

ideal gas
intermolecular energy

Total energy of gas $E = E_{\text{ig.}} + E_{\text{internal}}$

$$E_{\text{ig.}} = \frac{3}{2} N k T + E_{\text{lib}} + E_{\text{rot}}$$

\hookrightarrow translational degrees of freedom

$E_{\text{ig.}}$ depends on T but not on density

Any density dependence of E comes from E_{internal} .

local density at P distant r from a molecule at O is $g(r)$; The infinitesimal no. of molecules in an infinitesimal volume dC centered at P is $g(r) dC$. Potential energy of interaction of any molecule in this volume dC with molecule at O is $\phi(r)$; Total potential energy of interaction between molecule at O and all molecules within dC is $\phi(r) g(r) dC$. Sum of energies of interaction of the molecule at O with all other molecules of the gas is the (integral)
sum of this over all such volume elements dC at all such points P in space:

$$P \int g(r) \phi(r) dC$$

Multiplying by total number of molecules N (each one playing the role of central molecule at O) and dividing by 2 (\because every interaction is counted twice) \rightarrow Integration in polar

$$E_{\text{internal}} = \frac{N_p}{2} \int g(r) \phi(r) dC$$

ω -ordinates over all θ, ϕ
 $dC = r^2 \sin \theta d\theta d\phi dr$

For spherical molecules, interaction is spherically symmetric

\therefore Integrating over θ (0 to π in polar angle) and ϕ (0 to 2π in azimuthal angle) can be performed to give 4π .

$$\therefore E_{\text{internal}} = 2\pi N_p \int_0^{\infty} r^2 g(r) \phi(r) dr + \dots$$

\hookrightarrow higher order terms

Upper limit to ∞ justified even though box of gas not infinitely

large, because $\phi(r)$ becomes zero after very small distances and r is very large compared to these length scales.

$$\text{Now } E_{\text{internal}} = 2\pi\rho \int_0^{\infty} e^{-\phi(r)/kT} \cdot \phi(r) r^2 dr + \dots$$

interaction energy per molecule

(valid even if V and $N \rightarrow \infty$
at given $p = N/V$)

higher order terms with

p^2, p^3, \dots dependence.

To leading order in p , E_{internal}/N is $\propto p$. When $p \rightarrow 0$
 $E_{\text{internal}} \rightarrow 0$, $E \rightarrow E_{\text{rig}}$.

density p can be changed at fixed N by decreasing volume

$$\begin{aligned} \left(\frac{\partial E}{\partial V} \right)_{T,N} &= \left(\frac{\partial E}{\partial (N/p)} \right)_{T,N} = \frac{\partial (E/N)}{\partial (1/p)} = -p^2 \left(\frac{\partial (E/N)}{\partial p} \right) \\ &= -p^2 \left(\frac{\partial (E_{\text{internal}}/N)}{\partial p} \right) \quad \because \text{only } E_{\text{internal}} \text{ is density-dependent.} \end{aligned}$$

$$\therefore \left(\frac{\partial E}{\partial V} \right)_{T,N} = -2\pi p^2 \int_0^{\infty} e^{-\phi(r)/kT} \phi(r) r^2 dr + \dots$$

correction terms of order p^3, p^4, \dots

$$\text{We know } \left(\frac{\partial E}{\partial V} \right)_{T,N} = -p + T \left(\frac{\partial p}{\partial T} \right)_{V,N}$$

$$= - \left(\frac{\partial (p/T)}{\partial (1/T)} \right)_p = - \left(\frac{\partial (p/kT)}{\partial (1/kT)} \right)_p$$

$$\text{Now } \int_0^{\infty} e^{-\phi(r)/kT} \phi(r) r^2 dr = \frac{\partial}{\partial (1/kT)} \left(\int_0^{\infty} (1 - e^{-\phi(r)/kT}) r^2 dr \right)$$

constant / to ensure as $r \rightarrow \infty$ $\phi(r) \rightarrow 0$
integrand goes to zero.

$$\therefore \left(\frac{\partial(p/kT)}{\partial(1/kT)} \right)_p = 2\pi p^2 \left(\int_0^\infty (1-e^{-\phi(r)/kT}) r^2 dr \right) + \dots$$

higher order terms

Thus, the two quantities in RHS and LHS parentheses are equal to within a constant.

$$\therefore \frac{p}{kT} = h(p) + 2\pi p^2 \int_0^\infty (1-e^{-\phi(r)/kT}) r^2 dr + \text{corrections of order } p^3, p^4, \dots$$

where $h(p)$ is a function of p but independent of temperature.

As $p \rightarrow 0$ we must have

$$\frac{p}{kT} = \frac{N}{V}$$

$$\therefore h(p) = p.$$

Therefore,

$$\frac{p}{kT} = p \left(1 + 2\pi p \int_0^\infty (1-e^{-\phi(r)/kT}) r^2 dr + \text{corrections of order } p^2, p^3, \dots \right)$$

This is the virial series since $p = N/V$

$$\therefore B(T) = 2\pi \int_0^\infty (1-e^{-\phi(r)/kT}) r^2 dr$$

Let's calculate $B(T)$ for a square well potential.

$$\therefore B(T) = 2\pi \left[\int_0^{r_1} (1-e^{-\phi(r)/kT}) r^2 dr + \int_{r_1}^{r_2} (1-e^{-\phi(r)/kT}) r^2 dr + \int_{r_2}^\infty (1-e^{-\phi(r)/kT}) r^2 dr \right]$$

$$\begin{aligned}
 \therefore B(T) &= 2\pi \left[\int_0^{\sigma_1} r^2 dr + \int_{\sigma_1}^{\sigma_2} (1 - e^{-\epsilon/kT}) r^2 dr + \int_{\sigma_2}^{\infty} r^2 dr \cdot 0 \right] \\
 &\quad \underbrace{\qquad}_{\phi(r)=\infty} \quad \underbrace{\qquad}_{\phi(r) = -\epsilon} \quad \underbrace{\qquad}_{\phi(r) = 0} \\
 &= 2\pi \left(\frac{\sigma_1^3}{3} + (1 - e^{-\epsilon/kT}) \frac{(\sigma_2^3 - \sigma_1^3)}{3} + 0 \right) \\
 &= \frac{2\pi}{3} (\sigma_1^3 + (1 - e^{-\epsilon/kT})(\sigma_2^3 - \sigma_1^3))
 \end{aligned}$$

At high enough temperatures, thermal energy kT is much greater than the depth ϵ of the attractive well in the potential $\therefore e^{-\epsilon/kT} \approx (1 + \epsilon/kT)$

$$\therefore B(T) \approx \frac{2\pi}{3} \left[\sigma_1^3 - (\sigma_2^3 - \sigma_1^3) \frac{\epsilon}{kT} \right]$$

This shows us the temperature dependence of $B(T)$.

Now $B(T)$ can be measured by experiment as well. By fitting the experimental data with above expression (note there are three adjustable parameters) shows agreement when $\sigma_2 \sim 1.5 \sigma_1$. Similarly experiment can be fit to $B(T)$ obtained from a Lennard Jones potential (only two adjustable parameters r_0 and ϵ) without much trouble. Values of r_0 and ϵ obtained from fit are meaningful. $\epsilon \Rightarrow$ depth of attractive well and $\sigma \approx 0.9r_0$, molecule's diameter.

Thus, at high temperature $B(T)$ takes the form.

$$B(T) = b - a/kT$$

$$\text{where } b = (2\pi/3) \sigma_1^3 \quad a = (2\pi/3) (\sigma_2^3 - \sigma_1^3) \epsilon$$

\therefore Introducing $B(T)$ into gas law to correct for non-ideality.

$$\frac{P}{kT} = \frac{N}{V} \left(1 + \frac{N}{V} \left(b - \frac{a}{kT} \right) \right)$$

$$\Rightarrow \frac{P}{kT} + \frac{aN^2}{V^2 kT} = \frac{N}{V} \left(1 + \frac{bN}{V} \right)$$

$$\therefore \frac{\left(P + \frac{aN^2}{V^2} \right)}{kT} \frac{1}{\left(1 + \frac{bN}{V} \right)} = \frac{N}{V}$$

when $bN \ll V$ (low density limit).

$$\frac{1}{1 + \frac{bN}{V}} \approx 1 - \frac{bN}{V}$$

$$\therefore \underbrace{\left(P + \frac{aN^2}{V^2} \right) (V - bN)}_{=} = NkT$$

known as the van-der Waal's equation of state.

Origin of VDW equation of state

For ideal gas

$$Q = \frac{q^N}{N!} \quad q = \frac{V}{\lambda^3}$$

Let's modify q to account for intermolecular forces & then still assume particles independent of each other

Two modifications

- 1) Replace V by a free volume V_f . Not all volume is available for motion for a given molecule.
- 2) Correct partition function by a Boltzmann factor ~~$e^{-E_{internal}/kT}$~~

intermolecular
interactions
felt by single
particle

(potential energy
of interaction)

$$\text{Now } 2E_{internal} = - \int_{r_0}^{\infty} \varepsilon \left(\frac{r_0}{r}\right)^6 \frac{N}{V} 4\pi r^2 dr$$

Assumptions: No molecules close to our molecule upto distance r_0 \therefore hard-spheres of radius

"repulsive
shell"

$\sim r_0$

gross approximation
fine at low densities

From r_0 to ∞ molecules randomly distributed. So average density of molecules in this region is $\frac{N}{V}$

of molecules at distances from r to $r+dr$ from our chosen molecule is $4\pi r^2 dr$. These molecules (in the "attractive shell") give rise to the above potential energy of attraction (-ve sign)

$$\therefore 2E_{internal} = \varepsilon r_0^6 \frac{N}{V} 4\pi \cancel{\frac{1}{3}} \left(0 - \frac{1}{r_0^3} \right)$$

$$(2E_{internal}) = - \frac{4\pi}{3} \varepsilon r_0^3 \frac{N}{V}$$

Only half of this intermolecular energy can be counted for each

$$\therefore E_{internal} = - \frac{2\pi}{3} \varepsilon r_0^3 \frac{N}{V}$$

Let's say $E_{\text{internal}} = -a_v \frac{N}{V}$ where $a_v = \frac{2\pi\epsilon r_0^3}{3}$

Now for non-ideal gas in low density limit

$$Q = \frac{q^N}{N!} \quad q = \frac{V_f e^{-E_{\text{internal}}/kT}}{\lambda^3}$$

$$\ln Q = N \ln \frac{V_f}{\lambda^3} - \frac{N E_{\text{internal}}}{kT} - N \ln N + N$$

now $V_f = V - Nb$ → a "molecular volume" of interaction

$$\therefore \ln Q = N \ln \frac{(V - Nb)}{\lambda^3} - \frac{N E_{\text{internal}}}{kT} - N \ln N + N$$

$$P = \frac{kT \partial \ln Q}{\partial V} = kT \left[\left(\frac{N}{V - Nb} \right) - \frac{1}{kT} \frac{\partial (-a_v N^2/V)}{\partial V} - 0 \right]$$

$$\therefore P = \frac{NkT}{V - Nb} + \frac{a_v N^2}{V^2} (-1)$$

$$\therefore \left(P + \frac{a_v N^2}{V^2} \right) (V - Nb) = NkT$$

Van der Waals eq.



same as that obtained from $B(T)$ of form

$$b - \frac{a}{kT}$$

$$b = \underbrace{\frac{2\pi}{3} \sigma_1^3}$$

Volume of repulsive
core

(with a correction factor
of 2)

$$a = \underbrace{\frac{2\pi}{3} (\sigma_2^3 - \sigma_1^3)} \varepsilon$$

Volume of attractive
shell (with a

correction factor of 2)

Note other thermodynamic quantities can also be evaluated for the non-ideal gas.