"Virial Coefficients"

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Theory of Imperfect gases and the virial coefficients:-

① Let us consider a monoatomic gas consisting of N molecules each of mass m, contained in a vessel of volume V at temp. T; We assumed that T is sufficiently high and the density $n = N/V$ is sufficiently low that the gas can be treated by classical statistical mechanics*.

The gas molecules interacting via a pairwise potential. We ~~have~~ denote the potential energy of interaction between molecules i and j as

$U_{(ij)} = U(r_{ij})$ and assume that it depends only on thus relative separation $\vec{r}_{ij} = |\vec{r}_i - \vec{r}_j|$ is the magnitude of the separation vectors between i^{th} and j^{th} molecule. We assume further that U is the simply given by the sum of all interaction between pairs of molecules.

Thus $U = u_{12} + u_{13} + u_{14} + \cdots + u_{23} + u_{24} + \cdots$

$$U = \sum_{\substack{i=1 \\ i<j}}^{N} \sum_{j=1}^{N} u_{ij} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} u_{ij} \qquad \text{——— (1)}$$

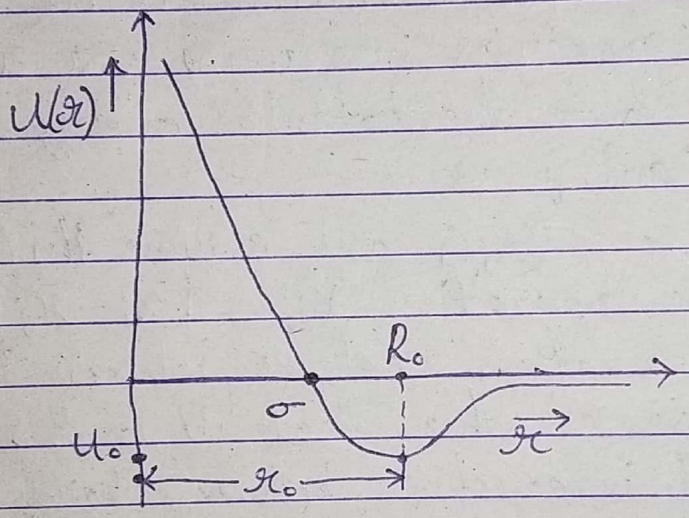
The energy of the Hamiltonian of this system is written in the form

$$H = K + U$$

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{\text{Pair}} u \qquad \text{——— (2)}$$

where $K = \frac{1}{2m}\sum_{i=1}^{N} p_i^2$

The potential corresponds to an attractive force at large distances and a ~~large~~ very strong repulsion at short distances. A typical $U(r)$ is shown in the fig①.



Fig(1)

In eqn ② the first term is the K.E. of the gas particle and 2nd term is the P.E. of their ~~P.E.~~ mutual interaction. In monoatomic gas, $U(r)$ is the only function of the distance between atoms. Let the P.E. $U(r)$ be written as a ~~term~~ sum of terms each depending only on the distances apart (r_{ij}) of the two molecule i and j. The P.E. of interaction between a pair of molecules has the general shape as shown in Fig①. It is strongly repulsive, when the molecules are very close together and more

weakly attractive at large separation. The P.E. of three particles molecules all close together is the same as that of their independent pairs, which can be form of the group of three. In the assembly of N molecules, there are $\frac{1}{2}N(N-1)$ different ~~pair~~ pairs, which can be formed. So this assumption is that $U(r_{ij})$ is the sum of $\frac{1}{2}N(N-1)$ terms namely,

$$U(r_{ij}) = \sum_{i>1}^{N} \sum_{j\geq 1}^{N-1} u(r) \qquad \text{——— (2a)}$$

The function $u(r)$ has the same general characteristic form for all, neutral chemically ~~stand~~ saturated molecules. It is zero for large values of r decreasing to minimum negative value at distance r_0 of few Å units and then decreases rapidly as r decreases to very high positive value for smaller distance of approach as shown in Fig ①.

The canonical partition function Z for all N identical molecules is given by,

$$Z = \frac{1}{[N} \int \left\{ \frac{d^{3N}p_i \cdot d^{3N}r_i}{h^{3N}} e^{-\sum p_i^2/2mkT - \sum_{pair} u(r_{ij})/kT} \right\}$$

$$= \frac{1}{[N} \cdot \frac{1}{h^{3N}} \int_{-\infty}^{\infty} e^{-\sum_i p_i^2/2mkT} d^{3N}p_i \int e^{-u(r_{ij})/kT} \cdot d^{3N}r_i$$

$$= \frac{1}{[N} \frac{1}{h^{3N}} \left[\left\{ \int_{-\infty}^{\infty} e^{-p_i^2/2mkT} \cdot dp_i \right\}^{3N} \int \left\{ e^{-u(r_{ij})/kT} \cdot dr_i \right\}^{3N} \right.$$

$\because \int_{-\infty}^{\infty} e^{-\alpha x^2} \cdot dx = \sqrt{\frac{\pi}{\alpha}}$, $3N$ = D.O.F.

So,

$$Z = \frac{1}{N!} \frac{1}{h^{3N}} \left\{ (2\pi mkT)^{1/2} \right\}^{3N} \left\{ e^{-\sum_{Pair} U(r_{ij})/kT} \cdot dr_i \right\}^{3N}$$

$$= \frac{V^N}{N!} \left(\frac{2\pi kT}{h^2} \right)^{3N/2} \cdot \frac{1}{V^N} \int d^{3N} r_i \, e^{-\sum_{Pair} U(r_{ij})/kT} \quad \text{——— (3)}$$

$$Z = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \cdot Z_q \quad \text{——— (4)}$$

where,

$$Z_q = \frac{1}{V^N} \int d^{3N} r_i \, e^{-\sum_{Pair} U(r_{ij})/kT} \quad \text{——— (5)}$$

$$Z_q = \frac{1}{V^N} \int e^{-\sum U(r_{ij})/kT} \, d\tau_1 \, ---- \, d\tau_N$$

where $d\tau_i = dx_i \, dy_i \, dz_i$

The integral (5) depends upon the configuration of the molecules and hence is called the configuration integral. Eqn (4) represents the general expression for the partition function of an assembly of actual gas molecules. The form of the partition function Z depends upon the the configuration integral Z_q.

Substituting the value $U_{r_{ij}}$ from eqn (2a) in eqn (5), we get

$$Z_q = \frac{1}{V^N} \int \exp\left(-\sum_{i=1}^{N} \sum_{j=1}^{N-1} u r_{ij}/kT \cdot dT_1 \cdots dT_N \right) \quad \text{——— (6)}$$

Obviously the exponent of the integrand in above eqⁿ is sum of terms and then the integrand itself is a product. However the coordinate of two molecules occur in each term of the product and the coordinate of each molecule occur in (N-1) different terms of the product. The complete integral is not be written as a product of integral like momenta integral.

We may write

$$e^{-u(r)/kT} = \prod_{N \geq i > j \geq 1} e^{-u(r_{ij})/kT} \quad \text{——— (7)}$$

each term $e^{-r_{ij}/kT}$ approaches unity for large values of arguments r_{ij} for which $u(r_{ij})$ approachs zero.

Thus we may write

$$e^{-u(r_{ij})/kT} = (1 \pm f_{ij}) \quad \text{——— (8)}$$

Eqⁿ (3) may be written as

$$Z = \frac{V^N}{\lfloor N} \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \cdot \frac{1}{V^N} \int d^{3N} r_i \prod_{\text{Pair}} (1 + f_{ij}) \quad \text{——— (9)}$$

———→

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——→

In eqn (9), we have used the definition of $f(r)$ from $f(r) = e^{-\beta V(R)} - 1$ (an auxilliary) and introduced the notation $f(r_{ij}) = f_{ij}$ in the last line.

The free energy is

$$F = -kT \log Z$$

$$F = -kT \log \left[\frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \left\{ \frac{1}{V^N} \int d^{3N} r_i \cdot \prod_{\text{Pairs}} (1 + f_{ij}) \right\} \right]$$

$$= -kT \left[\log V^N + \log \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \left\{ \frac{1}{V^N} \int d^{3N} r_i \right. \right.$$

$$= -kT \left[\log V^N + \log \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} - \log [N!] - kT \left[\log \left(\frac{1}{V^N} \right) \int d^{3N} r_i \right. \right.$$

$$\left. \left. \prod_{\text{Pairs}} (1 + f_{ij}) \right\} \right]$$

$$= -NkT \log V - \frac{3}{2} NkT \log \left(\frac{2\pi mkT}{h^2} \right) + NkT \log N - NkT$$

$$- kT \log \frac{1}{V^N} \int d^{3N} r_i \prod_{\text{Pairs}} (1 + f_{ij}) \qquad \text{---------- (10)}$$

and the pressure P follows as

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

$$= \frac{NkT}{V} + kT \frac{\partial}{\partial V} \log \frac{1}{V^N} \int d^3 r_i \prod_{\text{Pairs}} (1 + f_{ij})$$

$$= \frac{NkT}{V}\left[1 + \frac{V}{N}\frac{\partial}{\partial V}\log\frac{1}{V^N}\int d^3r_i \prod_{Pairs}(1+f_{ij})\right]$$

$$P = \frac{NkT}{V}\left[1 + V\frac{\partial \bar{F}}{\partial V}\right] \quad \text{——— (11)}$$

where $$\bar{F} = \frac{1}{N}\log\frac{1}{V^N}\int d^3r_i \prod_{Pairs}(1+f_{ij}) \quad \text{——— (12)}$$

At this result, we have an exact result. If $u_{ij} = 0$, $f_{ij} = 0$ and hence $\bar{F} = 0$, giving back the ideal gas law. Since $\bar{F}$ can not be exactly obtained for any non zero u_{ij}. We try to get a handle on the problem by assuming that u_{ij} is small and hence f_{ij} is small. Accordingly, we retain only the $O(f)$ terms in eqn (12) and find,

$$\bar{F} = \frac{1}{N}\log\frac{1}{V^N}\int d^{3N}r_i\left(1 + \prod_{Pairs} f_{ij}\right)$$

from eqn (5),

$$Z_q = \frac{1}{V^N}\int e^{-\sum u(r_{ij})/kT}\, d\tau_1 \cdots\cdots d\tau_N$$

and from (8), $e^{-u(r_{ij})/kT} = (1+f_{ij})$

$$\therefore Z_q = \frac{1}{V^N}\int\cdots\int d\tau_1 \cdots\cdots d\tau_N + \int_{N\geq i\geq j} f_{ij}\, d\tau_1 \cdots d\tau_N$$

——— (13)

As the configuration space allowed to each molecule, is the of the system. (First integration for all the N molecules

is V^N).

For an assembly of N molecules the total number of interaction terms of the type $(f_{r_{ij}})$ is equal to $\frac{1}{2}N(N-1)$ and the integration over each of these terms give the same value.

Hence eqn (13) may be written as

$$Z_q = \frac{1}{V^N}\left[V^N + \frac{1}{2}N(N-1)\int\int f_{ij}\, d\tau_2 \cdots d\tau_N\right] \quad \text{——— (14)}$$

Similarly eqn (12) may be written as

$$\bar{F} = \frac{1}{N}\log\frac{1}{V^N}\left[V^N + \frac{1}{2}N(N-1)\int\cdots\int f_{ij}\, d\tau_1 \cdots d\tau_N\right] \quad \text{——— (15)}$$

If $u(r)$ were identically zero for all values of r, then the function $(f_{ij})^s$ would be zero and the value of integration in above equation would be zero. Thus configuration integral Z_q would be equal to V^N. This is the case a perfect gas.

As f_{ij} depends only on the coordinates (x_i, y_i, z_i) and (x_j, y_j, z_j) of the i^{th} and j^{th} molecules, the remaining $(N-2)$ terms ~~instead~~ inside the integrals.

When integrated over the configration space would give V^{N-2}, Since for each term containing one f_{ij} integration over the configuration space of a molecule other than i or j leads to V as a factor.

Hence eq^n (15) takes the form

$$\bar{F} = \frac{1}{N}\log\frac{1}{V^N}\left[V^N + \frac{1}{2}N(N-1)\cdot V^{N-2}\int f_{ij}\, d\tau_i \cdot d\tau_j\right] \quad \text{——— (15A)}$$

In order to evaluate the integral, we shall use spherical coordinates. ~~be at the molecule~~ Let the origin of spherical coordinates be at the molecules j and let us assume that the function f_{ij} drops rapidly to zero as inter-molecular distance r_{ij} become large.

$$\begin{aligned} d\tau_i &= dx_i\, dy_i\, dz_i \\ &= dr \cdot r d\theta \cdot r\sin\theta \cdot d\theta\, d\phi \\ &= r^2 dr \sin\theta \cdot d\theta d\phi \end{aligned}$$

Therefore we may write

$$\begin{aligned} \int f_{ij}\, d\tau_i &= \int\int\int f(r)\, r^2 dr \sin\theta \cdot d\theta\, d\phi \\ &= \int_0^\infty f(r)\, r^2 \cdot dr \int_0^\pi \sin\theta \cdot d\theta \int_0^{2\pi} d\phi \\ &= \int_0^\infty f(r)\, r^2 \cdot dr \cdot (2) \cdot 2\pi \\ &= \int_0^\infty f(r) 4\pi r^2 \cdot dr = \beta \quad \text{(suppose)} \quad \text{——— (16)} \end{aligned}$$

The integral β has the dimension of the position at molecule i, at least to within a few angstorm of the wall of the gas containing vessel, so that

$$\iint f_{ij}\, d\tau_i\, d\tau_j = \int \beta\, d\tau_j = \beta V \qquad (17)$$

Now eqn (15) may be written as,

$$\bar{F} = \frac{1}{N} \log \frac{1}{V^N} \left[V^N + \frac{1}{2} N(N-1) V^{N-2} \cdot \beta V \right]$$

$$\bar{F} = \frac{1}{N} \log \frac{1}{V^N} \left[V^N \left\{ 1 + \frac{1}{2} N^2 \frac{\beta}{V} \right\} \right]$$

$$\because \log\left(1 + \frac{N^2\beta}{V}\right) \approx \frac{1}{2} N^2 \beta / V$$

Similarly (15A) may be written as,

$$\bar{F} = \frac{1}{N} \log \frac{1}{V^N} \left[V^N + \frac{N^2 V^{N-1}}{2V} \int f(r)\, d^3 r \right]$$

taking V^N as common,

$$\bar{F} = \frac{1}{N} \log \left[1 + \frac{N^2}{2V} \int f(r)\, d^3 r \right]$$

where we have approximate the number of pairs $N(N-1)/2$ by $N^2/2$ for large N, evaluating the derivative $\frac{\partial \bar{F}}{\partial V}$ to $O(F)$, we find $(\partial \bar{F}/\partial V)$ to $O(F)$

We find, $$\left(\frac{\partial \bar{F}}{\partial V}\right) = \frac{-N}{2V^2} \int f(r)\, d^3 r \qquad (18)$$

The eqⁿ of state, eqⁿ (11) now becomes by putting eqⁿ (18),

$$\frac{PV}{NkT} = 1 - \frac{N}{2V}\int f(r)\, d^3r \qquad \text{——— (19)}$$

A phenomenological eqⁿ of state for the real gas is - Vander - waals eqⁿ, which reads,

$$\left(P + \frac{a}{V^2}\right)(V-b) = NkT \qquad \text{——— (20)}$$

where 'a' and 'b' are constants for a given gas, we can rewrite this eqⁿ of state as,

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

$$= \frac{NkT}{V}\left(1 + \frac{b}{V}\right) - \frac{a}{V^2} + o\left(\frac{1}{V^3}\right)$$

$$= \frac{NkT}{V} + \frac{bNkT - a}{V^2} + \text{------}$$

——— (21)

To see how this compare with eqⁿ (19), we need to have an expression for $f(r)$, we make the approximation,

$$f(r) = \begin{cases} -1, & \text{for } r < \sigma \\ -(1 - e^{-\beta V(r)}), & \text{for } r > \sigma \end{cases}$$

——— (22)

leading to

$$\int f(r)\, d^3r = -\frac{4}{3}\pi\sigma^3 - 4\pi \int_0^\infty r^2 \left(1 - e^{-\beta V(r)}\right) \cdot dr$$

put this value in (19)

and,

$$\frac{PV}{NkT} = 1 + \frac{2\pi}{3}\frac{N}{V}\sigma^3 - \frac{2\pi N}{V}\int_0^\infty r^2 \left(e^{-\beta V(r)} - 1\right) \cdot dr$$

or

$$\frac{PV}{NkT} = 1 + \frac{2\pi}{3}\frac{N}{V}\sigma^3 - \frac{2\pi N}{VkT}\int \{-v(r)\} r^2 \cdot dr$$

——— (23)

for weak potentials, i.e., $v \ll kT$.

note that $-\int v(r)\, r^2 \cdot dr$ is positive definite.

since beyond σ, $v(r)$ is attractive.

Thus an expansion in inverse powers of V, eqn (23) has the same structure as vander waals eqn to the lowest order, then we identify,

$$b = \frac{2}{3}\pi N^3 \sigma \qquad \text{——— (24a)}$$

& $a = 2\pi N^2 \int_0^\infty \{-v(r)\} r^2 . dr$ ——— (24)

If we could retain all powers of f, i.e. considered arbitrarily strong potentials. We would generate an eqn of state of the form

$$\frac{P}{nkT} = 1 + A_1 n + A_2 n^2 + \text{-------} \quad \text{——— (25)}$$

where $n = N/V$ is the no. of density.

The various $A_1, A_2, \text{----}$ etc. are known as "virial coefficient". The interesting feature is that, A_1 has a zero at a finite temp. This has verified experimentally.