Structure in the Density Profile at the Liquid-Metal–Vapor Interface

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(Received 1 June 1981)

This paper presents the results of Monte Carlo simulations of a pseudoatom model of the liquid-metal–vapor interface. The surface density profile is found to have stable density oscillations, with spacing about one atomic diameter, extending several layers into the bulk liquid. This effect is ascribed to the presence of the "structure-independent" electronic energy, which is characteristic of simple metals, in the effective Hamiltonian for the classical pseudoatoms.

PACS numbers: 68.10.Jy, 61.20.Ja, 61.25.Mv

Within the last ten years there has been a dramatic increase in our understanding of the properties of the surfaces of crystalline metals and semiconductors,[1] and of the liquid-vapor interface of a simple dielectric.[2] However, our understanding of the liquid-metal–vapor interface remains primitive. All the jellium[3] or pseudoatom[4] theories proposed to date predict interfacial density profiles that are extremely narrow, indeed considerably smaller in width than that measured by Lu and Rice[5] for the liquid-vapor interface of mercury. A recently proposed phenomenological density-functional theory[6] is in much better agreement with the experimental results, but it is arguable that the model omits essential characteristics of real liquid metals. Moreover, none of these theories has been able to adequately address a more interesting question than the width of the surface transition zone, namely the possibility of local ordering at the liquid-vapor interface. A number of experiments have been interpreted so as to suggest that such ordering might exist in some cases.[7-9]

There are several reasons why the surface zone of a liquid metal might be expected to possess significant structure, even though in a liquid dielectric the interfacial density profile is monotonic. In contrast to argonlike fluids, the effective interactions near the surface of a liquid metal vary drastically, since they depend sensitively on the conduction-electron density. Indeed, there is presumably a metal-insulator transition that occurs across the interface, resulting in interactions in the vapor of a totally different character from those in the metallic liquid. Finally, the conduction electrons, which give liquid metals surface tensions orders of magnitude higher than those of simple liquid dielectrics, exert a powerful restoring force on deviations from the minimum-energy surface structure. This could in itself give rise to ordering, and the suppression of capillary wave motion by the high surface tension will tend to prevent the washing out of any such structure.

The work we describe is an attempt to extend pseudopotential theory,[10] which has been successful at explaining many of the bulk properties of simple metals, to the description of the liquid metal surface. A similar attempt was made by Evans and Kumaravadivel,[4] but they assumed a monotonic ionic density profile and were forced to make numerous additional approximations to obtain numerical results, which we avoid by using computer simulation techniques. In contrast to earlier work, we find that this pseudoatom model predicts highly structured interfacial profiles, with density oscillations extending several atomic diameters into the bulk liquid.

Our theory begins with the expression from pseudopotential theory for the effective potential energy of classical ions at positions $\{\vec{R}_i\}$ moving in a neutralizing cloud of electrons[11]:

$$V_{\text{eff}}(\{\vec{R}_i\}) = U_0[n_{\text{el}}{}^0(\vec{r}), n_+{}^0(\vec{r})] + \sum_{i<j} \varphi_{\text{eff}}(\vec{R}_i, \vec{R}_j; n_{\text{el}}{}^0(\vec{r}), n_+{}^0(\vec{r})). \tag{1}$$

The first term in (1), the so-called structure-independent energy, which is characteristic of simple metals, depends only on the electronic density $n_{\text{el}}{}^0(\vec{r})$ and the neutralizing positive density $n_+{}^0(\vec{r})$ of a reference system. This expression follows from the linear-response approximation to the exact (coupling parameter) relation between the free energy of a system in which the electrons interact with weak ionic pseudopotentials and a reference continuum (jellium) system. U_0 contains the electronic free energy of the reference system, along with several terms terms left over from the separation of the effective pair potentials from the coupling-parameter expression. The reference system about which the perturbation expansion is normally made is the uniform electron gas; however, the expressions are equally valid for a nonuniform system. In particular, for a system with a free surface the natural reference system is one which also has a surface, i.e., a "relaxed jellium." We note that the term "structure-independent" energy is misleading, in that it implies a lack of dependence of U_0 on the positions of the pseudoatoms. The reference jellium density $n_+{}^0(\vec{r})$ must, however, depend on the ionic positions in some average way. For a bulk metal $n_+{}^0$ is just the mean density. For a metal surface, $n_+{}^0(\vec{r})$ must similarly represent a smoothed-out ionic density profile, and in this way U_0 does depend significantly on the spatially averaged instantaneous positions of the pseudoatoms. Because of its dependence on $n_+{}^0(\vec{r})$, we expect U_0 to restrain atomic movements away from the minimum-energy surface density profile, just as in a bulk metal U_0 restrains atomic motions that change the bulk density.

We begin our analysis by assuming that the positive-ion and electron reference profiles coincide: $n_+{}^0(\vec{r}) = n_{\mathrm{el}}{}^0(\vec{r}) = n_0(\vec{r})$. We base this assumption on the finding by Allen and Rice that the self-consistent electron and positive charge distributions in relaxed jellium maintain local charge neutrality to a very good approximation.[3] Next we adopt local density approximations, with gradient corrections,[12] to the structure-independent energy density and the effective pair potentials,

$$U_0[n_0(\vec{r})] \cong \int d^3r\, n_0(\vec{r})\{u_0(n_0(\vec{r})) + u_1(n_0(\vec{r}))\,|\vec{\nabla} n_0(\vec{r})|^2 + \ldots\}, \tag{2}$$

$$\varphi_{\mathrm{eff}}(\vec{R}_i, \vec{R}_j; n_0(\vec{r})) \cong \varphi_{\mathrm{eff}}(R_{ij}; \tfrac{1}{2}[n_0(\vec{R}_i) + n_0(\vec{R}_j)]). \tag{3}$$

Finally, we make some simple approximations to treat the metal-insulator transition. When the reference density $n_0(\vec{r})$ at an atomic position is less than a metal-insulator transition density, which we take to be the liquid-vapor critical density, that atom is taken to interact with its neighbors via a Born-Mayer potential[13] and with the metallic liquid surface via a van der Waals potential.[14] The coefficient of r^{-3} in the van der Waals potential is calculated with use of the Lifshitz expression[15] and the frequency-dependent polarizability of the atom (in our case sodium[16]).

The use of gradient expansions in surface problems has been subjected to deserved criticism,[17] as the electron density varies quite rapidly near the interface. However, several investigators have obtained good results with it,[18] and the gradient expansion of the kinetic energy for a linear-potential model of the jellium surface gives very good agreement with the exact results.[19] For the purposes of this calculation (2) should be adequate, since errors in the surface energy due to the gradient expansion will give rise to only minor quantitative errors in the simulated profiles. As a test, we repeated the calculations of Allen and Rice[3] using the density functional expresssions rather than the Schrödinger equation representation. Using a hyperbolic tangent profile as a trial function, we found minimum-energy surface density profiles with widths differing from those of Allen and Rice by only five percent or less.

We have carried out calculations of the structure-independent energy per atom for bulk sodium as a function of the electron density using the optimized model potential (OMP) of Heine and Abarenkov[20] and Shaw and Harrison,[21] the Vashishta-Singwi correlation energy,[22] and full effective-mass corrections.[23] We use the first and second gradient corrections for the kinetic energy of the electron gas,[19] and the Gupta-Singwi coefficients for the first two gradient terms in the exchange-correlation energy.[24] We ignore any gradient corrections due to the nonlocality of the pseudopotential.

We have similarly calculated $\varphi_{\mathrm{eff}}(R; n_0)$ for sodium over a range of densities using the OMP with full effective-mass corrections and the Vashishta-Singwi local-field correction for exchange and correlation.[22] As a test, we used this pair potential in a simulation of bulk liquid sodium and obtained a pair correlation function that compares very well with experimental data.[25]

We have carried out the computer simulations using a 256-atom cluster. The spherical geometry affords a large surface area without requiring a prohibitively large number of particles and also avoids boundary effects. For the reference density profile we use the three-parameter function $n_0(r) = n_b/\{1 + \exp[(r - R_0)/\delta]\}$. Prior to the simulations, tables are generated of $U_0[n_b, R_0, \delta]$ and of $\varphi_{\mathrm{eff}}(R; n_0)$. For each configuration during the simulation, the reference profile parameters are determined self-consistently by performing a quasianalytic least-squares fit to the cumulative density profile $N(R) = \int_0^R n(r) 4\pi r^2 dr$.

U_0 is then calculated by interpolation from the tables, along with the pair energies as prescribed by Eq. (3). The total resultant energy is used to generate the Markov chain of Monte Carlo configurations according to the standard prescription.[26]

We have carried out Monte Carlo simulations consisting of 2.56×10^6 configurations each at two temperatures, 100 °C (just above the melting point) and 200 °C. The calculated density profiles are plotted in Figs. 1(a) and 1(b) along with the average parametric reference profiles. In both cases we find highly structured surface density profiles, with stable oscillations extending several atomic diameters into the bulk liquid. The distance between adjacent layers is roughly one atomic diameter. The sharp outermost spike corresponds to atoms positioned where the reference jellium profile passes through the metal-insulator transition density, and the pair interactions change abruptly; the spike may be an artifact induced by the spherical uniformity of the imposed metal-insulator transition. If we accept the spike as real, it is most appropriate to think of these atoms as lying in a metal-nonmetal transition zone, neither metallic nor vaporized. The integrated area of this peak corresponds to roughly 50% and 20% of a monolayer, respectively, at the two temperatures.

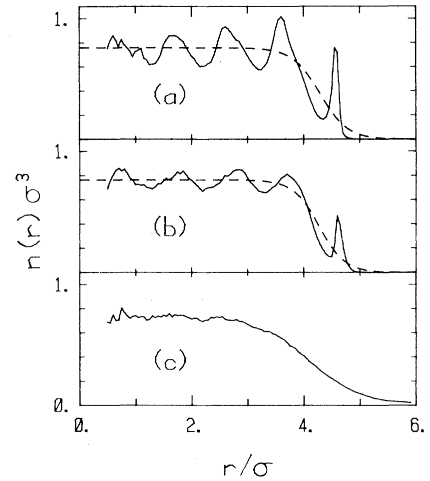

FIG. 1. Scaled density profiles for two 256-atom models of a liquid sodium cluster: (a), (b) Model containing local density approximations to the structure-independent energy and effective pair potentials, at 100 °C and 200 °C, respectively; (c) model containing density-independent pair interactions only, at 100 °C. Solid curves: atomic density profiles. Broken curves in (a) and (b): average parametric reference density profiles. Scaling length (atomic diameter) $\sigma = 3.108$ Å.

The density profiles we find are strongly reminiscent of the layering that occurs in a fluid in contact with a hard wall.[27] Indeed, we believe that the density oscillations are principally due to the effective confinement of the ions due to the structure-independent electron energy. It is as if the surface is so "tight" that it acts as a smooth wall for the liquid. Other mechanisms that have been proposed for ordering at the interface, such as Friedel oscillations in the electronic density,[3] which are absent from our model, may play some role in determining the surface density profiles of real metals.

In addition to the calculations described above, we have carried out simulations of two simpler models of liquid metal clusters: One treats the structure-independent energy as before but uses a density-independent pair potential, and the other, even simpler, uses density-independent pair interactions only. In the first case we find results very similar to those in Figs. 1(a) and 1(b). The sharp peak at the metal-insulator transition is missing, naturally, but again there are strong density oscillations, with spacing about one one atomic diameter, extending into the bulk. In the second case, plotted in Fig. 1(c), we find a smooth density profile about two atomic diameters wide, which is very similar to that found in simulations of argonlike fluids. Both of these results point to the crucial role played by the structure-independent energy. Collectively, our results also suggest that although the details of the interfacial profile may depend on the specific interactions, layering can develop simply as a consequence of the confining effects of the conduction electrons, and could be a general phenomenon.

Our model suffers from several limitations, which should be removed in a complete theory. The treatment of the electrons and ions is not fully self-consistent in that we assume the positive-ion and electron reference profiles to coincide, rather than calculating the minimum-energy electron profile for a given ion profile. The breakdown of this local electroneutrality assumption could lead to the failure of some of the approximations which yield Eq. (1). In particular, certain one-body terms in the effective Hamiltonian could begin to become important. In addition, our treatment of the metal-insulator transition is *ad hoc*, and the spherical uniformity which is imposed on the system by the choice of parametric reference profile is artificial.

There are a number of important questions about the liquid metal surface, such as the nature of the dipole layer, which this study does not address. However, we believe that it points to a very interesting phenomenon, surface ordering, which has far-reaching implications for a satisfactory description of the liquid metal surface. For example, the possible existence of a fractional monolayer of "hybrid-state" atoms, and the large entropy associated with quasidegeneracy of configurations in this monolayer, implies that a positive excess surface entropy need not necessarily correspond to a lack of surface ordering.

This research has been supported in part by the National Science Foundation and in part by the National Resource for Computation in Chemistry. We have also benefited from facilities provided by the National Science Foundation for materials research at the University of Chicago. One of us (M.P.D.) has been supported by a Fannie and John Hertz Foundation predoctoral fellowship.

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