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# Solid-fluid equilibrium: new perspectives from molecular theory

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**Abstract**

Some recent developments in the molecular modeling of solid-fluid phase equilibrium are reviewed. Theoretical approches to solid phase thermodynamics and solid-fluid equilbria are described as well as methods for studying solid phases by computer simulation. Applications to the study of solid-fluid equilibrium in systems of nonspherical molecules and to predicting solid-fluid phase diagrams for mixtures are described.

## 1. INTRODUCTION

Historically, research in phase equilibrium thermodynamics has focused principally on fluid phase systems, reflecting the importance of fluid phase separations in the chemical process industries. Rather less attention has been given to the prediction of solid-fluid equilibria. Processes involving solids are less common than entirely fluid phase processes, especially in petrochemical processing. Nonetheless, there are numerous instances where solids appear directly as reactor products or where components in a liquid phase mixture are more easily separated via crystallization. Crystallization may be preferred to distillation for components with melting points close to ambient temperatures since the energy requirements for crystallization (if measured by the enthalpies of vaporization and crystallization) may typically be lower by a factor of three to four. Crystallization is sometimes a useful alternative for components which decompose before boiling, as well as for closely boiling components such as in mixtures of isomers. With the gradual increase in the importance of specialty chemicals and biochemical processing to the chemical industry the number of processes involving solids is likely to increase rapidly. Of course modeling crystallization separations is significantly more complex than modeling distillation since transport and kinetic effects play a much greater role in relation to the phase equilibria. Nevertheless, knowledge of multicomponent solid-fluid phase equilibrium is a critical ingredient in the design of crystallization separations.

Techniques from statistical mechanics now play a significant role in the modeling of fluid phase equilibrium for chemical process design and this paper describes how such techniques can be used to study solid-fluid equilibrium also. We review several methods for calculating solid-fluid equilibria using statistical mechanics. Applications are described to two problems which have featured prominently in our recent research: i) How the shape of molecules determines solid-fluid equilibrium; ii) Prediction of solid-fluid equilibrium for mixtures.

Our interest in the first of these problems arose in part from earlier work on the development of methods for calculating the free energies of fluids where the molecules have nonspherical shape as well as electrostatic interactions [1]. During the course of this work we looked at the departures from two parameter corresponding states in single component vapor-liquid equilibrium as a function of anisotropy in the intermolecular forces. The question of how departures from corresponding states in the melting line and especially the ratio of the triple point temperature to critical temperature, $T_t/T_c$, might be determined by details of the intermolecular forces is an important extension of this work. In the case of

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the classical rare gases $T_t/T_c$ is always about 0.55 but for nonspherical molecules values both substantially higher and substantially lower than this are found. For example, in the case of ethane $T_t/T_c \sim 0.3$ whereas for carbon dioxide $T_t/T_c \sim 0.7$. Such variations reflect departures from corresponding states behavior in both the vapor-liquid and solid-liquid equilibria. Statistical mechanical calculations for molecular models which include anisotropic intermolecular forces can reveal useful information about these effects.

A major feature of solid-fluid equilibria for mixtures is that complete miscibility at all compositions in the solid phase is the exception rather than the rule. Such complete miscibility requires that both components can be accommodated on a substitutionally disordered crystal structure. This is difficult to achieve except when the components are similar in molecular size and shape. Ordered solid solutions (or compounds) where the molecules of each component lie on the sites of interpenetrating sublattices are restricted to fixed solid compositions and their presence leads to complex phase diagrams involving equilibria between the liquid mixture and various solid phases involving the pure component solids, disordered solid solutions and ordered solid solutions. The simplest cases are those where the components show no miscibility in the solid phase [2] and a single eutectic point. Then calculation of the phase equilibria requires only the chemical potentials in the liquid mixture and those of the pure solids. In an engineering context this is often done by using an activity coefficient model for the liquid mixture with subcooled liquid reference states for the pure solid solutes. The solid phase fugacities can then be approximated by their (ideal gas) values on the sublimation curve at the temperature of interest [2]. This calculation parallels the case of vapor-liquid equilibrium for a mixture with a heterogeneous azeotrope and complete immiscibility in the liquid phase. Of course, predicting the occurrence of complete immiscibility is another matter. For more complex cases with partial miscibility in the solid phase, models which are capable of treating the detailed solution thermodynamics of the solid phase are required. This is again an area where statistical mechanics can provide much useful information.

In the first section of this paper we describe some theoretical approaches to solid-fluid equilibrium. Two approaches are described. One approach uses approximations to the partition function especially appropriate to the solid state and generally referred to as cell theories. The other approach treats the solid as a highly inhomogeneous fluid which is treated in the context of classical density functional theory. Next we discuss computer simulation techniques for studying solid phases, focusing especially on calculations of the free energy and on the determination of the equilibrium structure of the solid. We then move on to some applications. The first is the influence of molecular shape upon solid-fluid equilibrium. The second deals with solid-fluid equilibrium in mixtures. In both these applications a strong emphasis on the importance of packing effects arising from the repulsive forces between molecules. In particular we show how the packing effects associated with molecular shape play an important role in determining solid-fluid equilibrium. As a first approximation to the influence of attractive forces is given by mean field or generalized van der Waals theory. In addition we show how most of the known types of solid-fluid phase behavior of binary mixtures, including compound formation, can arise from packing effects arising from molecular size differences.

## 2. THEORIES OF SOLID-FLUID EQUILIBRIUM

The approaches we describe start from the premise that quite accurate statistical mechanical equations of state (e.g. from perturbation or integral equation theories) are available for obtaining liquid state thermodynamic properties, so that the focus can be placed on determining the solid phase properties. This is clearly the case for spherical molecules, as well as for some simpler nonspherical molecules and idealized models of chain molecules.

### 2.1. Cell Theory

There is an extensive literature spanning a period from the mid 1930's to the mid 1960's which describes efforts to develop theories for the free energies of liquids by assuming that the volume of the system was divided into cells on a lattice. At the simplest level the partition function can then be calculated by assuming independent motion of the molecules in a potential field created by the neighboring molecules assumed fixed to their lattice sites. Much of this work is reviewed in a monograph by Barker [3]. We now know that such efforts were of limited utility in developing the theory of liquids which is now firmly based in the language of the radial distribution function [4]. In fact the cell theories are a more appropriate description of solids rather than fluids and the recognition of this fact leads to some very useful results for the thermodynamic properties of solids.

The simplest of the cell theories is that first suggested by Lennard-Jones and Devonshire (LJD) [5,6]. In this approximation the configurational partition function may be written as a product of cell partition functions for single molecules moving in a cage formed by neighboring molecules fixed on their lattice sites. We have

$$Z(N,V,T) = e^{-U_0/kT} q^N \tag{1}$$

where $U_0$ is the static lattice energy of the solid at the density of interest and q is the cell partition function given by

$$q = \int e^{-[\phi(\mathbf{r})-\phi(\mathbf{r}_0)]/kT} d\mathbf{r} \tag{2}$$

where $\phi(\mathbf{r})$ is the potential energy experienced by the molecule in its cell at position $\mathbf{r}$ and $\mathbf{r}_0$ is the location of the center of the cell. This approximation essentially treats the solid as if each molecule experiences a potential energy field generated by the neighboring molecules on their static lattice sites.

The LJD theory in combination with perturbation theory for the liquid state free energy has been applied to the calculation of solid-fluid equilibria for the Lennard-Jones 12-6 potential by Henderson and Barker [7]. The results were compared with simulations by Hansen and Verlet [8] and the agreement found to be quite good. Hansen and Verlet also showed that the solid free energies predicted by the LJD theory were in good agreement with the simulation results. Previously Hoover and Ree [9] had shown that it leads to accurate results for hard spheres also.

Recently we have extended the cell theory to mixtures. Consider a n component mixture consisting of $N_1$ molecules of type 1, $N_2$ molecules of type 2, ..., $N_n$ molecules of type n placed on a lattice characterized with coordination number z. We assume that a cell is characterized by the species of the central particle and by the composition and configuration of the z nearest neighbors. The configurational partition function of the system can then be written :

$$Z = \left(\frac{N!}{N_1!N_2!\ldots N_n!}\right) \prod_i q_i^{NP_i} \tag{3}$$

where $q_i$ is the partition function of cell i and $P_i$ is the probability of observing cell i. We approximate the $P_i$'s as :

$$P_i = x_c x_1^{s_{i1}} x_2^{s_{i2}} \ldots x_n^{s_{in}} \tag{4}$$

along with the constraint:

$$\sum_{j=1}^{n} s_{ij} = z \tag{5}$$

where $x_j$ denotes the mole fraction of species j, the subcript c refers to the species of the central particle and $s_{ij}$ is the number of particles of type j in the nearest neighbor shell of cell i. Our approximation for the cell probabilities is the same as that used in the Bragg-Williams or mean field theory for the partition function of a binary alloy [10]. Once the set of cell partition functions has been determined at a given density, the total partition function and Helmholtz energy can be determined for all compositions at that density. Even for a binary mixture there are a very large number of cell partition functions to be computed but we have shown that these contributions can be calculated simultaneously. This simple theory leads to impressive results for the properties of hard sphere mixtures [11,12] and the extension to more complex systems is relatively straightforward.

### 2.2. Density Functional Theory

There has been considerable recent interest in the application of the classical density functional theories to the calculation of solid-fluid equilibria. Recent reviews of this approach have been given by Evans [13] and Haymet [14] which provide much more detail than can be provided in this very brief review. The basic physical idea underlying this approach is that the influence of pair correlations upon the molecular density distribution in the melting solid is similar to that seen in the freezing liquid. Thus information about the structure of one equilibrium phase could be used to calculate the free energy of the other. Since there are some tractable routes to the pair correlations in liquids [4] it makes sense to use the liquid as the reference state for the calculation.

The key to the practical application of the method is the development of suitable parameterization of the excess Helmholtz free energy functional, $A_{ex}[\rho]$, for the nonuniform system of interest. Two kinds of approach have been taken. In one approach the Helmholtz energy is approximated by a functional Taylor expansion usually truncated at second order [14]. We have

$$A_{ex}[\rho] = A_{ex}(\rho_L) + \frac{\mu_{ex}(\rho_L)}{kT} \int d\mathbf{r}\Delta\rho(\mathbf{r}) - \frac{kT}{2} \int\int d\mathbf{r}d\mathbf{r}' c(|\mathbf{r}-\mathbf{r}'|;\rho_L)\Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r}') \tag{6}$$

where $\rho_L$ is the density of the bulk liquid, $\mu_{ex}(\rho)$ is the excess chemical potential, $\Delta\rho(\mathbf{r})$ is the difference between the solid density at point $\mathbf{r}$ and that of the bulk liquid, and $c(|\mathbf{r}-\mathbf{r}'|;\rho_L)$ is the direct correlation function of the bulk liquid. The principal difficulty with this approach is that little is known about the convergence of the functional Taylor expansion and calculations beyond second order are quite complex.

In the other approach, known as weighted density functional theory, the Helmholtz energy is approximated in a nonperturbative manner [13]. This is done by writing

$$A_{ex}[\rho] = \int d\mathbf{r}\rho(\mathbf{r})\psi[\overline{\rho}(\mathbf{r})] \tag{7}$$

where $\rho(\mathbf{r})$ is the single molecule density, $\psi[\rho]$ is the Helmholtz energy density for a uniform system with density $\rho$ and $\overline{\rho}(\mathbf{r})$ is the weighted density defined via

$$\overline{\rho}(\mathbf{r}) = \int d\mathbf{r}' w(|\mathbf{r}-\mathbf{r}'|;\overline{\rho}(\mathbf{r}))\rho(\mathbf{r}') \tag{8}$$

Here $w(|\mathbf{r}-\mathbf{r}'|;\overline{\rho}(\mathbf{r}))$ is a weight function. Various prescriptions are used for determining this weight function, which make use of known results for the free energy of homogeneous fluid as a boundary condition which the weight function must satisfy. This approach does not suffer from the difficulties associated with convergence of the functional Taylor expansion. On the other hand, there is a certain arbitrariness in the choice of the weight function.

Density functional theories of freezing have generated a number of interesting results, especially in treating single component atomic fluids and for hard sphere mixtures [14]. Moreover, research in this area has contributed to renewed interest in the whole area of solid-fluid equilbrium. The application of these techniques to solid-fluid equilibria in more complex systems with nonspherical molecules, although formally possible (Chandler et al., 1986a,b; Smithline et al., 1988) may well be limited by the complexity of the calculations and the lack of truly accurate information about the direct correlation functions of complex liquids.

## 3. SOLID-FLUID EQUILBRIUM VIA COMPUTER SIMULATION

The application of Monte Carlo and molecular dynamics techniques to solid-fluid equilibrium has a history as long as that of the techniques themselves [17-20]. In fact the issue of whether hard sphere systems exhibit fluid-solid equilibria was a strong motivation for the development of the techniques. The evidence accumulated from such studies for the existence of the freezing transition is one of the most important developments in our understanding of condensed phase systems. The early studies concentrated upon the observation of two branches in the hard sphere equation of state. Subsequently, calculations of the free energies [9] provided convincing evidence for the transition.

For single component systems the basic problem in using computer simulations in studies of solid-fluid equilibria is that of determining the chemical potentials associated with the solid and fluid branches of the PVT equation of state. The straightforward approach is to determine the chemical potential via integration of the isothermal Gibbs-Duhem equation. In the case of the solid this cannot be done directly since the path of integration passes through the first order phase transition, the location of which is sought in the calculation. Three strategies have been used to circumvent this difficulty. The feature which these methods have in common is the construction of a reversible path from the solid state of interest to a reference state with known free energy. The earliest approach was that of Hoover and Ree [9]. They carried out simulations of a single occupancy hard sphere cell model, essentially the model which is solved approximately in the cell theories. The system has an equation of state which is indistinguishable from that of a hard sphere solid at high densities but at lower densities goes smoothly to that of a single occupancy lattice gas, thus providing a reversible path between a zero density ideal gas and the solid. This work has ben extended to hard sphere mixtures by Kofke [31]. Unfortunately this method does not seem to be applicable to potentials without hard sphere cores.

For systems where the intermolecular potentials are continuous and where the solid phase of interest remains stable at low temperature, an alternative is to use the fact that at low temperatures the solid will be harmonic (this will not be true for discontinuous potentials such as hard spheres or square wells) and its free energy can be computed via the methods of lattice dynamics [21]. The free energy difference between low and higher temperatures can then be obtained by integration of the Gibbs-Helmholtz equation. The principal difficulties with this approach lie in the complexity of the lattice dynamics calculations for anything except simple atomic systems and the restriction to solid phases which are stable at low temperature.

An especially elegant approach is that suggested by Frenkel and Ladd [22]. They have shown that it is possible to construct an external field in such a way that as the field is switched on, the solid is reversibly transformed into a classical Einstein crystal where the free energy is that of an assembly of independent classical harmonic oscillators and can be obtained in closed form (in the case of spherical molecules) or by a simple numerical integration (in the case of nonspherical molecules). The method can be applied to all kinds of potentials including systems with attractive forces [23] and nonspherical molecules [24, 25]. By combining with methods for performing thermodynamic integrations over composition it can also be extended to mixtures [26].

One of the key problems in calculating the free energy of solids is the determination of the most stable crystal structure. The simulation methods which we have just described are carried out for an assumed crystal structure. Thus it might be necessary to consider a variety of crystal structures in order to locate the structure of lowest free energy. Alternatively, one can incorporate structural relaxations into molecular dynamics and Monte Carlo simulations, as was first suggested by Parinello and Rahman [27]. Ordinarily such structural relaxations are suppressed by the use of a fixed simulation box shape and the periodic boundaries. The basic idea in the Parinello-Rahman approach is simply to allow the simulation cell to change shape during the calculation. Such a shape change can be incorporated into the equations of motion in isobaric molecular dynamics or as a trial move in isobaric Monte Carlo simulations [29, 30].

The methods described above will permit the calculation of solid-fluid equilibrium at a single temperature for a single component system. For systems with attractive forces we are faced with the task of repeating the calculation for each isotherm under consideration. Recently, Kofke and coworkers [32] have shown how, given the phase coexistence properties at one temperature, these properties may be obtained at other temperatures by numerical integration of the Clapeyron equation using predictor-corrector methods. This approach, referred to as the Gibbs-Duhem integration technique, offers considerable promise for evaluating solid-fluid equilibrium over a range of temperatures, and can be extended to mixtures.

## 4. MOLECULAR SIZE EFFECTS ON SOLID-FLUID EQUILIBRIUM IN MIXTURES

One of the most important recent applications of statistical mechanics to the calculation of solid-fluid equilibrium has been mixtures of hard spheres of different sizes. The importance of molecular size difference in determining the stability of solid state mixtures has been recognized for some time [28]. It is only recently that it has been possible to quantify the effects precisely through calculations on hard sphere mixtures in the solid state. Such mixtures have been studied via density functional theory [33–36], cell theory [11, 12] and by Monte Carlo simulation [26, 31, 37]. The remarkable conclusion to be drawn from this work is that binary hard sphere mixtures exhibit most of the kinds of solid-fluid phase equilibrium exhibited by real binary mixtures.

Before discussing this phase behavior in more detail it is worthwhile to discuss the significance of the hard sphere model of freezing in a little more detail. Starting with the work of Alder and Wainwright [19], Wood and Jacobsen [20], and Hoover and Ree [9] the existence of a first order freezing transition for hard spheres has been established. Hard spheres exhibit a low density disordered fluid phase and a high density ordered solid phase. The pressure density isotherm for hard spheres is qualitatively similar to that for a simple substance such as argon or nitrogen at temperatures well above the critical temperature. The freezing of hard spheres provides a fundamental geometric picture of the freezing of simple molecules by isothermal compression. For hard spheres the effect of increasing pressure in the solid phase is analagous to the effect of decreasing temperature in a system with attractive forces. In fact the pressure in a hard sphere system can be regarded as an inverse temperature. Longuet-Higgins and Widom [38] showed how a quite accurate picture of the full phase diagram for argon could be obtained by starting with the hard sphere equation of state for both solid and fluid states and adding a mean field term to describe the effect of the attractive forces. This was probably the first example of what is now commonly referred to as a generalized van der Waals equation of state.

Returning now to mixtures, Figure 1 shows pressure versus composition phase diagrams of binary hard sphere mixtures. These results were calculated by using the cell theory for the solid phase and an accurate equation of state for the fluid phase [39]. This approach generates very good agreement with Monte Carlo simulation results [11, 12]. Six types of behavior are shown. For a size ratio $\alpha = \sigma_2/\sigma_1$ of 0.97 (Figure 1a.) a simple spindle phase diagram is seen. Notice that at a given pressure the mole fraction of the larger spheres is higher in the solid phase since the larger spheres have the lower pure component freezing pressure. As $\alpha$ is lowered to 0.92 we see the occurrence of an azeotrope (Figure 1b.). At lower values of $\alpha$ a simple eutectic with complete immiscibility in the solid phase is seen as shown for example for $\alpha = 0.73$ in Figure 1d. At intermediate values of $\alpha$ partial miscibility is also seen in the solid phase (see Figure 1c.). Perhaps the most remarkable feature of the hard sphere mixture phase diagrams is the formation of substitutionally ordered solid solutions or compounds. Theoretical phase diagrams [12] for hard sphere mixtures with compound formation are shown in Figures 1e and 1f. Three types of compound have been found to be stable with stoichiometries AB, $AB_2$ and $AB_{13}$ [12, 37]. These compounds are stabilized by packing effects on the free energy for mixtures of spheres of different sizes. The compounds with stoichiometries $AB_2$ and $AB_{13}$ have been observed experimentally in some samples of natural opal, in colloidal systems [41] and more recently in mixtures of $C_{60}$ with cyclohexane [42].

Some time ago Matsuoka [43] presented a survey of solid-fluid equilibrium based on data for about 1500 binary organic mixtures. In this survey he identified six important classes of phase diagram. Hard sphere mixtures exhibit all but one of these classes. Thus we may conclude that hard sphere mixtures provide

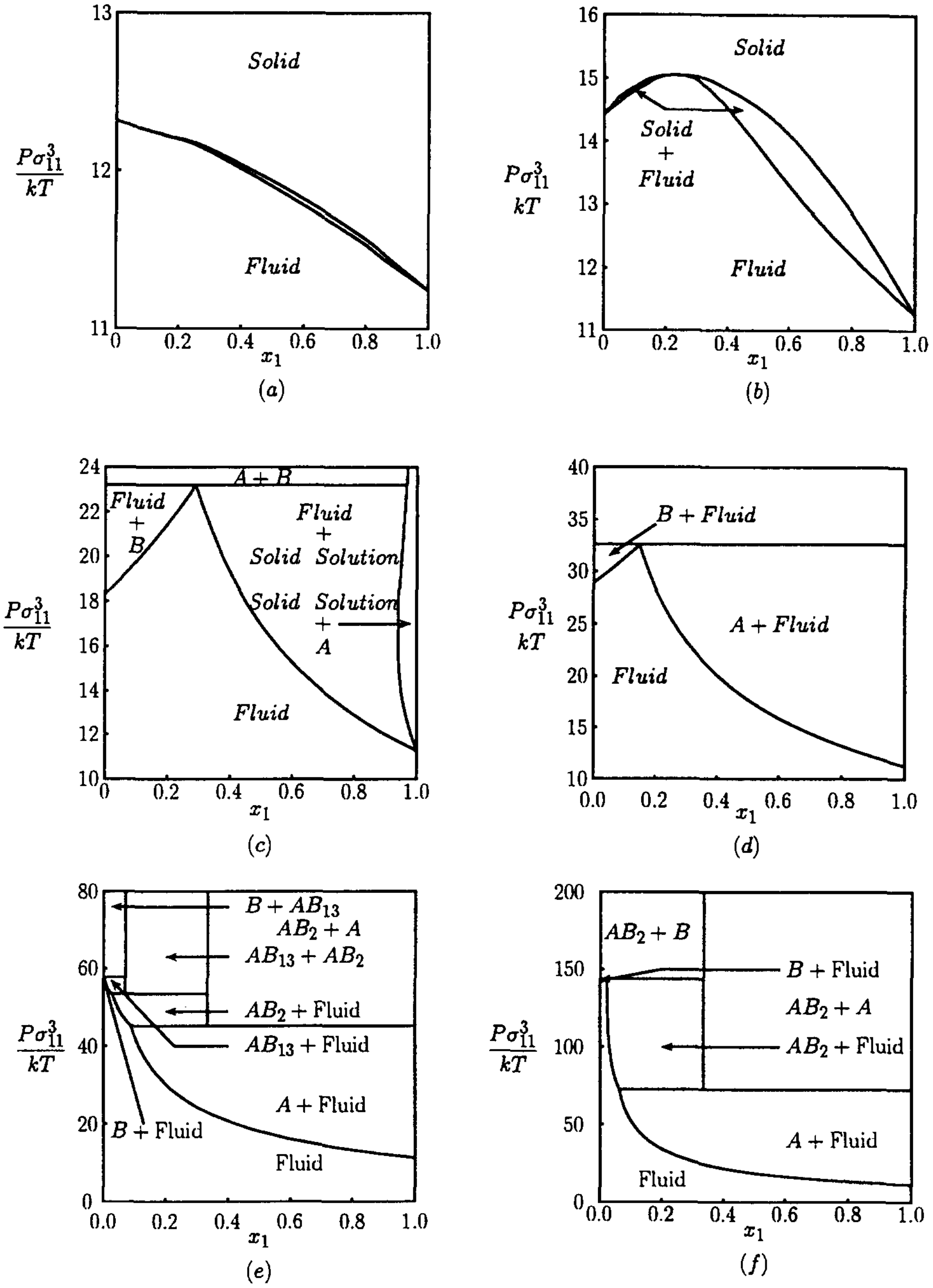

Figure 1. Solid-fluid phase diagrams for binary hard sphere mixtures obtained by using the cell theory for the solid phase and the equation of state of Mansoori et al. [39] for the fluid phase [11,12]. The systems depicted are: a) $\alpha = 0.97$; b) $\alpha = 0.92$; c) $\alpha = 0.85$; d) $\alpha = 0.73$; e) $\alpha = 0.58$; f) $\alpha = 0.43$.

a good starting point for understanding the solid-fluid phase diagrams in more complex mixtures. What seems to be missing in the hard sphere mixture is the presence of compounds which melt congruently. The hard sphere compounds studied thus far become unstable before the melting point is reached.

## 5. MOLECULAR SHAPE AND SOLID-FLUID EQUILIBRIUM

In extending theoretical approches for solid-fluid equilibrium to more complex molecules it is important to identify which are the important effects which need to be taken into account. In this section we consider the effect of molecular shape. A useful model for nonspherical molecular shape which is readily extended to the case of polar or long chain molecules is the interaction site formalism [44]. In this formalism a nonspherical molecule is regarded as a collection of interaction sites and the intermolecular potential between two molecules is then a sum of site-site potentials. The simplest such model for the effect of molecular shape is provided by the hard dumbbell model which consists of two hard spheres, each of diameter $\sigma$, connected by a rigid bond of length L. The key parameter describing the nonsphericity in this model is $L^* = L/\sigma$. The model describes much of the physics of solid-fluid equilibrium in systems of diatomic and other small nonspherical molecules. Recent work, using both Monte Carlo simulation [25,45,46] and cell theory [47], has shown how the solid-fluid phase equilibrium for this model changes with $L^*$.

The results are illustrated in Figure 2 which presents Monte Carlo simulations [25,45,46] for the coexistence densities and pressures versus $L^*$. The values for $L^* = 0$ are those for hard spheres. Hard dumbbells exhibit two kinds of solid phase. One which is characterized by a low degree of orientational order is analogous to the plastic crystal phases formed in the freezing of liquid nitrogen or oxygen. The plastic crystal phase is stable only for shorter bond lengths. It becomes unstable with respect to orientationally ordered phases, which allow the dumbbells to reach their maximum packing density, for larger values of $L^*$ and at high pressure. The orientationally ordered phases are closely related to the orthorhombic phases exhibited by the diatomic halogens and ethane. One of the interesting features of Figure 2a is the decrease in the density change on freezing into the plastic crystal phase as $L^*$ increases. A value of $L^* \sim 0.33$ is often used in diatomic models of nitrogen and it appears that the effects present in the hard dumbbell model can account for the decrease in the density change on freezing between argon and nitrogen.

The properties of hard dumbbells can be used as the reference system for a generalized van der Waals [38,48] treatment of the effect of molecular shape upon solid fluid equilibrium for systems with attractive intermolecular forces. This is accomplished via the following approximation for the Helmholtz free energy per molecule:

$$\frac{A}{NkT} = \frac{A_0}{NkT} - a\rho \tag{9}$$

where $A_0$ is the Helmholtz energy for the hard dumbbell system and $a$ is a parameter describing the effect of the attractive forces. This equation predicts both vapor-liquid and solid-fluid equilibrium. The solid-fluid equilibrium emerges via the hard dumbbell equation of state. As an illustration of the results which can be obtained from this model, Figure 3 shows phase diagrams for three systems obtained from this theory represented on a $T/T_c$ versus $\rho/\rho_c$ diagram. The systems considered correspond to three values of $L^* = 0, 0.3$ and $0.6$ representing argon, nitrogen and chlorine respectively. Clearly, in going from argon to nitrogen the theory predicts an increase in the triple point density and decreases in the triple point temperature and fractional density changes on freezing. This agrees with what is seen experimentally. This theory has been modified to account for the effect of a large quadrupole moment [48–50]. When this is done the phase diagrams of acetylene and carbon dioxide can be accounted for quite realistically.

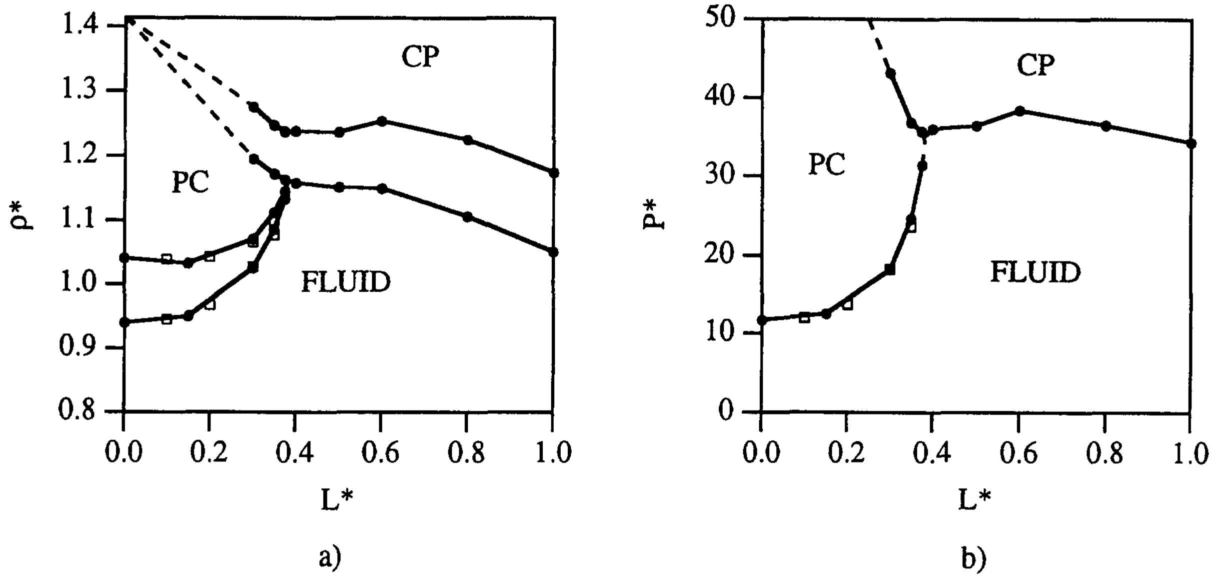

Figure 2. Solid-fluid equilibrium for the hard dumbbell model from Monte Carlo simulation [25,46]: a) coexistence densities; b) coexistence pressures.

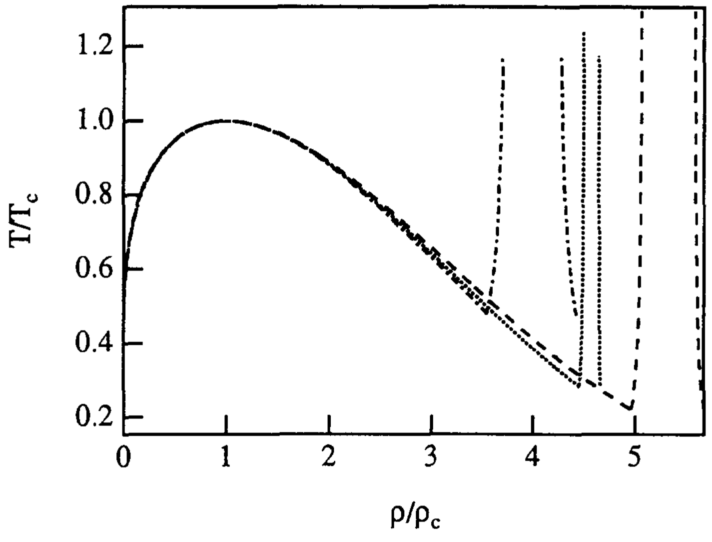

Figure 3. Corresponding states phase diagrams from the generalized van der Waals theory using the hard dumbbell reference system [48]. Three systems are shown: $L^*=0$ representative of argon (dot dash curve); $L^*=0.3$ representative of nitrogen (dotted curve); $L^*=0.6$ representative of chlorine (dashed curve).

## 6. SUMMARY AND DISCUSSION

The methods of statistical mechanics can provide much useful information concerning solid-fluid phase equilibrium and in this paper we have reviewed several theoretical and molecular simulation methods for accomplishing this. To illustrate the kinds of insights obtained we have presented applications to the prediction of solid-fluid phase diagrams for binary mixtures and to predicting the influence of molecular shape on solid-fluid phase equilibrium.

Studies of binary hard sphere mixtures show that these simple systems exhibit much of the complex behavior seen in the solid-fluid phase diagrams for real mixtures, including azeotropy, eutectics and compound formation. The hard sphere compounds do not exhibit congruent melting. Extending the theory developed for hard sphere mixtures to more complex systems (with attractive forces and/or nonspherical molecules) and determining the additional effects required to increase the stability of compounds are subjects of ongoing research.

The generalized van der Waals theory with the hard dumbbell reference system provides a good starting point for understanding the influence of molecular shape upon solid-fluid phase equilibrium. In particular the theory explains the lower values of $T_t/T_c$ for nonspherical molecules and the small density change when molecules like nitrogen freeze into plastic crystals. We are currently extending this approach to flexible chain molecules representative of the normal alkanes.

## 7. ACKNOWLEDGMENTS

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