9.C.1. Virial Expansion and Cluster Functions

For a fluid described by the Hamiltonian (9.1), the grand partition function is given by [c.f. (7.112)]

$$Z_\mu(T, V) = \sum_{N=0}^{\infty} \frac{1}{N!} Z_N e^{\beta \mu N}$$
$$= \sum_{N=0}^{\infty} \frac{1}{N!} \int d\boldsymbol{p}^N \int d\boldsymbol{q}^N e^{-\beta(H-\mu N)} \tag{9.9a}$$

where μ is the chemical potential and $N!$ is the Gibbs counting factor [see (7.12) in §7.B]. Using (9.2c), we have

$$Z_\mu(T, V) = \sum_{N=0}^{\infty} \frac{1}{N!} z^N Q_N(V, T) e^{\beta \mu N} \tag{9.9b}$$

Caution: Reichl used μ' to denote the chemical potential and μ to denote the molar chemical potential equal to $\mu' n v$, where $n = \frac{N}{V}$ and v is the molar volume [see (2.63) of §2.E].

Using the thermal wavelength defined as [see (5) of Exercise 7.3, §7.D.2]

$$\lambda_T = h \sqrt{\frac{\beta}{2 \pi m}} \tag{9.9c}$$

(9.7c) of §9.B becomes

$$z = \left(\frac{h}{\lambda_T} \right)^3 \tag{9.9d}$$

so that (9.9b) becomes

$$Z_\mu(T, V) = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{h}{\lambda_T} \right)^{3N} Q_N(V, T) e^{\beta \mu N} \tag{9.9}$$

For a short range potential of range R,

$$\mathcal{V}(q_{ij}) = 0 \qquad \text{for} \qquad q_{ij} \gg R$$
$$\rightarrow \qquad e^{-\beta \mathcal{V}(q_{ij})} = 1 \qquad \text{for} \qquad q_{ij} \gg R$$

Therefore, it is convenient to define

$$f(q) = e^{-\beta \mathcal{V}(q)} - 1$$

with the shorthand

$$f_{ij} = e^{-\beta \mathcal{V}(q_{ij})} - 1 \tag{9.10}$$

Note that

$$f(q) = 0 \qquad \text{for} \qquad q \gg R$$

Furthermore, if $\mathcal{V}$ has a hard core of radius σ so that

$$\mathcal{V}(q) \to \infty \qquad \text{for} \qquad q \ll \sigma$$

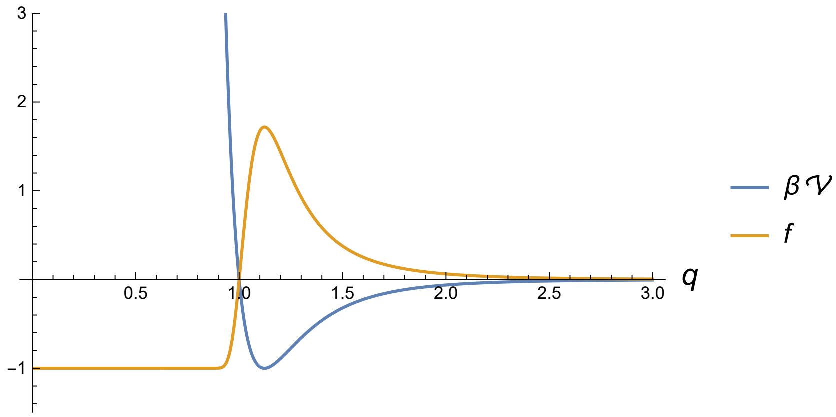
we have

$$f(q) \to -1 \qquad \text{for} \qquad q \ll \sigma$$

The case for the Lennard-Jones (6-12) potential

$$\mathcal{V}(q) = 4 \epsilon \left[\left(\frac{\sigma}{q} \right)^{12} - \left(\frac{\sigma}{q} \right)^6 \right]$$

with $\epsilon = \sigma = 1$, is plotted below [see "9.C.1._Code.nb"]. The hard-core radius, defined by $\mathcal{V}(q_c) = 0$, is given by $q_c = \sigma$.



Using

$$e^{-\beta \mathcal{V}^N} = \exp\left[-\beta \sum_{(i,j)}^{N(N-1)/2} \mathcal{V}(q_{ij})\right] = \prod_{(i,j)}^{N(N-1)/2} e^{-\beta \mathcal{V}(q_{ij})}$$

$$= \prod_{(i,j)}^{N(N-1)/2} (1 + f_{ij})$$

we can write the configuration integral [see (9.5)] as

$$Q_N(V, T) = \int d\,\boldsymbol{q}^N \prod_{(i,j)}^{N(N-1)/2} (1 + f_{ij}) \tag{9.11}$$

In general, the configuration integral takes the form

$$Q_N(V, T) = \int d\,\boldsymbol{q}^N\, W_N(\boldsymbol{q}^N) \tag{9.12}$$

so that (9.9b) becomes

$$Z_\mu(T, V) = \sum_{N=0}^{\infty} \frac{1}{N!} z^N e^{\beta \mu N} \int d\,\boldsymbol{q}^N\, W_N(\boldsymbol{q}^N) \tag{9.13}$$

The cumulant expansion of the grand partition function is defined as [c.f. (4.18)]

$$Z_\mu(T, V) = \exp\left[\sum_{N=0}^{\infty} \frac{1}{N!} z^N e^{\beta \mu N} \int d\,\boldsymbol{q}^N\, U_N(\boldsymbol{q}^N)\right] \tag{9.14}$$

where $U_N(\boldsymbol{q}^N)$ is called a cluster (or Ursell) function.

This leads to the corresponding expansion of the grand potential [see (7.111)]

$$\Omega(T, V, \mu) = -k_B T \ln Z_\mu(T, V)$$

$$= -k_B T \sum_{N=0}^{\infty} \frac{1}{N!} z^N e^{\beta \mu N} \int d\,\boldsymbol{q}^N\, U_N(\boldsymbol{q}^N) \tag{9.15}$$

The cumulant expansion [see §4.D.3]

$$\langle e^{-\alpha x} \rangle = \sum_{n=0}^{\infty} \frac{(-\alpha)^n}{n!} \langle x^n \rangle = \exp\left(\sum_{n=1}^{\infty} \frac{(-\alpha)^n}{n!} C_n\right)$$

can be calculated using *Mathematica* [see "9.C.1._Code.nb"]. The first few terms are

$$
\begin{aligned}
C_1 &= \langle x \rangle \\
C_2 &= \langle x^2 \rangle - \langle x \rangle^2 \\
C_3 &= \langle x^3 \rangle - 3 \langle x^2 \rangle \langle x \rangle + 2 \langle x \rangle^3 \\
C_4 &= \langle x^4 \rangle - 4 \langle x^3 \rangle \langle x \rangle + 12 \langle x^2 \rangle \langle x \rangle^2 - 3 \langle x^2 \rangle^2 - 6 \langle x \rangle^4 \\
C_5 &= \langle x^5 \rangle - 5 \langle x^4 \rangle \langle x \rangle + 20 \langle x^3 \rangle \langle x \rangle^2 - 60 \langle x^2 \rangle \langle x \rangle^3 \\
&\quad + 30 \langle x^2 \rangle^2 \langle x \rangle - 10 \langle x^2 \rangle \langle x^3 \rangle + 24 \langle x \rangle^5
\end{aligned}
\tag{9.15a}
$$

Inverting these gives

$$
\begin{aligned}
\langle x \rangle &= C_1 \\
\langle x^2 \rangle &= C_1^2 + C_2 \\
\langle x^3 \rangle &= C_1^3 + 3 C_2 C_1 + C_3 \\
\langle x^4 \rangle &= C_1^4 + 6 C_2 C_1^2 + 4 C_3 C_1 + 3 C_2^2 + C_4 \\
\langle x^5 \rangle &= C_1^5 + 10 C_2 C_1^3 + 10 C_3 C_1^2 + 15 C_2^2 C_1 + 5 C_4 C_1 + 10 C_2 C_3 + C_5
\end{aligned}
\tag{9.15b}
$$

These can be used to obtain relations between W_N & U_N. Since the calculations can be quite involved, we shall simplify the notations with the shorthands

$$g(\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{q}_N) = g(1, 2, \ldots, N) \qquad \text{for all functions } g$$

$$\int d\boldsymbol{q}\; g(\boldsymbol{q}) = \int d1\, g(1)$$

With the substitutions

$$Z_\mu(T, V) \to \langle e^{-\alpha x} \rangle \qquad z e^{\beta\mu} \to -\alpha$$

$$\int d\boldsymbol{q}^N W_N(\boldsymbol{q}^N) \to \langle x^N \rangle \qquad \int d\boldsymbol{q}^N U_N(\boldsymbol{q}^N) \to C_N$$

we have

$$\int d1\, U_1(1) = \int d1\, W_1(1)$$

$$\to \quad U_1(1) = W_1(1) \tag{9.16}$$

$$\int d1 \int d2\, U_2(1,2) = \int d1 \int d2\; W_2(1,2) - \left(\int d1\, W_1(1) \right)^2$$

$$\to \quad U_2(1,2) = W_2(1,2) - W_1(1)\, W_1(2) \tag{9.17}$$

Note that inside an integral, $\boldsymbol{q}_j$ are dummy variables so that

$$\left(\int d1\, W_1(1) \right)^2 = \int d1 \int d2\, W_1(1)\, W_1(2) \tag{9.17a}$$

$$
\begin{aligned}
\int d1 \int d2 \int d3\, U_3(1,2,3) &= \int d1 \int d2 \int d3\, W_3(1,2,3) \\
&\quad -3 \left(\int d1\, W_1(1) \right) \left(\int d1 \int d2\, W_2(1,2) \right) + 2 \left(\int d1\, W_1(1) \right)^3
\end{aligned}
$$

$$
\begin{aligned}
\to \quad U_3(1,2,3) &= W_3(1,2,3) - W_1(1)\, W_2(2,3) - W_1(2)\, W_2(3,1) \\
&\quad - W_1(3)\, W_2(1,2) + 2\, W_1(1)\, W_1(2)\, W_1(3)
\end{aligned}
\tag{9.18}
$$

Note that we have symmetrized the $3\, W_1\, W_2$ term since the order of the arguments in U_N should be immaterial.

Inverting, we have

$$W_1(1) = U_1(1) \tag{9.19}$$

$$W_2(1,2) = U_2(1,2) + W_1(1)\, W_1(2)$$

$$= U_2(1,2) + U_1(1)\, U_1(2) \tag{9.20}$$

$$W_3(1,2,3) = U_3(1,2,3) + U_1(1)\, W_2(2,3) + U_1(2)\, W_2(3,1) + U_1(3)\, W_2(1,2) - 2\, U_1(1)\, U(2)\, U_1(3)$$

$$= U_3(1,2,3) + U_1(1)\,[\, U_2(2,3) + U_1(2)\, U_1(3)\,] + U_1(2)[\, U_2(3,1) + U_1(3)\, U_1(1)\,] + U_1(3)[\, U_2(1,2) + U_1(1)\, U_1(2)\,] - 2\, U_1(1)\, U(2)\, U_1(3)$$

$$= U_3(1,2,3) + U_1(1)\, U_2(2,3) + U_1(2)\, U_2(3,1) + U_1(3)\, U_2(1,2) + U_1(1)\, U(2)\, U_1(3) \tag{9.21}$$

Obviously, these can also be obtained directly from (9.15b) with proper symmetrization.

Comparing (9.11) with (9.12) gives

$$W_N(1, \ldots, N) = \prod_{(i,j)}^{N(N-1)/2} (1 + f_{ij}) \tag{9.22}$$

so that

$$W_1(1) = 1 \tag{9.23}$$

$$W_2(1,2) = 1 + f_{12} \tag{9.24}$$

$$W_3(1,2,3) = (1 + f_{12})\,(1 + f_{13})\,(1 + f_{23}) \tag{9.25}$$

$$= 1 + f_{12} + f_{13} + f_{23} + f_{12}\, f_{13} + f_{12}\, f_{23} + f_{13}\, f_{23} + f_{12}\, f_{13}\, f_{23} \tag{9.25a}$$

$$W_4(1,2,3,4) = (1 + f_{12})\,(1 + f_{13})\,(1 + f_{14})\,(1 + f_{23})\,(1 + f_{24})\,(1 + f_{34}) \tag{9.26}$$

Since there are $\frac{1}{2} N(N-1)$ factors of $(1 + f_{ij})$ in W_N, there will be $2^{N(N-1)/2}$ terms if we expand it.

The cluster functions can be obtained using (9.16-8),

$$U_1(1) = 1 \tag{9.27}$$

$$U_2(1,2) = 1 + f_{12} - 1$$

$$= f_{12} \tag{9.28}$$

$$U_3(1,2,3) = (1 + f_{12})\,(1 + f_{13})\,(1 + f_{23}) - (1 + f_{12}) - (1 + f_{13}) - (1 + f_{23}) + 2$$

$$= f_{12}\, f_{13} + f_{12}\, f_{23} + f_{13}\, f_{23} + f_{12}\, f_{13}\, f_{23} \tag{9.29}$$

Now, since $1 = e^{-\beta \mathcal{V}(q_{ij})}\big|_{\mathcal{V}=0}$, the Taylor expansion

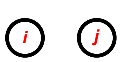
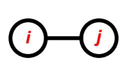
$$e^{-\beta \mathcal{V}(q_{ij})} = \sum_{n=0}^{\infty} \frac{1}{n!} (-\beta \mathcal{V})^n = 1 + f_{ij}$$

can be interpreted as the sum of the contributions from 2 states of the pair of particles i & j :

1 : i & j out of interaction range.

f_{ij} : i & j within interaction range.

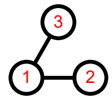
which can be represented graphically as

$1 =$  $f_{ij} =$ 

where the particles are represented by labelled circles (vertices).

From (9.22), we see that W_N is a sum of all possible graphs that can be formed from N particles such that each pair i & j can either be unconnected (1) or connected (f_{ij}).

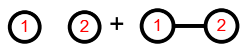
For example, the term $f_{12}\, f_{13}$ in W_3 should be taken as $f_{12}\, f_{13}\, (f_{23} = 1)$ so that

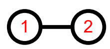
$f_{12}\,f_{13} =$ 

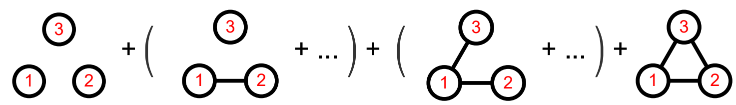
The general proof is quite involved, but one can verify by inspection (for small N) that U_N is the sum of all connected graphs of N particles. A graph is connected if every vertex in it is connected to every other vertex by at least one path (sequence of joined lines). In physical terms, every particle is interacting, directly or in-directly, with every other particle. Such a group of particles is called a cluster, and U_N, a cluster function.

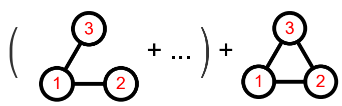
Thus,

$W_1(1) = U_1(1) =$ 

$W_2(1, 2) =$ 

$U_2(1, 2) =$ 

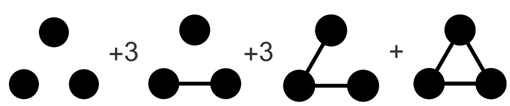
$W_3\,(1, 2, 3) =$ 

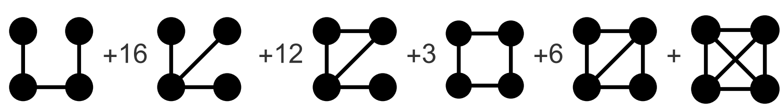
$U_3(1, 2, 3) =$  (9.33a)

where "..." denotes terms that are obtained by permuting the vertex labels of the graph shown.

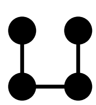
Mathematica codes for drawing these graphs can be found in “graphics.nb”.

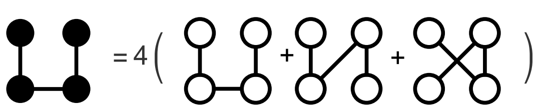
In some discussions, labels of the vertices are unimportant or even distracting. In which case, particles can be represented by black dots, e.g.,

$W_3 =$  (9.33)

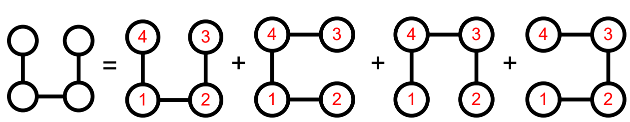
$U_4 = 12$  (9.38)

where the number in front of a graph is its multiplicity (number of topologically equivalent graphs).

For example,  means all graphs with a chain of length 3. If we use a graph of un-labelled circles to denote the set of graphs that have the same shape, we have

12  (9.38a)

where

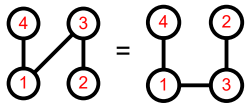
4 

$$= f_{41}\,f_{12}\,f_{23} + f_{34}\,f_{41}\,f_{12} + f_{23}\,f_{34}\,f_{41} + f_{12}\,f_{23}\,f_{34}$$

and similarly for the other two graphs.

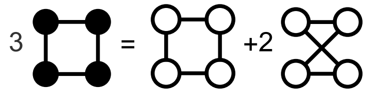
Note that we have assumed the vertex labels are fixed.

If we allow permutations on vertex labels, then

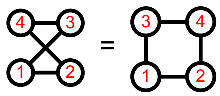


In fact, as implied in (9.33a), all members of a black-dot-graph are related by label permutations. They are therefore called topologically equivalent. Dividing them into subgroups by shape, as in (9.38a), works only if we fixed the vertex labels.

Another example is,



If we allow permutations on vertex indices, then



So far, we have shown how to draw graphs given the algebraic expression. However, the real advantage of using graphs is the reverse: draw graphs by connecting dots according to some rules based on physical considerations, and then translate them into algebraic expressions for calculations.

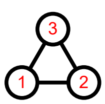
The cumulant expansion (9.14) is a vast improvement over (9.13) because all redundant terms associated with disjointed (or non-connected) graphs are dropped. In practical terms, (9.14) converges much faster than (9.13).

We now turn to another important property of clusters:

The integral over all coordinates of a cluster is proportional to the volume V.

The reason for this is simple. Since f_{ij} are functions of relative coordinates, the integral over the center of mass (CM) coordinate gives V. Furthermore, since all particles interact with each other in a cluster, the number of coordinates required to describe the cluster cannot be further reduced. QED.

As an example,

$$\int d\,1 \int d\,2 \int d\,3$$ 

$$= \int d\,1 \int d\,2 \int d\,3\; f_{12}\, f_{23}\, f_{31}$$

$$= \int d\,\boldsymbol{Q} \int d\,\boldsymbol{q}_{12} \int d\,\boldsymbol{q}_{23}\, f_{12}\, f_{23}\, f(\boldsymbol{q}_{12} - \boldsymbol{q}_{23})$$

$$= V \int d\,\boldsymbol{q}_{12} \int d\,\boldsymbol{q}_{23}\, f_{12}\, f_{23}\, f(\boldsymbol{q}_{12} - \boldsymbol{q}_{23})\, J$$

where J is the Jacobian of the coordinate transformation and

$$\boldsymbol{Q} = \frac{1}{3}(\boldsymbol{q}_1 + \boldsymbol{q}_2 + \boldsymbol{q}_3)$$

is the CM coordinate.

Thus, a disjointed graph composed of n clusters is proportional to V^n.

The cluster integral, defined by

$$b_N(T, V) = \frac{1}{V N!} \int d\,1 \ldots \int d\,N\, U_N(1, \ldots, N) \qquad (9.39)$$

is therefore independent of V.

(9.15) thus becomes

$$\Omega(T, V, \mu) = -k_B T V \sum_{N=0}^{\infty} z^N e^{\beta \mu N} b_N(T, V) \qquad z = \left(\frac{h}{\lambda_T}\right)^3 \qquad (9.40)$$

The pressure is therefore [see (2.122) of §2.F.5]

$$P = -\frac{\Omega(T, V, \mu)}{V} = k_B T \sum_{N=0}^{\infty} z^N e^{\beta \mu N} b_N(T, V) \qquad (9.41)$$

and the particle density [see (2.126) of §2.F.5]

$$\frac{\langle N \rangle}{V} = -\frac{1}{V}\left(\frac{\partial \Omega}{\partial \mu}\right)_{T V} = \sum_{N=0}^{\infty} N z^N e^{\beta \mu N} b_N(T, V) \qquad (9.42)$$

The virial expansion of the equation of state is a density expansion [see (2.11) of §2.C.2]

$$\frac{P V}{\langle N \rangle k_B T} = \sum_{j=1}^{\infty} B_l(T) \left(\frac{\langle N \rangle}{V}\right)^{j-1} \qquad (9.43)$$

In the thermodynamic limit,

$$\lim_{\langle N \rangle, V \to \infty} \frac{\langle N \rangle}{V} = \rho = \text{const}$$

we set

$$\lim_{V \to \infty} b_j(T, V) = \tilde{b}_j(T)$$

so that (9.41-3) become

$$P = k_B T \sum_{N=0}^{\infty} z^N e^{\beta \mu N} \tilde{b}_N(T)$$

$$\rho = \sum_{N=0}^{\infty} N z^N e^{\beta \mu N} \tilde{b}_N(T)$$

$$\sum_{n=0}^{\infty} z^n e^{\beta \mu n} \tilde{b}_n(T) = \sum_{j=0}^{\infty} B_j(T) \left(\sum_{m=0}^{\infty} m z^m e^{\beta \mu m} \tilde{b}_m(T)\right)^j \qquad (9.44)$$

Setting the coefficient of each power of $z e^{\beta \mu}$ to zero, one get a series of equations for $B_j(T)$. The first 6 of which are [see “Code.nb]

$$\begin{aligned}
0 &== -B_0 + \tilde{b}_0 \\
0 &== \tilde{b}_1 - B_1 \tilde{b}_1 \\
0 &== -B_2 \tilde{b}_1^2 + \tilde{b}_2 - 2 B_1 \tilde{b}_2 \\
0 &== -B_3 \tilde{b}_1^3 - 4 B_2 \tilde{b}_1 \tilde{b}_2 + \tilde{b}_3 - 3 B_1 \tilde{b}_3 \\
0 &== -B_4 \tilde{b}_1^4 - 6 B_3 \tilde{b}_1^2 \tilde{b}_2 - 4 B_2 \tilde{b}_2^2 - 6 B_2 \tilde{b}_1 \tilde{b}_3 + \tilde{b}_4 - 4 B_1 \tilde{b}_4 \\
0 &== -B_5 \tilde{b}_1^5 - 8 B_4 \tilde{b}_1^3 \tilde{b}_2 - 12 B_3 \tilde{b}_1 \tilde{b}_2^2 - 9 B_3 \tilde{b}_1^2 \tilde{b}_3 - 12 B_2 \tilde{b}_2 \tilde{b}_3 \\
&\quad - 8 B_2 \tilde{b}_1 \tilde{b}_4 + \tilde{b}_5 - 5 B_1 \tilde{b}_5
\end{aligned} \qquad (9.44a)$$

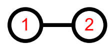
With the help of [see (9.39) & (9.27)]

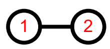
$$\tilde{b}_0(T) = \tilde{b}_1(T) = 1$$

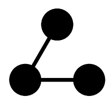
they can be solved using *Mathematica* [see "graphics.nb"]. The first 5 solutions are

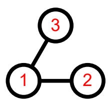
$$
\begin{aligned}
B_0 &= 1 \\
B_1 &= 1 \\
B_2 &= -\tilde{b}_2 \\
B_3 &= -2\left(\tilde{b}_3 - 2\,\tilde{b}_2^2\right) \\
B_4 &= -20\,\tilde{b}_2^3 + 18\,\tilde{b}_3\,\tilde{b}_2 - 3\,\tilde{b}_4 \\
B_5 &= -2\left(-56\,\tilde{b}_2^4 + 72\,\tilde{b}_3\,\tilde{b}_2^2 - 16\,\tilde{b}_4\,\tilde{b}_2 - 9\,\tilde{b}_3^2 + 2\,\tilde{b}_5\right)
\end{aligned}
\qquad (9.44b)
$$

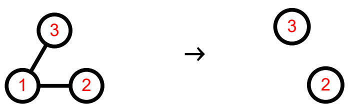
Using (9.39), we have

$$\tilde{b}_2(T) = \frac{1}{V\,2!}\int d\,1 \int d\,2$$ 

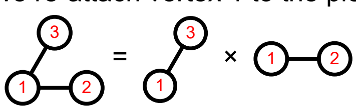
$$= \frac{1}{2}\int d\,\boldsymbol{q}_{12}$$  (9.44c)

$$\tilde{b}_3(T) = \frac{1}{V\,3!}\int d\,1 \int d\,2 \int d\,3 \;\Big(\; 3$$  $\Big)$

Now, a graph like  can be broken into two pieces by taking one vertex and the associated lines away. For example, taking vertex 1 away gives



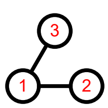
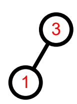
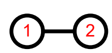
When we re-attach vertex 1 to the pieces, we get

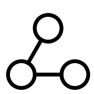
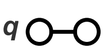


Algebraically, this means $\boldsymbol{q}_1$ can be isolated using the transform

$$(\boldsymbol{q}_1,\ \boldsymbol{q}_2,\ \boldsymbol{q}_3) \to (\boldsymbol{q}_1,\ \boldsymbol{q}_{12},\ \boldsymbol{q}_{13})$$

so that

$$\frac{1}{V}\int d\,1 \int d\,2 \int d\,3$$  $= \left(\int d\,\boldsymbol{q}_{13}\right.$  $\left.\right)\left(\int d\,\boldsymbol{q}_{12}\right.$  $\left.\right)$ (9.44d)

or $$\frac{1}{V}\int d\,1 \int d\,2 \int d\,3$$  $= \left(\int d\,\boldsymbol{q}\right.$  $\left.\right)^2$

Moreover, (9.44d) remains valid if we replace vertices 2 & 3 with arbitrarily complicated & different clusters. And the same if we add more vertices to join vertex 1.

The conclusion is that, if a cluster can be broken into multiple pieces by taking one vertex and the associated lines away, then its cluster integral is a product of integrals of clusters made from re-attaching the cut-off vertex to each of the broken pieces. We shall call such a cluster loose.

In contrast, a cluster that is not loose is called a tight (or star) cluster.

A happy result is that in the virial expansion, all loose cluster integrals are cancelled out so that only integrals of tight clusters contribute. We shall take this on faith and check it for individual cases.

Inspection of (9.44a) quickly shows that for B_j, only the term $\tilde{b}_j$ can contain star clusters. Denoting the star cluster integral with a superscript $*$, we have

$$B_j = c_j\, \tilde{b}_j^* \qquad (9.49a)$$

where the coefficient

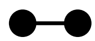
$$c_j = \frac{(1-j)\, B_1}{\tilde{b}_1^j} = -(j-1)$$

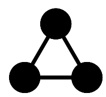
can be deduced from the $(j+1)^{\text{th}}$ equation in (9.44a).

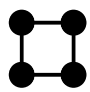
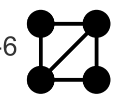
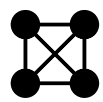
In analogy with (9.39), we define the star function $U_N^*(\boldsymbol{q}^N)$ by

$$\tilde{b}_N^* = \lim_{V\to\infty} \frac{1}{V\,N!} \int d\,1 \ldots \int d\,N\, U_N^*(1,\ \ldots,\ N) \qquad (9.49b)$$

The associated star graphs can be obtained easily from the graphs for U_N.

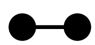
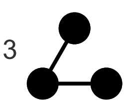
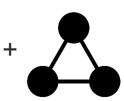
$U_2^*(1,\,2) =$  (9.51)

$U_3^*(1,\,2,\,3) =$  (9.52)

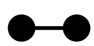
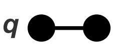
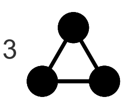
$U_4^*(1,\,2,\,3,\,4) =$ 3  +6  +  (9.53)

To check the validity of (9.49a) for $j = 3$, we get from (9.44b) that

$B_3 = 4\,\tilde{b}_2^2 - 2\,\tilde{b}_3$

$= 4\left(\frac{1}{2\,V}\int d\,1 \int d\,2\right.$  $\left.\right)^2 - \frac{2}{3!\,V}\int d\,1 \int d\,2 \int d\,3\ ($ 3  +  $)$

[(9.33) used.]

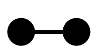
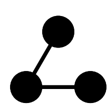
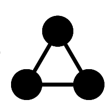
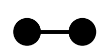
$= \left(\int d\,\boldsymbol{q}\right.$  $\left.\right)^2 - \left(\int d\,\boldsymbol{q}\right.$  $\left.\right)^2 - \frac{1}{3\,V}\int d\,1 \int d\,2 \int d\,3$ 

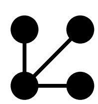
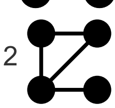
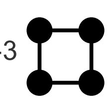
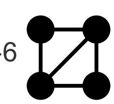
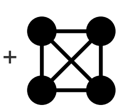
[(9.44c-d) used.]

$= -2\,\tilde{b}_3^*$ [(9.49b) & (9.52) used.]

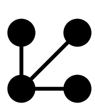
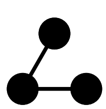
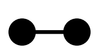
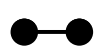
To simplify the notations, we shall leave out the integrals in the proof for $j = 4$.

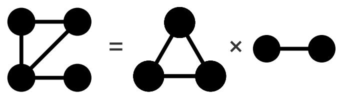
$B_4 = -20\,\tilde{b}_2^3 + 18\,\tilde{b}_3\,\tilde{b}_2 - 3\,\tilde{b}_4$

$= -20\left(\frac{1}{2}\right.$  $\left.\right)^3 + \frac{18}{3!\quad 2!}($ 3  +  $)($  $)$

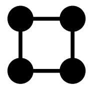
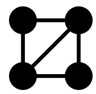
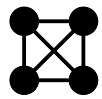
$-\frac{3}{4!}($ 16  +12  +3  +6  +  $)$

Using

 =  ×  $= ($  $)^3$



we have

$B_4 = -\frac{3}{4!}\Big($ 3  +6  +  $\Big)$

$= -3\,\tilde{b}_4^*$