CHAPTER I

THEORY OF IMPERFECT GASES

1.1 Introduction

All the thermodynamic properties of a system are determinable from a knowledge of the partition function. For an equilibrium one-component quasi-classical system the \( N \)-body partition function is given in terms of the phase integral as

\[
Z_N = \frac{1}{N! h_0^{3N}} \int \exp \left( -\beta H \right) d\Omega,
\]

where the Hamiltonian of the system is

\[
H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \Phi_N(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N),
\]

and provided it is separable into its kinetic and configurational components as (1.1.2) implies, then determination of \( Z_N \) reduces to evaluation of the configurational integral \( Z_Q \)

\[
Z_N = \left( \frac{2\pi m k T}{h_0^2} \right)^{3N/2} Z_Q,
\]

where

\[
Z_Q = \frac{1}{N!} \int \exp \left[ -\beta \Phi_N(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N) \right] d\Omega.
\]

This is where the problem begins, for what do we write for

\[
\Phi_N(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N) \?
\]

The total configurational energy is, of course, dependent upon the total configuration \( \{\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N\} \), and this is quite unknown. A certain simplification is obtained by assuming pairwise additivity of the interatomic potential, such that

\[
\Phi_N(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N) = \sum_{i=1}^{N} \sum_{i>j}^{N} \Phi(|\mathbf{q}_i - \mathbf{q}_j|),
\]

where \( \Phi(|\mathbf{q}_i - \mathbf{q}_j|) \) is the potential developed between the pair \( ij \).

However, if we consider the physical situation a little more closely
we find we are able to effect a series solution for $Z_N$, or $Z_Q$ in particular, where the various terms have immediately identifiable physical roles.

1.2 The cluster expansions

The cluster expansion of the classical partition function is an important conceptual tool in the mathematical analysis of dense fluids as we shall see later. Its physical significance and immediate applicability is most apparent in the case of low density imperfect gases, and we introduce it here in terms of the Mayer $f$-function\(^{(1)}\), although there are several variations\(^{(8-8)}\) on the cluster expansion method.

We take advantage of the pair potential expression of $\Phi_N$ given in (1.1.5). Under these circumstances

$$\exp(-\beta\Phi_N) = \prod_{i>j}^N N \exp\left(-\frac{\Phi}{kT}(r_{ij})\right).$$  \hspace{1cm} (1.2.1)

We now define the Mayer $f$-function as

$$f(r_{ij}) = \exp\left(-\frac{\Phi}{kT}(r_{ij})\right) - 1.$$  \hspace{1cm} (1.2.2)

Notice that $f_{ij}$ is a short range function, of the order of the range of the pair potential and is practically zero unless two or more molecules are close to each other. Further it is a bounded function; that is as $r_{ij} \to 0$, so $f_{ij} \to -1$ even though the repulsive forces between atoms cause $\Phi(r_{ij})$ to become large and positive.

From (1.2.2), the $N$-body partition function may be written

$$Z_N = \frac{1}{N!} \left(\frac{2\pi mkT}{\hbar^2}\right)^{3N/2} \int ... \int \prod_i \prod_j (1 + f_{ij}) \, d\mathbf{x}...d\mathbf{N}.$$  \hspace{1cm} (1.2.3)

Here we have used $\int ... \int d\mathbf{x}...d\mathbf{N}$ to signify integration over all positions of molecules $1...N$.

Expansion of the integrand gives

$$\prod_{n 

\prod_{i>j>1} (1 + f_{ij}) = 1 + \sum_i \sum_j f_{ij} + \sum_i \sum_j \sum_k f_{ij}f_{ik} + ...$$

$$+ \sum \sum \sum f_{ij}f_{kl} ... f_{mn} ...$$  \hspace{1cm} (1.2.4)
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The general product in this series consists of the sum over all connected products of the same order, \( n \). By this we mean the sum over all \( n \)-body clusters which are topologically distinct. The expansion (1.2.4) can be split up and reassembled in irreducible clusters of the following forms:

\[
\begin{align*}
\{ \circ \circ \} & \quad 2\text{-body clusters between molecules } i, j, \\
\{ \bigcirc \} & \quad 3\text{-body clusters between molecules } i, j, k, \\
\{ \bigcirc \bigcirc \bigcirc \} & \quad 4\text{-body clusters between molecules } i, j, k, l
\end{align*}
\]

(1.2.5)

and so on. An irreducible cluster is defined by a mapping or graph in which each point or molecule is connected by an \( f \)-bond to at least two other points. For completeness, the exceptional case of two interacting molecules is included as the lowest irreducible cluster. Thus

\[
\begin{align*}
\bigcirc & , \\
\bigcirc \bigcirc & , \\
\bigcirc \bigcirc \bigcirc &
\end{align*}
\]

are not irreducible clusters since the first can be decomposed into two 2-body irreducible clusters, the second into a 3-body and a 2-body irreducible cluster, and the third into two 3-body irreducible clusters.

The number of topologically distinct clusters in each \( n \)-body subset increases rapidly with \( n \). Thus there are three 4-body clusters, ten 5-body clusters, and fifty-six 6-body clusters. A recent development by Ree and Hoover\(^6\) enables a drastic reduction to be made in the number of clusters in each subset which need to be evaluated, thereby simplifying the evaluation of the cluster integrals. We shall return to Ree and Hoover’s work later.

Each cluster within a given subset is weighted according to the frequency of its occurrence in the expansion (1.2.4). The combinatorial algebra necessary to establish the general expansion (1.2.4) in terms of the correctly weighted \( n \)-body subsets (1.2.5) is formidable, but is discussed in several reviews\(^1,4,7\). Further, the \( n \)-body subset must be divided by \( n! \) to account for the indistinguishability
of topologically identical permutations of the \( n \) molecules in the cluster. Cyclic permutation of the labels on the 3-body subset

\[
\begin{array}{ccc}
\bigcirc & \bigcirc & \bigcirc \\
\text{k} & \text{i} & \text{j} \\
\text{i} & \text{j} & \text{k}
\end{array}
\]

does not produce a topologically distinct diagram. In the evaluation of the quasi-classical partition function we must only sum over physically distinct states. Otherwise we shall be confronted with a discrepancy between the predicted and observed entropies and free energies—the Gibbs paradox.

The partition function in the cluster expansion may then be written, from (1.2.3), (1.2.4):

\[
Z_N = \left( \frac{2\pi kT}{\hbar^2} \right)^{3N/2} \int \cdots \int \left\{ 1 + \frac{1}{2!} \frac{N!}{(N-2)!} \phi^{\circ\circ} + \frac{N!}{3!} \frac{N!}{(N-3)!} \phi^{\circ\circ\circ} \right\} \, \phi \cdots \phi.
\]

The coefficients of the various subsets

\[
\frac{N!}{(N-2)!}!, \frac{N!}{(N-3)!}!, \ldots, \frac{N!}{(N-n)!}!
\]

represent the number of ways the \( n \)-body cluster may be formed from the complete set of \( N \) molecules. Notice the absence of the quasi-classical indistinguishability factor \((N!)^{-1}\) from the right hand side of (1.2.6): indistinguishability is being taken care of termwise in the cluster expansion. The weighting factors are given in the 4-body subset. Integration over the expansion yields

\[
Z_N = \left( \frac{2\pi kT}{\hbar^2} \right)^{3N/2} \left\{ V^N + \frac{N}{2!} (N-1) V^{N-1} \Delta + \cdots \right\},
\]

where the cluster integrals are defined as follows:

\[
\begin{align*}
\langle 12 \rangle &= \int \phi^{\circ\circ} \, d2 = \int f_{12} \, d2, \\
\langle 12, 3 \rangle &= \int \phi \, d3 = \int \int f_{12} f_{23} \, d2 \, d3, \\
\langle 12, 3, 4 \rangle &= \int \int \phi \, d4 = \int \int \int f_{12} f_{13} f_{14} \, d2 \, d3 \, d4.
\end{align*}
\]
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Then,
\[
\ln Z_N = N \ln V + \ln \left( 1 + \frac{N(N-1)}{2!} \frac{1}{V^2} \Delta + \cdots \right) + \frac{3N}{2} \ln (2\pi m k T/h_0^2). \tag{1.2.9}
\]

The equation of state is determined from the usual relationship
\[
P = \frac{1}{\beta} \left( \frac{\partial \ln Z_N}{\partial V} \right)_T, \quad \text{where} \quad \beta = (kT)^{-1}. \tag{1.2.10}
\]

Since \( N \) is very large we may write \( N^2 \) for \( N(N-1) \), etc. and for \( x \ll 1 \), \( \ln (1 + x) \sim x \), whereupon from (1.2.9), (1.2.10)
\[
P = \frac{NkT}{V} - \frac{N^2 k T}{2! V^2} \Delta - \frac{2N^3 k T}{3! V^3} \Delta - \cdots = \frac{NkT}{V} \left( 1 - \frac{N}{V} \frac{1}{2!} \Delta - \frac{N^2}{V^2} \frac{1}{3!} \Delta - \cdots \right) \tag{1.2.11}
\]

which is, of course, the virial expansion:
\[
P = \frac{NkT}{V} \left( 1 + \frac{N}{V} B_2(T) + \frac{N^2}{V^2} B_3(T) + \cdots \right), \tag{1.2.12}
\]

where \( B_2(T), B_3(T), \ldots \) are the virial coefficients.

We should point out that in applying the approximation
\[
\ln (1 + x) \sim x
\]
to (1.2.9), we require not only that the density \( N/V \) is small, but also that the quantity \( N \) is also small.

Identifying (1.2.11) and (1.2.12) we have the following cluster expansion for \( P \):
\[
\frac{P}{\rho k T} = 1 - \sum_{l=2}^{L-1} \frac{1}{l} \beta_l \rho^{l-1}, \tag{1.2.13}
\]

where
\[
\beta_l = \frac{1}{(l-1)!} \int \cdots \int (\Sigma f_{ij}) \rho^l d^2 \cdots dI, \tag{1.2.14}
\]

the sum of products of \( f_{ij} \) being taken over irreducible clusters. The physical significance of the second and subsequent terms in the virial expansion may clearly be attributed to the existence of
clusters of $2, 3, 4, \ldots$ molecules in simultaneous interaction. This is not to say, of course, that the clusters of molecules remain in permanent association: they will in fact be continuously forming and collisionally disrupting. But as the density of the gas increases the probability of an $n$-body encounter increases, and the gas departs from idealism.

This approach to the equation of state depends essentially upon $\rho$ being small, that is, below the critical density. As the density increases the convergence deteriorates, and it has now been confirmed that the expansion diverges at high densities and is inapplicable as such at liquid densities. The radius of convergence of this series has been investigated by Penrose, and by Lebowitz and Penrose.

1.3 The Ursell development

Historically earlier than the Mayer $f$-function cluster expansion of the partition function, the Ursell expansion of the configurational integral in terms of $\mathcal{U}$-functions again enables the partition function to be written as a series of cluster integrals. The Ursell approach is, however, more general in that it does not assume additivity of the pair potential. Further this method may be extended to include quantum mechanical systems. The Mayer $f$-function method appears as a special case of the Ursell development.

Ursell has shown that the $N$-body Boltzmann factor appearing in the configurational integral may be expressed as a sum of products of $\mathcal{U}$ functions:

$$W(1 \ldots N) = \exp (-\Phi_N/kT), \quad \text{(1.3.1)}$$

where

$$\begin{align*}
\mathcal{U}(1) &= W(1), \\
\mathcal{U}(12) &= W(12) - W(1) W(2), \\
\mathcal{U}(123) &= W(123) - W(12) W(3) - W(23) W(1) - W(31) W(2) \\
&\quad + 2W(1) W(2) W(3), \\
\mathcal{U}(1234) &= \ldots
\end{align*} \quad \text{(1.3.2)}$$

It is important to note that the Boltzmann expansion of the $n$-body $\mathcal{U}$-function does not imply permutation of the $n$ molecules within
the group. In the case of $\mathcal{U}(123)$ the expansion is expressed in terms of one 3-body cluster, 3 groups of 2-body and 1-body clusters, and one group of 1-body clusters. The coefficients before the various terms are $(-1)^{n-1}(n-1)!$ where $n$ is the number of groups in the term. There are several properties of this expansion which should be noted. Groups of single particle clusters such as $W(1)$, and $W(1)W(2)$, physically represent the Boltzmann factors of isolated non-interacting particles whose potential may be taken as zero, in which case, $W(1) = W(1)W(2) = \ldots = 1$. Further the function $\mathcal{U}(1 \ldots k)$ is zero for separated configurations; i.e. for all configurations wherein the $k$ molecules are separated into two or more groups at such distances that no interactive coupling exists between the molecules of the several groups. In a dilute gas, for example, where 2-body collisions are frequent but 3-body collisions are rare, the functions $\mathcal{U}(123)$ vanish, as do all $\mathcal{U}$-functions of higher order. The $N$-body Boltzmann factor $W(1 \ldots N)$ would then be expressed entirely in terms of one and two particle $\mathcal{U}$-functions. And if we were only interested in the second virial coefficient involving binary collisions, we should discard all $\mathcal{U}$-functions involving three or more molecules.

The Boltzmann factors for $1, 2, 3, \ldots$ particles in terms of the functions may be obtained by inverting (1.3.2) giving

\[
\begin{align*}
W(1) &= \mathcal{U}(1) = 1, \\
W(12) &= \mathcal{U}(12) + \mathcal{U}(1) \mathcal{U}(2), \\
W(123) &= \mathcal{U}(123) + \mathcal{U}(12) \mathcal{U}(3) + \mathcal{U}(23) \mathcal{U}(1) + \mathcal{U}(31) \mathcal{U}(2) \\
&\quad + \mathcal{U}(1) \mathcal{U}(2) \mathcal{U}(3), \\
&\quad \ldots \\
&= (1.3.3)
\end{align*}
\]

We can express (1.3.3) diagrammatically, where the bond now represents the $\mathcal{U}$-function, and the unbonded circles represent the isolated particles:

\[
\begin{align*}
W(1) &= o, \\
W(12) &= o-o+ o o, \\
W(123) &= o o o + 3 o o + o o o,
\end{align*}
\]

(1.3.4)

where the factor 3 accounts for the degeneracy of the diagram.
The *distinguishable* $N$-body Boltzmann factor is then

$$W(1 \ldots N) = \left\{ \frac{N!}{N!} \cdot \frac{(N-2)!}{2! \cdot N!} \cdot \frac{(N-3)!}{3! \cdot N!} \cdot \ldots \right\}.$$ (1.3.5)

The number of ways of arranging $N$ molecules $n$ at a time is $N!/(N-n)!$, and the number of arrangements of the $n$ within themselves is $n!$. Since these are topologically identical configurations and in the partition function we must sum only over physically distinct states, we must divide by this figure, giving the factors in (1.3.5). The schematic clusters $\circ \circ$, $\circ \circ \circ$, $\ldots$ represent the sum of all two-, three-, $\ldots$ body clusters which develop in the series—we shall return to this point shortly. The unbonded molecules, since they are physically excluded from the interaction, do not contribute to the cluster integrals. The configurational $N$-body partition function $Z_Q$ is obtained by integrating (1.3.5) over the whole of the volume $V$ available to each of the $N$ molecules, thus:

$$Z_Q = \frac{1}{N!} \int W(1 \ldots N) \, dV \ldots dV$$

$$= \left\{ V^N \cdot \frac{N(N-1)}{2!} V^{N-1} \cdot \cdot \cdot \right\}$$

$$+ \frac{N(N-1)(N-2)}{3!} V^{N-2} \cdot \cdot \cdot + \ldots \right\}. \quad (1.3.6)$$

The full circles represent integration over the bonded cluster. The $V^{N-n}$ arise from integration over the $(N-n+1)$ isolated centres, relative to molecule $i$.

In the course of the expansion (1.3.5), some regrouping has been done to incorporate into the 3-body cluster, for example, such terms as $\bigwedge_{b}$ which do not appear in (1.3.4). These terms have arisen from a special case of the four-body $(ijkl)$ cluster for which,
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say, \( j = k \). As in the case of the \( f \)-function analysis, the combinatorial algebra leading to the reclassification in (1.3.5) is considerable.

Writing

\[
Z_Q = \frac{V^N}{N!} \left( 1 + \frac{N^2}{2!V} \bullet \bullet + \frac{N^3}{3!V^2} \bullet \bullet \bullet + \ldots \right),
\]

then the equation of state follows directly:

\[
P = kT \left( \frac{\partial \ln Z_Q}{\partial V} \right)_T = \frac{NkT}{V} \left( 1 - \frac{N}{2!V} \bullet \bullet \bullet - \frac{2N^2}{3!V^2} \bullet \bullet \bullet \bullet \bullet \bullet - \ldots \right),
\]

where the virial coefficients are given by

\[
B_2(T) = -\frac{1}{2!} \bullet \bullet \bullet
\]

\[
B_3(T) = -\frac{2}{3!} \bullet \bullet \bullet \bullet \bullet \bullet, \quad \text{etc.}
\]

It now remains to identify the cluster integrals \( \bullet \bullet \bullet \), \( \bullet \bullet \bullet \bullet \bullet \bullet \), ... over the \( U \)-functions. The 3-body cluster integral is, for example, given by

\[
\frac{2}{3!} \int \int \mathcal{U}'(123) \, dz \, d\xi,
\]

where integration is relative to \( 1 \). The prime signifies the augmented \( U \)-function since it incorporates terms of the form \( \partial U \) arising during the regrouping in (1.3.5). Referring to (1.3.2), and recalling that the single particle Boltzmann factors are unity, it may be quite easily shown that

\[
\mathcal{U}'(123) = W(123) - W(12) \, W(13) - W(23) \, W(12)
- W(13) \, W(23) + W(12) + W(13) + W(23) - 1. \quad (1.3.11)
\]

If we define the \( l \)-body Ursell function as \( \mathcal{U}[l] \), then it may be shown, quite generally, that the virial coefficients are directly expressible in terms of these cluster integrals, the \( j \)th virial coefficient being given as a combination of the cluster integrals \( b_1, b_2, \ldots, b_j \), where

\[
b_l = \frac{1}{l!} \int \int \int \mathcal{U}(1,2,\ldots,l) \, dz \, d\xi \ldots d\eta. \quad (1.3.12)
\]
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For example, the second virial coefficient $B_2(T)$ is, from (1.3.2),

$$B_2(T) = -\frac{1}{2!}\int \mathcal{V}'(12) \, d2 = -\frac{1}{2!} \int [W(12) - 1] \, d2$$

$$= -\frac{1}{2!} 2b_2 = -\frac{1}{2} \beta_2$$  \hspace{1cm} (1.3.13)

and the third virial coefficient,

$$B_3(T) = -\frac{2}{3!} \int \int \mathcal{V}'(123) \, d2 \, d3 = -\frac{2}{3!} (3b_3 - 6b_2^2) = -\frac{2}{3} \beta_3$$  \hspace{1cm} (1.3.14)

and it may be shown (the complexity of the combinatorial algebra here becoming apparent),

$$B_4(T) = -\frac{3}{4!} \int \int \int \mathcal{V}'(1234) \, d2 \, d3 \, d4$$

$$= -\frac{3}{4!} (4b_4 - 2b_4 b_2 - \frac{8}{3} b_3^2) = -\frac{3}{4} \beta_4.$$  \hspace{1cm} (1.3.15)

The virial equation of state may therefore be written

$$\frac{P}{\rho kT} = 1 - \sum_{l=2} \frac{(l-1)!}{l} \beta_l \rho^{l-1},$$  \hspace{1cm} (1.3.16)

where

$$\beta_l = \frac{1}{(l-1)!} \int \ldots \int \mathcal{V}'(1 \ldots l) \, d2 \ldots d_l$$  \hspace{1cm} (1.3.17)

(compare this with $b_2$ (1.3.12)). Equation (1.3.16) is seen to be identical to the Mayer f-function virial expression (1.2.14), provided the identification

$$\int \ldots \int \mathcal{V}'(1 \ldots l) \, d2 \ldots d_l = \int \ldots \int (\Sigma \Pi f_{ij}) \, d2 \ldots d_l$$  \hspace{1cm} (1.3.18)

is made. Clearly, $(\Sigma \Pi f_{ij})$ represents $\mathcal{V}'(1 \ldots l)$ in the approximation of pairwise additivity. Noting that

$$f_{ij} = \exp\left( -\frac{\Phi_{ij}}{kT} \right) - 1 = W(ij) - 1,$$  \hspace{1cm} (1.3.19)

then the 3-body Mayer expansion is, from the right hand side of (1.3.18),

$$(W(12) - 1)(W(23) - 1)(W(31) - 1)$$


$$- W(23) W(31) + W(12) + W(23) + W(31) - 1$$  \hspace{1cm} (1.3.20)