

SUNY CEAS Report # 636, September 1992

LIQUID-STATE THEORY FOR SOME NON-EQUILIBRIUM PROCESSES

James A. Given and George Stell

Department of Chemistry
State University of New York at Stony Brook
Stony Brook, New York 11794-3400

ABSTRACT

Recent advances in liquid-state theory permit the calculation of thermodynamic quantities and correlation functions for systems in which some of the degrees of freedom are quenched, or frozen in place, while the rest are annealed. Basic examples include models for fluids in porous media, crystals containing quenched impurities, and spin glasses. We further extend these methods to treat materials constructed in layers, each layer being added to the system and allowed to equilibrate, then frozen in place before the next layer is added. We discuss sequentially adsorbed systems as an important class of examples.

INTRODUCTION

Amorphous matter is ubiquitous in nature.¹ Indeed, if an amorphous system is defined as a system lacking long-range positional order of its particles, but possibly with ordering among the other degrees of freedom that characterize a particle, then matter generically is amorphous, and the ordered solid-state is seen to be rather specialized! Under such a definition, amorphous systems include complex biological fluids, such as blood and milk, complex construction materials, such as cement and plastics, and even solid-state materials such as glasses and amorphous alloys. Research in recent years²⁻⁸ has shown that one can extend to the general category of amorphous materials the techniques developed during the past several decades to study the properties of simple, equilibrated fluids. These techniques include virial expansions for the bulk properties, integral equations for the correlation functions, and sequences of upper and lower bounds for all of these objects.

Extension of equilibrium liquid-state methods to a general class of disordered materials presents one immediate problem: one can no longer assume the positions of particles are determined by the same equilibrium distribution as the other degrees of freedom characterizing those particles. Attempts to extend liquid-state methods to disordered or partly quenched systems⁴⁻¹⁰ must confront the fact that expressions for the free energy and correlation functions of such systems are not in the form familiar from

equilibrium statistical mechanics, that is, a single average over states of the system, with each state weighted by its Boltzmann weight. Rather the free energy and correlation functions take the form of double averages: one first calculates these quantities by averaging over all values of the annealed degrees of freedom, keeping the quenched degrees of freedom constant.⁶ The quantities thus obtained are then averaged over all values of the quenched degrees of freedom. In this paper we will discuss a recently developed approach to this problem, namely the "liquid-state" version of the replica method. This method allows us to rewrite the double averages just described, as single averages of a type familiar from equilibrium statistical mechanics. We shall also discuss a complementary approach that is an extension of a very old method first used by Boltzmann¹¹ in treating equilibrium problems. This second method yields a set of Kirkwood-Salsburg equations that facilitate the exploration of rigorous results. This approach also yields a class of approximate integral equations for the pair distribution function.

The replica method was originally developed to treat model systems on a lattice¹² in which the exchange interaction strengths between lattice sites were chosen from a fixed random distribution. It involved integrating out the random exchange interactions to yield a non-random effective interaction between sites. The liquid-state replica method,^{4,5,9} on the other hand, is applied to systems in which some of the particles have been quenched or frozen in position with a distribution corresponding to a different temperature, and a different pairwise interaction, from that characterizing the other particles in the system. Application of the replica method to liquid-state systems, rather than averaging out the quenched degrees of freedom, places all degrees of freedom on an equal footing by mapping a partly quenched system onto a limiting case of a fully equilibrated system, to be called the replicated system. The replica method, when applied to a partly quenched system, thus "erases" the distinction between quenched and annealed particles, allowing us to deal with a fully equilibrated system containing both kinds of particles. The standard machinery of equilibrium liquid-state theory can then be applied to this replicated system.

Of course, not all spatially disordered system can be simply idealized in the way just described, as a mixture of two fractions of particles, one of them "quenched" and one "annealed." However, many systems, both of practical and theoretical interest, can be described as being constructed in layers,⁴ which are added successively to the system volume, each being brought into an equilibrium with the layers already present, then quenched in place, before the next layer is added. We emphasize that each layer of particles may have its own effective pairwise interaction, and its own effective temperature.¹³ The liquid-state replica method can be applied repeatedly to such a layered system, each time "erasing" one of the boundaries between layers, until a fully equilibrated system results. Disordered systems that accord with the picture just described include Eden clusters, diffusion-limited aggregates,¹⁴ chemical reaction models,¹⁵ porous materials,¹⁶ sequential adsorption processes,^{4,17,18} and sequential polymerization.⁵ The description along these lines, of certain irregular porous materials such as Berea sandstones,^{14,16} also relies on a picture of successive aggregation. As can be seen from the description of the "layering" common to the formation of all the systems we can conveniently describe by replication, an absence of development in time of the structure of the system, once it is formed, is also a common feature, despite the nonequilibrium character of such systems. In this sense, such systems are all "preparation procedure" and no "dynamics".¹⁹

In this paper, we will describe the continuum replica method and develop the effective equilibrium picture that results from applying it to a two-layer system. We extend this scheme in two directions. First, we use chemical-association techniques to apply our method to a model spin glass, in which the quenched and annealed degrees of freedom belong to the same set of particles. Second, we sketch the features of a model in which each particle is a separate layer, namely the class of sequentially adsorbed systems. For the case of sequential adsorption, we shall also introduce the Kirkwood-Salsburg equations to illustrate some of the features those equations that

are common to both equilibrated and non-equilibrated systems, as well as the way the features that differentiate such systems from one another appear in the Kirkwood-Salsburg equations.

LIQUID-STATE THEORY FOR PARTLY QUENCHED SYSTEMS

In this section we develop the liquid state replica method⁴ in its most natural setting, namely a system in which some of the particles are quenched or frozen in place and the others are annealed, or allowed to equilibrate. The result of applying this method is to map a partly quenched system onto a limiting case of a fully equilibrated system with additional "replicated" degrees of freedom. This mapping in turn yields Mayer expansions for the free energy and correlation functions of partly quenched systems. It also yields a set of integral equations, the replica Ornstein-Zernike (ROZ) equations, satisfied by the correlation functions.

We consider then a mixture of two species, one quenched and one annealed, which we denote species '0' and species '1', respectively. Species 0 particles are quenched in place with the spatial correlations corresponding to a temperature T and pairwise interaction $v_{00}(ij)$. Species-1 particles have pairwise interactions $v_{10}(ij)$, $v_{11}(ij)$ with the quenched particles and with each other, respectively. Here the arguments i and j represent the configurations of the particles labelled i and j . The average free energy of our two-species system is

$$-\beta F = \ln Z_{TOTAL} = \frac{1}{Z'} \int e^{-\beta H_{00}} \ln Z_1 d\vec{0} \quad (2.1)$$

with

$$Z' \equiv \int e^{-\beta H_{00}} d\vec{0} \quad (2.2)$$

and

$$Z_1 \equiv \int e^{-\beta [H_{01} + H_{11}]} d\vec{1} \quad (2.3)$$

Here we write H_{ij} for the sum of all pairwise interactions between particles of species i and species j . Also, we write $d\vec{0}$, $d\vec{1}$, to represent integration over all the positions of particles of species 0 and 1, respectively. The average in (2.1) is difficult to treat analytically because of the presence, under the integral sign, of the logarithm. We thus make use of the replica trick, which consists of replacing the logarithm with an exponential by using the identity

$$\ln Z \equiv \lim_{n \rightarrow 0} \frac{1}{n} [Z^n - 1] \quad (2.4)$$

Substituting (2.4) into (2.1) gives, for the total partition function

$$\ln Z_{TOTAL} = \lim_{n \rightarrow 0} \frac{1}{n} \int \left\{ \exp \left[-\beta \sum_{i=1}^n [H_{01}^{(i)} + H_{11}^{(i)}] \right] - 1 \right\} \exp[-\beta H_{00}] \{d\vec{1}\} d\vec{0} \quad (2.5)$$

The variables describing species 1 have been replicated and now appear in n copies, in accordance with (2.4). The notation $\{d\vec{1}\}$ indicates an integration over the n sets of position variables corresponding to these particles.

We first note that the expression on the RHS of (2.5) is, in fact, a limiting case of the equilibrium partition function for a particular system, namely the system with Hamiltonian

$$H = \sum_{\langle i,j \rangle} v_{00}(x_{ij}) + \sum_{\alpha=1}^n \sum_{\langle i,j \rangle} v_{0\alpha}(x_{ij}) + \sum_{\alpha,\beta=1}^n \sum_{\langle i,j \rangle} v_{\alpha\beta}(x_{i,j}) \delta_{\alpha\beta} \quad (2.6)$$

This system is a mixture of a one-component fluid (the quenched species) with an n -component fluid, given by n identical copies or replicas of the annealed species. Each pair of particles has the same pairwise interaction in this replicated system as in the partly quenched model from which it was derived **except that a pair of annealed particles from different replicas has no interaction** (because of the Kronecker delta $\delta_{\alpha\beta}$ in the last term on the RHS). Thus the system of type 0 particles, i.e., the original quenched phase, can be thought of as a “solvent” which mediates interactions between the different type 1 components. This analogy is apt in the sense that a quenched phase, like a solvent, can induce effective interactions that are both long-range and many-body.

We now find it conceptually useful to again recast the problem, describing the n -replica fluid of type 1 particles as being instead a one-component fluid whose particles have a discrete internal degree of freedom which we call ‘spin’. The spin of a type 1 particle i , which we write σ_i , is just another name for what we previously called its replica index. The conceptual change here is the reverse of that originally used by Onsager²⁰ in his treatment of liquid crystals: Onsager treated molecules with different orientations as members of different species; we are treating particles from different replicas as members of a single species differing only by values of a fictitious internal coordinate. This description is equivalent to the original one, in which the number of particles in each replica was held constant, because we work in the grand canonical ensemble.

Thus in considering Mayer expansions for the properties of this system, each internal vertex, or root point, associated with a type 1 particle will be accompanied by both a spatial integration over its position and a summation over its spin state. Also, because of the spin-dependence of the last term in the Hamiltonian (2.6), each pair of root points of type 1 that are connected by a Mayer bond must be in the same spin state.

We pause to comment upon the peculiar spin-dependent potential, given by the last term in eqn. (2.6), which acts between pairs of type 1 particles; we have previously^{2-4,21-23} described this as a generalized Widom-Rowlinson interaction. The original Widom-Rowlinson model was introduced as a model of phase separation;²¹ it involved a mixture of particles of two different species (or ‘spin states’) with a repulsive interaction between particles in **different** species. However, n -species generalizations such as that used here occur frequently in the theory of random media.^{24,25} They are actually continuum generalizations of the ferromagnetic Potts model.²² A basic insight of the work described here is that the continuum version of the well-studied replica method, used for treating many quenched random systems, falls within the same framework. It is a limiting case of an **anti-Widom Rowlinson model**, so-called because repulsive interactions are present between particles in the same species, rather than those in different species. This model is a continuum generalization of the **anti-ferromagnetic** Potts model. The intriguing notion suggested by these mappings, namely that there are two basically different kinds of models for randomly disordered materials, is still under study. It is also important to note that both of these well-studied classes of non-equilibrium systems are isomorphic to Hamiltonian models with pair interactions that define **non-additive** particle diameters; this is seen to be a general trait of such systems.

Here we note that the quenched two-phase system discussed in this section is the $n \rightarrow 0$ limit of the mixture just described, in the sense implied by eqn. (2.5). This relation provides explicit formulae for the coefficients in the virial expansions of the basic physical quantities. The Kronecker delta occurring in the interaction (2.6) ensures that any pair of species-1 particles connected by a Mayer bond must be in the same spin state. Since each group of such particles in a Mayer graph that are connected by bonds into a cluster will be weighted by a factor of n by the summation over spin states, the only graphs making a non-zero contribution in the $n \rightarrow 0$ limit will be those having all the species-1 particles connected directly or indirectly by Mayer bonds. By a similar argument, the graphs contributing to the correlation functions are precisely

those in which each species-1 particle is connected, directly or indirectly, to a root point by a chain of Mayer bonds passing only through species-1 particles.

The lowest-order example of such functions is the density, for which the corresponding Mayer graphs are those with a single root point. A set of Ornstein-Zernike equations has been developed⁹ by exploiting the description just given for the structure of the Mayer graphs that contribute to the correlation functions.

We can derive these equations, called the replica Ornstein-Zernike (ROZ) equations⁹ satisfied by the correlation functions of a partly quenched system. To do this, we write down the OZ equations for the replicated $(n+1)$ -species system with Hamiltonian (2.6), isolate the n -dependence of these equations (by grouping together identical terms), and take the $n \rightarrow 0$ limit. The resulting ROZ equations are:

$$h^{00} = c^{00} + \rho c^{00} \otimes h^{00} \quad (2.7)$$

$$h^{01} = c^{01} + \rho c^{00} \otimes h^{01} + \rho c^{01} \otimes h^{11} - \rho c^{01} \otimes h^{12} \quad (2.8)$$

$$h^{10} = c^{10} + \rho c^{10} \otimes h^{00} + \rho c^{11} \otimes h^{10} - \rho c^{12} \otimes h^{10} \quad (2.9)$$

$$h^{11} = c^{11} + \rho c^{01} \otimes h^{01} + \rho c^{11} \otimes h^{11} - \rho c^{12} \otimes h^{12} \quad (2.10)$$

$$h^{12} = c^{12} + \rho c^{01} \otimes h^{01} + \rho c^{11} \otimes h^{12} + \rho c^{12} \otimes h^{11} - 2\rho c^{12} \otimes h^{12} \quad (2.11)$$

Here both the superscripts 1 and 2 refer to identical species-1 particles. The notation naturally arises as a result of dealing with replicas of species-1 particles, but is artificial in the limit $n \rightarrow 0$. We shall switch to more natural notation immediately. The symbol \otimes denotes both a spatial convolution and an integral over the spin of the intermediate particle. That is, we have

$$f \otimes g \equiv \int d^3x_2 \frac{d\Omega_2}{\Omega} f(x_1, s_1, x_2, s_2) g(x_2, s_2, x_3, s_3) \quad (2.12)$$

The integral $d\Omega_2$ is over the orientation of the vector spin s_2 . The quantity Ω is a normalizing factor $\Omega = \int d\Omega_2$ which we have extracted from the fugacity of a 'spin'; it turns the integral over spin orientation into an average over this quantity.

We prefer to rewrite the ROZ equations in a way that is more felicitous and moreover emphasizes their graphical structure. To do this, it is useful to identify the function we shall denote here as c_b , which is represented by the subset of c_{11} graphs such that all paths between the two white species-1 vertices pass through at least one ρ_0 -vertex. We further identify the function represented by the corresponding subset of h_{11} graphs as h_b and write

$$c_{11}(12) = c_c(12) + c_b(12) \quad (2.13)$$

$$h_{11}(12) = c_c(12) + h_b(12) \quad (2.14)$$

so that between the two white vertices of every c_c and h_c graph there is at least one unbroken path free of ρ_0 -vertices (the subscripts 'c' and 'b' denote 'connected' and 'blocking', respectively.) We can then rewrite the ROZ equations as

$$h_{00} = c_{00} + c_{00} \rho_0 \otimes h_{00} \quad (2.15)$$

$$h_{10} = c_{10} + \rho_0 c_{10} \otimes h_{00} + \rho_1 c_c \otimes h_{10} \quad (2.16)$$

$$h_{11} = c_{11} + \rho_0 c_{10} \otimes h_{01} + \rho_1 c_c \otimes h_{11} + \rho_1 c_b \otimes h_c \quad (2.17)$$

$$h_c = c_c + \rho_1 c_c \otimes h_c \quad (2.18)$$

where, by symmetry, $c_{01} = c_{10}$ and $h_{01} = h_{10}$.

An alternative equation for h_{01} that can be derived from using (2.12-13) in (2.19) is

$$h_{01} = c_{01} + \rho_0 c_{00} \otimes h_{01} + \rho_1 c_{01} \otimes h_c. \quad (2.19)$$

When c_{00} , c_{01} , c_{11} , c_c and the $\{\rho_i\}$ are prescribed, (2.15-18) are a closed set of equations for h_{00} , h_{01} , h_{11} , and h_c . For some $v_{\alpha\beta}$ a reasonable approximation in the ROZ equations is given by the assumption

$$c_b(12) = 0. \quad (2.20)$$

This approximation is implied by the Percus-Yevick (PY) closure, as well as the mean-spherical approximation (MSA) closure. We shall refer to the approximation (2.20) as the Madden-Glandt (MG) approximation. There is a class of approximate closures of the ROZ equations that imply $c_b(x) = 0$; within the context of such a closure the Madden-Glandt approximation is exact. This class of closures includes the Percus Yevick (PY) closure, $c_{ij} = f_{ij} y_{ij}$, where f_{ij} is the Mayer function, and the cavity function y_{ij} is defined by the equation

$$h_{ij} + 1 \equiv (f_{ij} + 1)y_{ij} \quad (2.21)$$

It also includes the mean-spherical approximation,

$$h_{ij} = -1, \quad x_{ij} < R_{ij} \quad (2.22)$$

$$c_{ij} = \beta v_{ij}, \quad x_{ij} > R_{ij} \quad (2.23)$$

Here v_{ij} is the pair potential, x_{ij} is the distance between particle centers and R_{ij} is the average of hard core diameters. However, the hypernetted chain (HNC) approximation is not among this class of closures.

A fundamental fact about the MG approximation is this: in a sense to be made precise, the only difference between the MG OZ equations and the equilibrium OZ equations is in the quenched system input. In a quenched system, the functions h_{00} and c_{00} are supplied "externally", i.e., they are not influenced by the behavior of the annealed degrees of freedom. If we take these functions as input and proceed to solve both the MG OZ equations and the equilibrium OZ equations for the functions h_{01} , h_{11} (using the same closure) the results will be identical. This shows that the MSA (which implies the MG approximation) is "blind" to the difference between partly quenched and annealed systems.

This raises the question: what systems will exhibit appreciable " c_b effects," that is, effects that go beyond the effect of the quenched system input? The discussion above implies that such effects should be most pronounced for partly quenched systems in which the most natural closure lies outside the class discussed above, for which the MG approximation is exact. Specifically, we consider the class of systems in which the quenched species consists of randomly centered particles ($f_{00} = 0$, ρ_0 spatially uniform) that freely overlap each other but are impenetrable to the annealed particles. Such a partly quenched system gives a natural model for a fluid adsorbed in a porous medium, the annealed and quenched particles representing, respectively, the fluid atoms, and the partly overlapping inclusions that make up the porous matrix. For this system, one can calculate c_b exactly in the limit $\rho_1 \rightarrow 0$ by summing the Mayer graphs that contribute to this quantity. Such Mayer graphs consist of two or more ρ_1 -vertices, each connected to both of the root points. The sum of such graphs is easily obtained. It is

$$c_b(12) = \exp[\rho_0 O^\circ] - 1 - \rho_0 O^\circ \quad (2.24)$$

where $O^\circ(12)$ is the "overlap volume" integral

$$O^\circ(12) = \int d3 f_{10}(13) f_{01}(32) \quad (2.25)$$

Physically, this contribution to c_b represents an effective attraction among the annealed particles due to the presence of the inclusions that make up the porous matrix; this effect is substantial for large matrix particles, especially at low density of adsorbed fluid, for the intermediate to high densities of matrix inclusions that characterize many microporous materials. (We note that the HNC closure for c_{11} is exact whenever (2.24) is.)

We are now studying simulations of such a porous medium. For low fluid density but moderate matrix density, the approximation given by (2.24) is superior to the MG approximation. However, both approximations underestimate the contact values of correlation functions. At higher fluid particle densities, the two approximations become very similar. For a more general class of matrix particles we are further investigating a reference-system closure, in which the reference system is the pure species-0 system into which a single pair of species-1 particles are inserted. We represent the direct correlation function c_{ij} as follows:

$$c_{ij} = f_{ij}y_{ij} + d_{ij} \quad (2.26)$$

The function d_{11} is zero in the PY approximation. We note that this function contains all the terms in c_b because, by definition, it contains all the terms in c_{11} that lack a Mayer bond between the roots and all contributions to c_b , by definition, have this property. Approximating c_b by the reference-system d_{11} appears especially promising for hard-sphere interactions among matrix particles.

Another limit in which (2.24) gives an exact result for $c_{11}(x)$ is that of an ideal fluid of noninteracting atoms, again adsorbed in a rigid matrix of freely overlapping inclusions. In this case we also have $c_{11} = c_{12}$, $c_{01} = f_{01}$, (with f_{01} the Mayer bond) and $c_{00} = 0$. This is the quenched-annealed version of the Widom-Rowlinson model.

SPIN GLASS

We consider¹⁰ each atom in a spin glass²⁵ to be a tightly associated pair of "pseudoatoms", one of which we call a 'spin', the other of which we call an 'atom'. We will relax the association between these pseudoatoms, use the replica method described in Section 2 to write the free energy and correlation functions of the spin glass in terms of the corresponding quantities for an equilibrium mixture of particles, then impose the constraint of complete association.

The interaction $v_{11}(ij)$ between a pair of spins i and j is taken to be the sum of a classical Heisenberg interaction and a spin-independent excluded-volume interaction (taken here to be of hard-sphere type):

$$v_{11}(ij) = v_{HS}(x_{ij}) + J(x_{ij})(\vec{s}_i \cdot \vec{s}_j) \quad (3.1)$$

where the dot product between the vector spins located at atoms i and j is multiplied by the separation-dependent exchange coupling $J(x_{ij})$. In many materials a reasonable form for $J(x)$ is provided by the sinusoidally modulated Yukawa coupling

$$J(x) = \frac{\exp[-\kappa x]}{x^p} \sin(\alpha x + \theta) \quad (3.2)$$

The interatomic interaction $v_{00}(x)$ is taken to be hard-core at short range; the long-range tail $v_{LR}(x)$ can be left arbitrary

$$v_{00}(x_{ij}) = v_{LR}(x_{ij}) + v_{HS}(x_{ij}) \quad (3.3)$$

Finally, the interaction v_{01} is taken to be an extremely strong, short-range attractive force binding a spin to the center of an atom. The presence of a hard-core

component in both the spin-spin and atom-atom potentials ensures that no complexes containing more than one atom and one spin may form.

The continuum replica method provides an explicit mapping of the spin glass onto a limiting case of an equilibrium Hamiltonian system, to be called the replicated system. Specifically, this is an $(n + 1)$ -species mixture, consisting of one copy of the quenched species, i.e., of the atoms, together with n copies of the annealed species, i.e., the spins. Here quenched and annealed particles have the same pairwise interactions that they have in the partly quenched system being studied, **except** that annealed particles from different replicas do not interact. In the complete association limit, the replicated system is entirely composed of tightly bound complexes, each consisting of an atom, together with one spin from **each** of the replicas.

We discuss two complementary approaches to developing integral equations for the correlation functions of the spin glass. The first is a version, for partly quenched systems, of the RISM approximation.^{26,27} It has the advantage of simplicity, and aids both intuition (in the formation of closures) and the process of numerical solution. It has the disadvantage of not providing a direct correlation function that can be expressed as a resummation of Mayer perturbation theory, i.e., of not being "proper," in the language of interaction site theory.^{28,29} The second approach remedies that difficulty; it uses the chemical association³⁰ formalism of Wertheim^{31,32} to develop a set of four coupled integral equations for the different terms contributing to h_{11} . The theory involves four direct correlation functions that correspond to these terms.

We first develop a RISM-like equation for the spin glass. It is natural to use site-site notation, with subscripts '0' and '1' for sites that are atoms and spins, respectively. The site-site formalism allows us to treat atoms and spins as separate particles, eg., for the purpose of applying the replica method, and yet be able to separate out the delta-function contributions to correlation functions from spins and atoms that are bound together. It is thus natural to use the SSOZ equations for spin glass correlation functions. However, because of the high degree of symmetry possessed by the Heisenberg spin glass, the distinction between the OZ and SSOZ equations will not be important here. This is discussed below.

It is useful to write for any pair correlation function $a(12)$

$$a(12) = \bar{a}(12) + \tilde{a}(12) \quad (3.4)$$

where $\bar{a}(12)$ is an average over the orientation Ω_i of both particles

$$\bar{a}(12) = \int a(12) d\Omega_1 d\Omega_2 / \Omega^2, \Omega = \int d\Omega_i \quad (3.5)$$

In the complete association limit, the positions of atoms and spins must coincide. Thus, we have for a general interaction

$$\bar{h}_{11} = \bar{h}_{10} = h_{00} \quad (3.6)$$

Also, for interactions having the symmetry of the Heisenberg interaction, we have

$$\tilde{h}_{10} = \tilde{h}_b = 0 \quad (3.7)$$

where our notation is the same as in (2.15-2.18).

Using eqns. (3.6-7) in eqn. (2.17), we can write a simple Ornstein-Zernike (OZ) equation for \tilde{h}_{11}

$$\tilde{h}_{11} = \tilde{c}_{11} + \rho \tilde{c}_{11} \otimes \tilde{h}_{11} \quad (3.8)$$

Adding eqns. (3.6) and (2.7) gives an OZ equation for $h(12)$ itself,

$$h = c + \rho c \otimes h, \quad (3.9)$$

where $h = h_{00} + \tilde{h}_{11}$ and $c \equiv c_{00} + \tilde{c}_{11}$. It follows that in the mean-spherical approximation, the spin-spin correlation function for a spin fluid and a spin glass are identical,

assuming the two have identical atom-atom correlation functions. This was surmised in [33].

Appropriate closures of PY and HNC (hypernetted chain) type for the spin glass³³ have been developed. We do not derive these here, but simply present two simple examples. For the PY-type closure one has

$$\tilde{c} = f(g - c) - \overline{f(g - c)} \quad (3.10)$$

where $g = h + 1$. For long-range $J(x_{ij})$, one might expect the analogous HNC-type closure to prove more accurate. This is given by

$$\tilde{c} = h - \ln y - \overline{(h - \ln y)} \quad (3.11)$$

where $g = (f + 1)y$.

In order to extend this treatment in a systematic manner, it is important to develop a proper integral-equation treatment of the spin glass. This involves classifying the Mayer graphs that contribute to h_{11} into four types, according to whether they have neither, one, or both of the root points (representing spins) in such a graph connected directly to type 0 vertices (representing atoms.) The corresponding decomposition of h_{11} is

$$h_{11} = h_{11}^{00} + h_{11}^{01} + h_{11}^{10} + h_{11}^{11}. \quad (3.12)$$

The quantities $\{h_{11}^{ij}\}$ obey a coupled set of OZ equations which generalize (3.8)

$$\tilde{h}_{11}^{ij} = \tilde{c}_{11}^{ij} + \tilde{c}_{11}^{ik} \otimes \rho^{kl} \tilde{h}_{11}^{lj}. \quad (3.13)$$

Here we have $\rho^{00} = \rho^{01} = \rho^{10} = \rho$ and $\rho^{11} = 0$.

SEQUENTIAL ADSORPTION PROCESSES

The adsorption of large molecules and molecular aggregates, such as polymers, colloids, and proteins, to 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)**.¹⁸ 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. This is the simplest RSA model. We generalize this model in two ways: first, by allowing a longer-range potential interaction between particles; second, by allowing for a finite probability of rearrangement. The former generalization is a natural way to allow the adsorption of charged particles; the latter gives a model that smoothly interpolates between an equilibrium hard-sphere system and a sequential adsorption system. As described in the Introduction, we can develop liquid-state theory for this process by viewing it as an extreme case of a system constructed in layers: here, each particle constitutes a separate component or layer, and the graphical rules developed in Section 2 for the two-layer system must be generalized.⁴ Some reflection shows that we get prescriptions for the graphs contributing to both the free energy and the correlation functions if we replace the term "annealed path" in the prescriptions for the two-layer system by the term "uphill path", where 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 successive particles are given species labels in the order in which they are introduced.)

We map the general RSA model just described onto a Hamiltonian system. Consider a system of particles bearing spins σ_i which can take any of n discrete values, such that particles i and j , $i < j$, have interaction

$$V_{ij}(x) = v(x)\delta_{\sigma_i,1} + \phi(x) \quad (4.1)$$

We consider this system to be a multi-species mixture, with each particle belonging to a distinct "species" labelled by its particle number. In the $n \rightarrow 0$ limit, the thermodynamic quantities of this model become the basic physical quantities that describe RSA. For example, we have the formulas for the adsorption rate Φ :

$$\Phi = \lim_{n \rightarrow 0} \frac{\rho}{z} \quad (4.2)$$

with z the fugacity and ρ the density of the mixture (4.1).

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 (4.1) is zero, the interaction 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.

We have two paths that lead to integral equations for the correlation functions in RSA. The first is to derive the ROZ equations by using the Hamiltonian mapping defined by eqn. (4.1). The second is to write the Kirkwood-Salsburg hierarchy for this process, again using the Hamiltonian (4.1), and then to expand in a functional Taylor series the left-hand side of the second of the hierarchy around the lhs of the first. We will sketch both approaches.

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 $n \rightarrow 0$ 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:

$$g_{ij}^{11}(x) \rightarrow_{n \rightarrow 0} g_{ij}(x) \equiv g_{ij}^b(x) + g_{ij}^c(x) \quad (4.3)$$

$$g_{ij}^{i1}(x) \rightarrow_{n \rightarrow 0} g_{ij}^b(x) \quad (4.4)$$

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 (4.1): it consists of all labelled, two-rooted graphs satisfying the uphill constraint. 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. Combining eqns. (4.3) and (4.4) gives

$$[g_{ij}^{11}(x) - g_{ij}^{i1}(x)] \rightarrow_{n \rightarrow 0} g_{ij}^c(x) \quad (4.5)$$

This function occurs in the topological reduction of the Mayer expansion.

By virtue of the isomorphism we establish onto the many body system defined by the Hamiltonian (4.1), 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,²³ 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

$$\rho_i = i/V \quad (4.6)$$

In the thermodynamic limit, each intermediate summation 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

$$g_{ij}(x, \rho) = g_{ij}(x, \rho_j) \quad (4.7)$$

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

The ROZ equations satisfied by the functions $h_{ij}^b \equiv g_{ij}^b - 1$ and $h_{ij}^c \equiv g_{ij}^c - 1$ can be obtained by writing down the Ornstein-Zernike equations for the correlation functions of a polydisperse system with pairwise interaction (4.1), and taking the RSA limit $n \rightarrow 0$. We rewrite these immediately in terms of the definitions (4.3 - 4.5):

$$h_{ij}^c = c_{ij}^c + \int_{\rho_i}^{\rho_j} [c_{ik}^c \otimes h_{kj}^c] \quad (4.8)$$

$$h_{ij}^b = c_{ij}^b + \int_0^{\rho_i} [c_{ki}^c \otimes h_{kj}^c + c_{ki}^c \otimes h_{kj}^b + c_{ki}^b \otimes h_{kj}^c] d\rho_k + \int_{\rho_i}^{\rho_j} [c_{ik}^b \otimes h_{kj}^c] d\rho_k \quad (4.9)$$

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).

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,¹¹ 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 Salsburg considered the full series of the Φ_n for arbitrary pair potentials in an equilibrated system.

$$\Phi_n(x_1; x_2 \dots x_n) = e_n(x_1; x_2 \dots x_n) \sum_{s=0}^{\infty} \frac{1}{s!} \int dx_{n+1} \dots dx_{n+s} \prod_{i=1}^n f(x_i x_{n+s}) \rho_{n+s-1}(x_2 \dots x_{n+s}) \quad (4.10)$$

Here

$$e_n(x_1; x_2 \dots x_n) = \prod_{i=2}^n [1 + f(x_1 x_i)] \quad (4.11)$$

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

$$\frac{\rho_n(x_1 \dots x_n)}{\rho_1(x_1)} = \frac{\Phi_n(x_1; x_2 \dots x_n)}{\Phi_1(x_1)} \quad (4.12)$$

as the closure of (4.10). In the spatially uniform case this reduces to

$$\rho_n(x_1 \dots x_n)/\rho = \Phi_n(x_1; x_2 \dots x_n)/\Phi_n \quad (4.13)$$

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

$$\frac{\partial \rho_n(x_1 \dots x_n)}{\partial \rho} = \sum_{k=1}^n \Phi_n(x_1; x_1 \dots x_{k-1}, x_{k+1} \dots x_n)/\Phi \quad (4.14)$$

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

$$\Phi_n(x_1; x_2 \dots x_n) = \Psi_n(x_1/x_2 \dots x_n) \rho_{n-1}(x_2 \dots x_n) \quad (4.15)$$

In particular

$$\Psi_2(x_1/x_2) = \Phi_2(x_1; x_2)/\rho_1(x_2) \quad (4.16)$$

and in a uniform system

$$\Psi_2(x_1/x_2)/\Phi = G(x_1/x_2) = G(x_{12}) \quad (4.17)$$

where $G(x_{12})$ is a radial distribution function. In a uniform equilibrium system we would have simply

$$G(x_{12}) = \rho(x_1 x_2) / \rho^2 \quad (4.18)$$

but from (4.14) and (4.17) we have instead

$$2G(x_{12}) = \frac{1}{\rho} \frac{\partial \rho(x_1 x_2)}{\partial \rho} \quad (4.19)$$

or

$$G(x_{12}) = g(x_{12}) + \frac{\rho}{2} \frac{\partial g(x_{12})}{\partial \rho} \quad (4.20)$$

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

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

$$\Phi Y(0) = 1 \quad (4.21)$$

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

$$\rho G(x_1/x_2) = \sum_{i=1}^j \rho_i g_{ij}(x) \quad (4.22)$$

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

$$\rho_j G(x_1/x_2, \rho_j) = \int_0^{\rho_j} g_{mj}(x_1, x_2, \rho_m, \rho_j) d\rho_m \quad (4.23)$$

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

$$\begin{aligned} \rho^2 g(x_1, x_2) &= \sum_{j=1}^{N-1} \rho_j [G(x_1/x_2, \rho_j) + G(x_2/x_1, \rho_j)] \\ &= \sum_{i,j=1}^{N-1} \rho_i \rho_j g_{ij}(x_1, x_2, \rho_i, \rho_j) \end{aligned} \quad (4.24)$$

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

$$\rho^2 g(x_1, x_2) = \int_0^{\rho} [G(x_1/x_2, \rho_i) + G(x_2/x_1, \rho_i)] d\rho_i \quad (4.25)$$

From (4.10) 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 .

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 $V A_n$, where

$$A_n(x_1/x_2 \dots x_n) = \frac{\Psi_n(x_1/x_2 \dots x_n)}{e_n(x_1; x_2 \dots x_n)} \quad (4.26)$$

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

$$A_1(x_1/x_2) = \Phi Y(x_{12}) \quad (4.27)$$

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

$$\begin{aligned} A_1(x_1/x_2) &= \Phi_1(x_1) + \int \frac{\delta\Phi_1(x_1)}{\delta\rho(x_3)} [\rho(x_3x_2) - \rho(x_3)] dx_3 \\ &+ \frac{1}{s!} \int \frac{\delta^s\Phi_1(x_1)}{\prod_{i=3}^{s+2} \delta\rho(x_i)} \prod_{i=3}^{s+2} [(\rho(x_ix_2) - \rho(x_i))] dx_i + \dots \end{aligned} \quad (4.28)$$

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

$$\frac{\delta^s c_1(x_1)}{\delta\rho(x_2) \dots \delta\rho(x_{s+1})} = c_{s+1}(x_1; x_2 \dots x_{s+1}) \quad (4.29)$$

Using (4.27) and (4.28), yields, in the uniform case,

$$\begin{aligned} Y(x_{12}) &= 1 + \rho \int c_2(x_1; x_3) h(x_3x_2) dx_3 \\ &+ \frac{\rho^2}{2} \int [c_3(x_1; x_3x_4) - c_2(x_1; x_2)c_2(x_1; x_3)] h(x_3x_2) h(x_4x_2) dx_3 dx_4 \dots \end{aligned} \quad (4.30)$$

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

$$Y(x_{12}) = 1 + \rho \int c_2(x_1; x_3) h(x_3x_2) dx_3 \quad (4.31)$$

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 (4.30) 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

$$c_2(x_1; x_2) = f(x_{12}) [G(x_1/x_2) - c_2(x_1; x_2)] \quad (4.32)$$

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

$$c_2(x_1; x_2) = 0 \quad (4.33)$$

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 (4.31), (4.32), and (4.19) yield a unique approximation for soft- as well as hard- core particles.

CONCLUSIONS

We have developed very general techniques for mapping a class of nonequilibrium

problems into equilibrium statistical mechanics. We are now studying various approximations and closures of the equations presented here. Still before us is the task of incorporating phase-transition behavior³⁴ into our account of systems with quenched disorder.

ACKNOWLEDGMENTS

J.G. is grateful to the National Science Foundation for their support of this work. G.S. gratefully acknowledges financial support from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

REFERENCES

1. G. Stell, A.M.S., Statistical mechanics applied to random-media problems, in: "AMS-SIAM Workshop on Random Media", G. Papanicolaou, ed., New York, AMS, (1991).
2. J.A. Given and G. Stell, Towards a realistic, general, continuum theory of clustering, in: "On Clusters and Clustering: from Atoms to Fractals", P. Reynolds ed., North Holland, New York (1991).
3. B.C. Xu and R.M. Stratt, Liquid theory for band structure in a liquid, *J. Chem. Phys.* 91:5613 (1989).
4. J.A. Given, Liquid-state methods for random media: I. random sequential adsorption, *Phys. Rev. A* 45:816 (1991).
5. J.A. Given, Liquid-state methods for random media: II. spin glasses, *J. Chem. Phys.* 96:2287 (1992).
6. W.A. Madden and E.D. Glandt, Distribution functions for fluids in random media, *J. Stat. Phys.* 51:537 (1988).
7. W.A. Madden, Fluid distributions in random media: arbitrary matrices, *J. Chem. Phys.* 96:5422 (1992).
8. L.A. Fanti, E.D. Glandt, and W.G. Madden, Fluids in equilibrium with disordered porous materials: integral equation theory, *J. Chem. Phys.* 51:537 (1988).
9. J.A. Given and G. Stell, Comment on: fluid distributions in two-phase random media: arbitrary matrices, *J. Chem. Phys.* 96: (to appear, Sept. 1992).
10. J.A. Given and G. Stell, A realistic model for a spin glass, in: "Complex Fluids: MRS Symposium Proceedings", Materials Research Society, Pittsburg, 1991.
11. G. Stell, Mayer-Montroll equations (and some variants) through history for fun and profit, in: "The Wonderful World of Stochastics", M.F. Schlesinger and G.H. Weiss eds., North Holland, Amsterdam (1985).
12. M. Mezard, G. Parisi, and M.A. Virasoro, "Spin Glass Theory and Beyond", World Scientific, Singapore (1987).
13. R. Kraichnan and S.Y. Chen, Is there a statistical mechanics of turbulence?, *Physica D* 37:160 (1989).
14. H.E. Stanley and N. Ostrowsky, "Random Fluctuations and Pattern Growth: Experiments and Models", Kluwer Academic, Norwell MA (1988).
15. K. Kang, S. Redner, P. Meakin, and F. Leyvraz, Long-time crossover phenomena in coagulation kinetics, *Phys. Rev. A* 33:1171 (1986).
16. See e.g. E. Guyon, C.D. Mitescu, J.P. Hulin, and S. Roux, *Physica D* 38:172 (1989).
17. G. Tarjus, P. Schaaf, and J. Talbot, Random sequential addition: a distribution function approach, *J. Stat. Phys.* 63:167 (1991).
18. J.W. Evans, (to appear, *Reviews of Mod. Phys.*).
19. P.L. Garrido, J.L. Lebowitz, C. Maes, and H. Spohn, Long-range correlations for conservative dynamics, *Phys. Rev. A* 42:1954 (1990).

20. L. Onsager, *Ann. N.Y. Acad. Sci.* 51:627 (1949).
21. B. Widom and J.S. Rowlinson, New model for the study of liquid-vapor phase transitions, *J. Chem. Phys.* 52:1670 (1970).
22. J.A. Given and G. Stell, The continuum Potts model and continuum percolation, *Physica A* 161:152 (1989).
23. J.A. Given, I.C. Kim, S. Torquato, and G. Stell, Comparison of analytic and numerical results for the mean cluster density in continuum percolation, *J. Chem. Phys.* 93:5128 (1990).
24. R. Fisch and A.B. Harris, Critical behavior of random resistor networks near the percolation threshold, *Phys. Rev.* B18:416 (1978).
25. K. Binder and A.P. Young, Spin glasses: experimental facts, theoretical concepts and open questions, *Rev. Mod. Phys.* 58:801 (1986).
26. D. Chandler, H.C. Anderson, Optimized cluster expansion for classical fluids III molecular fluids, *J. Chem. Phys.* 57:1930 (1972).
27. D. Chandler and L. Pratt, Statistical mechanics of chemical equilibrium and the intramolecular structure of non-rigid molecules in condensed phases, *J. Chem. Phys.* 65:2925 (1976).
28. P.T. Cummings, G.P. Morriss, and G. Stell, Solution of the site-site Ornstein-Zernike equation for non-ideal dipolar spheres, *J. Phys. Chem.* 86:1696 (1982).
29. L. Pratt, Connection between central-force model treatment of polyatomic molecular liquids and the interaction-site cluster expansion, *Mol. Phys.* 43:1163 (1981).
30. H.C. Andersen, Cluster expansions for hydrogen-bonded fluids II. dense liquids, *J. Chem. Phys.* 61:4985 (1974).
31. M.S. Wertheim, Fluids with highly directional attractive forces IV. equilibrium polymerization, *J. Stat. Phys.* 42:477 (1986).
32. M.S. Wertheim, Integral equation for the Smith-Nezbeda model of associated fluids, *J. Chem. Phys.* 88:1145 (1988).
33. P.T. Cummings and G. Stell, Mean spherical approximation for a model liquid metal potential, *Mol. Phys.* 43:1267 (1981). See Section 4.
34. S.H. Adachi, A.E. Panson, and R.M. Strat, The effect of an unusual type of quenched disorder on phase transitions: illustration in a mixed-valence system, *J. Chem. Phys.* 88:1134 (1988).