CHAPTER II

THE PARTITION FUNCTION

The Partition Function [1]

By definition of the entropy in statistical mechanics, we have equation (1.32)

$$S = Nk \ln \sum_i g_i e^{-\epsilon_i/kT} + \frac{E}{T} \qquad ----(2.1)$$

From thermodynamics, the Helmholtz free energy, A, is defined by

$$A = E - TS$$

Thus,

$$A = -Nk T \ln \sum_i g_i e^{-\epsilon_i/kT} \qquad ----(2.2)$$

or

$$A = - Nk T \ln Q \qquad ----(2.3)$$

where Q is called the partition function.

The partition function, Q, is defined by

$$Q = \sum_i g_i e^{-\epsilon_i/kT} \qquad ----(2.4)$$

For a system of s degrees of freedom the energy surfaces

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[1] Henry Eyring, Douglas Henderson, Betsy Jones Stover, and Eward H. Eyring Statistical Mechanics and Dynamics (New York: John Wiley and Sons, Inc., 1964), pp. 92-110

corresponding to allowed states subdivide μ space into regions of volume h^S (h is Planck's constant). Therefore, we would expect that

$$\epsilon_i \longrightarrow \epsilon(p,q)$$

$$g_i \longrightarrow d\,\omega/h^S = dq_1 \ldots dp_s/h^S \quad \text{-----}(2.5)$$

in making the transition to an integral.

Thus, the partition function becomes

$$Q = \sum_i g_i \, e^{-\epsilon_i/kT} \qquad \text{(quantum)} \qquad \text{-----}(2.6)$$

$$Q = \frac{1}{h^S} \int e^{-\epsilon/kT} \, d\omega \quad \text{(classical)} \qquad \text{-----}(2.7)$$

For the case of a system of non-localized particles such as a gas, we must divide W by N! . This is equivalent to replacing $(Q)^N$ by

$$\frac{(Q)^N}{N!}$$

Thus, the equation (2.3) and (2.1) become

$$A = -Nk\,T\,\ln Q + kT\,\ln N! \qquad \text{-----}(2.8)$$

$$S = Nk\,\ln Q - k\,\ln N! + \frac{E}{T} \qquad \text{-----}(2.9)$$

We now consider a perfect monatomic gas enclosed in a volume V. The energy of one atom of this perfect monatomic gas is given by

$$\epsilon = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + U$$

where

$$U \; = \; 0, \quad \text{inside } V$$

$$U \; = \; \infty, \quad \text{outside } V$$

The partition function becomes

$$Q \; = \; \frac{1}{h^3} \int_{-\infty}^{\infty} e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} \, dp_x dp_y dp_z \int_V dx \, dy \, dz$$

$$= \; \frac{V}{h^3} \int_{-\infty}^{\infty} e^{-p_x^2/2mkT} \, dp_x \int_{-\infty}^{\infty} e^{-p_y^2/2mkT} \, dp_y \int_{-\infty}^{\infty} e^{-p_z^2/2mkT} \, dp_z$$

$$Q \; = \; \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \qquad\qquad \text{-----(2.10)}$$

The Helmholtz function for N molecules is

$$A \; = \; -NkT \ln \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V + kT \ln N! \qquad \text{-----(2.11)}$$

We also obtain the Sackur -- Tetrode equation

$$S \; = \; \frac{E-A}{T} = \frac{5}{2} Nk + Nk \ln \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V - Nk \ln N \;\text{---(2.12)}$$

The partition function for the canonical ensemble

We can extend our definition of entropy to the case
of the canonical ensemble by defining the entropy of a
canonical ensemble whose mean energy is E as being equal to
the entropy of microcanonical ensemble with energy E. We
may do this because from thermodynamics we know that the

entropy is quite independent of whether the system is isolated or in thermal contact with a heat reservoir.

By definition of the entropy, S, we have

$$S = k \ln \frac{\delta\Omega}{h^{Ns}} \qquad \qquad ----(2.13)$$

N being the number of particles in the system, s the number of degrees of freedom of each particle, and $\delta\Omega$ the volume of phase space corresponding to energies between E and E + δE. We can gain an estimate for $\delta\Omega$ by requiring that δE be equal to the range of reasonably probable values of the energy of the canonical ensemble, i.e. by requiring that

$$\rho(E) \, \delta\Omega = 1 \qquad \qquad ----(2.14)$$

Equation (2.14) follows from the fact that we know that the particles of the microcanonical ensemble must lie in $\delta\Omega$ and their density $\rho(E)$ in $\delta\Omega$ is a constant. Hence,

$$\delta\Omega = 1/\rho(E) = e^{E/kT}/C \qquad \qquad ----(2.15)$$

and

$$S = k \ln (e^{E/kT}/h^{Ns}C) = -k \ln h^{Ns} C + E/T \quad ----(2.16)$$

Thus, $\quad A = E - TS \qquad = k T \ln C \, h^{Ns} \qquad ----(2.17)$

But we have the normalization condition,

$$\int C e^{-E/kT} d\Omega = 1 \qquad \qquad ----(2.18)$$

and so since C is a constant,

$$\frac{1}{C} = \int e^{-\epsilon/kT} \, d\Omega \qquad \qquad ----(2.19)$$

Hence we have

$$A = -kT \ln Q_c \qquad \text{----(2.20)}$$

where

$$Q_c = \frac{1}{h^{Ns}} \int e^{-\epsilon/kT} \, d\Omega \qquad \text{----(2.21)}$$

Q_c is called the system partition function and plays a role similar to the partition function, Q, for one particle, except that

$$Q_c = (Q)^N \qquad \text{----(2.22)}$$

for a system of localized particles.

For the case of non-localized particles we have

$$Q_c = (Q)^N/N! \qquad \text{----(2.23)}$$

Next, we consider the perfect monatomic gas, enclosed in a volume V, and apply the method of the canonical ensemble. We must evaluate

$$Q_c = \frac{1}{h^{3N}N!} \int e^{-\epsilon/kT} \, d\Omega \qquad \text{----(2.24)}$$

The energy of the system is

$$\epsilon = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U \qquad \text{----(2.25)}$$

where

$$U = 0 \qquad \text{inside V}$$

$$U = \infty \qquad \text{outside V}$$

Now

$$d\Omega = \prod_{i=1}^{3N} dq_i \, dp_i \qquad \text{-----(2.26)}$$

Thus,

$$Q_c = \frac{V^N}{h^{3N} N!} \int e^{-\sum_i p_i^2/2mkT} \prod_i d p_i$$

$$= \frac{V^N}{h^{3N} N!} \prod_i \int_{-\infty}^{\infty} e^{-p_i^2/2mkT} \, d p_i$$

$$Q_c = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3/2N} \qquad \text{-----(2.27)}$$

Thus, the Helmholtz function for N particles is

$$A = -NkT \ln \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V + NkT \ln N - NkT \qquad \text{---(2.28)}$$

We also obtain the Sackur-Tetrode equation,

$$S = (E-A)/T = 5/2 \, Nk + Nk \ln(2\pi mkT/h^2)^{3/2} V - Nk \ln N$$

$$\text{-----(2.29)}$$

The partition function for the grand canonical ensemble

We define the entropy of a grand canonical ensemble as being equal to the entropy of a microcanonical ensemble whose energy and number of particles is equal to the average energy and average number of particles of the grand canonical ensemble. This is a necessary definition since any other would imply that the entropy of a system depended upon its surroundings.

$$S = k \ln (\delta\Omega / h^{\bar{\bar{N}}s}) \qquad \text{-----}(2.30)$$

where $\delta\Omega$ is the volume of phase space corresponding to energies between E and $E + \delta E$ and $\mathbf{s}$ is the number of degrees of freedom of a particle. We can obtain on estimate of $\delta\Omega$ by requiring that

$$\rho(E, \bar{N}) \; \delta\Omega = 1 \qquad \text{-----}(2.31)$$

Hence,
$$S = k \ln (e^{E/kT} / h^{\bar{\bar{N}}s} \; C \; e^{\mu\bar{\bar{N}}/kT})$$

$$= E/T - \mu\bar{N}/T - k \ln C \; h^{\bar{\bar{N}}s} \qquad \text{-----}(2.32)$$

But,

$$E - TS = A = \mu\bar{N} + kT \ln C \; h^{\bar{\bar{N}}s} \qquad \text{-----}(2.33)$$

Following Gibbs we define the grand partition function Q_{gc} by

$$C = 1/h^{\bar{\bar{N}}s} \; Q_{gc}$$

But

$$\frac{1}{h^{\bar{\bar{N}}s}} = \sum_{N=0}^{\infty} \frac{1}{h^{Ns}} \int \rho(N, \epsilon) \; d\Omega$$

and so

$$Q_{gc} = \sum_{N=0}^{\infty} \frac{e^{\mu N/kT}}{h^{Ns}} \int e^{-\epsilon/kT} \; d\Omega \qquad \text{-----}(2.34)$$

Thus, Eq. (2.33) becomes

$$A = \mu\bar{N} - kT \ln Q_{gc} \qquad \text{-----}(2.35)$$

But the Gibb's free energy is defined by

$$G = A + pV$$

and

$$G = \mu \bar{N}$$

so we have

$$pV = kT \ln Q_{gc} \qquad \text{------}(2.36)$$

We now consider the perfect monatomic gas and apply the method of grand canonical ensemble. We have

$$Q_{gc} = \sum_{N=0}^{\infty} \frac{e^{\mu N/kT}}{N! \; h^{3N}} \int e^{-E/kT} \, d\Omega = \sum_{N=0}^{\infty} e^{\mu N/kT} Q_c$$

$$\text{------}(2.37)$$

But we have seen that

$$Q_c = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}N}$$

Hence

$$Q_{gc} = \sum_{N=0}^{\infty} \frac{1}{N!} \left[e^{\mu/kT} V \left(\frac{2\pi \, mkT}{h^2} \right)^{3/2} \right]^N$$

$$= \exp \left[e^{\mu/kT} V \left(\frac{2\pi \, mkT}{h^2} \right)^{3/2} \right] \quad \text{------}(2.38)$$

So we have

$$\bar{N} = kT \left[\frac{\partial}{\partial \mu} \left\{ e^{\mu/kT} V \left(\frac{2\pi \, mkT}{h^2} \right)^{3/2} \right\} \right]_{V,T}$$

$$= e^{\mu/kT} V \left(\frac{2\pi \, mkT}{h^2} \right)^{3/2} \qquad \text{------}(2.39)$$

or

$$\mu = kT \ln \left[\bar{N} \Big/ \left\{ V \left(\frac{2\pi \, mkT}{h^2} \right)^{3/2} \right\} \right] \text{------}(2.40)$$

Also

$$p V = k T \ln Q_{gc} = k T \, e^{\mu/kT} \, V \left(\frac{2\pi \, mkT}{h^2} \right)^{3/2}$$

which combined with Eq.(2.39) yields the perfect gas law

$$p V = \bar{N} k T \qquad\qquad ----(2.41)$$

We can also obtain the Sackur - Tetrode equation

$$S = \frac{5}{2} \bar{N}k + \bar{N}k \, \ln\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V - \bar{N}k \, \ln \bar{N} \quad ----(2.42)$$

The Approximate Statistical Treatment for Real Gas[2]

A gas composed of N indentical molecules in a volume V will be considered. Since the essential features of an imperfect gas are observed in the noble monatomic gases as well as in the more complicated polyatomic gases, it will be simpler to choose a monatomic one as an example, and to assume that the molecules treated have no excited internal degrees of freedom. Since, further, the behavior of the imperfect gas is not due to quantized energy levels, but occurs at temperatures and volumes, in the heavier gases at least, for which the classical eqations are valid, we shall use the classical integration methods throughout.

The 3N cartesian coordinates of the molecules, and their conjugated momenta, will be used. The indices i and j

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[2] Joseph Edward Mayer and Maria Geoppert Mayer. Statistical Mechanics (New York ; John Wiley and Sons, Inc., 1940), pp.263-266

as subscripts will indicate the molecules i and j. The Hamiltonian contains the sum of 3N kinetic energy terms $p^2/2m$. The additional potential – energy terms, [unclear] functions of the coordinates alone, will be responsible for the difference between the equations derived and those of the perfect gas. The phase integral Q_c may be integrated at once over the 3N momenta from minus to plus infinity, leading to

$$Q_c = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}N} \frac{Q_N}{N!} \quad\quad\text{----(2.43)}$$

The configuration integral Q_N is

$$Q_N = \int\int\cdots\int e^{-U(q)/kT} \, d\tilde{r}_1 \ldots \tilde{r}_i \ldots d\tilde{r}_N \quad\text{----(2.44)}$$

which

$$d\tilde{r}_i = dx_i \, dy_i \, dz_i \quad\quad\text{----(2.45)}$$

and $U(q)$ is the potential energy of the system.

The potential energy, $U(q)$, will be assumed to have certain simplified characteristics, which are probably almost exactly obeyed in almost all real gases composed of chemically saturated molecules. It will first be assumed that $U(q)$ can be written as a sum of terms, each depending only on the distance apart r_{ij} of two molecules i and j. This assumes that the potential of three molecules, all close together, is the same as that of three independent pairs of molecules having the same distances apart as the three pairs which

can be formed of the group of three. In the system of N
molecules there are $\frac{1}{2}$ N(N-1) different pairs which can be
formed, so that this assumption is that U(q) is the sum of
$\frac{1}{2}$ N(N-1) terms, namely,

$$U(q) = \sum_{\substack{i=N \\ i>j}} \sum_{\substack{j=N-1 \\ j=1}} u(r_{ij}), \qquad\qquad ----(2.46)$$

where $u(r_{ij})$ is the potential energy of the pair of molecules
i and j as a function of their distance apart r_{ij}.

The function u(r) has the same general characteristic
form for all neutral, chemically saturated molecules. It is
zero for large values of the argument r, decreasing to a
minimum negative value at a distance r of a few Angström
units, and then increasing rapidly, as r decreases, to very
high positive values for smaller distances of approach.

With (2.46) for U(q) the exponent of the integrand in
(2.44) for Q_N is a sum of terms. The integrand itself is
then a product. However, the coordinates of two molecules
occur in each term of the product, and the coordinates of
each molecule occur in N-1 different terms of the product.
The complete integral is not to be written as a product of
integrals as were the momenta integrals. One may write

$$e^{-U(q)/kT} = \prod_{N \geq i > j \geq 1} e^{-u(r_{ij})/kT} \qquad\qquad ----(2.47)$$

Each term $e^{-u(r_{ij})/kT}$ becomes unity for large values of the
argument r_{ij}, for which $u(r_{ij})$ is zero, so that it is

convenient to define a function,

$$f(r_{ij}) = f_{ij} = e^{-u(r_{ij})/kT} - 1, \qquad \text{-----}(2.48)$$

which becomes zero for large values of r_{ij}. Since

$$e^{-u(r_{ij})/kT} = 1 + f_{ij},$$

equation (2.47) may be written as

$$e^{-U(q)/kT} = \prod_{N \geqslant i > j \geqslant 1} (1 + f_{ij}). \qquad \text{-----}(2.49)$$

This product may be expanded into a sum of terms,

$$e^{-U(q)/kT} = 1 + \sum_{N \geqslant i > j \geqslant 1} f_{ij} + \Sigma \Sigma f_{ij} f_{i'j'} + \ldots, \qquad \text{-----}(2.50)$$

in which each term becomes zero if the argument r_{ij} is large for any pair ij occurring as a function f_{ij} in the term. Using (2.50) in (2.44), we obtain

$$Q_N = \int \int \ldots \int \left[1 + \sum_{N \geqslant i > j \geqslant 1} f_{ij} + \ldots \right] d\vec{r}_1 \ldots d\vec{r}_i \ldots d\vec{r}_N \qquad \text{-----}(2.51)$$

For example of calculating Q_N, we may assume that the contribution to the integral of the unity, and the $\frac{1}{2}N(N-1)$ terms containing only one f_{ij}, need be considered, and that all the other terms may be neglected. The integration over the unity leads to a factor V for each molecule, since the configuration space allowed to each molecule is the volume of the system. The product of these factors for all N molecules is V^N. If $u(r)$ were indentically zero for all r's, then all the f_{ij}'s would be zero and this term alone would be present.

The integration over each of the $\frac{1}{2} N(N-1)$ different f_{ij}'s gives the same value. For each such term, containing one f_{ij}, integration over the configuration space of a molecule other than i or j leads to V as a factor. There are N-2 such molecules, so that the term is

$$V^{N-2} \int \int f_{ij} \, d\bar{r}_i \, d\bar{r}_j.$$

Now f_{ij} drops rapidly to zero as r_{ij} becomes large, so that, if the position of i does not happen to be within molecular distance of the walls of the vessel,

$$\int \int f_{ij} \, d\bar{r}_j = \int_0^\infty f(r) \, 4\pi r^2 \, dr = \beta \qquad \text{-----(2.52)}$$

since $d\bar{r}_j$ can be expressed in spherical coordinates with molecule i as a center, and the integration over the angles performed. The integral β has the dimensions of volume. β is independent of the position of molecule i, at least to within a few Angströms of the wall, so that

$$\int \beta \, d\bar{r}_i = \beta V.$$

There are $\frac{1}{2} N(N-1)$ such terms, and since N is very large this is practically $\frac{1}{2} N^2$. One may write

$$Q_N = V^N (1 + \tfrac{1}{2} N^2 \tfrac{\beta}{V}),$$

or

$$Q_N = N^N v^N (1 + \tfrac{1}{2} N \tfrac{\beta}{V}), \qquad \text{-----(2.53)}$$

with the introduction of the volume per molecule, v,

$$v = \frac{V}{N} .$$ $\qquad$ ----(2.54)

The cluster integrals b_1^3

We shall now consider the general term of the sum

$$e^{-U(q)/kT} = 1 + \sum_{n \geq i \geq j \geq 1} f_{ij} + \Sigma\Sigma f_{ij} f_{i'j'} + \ldots \text{---}(2.55)$$

It is convenient to make a one – to – one correspondence between the terms of this sum, which are composed of a definite product of the particular functions, f_{ij}, and certain diagrams which may be drawn in a plane. If all the N molecules are represented by numbered circles in a figure such as Fig.1, and a line is drawn between the two circles i and j for every function f_{ij} occurring in the term, then every term
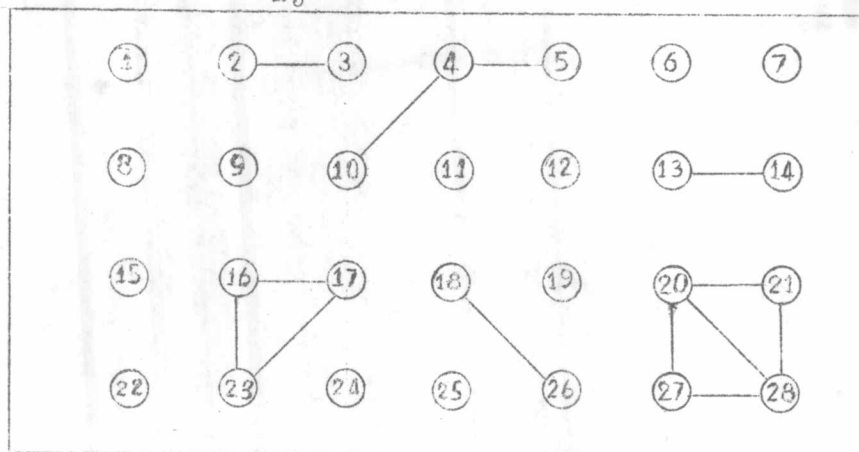

Figure 1   Diagram corresponding to the term in (2.55)

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[3] Ibid., pp.278-280

of the sum (2.55) may be represented by one such figure, and every figure corresponds to exactly one term of the sum.

The first term, unity in the sum, corresponds to the figure which has no line. The $\frac{1}{2} N(N-1)$ figures which can be drawn with only one line connecting any two of the numbered circles correspond each to one of the $\frac{1}{2} N(N-1)$ different terms containing only one f_{ij}.

The functions f approach zero for large values of their arguments r_{ij} (large compared to molecular distances of 10^{-8} cm.). The contribution to the configuration integral Q_N of one term arises, therefore, only from that part of the space for which all the distances represented by a line of the figure are small. We may speak of the molecules which are connected by lines in the figure, or functions f_{ij} in the term, as being bound to each other in that term.

In any specified figure, that is, any specified product of f_{ij}'s, such as that sketched in Fig.1, there will be groups of clusters of molecules which are all bound to each other directly or indirectly by lines, and not bound to any molecules which are not members of the cluster. Such molecules will be said to be part of a cluster, and by this criterion every molecule of any figure may be said to be one of a cluster of a certain number of molecules.

The simplest cluster is that consisting of a single molecule, not bound to any other, that is, its index does

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not occur as a subscript to any f in the term. The number of these single clusters of one molecule each, in any term, will be designated by m_1.

The cluster of two consists of a bound pair of molecules, neither of which is bound to any other molecule. In the term the two indices i and j of the molecules in one cluster of two occur as subscripts to the same f, but to no other f. The number of such clusters of two will be called m_2.

A cluster of three specified molecules, i, j, and k, may be formed in any of four ways:

$$f_{ij}f_{ik} \qquad f_{ij}f_{jk} \qquad f_{ik}f_{jk} \qquad f_{ij}f_{jk}f_{ik}$$
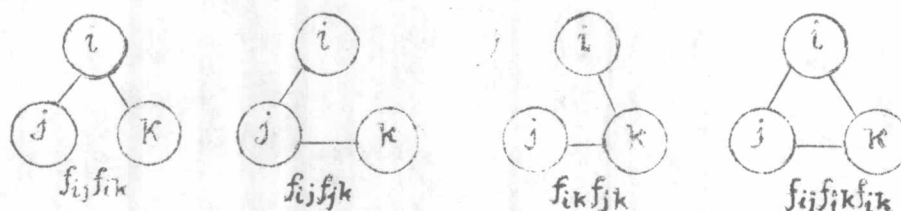
The terms in which the same molecules are bound to each other in the clusters have in common the property that they differ from zero only in that part of the configuration space for which the molecules in the same cluster are close to each other. Since the larger clusters may be formed from the same molecules in several ways, there will be a considerable number of such terms. We now propose to collect these terms together.

In any term the number of clusters of 1 molecules

each will be designated by m_1. The total number N of molecules is the sum of the number per cluster 1, times the number of clusters of this size m_1, or

$$N = \sum_{1=1}^{1=N} 1\, m_1 \qquad \text{----}(2.56)$$

The integrals over the molecules which are in different clusters of one term will be independent of each other, since the clusters are so defined that the integrand contains no functions that depend on the coordinates of two molecules in different clusters. The integral of the term will be a product of the integrals over the molecules in the same cluster. We shall sum the integrals of all the products that occur when the same 1 molecules are in one cluster and designate this the cluster integral b_1 after multiplication by a normalization factor 1/1!V. That is, the cluster integral b_1 is defined as

$$b_1 = \frac{1}{1!V} \iint \cdots \int \sum_{1 \geqslant i > j \geqslant 1} \prod f_{ij}\, d\bar{r}_1 \cdots d\bar{r}_1 \qquad \text{----}(2.57)$$

some over all products

consistent with single cluster.

The dimension of b_1 is volume to the power 1 - 1. There are at least 1-1 f's in the product, and at most $\frac{1}{2}\, 1(1-1)$ f's in any term of the integrand of the cluster integral.

The first three cluster integral are

$$b_1 = \frac{1}{V} \int d\bar{r}_1 = 1, \qquad \text{-----(2.58)}$$

$$b_2 = \frac{1}{2V} \iint f(r_{12}) \, d\bar{r}_2 \, d\bar{r}_1 = \frac{1}{2} \int_0^\infty 4\pi r^2 f(r) dr, \qquad \text{-----(2.59)}$$

$$b_3 = \frac{1}{6V} \iiint (f_{31}f_{21} + f_{32}f_{31} + f_{32}f_{21} + f_{32}f_{31}f_{21})$$
$$d\bar{r}_1 \, d\bar{r}_2 \, d\bar{r}_3 . \qquad \text{----(2.60)}$$

The equation for the cluster integrals in terms of irreducible integrals β_k [4]

Equations (2.58) and (2.59) for b_1 and b_2 respectively, show that no difficulty is encountered in evaluating the first two numbers of the series. The third cluster integral b_3, (2.60), however, is appreciably more complicated. It has already been mentioned that all the first three of the four terms making up b_3 had the same numerical value of $V\beta^2$. This can be readily seen.

Consider the integral of the first term which is

$$\iint f_{31}f_{21} \, d\bar{r}_1 \, d\bar{r}_2 \, d\bar{r}_3 . \qquad \text{----(2.61)}$$

The coordinates of particle 3 occur in the integrand only in f_{31}, and only as the distance r_{31} from the position of particle 1. The function f_{31} drops rapidly to zero as this distance becomes large, so that integration over the space $d\bar{r}_3$

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[4] Ibid., pp.278-280

leads to a definite integral as a factor. This integral will be designated as β_1, and it is the first of a series of irreducible integrals β_k which will be introduced. It is

$$\beta_1 = \int f_{31} \, d\bar{r}_3 = \int_0^\infty 4\pi \, r^2 f(r) dr, \qquad \text{----}(2.62)$$

since the volume element $d\bar{r}_3$ may be replaced by $4\pi \, r_{13}^2 \, dr_{13}$.

Similarly, in this term (2.61), integration over $d\bar{r}_2$ leads to the factor β_1, and integration over the coordinates of the last particle, $d\bar{r}_1$, gives the factor V. The term (2.61) is then

$$\iiint f_{31} f_{21} \, d\bar{r}_1 \, d\bar{r}_2 \, d\bar{r}_3 = V \, \beta_1^2 \qquad \text{----}(2.63)$$

From (2.59) and (2.62) it is seen that $b_2 = \frac{1}{2}\beta_1$, so that the term (2.61) is just $V(2b_2)^2$.

All three of the first three terms of b_3, equation (2.60) may be handled in exactly the same manner, and lead to the same numerical values after integration. The last term, however, has an entirely different value, and will be used to define β_2, the second irreducible integral, as

$$\iiint f_{32} f_{31} f_{21} \, d\bar{r}_1 \, d\bar{r}_2 \, d\bar{r}_3 = 2V \beta_2. \qquad \text{----}(2.64)$$

With this nomenclature one obtains

$$b_3 = \frac{1}{2} \beta_1^2 + \frac{1}{3}\beta_2 \qquad \text{----}(2.65)$$

In general, any single one of the terms making up the

integrand of the cluster integral b_1 can be represented by a figure of 1 numbered circles, with a line connecting the circles for every function f_{ij} in the term. In order to be a member of the cluster integral the figure must have every circle connected by at least one line to other circles, and all circles must be directly or indirectly connected by lines. Such a figure is drawn in Fig.2, for $1 = 8$.
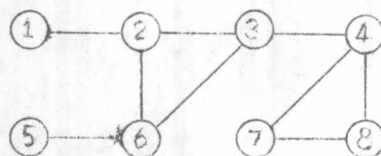

Figure 2. One term in the integrand of b_8.

If, in such a diagram, any circles are connected by only one line to other circles, as 1 and 5 are in the figure shown, integration over the coordinates of these particles in the corresponding term gives factors β_1 for each to the total integral of the term. If two particles, such as 7 and 8 of the figure, are joined by a line, and both joined to a common particle, as 4, by lines, but to no other circles, then integration over the coordinates of these two (7 and 8) contributes the factor β_2 to the integral of the term. Subsequent integration over the other particles allows similar factoring of the integral into a product of simpler integrals. For instance, in the figure shown, the contributions of integration in the order indicated are as follow: integration

over $d\bar{r}_1$ give β_1, over $d\bar{r}_5$ give β_1, over $d\bar{r}_7$ and $d\bar{r}_8$ gives β_2, over $d\bar{r}_4$ gives β_1, over $d\bar{r}_2$ $d\bar{r}_3$ gives β_2, and final integration over $d\bar{r}_6$ leads to the factor V. The value of the integral over all eight particles, of the term represented by the figure, is

$$\beta_1^3 \, \beta_2^2 \, V.$$

The normalization factor in front of the integral is, from (2.57), 1/8! V, so that the contribution to b_8 of this term is

$$\frac{1}{8!} \, \beta_1^3 \, \beta_2^2.$$

In general, it will frequently happen that two groups of molecules in a figure are singly connected, that is, they have one molecule in common, but there are otherwise no lines between molecules of the different groups. If the coordinates of the common particle are thought of as fixed, and the integration performed over the other particles, the integration of the two groups is quite independent and the integral corresponding to the picture reduces to a product of two integrals. In this manner the integral over any figure consistent with the cluster may be analyzed into a product of integrals over groups of particles to which this process can no longer be applied and which shall therefore be termed irreducible integrals. In the figure corresponding to an irreducible integral, which we shall term a frame, every

circle is connected with at least two others, except of course in β_1. The frame is said to be at least doubly connected, that is, one can go from any one circle of the frame to every other by two or more entirely independent paths of lines which do not cross at any circle.

The irreducible integral β_k is defined as an integral over the configuration space of k+1 particles, multiplied by a normalization factor. The normalization factor is 1/k! V. The integrand is the sum of all products of f_{ij}'s of k+1 particles which cannot be further reduced into a product of integrals. This means that in the corresponding figure all the circles are more than singly connected.

The definition may be written as

$$\beta_k = \frac{1}{k!V} \int\int \cdots \int \sum_{k+1 \geq i > j \geq 1} \Pi f_{ij} \, d\bar{r}_1 \cdots d\bar{r}_{k+1}. \quad \text{------}(2.66)$$

All products which are more than singly connected.

The dimensions of β_k are volume to the power k.

The first three irreducible integrals are

$$\beta_1 = \frac{1}{V} \int\int f_{12} \, d\bar{r}_1 \, d\bar{r}_2 = \int_0^\infty 4\pi r^2 f(r) dr \quad \text{----}(2.67)$$

$$\beta_2 = \frac{1}{2V} \int\int\int f_{32} f_{31} f_{21} \, d\bar{r}_1 \, d\bar{r}_2 \, d\bar{r}_3 \quad \text{----}(2.68)$$

$$\beta_3 = \frac{1}{6V} \int\int\int\int (3 f_{43} f_{32} f_{21} f_{41} + 6 f_{43} f_{32} f_{21} f_{41} f_{31}$$
$$+ f_{43} f_{32} f_{21} f_{41} f_{31} f_{42}) \, d\bar{r}_1 d\bar{r}_2 d\bar{r}_3 d\bar{r}_4 \text{--}(2.69)$$

The origin of the coefficients 3 and 6 in β_3 is due to the fact that there are respectively 3 and 6 products, differing only in the numbering of the particles, containing the same number of the functions f as these terms, and leading to the same numerical values after integration. This can be seen in Fig.3, which shows the ten diagrams corresponding to the ten irreducible products with make up β_3.
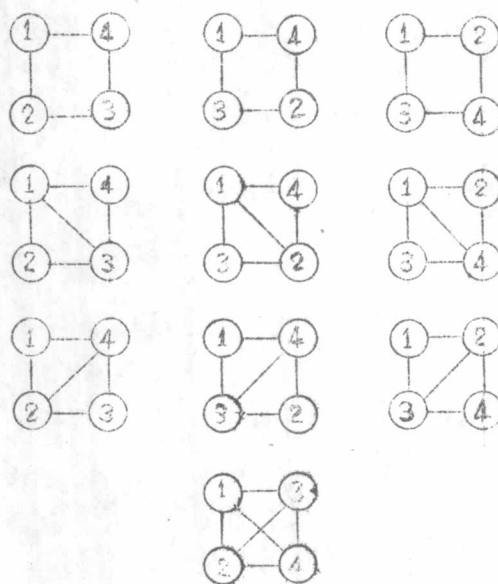

Figure 3. The ten terms composing β_3.