Chapter 7: Part B
Simple applications of statistical mechanics

Zhi-Jie Tan

Wuhan University

2019 spring semester

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:

$$Z = \sum_{r} e^{-\beta E_r}$$

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

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

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

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

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

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

volume of cells in phase space

a, if energy changes by a constant ε_0

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

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

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

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

$U \to 0$ ⇒ 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:

$U(r_1,\ldots,r_N) \mathrel{!=} 0$

It is difficult to carry out the integral over

$r_1, \ldots, r_N$

U=0

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

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

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

Partition function for a single molecule

General method of approach

7.2 calculation of thermodynamic quantities

Partition function:

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

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

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

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

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

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

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

General method of approach

7.2 calculation of thermodynamic quantities

Partition function:

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

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

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

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

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

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

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

General method of approach

7.2 calculation of thermodynamic quantities

Entropy from partition function:

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

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

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

Not correct !!! ???

General method of approach
7.3 Gibbs paradox

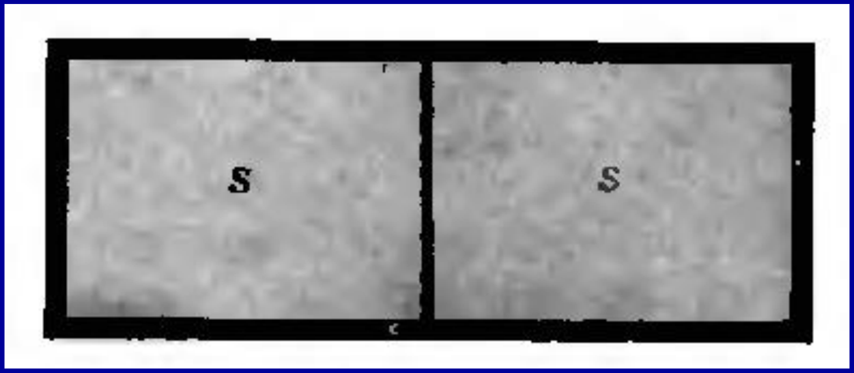
$$S = Nk\left[\ln V + \frac{3}{2}\ln T + \sigma\right]$$

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

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

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

Why ?????

General method of approach
7.3 Gibbs paradox

In above discussion, the particles are treated as distinguishable .

If treat particles indistinguishable, then

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

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

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

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

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

General method of approach
7.4 Validity of classical approximation

Heisenberg uncertainty principle

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

a classical description

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

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

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

Mean inter-molecule distance

de Broglie wavelength

General method of approach
7.4 Validity of classical approximation

$\bar{R}$

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

$\bar{p}$

$\bar{\lambda}$

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

Classic condition

Requirements:

Dilute;

High T;

m is not too small

General method of approach
7.4 Validity of classical approximation

Numerical estimates
He 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

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

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

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

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

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

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

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

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

Large mass, less strong Brownian motion

The equi-partition theorem

7.6 Simple applications

Harmonic oscillator

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

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

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

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

Quantum theory

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

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

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

The equi-partition theorem

7.6 Simple applications

Harmonic oscillator

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

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

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

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

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

The equi-partition theorem

7.6 Simple applications

Harmonic oscillator

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

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

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

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

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

expansion

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

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

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

The equi-partition theorem

7.6 Simple applications

Harmonic oscillator

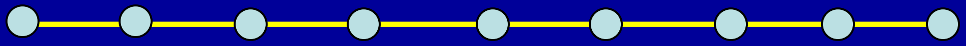
$$\boxed{\beta\hbar\omega = \frac{\hbar\omega}{kT} \gg 1}$$

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

T->0, E-→ energy of ground state $\frac{1}{2}\hbar\omega$

The equi-partition theorem
7.7 Simple applications
Specific heats of solids

Consider a solid with N_A atoms per mole;
At nonzero T,
there are lattice vibrations.



Suppose vibration is small,

$$\boxed{E = \sum_{i=1}^{3N_a} \left(\frac{p_i^2}{2m} + \frac{1}{2} \kappa_i q_i^2 \right)}$$

Kinetic energy **Potential energy**

The equi-partition theorem

7.7 Simple applications

Specific heats of solids

$$E = \sum_{i=1}^{3N_o} \left(\frac{p_i^2}{2m} + \frac{1}{2}\kappa_i q_i^2 \right)$$

If the T is high enough (room T is enough),
<u>Equi-partition theorem</u>

$$\bar{E} = 3N_o[(\tfrac{1}{2}kT) \times 2]$$
$$\bar{E} = 3N_o kT = 3RT$$

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

At very high T, all simple solids have the same Cv of 3R-----------Law of Dulong and Petit

The equi-partition theorem
7.7 Simple applications
Specific heats of solids

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

Table 7·7·1 Values of c_p (joules mole^{-1} deg^{-1}) for some solids at $T = 298°K$*

Solid	c_p	Solid	c_p
Copper	24.5	Aluminum	24.4
Silver	25.5	Tin (white)	26.4
Lead	26.4	Sulfur (rhombic)	22.4
Zinc	25.4	Carbon (diamond)	6.1

* "American Institute of Physics Handbook," 2d ed., McGraw-Hill Book Company, New York, 1963, p. 4–48.

3R=25 joules/mole deg

The equi-partition theorem

7.7 Simple applications

Specific heats of solids

Harmonic oscillator

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

However, it is not valid at lower T

In fact, Cv ------>0 as T ---->0

$$\kappa_i = m\omega^2$$

Einstein model:

Assumption: all atoms vibrate with same frequency ω

$$\bar{E} = 3N_a\hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right)$$

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial \beta}\right)_V \frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}\left(\frac{\partial \bar{E}}{\partial \beta}\right)_V$$

The equi-partition theorem

7.7 Simple applications

Specific heats of solids

$$c_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \left(\frac{\partial \bar{E}}{\partial \beta}\right)_V \frac{\partial \beta}{\partial T} = -\frac{1}{kT^2}\left(\frac{\partial \bar{E}}{\partial \beta}\right)_V$$

$$= -\frac{3N_a\hbar\omega}{kT^2}\left[-\frac{e^{\beta\hbar\omega}\hbar\omega}{(e^{\beta\hbar\omega}-1)^2}\right]$$

$$\beta\hbar\omega = \frac{\hbar\omega}{kT} \equiv \frac{\Theta_E}{T}$$

$$c_V = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)^2}$$

The equi-partition theorem

7.7 Simple applications

Specific heats of solids

$$c_V = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)^2}$$

for $T \gg \Theta_E$,

$$c_V \to 3R$$

for $T \ll \Theta_E$,

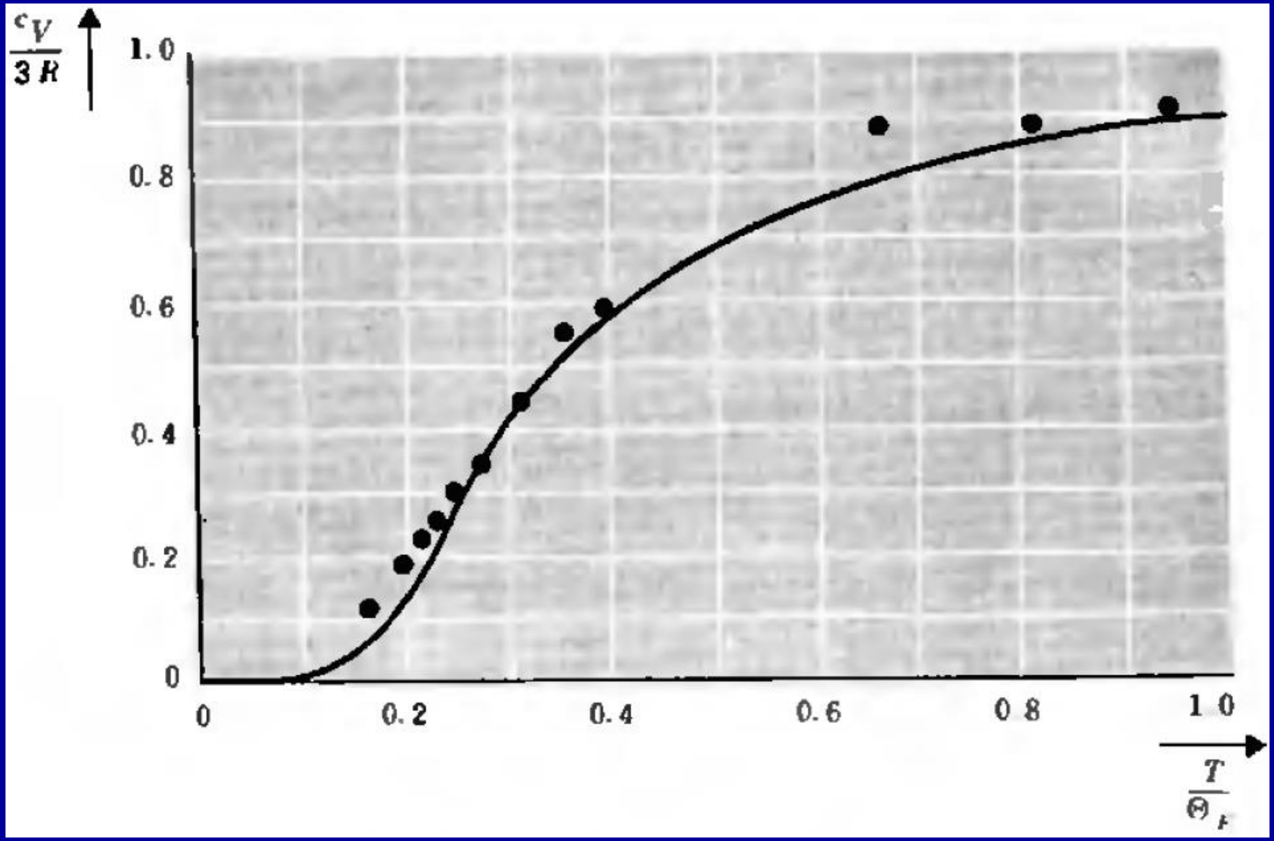
$$c_V \to 3R\left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T}$$

The equi-partition theorem

7.7 Simple applications

Specific heats of solids

$$c_V = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{\left(e^{\Theta_E/T}-1\right)^2}$$



The equi-partition theorem

7.7 Simple applications

Specific heats of solids

$$c_V \to 3R\left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T}$$

as $T \to 0$. Cv decreases to Zero exponentially

In reality, $c_V \propto T^3$ as $T \to 0$.

Reason: the model assumes that all atoms vibrate with the same frequency!!!

More accurate model was proposed by Debye!

The equi-partition theorem

7.8 Simple applications

General calculation of magnetization

Considering N non-interacting atoms at T and in external H (in z)

$$\boxed{\epsilon = -\boldsymbol{\mu} \cdot \boldsymbol{H}}$$

$$\boldsymbol{\mu} = g\mu_0 \boldsymbol{J}$$

$$\boxed{\epsilon = -g\mu_0 \boldsymbol{J} \cdot \boldsymbol{H} = -g\mu_0 H J_z}$$

$$J_z = m$$

$$m = -J, -J+1, -J+2, \ldots, J-1, J$$

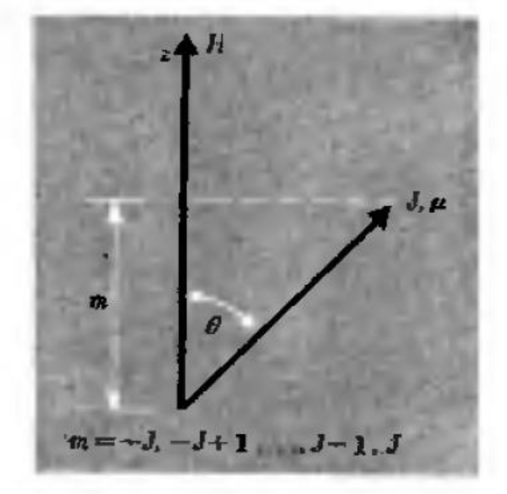
The equi-partition theorem
7.8 Simple applications
General calculation of magnetization

Considering N non-interacting atoms at T and in external H (in z)

$$\boldsymbol{\epsilon} = -\boldsymbol{\mu}\cdot\boldsymbol{H}$$

$$\boldsymbol{\mu} = g\mu_0\boldsymbol{J}$$

$$\boldsymbol{\epsilon} = -g\mu_0\boldsymbol{J}\cdot\boldsymbol{H} = -g\mu_0 H J_z$$



$$J_z = m$$

$$m = -J, -J+1, -J+2, \ldots, J-1, J$$

The equi-partition theorem

7.8 Simple applications

General calculation of magnetization

$$\epsilon_m = -g\mu_0 H m$$

$$P_m \propto e^{-\beta\epsilon_m} = e^{\beta g\mu_0 H m}$$

$$\mu_z = g\mu_0 m$$

$$\bar{\mu}_z = \frac{\sum_{m=-J}^{J} e^{\beta g\mu_0 H m}(g\mu_0 m)}{\sum_{m=-J}^{J} e^{\beta g\mu_0 H m}}$$

The equi-partition theorem

7.8 Simple applications

$$\bar{\mu}_z = \frac{\sum_{m=-J}^{J} e^{\beta g\mu_0 Hm}(g\mu_0 m)}{\sum_{m=-J}^{J} e^{\beta g\mu_0 Hm}}$$

General calculation of magnetization

$$\sum_{m=-J}^{J} e^{\beta g\mu_0 Hm}(g\mu_0 m) = \frac{1}{\beta}\frac{\partial Z_a}{\partial H}$$

$$Z_a \equiv \sum_{m=-J}^{J} e^{\beta \mu_0 Hm}$$

$$\bar{\mu}_z = \frac{1}{\beta}\frac{1}{Z_a}\frac{\partial Z_a}{\partial H} = \frac{1}{\beta}\frac{\partial \ln Z_a}{\partial H}$$

Define

$$\eta \equiv \beta g\mu_0 H = \frac{g\mu_0 H}{kT}$$

$$Z_a = \sum_{m=-J}^{J} e^{\eta m} = e^{-\eta J} + e^{-\eta(J-1)} + \cdots + e^{\eta J}$$

The equi-partition theorem

7.8 Simple applications

$$\sinh y = \frac{e^{y} - e^{-y}}{2}$$

General calculation of magnetization

$$Z_a = \sum_{m=-J}^{J} e^{\eta m} = e^{-\eta J} + e^{-\eta(J-1)} + \cdots + e^{\eta J}$$

$$Z_a = \frac{e^{-\eta J} - e^{\eta(J+1)}}{1 - e^{\eta}}$$

$$Z_a = \frac{e^{-\eta(J+\frac{1}{2})} - e^{\eta(J+\frac{1}{2})}}{e^{-\frac{1}{2}\eta} - e^{\frac{1}{2}\eta}}$$

$$Z_a = \frac{\sinh\,(J+\frac{1}{2})\eta}{\sinh \frac{1}{2}\eta}$$

$$\ln Z_a = \ln \sinh\,(J+\tfrac{1}{2})\eta - \ln \sinh \tfrac{1}{2}\eta$$

The equi-partition theorem

7.8 Simple applications

$$\ln Z_a = \ln \sinh (J+\tfrac{1}{2})\eta - \ln \sinh \tfrac{1}{2}\eta$$

General calculation of magnetization

$$\bar{\mu}_z = \frac{1}{\beta}\frac{\partial \ln Z_a}{\partial H} = \frac{1}{\beta}\frac{\partial \ln Z_a}{\partial \eta}\frac{\partial \eta}{\partial H} = g\mu_0 \frac{\partial \ln Z_a}{\partial \eta}$$

$$\bar{\mu}_z = g\mu_0 \left[\frac{(J+\frac{1}{2})\cosh (J+\frac{1}{2})\eta}{\sinh (J+\frac{1}{2})\eta} - \frac{\frac{1}{2}\cosh \frac{1}{2}\eta}{\sinh \frac{1}{2}\eta}\right]$$

$$\boxed{\bar{\mu}_z = g\mu_0 J B_J(\eta)}$$

where $B_J(\eta) \equiv \frac{1}{J}\left[\left(J+\frac{1}{2}\right)\coth\left(J+\frac{1}{2}\right)\eta - \frac{1}{2}\coth\frac{1}{2}\eta\right]$

The equi-partition theorem

$$\bar{\mu}_z = g\mu_0 J B_J(\eta)$$

7.8 Simple applications

General calculation of magnetization

$$\coth y = \frac{\cosh y}{\sinh y} = \frac{e^y + e^{-y}}{e^y - e^{-y}}$$

For $y \gg 1$, $\Rightarrow$ $e^{-y} \ll e^y$ and $\coth y = 1$

For $y \ll 1$,

$$\coth y = \frac{\boxed{1 + \frac{1}{2}y^2} + \cdots}{\boxed{y + \frac{1}{6}y^3} + \cdots}$$

$\Rightarrow$

$$\coth y = \frac{1}{y} + \frac{1}{3}y$$

The equi-partition theorem
7.8 Simple applications

$$\bar{\mu}_z = g\mu_0 J B_J(\eta)$$

General calculation of magnetization

for $\eta \gg 1$,

$$B_J(\eta) = \frac{1}{J}\left[\left(J+\frac{1}{2}\right)-\frac{1}{2}\right] = 1$$

$\eta \ll 1$,

$$B_J(\eta) = \frac{(J+1)}{3}\eta$$

$$\bar{M}_z = N_0\bar{\mu}_z = N_0 g\mu_0 J B_J(\eta)$$

for $g\mu_0 H/kT \ll 1$,

$$\bar{M}_z = \chi H$$

The equi-partition theorem

7.8 Simple applications

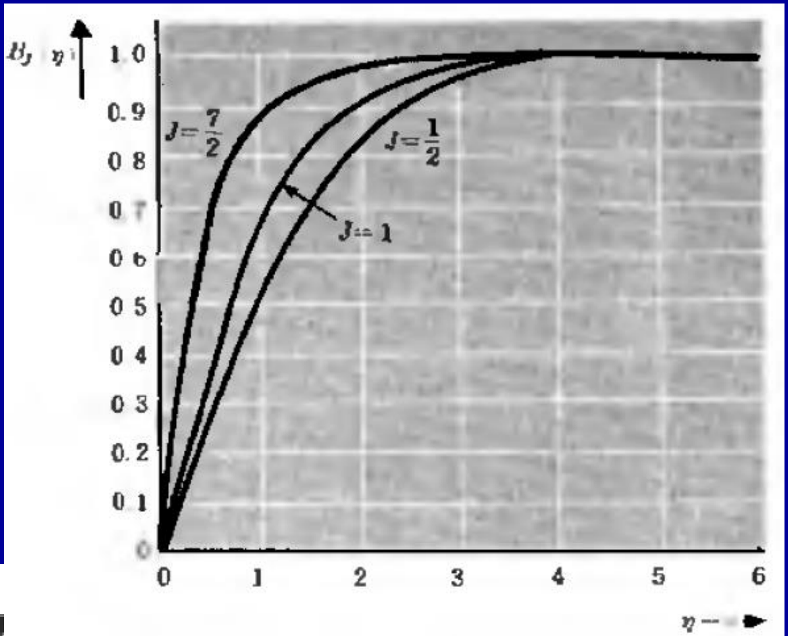
General calculation of magnetization

for $g\mu_0 H/kT \ll 1$,

$$\bar{M}_z = \chi H$$

$$\boxed{\chi = N_0 \frac{g^2 \mu_0^2 J(J+1)}{3kT}}$$

Curie Law



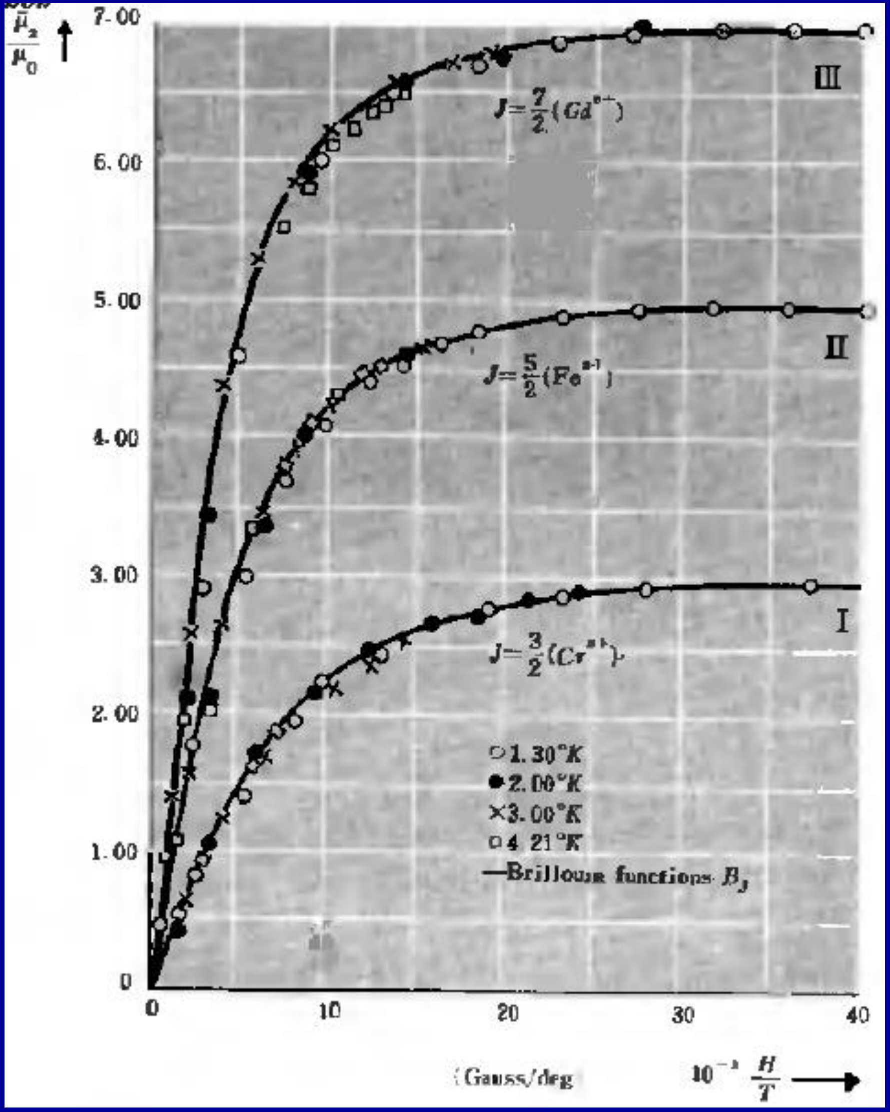
$g\mu_0 H/kT \gg 1$,

$$\bar{M}_z \to N_0 g \mu_0 J$$

The equi-partition theorem

7.8 Simple applications

General calculation of magnetization



Kinetic theory of dilute gas in equilibrium
7.9 Maxwell velocity distribution

A molecule of mass m at *r* with momentum p;
If there is no external field

$$\epsilon = \frac{p^2}{2m} + \epsilon^{(int)}$$

Kinetic energy **Intra-molecule energy**

$$P_s(\mathbf{r},\mathbf{p})\, d^3\mathbf{r}\, d^3\mathbf{p} \propto e^{-\beta[p^2/2m+\epsilon_s^{(int)}]}\, d^3\mathbf{r}\, d^3\mathbf{p}$$
$$\propto e^{-\beta p^2/2m}\, e^{-\beta\epsilon_s^{(int)}}\, d^3\mathbf{r}\, d^3\mathbf{p}$$

$$\boxed{P(\mathbf{r},\mathbf{p})\, d^3\mathbf{r}\, d^3\mathbf{p} \propto e^{-\beta(p^2/2m)}\, d^3\mathbf{r}\, d^3\mathbf{p}}$$

Kinetic theory of dilute gas in equilibrium
7.9 Maxwell velocity distribution

$f(\mathbf{r},\mathbf{v})\, d^3\mathbf{r}\, d^3\mathbf{v} \equiv$ the mean number of molecules with center of mass position between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$, and velocity between $\mathbf{v}$ and $\mathbf{v} + d\mathbf{v}$.

$$\boxed{f(\mathbf{r},\mathbf{v})\, d^3\mathbf{r}\, d^3\mathbf{v} = C e^{-\beta(mv^2/2)}\, d^3\mathbf{r}\, d^3\mathbf{v}}$$

$$\int_{(\mathbf{r})} \int_{(\mathbf{v})} f(\mathbf{r},\mathbf{v})\, d^3\mathbf{r}\, d^3\mathbf{v} = N$$

$$C \int_{(\mathbf{r})} \int_{(\mathbf{v})} e^{-\beta(mv^2/2)}\, d^3\mathbf{v}\, d^3\mathbf{r} = N$$

Kinetic theory of dilute gas in equilibrium
7.9 Maxwell velocity distribution

$$CV\left(\int_{-\infty}^{\infty} e^{-\frac{1}{2}\beta m v_x^2}\, dv_x\right)^3 = CV\left(\frac{2\pi}{\beta m}\right)^{\frac{3}{2}} = N$$

$$C = n\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}}, \qquad n \equiv \frac{N}{V}$$

$$f(\mathbf{v})\, d^3\mathbf{r}\, d^3\mathbf{v} = n\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{1}{2}\beta m v^2}\, d^3\mathbf{r}\, d^3\mathbf{v}$$

$$\boxed{f(\mathbf{v})\, d^3\mathbf{r}\, d^3\mathbf{v} = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mv^2/2kT}\, d^3\mathbf{r}\, d^3\mathbf{v}}$$

Kinetic theory of dilute gas in equilibrium

7.9 Maxwell velocity distribution

$$f(\mathbf{v})\, d^3\mathbf{r}\, d^3\mathbf{v} = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, d^3\mathbf{r}\, d^3\mathbf{v}$$

f depends only on *v* instead of v

Then

$$f(\mathbf{v}) = f(v)$$

Maxwell velocity distribution for a molecule of a dilute gas in equilibrium

Kinetic theory of dilute gas in equilibrium
7.10 related velocity distributions and mean values

$g(v_x)\,dv_x$ = the mean number of molecules per unit volume with x component of velocity in the range between v_x and $v_x + dv_x$, irrespective of the values of their other velocity components.

$$\boxed{g(v_x)\,dv_x = \int_{(v_y)} \int_{(v_z)} f(\mathbf{v})\,d^3\mathbf{v}}$$

$$= n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int_{(v_y)} \int_{(v_z)} e^{-(m/2kT)(v_x^2+v_y^2+v_z^2)}\,dv_x\,dv_y\,dv_z$$

$$= n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mv_x^2/2kT}\,dv_x \int_{-\infty}^{\infty} e^{-(m/2kT)v_y^2}\,dv_y \int_{-\infty}^{\infty} e^{-(m/2kT)v_z^2}\,dv_z$$

$$= n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mv_x^2/2kT}\,dv_x \left(\sqrt{\frac{2\pi kT}{m}}\right)^2$$

Kinetic theory of dilute gas in equilibrium

7.10 related velocity distributions and mean values

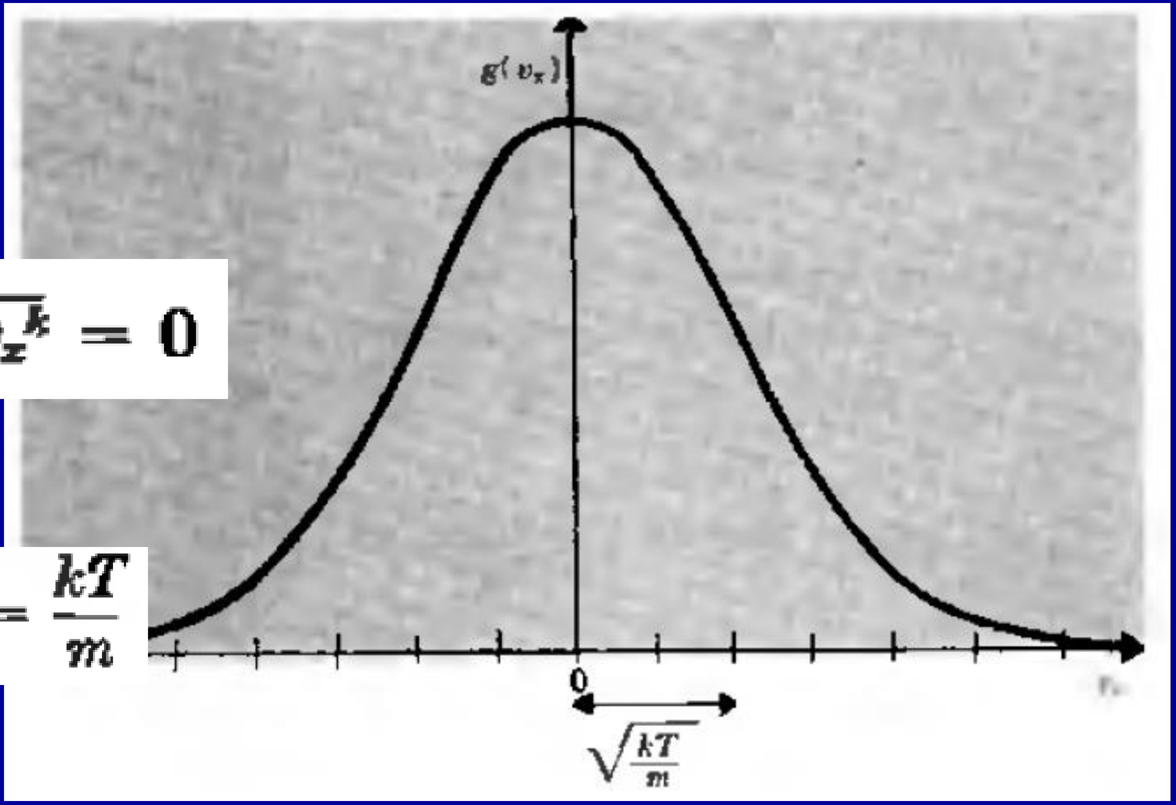
$$g(v_x)\,dv_x = n\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-mv_x^2/2kT}\,dv_x$$

discussions:

$$\int_{-\infty}^{\infty} g(v_x)\,dv_x = n$$

$$\bar{v}_x = \frac{1}{n}\int_{-\infty}^{\infty} g(v_x)\,v_x\,dv_x \qquad \overline{v_x^k} = 0$$

$$\overline{v_x^2} = \frac{1}{n}\int_{-\infty}^{\infty} g(v_x)\,v_x^2\,dv_x = \frac{kT}{m}$$



Kinetic theory of dilute gas in equilibrium
7.10 related velocity distributions and mean values

$$g(v_x)\,dv_x = n\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-mv_x^2/2kT}\,dv_x$$

$$\frac{f(\mathbf{v})\,d^3\mathbf{v}}{n} = \left[\frac{g(v_x)\,dv_x}{n}\right]\left[\frac{g(v_y)\,dv_y}{n}\right]\left[\frac{g(v_z)\,dv_z}{n}\right]$$

Distribution of speed

$F(v)\,dv$ = the mean number of molecules per unit volume with a speed $v = |\mathbf{v}|$ in the range between v and $v + dv$.

Kinetic theory of dilute gas in equilibrium
7.10 related velocity distributions and mean values

Distribution of speed

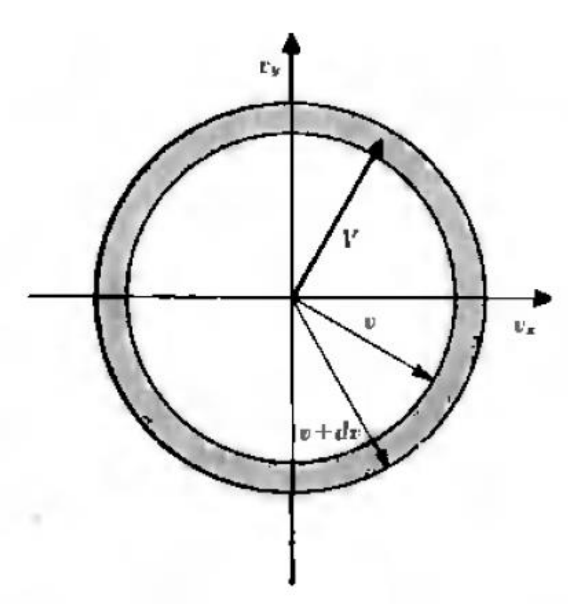
$$F(v)\,dv = \int' f(\mathbf{v})\,d^3\mathbf{v}$$

$$v < |\mathbf{v}| < v + dv$$

$$4\pi v^2\,dv$$

$$F(v)\,dv = 4\pi f(v) v^2\,dv$$

$$F(v)\,dv = 4\pi n \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2\, e^{-mv^2/2kT}\,dv$$



Kinetic theory of dilute gas in equilibrium
7.10 related velocity distributions and mean values

Mean values

$$\bar{v} = \frac{1}{n}\iiint f(\mathbf{v})\, v\, d^3\mathbf{v}$$

$$\bar{v} = \frac{1}{n}\int_0^\infty F(v)\, v\, dv$$

$$\bar{v} = \frac{1}{n}\int_0^\infty f(v)\, v \cdot 4\pi v^2\, dv = \frac{4\pi}{n}\int_0^\infty f(v)\, v^3\, dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty e^{-mv^2/2kT}\, v^3\, dv \qquad \text{by } (7\cdot 9\cdot 10)$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\cdot\frac{1}{2}\left(\frac{m}{2kT}\right)^{-2} \qquad \text{by } (\mathrm{A}\cdot 4\cdot 6)$$

$$\boxed{\bar{v} = \sqrt{\frac{8}{\pi}\frac{kT}{m}}}$$

$$\boxed{\overline{v^2} = \frac{1}{n}\int f(\mathbf{v})\, v^2\, d^3\mathbf{v} = \frac{4\pi}{n}\int_0^\infty f(v)\, v^4\, dv}$$

Kinetic theory of dilute gas in equilibrium 7.10 related velocity distributions and mean values

Mean values

$$\boxed{\overline{v^2} = \frac{1}{n}\int f(v)v^2\, d^3v = \frac{4\pi}{n}\int_0^\infty f(v)v^4\, dv}$$

$$\overline{\tfrac{1}{2}mv^2} = \overline{\tfrac{1}{2}m(v_x{}^2 + v_y{}^2 + v_z{}^2)}$$

$$\tfrac{1}{2}m\overline{v^2} = \tfrac{3}{2}kT$$

$$\overline{v^2} = \frac{3kT}{m}$$

Most probable v

$$\boxed{\frac{dF}{dv} = 0}$$

$$2v\, e^{-mv^2/2kT} + v^2\left(-\frac{m}{kT}v\right)e^{-mv^2/2kT} = 0$$

$$\boxed{\tilde{v}^2 = \frac{2kT}{m}}$$

$$\tilde{v} = \sqrt{\frac{2kT}{m}}$$

Kinetic theory of dilute gas in equilibrium
7.10 related velocity distributions and mean values

$$v_{rms} \equiv \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$$

$$\bar{v} = \sqrt{\frac{8}{\pi}\frac{kT}{m}}$$

$$\tilde{v} = \sqrt{\frac{2kT}{m}}$$

$$\left.\begin{array}{ccccc} v_{rms} & : & \bar{v} & : & \tilde{v} \\ \sqrt{3} & : & \sqrt{\frac{8}{\pi}} & : & \sqrt{2} \\ 1.224 & : & 1.128 & : & 1 \end{array}\right\}$$

For nitrogen (N_2) gas at room temperature (300°K) one finds by (7·10·16), using $m = 28/(6 \times 10^{23})$ g, that

$$v_{rms} \approx 5 \times 10^4 \text{ cm/sec} \approx 500 \text{ m/sec} \qquad (7\cdot10\cdot19)$$

a number of the order of the velocity of sound in the gas.

Class-work

P 282 7.8

Homework

P 282 7.10,12,14--19