

V.B The Cluster Expansion

For short range interactions, specially with a hard core, it is much better to replace the expansion parameter $\mathcal{V}(\vec{q})$ by $f(\vec{q}) = \exp(-\beta\mathcal{V}(\vec{q})) - 1$, which is obtained by summing over all possible number of bonds between two points on a cumulant graph. The resulting series is organized in powers of the density N/V , and is most suitable for obtaining a *virial expansion*, which expresses the deviations from the ideal gas equation of state in a power series

$$\frac{P}{k_B T} = \frac{N}{V} \left[1 + B_2(T) \frac{N}{V} + B_3(T) \left(\frac{N}{V} \right)^2 + \dots \right]. \quad (\text{V.14})$$

The temperature dependent parameters, $B_i(T)$, are known as the *virial coefficients* and originate from the inter-particle interactions. Our initial goal is to compute these coefficients from first principles.

To illustrate a different method of expansion, we shall perform computations in the grand canonical ensemble. With a macro-state $M \equiv (T, \mu, V)$, the grand partition function is given by

$$\mathcal{Q}(\mu, T, V) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z(N, T, V) = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\lambda^3} \right)^N \mathcal{S}_N, \quad (\text{V.15})$$

where

$$\mathcal{S}_N = \int \prod_{i=1}^N d^3 \vec{q}_i \prod_{i < j} (1 + f_{ij}), \quad (\text{V.16})$$

and $f_{ij} = f(\vec{q}_i - \vec{q}_j)$.

The $2^{N(N-1)/2}$ terms in \mathcal{S}_N can now be ordered in powers of f_{ij} as

$$\mathcal{S}_N = \int \prod_{i=1}^N d^3 \vec{q}_i \left(1 + \sum_{i < j} f_{ij} + \sum_{i < j, k < l} f_{ij} f_{kl} + \dots \right). \quad (\text{V.17})$$

An efficient method for organizing the perturbation series is to represent the various contributions diagrammatically. In particular we shall apply the following conventions:

(a) Draw N dots labelled by $i = 1, \dots, N$ to represent the coordinates \vec{q}_1 through \vec{q}_N ,

$$\begin{array}{ccccccc} \bullet & \bullet & & \bullet & & & \\ 1 & 2 & \cdots & N & & & \end{array}$$

(b) Each term in eq.(V.17) corresponds to a product of f_{ij} , represented by drawing lines connecting i and j for each f_{ij} . For example, the graph,

$$\begin{array}{ccccccc} \bullet & \bullet - \bullet & \bullet - \bullet - \bullet & & \bullet & & \\ 1 & 2 & 3 & 4 & 5 & 6 & \cdots & N \end{array},$$

represents the integral

$$\left(\int d^3 \vec{q}_1 \right) \left(\int d^3 \vec{q}_2 d^3 \vec{q}_3 f_{23} \right) \left(\int d^3 \vec{q}_4 d^3 \vec{q}_5 d^3 \vec{q}_6 f_{45} f_{56} \right) \cdots \left(\int d^3 \vec{q}_N \right) .$$

As the above example indicates, the value of each graph is the product of the contributions from its *linked clusters*. Since these clusters are more fundamental, we reformulate the sum in terms of them by defining a quantity b_ℓ , equal to the *sum over all ℓ -particle linked clusters* (one-particle irreducible or not). For example

$$b_1 = \bullet = \int d^3 \vec{q} = V, \quad (\text{V.18})$$

and

$$b_2 = \bullet - \bullet = \int d^3 \vec{q}_1 d^3 \vec{q}_2 f(\vec{q}_1 - \vec{q}_2). \quad (\text{V.19})$$

There are four diagrams contributing to b_3 , leading to

$$\begin{aligned} b_3 = \int d^3 \vec{q}_1 d^3 \vec{q}_2 d^3 \vec{q}_3 [& f(\vec{q}_1 - \vec{q}_2) f(\vec{q}_2 - \vec{q}_3) + f(\vec{q}_2 - \vec{q}_3) f(\vec{q}_3 - \vec{q}_1) + f(\vec{q}_3 - \vec{q}_1) f(\vec{q}_1 - \vec{q}_2) \\ & + f(\vec{q}_1 - \vec{q}_2) f(\vec{q}_2 - \vec{q}_3) f(\vec{q}_3 - \vec{q}_1)]. \end{aligned} \quad (\text{V.20})$$

A given N -particle graph can be decomposed to n_1 1-clusters, n_2 2-clusters, \cdots , n_ℓ ℓ -clusters, etc. Hence,

$$\mathcal{S}_N = \sum_{\{n_\ell\}'} \prod_{\ell} b_\ell^{n_\ell} W(\{n_\ell\}), \quad (\text{V.21})$$

where the restricted sum is over all *distinct divisions of N points* into a set of clusters $\{n_\ell\}$, such that $\sum_{\ell} \ell n_\ell = N$. The coefficients $W(\{n_\ell\})$ are the number of ways of assigning N particle labels to groups of n_ℓ ℓ -clusters. For example, the divisions of 3 particles into a 1-cluster and a 2-cluster are

$$\begin{array}{ccc} \bullet & \bullet - \bullet & \bullet \\ 1 & 2 \quad 3 & 2 \end{array}, \quad \begin{array}{ccc} \bullet - \bullet & & \bullet \\ 1 \quad 3 & & 3 \end{array}, \quad \text{and} \quad \begin{array}{ccc} \bullet & \bullet - \bullet & \\ 3 & 2 \quad 1 & \end{array}.$$

All above graphs have $n_1 = 1$ and $n_2 = 1$, and contribute a factor of $b_1 b_2$ to \mathcal{S}_3 ; thus $W(1, 1) = 3$.

In general, $W(\{n_\ell\})$ is the number of distinct ways of grouping the labels $1, \dots, N$ into bins of n_ℓ ℓ -clusters. It can be obtained from the total number of permutations, $N!$, after dividing by the number of equivalent assignments. Within each bin of ℓn_ℓ particles, equivalent assignments are obtained by: (i) permuting the ℓ labels in each subgroup in $\ell!$

ways, for a total of $(\ell!)^{n_\ell}$ permutations; and (ii) the $n_\ell!$ rearrangements of the n_ℓ subgroups. Hence,

$$W(\{n_\ell\}) = \frac{N!}{\prod_\ell n_\ell! (\ell!)^{n_\ell}}. \quad (\text{V.22})$$

(We can indeed check that $W(1, 1) = 3!/(1!)(2!) = 3$ as obtained above.)

Using the above value of W , the expression for \mathcal{S}_N in eq.(V.21) can be evaluated. However, the restriction of the sum to configurations such that $\sum_\ell \ell n_\ell = N$ complicates the evaluation. Fortunately, this restriction disappears in the expression for the grand partition function in eq.(V.16),

$$\mathcal{Q} = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}}{\lambda^3} \right)^N \sum_{\{n_\ell\}} \frac{N!}{\prod_\ell n_\ell! (\ell!)^{n_\ell}} \prod_\ell b_\ell^{n_\ell}. \quad (\text{V.23})$$

The restriction in the second sum is now removed by noting that $\sum_{N=0}^{\infty} \sum_{\{n_\ell\}} \delta_{\sum_\ell \ell n_\ell, N} = \sum_{\{n_\ell\}}$. Therefore,

$$\begin{aligned} \mathcal{Q} &= \sum_{\{n_\ell\}} \left(\frac{e^{\beta\mu}}{\lambda^3} \right)^{\sum_\ell \ell n_\ell} \prod_\ell \frac{b_\ell^{n_\ell}}{n_\ell! (\ell!)^{n_\ell}} = \sum_{\{n_\ell\}} \prod_\ell \frac{1}{n_\ell!} \left(\frac{e^{\beta\mu} b_\ell}{\lambda^3 \ell!} \right)^{n_\ell} \\ &= \prod_\ell \sum_{\{n_\ell\}} \frac{1}{n_\ell!} \left[\left(\frac{e^{\beta\mu}}{\lambda^3} \right)^\ell \frac{b_\ell}{\ell!} \right]^{n_\ell} = \prod_\ell \exp \left[\left(\frac{e^{\beta\mu}}{\lambda^3} \right)^\ell \frac{b_\ell}{\ell!} \right] \\ &= \exp \left[\sum_{\ell=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3} \right)^\ell \frac{b_\ell}{\ell!} \right]. \end{aligned} \quad (\text{V.24})$$

The above result has the simple geometrical interpretation that the sum over all graphs, connected or not, equals the exponential of the sum over *connected* graphs. This is a quite general result that is also related to the graphical connection between moments and cumulants discussed in sec.II.B.

The grand potential is now obtained from

$$\ln \mathcal{Q} = -\beta \mathcal{G} = \frac{PV}{kT} = \sum_{\ell=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3} \right)^\ell \frac{b_\ell}{\ell!}. \quad (\text{V.25})$$

In eq.(V.25), the extensivity condition is used to get $\mathcal{G} = E - TS - \mu N = -PV$. Thus the terms on the right hand side of the above equation must also be proportional to the volume V . This can be explicitly verified by noting that in evaluating each b_ℓ there is an

integral over the center of mass coordinate that explores the whole volume. For example, $b_2 = \int d^3\vec{q}_1 d^3\vec{q}_2 f(\vec{q}_1 - \vec{q}_2) = V \int d^3\vec{q}_{12} f(\vec{q}_{12})$. Quite generally, we can set

$$\lim_{V \rightarrow \infty} b_\ell = V \bar{b}_\ell, \quad (\text{V.26})$$

and the pressure is now obtained from

$$\frac{P}{kT} = \sum_{\ell=1}^{\infty} \left(\frac{e^{\beta\mu}}{\lambda^3} \right)^\ell \frac{\bar{b}_\ell}{\ell!}. \quad (\text{V.27})$$

The linked cluster theorem ensures $\mathcal{Q} \propto V$, since if any non-linked cluster had appeared in $\ln \mathcal{Q}$, it would have contributed a higher power of V .

Although an expansion for the gas pressure, eq.(V.27) is quite different from eq.(V.14) in that it involves powers of $e^{\beta\mu}$ rather than the density $n = N/V$. This difference can be removed by solving for the density in terms of the chemical potential, using

$$N = \frac{\partial \ln \mathcal{Q}}{\partial(\beta\mu)} = \sum_{\ell=1}^{\infty} \ell \left(\frac{e^{\beta\mu}}{\lambda^3} \right)^\ell \frac{V \bar{b}_\ell}{\ell!}. \quad (\text{V.28})$$

The equation of state can be obtained by eliminating the *fugacity* $x = e^{\beta\mu}/\lambda^3$, between the equations

$$n = \sum_{\ell=1}^{\infty} \frac{x^\ell}{(\ell-1)!} \bar{b}_\ell, \quad \text{and} \quad \frac{P}{kT} = \sum_{\ell=1}^{\infty} \frac{x^\ell}{\ell!} \bar{b}_\ell, \quad (\text{V.29})$$

using the following steps:

(a) Solve for $x(n)$ from $(\bar{b}_1 = \int d^3\vec{q}/V = 1)$

$$x = n - \bar{b}_2 x^2 - \frac{\bar{b}_3}{2} x^3 - \dots. \quad (\text{V.30})$$

The perturbative solution at each order is obtained by substituting the solution at the previous order in eq.(V.30),

$$\begin{aligned} x_1 &= n + \mathcal{O}(n^2) \\ x_2 &= n - \bar{b}_2 n^2 + \mathcal{O}(n^3) \\ x_3 &= n - \bar{b}_2(n - \bar{b}_2 n)^2 - \frac{\bar{b}_3}{2} n^3 + \mathcal{O}(n^4) = n - \bar{b}_2 n^2 + (2\bar{b}_2^2 - \frac{\bar{b}_3}{2}) n^3 + \mathcal{O}(n^4). \end{aligned} \quad (\text{V.31})$$

(b) Substitute the perturbative result for $x(n)$ into eq.(V.29), yielding

$$\begin{aligned}
\beta P &= x + \frac{b_2}{2}x^2 + \frac{b_3}{6}x^3 + \dots \\
&= n - b_2n^2 + (2b_2^2 - \frac{b_3}{2})n^3 + \frac{b_2}{2}n^2 - b_2^2n^3 + \frac{b_3}{6}n^3 + \dots \\
&= n - \frac{b_2}{2}n^2 + (b_2^2 - \frac{b_3}{3})n^3 + \mathcal{O}(n^4).
\end{aligned} \tag{V.32}$$

The final result is in the form of the virial expansion of eq.(V.14),

$$\beta P = n + \sum_{\ell=2}^{\infty} B_{\ell}(T)n^{\ell}.$$

The first term in the series reproduces the ideal gas result. The next two corrections are

$$B_2 = -\frac{b_2}{2} = -\frac{1}{2} \int d^3\vec{q} \left(e^{-\beta\mathcal{V}(\vec{q})} - 1 \right), \tag{V.33}$$

and

$$\begin{aligned}
B_3 &= b_2^2 - \frac{b_3}{3} \\
&= \left(\int d^3\vec{q} \left(e^{-\beta\mathcal{V}(\vec{q})} - 1 \right) \right)^2 \\
&\quad - \frac{1}{3} \left[3 \int d^3\vec{q}_{12} d^3\vec{q}_{13} f(\vec{q}_{12}) f(\vec{q}_{13}) + \int d^3\vec{q}_{12} d^3\vec{q}_{13} f(\vec{q}_{12}) f(\vec{q}_{13}) f(\vec{q}_{12} - \vec{q}_{13}) \right] \\
&= -\frac{1}{3} \int d^3\vec{q}_{12} d^3\vec{q}_{13} f(\vec{q}_{12}) f(\vec{q}_{13}) f(\vec{q}_{12} - \vec{q}_{13}).
\end{aligned} \tag{V.34}$$

The above example demonstrates the cancellation of the one particle reducible cluster that appears in b_3 . While all clusters (reducible or not) appear in the sum for b_{ℓ} , as demonstrated in the previous section, only the *one particle irreducible* ones can appear in an expansion in powers of density. The final expression for the ℓ^{th} virial coefficient is

$$B_{\ell}(T) = -\frac{(\ell-1)}{\ell!} \bar{d}_{\ell}, \tag{V.35}$$

where \bar{d}_{ℓ} is defined as the sum over all one-particle-irreducible clusters of ℓ points. Note that in terms of \bar{d}_{ℓ} , the partition function can be organized as

$$\ln Z = \ln Z_0 + V \sum_{\ell=2}^{\infty} \frac{n^{\ell}}{\ell!} \bar{d}_{\ell}, \tag{V.36}$$

reproducing the above virial expansion from $\beta P = \partial \ln Z / \partial V$.