

EQUILIBRIUM THEORY OF CLASSICAL FLUIDS

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In their first exposure to statistical mechanics, chemists are introduced to ensembles and partition functions and their relation to thermodynamic quantities. The canonical distribution function is derived using the ergodic hypothesis and the molecular partition function is defined as $Z = \sum_i e^{-\beta E_i}$, where E_i s are the energy levels of the molecule and $\beta^{-1} = k_B T$ where k_B is the Boltzmann constant and T , the absolute temperature. The statistical mechanical entropy is defined as $S = -k_B \sum_i p_i \ln p_i$ where $p_i = e^{-\beta E_i} / Z$. The internal energy is then obtained as $-\partial \ln Z / \partial \beta$ and all the other thermodynamic properties including equilibrium constant for reactions such as $A + B \leftrightarrow C + D + E$ are obtained in terms of the partition functions. The partition functions of quantum statistics are derived by taking into account the indistinguishability of particles and the constraint that more than one spin half particle can not occupy any given quantum state^{la-1f}.

The framework of partition functions and molecular energy levels is very well suited for a collection of molecules in an ideal gas system. In a discussion involving a real system such as a dense gas, a liquid or a solid, the main feature is the intermolecular interaction which is absent in ideal gases. The focus then, is not on the energy levels of isolated molecules but on the properties of the bulk system as a whole using the full information on the intermolecular forces. It is however possible to calculate the energy levels of a given molecule, eg. water, in the presence of other neighbouring water molecules. But, such a calculation of these modified energy levels describes the behaviour of this single molecule in the presence of a cluster of surrounding interacting molecules rather than the behaviour of the medium as a whole. To describe the behaviour of the medium as a whole we need to take into account all the interparticle interactions. We shall begin with a classical description of fluids and also briefly comment on quantum corrections. An alternative is to describe the infinite system quantum mechanically and there is considerable success of late of methods which are hybrids of classical and quantum mechanical methods.

The properties of liquids are obtainable from interparticle distribution functions¹⁻⁶. These distribution function are determined by the interparticle interaction potentials. The total intermolecular energy in a liquid containing N particles may be written as the sum of all pair potentials, all triplets potentials, and so on, i.e.,

$$U_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \sum_i u_i(\mathbf{r}_i) + \sum_{i < j} u_{i,j}(\mathbf{r}_i, \mathbf{r}_j) + \sum_{i < j < k} u_{i,j,k}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots \quad (4.1)$$

The commonest decomposition of U_N is in terms of the pair potentials. The first term is the sum over the one body potentials, the second term is the sum over all pair interaction terms and the third term is the sum over all three body potentials. When pair potentials are inadequate, effective pair potentials are used. The triplets or the

three body potentials are difficult to calculate accurately and are relevant only when all the three particles are very close to one another.

The determination of these potential energy functions by quantum chemical calculation constitutes an important research area in theoretical chemistry. An alternative to this ab initio approach is the determination of the thermodynamic properties from empirical potentials and adjust the empirical parameters so that the calculated thermodynamic properties derived using these potentials agree with the experimental thermodynamic data. A common practice is to start with the ab initio pair potentials and adjust some parameters therein so that the bulk properties are reproduced accurately.

Both the canonical (N, V, T fixed ; N = number of particles, T = absolute temperature and V is the volume of the system) and the grand canonical (μ, V, T fixed ; μ is the chemical potential) ensembles can be used to describe the equilibrium distribution functions. We shall begin with the canonical ensemble. The classical canonical partition function $Q_N (V, T)$ for a system of N identical particles is defined as,

$$Q_N (V, T) = \frac{1}{N!} \cdot \frac{1}{h^{3N}} \int \dots \int e^{-\beta H(\mathbf{r}^N, \mathbf{p}^N)} d\mathbf{r}^N d\mathbf{p}^N \quad (4.2)$$

where h = Planck's constant, \mathbf{r}^N and \mathbf{p}^N are the position and velocities respectively of the N particles, and H is the hamiltonian of the N particle system. The factor h^{-3N} is necessary if Q has to go over correctly to its quantum mechanical analogues and $N!$ accounts for the indistinguishability of the particles. It will be noticed that summation over states \sum_i is replaced by

$(N!h^{3N})^{-1} \int \dots \int d\mathbf{r}^N d\mathbf{p}^N$ with the integration over the whole phase space. The hamiltonian can be written as the sum of kinetic energies and potential energies of the particles.

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U_N (r_1, r_2, \dots, r_N) \quad (4.3)$$

The kinetic energy terms can be integrated to yield $Q = Z_N / (\Lambda^{3N} N!)$ for a homogeneous one component system. In this expression for Q , Z_N is the configuration integral is defined by

$$Z_N = \int \dots \int e^{-\beta U_N(r_1, r_2, \dots, r_N)} dr_1 dr_2 \dots dr_N \quad (4.4)$$

and $\Lambda = (2\pi m kT / h^2)^{1/2}$ is the de Broglie thermal wavelength. This wavelength roughly indicates the extent to which the particle spreads out in configuration space $\{\mathbf{r}^N\}$ at a given temperature. A comparison of Λ with the mean interparticle separation $a \cong (N/V)^{-1/3}$ indicates whether a classical description of liquids is justified. A value of $\Lambda/a = 0.97$ for H_2 and 0.035 for potassium at their respective triple points indicates that the classical hypothesis may work well only in the case of the latter. In the case of ideal gas, $e^{-\beta U_N} = 1$ as $U_N = 0$ and $Z_N = V^N$ and $Q_N^{id} = V^N / (\Lambda^{3N} N!)$.

For a real system, Q_N may be rewritten as $Q_N = Q_N^{id} Z_N / V_N \dots (4.5)$

(4.5)

The Helmholtz free energy is then given by

$$A = -kT \ln Q_N = A^{id} + A^{ex} \quad (4.6)$$

Where

$$A^{id} = -kT \ln Q_N^{id} \text{ and } A^{ex} = -kT \ln \frac{Z_N}{V^N} \quad (4.7)$$

The remaining thermodynamic quantities can now be calculated as

$$p = -(\partial A / \partial V)_T, S = -(\partial A / \partial T)_V \quad (4.8)$$

The canonical ensemble probability density $f_o^N(\mathbf{r}^N, \mathbf{p}^N)$ and the canonical configuration probability density $P_N^{(N)}$ are defined by the following relations :

$$f_o^{(N)}(\underline{\tilde{r}}^N, \underline{\tilde{p}}^N) = \frac{1}{h^{3N} N!} \frac{e^{-\beta H(\underline{\tilde{r}}^N, \underline{\tilde{p}}^N)}}{Q_N} \quad (4.9)$$

$$P_N^{(N)}(\underline{\tilde{r}}^N) = \frac{e^{-\beta U_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)}}{Z_N} \quad (4.10)$$

The quantity $P_N^{(N)}(\underline{\tilde{r}}^N) d\underline{\tilde{r}}^N = P_N^{(N)}(r_1, r_2, \dots, r_N) dr_1, dr_2, \dots, dr_N$ gives the probability of finding, simultaneously, molecule 1 in volume element dr_1 about the position vector $\mathbf{r}_{\sim 1}$ (which is written in other places as simply \mathbf{r}_1), molecule 2 in

volume element dr_2 about $\mathbf{r}_{\sim 2}$, ... and finally molecule N in a volume element

dr_N about the position vector $\mathbf{r}_{\sim N}$. The symbol $\mathbf{r}_{\sim N}^N$ represents the collection of

vectors $(\mathbf{r}_{\sim 1}, \mathbf{r}_{\sim 2}, \dots, \mathbf{r}_{\sim N})$. This quantity P_N is the classical N particle probability distribution function (where indistinguishability, occupation of states, minimum volumes in phase space and so on do not appear at all) and the average value of any dynamical variable is obtained as

$$\langle U \rangle = \int \dots \int U_N P_N^{(N)} d\underline{\tilde{r}}^N \quad (4.11)$$

The function $P_N^{(N)}$ contains just too much information for direct application in the calculation of bulk properties ; not to mention the fact that it is extremely difficult to calculate . The $P_N^{(N)}$ is very similar to the square of the absolute value of the N particle wave function, i.e. $\psi_N^* \psi_N$. The averaging process, however is the different in the two cases. In the quantal case, the operator for the quantity whose average or expectation value is sought is inserted between ψ_N^* and ψ_N and the intergrations are performed after the operator operates on ψ_N . The determination of the reduced probability distribution functions $P_N^{(n)}$'s is the main aim of this chapter and we shall restrict primarily to $P_N^{(2)}$. We define only $P_N^{(2)}$ here and the $P_N^{(n)}$'s for $n > 2$ can be defined by analogy

$$P_N^{(2)}(r_1, r_2) = \int dr_3 \int dr_4 \dots \int dr_N P_N^{(N)}(r_1, r_2, \dots, r_N) \quad (4.12)$$

Here, all coordinates other than those for particles 1 and 2 are integrated out. The value of $P_N^{(2)}(r_1, r_2)$ gives the probability of finding simultaneously a molecule in volume element $d\tilde{r}_1$ at \tilde{r}_1 and another molecule in volume element dr_2 at r_2 irrespective of the coordinates of the remaining particles.

The pair correlation function or the radial distribution function (RDF) $g_N^{(2)}(r_1, r_2)$ or $g(r_1, r_2)$ or $g^{(2)}$ or simply g is more useful in dense fluids than $P_N^{(2)}$ because $P_N^{(2)}$ is a very sharply peaked function which is negligibly small in most of the configuration space. The ratio $P_N^{(n)}(r_1, \dots, r_n) / (P_N^{(1)}(r_1) \dots P_N^{(1)}(r_n))$ which is referred to as the n-body correlation function or the n-body distribution function, is much better behaved and is a good function for describing the structure of fluids.

In uniform and homogeneous systems,

$$P_N^{(1)}(r_1) = \frac{\int dr_2 dr_3 \dots e^{-\beta U_N(\mathbf{r}^N)}}{Z_N} = 1/V \quad (4.13)$$

This is really, independent of the position vector \tilde{r}_1 . This is a consequence of translational invariance. The RDF is then given by

$$g(r_1, r_2) = P_N^{(2)} V^2 \quad (4.14)$$

For isotropic systems, $g(r_1, r_2) = g(|r_1 - r_2|) = g(r)$. When all the particles are far apart, $P_N^{(n)} \cong (P_N^{(1)})^n$ and $g \rightarrow 1$. When the particles are very close to one another, $U_N \rightarrow \infty$ and the Boltzmann factors tends to 0 and thus $g(r) \rightarrow 0$ as $r \rightarrow 0$. The

property that $\tilde{g}_N^n(\tilde{r}^n)$ has significant variation when the n particles under

consideration are all clustered together is referred to as the cluster property and this property is used in cluster expansion for various correlation functions and thermodynamic properties.

Before going into the methods of determining g 's, we will describe how the pressure and the compressibility of a system can be obtained in terms of the RDF.

Equations of State:

To obtain the virial equation of state, one begins with the virial function of

Clausius $V(\tilde{r}^N) = \sum_{i=1}^N \tilde{r}_i \cdot \tilde{F}_i$ where \tilde{r}_i is the position of the particle i and \tilde{F}_i , the

force acting upon it. The time average of the virial V , V_t or V_{total} may be shown to be equal to $-3Nk_B T$, by writing F_i as md^2r_i/dt^2 , integrating by parts and using the equipartition principle. The ensemble average of the virial is given by the sum of $\langle V_{ext} \rangle$ and $\langle V_{int} \rangle$. In a cubic box, the external force on each wall is given by the product of the pressure P and the wall area L^2 , i.e., $= PL^2$ where L is the length of the wall. This force is exerted when the particles are at $\pm L$ and thus, the contribution to the virial from external forces is $3PV$. The contribution to the average of the virial from intermolecular potential is

$$\langle V_{int} \rangle = \left\langle \sum_{i=1}^N r_i \cdot \nabla_i U_N(\underline{r}^N) \right\rangle \quad (4.15)$$

$$\begin{aligned} \langle V \rangle_t &= \langle V_{ext} \rangle + \langle V_{int} \rangle \\ -3Nk_B T &= -3P V + \langle V_{int} \rangle \\ \text{or } -3 P V &= 3Nk_B T + \langle V_{int} \rangle \end{aligned} \quad (4.16)$$

$$\text{or } \frac{\beta P}{\rho} = 1 - (\beta / 3N) \sum_{i=1}^N r_i \cdot \nabla_i U(\underline{r}^N) \quad (4.17)$$

This is the virial equation of state. A more elegant way of obtaining this is from

$$p = -(\partial A / \partial V)_{T,N} = \beta^{-1} \frac{\partial}{\partial V} \ln Z \quad \text{or} \quad \beta Z p = \frac{\partial}{\partial V} \int d\underline{r}^N e^{-\beta U_N(\underline{r}^N)}$$

In a cubic box of length L, $dV = 3 L^2 dL$ and by suitable manipulations, the virial equation of state can be recovered.

To obtain the virial equation of state for pairwise additive potential average value of $\sum_i r_i \cdot \nabla_i U_N(\underline{r}^N) = \sum_i r_i \cdot \nabla_i (\sum_{KL} u(r_{KL}))$

$$\frac{1}{Z} \int e^{-\beta U_N(\underline{r}^N)} (\sum_i r_i \cdot F_i) = \sum_i \sum_{j \neq i} \frac{1}{Z_N} \int d\underline{r}^N e^{-\beta U_N(\underline{r}^N)} r_{i,j} \cdot \nabla_{ij}(r_{ij}) \quad (4.18)$$

$$\text{as } \nabla_i U(r_{ij}) = \nabla_{ij} U(r_{ij})$$

Each term in the summation yields the same value and the result is

$$\frac{1}{Z} \frac{N(N-1)}{2} \int dr_1 \cdot dr_2 \frac{dU(r_{12})}{dr_{12}} \left[\frac{1}{Z_N} \int \dots \int e^{-\beta U_N(\underline{r}^N)} dr_3 dr_4 \dots dr_N \right] \quad (4.19)$$

The term in the square brackets on right is $g(r_1, r_2)$. For homogeneous fluids, $g(r_1, r_2) = g(r)$, as integration over one variable can be performed because of translational invariance and the result is

$$\frac{\beta P}{\rho} = 1 - \frac{2}{3} \pi \beta \rho \int_0^\infty dr g(r) r^3 \frac{dU(r)}{dr} \quad (4.20)$$

This equation is valid only for purely additive forces. An equation of state which does not depend on such an approximation is the compressibility equation of state which is

$$k_B T \rho \chi_T = 1 + \rho \int [g^2(r) - 1] dr = \frac{\langle N^2 \rangle - \langle N \rangle^2}{N} \quad (4.21)$$

The isothermal compressibility χ_T is $-\frac{1}{V} (\partial V / \partial P)_T$. These two equations are the main routes to calculate thermodynamic quantities. A discrepancy between them indicates that either that the pair wise approximation is not valid or that the g

obtained from any of the approximation schemes is not of very good quality. The compressibility equation of state is obtained by using the grand canonical probability distribution functions and calculating the number fluctuations in the grand ensemble.

There are a large number of methods for determining $g^{(2)}(r)$. Numerical simulation methods are presented in chapter 5. In the non-simulation methods such as the integral equation and perturbation theories $g^{(2)}$ is not evaluated from its formula mentioned but from certain approximate relations between $g^{(2)}$ and $g^{(3)}$ or relations between $g^{(2)}$ and other more tractable quantities such as the potential function and the direct correlation function which needs to be defined.

The Ornstein Zernicke equation which was introduced in 1917, has become a very powerful tool for calculating the structure of liquids. Before we discuss this equation by using functional derivatives and diagrammatic methods, we shall mention the Yvon Born Green Equation (YBG) which may be derived by elementary methods. The solutions of this equation have been revived recently when it was discovered that they are useful in describing critical phenomenon.

Relation between the compressibility and the distribution functions

In the grand canonical ensemble ,

$$\Xi = \sum_{N \geq 0} \frac{e^{\beta \mu N}}{N! h^{3N}} \int \dots \int e^{-\beta H(\underline{r}^N, \underline{p}^N)} d\underline{r}^N d\underline{p}^N \quad (4.22)$$

$$= \sum_{N \geq 0} \frac{e^{\beta \mu N}}{N! h^{3N}} Q_N(V, T) = \sum_{N \geq 0} \frac{z^N}{N!} Z_N(V, T) \quad (4.22)$$

where, $z = \frac{e^{\beta \mu}}{\Lambda^3}$ which is the activity or the fugacity. (4.23)

The probability of finding the system containing N particles regardless of their locations and momenta, $P(N)$, is obtained by integration $f_o(N, \underline{r}^N, \underline{p}^N)$ over \underline{r}^N and \underline{p}^N , which is

$$P(N) = \iint f_o(N, \underline{r}^N, \underline{p}^N) d\underline{r}^N d\underline{p}^N \quad (4.24)$$

where, $f(N, \underline{r}^N, \underline{p}^N) = \frac{e^{\beta \mu N} e^{\beta H(\underline{p}^N, \underline{r}^N)}}{N! h^{3N} \Xi}$ (4.25)

$$P(N) = \frac{z^N}{\Xi N!} Z_N(V, T) \quad (4.26)$$

$$\langle N \rangle = \sum_{N=0}^{\infty} N P(N) = \frac{z}{\Xi} \frac{\partial \Xi}{\partial z} = \frac{\partial \ln \Xi}{\partial \beta \mu} \quad (4.27)$$

The dispersion of N about this average value is given by

$$\frac{\partial \langle N \rangle}{\partial (\beta \mu)} = \frac{\partial^2 \ln \Xi}{\partial (\beta \mu)^2} = \langle N^2 \rangle - \langle N \rangle^2 \quad (4.28)$$

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{\partial \langle N \rangle}{\langle N \rangle \partial (\beta \mu)} \quad (4.29)$$

The total number of particles in the system may be identified as $\langle N \rangle$. In the thermodynamic limit, $\langle N \rangle \rightarrow \infty$, $V \rightarrow \infty$, $\langle N \rangle / V = \rho$ (which is fixed), the averages in the grand canonical, canonical and the microcanonical ensembles become equal. It is to be shown that equation (4.28) is related to the compressibility of the system.

Defined the thermodynamic potential as

$$\Omega = A - N\mu = G - PV - N\mu = -PV \quad (4.30)$$

(shown by using Euler's theorem on homogeneous functions or using $G = N\mu$)

$$dG = -SdT + VdP + \mu dN \quad (4.31)$$

$$d\Omega = -PdV - SdT - N d\mu \quad (4.32)$$

$$= -PdV - V dp \quad (4.33)$$

$$\text{or} \quad N d\mu + SdT = V dP \quad (4.34)$$

and at constant temperature, $N d\mu = V dP$

If the volume too is held constant, dP and $d\mu$ both depend only on dN . Thus, we can write,

$$d\mu = (\partial\mu / \partial N)_{T,V} dN \quad \text{and} \quad dp = (\partial p / \partial N)_{T,V} dN \quad (4.35)$$

$$\therefore N (\partial\mu / \partial N)_{T,V} = V (\partial p / \partial N)_{T,V} = V (\partial p / \partial \rho)_{T,V} (\partial \rho / \partial N)_{T,V} \quad (4.36)$$

$$= (\partial p / \partial \rho)_{T,V} = (\partial p / \partial \rho)_{N,T} = (\partial p / N \partial [1/V])_{T,V} = (-V^2 / N) (\partial p / \partial V)_T \quad (4.37)$$

$$= (V / N) / [(-1/V) (\partial V / \partial P)_T] = (V / N) / \chi_T = 1 / (\rho \chi_T) \quad (4.38)$$

or $\rho \chi_T = (1/N) (\partial N / \partial \mu) = \beta (1/N) (\partial N / \partial \beta \mu) = \beta (1 / \langle N \rangle) (\partial \langle N \rangle / \partial \beta \mu)$

And using eq. (4.29), we get,

$$\rho k_B T \chi_T = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \quad (4.39)$$

To obtain the compressibility equation of state in terms of the distribution functions, let us begin with the definition of the canonical reduced probability function,

$$P_N^{(n)}(r^n) = Z_N^{-1} \int \dots \int dr_{n+1} dr_{n+2} \dots dr_N e^{-\beta U_N(r_1, r_2, \dots, r_N)} \quad (4.40)$$

With the normalization,

$$\int \dots \int P_N^{(n)}(r^n) dr_1 dr_2 \dots dr_n = 1 \quad (4.41)$$

Certain other functions are defined in terms of $P_N^{(n)}$ which are found to be more useful in calculations of thermodynamic properties. One such function is the n -particle density $\rho_N^{(n)}(r^n)$ defined as

$$\rho_N^{(n)}(r^n) = \frac{N!}{(N-n)!} P_N^{(n)}(r^n) \quad (4.42)$$

The factorials account for all the permutations of the particles. The normalization of $\rho_N^{(n)}$ is given by

$$\int \rho_N^{(n)} d\tilde{r}^n = \frac{N!}{(N-n)!} \quad (4.43)$$

For a homogeneous system, $\rho_N^{(1)}(r_{\sim 1}) = \frac{N}{V}$ which is the particle number density of the system. The pair distribution function which was defined earlier as :

$$g_N^n(r_{\sim}^n) = V^n P_N^n(r_{\sim}^n) \quad (4.44)$$

now becomes, for homogeneous systems,

$$g_N^{(2)}(r_{\sim}^2) = g_N^{(2)}(r_{\sim 1}, r_{\sim 2}) = \rho^{-2} \rho_N^{(2)}(r_{\sim}^2) \quad (4.45)$$

To study fluctuations in the number of particles, we need to switch to the grand canonical ensemble wherein the n-particle densities are defined as

$$\rho^{(n)}(r_{\sim}^n) = (1/\Xi) \sum_{N \geq n} \frac{z^n}{N!} Z_N P_N^{(n)}(r_{\sim}^n) \quad (4.46)$$

$$= (1/\Xi) \sum_{N \geq n} \frac{z^n}{(N-n)!} \int \dots \int e^{-\beta V_n(r_{\sim}^n)} d r_{\sim n+1} \dots d r_N \quad (4.47)$$

The normalization for the grand density is

$$\int \dots \int \rho^{(n)}(r_{\sim}^n) d r_{\sim}^n = \langle N! / (N-n)! \rangle \quad (4.48)$$

which may be verified by recalling that $P(N) = (1/\Xi) \frac{z^N}{N!} Z_N(V, T)$

Using this normalization factor, we may evaluate the following expression

$$\iint d r_{\sim 1} d r_{\sim 2} \left[\rho^{(2)}(r_{\sim 1}, r_{\sim 2}) - \rho^{(1)}(r_{\sim 1}) \rho^{(1)}(r_{\sim 2}) \right] = \langle N! / (N-2)! \rangle - \langle N \rangle^2 \quad (4.49)$$

$$= \langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2 \quad (4.50)$$

For a homogeneous system, $\rho^{(1)}(r) = \langle N \rangle / V = \rho$.

$$\rho^{(2)}(r_{\sim 1}, r_{\sim 2}) = \rho^2 g^{(2)}(r_{\sim 1}, r_{\sim 2}) = \rho^2 g^{(2)}(r_{\sim}) = \rho^2 g(r_{\sim}) \quad (4.51)$$

Using the above formula for $g^{(2)}$, eq. (4.49) can now be written as,

$$\rho^2 \iint (g^2(r_1, r_2) - 1) d r_1 d r_2 = \langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2 \quad (4.52)$$

Dividing both sides by $\langle N \rangle$, taking the term of unity to the left side and using translational invariance to take a factor of V outside the integral on the left side, we get,

$$1 + \rho \int (g^2(r) - 1) d r = (\langle N^2 \rangle - \langle N \rangle^2) / \langle N \rangle = \rho k_B T \chi_T \quad (4.53)$$

This is the compressibility equation in terms of the pair distribution function. The following procedure enables to get pressure from the values of compressibility.

$$\frac{1}{\rho} \left(\frac{\partial \rho}{\partial P} \right)_T = \frac{1}{(N/V)} \frac{\partial (N/V)}{\partial P} = \frac{-V}{V^2} \left(\frac{\partial V}{\partial P} \right)_T \quad (4.54)$$

Using the definition of $\chi_T = (-1/V) (\partial P / \partial V)_T$, we get,

$$\frac{\partial P}{\partial \rho} = \frac{1}{\rho \chi_T}; \quad (4.55)$$

Integrating the above equation,

$$p(\rho) = \int_0^p 1/(\rho^* \chi_T) d\rho^* \quad (4.56)$$

This gives $p = p(\rho)$ which is an equation of state in terms of the pair distribution function alone, and does not make any reference to the pairwise additivity approximation.

The YBG Equation:

In the formula $g^{(2)}(r)$ or $g(r)$,

$$g(r) = \frac{N!}{\rho^2 (N-2)!} \int \dots \int e^{-\beta U_N(\mathbf{r}^N)} d\mathbf{r}_3 \dots d\mathbf{r}_N = \frac{\rho^{(2)}(r)}{\rho^2} \quad (4.57)$$

it is extremely difficult to carry out the integration on the right hand side. Yvon, Born and Green (YBG) differentiated the equation with respect to (\mathbf{r}_1) to get

$$\frac{\partial g(r)}{\partial \mathbf{r}_1} = -\frac{N!}{kT \rho^2 (N-2)!} \int \dots \int \frac{\partial U_N}{\partial \mathbf{r}_1} e^{-\beta U_N(\mathbf{r}^N)} d\mathbf{r}_3 \dots d\mathbf{r}_N \quad (4.58)$$

This may be further simplified if the potential U_N is pairwise additive. In that case,

$$\frac{\partial U_N}{\partial \mathbf{r}_1} = \sum_{j=2}^N \frac{\partial U_{1j}}{\partial \mathbf{r}_1} = \frac{\partial U(r_{12})}{\partial \mathbf{r}_1} + \sum_{j=3}^N \frac{\partial U(r_{1j})}{\partial \mathbf{r}_1} \quad (4.59)$$

$$kT \frac{\partial g(r_{12})}{\partial \mathbf{r}_1} + \frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} \left[\frac{N!}{\rho^2 (N-2)!} \int \dots \int e^{-\beta U_N(\mathbf{r}^N)} d\mathbf{r}_3 \dots d\mathbf{r}_N \right] + \frac{1}{\rho^2} \frac{N!}{(N-2)!} \sum_{j=3}^N \int \dots \int \frac{\partial \phi_{1j}}{\partial \mathbf{r}_1} e^{-\beta U_N(\mathbf{r}^N)} d\mathbf{r}_3 \dots d\mathbf{r}_N = 0 \quad (4.60)$$

The second and the third terms contain $g^{(2)}$ and $g^{(3)}$ respectively. By using their definition, we get

$$kT \frac{\partial g(r_{12})}{\partial \mathbf{r}_1} + \frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} g(r_{12}) + \rho \int \frac{\partial \phi(r_{12})}{\partial \mathbf{r}_1} g^{(3)} d\mathbf{r}_3 = 0 \quad (4.61)$$

This may be generalised to the equation for $g^{(n)}$ in terms of $g^{(n+1)}$ and the derivatives of the potential with respect to $r_{\sim 1}$. A very useful approximation, whose validity has always been questioned, is the Kirkwood approximation for $g^{(3)}(r_{\sim 1}, r_{\sim 2}, r_{\sim 3})$ in terms of $g^{(2)}$ s as :

$$g^{(3)}(r_{\sim 12}, r_{\sim 23}, r_{\sim 31}) = g(r_{12}) g(r_{23}) g(r_{31}) \quad (4.62)$$

Using this approximation, we get the YBG equation

$$kT \frac{\partial g(r_{12})}{\partial r_{\sim 1}} + \frac{\partial \phi(r_{12})}{\partial r_{\sim 1}} g(r_{\sim 12}) + \rho \int \frac{\partial \phi(r_{13})}{\partial r_{\sim 1}} g(r_{12}) g(r_{23}) g(r_{31}) d r_{\sim 3} = 0$$

As alternatives to the YBG equation, which is an integro-differential equation which is difficult to solve and wherein additional approximations are necessary, expansions of $g^{(2)}$ in powers of density were sought. In the process of all this search, several equations have been derived and the structure of all these equations has become more transparent by the use of functional derivatives and diagrammatic techniques. The functional derivatives will now be defined and their representation in terms of diagrams will be given. Certain lemmas involving the diagrams, are used to obtain more convergent series for the pair distribution functions. The numerical methods used in solving these equations will be discussed.

Functional Derivatives

A functional is a function of a function and is a quantity which does not depend on one or two values of the function, but on the entire range of the function. A typical example is an integral below which is the second virial coefficient.

$$B_{(2)} = - 2 \pi \int_0^{\infty} [e^{-\beta U(r)} - 1] r^2 dr \quad (4.64)$$

Here, $B_{(2)}$ is a functional, $U(r)$, a function and r is the independent variable. It is well known that if the value of $U(r)$ is changed at one point (value) of r or finitely many values of r , the integral B_2 is unchanged in magnitude. In fact, the function $U(r)$ has to be changed at each value of r to change B_2 . The variation in f at each point a may be written as

$$f'(a) = f(a) + C_a \delta(x-a), \quad C_a \in (-\infty, \infty) \quad (4.65)$$

where $\delta(x-a)$ is the Dirac delta function with the following properties

$$\delta(x-a) = 0 \text{ if } x \neq a, \text{ and} \quad (4.66)$$

$$\int_{-\infty}^{\infty} f(x) \delta(x-a) dx = f(a) \quad (4.67)$$

It is a function which is zero everywhere except at $x = a$ and whose integral from $-\infty$ to $+\infty$ equals unity. The delta function can be developed as the limit of a normalized

Gaussian function as its width goes to zero. The subscript on C implies that the value of C may be different for each point a on the interval under consideration.

The change in the functional when the function changes over its range is given by adding the contribution to the change in the functional over the full range of the function. In mathematical terms,

$$\delta F = \int \frac{\delta F}{\delta f(x)} \delta f(x) dx \quad (4.68)$$

where $\frac{\delta F}{\delta f}$ is the functional derivative of F, $\frac{\delta F}{\delta f} \delta f(x)$ gives the change of F near x and the total change in the functional is obtained by adding the changes in the functional over the whole range of the function.

The meaning of the above equations may become clearer by comparing them with the case of a discrete sum such as the partition function $Q = \sum e^{-\beta E_k}$.

$$\frac{\partial Q}{\partial E_k} = -\beta e^{-\beta E_k}, \delta Q = \sum \frac{\partial Q}{\partial E_k} \delta E_k \text{ where } \delta E_k = e_k = \text{change in } E_k \quad (4.69)$$

Where $e_k = E_k - E_k'$, the change in E_k . If k is a continuous variable, summation over k can be replaced by integration over k , i.e., $\sum_k \rightarrow \int dk$ and the total change in Q is given by

$$\delta Q = \int (\partial Q / \partial E(k)) e(k) dk \quad (4.70)$$

To calculate the functional derivative, it is best to write the variation in the functional in the form indicated in eq. (4.68) above, and then pick the derivative from the right hand side.

Some useful rules in calculating the functional derivatives are :

The chain rule,

$$\frac{\delta F}{\delta f(r)} = \int \frac{\delta F}{\delta g(r')} \frac{\delta g(r')}{\delta f(r)} dr' \quad (4.71)$$

wherein the independent variable now is a vector variable \underline{r}' rather than the scalar variable as in (4.68). Also

$$\frac{\delta f(\underline{r}')}{\delta f(\underline{r})} = \delta(\underline{r} - \underline{r}') \quad (4.72)$$

which is a generalisation of $\frac{\partial x_i}{\partial x_j} = \delta_{ij}$.

Three examples will now be considered.

$$\frac{\delta B_2}{\delta v(r')} = -\frac{1}{2} \int_0^\infty \frac{\delta [4\pi r^2 (e^{-\beta v(r)} - 1)]}{\delta v(r)} \frac{\delta v(r)}{\delta v(r')} dr \quad (4.73)$$

The quantity in the brackets is a function of $v(r)$. In that the case $\delta[\]/\delta v(r)$ becomes $d[\]/d v(r)$ which in this case is $-\beta 4\pi r^2 e^{-\beta v(r)}$. By substituting, we get

$$\frac{\delta B_2}{\delta v(r)} = 2\pi \beta r^2 e^{-\beta v(r)} \quad (4.74)$$

Let the functional F be an integral over a product of functions $f(r_i)$

$$\text{Let } F = \int \dots \int \prod_{i=1}^N f(r_i) \, d\mathbf{r}_{\sim 1} \dots d\mathbf{r}_{\sim N} \quad (4.75)$$

If each function $f(r_i)$ is changed to $f(r_i) + \delta f(r_i)$, then the change in the functional is given by

$$F + \delta F = \int \dots \int \prod_{i=1}^N [f(r_{\sim i}) + \delta f(r_{\sim i})] d\mathbf{r}_{\sim 1} d\mathbf{r}_{\sim 2} \dots d\mathbf{r}_{\sim N} \quad (4.76)$$

Expanding the product and keeping only the first three terms,

$$\begin{aligned} &= \int \dots \int \prod_{i=1}^N f(r_{\sim i}) d\mathbf{r}_{\sim 1} \dots d\mathbf{r}_{\sim N} + \sum_{j=1}^N \int \dots \int d\mathbf{r}_{\sim N} \frac{\delta f(r_j)}{f(r_j)} \prod_{i=1}^n f(r_{\sim i}) \\ &\quad + \sum_{j,k=1}^N \int \dots \int d\mathbf{r}_{\sim N} \frac{\delta f(r_j) \delta f(r_k)}{f(r_j) f(r_k)} \prod_{i=1}^n f(r_i) \end{aligned} \quad (4.77)$$

Since $r_{\sim j}$ is an integration variable each term in the summation of second and higher terms is equal. Retaining terms only to first order and cancelling F on either side we have, for the first and the second functional derivatives:

$$\delta F / \delta f(r) = N \int \dots \int d\mathbf{r}_2 \dots d\mathbf{r}_N \prod_{i=2}^N f(r_i) \quad (4.78)$$

Extending to the second functional derivative, we get,

$$\delta F / \delta f(r) \delta f(r') = N(N-1) \int \dots \int d\mathbf{r}_3 \dots d\mathbf{r}_N \prod_{i=3}^N f(r_i) \quad (4.79)$$

In the next section, the lemmas used for analysing and transforming the functionals using diagrammatic representations of the functionals are given. The purpose of the exercise is to obtain convenient expressions for the pair distribution so that the cluster expansion for the distribution function functions or the approximations for them can be evaluated and used for the estimation of structure factors and thermodynamic functions.

REFERENCES

1. J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, Second Edition, Academic Press, 1986
2. H. L. Friedman, *A Course in Statistical Mechanics*, Prentice Hall, 1985
3. C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids*, Clarendon Press, Oxford, 1984

4. J. K. Percus, in *The Equilibrium Theory of Classical Fluids*, (H. L. Frisch and J. L. Lebowitz, eds), W.A. Benjamin, New York, 1964
5. M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids*, Oxford University Press, 1985
6. D. Chandler, *Statistical Mechanics*, Oxford University Press, 1984