CHEMICAL EQUILIBRIUM

Consider an arbitrary chemical reaction;

$$\nu_1 \overline{X}_1 + \nu_2 \overline{X}_2 \rightleftharpoons \nu_3 \overline{X}_3 + \nu_4 \overline{X}_4 \qquad \nu_i \text{ all positive}$$

OR, for arbitrary n;

$$\sum_{i=1}^{n} \nu_i \overline{X}_i = 0 \quad \text{where} \quad \begin{cases} \nu_i > 0 \text{ products} \\ \nu_i < 0 \text{ reactants} \end{cases}$$

Example! $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

$\nu_{H_2} = -1$

$\nu_{O_2} = -\frac{1}{2}$

$\nu_{H_2O} = +1$

So

$$\sum \nu_i \overline{X}_i = H_2O - H_2 - \frac{1}{2}O_2 = \phi.$$

Can use this formalism for expressions like

$$\Delta H_R^\theta = \sum \nu_i \Delta H_f^\theta$$

$$\Delta S = \int \nu_i C_{p_i} dT$$

etc.

Extent of Reaction

At an arbitrary time τ, the amount, $n_i(\tau)$ present in a reaction is given by;

$$n_i(\tau) = n_i(0) + \nu_i \xi(\tau)$$

$\xi(\tau)$ is the 'extent of reaction' parameter ξ is zero at time ϕ, ie $\xi(0) = \phi$, ξ when one equivalent of reaction has occurred at $\tau = \tau'$, then $\xi(\tau') = 1$.

Criterion for Equilibrium

We have, for the Helmholtz energy, $A = A(T, V, n, \dots)$

$$dA = -SdT - PdV + \sum \mu_i dn_i = \sum \mu_i dn_i \quad \text{const } T,V$$

$$\mu_j = \left(\frac{\partial A}{\partial n_j} \right)_{T,V,n_{i\neq j}}$$

Now since,

$$n_i(\tau) = n_i(0) + \nu_i \xi(\tau).$$

Then,

$$dn_i = \nu_i d\xi \quad \text{all } i$$

and, at const. T, V,

$$dA = \sum \mu_i dn_i = \sum \mu_i \nu_i d\xi \quad \text{or} \quad \left(\frac{\partial A}{\partial \xi}\right)_{T,V} = \sum \mu_i \nu_i$$

$\xi(\tau)$ is a very useful function which allows a natural entry into non-equilib. Thermo. Since we can define

$$\text{Reaction rate} \equiv \overline{\nu} = \frac{d\xi(\tau)}{d\tau}$$

The condition for equilibrium for a ~~chemical~~ chemical reaction is:

$$\rightarrow \left(\frac{\partial A}{\partial \xi}\right)_{T,V} = \sum \mu_i \nu_i = \phi \quad \text{const. } T, V; \quad \mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j \neq i}}$$
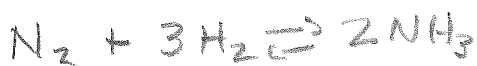
OR, alternatively,

$$dG = -SdT + Vdp + \sum \mu_i dn_i = \sum \mu_i dn_i \quad \text{const } T, P$$

so, by analogy with $\Delta G_{T,P} = \sum \mu_i \nu_i = 0$

$$\rightarrow \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum \mu_i \nu_i = \phi \quad \text{const } T, P; \quad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}$$

Example

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Equilibrium implies that:

$$\sum \nu_i \mu_i = 2\mu_{NH_3} + 3\mu_{H_2} - \mu_{N_2} = 0$$

Equilibrium Constant for an Ideal Gas Mixture

For an N component system all of which are independent (ideal gas mixtures only) we can write [*] for the system P.f. (the various species are distinguishable) — like $Q = q_A \cdot q_B \cdots$

$$\underbrace{Q(N_1, N_2, \cdots T, V)}_{\text{P.f. for multiple disti. species}} = \underbrace{\prod_i Q(N_i, T, V)}_{\text{Distr. system! P.f.'s}} = \underbrace{\prod_i q_i^{N_i}(V,T) / N_i!}_{\text{Indist. species for each}}$$

where q_i is the cmB particle P.f. for component i.

$$A = -kT \log Q = -kT \log \prod_i Q(N_i, T, V)$$

$$= -kT \sum_i \log \frac{q_i^{N_i}(T,V)}{N_i!} \qquad (\log \prod = \sum_i \log s)$$

Now $dA = -SdT - PdV + \sum \mu_i dN_i$ so we have

$$\mu_j = \left(\frac{\partial A}{\partial N_j}\right)_{i \neq j, T, V} = -kT \sum_i \frac{\partial}{\partial N_j}\left[N_i \log q_i - N_i \log N_i + N_i\right]$$

OR
$$\mu_j = -kT \log \frac{q_j(T,V)}{N_j} \qquad \text{for the } j\text{th component}$$

On the previous page we had for our condition for equilibrium

$$\sum_i \mu_i \nu_i = \sum_i \nu_i \left(-kT \log \frac{q_i}{N_i}\right) = \phi \quad \text{const. } T, V$$

Expanding the RHS gives;

$$\prod_i N_i^{\nu_i} = \prod_i q_i^{\nu_i} \qquad \text{where the } \nu_i \text{ are signed.}$$
AND N_i is the no. of particles of the ith component in the gas.

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[*] Note: we assume the gases etc. to be independent in the _initial_ and _final_ states. The fact that they react to produce a product and are certainly not independent then has no bearing on this assump.

This expression

$$\prod_i N_i^{\nu_i} = \prod_i q_i^{\nu_i}$$

looks a lot like an equilibrium constant expression.

Suppose we now define a concentration or particle density by the equation,

$$\rho_j \equiv \frac{N_j}{V} \quad - \text{concentration of the } j^{th} \text{ species}$$

which we substitute into the previous equation to get

$$\prod_i N_i^{\nu} = \prod_i \rho_i^{\nu_i} V_i^{\nu_i} = \prod_i q_i^{\nu_i} \quad OR \quad \prod_i \left(\frac{N_i}{V_i}\right)^{\nu_i} = \prod_i \left(\frac{q_i}{V_i}\right)^{\nu_i}$$

OR rearranging we have equilibrium constant, K_c

$$\prod_i \rho_i^{\nu_i} = \prod_i \left(\frac{q_i}{V}\right)^{\nu_i} \equiv K_c(T) \quad \text{which is justified}$$

since K_c is usually defined as

$$K_c(T) = \frac{\prod_i a_i^{\nu_i} (Prod)}{\prod_i a_i^{\nu_i} (React)} = \prod_i a_i^{\nu_i} (equilib) \approx \prod_i [conc.]^{\nu_i}$$

$$\underbrace{\qquad\qquad}_{\text{all } \nu_i > 0} \qquad \underbrace{\qquad}_{\nu_i \text{ are signed}} \qquad \underbrace{\qquad}_{\text{ideal gas mixture}}$$

Thus:

$$\longrightarrow K_c(T) = \prod_i \left(\frac{q_i}{V}\right)^{\nu_i} \quad OR$$

$$\longrightarrow K_p(T) = (kT)^{\Delta\nu} K_c(T) \quad \text{where } K_p \equiv \prod_i P_i^{\nu_i} \quad \begin{array}{l} \text{Meas.} \\ P_i - \text{press of the} \\ i^{th} \text{ gas in the} \\ \text{mixture} \end{array}$$

and, $\Delta\nu = \sum_i \nu_i = \sum_i \nu_i (Prod) - \sum_i \nu_i (React's)$

Summary

Condition for Equilib for a chemical Reaction

$$dA = \sum_i \mu_i \, dn_i \quad \text{const } T, V, n_{i \neq j}$$

$$dn_i = \nu_i \, d\xi_i$$

$$\left(\frac{\partial A}{\partial \xi}\right)_{T,V} = \sum_i \mu_i \nu_i = 0 \quad \text{const } T, V, \quad \mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j \neq i}}$$

Equilibrium Const

For an arbitrary reaction

$$\sum_i \nu_i \overline{X}_i = 0 \quad \begin{cases} \nu_i > 0 \quad \text{Products} \\ \nu_i < 0 \quad \text{reactants} \end{cases}$$

we have

$$K_c = \frac{\prod_i a_i^{\nu_i} (Prod)}{\prod_j a_j^{\nu_j} (React)} = \prod_i a_i^{\nu_i} (equilib) = \prod_i \{conc\}_i^{\nu_i}$$

Partition Function

$$Q(N_1, N_2, \ldots T, V) = \prod_i Q(N_i, T, V) = \prod_i \frac{q_i^{\nu_i}(V,T)}{N_i!}$$

so

$$A = -kT \sum_i \frac{\log q_i^{N_i}(T,V)}{N_i!} \quad \text{as } A = -kT \log Q$$

Introduction of The P.F into K_c

$$\mu_j = \left(\frac{\partial A}{\partial N_j}\right)_{T,V,N_{j \neq i}} = -kT \log \frac{q_j(T,V)}{N_j}$$

But

$$\sum_i N_i \mu_i = \sum_i \nu_i \left(-kT \log \frac{g_i}{N_i} \right) = 0 \qquad const, T,V.$$

Exanding gives:

$$\prod_i N_i^{\nu_i} = \prod_i g_i^{\nu_i}$$

N_i = # particles of the ith component in the gas phase

Now defining a conc. term $\rho_i = \frac{N_i}{V}$ we can write

$$K_c = \prod_i [conc]^{\nu_i} = \prod_i \left(\frac{g_i}{V} \right)^{\nu_i} \qquad OR$$

$$K_p = (kT)^{\Delta\nu} K_c = (kT)^{\Delta\nu} \prod_i \left(\frac{g_i}{V} \right)^{\nu_i}$$

And thus we have the saga of the equilibrium constant and the partition function.

Examples

1) Dimerization of Sodium vapor at 1000k; 1atm.

$$2Na \rightleftarrows Na_2 \qquad \upsilon_{Na_2} = +1 ; \quad \upsilon_{Na} = -2 ; \quad \Delta\upsilon = \sum \upsilon_i = 1-2 = -1$$

$$K_p(T) = \frac{P_{Na_2}}{P_{Na}^2} = (kT)^{\Delta\upsilon} K_c(T)$$

$$K_c(T) = \prod \left(\frac{q_i}{V}\right)^{\upsilon_i} \quad so$$

$$K_p(T) = (kT)^{-1} K_c = \frac{1}{kT}\left(\frac{q_{Na_2}/V}{q_{Na}^2/V^2}\right)$$

Now :

$$q_{Na}(T,V)_{\substack{monoatomic \\ gas}} = q_T V q_{elec}$$

$$q_{Na_2}(T,V)_{\substack{diatomic \\ gas}} = q_T V \left(\frac{T}{2\theta_r}\right)\left(1 - e^{-\theta_r/T}\right)^{-1} e^{D_0/kT}$$

↑ $\sigma = 2$ homonuclear diatomic is used because There are extensive tables of D_0 available.

where $D_0 = D_e - \frac{1}{2}h\nu$ and

In addition we have:

Na

$MW = 23$, $q_{elec.} = w_{e1} + w_{e2} e^{-\epsilon_{e2}/kT} \approx w_{e1}$

where $w_{e1} = 2$, $w_{e2} = 2$, $\underline{\epsilon_{e2} = 16956.183 cm^{-1}}$

<u>can ignore</u>

Na_2

$\theta_r = 229°K$; $\theta_r = 0.221k$, $D_0 = 17.3$ kcal/mole

Calculation gives a K_p value of

$$K_p = 0.50 \text{ atm}^{-1} = 0.0049 \text{ kPa}^{-1}$$

which is in fair agreement w̄ the experimental value of 0.47 atm^{-1}. At $1200°K$, $K_p(calc) = 0.11$ vs 0.10 exp. Since measurements of K_p etc. are difficult, $K_p(calc.)$ is usually considered more accurate.

2) Reaction Involving Polyatomic Molecules

$$H_2 + \tfrac{1}{2}O_2 \rightleftharpoons H_2O$$

$$K_p = \frac{q_{H_2O}/V}{(kT)^{1/2}(q_{H_2}/V)(q_{O_2}/V)^{1/2}}$$

$$\frac{q_{H_2}}{V} = \left(\frac{2\pi m_{H_2}kT}{h^2}\right)^{3/2}\left(\frac{T}{\sigma_{H_2}\Theta_{r,H_2}}\right)\left(1-e^{-\Theta_{v,H_2}/T}\right)^{-1}e^{D_{0,H_2}/RT}$$

$$= 2.80\times10^{26} e^{D_{0,H_2}/RT}$$

$$\frac{q_{O_2}}{V} = \left(\frac{2\pi m_{O_2}kT}{h^2}\right)^{3/2}\left(\frac{T}{\sigma_{O_2}\Theta_{r,O_2}}\right)\left(1-e^{-\Theta_{r,O_2}/T}\right)^{-1}3e^{D_{0,O_2}/RT}$$

$$= 2.79\times10^{30} e^{D_{0,O_2}/RT}$$

$$\frac{q_{H_2O}}{V} = \left(\frac{2\pi m_{H_2O}kT}{h^2}\right)^{3/2}\frac{\pi^{1/2}}{\sigma_{H_2O}}\left(\frac{T^3}{\Theta_A^{H_2O}\Theta_B^{H_2O}\Theta_C^{H_2O}}\right)^{1/2} *$$

$$\prod_{j=1}^{3}\left(1-e^{-\Theta_{v,j,H_2O}/T}\right)^{-1}e^{D_{0,H_2O}/RT}$$

$$= 5.33\times10^{29} e^{D_{0,H_2O}/RT}$$

<u>Note</u>

$\sigma_{H_2} = \sigma_{O_2} = 2$

$\sigma_{H_2O} = 2$

The computed value for k_p is 4.8×10^5 $atm^{-1/2}$ at $1500°K$, again, in fair agreement w $k_p(meas) = 5.7$ $atm^{-1/2}$. Here the experimental values are probably better. Improved results require correcting for centrifugal distortion & the use of the Morse potential.

Thermodynamic Tables

Most tables are based in large part on s.m. calculations based on spectroscopic data + certain calorimetric data such as enthalpies of phase transitions etc. We wish to derive a relationship between certain quantities in the tables and our partition functions.

From

1) $\sum' \nu_i \mu_i = 0$ const T, V etc.

we have

$$\mu_i = \mu_i^\ominus + KT \log a_i = \mu_i^\ominus + KT \log \frac{f_i}{f_i^\ominus} = \mu_i^\ominus + KT \log f_i \text{ as } f_i^\ominus \equiv 1$$

since the s.s. (ie $a_i = 1$) occurs when $f_i = f_i^\ominus = 1$.

If the gas is ideal $f_i = P_i$ for all P_i so

2) $\mu_i = \mu_i^\ominus + KT \log P_i$

Eqn 2 into 1 gives

$$\sum \nu_i \mu_i^\ominus = -KT \sum \log P_i^{\nu_i} = -KT \log \prod P_i^{\nu_i}$$

where, defining

$$\Delta G_{T,P}^\ominus \equiv \sum \nu_i \mu_i^\ominus = \Delta \mu^\ominus$$

$$K_P \equiv \prod_i P_i^{\nu_i} \text{ where } \nu_i \text{ carry their own sign and } P_i \text{ are equilib pressures.}$$

so

3) $\Delta G_{T,P}^\ominus = -KT \log K_P = \Delta \mu^\ominus$

which is the usual expression for K_P.

Now, as we have seen, for an arb. ideal gas (P77)

$$\mu = -kT \log\left(\frac{q}{N}\right) \quad \text{ideal gas, OR}$$

4) $\mu = -kT \log\left(\frac{q}{V} \cdot \frac{V}{N}\right) = -kT \log\left(\frac{q}{V} \cdot kT\right) + kT \log P \quad \text{using } \frac{V}{N} = \frac{kT}{P}$

which in comparison w equ 2 identifies

5) $\mu^{\ominus}(T) = -kT \log\left(\frac{kTq}{V}\right)$ ie the stn. chem. pot. for the ideal gas and, incedentally equals zero for any element in its stn. state irrespective of T, by convention.

In (4), P is usually tabulated in atm. For SI. units in 4, we mult. P by $101325 \equiv C$ or alternatively divide q by C ie.

6) $\mu \text{(SI. units)} = -kT \log\left(\frac{q kT}{CV}\right) + kT \log P\text{(atm)}$

ENERGY ZERO

Our previous zero's include:

The value $\epsilon = 0$ for translation (n=0), rotation (J=0) and electronic ($\epsilon_0 = 0$) and ½ hv for vibration (n=0). In addition we chose the isolated g.s. atoms at ∞ when studying Xal's in which case we set $\epsilon_{el}\text{(elec.)} = -D_e$

The problem is that we would like to tabulate $\Delta G^{\ominus}$ data indept. of energy zero's. We do this by first separating the portions of the P.f. which depend on an arbitrary zero from those which use $\epsilon = 0$ as their minimum.

We can ignore $q_T(T,V)$ & q_R since these are already referenced to $\epsilon = 0$. We then write for q_V

$$q_V(T) = \prod_i \frac{e^{-\theta_{v,i}/2T}}{(1-e^{-\theta_{v,i}/T})} = \prod_i (1-e^{-\theta_{v,i}/T})^{-1} \cdot \underbrace{e^{-\Sigma \theta_{i,v}/2T}}_{\text{g.s. Term}}$$

$$= q_V^0(T) e^{-\frac{1}{2}\sum_i \frac{h\nu_i}{kT}}$$

where $\theta_V = \frac{h\nu}{k}$ & $q_V^0(T)$ is the $\epsilon = 0$ referenced p.f for vib.

and for $q_e(T)$

$$q_e = W_{e1} e^{-\epsilon_{e1}/kT} + W_{e2} e^{-\epsilon_{e2}/kT} + \cdots$$

Now usually we choose the btm. of the well as the energy zero rel. to ∞ so

$$\epsilon_{e1} = -D_e \quad \text{for the ground elec. state}$$

so

$$q_e = W_{e1} e^{D_e/kT} + W_{e2} e^{-\epsilon_{e2}/kT} + W_{e3} e^{-\epsilon_{e3}/kT} + \cdots$$

where we can define:

$$\Delta \epsilon_{ei} = \epsilon_{ei} - \epsilon_{e1} = \epsilon_{ei} + D_e \quad \text{so} \quad \epsilon_{ei} = \Delta \epsilon_{ei} - D_e$$

Hence

$$q_e = W_{e1} e^{D_e/kT} + W_{e2} e^{D_e/kT} \cdot e^{-\Delta \epsilon_{e2}/kT} + W_{e3} e^{D_e/kT} e^{-\Delta \epsilon_{e3}/kT} + \cdots$$

$$= e^{D_e/kT} \left[W_{e1} + W_{e2} e^{-\Delta \epsilon_{e2}/kT} + e^{-\Delta \epsilon_{e3}/kT} + \cdots \right]$$

$$= e^{D_e/kT} q_e^0(T) \quad \text{where all } \Delta \epsilon_{e,i} \text{ are now referenced to } \epsilon_{e1} = 0$$

We can now write

$$q(T,V) = q_T^0 \cdot q_r^0 \cdot q_v^0 \cdot q_e = e^{\overbrace{D_e/kT - \frac{1}{2}\sum^i \frac{h\nu_i}{kT}}^{\text{energy zero scale factor}}} \prod_{\text{modes}} q_i^0$$

where each q^0 has $\epsilon = 0$ as its reference.

More generally we can define an arbitrary zero which may differ from $D_0 = [D_e - \frac{1}{2}\sum h\nu_i]$ & call it simply ϵ^0

Hence, for each molecule we have

$$q(T,V) = \prod_{\text{modes}} q_i^0 \cdot e^{-\epsilon^0/kT}$$

In this case, (6) reads

7) $\mu - \epsilon_0^0 = - kT \log\left(\dfrac{g^0 kT}{cv}\right) + kT \log P(atm)$ ϵ_0 in Joules.

where we see that, since $\displaystyle\lim_{T \to 0} T \log T \to 0$, then

$\displaystyle\lim_{T \to 0} \mu \to \epsilon_0^0$ justifying the <u>subscript</u> on ϵ_0^0.

On a molar bases, we have for each pure substance involved in a reaction (since $G_i = \mu_i N$)

8) $G - E_0^0 = - RT \log\left(\dfrac{g^0 kT}{cv}\right) + RT \log P(atm)$

Finally, if we agree to a stn. state we can tabulate $G - E_0^0$ values for computation purposes.

We choose the most stable form of the compound at $P = 1 \times 10^5$ Pa $\equiv 1$bar. as it exists at 25°C. The chemical potential of this compound in this 25°C "state" is zero & This is then true at all temperatures for $P = 1$ bar. Hence, $H_2(g)$ has a zero $\mu = \mu^0$ at $f = 1$ or $P = 1$ (hypothetical I.G.) at all temperatures. Consistent w this convention is setting $E_0^0 = 0$ at $T = 0$ for <u>elements</u> in their stn. state. This follows because by convention μ(element) = 0 in the s.s. at all temp.'s

Since from (7), The RHS $\to 0$ as $T \to 0$ and if by convention $\mu = 0$ then ϵ_0^0 (or E_0^0) = 0 for consistency,

Thus one may tabulate $G - E_0^0$ or better $(G - E_0^0)/T$ which varies more slowly vs T together w E_0^0 ($\equiv 0$ for elements) which represents the enthalpy of formation H_0^0 (T=0) at 0°K. rel. to the elem. at 0°K. for any compound of choice $\Delta H_f^0 (0) \equiv E_0^0$ as $H_0^0 \equiv E_0^0$ at 0°K since as $T \to 0$, $PV \to 0$ for any gas. E_0^0 will also represent the heat of vapourization or sublimation of an element not in its s.s. (see text)

For our ideal gases then, in their s.s. (from 8)

$$G^0 - E_0^0 = -RT \log \left\{ \frac{\mathcal{S}^0}{V} \cdot \frac{kT}{c} \right\} \quad \text{since} \quad P = 1 \text{ atm by defn.}$$

and hence $G^0 - E_0^0$ is indept. of the energy zero. Since the RHS refers to P.f.'s referenced to zero energy at $T = 0K$.

We then have:

$$\Delta G^\ominus = \sum \nu_i \mu_i^\ominus = \sum \nu_i G_i^\ominus = -RT \log k_P$$

We may also write:

$$-R \log k_P = \sum' \nu_i \left(\frac{G_i^0 - E_{0i}^0}{T} \right) + \frac{1}{T} \sum' \nu_i E_{0,i}^0 \qquad \nu_i - \begin{array}{l} + \text{ prod} \\ - \text{ react.} \end{array}$$

$$= \Delta \left(\frac{G^0 - E_0^0}{T} \right) + \frac{\Delta E_0^0}{T}$$

where $\dfrac{G^0 - E_0^0}{T}$ is tabulated vs T.

Study problems in text.

Quantum Statistics of Non-Interacting Dependent Particles

Since all real particles are either Bosons or Fermions, depending on specific symmetry requirements, we need to develop this topic. As an alternative to deriving the statistics from a knowledge of the degeneracy much as we did for Boltzmann statistics, we will use the GPF which is a more direct approach.

As we have seen

$$\Xi(T,V,\mu) = \sum_{N=0}^{\infty} {\sum_{j(\text{system states})}}' e^{-\rho E_j(N,V)} \cdot e^{\beta N \mu}$$

all const at equilib.
N_j & E_j can vary

$$= \sum_{N=0}^{\infty} {}' Q(N,V,T) e^{\beta \mu N} \qquad Q - \text{canonical P.f.}$$

$$= \sum_{N=\emptyset}^{\infty} \lambda^N Q(N,V,T) = \sum_{N=0}^{\infty} {}' \lambda^N(\mu) {\sum_{\{n_i\}}}' e^{-\beta \sum_i n_i \epsilon_i} \qquad \text{where } \lambda = e^{\mu \beta}$$

ie, the absolute activity

$$E_j(N,V) = {\sum_i}' n_i^j \epsilon_i$$

which emphasis that the sum is not independent of N, ie, the value of N in the first sum determines the values for the possible set of $\{n_k\}$ values, ie the set of distribution numbers for which

$${\sum_i}' n_i = N \text{ and } \sum_i n_i \epsilon_i = E.$$ Here n_i^j denote the number of particles in the ith particle state with energy ϵ_i of the jth system state.

We can now rewrite the expression

$$\Xi = \sum_{N=0}^{\infty} \lambda^N \sum_{\{n_k\}} e^{-\beta \sum_i n_i \epsilon_i} \quad \text{and} \quad \sum_i n_k = N \quad \text{where } N \text{ is a variable,}$$

$$\lambda = e^{\beta \mu}$$

as

$$\Xi = \sum_{N=0}^{\infty} \sum_{\{n_k\}} \lambda^{\sum_i n_i} e^{-\beta \sum_i n_i \epsilon_i} = \sum_{N=0}^{\infty} \sum_{\{n_k\}} \prod_k^{\substack{\text{particle}\\\text{states}}} \left(\lambda e^{-\beta \epsilon_k}\right)^{n_k}$$

$$= \sum_{n_1=0}^{n_1 \max} \sum_{n_2=0}^{n_2 \max} \cdots \prod_k \left(\lambda e^{-\beta \epsilon_k}\right)^{n_k} = \sum_{n_1=0}^{n_1 \max}\left(\lambda e^{-\beta \epsilon_1}\right)^{n_1} \sum_{n_2=0}^{n_2 \max}\left(\lambda e^{-\beta \epsilon_2}\right)^{n_2} \cdots$$

OR

$$\Xi(V,T,\mu) = \prod_{k=1}^{\infty} \sum_{n_k=0}^{n_k \max} \left(\lambda e^{-\beta \epsilon_k}\right)^{n_k} \quad \text{for a final result}$$

Comment: We need to justify the equality

$$\sum_{N=0}^{\infty} \sum_{\{n_k\}} \prod_{k=1}^{\substack{\text{particle}\\\text{states}}} \left(\lambda e^{-\beta \epsilon_k}\right)^{n_k} = \prod_{k=1}^{\infty} \sum_{n_k=0}^{n_k \max} \left(\lambda e^{-\beta \epsilon_k}\right)^{n_k}$$

(no. particles in the kth particle state)

Assume 4 particles distributed over 2 particle states, ϵ_1 & ϵ_2, where $n_k(\max) = 2$. Then, defining $a_k = \lambda e^{-\beta \epsilon_k}$ we have

$$\sum_{N=0}^{4} \sum_{\{n\}} \prod_{k=1}^{2} a_k^{n_k} \neq \prod_{k=1}^{2} \sum_{n_k=0}^{2} a_k^{n_k}$$

sum over all valid sets $\{n_k\}$

Looking first at the RHS expression, we have

$$\prod_{k=1}^{2} \sum_{n_k=0}^{2} a_k^{n_k} = \underbrace{(a_1^0 + a_1^1 + a_1^2)}_{\substack{k=1, n_k=0,1,2 \\ \text{particle state 1}}} \underbrace{(a_2^0 + a_2^1 + a_2^2)}_{\substack{k=2, n_k=0,1,2 \\ \text{particle state 2}}}$$

$$= 1 + a_1 + a_2 + a_1^2 + a_1 a_2 + a_2^2 + a_1 a_2^2 + a_1^2 a_2^2 + a_1^2 a_2$$

For the LHS, we have:

$$\sum_{N=0}^{4} \sum_{\{n\}=\phi}^{} \prod_{k=1}^{2} a_k^{n_k}$$

which requires we look at all acceptable $\{n_k\}$ values consistent w the fact that $N = 0,1,2,3,4$ & $\sum n_i = 4$ and that $n_k \, max = 2$ ie, no more than 2 particles/state.

We have

N	n_1	n_2
0	ϕ	ϕ
1	1	0
	0	1
	1	1
2	2	0
	0	2
3	2	1
	1	2
4	2	2

Note that:
$n_1 = \phi$, $n_2 = 3$ or $n_1 = 1$ $n_2 = 3$ are not acceptable when $N = \sum n_i = 3$ or 4 as $n_j (max) = 2$.

So Now ⊛

$$\sum_{N=0}^{4} \sum_{\substack{n_1, n_2 \\ \sum n_i = 4}} \prod_{k=1}^{2} a_k^{n_k} = \sum_{i}^{4} a_1^{n_1} a_2^{n_2}$$

$\{n_1, n_2\} = 0,1,2,3,4, \; \xi_i \; n_1(max) = n_2(max) = 2$
corresponding to $N = \emptyset, 1, 2, 3, 4$

$$= \sum_{n_1=0}^{2} a_1^{n_1} \sum_{n_2=0}^{2} a_2^{n_2} \qquad a_k = \lambda e^{-\beta \epsilon_k}$$

$$= \left(a_1^0 + a_1^1 + a_1^2\right)\left(a_2^0 + a_2^1 + a_2^2\right)$$

which is identical to the RHS.

OR using ⊛ directly we get

$$a_1^0 a_2^0 + a_1^0 a_2^1 + a_1^1 a_2^0 + a_1^1 a_2^1 + a_1^2 a_2^0 + a_1^0 a_2^2 + a_1^1 a_2^2 + a_1^2 a_2^1 + a_1^2 a_2^2$$

which, if factored gives the same thing as the RHS

Conclusion

We can now write:

$$\Xi = \prod_{k=1}^{\infty} \sum_{n_k=0}^{n_k \, max} \left(\lambda e^{-\beta \epsilon_k}\right)^{n_k}$$

where n_k is the number of particles in the kth particle state and depends on the nature of the particles of interest.

Fermi - Dirac Statistics

Here, according to the Pauli Exclusion Principle, $n_k = 0$ or 1 so $n_k(\max) = 1$ and $\left(\lambda = e^{\beta\mu}\right)$

$$\Xi_{F.D.} = \prod_K^\infty \sum_{n_K=0}^1 (\lambda e^{-\beta\epsilon_K})^{n_{K_1}}$$

$$= \prod_K \left[(\lambda e^{-\beta\epsilon_K})^0 + (\lambda e^{-\beta\epsilon_K})^1\right]$$

$$= \prod_K (1 + \lambda e^{-\beta\epsilon_K})$$

Bose Einstein Statistics

Here, $n_K = 0$ to $n_K = N = \infty$ so

$$\Xi_{BE} = \prod_K^\infty \sum_{n_K=0}^\infty (\lambda e^{-\beta\epsilon_K})^{n_K} \quad \text{and since } \sum_{J=0}^\infty x^J = \frac{1}{1-x} \text{ we have}$$

$$\Xi_{BE} = \prod_K^\infty (1 - \lambda e^{-\beta\epsilon_K})^{-1} \quad \text{for } \lambda e^{-\beta\epsilon_K} < 1$$

OR, for both statistics, we have:

$$\Xi = \prod_K^\infty (1 \pm \lambda e^{-\beta\epsilon_K})^{\pm 1} \begin{cases} + & FD \\ - & BE \end{cases}$$

where Ξ is a system P.f. in terms of particle eigenstates. There is no equivalent single particle P.f. equivalent to g^i for qtm. statistics.

Thermodynamic Functions

From

$$d(PV) = SdT + Nd\mu + PdV \qquad (P13,21)$$

we have

$$\bar{\Pi}_{thermo.} = N = \left(\frac{\partial(PV)}{\partial\mu}\right)_{T,V} \qquad \text{and}$$

$$PV = kT\log\Xi = kT\log\left[\prod_k (1 \pm \lambda e^{-\beta\epsilon_k})^{\pm 1}\right] \quad \text{and}$$

$$\lambda = e^{\mu/kT} \quad \text{absolute activity}$$

So

$$\bar{N} \equiv N = \sum_k \bar{C}_k = kT\left(\frac{\partial\log\Xi}{\partial\mu}\right)_{V,T} = \lambda\left(\frac{\partial\log\Xi}{\partial\lambda}\right)_{V,T}$$

1) $$= \sum_k \frac{\lambda e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}} = \text{AVG. NO. PARTICLES IN A SYSTEM}$$

Thus, the average occupancy of the kth particle state is:

2) $$\bar{C}_k = \frac{\lambda e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}} \quad \text{and where} \quad \bar{C}_k = \eta_{k,N} \quad \eta_k = \begin{array}{l}\text{prob. of the} \\ k^{th} \text{ state} \\ \text{being occupied}\end{array}$$

from which it follows:

$$\bar{E}_{SYS} = N\bar{\epsilon} = N\sum_k \eta_k \epsilon_k = \sum_k N\eta_k \epsilon_k = \sum_k \bar{C}_k \epsilon_k \quad OR$$

3) $$\bar{E}_{SYS} = \sum_k \frac{\lambda \epsilon_k e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}} = \text{AVG. ENERGY OF A SYSTEM}$$

4) $$PV = kT\log\Xi = \pm kT\sum_k \log[1 \pm \lambda e^{-\beta\epsilon_k}]$$

Note that the probability of the kth quantum state is:

5) $$\eta_k = \frac{\bar{C}_k}{N} = \frac{\lambda N^{-1} e^{-\beta\epsilon_k}}{1 \pm \lambda e^{-\beta\epsilon_k}} = \begin{array}{l}\text{PROB. OF THE } k^{th} \text{ PARTICLE} \\ \text{STATE}\end{array}$$

CLASSICAL LIMIT

The condition for __Boltzmann (corrected)__ statistics to apply was that $\bar{c}_j \ll 1$ ie, when the average particle state was unoccupied, a condition that held in the limit of high temperature and low density.

Specifically, since

$$\bar{c}_j = \frac{\lambda e^{-\beta \varepsilon_j}}{1 \mp \lambda e^{-\beta \varepsilon_j}}$$

then the condition on $\bar{c}_j$, ie

$\bar{c}_j \ll 1$ or $\bar{c}_j \to \phi$ is achieved when

$\lambda \to \phi$ implying, since $\lambda = e^{\beta \mu}$ that $\mu \to -\infty$.

Example

For an ideal gas, we have:

$$\mu_{IG}(T, P) = \mu^{\Theta}(T) + KT \log P \quad \text{and}$$

$$\mu^{\Theta}(T) = -KT \log \left(\frac{Q}{N}\right)^* = -KT \log \left[q_{INT} \cdot \frac{1}{\Delta^3 \rho} \right]$$

where $\Delta = \left(\frac{h^2}{2\pi m KT}\right)^{\frac{1}{2}}$ and $\rho = \frac{N}{V}$.

Thus when T or $m \to \infty$, $\Delta \to \phi$ or when $\rho \to \phi$ then $\frac{1}{\Delta^3 \rho} \to \infty$

$\mu \to -\infty$ and $\lambda \to \phi$ as required.

$* \quad \mu(T, P) = -KT \left(\frac{\partial \log Q}{\partial N}\right)_{V, T}$

Thus when λ is small $(\rightarrow \emptyset)$, Eqn 2., p 8.12 becomes:

1) $\bar{c}_k = \dfrac{\lambda e^{-\beta \epsilon_k}}{1 \pm \lambda e^{-\beta \epsilon_k}} \longrightarrow \lambda e^{-\beta \epsilon_k}$ small λ, implying $\bar{c}_k \ll 1$
$(\rightarrow \emptyset)$

Now we get λ by summing as usual, ie

$$\sum_k \bar{c}_k = \sum_k N \eta_k = N = \lambda \sum_k e^{-\beta \epsilon_k} \text{small } \lambda$$

OR

2) $\lambda = \dfrac{N}{\sum e^{-\beta \epsilon_k}}$ when $\lambda \rightarrow \emptyset$

$\bar{c}_k = \lambda e^{-\beta \epsilon_k}$ small λ
$N = \lambda \sum e^{-\beta \epsilon_k}$ " "

So, 2 into 1 gives

$$\dfrac{\bar{c}_k}{N} = \dfrac{e^{-\beta \epsilon_k}}{\underbrace{\sum e^{-\beta \epsilon_k}}_{q}} = \dfrac{\eta_k N}{N} = \eta_k$$ which is the prob. of the kth particle state.

OR prob. of the kth particle$^{\text{state}} \equiv \eta_k = \dfrac{e^{-\beta \epsilon_k}}{q}$ where $q = \sum e^{-\beta \epsilon_k}$ ie
state being occupied   & q is a single particle partition function

Limit BE/FD $\rightarrow$ MB/CMB
$\rho \rightarrow 0$
$T \rightarrow \infty$
$m \rightarrow \infty$
$\bar{c} \ll 1$ or $\lambda \rightarrow \emptyset \Rightarrow \mu^\circ \rightarrow -\infty$

Finally, it is possible to show in the limit of small λ, that

$$\bar{E} = \sum_k \dfrac{\lambda \epsilon_k e^{-\beta \epsilon_k}}{1 \pm \lambda e^{-\beta \epsilon_k}} \longrightarrow \dfrac{\sum_i \epsilon_k e^{-\beta \epsilon_k}}{q} \text{and}$$

$$PV = \pm kT \sum_k \log[1 \pm \lambda e^{-\beta \epsilon_k}] \longrightarrow NkT$$

$$\Xi = \prod_i (1 \pm \lambda e^{-\beta \epsilon_k})^{\pm 1} \longrightarrow \sum_{N=0}^{\infty} Q(N,V,T) \lambda^N \equiv GPF$$

Statistics

$$\Omega_{Boltz} = N! \prod_K (\omega_K)^{n_K} / n_K! \longrightarrow \frac{n_j}{\omega_j} = N e^{-(\epsilon_j - \mu)/kT}$$
(Dist. Particles)   (levels)

$$\Omega_{BE} = \prod_K (n_K + \omega_K - 1)! / [(\omega_K - 1)! \, n_K!] \longrightarrow \frac{n_j}{\omega_j} = \left\{ e^{-(\epsilon_j - \mu)/kT} - 1 \right\}^{-1}$$

$$\Omega_{FD} = \prod_K \omega_K! / [(\omega_K - n_K)! \, n_K!] \longrightarrow \frac{n_j}{\omega_j} = \left\{ e^{-(\epsilon_j - \mu)/kT} + 1 \right\}^{-1}$$

Also, when $\zeta \ll 1$

$$\log \Omega_{BE} = \log \Omega_{FD} = \underbrace{\log [\Omega_{Boltz}/N!]}_{CMB}$$

where $\dfrac{n_j}{\omega_j}$ (CMB) $= e^{-(\epsilon_j - \mu)/kT}$ indist. particles, $\zeta \ll 1$

Comment:

$\lambda = e^{\beta \mu}$ can be used as a measure of the degree of quantum behavior of a system. Specifically,

$\lambda \ll 1$ Classical or near-classical behavior

$\lambda \gtrsim 1$ quantum mechanical behavior.

Weakly Degenerate Ideal Fermi-Dirac Gas

Our basic eqns are now:

$$\Xi(V, T, \lambda) = \prod_{k} \left(1 + \lambda e^{-\beta \epsilon_k}\right)$$

$$N = \sum_{k} \frac{\lambda e^{-\beta \epsilon_k}}{1 + \lambda e^{-\beta \epsilon_k}}$$

$$\overline{n}_k \equiv \overline{c}_k = \frac{\lambda e^{-\beta \epsilon_k}}{1 + \lambda e^{-\beta \epsilon_k}}$$

$$E = \sum \frac{\lambda \epsilon_k e^{-\beta \epsilon_k}}{1 + \lambda e^{-\beta \epsilon_k}}$$

$$PV = kT \sum_{k} \log\left(1 + \lambda e^{-\beta \epsilon_k}\right) \qquad \text{and} \qquad \lambda = e^{\mu/kT}$$

Defn.

A weakly degenerate Fermi gas is one in which λ is small enough that we can expand λ in a series.

The ϵ_k values are the ϵ values for a particle in a box, ie

$$\epsilon_{n_x, n_y, n_z} = \frac{h^2}{8 m V^{2/3}} \left(n_x^2 + n_y^2 + n_z^2\right) \quad n_x, n_y, n_z = 1, 2, \cdots$$

We again treat these energy states as continuous for large V ⊛ (or R = radius of the $1/8$ quadrant) so we have

$$N = 2\pi \left(\frac{2m}{h^2}\right)^{3/2} V \int_0^\infty \frac{\lambda \epsilon^{1/2} e^{-\beta \epsilon}}{1 + \lambda e^{-\beta \epsilon}} d\epsilon$$

$$PV = 2\pi kT \left(\frac{2m}{h^2}\right)^{3/2} V \int_0^\infty \epsilon^{1/2} \log\left[1 + \lambda e^{-\beta \epsilon}\right] d\epsilon$$

where we have used $\phi(\epsilon, \Delta \epsilon) = \frac{4\pi V}{h^3} \left(2m^3 \epsilon\right)^{1/2} d\epsilon$ for the number of states between ϵ & $\epsilon + d\epsilon$, and the recognition that λ is a continuous function of ϵ.

⊛ Not large T as before

Neither of these two integrals can be expressed in closed form so we instead expand the terms $(1 + \lambda e^{-\beta \epsilon})$ & the log() as a power series in λ, and integrate term by term to get

$$\frac{N}{V} = \rho = \frac{1}{\Delta^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \lambda^l}{l^{3/2}} \qquad \text{valid for small } \lambda$$

$$\frac{P}{kT} = \frac{1}{\Delta^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \lambda^l}{l^{5/2}} \qquad '' \qquad '' \qquad ''$$

Our goal now is to solve the $\frac{N}{V} = \rho$ eq'n for λ to get $\lambda = \lambda(\rho)$. This requires reversion of the series in λ.

Assume

$$\lambda = a_0 + a_1 \rho + a_2 \rho^2 + \cdots \qquad \rho - \frac{N}{V} \text{ density}$$

and substitute this into the $\rho = \frac{1}{\Delta^3} \sum$ etc. to get

$$\Delta^3 \rho = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} (a_0 + a_1 \rho + a_2 \rho^2 + \cdots)^l}{l^{3/2}}$$

and find, upon equating like powers of ρ:

$$a_0 = 0$$
$$a_1 = \Delta^3$$
$$a_2 - \frac{a_1^2}{2^{3/2}} = \emptyset \quad \text{so} \quad a_2 = \frac{a_1^2}{2^{3/2}} = \left[\frac{\Delta}{2^{3/2}} \right]^2$$
$$a_3 = \frac{a_1 a_2}{\sqrt{2}} + \frac{a_1^3}{3^{3/2}} \quad \text{etc.}$$

So finally,

$$\lambda = \rho \Delta^3 + \frac{1}{2^{3/2}} (\rho \Delta^3)^2 + \left(\frac{1}{4} - \frac{1}{3^{3/2}} \right) (\rho \Delta^3)^3 + \cdots$$

Which on substitution into the expression (sub. $\lambda = \lambda(\rho)$)

ie, $\dfrac{P}{kT} = \dfrac{1}{\Lambda^3} \displaystyle\sum_{\ell=1}^{\infty} \dfrac{(-1)^{\ell+1}\lambda^\ell}{\ell^{5/2}}$ pressure agin

gives:

$$\frac{P}{kT} = \rho + \frac{\Lambda^3}{2^{5/2}}\rho^2 + \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right)\Lambda^6 \rho^3 + \cdots$$

Which can be compared w/ the usual density series

$$\frac{P}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$$

However, in a $\overset{\text{classical}}{\text{ideal}}$ gas all B_k are $\emptyset$ but in our weakly degenerate IDEAL Fermi gas, the interactions arise due to wave function overlap, ie symmetry effects. Unlike $B_2(T)_{\text{classical}}$ however, where $B_2(T)$ is negative denoting attractive forces, the term Λ^3 is positive implying a repulsive force. Since $B_2 \propto \Lambda^3 \sim \lambda^3_{\text{de Broglie}}$ then the smaller the value of λ, the less influence qtm. effects have - a fact we have already seen because $\lambda \ll$ particle separation was the case for class. statistics. Finally, by a similar analysis, the energy becomes:

$$\bar{E} = \frac{3}{2}NkT\left(1 + \frac{\Lambda^3}{2^{5/2}}\rho + \cdots\right)$$

Note that the leading term is the classical value for $\bar{E}$, ie $\frac{3}{2}NkT$ so everything else is a quantum correction for symmetry effects.

EXTENSION TO AN IDEAL WEAKLY DEGENERATE BOSE GAS

By a similar argument, one can show that

$$\frac{P}{KT} = \rho - \frac{\Lambda^3}{2^{5/2}} \rho^2 + \cdots$$

showing that $B_2(T)$ is negative in contrast w the FD case.

Likewise

$$E = \frac{3}{2} NKT \left(1 - \frac{\Lambda^3}{2^{5/2}} \rho + \cdots \right)$$
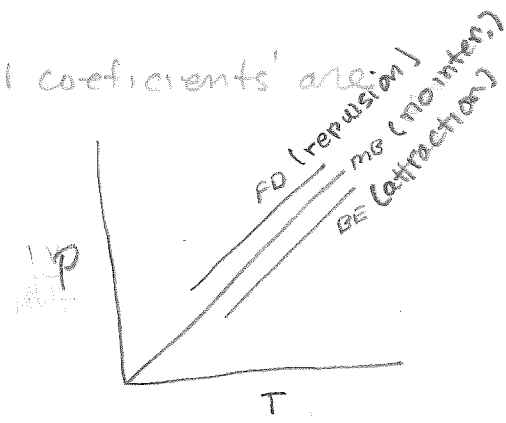
Where the "ideal quantum virial coefficients" are:

$$B_2(T) = 2^{-5/2} \Delta^3$$

$$B_3(T) = \left(\frac{1}{8} - \frac{2}{3^{5/2}}\right) \Delta^6$$

etc.

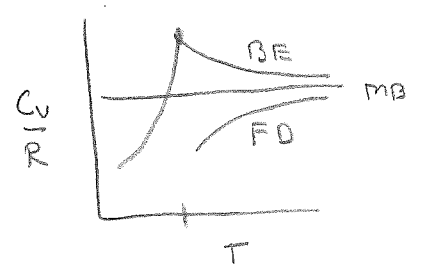Since $\Delta^3 = \left(\frac{h^2}{2\pi m kT}\right)^{3/2} > 0$ then the press. of a FD gas will

always be higher than a classical gas & the converse is true

for a BE gas, since then $B_2(T) > 0$ & $|B_a(T)| > |K_a(T)|$

Comments:

1) An ideal quantum gas shows an effective interaction due
to quantum or symmetry effects.

2) All gases w the exception of He & possibly H_2 are classical
all the way from the point of liquefaction to any arb. higher
temperature. For He & H_2 as T inc. the effect decreases,
ie only at low temp, is symmetry significant.

Gas		T/K	B(T) Classical 6-12 pot	B(T) Ideal quantum gas	
Bose	He^4	27.3	−4.87	0.5	
		256	11.13	0.017	
Bose	Ne	35.6	−66.2	0.03	
		392	12.1	8×10^{-4}	

In general, for large (relative) T, mass & small p, classical
behavior can be expected. In terms of the deg. factor λ,
one finds for normal gases where classical statistics hold,
that $\lambda \sim 10^{-5}$ & even under high compression $\lambda \sim 10^{-2}$. Even
so, intermolecular forces will mask the effect.

Imperfect Gases

We know experimentally that all real gases display ideal behavoir at low density, ie,

$$\underset{p \to 0}{\text{Limit}} \left(\frac{PV}{RT} \right)_{exp} \to 1$$

with the resulting equation of state:

$$PV = nRT$$

Attempts to account for non-ideality gave rise to two general equations of state, the virial expansions:

a) $\dfrac{PV_m}{RT} \equiv Z \text{ (compressibility)} = 1 + B_2(T)\rho + B_3(T)\rho^2 + \ldots$ Density Series $\rho = \dfrac{N}{V}$

b) $\dfrac{PV_m}{RT} = 1 + B_2'(T)P + B_3'(T)P^2 + \ldots$ Pressure series

where in general, the virial coeficient, $B_n(T)$ is given by:

$$B_n(T) = \frac{1}{(n-1)!} \left(\frac{\partial^{n-1} Z}{\partial \rho^{n-1}} \right)_{T, \rho \to \emptyset} \quad n = 2, 3, \ldots \quad \text{Thus } B_n = B_n(T) \text{ only}$$
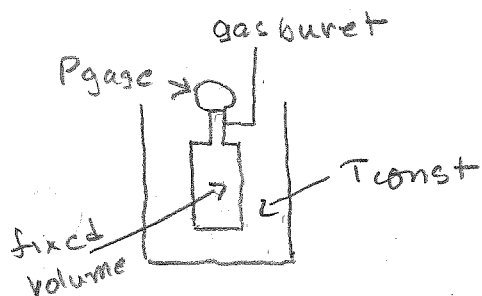$$\text{since } \rho \to 0 \text{ implies } V \to \infty.$$

corresponding to the Taylor series expansion of Z as a function of ρ.

Measurement of the Virial Coeficients B_2 and B_3

For the density series we have $Z = 1 + B_2 \rho + B_3 \rho^2$. OR,

$$\frac{Z-1}{\rho} = B_2 + \rho B_3 \quad \text{truncating } Z \text{ after the quadratic term.}$$
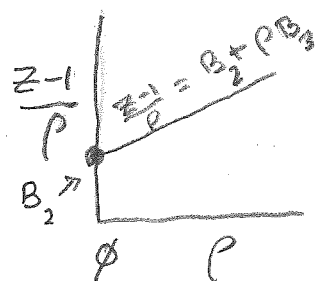
We now measure $Z \left(\equiv \dfrac{PV}{nRT} \right)$ AND $\rho \left(= \dfrac{N}{V} \right)$ as follows:

Measure P as a function of n (moles) for a fixed T & V & calc Z & ρ. Now change the temperature & repeat. Plot $\frac{Z-1}{\rho}$ vs ρ,

$$\frac{Z-1}{\rho} = B_2 + \rho B_3$$

B_2 = intercept which will vary $\underline{w}$ temperature.

B_3 = slope   ditto.

Temperature Dependence of $B_2(T)$

$B_2(T_B) = \phi$ but B_3 is not zero.

T_B for N_2 is @ room temp which means it is nearly ideal.

Comments

1) The 2nd & 3rd virial coef's are the only ones measured due to experimental difficulties with the measurements.

2) The 2nd V.C. $B_2(T)$ is the most important, $B_3(T)$ the next etc.

3) The value of the virial expansions is that one can relate them to the intermolecular interactions.

4) There are well over 300 equations of state, all of which are empirical & are used for specific purposes esp. in chemical engineering. Only the virial eqns have a molecular basis.

Derivation of The Virial Equation – Summary.

1) Starting $\underline{w}$ The GPF

1.1 $\quad \Xi(V,T,\mu) = \sum_{N=0}^{\infty} Q(N,V,T) \lambda^N = 1 + \sum_{N=1}^{\infty} Q_N(V,T) \lambda^N$

where $N=0 \Rightarrow E_j = \sum_i n_i \epsilon_i = \phi$, ie $Q(\phi,V,T) = 1$

And from $d(PV) = SdT + Nd\mu + pdv$ we get

1.2 $\quad \dfrac{PV}{KT} = \log \Xi \quad$ and

1.3 $\quad N = KT \left(\dfrac{\partial \log \Xi}{\partial \mu} \right)_{V,T} = \lambda \left(\dfrac{\partial \log \Xi}{\partial \lambda} \right)_{V,T}$

2) Now define a new variable z as:

2.1 $\quad z = \lambda Q_1 / V \qquad Q_1 -$ single particle partition function

we sub. into 1.1 to get

2.2 $\quad \Xi(V,T,\mu) = 1 + \sum_{N=1}^{\infty} \left(\dfrac{Q_N V^N}{Q_1^N} \right) z^N \quad$ as $\lambda^N = \left(\dfrac{VZ}{Q_1} \right)^N$

3) Define

$\quad Z_N = N! \left(\dfrac{V}{Q_1} \right)^N Q_N \qquad$ so 2.2 becomes

$\quad \Xi = 1 + \sum_{N=1}^{\infty} \dfrac{Z_N(V,T)}{N!} z^N \qquad$ $Z_N -$ config. integral

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad z -$ activity

From 1.2 we then write:

3.1 $\quad \Xi = \exp\left(\dfrac{PV}{KT} \right) = 1 + \sum_{N=1}^{\infty} \dfrac{Z_N(V,T)}{N!} z^N$

We now assume we can expand p as a power series in Z to get:

3.2 $\quad P = kT \sum_{j=1}^{\infty} b_j Z^j = kT[b_1 Z + b_2 Z^2 + \cdots]$

and me substitute in to 3.1, ie,

3.3 $\quad \Xi = \exp\left[\frac{V}{kT} \cdot kT \sum_{j=1}^{\infty} b_j Z^j\right] = 1 + \sum_{N=1}^{\infty} \frac{Z_N(V,T)}{N!} Z^N$

Expanding both sides of 3.3 & equating like powers of Z gives

$b_1 = (1! V)^{-1} Z_1 = 1$

$b_2 = (2! V)^{-1} (Z_2 - Z_1^2)$

4) Our goal is to expand $P = kT \sum_{j=1}^{\infty} b_j Z^j$ in terms of $\rho = \frac{N}{V}$ instead of Z.

This leads to

4.1 $\quad \rho = \frac{N}{V} = \frac{\lambda}{V}\left(\frac{\partial \log \Xi}{\partial \lambda}\right)_{V,T} = \frac{Z}{kT}\left(\frac{\partial P}{\partial Z}\right)_{V,T} = \sum j b_j Z^j$

we Now have $P \& \rho$ as functions of Z.

5) We now want $P = P(\rho)$.

This involves eliminating Z between the two series (3.2) and (4.1).

Procedure

a) Expand $Z = Z(\rho)$ as a power series in ρ, ie $Z = a_1 \rho + a_2 \rho^2 + \cdots$

b) Sub. into (4.1)

c) Collect like coef's of ρ, ie get $a_1 = 1, a_2 = -2b_2, a_3 = -3b_3 + 8b_2^2$ etc, which gives $Z(\rho) = \rho - 2b_2 \rho^2 + \cdots$ which we sub. into 3.2, to get $P/kT = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$ which is the virial eq'n.

Virial Coefficients in The Classical Limit

We consider monoatomic gases only. We start $\underline{w}$ the usual expression for Q_1, ie,

$$Q_N = \frac{1}{N! \, h^{3N}} \int \cdots \int e^{-\beta H} \prod_{i=1}^{N} d\bar{p}_i \, d\bar{r}_i \qquad \text{Classical P.F.}$$

which, assuming $N=1$ and that $Z_{1N} = \int \cdots \int e^{-U_N/kT} \prod_{i=1}^{N} d\bar{r}_i$, our configurational integral term reduces to

$$Z_1 = V \quad \underline{w} \; U_N \equiv \emptyset, \text{ gwing}$$

$$Q_1(V,T) = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} V \equiv \frac{V}{\Delta^3}$$

For $N > 1$ we have as we have seen much earlier in mentor

$$Q_N(V,T) = \frac{Z_{1N}}{N! \, \Delta^{3N}} = \frac{1}{N!} \left(\frac{Q_1}{V} \right)^N Z_N \quad \begin{array}{l} \text{in agreement } \underline{w} \text{ me} \\ \text{def}^n \text{ of } Z_N, \; p125 \end{array}$$

uluch justifies the defn. on p 125 for Z_N.

SECOND VIRIAL Coefficient $B_2(T)$

We have already seen that

$$B_2(T) = -b_2 = -(2! \, V)^{-1} \left[Z_2 - Z_1^2 \right]$$

where

$$Z_1 = \int dr_1 = V$$

$$Z_2 = \int \int e^{-u(r_{12})/kT} d\bar{r}_1 \, d\bar{r}_2$$

$$B_2(T) = -\frac{1}{2V} \left[\int \int e^{-u(r_{12})/kT} d\bar{r}_1 d\bar{r}_2 - \int \int d\bar{r}_1 d\bar{r}_2 \right] \quad \begin{array}{l} \text{writing } Z_1^2 \text{ as} \\ \left[\int d\bar{r}_1 \right]^2 = \int \int d\bar{r}_1 d\bar{r}_2 \end{array}$$

OR

$$B_2(T) = -\frac{1}{2V} \iint \left[e^{-\beta u(r_{12})} - 1 \right] d\vec{r_1} d\vec{r_2}$$

Now, since $u(r_{12})$ is a 2 particle potential function that goes to zero if r is much greater than a few molecular diameters (eg, 20 Å) when $d\vec{r_1}$ & $d\vec{r_2}$ are close to each other. we can work in terms of relative coordinates, ie,

$$\vec{r_{12}} = \vec{r_2} - \vec{r_1}$$

and write

$$B_2(T) = -\frac{1}{2V} \int d\vec{r_1} \int \left[e^{-\beta u(r_{12})} - 1 \right] d\vec{r_{12}}$$

and observe that $d\vec{r_{12}}$ is independent of where the two molecules are in the container except for wall effects which can be ignored for $V \to \infty$. Changing to spherical coordinates where $V = \frac{4}{3}\pi r^3$ we have

$$B_2(T) = -\frac{1}{2V} \int_0^V d\vec{r_1} \int_0^\infty \left[e^{-\beta u(r_{12})} - 1 \right] 4\pi r^2 dr$$

$$= -2\pi \int_0^\infty \left[e^{-\beta u(r)} - 1 \right] r^2 dr$$

whose integration now depends on a specific $u(r)$.

Potential Functions

The calc. of $B_2(T)$ requires a realistic potential function. In general, we know little of the N body potential function, ie

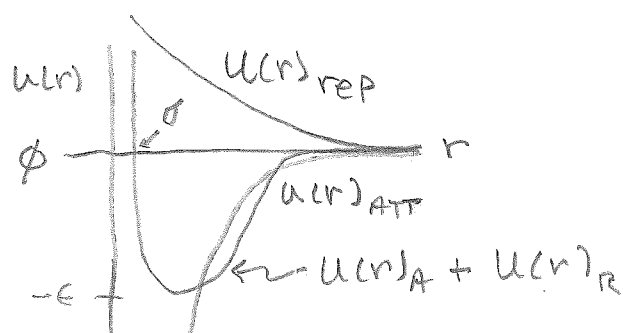$$U_N(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_N)$$

However, provided the density of the gas is low enough that 2 body collisions dominate, we can assume only pairwise interactions without the perturbing effects of other particles. Thus:

$$U_N(\bar{r}_1, \bar{r}_2, \ldots \bar{r}_N) \longrightarrow \sum_{1 \leq i < j \leq N} U(r_{ij})$$

where the sum is over pairs, of which there are $\frac{n(n-1)}{2}$.

Specific Potential Functions

In general, the potential of interaction, which is induced dipole – induced dipole (or dispersion forces) looks like, when plotted vs r

where $U(r)_{ATT} = -\dfrac{A}{r^6}$ from qtm. mechanics

$U(r)_{rep} = +\dfrac{B}{r^n}$, $9 \leq n \leq 15$ where $n=12$ is common

The form of the repulsive force is empirical since it is not known quantum mechanically (except for H).

Comments:

1) $B_2(T)$ is actually quite insensitive to n which makes $B_2(T)$ a poor choice to test various models of $U(r)$;
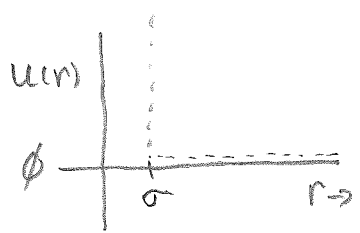
2) $U(r) = -\dfrac{A}{r^6} + \dfrac{B}{r^{12}}$ is called the 6-12 potential or Lennard-Jones. Devonshire potential & was the first realistic pot. proposed.

3) The computation of $B_2(T) = -2\pi \displaystyle\int_0^\infty \left[e^{-U(r)/kT} - 1\right] r^2 \, dr$ now involves choosing a $U(r)$ & integrating.

4) Note that $B_2 = -\dfrac{1}{2}\displaystyle\int_0^\infty \left[e^{-U(r)/kT} - 1\right] 4\pi r^2 \, dr = -\dfrac{1}{6kT}\displaystyle\int_0^\infty r U'(r) e^{-U(r)/kT} 4\pi r^2 \, dr$

where $U'(r) \equiv \dfrac{dU(r)}{dr}$
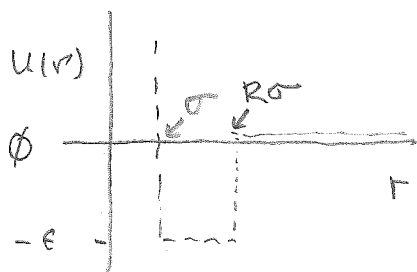
Model Potential Functions

i) Hard Spheres

$$U(r_{12}) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

$$B_2 = \dfrac{2\pi\sigma^3}{3} \neq f(T); \quad B_3 = \dfrac{5}{8}B_2^2; \quad B_4 = 0.2869\,B_2^3; \quad B_5 \approx 0.115\,B_2^4$$

ii) Square Well

This function at least attempts to mimic the attractive force, albeit with a constant $u(r)$ value, ϵ.

$$u(r) = \begin{cases} \infty & r < \sigma \quad \text{(hard sphere cutoff)} \\ -\epsilon & \sigma \leq r \leq R \quad \underline{w} \quad R \simeq 1.5 \text{ to } 2 \\ \emptyset & r > R\sigma \end{cases}$$

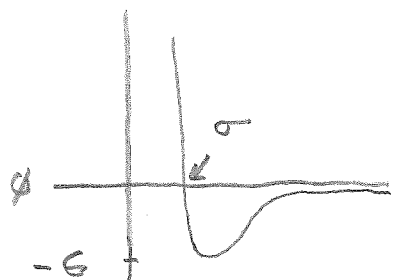$$B_2(T) = \frac{2\pi\sigma^3}{3}\left[1 - (R^3 - 1)(e^{\epsilon/kT} - 1)\right]$$

$B_2(T)$ is temperature dependent but shows no maximum in T. Also as $\epsilon \to \emptyset$, $B_2(T) \to B_2$ (hard sphere).

Surprisingly, the square well work quite well representing exp. data suggesting that $B_2(T)$ isn't very sensitive to $u(r)$. In fact, $B(T)$ generally (moderate densities) depends only on the ratio of the width to depth ie, the area under the $u(r) = 0$ region. However, other properties of a gas are more sensitive to the form of $u(r)$.

iii) L-J Potential (6-n potential)

General form is given by:

$$u(r) = \frac{n\epsilon}{n-6}\left(\frac{n}{6}\right)^{6/(n-6)}\left\{\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^6\right\}$$

$$u(r) = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right\} \quad \text{6-12 potential}$$

It is most convenient to define a reduced form for r & ε by the relationships:

$$r^* = \frac{r}{\sigma} \quad \text{and} \quad T^* = \frac{kT}{\epsilon}$$

for tabulation purposes since the expression for $B_2(T)$ cannot be integrated in closed form. Thus:

$$B_2(T) = -\frac{2\pi}{3kT} \int_0^\infty r^3 \frac{du}{dr} e^{-U(r)/kT} dr$$

$$= -\frac{2\pi}{3} \left\{ \frac{4\sigma^3}{T^*} \int_0^\infty r^{*2} \left[-\frac{12}{r^{*12}} + \frac{6}{r^{*6}} \right] \exp\left[-\left(\frac{4}{T^*}\right)\left(\frac{1}{r^{*12}} - \frac{1}{r^{*6}}\right) \right] \right\} dr^*$$

Now expand $\exp\left[\left(\frac{4}{T^*}\right) r^{*-6}\right]$ & integrate term by term:

$$B_2(T) = \frac{2\pi\sigma^3}{3} T^{*(-0.25)} \sqrt{2} \sum_{j \geq 0}' -\frac{2^j}{4j!} \Gamma\left[\frac{2j-1}{4}\right] T^{*\left(-\frac{j}{2}\right)}$$

$$= \frac{2\pi\sigma^3}{3} T^{*(-0.25)} \left[1.733 - 2.564\, T^{*\left(-\frac{1}{2}\right)} - 0.866\, T^{*(-1)} \right.$$

$$\left. - 4.27\, T^{*(-3/2)} - \ldots \right]$$

Convergence is rapid for $T^* > 4$ while $T^* = 0.3$ requires at least 30 terms for 5 significant figures.

Third Virial Coefficient

$B_3(T)$ arises as a result of 3 particle collisions where the potential function $U_3(r_1, r_2, r_3)$ is given by the expression,

$$U_3(r_1, r_2, r_3) = U(r_{12}) + U(r_{13}) + U(r_{23}) + \Delta U_c(r_{12}, r_{13}, r_{23})$$

$$\approx U(r_{12}) + U(r_{13}) + U(r_{23}) \text{ assuming pairwise additivity hold.}$$

The perturbation term $\Delta U_c(r_{12}, r_{13}, r_{23})$ arises when a 3rd particle interacts w/ a pair to influence the potential of pair interactions, We usually assume $\Delta U_c(r_{12}, r_{13}, r_{23}) \approx \emptyset$, pair-wise additivity
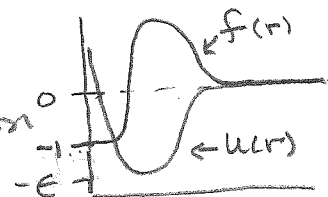
We have then:

$$B_3(T) = 4b_2^2 - 2b_3 = -\frac{1}{3V^2}\left[V\left(Z_3 - 3Z_{12}Z_1 + 2Z_1^3\right) - 3\left(Z_2 - Z_1^2\right)^2\right]$$

Define:

$$f_{ij} = f(r_{ij}) = e^{-U(r_{ij})/kT} - 1 \quad \text{Mayer function}$$

Then, for example:

$$Z_3 = \int\int\int e^{-U(r)/kT} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 = \int\int\int e^{-[U(r_{12}) + U(r_{13}) + U(r_{23})/kT]} \prod_{i=1}^{3} d\vec{r}_i$$

$$= \int\int\int (1 + f_{12})(1 + f_{13})(1 + f_{23}) d\vec{r}_1 d\vec{r}_2 d\vec{r}_3$$

$$= \int\int\int \left[f_{12}f_{13}f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12} + f_{23} + f_{13} + 1\right] \prod_{i=1}^{3} d\vec{r}_i$$

The procedure now is to subtract $3Z_{12}Z_1$ from Z_3. After a series of manipulations involving further subtractions, we can show that, since the subscripts are arbitrary:
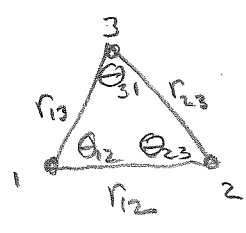
$$B_3(T) = -\frac{1}{3V}\int\int\int f_{12}f_{13}f_{23} \, dr_1 dr_2 dr_3$$

We note that $f_{ij} \to \emptyset$ if i & j are separated so $B_3(T)$ will be $\emptyset$ for large r unless all three particles are in close proximity.

The additive term, $\Delta u_c(r_{12}, r_{13}, r_{23})$ is given by

$$\Delta u_c = \text{const.} \int\int\int [\exp(-\textstyle\sum_i \text{Pairs})/kT - 1] * \exp(-U_{corr}/kT) * r_{12}\, r_{13}\, r_{23}\, dr_{12}\, dr_{13}\, dr_{23}$$

where $\Delta U_{corr} = \dfrac{\upsilon[1 + 3\cos\Theta_{12}\cos\Theta_{13}\cos\Theta_{23}]}{r_{12}^3\, r_{13}^3\, r_{23}^3}$

and $\upsilon = \dfrac{3}{4}\alpha\, C_6$ where $\alpha = $ static polarizability

$C_6 - $ leading term in the London dispersion energy.

The additive correction to the pairwise addition terms improves the agreement between computed & meas. third virial coefficients significantly.

The third virial coefficient is difficult to evaluate for a realistic potential although the method of Katsura using Fourier Transforms has been successful.
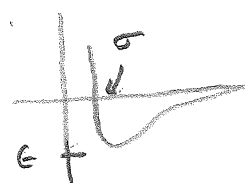
The Law of Corresponding States

We begin by assuming the potential function, $U(r)$ can be written:

$$U = \sum_{i,j}' U(r_{ij}) = \sum_{i,j}' \epsilon \phi\left(\frac{r_{ij}}{\sigma}\right)$$

where r_{ij} = dist. between molecular centers, ϵ, the depth of the potential well & σ the point where $U(r_{ij})$ crosses the $U(r)$ vs r line at ϕ.

and we assume pairwise additivity.

We now define the reduced variables B_2^* & T^* by:

$$B_2^*(T^*) = \frac{B_2}{b_0} \quad ; \quad b_0 = \frac{2}{3}\pi N \sigma^3$$

$$T^* = \frac{kT}{\epsilon}$$

Our basic assumption now is that the pair potential $\phi\left(\frac{r_{ij}}{\sigma}\right)$ is the same for all substances. The config. integral now reads

$$Z_N = \int \cdots \int e^{-U/kT} \prod_{i=1}^{N} dr_i$$

$$= \sigma^{3N} \int \cdots \int \exp\left\{-\frac{\epsilon}{kT} \sum' \phi\left(\frac{r_{ij}}{\sigma}\right)\right\} \prod_{i=1}^{N} d\left(\frac{\bar{r}_i}{\sigma^3}\right)$$

$$= \sigma^{3N} f\left(T^*, \frac{V}{\sigma^3}, N\right)$$

where we now assume that all molecules have the same f.

This men leads to a 'universal' partition function of the form

$$Q(N,V,T) = \left[\frac{\sigma^3 g\left(kT/\epsilon, V/\sigma^3\right)}{\underline{\Lambda^3}} \right]^N$$

and finally we have:

$$\frac{PV}{kT} = \left(\frac{V}{\sigma^3}\right)\left(\frac{\partial \log g}{\partial (V/\sigma^3)}\right)_{T^*}$$

ie, $\frac{PV}{kT}$ must be the <u>same</u> function of $T^* = kT/\epsilon$

and V/σ^3 for <u>all</u> substances that obey a 2 parameter potential function.

Table 12-5 text

Gas	$P_c V_c / kT_c$	
<u>He</u>	<u>0.300</u>	qtm. effects
He	0.296	
Ar	0.292	Similar
Xe	0.289	
CO_2	0.274	non-spherical
n-pentane	0.268	

Useful for estimating potential parameters.

Measurement of The Potential Parameters

Suppose we want to determine the parameters for The square well, i.e., ϵ, R and σ from measured values of $B_2(T)$ where

$$B_2(T) = \frac{2\pi\sigma^3}{3}\left[1 - (R^3-1)(e^{\epsilon/kT} - 1)\right]$$

Using a techniques for meas. $B_2(T)$ vs T we have:

B_2	T
=	=
=	=
=	=

Using NLR, you determine The best fit values for σ, R and ϵ as a function of T. One you have what you believe to be The 'best' values, you can plot $\frac{PV_m}{RT} = 1 + B_2(T)P$ to see how well $B_2(T)$ represents The data. You should also plot $B_2(T)$ vs T for which you should get an excellent fit.

LIQUID STATE THEORY
Distribution Functions

The radial distribution function is the basis for all modern theories of liquids as well as all other system involving interact[...]

Consider a system of N particles, volume V and Temperature T. If the particles are labelled, we can write:

1) $$P^N(\bar{r}_1, \dots \bar{r}_N) \prod_{i=1}^{N} d\bar{r}_i = \frac{e^{-\beta U_N(r_1, \dots r_N)} \prod_i d\bar{r}_i}{Z_N} \qquad \beta = kT$$

where $P^N(\ )$ is the prob. that particle 1 is at $\bar{r}_1$ in the range dr_1, particle 2 is at $\bar{r}_2$ in $d\bar{r}_2$, ... etc.

2) Z = configurational integral
$$= \int \dots \int e^{-U_N(\bar{r})/kT} \prod_i d\bar{r}_i \equiv V^N \text{ if } U(r_N) = \phi$$

Note that if we integrate (1) over all coord's $d\bar{r}_1 \dots d\bar{r}_N$ we get 1, ie P^N is normalized.

Now suppose we write eq'n 1 for just the first n particles ignoring the remaining $N-n$ particles. This gives the MARGINAL probability,

3) $$P^{(n)}(r_1, \dots, r_n) = \frac{\int \dots \int e^{-\beta U(r_1, \dots r_N)} \prod_{i=n+1}^{N} d\bar{r}_i}{Z_N}$$

where $P^{(n)}$ refers to the prob. that particle 1 is in dr_1 at r_1, ... particle n is in dr_n at r_n irrespective of the remaining $N-n$ particles.

We now remove the labels on the molecules, i.e., we correct eq'n 3 for distinguishability. Since the first molecule can go anywhere, we then have N choices, the 2nd, $N-1$ etc. or, are correction for indistinguishability is (ie assigning $N-n+1$ particles to N vol's dr_1, dr_2...

$$N(N-1)(N-2)\cdots N-n+1 = \frac{N!}{(N-n)!}$$

so (3) becomes:

$$4) \quad \underbrace{\rho^{(n)}(r_1, \cdots r_n)}_{\text{Particles indistinguishable}} = \frac{N!}{(N-n)!} \underbrace{\overbrace{\rho^{(n)}(r_1, \cdots r_n)}^{\text{Particles distinguishable}}}_{\text{marginal prob, eq'n 3}}$$

where now $\rho^{(n)}$ is the prob. that any molecule can be in $dr_1, \cdots$ etc.

The simplist dist. function is $\rho^{(1)}(r_1)$ which is the prob. that a molecule is at r_1 in dr_1. However all points in the fluid are equivalent so $\rho(r_1)$ is actually indept. of r_1. We then have:

$$\underbrace{\int \rho^{(1)}(r_1)\, dr_1}_{\substack{\text{Integral or prob. of} \\ \text{a single particle dist. fn.}}} = \frac{N!}{(N-1)!} \int \rho^{(1)}(r_1)\, dr_1 = N \int \rho^{(1)}(r_1)\, dr_1$$

$$N \frac{\int_{r_1}\left[\int\cdots\int e^{-()} \prod_{i=2}^{N} dr_i\right] dr_1}{Z_N} \quad \text{Using eq'n 3}$$

$$= N.$$

OR $\quad \int \rho^{(1)}(r_1)\, dr_1 = \rho^{(1)} V = N$ ie. $\rho^{(1)} = \frac{N}{V} = \rho$

where ρ is the density of the fluid.

Correlation Function; $g^{(n)}$

The correlation function serves as a measure of the interaction between molecules, ie, their 'correlation' and is defined as:

5) $\quad \rho^n g^{(n)}(r_1,\ldots,r_n) = \rho^{(n)}(r_1,\ldots,r_n)$ where $\rho^n = \dfrac{N^n}{V^n} = \text{density}^n$

$\rho^{(n)}$ eq'n 4

OR

6) $\quad g^{(n)}(r_1,\ldots,r_n) = \dfrac{V^n N!}{N^n (N-n)!} \cdot \underbrace{\dfrac{\displaystyle\int\cdots\int e^{-\beta U_N}\,dr_{n+1}\cdots dr_N}{Z_N}}_{\rho^{(n)}\ (eq'n\ 3)}$

Problem:

Show that $\dfrac{1}{V^n} g^{(n)}(r_1,\ldots,r_n)$ is normalized to:

$$\dfrac{V^n N!}{N^n (N-n)!} \approx 1 + O(N^{-1})$$

Radial Distribution Function $g^{(2)}(r) \equiv g(r)$

Consider now the case of $\rho^{(2)}(r_1,r_2)$. <u>For a fluid,</u> $\rho^{(2)}(r_1,r_2)$ is the prob. of a molecule being found at r_1 in dr_1 & any second molecule at r_2 in dr_2 ⊛ which, unlike a crystal, depends only on the distance between r_1 & r_2

ie $\quad \rho^2(r_1,r_2) = \rho^2(r_{12})$, spherically symm molecules

From (5) & (6) then

$$\rho^2 g^{(2)}(r_1,r_2) = \rho^{(2)}(r_1,r_2) = N(N-1)\dfrac{\displaystyle\int\cdots\int e^{(\cdot)}\prod_{i=3}^{N} dr_i}{Z_N}$$

⊛ Alternatively, $\rho^{(2)}(r_{12})$ is the conditional prob. that if there is a mole. at r_1 in dr_1, there will be a molecule at r_2 in dr_2

OR, on integrating both sides, we have

$$\int d\bar{r}_1 \int \rho^2 g^{(2)}_{(r_2)} d\bar{r}_2 = N(N-1)$$

$$= V \int \rho^2 g^{(2)} (r_{12}) dr_{12} = V \rho^2 \int_0^\infty 4\pi r^2 g(r) dr = N(N-1)$$

OR, having switched to relative spherical coord's,
and denoting $g^{(2)}(r)$ as $g(r)$, we have finally,
noting that $\frac{V}{N} = \rho^{-1}$

7) $\int_0^\infty \rho g(r) \cdot 4\pi r^2 dr = N-1 \approx N$ i.e. $g(r)$ is normalized to N

Note that:

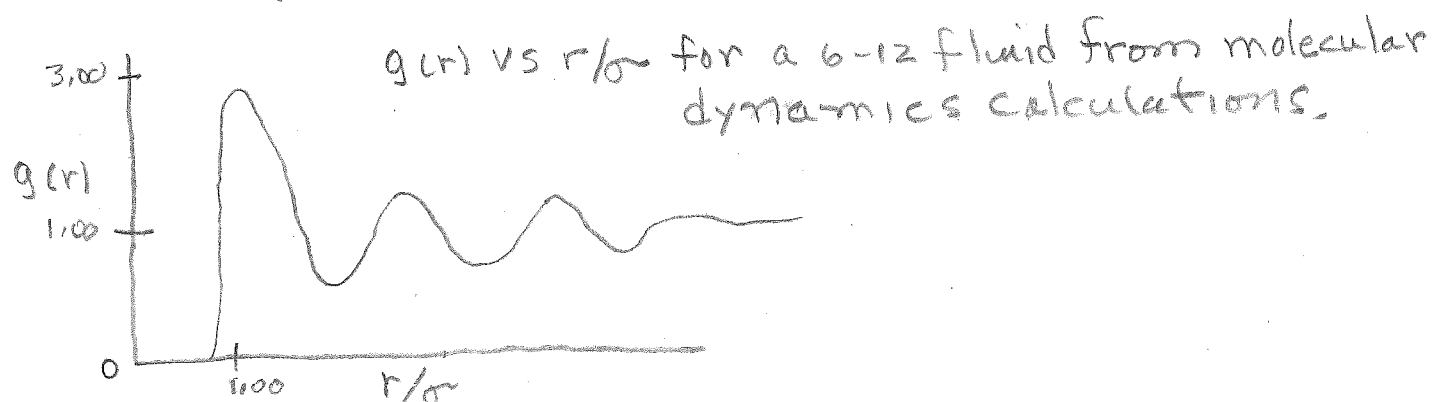$g(r) \to \phi$ as $r \to \phi$ since no two molecules can occupy the same point in space

$g(r) \to 1$ as $r \to \infty$ since there must be another molecule at $r = \infty$.

Interpretation of $g(r)$:

a) $\rho g(r) \cdot 4\pi r^2 dr$ is the number of molecules between r and $r+dr$ about a central molecule.

b) $\rho g(r)$ is the prob. of finding a 2nd molecule in dr given a molecule at r.

$g(r)$ vs r/σ for a 6-12 fluid from molecular dynamics calculations.

Note that:

Limit $r \to \emptyset$, $U(r) \to \infty$, $g(r) \to \emptyset$

Limit $r \to \infty$, $U(r) \to \emptyset$, $g(r) \to 1$

Problem: Show this from the definition of $g^{(2)}$.

Solution:

$$g^{(2)} = \frac{V^2}{N^2} \frac{N!}{(N-2)!} \frac{\int \cdots \int e^{-\beta U_N} dr_3 \cdots dr_N}{Z_N}$$

$$\simeq V^2 \left[\; \nearrow \; \right]$$

$\underline{U(r) \to \infty \text{ as } r \to \emptyset}$

$$g^{(2)} = V^2 \frac{\int \cdots \int e^{-\infty} \prod_3^N dr_i}{Z_N} \longrightarrow \emptyset$$

$\underline{U(r) \to \emptyset \text{ as } r \to \infty}$

$$g^{(2)} = V^2 \frac{\int \cdots \int e^{\emptyset} \prod_3^N dr_3 \cdots dr_N}{\int \cdots \int e^{-\emptyset} \prod_{i=1}^N dr_i} \longrightarrow \frac{V^2 \cdot V^{N-3+1}}{V^N} \longrightarrow 1$$

<u>Importance of $g(r)$</u>

1) $g(r)$ can be related to the Thermodynamic functions of a fluid (or gas)

2) $g(r)$ can be measured from Xray and Neutron scattering measurements.

Thermodynamics and g(r)

INTERNAL ENERGY, E

From: $Q_N = \dfrac{Z_N}{N! \, \Delta^{3N}}$

$$\Delta = \left[\frac{h^2}{2\pi m kT} \right]^{\frac{1}{2}}$$

$$E = -T^2 \left[\frac{\partial (A/T)_{N,U}}{\partial T} \right]$$

$$A = -kT \log Q_N$$

one can show that:

$$\bar{E} = \underbrace{\frac{3}{2} NkT}_{KE} + \underbrace{\bar{U}}_{PE}$$

where

$$\bar{U} = \frac{N(N-1)}{2 Z_N} \int \cdots \int e^{-U(r_1, r_2, \cdots r_N)/kT} \, u(r_{12}) \prod_{i=1}^{N} d\vec{r}_i$$

where we have assumed 'pair wise additivity'
and recognized that

$$U_N(r_1 \cdots r_N) = \sum_{1 \le i < j \le N} u(r_{ij}) = \frac{N(N-1)}{2} u(r_{12})$$

when integrated from 0 to ∞, ie all $\frac{N(N-1)}{2}$ terms
are identical. This $\overset{\text{is the}}{\wedge}$ one reason for assuming
pairwise additivity, otherwise we have a intractable
problem.

Rearranging we have:

8)' $\quad \bar{U} = \frac{N(N-1)}{2} \int\int u(r_{12}) \left[\frac{\int\cdots\int e^{-\beta u_N \prod_{i=3}^{N}} d\vec{r}_i}{Z_N} \right] d\vec{r}_1 d\vec{r}_2$

$$\rho^{(2)}(r_1, r_2) = \frac{N(N-1)}{2} \rho^{(2)}(r_1, r_2)$$

$$= \frac{N(N-1)}{2} \frac{\int\cdots\int e^{-\beta u_N \prod_{i=3}^{N}} d\vec{r}_i}{Z_N}$$

Eqn 8) now reads:

$$\bar{U} = \frac{1}{2} \int\int u(r_{12}) \rho^{(2)}(r_1, r_2) d\vec{r}_1 d\vec{r}_2$$

$$= \frac{N^2}{2V} \int_0^\infty u(r) g(r) 4\pi r^2 dr \quad \text{where we have used}$$

$$\rho^{(2)}(r_1, r_2) = \rho^2 g(r_1, r_2) \equiv \rho^2 g(r) = \frac{N^2}{V^2} g(r)$$

and switched to relative coordinates

So our total energy is then:

9) $\quad \dfrac{E}{NkT} = \dfrac{3}{2} + \dfrac{\rho}{2kT} \displaystyle\int_0^\infty u(r) g(r, T, \rho) \, 4\pi r^2 dr$

which emphasizes that $g(r)$ depends on r, T, ρ.

Pressure

From $dA = -SdT - pdV$ we have $P = -\left(\dfrac{\partial A}{\partial V}\right)_{T,V}$ so

$$\frac{P}{KT} = \left(\frac{\partial \log Q_N}{\partial V}\right)_{N,T} = \left(\frac{\partial \log Z_N}{\partial V}\right)_{N,T} \quad \text{as } Q_N = \frac{Z_N}{N!\,\Delta^{3N}}$$

$$= \frac{1}{Z_N}\left(\frac{\partial Z_N}{\partial V}\right)_{N,T} \quad \text{We now calculate } \left(\frac{\partial Z_N}{\partial V}\right)_{N,T}$$

We now assume a cube w.o. loss of generality

so

$$Z_N = \int_0^{V^{1/3}} \cdots \int_0^{V^{1/3}} e^{-\beta U(\bar{r}_1, \cdots \bar{r}_N)} dx_1\, dy_1\, dz_1, \cdots, dx_N\, dy_N\, dz_N$$

where

$$U(r_1 \cdots r_N) = \sum_{i<1}' U(r_{ij}) \quad \text{assuming pairwise additivity for } N(N-1)/2 \text{ pairs.}$$

and where

$$r_{ij} = \left[(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2\right]^{1/2}$$

$$= V^{1/3}\left[(x_i' - x_j')^2 + \cdots \text{etc.}\right]^{1/2} \quad \text{if we let } x_k = V^{1/3} x_k' \text{ etc.}$$

so $U(r)$ is now a function of V and the limits are from 0 to 1.

Thus Z_N can be written

$$Z_N = \left(V^{1/3}\right)^{3N}\int_0^1 \cdots \int_0^1 e^{-\beta U} dx_1' \cdots dz_N' \quad Z' \text{ refers to the } x' \text{ etc. coord's}$$

and

$$\underbrace{\left(V^{1/3}\right)^{3N}}_{= V^N}$$

$$\left(\frac{\partial Z_N}{\partial V}\right)_{T,N} = \underbrace{NV^{N-1}\frac{Z_N'}{V^N \equiv (V^{1/3})^{3N}}}_{\substack{\text{switching back} \\ \text{to the orig. coord's}}} - \underbrace{V^N \int_0^1 \cdots \int e^{-\beta U}\left(\frac{\partial U}{\partial V}\right) dx_1' \cdots dz_N'}_{\substack{\text{each triplet} \\ \text{gives a } V \text{ term} \\ \text{Next page}}}$$

$$= \frac{N}{V} Z_N = \frac{N}{V}\int \cdots \int e^{-\beta U} dx_1 \cdots dz_N$$

$$\left(\frac{\partial u}{\partial V}\right)_{N,T} = \sum_{1 \leq i < j \leq N}' \frac{du(r_{ij})}{dr_{ij}} \underbrace{\frac{dr_{ij}}{dV}}_{3V^{2/3}} = \sum_{1 \leq i < j \leq N}' \underbrace{\frac{r_{ij}'}{3V^{2/3}} \cdot \frac{1}{V^{1/3}} \frac{du(r_{ij})}{dr_{ij}}}$$

Change to orig. coords. gives $V^{-1/3}$.

ij^{th} derivative

$$= \sum_{1 \leq i < j \leq N}' \frac{r_{ij}}{3V} \frac{du(r_{ij})}{dr_{ij}}$$

We now have

$$\left(\frac{\partial Z_N}{\partial V}\right)_{T,N} = \frac{N}{V} Z_N - \frac{V^N}{V^N} \frac{\beta^{-1}}{3V} \int_0^{V^{1/3}} \cdots \int e^{-\beta u} \sum_{1 \leq i < j \leq N}' r_{ij} \cdot \frac{du(r_{ij})}{dr_{ij}} dx_1 \cdots dz_N$$

after changing $dx_1' \cdots dz_N'$ term back to original coords.
We now note again that the integrations are all the same⊗, and since we are interested in _pair_
correlation _function_, we can write, for $i=1$, $j=2$; on dividing by Z_N

$$\frac{P}{KT} = \frac{1}{Z_N}\left(\frac{\partial Z}{\partial V}\right)_{T,V} = \frac{N}{V}\frac{Z_N}{Z_N} - \frac{N(N-1)}{2 Z_N V} * \frac{1}{3VKT} \int\int r_{12} \frac{du(r_{12})}{dr_{2}} \left\{ \int \cdots \int e^{-\beta u} \prod_{i=3}^{N} d\vec{r}_i \right\} d\vec{r}_1 d\vec{r}_2$$

But, as before

$$\rho^{(2)}(r_1,r_2) = N(N-1) P^{(2)} = N(N-1) \underbrace{\frac{\int \cdots \int e^{-\beta u_N} \prod_{i=N+1}^{N} d\vec{r}_i}{Z_N}}_{\rho^{(2)}(r_1,r_2)}$$

$\overbrace{\qquad}^{P^{(2)}(r_1,r_2)}$

so finally, we have
oR

$$\frac{P}{KT} = \frac{1}{Z_N}\left(\frac{\partial Z_N}{\partial V}\right)_{T,V} = \frac{N}{V} - \frac{1}{6VKT}\int_V\int r_{12} u'(r_{12})\rho^{(2)}(r_1,r_2) dr_1 dr_2$$

But changing to relative coords & using the eq'n $\rho^{(2)}(r) = \rho^2 g^{(2)}(r)$
we get,

10) $\dfrac{P}{KT} = \rho - \dfrac{\rho^2}{6KT}\int_0^{\alpha} r u'(r) g(r) 4\pi r^2 dr$

⊗ $\dfrac{N(N-1)}{2}$

Virial Coefficients

Virial Coefficients

Other Thermodynamic Functions

Chemical Potential:

We begin by defining the coupling parameter q, which varies between 0 & 1 and defines the degree of interaction between molecule 1 and the other $N-1$ molecules in the system, ie,

$$U(r_1, \cdots r_N, q) = \sum_{j=2}^{N} q \, u(r_{1,j}) + \sum_{2 \leq i < j \leq N}' u(r_{i,j})$$

If we set $q = 0$ we effectively remove molecule 1 from the system, so for example, the config. integral Z can be differentiated as $Z_N(q=1)$ and $Z_{N-1}(q=0)$.

We now have

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V,T} \simeq \frac{A(N,V,T) - A(N-1,V,T)}{\Delta N(=1)}$$

$$= A(N,V,T) - A(N-1,V,T) \quad \text{since the least}$$
$$\text{value } \Delta N \text{ can take on is 1.}$$

Now

$$-\frac{A}{kT} = \log Z_N - \log N! - 3N \log \Lambda$$

which in conjunction with μ above leads to

11)
$$-\frac{\mu}{kT} = \log \frac{Z_N}{Z_{N-1}} - \log N - \log \Lambda^3$$

We also note that if $\xi = 0$, $u(\bar{r}, \xi) = \sum_{2 \le i < j \le N} u(\bar{r}_{ij})$

ie, molecule 1 is gone leading to:

$$Z_N(\xi = 1) = Z_N$$

$$Z_N(\xi = 0) = \int_0^\infty \left[Z_{N-1} \right] d\bar{r}_1 = V Z_{N-1}$$

Since $\xi = 0$ removes particle 1 but $d\bar{r}_1$ is still in the $\prod_{i=1}^{N} d\bar{r}_i$ so we integrate it out.

So eq'n 11 can be written:

12) $\log \dfrac{Z_N}{Z_{N-1}} = \log \dfrac{Z_N(\xi=1)}{Z_N(\xi=0)} + \overbrace{\log V} = \int_0^1 \left(\dfrac{\partial \log Z_N}{\partial \xi} \right) d\xi + \log V$

$$= \int_0^1 \dfrac{1}{Z_N} \dfrac{\partial Z_N}{\partial \xi} d\xi + \log V$$

Now

$$Z_N(\xi) = \int \cdots \int e^{-\beta u_N(\xi)} \prod_i d\bar{r}_i$$

and

$$\dfrac{\partial Z_N}{\partial \xi} = -\dfrac{1}{kT} \int \cdots \int e^{-\beta u_N(\xi)} \dfrac{\partial}{\partial \xi} \overbrace{\left[\sum_{j=2}^{N} \xi u(r_{1j}) + \sum_{2 \le i < j \le N} u(r_{ij}) \right]}^{\text{only contribution to } \frac{\partial}{\partial \xi}} \prod_{i=1}^{N} d\bar{r}_i$$

$u_N(\xi)$

Now divide by Z_N & recognize that all $N-1$ integrals are the same.

$$\dfrac{\partial \log Z_N}{\partial \xi} = -\dfrac{1}{NkT} \int\int_V u(r_{12}) \rho^{(2)}(r_1, r_2) d\bar{r}_1 d\bar{r}_2 \quad \text{since we want } g^{(2)}$$

13) $$= -\dfrac{\rho}{kT} \int_0^\infty u(r) g(r, \xi) 4\pi r^2 dr \quad \text{so, finally,}$$

sub. 13 into 12 & that result into 11, we get

14) $$\mu/kT = \log \rho \Lambda^3 + \dfrac{\rho}{kT} \int_0^1 \int_0^\infty u(r) g(r, \xi) 4\pi r^2 dr \, d\xi$$

Compressibility:

With the aid of the GPF one can show that the isothermal compressibility α_T is given by:

$$KT\rho\alpha_T = 1 + \rho \int [g(r) - 1] dr$$

Summary

Clearly, knowing $g(r)$ allows one to compute all of the thermodynamic functions for any pure fluid. What we want is an equation that would allow us to get $g(r)$ at any temperature from a knowledge of the interaction potential.

Kirkwood's Exact Integral Equation for $g(r)$ (1930's)

We start w/ the relationship:

$$\rho^{(n)}(1, 2, \cdots n; \xi) = \frac{N!}{(N-n)!} \frac{\int \cdots \int e^{-\beta U(\xi)} \prod_{i=n+1}^{N} d\vec{r_i}}{Z_N(\xi)}$$

$\underbrace{\rho^{(n)}(1, 2, \cdots n; \xi)}_{\text{same as } (r_1, \cdots r_n, \xi)}$

which is just eqn (4). We first differentiate WRT the coupling parameter ξ, integrate from 0 to ξ and set $n=2$. After an incredible amount of very messy mathematics, we get a coupled equation of the form

$$(15) \quad -KT \log g^{(2)}(1,2,\xi) = \xi U(r_{12}) + \rho \int_0^\xi \int_V U(r_{13}) \left[\frac{g^{(3)}(1,2,3,\xi)}{g^{(2)}(1,2,\xi)} - g^{(2)}(1,3,\xi) \right] d\xi d\vec{3}$$

which is eqn 13-40 of the text.

In general this equation writes $g^{(n-1)}$ in terms of $g^{(n)}$. Thus requiring that we know $g^{(n)}$ in order to compute $g^{(2)}$. We need therefore a method to break this 'hierarchy' of equations.

Potential of Mean Force

Define (compare w $g_0(r,T) = e^{-\beta u(r)}$ for a dilute gas.

$$g^{(n)}(r_1, \cdots r_n) \equiv e^{-\beta W^{(n)}(r_1, \cdots, r_n)} \left(= \frac{V^n N!}{N^n (N-n)!} \cdot \frac{\int \cdots \int e^{-\beta u_N} \prod_{i=n+1}^{N} dr_i}{Z_N} \right)$$

Now take logs of ↑ and compute:

$$f_j^{(n)} = -\nabla_j \omega^{(n)} = -\nabla_j \frac{g^{(n)}}{g^{(n)}} = \frac{\int \cdots \int e^{-\beta u}(-\nabla_j u)\, dr_{n+1} \cdots dr_N}{\int \cdots \int e^{-\beta u}\, dr_{n+1} \cdots dr_N} \qquad 1 \le j \le n$$

where $f_j^{(n)}$ is the 'mean force acting on particle $1 \le j \le n$,' when averaged over all possible configurations of the remaining $n+1$ to N particles (not the 1 to n particles.). Note that if $\rho \to \phi$ then particles i & j do not see the remaining $N-2$ particles, so $W^{(2)}(r) \to u(r)$, ie at low densities the mean potential becomes the simple direct potential.

Superposition Approximation

We now assume that

$$W^{(3)}(1,2,3) \approx W^{(2)}(1,2) + W^{(2)}(1,3) + W^{(2)}(2,3)$$

from which it follows that:

$$g^{(3)}(1,2,3) \approx g^{(2)}(1,2)\, g^{(2)}(1,3)\, g^{(2)}(2,3) \quad \leftarrow \text{indept. pair prob's.}$$
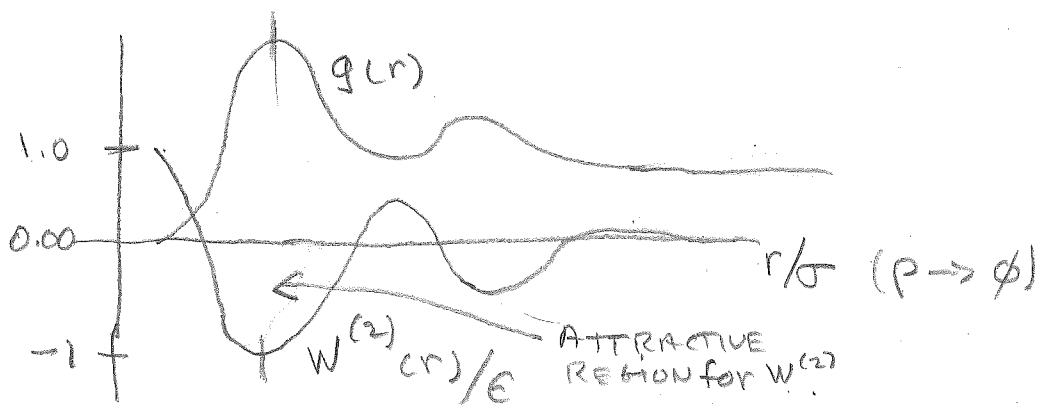
which is called the Kirkwood superposition approx. for $g^{(3)}$ & clearly better than assuming $g^{(3)}(1,2,3) = g^{(3)}(1)\, g^{(3)}(2)\, g^{(3)}(3)$.

Substitution of $g^{(3)}(1,2,3)$ into 15 then gives the famous Kirkwood integrodifferential eq^n

16) $-kT \log [g(r_{12}, \xi)] = \xi u(r_{12}) + \rho \int_0^{\xi} \int_V u(r_{13}) g(r_{13}; \xi) [g(r_{23}) - 1] d\vec{r_3} d\xi'$

where the n particle hierarchy is broken by the superposition approximation. This equation is exceedingly difficult to solve because in order to get $g(r_{12}, \xi)$ you also need to compute $g(r_{13}, \xi)$ & $g(r_{23})$.

Note that $g(r_{12}) = \exp[-\xi u(r_{12})/kT]$ as $\rho \rightarrow \phi$ (eq'n 16) implying that, since $g^{(2)}(r_1, r_2) = e^{-\rho W^{(2)}(r_1, r_2)}$ ($\rho 14$), then as $\rho \rightarrow 0$ $W(r_{12}) \rightarrow u(r_{12})$. In other words, in dense systems, you must use the 'potential of mean force' in the Boltzmann expression and it is only in dilute systems where $\rho \rightarrow \phi$ is $u(r_1, r_2)$ applicable. This can be seen in the following picture:

which shows how the Pot. of Mean force mirrors the $g(r)$. These curves are also typical of a fluid of hard spheres for which $u(r)$ is purely repulsive, but $W^{(2)}(r)$ actually shows an attractive region due to collisional asymmetry.

Born-Green-Yvon Equation

Another famous eq'n similar to the Kirkwood equation was derived by differentiating $\rho^{(n)}(1,2\cdots n,\xi)$ WRT the jth coord, instead of ξ as Kirkwood did. This lead to expression 13-47 in the text and which has the same complication of a hierarchial $g^{(n)}$.

Percus-Yevick Equation

This important equation came about by using the notion of a 'Direct correlation function' which can be derived from the GPF for an open system. This leads to the compressibility equation:

$$(16.1) \qquad KT\left(\frac{\partial \rho}{\partial P}\right)_T = 1 + \rho \int [g(r) - 1]\, d\bar{r}$$

and does not require the assumption of pairwise additivity, as everything up to now has.

We now define the 'Direct Correlation Function'

$$(17) \qquad h(r_{12}) = c(r_{12}) + \rho \int c(r_{13}) h(r_{23})\, d\bar{r_3}$$

or the Ornstein-Zernike eq'n.

Here $c(r_{12})$ is the direct correlation function and represents the interaction or correlation between particles 1 & 2 and pertains to low density interactions whereas $\rho \int \cdots d\bar{r}$ gives a measure of indirect correlations due to the presence of

long range interactions (actually a convolution of correlation functions). This equation is a difficult as the Kirkwood eq'n to solve, because of the indirect correlation term. This indirect term reflects how long range interactions modify or perturb particle 2. Thus influencing how particles 1 and 2 interact.

Equation (17) is the starting point for both the Percus-Yevick and hypernetted chain equations. See the text, P276 for details. We have then

$$y(r_{12}) = 1 + \rho \int f(r_{13}) y(r_{13}) h(r_{23}) d\bar{r}_3 \quad \text{Percus Yevick}$$

$$\text{or,} \quad \log y(r_{12}) = \rho \int \left[h(r_{13}) - \log g(r_{13}) - \frac{u(r_{13})}{kT} \right] [g(r_{23}) - 1] d\bar{r}_3$$

where:
$$f(r_{13}) = e^{-\beta u(r_{13})} - 1$$
$$y(r_{13}) = e^{-\beta u(r_{13})} g(r_{13}) \quad \text{etc. for } y(r_{12})$$

There are other integro differential equation that have been derived to facilitate the derivation of g(r) from first principles. These four reflect the nature of all of the derived expressions.

Tests of the Theory

All four equations give qualitatively acceptable results when compared with experimental data with no-one equation being vastly superior. The Kirkwood & BGV equations both use the superposition approximation whereas the PY & HNC eqn stem from the indirect correlation function.

Alternatively, in the limit of low density (ρ typical of gases, we can compute from the PY eqn for example, the virial coeficients, B_2, B_3 .. etc, for a gas of hard spheres. Table 13-2, P279 shows that all four equations agree with the exact values of B_2 & B_3 but all fail at B_4, B_5 etc.

In the case of the PY eqn, one can compute an exact equations for the pressure P from the pressure equation & from the compressibility equation. We have:

$$\frac{P}{\rho \kappa T} = \frac{1 + 2y + 3y^2}{(1-y)^2} \qquad \text{from pressure eqn (10)}$$

$$\frac{P}{\rho \kappa T} = \frac{1 + y + y^2}{(1-y)^3} \qquad \text{from compressibility eqn (16.1)}$$

and they are obviously not the same, $y = \frac{\pi \rho \sigma^3}{6}$ which reflects the approx. nature of the PY eqn.

Perturbation Theory

The concept of using perturbation theory for a problem requires that one have a 'standard' or known solution that is preferably exact for a problem that is similar to the unsolved problem.

In the case of liquids, the observation that the computed radial distribution function of a 'hard sphere' fluid is very similar to a 6-12 fluid or to an actual liquid from neutron scattering measurements, or from MD computations. We conclude from this that, since the 'hard sphere' potential is strictly repulsive, then the limi's share of a fluid's structure must be determined largely by 'repulsive force' while the attractive potential simply hold the molecules together in the fluid state.

This suggests that we think of a fluid's structure as determined by repulsive forces while the attractive forces can be treated as a perturbation.

Thus we can write:

$$U_N = U_N^{(0)} + U_N^{(1)}$$

where:

$U_N \equiv U_N(r_1, r_2, \ldots, r_N)$ is the total potential of interaction, $U_N^{(0)}$ is a 'hard sphere' potential and $U_N^{(1)}$ is the 'attractive potential', perturbation.

From the config. integral we have:

$$Z_N = \int \cdots \int e^{-\beta\, U_N(r_1, \ldots r_N)} \prod_{i=1}^{N} dr_i = \int \cdots \int e^{-\beta [U_N^{(0)} + U_N^{(1)}]} \prod_{i=1}^{N} dr_i$$

We now multiply & divide by $Z_N^{(0)} = \int \cdots \int e^{-\beta U_N^{(0)}} dr_1 \cdots dr_N$, e,

$$Z_N = Z_N^{(0)} * \frac{\int \cdots \int e^{-\beta [U_N^{(0)} + U_N^{(1)}]} dr_1 \cdots dr_2}{Z_N^{(0)}}$$

Which can be written as the avg. of $e^{-\beta U_N^{(1)}}$ OR,

$$Z_N = \underbrace{Z_N^{(0)}}_{\substack{\uparrow \\ Z_N \text{ for the} \\ \text{unperturbed system}}} \underbrace{\langle \exp(-\beta U_N^{(1)}) \rangle_0}_{\substack{\uparrow \text{ canonical average of the perturbation} \\ \text{over the unperturbed system.}}}$$

Now, assuming the exponential to be small, we can expand it, to get

$$\langle \exp(-\beta U_N^{(1)}) \rangle_0 = 1 - \beta \langle U_N^{(1)} \rangle_0 + \frac{\beta^2}{2!} \langle (U^{(1)})^2 \rangle_0 + \cdots -$$

Since,

$$A = -kT \log Q = -kT \log \frac{Z_N}{N! \Delta^{3N}} \quad \text{we have}$$

$$-\beta A = \log\left[\frac{Z_N^{(0)}}{N! \Delta^{3N}} \right] + \log \langle \exp(-\beta U_N^{(1)}) \rangle_0$$

$$= \underbrace{-\beta A_0}_{\substack{\uparrow \\ A \text{ ref system}}} \underbrace{-\beta A^{(1)}}_{\uparrow A \text{ pert.}}$$

18) Where $A^{(1)} = -kT \log \langle \exp(-\beta U_N^{(1)}) \rangle_0$

We now expand $A^{(1)}$ as a series in $\beta = \frac{1}{kT}$ to get

19) $A^{(1)} = \sum_{n=1}^{\infty} \frac{\omega_n}{n!} (-\beta)^{n-1}$

OR, taking the exponential of both sides, but $\wedge$ mult. by β first

19) $\exp(-\beta A^{(1)}) = \exp\left[\sum_{n=1}^{\infty} \frac{\omega_n}{n!} (-\beta)^n\right] = \sum_{n=0}^{\infty} \frac{(-\beta)^k}{k!} \langle (U_N^{(1)})^k \rangle_0$

Expanding & comparing like coefficients of β we have;

$\omega_1 = \langle U_N^{(1)} \rangle_0$

$\omega_2 = \langle (U_N^{(1)})^2 \rangle_0 - \langle U_N^{(1)} \rangle_0^2$

$\vdots$

so finally we can show that;

$A = A_0 + \omega_1 - \frac{\omega_2}{2kT} + O(\beta^3)$

which together with

$U_N^{(1)} = \sum_{i<j} u^{(1)}(r_{ij})$ pair potentials

and which, after some the usual change to relative coord's
we have

$$\langle U_N^{(1)} \rangle_0 = \frac{\rho^2 V}{2} \int u^{(1)}(r_{12}) \overbrace{g_0^{(2)}(r_{12})}^{\text{reference system}} d\bar{r}_{12}$$

Continuation requires a reference fluid & a perturbation.