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A Theory of Solid Solutions and Solid–Fluid Equilibria for Mixtures[1]

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We describe the application of a recently developed cell theory of solid solutions to the calculation of solid phase thermodynamics and solid–fluid phase equilibria for hard sphere mixtures. We focus on freezing into both substitutionally ordered and substitutionally disordered solid solutions. A comparison with Monte Carlo simulation results is presented.

KEY WORDS: cell theory; hard spheres; mixtures; solid–fluid equilibria.

1. INTRODUCTION

Two classes of approach have been taken in studies of solid–fluid equilibria. The most ambitious approach has been to calculate the properties of both phases within the context of a single theory. This is exemplified by the order–disorder theory of Lennard-Jones and Devonshire [1] which treats the fluid as a disordered solid and, more recently, by the density functional theory [2–4], which treats the solid as a highly inhomogeneous fluid, an idea originating from the work of Kirkwood and Monroe [5]. The density-functional-theory work has attracted considerable interest in recent years since it seems to provide a quite accurate picture of the solid structure while being based on accurate approximations for the fluid properties [2–4]. In contrast, the treatment of a fluid as a disordered solid is now considered to be incorrect since it imposes too high a degree of order on the fluid [6]. An alternative to these single-phase strategies is to treat the two phases by theories appropriate to each. This approach was initiated by

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Barker and Henderson [7], who used thermodynamic perturbation theory for the fluid phase and the cell theory for the solid phase. Although this approach is in some sense less satisfying than if a single theory is used for both phases, it does lead to quantitatively accurate results.

We have recently adapted the latter approach to the problem of solid-fluid equilibria in mixtures [8]. In this work an extension of the cell theory for binary mixtures in the solid state was developed. In the past this theory had only been applied to mixtures in the liquid state, for which it is inappropriate. The key feature of our work is that it takes into account the effect of composition fluctuations on the cell potential field. This is important in the treatment of molecules of different size freezing into substitutionally disordered solid solutions. Application to binary hard-sphere mixtures was considered. The fluid phase thermodynamic properties were determined from the equation of state for hard-sphere mixtures developed by Mansoori et al. [9]. The predictions obtained in this way are in good quantitative agreement with results from Monte Carlo simulations [10, 11].

In this paper we provide a brief review of the theory presented in detail in Ref. 8 and provide some additional results which illustrate the accuracy of the theory for hard-sphere mixtures freezing into substitutionally disordered solid solutions. In addition, we discuss the application of the approach to substitutionally ordered solid solutions or compounds.

Substitutionally ordered solid solutions play a very important role in the phase diagrams of mixtures in the solid state. They arise principally when the components have only limited miscibility as substitutionally disordered solids but where crystal structures of especially favorable stability can be formed by substitutional ordering of the components among the lattice sites. Such phases are often referred to as "compounds" since they correspond to fixed stoichiometric amounts of the pure components. While this designation is certainly appropriate for most inorganic solids of this type stabilized by covalent or ionic bonding, it is much less appropriate for mixtures of organic compounds and other systems where the structures are stabilized by van der Waals forces. For these systems the route to understanding and predicting the occurrence of ordered solid solutions lies in understanding how different types of molecular interactions can stabilize these structures.

Striking evidence for the importance of simple packing effects in the stability of ordered solid solutions comes from recent studies of the structure of some samples of natural opal [12, 13], which consists of packings of silica spheres, and of the flocculation of colloidal suspensions of spheres [14]. These studies suggest that hard sphere mixtures with size ratios of about 0.58 can form substitutionally ordered structures with stoichiometry

AB_2 and AB_{13}. This has recently been confirmed by Madden et al. [15, 16] using Monte Carlo simulation. Further evidence for the formation of substitutionally ordered solutions stabilized by van der Waals interactions is provided by studies of mixtures of helium and nitrogen at high pressure in which a substitutionally ordered structure with stoichiometry $\mathrm{He(N_2)_{11}}$ has been suggested [17]. In this work we describe an application of the cell theory to the AB_2 and AB_{13} structures of hard-sphere systems as well as to interstitial compounds such as the NaCl structure. A more detailed account of this work will appear elsewhere [18].

2. THEORY

Our theory is based on the assumption that the configurational partition function of a system of N molecules can be written as a product of cell partition functions for single molecules, each moving in a cage formed by its nearest neighbors fixed at their lattice sites. To generalize to substitutionally disordered solid mixtures, we introduce a mean-field approximation for the distribution of the molecules on the lattice sites. In this case, a particular cell is characterized by the type of its central particle and by the composition and distribution of the z nearest neighbors. Consequently, for a p-component mixture consisting of N_1 molecules of species 1, N_2 molecules of species 2,..., N_{p} molecules of species p placed on a lattice of coordination z, we can write the configurational partition function as

$$Z = \frac{N!}{N_1!\,N_2!\cdots N_{\mathrm{p}}!}\prod_j q_j^{NP_j} \tag{1}$$

where $q_j = \int_{\mathrm{cell}\,j} e^{-\beta\psi(\mathbf{r})}\,d\mathbf{r}$ is the partition function of cell j and P_j is the probability of observing cell j. ψ is the cell potential field, that is, the potential due to the rest of the lattice acting on the central particle. For the P_j's, we consider the following expression:

$$P_j = x_{\mathrm{c}} x_1^{s_{j1}} x_2^{s_{j2}} \cdots x_n^{s_{jn}} \tag{2}$$

with the constraint

$$\sum_{i=1}^{p} s_{ji} = z \tag{3}$$

where x_i denotes the mole fraction of species i and the subscript c refers to the type of the central particle. s_{ji} is the number of particles of species i present in the neighbor shell of cell j. It is worth noting at this point that our approximation for the cell probabilities is exactly that used in the

Bragg–Williams [19] approximation. This can be seen by evaluating Eq. (1) in the case of fixed central particles and only nearest-neighbor interaction. However, our theory goes beyond that approximation. By taking into account density effects, via the density dependence of the cell partition functions, and by considering all possible nearest-neighbor environments of a given molecule, we provide a more realistic treatment of size-difference effects and local fluctuations in composition in mixtures.

Once the set of cell partition functions has been determined at a given density, the Helmholtz free energy and all thermodynamic properties can be obtained for all compositions at that particular density. An apparent difficulty with this approach might be the large number of cell partition functions to compute, even in the simplest case of binary mixtures. This difficulty has been resolved by using a very efficient algorithm [8] which permits simultaneous computation, via Monte Carlo integration, of all partition functions for a given density.

For the case of substitutionally ordered solid solutions, this problem disappears due to the great reduction in cell types. Indeed, as each species occupies a given set of lattice points, there is only a limited number of possible environments for a molecule. Once these environments are determined, one can compute the corresponding cell partition functions as before. For example, in the case of AB_2 structure, only two types of cells remain: one with a large central particle and one with a small central particle. The probabilities of observing the different cells reduce, in this case, to the mole fractions of the different species. Thus, if q_1 and q_2 are the respective cell partition functions evaluated at a given density, the configurational partition function of the system, at that particular density, is given by

$$Z = q_1^{N/3} q_2^{2N/3} \tag{4}$$

where N is the total number of particles.

3. APPLICATION TO BINARY HARD SPHERE MIXTURES

3.1. Substitutionally Disordered Solid Solutions

We first consider substitutionally disordered binary mixtures of hard spheres of different sizes on a FCC lattice. We are interested in how the solid-phase thermodynamics and the solid-fluid phase equilibria change with α, the ratio of the smaller sphere diameter to that of the larger sphere. The solid solutions behave very differently from the fluid mixtures [8]. In particular, at constant pressure, the volume increases on mixing. The volume of mixing gets bigger as the size ratio decreases. Clearly in a solid mixture the molecules of different species do not have the same ability as in a fluid to rearrange and as a consequence the system expands on freezing at constant pressure. The size ratio α also has a large influence on the shape of the solid–fluid phase diagram of these systems [3, 8, 10, 11, 20–22]. For size ratios close to unity, the phase diagrams are of the spindle type. For $\alpha \approx 0.93$ an azeotrope appears. For a value of $\alpha \approx 0.85$ the diagram starts to exhibit a eutectic. Below $\alpha \approx 0.85$ the substitutionally disordered binary mixture is unstable and phase separates into two pure solid phases.

In Fig. 1, we present the P–x phase diagram corresponding to the case $\alpha = 0.93$, where P is the reduced pressure $P\sigma_{11}^3/kT$ and x_1 is the mole fraction in large spheres, along with a comparison with the Monte Carlo simulations of Kofke [11]. The cell theory result is in good agreement with simulations. In particular the shape of the diagram, as well as the composition of the azeotrope are correct. The theory is also capable of predicting correctly the densities at coexistence as shown in Fig. 2. The packing fraction η is defined as $\eta = (\pi/6)(N/V)(x_1\sigma_{11}^3 + (1-x_1)\sigma_{22}\alpha^3)$. The differences between the simulation results and theoretical predictions for lower values of x_1 are principally a reflection of scatter in the Monte Carlo results [23].

The main weakness of the cell theory at this point is that it does not allow for structural relaxations. Since each cell is a rigid entity which scales

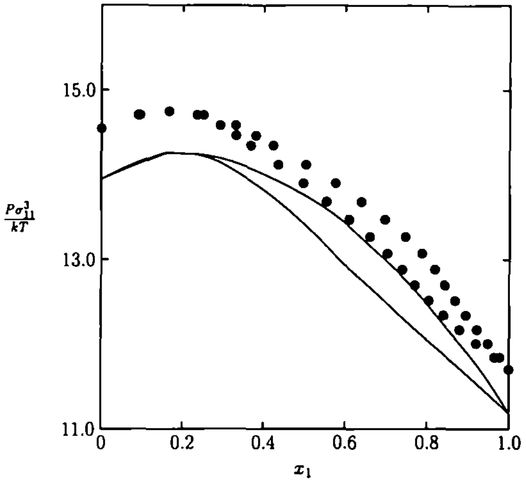

Fig. 1. Phase diagram for freezing of a binary hard sphere mixture of size ratio $\alpha = 0.93$ into a substitutionally disordered solid solution. The full lines represent the predictions of the cell theory and the circles are the results of Monte Carlo simulations [11]

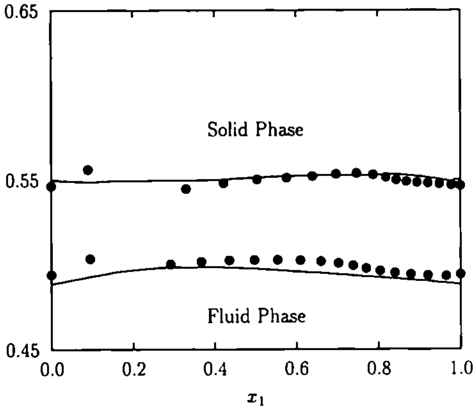

Fig. 2. The densities at equilibrium for the phase diagram in Fig. 1. The lines represents the predictions of the cell theory and the circles are the simulation results of Kofke [11].

with density; relaxation effects which naturally occur in Monte Carlo simulations are not allowed. As a consequence, particles do not have the possibility to rearrange themselves and the solid solution appears more nonideal than it would normally be. This effect is especially important for solutions of small size ratio which are dilute in the larger spheres. For example, in the case $\alpha = 0.85$ the cell theory predicts a zone of immiscibility as the composition in large spheres goes to zero, while the simulation results predict a small region of miscibility [8, 10]. Fortunately, this behavior occurs close to the limit of stability of those substitutionally disordered solid solutions.

3.2. Substitutionally Ordered Binary Hard Sphere Solid Solutions

It is somewhat remarkable that hard-sphere mixtures are able to pack in such an efficient way as to form substitutionally ordered solid solutions. The experimental discovery of hard sphere structures such as AB_2 and AB_{13} [12] for some size ratios and compositions, as well as earlier theoretical studies [13], confirmed that packing has a much greater importance in the stability of such structures than was believed before. It is now important to understand this in more detail and also why some structures are stable while others are not. Such an understanding would certainly provide a good basis for extrapolation to more complex systems, such as rare-gas mixtures and beyond.

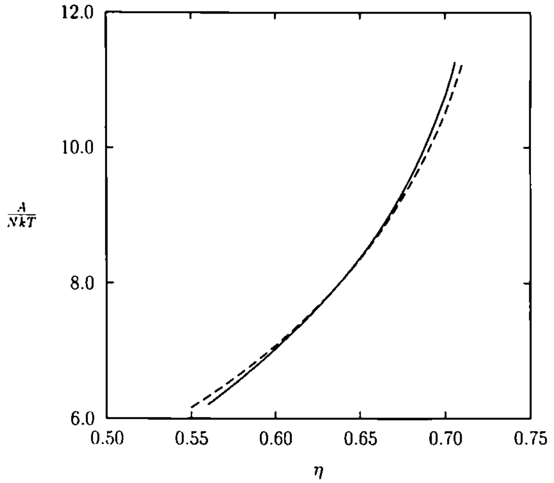

Fig. 3. The Helmholtz free energy of a substitutionally ordered solid solution of hard spheres of the type AB_{13} for a size ratio $\alpha = 0.58$. The full line gives the cell theory predictions while the dashed line represents the simulation results of Eldridge et al. [15].

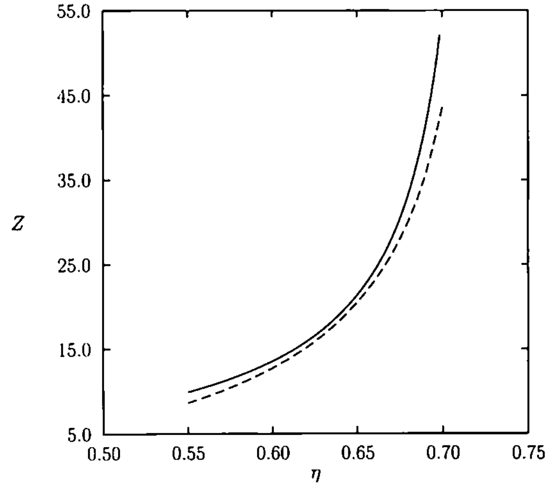

Fig. 4. Pressure of the substitutionally ordered solid solution of Fig. 3 vs density. The full line gives the cell theory predictions and the dashed line represents the simulation results of Eldridge et al. [15]

We believe the present theory to be a useful tool in such a study. Although this problem will be discussed in more detail elsewhere [18], we would like to present here some preliminary results in the case of a solid solution of the AB_{13} type, with a size ratio $\alpha = 0.58$, which was the subject of recent Monte Carlo simulation work [15, 16, 24]. In Fig. 3, we present the Helmholtz free energy of this system as a function of the packing fraction η. The agreement is quite good, especially at high density. In Fig. 4, we show the pressure as a function of density. Although the agreement is still quite good, the theory overpredicts the pressure and again this is due to the absence of structural relaxation in the theory. A preliminary calculation of the full phase diagram for this system, which also includes the AB_2 solid phase, indicates an excellent agreement with that presented by Eldridge et al. [24] using Monte Carlo simulations.

4. CONCLUSION

We have reviewed an extension of the cell theory of Lennard–Jones and Devonshire to mixtures. Through a mean-field approximation for the distribution of the particles on the lattice sites, we treat more realistically the local fluctuations in composition which arise in a mixture. Results in the case of binary hard sphere mixtures forming both substitutionally ordered and disordered solid solutions have been presented. Very good agreement with Monte Carlo simulations is obtained. We believe that this approach is a valuable tool in the study of the thermodynamics of solid solutions and in conjunction with a theory for fluid phase properties for the calculation of solid–fluid phase equilibria. Further studies of substitutionally ordered solid solutions are in progress and these will be presented in due course.

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