

Liquid-State Theory for Irreversible Surface Adsorption

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ABSTRACT

Random sequential adsorption (RSA) can be described as the $s \rightarrow 0$ limit of an s -species mixture of particles with a particular Hamiltonian. Here we use this mapping to systematically derive a general theory of sequentially adsorbed systems using a liquid-state approach. This theory generalizes the standard model of random sequential adsorption in several basic ways. We also exploit an approach to correlation pioneered by Boltzmann, which yields the Kirkwood-Salsburg hierarchy for the correlation functions of this model, from which we obtain further results that include bounds on convergence for the virial series. We further derive a Percus-Yevick type integral equations for the two-point correlation function of RSA. Finally, we use the virial theorem and zero-separation theorem for RSA to give a scaled-particle theory for this model.

1. Introduction

The adsorption of large molecules and molecular aggregates, such as polymers, colloids, and proteins, upon membranes and surfaces is frequently associated with a large binding energy so that the time needed for the surface involved to become saturated with particles is small compared to a typical desorption time. In such cases, the correlation

functions are substantially different from those associated with equilibrium. It has been shown to be a good approximation, at least in some cases, to use for such processes an idealized model known as **random sequential adsorption (RSA)**.¹⁻¹⁴ In this model, hard, i.e., non-overlapping particles are placed on a surface, one at a time, each in such a way that it does not overlap those already in place. Once placed, a particle is quenched, i.e., frozen in that location.

Previous approaches to RSA have been of two kinds. The first involves application of ideas from kinetic theory. Evans and coworkers¹¹ and Dickman et. al.⁷ have developed sets of kinetic equations to describe the RSA process both on lattice and in the continuum. A second approach to the RSA model uses probability theory and statistical geometry to exploit the fact that all interactions in that model are of the excluded-volume type. This was in fact the approach to RSA originally used by Widom;¹ It proves to be an application of a general method originally due to Boltzmann¹⁵, who used it to formulate a theory for the thermodynamics of hard-sphere systems at equilibrium. One of us has shown elsewhere¹⁶ how Boltzmann's program can be completed and generalized, and how, when so completed, it is related to the scaled-particle theory of Reiss, Frisch, and Lebowitz,¹⁷ the potential distribution method of Widom,¹ and the Kirkwood-Salsburg equations¹⁸ As discussed in some detail in ref. (16), a remarkable aspect of our generalizations of Boltzmann's method is that it is not limited to systems at equilibrium. This was exploited in the work of Torquato and Stell¹⁹ to obtain the n -point matrix functions for composite media in terms of n -particle probability distribution functions. These equations, which are of the Kirkwood-Salsburg and Mayer-Montroll type, are valid for both equilibrium and non-equilibrium systems. The first of these equations, from which the others can be derived by "turning on" extra particles into the system, gives a formula for the average space available to an $(N+1)^{st}$ particle being added to a system of N particles. (Boltzmann called this the available space.) Widom¹ used this equation as the starting point for his study of RSA, exploiting the fact that the available space is simply related to the adsorption

rate of particles. More recently, the Kirkwood-Salsburg equations have been used in the context of the RSA by Tarjus et. al.¹²

In this paper, we generalize and extend previous results on RSA by giving a complete, systematic liquid-state theory for this class of models. To do this, we combine two distinct theoretical approaches. The first is a differential replica method previously developed by one of us¹³ that enables us to reduce a large class of models containing quenched degrees of freedom^{13,21} to limiting cases of equilibrium, many-body systems. The second is the method of Boltzmann already described.

This work has several goals. One of them is to systematize and generalize a number of approximations and formal expansions that have previously appeared in the literature. In particular, we are able to obtain the general term in a number of fundamental expansions for RSA correlation functions. Another goal is to extend the standard RSA model described above in several directions, in order to give a more realistic treatment of the physical systems to which RSA can be applied. In real adsorption problems successive particles may interact with those already adsorbed via long-range, e.g., electrostatic, forces; thus their placement will not be random. The adsorption may proceed at a finite rate rather than the infinitesimal rate assumed by the naive RSA model, so that a nonzero density of particles will simultaneously be adsorbing. The short-range interactions may not be sufficiently repulsive to be modelled as hard-core; this may be very important at high adsorbate density. All of these effects can be treated naturally once we describe the general RSA process in terms of liquid-state theory.

Our final reason for discussing the RSA process in detail is that it represents an important example of class of models of disordered materials, for which the correlation functions do not correspond directly to an equilibrium Hamiltonian system, but which can nevertheless be treated using the methods of liquid-state equilibrium theory. This work is part of a long-term project of finding effective Hamiltonians for such materials in order to use the machinery of equilibrium statistical mechanics (integral equations, renormalized

perturbation theory, etc.) to calculate their properties.

The study of sequential adsorption was originally limited to one- and two- dimensional problems, i.e., to adsorption on lines and surfaces. However, the generality of our study makes it reasonable for us to frame our discussion here, except when noted otherwise, in d -dimensional space.

This paper is organized as follows: in Section 2, we use the method of differential quenching, essentially an iterated replica method, to develop a Mayer series for the particle adsorption rate. We show how to extend this calculation to the general RSA model mentioned above. We also give a representation for RSA as a limiting case of an equilibrium Hamiltonian system. In Section 3, we extend the development of Section 2 to give a set of two- point correlation functions for RSA. We discuss several sets of such functions that naturally enter the analysis of this system. Finally, we give a set of Ornstein-Zernike equations satisfied by the RSA correlation functions and suggest natural closures for them. In Section 4, we define n -point correlation functions for RSA, and give a set of Kirkwood-Salsburg equations these satisfy. In Section 5, we develop a scaled-particle theory for RSA. It is shown that scaled-particle theory for sequentially adsorbed systems, unlike that previously developed for equilibrium systems, is **nonlinear**. We solve the simplest approximation scheme of this kind numerically and discuss the solution. Section 6 gives a summary of our conclusions.

2. A Generalized Replica Method for RSA, and an Effective Hamiltonian

In this section we will use a recently developed generalization of the replica method to provide virial series for the particle adsorption rate and correlation functions of RSA. We will exhibit an s -state Hamiltonian spin model whose thermodynamic quantities and correlation functions become those of RSA in the singular limit $s \rightarrow 0$. Finally, we will then use this Hamiltonian formalism to discuss the very general RSA model described in the introduction.

RSA can be described¹³ as an example of a differentially quenched system, i.e., one

in which the system is repeatedly quenched after each particle is added and allowed to equilibrate. Such differentially quenched systems are readily treated by generalizations of the continuum or liquid-state replica method. Since the latter is not yet widely used, we explain its basic features, then give the generalization needed to treat RSA.

The liquid-state replica method¹³ converts quenched thermodynamic averages into standard thermodynamic averages in a system with an effective Hamiltonian. To see this let us consider a system whose particles are divided into two components or fractions, the first of which, termed component 1, is allowed to reach equilibrium at temperature T_1 as a result of pairwise interactions between particles at positions x_1 and x_2 of the form $v_{11}(x)$ with $x = x_2 - x_1$. (In the simplest case, v_{11} depends only on the magnitude of x , which is the distance between the particles.) We then quench component 1, or freeze it in place, before introducing component 2. Molecules of component 2 have the interaction $v_{22}(x)$ with each other and the interaction $v_{12}(x)$ with component 1 atoms. The mean free energy for this system is calculated by performing an ensemble average over the degrees of freedom of component 2 molecules, treating the degrees of freedom of component 1 molecules as parameters. The thermodynamic quantities calculated from this free energy are then averaged over the degrees of freedom associated with component 1 molecules to give the averaged thermodynamic quantities describing the two-component partly quenched system. This double ensemble average is computationally quite difficult. The liquid-state replica method¹³ converts this average into a single ensemble average. It has been shown that the Mayer expansions for the thermodynamic quantities for this two-component system are derived from the corresponding Mayer expansions for the fully equilibrated system by simply excluding from the calculation all graphs not obeying a particular constraint. Specifically, a Mayer graph is excluded if each vertex corresponding to a component 2 atom is not part of an unbroken chain of such vertices connected to a root vertex also of component 2. Madden and Glandt²² originally derived this result using a general argument from probability theory; a derivation was subsequently given

by us^{23,24} using the replica method developed in [13] and [21]. Further results on the quenched-annealed mixture obtained from the replica formalism can be found in ref. [25].

Sequentially adsorbed systems can be described as a generalization of this two-component system in which each molecule is a separate component. One can construct a sequentially adsorbed system by a process of differential quenching, in which one particle at a time is added to a surface containing the previously adsorbed particles and allowed to equilibrate before being quenched or frozen in place. Conversely, one can arrive at an effective equilibrium system for RSA by repeatedly applying the replica formalism, once for each particle, each application undoing a quench operation. From these considerations, it follows that the Mayer expansions for this system are derived from those for an equilibrium polydisperse or infinite-component system by discarding all Mayer graphs that do not obey a particular constraint.¹³ Specifically, a graph is discarded if it does not have at least one **uphill path** leading from each field point to a root point. An uphill path is defined to be a sequence of vertices, each successive pair connected by a Mayer bond, such that in traversing the path from field point to root point, the species labels of the vertices encountered increase monotonically. (Here, every particle in RSA is considered to belong to a different species, and they are given species labels in the order in which they are introduced.) We emphasize that this prescription for providing Mayer expansions for the bulk properties of partly quenched systems is extremely general. It applies to systems arrived at by an arbitrary annealing schedule, or sequence of quench operations. Interestingly enough, it seems that an isomorphism onto a non-additive spin system of the type provided here for RSA also exists for an arbitrary annealing schedule.

The adsorption rate Φ in RSA can be immediately related to the probability that a randomly chosen point is the center of a disk of diameter a which contains no particle centers, or equivalently, to the expected space available to the center of a disk of diameter a which is to be inserted into the system. For the usual case of hard particles, we find it useful to introduce a “fugacity” and “chemical potential” for RSA by means of the

equations

$$\Phi = \frac{\rho}{z} = e^{-\beta\mu}/\Lambda^3 \quad (2.1)$$

which is the relationship between ϕ and μ in an equilibrated system of hard particles. We discuss in detail the Mayer expansion of the adsorption rate; we will give the corresponding recipe for the RSA correlation functions in the next section. The coefficient of ρ^n in the Mayer expansion for $\beta\mu$ is given by $1/n!$ times the sum of all topologically distinct, single-rooted, labelled Mayer graphs. In the equilibrium theory of liquids,²⁶ the factor $1/n!$ results from the classical, i.e., indistinguishable nature of the particles. The labels on the field points can be any n distinguishable symbols; they need not be integers. In the RSA calculation, the labels on field points represent possible orderings of the n different species labels assigned to these vertices. For any such ordering, there are $N^n/n!$ possible assignments of species to the vertices in a Mayer graph. The root point is assigned to the last particle added to the system, i.e., to the species N . According to the uphill path constraint, this must be so, because no field point in any graph can be assigned to a species with bigger label, i.e., to a particle added later. Thus, apart from the uphill path constraint, which eliminates some labelled graphs, the Mayer expansion for the chemical potential in RSA is the same as that in an equilibrium, hard sphere system.

We now use this observation to directly map RSA onto a limiting case of an equilibrium system. We consider each particle in a many-body system to belong to a different species. Also, assume that associated with each particle is an internal "spin" degree of freedom σ_i that can take any of s different values, from 1 to s . Then we define a system with the pairwise interaction between the particle of species i and the particle of species j , $j > i$, to be given by

$$V_{ij}(x) = v_{HS}(x)\delta_{\sigma_i,1} \quad (2.2)$$

with $v_{HS}(x)$ a hard-disk interaction of range a . This somewhat unusual equilibrium system has the property that, in the limit $s \rightarrow 0$, all of its correlation functions (including the

one-point function ρ/z) become those of RSA. To see this, note that the sum over spin states weights each field point with a factor of s unless it is connected by a Mayer bond to a vertex corresponding to a species of larger index. Thus, only Mayer graphs satisfying this last condition will survive the $s \rightarrow 0$ limit. But this last condition is equivalent to the uphill path constraint. Incidentally, we note that the fact that the Hamiltonian (2.2) depends on particle labels is **not** unusual; it is a common occurrence in treating polydisperse systems.^{27,28}

In the $s \rightarrow 0$ limit, the thermodynamic quantities of this model become the basic physical quantities that describe RSA. For example, we have

$$\Phi = \lim_{s \rightarrow 0} \frac{\rho}{z} \quad (2.3)$$

also

$$p_{RSA} = \left. \frac{d}{ds} \right|_{s=0} p \quad (2.4)$$

Here the quantity p on the RHS of eqn. (2.4) is the equilibrium pressure for the Hamiltonian model defined by the interaction (2.2). The physical meaning of the RSA pressure p_{RSA} can be understood by imagining a large but finite realization of an RSA model using soft spheres in a box with hard walls. If one attempts to contract the walls of the box infinitesimally, the RSA pressure is the force per unit area that one encounters. This definition implies that the virial theorem, relating the RSA pressure to the two point correlation function of that model, will be valid. One can see this implication by using the rescaling proof of the virial theorem due to H.S. Green.²⁹

The Hamiltonian mapping just given suggests a natural generalization of RSA: we replace the pairwise interaction (2.2) between species i and j , $j > i$, with

$$V_{ij}(x) = v(x)\delta_{\sigma_i,1} + \phi(x) \quad (2.5)$$

The two potential functions in this model, $v(x)$ and $\phi(x)$, can be chosen independently to give a variety of interesting models. If the potential $v(x)$ in (2.5) is zero, the interaction (2.5) will give an equilibrium system with potential $\phi(x)$. If the potential $\phi(x)$

is zero, it gives various models of sequential adsorption. Choosing $v(x)$ to be a hard-sphere interaction gives the model usually called RSA. Choosing $v(x)$ to be the sum of a hard-sphere interaction and a Coulomb potential gives a model for the correlated but irreversible adsorption of charged, hard particles. This system could be realized experimentally by placing a static charge on small latex spheres, then allowing them to adsorb strongly onto a surface. We note that unless the potential $v(x)$ has a hard core, the resulting RSA model will have no jamming density. Nevertheless, one can ask whether the asymptotic behavior of the adsorption rate will still be a power law in the elapsed time, as it is in naive RSA.

In the general case, the interaction (2.5) corresponds to a model of correlated and partly reversible sequential adsorption. Allowing a general potential $\phi(x)$ that acts between each pair of particles independent of their spin state is equivalent to making the binding to the substrate partly reversible. To simulate this general two-potential RSA model e.g., on a computer, one begins with an arbitrary placement of particles on a surface, then evolves this distribution to a steady state by cycling through the particles in order of increasing species number and attempting to move each to a new location. If a candidate move involves placing particle i at x_i , it should be accepted with probability p determined by the Boltzmann factor

$$p = \exp[-\beta E(x_i)] / \int \exp[-\beta E(x_i)] d^3 x_i \quad (2.6)$$

where

$$E(x_i) \equiv \sum_{j < i} v(x_{ij}) + \sum_{j \neq i} \phi(x_{ij}) \quad (2.7)$$

Depending on the relative strength of the two interactions $v(x)$ and $\phi(x)$, this process will give a more or less reversible adsorption process.

Finally, we note an interesting class of models, now under study, which involve sequential adsorption on a substrate that is either porous or heterogeneous, so that only part of the surface is available for adsorption. We construct the RSA process as before as a system

with many layers or components, each consisting of a single particle. But instead of adding these components successively to a vacuum, we add them to a finite-density hard sphere system, which is itself defined to be the first layer in a generalized sequential adsorption process. The rules for calculating Mayer series for such generalized sequential adsorption processes have been described previously. The additional component of hard-sphere particles can be thought of as impurities or obstacles having the pairwise interactions $V_{11}(x)$, $V_{12}(x)$, resp. with each other and with the sequentially adsorbing particles. We choose $V_{12}(x)$ to be a hard-core interaction so as to exclude adsorption inside the obstacles. For $V_{11}(x)$, it is advantageous to use a parameterized potential that can range from no interaction to a hard-sphere interaction. The square-mound potential, $V_{11}(x) = 1/\tau_1$ for $x < 1$ and 0 for $x > 1$ is an example. The somewhat different choice that defines the permeable sphere model³⁰ has proven especially simple in the context of the Percus-Yevick approximation. Here $V_{11}(x) = 0$ for $x > 1$ but the condition on V_{11} for $x < 1$ is replaced by the condition that V_{11} yield the radial distribution function, $g_{11}(x) = \lambda$ for $x < 1$, $0 \leq \lambda \leq 1$.

3. Ornstein-Zernike Formalism for Sequential Adsorption

In this section, we define several different two-point correlation functions for RSA, each of which is useful in the analysis of this model. We also present an Ornstein-Zernike system for RSA and discuss it in terms of the Hamiltonian formalism presented in Section 2.

It is most natural to first define RSA correlation functions that are a limiting case of the correlation functions of the Hamiltonian model defined in Section 2. These functions inherit virial expansions, integral equations, etc., from the equilibrium correlation functions from which they are derived. One can then use these functions to study the detailed structure of an RSA model.

We define the two-point correlation function of the Hamiltonian system of Section 2 as follows: $g_{ij}^{\sigma_i \sigma_j}(x)$ is the probability density associated with finding a particle of species i in spin state σ_i and a particle of species j in spin state σ_j , the two of them separated by

a distance x . The $s \rightarrow 1$ limit of this function gives, depending on the spin indices σ_i and σ_j , two correlation functions useful in describing RSA. In this limit, the “species” of our original model become particle labels, describing the sequential order in which particles are placed. We will use the particle labels i and j , with the convention that $i < j$. We define two RSA correlation functions as follows:

$$g_{ij}^{11}(x) \equiv \rightarrow_{s \rightarrow 0} g_{ij}(x) \quad (3.1)$$

$$g_{ij}^{i1}(x) \equiv \rightarrow_{s \rightarrow 0} g_{ij}^b(x) \quad (3.2)$$

The function $g_{ij}(x)$ is the probability density associated with finding, in a realization of RSA, the i^{th} and j^{th} particle separated by a distance x . The Mayer series for this function is easily constructed using the Hamiltonian (2.5): it consists of all labelled, two-rooted graphs satisfying the uphill constraint, as specified in Section 2. A labelled Mayer graph is interpreted as an ordering on the particle labels; the field points in a labelled graph must be summed over all sets of particle labels that preserve this ordering. The function $g_{ij}^b(x)$ is a related function defined as the sum of the subset of Mayer graphs contributing to $g_{ij}(x)$ such that there exists **no** uphill path joining the two root points. Similarly, we have $g_{ij}^c(x)$ defined as the sum of the subset of Mayer graphs contributing to $g_{ij}(x)$ such that there exists **at least one** uphill path joining the two root points. Thus, we have by definition

$$g_{ij}(x) = g_{ij}^b(x) + g_{ij}^c(x) \quad (3.3)$$

(The subscripts ‘b’ and ‘c’ denote ‘blocked’ and ‘connected’, respectively, and refer to the path joining the root points.) Combining eqns. (3.1) and (3.3) gives

$$[g_{ij}^{11}(x) - g_{ij}^{i1}(x)] \equiv \rightarrow_{s \rightarrow 0} g_{ij}^c(x) \quad (3.4)$$

This function occurs in the topological reduction of the Mayer expansion, and is also important in the relations between thermodynamic quantities and RSA correlation

functions, for example the RSA compressibility theorem. We explore this relation after we develop the Ornstein-Zernike equations for the functions $\{g_{ij}(x)\}$ and $\{g_{ij}^c(x)\}$.

By virtue of the isomorphism we establish onto the many body system defined by the Hamiltonian (2.5), the RSA system has the structure of a polydisperse system. In such systems, each particle has, in addition to its position, an extra parameter characterizing it. In the standard examples of polydisperse systems,^{27,28} this parameter is the particle radius or orientation. Here, the extra parameter characterizing the i^{th} particle in the system is ρ_i , the density of the system at the time that particle was added. This density is given by

$$\rho_i = i/V \quad (3.5)$$

In the thermodynamic limit, each intermediate summations over the particles in the system occurring e.g. in the Mayer expansions can be replaced by an integration over the extra parameter ρ_i . The integration measure for such an integration is trivial because each particle added to the system corresponds to a distinct value of ρ_i . We henceforth assume this limit to be taken, and use as limits the densities ρ_i instead of particle labels i , density integrations instead of summations over particles, etc. Each specific correlation function $g_{ij}(x)$ is actually a function of three densities: ρ_i and ρ_j , the extra parameters characterizing the two root points, and ρ , the final particle density of the RSA system in which the correlation functions are computed. However, because each particle in a realization of RSA is independent of the particles placed **after** it, we have

$$g_{ij}(x) = g_{ij}(x, \rho) = g_{ij}(x, \rho_j) \quad (3.6)$$

for any $\rho > \rho_j$. In this equation and what follows, we will adopt the convention, unless stated otherwise, that $j > i$.

The Ornstein-Zernike equations satisfied by the functions $h_{ij} \equiv g_{ij} - 1$ and $h_{ij}^c \equiv g_{ij}^c - 1$ can be obtained by writing down the Ornstein-Zernike equations for the effective RSA Hamiltonian, as described in Section 2, and taking the RSA limit $s \rightarrow 0$:

$$h_{ij}^{11} = c_{ij}^{11} + \int_0^{\rho_j} \left[c_{ik}^{11} \otimes h_{kj}^{11} - c_{ik}^{1i} \otimes h_{kj}^{i1} \right] d\rho_k \quad (3.7)$$

$$h_{ij}^{i1} = c_{ij}^{i1} + \int_0^{\rho_j} \left[c_{ik}^{i1} \otimes h_{kj}^{11} - c_{ik}^{ii} \otimes h_{kj}^{i1} \right] d\rho_k \quad (3.8)$$

where \otimes denotes a spatial convolution integral. Here the quantities $c_{ij}(x)$, $c_{ij}^c(x)$ can be defined to be the sum of the subset of node-free diagrams contributing to $h_{ij}(x)$, $h_{ij}^c(x)$, respectively. For simplicity we define a standard form for a correlation function: we rewrite it, if necessary, so that the subscript on the left, e.g., 'i' in the case of h_{ik} , is smaller than the subscript on the right. Also, we express (3.7) and (3.8) in terms of the connected and blocking correlation functions $g_{ij}^c(x)$ and $g_{ij}^b(x)$, defined by eqns. (3.2) and (3.4), respectively. The resulting Ornstein-Zernike equations for RSA are:

$$h_{ij}^c = c_{ij}^c + \int_{\rho_i}^{\rho_j} \left[c_{ik}^c \otimes h_{kj}^c \right] \quad (3.9)$$

$$h_{ij}^b = c_{ij}^b + \int_0^{\rho_i} \left[c_{ki}^c \otimes h_{kj}^c + c_{ki}^c \otimes h_{kj}^b + c_{ki}^b \otimes h_{kj}^c \right] d\rho_k + \int_{\rho_i}^{\rho_j} c_{ik}^b \otimes h_{kj}^c \Big] d\rho_k \quad (3.10)$$

The functions $\{g_{ij}^b(x)\}$ and $\{g_{ij}^c(x)\}$ are specific RSA correlation functions, i.e., they give the probability density associated with finding a specific pair of particles at a separation x . These functions, like the correlation functions of any polydisperse system, depend upon an additional parameter, i.e., an extra density. One must solve (4.8-9) and then form the generic correlation function, or probability density associated with finding **any** two particles with separation x . It would be of great value to be able to rewrite the ROZ equations (4.8-9) directly in terms of generic correlation functions. This we have not been able to do. However, we have obtained a formally exact equation for the generic correlation functions by using the Kirkwood-Salsburg equations for RSA. We will define the generic correlation functions for RSA, give the Kirkwood-Salsburg equations for them, and then relate these functions to the specific functions that satisfy (4.8-9).

The functions $\{g_{ij}(x)\}$ and $\{g_{ij}^c(x)\}$ are natural 'atoms' or building blocks for generic RSA correlation functions, which are more directly useful. Thus the latter will be defined as sums of the former over the external particle indices i and j .

It is the direct correlation function c_{ij}^b , and the generic functions that result from summing it over particle labels that directly enter the analysis of thermodynamic quantities. The functional derivative expansion of the free energy function for RSA contains the hierarchy of generic correlation functions $g(x_1, \dots, x_n)$. In contrast, the functional derivative expansion of the thermodynamic potential, or equivalently, of the pressure, contains the hierarchy of functions $c^c(x_1, \dots, x_n)$. The function $c^c(x_1, \dots, x_n)$ is defined to be the subset of Mayer graphs that contribute to the function $c(x_1, \dots, x_n)$ and that also have an uphill path connecting the root point at x_n to each other root point. The $n = 2$ member of this hierarchy is just the function $h^c(x)$. To understand why functions with such constraints arise, we consider the $n = 2$ case in more detail. The Hamiltonian system defined by eqn. (2.5) obeys the standard functional relation

$$\frac{\delta}{\delta \rho(x_1)} \mu(x_2) = \delta(x_1, x_2) / \rho(x_1) - c_{ij}^c(x_1, x_2) \quad (3.11)$$

In the limit in which the number of spin states s is set equal to zero, this eqn. becomes

$$\frac{\rho}{\Phi} \frac{d\Phi}{d\rho} = 1 - \rho \int dx_1 c_{ij}^c(x_1, x_2) \quad (3.12)$$

which is the compressibility relation for RSA. The occurrence in this equation of the function $c_{ij}^c(x)$ can be understood as follows: the Mayer series for the derivative of a quantity is obtained from the Mayer series for the quantity itself by producing, for each Mayer graph having k field points, a set of k Mayer graphs, each of which has one of those field points replaced by a root point. In the Mayer expansion for $\Phi(x_1)$, each field point is connected by an uphill path to the single root point at x_1 . When such a field point becomes a root point, as a result of the differentiation in equation (3.14), there will still be such an uphill path between the two resulting root points. Thus, the graphs that result will all belong to $c^c(x_1, x_2)$.

4. Kirkwood-Salsburg Equations and Their Structure

In this section, we develop a Kirkwood-Salsburg hierarchy for random sequential adsorption. A discussion of this hierarchy has already appeared in which the general

Kirkwood-Salsburg structure discussed in reference (16) is considered in the context of RSA. Our treatment here will focus upon some aspects of this structure that are peculiar to its appearance in the treatment of RSA, in particular the basic distinction between generic and specific correlation functions. Also, we give several approximate integral equations for the two-point correlation function, which we derive from approximate closures of this hierarchy.

Consider the function $\Phi_n(x_1; x_2 \dots x_n)$ that represents the probability density associated with being able to insert at position x_1 an extra particle into a system consisting of $N + n$ particles, with $n - 1$ of them found at x_2, \dots, x_n , respectively. [We shall write $\Phi_1(x)$ for Φ_n in the absence of the $n - 1$ particles at prescribed locations; in a spatially homogenous system in which $\Phi_1(x_1)$ is independent of x_1 we shall simply write Φ for $\Phi_1(x_1)$.]

There is a way of representing such functions as a series that goes back to Boltzmann,¹² who considered the first few terms in such a representation of Φ_1 and Φ_2 for a hard-sphere system in equilibrium. Subsequently Kirkwood and Salsburg¹⁸ considered the full series of the Φ_n for arbitrary pair potentials in an equilibrated system. We can derive the corresponding Kirkwood-Salsburg equations for RSA by directly applying Boltzmann's method, as developed in ref. [16], to the RSA problem. (Alternatively we can apply the argument to the replica system and take the $s \rightarrow 0$ limit.) The result is

$$\Phi_n(x_1; x_2 \dots x_n) = e_n(x_1; x_2 \dots x_n) \sum_{s=0}^{\infty} \frac{1}{s!} \int dx_{n+1} \dots dx_{n+s} \prod_{s=1}^n f(x_i x_{n+s}) \rho_{n+s-1}(x_2 \dots x_{n+s}) \quad (4.1)$$

Here

$$e_n(x_1; x_2 \dots x_n) = \prod_{i=2}^n [1 + f(x_1 x_i)] \quad (4.2)$$

and the $\rho_n(x_1 \dots x_n)$ are **generic** n -particle probability density functions associated with finding n unspecified particles at positions $x_1 \dots x_n$. On the other hand the Φ_n have an intrinsically **specific** quality in the sense that they specifically refer to the extra particle,

which must be the **last** of the particles being inserted into the system. We could replace Φ_n by a fully specific probability density by referring to specified (i.e., labelled) particles at $x_2 \dots x_n$. This would define a function that differs from Φ_n only through a trivial change in normalization; Φ_n already has the symmetry properties of its specific version. Strictly speaking, however, it is neither fully specific or fully generic. We shall refer to such functions as “mixed.” In RSA the most important mixed functions are those, like the Φ_n , that refer to one **last** particle, with the rest of the particles unspecified.

In a system of particles at equilibrium that are identical except for labelling, the entire difference between specific and generic functions is just a trivial one of normalization, because particle labelling can be done in any order — order is of no consequence. This implies that Φ_n is very simply related to ρ_n . One has

$$\frac{\rho_n(x_1 \dots x_n)}{\rho_1(x_1)} = \frac{\Phi_n(x_1; x_2 \dots x_n)}{\Phi_1(x_1)} \quad (4.3)$$

as the closure of (4.1). In the spatially uniform case this reduces to

$$\rho_n(x_1 \dots x_n)/\rho = \Phi_n(x_1; x_2 \dots x_n)/\Phi_n \quad (4.4)$$

In the case of RSA, on the other hand, the ordering of the particles constitutes the whole problem! As a result the generic ρ_n are related to the Φ_n via a combination transformation that takes this ordering into account. This can be carried out term by term in the density expansion of ρ_n and summarized in terms of a single differentiation with respect to ρ , which yields the coefficients that are found in the expansion of Φ_n , which the latter are appropriately symmetrized. Considering only the spatially uniform case for simplicity, we have

$$\frac{\partial \rho_n(x_1 \dots x_n)}{\partial \rho} = \sum_{k=1}^n \Phi_n(x_1; x_1 \dots x_{k-1}, x_{k+1} \dots x_n)/\Phi_n \quad (4.5)$$

We shall find it convenient to introduce the probability densities $\Psi_n(x_1/x_2 \dots x_n)$ associated with being able to insert a particle into the system at position x_1 in the presence

of $n - 1$ particles at positions x_2, \dots, x_n , respectively. One has

$$\Phi_n(x_1; x_2 \dots x_n) = \Psi_n(x_1/x_2 \dots x_n) \rho_{n-1}(x_2 \dots x_n) \quad (4.6)$$

In particular

$$\Psi_2(x_1/x_2) = \Phi_2(x_1; x_2)/\rho_1(x_2) \quad (4.7)$$

and in a uniform system

$$\Psi_2(x_1/x_2)/\Phi = G(x_1/x_2) = G(x_{12}) \quad (4.8)$$

where $G(x_{12})$ is a radial distribution function that depends on the positions x_1 and x_2 only through their absolute difference $|x_1 - x_2|$ which we shall write as x_{12} or x as appropriate.

In a uniform equilibrium system we would have simply

$$G(x_{12}) = \rho(x_1 x_2)/\rho^2 \quad (4.9)$$

but from (4.5) and (4.8) we have instead

$$2G(x_{12}) = \frac{1}{\rho} \frac{\partial \rho(x_1 x_2)}{\partial \rho} \quad (4.10)$$

or

$$G(x_{12}) = g(x_{12}) + \frac{\rho}{2} \frac{\partial g(x_{12})}{\partial \rho} \quad (4.11)$$

where $\rho(x_1 x_2) = \rho^2 g(x_{12})$, so $g(x_{12})$ is the generic two-particle distribution function.

In equilibrium systems, the cavity function gives the probability density associated with finding a cavity of diameter a at position x_2 , with **some** particle at position x_1 . In such systems, this function is derived from the equilibrium two-point correlation function $g(x_1, x_2)$ by dividing out the Boltzmann factor for the direct interaction between root points. In RSA, these two functions are related in a nontrivial manner, as we now explain. In an equilibrium hard-sphere system, a cavity is equivalent to a hard sphere of twice its radius, except that a pair of cavities may freely overlap, while a pair of hard spheres may

not. Similarly, in RSA, we may establish an equivalence between a hard sphere particle and a cavity, providing that that particle is the last one placed; while a cavity may not overlap particles placed before it is (by definition), it may readily be overlapped by particles placed after it is. (Just as in equilibrium, a pair of cavities may freely overlap, but this fact will not be relevant to our treatment of RSA, because we will discuss the cavity-particle distribution function, but not the cavity-cavity distribution function.) In other words, the natural extension to RSA of the equilibrium concept of a cavity is that of a cavity interacting only with those particles having smaller labels than it. A cavity of diameter a in RSA is thus associated with a hard-sphere particle of species $(N + 1)$, i.e., it is a cavity associated with the **next** particle to be added to the system.

Thus we have both a mixed cavity function $Y(x) = G(x)/[1 + f(x)]$ and a generic cavity function $y(x) = g(x)/[1 + f(x)]$. It is the former that appears in a more fundamental way in our theory. In particular we have the zero-separation condition for hard-particle RSA

$$\Phi Y(0) = 1 \tag{4.12}$$

from (4.10) with $n = 2$ as well as its obvious generalization to $n > 2$.

We now relate the generic and specific correlation functions. Thus, from its definition, we can express $G(x_1/x_2)$ as

$$\rho G(x_1/x_2) = \sum_{i=1}^j \rho_i g_{ij}(x) \tag{4.13}$$

In the limit of large N , this can be rewritten in terms of an integral over density:

$$\rho_j G(x_1/x_2, \rho_j) = \int_0^{\rho_j} g_{mj}(x_1, x_2, \rho_m, \rho_j) d\rho_m \tag{4.14}$$

The generic distribution function $g(x)$ is the probability density associated with finding

any two particles at positions x_1 and x_2 ; it can be expressed in terms of the $\{g_{ij}(x)\}$ as

$$\begin{aligned}\rho^2 g(x_1, x_2) &= \sum_{j=1}^{N-1} \rho_j [G(x_1/x_2, \rho_j) + G(x_2/x_1, \rho_j)] \\ &= \sum_{i,j=1}^{N-1} \rho_i \rho_j g_{ij}(x_1, x_2, \rho_i, \rho_j)\end{aligned}\tag{4.15}$$

This can also be rewritten in terms of an integral over density:

$$\rho^2 g(x_1, x_2) = \int_0^\rho [G(x_1/x_2, \rho_i) + G(x_2/x_1, \rho_i)] d\rho_i\tag{4.16}$$

This is equivalent to the statement that the rate of creation of pairs of particles at positions x_1 and x_2 is proportional to the probability density associated with finding a particle and a cavity, one at x_1 and one at x_2 . We can rewrite the last equation in a way that stresses this interpretation by using the definition of the adsorption rate

$$\Phi \frac{d}{d\rho_j} (\rho_j^2 g(x, \rho_j)) = k [Y_j(x_1, x_2, \rho_j) + Y_j(x_2, x_1, \rho_j)]\tag{4.17}$$

From (4.1) one can also obtain a number of interesting rigorous results for non-negative pair potentials, for which the remainder terms in the series alternate in sign, yielding rigorous upper and lower bounds on Φ_n . The authors have previously discussed the use of the Kirkwood-Salsburg hierarchy to treat continuum sphere percolation, which can also be transformed into a limiting case of a Potts model. Upper and lower bounds on the correlation functions, as well as a lower bound on the radius of convergence of the Mayer series were also obtained for that model.

For hard particles, the function $\Psi_n(x_1/x_2 \dots x_n)$ has the significance of being the volume available to the center of the particle to be inserted at x_1 , given particles fixed at x_2, \dots, x_n , divided by V , the volume of the box in which the system is contained. It is also useful to consider the volume available to the center of a cavity of the same size as a particle. This is just VA_n , where

$$A_n(x_1/x_2 \dots x_n) = \frac{\Psi_n(x_1/x_2 \dots x_n)}{e_n(x_1; x_2 \dots x_n)}\tag{4.18}$$

with $A_1(x_1) = \Phi_1(x_1)$. We have, in a uniform system,

$$A_1(x_1/x_2) = \Phi Y(x_{12}) \quad (4.19)$$

To generate an exact functional expansion that yields a Percus-Yevick equation upon truncation, we can consider $A_1(x_1/x_2)$ expanded around its value $\Phi_1(x_1)$ when the particle at x_2 is turned off. We have

$$\begin{aligned} A_1(x_1/x_2) &= \Phi_1(x_1) + \int \frac{\delta \Phi_1(x_1)}{\delta \rho(x_3)} [\rho(x_3 x_2) - \rho(x_3)] dx_3 \\ &+ \frac{1}{s!} \int \frac{\delta^s \Phi_1(x_1)}{\prod_{i=3}^{s+2} \delta \rho(x_i)} \prod_{i=3}^{s+2} [(\rho(x_i x_2) - \rho(x_i))] dx_i + \dots \end{aligned} \quad (4.20)$$

The mixed direct correlation functions $c_n(x_i; x_2 \dots x_n)$ are generated by $\ln \Phi(x_i) = c_1(x_i)$

$$\frac{\delta^s c(x_1)}{\delta \rho(x_2) \dots \delta \rho(x_{s+1})} = c_{s+1}(x_1; x_2 \dots x_{s+1}) \quad (4.21)$$

Using (4.28) and (4.29), yields, in the uniform case,

$$\begin{aligned} Y(x_{12}) &= 1 + \rho \int c_2(x_1; x_3) h(x_3 x_2) dx_3 \\ &+ \frac{\rho^2}{2} \int \left[c_3(x_1; x_3 x_4) - c_2(x_1; x_2) c_2(x_1; x_3) \right] h(x_3 x_2) h(x_4 x_2) dx_3 dx_4 \dots \end{aligned} \quad (4.22)$$

Truncation after the first non-trivial terms yields a Percus-Yevick approximation suitable for RSA

$$Y(x_{12}) = 1 + \rho \int c_2(x_1; x_3) h(x_3 x_2) dx_3 \quad (4.23)$$

In equilibrium, where $Y(x) = y(x)$, this relation defines a unique approximation when combined with the OZ equation which identifies the correlation terms as $h - c_2$, yielding $y = 1 + h - c_2$. For hard particles in equilibrium, this yields a good approximation $c_2 = 0$ outside the hard core, where $y = 1 + h$. Inside the core it yields the result $y = c_2$. This represents a very poor approximation for y ; however inside the core, the PY approximation is very useful in situations in which knowledge of y inside the core is not needed. In the case of RSA, the OZ equations do not have as simple a form. In particular, the convolution

on the LHS of (4.22) is not equal to $h - c_2$. Instead of obtaining a unique approximation via the OZ equations, it is more convenient to obtain one directly by introducing the closure

$$c_2(x_1; x_2) = f(x_{12})[G(x_1/x_2) - c_2(x_1; x_2)] \quad (4.24)$$

For hard particles, this simply says that $G = 0$ inside the core, which is identically true, and that

$$c_2(x_1; x_2) = 0 \quad (4.25)$$

outside the core, which is likely to be a good approximation for the same reasons that the PY approximation is good for hard particles in equilibrium. Equations (4.23), (4.24), and (4.10) yield a unique approximation for soft- as well as hard- core particles.

5. Scaled-Particle Theory for RSA

In this section we derive the virial theorem for RSA, along with a number of other identities that constrain the behavior of the two-point cavity function $Y(x_1/x_2)$ at small distances. This information is then used to construct a scaled-particle theory for RSA. In this section we will specialize to the case of adsorption of three-dimensional spheres in a volume.

The virial theorem for RSA is readily developed by using the Hamiltonian representation of Section 2. Writing down the virial theorem for the many-body spin system discussed in that section, taking an s -derivative and setting $s \rightarrow 0$ gives

$$\beta p_{RSA} = \rho + \frac{1}{2} \left(\frac{4}{3} \pi a^3 \right) \rho^2 g(a) \quad (5.1)$$

where $g(x)$ is the correlation function for RSA defined in eqn. (3.8). The $g(x)$ is a discontinuous function with a discontinuity at a ; by $g(a)$ we mean $\lim g(x)$ as $x \rightarrow a$ from above. The p_{RSA} is the "excess pressure". The latter quantity has a physical interpretation that is developed in Section 2. That development also implies that the Gibbs-Duhem relation is valid for RSA. If one takes a ρ -derivative of both sides of eqn. (5.1), and uses

the Gibbs-Duhem relation for RSA

$$\frac{d(\beta p)}{d\rho} = 1 - \frac{\rho}{\Phi} \frac{d\Phi}{d\rho} \quad (5.2)$$

on the LHS and eqn. (3.8) on the RHS, the result is

$$\rho \frac{d}{d\rho} \Phi = -\left(\frac{4}{3}\pi a^3\right)Y(a) \quad (5.3)$$

Here we have used translation invariance to write for simplicity $Y(x_1/x_2) = Y(x)$ where $x = |x_2 - x_1|$. Equation (5.3) is the virial theorem for RSA. It can be given a more direct interpretation in terms of geometric probability theory by noting that Φ is a function only of the dimensionless quantity ρa^3 , and using this fact to rewrite the derivative on the LHS of eqn. (5.2)

$$\frac{d}{da} \Phi = -(4\pi a^2)Y(a) \quad (5.4)$$

This equation has the following interpretation: Φ is the probability that a point chosen at random is the center of a cavity of radius a that is free of particle centers. Increasing the diameter of each particle slightly will cause a point to stop satisfying this condition precisely when the cavity drawn around that point first makes contact with a particle. The probability that a circle of radius a drawn about a point chosen at random in a realization of RSA will just satisfy this last condition is precisely given by the RHS of eqn. (5.3).

According to equation (5.3), knowledge of the function $Y(a)$ is equivalent to knowledge of the adsorption rate $\Phi(\rho)$. We parallel the equilibrium scaled-particle theory for the hard sphere system in order to find further constraints on the behavior of the function $Y(a)$.

An identity¹⁷ true for any system containing only hard-particle interactions relates the excess pressure of such a system to the density of particles near a wall. This identity can be written

$$\beta p_{RSA} = \rho Y(\infty) \quad (5.5)$$

We also generalize the adsorption rate Φ : define $p_0(\lambda)$ to be the probability density associated with finding, around a randomly chosen point, a cavity of radius **at least** λ , that is empty of particle centers. An identity for the excess activity of hard-sphere particles then gives

$$p_0(a) = \Phi \quad (5.6)$$

We borrow a basic probabilistic argument from equilibrium scaled-particle theory¹⁷ to give a relation between p_0 and $Y(\lambda)$:

$$-\ln p_0(\lambda) = \rho \int_0^\lambda 4\pi\lambda'^2 Y(\lambda') d\lambda' \quad (5.7)$$

The quantity $p_0(\lambda)$ can be expanded in a Kirkwood-Salsburg series exactly parallel to eqn. (4.2). When this is combined with eqn. (5.7), it gives conditions on $Y(\lambda)$ and its derivatives at $\lambda = a/2$:

$$Y = \frac{1}{1 - (\pi a^3 \rho / 6)} \quad \lambda \leq \frac{a}{2} \quad (5.8)$$

$$\left. \frac{dY}{dx} \right|_{\lambda=a/2} = \frac{\pi a^2 \rho}{[1 - (\pi a^3 \rho / 6)]^2} \quad (5.9)$$

$$\left. \frac{d^2 Y}{dx^2} \right|_{\lambda=a/2} = \frac{4\pi a \rho}{[1 - (\pi a^3 \rho / 6)]^2} + \frac{2\pi^2 a^4 \rho^2}{[1 - (\pi a^3 \rho / 6)]^3} - \frac{8\pi a \rho}{[1 - (\pi a^3 \rho / 6)]} g(a+) \quad (5.10)$$

Note that eqn. (5.10) relates the cavity function to the generic correlation function $g(x)$. The relation (3.8) allows one to eliminate $g(a)$ from these equations and thereby obtain a closed set involving only the function $Y(\lambda)$. Note, however, that the nonlinear nature of equations (3.8) and (5.2) in the unknowns implies that, unlike the scaled-particle theories of equilibrium hard spheres and sphere percolation, the scaled-particle theory of sequential adsorption processes (and of partly quenched systems in general) will be *nonlinear*.

Using the above relations, one develops a scaled-particle theory as follows: the function $Y(\lambda)$ on the interval $[a/2, a]$ is approximated by a low-order polynomial in the variable (a/λ) :

$$Y(\lambda) = \sum_{n=1} A_n \left(\frac{a}{\lambda}\right)^n \quad (5.11)$$

The coefficients $\{A_n\}$ are then determined as functions of the density using some subset of the relations (5.2-3), (5.5), (5.8) and (5.9-10). We illustrate this by developing a low-order scaled-particle theory of this kind. We take $n = 3$ in equation (5.11), and use the constraint equations (5.2-3), (5.5), and (5.8). Substituting the expansion (5.11) into the virial theorem for RSA, equation (5.3), gives

$$\eta \frac{d}{d\eta} \Phi = -\eta [A_0 + A_1 + A_3] \quad (5.12)$$

where η , the dimensionless density, is given by $\eta = \frac{\pi}{6} \rho a^3$. Φ can be expressed in terms of the $\{A_n\}$ using the Gibbs-Duhem relation for RSA, equation (5.2). This gives

$$\Phi = \frac{-8[A_0 + A_1 + A_3]}{1 - A_0 - \eta(d/d\eta)A_0} \quad (5.13)$$

The boundary conditions (5.8) and (5.9) can be used to eliminate A_1 and A_3

$$A_1 = \frac{1}{8} [6C_1 + C_2 - 6A_0] \quad (5.14)$$

$$A_3 = \frac{1}{32} [2A_0 - 2C_1 - C_2] \quad (5.15)$$

Here we have used C_1 and C_2 as abbreviations for the constants on the RHS of equations (5.8) and (5.9), respectively. Equation (5.12) then becomes a second-order, nonlinear differential equation in η for the quantity A_0 . Numerical solution of this equation gives the behavior shown in Figure 1. The adsorption rate Φ , as given by this theory, is a rapidly but smoothly increasing function of the density η . Unfortunately, at this level of approximation, the theory does not yet show a singularity corresponding to the jamming density. It remains to be seen whether higher-order approximations of this kind can capture this singularity.

6. Conclusions

RSA is a limiting case of a many-body Hamiltonian system. Using this fact, one can construct a complete liquid-state theory for it. We have defined the basic types

of correlation function needed for an analysis of the structure of RSA. These satisfy a Kirkwood-Salsburg hierarchy of integral equations. We give several closures of this hierarchy which result in integral equations for the two-point correlation function. We also give a zero-separation theorem, a virial theorem, and other exact constraints on any approximate theory of RSA. These are used to provide the basis for a scaled-particle theory.

The purely geometric aspects of sequential adsorption, i.e., those imposed by the excluded-volume effect, have been explored previously. Here we provide a basic extension of the class of models that can be treated to include continuous potentials between adsorbing particles. We can thus treat at arbitrary temperature models that were previously accessible only at zero temperature. For example, the sequential adsorption of charged colloidal particles requires the inclusion of both short-range attractive forces and long-range Coulomb forces.

Recently, a new description of the continuum spin glass has been developed by combining methods for treating partly quenched systems with methods for treating chemical association. As we have described in a previous publication, a similar combination of techniques will allow one to treat the most commonly studied sequential aggregation models, including the Eden model.

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References

- [1] B. Widom, *J. Chem. Phys.* **44**, 3888, (1966)
- [2] J.J. Gonzalez, P.C. Hemmer, and J.S. Høye, *J. Chem. Phys.* **3**, 228 (1974)
- [3] J. Feder, and I. Giaever, *J. Colloid and Interface Sci.* **78**, 144 (1980); E.L. Hinrichsen,

- J. Feder, and T. Jossang, *J. Stat. Phys.* **44**, 793 (1986)
- [4] Y. Pomeau, *J. Phys.* **A13**, L193 (1980)
- [5] R. Swendsen, *Phys. Rev.* **A24**, 504 (1981)
- [6] J. Schaaf and J. Talbot, *Phys. Rev. Lett.* **62**, 175 (1989); *J. Chem. Phys.* **91**, 4401 (1989)
- [7] R.L. Dickman, J.S. Wang, and I. Jensen, "Random Sequential Adsorption: Series and Virial Expansions", *J. Chem. Phys.* **94** (1991)
- [8] B.S. Brosilow, R.M. Ziff, and R.D. Vigil, *Phys. Rev.* **A43**, (1991)
- [9] V. Privman, J.S. Wang, P. Nielaba, *Phys. Rev.* **B43**, 3366 (1991)
- [10] P. Meakin, J.L. Cardy, E. Loh, and D.J. Scalapino, *J. Chem. Phys.* **86**, 2380 (1987)
- [11] J.W. Evans, and R.S. Nord, *J. Stat. Phys.* **38**, 681 (1985); J.W. Evans, *P.R. Lett.* **62**, 2642 (1989)
- [12] G. Tarjus, P. Schaaf, and J. Talbot, *J. Stat. Phys.* **63**, 167 (1991)
- [13] J.A. Given, *Phys. Rev. A* **45**, 816 (1992)
- [14] J. Talbot, P. Schaaf, and G. Tarjus, *Mol. Phys.* **72**, 1397 (1991); P. Schaaf and J. Talbot, *Phys. Rev. Lett* **62**, 175 (1990)
- [15] L. Boltzmann, *Lectures Gas Theory*, University of California Press, Berkely, 1964
- [16] G. Stell, "Mayer-Montroll Equations (and Some Variants) Through History for Fun and Profit", in *The Wonderful World of Stochastics*, ed. by M.F. Schlesinger and G.H. Weiss (North Holland, Amsterdam, 1985)
- [17] H. Reiss, H.L. Frisch and J.L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959)
- [18] J.G. Kirkwood and Z.W. Salsburg, *Disc. Faraday Soc.* **15**, 28 (1953)
- [19] S. Torquato and G. Stell, *J. Chem. Phys.* **77**, 2071 (1982); **78**, 3062 (1983)
- [20] J.A. Given and G. Stell, *J. Chem. Phys.* **92**, 4433 (1990); J. A. Given and G. Stell, *J. Stat. Phys.* **59**, 981 (1990)
- [21] J.A. Given, *J. Chem. Phys.* **96**, 2287 (1992)
- [22] W.A. Madden and E.D. Glandt, *J. Stat. Phys.* **51**, 537 (1988)

- [23] J.A. Given and G. Stell, SUNY CEAS Report # 636, September 1992. To appear in Vol. 8 of the Condensed Matter Theories Series (Plenum Press, N.Y., 1993)
- [24] J.A. Given and G. Stell, J. Chem. Phys. **97**, 4573 (1992)
- [25] J.A. Given and G. Stell (to appear)
- [26] G. Stell, in *Equilibrium Theory of Classical Fluids*, ed. by H. Frisch and J. Lebowitz, (W.A. Benjamin, N.Y., 1964)
- [27] L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949)
- [28] See e.g. P.A. Rikvold and G. Stell, Chem. Engr. Comm. **51**, 233 (1987) and references. (polydisperse)
- [29] *Statistical Mechanics*, T.L. Hill, (McGraw Hill, New York, 1956)
- [30] R.H. Swendsen and W. Klein, Phys. Rev. A **13**, 872 (1976)