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Nonlinear theory of metal-solvent interface using the density functional approach

Sanjib Senapati and Amalendu Chandra
Department of Chemistry, Indian Institute of Technology, Kanpur, Uttar Pradesh 208016, India

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A nonlinear theory for the calculation of spatial and orientational structure of a dipolar solvent near a metal surface is developed by using the density functional approach. The theory is based on a weighted density approximation for the isotropic part of the density and the anisotropic part is calculated by using a perturbative approach. The theory, however, retains the full nonlinear dependence of the inhomogeneous solvent structure on the field produced by the metal surface and also on solvent-solvent interactions. Explicit numerical results are obtained for the number density and polarization of a dipolar solvent near a metal surface. The number density of the solvent near the surface is found to increase with increase of the electrostatic field of the metal, which is a nonlinear effect. The polarization is also found to increase nonlinearly with the metal field and exhibits the presence of pronounced orientational order near the metal surface. [S1063-651X(99)02403-4]

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I. INTRODUCTION

A detailed description of the structure and dynamics of a dipolar liquid near a metal surface is of primary importance in electrochemistry and surface science. The inhomogeneous field of a metal surface can influence the structure and dynamics at the molecular level and as a result the behavior of an interfacial medium can be very different from that of a bulk liquid. The approach of a molecule to a metal surface is an important step in many physical and chemical processes such as adsorption and heterogeneous electron transfer reactions [1] and the rates of such processes are expected to be influenced by the molecular properties of the metal-solvent interface. In the present paper, we focus on the structural properties of a metal-solvent interface.

The modifications of the structure of a dipolar solvent near a metal surface have been the subject of much attention in the recent past, both experimentally and theoretically. Toney and co-workers [2,3] measured the spatial and orientational structure of water molecules near silver surfaces by means of *in situ* x-ray scattering. They found that water density near the surface is significantly higher than the bulk density, which implies that the hydrogen bonding network is disrupted in the water layer next to the charged surfaces. Also, pronounced orientational structure was found in their experiments. Similar orientational order was also found for water molecules near gold surfaces by Ataka, Yotsuyanagi, and Osawa [4] by means of surface-enhanced infrared absorption spectroscopy. In the past decade, molecular dynamics (MD) and Monte Carlo (MC) simulations have been employed to investigate the structural properties of dipolar solvents near metal surfaces [5–12]. In these studies, the liquid is usually treated by employing one of the standard water models and the surface-water interaction is modeled in different ways. Many models of metal-water interaction are based on the calculations of a water molecule with a metal cluster. Metal-water interactions have also been modeled assuming a planar surface with a uniform distribution of Lennard-Jones particles for the metal atoms or site-site potentials acting between the metal and water molecules. In one such recent study, Xia and Berkowitz [11] carried out MD simulations of the SPC/E model of water [13] near charged platinum surfaces and found no dramatic increase of water density near the surfaces. Also, no significant disruption of hydrogen bonding near the charged surfaces was found. Clearly, our understanding of the structure of dipolar solvents near metal surfaces is far from complete and many basic questions remain.

There has also been a good deal of interest in developing theories of the metal-solvent interface. In their early work, Badiali, Rosinberg, and Goodisman [14] considered continuum dielectric models and Schmickler [15] treated monolayers of discrete dipoles on a metal surface. In further studies, Badiali *et al.* [16] and others [17–19] considered a metal-solution interface by considering the molecularity of the solution. Although these studies demonstrated the importance of treating the liquid at a molecular level, they did not properly couple the solution structure at interface to the electronic structure of the metal. In a further significant advance, Berard *et al.* [20] investigated the structure of a dipolar solvent near a metal surface by including the coupling between the interfacial solvent structure and the electron density of the metal. These authors treated the metal by employing the so-called jellium model, which was then solved by using the general self-consistent approach of Gies and Gerhardts [21] for metal slabs of finite thickness. The solvent structure was obtained by employing the reference hypernetted chain (RHNC) approximation [22] taking account of metal-solvent interaction. The solvent structure at the interface was found to be significantly altered by electrostatic interactions with the metal surface.

An alternative approach to the study of a solid-liquid interface is the density functional theory (DFT), which has been recognized as a versatile tool for the description of the structure and properties of inhomogeneous systems [23]. A recent development in the density functional theory is the so-called weighted density approximation (WDA) [23–30]. This is a nonperturbative approach in which one assumes that a system with an inhomogeneous density distribution can be locally mapped to a corresponding uniform system with a position-dependent effective density. Two recent weighted density schemes that have been quite successful are due to Tarazona [27] and Ashcroft and co-workers [28,29]. The first approach is based on an evaluation of excess free-energy density from the corresponding expression of the uniform system using the effective density and the approach of Ashcroft and co-workers is based on a calculation of the first-order correlation function of an inhomogeneous system using the corresponding expression for a uniform system. The density functional approaches using WDA have been quite successful in predicting the structure of neutral inhomogeneous hard sphere fluids and ionic solutions near solid surfaces and, very recently, have been extended to study dipolar fluids near charged surfaces [31,32]. Similar studies have not yet been carried out to investigate the structure and properties of a metal-solvent interface.

In this work, we present a nonlinear theory for the solvent structure and polarization near a metal surface by using classical DFT for the solvent and quantum DFT for the metal. The theory is based on a weighted density approximation for the isotropic correlation and a perturbative approximation for the dipolar electrostatic contribution to the first-order correlation function of the inhomogeneous solvent. The theory, however, retains the full nonlinear dependence of the interfacial solvent structure on the metal potential and also on solvent-solvent interactions. The metal potential is calculated by modeling the metal as a jellium that is then solved by using the general quantum density functional approach of Hohenberg-Kohn-Sham [33,34]. Self-consistent equations are derived for the solvent density, polarization, and metal electron density. The final equations are solved iteratively and results are obtained for the density and polarization of the interfacial solvent.

The organization of the rest of the paper is as follows. In Sec. II, we present the theory and the numerical results are discussed in Sec. III. We summarize our conclusions in Sec. IV.

II. THEORY

We consider a solvent consisting of nonpolarizable dipolar molecules that are confined between two metal surfaces. The separation between the surfaces is large enough so that the structure at one surface is not affected by that at the other surface. The solvent molecules are characterized by the so-called dipolar hard-sphere potential where dipolar molecules interact through a short-range hard-sphere interaction and a long-range dipole-dipole interaction potential. The solvent molecules also interact with the two metal surfaces, which are considered to be infinite walls located at positions z' and z'' along the z axis, and the x and y axes are parallel to the surfaces. For this geometry, the wall-solvent interaction potential depends on the z coordinate of the solvent molecule and on its orientation (Ω) and can be written as

$$u(z,\Omega)=u'(z,\Omega)+u''(z,\Omega), \tag{1}$$

where u' and u'' represent the interaction of a solvent particle with walls located at $z=z'$ and $z=z''$, respectively. Both u' and u'' include a short-range isotropic part and an electrostatic anisotropic part. The short-range isotropic part is described by a hard-wall–hard-sphere interaction and the anisotropic part represents the interaction of a dipole with the metal electrostatic field generated by the nonuniform electron density of the metal surface. Thus $u'(z,\Omega)$ can be written as

$$u'(z,\Omega)=u_{\mathrm{hw}}(|z-z'|)-E'(z)\cdot\mu, \tag{2}$$

where $u_{\mathrm{hw}}(|z-z'|)$ is infinity for $|z-z'|<\sigma/2$ and zero otherwise and $E'(z)$ is the electric field produced at z by the metal surface located at z'. σ and μ are, respectively, the diameter and dipole vector of a solvent molecule with orientation Ω.

We denote $\rho(\mathbf{r},\Omega)$ as the position- and orientation-dependent number density of the solvent. In DFT, the grand potential of this system at fixed temperature, volume, external field, and chemical potential can be exactly expressed as a functional of the inhomogeneous density distribution

$$\bar{\Omega}[\rho(\mathbf{r},\Omega)]=F[\rho(\mathbf{r},\Omega)]+\int d\mathbf{r}\,d\Omega \times\rho(\mathbf{r},\Omega)[u(\mathbf{r},\Omega)-\bar{\mu}], \tag{3}$$

where $u(\mathbf{r},\Omega)$ is the external potential, $\bar{\mu}$ is the chemical potential, and T is the temperature. The intrinsic Helmholtz free energy $F[\rho(\mathbf{r},\Omega)]$ is a universal functional of density and consists of two components,

$$F[\rho(\mathbf{r},\Omega)]=F^{\mathrm{id}}[\rho(\mathbf{r},\Omega)]+F^{\mathrm{ex}}[\rho(\mathbf{r},\Omega)], \tag{4}$$

where the ideal gas free-energy functional $F_{\mathrm{id}}[\rho(\mathbf{r},\Omega)]$ is given by

$$F^{\mathrm{id}}[\rho(\mathbf{r},\Omega)]=\beta^{-1}\int d\mathbf{r}\,d\Omega\,\rho(\mathbf{r},\Omega) \times\{\ln 4\pi\lambda^3\rho(\mathbf{r},\Omega)-1\}, \tag{5}$$

where $\beta=1/k_BT$, k_B is Boltzmann constant and λ is the thermal de Broglie wavelength. The excess free energy $F^{\mathrm{ex}}[\rho(\mathbf{r},\Omega)]$ includes the contribution from intermolecular interactions and it defines the direct correlation functions of different order through functional derivatives, the most important ones being the first- and second-order correlation functions defined by [22]

$$c^{(1)}(\mathbf{r},\Omega;[\rho(\mathbf{r},\Omega)])=-\beta\frac{\delta F^{\mathrm{ex}}[\rho]}{\delta\rho(\mathbf{r},\Omega)}, \tag{6}$$

$$c^{(2)}(\mathbf{r},\mathbf{r}',\Omega,\Omega')=-\beta\frac{\delta^2F^{\mathrm{ex}}[\rho]}{\delta\rho(\mathbf{r},\Omega)\,\delta\rho(\mathbf{r}',\Omega')}. \tag{7}$$

Minimizing the grand potential of Eq. (3) with respect to density and evaluating the chemical potential for the uniform bulk density, one obtains an expression for the equilibrium density of the dipolar fluid between the two surfaces. Since the density variation is only along the perpendicular (z) direction, one can write the following expression for the inhomogeneous density:

$$\rho(z,\Omega)=\frac{\rho_0}{4\pi}\exp[-\beta u(z,\Omega) +c^{(1)}(z,\Omega;[\rho(z,\Omega)])-c^{(1)}(\rho_0/4\pi)], \tag{8}$$

for $\sigma/2 < z < (L-\sigma/2)$ and $\rho(z,\Omega)=0$ otherwise, where L is the separation between the two metal surfaces along the z direction. The application of the density functional method can now proceed by the search for a self-consistent solution of Eq. (8). The above equation is a formally exact relation that, in principle, may be solved for $\rho(z,\Omega)$ if the functional $c^{(1)}$ is known. In practice, however, $c^{(1)}$ is generally unknown for inhomogeneous systems and so must be approximated. The simplest approximation of $c^{(1)}(\mathbf{r},\Omega;[\rho(\mathbf{r},\Omega)])$ of an inhomogeneous system involves a perturbative expansion (up to first order) in terms of the density inhomogeneity that makes use of the second-order direct correlation function of the corresponding homogeneous system and is given by

$$c^{(1)}(\mathbf{r},\Omega;[\rho(\mathbf{r},\Omega)])-c^{(1)}(\rho_0/4\pi) = \int d\mathbf{r}' d\Omega' \tilde{c}^{(2)}(\mathbf{r}-\mathbf{r}',\Omega,\Omega')\left(\rho(\mathbf{r}',\Omega')-\frac{\rho_0}{4\pi}\right), \tag{9}$$

where $\tilde{c}^{(2)}(\mathbf{r}-\mathbf{r}',\Omega,\Omega')$ is the second-order direct correlation function of the homogeneous liquid. The z-dependent first-order correlation function $c^{(1)}(z,\Omega;[\rho(z,\Omega)])$ can be obtained by integrating Eq. (9) over x and y coordinates. For convenience, we write the second-order direct correlation function in terms of angular functions as follows:

$$\begin{aligned}\tilde{c}^{(2)}(\mathbf{r}-\mathbf{r}',\Omega,\Omega') = {} & c^{0000}(|\mathbf{r}-\mathbf{r}'|) \\ & + c^{110}(|\mathbf{r}-\mathbf{r}'|)\phi^{110}(\Omega,\Omega') \\ & + c^{112}(|\mathbf{r}-\mathbf{r}'|)\phi^{112}(\Omega,\Omega',\hat{\mathbf{r}}),\end{aligned} \tag{10}$$

where the angular functions $\phi^{110}(\Omega,\Omega')=(\hat{\boldsymbol{\mu}}\cdot\hat{\boldsymbol{\mu}}')$ and $\phi^{112}(\Omega,\Omega',\hat{\mathbf{r}})=3(\hat{\boldsymbol{\mu}}\cdot\hat{\mathbf{r}})(\hat{\boldsymbol{\mu}}'\cdot\hat{\mathbf{r}})-(\hat{\boldsymbol{\mu}}\cdot\hat{\boldsymbol{\mu}}')$, $\hat{\boldsymbol{\mu}}$ and $\hat{\boldsymbol{\mu}}'$ are the unit vectors along dipole moments of particles located at $\mathbf{r}$ and $\mathbf{r}'$, and $\hat{\mathbf{r}}=(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$. In Eq. (10), $c^{000}(|\mathbf{r}-\mathbf{r}'|)$ represents the isotropic or hard-sphere part and the second and third terms represent the anisotropic or dipolar parts of the direct correlation function the analytical solutions of which are available within integral equation theories such as mean spherical approximation (MSA) [35].

An alternative to Eq. (9) is to adopt the WDA in which $c^{(1)}(z,\Omega;[\rho(z,\Omega)])$ for the inhomogeneous density is obtained by evaluating the corresponding expression $\tilde{c}^{(1)}$ for the homogeneous fluid at an effective density $\overline{\rho}(z,\Omega)$. Thus, we write

$$\begin{aligned}& c^{(1)}(z,\Omega;[\rho(z,\Omega)])-c^{(1)}(\rho_0/4\pi) \\ & = \tilde{c}^{(1)}(\overline{\rho}(z,\Omega))-\tilde{c}^{(1)}(\rho_0/4\pi).\end{aligned} \tag{11}$$

Although the perturbative approximation, Eq. (9), is simpler to deal with, WDA has been known to provide a better treatment for the hard-sphere correlation contributions. Therefore, we decompose the total first-order direct correlation function into two parts: $c^{(1)}=c_{\text{hs}}^{(1)}+c_{\text{ex}}^{(1)}$, where $c_{\text{hs}}^{(1)}$ is the isotropic hard-sphere contribution to the first-order direct correlation function and $c_{\text{ex}}^{(1)}$ represents the remaining anisotropic (or excess) contribution which arises from the explicit dipole-dipole electrostatic interactions and also from the coupling of electrostatic and hard-sphere interactions. We adopt a partially nonperturbative approach in which we evaluate the isotropic hard-sphere contribution $c_{\text{hs}}^{(1)}$ using WDA and the remaining anisotropic part $c_{\text{ex}}^{(1)}$ through a perturbative approach by using an equation similar to Eq. (9) but involving only the anisotropic terms of the second-order direct correlation function. The expression for the inhomogeneous density can now be written in the following form:

$$\begin{aligned}\rho(z,\Omega) = \frac{\rho_{\text{hs}}(z)}{4\pi}\exp\Big[& -\beta u(z,\Omega) \\ & + \int dx\, dy\, d\mathbf{r}'\, d\Omega' [c^{110}(|\mathbf{r}-\mathbf{r}'|;\rho_0) \\ & \times \phi^{110}(\Omega,\Omega') + c^{112}(|\mathbf{r}-\mathbf{r}'|,\rho_0) \\ & \times \phi^{112}(\Omega,\Omega',\hat{r})](\rho(z',\Omega)-\rho_0/4\pi)\Big]\end{aligned} \tag{12}$$

and

$$\rho_{\text{hs}}(z)=\rho_0 \exp[c_{\text{hs}}^{(1)}(\overline{\rho_{\text{hs}}}(z))-c_{\text{hs}}^{(1)}(\rho_0)], \tag{13}$$

where $c_{\text{hs}}^{(1)}(\overline{\rho_{\text{hs}}}(z))$ refers to the hard-sphere contribution to the first-order correlation function defined through WDA at an effective density $\overline{\rho_{\text{hs}}}(z)$ obtained as the weighted average $\overline{\rho_{\text{hs}}}(z)=\int dz' \rho_{\text{hs}}(z')w(|z-z'|)$ where $w(z-z')$ is a planar averaged weight function for the hard-sphere density. There are several ways to calculate the weight function, the most successful among them are those of Tarazona [27] and of Ashcroft and co-workers [28,29]. In the WDA proposed by Tarazona [27], $c_{\text{hs}}^{(1)}(z;\overline{\rho}(z))$ is calculated by calculating the hard-sphere contribution to the excess free-energy density f_{hs} [defined through $F_{\text{hs}}^{\text{ex}}=\int d\mathbf{r}\,\rho(\mathbf{r})f_{\text{hs}}(\mathbf{r})$] of the uniform system using the effective density $\overline{\rho}$. In this scheme, the first-order correlation functions are given by

$$\begin{aligned}c_{\text{hs}}^{(1)}(z;\overline{\rho}) = {} & -\beta f_{\text{hs}}[\overline{\rho}(z)]-\beta\int dz' \rho(z') f'_{\text{hs}}[\overline{\rho}(z)] \\ & \times \frac{w(z-z';\overline{\rho}(z'))}{1-\overline{\rho_1}(z')-2\overline{\rho_2}(z')\overline{\rho}(z')},\end{aligned} \tag{14}$$

$$c_{\text{hs}}^{(1)}[\rho_0] = -\beta f_{\text{hs}}[\rho_0]-\beta\rho_0 f'_{\text{hs}}[\rho_0], \tag{15}$$

where f'_{hs} is the derivative of f_{hs}. The expression for the weight function in this approach is given by the second-order expansion

$$\begin{aligned}w(|z-z'|;\overline{\rho}(z)) = {} & w^{(0)}(|z-z'|)+w^{(1)}(|z-z'|)\overline{\rho}(z) \\ & + w^{(2)}(|z-z'|)\overline{\rho}(z)^2,\end{aligned} \tag{16}$$

with the density-independent component weight functions normalized as $\int dz' w^{(i)}(z-z')=\delta_{i,0}$. The weighted density $\overline{\rho}(z)$ in this scheme can be expressed as

$$\overline{\rho}(z) = \frac{2\overline{\rho}^{(0)}(z)}{[1-\overline{\rho}^{(1)}(z)]+[(1-\overline{\rho}^{(1)}(z))^2-4\overline{\rho}^{(0)}(z)\overline{\rho}^{(2)}(z)]^{1/2}}, \tag{17}$$

where $\overline{\rho}^{(i)}(z)=\int dz'\rho(z')w^{(i)}(|z-z'|)$, $i=0,1,2$. Explicit expressions for the density-independent component weight functions are available in the literature [27,30]. In the present work, we have implemented the above scheme for the calculation of the hard-sphere part of the solvent density.

We now expand the position and orientation dependent density $\rho(z,\Omega)$ in the basis set of spherical harmonics $Y_{lm}(\Omega)$ as follows [36]:

$$\rho(z,\Omega)=\sum_{lm} a_{lm}(z)Y_{lm}(\Omega). \tag{18}$$

Clearly, the angle averaged number density $\rho(z)=\int d\Omega\,\rho(z,\Omega)=\sqrt{4\pi}a_{00}(z)$ and the solvent polarization $P(z)$ is related to $a_{10}(z)$ by the following relation $P(z)=\sqrt{4\pi/3}\mu a_{10}(z)$. Substitution of Eq. (18) and explicit forms of angular functions ϕ^{110} and ϕ^{112} into Eq. (12) and carrying out the angular integrations give the following simplified expressions for the density components:

$$a_{00}(z)=\frac{\rho_{\mathrm{hs}}(z)}{\sqrt{4\pi}}\,\frac{\sinh\{\beta\mu E(z)+I_1(z)+I_2(z)\}}{\beta\mu E(z)+I_1(z)+I_2(z)}, \tag{19a}$$

$$a_{10}(z)=\left(\tfrac{3}{4}\right)^{1/2}\rho_{\mathrm{hs}}(z)\Bigg(\frac{\cosh\{\beta\mu E(z)+I_1(z)+I_2(z)\}}{\beta\mu E(z)+I_1(z)+I_2(z)} \times\frac{\sinh\{\beta\mu E(z)+I_1(z)+I_2(z)\}}{[\beta\mu E(z)+I_1(z)+I_2(z)]^2}\Bigg), \tag{19b}$$

where $E(z)$ is the electrostatic field of the metal surfaces and $I_1(z)$ and $I_2(z)$ are given by

$$I_1(z)=\int dz'a_{10}(z')c^{110}(z-z') \tag{20a}$$

and

$$I_2(z)=\int dx\,dy\,d\mathbf{r}'a_{10}(z')c^{112}(|\mathbf{r}-\mathbf{r}'|)\left(\frac{3|z-z'|^2}{|\mathbf{r}-\mathbf{r}'|^2}-1\right), \tag{20b}$$

where $c^{110}(z-z')$ is obtained from $c^{110}(|\mathbf{r}-\mathbf{r}'|)$ by integrating over x and y coordinates. In the present work, MSA solutions are used for $c^{110}(|\mathbf{r}-\mathbf{r}'|)$ and $c^{112}(|\mathbf{r}-\mathbf{r}'|)$ [35]. One can also calculate the quantity $\langle\cos\theta\rangle_z$, the average value of $\cos\theta$ for a solvent molecule at a given value of the position z from the surface. $\langle\cos\theta\rangle_z$ can be written in terms of position and orientation dependent density as

$$\langle\cos\theta\rangle_z=\frac{\int d\Omega(\cos\theta)\rho(z,\Omega)}{\int d\Omega\rho(z,\Omega)}=\mathcal{L}[\beta\mu E+I_1(z)+I_2(z)], \tag{21}$$

where $\mathcal{L}$ refers to the Langevin function, defined as $\mathcal{L}(x)=\coth(x)-x^{-1}$. The expression for $\langle\cos\theta\rangle_z$ in the above equation includes the effects of dielectric saturation [37] in the presence of a strong metal field, since $\langle\cos\theta\rangle_z$ in the Langevin form approaches the saturated value of unity at large field strengths.

We note that the full nonlinearity of Eq. (12) is retained in Eq. (19). Equations (19)–(21) are the key results of this work which constitute a set of nonlinear equations for the calculation of number density, polarization, and average orientation of a molecule near metal surfaces. The above equations can be solved iteratively once the metal electrostatic field $E(z)$ is known. We note that $E(z)=-(\partial/\partial z)V(z)$, where $V(z)$ is the metal electrostatic potential that satisfies the Poisson equation

$$\frac{d^2}{dz^2}V(z)=-4\pi\rho_c(z), \tag{22}$$

where $\rho_c(z)$ is the charge density of the metal. An explicit modeling of the electronic structure of the metal is now necessary in order to calculate the charge density and the metal field. Following Berard *et al.* [20], we model the metal walls by semi-infinite jellium slabs of width $2z_w$. The jellium model consists of a uniform background of positive charge density ρ_+ which represents the metal nuclei and core electrons and the associated valence electron density $\rho_e(z)$. The valence electron density is calculated by using density functional theory [33,34]. In this approach, the electron density is calculated by solving the effective one-electron Schrödinger equation

$$-\frac{\hbar^2}{2m_e}\frac{d^2}{dz^2}\psi_n(z')+V_{\mathrm{eff}}(z')\psi_n(z')=\epsilon_n\psi_n(z'), \tag{23}$$

where ψ_n and ϵ_n are the one-electron normalized eigenfunction and energy eigenvalue for the nth state and m_e is the mass of an electron. z' denotes the z coordinate with origin at the center of the metal slab. $V_{\mathrm{eff}}(z')$ is the effective potential, which is given by

$$V_{\mathrm{eff}}(z')=V_{\mathrm{jel}}(z')+V_{\mathrm{xc}}(z')+V_{\mathrm{dip}}(z'), \tag{24}$$

where $V_{\mathrm{jel}}(z')$ represents instantaneous interaction of an electron with the field of the jellium, $V_{\mathrm{xc}}(z')$ is the exchange and correlation potential, and $V_{\mathrm{dip}}(z')$ is the average interaction energy of the electron with the dipolar solvent. The valence electron density $\rho_e(z')$ is given by

$$\rho_e(z')=\frac{m_e}{\pi\hbar^2}\sum_{\epsilon_n<\epsilon_F}(\epsilon_F-\epsilon_n)|\psi_n(z')|^2, \tag{25}$$

where ϵ_F is the Fermi energy, which is obtained from the following equation:

$$\epsilon_F=\frac{2\pi\hbar^2\rho+z_w}{m_e n_F}+\sum_{\epsilon_n<\epsilon_F}\frac{\epsilon_n}{n_F}, \tag{26}$$

where n_F is the number of eigenstates with energy $\epsilon_n<\epsilon_F$. Equation (26) is obtained by using the charge neutrality condition.

In the present work, we have used the local density approximation with Wigner's expression for the exchange and correlation energy [38],

$$V_{\mathrm{xc}}(z')=-e^2\left(\frac{0.611}{r_s(z')}+0.147\frac{4r_s(z')+23.4a_0}{[r_s(z')+7.8a_0]^2}\right), \tag{27}$$

where $r_s(z')=[4\pi\rho_e(z')/3]^{-1/3}$, e is the magnitude of electronic charge, and a_0 is the Bohr radius. The interaction of an electron with the solvent dipoles is given by [20]

$$V_{\mathrm{dip}}(z')=\frac{2\pi\rho_0\mu e}{3}\left(\int_0^{z'}g_{\mathrm{ws}}^{011}(z)dz-\int_{z'}^{\infty}g_{\mathrm{ws}}^{011}(z)dz\right), \tag{28}$$

where $g_{\mathrm{ws}}^{011}(z)$ is the (011) component of the following Legendre polynomial expansion of the metal-solvent correlation function

$$g_{\mathrm{ws}}(z,\theta)=\sum_n(-1)^n g_{\mathrm{ws}}^{011}(z)P_n(\cos\theta), \tag{29}$$

where $P_n(\cos\theta)$ is the Legendre polynomial of order n. We note that the solvent polarization $P(z)$ is related to $g_{\mathrm{ws}}^{011}(z)$ by the following relation:

$$P(z)=-\frac{2\mu\rho_0}{3}g_{\mathrm{ws}}^{011}(z). \tag{30}$$

Clearly, the metal potential depends on the solvent polarization, which, in turn, depends on the potential of the metal surface. Thus, the above equations for the metal potential and the solvent structure are solved self-consistently through iteration. Initially, the metal potential is calculated by replacing the dipolar fluid by vacuum. The dipolar liquid was then introduced and the Eq. (19) was solved for the solvent density and polarization. After this initial calculation, $V_{\mathrm{dip}}(z')$ was evaluated using Eq. (28) and the new electron distribution was calculated by solving Eqs. (23) and (25). The metal potential was calculated from the new electron distribution by using Eq. (22) and the corresponding metal field was used in the next set of solutions of Eq. (19) and this iterative process was continued until convergence was attained.

III. NUMERICAL RESULTS

The dipolar solvents studied in this work can be specified by specifying the values of the reduced parameters: reduced dipole moment $\mu^*=\sqrt{\mu^2/k_BT\sigma^3}$ and the reduced bulk density $\rho_0^*=\rho_0\sigma^3$ and the metal is described by the Wigner-Seitz radius $r_s=(3/4\pi\rho_+)^{1/3}$. The solvent in the present calculations is characterized by $\mu^*=1.29$ and $\rho_0^*=0.74$. We have, however, used three different values of the reduced Wigner-Seitz radius r_s^* $(=r_s/a_0$ where a_0 is the Bohr radius) for the metal surfaces.

In Fig. 1, we have plotted the results of $\rho(z)$ for three different values of reduced Wigner-Seitz radius $r_s^*=2.65$, 3, and ∞. We note that $r_s=\infty$ corresponds to a nonmetallic or an inert surface. It is seen that the solvent density profiles are highly nonuniform near the metal surface. Also, the density at the surface increases with decrease of r_s, which is more clearly shown in the inset. This implies that electrostatic field of the metal surface attracts the solvent molecules and leads to a stronger physisorption at the metal surface. Also, the profiles of $\rho(z)$ show pronounced oscillations in the interfacial region indicating layering of the solvent structure at microscopic level induced by the metal field. We next discuss the results of solvent polarization which are shown in Fig. 2.

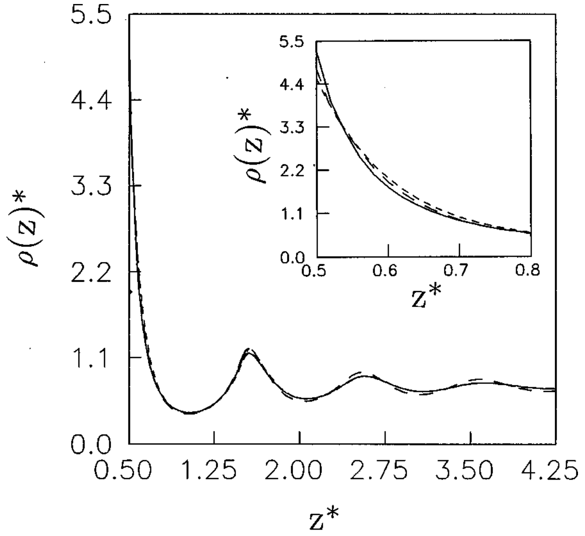

FIG. 1. The variation of solvent density with distance from the metal surface. The solid, long-dashed, and short dashed curves are for $r_s^*=2.65$, 3.0, and ∞, respectively. The reduced distance $z^*=z/\sigma$. Other reduced quantities are defined in the text.

The solvent polarization is found to be most significant near the surface and then it oscillates until the bulk value is reached. The results seem to depend rather strongly on the strength of the metal field characterized by the value of r_s. Also, the polarization increases with decrease of r_s in a nonlinear fashion. In Fig. 3, we have plotted the quantity $\langle\cos\theta\rangle_z$ against z for two different values of the Wigner-Seitz radius r_s. We note that there is no polarization for $r_s=\infty$ and hence $\langle\cos\theta\rangle_z$ is zero for this particular value of r_s. For smaller values of r_s, the molecules near the surface are found to be significantly oriented. This is in agreement with the results of recent molecular dynamics simulations of simple dipolar liquids near metal surfaces [12]. Also, the profiles of $\langle\cos\theta\rangle_z$ are seen to oscillate with distance from the surface, which can be attributed to the interplay between the metal-solvent and solvent-solvent interactions. This is, again, in agreement with the results of recent MD simulations [12].

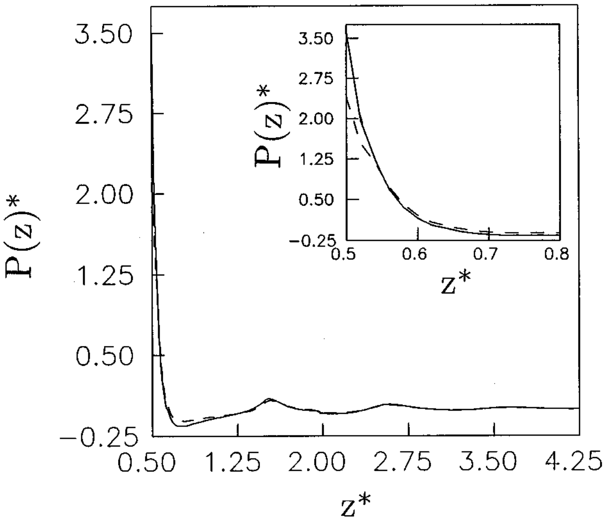

FIG. 2. The variation of solvent polarization with distance from the metal surface. The solid and dashed curves are for $r_s^*=2.65$ and 3.0, respectively.

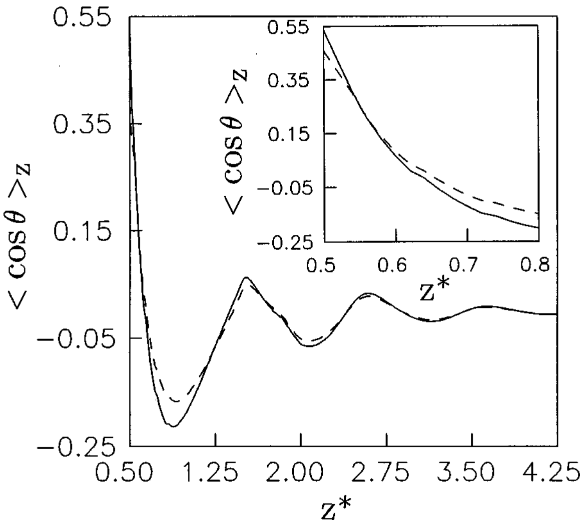

FIG. 3. The variation of $\langle \cos\theta \rangle_z$ with distance from the metal surface where θ is the average angle that a solvent molecule makes with the direction of the metal field. The different curves are as in Fig. 2.

IV. SUMMARY AND CONCLUSIONS

We summarize the main results of this work. We have developed a nonlinear theory for the calculation of structure of a metal-solvent interface by using classical density functional theory for the solvent and quantum density functional theory for the metal. Our approach to the interfacial structure is based on a weighted density approximation for the isotropic part of the solvent density and the anisotropic (or dipolar) part is calculated by using a perturbative approach. The theory, however, retains the full nonlinear dependence of the interfacial solvent density and polarization on the metal electrostatic potential and solvent-solvent interactions. The metal potential arises from the inhomogeneous electron density at the surface, which is influenced by the solvent; the solvent structure, in turn, is influenced by the metal; and the entire system is solved self-consistently until convergence is attained. It is found that the number density of the solvent near the metal surface is significantly higher than the bulk density that occurs due to strong physisorption. The polarization is found to depend nonlinearly on the electrostatic field of the metal and exhibits the presence of pronounced orientational order of solvent molecules near the metal surface. This is most important in the first layer at the metal surface where the solvent dipoles tend to align parallel to the surface normal. This is in agreement with the results of earlier theoretical calculations based on integral equation theory and computer simulations. We note that a nonlinear theory for metal-solvent interface based on a density functional approach is presented here for the first time.

The theory presented in this paper can be extended to the study of more complex metal-solvent interfaces. For example, it will be interesting to investigate the structure of an ion-dipole mixture and a binary dipolar liquid near a metal surface. The interfacial structure of such systems is expected to be rather complex and interesting because of preferential physisorption of one species against the other at the metal surface. Work in these directions is in progress.

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