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Longitudinal density distribution in the liquid-vapor interface of a dilute alloy of Tl in Ga

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We report the results of self-consistent Monte Carlo simulations of the density distribution along the normal to the liquid-vapor interface of a dilute binary alloy of Tl in Ga. The results of the simulation are in agreement with those obtained from experimental studies reported by Yang *et al.* [Phys. Rev. E **67**, 212103 (2003)]. In particular, our calculations reproduce the positions and relative amplitudes of the density strata in the liquid-vapor interface and the finding that the excess Tl forms a complete monolayer that is its outermost layer. The amplitudes of the density oscillations are overestimated by the simulations, which we attribute in part to the small size of the surface of the simulation sample and in part to residual inaccuracies in the pseudopotential employed.

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I. INTRODUCTION

This paper presents the results of a theoretical study of the density distribution along the normal to the liquid-vapor interface of a dilute Tl in Ga alloy. The motivations for this study, which complements the experimental study of that interface reported by Yang *et al.*,[1] are (1) to further test the generic predictions of the pseudopotential-based self-consistent Monte Carlo simulation analysis of Rice and co-workers[2] against experimental data, and (2) to test the particular pseudopotential that they have widely used.

Despite extensive effort,[3] there is not any satisfactory "analytic" theoretical description of the structure of the liquid-vapor interface of a pure metal. By "analytic" we mean a description that is derived, albeit by numerical solution, from some integral equation representation, or other explicit representation, of the longitudinal (along the normal) and transverse (in the plane) density distributions in the interface. Moreover, there is no report of an analytic approach to the prediction of the transverse and longitudinal density distributions in the liquid-vapor interface of a binary alloy. The major elements of our current theoretical understanding of the structure of the liquid-vapor interface of a binary alloy come from self-consistent Monte Carlo simulations of the type introduced by Rice and co-workers.[2] This method, which is based on the pseudopotential representation of the interactions in the liquid metal, has previously been employed in theoretical studies of the binary alloys of Bi, In, Sn, and Pb in Ga.[4–7] The common features of the results obtained are: (1) that the distribution of the total ion density along the normal to the interface (the longitudinal density distribution) is stratified for 3–4 atomic diameters into the bulk liquid, (2) that the component of the mixture that is in excess in the interface forms a monolayer which is the outermost layer of the liquid-vapor transition region, and (3) that the segregated monolayer in the liquid-vapor interface is a liquid. These predictions have been verified by experimental studies of those alloys.[11–13] The interface structure of a dilute alloy of Pb in Ga shows all these features above 341 K, while below 341 K the segregated monolayer is a hexagonal crystal.[14,15] Recent experimental studies of Yang *et al.* are consistent with the previous findings in that in a dilute alloy of Tl in Ga the outermost layer of the interface is a monolayer of pure Tl that forms a two-dimensional hexagonal crystal when the temperature is below 297 K and a disordered (hexatic or liquid) phase above that temperature.

Given that the pseudopotential representation of the interactions in an inhomogeneous metal necessarily employs several approximations, it is worthwhile testing the predictions derived from that representation for many different systems against experimental data, with the explicit goal of finding failures that guide improvement of the theoretical representation (see Table I). For example, recent studies of diffuse x-ray scattering from the liquid-vapor interface of Ga (Ref. 16) show that the asymptotic form of the pseudopotential used by Rice and co-workers needs improvement. Although improving the pseudopotential in this fashion will not affect the density distribution along the normal to the liquid-vapor interface, which is primarily determined by the electron-density-dependent one-body term in the pseudopotential and by the short-ranged pair interactions, it likely will affect the prediction of the melting temperature of any possible ordered structure in the liquid-vapor interface, e.,g., the melting temperature of the crystalline phase of Pb monolayer that forms the outer stratum of the liquid-vapor interface of a dilute Pb in Ga alloy.

TABLE I. Pseudopotential parameters (in atomic units, a.u.), $r_{\max}$ is the maximum value of r in the radial wave function, E_{11} is the spectroscopic term of the state $|11\rangle$. For details please refer to Refs. 13–15.

	1	E_{11}	R_1	B_{11}	$r_{\max}$
Ga	0	1.128 6023	1.9	1.546 51	35.0
	1	1.105 0598	0.5	4.344 04	45.0
	2	0.472 1357	2.0	0.335 13	55.0
Tl	0	1.095 1172	2.0	1.487 98	35.0
	1	0.714 0641	2.3	1.306 32	45.0
	2	0.433 5180	2.9	1.058 15	55.0

We report the results of self-consistent Monte Carlo simulations of the density distribution along the normal to the liquid-vapor interface of a dilute binary alloy of Tl in Ga; the methodology we used was the same as in previous studies by Rice and co-workers.[2] The results of our simulation studies are in agreement with those obtained from experimental studies reported by Yang *et al.*[1] In particular, our calculations reproduce the positions of the density strata in the interface, the relative amplitudes of the first two strata, and the finding that the excess Tl forms a complete monolayer that is the outermost layer of the interface. As in previous studies,[4–10] the predicted amplitudes of the density strata are larger than those observed, which we attribute in part to the small size of the surface of the simulation sample which cannot support long-wavelength capillary excitations, and in part to residual inaccuracies in the pseudopotential employed. Because the surface area of our simulation sample is small it cannot support an in-plane structure that requires long-range correlation. Furthermore, it is rarely the case that an *ab initio* pseudopotential representation of the properties of a metal of the type we have used leads to very accurate prediction of the bulk metal melting point. For these reasons, we have not attempted to account for the experimental finding that below 297 K the Tl monolayer forms a hexagonal two-dimensional crystal.

II. METHODOLOGY

The pseudopotential theory of the liquid-vapor interface of a metal has been described in earlier papers[2,4–7] to which the reader is referred to for details. It suffices to say that we have used the nonlocal energy-independent pseudopotential proposed by Woo *et al.*[17]

The self-consistent Monte Carlo simulations of the liquid-vapor interface of the Tl in Ga alloy were carried out in the same fashion as our earlier studies.[2,4–10] The details pertinent to the study reported in this paper are as follows. The model system consisted of a slab of 1000 ions and 3000 electrons. The dimensions of the simulation slab were $L_0 \times L_0 \times 2L_0$ in the x, y, and z directions. The slab contains two free surfaces in the positive and negative z direction (normal to the two liquid-vapor interfaces) so that the area of each liquid-vapor interface is $\sigma = L_0 \times L_0$. Conventional periodic boundary conditions were applied in the x and y directions. In fact, periodic conditions were also applied in the z direction, but at distances so far from the liquid-vapor interfaces that the description of those interfaces as free is valid. L_0 was chosen such that the average density of ions in the slab matched the density of the dilute binary alloy at the simulation temperature. The center of mass of the simulation system was located at the origin of the coordinates ($x=0$, $y=0$, $z=0$). We generated the initial well-mixed configuration of the ion cores by placing them at random positions within the boundaries of the simulation slab, subject to the constraint that no ion core-ion core separation was less than the ion core diameter.

The simulations were carried out using the Metropolis scheme[18] and a force bias Monte Carlo algorithm to eliminate the overlaps between ion cores. The trial configurations were generated by randomly displacing a selected ion; the magnitude of the ionic displacement was chosen to lead to convergence to equilibrium with a reasonable overall acceptance ratio for the trial configurations. A simulation pass is defined to be 1000 ionic configurations. Using this unit, the simulations were carried out up to 95 000 passes. The results reported here were obtained as an average over all the passes except the initial 5000.

Before describing the simulation results, it is necessary to make a few remarks concerning the composition of the simulated sample. The experimental data to be used for comparison come from x-ray reflectivity studies of a dilute Tl in Ga alloy with a Tl concentration of about 0.014 atom % at $T=313$ K. To mimic this macroscopic composition a double-ended simulation sample containing only 1000 atoms would have less than one Tl atoms, hence generation of complete Tl monolayer coverage of the interface, as is expected from the experimental results, would be impossible. This anomaly is, obviously, a consequence of the limited size of the simulation sample. A simulation sample large enough to permit monolayer coverage of the surface with the specified bulk concentration of Tl would have to have at least one million atoms, which is much too large for our computational resources. Following the procedure used by Zhao and Rice,[8–10] we constructed an alloy with composition $Ga_{0.86}Tl_{0.14}$ to ensure that complete coverage of the liquid-vapor interface by Tl is a possible outcome of the simulations. This procedure was successful in previous studies of the structures of the liquid-vapor interfaces of binary alloys of Bi, Pb, and Sn in Ga. As in those earlier studies, the larger solute concentration did not lead to solute atom clustering or any other precursor signatures of bulk phase separation during the evolution of the system to equilibrium.

Our simulation sample consists of 1000 atoms configured in 14 layers. The use of many layers with small surface area is a compromise between achieving true bulk liquid behavior in the central portion of the simulation cell and the capability of our computational resources. Since the surface layer holds about 70 atoms, surface structures that are defined by long-range correlations cannot be supported. This is one of the sources of the failure of previous simulations, as well as the one reported herein, to predict any low-temperature monolayer crystalline structure. We believe that an even more important source for this discrepancy is residual inaccuracy of the pseudopotentials used. It is likely that the melting temperatures of the monolayers supported by our pseudopotentials, lie, in each of the alloys considered to date, below the temperature range explored in the experimental studies. For example, a recent simulation study[20] of the structure and properties of an isolated Pb monolayer using the same type of pseudopotential and simulation methodology as employed in this paper, and with up to 20 000 atoms, yields a melting temperature of 251.7 K, and of a Pb on Ga bilayer yields a melting temperature of 413 K. The observed melting temperature of a monolayer of Pb segregated in the liquid-vapor interface of a dilute Pb in Ga alloy is 341 K.

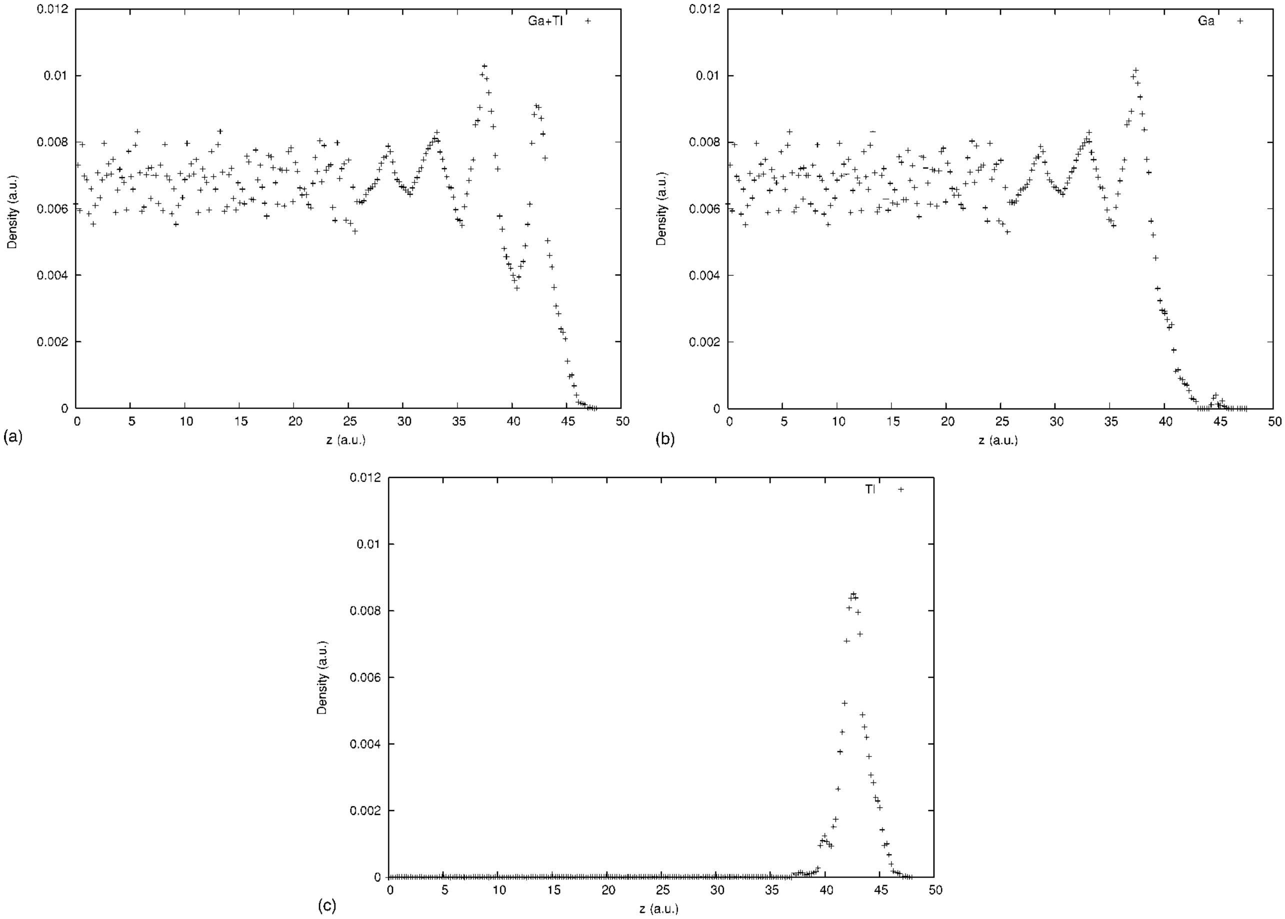

FIG. 1. Longitudinal density profiles in the liquid-vapor interface of $Ga_{0.86}Tl_{0.14}$; (a) the total ion distribution, (b) the Ga ion distribution, and (c) the Tl ion distribution.

III. RESULTS AND DISCUSSION

The longitudinal density distribution of the ions was obtained from a histogram of the distance between a particle and the center of the mass of the slab; the density profiles in the $+z$ and $-z$ directions were averaged to obtain density distributions shown in Fig. 1. Figure 1(a) displays the overall longitudinal density distribution, and Figs. 1(b) and 1(c) the longitudinal density distributions of the Ga and Tl atoms, respectively. The noise in the Ga longitudinal density distribution in the interior of the slab (fifth and deeper layers) is similar to that found in earlier simulations.[8–10] It is consistent with the expected fluctuations in a uniform fluid when sampling strata that are smaller than an ionic diameter are employed, since each stratum contains only a few atomic centers, and there is no force constraining movement of atoms between strata. The fluctuations in the strata that define the inhomogeneous liquid-vapor interface are damped by the increased difficulty, relative to a uniform fluid, of atomic movement between strata. Put another way, the fluctuations are damped by the force that generates the strata (determined by the electron-density variation of the one-body potential energy in the pseudopotential representation).

We remind the reader that the simulated Tl in Ga alloy has the atom ratio $Tl/Ga=0.14/0.86$, for the reason specified in the last section. As found experimentally, a complete monolayer of Tl forms the outermost layer of the liquid-vapor interface. We show in Fig. 2 a comparison of the calculated and experimental longitudinal density distributions for the case $T=315$ K. The agreement between the observed and predicted longitudinal density profile is generally good. In particular, the observed number, positions, and the relative amplitudes of the density strata are well reproduced by the simulation results, but the predicted amplitudes of the strata are larger than is observed. The failure to quantitatively reproduce the amplitudes of the outermost strata in the liquid-vapor interfaces of metals and alloys has been found in previous simulation studies.[8–10] As before, we attribute the differences noted between theory and experiment in large part to the inability of the simulation sample to support the long-wavelength capillary waves which determine the temperature dependencies of the amplitudes and widths of the peaks in the longitudinal density distribution, and to a lesser extent to residual inadequacies and inaccuracies of the pseudopotential representation of the inhomogeneous liquid metal.

Despite its extensive use in condensed-matter theory, not a lot can be said about the accuracy of the pseudopotential representation. The difficulty in assessing the accuracy of that representation is a consequence of the direct nature of the available tests, e.g., comparison of predicted and observed condensed phase structure. For the cases of interest to

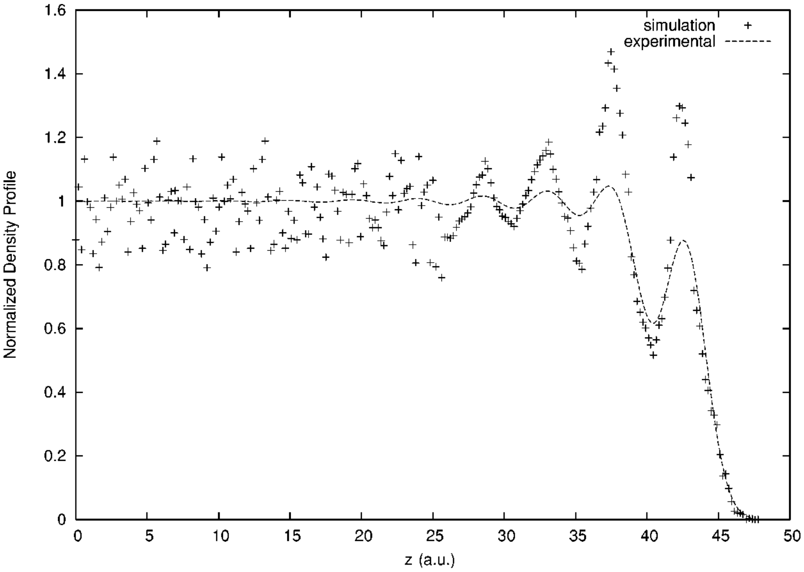

FIG. 2. Comparison of the simulated and experimental longitudinal density profile of the interface of the $Ga_{0.86}Tl_{0.14}$ alloy.

us, namely liquid metals and alloys, it has been shown that the pseudopotential we have used gives a very accurate prediction of the bulk liquid pair-correlation functions of all the systems studied, Tl, Al, Ga, and Pb.[19] While important, that comparison is weighted towards testing the repulsive region of the effective pair interaction. It is also found[19] that the predicted longitudinal density distribution in the liquid-vapor interfaces of Tl is more sharply stratified than is that in Ga, despite the great similarities in the bulk liquid pair-correlation functions of these two liquids. No experimental study of the longitudinal density distribution in the liquid-vapor interface of pure Tl has been reported. We speculate that the predicted amplitudes of the density strata of the liquid-vapor interface of Tl (and by extension of Tl in Ga) are too large by a greater amount than in the case of Ga because the Tl pseudopotential we used is somewhat more inaccurate than the Ga pseudopotential we used. Possible sources of inaccuracy of the form of the pseudopotential we have used include neglect of the metal-to-nonmetal transition across the liquid-vapor interface, inadequacies in the asymptotic form of the potential, neglect of core polarization in the interaction, and inadequacies in the representation of the kinetic, exchange, and correlation energies of the inhomogeneous electron distribution.

Consider first the neglect of the metal-to-nonmetal transition. Its pertinence arises from the fact that the vapor in equilibrium with a liquid metal is composed of atoms, or in some cases a mixture of atoms and diatomic molecules; hence it is necessary that there be a transition in electronic structure across the liquid-vapor interface in which the delocalized electrons that characterize the liquid phase become localized. Although the pseudopotential representation does not describe that transition, the density distribution of the outermost stratum of the liquid-vapor interface has a very rapid fall from the peak liquid density to sensibly zero density, typically in a distance that is a small fraction of an atomic diameter. Accordingly, it seems very unlikely that the delocalized-to-localized electron transition occurs in that stratum. Although studies of the diffuse scattering from the liquid-vapor interface of Ga (Ref. 16) show that the asymptotic form of the Woo-Wang-Matsuura pseudopotential[17] does not account for the experimental observations, a simple modification of that asymptotic form does account for the experimental observations. That modification does not alter the repulsive region of the effective pair interaction, hence does not affect the structural features found in the simulation studies.

Consider now the neglect of core polarization; its contribution to the energy is usually small compared to the screened direct interaction between the ion cores and the indirect interaction that is sometimes called the band-structure energy. To account for core-core repulsion and core polarization it is common to add to the effective pair potential obtained from the pseudopotential a Born-Mayer-type energy term that is parametrized to fit, say, the heat of vaporization. It is not known whether this form for the core-core repulsion and core-polarization energy is equally accurate for all the species of interest to us. In particular, there is no direct test of the approximation that must be used to obtain the parameters of the Born-Mayer interaction between the unlike ion cores of Ga and Tl.

Finally, although the representations of the kinetic, exchange, and correlation energies of the inhomogeneous electron distribution we have used are the best available, each involves gradient corrections, and the gradients in the liquid-vapor interface are large. There is room for improvement of these approximations.

In conclusion, the use of the pseudopotential representation coupled with self-consistent Monte Carlo simulations appears to adequately account for all the major physical phenomena in a dense inhomogeneous mixture of ion cores and electrons, and thereby provides a rather good, but not perfect, description of the liquid-vapor interface of diverse dilute alloys.

ACKNOWLEDGMENT

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