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Role of the surface electronic response function on treatments of the liquid-vapor interface of alkali metals

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We present a treatment of the surface of liquid alkali metals based on a perturbative expansion to second order in the electron-ion pseudopotential. We make a simple direct approximation for the inhomogeneous electronic response function, in contrast to previous work which approximates the effective pair interaction. It is found that the surface tension, obtained by using a nonmonotonic parametrization of the ionic profile, is in good agreement with the experimental value and improves the results of the previous approaches.

I. INTRODUCTION

A satisfactory description of the liquid-vapor interface of alkali metals requires a second-order perturbative calculation in the electron-ion pseudopotential.[1-3] The initial work of Hasegawa and Watabe[1] was improved by Chacón *et al.*[2] taking an electronic reference system that reflected the change induced by the pseudopotential averaged over the ionic configurations. The main advantage of that method is that it makes the theory less sensitive to changes in the pseudopotential, as was shown by Lai.[3] These treatments use hard spheres as an ionic reference system and approximate the effective pair interaction ϕ_{eff} instead of, directly, the exact electronic surface screening. Thus,

$$\phi_{\text{eff}}(\mathbf{R_1},\mathbf{R_2}) = \phi_{\text{eff}}^{\text{bulk}}(|\mathbf{R_1}-\mathbf{R_2}|;n_{\text{aver}}) \tag{1}$$

is used, which replaces the exact effective pair interaction at the surface by that of the bulk pair effective interaction evaluated at an average electronic density n_{aver} (hereafter approximation α).

All these treatments use monotonic functions to describe the ionic density profiles and predict acceptable values for the surface tension but unrealistically small ionic profile widths. This failure could be due to the use of monotonic functions to describe the density profile since the Monte Carlo simulations[4] and also x-ray and neutron scattering experiments[5,6] suggest the existence of a nonmonotonic ionic density profile. One alternative source of error could be the approximation used to describe the electronic surface screening.

Recently we have analyzed the first issue improving the method of Chacón *et al.*[2] in order to develop a model capable of describing the surface tension when the ionic profile is nonmonotonic,[7] but retaining approximation α. We found that the surface tension calculated was in good agreement with the experimental values if we constrained the minimization procedure to exponential parametrizations for the ionic profile. Choosing a more flexible parametrization for the ionic profile yields poor results for alkali metals since the surface tension is halved. This fact suggests that it is necessary to improve the formulation of the free energy functional. However this conclusion appears to be contradicted by the good values for the surface tension obtained by Hasegawa,[8] using the one component plasma as an ionic reference system and an nonmonotonic parametrization for the ionic profile width. The trouble is that Hasegawa uses an inflexible parametrization for the ionic profile; if we use this parametrization in our theory, the surfaces tensions obtained are very similar to those of Hasegawa, but the real minimun of the free energy functional is lower.

At present, we think that an improved description of the surface screening is required. A first step toward this goal consists of approximating directly the inhomogenous electronic response function, instead of the effective pair potential (approximation α). A partial study of the approximation was done by Foiles and Ashcroft,[9] when using the approximation α they do not find convergent minimization for polyvalents metals. In order to analyze the origin of this behavior, they calculated the self-energy approximating the pair interaction potential and also using a direct approximation for the surface electronic response function. They concluded that to understand the polyvalent metals an accurate calculation of the self-energy is crucial whereas for the alkali metals this quantity is less important. We think that when we use a flexible nonmonotonic parametrization for the ionic profile, the accuracy of the surface electronic response in a surface tension calculation is as important for the alkali metals as it is for the polyvalent metals. We also note that it is not completely correct to analyze the self-energy contribution alone since the effect in the self-energy due to an approximate response function is of the same order as that in the pair interaction contribution.

In this work we have introduced a simple approximation to analyze the role of the surface screening description in the study of the liquid alkali-metal surfaces.

II. THEORY

The present model is based on the theory developed by us[7] in order describe the surface tension when the ionic profile is nonmonotonic. The following presentation is and that photoemission data identified occupied states

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focused on the modifications to previous work necessary to incorporate our improvements; the details of the model can be found in Ref. 7.

The surface tension σ of a liquid metal is given by

$$\sigma = \sigma_{\rm hs} + \sigma_{\rm jell} + \sigma_{\rm eff} + \sigma_{\rm self}, \tag{2}$$

where $\sigma_{\rm hs}$ and $\sigma_{\rm jell}$ are the contributions to the surface tension of the hard-sphere and the electronic reference system, respectively. The last two terms, the self-energy contribution $\sigma_{\rm self}$ and the contribution due to the effective pair interaction $\sigma_{\rm eff}$, depend on the surface electronic response function and, therefore, they will be changed in this work.

The evaluation of the electronic response function at the surface of a liquid metal is a difficult task. To bypass this problem we will use an approximation that has shown its validity in studies of the surface of solid metals. Rose and Dobson[10] proposed a simple approximation that consists of replacing the exact inhomogeneous electronic response function χ^s with the homogeneous one χ^B but evaluated at an electronic density averaged over the electronic positions. They write, if we take the z axis perpendicular to the surface,

$$\begin{aligned}\chi^s(r_{xy}, z_1, z_2) &\simeq \chi^{\rm bulk}[r_{xy}, z_1 - z_2; n_{\rm aver}(z_1, z_2)] \\ &= \chi^B[|\mathbf{r}_1 - \mathbf{r}_2|; n_{\rm aver}(z_1, z_2)],\end{aligned} \tag{3}$$

where r_{xy} is the radius in the plane x-y, and

$$n_{\rm aver}(z_1, z_2) = \frac{1}{2}[n(z_1) + n(z_2)]. \tag{4}$$

This approximation has improved the description of the dependence of the surface energy on the crystallographic face; also, its quality has been tested against the self-consistent results.[11] The aim of the present work is to evaluate the effect on $\sigma_{\rm self}$ and $\sigma_{\rm eff}$ in making approximation (3) instead of approximating the effective potential. As a first step, and in order to make the calculation more tractable, we introduce the further simplification of assuming that the electronic density distribution we use in (4) to evaluate the response function is a step function:

$$n^{\rm step}(z) = \begin{cases} n_B, z < 0 \\ 0, \quad z \geq 0, \end{cases} \tag{5}$$

where n_B is the bulk electronic density. Hereafter we will name this approximation β. In this approach the self-energy contribution to the surface tension is given by

$$\sigma_{\rm self} = \frac{1}{2}(2E_{\rm self} - E_{\rm self}^{\rm bulk}), \tag{6}$$

with

$$E_{\rm self} = \frac{1}{2}\int_{-\infty}^{\infty} dZ\rho(Z)\int_{-\infty}^{\infty} dz_y \Phi(Z, z_y) \tag{7}$$

and

$$\begin{aligned}\Phi(Z, z_y) = 2\pi^2 &\int_0^{\infty} dr r^2 \chi^B[r; n^{\rm step}(Z + z_y)] \\ &\times \int_{|z_y|}^{\infty} dy y v_{\rm ps}(y) \int_0^{\pi} d\theta v_{\rm ps}(|\mathbf{r} + \mathbf{y}|)\sin\theta.\end{aligned} \tag{8}$$

Aschroft's empty-core model[12] is used for the pseudopotential $v_{\rm ps}$, and the static bulk electronic response function χ^B employed is that proposed by Geldart and Vosko.[13] The second term changed in this work corresponds to the contribution due to the effective pair interaction

$$\sigma_{\rm pair} = \frac{1}{2}(2E_{\rm eff} - E_{eff}^{\rm bulk}), \tag{9}$$

where

$$E_{\rm eff} = \pi \int_{-\infty}^{\infty} dZ\rho(Z) \int_{-\infty}^{\infty} dZ_T \rho(Z + Z_T)\Phi_{\rm pair}(Z, Z_T) \tag{10}$$

and

$$\Phi_{\rm pair}(Z, Z_T) = \int_{|Z_T|}^{\infty} dT \Phi_{\rm ind}(Z, Z_T, T)[g_{\rm hs}(T) - 1]. \tag{11}$$

$g_{\rm hs}$ is the radial distribution function of the bulk hard-spheres reference liquid, and $\Phi_{\rm ind}$ is given by

$$\begin{aligned}\Phi_{\rm ind}(Z, Z_T, T) = \int d\mathbf{r} \int & d\mathbf{r}' v_{\rm ps}(|\mathbf{r} - \mathbf{R}|) \\ &\times v_{\rm ps}(|\mathbf{r}' - \mathbf{T} - \mathbf{R}|) \\ &\times \chi^B[|\mathbf{r} - \mathbf{r}'|; n^{\rm step}(\mathbf{r})].\end{aligned} \tag{12}$$

Z and Z_T are the z component of $\mathbf{R}$ and $\mathbf{T}$, respectively.

III. NUMERICAL RESULTS

The bulk parameter values used in this work are those of Ref. 7. The ionic profile is determined by the minimization of the surface tension given in Eq. (2). The main advantage of the electronic reference system developed by Chacón *et al.* and used in this work, is that for a fixed ionic profile, the electronic profile is obtained by minimizing $\sigma_{\rm jell}$, which does not depend on the surface electronic response function. That means that for a fixed ionic profile, and within linear response theory, the electronic density profile is independent of the approximation used for the surface response function. Therefore, the electronic density profile depends on the surface response function only through the changes in the ionic density profile. When we change the approximation for the surface response function, a new ionic density profile minimizes the surface tension, and so we have a new electronic density profile. The electronic minimization of $\sigma_{\rm jell}$ is carried out using the conjugate gradient method modified by Tarazona and Chacón.[14] It is worth noting that the step function used previously [Eq. (5)] is only a way to approximate the surface response function.

We assume the following functional form for the ionic profile:

$$\rho(z) = \begin{cases} \rho_B\{1 - \frac{1}{2}\exp[(z + C)/M] + A_1 \exp[(\frac{z - A_2 + C}{A_3})^2]\}, z < 0 \\ \rho_B\{\frac{1}{2}\exp[(-z + C)/M] + A_1 \exp[(\frac{z - A_2 + C}{A_3})^2]\}, \quad z \geq 0, \end{cases} \tag{13}$$

TABLE I. Calculated surface tension σ using approximations α or β and comparison with experimental values (all units are erg cm^{-2}).

Metal	Approximation α σ_{self}	 σ_{eff}	 σ	Approximation β σ_{self}	 σ_{eff}	 σ	Experiments σ
Na	-65	-672	111	201	-871	187	191
K	-64	-596	50	134	-312	130	115
Cs	15	43	54	87	-244	98	70

where ρ_B is the bulk ionic density. One of the five parameters is eliminated by the requirement that the Gibbs dividing surface must be located at $z = 0$, thus the parametrization has four free parameters that are determined by the minimization condition. As shown by Gómez and Chacón[7] this parametrization is more flexible than others used in previous work.

Table I shows the surface tension values for some alkali metals obtained with the present model and also, as a comparison, the results obtained in our previous work using the same parametrization but making surface approximation on Φ_{pair} instead of on the surface response function. The results of the present approach are in good agreement with the experimental values, showing that this approximation represents an improvement over the previous one. The relative error of our results compared to experiments increases with the atomic number. Except for sodium our results are bigger than experiments, so a better parametrization of the ionic profiles could improve the results.

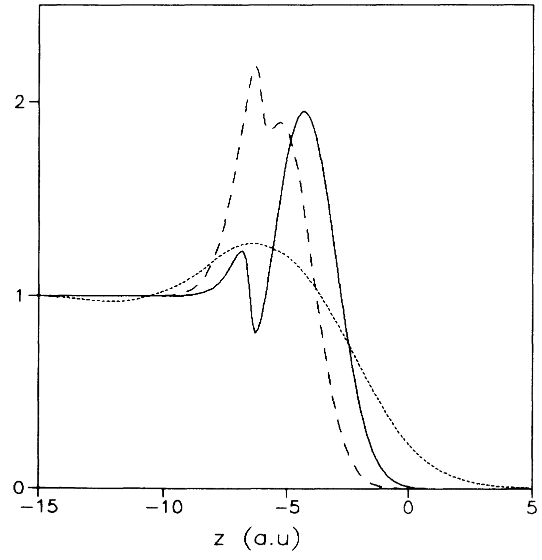

FIG. 1. Results of variational calculations for the normalized ionic density profiles of the potassium with z in atomic units. Dashed line, approximation α; full line, approximation β. For approximation β, the dotted line shows the electronic profile. This profile is obtained minimizing σ_{jell} with the ionic profile given by the full line.

In the work of Foiles and Aschroft,[9] which analyzes the σ_{self} term, they noted that the effects of directly approximating the electronic response function are very important in polyvalent metals. Our results show that this effect is also very important for alkali metals. On the other hand, introducing approximation β modifies σ_{self} as well as σ_{eff}, with the contribution of these modifications to the surface tension being similar. Therefore, if we want to study the role of the electronic surface response function in the surface tension we cannot study the term σ_{self} alone. It is necessary to study σ_{self} and σ_{eff} consistently, that means within the same approximation. We have calculated the surface tension using approximation β for σ_{self} and the approximation α for σ_{eff}; the results became drastically worse.

Figure 1 shows the density profiles for potassium using approximations α and β. For both approximations the height of the first peak is very high. We can see that approximation β does not prevent the exaggerated growth of the first peak for monovalent metals. We think that this behavior could not be due to the Dobson and Rose approximation [Eq. (3)] but rather to our simplification [Eq. (5)], which makes the surface electron-response function independent of the electronic profile as it is evaluated for a step profile.

Based on the encouraging results obtained in this work it appears that our simplification model of the Dobson and Rose model gives very good results for the surface tension of alkali metals. At present we are attempting to include in our theory the original Dobson and Rose description, without using the step function, in order to study if it will correct the height of the first peak of the ionic profile.

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