PHYSICAL REVIEW A VOLUME 45, NUMBER 2 15 JANUARY 1992

Liquid-state methods for random media: Random sequential adsorption

James A. Given
Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11734

(Received 14 June 1991)

A large number of statistical models of current interest in physics can be characterized as *differentially quenched* systems. They are prepared by successively introducing into a volume one fraction after another of the particles in a many-body system, each successive fraction being equilibrated while all the earlier fractions are kept frozen in place. Examples of current interest include self-avoiding walks, chemical association models, growth models, and models of random sequential adsorption (RSA). In this paper, we develop generalizations of the replica method adequate for calculating the properties of such systems. These are applied to RSA, resulting in both virial series and integral equations for the physical quantities describing this system. We extend the virial series for the adsorption rate to give excellent agreement with simulation results at all densities.

PACS number(s): 05.20.−y

I. INTRODUCTION

This paper is part of an ongoing project [1] of extending the methods of liquid-state physics (integral equations, renormalized perturbation theory, etc.) to apply to continuum systems with quenched disorder. Such systems include engineering composites, porous materials, gels, amorphous materials, spin glasses, etc.

There are two broad classes of goals motivating this research, one of which is practical, the other of which is rooted in fundamentals. From a practical point of view, it is important to have algorithms to calculate the bulk properties of random materials given statistical information about their composition. From a more basic point of view, research has focused on the nature of the continuous transitions, such as the percolation transition and the glass transition, found in quenched random systems. One wants to know whether these transitions display a substantial and computationally powerful resemblance to those found in equilibrium systems near their critical point, or whether the resemblance is limited to superficial analogies based on the occurrence in both of a diverging correlation length. In particular, it has been shown that the spectrum of critical exponents associated with different moments of the order parameter is concave up in thermal critical phenomena and concave down in quenched random materials [2]. Furthermore, at least in two dimensions [2], this behavior can be traced to the existence of an infinity of dangerous irrelevant operators which can greatly complicate the analysis of the asymptotic scaling. This could present major problems to workers trying to incorporate a description of the scaling region into a unified picture of a random system over its entire phase diagram [3]. Clearly, it is important to develop methods for exploring these questions in detail for specific models.

In considering these questions, the present author has noted a property found in a large class of disordered systems, many of which exhibit the anomalous scaling phenomena just mentioned. Specifically, many of these are examples of *differentially quenched* systems. These are defined to be many-body systems prepared by the following procedure: one adds to the system volume a small fraction of the total number of particles in the system, allows them to equilibrate, then quenches or freezes them in place. The next fraction of particles is then added to the system and allowed to equilibrate in the presence of the first fraction added. They are frozen in place before the next fraction is added. Many successive fractions or layers are added to the system in this manner until the desired density is achieved. If each successive fraction is infinitesimal, we will refer to a system prepared in this way as a differentially quenched system.

Using a useful thermal picture, we may think of each successive layer or fraction as being much "hotter" than the "cold" layers already in place. Certainly, this particular physical circumstance gives a realization of the preparation procedure just described. However, the occurrence of differential quenching is not limited to systems supporting a wide variation in local temperature [4]. We readily imagine that external constraints (or internal conservation laws) impose the successive or stepwise equilibration procedure that we denote as a differential quenching. Under these circumstances, the successive fractions of particles may equilibrate at temperatures provided by an arbitrary annealing schedule. For example, each fraction may equilibrate at the same local temperature as, for example, in the case of differentially quenched hard-sphere systems. These will be an important class of the examples we discuss. Also, the initial fraction of particles in a differentially quenched system may be distributed according to an arbitrary nonequilibrium distribution function.

Disordered systems that accord with the picture discussed here [5] include Eden clusters, diffusion-limited aggregates, chemical reaction models [6], porous materials [7], sequential adsorption processes, self-avoiding walks, and turbulent cascades [8]. The description along these lines, of certain irregular porous materials such as Berea sandstones [7], relies on a picture of successive aggregation. Most of the other examples will be discussed either below, or in a companion paper to this one [9]. The latter treats examples which we formulate as Hamiltonian systems by adding certain chemical association techniques to the methods developed here.

We pause to discuss the turbulent cascade, which is not obviously related to the general scenario just sketched. The standard picture of such a cascade [8] is that of a system of eddies with a very large range of characteristic wavelengths or wave numbers. The cascade successively transfers energy, in a roughly local fashion, from eddies corresponding to each decade of wave number to eddies corresponding to smaller wave numbers. Because the effective kinetic energy (or temperature of different eddies) is a rapidly varying function of their wave number (it varies as $k^{-11/3}$), successive decades of wave numbers play the role of successively quenched fractions in the picture drawn above. The turbulent cascade thus has the general structure we have described when considered in wave number space; the Rayleigh-Benard system and other systems in local equilibrium under strong thermal gradients will show a corresponding structure in configuration space [4]. However, because the turbulent cascade has no Hamiltonian structure, treating it will require a basic extension of the methods used here, which rely on the presence of such a structure.

This paper is organized as follows: in Sec. II, we develop an effective thermodynamics, using the replica method, for a two-species system, one species of which is quenched. This system, in addition to being a basic building block of the more complex systems to follow, has itself been successfully applied as a model for fluid partitioning of solute particles between a solvent and a porous material. In Sec. III, we generalize this model to a multispecies model, which realizes the differential quenching picture in a general Hamiltonian model. In particular, when the interactions are provided by hard-sphere potentials, we get an exact description, in terms of virial series, of the random sequential adsorption (RSA) models extensively studied as models of irreversible binding to substrates [10–20]. Section IV will present the Ornstein-Zernike equations for the correlation functions of the RSA system and discuss one possible closure. Section V mentions some consequences and extensions of this work.

Paper II of this series exploits ideas from the theory of chemical association [21] to relax the constraint that the "hot" and "cold" degrees of freedom must each correspond to the positions of a subset of the particles in the system. This extension of our concepts will allow us to treat the Miller-Abrahams model of electron hopping in amorphous media [22], self-avoiding walks, the Eden model, and the continuum spin glass as examples of our general picture. We do this by considering a general model in which each particle of an arbitrary many-body system is represented as a fictitious bound state of two pseudoparticles, each of which is associated with a subset of the degrees of freedom normally attributed to a single particle. For example, a magnetic atom with a point dipole at its center may be described as a bound state of a hard-sphere particle and a point dipole. This description then allows one "species" to be quenched (i.e., the hard-sphere particles) and the other to be annealed (i.e., the point dipoles) thus giving a realistic description of a continuum spin glass. This process offers a powerful extension of the methods developed in this paper.

Paper III of this series will use further extensions of the ideas already developed to treat diffusion-limited aggregation and void percolation within the same effective equilibrium framework.

II. PROPERTIES OF A BASIC, QUENCHED TWO-SPECIES SYSTEM

In this section, we will use the replica method [23] to calculate the properties of a mixture of two species, one of which is quenched and the other annealed. This system was studied from a different, more probabilistic perspective by Madden and Glandt [24] and used by them to calculate the partition coefficient of a spherical solute divided between a homogeneous fluid phase and a porous material soaked with the same fluid [25]. We present here complete prescriptions for virial expansions of the effective properties of this system. We also sketch the exact analytic solution, in the mean-spherical approximation, of the Ornstein-Zernike equations for the system correlations functions. The technical details of this solution are planned to be published separately [26].

The two species in the system discussed here should be thought of as fractions of the particles in a many-body system, physically identical, but equilibrated at much different temperatures. This system will be a basic building block of the general differentially quenched system discussed in the next section. We will show that the quenched averages describing such a system can be rewritten in terms of the annealed, or equilibrium averages describing a related two-species system.

We consider then a mixture of two species which has the pairwise interaction potentials $v_{ij}(x), i,j=1,2$. Throughout this paper, species will be numbered according to their "temperature," i.e., to their order of introduction into the system, with the fraction introduced later always having the higher species index and thus the higher temperature or level of activity. The average free energy of our two-species system is

$$-\beta F = \ln Z_{\mathrm{tot}} = \frac{1}{Z'} \int e^{-\beta H_{11}} \ln Z_1 d1 \ , \tag{2.1}$$

with

$$Z' \equiv \int e^{-\beta H_{11}} d1 \tag{2.2}$$

and

$$Z_1 \equiv \int e^{-\beta (H_{12}+H_{22})} d2 \ . \tag{2.3}$$

Here we write H_{ij} for the sum of all pairwise interactions between particles of species i and species j. Also, we write $d1, d2$, to represent integration over all the positions of particles of species 1 and 2, 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 [23], which consists of replacing the logarithm with an exponential by using the identity

$$\ln Z \equiv \lim_{s\to 0}\frac{1}{s}(Z^s-1)\ . \tag{2.4}$$

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

$$\ln Z_{\text{tot}} = \lim_{s\to 0}\frac{1}{s}\int\left[\exp\left[-\beta\sum_{i=1}^{s}(H_{12}^{(i)}+H_{22}^{(i)})\right]-1\right]\otimes e^{-\beta H_{11}}\{d2\}d1\ . \tag{2.5}$$

The variables describing species 2 have been replicated and now appear in s copies, in accordance with (2.4). The notation $\{d2\}$ indicates an integration over the s sets of position variables corresponding to these particles.

As we will discuss in later sections, the partition function (2.5) is a basic building block for several of the quenched systems to be treated. Here we first discuss the virial expansions of the various physical quantities that describe this model. We will then discuss the analytic solution of the mean-spherical approximation (MSA) for the correlation functions of this model.

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

$$H=\sum_{\langle i,j\rangle}v_{11}(x_{ij})+\sum_{\langle i,j\rangle}v_{12}(x_{ij}) + \sum_{\langle i,j\rangle}v_{22}(x_{ij})\otimes\delta_{\sigma_i\sigma_j}\ . \tag{2.6}$$

This system is a mixture of a simple, i.e., a one-component, fluid with an s-component fluid. Particles of the one-component fluid (the s-component fluid) bear the subscript 1 (2). We have denoted by σ_i the number of the component to which the ith particle of type 2 belongs. The Kronecker δ on the RHS of Eq. (2.6) then indicates that pairs of type-2 particles only interact when they belong to the same component. Thus the system of type-1 particles, i.e., the original quenched phase, can be thought of as a "solvent" which mediates interactions between the different type-2 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. According to Eq. (2.5), the equilibrium free energy of the system just described becomes, in the $s\to 0$ limit, the average free energy of the quenched, two-phase system described in this section.

We now find it conceptually useful to again recast the problem, describing the s-component fluid of type 2 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-2 particle i, which we write σ_i, is just another name for what we previously called its component. The conceptual change here is the reverse of that originally used by Onsager [27] in his treatment of anisotropic colloidal systems: Onsager treated colloidal particles with different orientations as members of different species; we are treating particles from different components as members of a single species differing only by values of a fictitious internal coordinate. These two descriptions are equivalent because we work only in the grand canonical ensemble; however, one must in general take into account the entropy of mixing between different components when translating between the two descriptions. Thus in considering Mayer expansions for the properties of this system, each internal vertex, or root point, associated with a type-2 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 2 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 Eq. (2.6), which acts between pairs of type-2 particles; we have previously [1,28] described this as a generalized Widom-Rowlinson interaction. The original Widom-Rowlinson model was introduced as a model of phase separation [29]; it involved a mixture of particles of two different species (or "spin states") with a repulsive interaction between particles in *different* species. However, s-species generalizations such as that used here occur frequently in the theory of random media [28]. They are actually continuum generalizations of the ferromagnetic Potts model [30]. 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 *antiferromagnetic* 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. Here we note that the quenched two-phase system discussed in this section is the $s\to 0$ limit of the mixture just described, in the sense implied by Eq. (2.5). We will realize the analytic continuation implied by Eq. (2.5) by expanding the physical properties of this mixture in virial series, taking the $s\to 0$ limit of each term, and, in certain cases, resumming the virial series to give integral equations. The same prescription provides explicit formulas for the coefficients in the virial expansions of the basic physical quantities. The Kronecker δ occurring in the interaction (2.6) ensures that any pair of species 2 (or Widom-Rowlinson) 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 s by the summation over spin states, the only graphs making a nonzero contribution in the $s \rightarrow 0$ limit will be those having all the species-2 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-2 particle is connected, directly or indirectly, to a root point by a chain of Mayer bonds passing only through species-2 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 developed [24,25] by exploiting the description just given for the structure of the Mayer graphs that contribute to the correlation functions. This is precisely the $s \rightarrow 0$ limit of the Ornstein-Zernike system obeyed by a mixture of a hard-sphere fluid and an s-state Widom-Rowlinson fluid. The correlation functions for both the Widom-Rowlinson fluid and the pure hard-sphere fluid [31] satisfy Ornstein-Zernike equations that are exactly solvable in the mean-spherical approximation. We have extended these calculations to treat the mixture discussed here; the exact solution of the MSA for this system will be discussed separately [26].

In an earlier study [24], the two-phase system described here was used to model the partition of a solute between a porous medium and a homogeneous liquid. The porous medium is modeled as a thermally quenched species of particles that do not interact with each other, but have a hard-sphere repulsive interaction with the annealed solute particles. The latter thus percolate through a matrix of overlapping spheres. The system has been studied numerically [25]; we are now extending this work using the exact solution.

III. ANALYTICAL FORMULAS FOR RANDOM SEQUENTIAL ADSORPTION

In this section, we extend the model of Sec. II to describe a mixture of many species. This provides an analytic framework for calculating the properties of systems constructed by differential quenching. We first develop a formalism general enough to handle all the models described by differential quenching. This formulation is then used to treat a basic example, namely, random sequential adsorption. In particular, we present virial expansions for the properties of a sequentially absorbed system of hard disks.

It is straightforward to generalize the two-temperature model of Sec. II to a model involving multiple fractions, with the system being quenched before adding each successive fraction. As in Sec. II, we will describe a multiply quenched system as a system of s species, with the particles of a specific species k being equilibrated at a temperature T_k, the particles of species $i, i<k$ being already thermalized and frozen in place. We find it valuable conceptually to bear in mind the case in which the $\{T_k\}$ obey the inequality

$$T_i \gg T_j, \quad i>j \tag{3.1}$$

so that the sudden change in local temperature as one moves from one fraction to the next brings about the differential quenching. However, as we have emphasized, this case is not even general enough to handle all the differentially quenched systems treated in this paper. In a more general scenario, the nonequilibrium development of the system has prevented the equilibration of different layers with each other, thus externally imposing the differential quenching we assume. The variation of local temperature with particle fraction will be called the "annealing schedule," in order to emphasize this aspect of differential quenching; here we have generalized a term used in the simulated annealing algorithms [23]. The choice of annealing schedule will depend upon the specific physical application.

One readily constructs Mayer expansions for the properties of the general differentially quenched system by recursively applying the continuum replica method developed in Sec. II. Applying this method $n-1$ times to a differentially quenched system of n fractions gives formulas for the thermodynamic quantities of this system in terms of the thermodynamics of an effective equilibrium system of n species, of which all but one have been replicated into a mixture of s components, as in Sec. II. The only residue of the nonequilibrium nature of the problem being studied is the absence from the Mayer expansions of the system of all graphs not satisfying certain constraints. We will present these constraints for a general differentially quenched system. The graphical expansions for the general n-fraction mixture are specified by the requirement that we be able to divide this mixture, in all possible ways into a "hot species," comprising the top k fractions or species, and a "cold species," which is a mixture of the remaining $n-k$ different fractions or species. Making such a division, for any value of k, should yield the constraints derived in Sec. II for the two-temperature, i.e., two-fraction system. In general, the graphical expansions for the physical quantities of a quenched system can be derived from the corresponding expansions for an equilibrium system by deleting all the labeled Mayer graphs that do not obey certain constraints. Explicitly, the constraint on graphs contributing to the free energy of the n-species system is as follows.

(1) Free energy constraint: All the vertices corresponding to particles of a particular species (except for the first species, which was not replicated) must be connected together by Mayer bonds, i.e, they must form a connected subcluster. Also, there must be at least one vertex corresponding to a particle of a species other than species 1. Finally, for each species except for the last at least one particle of that species must be connected to a particle with larger species number, i.e., to a particle from a hotter fraction.

Similarly, the constraint on graphs contributing to the correlation functions of the s-species system is as follows.

2. Correlation function constraint: Each field point corresponding to a particle of, say, species m, must be connected to a root point by a path, i.e., a succession of directed Mayer bonds, such that the kth bond starts at a particle of species i_k and ends at a particle of species j_k, with $j_k \geq i_k$. We will call this an "uphill path." See Fig. 1.

Except for these constraints, the Mayer expansions involved are just those corresponding to an equilibrium s-species mixture. Such a mixture has the grand partition function [32]

$$\Xi=\sum_n \frac{1}{n!}\,\frac{z_1^{i_1}z_2^{i_2}\ldots z_n^{i_n}}{i_1!i_2!\ldots i_n!}Z_{i_1i_2\ldots i_n}\ . \tag{3.2}$$

Here $Z_{i_1\ldots i_n}$ is the canonical partition function for a system having i_1 particles of species 1, i_2 particles of species 2, etc. The average free energy for the multiply quenched system considered here is placed in precisely this form by $(n-1)$ applications of the replica method described in Sec. II. The constraints on the Mayer graphs arise, as in the 2-species case considered in that section, from considering which graphs survive the successive $s\rightarrow 0$ limits.

The Mayer expansion for the free energy of this differentially quenched system is then given by

$$F=\sum_n \frac{1}{n!}\,\frac{z_1^{i_1}z_2^{i_2}\ldots z_n^{i_n}}{i_1!i_2!\ldots i_n!}\mathcal{S}_1\ , \tag{3.3}$$

where $\mathcal{S}_1$ is the sum of all connected, topologically distinct graphs, in general reducible, containing i_1 vertices of species $1,\ldots,i_n$ vertices of species n, with vertices labeled by particle number and species, the species labels obeying the constraint above. The expansions for the correlation functions are directly analogous.

Many differentially quenched systems have the property that each quenched fraction comprises only a single particle. These include self-avoiding walks, the Eden model, and the simplest cases of both diffusion-limited aggregation (DLA) and of random sequential adsorption. (The general case of the last two models involves the deposition of particles at a finite rate, and thus requires the general formalism just developed.) Differentially quenched systems with this constraint have Mayer expansions similar in many ways to those of systems polydisperse in size or orientation, which have been described analytically by treating each type of particle as a different species [33]. We will now illustrate this by developing the explicit Mayer expansions for the properties of random sequential adsorption of disks on a surface.

The properties of RSA are simpler when the interactions between particles are of exclusion type, i.e., when the corresponding pairwise Boltzmann factors take only the values 0 and 1. In this case, we can use certain identities of a kind familiar from statistical geometry [34] and scaled-particle theory [35] to simplify the expressions for the basic thermodynamic quantities. These quantities are the direct analogs, for RSA, of the activity and the pressure. As we now show, these are directly related to the adsorption rate, and to the contact value of the two-point function.

We define RSA in the continuum by making attempts at a constant rate to place disks on a surface. Each attempt consists of choosing at random a point on the surface as a candidate for the center of a newly placed particle. Define ϕ_k to be the probability that an attempt to place the kth particle in the system will succeed i.e., that the candidate center will be at the center of a cavity (a region free of other centers) of radius at least equal to a. Because such a cavity is functionally identical to a hard-sphere particle, the probability ϕ_k is closely related to the fugacity of a hard-sphere particle in this system. The quantity ϕ_k, which is called the available volume fraction, is then identical to the rate of adsorption, on the surface, of new disks. It is clear that this quantity gives, for large k, the rate at which random encounters between substrate and particles will result in binding to the substrate. Then for any hard-particle model, the available volume fraction ϕ_k is given by

$$\phi_k=\frac{\rho_k}{z_k}\ , \tag{3.4}$$

where one has, for the activity z_k of the kth particle placed in a realization of the RSA:

$$z_k=\frac{e^{\beta\mu_k}}{\Lambda^3}\ . \tag{3.5}$$

Here ρ_k, the density of particles in the kth species, is by construction equal to $1/V$, with V the total system volume. Similarly, μ_k is the chemical potential of the kth particle placed; we will present a Mayer expansion for this quantity. Finally, Λ is the standard thermal wavelength.

The fugacity expansion (3.3) is not very useful for studying RSA because the activities $\{z_k\}$ will, in general, all be different. However, the standard topological reduction to star graphs, modified by the constraints on admissible graphs, allow us to replace all $\{z_k\}$ vertices with $\{\rho_k\}$ vertices. Specifically, we have

$$\ln\left[\frac{z_k}{\rho_k}\right]=\mathcal{S}_2\ , \tag{3.6}$$

which is the sum of all irreducible, labeled, singly rooted graphs such that the vertices correspond to ρ_k factors, for which the origin is not an articulation point, and for which the particle labels obey constraint (2) above. This reduction is especially valuable because, as already noted, the $\{\rho_k\}$ are all equal to $(1/V)$. Finally, combining (3.4) and (3.6) gives a virial expansion for the accessible volume fraction ϕ_v

$$\phi_v=\exp\left[\sum_{k=1}^{\infty}\beta'_k\rho^k\right]\ , \tag{3.7}$$

where the β'_k are

$$\beta'_k=\frac{1}{k!}\mathcal{S}_3\ , \tag{3.8}$$

where $\mathcal{S}_3$ is the sum of all irreducible, singly rooted topologically distinct labeled star graphs with k vertices, such that the labeling obeys constraint (2) above.

The formulas (3.3)–(3.6) then give the virial expansion for the chemical potential of RSA in two dimensions:

$$\beta\mu = -4\eta - 4.692\,027\eta^2 - 6.694\,561\eta^3 + 14.770\,89\eta^4 + O(\eta^5)\,, \tag{3.9}$$

where $\eta = \pi a^2 \rho/4$ is the dimensionless density of disks. Substituting this formula into (3.4) and (3.5) and expanding then gives the virial series for ϕ_v:

$$\phi_v = 1 - 4\eta + 3.307\,973\eta^2 + 1.406\,876\eta^3 + 0.720\,565\eta^4 + O(\eta^5)\,. \tag{3.10}$$

This formula agrees with previous work [17] through terms in η^3; the η^4 term is new. The best Padé approximants to (3.10) now agree with available simulation data to the accuracy of that data. A graph of that data versus several approximations derived from Eq. (3.10) is shown as Fig. 2. A [3,2] Padé fit to this formula gives for the jamming density the value $\eta_c = 0.5478$ as compared to the value 0.5470 obtained from simulation data. It is quite interesting that the formulas (3.8) and (3.10) have been derived by Dickman, Wang, and Jensen [10] using an operator, or Fock space formalism apparently unrelated to the approach taken here. In fact, their general approach to growth models, built upon the concepts of rate equations and state transitions, is opposite in philosophy from the approach used here, in which we map growth models onto equivalent equilibrium systems. Also, their work exploits the Mayer series in fugacity (or time); we find it more economical to calculate the virial series for $\phi_v(\eta)$, then revert to give $\phi_v(t)$.

We can also obtain the scaling behavior of physical quantities at densities near to the jamming limit. Both analytically [13,15] and numerically [14] it is known that the jamming density in continuum RSA is approached in power-law fashion as a function of time:

$$(\eta_c - \eta) \sim t^{-(1/d)}\,, \tag{3.11}$$

where d is the spatial dimension. From this result and the interpretation of ϕ_v as an adsorption rate it then follows that

$$\phi_v \sim (\eta_c - \eta)^{d+1}\,. \tag{3.12}$$

Similarly, from Eq. (3.5) we get

$$\mu \sim (d+1)\ln(\eta_c - \eta)\,. \tag{3.13}$$

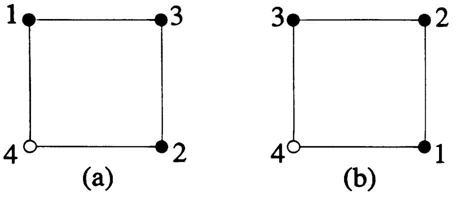

FIG. 1. Two labeled Mayer graphs that contribute to the equilibrium density expansion for the chemical potential. The one on the right contributes to the corresponding expansion for RSA; the one on the left does not.

We can also define the pressure corresponding to the RSA ensemble by using its relation to the grand partition function Ξ:

$$\beta p = \ln\Xi\,. \tag{3.14}$$

The virial series for the pressure is then obtained immediately from the virial series for the free energy obtained in Sec. II. Examination of the constraints (1) and (2) given in that section then shows that they preserve the Gibbs-Duhem relation

$$\frac{\partial p}{\partial \rho} = \rho\frac{\partial \mu}{\partial \rho}\,. \tag{3.15}$$

This relation then shows that the logarithmic singularity in the chemical potential is also present in the pressure. Because the virial theorem relating the pressure to the contact value of the correlation function is also preserved by these constraints, this gives a new prediction for the rate at which this latter quantity becomes singular.

The approach of a continuum sequentially absorbed system to its jamming limit is an interesting candidate for the study of glass-liquid transitions. In order to achieve densities higher than the hard-sphere freezing density, it has been suggested [36] that one begin the RSA procedure with a finite-density, equilibrium, hard-sphere system. We note that this more general system is easily described within our framework. It is simply a differentially quenched system in which one phase has finite density. The resulting graph-theoretic formalism is easily developed as a two-species mixture of the equilibrium fluid and the RSA system developed in Sec. III. Or it can be developed *ab initio* as a specific case of the general system developed in Sec. II.

It is also interesting that the fourth term in the expansion (3.9) differs in sign from the first three terms. It has been argued that the corresponding equilibrium virial series may also show such alternation in sign [37], but the first seven terms in that expansion do not yet show such behavior. The RSA model studied here and the continuum sphere percolation problem are just two of a large family of quenched statistical models whose virial series involve the same Mayer integrals as those found in the equilibrium hard-sphere fluid, but with different combinatoric prefactors. One can define a similar correspondence for any purely repulsive potential. It would be of basic importance to obtain the values of the Mayer integrals up to a very high order for at least one such repulsive model potential, in order to make a comparative study of the analytic structures of these various closely related problems. Efforts to do this for the potential having a Gaussian f bond are now in progress; it is expected that they will shed light on such matters.

The sequential adsorption model explored in this paper is perhaps the simplest nontrivial example of the differentially quenched system we discuss in the Introduction. We chose to explore it in detail even though its basic features have already been elucidated, because it provides a simple testing ground for the approach introduced here. We emphasize that many apparently more complex models are easily incorporated within our framework. For example, if one begins with an equilibrium hard-sphere system at finite density and uses this system as a substrate for the random sequential adsorption process, a higher jamming density is obtained than in the simpler model studied here. This more general model has been used [36] to study the glassy state of matter. We can immediately calculate the properties of this model using the framework developed in this paper: the equilibrium hard-sphere system is the first fraction in a differentially quenched system, while all the successive fractions have but one particle each. Similarly, we can study sequential adsorption on a random, porous substrate [24] using another variation in this approach.

Finally, it is important conceptually to know whether the RSA or other differentially quenched systems have a representation as a limit of a Hamiltonian model, like the representation provided in Sec. II for the two-temperature model in terms of the Widom-Rowlinson model. There is some evidence that the RSA is related to a limiting form of the chiral Potts model [38], but this matter is still being studied. Such representations exist for all the other forms of the replica technique. It would be useful to know whether the same is true of the replica techniques explored here.

In fact, RSA models have a simple Hamiltonian representation. Consider a system of particles, each of which can be in any of s internal states, or "spin states." The interaction potential between particle i and particle j, with $j > i$, is taken to be $v(x_{ij})\,\delta_{\sigma_i 1}$. Here $v(x)$ is a hard-sphere potential and σ_i is the spin state of particle i. In the $s \rightarrow 0$ limit, the thermodynamic quantities describing this model become the physical quantities describing RSA.

IV. ORNSTEIN-ZERNIKE RELATIONS FOR RANDOM SEQUENTIAL ADSORPTION

In this section, we derive a set of Ornstein-Zernike equations obeyed by the correlation functions for RSA. We also present the natural extension to this system of the mean-spherical approximation.

The standard method in liquid-state theory of characterizing the structure of a system is to calculate the correlation functions. Thus, in the project of extending liquid-state theory to describe materials with quenched disorder [1], considerable effort has been devoted to finding exact integral equations [28,36,9] and suitable closures for the correlation functions describing such systems. To construct integral equations for RSA, we first recall the constraint (2) on labeled Mayer graphs that contribute to the two-point correlation function $h(x)$. We rephrase this as follows: allowed graphs are two-rooted, irreducible, labeled Mayer graphs such that each field point has an uphill path connecting it to at least one of the root points. By an "uphill path" we mean a sequence of Mayer bonds passing through increasing particle labels. We may divide such graphs into two classes: those that contain an uphill path from one root point to the other, and those that do not. Denote by $2h_1(x)$ the sum of the first set of labeled graphs and by $h_2(x)$ the sum of the second set. We include a factor of 2 in the former piece of notation because an uphill path may go from root point 1 to root point 2 or vice versa (but not both). Similarly, define $c_1(x)$ $[c_2(x)]$ to be the sum of the node-free graphs included in $h_1(x)$ $[h_2(x)]$. Then we have

$$h_{\mathrm{RSA}}(x)=2h_1(x)+h_2(x) \qquad (4.1)$$

by definition. We can write a set of equations analogous to the usual Ornstein-Zernike equations by sorting the labeled graphs included in the functions h_1, h_2: each such graph will have a certain number of node points (possibly zero), and from each node point there must be at least

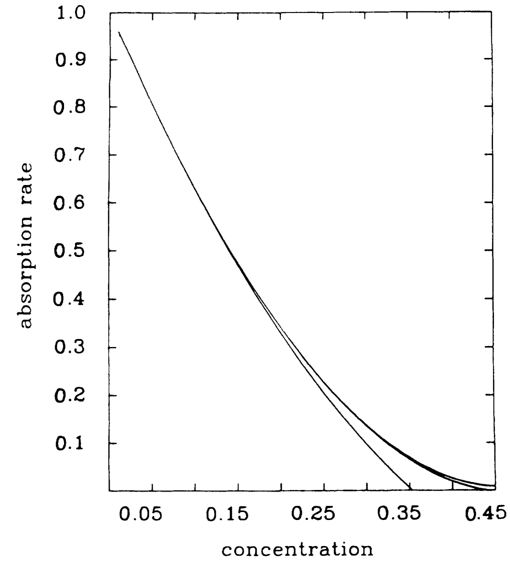

FIG. 2. Several approximants to the adsorption rate in the RSA of disks. From bottom to top, these are the first three, four, and five terms of Eq. (9), respectively. Here we plot the rate of successful adsorption, i.e., the probability that a placement will be successful, vs the dimensionless density of disks $\eta=\pi a^2\rho/4$. On this plot, the simulation data are indistinguishable from the Padé approximant in the top curve.

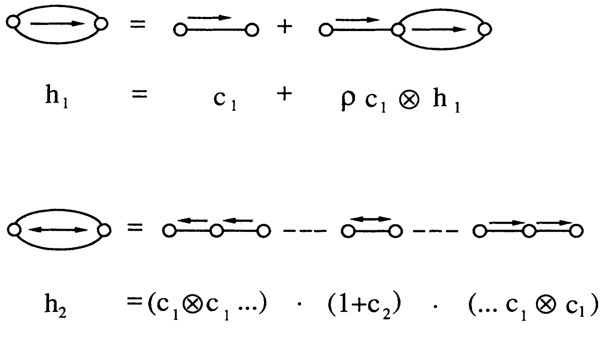

FIG. 3. Diagrammatic structure of the Ornstein-Zernike equations (4.2) and (4.3). The bold lines connecting root points denote c functions; the blobs denote h functions. An arrow pointing from left to right indicates an uphill path from one root point to the other. A two-way arrow indicates that both root points of the corresponding function are terminal points for uphill paths from some of the field points involved. See discussion above Eq. (4.1).

one uphill path to a root point. The general structure of the $\{h_i\}$ is easily found: it is shown in Fig. 2. The resulting Ornstein-Zernike equations are simpler in k space because they are based on convolutions (see Fig. 3). They are

$$\hat{h}_1=\frac{\hat{c}_1}{1-\rho\hat{c}_1}\ , \tag{4.2}$$

$$1+\rho\hat{h}_2=\frac{1}{1-\rho\hat{c}_1}(1+\rho\hat{c}_2)\frac{1}{1-\rho\hat{c}_1}\ , \tag{4.3}$$

where $\hat{h}_i$ is the Fourier transform of $h_i, i=1,2$. These equations can be solved, e.g., by using the mean-spherical approximation to form a closure:

$$h_i=0,\quad x<a \tag{4.4}$$

$$c_i=0,\quad x>a \tag{4.5}$$

for $i=1,2$. However, it seems clear that a better closure would be obtained by approximating the short-range structure in $h_i(x)$ using, e.g., scaled-particle theory [35], then using the analog of Perram's method for Eqs. (4.2) and (4.3) to complete the calculation. These methods are under investigation.

V. CONCLUSIONS

We have developed a basic generalization of the replica method which should be valuable for describing systems far from equilibrium. Here, this method is applied to random sequential adsorption and used to develop virial series for the adsorption rate and the contact value of the correlation function. The sequel to this paper [9] applies similar techniques to aggregation models, using an extension of the chemical association formalism.

ACKNOWLEDGMENTS

I would like to thank the National Science Foundation for funding this research. I thank Per Hemmer, Ron Dickman, Vladimir Privman, Bob Kraichnan, Eduardo Glandt, Bill Madden, and George Stell for discussions of this work. I am grateful to Kare Olaussen and the faculty of the Institue for Theoretical Physics, NTH, Trondheim, Norway, for extending their hospitality while I finished this work.

---

[1] For a review, see J. A. Given and G. Stell, in *On Clusters and Clustering: from Atoms to Fractals,* edited by P. Reynolds (North-Holland, New York, in press).

[2] B. Duplantier and A. W. Ludwig, Phys. Rev. Lett. **66**, 247 (1991).

[3] A. Parola and L. Reatto, Europhys. Lett. **3**, 1185 (1987); Z. Y. Chen, A. Abbaci, S. Tang, and J. V. Sengers, Phys. Rev. A **42**, 4470 (1990).

[4] Both a system in a strong thermal gradient and a system quenched deep into a metastable region can be described using the differential quenching paradigm. Such systems have in common the occurrence of long equilibration times (when measured in the proper units), although the general conditions under which a nonequilibrium system will show scaling behavior are still being explored. For a good recent discussion, see J. Grinstein (unpublished).

[5] H. E. Stanley and N. Ostrowsky, *Random Fluctuations and Pattern Growth: Experiments and Models* (Kluwer Academic, Norwell, MA, 1988).

[6] K. Kang, S. Redner, P. Meakin, and F. Leyvraz, Phys. Rev. A **33**, 1171 (1986).

[7] See, e.g., E. Guyon, C. D. Mitescu, J. P. Hulin, and S. Roux, Physica D **38**, 172 (1989); D. L. Johnson, J. Koplik, and R. Dashen, J. Fluid Mech. **176**, 379 (1987).

[8] R. Kraichnan and S. Y. Chen, Physica D **37**, 160 (1989).

[9] J. A. Given, J. Chem. Phys. (to be published).

[10] R. L. Dickman, J. S. Wang, and I. Jensen, J. Chem. Phys. **94**, 8252 (1991).

[11] B. S. Brosilow, R. M. Ziff, and R. D. Vigil, Phys. Rev. A **43**, 631 (1991).

[12] B. Widom, J. Chem. Phys. **44**, 3888 (1966).

[13] R. Swendsen, Phys. Rev. A **24**, 504 (1981).

[14] Y. Pomeau, J. Phys. A **13**, L193 (1980).

[15] J. Feder and I. Giaever, J. Coloid Interface Sci. **78**, 144 (1980); E. L. Hinrichsen, J. Feder, and T. Jossang, J. Stat. Phys. **44**, 793 (1986).

[16] J. J. Gonzalez, P. C. Hemmer, and J. S. Hoye, J. Chem. Phys. **3**, 228 (1974).

[17] J. Schaaf and J. Talbot, Phys. Rev. Lett. **62**, 175 (1989); J. Chem. Phys. **91**, 4401 (1989).

[18] V. Privman, J. S. Wang, and P. Nielaba, Phys. Rev. B **43**, 3366 (1991); M. C. Bartelt and V. Privman, J. Chem. Phys. **93**, 6820 (1990).

[19] P. Meakin, J. L. Cardy, E. Loh, and D. J. Scalpino, J. Chem. Phys. **86**, 2380 (1987).

[20] J. W. Evans and R. S. Nord, J. Stat. Phys. **38** 681 (1985); J. W. Evans, Phys. Rev. **62**, 2642 (1989).

[21] H. C. Andersen, J. Chem. Phys. **59**, 4714 (1973); M. W. Wertheim, J. Stat. Phys. **35**, 19 (1984); **35**, 34 (1984).

[22] J. M. Ziman, *Models of Disorder* (Cambridge University Press, Cambridge, 1979).

[23] M. Mezard, G. Parisi, and M. A. Virasoro, *Spin Glass Theory and Beyond* (World Scientific, Singapore, 1987).

[24] W. A. Madden and E. D. Glandt, J. Stat. Phys. **51**, 537 (1988).

[25] L. A. Fanti, E. D. Glandt, and W. G. Madden, J. Chem. Phys. **51**, 537 (1988).

[26] J. A. Given (unpublished).

[27] L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).

[28] J. A. Given and W. Klein, J. Chem. Phys. **90**, 1116 (1989); J. A. Given, I. C. Kim, S. Torquato, and G. Stell, *ibid.* **93**, 5128 (1990).

[29] B. Widom and J. S. Rowlinson, J. Chem. Phys. **52**, 1670 (1970).

[30] For some of the deep relationships between the Potts model and the replica method, see A. B. Harris, Phys. Rev. B **28**, 2614 (1983); J. Rudnick and G. Gaspari, J. Stat. Phys. **42**, 833 (1986).

[31] M. Wertheim, J. Math. Phys. **5**, 643 (1964); S. Ahn and J. L. Lebowitz, J. Chem. Phys. **60**, 523 (1974).

[32] See, e.g., S. Baer and J. L. Lebowitz, J. Chem. Phys. **44**, 3474 (1964).

[33] See, e.g., P. A. Rikvold and G. Stell, Chem. Eng. Commun. **51**, 233 (1987) and references cited therein.

[34] G. Stell in *The Wonderful World of Stochastics,* edited by M. F. Schlesinger and G. H. Weiss (North-Holland, Amsterdam, 1985).

[35] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).

[36] G. Tarjus, P. Schaaf, and J. Talbot, J. Stat. Phys. **63**, 167 (1991); J. Talbot, P. Schaaf, and G. Tarjus, Mol. Phys. **72**, 1397 (1991).

[37] J. E. Kilpatrick, Adv. Chem. Phys. **20**, 39 (1971).

[38] D. K. Arrowsmith and J. W. Essam. Phys. Rev. Lett. **65**, 3068 (1990).