Virial expansion for dilute gas.

First review BE gas:

$$Z_G = \prod_k \frac{1}{1 - z e^{-\beta \varepsilon_k}} \qquad z = e^{\beta\mu} < 1 \qquad \varepsilon_k = \frac{\hbar^2 k^2}{2m} \qquad k \in \frac{2\pi}{L}\mathbb{Z}^3$$

$$\frac{\log Z_G}{V} \to \int \frac{d^3\vec{k}}{(2\pi)^3} \log \frac{1}{1 - z e^{-\beta\varepsilon_k}}$$

$$= \frac{4\pi}{(2\pi)^3} \int_0^\infty \underbrace{r^3 \frac{dr}{r}}_{\varepsilon^{3/2} \frac{1}{2}\frac{d\varepsilon}{\varepsilon}} \left(-\log\left(1 - z e^{-\beta \underbrace{\frac{\hbar^2}{2m} r^2}_{\varepsilon}}\right)\right)$$

$$= \frac{4\pi}{(2\pi)^3} \frac{1}{2} \left(\frac{2m}{\hbar^2 \beta}\right)^{3/2} \underbrace{\int_0^\infty x^{3/2} \frac{dx}{x} \left(z e^{-x} + \frac{z^2 e^{-2x}}{2} + \frac{z^3 e^{-3x}}{3} + \cdots\right)}_{\underbrace{\Gamma(3/2)}_{\frac{1}{2}\sqrt{\pi}} \left[z + \frac{z^2}{2^{5/2}} + \frac{z^3}{3^{5/2}} + \cdots\right]}$$

$$\frac{\log Z_G}{V} \longrightarrow \underbrace{\left(\frac{mk}{2\pi \hbar^2}\right)^{3/2}}_{c} T^{3/2} \left[z + \frac{z^2}{2^{5/2}} + \cdots\right]$$

The basic equations are

$$p\beta = \lim_{V\to\infty} \frac{\log Z_G}{V} = c\, T^{3/2} \left[z + \frac{z^2}{2^{5/2}} + \cdots\right]$$

$$\rho = \lim \frac{N}{V} = z \frac{\partial}{\partial z}\left(\lim \frac{\log Z_G}{V}\right) = c\, T^{3/2} \left[z + \frac{z^2}{2^{3/2}} + \cdots\right]$$

and we eliminate z from these to get the equation of state.

Next consider the grand canonical partition fn. for a classical imperfect gas

$$Z_G = \sum_{N=0}^{\infty} \frac{z^N}{N!} \int e^{-\beta\left(\frac{p^2}{2m} + U_N\right)} \frac{d\vec{p}^{\,N}\, d\vec{q}^{\,N}}{h^{3N}}$$

$$= \sum_{0}^{\infty} \frac{z^N}{N!} \Big(\underbrace{\frac{1}{h^3}\left(\frac{m}{\beta}\right)^{3/2}(2\pi)^{3/2}}_{\left(\frac{km}{2\pi \hbar^2}\right)^{3/2} T^{3/2}} \Big)^N \int e^{-\beta U_N}\, d^N\vec{q}$$

same C

Thus if we put $u = zcT^{3/2}$ we have

$$Z_G = 1 + u a_1 + \frac{u^2}{2} a_2 + \frac{u^3}{3} a_3 + \cdots$$

where $a_N(T,V) = \int e^{-\beta U_N}\, d^N\vec{q}$

$$\log Z_G = \left(u a_1 + \frac{u^2}{2} a_2 + \frac{u^3}{6} a_3\right) - \frac{1}{2}\left(u a_1 + \frac{u^2}{2} a_2\right)^2 + \frac{1}{3}(u a_1)^3 + \cdots$$

$$\frac{\log Z_G}{V} = \frac{u a_1}{V} + \frac{u^2}{2} \underbrace{\frac{(a_2 - a_1^2)}{V}}_{\downarrow} + \frac{u^3}{3!} \underbrace{\frac{(a_3 - 3a_1 a_2 + 2a_1^3)}{V}}_{\downarrow} + \cdots$$

$$\lim \frac{\log Z_G}{V} = u + \frac{u^2}{2} h_1(T) + \frac{u^3}{3!} h_2(T) + \cdots$$

Then the equation of state is obtained by eliminating u from the 2 equations

$$p\beta = u + \frac{u^2}{2} h_1 + \frac{u^3}{3!} h_2 + \cdots$$

$$\rho = u + u^2 h_1 + \frac{u^3}{2} h_2 + \cdots$$

$$u = \rho - u^2 h_1 - \frac{u^3}{2} h_2$$ solve by iteration:

$$u^{(1)} = \rho - \rho^2 h_1 - \frac{\rho^3}{2} h_2$$

$$u^{(2)} = \rho - \left(\rho - \rho^2 h_1 \text{[redacted]} - \frac{\rho^3}{2} h_2\right)^2 h_1 - \left(\rho - \cdots\right)^3 \frac{h_2}{2}$$

$$= \rho - \left(\rho^2 - 2\rho^3 h_1\right) h_1 - \rho^3 \frac{h_2}{2}$$

$$u = \rho - \rho^2 h_1 + \rho^3\left(2h_1^2 - \frac{h_2}{2}\right) + \cdots$$

Then

$$p\beta = \rho - \rho^2 h_1 + \rho^3\left(2h_1^2 - \frac{h_2}{2}\right) + \frac{1}{2}\left(\rho - \rho^2 h_1 +\right)^2 h_1 \text{[redacted]} + \frac{\rho^3}{6} h_2$$

$$= \rho + \rho^2\left(-h_1 + \frac{h_1}{2}\right) + \rho^3\left(2h_1^2 - \frac{h_2}{2} \text{[redacted]} - h_1^2 + \frac{h_2}{6}\right)$$

$$\boxed{p\beta = \rho + \rho^2\left(-\frac{h_1}{2}\right) + \rho^3\left(h_1^2 - \frac{h_2}{3}\right) + \cdots}$$

[redacted] Let's suppose the [redacted] atoms of the gas [redacted] interact via a 2 body potential, so that the potential energy of atoms at positions $\vec{q}_1, \ldots, \vec{q}_N$ is

$$U_N(\vec{q}_1, \ldots, \vec{q}_N) = \frac{1}{2} \sum_{i \neq j} U(\vec{q}_i, \vec{q}_j)$$

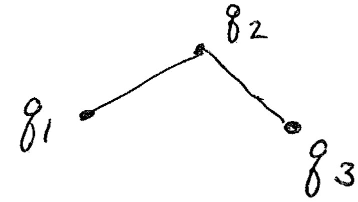
Go back to the grand partition fn.

$$Z_G = \sum_{N \geq 0} u \text{[redacted]}^N \frac{1}{N!} \int e^{-\beta U_N} d\vec{q}_1 \ldots d\vec{q}_N$$

One should think of this as a sum over all sequences $\vec{q}_1, \ldots\ldots, \vec{q}_N$ and all N. The contribution belonging to this sequence can be written

$$\prod_{i<j} e^{-\beta U(q_i, q_j)} = \prod_{i<j} (1 + T_{ij})$$

where $T_{ij} = e^{-\beta U(q_i, q_j)} - 1$. Expand out the product and one gets terms which can be described by a Mayer graph:



gives $T_{12} T_{23}$

So now we see that the N-th term of Z_G is z^N times the sum over all Mayer graphs of the appropriate product of the T-factors divided by the order of the symmetry group Σ_N. The graphs have the vertices ordered, but we get the same sum if we consider distinct unordered graphs and divide by the symmetry factor. e.g. $N=2$ gives

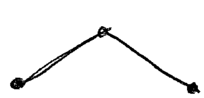
 contributes $\dfrac{V^2}{2} = a_1^2/2$

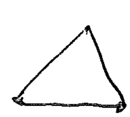
 " $\dfrac{1}{2}\int \left(e^{-\beta V(\vec{q}_1, \vec{q}_2)} - 1\right) d\vec{q}_1 d\vec{q}_2$

and $N=3$ gives $= \frac{1}{2}(a_2 - a_1^2)$

 $\dfrac{V^3}{6} = a_1^3/6$

 $V \cdot \dfrac{a_2 - a_1^2}{2}$





$\Big\}$ contributes the rest of $\dfrac{a_3}{6}$ $= \dfrac{a_3}{6} - \dfrac{a_1(a_2 - a_1^2)}{2} - \dfrac{a_1^3}{6}$

$$= \frac{1}{6}\left(a_3 - 3a_1 a_2 + 2a_1^3\right)$$

It should follow by the linked cluster thm. argument that $\log Z_G$ is given by linked clusters:

$$\log Z_G = u(\cdot) + u^2 \frac{1}{2!}(\bullet\!\!-\!\!\bullet) + u^3\left(\frac{1}{2}(\wedge) + \frac{1}{3!}(\triangle)\right)$$

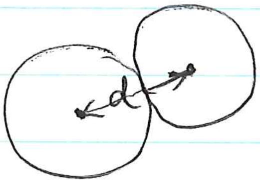
$$+ u^4\left(\frac{1}{2}(\sqcap) + \frac{1}{3!}(\prec) + \frac{1}{2!}(-\!\triangleleft)\right.$$

$$\left. + \frac{1}{8}(\square) + \frac{1}{2\cdot 2}(\boxslash) + \frac{1}{4!}(\boxtimes)\right) + \cdots$$

Example: Suppose our gas made up of hard spheres of diameter d. Since we take an infinite volume limit, we don't care about the excluded volume near the boundary of V. Thus

$$\frac{(\cdot)}{V} = \frac{a_1}{V} \longrightarrow 1$$

Now
$$U(\vec{q}_1, \vec{q}_2) = \begin{cases} +\infty & \text{if } |q_1 - q_2| \leq d \\ 0 & \text{if } |q_1 - q_2| > d \end{cases}$$



so that

$$e^{-\beta U(q_1, q_2)} - 1 = \begin{cases} -1 & \text{if } |q_1 - q_2| < d \\ 0 & \text{if } |q_1 - q_2| > d. \end{cases}$$

Thus

$$(\bullet\!\!-\!\!\bullet) = \int \left(e^{-\beta U(q_1, q_2)} - 1\right) d\vec{q}_1\, d\vec{q}_2$$

$$= -\int_{|q_1 - q_2| < d} d\vec{q}_1\, d\vec{q}_2 = -\int dq_1 \underbrace{\frac{4}{3}\pi d^3}_{v} = -Vv$$

It's helpful to think of the volume as being a torus, so as to simplify the surface effects which disappear in the ∞ volume limit. Next

$$(\wedge) = \int_{\substack{|q_1-q_2|<d \\ |q_2-q_3|<d}} (-1)^2 dq_1\, dq_2\, dq_3 = V v^{-2}$$

The integral

$$\triangle = -\int_{\substack{|q_1-q_2|<d \\ |q_2-q_3|<d \\ |q_1-q_3|<d}} d\vec{q}_1\, d\vec{q}_2\, d\vec{q}_3$$

can be worked out.

[redacted] Standard formulas (from McQuarrie - Stat. Thermo.) [redacted]

$$\left.\begin{aligned} p\beta &= z + b_2 z^2 + b_3 z^3 + \cdots \\ \rho &= z + 2b_2 z^2 + 3b_3 z^3 + \cdots \end{aligned}\right\} \quad z \text{ here is my } u \text{ above}$$

when [redacted] z is eliminated from these we get

$$p\beta = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \cdots$$

Therefore

$$B_2 = -b_2$$

$$B_3 = 4b_2^2 - 2b_3$$

and the b_n are given by cluster integrals

$$\frac{\log Z_G}{V} = u + u^2 \underbrace{\frac{1}{V}\frac{1}{2!}(\bullet\!\!-\!\!\bullet)}_{b_2} + u^3 \frac{1}{V} [redacted] \underbrace{\left(\frac{1}{2}(\wedge) + \frac{1}{3!}(\triangle)\right)}_{b_3}$$

July 24, 1980

There is evidently an analogue of 1PI for cluster integrals. Thus it is necessary to finally understand vertex functions, 1PI graphs, etc.

First review imperfect gas virial expansion using the standard notation (McQuarrie). The grand partition function is

$$Z_{gr}(T,V,z) = \sum_{N\geq 0} \frac{z^N}{N!} \underbrace{\int e^{-\beta U_N} d\vec{q}_1 \cdots d\vec{q}_N}_{Z_N(T,V)}$$

where z is the activity and is to be adjusted so as to give the correct no. of particles. Recall

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

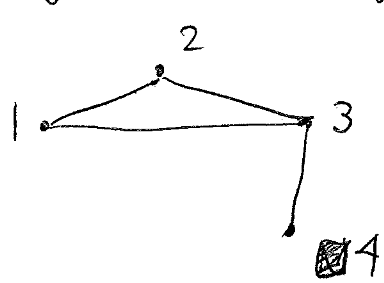
The N particle potential U_N is assumed to be a sum of pairwise potentials hence

$$e^{-\beta U_N} = \prod_{1\leq i<j\leq n} (1+f_{ij})$$

where

$$f_{ij} = e^{-\beta U(q_i, q_j)} - 1 = e^{-\beta U(r)} - 1 \qquad r = |q_i - q_j|$$

is the Mayer-function. If we put this expression for $e^{-\beta U_N}$ into Z_{gr}, then Z_{gr} becomes a sum of cluster integrals, belonging to diagrams



$$\longmapsto \frac{z^4}{4!}\int f_{12} f_{23} f_{13} f_{34}\, d\vec{q}_1 \cdots d\vec{q}_4$$

with labelled vertices.

Because of the linked cluster theorem one has

$$\log Z_{gr} = \text{sum of connected diagrams}$$

Each of the cluster integrals contains a factor V by translational invariance, so assuming the Mayer fn. goes to 0 at ∞ fast enough the infinite volume limit $\exists$.

$$\lim_{V\to\infty} \frac{\log Z_{gr}}{V} = z + b_2 z^2 + b_3 z^3 + \cdots$$

where b_N is the sum of the connected N fold cluster integrals divided by V. $\therefore$

$$b_2 = \frac{1}{2}(\bullet\!-\!\bullet) = \frac{1}{2}\int_0^\infty \left(e^{-\beta U(r)}-1\right) 4\pi r^2 dr$$

$\left(= -\frac{2\pi\sigma^3}{3}\right.$ for hard sphere of radius $\left.\sigma\right)$

$$b_3 = \frac{1}{2}(\bullet\!-\!\bullet\!-\!\bullet) + \frac{1}{6}(\triangle)$$

We then get the equations

$$p\beta = \lim_{V\to\infty}\frac{\log Z_{gr}}{V} = z + b_2 z^2 + b_3 z^3 + \cdots$$

$$\rho = \lim_{V\to\infty}\frac{N}{V} = z + 2b_2 z^2 + 3b_3 z^3 + \cdots$$

and eliminating z from these two equation gives the virial expansion

$$p\beta = \rho + B_2\rho^2 + B_3\rho^3 + \cdots$$

where $B_n = B_n(T)$.

The point is that the virial coefficients B_n are given by cluster integrals involving connected graphs which do not become disconnected when any vertex is removed. Thus

$$B_2 = -b_2 = -\frac{1}{2}(\bullet\!-\!\bullet)$$

$$B_3 = 4b_2^2 - 2b_3 = (\bullet\!-\!\bullet)^2 - 2\left(\frac{1}{2}(\wedge) + \frac{1}{6}(\triangle)\right)$$

$$= -\frac{1}{3}(\triangle)$$

This is the theorem that I want to understand.

Let's review the simplest situation with vertex functions:

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

Here λ is a parameter and the integral is to be evaluated formally as an asymptotic series in λ. Suppose

$$f(x) = \frac{1}{2}ax^2 + \frac{1}{3!}bx^3 + \frac{1}{4!}cx^4 + \cdots$$

whence

$$Z(J) = \int e^{-\frac{\lambda a}{2}x^2}\, e^{\lambda J x - \frac{1}{3!}\lambda b x^3 - \frac{1}{4!}\lambda c x^4 - \cdots}\,dx.$$

The second exponential is expanded as a power series in λ, and the Gaussian integrals are evaluated by Wick's thm. to get

$$\log\left(\frac{Z(J)}{\int e^{-\frac{\lambda a x^2}{2}}}\right) = \text{connected diagrams where vertex}$$

of mult 1	contributes	λJ
3	"	$-\lambda b$
4	"	$-\lambda c$

and each edge contributes $\dfrac{1}{\lambda a}$

The power of λ is $\#$vertices $-$ $\#$edges $= 1 - \#$ loops for a connected graph.

Suppose V_n vertices of mult. n.

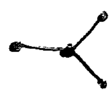
$$\# \text{vert} = V_1 + V_3 + V_4 + \cdots$$

$$\# \text{edges} = \tfrac{1}{2}V_1 + \tfrac{3}{2}V_3 + \tfrac{4}{2}V_4 + \cdots$$

$$1 - \# \text{loops} = \tfrac{1}{2}V_1 - \tfrac{1}{2}V_3 - V_4 - \tfrac{3}{2}V_5 - \cdots$$

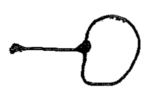
The coeff. of λ is given by tree graphs:

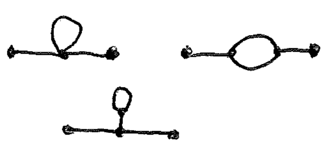
$V_1 = 2$  $\quad \frac{1}{2}\frac{J^2}{a}$

$V_1 = 3$  $\quad \frac{-b}{6}\frac{J^3}{a^3}$

$V_1 = 4$  $\quad -\frac{c}{24}\frac{J^4}{a^4} + \frac{b^2}{8}\frac{J^4}{a^5}$

The coeff of λ^0 is given by 1-loop graphs

$V_1 = 1$  $\quad \frac{-b}{2}\frac{J}{a^2}$

$V_1 = 2$  $\quad -\frac{c}{4}\frac{J^2}{a^3} + \frac{b^2}{4}\frac{J^2}{a^4} + \frac{b^2}{4}\frac{J^2}{a^4}$

Two loop graphs

$V_1 = 0$ 

Then one has

$$Z(J) = \sqrt{\frac{2\pi}{\lambda a}}\, \exp\Big\{ \lambda\Big(\frac{1}{2a}J^2 + \Big(-\frac{b}{6a^3}\Big)J^3 + \Big(-\frac{c}{24}\frac{J^4}{a^4} + \frac{b^2}{8}\frac{J^4}{a^5}\Big) + \cdots\Big)$$
$$- \frac{1}{2}\Big(\frac{bJ}{a^2} + \Big(\frac{c}{2a^3} - \frac{b^2}{a^4}\Big)J^2 + \cdots\Big) \Big\}$$

We can check this by applying the Laplace method to $\quad Z(J) = \int e^{\lambda(Jx - f(x))}\,dx$

Define x_c to be the critical point, so that

$$J = f'(x_c) = a x_c + \frac{1}{2} b x_c^2 + \frac{1}{6} c x_c^3 + \cdots$$

We can solve this for x_c by iteration

$$x_c = \frac{J}{a} - \frac{1}{2}\frac{b}{a} x_c^2 - \frac{1}{6}\frac{c}{a} x_c^3 - \cdots$$

$$x_c^{(1)} = \frac{J}{a}$$

$$x_c^{(2)} = \frac{J}{a} - \frac{1}{2}\frac{b}{a}\frac{J^2}{a^2} - \frac{1}{6}\frac{c}{a}\frac{J^3}{a^3} -$$

$$x_c^{(3)} = \frac{J}{a} - \frac{1}{2}\frac{b}{a}\left(\frac{J}{a} - \frac{1}{2}\frac{b}{a}\frac{J^2}{a^2}\right)^2 - \frac{1}{6}\frac{c}{a}\frac{J^3}{a^3}$$

$$\therefore \quad x_c = \frac{J}{a} + \left(-\frac{1}{2}\frac{b}{a}\right)\frac{J^2}{a^2} + \left(\frac{1}{2}\frac{b^2}{a^2} - \frac{1}{6}\frac{c}{a}\right)\frac{J^3}{a^3} + O(J^4)$$

Put

$$g(x) = Jx - f(x)$$

$$g''(x_c) = -f''(x_c) = -\left(a + b x_c + \frac{1}{2} c x_c^2 + \cdots\right)$$

$$f''(x_c) = a + b\left(\frac{J}{a} + \left(-\frac{1}{2}\frac{b}{a}\right)\frac{J^2}{a^2}\right) + \frac{1}{2} c \frac{J^2}{a^2}$$

$$= a + \frac{b}{a} J + \left(-\frac{1}{2}\frac{b^2}{a^3} + \frac{c}{2a^2}\right) J^2 + \cdots$$

Then

$$Z(J) = e^{\lambda(J x_c - f(x_c))} \underbrace{\int e^{\lambda\left(-\frac{f''(x_c)}{2}\right)(x - x_c)^2 + \cdots} dx}_{\sqrt{\frac{2\pi}{\lambda f''(x_c)}}}$$

Now

$$\frac{d}{dJ}\left(J x_c - f(x_c)\right) = x_c$$

so

$$J x_c - f(x_c) = \frac{J^2}{2a} + \left(-\frac{1}{6}\frac{b}{a^3}\right) J^3 + \left(\frac{1}{8}\frac{b^2}{a^5} - \frac{1}{24}\frac{c}{a^4}\right) J^4$$

$$\log \frac{f''(x_c)}{a} = \log\left(1 + \frac{b}{a^2}J + \left(-\frac{1}{2}\frac{b^2}{a^4} + \frac{1}{2}\frac{c}{a^3}\right)J^2 + \cdots\right)$$

$$= \frac{b}{a^2}J + \left(-\frac{1}{2}\frac{b^2}{a^4} + \frac{1}{2}\frac{c}{a^3}\right)J^2 - \frac{1}{2}\frac{b^2}{a^4}J^2$$

$$= \frac{b}{a^2}J + \left(-\frac{b^2}{a^4} + \frac{1}{2}\frac{c}{a^3}\right)J^2 + O(J^3)$$

$\therefore$ Everything checks.

But more important than x_c (= classical solution) is

$$\langle x \rangle = \frac{\int x e^{\lambda(Jx - f(x))}\,dx}{\int e^{\lambda(Jx - f(x))}\,dx} = \frac{1}{\lambda}\frac{d}{dJ}\log Z(J)$$

July 25, 1980

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

where λ is a variable in which we have an asymptotic expansion. We are interested in the ~~moments~~ variable

$$\langle x \rangle = \frac{1}{\lambda}\frac{\partial}{\partial J}\log Z = \frac{\int x e^{\lambda(Jx-f(x))}dx}{\int e^{\lambda(Jx-f(x))}dx}$$

and in the higher moments

$$\langle x^n \rangle = \frac{1}{n!}\left(\frac{1}{\lambda}\frac{\partial}{\partial J}\right)^n Z \Big/ Z.$$

Hence it makes sense to replace $Z(J)$ by

$$Z(J) = \frac{\int e^{\lambda(Jx-f(x))}dx}{\int e^{-\lambda f(x)}dx}$$

so that $F(0) = 0$. Also we have

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

where

$$\lambda f(x/\lambda) = \frac{1}{2}\frac{a}{\lambda}x^2 + \frac{1}{6}\frac{b}{\lambda^2}x^3 + \cdots$$

It follows that whatever grading is specified by powers of λ can also seen by regarding a of degree 1 b of degree 2, etc. So we might as well take $\lambda = 1$, so let us redefine

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

Then $F(J) =$ sum over connected diagrams having at least one vertex of multiplicity 1.

July 26, 1980

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

where $f(x) = \frac{1}{2}ax^2 + \frac{1}{6}bx^3 + \cdots$

Then we know $F(J)$ is a sum of terms described by connected diagrams in which the vertices contribute $J, (-b), (-c)$ and the edges $\frac{1}{a}$. Then [redacted]

$$\underset{\substack{\uparrow \\ \text{no. of} \\ \text{loops}}}{1-\ell} = \underset{\substack{\uparrow \\ \text{no. of vertices}}}{(v_1 + v_3 + \cdots)} - \underbrace{\tfrac{1}{2}(v_1 + 3v_3 + \cdots)}_{\text{no. of edges}}$$

[redacted]

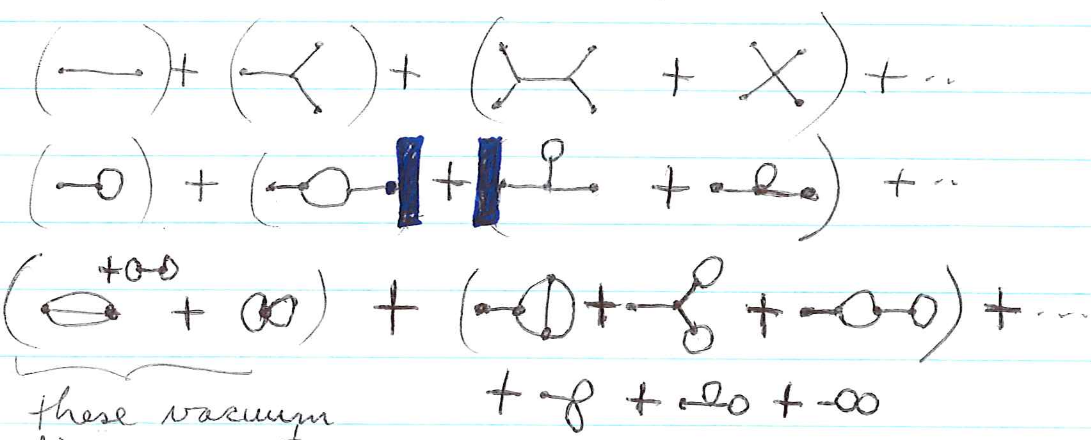
$$1-\ell = \frac{1}{2}v_1 - \frac{1}{2}v_3 - v_4 - \frac{3}{2}v_5 - \cdots$$

is the homogeneity degree of a diagram. Review the diagrams

$\ell = 0$

$\ell = 1$

$\ell = 2$



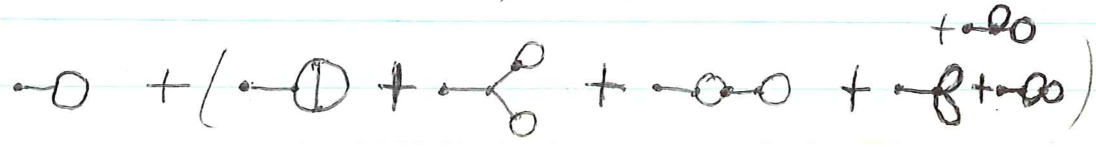
these vacuum diagrams get removed by denom.

Thus we can write

$$F = JF_1 + J^2 \text{[redacted]} \frac{F_2}{2!} + J^3 \frac{F_3}{3!} + \cdots$$

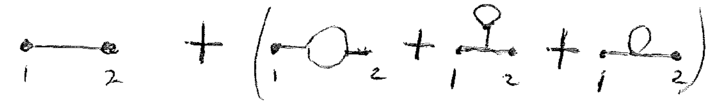
where F_n = connected diagram with n labelled multiplicity 1 vertices. [redacted]

For example

$F_1 =$ 

$$F_1 \; [redacted] = \frac{-b}{2a^2} + \frac{(-b)^3}{2a^5} + \frac{(-b)^3}{8a^5} + \frac{(-b)^3}{4a^5} + \frac{(-d)}{8a^3} + \frac{(-b)(-c)}{4a^4} + \frac{(-b)(-c)}{4a^4}$$

$F_2 =$ [redacted]



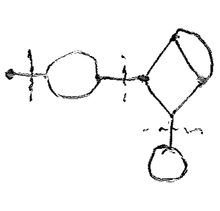
$$= \frac{1}{a} + \frac{(-b)^2}{2a^4} + \frac{(-b)^2}{2a^4} + \frac{(-b)^2}{2a^4} + \cdots$$

[redacted] A graph is (1PI) irreducible if removing an edge doesn't disconnect it. Let Γ_n be the sum of contributions from irreducible graphs with n labeled external vertices. We have

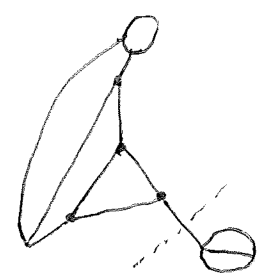
$$\langle x \rangle = \frac{\partial F}{\partial J} = F_1 + JF_2 + \frac{J^2}{2!}F_3 + \cdots$$

which is a sum over connected diagrams having 1 labeled external vertex. Thus $F_n/(n-1)!$ represents conn. graphs with 1 external vertex and n-vertices of mult. 1, the others being unlabelled.

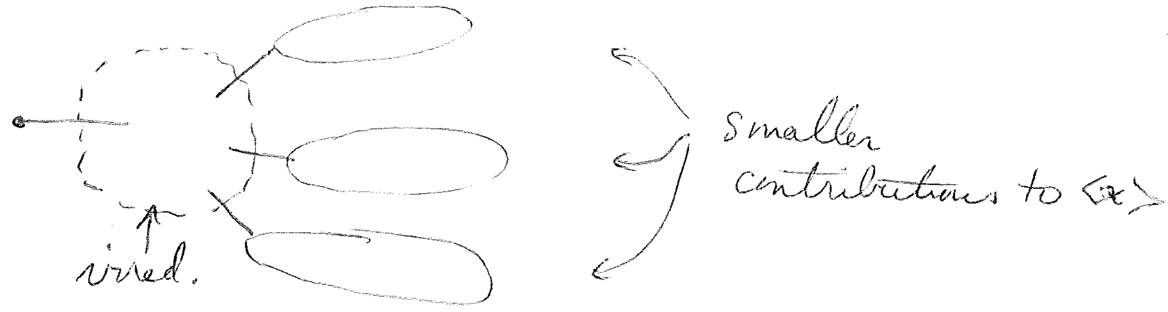
Given any connected graph, [redacted] we can look at those edges whose removal disconnects the graph. The graph [redacted] collapses onto a tree, the fibres being the maximal irreducible subgraphs. For example:



or



Next suppose given a connected graph with 1 external vertex, i.e. a contribution to $\langle x \rangle$. Then we can look at the irreducible component into which this vertex is connected, and so we get



This gives us the equation

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

Note that Γ_1 doesnot include —• by definition. This definition makes all the Γ_n independent of J.

Tomorrow we should check these formulas.

July 27, 1980

More vertex functions.

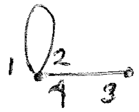
$$Z(J) = e^{F(J)} = \int e^{Jx - f(x)}dx \Big/ \int e^{-f(x)}dx$$

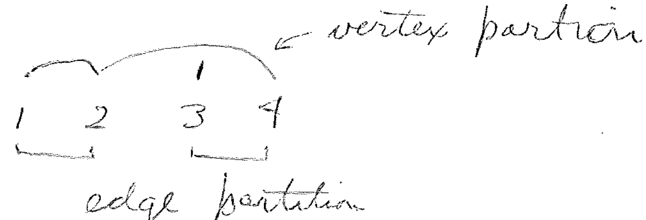
where $f(x) = \frac{a}{2}x^2 + \frac{b}{3!}x^3 + \cdots\cdots\cdots$.

$$\int e^{-\frac{a}{2}x^2 + (Jx - \frac{b}{3!}x^3 - \cdots)}dx$$

$$= \int e^{-\frac{a}{2}x^2} \underbrace{\sum_N \frac{1}{N!}\left(Jx - \frac{b}{3!}x^3 - \cdots\right)^N}_{\sum_{n_1, n_3, \ldots} \frac{J^{n_1}}{n_1!} \frac{1}{n_3!}\left(\frac{-b}{3!}\right)^{n_3} \cdots \quad x^{n_1 + 3n_3 + \cdots}} dx$$

We need another way to describe the term belonging to $n_1, n_3, \ldots\ldots$ after integrating $\int e^{-\frac{a}{2}x^2} x^N dx$ using Wick's thm. One takes the set $\{1, \ldots, N\}$ and partitions it into 2 element subsets, and also partitions it into n_j ~~blocks~~ subsets of size j. Hence N must be even. We can identify the pair consisting of these two partitions (the edge partition and the vertex partition) with a graph having n_j vertices of multiplicity j, and on which the ends of the edges have been ordered.





If we let the symmetric group Σ_N act, the orbits are the different graphs with n_j vertices of mult. j, and the isotropy group of a "labeled graph" is the symmetry group of the graph.

It seems better to start with the $n_1, n_3, \dots$ term of the series. Take the set $\{1, \dots, N\}$ and consider the unique partition into n_j blocks of size j so that the blocks are segments and so that the blocks occur in order of increasing size. e.g.

$$\underbrace{1 \mid 2 \mid 3}_{n_1 = 3} \mid \underbrace{4\ 5\ 6 \mid 7\ 8\ 9}_{n_3 = 2} \mid \underbrace{10\ 11\ 12\ 13}_{n_4 = 1}$$

The subgroup $\Sigma_{\{n_1, n_3, \dots\}}$ of Σ_N fixing this partition is of order

$$\left| \Sigma_{\{n_1, n_3, \dots\}} \right| = n_1!\, (3!)^{n_3} n_3! \cdots (j!)^{n_j} n_j!$$

This subgroup acts on all possible edge partitions and

$$\int e^{-\frac{a}{2}x^2} x^N dx = \sqrt{\frac{2\pi}{a}} \sum \frac{1}{a^{N/2}}$$

where the sum is over all possible edge partitions. Thus forgetting the $\sqrt{\frac{2\pi}{a}}$ factor, the $n_1, n_3, \dots$ term contribution is

$$\frac{1}{\left| \Sigma_{\{n_1, n_3, \dots\}} \right|} J^{n_1} (-b)^{n_3} (-c)^{n_4} \cdots \sum_{\substack{\text{edge} \\ \text{partitions}}} \frac{1}{a^N} .$$

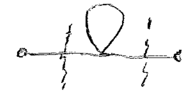
$$= \frac{1}{N!} J^{n_1} (-b)^{n_3} (-c)^{n_4} \cdots \sum_{\substack{\text{edge + vertex} \\ \text{partitions}}} \frac{1}{a^N}$$

By standard arguments this can be written as a sum over the orbits where one divides by the order of the isotropy group. One proves linked cluster thm. which says that $F(J) =$ sum of connected graph contributions

So the next thing is to decompose graphs into irreducible graphs. It will be useful to write

$$F(J) = \frac{F_1}{a} J + \frac{F_2}{2!}\left(\frac{J}{a}\right)^2 + \frac{F_3}{3!}\left(\frac{J}{a}\right)^3 + \cdots$$

so that F_n is the sum of contributions from graphs having exactly n vertices of mult 1 assigned a definite order. Moreover the J factor and the $\frac{1}{a}$ factor for each such vertex and associated edge are omitted. What this means is that each mult. 1 vertex is separated off and numbered: For example

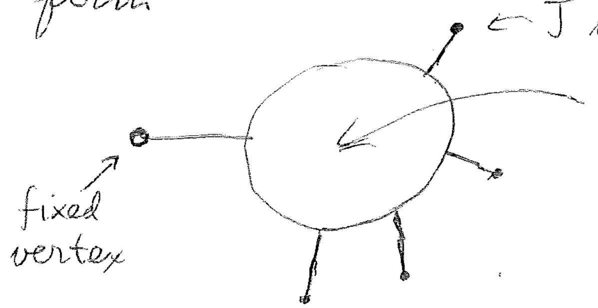
 is decomposed: 

and the resulting contribution to F_2 is  $= \frac{(-c)}{2a}$

Then

$$\langle x \rangle = \frac{dF}{dJ} = \frac{F_1}{a} + \frac{F_2}{a^2} J + \frac{F_3}{a^3}\frac{J^2}{2!} + \cdots$$

and $\frac{1}{a}\frac{F_n}{(n-1)!}\left(\frac{J}{a}\right)^{n-1}$ is the sum over graphs of the form



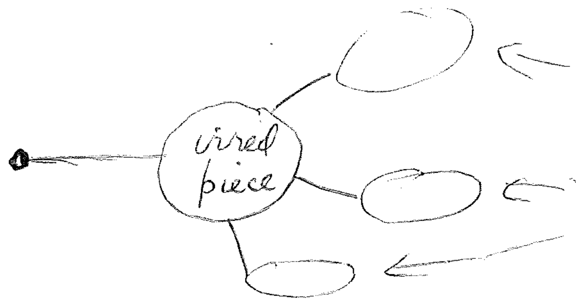
typical term in F_n (no mult. 1 vertices)

This situation has obvious symmetry factor $(n-1)!$

Now we let Γ_n be the irreducible graph part of F_n. We then get the key equation

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

representing the fact that if we go from the fixed vertex then we come to an irreducible piece



smaller graphs contributing to $\langle x \rangle$

and if we order the edges exiting from the irred. pieces we get smaller pieces of $\langle x \rangle$.

Let's compute: $\ell - 1 + \frac{1}{2} v_1 = \frac{1}{2} v_3 + v_4 + \frac{3}{2} v_5 + \cdots$

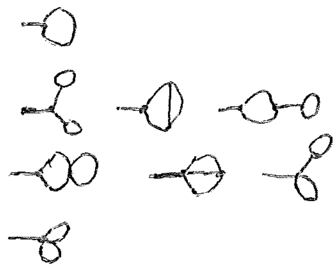
$v_1 = 1$ $\quad$ $\ell = 0$ none

$\ell = 1$ $\quad$ $v_3 = 1$

$\ell = 2$ $\quad$ $v_3 = 3$

$v_3 = 1,\ v_4 = 1$

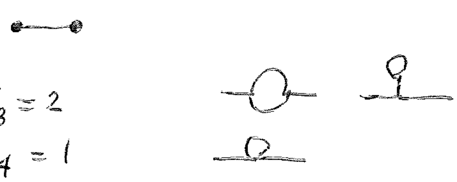
$v_5 = 1$



$v_1 = 2$ $\quad$ $\ell = 0$

$\ell = 1$ $\quad$ $v_3 = 2$

$v_4 = 1$



$v_1 = 3$ $\quad$ $\ell = 0$

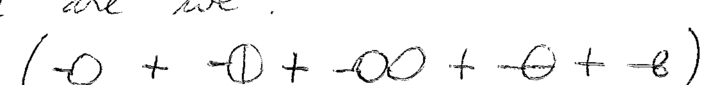
We have to be careful about in $\frac{F_2}{a^2} \frac{J^2}{2!}$

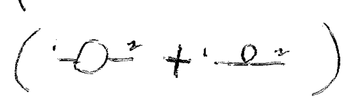
If we decompose it we get a term $\overset{\cdot}{-}{}^2 = a$ in F_2 which we want to exclude from Γ_2. Notice that the corresponding term in $\langle x \rangle$ is

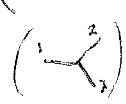
 $\quad \frac{J}{a}$

which has been included in the key equation.

So where are we?

$\Gamma_1 =$  thru 2 loops

$\Gamma_2 =$  thru 1 loop

$\Gamma_3 =$  thru 0 loops. etc.

The key equation can be written

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

and it shows that the Γ_n give the series for J as a function of $\langle x \rangle$.

July 28, 1980

Return to a monatomic gas. The grand partition function is

$$Z_{gr} = \sum \frac{z^N}{N!} \underbrace{\int e^{-\beta U_N} dq_1 \cdots dq_N}_{Z_N}$$

where $U_N(q_1, \ldots, q_N) = \sum_{1 \le i < j \le N} U(|q_i - q_j|)$. One puts

$$e^{-\beta U(r)} = 1 + f(r) \qquad f \text{ called the Mayer function.}$$

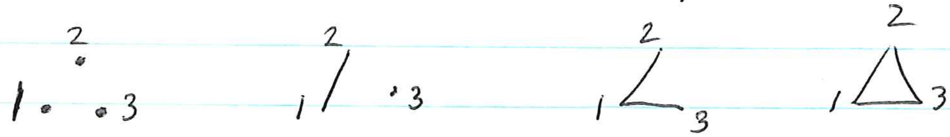
and

$$e^{-\beta U_N} = \prod_{1 \le i < j \le N} (1 + f_{ij}) \qquad f_{ij} = f(|q_i - q_j|)$$

$$= \sum_X{}' \prod_{\sigma \in X} f_\sigma$$

where X ranges over the subsets of the set of 2 element subsets of $\{1, \ldots, N\}$. Such an X can be identified with a graph having vertices $\{1, \ldots, N\}$ and at most one edge between two vertices. There are $2^{N(N-1)/2}$ such X. For $N = 2$ we have

and for $N = 3$ we have 8 possibilities



1 poss.   3 of this   3 of this   1 poss.

The group Σ_N acts on the set of X and the orbits can be identified with isom classes of these graphs. Moreover

$$\frac{1}{N!} \sum_X{}' \int \prod_{\sigma \in X} f_\sigma \, dq_1 \cdots dq_N$$

can be written as a sum over the different iso. classes weighted by the order of the autom. gp. of the graph.

Question: Can one handle a general family U_N of potentials?

The physical idea is that the interaction between particles is short range and so [redacted] the interaction energy associated to a configuration $q_1, \ldots, q_N$ should [redacted] depend first on the way the particles clump together. This gives us a partition of $\{1, \ldots, N\}$

Now there is no reason why $q_1, \ldots, q_N$ have to be continuous variables. In lattice gases they can be discrete. Simplest model would appear to allow only coallescing q_i to contribute to the interaction energy. So suppose we allow q to run over a group like $A = \mathbb{Z}/L\mathbb{Z}$ and that we give the energy for each group of atoms at the same spot.

Take $n=2$. Then

$$U_2(q_1, q_2) = \begin{cases} 0 & \text{if } q_1 \neq q_2 \\ u_2 & \text{if } q_1 = q_2 \end{cases}$$

$$U_3(q_1, q_2, q_3) = \begin{cases} 0 & q_1, q_2, q_3 \text{ distinct} \\ u_2 & \text{if two are equal} \\ u_3 & \text{if three are equal} \end{cases} \qquad \text{etc.}$$

Now it seems to be convenient to compute the contribution from a graph by assigning all values of $q_1, q_2, \ldots, q_N$ to the vertices. But first maybe we should see if the partition function defined in the above way can be computed.

$$Z_2 = \sum_{q_1, q_2 \in \mathbb{Z}/L\mathbb{Z}} e^{-\beta U_2} = L^2 - L + Le^{-\beta u_2} = L^2 + L(e^{-\beta u_2} - 1)$$

$$Z_3 = \sum e^{-\beta U_3} = \text{[redacted]}\; L(L-1)(L-2)$$
$$+ 3L(L-1)e^{-\beta u_2} + Le^{-\beta u_3}$$

$$e^{-\beta U_3} = 1 + \delta(q_1 - q_2)(e^{-\beta u_2} - 1) + \delta(q_2 - q_3)(e^{-\beta u_2} - 1) + \delta(q_1 - q_3)(e^{-\beta u_2} - 1)$$
$$+ \delta(q_1, q_2, q_3)(e^{-\beta u_3} - 3e^{-\beta u_2} + 2)$$

$$Z_3 = \sum e^{-\beta u_3} = L^3 + 3L^2(e^{-\beta u_2} - 1) + L(e^{-\beta u_3} - 3e^{-\beta u_2} + 2)$$

In this particular situation the diagrams of order n [redacted] should [redacted] be in 1-1 correspondence with partitions of $\{1, 2, \ldots, n\}$. There should be no distinction between Λ and Δ.

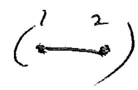
We want the decomposition of a graph into its connected components to lead to a linked cluster theorem. Hence it is essential that when we decompose a graph the contribution should be the product of the contributions from the components. Thus from the graph $\overset{1}{\bullet}\!\!-\!\!\overset{2}{\bullet}$ we get the contribution $L(e^{-\beta u_2} - 1)$ and from $\overset{1}{\bullet}\!\!-\!\!\overset{2}{\bullet}\;\; \overset{3}{\bullet}\!\!-\!\!\overset{4}{\bullet}$ we must get $(L(e^{-\beta u_2} - 1))^2$. This probably means that the energy when $q_1 = q_2$, $q_3 = q_4$, and when there are no further coincidences must be $u_2 + u_2$.

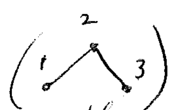
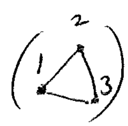
Let's go back to the standard case. We have a linked cluster thm.

$$p\beta = \frac{\log Z_{gr}}{V} = \text{contributions from connected diagrams}$$
$$= F_1 z + \frac{F_2}{2!} z^2 + \cdots$$

where

$$F_1 = (\,\cdot\,) = 1$$

$$F_2 = $$  $$= \int f(|q|)\,dq$$

$$F_3 = $$  + other perms $$+$$  $$= 3\left(\int f\,dq\right)^2 + \int_{q_1=0} f_{12} f_{13} f_{23}\, dq_2\, dq_3$$

Now

$$\rho = z\frac{\partial}{\partial z} \frac{\log Z_{gr}}{V} = 1 + F_2 z^2 + \frac{F_3}{2!} z^3 + \cdots$$

and this can be described a sum of contributions from connected graphs with 1 vertex fixed.

July 29, 1980

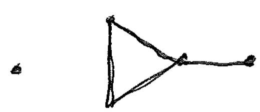
Mayer cluster expansion.

$$Z_{gr} = \sum \frac{z^N}{N!} \int e^{-\beta U_N} dq_1 \cdots dq_N$$

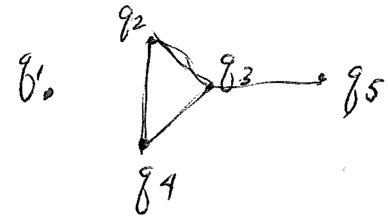
$$e^{-\beta U_N} = \prod_{1 \le i < j \le N} (1 + f_{ij})$$

$$f_{ij} = f(|q_i - q_j|) \quad \text{where } f(r) = e^{-\beta U(r)} - 1$$

Thus Z_{gr} is a sum of terms, each term belonging to an iso. class of graphs having at most one edge between two vertices. To compute the term belonging to a graph e.g.



one assigns coordinates to the vertices:



then takes the product of the f-factors belonging to the edges:

$$f(|q_2 - q_4|)\, f(|q_2 - q_3|)\, f(|q_3 - q_4|)\, f(|q_3 - q_5|)$$

or $\quad f_{24} f_{23} f_{34} f_{35} \quad$ for short

then integrates over all possible coordinates, and divides by the symmetry factor of the graph, and multiplies by z for each vertex

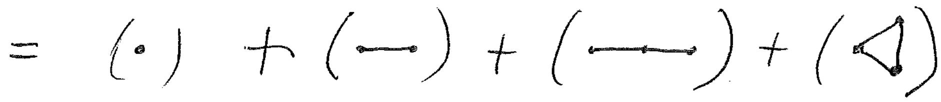
$$z^5 \frac{1}{2} \int f_{24} f_{23} f_{34} f_{35} \, dq_1 \cdots dq_5$$

The linked cluster thm. tells us that

$$Z_{gr} = \exp(\text{conn. diagram terms})$$

Notice that for a connected diagram the integral contains a factor of V. We will divide out by this in computing contributions.

$$P\beta = \frac{\log Z_{gr}}{V} = \text{sum of connected diagram terms}$$



$$= z + \frac{z^2}{2}\int f(|q|)\,dq + \frac{z^3}{2}\left(\int f\right)^2 + \frac{z^3}{6}\frac{1}{V}\int f_{12}f_{13}f_{23}\,dq_1dq_2dq_3$$

$$= z + \frac{a}{2}z^2 + \left(\frac{a^2}{2} + \frac{b}{6}\right)z^3 + \cdots$$

where we put

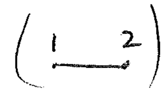
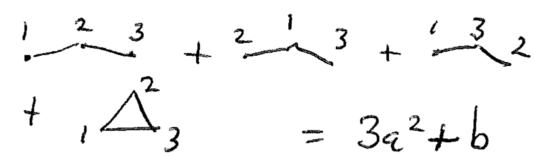
$$a = \int f(|q|)\,dq$$

$$b = \frac{1}{V}\int f_{12}f_{13}f_{23}\,dq_1 \cdot dq_3$$

We can write

$$p\beta = \frac{\log Z_{gr}}{V} = z + F_2\frac{z^2}{2!} + F_3\frac{z^3}{3!} + \cdots$$

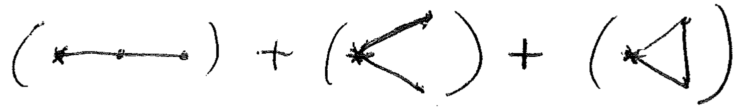
where F_n = sum of terms belonging to connected graphs which have the n vertices $1, 2, \ldots, n$.

Thus $F_2 =$  $= a$ $\qquad F_3 =$  $= 3a^2 + b$

The density is given by

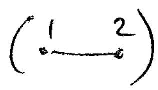
$$\rho = \frac{N}{V} = z\frac{\partial}{\partial z}\frac{\log Z_{gr}}{V} = z + F_2\frac{z^2}{1!} + F_3\frac{z^3}{2!} + \cdots$$

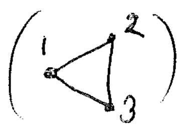
and $\dfrac{F_n}{(n-1)!}$ = sum of terms belonging to conn. graphs with n vertices one of which is labeled. (pointed connected graphs).

e.g. $\dfrac{F_3}{2!} =$ 

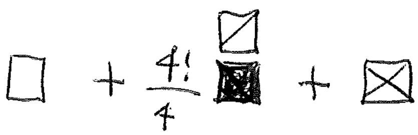
$$= a^2 + \frac{a^2}{2} + \frac{b}{2} = \frac{3a^2+b}{2}$$

Now we want to bring in the fact that in a connected graph there are vertices whose removal disconnects the graph. Let us denote by Γ_n the sum of the terms belonging to connected graphs with vertices $1,\dots,n$ which are doubly-connected in the sense that removing any vertex leaves them connected.

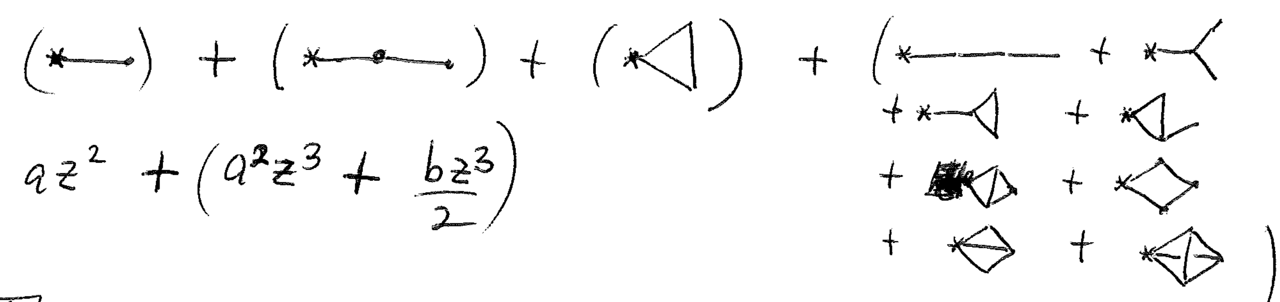
$\Gamma_2 =$  $= a$

$\Gamma_3 =$  $= b$

$\Gamma_4 =$  with all ways of labeling the vertices.

$= \frac{4!}{8}$ 

Let us consider the graphs contributing to g, that is, pointed connected graphs, which remain connected when the basepoint is removed. Let Y be the part of g which is the sum of the terms belonging to these graphs, so the z factors are in:

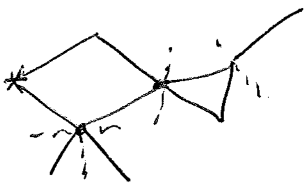
$Y =$ 

$$= az^2 + \left(a^2z^3 + \frac{bz^3}{2}\right)$$

The first equation is that

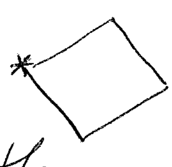
$$\boxed{Y = z\left(\Gamma_2 \rho + \Gamma_3 \frac{\rho^2}{2!} + \Gamma_4 \frac{\rho^3}{3!} + \cdots\right)}$$

To see this we take a graph which is pointed and connected and such that removing the basept. doesn't disconnect the graph. Let us consider the vertices whose removal disconnects the graph, let's called these vertices critical.

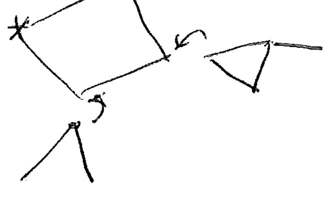


A vertex ^{A} is critical when there exists another vertex ^{B} such that all paths from the basept to B must pass thru A. There is a nice way to separate a graph at critical vertices. ~~Let's do this and look at the component containing the basepoint. It is doubly-connected so, given its ordering gives us a term of Γ_ρ. At each of its vertices except * there is attached a smaller pointed connected graph~~

Let us consider the subgraph consisting of all vertices ^{A} which remain connected to the basepoint * no matter what other vertex is removed besides A and *. In the above example we get



If we order the vertices ~~starting~~ with $* = 1$, then we get an element of Γ_ρ. Moreover at each of the vertices other than * is attached a term of ρ e.g.



We divide by $(p-1)!$ to allow for the choice of ordering of the other vertices.

This explains the formula at the top of the preceding path. Check thru degree 3:

$$Y = az^2 + \left(a^2z^3 + \frac{bz^3}{2}\right)$$

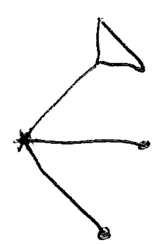
$$z\left(\Gamma_2\rho + \Gamma_3\frac{\rho^2}{2} + \cdots\right) = z\left(a\left(z + az^2\right) + \overset{b}{\overset{\shortparallel}{\Gamma_3}}\frac{z^2}{2}\right)$$

$$= az^2 + a^2z^3 + b\frac{z^3}{2} \quad \checkmark$$

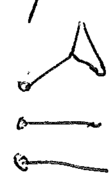
The next equation concerns the graphs in ρ, i.e. pointed connected graphs, for which the base point is critical. This will give the equation

$$\boxed{\rho = z\,e^{Y/z}}$$

Example



Separate this at the basepoint



and one gets a collection of terms belonging to Y except there is a z-factor missing. Check:

$$\rho = \left(z + az^2 + \frac{3a^2+b}{2}z^3 + \cdots\right)$$

$$z\,e^{Y/z} = z\,e^{\left(az + (a^2+\frac{b}{2})z^2 + \cdots\right)}$$

$$= z\left(1 + az + \left(a^2+\tfrac{b}{2}\right)z^2 + \frac{1}{2!}a^2z^2\right)$$

$$= z\left(1 + az + \left(\frac{3a^2}{2}+\frac{b}{2}\right)z^2 + \cdots\right) \quad \checkmark$$

Combine the equations to get

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

or

$$z = \rho e^{-\Gamma(\rho)}$$

Then

$$\frac{1}{z}\frac{dz}{d\rho} = \frac{d}{d\rho}\left(\log \rho - \Gamma(\rho)\right) = \frac{1}{\rho} - \frac{d\Gamma}{d\rho}$$

But

$$\frac{dF}{d\rho} = \frac{dF}{dz}\cdot\frac{dz}{d\rho} = z\frac{dF}{dz}\cdot\frac{1}{z}\frac{dz}{d\rho}$$

$$= \rho\left(\frac{1}{\rho} - \frac{d\Gamma}{d\rho}\right) = 1 - \rho\frac{d\Gamma}{d\rho}$$

$$= 1 - \Gamma_2\rho - \Gamma_3\rho^2 - \Gamma_4\frac{\rho^3}{2!} \cdots - \Gamma_{n+1}\frac{\rho^n}{(n-1)!} - \cdots$$

$$\therefore \quad F = \rho - \Gamma_2\frac{\rho^2}{2} - \Gamma_3\frac{\rho^3}{3} - \Gamma_4\frac{\rho^4}{4\cdot 2!} \quad - \Gamma_{n+1}\frac{\rho^{n+1}}{(n+1)(n-1)!}$$

Therefore we get the [redacted] virial expansion

$$\frac{p}{kT} = \rho + B_2\rho^2 + B_3\rho^3 + \cdots$$

where $B_n =$ [redacted] $-(n-1)\dfrac{\Gamma_n}{n!}$ and Γ_n is the sum of the edge contributions from [redacted] doubly connected graph with vertices $1, \ldots, n$.

$B_2 = -\Big($ $\Big) = -\frac{1}{2} a$

$B_3 = -\frac{2}{[redacted]}\Big($  $\Big) = -\frac{1}{3} b$

$B_4 = -3\Big[\Big($ $+$  $+$  $\Big)\Big]$