Structure and dynamics of the interface between a binary hard-sphere crystal of NaCl type and its coexisting binary fluid

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Molecular dynamics simulations are performed to study the [100] and [111] orientations of the crystal-melt interface between an ordered two-component hard sphere with a NaCl structure and its coexisting binary hard-sphere fluid. The diameter ratio of the two types of hard spheres making up the mixture is taken to be $\alpha = 0.414$. This work complements our earlier interface simulations [J. Chem. Phys. 116, 3410] for the same diameter ratio at lower pressures where the smaller component is immiscible in the solid and the fluid mixture coexists with a pure FCC crystal of large particles. Density profiles and diffusion coefficient profiles are presented for the AB interfacial system. We find that for this system, the transition from crystal-like to fluid-like behavior of both the density and diffusion constant profiles occurs over a narrower region than that seen in our previous studies [J. Chem. Phys. 116, 3410] of the FCC/binary fluid system. But similar to what was found in the FCC/binary fluid interface the transition region for the large particle diffusion constant is shifted about 1.0$\sigma_A$ toward the fluid phase relative to that for the small particles.

I. INTRODUCTION

The kinetics of crystal growth and nucleation from the melt is highly dependent upon the structure, dynamics and thermodynamics of the crystal-melt interface. Given the difficulties in obtaining unambiguous information from experiments, most of what is currently known about the microscopic phenomenology of such interfaces is obtained via computer simulation. Although most simulation studies have focused on single component systems, there has been recent interest in multicomponent interfaces. All of these studies have involved crystal phases that are either disordered or pure face-centered cubic (FCC) lattices. In this work we present results for the structure and dynamics of the interface between an ordered two-component hard-sphere crystal with a sodium chloride (NaCl) structure and a binary hard-sphere fluid. Such a system can be viewed either as a prototype to understand the interface between inter-metallic compounds and their coexisting fluid phases or as a model two-component colloidal dispersion.

The hard-sphere interaction was chosen for this study since it is an important reference model for the study of simple liquid and liquid mixtures. This is especially true with regard to phenomena associated with the freezing transition. For example, it has been recently shown that the interfacial free energy of close-packed metals can be described with quantitative accuracy using a hard-sphere model. In addition, recent phase boundary calculations have shown that binary hard spheres form a wide range of crystal structures depending on the ratio, $\alpha = \sigma_B/\sigma_A$, of the diameter of the small spheres (labeled B), $\sigma_B$ to that of the larger spheres (labeled A), $\sigma_A$. A substitutionally disordered FCC crystal is the stable phase for $1.0 > \alpha > 0.85$ while for $\alpha < 0.85$, only ordered crystal structures are seen to be stable, including AB, AB$_2$ and AB$_{13}$ structures. A detailed study of the disordered FCC crystal/melt interface for $\alpha = 0.9$ has been recently reported.

In this work, we examine two-component hard-sphere mixtures with a considerably larger size asymmetry of $\alpha = 0.414$. This size ratio is significant in the theory of binary alloys in that it is the largest asymmetry in which the small spheres can be accommodated in the interstitials of a densest close-packed crystal of larger spheres. The phase diagram for this value of $\alpha$ has been determined as a function of pressure and mole fraction using MC and MD simulations by Trizac and coworkers and is reproduced in Fig. 2. At low pressures, the binary fluid coexists with a pure FCC crystal of large spheres, whereas at higher pressures (above $50kT/\sigma_A^3$) the coexisting solid phase is an ordered 1:1 crystal of the sodium chloride (NaCl) type. Earlier cell theory calculations also predicted the stability of the NaCl at this diameter ratio. Other AB structures such as the CsCl and the zinc blende have been shown to be unstable at this diameter ratio. Throughout the text we will be using AB to also refer to the NaCl structure.

A detailed study of the low pressure pure FCC/binary fluid system has been recently reported. In that work, the coexistence between the crystal and an approximately 1:1 binary mixture was examined, corresponding to a pressure of $20.1kT/\sigma_A^3$, which is approximately twice the coexistence pressure ($11.5kT/\sigma$) of the pure single component system. As the pressure is increased the mole fraction of large spheres in the fluid phase, $X_A^f$, decreases, and at a pressure of about $50kT/\sigma_A^3$, the fluid coexists with an AB crystal of NaCl type (see Fig. 2). In this work, we examine in detail the microscopic structure

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and dynamics of the interface between the high pressure AB crystal and its melt. To do this, we have chosen a point in the phase diagram with \(X_A^f = 0.097\). At this mole fraction, the fluid coexists with the NaCl crystal at a pressure of 53 \(kT/\sigma_A^3\). Details of the simulation methodology and interface equilibration procedure are outlined in the next section followed by presentation of the results of the study in Section III and concluding remarks in section IV.

II. SIMULATION DETAILS

Molecular-dynamics simulations are performed on a two-component system of hard spheres of differing diameters, \(\sigma_A\) and \(\sigma_B\), with \(\sigma_A < \sigma_B\) (Type A particles are assumed to be the larger spheres). The interaction potential between two spheres is defined by the following pairwise interaction potential

\[
\phi_{ij}(r) = \begin{cases} 
\infty & , r \leq \sigma_{ij} \\
0 & , r > \sigma_{ij} 
\end{cases},
\]

where \(i, j \in \{A, B\}\), \(r\) is the distance between the centers of the two interacting spheres, and \(\sigma_{ij} = (\sigma_i + \sigma_j)/2\) is the distance of closest possible approach between two spheres with diameter \(\sigma_i\) and \(\sigma_j\), respectively. The system is completely defined by specifying the diameter ratio \(\alpha \equiv \sigma_B/\sigma_A\), the mole fraction of large particles, \(x_A\) and the total number density, \(\rho\). The total volume occupied by the hard spheres relative to the volume available to the system is given by the packing fraction,

\[
\eta = \frac{\pi \sigma_A^3}{6} \rho \left[ x_A + (1 - x_A) \alpha^3 \right],
\]

where \(\rho = \rho_A + \rho_B = N/V\) is the total density, \(x_A\) is the mole fraction of the larger species, and \(\alpha = \sigma_B/\sigma_A\) is the diameter ratio.

The procedures for interface construction and equilibration of binary interfaces employed in this study are similar to those used in our earlier work[44] on the low-pressure coexistence in this system (single component FCC \((x_A = 1)/\)binary fluid mixture). Since the general interface preparation process is described at length in that work, only those details specific to the current system are described here. The interested reader is encouraged to consult reference[44] for a more complete description.

To construct an interface, fluid and crystal blocks are prepared separately using the calculated coexistence conditions. At a pressure of 53 \(kT/\sigma_A^3\), we independently determined the packing fractions of the coexisting crystal and fluid to be \(\eta_c = 0.683\) and \(\eta_f = 0.490\), respectively. In the preparation of a fluid block, it is a usual practice to initially position particles in a lattice at a density lower than coexistence. As the system is allowed to equilibrate the lattice melts, giving a fluid configuration, which is then compressed to the coexistence density. For the system under study here this procedure is not feasible since the size asymmetry \((\alpha = 0.414)\) and the mole fraction of small particles \((X_B^f = 0.903)\) in the fluid system are both large. (It should be noted that for this value of \(\alpha\) the large sphere volume is over 14 times that of the small particle.) To construct the fluid phase we began with an FCC lattice of small particles at a number density equal to the desired total number density of the fluid mixture. A number of particles, corresponding to the target mole fraction of large spheres, are then chosen at random from this lattice. A molecular dynamics run is started from this initial configuration and the diameter of randomly chosen particles is periodically increased until the correct large sphere diameter is attained. The amount of increase in the diameter at each stage depends on the maximum increase that is possible without creating particle overlap. The preparation of the crystal is straightforward as the small particles easily inserted into the interstitial sites of the large sphere FCC lattice.

After equilibration of separate crystal and fluid systems, they are placed in contact within the simulation box. Due to the periodic boundary conditions, two interfaces are formed. Note that packing fraction used in the preparation of the initial fluid block is slightly different from the predicted \(\eta_f\) since a gap of 1\(\sigma_A\) is placed between the crystal and fluid blocks to avoid any initial overlap that may occur when the two blocks are.
TABLE I: Number of particles and dimensions of the simulation box

|  | N° | N° | L_z/σ_A | L_y/σ_A | L_z/σ_A |
|---|---|---|---|---|---|
| [100] | 7056 | 14976 | 10.41 | 10.41 | 53.02 |
| [111] | 7200 | 15552 | 10.51 | 10.92 | 51.44 |

combined. The fluid particles are then allowed to move while the large particles are fixed so the initial gaps are then filled with the fluid particles. The initial fluid packing fraction is adjusted until an unstressed bulk crystal is obtained when the two blocks are combined and equilibrated.

In this study, we examine both the [100] and [111] orientations of this NaCl crystal/binary fluid interface. For reference, we define the z-axis to be perpendicular to the interfacial plane. Periodic boundary conditions are applied in x, y, and z directions. The length in the z-direction, L_z, is a sum of lengths of the two separate blocks in the z-direction and the 2σ_A-gap initially left between the two blocks. The total number of particles used are 22,032 and 22,752 for the [100] and [111] orientations, respectively. The details of the system sizes used are summarized in Table I. As the systems studied are large, we have implemented the cell method technique to efficiently carry out the molecular-dynamics simulations. Equilibration was done for about 4 × 10^5 collisions per particle(cpp). During sampling, the run was divided into blocks of 2600 cpp each. The sampling run was over a length of 30 blocks, but since each block gives two independent measures of interfacial properties when the system is properly folded at the center of the crystal, the results reported are averages taken over 60 samples.

In the course of such simulations the position of the interfacial plane can shift due to Brownian motion or due to melting or freezing of the crystal. To prevent such motion from artificially broadening the interfacial profiles it is necessary to monitor the position of the interfacial plane during the sampling runs. The standard measure of interfacial position for a planar interface is the Gibbs dividing surface defined for a multicomponent system as the value of z where the surfaces excess number of “solvent” particles is zero. However, accurate calculation of the Gibbs dividing surface requires relatively long simulation runs and is then unsuitable for a method of monitoring the time dependence of interfacial position. In our previous studies, we find that a more suitable measure can be obtained from measurement of orientational order parameter profile as a function of z. The orientational order parameter is defined as follows

\[ q_n(z) = \frac{1}{N_z} \sum_{i,j,k} \cos \left[ n\theta_{xy}(i,j,k) \right], \]

where \( n = 4 \) for the [100] orientation and \( n = 6 \) for the [111] orientation. \( i, j \) and \( k \) are nearest neighbor large particles, \( \theta_{xy}(i,j,k) \) is the bond angle formed by \( i, j \) and \( k \) projected on the \( x, y \) plane, and \( N_z \) is the total number of particles that form bond angles. The average is taken over the number of angles found between \( z - \Delta z/2 \) and \( z + \Delta z/2 \), where \( \Delta z \) is equal to the layer spacing of the bulk crystal.

We show in Fig. 2 the order parameters, \( q_4 \) and \( q_6 \), of the two particle types for the [100] (upper panel) and [111] (lower panel) orientations. As expected \( q_4 \) (\( q_6 \)) is small in the [111] ([100]) interface where 6-fold (4-fold) symmetry dominates. We define the interfacial position relative to the midpoint of the orientational order profile for the large particles. That is, \( z = 0 \) in all of the \( z \)-dependent profiles presented in this study is defined as the point at which the orientational order parameter has decayed halfway from its crystal to fluid value. This order parameter is suitable as a measure of interfacial position since it is smoothly monotonically decreasing and can be calculated accurately for very short runs. The parameter profiles of the small particles are not smoothly varying because at the interfacial region, some number of small particles cluster together to occupy large particle vacancies at the interfacial region (as will be seen in the density plots presented in the next section) disrupting the smooth transition from crystal-like to fluid-like value of the orientational order parameter.

Analysis of the interfacial position as a function of time shows that during the equilibration run the crystal exhibits some initial growth, but quickly stabilizes before the averaging runs are begun. Brownian motion of the

![FIG. 2: Large (dotted) and small (solid) particle orientational order parameter profiles, \( q_4 \) (circle) and \( q_6 \) (square) for the [100] and [111] interfacial orientations. The point \( z = 0 \) is the location of the interfacial plane as calculated from the large particle order parameter profile.](image)
solid phase, as monitored by motion of the inner layers of the crystal, was found to be negligible due to the large system size and no correction was necessary.

III. SIMULATION RESULTS FOR THE [100] AND [111] INTERFACES

A. Structure: Density profiles and contour plots

The structural variation of the system across the interface is determined by calculating the density profile for each particle type.

\[ \rho_i(z) = \frac{<N_i(z)>}{L_x L_y \Delta z} \]  

(4)

where \( i \) denotes a particle type, \( \Delta z \) is 1/25 of the crystal layer spacing, \( <N_i(z)> \) is the average number of particles of type \( i \) in the region between \( z - \Delta z/2 \) and \( z + \Delta z/2 \).

The density profiles of the two particle types are shown in Fig. 3(a) and (b) for the [100] and [111] orientations, respectively. As expected for an NaCl-type lattice, the small and large particle peaks are in phase in [100] and exactly out of phase in [111]. This is similar to the registry of particle density peaks found at the interfacial region of the lower pressure pure FCC/binary fluid system. Due to the higher pressures in this study, the crystal peaks are much sharper than those seen in the lower pressure binary system or in the single component interface. The small side peaks in the NaCl density are due to the filling of large particle vacancies in the lattice structure with several smaller particles - as discussed below. In order to reveal any change in the lattice spacing through the interface and to index the interfacial planes for later use, vertical dotted lines separated by the bulk crystal lattice spacing were added to Fig. 3. Labels a to i in the [100] profile marks some layers whose cross-sectional density distributions have been determined and will be discussed later. For both orientations, there is no discernible change in the lattice spacing as the interface is traversed from crystal to fluid, in contrast to what was seen in our previous studies where the crystal was either a pure or disordered FCC lattice. In those studies there was a significant increase in the lattice spacing in the [100] orientation as the fluid side of the interface was approached.

The oscillations in the fine scale density profiles shown in Fig. 3 make it difficult to see the overall trend in bulk density, so we have processed these profiles using a Finite Impulse Response filter to reveal the non-oscillatory component of the density variation. The resulting filtered density profiles are shown in Fig. 4. The 10-90 width of these bulk density profiles provides a measure of the interfacial width. (The 10-90 width of a monotonically varying interfacial profile is the distance over which the profile changes from 10% to 90% of the higher of two coexisting bulk values, relative to the lower bulk value.) The 10-90 width derived from the large particle density profile of the [100] orientation [see Fig. 4(a)] is 2.6σA, corresponding to the region between \( z = -2.2\sigma_A \) to \( z = 0.4\sigma_A \). For the small particles the 10-90 width is smaller at 2.3σA and the 10-90 region (\( z = -1.7\sigma_A \) to \( z = 0.6\sigma_A \)) is shifted slightly toward the fluid, relative to the 10-90 region of the large spheres. Combining these two regions, the interfacial region of the [100] ori-
orientation defined by the densities has a width of 2.8σ_A. The total interfacial width defined for the densities for the [111] orientation (2.9σ_A) is not significantly different than that for [100]. The interfacial widths of the large particle density profiles are identical to those found in our earlier lower pressure FCC/binary fluid interface study for the same diameter ratio, but narrower than the 3.3σ widths found in the single component system. In contrast, the small particle interfacial widths found here are much smaller than those found in the lower pressure study, where they were found to be about 3.3σ_A. As a consequence, the overall interface for the NaCl/fluid is slightly narrower than the lower pressure pure FCC/fluid interface.

To get a detailed understanding of the structural transition across the interface between the two coexisting phases, we have determined the cross-sectional density distributions within layers parallel to the interfacial plane. For each layer, the 2-D density distribution is defined as

$$\rho_i(x, y) = \frac{<N_i^z(x, y)>}{\Delta x \Delta y \Delta z}$$  \hspace{1cm} (5)

where \(i\) denotes a particle type, \(\Delta x = \Delta y = 0.12\sigma_A\), \(\Delta z\) is the crystal layer spacing, which is 0.74σ_A for [100]. The average number of particles of type \(i\) in the volume given by \(\Delta x \Delta y \Delta z\) is \(<N_i^z(x, y)>\). In Figs. 5 and 6 are density contour plots of the [100] interface for the large and small particles, respectively. Layers a to i are as labeled in Fig. 3(a), where a is deep into the bulk crystal, 

\(i\) is in the bulk fluid and b to h are interfacial regions. The decrease in density peak height of the large (Type A) spheres in Fig. 5 starting at layer b is initially due to the presence of lattice vacancies as shown in Fig. 5. Small particle vacancies also start to appear in layer b of Fig. 6. We also find by comparing Figs. 3 and 6 for layers c and d that the side peaks appearing at these layers are due to the accumulation of small particles in the large sphere vacancies. The structure of this vacancy filling is interesting in that the large particle is typically replaced.
by 6 small particles (although a small number of vacancies filled with 5 or 7 small spheres do occur) with little disturbance to the surrounding lattice. This can be seen in Fig. 3, where a snapshot of one of these filled vacancies in layer c is shown. A uniform 2-D density distribution begins to develop in layer G for both particle types indicating that, although the z-dependent density profiles still have some oscillations in this region, the structure is that of an inhomogeneous fluid at a wall.

Of particular interest to materials scientists is the degree of interfacial segregation - the preferential adsorption (or desorption) of one component (usually the “solute”) at the interface. This quantity is defined relative to the Gibbs dividing surface. The Gibbs dividing surface of a planar interface is defined as the plane along the z-axis giving a vanishing surface excess solvent particle number, $\Gamma^\text{solv}$, defined in the equation

$$N^\text{solv} / A = \rho^\text{solv}_c z + \rho^\text{solv}_L (L_z - z) + \Gamma^\text{solv}$$

where $N^\text{solv}$ is the total number of solvent particles, $A$ is the area of the interface, $\rho^\text{solv}_c$ and $\rho^\text{solv}_L$ are the bulk densities, $z$ is the location of the interface assuming the length of the simulation box runs from 0 to $L_z$. Defining the small particles as the “solute”, we find that the Gibbs dividing surfaces are at $z = -0.49\sigma_A$ and $z = -0.93\sigma_A$ relative to the position calculated from the large particle order parameter for the [100] and [111] orientations, respectively. Surface excess of the “solute” particles, $\Gamma^A$ was found to be negligible, indicating the absence of interfacial segregation, a result that is consistent for other crystal/melt systems that have been investigated.

B. Transport: Diffusion coefficient profiles

Inhomogeneities in the transport properties within the interfacial region can be examined by calculating $z$-dependent diffusion coefficient profiles, defined for a particle of type $i$ by

$$D_i(z) = \lim_{t \to \infty} \frac{1}{6N_i(z)} \frac{d}{dt} \sum_{j=1}^{N_i(z)} \langle |r_j(t) - r_j(t_0)|^2 \rangle .$$

The term in the summation is the mean-squared displacement over a time interval $t - t_0$ of a total of $N_i$ type $i$ particles located between $z - \Delta z/2$ and $z + \Delta z/2$ at time $t_0$, where $\Delta z$ is the layer spacing in [100] and is twice the layer spacing in [111].

Figure 8(a) shows the diffusion coefficient profiles for the current study (dotted lines), including for comparison the results previously reported for the lower pressure FCC/binary fluid interface (solid lines). Only the [100] results are shown as the diffusion profiles for the [111] interfaces are not statistically different. The error bars are small and so are not shown for clarity of the plots. The bulk fluid value for the large particles in the lower pressure FCC/binary fluid system is $0.012(kT\sigma_A^2/m)^{1/2}$ and that for the small particles is $0.050(kT\sigma_A^2/m)^{1/2}$. Since the AB/fluid system has a higher pressure and larger fluid packing fraction, the bulk fluid diffusion coefficient values are lower: $0.008(kT\sigma_A^2/m)^{1/2}$ for the large particles and $0.029(kT\sigma_A^2/m)^{1/2}$ for the small particles. The difference in magnitude between the small and large particle diffusion constants makes it difficult to compare the two diffusion profiles. For a clearer comparison in Fig. 8(b) we plot the data in Fig. 8(a) normalized relative to the bulk fluid values. Traversing the system from fluid to crystal, we find a region of width greater than $1\sigma_A$ where the small particles have nonzero diffusion coefficient while the large particles have effectively zero diffusion. Both high- and low-pressure systems exhibit this shift in the change from crystal-like to fluid-like motion of the two particle types.

As was done for structural transition, we can also define the extent of dynamical transition by determining the 10-90 region from diffusion coefficient profiles. From the diffusion coefficient profile of the large particles this region starts from $z = -0.7\sigma_A$ up to $z = 1.3\sigma_A$, resulting to a width equal to $2.0\sigma_A$ and centered at $z = 0.3\sigma_A$. The small particles define an interfacial region that starts from $z = -2.2\sigma_A$ and ends at $z = 0.6\sigma_A$. These boundaries give a width of $2.8\sigma_A$, which is 40% greater than the width from diffusion of the large particles. Also, the midpoint is shifted by $1.1\sigma_A$ to the fluid side relative to the midpoint of the region defined by the large particles.

As in our previous studies on hard-sphere
diffusion is shifted by about 1. The same region, while the transition for the large particle is observed over approximately the densities for both particle types and the diffusion of FCC/binary fluid simulations in that the transition of to the corresponding plot for our earlier low-pressure interfacial width, this plot is qualitatively quite similar the [100] interface. Except for differences in the overall to unity in the bulk crystal and zero in the bulk fluid for profiles, normalized such that we have all values equal to unity in the crystal and zero in the bulk fluid for the [100] interface. Except for differences in the overall interfacial width, this plot is qualitatively quite similar to the corresponding plot for our earlier low-pressure FCC/binary fluid simulations in that the transition of densities for both particle types and the diffusion of the small particles is observed over approximately the same region, while the transition for the large particle diffusion is shifted by about \(1\sigma_A\) (1.3\(\sigma_A\) in the earlier study). Another notable feature in this plot is that the transition for the orientational order parameter, which we use to locate the interfacial plane, occurs at about the center of these two transition regions.

IV. SUMMARY

Using molecular-dynamics simulation, we have investigated the structure and dynamics of the [100] and [111] crystal-melt interfaces of the AB(NaCl)/binary fluid system for a two-component hard-sphere system in which the ratio of small to large particle diameter is \(\alpha = 0.414\). This system was at a pressure of \(53kT/\sigma_A^3\) that is at the lower range of the NaCl crystal/fluid coexistence region. These simulations complement our earlier work on the pure FCC/binary fluid interface found in this same system at lower pressure \((20.1kT/\sigma_A^3)\). We find that the higher pressure AB/binary-fluid interface has a narrower interfacial region of \(3.5\sigma_A\) compared to the lower pressure FCC/binary fluid system at the same diameter ratio, which had an interfacial region of width \(4.8\sigma_A\). In addition, the crystal side of the higher pressure binary interface exhibited much higher vacancy defect concentrations than either the low pressure binary system or the single-component interface. In the interfacial region, all vacancies in the large particle lattice were found, with little distortion in the surrounding lattice, to be filled with an average of 6 small particles. Similar to what was seen in the lower pressure FCC/binary fluid interface, the transition regions for both density profiles and the small particle diffusion constant are approximately coincident whereas the diffusion profile for the large particles is shifted relative to the others by about \(1\sigma_A\) toward the liquid side of the interface.

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