August 5, 1980

$$Z = \sum \frac{1}{n!}\int d^n q\, e^{-\beta U_n(q)} \prod_1^n z(q_i)$$

Assuming $U_n(q) = \sum'_{i<j} U_2(q_i, q_j)$ we have

$$e^{-\beta U_n(q)} = \prod_{i<j}(1+f_{ij})$$

and so Z can be interpreted as a sum over graphs. Also $\log Z$ can be interpreted as a sum over connected graphs.

$$\log Z = \sum \frac{1}{n!}\int d^n q \prod_1^n z(q_i) \left(\begin{array}{l}\text{sum over} \\ \text{conn. graphs} \\ \text{with vertices } q_1,\dots,q_n \\ \text{factor } f(r_{ij}) \\ \text{for each edge.}\end{array}\right) \qquad r_{ij} = |q_i - q_j|$$

The Green's functions are defined by

$$G^c_n(x_1,\dots,x_n) = \frac{\delta^n}{\delta z(x_1)\cdots\delta z(x_n)} \log Z \Big|_{\text{set } z(x)=z \text{ all } x}$$

So

$$G^c_1(x) = \frac{\delta \log Z}{\delta z(x)} = \sum \frac{z^n}{n!}\int d^n q \left\{\begin{array}{l}\text{sum over conn. graphs} \\ \text{with vertices } x, q_1,\dots,q_n\end{array}\right\}$$

Recall from p. 961 that

$$\log Z = (\cdot) + (\bullet\!\!-\!\!\bullet) + (\bullet\!\!-\!\!\bullet\!\!-\!\!\bullet + \triangleleft)$$

$$= z\int d^1q + \frac{z^2}{2}\int d^2q\, f_{12} + z^3\left(\frac{1}{2}\int d^3q\, f_{12}f_{23} + \frac{1}{6}\int d^3q\, f_{12}f_{13}f_{23}\right) + \cdots$$

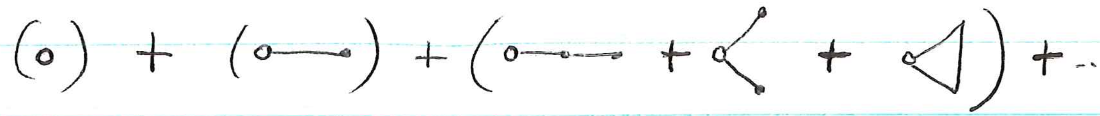
Put

$$a = \int f(|q|)\,dq = \frac{1}{V}\int d^2q\, f_{12}, \qquad b = \frac{1}{V}\int d^3q\, f_{12}f_{13}f_{23}$$

Then

$$\frac{\log Z}{V} = z + \frac{z^2}{2}a + \frac{z^3}{6}(3a^2+b)+\cdots$$

Also

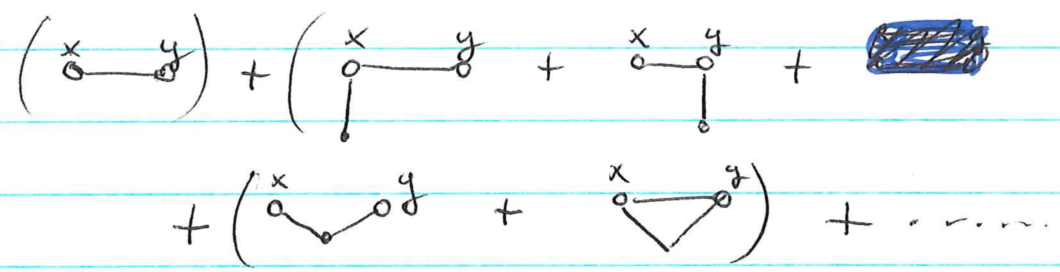
$G_1^c(x) =$ 

$$= 1 + z\int dq\, f(x,q) + \Big(z^2\int d^2q\, f(x,q_1)f(q_1,q_2) + \frac{z^2}{2}\int d^2q\, f(x,q_1)f(x,q_2) + \frac{z^3}{2}\int d^2q\, f(x,q_1)f(x,q_2)f(q_1,q_2)\Big)+\cdots$$

$$= 1 + za + z^2a^2 + \frac{z^2a^2}{2} + \frac{z^3}{2}b + \cdots$$

Note $G_1^c(x) = G_1(x) = \rho/z$ where $\rho = \frac{N}{V}$ is the density.

Next

$G_2^c(x,y) =$ 

$$= f(x,y) + \Big(z\int dq\, f(x,y)f(x,q) + z\int dq\, f(x,y)f(y,q) + z\int dq\, f(x,q)f(y,q) + z\int dq\, f(x,q)f(y,q)f(x,y)\Big)+\cdots$$

Introduce

$$\alpha(x,y) = \int dq\, f(x,q)f(q,y)$$

This depends only upon $|x-y|$. Then

$$\int dy\,\alpha(x,y) = \int dq\, f(x,q)\underbrace{\int dy\, f(q,y)}_{a} = a^2$$

and $\int dx dy\, f(x,y)\,\alpha(x,y) = \int dx dy\, d\xi\, f(x,y) f(x,\xi) f(y,\xi) = V \cdot b$

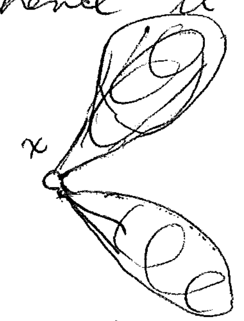
So

$$G_2^c(x,y) = f(x,y)\left[1 + 2az + z\alpha(x,y)\right] + z\alpha(x,y) + \cdots$$

Let's try to construct the vertex functions. First recall what we did on 963. It will probably be useful to keep a general $z(x)$ when possible. Recall that

$$G_1^c(x) = \frac{\rho(x)}{z(x)}$$

where $\rho(x)$ = density at x. A diagram contributing to $G_1^c(x)$ may become disconnected when the x-vertex is remove, hence it is a wedge:



This leads to the formula

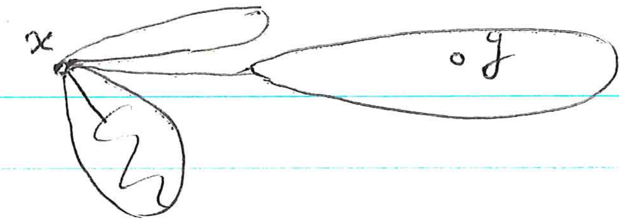
$$G_1^c(x) = \frac{\rho(x)}{z(x)} = e^{Y(x)}$$

where $Y(x)$ is the sum from the graphs which don't disconnect upon removing x. Also

$$Y(x) = \sum_{n\geq 0} \int \Gamma_{n+1}(x, x_1, \ldots, x_n)\, \frac{\rho(x_1)\cdots\rho(x_n)}{n!}\, d^n x$$

where $\Gamma_{n+1}(x, x_1, \ldots, x_n)$ denotes the contribution from star or doubly-connected graphs having the vertices $x, \ldots, x_n$

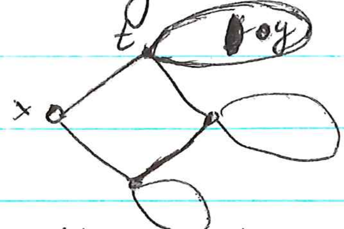
In the same spirit consider a graph contributing to $G_2^c(x,y)$, and split it at the x vertex:



This shows that

$$G_2^c(x,y) = G_1^c(x)\, G_2^{c*}(x,y)$$

where the $*$ means x-removal doesn't disconnect. A graph contributing to $G_2^{c*}(x,y)$ has the form



of a star with ρ terms at all but one vertex and at this vertex a smaller graph in $G_2^{c}(x,y)$

$$G_2^{c*}(x,y) = \sum_{n\geq 0} \iint \Gamma_{n+2}(x, t, x_1, \dots, x_n)\, \frac{\rho(x_1)\cdots\rho(x_n)}{n!}\, d^n x\, dt \times \left[z(t)\, G_2^c(t,y) + \delta(t-y) \right]$$

or

$$\frac{G_2^c(x,y)}{G_1^c(x)} = \sum_{n\geq 0} \frac{1}{n!} \int d^n x\, dt\, \Gamma_{n+2}(x, x_1, \dots, x_n, t)\, \rho(x_1)\cdots\rho(x_n) \left[\rho(t)\, \frac{G_2^c(t,y)}{G_1^c(t)} + \delta(t-y) \right]$$

When all the $z(x) = z$, then $\rho(x) = \rho$ and $G_1^c(x) = \frac{\rho}{z}$ so this becomes

$$G_2^c(x,y) = \sum_{n\geq 0} \frac{\rho^{n+1}}{n!} \int dt\, \Gamma_{n+2}(x,t)\, G_2^c(t,y)$$

+ extra term.

where $\Gamma_{n+2}(x,t)$ denotes star graphs contributions with vertices $x, z_1, \ldots, z_n, t$.

Missing from the above is the case when t is the fixed vertex y. We have

$$\frac{G_2^c(x,y)}{G_1^c(x)} = \sum_{n\geq 0} \frac{1}{n!}\int d^n x\, dt\, \Gamma_{n+2}(x, x_1 \ldots x_n, t)\, \rho(x_1)\cdots\rho(x_n)\rho(t)\, \frac{G_2^c(t,y)}{G_1^c(t)}$$

$$+ \frac{1}{n!}\int d^n x\, \Gamma_{n+2}(x, x_1, \ldots, x_n, y)\, \rho(x_1)\cdots\rho(x_n)$$

so when $z(x) = z$ and $\rho(x) = \rho$ for all x we have

$$\frac{G_2^c(x,y)}{G_1^c} = \sum_{n\geq 0} \frac{\rho^{n+1}}{n!}\int dt\, \Gamma_{n+2}(x,t)\, \frac{G_2(t,y)}{G_1^c} + \sum_{n\geq 0}\frac{\rho^n}{n!}\Gamma_{n+2}(x,y)$$

still not correct see p.4 below

<u>August 6, 1980</u>

$$Z = \sum_n \frac{1}{n!} \int d^n q \; \underbrace{e^{-\beta U_n(q)}}_{\prod_{i<j}(1+f_{ij})} \prod_{j=1}^{n} z(q_j)$$

can be interpreted as a "sum" over Mayer diagrams.

$$\log Z = \sum_n \frac{1}{n!} \int d^n q \;\; C_n(q) \prod z(q_j)$$

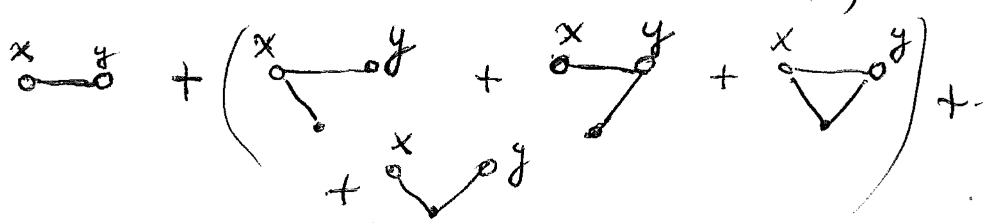
where $C_n(q)$ is the part of $\prod_{i<j}(1+f_{ij})$ belonging to connected diagrams.

The Green's (connected) functions are defined by

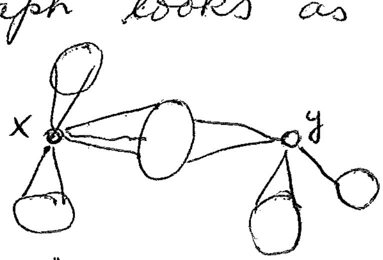
$$G_1^c(x_1, \dots, x_k) = \frac{\delta^k}{\delta z(x_1) \cdots \delta z(x_k)} \log Z$$

$$= \sum_n \frac{1}{n!} \int d^n q \;\; \underset{k+n}{C}(x_1, \dots, x_k, q) \prod_1^n z(q_j)$$

Thus $G_1^c(x) =$ 

Look at $G_2^c(x,y) =$ 

If the x vertex is removed from a graph, then it splits into components exactly one of which contains the y-vertex. Similarly if we remove the y-vertex. Thus the graph looks as follows.

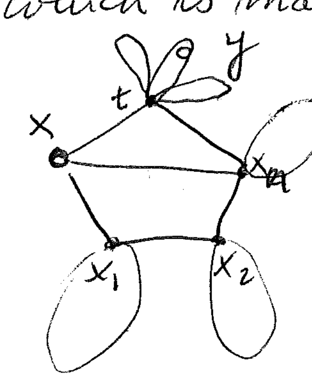


This shows that $G_1^c(x)\, G_1^c(y)$ occurs naturally as a factor of $G_2^c(x,y)$.

~~From now on let's drop the c superscript.~~

$$\cancel{G_2^c(x,y) \longmapsto G_2(x,y).}$$

So let's take a graph occurring in $G_2^c(x,y)/G_1^c(x)$, i.e. the x-vertex is not critical; (critical means the graph becomes disconnected when the vertex is removed). Then we look at the "star" (doubly-connected subgraph which is maximal) containing x. Any path from x to y passes thru one of its vertices, call it t, and label the rest $x_1, \dots, x_n$. At each x_i we get the contribution



$$\rho(x_i) = z(x_i)\, G_1^c(x_i).$$

At t, there are two possibilities. If the t-vertex is $\neq$ the y-vertex we get the contribution

$$z(t)\, G_2^c(t,y) = \rho(t) \frac{G_2^c(t,y)}{G_1(t)}$$

If t-vertex = y-vertex, the contribution is

$$\frac{\rho(y)}{z(y)} = G_1^c(y)$$

Hence we get

$$\frac{G_2^c(x,y)}{G_1^c(x)} = \sum_n \frac{1}{n!} \int d^n x\, dt\, \Gamma_{n+2}(x, x_1, \dots, x_n, t) \prod_{i=1}^n \rho(x_i)$$

$$\times \left\{ \rho(t) \frac{G_2^c(t,y)}{G_1^c(t)} + \delta(t-y)\, G_1^c(y) \right\}$$

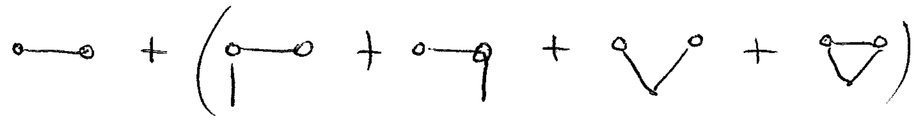
This can be written more simply

$$\frac{G_2^c(x,y)}{G_1(x)G_1(y)} = \sum_n \frac{1}{n!}\int d^n x \, dt \, \Gamma_{n+2}(x, x_1, \dots, x_n, t)\left\{\prod_{i=1}^n \rho(x_i)\right\}\rho(t)\,\frac{G_2^c(t,y)}{G_1(t)G_1(y)}$$

$$+ \sum_n \frac{1}{n!}\int d^n x \, \Gamma_{n+2}(x, x_1 \dots x_n, y)\prod_{i=1}^n \rho(x_i)$$

Assuming translation invariance for f_{ij} and $z(x)$, we get

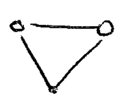
$$\boxed{\frac{G_2^c(x,y)}{(G_1)^2} = \sum_n \frac{\rho^n}{n!}\Gamma_{n+2}(x,y) + \sum_n \frac{\rho^{n+1}}{n!}\int dt \, \Gamma_{n+2}(x,t)\,\frac{G_2^c(t,y)}{(G_1)^2}}$$

<u>Check:</u> $G_2^c(x,y) =$ 

$$= f(x,y) + f(x,y)\,2za + z\underbrace{\int dq\, f(x,q) f(y,q)}_{\alpha(x,y)} + z f(x,y)\alpha(x,y)$$

$$a = \int f(x,q)\,dq \qquad\qquad + O(z^2)$$

Now $\Gamma_2(x,y) =$  $= f(x,y)$

$\Gamma_3(x,y) =$  $= f\alpha$

recall the Γ_n don't involve z.

$G_1 =$  $+ \cdots = 1 + za + O(z^2)$

$$\therefore \frac{G_2^c(x,y)}{(1+za)^2} = f + \underbrace{\rho}_{z+O(z^2)}(f\alpha) + \underbrace{\rho}_{z+O(z^2)}\int dt\, f(x,t)\big(f(t,y) + O(z)\big)$$

$$= f + z(f\alpha + \alpha) + O(z^2)$$

$$G_2^c(x,y) = f + 2zaf + zf\alpha + z\alpha + O(z^2) \qquad \text{checks.}$$

Pair correlation function:

Recall $n(x)$ is the "function" on $SP(X)$ which assigns to each configuration its density at x, so that

$$\rho_1(x) = \langle n(x) \rangle = z(x)\, G_1(x)$$

is the expected density at x. For $x \neq y$

$$\rho_2(x,y) = \langle n(x)\, n(y) \rangle = z(x) z(y) G_2(x,y)$$

Put
$$g_2(x,y) = \frac{\langle n(x)\, n(y)\rangle}{\langle n(x)\rangle \langle n(y)\rangle} = \frac{G_2(x,y)}{G_1(x) G_1(y)}$$

If $n(x)$, $n(y)$ are independent random variables, then $g_2(x,y) = 1$. Standard notion in the translation + rotation invariant case:

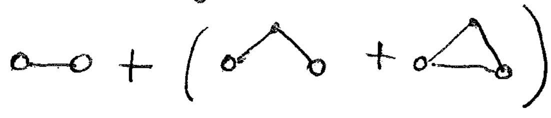
$$g(r) = g_2(x,y) \qquad r = |x-y|$$

Now
$$G_2(x,y) = G_1(x) G_1(y) + G_2^c(x,y)$$

so
$$g(r) = 1 + \underbrace{\frac{G_2^c(x,y)}{G_1(x)G_1(y)}}_{h(r)}$$

This defines $h(r)$:

Notice that we can expect $g(r) \to 1$ as $r \to \infty$ and hence $h(r) \to 0$ at ∞. We have already worked out the diagrams contributing to $h(r)$ – they are connected and do not have x, y as critical vertices. Thus

$h(r) =$  $+ \cdots$

But on page 4 we derived an

integral equation for $h(r) = \cancel{\frac{G_2^c(x,y)}{G_1^c(x)\,G_1^c(y)}}\ \frac{G_2^c(x,y)}{(G_1^c)^2}$
which can be written

$$h(x,y) = c(x,y) + \rho \int dt\; c(x,t)\, h(t,y)$$

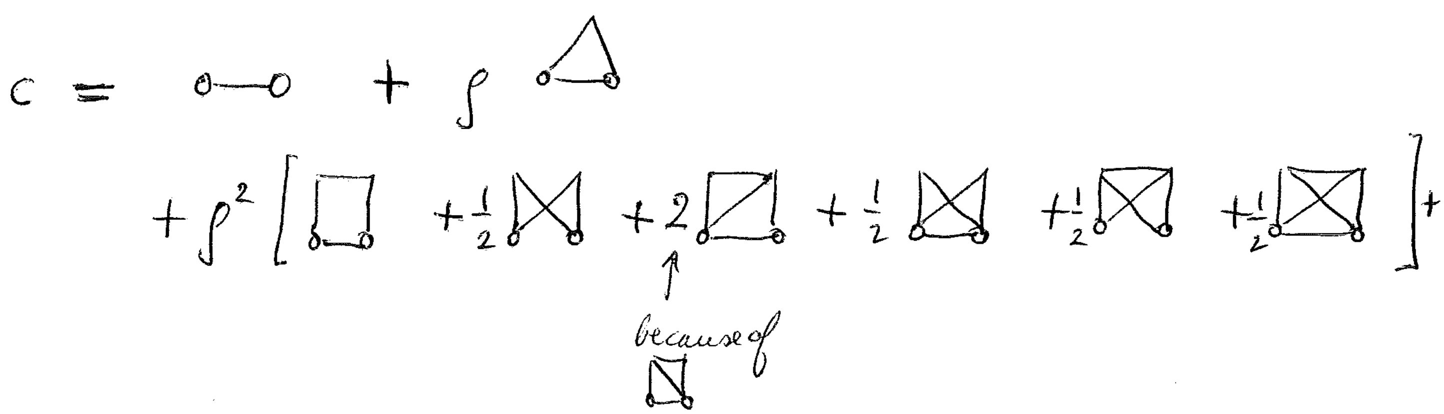
or

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})\, h(r_{23})\, d\vec{r}_3$$

which is called the <u>Ornstein-Zernike</u> equation. This equation can be taken as the definition of c. We showed that

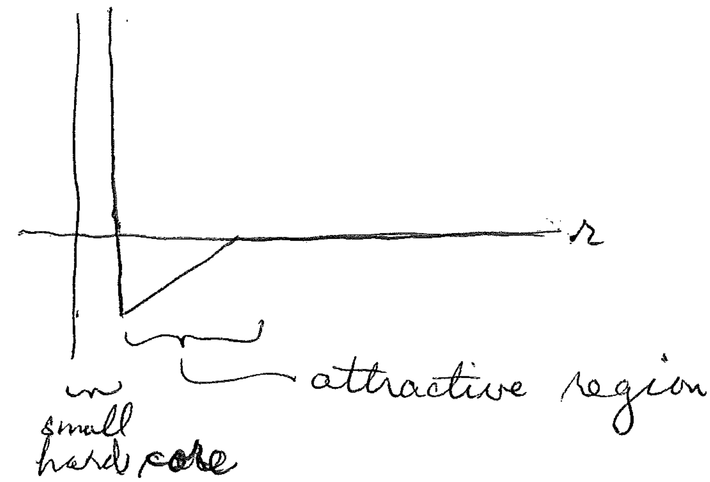
$$c(x,y) = \sum \frac{\rho^n}{n!} \Gamma_{n+2}(x,y)$$

c is called the <u>direct correlation</u> fn. and in diagrams is



August 7, 1980

van der Waals forces. Suppose we have a gas of small particles which attract each other. Say the interatomic potential looks as follows:

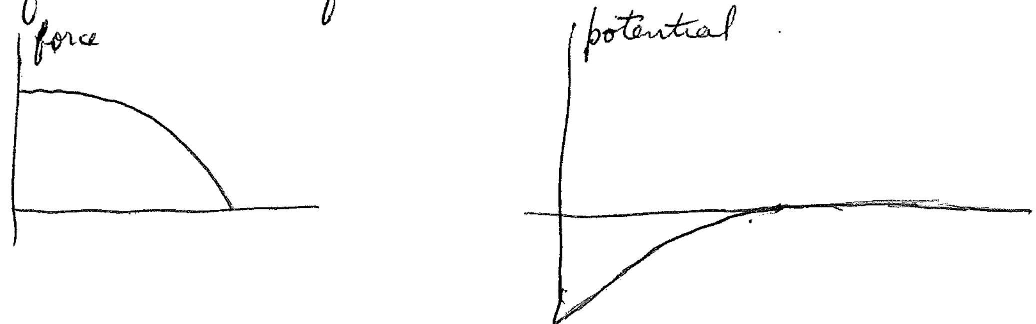


For the moment ignore the hard core.

The effect of the attractive interaction is to produce a surface effect which should reduce the pressure. Thus an atom in the middle is attracted on all sides

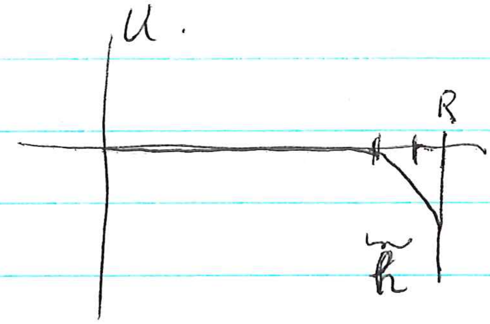
but an atom on the walls is attracted away from the walls.

My first idea is to compute the force on an atom assuming the other atoms are distributed uniformly with density $\rho = N/V$. Thus I am trying to find an effective 1-body potential. Picture of net normal force as a function of distance from walls



So if $U(q)$ denotes the effective potential, we want to compute the pressure assuming the atoms don't otherwise interact. The partition fn. is

$$Z_1 = C\beta^{-\frac{3}{2}} \int e^{-\beta U(q)}\, dq$$



distance from center.

Imagine the volume is a sphere of radius R

$$\int e^{-\beta U(q)}\, dq \doteq \int (1 - \beta U(q))\, dq$$

$$= V - \beta \int U(r)\, 4\pi R^2\, dr$$

Now $U(r)$ should be approximated by something linear in h. Also it should be proportional to the density because the force is. Thus put

$$U(r) = -C\rho h$$

and we get

$$\int e^{-\beta U(q)}\, dq \doteq V + C\beta\rho\, 4\pi R^2 \overbrace{\int_0 h\, dh}^{\text{fixed amount}}$$

$$\doteq V + C\beta\rho\, V^{2/3} \qquad = V(1 + C\beta N V^{-4/3})$$

where C is some constant.

The N particle partition fn. is

$$\log Z_N = -\frac{3}{2} N \log\beta + N \log V + \underbrace{N \log(1 + C\beta N V^{-4/3})}_{\doteq\, C\beta N^2 V^{-4/3}}$$

so

$$p\beta = \frac{\partial}{\partial V}\log Z_N = \frac{N}{V} - \frac{4}{3}C\beta N^2 V^{-7/3}$$

which leads to the equation of state

$$\Big(p + \frac{4}{3}C\underbrace{N^2 V^{-7/3}}_{\rho^2 V^{-1/3}}\Big) = \frac{NkT}{V}$$

What's strange about this is the $V^{-1/3}$ factor. Probably this is due to the fact that at surface $u<0$ so the density should be higher

Derivation from virial expansion. First note the standard derivation of van der Waals goes as follows. [redacted] ~~attractive forces give~~ basic assumption is that one has an ideal gas law

$$p'V' = NkT$$

with a modified pressure and volume. Thus we have independent particles. Each particle moves in a volume $V' = V -$ volume taken up by others $= V - Nb$. The pressure on a single molecule $p' = p +$ attractive part. The attractive part depends on the number of molecules in the surface layer and the number of molecules pulling these in the inner layer. Both numbers are proportional to the density hence

$$p' = p + a\rho^2$$

Thus the van der Waals equation is

$$(p + a\rho^2)(V - Nb) = NkT$$

or $$\frac{1}{kT}(p + a\rho^2) = \frac{N}{V - Nb} = \frac{\rho}{1 - \rho b}$$

$$\frac{p}{kT} = \rho - \left(\frac{a}{kT} - b\right)\rho^2 + O(\rho^3)$$

But now recall the virial expansion:

$$\rho = z e^{\Gamma(\rho)} \qquad \Gamma(\rho) = \Gamma_2\rho + \Gamma_3\frac{\rho^2}{2!} + \Gamma_4\frac{\rho^3}{3!} + \cdots$$

$p\beta = \frac{\log Z_{gr}}{V} = F(z)$. If $F(z) = G(\rho)$, then

$\rho = zF'(z)$ $\qquad F'(z)\frac{dz}{d\rho} = G'(\rho) \qquad \frac{1}{\rho} = \frac{1}{z}\frac{dz}{d\rho} + \Gamma'(\rho)$

$$\therefore\ G'(\rho) = \frac{\rho}{z}\frac{dz}{d\rho} = 1 - \rho\Gamma'(\rho) = 1 - \Gamma_2\rho - \Gamma_3\rho^2 - \Gamma_4\frac{\rho^2}{2!} - \cdots$$

and so the equation of ~~states~~ is

$$p\beta = \rho - \Gamma_2\frac{\rho^2}{2} - \Gamma_3\frac{\rho^3}{3} - \Gamma_4\frac{\rho^4}{4\cdot 2!} - \Gamma_5\frac{\rho^5}{5\cdot 3!} - \cdots$$

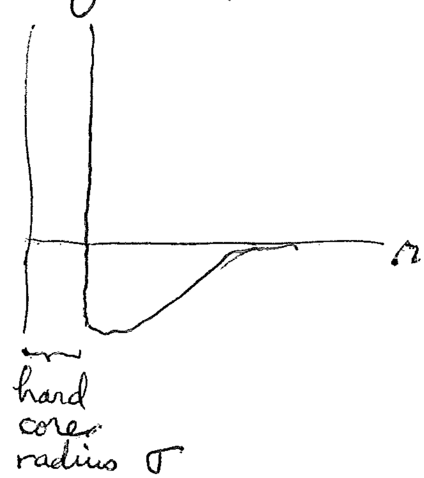
Hence van der Waals is obtained from

$$\frac{\Gamma_2}{2} = -b + \frac{a}{kT}$$

But we know that

$$\Gamma_2 = \int_0^\infty \left(e^{-\beta u(r)} - 1\right) 4\pi r^2\,dr$$

so in the case of a potential



we get

$$\Gamma_2 = -\frac{4\pi}{3}\sigma^3 + \underbrace{\int_\sigma^\infty -\beta U(r)\, 4\pi r^2 dr}_{\text{proportional to } \frac{1}{kT}} + O(\beta^2)$$

which gives van der Waals. The interesting point is the factor of 2:

$$b = \frac{1}{2}\,\frac{4\pi}{3}\sigma^3$$

Question: Suppose we have an imperfect gas and we would like to understand its behavior approximately as a gas of independent particles moving in some kind of effective potential. The effective potential $U_{eff}(q)$ gives the average effect of the molecules of the gas upon the particle at q. In the present case the effective potential is independent of q by translation invariance and coincides with the chemical potential μ, i.e. the energy required to insert a particle into the gas.

Recall that

$$p\beta = \frac{\log Z_{gr}}{V} = z + F_2 \frac{z^2}{2!} + \cdots$$

where

$$z = e^{\beta\mu} \int e^{-\beta \frac{p^2}{2m}} \frac{dp\, dq}{(2\pi\hbar)^3} = \left(\frac{mk}{2\pi\hbar^2}\right)^{3/2} T^{3/2} e^{\beta\mu}$$

and μ is adjusted to give the density

$$\rho = z + F_1 z^2 + F_2 \frac{z^3}{2!} + \cdots$$

We showed that

$$z = \rho\, e^{-\Gamma(\rho)} \qquad \Gamma(\rho) = \Gamma_2 \rho + \Gamma_3 \frac{\rho^2}{2!} + \cdots$$

and that
$$p\beta = \rho - \Gamma_2 \frac{\rho^2}{2} - \Gamma_3 \frac{\rho^2}{3} - \cdots$$

Now that we know the chemical ~~potential~~ μ let us compute the behavior of an ideal gas with ~~the same density and~~ this chemical potential μ or activity z

$$\tilde{p}\beta = z \qquad \text{where } z = \rho e^{-\Gamma(\rho)}$$

Here $\tilde{p}$ is the approximate pressure. Thus

$$\tilde{p}\beta = \rho e^{-\Gamma(\rho)} = \rho\left[1 - \left(\Gamma_2\rho - \Gamma_3\frac{\rho^2}{2}\right) + \frac{1}{2}(\Gamma_2\rho)^2 \cdots\right]$$

$$= \rho - \Gamma_2\rho^2 + \left(-\frac{\Gamma_3}{2} + \frac{\Gamma_2^2}{2}\right)\rho^3$$

This is off by a factor of 2 already at the ρ^2 level.

August 9, 1980

effective or pseudo-potential:

Idea: Consider

$$Z(J) = \int e^{Jx - f(x)}\,dx \Big/ \int e^{-f(x)}\,dx = e^{F(J)}$$

where $f(x) = a\frac{x^2}{2} + b\frac{x^3}{3!} + \cdots$ and $a > 0$. Then

[redacted] $$F(J) = F_1 J + F_2 \frac{J^2}{2!} + F_3 \frac{J^3}{3!} + \cdots$$

where F_n is a sum over connected diagrams having n labeled external (i.e. mult. 1) vertices.

$$\langle x\rangle = \frac{dF}{dJ} = F_1 + F_2 J + F_3 \frac{J^2}{2!} + \cdots$$

$$= \frac{1}{a}\Gamma_1 + \frac{J}{a} + \frac{1}{a}\Gamma_2 \langle x\rangle + \frac{1}{a}\Gamma_3 \frac{\langle x\rangle^2}{2!} + \cdots$$

$$J = -\Gamma_1 + (a - \Gamma_2)\langle x\rangle + (-\Gamma_3)\frac{\langle x\rangle^2}{2!} \cdots$$

Here Γ_n is [redacted] a sum over 1PI diagrams having n external lines [redacted] which are ordered.

Introduce the Legendre transform

$$\Gamma(\langle x\rangle) = \langle x\rangle J - F(J)$$

so that

$$\frac{d\Gamma}{d\langle x\rangle} = J$$

Thus

$$\Gamma(\langle x\rangle) = (-\Gamma_1)\langle x\rangle + (a - \Gamma_2)\frac{\langle x\rangle^2}{2!} + (-\Gamma_3)\frac{\langle x\rangle^3}{3!} + \cdots$$

Now Γ is called the <u>pseudo-potential.</u> Why?

x is describing configurations of our system, and

$f(x)$ is the energy of [redacted] the configuration x. [redacted] Hence if there were no "fluctuations" (thermal or quantum-mechanical) one would expect to see the system in the configuration of minimum potential energy, i.e. where $f'(x) = 0$. In this case $f(x) = a\frac{x^2}{2} + \cdots$ the configuration of minimum energy is $x = 0$.

[redacted]

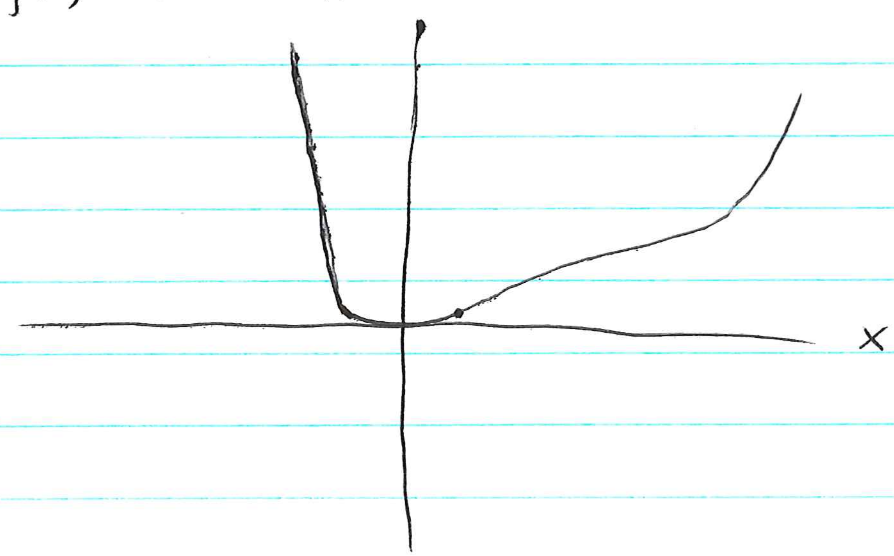
But because of fluctuations the system can be found in many [redacted] configurations, the probability density being

$$e^{-f(x)} \Big/ \int e^{-f(x)} dx$$

whose generating function is $Z(J)$. So the expected configuration is

$$\langle x \rangle_{J=0} = \frac{\int x e^{-f(x)} dx}{\int e^{-f(x)} dx} = \left.\frac{dF}{dJ}\right|_{J=0}$$

This is F_1, which is not necessarily zero, e.g. when $f(x)$ looks like



Thus $f'(x) = 0$ does not give [redacted] the observed average value $\langle x \rangle$. However because of

$$\frac{d\Gamma}{d\langle x\rangle} = J$$

it follows that $J=0$ corresponds to an extremal value for $\Gamma(\langle x\rangle)$, the pseudo-potential.

Another view is as follows. Suppose we apply a uniform force J to the particle, so that the potential energy of the configuration x is $f(x)-Jx$, and the equilibrium position given by

(*) $$f'(x) = J$$

i.e. where J balances the force $-f'(x)$. In the presence of fluctuations, the equilibrium position is

$$\langle x\rangle = \int x\, e^{\beta(Jx-f(x))}dx \Big/ \int e^{\beta(Jx-f(x))}dx$$

$$= \frac{1}{\beta}\frac{d}{dJ}\log Z(J) \qquad Z(J) = \frac{\int e^{\beta(Jx-f(x))}dx}{\int e^{-\beta f(x)}dx}$$

$$= \frac{d}{dJ}\left(\frac{\log Z(J)}{\beta}\right)$$

This makes $\langle x\rangle$ a function of the applied field J and the pseudo-potential $\Gamma(\langle x\rangle)$ generalizes * :

$$\frac{d\Gamma}{d\langle x\rangle} = J$$

Thus $\langle x\rangle$ is the position at which the pseudo-force $-\Gamma'(\langle x\rangle)$ is balanced by the applied field J.

The pseudo-potential is $\Gamma(\langle x\rangle) = \langle x\rangle J - \frac{\log Z}{\beta}$

August 10, 1980

To understand Brownian motion on the line in a potential $V(x)$:

We have this 1-dimensional system coupled to a heat reservoir. We are ignorant of the details of the coupling and so proceed by making statistical assumptions. One of these is that all states of the combined system of a given large energy are equally probable. This leads as we have seen to the Maxwell-Bolzmann distribution in phase space for the states of the Brownian particle.

Let's next suppose that at times $t = n\tau$ $\quad n \in \mathbb{N}$ the particle receives a "collision" from the heat reservoir which changes its momentum at that time. Thus we have a random walk. We start at $t=0$ at position x_0 and then pick a momentum consistent with Maxwell distribution, then let the particle move for a time τ to a position x_1. Then pick a new momentum, etc.

Let's try to see what this does for $V = 0$. We start at x_0 and we want to find $p(x, n\tau; x_0, 0) \times dx$, the probability of reaching x in n-steps. So we need the probability distribution of one step. If the initial and final positions are x', x resp. then

$$x = x' + \frac{p}{m}\tau \qquad \text{or} \qquad p = m\left(\frac{x-x'}{\tau}\right)$$

where p is the momentum. p has the distribution

$$e^{-\beta\frac{p^2}{2m}} \frac{dp}{\sqrt{2\pi\, m/\beta}} \qquad\qquad dp = \frac{m}{\tau}dx$$

so x has the distribution

$$e^{-\beta\frac{1}{2m}\left(m\frac{x-x'}{\tau}\right)^2} \frac{m}{\tau}\frac{dx}{\sqrt{2\pi\, m/\beta}}$$

$$= e^{-\frac{\beta}{2} m \frac{(x-x')^2}{\tau^2}} \frac{m}{\tau} \frac{dx}{\sqrt{2\pi m/\beta}}$$

Unfortunately the variance is proportional to τ^2 instead of τ, and so we won't be able to take a limit as $\tau \to 0$ and $n\tau \to t$.

The probability distribution $p(x,t)\,dx$ for the position of the Brownian particle at time t satisfies an integral equation

$$p(x,t) = \int K(xt; x't')\, p(x',t')\, dx'$$

which expresses the fact we have a Markov process, i.e. the probability of finding it at xt given that it was at $x't'$ does not depend on its earlier history. Rewrite this

$$p(x, t+\Delta t) = \int K(x, t+\Delta t; x-\Delta x, t)\, p(x-\Delta x, t)\, d\Delta x$$

and use that for Δt small this should be peaked near $\Delta x = 0$, so that we can use the approx.

$$p(x-\Delta x, t) = p(x,t) - \frac{\partial p}{\partial x}(x,t)\,\Delta x + \frac{1}{2}\frac{\partial^2 p}{\partial x^2}(x,t)\,\Delta x^2.$$

Then

$$p(x,t+\Delta t) = \int K(x, t+\Delta t; x-\Delta x, t) \Big\{ \qquad\qquad \Big\}\, d\Delta x$$

$$= p(x,t) - \lambda \frac{\partial p}{\partial x} + \frac{1}{2}\mu \frac{\partial^2 p}{\partial x^2}$$

where λ, μ are the first and second moments of the distribution $K(x, t+\Delta t; x-\Delta x, t)$ of Δx.

Now as $\Delta t \to 0$ we expect λ and μ to be proportional to Δt say

(*) $$\frac{\lambda}{\Delta t} \to a \qquad \frac{\mu}{\Delta t} \to b$$

hence we get the equation

$$\frac{\partial p}{\partial t} = a\frac{\partial p}{\partial x} + \frac{1}{2} b \frac{\partial^2 p}{\partial x^2}$$

To justify (*) consider a random walk x of N steps made of increments (independent) of mean $\bar{a}$ and second moment ~~[illegible]~~ $\bar{b}$. Then

$$\langle x\rangle = \sum \langle x_i\rangle = N\bar{a}$$

$$\langle x^2\rangle = N\bar{b} + 2\frac{N(N-1)}{2}\bar{a}^2 = (Na)^2 + N(\bar{b}-\bar{a}^2)$$

~~Let $N \to \infty$ and let a, b be varied so that $\lambda = \langle x\rangle$, $\mu = \langle x^2\rangle$ remain fixed. Then $a = \frac{\lambda}{N}$~~

Suppose N is very large and let us consider the first $(\Delta t)N$ steps in this random walk, and let x' be the resulting position. Then if λ, μ are the moments

$$\lambda = \langle x'\rangle = (\Delta t\, N)\bar{a}$$

$$\mu = \langle x'^2\rangle = (\Delta t\, N\bar{a})^2 + \Delta t\, N(\bar{b}-\bar{a}^2)$$

and we see that $\frac{\lambda}{\Delta t} = \langle x\rangle$, $\frac{\mu}{\Delta t} = \Delta t\langle x\rangle^2 + (\langle x^2\rangle - \langle x\rangle^2)$

which justifies (*) in this example.

Consider this example more closely. Let's start from the beginning. We have a random walk on the line with N steps

$$x = \sum_{i=1}^{N} x_i$$

where the x_i are independent random variables. Let us associate to N a time $t = N\tau$ and think of the probability distribution of x as the probability [redacted] $p(x,t)\,dx$ of finding the particle in the range $[x, x+dx]$ at time t. Now what I want to do is let $\tau \to 0$ and have $p(x,t)dx$ converge.

Because the [redacted] x_i are independent the central limit theorem says that $p(x,t)\,dx$ has to be a Gaussian random variable to a good approximation[redacted]. Let's take the simplest case where x_i is a Gaussian r.v. with mean $\langle x_i \rangle = a$ and variance $\langle x_i^2 \rangle - \langle x_i \rangle^2 = b$. Then $p(x,t)$ is Gaussian with $\langle x \rangle = Na$, $\langle x^2 \rangle - \langle x \rangle^2 = Nb$. So now let $\tau \to 0$ so that $\frac{a}{\tau} = \alpha$, $\frac{b}{\tau} = \beta$ and in the limit $p(x,t)$ is Gaussian with

$$\langle x \rangle = t\alpha \qquad \langle x^2 \rangle - \langle x \rangle^2 = t\beta$$

So if we start off with a $\delta(x)$-distribution at $t=0$ we get

$$p(x,t) = \frac{1}{\sqrt{2\pi t\beta}}\, e^{-\frac{(x-t\alpha)^2}{2t\beta}}$$

August 11, 1980

Let review linear response theory. Suppose we have a system described by a Hamiltonian H_0 and we are interested in some quantity [redacted] described by an operator A. [redacted] Work at $T=0$ so the system is in its ground state. When we measure A we get the mean value

$$\langle A \rangle = \langle \Psi_0 | A | \Psi_0 \rangle \big/ \langle \Psi_0 | \Psi_0 \rangle$$

where Ψ_0 is the ground state vector. This quantity $\langle A \rangle$ does not change in time.

Now let's suppose we have a weak time-dep. perturbation so the system is described by

$$H = H_0 + \delta H(t)$$

Assume $\delta H(t) = 0$ for $t < 0$ and the system starts out in the ground state. To first order the Schroedinger vector describing the system at time t is

$$\Psi(t) = \text{[redacted]}\, e^{-iH_0 t}\Psi_0 - i\int_{-\infty}^{t} dt_1\, e^{-iH_0(t-t_1)}\,\delta H(t_1)\, e^{-iH_0 t_1}\Psi_0$$

and the expected value of A at time t is

$$\langle \Psi(t) | A | \Psi(t) \rangle = \langle \Psi_0 | A | \Psi_0 \rangle - i\int_{-\infty}^{t} dt_1 \langle \Psi_0 | e^{iH_0 t} A e^{-iH_0(t-t_1)}\,\delta H(t_1)\, e^{-iH_0 t_1} | \Psi_0 \rangle$$

$$+ i\int_{-\infty}^{t} dt_1 \langle \Psi_0 | e^{iH_0 t_1}\,\delta H(t_1)\, e^{iH_0(t-t_1)} A\, e^{-iH_0 t} | \Psi_0 \rangle$$

Thus if we put $\delta\langle A\rangle(t) = \langle \Psi(t) | A | \Psi(t) \rangle - \langle \Psi_0 | A | \Psi_0 \rangle$ we get the response formula

$$\boxed{\delta\langle A\rangle(t) = -i\int_{-\infty}^{t} dt_1 \langle[\tilde{A}(t), \tilde{\delta H}(t_1)]\rangle}$$

where $\tilde{A}(t) = e^{iH_0 t} A e^{-iH_0 t}$, $\tilde{\delta H}(t_1) = e^{iH_0 t_1}\delta H(t_1) e^{-iH_0 t_1}$

Typically $\delta H(t) = f(t) B$ where B is a fixed (usually hermitian) operator and $f(t)$ is a fn. $=0$ for $t<0$. Then we get

$$\delta\langle A\rangle(t) = -i\int_{-\infty}^{t} \langle[\tilde{A}(t), \tilde{B}(t_1)]\rangle f(t_1)\,dt_1$$

$$= \int_{-\infty}^{\infty} K(t-t_1)\, f(t_1)\,dt_1$$

where
$$K(t) = -i\langle[\tilde{A}(t), B]\rangle\theta(t)$$
and we have used invariance of $\langle\ \rangle$ under H_0

Now introduce Fourier transforms

$$f(t) = \int \frac{d\omega}{2\pi} e^{-i\omega t}\hat{f}(\omega).$$

$$\hat{f}(\omega) = \int dt\, f(t) e^{i\omega t}$$ analytic for $\mathrm{Im}\,\omega > 0$

and we have
$$\widehat{\delta\langle A\rangle}(\omega) = \hat{K}(\omega)\hat{f}(\omega)$$

where $$\hat{K}(\omega) = \int_0^{\infty} dt\left(-i\langle[\tilde{A}(t), B]\rangle\right)e^{i\omega t}$$ is analytic for $\mathrm{Im}\,\omega > 0$.

Suppose $H_0 = \sum E_n |n\rangle\langle n|$ $\qquad |0\rangle = \Psi_0$

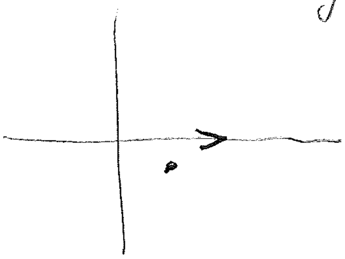
then $\tilde{A}(t) = e^{iH_0 t} A e^{-iH_0 t} = \sum_m |m\rangle e^{iE_m t} \langle m|A|n\rangle e^{-iE_n t} \langle n|$

$$\langle \tilde{A}(t) B \rangle = \sum e^{-i(E_n - E_0)t} \langle 0|A|n\rangle\langle n|B|0\rangle$$

$$\langle B \tilde{A}(t) \rangle = \sum e^{i(E_n - E_0)t} \langle 0|B|n\rangle\langle n|A|0\rangle$$

$K(t) = -i \langle [\hat{A}(t), B] \rangle \theta(t)$. Notice that by contour integration

$$\int \frac{d\omega}{2\pi} e^{-i\omega t} \frac{1}{\omega - E + i0^+} = e^{-iEt}\theta(t) \frac{-2\pi i}{2\pi}$$
$$= -ie^{-iEt}\theta(t).$$



Hence

$$\hat{K}(\omega) = \sum_n \left(\frac{\langle 0|A|n\rangle\langle n|B|0\rangle}{\omega - (E_n - E_0) + i0^+} - \frac{\langle 0|B|n\rangle\langle n|A|0\rangle}{\omega + (E_n - E_0) + i0^+} \right)$$

All the above has to be connected with examples. Previously I have looked at a fermi gas, ~~[illegible]~~ specifically an electron gas. The operators A were the particle density $\rho(x) = \psi(x)^* \psi(x)$ at different points. The B operators were the same, because I wanted the response to an applied electric field with potential $\varphi(x,t)$. The perturbing Hamiltonian was

$$\delta H = e\int \rho(x)\varphi(x,t)\,dx$$

Let's look at a simpler example. Take 1-dimensional motion of a single particle. Here A will be the position x. The perturbation will be a constant in space force field so that

$$\delta H(t) = x\, f(t)$$

and $B =$ the position operator x. (Notice that this is the sort of situation encountered in the reaction of electrons in [redacted] atoms to visible light.

red end of visible spectrum	8000 Å
near ultra-violet	2600 Å.

Hence an electromagnetic field of visible light is essentially constant over the dimensions of an atom.)

4000 – 7000 Å is a better estimate of the wavelengths of visible light.