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A REVIEW OF INTEGRAL EQUATIONS DESCRIBING THE RADIAL DISTRIBUTION FUNCTION OF FLUIDS

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ABSTRACT

The radial distribution function is of primary importance in statistical mechanics both for calculating thermodynamic properties as well as for investigating structure. However, the mathematical description of the radial distribution function is difficult. Several descriptions involving integral equations have been developed. This paper examines some of the integral equations and details some points of their derivations. The most popular family of integral equations, developed from the Ornstein Zernike integral equation, receives the most attention. In addition, this paper describes the application of these integral equations to electrolyte solutions.

NOMENCLATURE

c(r):	The direct correlation function
g(r):	The radial distribution function
h(r):	Equal to g(r)-1
J:	Any thermodynamic property
k:	Boltzmann's Constant
N:	The number of molecules and ions in a system
p:	The probability associated with a state
q:	A position coordinate in 3-dimensional space
Q:	The partition function
r:	Used to denote some distance
T:	Temperature
$u(r)$:	Pair potential
U_c :	The configurational internal energy
V:	Volume
$w^{(n)}$(r):	The mean force
Z:	The configurational partition function
β:	A constant equal to kT
ρ:	Number density of system
σ:	Hard sphere diameter

INTRODUCTION

In statistical mechanics, a theoretical description of thermodynamic properties based upon molecular phenomena is obtained through the use of probability. Any thermodynamic property can be described using the summation of individual property values, J_i, multiplied by their probability, p_i, as below:

$$<J> = \Sigma J_i p_i \tag{1}$$

The probability term in (1) is calculated from the partition function, Q, which is comprised of several parts. Some parts of Q, including the translational and internal contributions, can be obtained fairly easily. The most difficult portion of Q to obtain is the configurational contribution, Z.

Z is defined by

$$Z = \int \ldots \int e^{-\beta U} dq^{3N} \tag{2}$$

where β is a temperature dependent constant, U is the molecular potential energy, and q^{3N} are the position coordinates for all the molecules in the system being described.

Z, the configurational contribution to Q, can be related to the configurational contribution to any of the thermodynamic functions. For example, the configurational potential energy, U_c, can be related to Z by

$$U_c = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{N,V} \tag{3}$$

where k is Boltzmann's Constant, T, is temperature, N is the number of molecules being examined, and V is the volume.

When U_c is calculated in this manner, it yields an equation that can be manipulated with various assumptions to yield

$$U_c = \frac{1}{2} \iint u\left(r_1 r_2\right) \rho^{(2)}\left(r_1 r_2\right) dr_1 dr_2 \tag{4}$$

where $u(r_1,r_2)$ is the potential energy between two molecules (described by some model) and $\rho^{(2)}(r_1,r_2)$ is the probability of two molecules being at the positions designated by r_1 and r_2. In reaching the form of (4), a transition was made to a spherical coordinate system so radii (r_1 and r_2) can be used to describe positions.

If there is no correlation in position between the molecules, then $\rho^{(2)}(r_1,r_2)$ is simply equal to the density of the system squared. That is, the probability of finding molecules in a certain volume is uniform throughout the system and is equal to the density of the system. It is sensible therefore to define a function that describes how strongly correlated the positions of molecules are. It is called the pair correlation function:

$$g(r) = \frac{\rho^{(2)}}{\rho^2} \tag{5}$$

where ρ is the density of the solution. If there is radial symmetry in the system, $g(r)$ is called the *radial distribution function*. Any thermodynamic function can be derived in terms of g. Using (5), the form of (4) may further be reduced to

$$U_c = 2\pi\rho N \int_0^\infty u(r)\, g(r)\, r^2 dr \tag{6}$$

where the location of one molecule was set at the origin thereby reducing one integral to the volume of a sphere.

When $g(r)$ is equal to 1, there is no correlation between the molecule at the origin and the molecules at radius r. When g(r) is greater or less than 1, the density of molecules at radius r is greater or less than the bulk density and there is correlation. The g(r) function is a measure of how much affect one molecule has on the positions of other molecules.

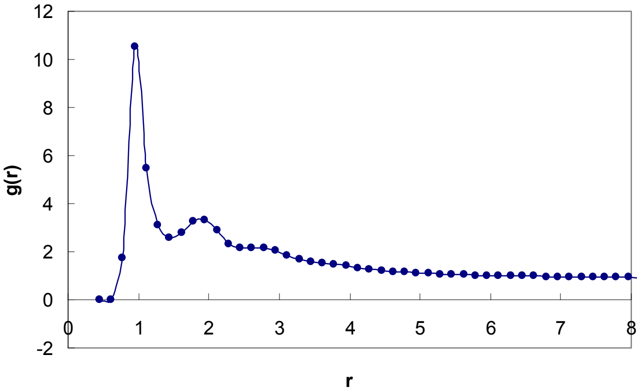

Figure 1: Plot of the radial distribution function obtained by the author through Monte Carlo simulation of a NaCl solution. This plot shows g(r) for the interactions between Na^+ ions and water. The high peak at r ≈ 1 indicates Na^+ has a strong effect on water molecules at this distance. The smaller peak at r ≈ 2 indicates an influence on water molecules at this distance, but this influence is not as strong.

The pair potential, u(r), can be calculated using any of a large group of models that are simple in form. For example, the *Hard-Sphere Model* and the *Lennard-Jones Model* are among the most popular.

INTEGRAL EQUATIONS FOR RADIAL DISTRIBUTION FUNCTION

The challenge in using this approach to calculate thermodynamic properties is in determining a function for g(r). Several methods have been derived yielding various integral equations.

Kirkwood Equation

The derivation of the *Kirkwood Equation* is long and beyond the scope of this paper. However, the form of the equation is interesting and is shown below for completeness.

$$-kT\, ln\left[g(r_{12},\xi)\right] = \xi u(r_{12}) + \ldots$$
$$\rho \int_0^{\xi}\int_V u(r_{13})\, g(r_{13};\xi')\left[g(r_{23})-1\right] dr_3\, d\xi' \tag{7}$$

A coupling parameter, ξ, was introduced in the development of the equation. The ξ variable is a “switch” of sorts that changes the function between different particles. The equation is a nonlinear integral equation and must be solved numerically. No analytic solution is available.

Another integral equation, the *Born-Green-Yvon Equation* , is similar but is not derived using a coupling parameter. It too is complicated and nonlinear, and it will not be shown here.

Direct Correlation Function Equations

In 1914, Ornstein and Zernike proposed another formulation of g(r) through a direct correlation function. In doing so, they define a function h(r) such that

$$h(r) = g(r) - 1 \tag{8}$$

The advantage to h(r) versus g(r) is that h(r) approaches zero as the local density of a fluid tends towards the bulk density.

The function h(r) is divided into two theoretical parts; one part is called the indirect correlation, and the other part is called the direct correlation. The direct correlation function, c(r), describes the influence of one molecule directly on another. The indirect portion of h(r) is a measure of the influence on a molecule broadcast through the influence of a third molecule.

In other terms, $h_{12}(r)$, describes the total influence molecule 1 exerts on molecule 2 at a distance r. The direct correlation function, $c_{12}(r)$, describes only the direct pairwise influence that molecule one exerts on molecule 2. The indirect portion of $h_{12}(r)$ describes the influence exerted by a third molecule, molecule 3, on molecule 2 as a result of the influence of molecule 1 on molecule 3. See Figure 2 for an illustration.

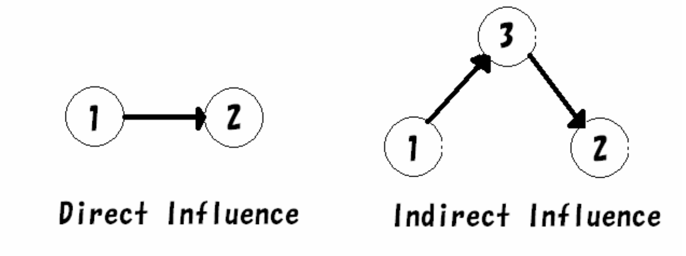

Figure 2: The direct influence on molecule 2 is described by c_{12}(r). The indirect influence is described by (9) and is the influence from molecule 1 propagated through molecule 3.

The function h_{12}(r) may then be described by summing the direct correlation function, c_{12}(r), with all the indirect interactions from all the other molecules in the system. The summation of the indirect interactions is described using an integral. If we call the indirect influence function I_3(r$_3$), then the integral representation can be described as:

$$I_3(r_3) = \rho\int c_{13}(r)h_{23}(r)dr_3 \tag{9}$$

This formulation makes conceptual sense. The c_{13}(r) function describes the effect that molecule 1 has on molecule 3. This is the indirect effect that will be propagated onto molecule 2. The h_{23}(r) function describes how strongly molecule 3 interacts with molecule 2 and therefore how much the effect described by c_{13}(r) will be felt by molecule 2. The integral sums the effects over all positions for molecule 3.

Put together, these terms constitute the *Ornstein-Zernike Integral Equation* (10). This equation is the basis for the most commonly used integral equations when describing the radial distribution function.

$$h_{12}(r) = c_{12}(r) + \rho\int c_{13}(r)h_{23}(r)dr_3 \tag{10}$$

Equations Derived From Ornstein-Zernike Equation

The Ornstein-Zernike equation, (10), is not solvable as given because there are two separate unknown functions, *h* and *c*. It is necessary, therefore, to provide a closure to this equation in a form that will relate the two unknown functions to each other. There are several theoretical methods for doing so.

One closure yields the *Percus-Yevick* equation. In defining this closure, a new function is defined, *w*(r).

$$w^{(n)}(r) = \frac{ln\left[g^{(n)}(r_1,....,r_n)\right]}{-\beta} \tag{11}$$

The function $w^{(i)}$ is the mean force acting on molecule 1 from molecule i with the averaged forces from all the other molecules in the solution added. If the *g*(r) function is broken into a direct and indirect component, the following formulation for *c*(r) is obtained:

$$c(r) = e^{-\beta w(r)} - e^{-\beta[w(r)-u(r)]} \tag{12}$$

or

$$c(r) = g(r)\left(1 - e^{\beta u(r)}\right) \tag{13}$$

The first term in (12) is a rearranged form of (11) equaling to *g*(r). The second term is *g*(r) with the pairwise, direct, potential removed thereby describing the indirect influence. Thus, (12) describes only the direct interaction part of *g*(r). This relates *c*(r) to *g*(r) as in (13) and only requires a model for the pair potential, *u*(r). The approximation inherent in the Percus-Yevick closure is in assuming that the direct interaction can be removed from the total interaction by subtracting the pair potential.

The *Hyper-netted Chain Equation* is obtained similarly through an expansion on (12). In this case, *c*(r) is related to *g*(r) by the following closure:

$$c(r) = g(r) - 1 - \beta u(r) - ln\left[g(r)\right] \tag{14}$$

Introduction of either of these closures into the Ornstein Zernike equations yield a closed integral equation. Again, these nonlinear equations can only be evaluated numerically because no analytical solution is available.

The Percus-Yevick integral equation can be solved analytically if one introduces a hard-sphere approximation. This approximation affects only the pair potential, *u*(r), in the equation. According to the hard sphere approximation:

$$\begin{aligned} u(r) &= \infty \qquad \text{for } r \le \sigma \\ u(r) &= 0 \qquad \text{for } r > 0 \end{aligned} \tag{15}$$

The solution using this approximation involves a Laplace Transform of the equation and then a lengthy proof to show that a piecewise analytic solution and an inverse Laplace Transform exist. The end goal is to use the resultant *g*(r) description to develop an equation of state from which all thermodynamic functions may be derived.

Integral Equations for Electrolyte Solutions

This approach is extended in a method used to describe electrolyte solutions. In doing so, the workers in this field have defined a model for solutions called the *primitive model*. The primitive model assumes a hard sphere pair potential, as described in (15) and simply averages the σ for each molecule coming into contact with each other. Thus, if a cation and an anion were to come into contact with each other then the s for the interaction would be defined as

$$\sigma = (\sigma_+ + \sigma_-)0.5 \tag{16}$$

where the + and – designators refer to the cation and anion respectively. In addition, a coulombic potential (17) is added to the pair potential to describe the added attractions and repulsions from the charged species.

$$u_{coulombic}(r) = \frac{q_1 q_2}{r\varepsilon} \tag{17}$$

The subscripts 1 and 2 in (17) refer to separate charged species, r refers to the distance between species 1 and 2, and ε is the dielectric constant of the solvent.

The *restricted primitive model* consists of all the same assumptions as the primitive model and also assumes the hard sphere diameters of all ions in solution are equal. Both of these models are good in dilute solutions where the hard sphere approximation becomes close to exact.

A popular model for describing the radial distribution function of electrolyte solutions is the M*ean Spherical Model*. The mean spherical model utilizes either the primitive or the restricted primitive description of ions and makes two new assumptions. First, the model assumes that the radial distribution function is equal to zero at radii less than the hard sphere diameter (18).

$$g(r) = 0 \qquad \text{for} \quad r < 0 \tag{18}$$

This assumption is exact for a hard sphere fluid and so is good at low densities.

The second approximation consists of defining a simple closure for the Ornstein Zernike equation:

$$c(r) = -\beta u(r) \tag{19}$$

When σ goes to zero, this yields the same result as the Debye-Huckel theory which describes the theoretical limit of dilute solutions.

Because the closure to this equation is simple in form, it can be solved analytically. Forms of the solution to this equation have been developed that, while complicated, yield an explicit solution to the problem.

The Percus-Yevick and Hyper-netted Chain equations, when adjusted to describe electrolyte solutions, are more accurate, in general, than the Mean Spherical Model, but they are less useful in many engineering applications because they require a numeric solution.

CONCLUSIONS

Many integral equations have been derived for the description of the radial distribution function. The Kirkwood and the Born-Green-Yvon Equations are older and, in general, more complicated than others. The more popular integral equations have been derived from the Ornstein-Zernike equation. These include the Percus-Yevick and Hyper-netted Chain equations.

All of these equations are not solvable analytically. Though less accurate, except in dilute solutions, the Mean Spherical Model provides an analytical solution to the Ornstein Zernike equation. This model is particularly useful when applied to electrolyte solutions.

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