Chapter 7: Part A
Simple applications of statistical mechanics

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General method of approach
7.1 Partition function and their properties

- **system in contact with a heat reservoir at a specified T**

- **Isolated system has fixed energy and mean values are related to its T**

Partition function:

$$Z = \sum_r e^{-\beta E_r}$$

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$$đW = \frac{1}{\beta Z}\frac{\partial Z}{\partial x}dx = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}dx$$

$$S = k(\ln Z + \beta \bar{E})$$

$$F = \bar{E} - TS = -kT \ln Z$$

Unrestricted sum

General method of approach

7.1 Partition function and their properties

- If one know the particles and interactions, it is possible to find the quantum states and evaluate the sum for Z

- But it is a formidable task to do for a liquid where molecules interact with each other strongly

General method of approach
7.1 Partition function and their properties

In classical approximation

$$E(q_1, \ldots, q_f, p_1, \ldots, p_f)$$

$$\boxed{Z = \int \cdots \int e^{-\beta E(q_1, \ldots, p_f)} \frac{dq_1 \cdots dp_f}{h_0^f}}$$

volume of cells in phase space

a, if energy changes by a constant ε_0

$$E_r^* = E_r + \epsilon_0.$$

$$\boxed{\begin{gathered} Z^* = \sum_r e^{-\beta(E_r+\epsilon_0)} = e^{-\beta\epsilon_0} \sum_r e^{-\beta E_r} = e^{-\beta\epsilon_0} Z \\ \ln Z^* = \ln Z - \beta\epsilon_0 \end{gathered}}$$

General method of approach

7.1 Partition function and their properties

In classical approximation

$$Z \equiv \sum_r e^{-\beta E_r}$$

$$E(q_1, \ldots, q_f, p_1, \ldots, p_f)$$

$$q_1 \in [q_1, q_1 + \delta q_1]; \;\; p_1 \in [p_1, p_1 + \delta p_1]$$

$$\delta q_1 \cdot \delta p_1 = h_0$$

Every Sum has the number of $dq_1 dp_1 / \delta q_1 \delta p_1 = dq_1 dp_1 / h_0$

General method of approach
7.1 Partition function and their properties

In classical approximation

$$E_r^* = E_r + \epsilon_0.$$

$$Z^* = \sum_r e^{-\beta(E_r+\epsilon_0)} = e^{-\beta\epsilon_0}\sum_r e^{-\beta E_r} = e^{-\beta\epsilon_0}Z$$

$$\ln Z^* = \ln Z - \beta\epsilon_0$$

$$\bar{E}^* = -\frac{\partial \ln Z^*}{\partial\beta} = -\frac{\partial \ln Z}{\partial\beta} + \epsilon_0 = \bar{E} + \epsilon_0$$

$$S^* = k(\ln Z^* + \beta\bar{E}^*) = k(\ln Z + \beta\bar{E}) = S$$ unchanged!

All expressions for generalized forces unchanged!
Since they only involves lnZ

General method of approach

7.1 Partition function and their properties

In classical approximation

b, subsystems A interacts with A' weakly

A in r and A' in s states

$$E_{rs} = E_r' + E_s''$$

$$Z = \sum_{r,s} e^{-\beta(E_r'+E_s'')} = \sum_{r,s} e^{-\beta E_r'} e^{-\beta E_s''} = \left(\sum_r e^{-\beta E_r'}\right)\left(\sum_s e^{-\beta E_s''}\right)$$

$$Z = Z'Z''$$

$$\ln Z = \ln Z' + \ln Z''$$

General method of approach

7.2 calculation of thermodynamic quantities

A gas of identical monatomic molecules of mass m in volume V. Position vector—r; Momentum p.

$$\boxed{E=\sum_{i=1}^{N}\frac{p_i^2}{2m}+U(r_1,r_2,\cdots,r_N)}$$

Kinetic energy Potential energy

$U\rightarrow 0$ ⇨ an ideal gas.

In the following, discuss it classically

General method of approach

7.2 calculation of thermodynamic quantities

Partition function:

$$Z' = \int \exp\left\{-\beta\left[\frac{1}{2m}(p_1^2 + \cdots + p_N^2) + U(\mathbf{r}_1, \ldots, \mathbf{r}_N)\right]\right\} \frac{d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N \, d^3\mathbf{p}_1 \cdots d^3\mathbf{p}_N}{h_0^{3N}}$$

$$Z' = \frac{1}{h_0^{3N}} \int e^{-(\beta/2m)p_1^2} d^3\mathbf{p}_1 \cdots \int e^{-(\beta/2m)p_N^2} d^3\mathbf{p}_N \int e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)} d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N$$

$$\boxed{\int_{-\infty}^{\infty} e^{-(\beta/2m)p^2} d^3\mathbf{p}}$$

General method of approach
7.2 calculation of thermodynamic quantities

Partition function:

$U(r_1,\ldots,r_N) \neq 0$

It is difficult to carry out the integral over $r_1, \ldots, r_N$

$U=0$

$$\int d^3\mathbf{r}_1 \cdots d^3\mathbf{r}_N = \int d^3\mathbf{r}_1 \int d^3\mathbf{r}_2 \cdots \int d^3\mathbf{r}_N = V^N$$

$$Z' = \zeta^N$$
$$\ln Z' = N \ln \zeta$$

$$\zeta \equiv \frac{V}{h_0^3} \int_{-\infty}^{\infty} e^{-(\beta/2m)p^2} \, d^3\mathbf{p}$$

Partition function for a single molecule

General method of approach
7.2 calculation of thermodynamic quantities

Partition function:

$$\zeta \equiv \frac{V}{h_0^3} \int_{-\infty}^{\infty} e^{-(\beta/2m)p^2}\, d^3\mathbf{p}$$

$$\int_{-\infty}^{\infty} e^{-(\beta/2m)p^2}\, d^3\mathbf{p} = \iiint_{-\infty}^{\infty} e^{-(\beta/2m)(p_x^2+p_y^2+p_z^2)}\, dp_x\, dp_y\, dp_z$$

$$= \int_{-\infty}^{\infty} e^{-(\beta/2m)p_x^2}\, dp_x \int_{-\infty}^{\infty} e^{-(\beta/2m)p_y^2}\, dp_y \int_{-\infty}^{\infty} e^{-(\beta/2m)p_z^2}\, dp_z$$

$$= \left(\sqrt{\frac{\pi 2m}{\beta}}\right)^3 \quad \text{by } (A \cdot 4 \cdot 2)$$

$$\zeta = V\left(\frac{2\pi m}{h_0^2 \beta}\right)^{3/2}$$

$$\ln Z' = N \ln \zeta$$

General method of approach

$$\ln Z' = N \ln \xi$$

7.2 calculation of thermodynamic quantities

Partition function:

$$\boxed{\ln Z' = N\left[\ln V - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi m}{h_0^2}\right)\right]}$$

$$\bar{p} = \frac{1}{\beta}\frac{\partial \ln Z'}{\partial V} = \frac{1}{\beta}\frac{N}{V}$$

$$\bar{p}V = NkT$$

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln Z' = \frac{3}{2}\frac{N}{\beta} = N\bar{\epsilon}$$

$$\boxed{\bar{\epsilon} = \frac{3}{2}kT}$$

$$C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \frac{3}{2}Nk = \frac{3}{2}\nu N_0 k$$

$$c_V = \frac{3}{2}R$$

General method of approach
7.2 calculation of thermodynamic quantities

Entropy from partition function:

$$S = k(\ln Z' + \beta \bar{E}) = Nk\left[\ln V - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi m}{h_0^2}\right) + \frac{3}{2}\right]$$

$$S = Nk[\ln V + \tfrac{3}{2}\ln T + \sigma]$$

$$\sigma \equiv \frac{3}{2}\ln\left(\frac{2\pi m k}{h_0^2}\right) + \frac{3}{2}$$

Not correct !!! ???

General method of approach
7.3 Gibbs paradox

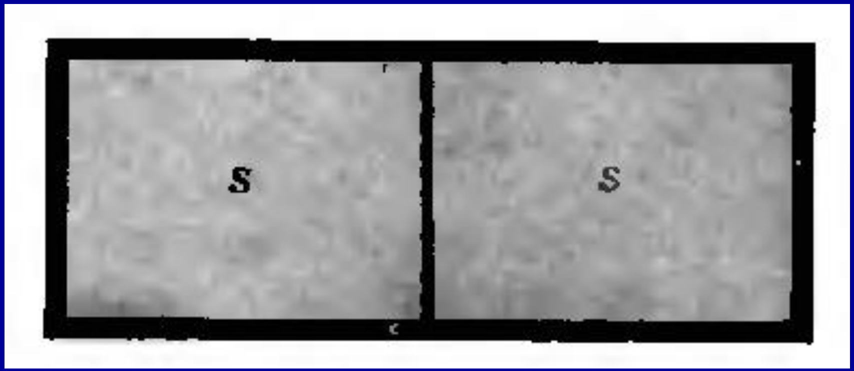
$$S = Nk\left[\ln V + \frac{3}{2}\ln T + \sigma\right]$$

$$\sigma \equiv \frac{3}{2}\ln\left(\frac{2\pi mk}{h_0^2}\right) + \frac{3}{2}$$

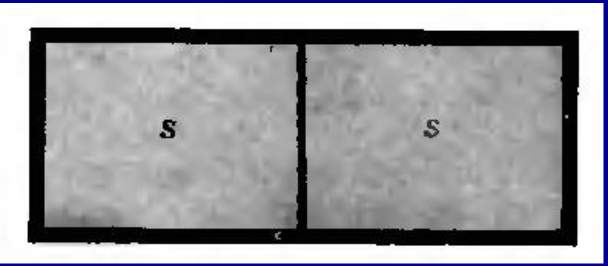
1, T->0, S -> - infinity ; not valid at low temperature

2, S does not behaves as an extensive quantity

$$S = S' + S''$$



General method of approach
7.3 Gibbs paradox



Equal parts

$$S' = S'' = N'k[\ln V' + \tfrac{3}{2}\ln T + \sigma]$$

2 parts

$$S = 2N'k[\ln (2V') + \tfrac{3}{2}\ln T + \sigma]$$

as 1

$$\boxed{S - 2S' = 2N'k\ln(2V') - 2N'k\ln V' = 2N'k\ln 2}$$

Why ?????

General method of approach

7.3 Gibbs paradox

In above discussion, the particles are treated as distinguishable .

If treat particles indistinguishable, then

$$Z = \frac{Z'}{N!} = \frac{\zeta^N}{N!}$$

$$\ln Z = N \ln \zeta - \ln N!$$
$$\ln Z = N \ln \zeta - N \ln N + N$$

$$S = kN[\ln V + \tfrac{3}{2} \ln T + \sigma] + k(-N \ln N + N)$$

$$S = kN\left[\ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma_0\right]$$

$$\sigma_0 \equiv \sigma + 1$$

General method of approach
7.4 Validity of classical approximation

Heisenberg uncertainty principle

$$\boxed{\Delta q\, \Delta p \gtrsim \hbar}$$

a classical description

$$\bar{R}\bar{p} \gg \hbar$$

$$\boxed{\bar{R} \gg \bar{\lambda}}$$

$$\bar{\lambda} = 2\pi \frac{\hbar}{\bar{p}} = \frac{\hbar}{\bar{p}}$$

Mean inter-molecule distance

de Broglie wavelength

General method of approach

7.4 Validity of classical approximation

$\bar{R}$

$$\bar{R}^3 N = V$$

$$\bar{R} = \left(\frac{V}{N}\right)^{1/3}$$

$\bar{p}$

$\bar{\lambda}$

$$\frac{1}{2m}\bar{p}^2 \approx \bar{\epsilon} = \frac{3}{2}kT$$

$$\bar{p} \approx \sqrt{3mkT}$$

$$\bar{\lambda} \approx \frac{h}{\sqrt{3mkT}}$$

Classic condition

$$\left(\frac{V}{N}\right)^{1/3} \gg \frac{h}{\sqrt{3mkT}}$$

<u>Requirements:</u>

Dilute;

High T;

m is not too small

General method of approach
7.4 Validity of classical approximation

Numerical estimates

<u>He</u> gas at room temperature and pressure

mean pressure $\bar{P} = 760$ mm Hg $\approx 10^6$ dynes/cm^2

temperature $T \approx 300°K$; hence $kT \approx 4 \times 10^{-14}$ ergs

molecular mass $m = \dfrac{4}{6 \times 10^{23}} \approx 7 \times 10^{-24}$ grams

$$\frac{N}{V} = \frac{\bar{P}}{kT} = 2.5 \times 10^{19} \text{ molecules/cm}^3$$

$\bar{R} \approx 34 \times 10^{-8}$ cm by (7·4·5)

$\bar{\lambda} \approx 0.6 \times 10^{-8}$ cm by (7·4·6)

$$\bar{R} \gg \bar{\lambda}$$

General method of approach
7.4 Validity of classical approximation

Numerical estimates

Electron in conductor: 7000 times less than He in mass

$$\bar{\lambda} \approx (0.6 \times 10^{-8})\sqrt{7000} \approx 60 \times 10^{-8} \text{ cm}$$

$$\bar{R} \approx 2 \times 10^{-8} \text{ cm}$$

Electron in metal form a very dense gas

The equi-partition theorem
7.5 Proof of the theorem

A system of f coordinates q_k and f momentum p_k

$$E = E(q_1, \ldots, q_f, p_1, \ldots, p_f)$$

Splits additively into the form

$$\begin{cases} E = \epsilon_i(p_i) + E'(q_1, \ldots, p_f) \\ \epsilon_i(p_i) = bp_i^2 \end{cases}$$

$$\Rightarrow \quad \bar{\epsilon}_i = \frac{\int_{-\infty}^{\infty} e^{-\beta E(q_1, \ldots, p_f)} \epsilon_i \, dq_1 \cdots dp_f}{\int_{-\infty}^{\infty} e^{-\beta E(q_1, \ldots, p_f)} \, dq_1 \cdots dp_f}$$

The equi-partition theorem

7.5 Proof of the theorem

$$\bar{\epsilon}_i = \frac{\int_{-\infty}^{\infty} e^{-\beta E(q_1,\ldots,p_f)}\epsilon_i \, dq_1 \cdots dp_f}{\int_{-\infty}^{\infty} e^{-\beta E(q_1,\ldots,p_f)} \, dq_1 \cdots dp_f}$$

$$\bar{\epsilon}_i = \frac{\int e^{-\beta(\epsilon_i+E')}\epsilon_i \, dq_1 \cdots dp_f}{\int e^{-\beta(\epsilon_i+E')} \, dq_1 \cdots dp_f}$$

$$= \frac{\int e^{-\beta\epsilon_i}\epsilon_i \, dp_i \int e^{-\beta E'} \, dq_1 \cdots dp_f}{\int e^{-\beta\epsilon_i} \, dp_i \int e^{-\beta E'} \, dq_1 \cdots dp_f}$$

$$\bar{\epsilon}_i = \frac{\int e^{-\beta\epsilon_i}\epsilon_i \, dp_i}{\int e^{-\beta\epsilon_i} \, dp_i}$$

$$\bar{\epsilon}_i = \frac{-\frac{\partial}{\partial\beta}\left(\int e^{-\beta\epsilon_i} \, dp_i\right)}{\int e^{-\beta\epsilon_i} \, dp_i}$$

$$\bar{\epsilon}_i = -\frac{\partial}{\partial\beta}\ln\left(\int_{-\infty}^{\infty} e^{-\beta\epsilon_i} \, dp_i\right)$$

The equi-partition theorem
7.5 Proof of the theorem

$$\bar{\epsilon}_i = \frac{-\frac{\partial}{\partial\beta}\left(\int e^{-\beta\epsilon_i}\,dp_i\right)}{\int e^{-\beta\epsilon_i}\,dp_i}$$

$$\bar{\epsilon}_i = -\frac{\partial}{\partial\beta}\ln\left(\int_{-\infty}^{\infty} e^{-\beta\epsilon_i}\,dp_i\right)$$

$$y \equiv \beta^{\frac{1}{2}} p_i.$$

$$\int_{-\infty}^{\infty} e^{-\beta\epsilon_i}\,dp_i = \int_{-\infty}^{\infty} e^{-\beta b p_i^2}\,dp_i = \beta^{-\frac{1}{2}}\int_{-\infty}^{\infty} e^{-by^2}\,dy$$

$$\ln\int_{-\infty}^{\infty} e^{-\beta\epsilon_i}\,dp_i = -\tfrac{1}{2}\ln\beta + \ln\int_{-\infty}^{\infty} e^{-by^2}\,dy$$

unrelated to β

$$\bar{\epsilon}_i = -\frac{\partial}{\partial\beta}\left(-\frac{1}{2}\ln\beta\right) = \frac{1}{2\beta}$$

$$\bar{\epsilon}_i = \tfrac{1}{2}kT$$

equi-partition theorem

The equi-partition theorem

7.6 Simple applications

Mean kinetic energy of a molecule in a gas

$$K = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$$

$$\bar{K} = \tfrac{3}{2}kT$$

Ideal gas

$$\bar{E} = N_a(\tfrac{3}{2}kT) = \tfrac{3}{2}RT$$

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \frac{3}{2}R$$

The equi-partition theorem

7.6 Simple applications

Brownian motion

$$\bar{v}_x = 0$$

$$\overline{\tfrac{1}{2} m {v_x}^2} = \tfrac{1}{2} kT \qquad \text{or} \qquad \overline{{v_x}^2} = \frac{kT}{m}$$

Large mass, less strong Brownian motion

The equi-partition theorem

7.6 Simple applications

Harmonic oscillator (1D)

$$E = \frac{p^2}{2m} + \frac{1}{2}\kappa_0 x^2$$

$$\text{mean kinetic energy} = \frac{1}{2m}\overline{p^2} = \tfrac{1}{2}kT$$

$$\text{mean potential energy} = \tfrac{1}{2}\kappa_0\overline{x^2} = \tfrac{1}{2}kT$$

$$\bar{E} = \tfrac{1}{2}kT + \tfrac{1}{2}kT = kT$$

Quantum theory

$$E_n = (n + \tfrac{1}{2})\hbar\omega$$

$$n = 0, 1, 2, 3, \ldots$$

$$\omega = \sqrt{\frac{\kappa_0}{m}}$$

The equi-partition theorem

7.6 Simple applications

Harmonic oscillator

$$Z \equiv \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\beta\hbar\omega}$$

$$\bar{E} = \frac{\sum_{n=0}^{\infty} e^{-\beta E_n} E_n}{\sum_{n=0}^{\infty} e^{-\beta E_n}} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z$$

$$Z = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = e^{-\frac{1}{2}\beta\hbar\omega}(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots)$$

$$Z = e^{-\frac{1}{2}\beta\hbar\omega}\frac{1}{1 - e^{-\beta\hbar\omega}}$$

$$\ln Z = -\frac{1}{2}\beta\hbar\omega - \ln(1 - e^{-\beta\hbar\omega})$$

The equi-partition theorem

7.6 Simple applications

Harmonic oscillator

$$Z = e^{-\frac{1}{2}\beta\hbar\omega}\frac{1}{1-e^{-\beta\hbar\omega}}$$

$$\ln Z = -\tfrac{1}{2}\beta\hbar\omega - \ln\left(1-e^{-\beta\hbar\omega}\right)$$

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln Z = -\left(-\frac{1}{2}\hbar\omega - \frac{e^{-\beta\hbar\omega}\hbar\omega}{1-e^{-\beta\hbar\omega}}\right)$$

$$\bar{E} = \hbar\omega\left(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega}-1}\right)$$

$$\beta\hbar\omega = \frac{\hbar\omega}{kT} \ll 1$$

$$\bar{E} = \hbar\omega\left[\frac{1}{2}+\frac{1}{(1+\beta\hbar\omega+\cdots)-1}\right] \approx \hbar\omega\left[\frac{1}{2}+\frac{1}{\beta\hbar\omega}\right]$$

$$\approx \hbar\omega\left[\frac{1}{\beta\hbar\omega}\right] \qquad \text{by virtue of } (7\cdot6\cdot13)$$

$$\bar{E} = \frac{1}{\beta} = kT$$

The equi-partition theorem

7.6 Simple applications

Harmonic oscillator

$$\boxed{\beta\hbar\omega = \frac{\hbar\omega}{kT} \gg 1}$$

$$\bar{E} = \hbar\omega\left(\frac{1}{2} + e^{-\beta\hbar\omega}\right)$$

T->0, E-→ energy of ground state

Class-work

P 282 7.2

Homework

P 282   7.1,7.3-7.7