

**The Replica Ornstein-Zernike Equations
and the Structure of Partly Quenched Media**

James A. Given^{1,a} and George R. Stell^{2,b}

¹ Department of Chemistry, SUNY - Stony Brook,
Stony Brook, New York, 11794-3400

² Gruppe for Teoretisk Fysikk, Universitetet i Trondheim,
7034 Trondheim - NTH, Norway

SUNY CEAS Report # 640, Sept, 1992

Abstract

We derive the replica Ornstein-Zernike equations (ROZ) satisfied by the two-point correlation functions for a partly quenched system, i.e., a system in which some of the particles are quenched, or frozen in place, and some are annealed, or allowed to equilibrate. A formally exact closure for these equations is given. A set of integral equations given by Madden and Glandt are recovered as an approximation to the exact ROZ equations. We discuss the fundamental status of this approximation. We also present new exact relations that express the thermodynamic quantities of partly quenched media in terms of the correlation functions in such media.

Permanent address:

^a Thermophysics Division, NIST, Gaithersburg, Maryland 20899, USA,

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

1. Introduction

This paper is part of an ongoing project^{1,2} 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. Many such materials can be regarded as being constructed in layers,^{3,4} each layer being added to those already in place and allowed to equilibrate, then frozen in place before the next layer is added. We have in mind here not stratified media, in which the layers are spatially separated, but homogeneous media in which the different layers interpenetrate; such media are distinguished from equilibrium mixtures in that they are formed by a step-by-step annealing or equilibration process. The simplest such system consists of just two layers, one quenched and one annealed. The basic idea is that the particles in the quenched layer constitute a random matrix through which the particles in the annealed layer move. A simple mixture of this kind, in which quenched and annealed particles possess only excluded-volume interactions, has already been studied⁵⁻⁷ as a possible model for the behavior of fluid in a micro-porous material.^{8,9} It is natural to ask whether the correlation functions of such partly quenched systems obey integral equations of the Ornstein-Zernike type.

The subject of partly quenched systems is discussed in a pair of papers by Madden and Glandt⁵ and Madden⁶. The quenched matrix of immobile particles in the mixtures considered in reference 5 is assumed to have been formed by a quench from an equilibrium distribution; that is, the quenched particles are distributed according to an equilibrium ensemble corresponding to a fixed potential distribution. Madden subsequently⁶ generalized this formalism to the case in which the distribution of quenched particles is essentially arbitrary and is specified only through its correlation functions.

In both of these papers various exact cluster expansions are derived for the correlation functions associated with the mixture and a set of Ornstein-Zernike equations are considered. Here we point out that the Ornstein-Zernike equations given in reference 5 are

**The Replica Ornstein-Zernike Equations
and the Structure of Partly Quenched Media**

James A. Given^{1,a} and George R. Stell^{2,b}

¹ Department of Chemistry, SUNY - Stony Brook,
Stony Brook, New York, 11794-3400

² Gruppe for Teoretisk Fysikk, Universitetet i Trondheim,
7034 Trondheim - NTH, Norway

Abstract

We derive the replica Ornstein-Zernike equations (ROZ) satisfied by the two-point correlation functions for a partly quenched system, i.e., a system in which some of the particles are quenched, or frozen in place, and some are annealed, or allowed to equilibrate. A formally exact closure for these equations is given. A set of integral equations given by Madden and Glandt are recovered as an approximation to the exact ROZ equations. We discuss the fundamental status of this approximation. We also present new exact relations that express the thermodynamic quantities of partly quenched media in terms of the correlation functions in such media.

Permanent address:

^a Thermophysics Division, NIST, Gaithersburg, Maryland 20899, USA,

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

not the exact Ornstein-Zernike equations associated with the cluster expansions therein. Instead they correspond to an approximation in which a certain class of terms is neglected in the cluster expansion of the direct correlation function $c_{11}(12)$ for annealed particles. This approximation seems to have a fundamental status; it has since been derived by several other rather different methods. Here we follow a line of thought developed in various earlier works^{3,4,10} of ours by using the replica method for liquid-state systems to give the exact Ornstein-Zernike equations for a partly quenched system. We refer to the latter as the replica Ornstein-Zernike (ROZ) equations.

The replica method¹³ exploits a mathematical isomorphism between a partly quenched system and a corresponding fully equilibrated system. Precisely stated, the thermodynamic quantities and correlation functions for a partly quenched system are given by the $s \rightarrow 0$ limit of a corresponding equilibrium system, called the replicated system. This system is a mixture of a one-component fluid (the quenched species) with an s -component fluid, given by s 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. In particular, if we write down the standard Ornstein-Zernike equations for the correlation functions of the replicated system, group together identical terms, and take the $s \rightarrow 0$ limit, we get a system of integral equations exactly satisfied by the correlation functions of the partly quenched system. These are satisfied by the set of functions $[\{h_{ij}\}, \{h_{0i}\}, h_{00}]$. (Here we use the subscript '0' for the quenched particles and the subscripts '1' through 's' for the s copies, or replicas, of the annealed particles. Thus $h_{ij}(x)$ density associated with finding a particle from replica i and a particle from replica j separated by a distance x . Similarly, the function $h_{0i}(x)$ gives the probability density associated with finding a particle from the quenched species and a particle from replica i separated by a distance x . We refer both to the Ornstein-Zernike equations for the replicated system and to the $s \rightarrow 0$ limit of these equations, which describes partly

quenched systems, as the **replica Ornstein-Zernike (ROZ)** equations.

In the limit $s \rightarrow 0$, the replicated system becomes simply an equilibrium system containing only the quenched particles. Similarly, the correlation function $h_{00}(x)$ for the replicated system becomes, in this limit, the correlation function for the quenched particles. However, the correlation functions $h_{11}(x)$ and $h_{12}(x)$, giving respectively, the correlation between a pair of annealed particles in the same replica and a pair of particles in different replicas, have a highly nontrivial $s \rightarrow 0$ limit. To see this, note that the function $h_{12}(x)$ describes the correlation between a pair of annealed particles that belong to different replicas. (In this paper, we consider only replica-symmetric solutions, in which $h_{ij} = h_{12}$ for i and j any two replica indices.) A pair of particles in two different replicas interact only indirectly, through the mediation of the quenched particles and the particles in the $(s - 2)$ additional replicas. The solution for the function $h_{12}(x)$ in this mixture can be obtained by standard methods of liquid-state theory, i.e. Mayer expansions and integral equations. This solution will be nontrivial even in the $s \rightarrow 0$ limit, although this limit (involving a background containing $s - 2 = -2$ replicas) clearly does not correspond to any physically realizable equilibrium mixture.

In this paper we explore some basic interactions between liquid-state theory and the theory of replicas. Readers interested in such interactions should also explore the recent work of Stratt et. al.,^{12,13} in which methods complementary to those described here are developed.

This paper is organized as follows: in Section 2, we first review the continuum replica method and show how it can be used to obtain the properties of partly quenched systems. We show that each partly quenched system of the type studied here (in which the quenched and annealed degrees of freedom belong to different particles) is isomorphic to a limiting case of a corresponding fully equilibrated system, to be called the replicated system. We use the standard Ornstein-Zernike equations for the replicated system to give the replica Ornstein-Zernike (ROZ) equations for the original partly quenched system. We

then rewrite the ROZ equations using the language of percolation theory. This terminology suggests useful closures for a large class of disordered systems; we give an important illustration of this. In Section 3, we discuss various natural types of closure approximations for equations of this kind. We discuss the Madden-Glandt approximation, which is a basic approximation to the ROZ equations. Section 4 discusses the relationships between correlation functions and thermodynamic quantities that hold for partly quenched systems. Section 5 gives our conclusions and directions for further research.

2. Derivation of the Replica Ornstein-Zernike Equations

In this section, we review the continuum replica method³ and use it to extend liquid-state theory to partly quenched systems. We show that a partly quenched system is isomorphic to a limiting case of a corresponding equilibrium system, to be called the replicated system. Using this mapping, we provide a set of replica Ornstein-Zernike (ROZ) equations exactly satisfied by the correlation functions of a partly quenched system. We rewrite the ROZ equations in terms of a generalized percolation formalism that should be valuable for finding approximate closures in certain disordered media.

We consider a system containing two species of particles, one quenched or frozen in place and the other annealed or allowed to equilibrate. This system has the pairwise interaction potentials $v_{11}(x)$, $v_{12}(x)$, $v_{22}(x)$, respectively, between a pair of quenched particles, a pair of annealed particles, and a quenched and an annealed particle, respectively. The Helmholtz free energy of this two-species system is given by

$$-\beta F = \ln Z_{TOTAL} = \frac{1}{Z'} \int e^{-\beta H_{11}} \ln Z_1 d\vec{1} \quad (2.1)$$

with

$$Z' \equiv \int e^{-\beta H_{11}} d\vec{1} \quad (2.2)$$

and

$$Z_1 \equiv \int e^{-\beta[H_{12}+H_{22}]} d\vec{2} \quad (2.3)$$

Here we write H_{ij} for the sum of all pairwise interactions between particles of species i and species j . Also, we write $d\vec{1}$, $d\vec{2}$, 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 trick¹³, which consists of replacing the logarithm with an exponential by using the identity

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

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

$$\ln Z_{TOTAL} = \lim_{s \rightarrow 0} \frac{1}{s} \frac{1}{Z'} \int \left\{ \exp \left[-\beta \sum_{i=1}^s [H_{12}^{(i)} + H_{22}^{(i)}] \right] - 1 \right\} \otimes e^{-\beta H_{11}} \{d\vec{2}\} d\vec{1} \quad (2.5)$$

The variables describing species 2 have been replicated and now appear in s copies, in accordance with (2.4). The notation $\{d\vec{2}\}$ indicates an integration over the s 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

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

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 (resp. the s -component fluid) bear the subscript 1 (resp. 2). We have denoted by σ_i the number of the component to which the i^{th} particle of type 2 belongs. The Kronecker delta on the RHS of eqn. (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.

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 Onsager¹⁴ 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; however, one must be careful to appropriately take into account the entropy of mixing between different components when going from one to the other description. 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.

The Hamiltonian (2.6) is a continuum version of the lattice Potts model, much studied as a model of magnetic ordering. When the number of replicas s is set equal to 2, this model is equivalent to the Widom-Rowlinson model, a basic model for liquid-liquid phase separation. The connection between this class of models and various basic problems in the theory of disordered media was first pointed out by Fortuin and Kastelyn;³² the demonstration³ that a large class of partly quenched systems are also related to these models suggests many new prospects for understanding their properties. We note here two limitations to the work that has been done so far. First, the pairwise interaction in (2.6) is highly **non-additive**. The development of liquid-state theory for such interactions, in particular, the establishment of good thermodynamic perturbation theories and good integral equation closures, is not nearly as advanced as for the case of additive potentials.

The fundamental methods available²³ for the study of additive excluded-volume interactions are only with great difficulty being extended to non-additive systems. Preliminary indications^{33,34} are that the analytic structure of non-additive models is far more complex than that of additive models. Second, the isomorphisms established here imply that symmetry-breaking transitions in the generalized Widom-Rowlinson model are related to sudden changes of behavior in partly-quenched systems. One example of the latter may be the loss of ergodicity encountered in simulating highly constrained systems. Thus, the phase structure of these generalized Widom-Rowlinson models is of direct relevance to the study of disordered systems. Unfortunately, simulation studies of these models have not yet been performed in detail.

The continuum replica method also provides virial expansions of the basic physical quantities for partly quenched systems. Namely, one takes the $s \rightarrow 0$ limit of the corresponding virial expansions for the replicated system. The result is that the Mayer expansions for a partially quenched system containing an annealed and a quenched species are identical to those for a fully equilibrated system containing the same two species except that all the Mayer graphs in the latter not obeying a specific constraint are missing in the former. We now derive this constraint.

The Kronecker delta occurring in the interaction (2.6) ensures that any pair of species 2 (or Widom-Rowlinson) vertices connected by a Mayer bond must be in the same spin state. Each group of such vertices 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. Graphs possessing only a single such cluster will survive the limiting operation in eqn. (2.5); only these will contribute to the pressure of a partly quenched system. 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. We refer to such a chain of Mayer bonds as an **annealed path** and say that the Mayer graphs must satisfy the **annealed-path**

condition.

A set of replica Ornstein-Zernike (ROZ) equations can be developed^{9,10} by using the description just given for the structure of the Mayer graphs that contribute to the correlation functions. One can use topological reduction directly to write the correlation functions as products of appropriately defined direct correlation functions. But the same results are obtained more easily by exploiting the isomorphism just obtained between a partly quenched system and its replicated system. In particular, the ROZ equations for the two-species system studied here are 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. We write down the Ornstein-Zernike equations for the replicated $(s+1)$ -species system with Hamiltonian (2.6), and isolate the s -dependence of these equations by grouping together identical terms. The result is

$$h^{00} = c^{00} + \rho c^{00} \otimes h^{00} + s \rho c^{01} \otimes h^{01} \quad (2.7)$$

$$h^{01} = c^{01} + \rho c^{00} \otimes h^{01} + \rho c^{01} \otimes h^{11} \\ + (s-1) \rho c^{01} \otimes h^{12} \quad (2.8)$$

$$h^{10} = c^{10} + \rho c^{10} \otimes h^{00} + \rho c^{11} \otimes h^{10} \\ + (s-1) \rho c^{12} \otimes h^{10} \quad (2.9)$$

$$h^{11} = c^{11} + \rho c^{01} \otimes h^{01} + \rho c^{11} \otimes h^{11} \\ + (s-1) \rho c^{12} \otimes h^{12} \quad (2.10)$$

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

The $s \rightarrow 0$ limit of these equations are the replica Ornstein-Zernike (ROZ) equations:

$$h^{00} = c^{00} + \rho c^{00} \otimes h^{00} \quad (2.12)$$

$$h^{01} = c^{01} + \rho c^{00} \otimes h^{01} + \rho c^{01} \otimes h^{11} \\ - \rho c^{01} \otimes h^{12} \quad (2.13)$$

$$h^{10} = c^{10} + \rho c^{10} \otimes h^{00} + \rho c^{11} \otimes h^{10} - \rho c^{12} \otimes h^{10} \quad (2.14)$$

$$h^{11} = c^{11} + \rho c^{01} \otimes h^{01} + \rho c^{11} \otimes h^{11} - \rho c^{12} \otimes h^{12} \quad (2.15)$$

$$h^{12} = c^{12} + \rho c^{01} \otimes h^{01} + \rho c^{11} \otimes h^{12} + \rho c^{12} \otimes h^{11} - 2\rho c^{12} \otimes h^{12} \quad (2.16)$$

It is natural to rewrite the ROZ equations using the language of percolation theory. This is especially valuable for deriving approximate closures in certain disordered-media problems. To do this, we define the functions c_c and c_b to be, respectively, the subset of graphs contributing to the function c_{11} that have, or do not have, respectively, an annealed path connecting their root points. Here the subscripts 'c' and 'b' denote 'connected' and 'blocking', respectively. We have borrowed the notations from percolation theory as we explain below. because $h_{12}(x)$ consists of precisely those graphs contributing to $h_{11}(x)$ that do not have an annealed path joining the two root points. We also define h_c and h_b as sums of the corresponding subsets of h_{11} graphs. By definition we have then

$$c_{11}(12) = c_c(12) + c_b(12) \quad (2.17)$$

$$h_{11}(12) = h_c(12) + h_b(12) \quad (2.18)$$

It also follows from these definitions that

$$h_{12}(12) = h_b(12) \quad (2.19)$$

By using the percolation terminology just defined, we can write the exact ROZ equations as

$$h_{00} = c_{00} + \rho_0 c_{00} \otimes h_{00} \quad (2.20)$$

$$h_{10} = c_{10} + \rho_0 c_{10} \otimes h_{00} + \rho_1 c_c \otimes h_{10} \quad (2.21)$$

$$h_{11} = c_{11} + \rho_0 c_{10} \otimes h_{01} + \rho_1 c_c \otimes h_{11} + \rho_1 c_b \otimes h_c \quad (2.22)$$

$$h_c = c_c + \rho_1 c_c \otimes h_c \quad (2.23)$$

where, by symmetry, $c_{01} = c_{10}$ and $h_{01} = h_{10}$. Here the symbol \otimes denotes a convolution.

An alternative equation for h_{01} that can be derived from (2.20-2.23) is

$$h_{01} = c_{01} + \rho_0 c_{00} \otimes h_{01} + \rho_1 c_{01} \otimes h_c. \quad (2.24)$$

When c_{00} , c_{01} , c_{11} , c_c and the $\{\rho_i\}$ are prescribed, (2.20-24) constitute the ROZ equations; they are a closed set of equations for h_{00} , h_{01} , h_{11} , and h_c .

We note that the separation of correlation functions into connected and blocking parts is natural in the description of many disordered and partly quenched systems. This separation was used by Hill¹⁶ in the description of continuum percolation phenomena; in that context, the connected and blocking functions have a direct geometric interpretation as probability densities. The present authors have extended the description of clustering given by continuum percolation theory² and also have applied that description to phenomena as diverse as sequential adsorption and spin-glass ordering.¹ It is useful in many such disordered systems to identify $h_c(x)$ and $h_b(x)$ as the “short-range” and “long-range” parts of the correlation function $h_{11}(x)$, and to use different approximation schemes or integral equation closures for each. We give here an intuitive explanation of the correlations included in each of the two new functions, the connected and blocking correlation functions. To do this we use as an example of a partly quenched system a fluid adsorbed in a porous medium,¹⁷⁻²¹ with the porous medium being constituted by the quenched particles, and the fluid being constituted by the annealed particles.⁵⁻⁷ The connected function $h_c(x)$ accounts for correlations between a pair of fluid particles that are transmitted through successive layers of fluid particles; the blocking function $h_b(x)$ accounts for correlations between fluid particles “blocked” or separated from each other by matrix particles. (We note that even though the matrix particles are immobile, they tend to order the fluid particles on either side of them and thus are capable of mediating correlations “through” a layer of matrix particles. At very low matrix porosities i.e., very high densities of matrix

particles, the volume accessible to fluid particles is divided into small cavities, each totally surrounded by matrix. In this limit, the function $h_c(x)$ describes correlations between fluid particles in the **same** cavity; the function $h_b(x)$ describes correlations between particles in **different** cavities. This sort of intuition leads naturally to closures that prove accurate for describing this system.²²

3. Approximate Closures of the ROZ Equations

In this section, we give a formally exact closure for the ROZ equations. We also discuss a fundamental approximation to the ROZ equations which was developed some time ago by Madden and Glandt.^{5,6} We discuss different approaches to forming approximate closures of the ROZ equations that also lead to the Madden-Glandt approximation.

Because the ROZ equations (2.20-23) are a particular limiting case of the equilibrium OZ equations, we may use the latter to write down formally exact closure relations²³ for the $\{c_{ij}\}$:

$$c_{ij} = \lim_{s \rightarrow 0} [f_{ij} y_{ij} + d_{ij}] \quad (3.1)$$

The quantities $\{f_{ij}\}$, $\{y_{ij}\}$, and $\{d_{ij}\}$ on the RHS of eqn. (3.1) are, resp., the Mayer f -functions, cavity functions, and tail functions, resp., of the $(s+1)$ -species replicated system discussed in Section 2. The Mayer expansions for these functions are given by the $s \rightarrow 0$ limit of the corresponding expansions. This immediately yields both Mayer expansions for these functions and approximate closures for the ROZ equations. For example, setting

$$d_{ij} = 0 \quad (3.2)$$

in eqn. (3.1) yields an analog for the ROZ equations of the equilibrium Percus-Yevick (PY) approximation. However, there are two features of the partly quenched systems studied here that caution us against naively applying the standard integral-equation closures to the ROZ equations. First, the potential interactions of the replicated system are in general highly non-additive. This is a general fact about disordered systems; as we discussed in Section 2, many of them are limiting cases of the highly non-additive Widom-Rowlinson

model. Second, the $s \rightarrow 0$ replica limit is, as already noted, unphysical in certain regards. It is thus unclear which if any of the standard closures will give good results for the systems studied here. This matter will be settled only through the detailed numerical studies now in progress.

If we make the approximation

$$c_b(x) = 0 \tag{3.3}$$

then $c_{11} = c_c$ in equations (2.12-2.16), and the last term in (2.15) vanishes. The resulting equations are the approximation to the replica Ornstein-Zernike equations that is studied in references 5. Specifically, (2.12-2.16) become the (30a), (30c), (30d), (30e) and (30b) of that work. (Madden and Glandt denote the function we call h_c by C_{ff} . Also, they use the subscripts 'f' and 'm', for 'fluid' and 'matrix', where we have used subscripts '1' and '0', respectively.)

We shall refer to the approximation (33), implicitly used in references 5 and 6, as the Madden-Glandt (MG) approximation. This approximation is also discussed by Chandler²⁴ who treats a mixture of a quenched and an annealed species by considering all the quenched particles to form a single "molecule," which is in equilibrium with the fluid. He then uses the equilibrium site-site Ornstein-Zernike (SSOZ)²⁵⁻²⁷ equations to calculate the correlation functions $h_{01}(x)$ and $h_{11}(x)$. This treatment is equivalent to the MG approximation because it assumes that the function $h_{00}(x)$ contains all of the non-equilibrium features of the calculation. In the case that the ratio of annealed to quenched particles is vanishingly small, e.g., if the quenched particles form a single polymer chain, this approximation is exact. This gives still another perspective on the MG approximation. (For a discussion of the use of the SSOZ theory in a partly quenched system, see reference 29.)

There is a class of approximate closures of the ROZ equations that imply the Madden-Glandt (MG) approximation $c_b(x) = 0$; 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

$$h_{ij} + 1 \equiv (f_{ij} + 1)y_{ij} \quad (3.4)$$

It also includes the mean-spherical approximation (MSA):

$$h_{ij} = -1, \quad x_{ij} < \sigma_{ij} \quad (3.5)$$

$$c_{ij} = -\beta v_{ij}, \quad x_{ij} > \sigma_{ij} \quad (3.6)$$

Here v_{ij} is the pair potential, x_{ij} is the distance between particle centers and σ_{ij} is the average of hard core diameters of species i and species j particles.

A fundamental fact about the MG approximation is this: in a sense to be made precise, the only difference between the MG Ornstein-Zernike equations and the equilibrium Ornstein-Zernike equations is in the quenched system input. In a quenched system, the functions h_{00} and c_{00} , and in general the degrees of freedom associated with the quenched particles, are determined by the dynamics of the quench, i.e., they are not influenced by the behavior of the annealed degrees of freedom as they would be if the quenched and annealed particles formed a totally equilibrated mixture. If we take these functions as input and proceed to solve both the MG Ornstein-Zernike equations and the equilibrium Ornstein-Zernike equations for the functions h_{01} , h_{11} (using the same closure) the results will be identical. This confirms a conjecture made previously by one of us,²⁷ during the study of approximate equations for the amorphous spin glass, that the MSA (which implies the MG approximation) is “blind” to the difference between a partly quenched system and the corresponding fully annealed system. We have obtained similar results in applying the MSA to other partly quenched systems, including a model for an electron hopping in a system of fixed impurities,²⁸ and an amorphous spin glass.²⁹

This raises the question: which systems require a nontrivial approximation for the function $c_b(x)$, or equivalently, which systems require for their description an assessment of explicit non-equilibrium effects? We have recently studied²² in detail a system for which

these effects are as large as possible, in a sense to be made precise. Consider in particular the following model^{9,30,31} for fluid adsorbed in a microporous material.³⁵ We model the fluid as an annealed species of particles that have no interactions with each other and hard-sphere interactions of range σ_{01} with the quenched particles constituting the matrix. The latter are taken to have no interaction among themselves, and thus to be frozen in place with the statistics of an ideal gas, i.e., with totally uncorrelated positions. Because of the excluded-volume interaction between fluid particles and matrix particles, the latter appear to the former to constitute a highly nontrivial porous structure. This model has the property that $c_c(x) = 0$, and thus

$$c_{11}(x) = c_b(x) \tag{3.7}$$

so that the correlations between the particles constituting the porous medium are given entirely by the function $c_b(x)$ which we have associated with explicitly non-equilibrium effects. This is intuitively reasonable, because the equilibrium mixture corresponding to this partly quenched system is completely trivial.

The model just discussed for fluid adsorbed in a porous medium has recently been the subject of a detailed study, in which the results of many approximate closures for the ROZ equations were compared with simulation data.²²

4. Thermodynamic Quantities of a Partly Quenched Mixture

In this section, we give formulas for the thermodynamic quantities of a partly quenched mixture in terms of weighted integrals over the correlation functions discussed in Section 2. In particular, we give formulas for the pressure and internal energy of a partly quenched mixture. We also provide the analog, for partly quenched systems, of the compressibility theorem.

The pressure p_{PQ} of a partly quenched system is closely related to the zero-replica limit of the corresponding replicated system. The exact relation is given by (2.1), from

which we find

$$\beta p_{PQ} = \left. \frac{d}{ds} \right|_{s=0} [\beta p_{REP} - \beta p_0] \quad (4.1)$$

Here p_{PQ} , p_{REP} , and p_0 are, respectively, the pressures of the partly quenched system, the replicated system, and the quenched species, considered in isolation. (Although the species-0 particles are quenched, or frozen in place, they are distributed according to an equilibrium Gibbs ensemble to which there corresponds a pressure; this is simply the pressure they would have if they were "unfrozen.") As in Section 2, the replicated system is an $(s+1)$ -species mixture, consisting of one copy of the quenched species (termed "species 0") together with s copies of the annealed species (termed "species 1 through s "). 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.

According to the replica method, as applied to a fluid mixture, we can relate the pressure of a partly quenched system to its correlation functions by applying the standard virial theorem to the corresponding replicated system, then taking the $s \rightarrow 0$ limit. The virial theorem for an equilibrium fluid mixture is given by

$$\beta p = \sum_i \rho_i - (\beta/6) \sum_{i \leq j} \rho_i \rho_j \int x \frac{d\phi_{ij}}{dx} g_{ij}(x) d^3x \quad (4.2)$$

For a hard sphere mixture, this becomes

$$\beta p = \sum_i \rho_i + (2\pi/3) \sum_{i \leq j} \rho_i \rho_j g_{ij}(\sigma_{ij}+) \sigma_{ij}^3 \quad (4.3)$$

For simplicity, we evaluate the pressure only in this case. When eqn. (4.3) is applied to the replicated system corresponding to a partly-quenched hard sphere mixture, and substituted in eqn. (4.1), the result is an expression for the fluid pressure.

$$\beta p_{PQ} = \rho_1 + (2\pi/3) [g_{01}(\sigma_{01}+) \rho_0 \rho_1 \sigma_{01}^3 + g_{11}(\sigma_{11}+) \rho_1^2 \sigma_{11}^3] \quad (4.4)$$

This formula deserves comment. The first term on the RHS gives the contribution from interactions of matrix particles and fluid particles; it can also be derived by considering the matrix as a highly convoluted “boundary” for the fluid particles. The second term on the RHS contains the contact value of the function $g_{11}(x)$ giving the density of fluid particle pairs in contact.

The same reasoning that leads to eqn. (4.1) also gives, for the internal energy per unit volume u the formula

$$\beta u_{PQ} = \left. \frac{d}{ds} \right|_{s=0} \beta u_{REP} \quad (4.5)$$

The internal energy of a mixture is given in general by

$$\beta u = (\beta/2) \sum_{i \leq j} \rho_i \rho_j \int \phi_{ij}(x) g_{ij}(x) d^3 x \quad (4.6)$$

For general soft potentials, the combination of (4.5) and (4.6) gives, for a partly quenched mixture, the formula

$$\beta u_{PQ} = (\beta/2) \rho_0 \rho_1 \int \phi_{01}(x) g_{01}(x) d^3 x + (\beta/2) \rho_1^2 \int \phi_{11}(x) g_{11}(x) d^3 x \quad (4.7)$$

In deriving eqn. (4.7), we again make use of the fact that different replicas do not interact, that is, $\phi_{ij} = 0$, $i, j \neq 0$. The result (4.7) is completely intuitive and serves mainly to check the formalism developed here. The results (4.4) and (4.7) have also been derived on a purely probabilistic basis.⁵

Finally, we derive the compressibility theorem for a partly quenched system. The compressibility theorem for the corresponding replicated system can be written

$$\frac{\partial \beta p_{PREP}}{\partial \rho_i} = 1 - \sum_{j=0}^s \rho_j \int d^3 x c_{ij}(x) \quad (4.8)$$

We first consider the variation with matrix density of the fluid pressure. To derive the compressibility corresponding to such a change, we set $i = 0$ in eqn. (4.8) and use eqn. (4.1), noting that the s -derivative commutes with the ρ_0 -derivative. The result is

$$\frac{\partial \beta p_{PQ}}{\partial \rho_0} = -\rho_1 \int d^3 x c_{01}(x) \quad (4.9)$$

Next, we consider the variation with fluid density of the fluid pressure. To do this, we use the identity

$$\left. \frac{\partial \beta p_{REP}}{\partial \rho_1} \right|_{s=0} = \frac{\partial \beta p_{PQ}}{\partial \rho_1} \quad (4.10)$$

Applying this to eqn. (4.8) gives the result

$$\frac{\partial \beta p_{PQ}}{\partial \rho_1} = 1 - \rho_1 \int d^3x c_{01}(x) + \rho_1 \int d^3x c_c(x) \quad (4.11)$$

where $c_c(x)$ is the connected part of $c_{11}(x)$, as defined below (2.1). To our knowledge, the formulae (4.9) and (4.11) have not been derived by methods other than the replica method used here. In considering fully equilibrated systems, certain important results (e.g., the equivalence of different definitions of key thermodynamic quantities and of different ensembles) hold only in the thermodynamic limit, in which the container becomes “infinite in all directions”, i.e., it contains a sphere, the radius of which can be made infinite. Because the quenched species of our model acts for the fluid species as a container that never becomes infinite in this sense, it is not clear whether such equivalences hold for our quenched-annealed mixture. The formal results of this section are subject to this cautionary observation and deserve further investigation in this connection. A closely related question involves the commutativity of the limits $s \rightarrow 0$ and $V \rightarrow \infty$, where V is the volume of the container used in defining the Z_{TOTAL} of eqn. (2.1). It also deserves further study.

5. Conclusions

We have shown that the replica method, when combined with standard liquid-state theory, allows the development of integral equations for the correlation functions of partly quenched systems. These equations, the replica Ornstein-Zernike(ROZ) equations, are developed here in detail. We discuss the advantages and disadvantages of a fundamental approximation for the ROZ equations which is due to Madden and Glandt. Finally, we give the formulas for thermodynamic quantities of a partly-quenched system in terms of the correlation functions for such a system.

The method of differential quenching,^{3,4} which is basically a repeated application of the replica method, extends the methods developed in this paper and yields ROZ equations for many other partly quenched systems. The simple partly quenched system discussed in this paper should be a valuable testing ground for closures to the ROZ equations. We intend soon to apply similar closures to more complex non-equilibrium systems.

Acknowledgements

J.G. is indebted to the National Science Foundation for support while G.S. gratefully acknowledges the support of the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy. We thank Bill Madden for his interest and encouragement, and for informative discussions. We thank Enrique Lomba both for valuable discussions of the closures discussed here and for his comments on this manuscript.

References

- * Present address: Thermophysics Division, NIST, Gaithersburg, MD 20899
- [1] J.A. Given and G. Stell, "Liquid-State Theory for Some Non-Equilibrium Processes," in the **XVIth International Workshop on Condensed-Matter Theories**, June 1992, (Plenum, N.Y. 1993).
 - [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] J.A. Given, *Phys. Rev. A* **45**, (1992) 816.
 - [4] J.A. Given, *J. Chem. Phys.* **96**, (1992) 2287.
 - [5] W.G. Madden and E.D. Glandt, *J. Stat. Phys.* **51**, (1988) 537.
 - [6] W.G. Madden, *J. Chem. Phys.* **96**, (1992) 5422.
 - [7] L.A. Fanti, E.D. Glandt and W.G. Madden, *J. Chem. Phys.* **93**, (1990) 5945. See also, R.D. Kaminsky and P.A. Monson, *J. Chem. Phys.* **95**, 2936 (1991).
 - [8] L.H. Zheng and Y.C. Chiew, *J. Chem. Phys.* **90**, (1989) 1; Y.C. Chiew and E.D.

- Glandt, J. Colloid Int. Sci. **99** (1984) 86.
- [9] H.L. Weissberg and S. Prager, Phys. Fluids **5**, (1962) 1390.
- [10] J.A. Given and G. Stell, J. Chem. Phys. **97**, (1992) 4573.
- [11] B.C. Xu and R.M. Stratt, J. Chem. Phys. **91**, (1989) 5613; R.M. Stratt, J. Chem. Phys. **80**, (1984) 5674.
- [12] R.M. Stratt, in "The Electronic Structure of Liquids", in Ann. Rev. Phys. Chem. **41**, (1990) 175-205.
- [13] S.F. Edwards, in **Polymer Networks**, eds. A.J. Chompff and S. Newman, (New York, Plenum Press, 1971); S.F. Edwards and P.W. Anderson, J. Phys. **F5**, 965 (1975); S.F. Edwards and R.C. Jones, J. Phys. **A9**, 1595 (1976); for further applications see the volume M. Mezard, G. Parisi, and M.A. Virasoro, *Spin Glass Theory and Beyond*, (World Scientific, Singapore, 1987).
- [14] L. Onsager, Ann. N.Y. Acad. Sci. **51**, (1949) 627.
- [15] B. Widom and J.S. Rowlinson, J. Chem. Phys. **52**, (1970) 1670.
- [16] T.L. Hill, **Statistical Mechanics**, (McGraw-Hill, New York, 1956).
- [17] D.J. Wilkinson, D.L. Johnson, and L.M. Schwartz, Phys. Rev. **B44**, (1991) 4960; K.R. McCall, D.L. Johnson, R.A. Guyer, Phys. Rev. **B44** (1991) 7344; D.L. Johnson, J. Koplik, and R. Dashen, J. Fluid Mech. **176**, (1987) 379.
- [18] E. Guyon, C.D. Mitescu, J.P. Hulin, S. Roux, Physica **D38**, (1989) 172.
- [19] R.T. Bonnecaz, J.F. Brady, J. Chem. Phys. **94**, (1991) 537.
- [20] P. Meakin, B. Sapoval, Phys. Rev. **A43**, (1991) 2993.
- [21] G.L. Dietrick, L.E. Scriven, and H.T. Davis, J. Chem. Phys. **85**, (1986) 2169; *ibid* **90**, (1989) 2370; R.B. Saeger, L.E. Scriven and H.T. Davis, Phys. Rev. **A44**, (1991) 5087.
- [22] E. Lomba, J.A. Given, G. Stell, J.J. Weis, D. Levesque, Phys. Rev. **E48**, 233 (1993).
- [23] G. Stell, in "The Equilibrium Theory of Classical Fluids", ed. by H.L. Frisch and J.L. Lebowitz, (Benjamin, N.Y., 1964).
- [24] D. Chandler, J. Physics B: Condensed Matter, **42**, (1991) F1.

- [25] D. Chandler and H.C. Andersen, *J. Chem. Phys.* **57**, (1972) 1930.
- [26] D. Chandler and L.R. Pratt, *J. Chem. Phys.* **69**, (1976) 2925.
- [27] J.Høye and G. Stell, *J. Chem. Phys.* **61**, (1974) 562.
- [28] J.A. Given, submitted for publication, *J. Chem. Phys.*
- [29] J.A. Given and G. Stell, "A Realistic Model for a Spin Glass", in: **Complex Fluids**, (Materials Research Society, Pittsburgh, Pa., 1992).
- [30] H. Reiss and P. Schaaf, *J. Chem. Phys.* **91**, 2514 (1989); P. Schaaf and H. Reiss, *J. Chem. Phys.* **92**, 1258 (1990).
- [31] J.A. Given and G. Stell, *J. Chem. Phys.* **94**, (1991) 3060.
- [32] C.M. Fortuin and P.W. Kastelyn, *Physica* **213**, (1972) 329.
- [33] A. Baram and J. Rowlinson, *Mol. Phys.* **74**, 707 (1991).
- [34] L. Blum, in private communication, has emphasized the importance of branch cut structures in studying the thermodynamic properties of non-additive models, considered as functions of density.
- [35] R. Dashen, P. Day, W. Kenyon, C. Straley, J. Willemsen, *Physics and Chemistry of Porous Media II: AIP Conf. Proc. Vol. 154*, eds. J.R. Banavar, J. Koplik, K.W. Winkler, AIP, New York, (1987).