

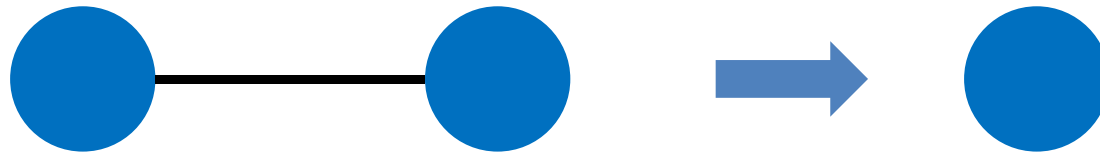
Chapter 20

Compressed Gases and Liquids

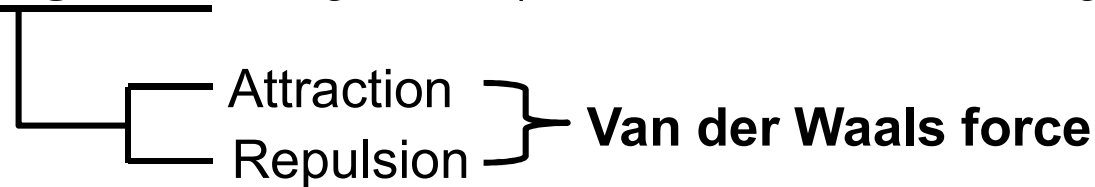
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20.1 Introduction

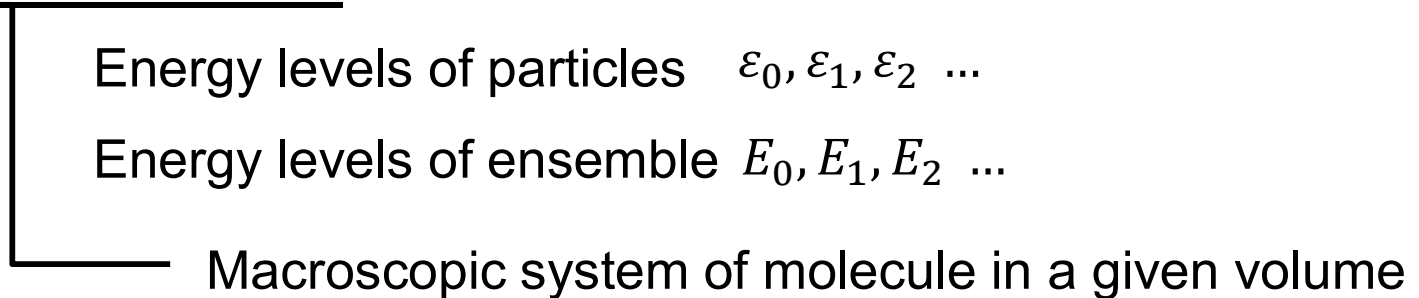


So far, **interacting forces** neglected (considered as an ideal gas)



In this chapter, the molecules of **nonideal gases, liquids, and solids** are considered with interacting forces and potential energies

Ensemble of molecules



20.2 Nonideal Gases

Intermolecular forces — $\left\{ \begin{array}{l} \text{Attraction} \\ \text{Repulsion} \end{array} \right.$

→ System of **dependent particles**

Energy of individual particles → Meaningless

Energy of ensemble of dependent particles → **Meaningful**

Energy of ensemble

: function of — $\left\{ \begin{array}{l} \text{Speed of molecule} \text{ — } \text{Translational } E \\ \text{Position of molecule} \text{ — } \text{Potential } E \end{array} \right.$

Not affected by internal degree of freedom —

20.2 Nonideal Gases

External partition function

$$Z_{ext} = Z_{trans} \times Z_p$$

Partition function for the ensemble

$$Z = Z_{ext} \times Z_{int} = Z_{ext} \times Z_{int}^N$$

N dependent particles occupying a total volume V

- $3N$ degrees of freedom for the ensemble

$$Z_{ext} = \frac{1}{N!} \left(\frac{1}{h^3} \right)^N \int \dots \int \exp \left[-\frac{E(p, q)}{kT} \right] \underbrace{dq_1 \dots dq_{3N}}_{\text{Indistinguishable}} \underbrace{dp_1 \dots dp_{3N}}_{\substack{dx_1 dy_1 dz_1 \\ dp_{x_1} dp_{y_1} dp_{z_1}}}$$

20.2 Nonideal Gases

External energy

$$E(p, q) = \frac{1}{2m} \sum_{i=1}^N (P_x^2 + P_y^2 + P_z^2)_i + \underbrace{E_P(q)}_{\substack{\text{Potential energy of the ensemble} \\ = f(3N \text{ coordinates of position})}}$$

$$\therefore Z_{ext} = \underbrace{\frac{1}{N!} \left(\frac{(2\pi mkT)^{3/2}}{h^3} \right)^N}_{Z_{trans}} \underbrace{\int \dots \int \exp \left[-\frac{E(p, q)}{kT} \right] dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}}_{\substack{\text{Configuration integral} \\ Z_P \text{ (potential partition function)}}}$$

If ideal gas, $E_P(q) = 0$

$$Z_P = V^N$$

20.2 Nonideal Gases

Potential energy of the ensemble

$$E_P(q) = \sum_{ij} \epsilon_P(r_{ij}) = \sum_{i>j}^{i=N} \sum_{j=1}^{j=N-1} \epsilon_P(r_{ij})$$

Potential energy due to interactions
between i & j molecules

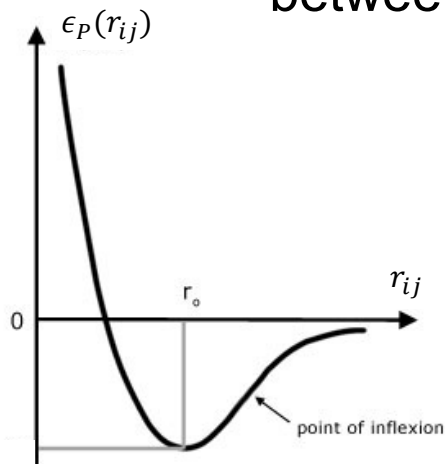


Fig. Intermolecular potential energy versus intermolecular distance (Ref. A-level Physics Tutor)

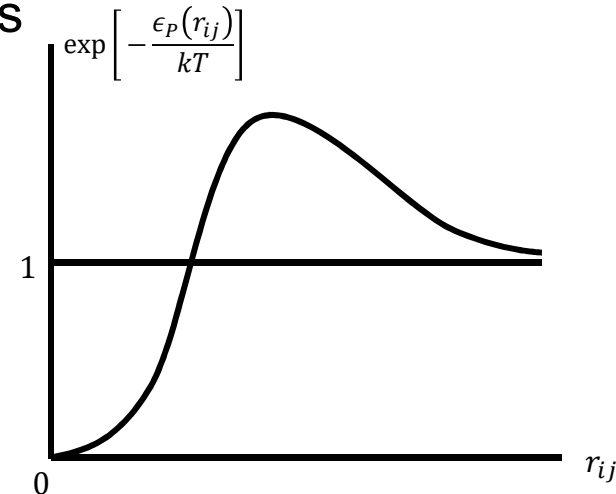


Fig. Intermolecular potential energy exponential versus intermolecular distance

20.2 Nonideal Gases

$$\begin{aligned}
 \therefore \exp \left[-\frac{E_P(q)}{kT} \right] &= \prod_{N \geq i > j \geq 1} \exp \left[-\frac{\epsilon_P(r_{ij})}{kT} \right] \\
 &= \prod_{N \geq i > j \geq 1} (1 + f_{ij}) \quad \text{where } f_{ij} = -1 + \exp \left[-\frac{\epsilon_P(r_{ij})}{kT} \right] \\
 &= 1 + \sum_{N \geq i > j \geq 1} f_{ij} + \dots \quad \text{if } |f_{ij}| \ll 1
 \end{aligned}$$

Potential partition function

$$Z_P = \int \dots \int \left[1 + \sum_{N \geq i > j \geq 1} f_{ij} + \dots \right] d\tau_1 \dots d\tau_j \dots d\tau_i \dots d\tau_N \quad \left\{ \begin{array}{l} d\tau_i = dx_i dy_i dz_i \\ dq_i = dx_i \\ dq_{i+1} = dy_i \\ dq_{i+2} = dz_i \end{array} \right.$$

20.2 Nonideal Gases

$$\begin{aligned}
 Z_P &= \int \dots \int \left[1 + \sum_{N \geq i > j \geq 1} f_{ij} + \dots \right] d\tau_1 \dots d\tau_j \dots d\tau_i \dots d\tau_N \\
 &= \underbrace{V^N}_{\text{Ideal gas}} + \underbrace{\frac{N(N-1)}{2}}_{\approx \frac{N^2}{2}} \underbrace{V^{N-2}}_{\text{Integral of residual}} \underbrace{\iint f_{ij} d\tau_i d\tau_j}_{N-2 \text{ terms}} \quad \text{For } r_{ij} \gg 1 \\
 & \quad \int_0^\infty f(r) 4\pi r^2 dr = \beta \\
 & \quad \iint f_{ij} d\tau_i d\tau_j = \int \beta d\tau_i = \beta V \\
 &= V^N \left(1 + \frac{N^2 \beta}{2V} \right)
 \end{aligned}$$

$$\therefore \ln(Z_P) = N \ln V + \ln \left(1 + \frac{N^2 \beta}{2V} \right)$$

Partition function for the ensemble

$$Z = \frac{Z_{trans}^N}{N!} \times Z_P (Z_{vib} Z_{rot} Z_{elec} Z_{nuc} Z_{chem})^N$$

20.2 Nonideal Gases

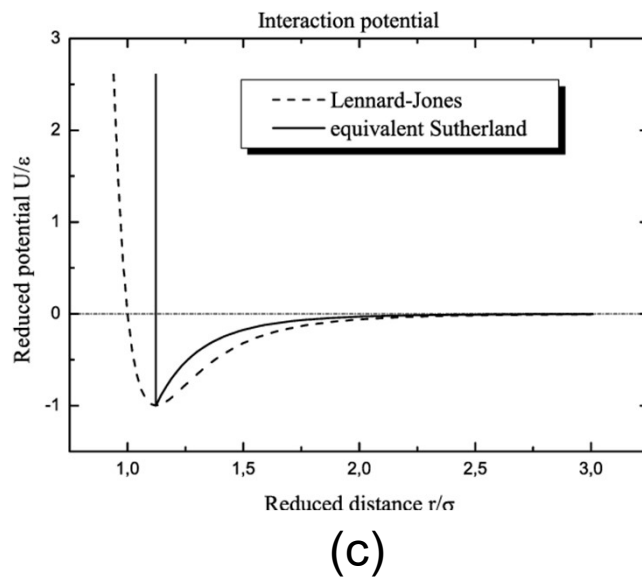
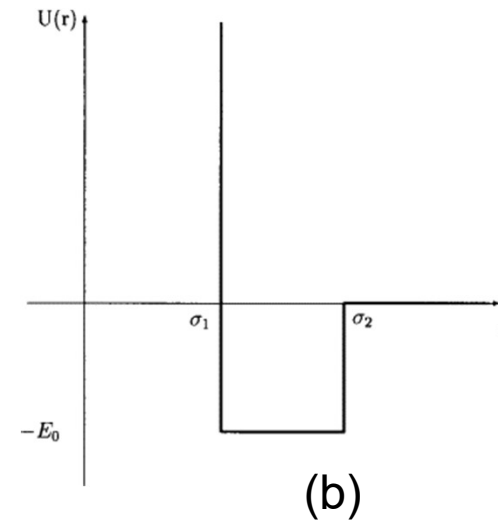
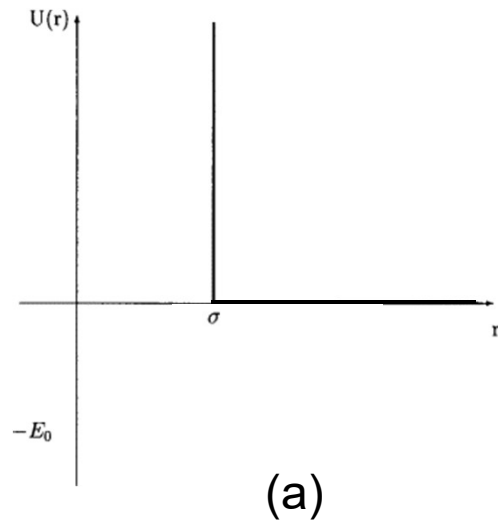


Fig. Intermolecular potential model
(a) hard-sphere (rigid-sphere) model
(b) square-well model
(c) Sutherland & Lennard-Jones model
(Ref. Science Direct, Research Gate)

20.3 Equations of State of Nonideal Gases

Pressure

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

Helmholtz energy

Z : total partition function

$$F = -kT \ln Z = -kT \left[\ln \left\{ \frac{Z_{trans}^N}{N!} \times Z_P (Z_{vib} Z_{rot} Z_{elec} Z_{nuc} Z_{chem})^N \right\} \right]$$

$$\text{where, } Z_{trans} = \frac{(2\pi mkT)^{3/2}}{h^3} \quad Z_P = N \ln V + \ln \left(1 + \frac{N^2 \beta}{2V} \right)$$

Since the only factor of Z dependent on V is Z_P ,

$$P = kT \left(\frac{\partial \ln Z_P}{\partial V} \right)_{T,N} = kT \left(\frac{N}{V} + \frac{-\frac{N^2 \beta}{2V^2}}{1 + \frac{N^2 \beta}{2V}} \right) \quad \because \ln(Z_P) = N \ln V + \ln \left(1 + \frac{N^2 \beta}{2V} \right)$$

20.3 Equations of State of Nonideal Gases

$$P = kT \left(\frac{N}{V} + \frac{-\frac{N^2\beta}{2V^2}}{1 + \frac{N^2\beta}{2V}} \right)$$

Assume $\frac{N^2\beta}{2V} \ll 1$

$$PV = NkT \left[1 - \frac{N\beta}{2V} \left\{ \underbrace{1 - \frac{N^2\beta}{2V} + \left(\frac{N^2\beta}{2V}\right)^2 - \dots}_{\approx 0} \right\} \right] \approx NkT \left(1 - \frac{1}{2} \beta \frac{N}{V} \right)$$

Van der Waals EOS

$$P = \frac{NkT}{V - Nb} - \frac{N^2a}{V^2}$$

$$\rightarrow \frac{PV}{NkT} = \left(\frac{1}{1 - \frac{Nb}{V}} \right) - \frac{Na}{kTV} \approx \left(1 + \frac{Nb}{V} \right) - \frac{Na}{kTV} = 1 + \frac{N}{V} \left(b - \frac{a}{kT} \right)$$

20.3 Equations of State of Nonideal Gases

Nonideal gas EOS

$$PV = NkT \left(1 - \frac{1}{2} \beta \frac{N}{V} \right)$$

Van der Waals EOS

$$PV = NkT \left[1 + \frac{N}{V} \left(b - \frac{a}{kT} \right) \right]$$

Virial form of Van der Waals equation

$$PV = NkT \left[1 + \frac{N}{V} B(T) + \frac{N^2}{V^2} C(T) + \dots \right] \quad \text{ignore from the third term}$$

If nonideal gas EOS and Van der Waals EOS is equal,

$$B(T) = b - \frac{a}{kT} = -\frac{\beta}{2} = -2\pi \int_0^{\infty} \left[\exp\left(-\frac{\epsilon_P(r)}{kT}\right) - 1 \right] r^2 dr$$

20.3 Equations of State of Nonideal Gases

Two hard spherical molecules diameter r_0 : infinite repulsion from 0 to r_0

$$\beta = \int_0^{\infty} \left[\exp\left(-\frac{\epsilon_P(r)}{kT}\right) - 1 \right] 4\pi r^2 dr$$

$$= -4\pi \int_0^{r_0} r^2 dr + 4\pi \int_{r_0}^{\infty} \left[1 - \frac{\epsilon_P(r)}{kT} \dots - 1 \right] r^2 dr$$

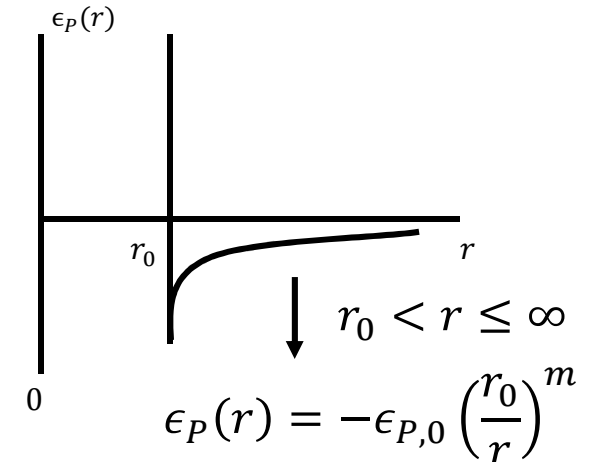
Assume $\epsilon_P(r) \ll kT$

$$= -\frac{4}{3}\pi r_0^3 - \frac{4\pi}{kT} \int_{r_0}^{\infty} \epsilon_P(r) r^2 dr$$

$$B(T) = b - \frac{a}{kT} = -\frac{\beta}{2} = \frac{2}{3}\pi r_0^3 + \frac{2\pi}{kT} \int_{r_0}^{\infty} \epsilon_P(r) r^2 dr$$

$$\therefore b = \frac{2}{3}\pi r_0^3 = 4v_0 \quad a = \frac{2\pi}{m-3} \epsilon_{P,0} r_0^3 = \frac{12}{m-3} \epsilon_{P,0} v_0$$

$$\text{where } v_0(\text{covolume}) = \frac{V_0}{N} = \frac{1}{N} \left[\frac{4\pi}{3} \left(\frac{r_0}{2}\right)^3 N \right]$$



$$\int_{r_0}^{\infty} \epsilon_P(r) r^2 dr$$

$$= -\epsilon_{P,0} r_0^m \int_{r_0}^{\infty} r^{2-m} dr$$

$$= \frac{-\epsilon_{P,0} r_0^m}{3-m} [r^{3-m}]_{r_0}^{\infty}$$

$$= \frac{\epsilon_{P,0} r_0^3}{3-m}$$

20.3 Equations of State of Nonideal Gases

Van der Waals isotherms

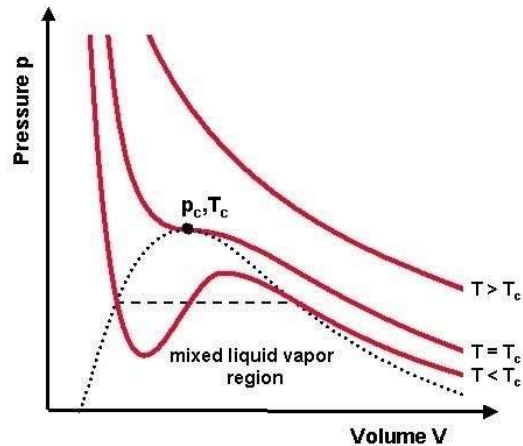


Fig. Van der Waals isotherms
(Ref. Quora.com)

For critical points of Van der Waals gases,

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

$$P = \frac{NkT}{V - Nb} - \frac{N^2 a}{V^2}$$

$$\rightarrow \frac{V_c}{N} = 3b, \quad kT_c = 3b, \quad P_c = \frac{a}{27b^2} \quad \frac{NkT_c}{P_c V_c} = \frac{8}{3}$$

$$\text{or } \frac{V_c}{N} = 12v_0, \quad kT_c = \frac{8}{9} \frac{\epsilon_{P,0}}{m-3}, \quad P_c = \frac{\epsilon_{P,0}}{36(m-3)v_0}$$

With reduced properties, $P_r = \frac{P}{P_c}$, $T_r = \frac{T}{T_c}$, $v_r = \frac{V}{V_c}$

$$\rightarrow \left(P_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r \quad \text{Law of corresponding states}$$

20.4 Compressed Gases

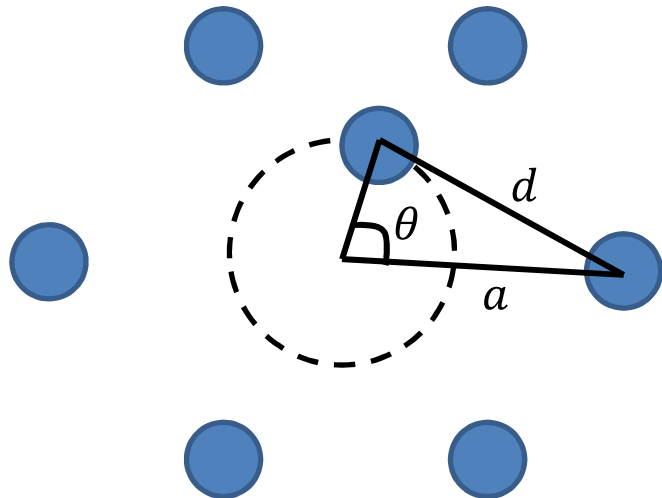
Previously, only interaction between the two molecules is considered for nonideal gases



$$\exp\left[-\frac{E_P(q)}{kT}\right] = \prod_{N \geq i > j \geq 1} \exp\left[-\frac{\epsilon_P(r_{ij})}{kT}\right] \quad Z_P = V^N \left(1 + \frac{N^2 \beta}{2V}\right)$$

For gases at high pressure, multiple interaction is considered

- Lennard-Jones and Devonshire cell theory



- Consider only the interactions with the nearest neighbors

- Spherically symmetric

a : mean distance between two close neighbors

d : intermolecular distance

20.4 Compressed Gases

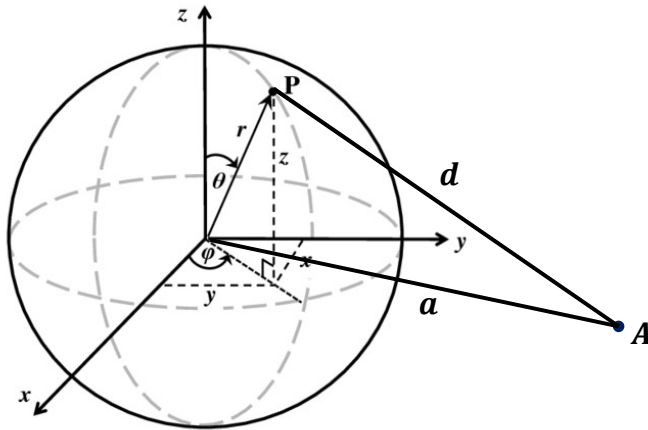


Fig. Spherical coordinate
(Ref. Research Gate)

Mutual potential of the two molecules

$$\begin{aligned}\bar{\epsilon}_P(r) &= \frac{1}{A} \int \epsilon_P(d) dA & d &= (a^2 + r^2 - 2ar\cos\theta)^{\frac{1}{2}} \\ &= \frac{1}{4\pi r^2} \int_0^\pi \int_0^{2\pi} \left[\epsilon_P(a^2 + r^2 - 2ar\cos\theta)^{\frac{1}{2}} \right] r^2 \sin\theta d\theta d\varphi \\ &= \frac{1}{2} \int_0^\pi \int_0^{2\pi} \left[\epsilon_P(a^2 + r^2 - 2ar\cos\theta)^{\frac{1}{2}} \right] r^2 \sin\theta d\theta d\varphi \\ &= \frac{1}{2} \int_0^\pi \epsilon_P(d) \sin\theta d\theta\end{aligned}$$

The average potential energy of the molecule in the cell

$$w(r) = c\bar{\epsilon}_P(r) = \frac{1}{2} c \int_0^\pi \left[\frac{A}{d^{12}} - \frac{B}{d^6} \right] \sin\theta d\theta$$

$\epsilon_{P,0}$: minimum potential energy
 r_0 : interparticle separation of $\epsilon_{P,0}$

c : number of immediate neighbors

$\epsilon_P(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$: Lennard-Jones Eq.

where $r_0 = \left(2 \frac{A}{B} \right)^{\frac{1}{6}}$ $|\epsilon_{P,0}| = \frac{B^2}{4A}$

20.4 Compressed Gases

$$w(r) = c\bar{\epsilon}_P(r) = \frac{1}{2}c \int_0^\pi \left[\frac{A}{d^{12}} - \frac{B}{d^6} \right] \sin\theta d\theta \quad d = (a^2 + r^2 - 2ar\cos\theta)^{\frac{1}{2}}$$

$$= -\frac{1}{2}c \left\{ \frac{aA}{10ra^{12}} \left[\left(1 + \frac{r}{a}\right)^{-10} - \left(1 - \frac{r}{a}\right)^{-10} \right] - \frac{aB}{4ra^6} \left[\left(1 + \frac{r}{a}\right)^{-4} - \left(1 - \frac{r}{a}\right)^{-4} \right] \right\}$$

$$\text{If } r \rightarrow 0, \quad w(0) = c \left(\frac{A}{a^{12}} - \frac{B}{a^6} \right)$$

$$\therefore w(r) - w(0) = c \left[\frac{A}{a^{12}} l(y) - \frac{B}{a^6} m(y) \right] = \Lambda \left\{ \left(\frac{V_1}{V} \right)^4 l(y) - 2 \left(\frac{V_1}{V} \right)^2 m(y) \right\}$$

where $y = r^2/a^2$

$$l(y) = (1 + 12y + 25.2y^2 + 12y^3 + y^4)(1 - y)^{-10} - 1$$

$$n(y) = (1 + y)(1 - y)^{-4} - 1$$

$$\left. \begin{aligned} \Lambda \left(\frac{V_1}{V} \right)^4 &= \frac{cA}{a^{12}} \\ 2\Lambda \left(\frac{V_1}{V} \right)^4 &= \frac{cB}{a^6} \end{aligned} \right\} \Lambda = \frac{cB^2}{4A} = c\epsilon_{P,0}$$

$$\left. \begin{aligned} \Lambda \left(\frac{V_1}{V} \right)^4 &= \frac{cA}{a^{12}} \\ 2\Lambda \left(\frac{V_1}{V} \right)^4 &= \frac{cB}{a^6} \end{aligned} \right\} \frac{V_1}{V} = \left(\frac{r_0}{a} \right)^3$$

$\epsilon_{P,0}$: minimum potential energy of two molecules with intermolecular distance r_0

V_1 : volume corresponding to intermolecular separation $a = r_0$

20.4 Compressed Gases

Potential partition function

$$Z_P = \int \dots \int \exp \left[-\frac{E(p, q)}{kT} \right] dq_1 \dots dq_{3N} dp_1 \dots dp_{3N} \ \& \ \exp \left[-\frac{E_P(q)}{kT} \right] = \prod_{N \geq i > j \geq 1} \exp \left[-\frac{\epsilon_P(r_{ij})}{kT} \right]$$

Potential partition function with average potential function

$$Z_P = \left[N 4\pi \int_0^{a/2} \exp \left\{ -\frac{w(r) - w(0)}{kT} \right\} r^2 dr \right]^N$$

$a/2$: higher limit for r
 a : mean distance between two close neighbors

$$= \left[2\pi N a^3 \int_0^{1/4} y^{1/2} \exp \left\{ \frac{\Lambda}{kT} \left[2 \left(\frac{V_1}{V} \right)^2 m(y) - \left(\frac{V_1}{V} \right)^4 l(y) \right] \right\} dy \right]^N \quad \text{where } y = r^2/a^2$$

Let this integral is equal to C

$$= [2\pi N \gamma C V]^N \quad \text{where } \gamma = a^3 \frac{N}{V} \text{ depends on the molecular arrangement}$$

Considering the ϵ_0 of the molecule located at the center of its cell

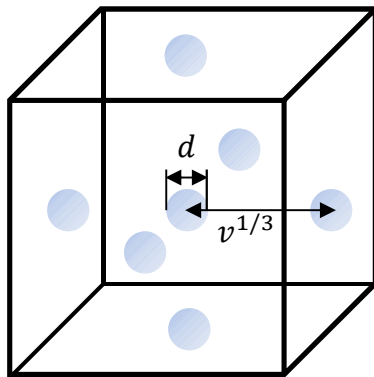
$$Z_P = \left[2\pi N \gamma C V \exp \left(\frac{\epsilon_0}{kT} \right) \right]^N$$

20.5 The Liquid Phase

Treatment of the liquid phase : **Free volume concept**

- The volume for the molecule to move within the cell under repulsive forces
- Assume that the structure of the liquid is pseudocrystalline

(face centered cubic lattice)



v : mean volume per molecule d : molecule diameter

$v^{1/3}$: intermolecular distance

Free volume per molecule

$$v_f = (2v^{1/3} - 2d)^3 = 8(v^{1/3} - d)^3 = \underline{b^3(v^{1/3} - d)^3}$$

generalized form

Total free volume

$$V_f = Nb^3(v^{1/3} - d)^3$$

b : determined by
molecular arrangement

20.5 The Liquid Phase

Potential partition function

$$Z_P = \int \dots \int \exp\left[-\frac{E(p, q)}{kT}\right] dq_1 \dots dq_{3N} dp_1 \dots dp_{3N} \quad \& \quad \exp\left[-\frac{E_P(q)}{kT}\right] = \prod_{N \geq i > j \geq 1} \exp\left[-\frac{\epsilon_P(r_{ij})}{kT}\right]$$

Potential partition function for a liquid

$$Z_P = V_f^N \left[\exp\left(\frac{\epsilon_{vap}}{kT}\right) \right]^N \quad \epsilon_{vap} : \text{hypothetical energy of vaporization at } T = 0 \text{ K}$$

Partition function for a liquid

$$Z_l = \frac{1}{N!} \left[\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} V_f \right]^N \left[Z_{int} \exp\left(\frac{\epsilon_{vap}}{kT}\right) \right]^N$$

Pressure

$$P = kT \left(\frac{\partial \ln Z_l}{\partial V} \right)_T = NkT \left(\frac{\partial \ln V_f}{\partial V} \right)_T + N \left(\frac{\partial \epsilon_{vap}}{\partial V} \right)_T$$

$$P - N \left(\frac{\partial \epsilon_{vap}}{\partial V} \right)_T = NkT \left(\frac{\partial \ln V_f}{\partial V} \right)_T = NkT \left[\frac{1}{V_f} \left(\frac{\partial V_f}{\partial V} \right)_T \right]$$

20.5 The Liquid Phase

Total free volume

$$V_f = Nb^3(v^{1/3} - d)^3 = b^3(V^{1/3} - dN^{1/3})^3$$

$$\left(\frac{\partial V_f}{\partial V}\right)_T = b^3 \times 3(V^{1/3} - dN^{1/3})^2 \times \frac{1}{3}V^{-2/3}$$

$$\frac{1}{V_f} \left(\frac{\partial V_f}{\partial V}\right)_T = bV_f^{-1/3}V^{-2/3}$$

$$P - N \left(\frac{\partial \epsilon_{vap}}{\partial V}\right)_T = NkT \left[\frac{1}{V_f} \left(\frac{\partial V_f}{\partial V}\right)_T \right] = NkT(bV_f^{-1/3}V^{-2/3})$$

$$\therefore V_f = \left[\frac{bNkT}{\left(P - N \left(\frac{\partial \epsilon_{vap}}{\partial V}\right)_T\right)} \right]^3 \times \frac{1}{V^2}$$

$$\text{Since } P \ll N \left(\frac{\partial \epsilon_{vap}}{\partial V}\right)_T \text{ \& } \left(\frac{\partial \epsilon_{vap}}{\partial V}\right)_T \approx -\frac{\epsilon_{vap}}{V}, \quad V_f = \left(\frac{bkT}{\epsilon_{vap}}\right)^3 V$$