where we use the property of the Gamma function

$$x\Gamma(x) = \Gamma(x+1)$$

The final result is

$$\pi^{n/2} = C_n \frac{n}{2}\Gamma\left(\frac{n}{2}\right) = C_n \Gamma(1+\frac{n}{2})$$

or

$$C_n = \frac{\pi^{n/2}}{\Gamma(1+\frac{n}{2})}$$

$$V_n(R) = \frac{\pi^{n/2} R^n}{\Gamma(1+\frac{n}{2})}$$

$$S_{n-1}(R) = \frac{n\pi^{n/2} R^{n-1}}{\Gamma(1+\frac{n}{2})}, \qquad S_n(R) = \frac{2\pi^{(n+1)/2} R^n}{\Gamma(\frac{n+1}{2})}$$

APPENDIX II Formula

$$\int\sqrt{\varepsilon_1}d\varepsilon_1\int\sqrt{\varepsilon_2}d\varepsilon_2......\int\sqrt{\varepsilon_N}d\varepsilon_N\theta(E-\varepsilon_1-\varepsilon_2-...-\varepsilon_N)=\frac{[\Gamma(\frac{3}{2})]^N}{\Gamma(\frac{3N}{2}+1)}E^{\frac{3N}{2}}$$

This formula can be derived using the Mathematica.

((**Mathematica**))

```
Clear["Global`*"];

f1 = √x1 √x2 ;
Integrate[Integrate[f1, {x2, 0, E1 - x1}],
  {x1, 0, E1}] // Simplify
```

$$\frac{E1^3\,\pi}{24}$$

```
f2 = √x1 √x2 √x3 ;
Integrate[
  Integrate[Integrate[f2, {x3, 0, E1 - x1 - x2}],
   {x2, 0, E1 - x1}], {x1, 0, E1}] // Simplify
```

$$\frac{4}{945}\,E1^{9/2}\,\pi$$

```
f3 = √x1 √x2 √x3 √x4 ;
Integrate[
  Integrate[
   Integrate[Integrate[f3,
     {x4, 0, E1 - x1 - x2 - x3}], {x3, 0, E1 - x1 - x2}],
   {x2, 0, E1 - x1}], {x1, 0, E1}] // Simplify
```

$$\frac{E1^6\,\pi^2}{11\,520}$$