

THE CONTRIBUTION OF SURFACE FIELD INDUCED DIPOLES TO FLUID-FLUID AND FLUID-SOLID ADSORPTIVE POTENTIALS AS MODELED BY NLDFT

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Introduction

It has been noted many times in the adsorption literature that the fluid-fluid interaction properties of an adsorbate are significantly affected by the surface of the underlying adsorbent [1,2,3]. In the case of an asymmetric polar molecule such as fluorotrichloromethane, dispersion forces alone may be sufficient to orient the adsorbate molecule, thus changing its effective fluid-fluid interaction on the surface, but the effect is also seen for the noble gases where no such asymmetry or polarity exists. Various explanations have been given, often under the label “multibody effects”. While several such attempts to quantitatively account for the observed perturbation using molecular modeling techniques have been successful to varying degrees, in the final analysis, all have been empirical in their implementation [4].

This paper revisits work done by de Boer [1] and later by Ross and coworkers [2] wherein the major cause of the perturbation is attributed to the presence of an electric field at the adsorbent surface. The direction of the electric field at a solid surface, where its effect has been directly measured by means of contact potentials, is such that it tends to orient dipoles, whether induced or permanent, in the adsorbed layer, with their positive ends farther away from the surface. This leads to the positive surface potential that has been found experimentally by Mignolet [5] and others. Even in the absence of a permanent dipole, the surface field has the effect of inducing a dipole moment in the adsorbed molecule:

$$\mathbf{m} = E\mathbf{x} \quad (1)$$

where μ is the dipole induced by surface field E and α is the polarizability of the adsorbed molecule. The existence of such parallel-oriented dipoles in the adsorbed film introduces a mutual repulsion that partially counteracts the normal, attractive dispersion potential between the adsorbed molecules. For argon on graphitized carbon black P-33, the induced dipole amounts to about 0.20 Debye, resulting in a significant (~12%) reduction of the net fluid-fluid potential near the solid surface.

Using submonolayer adsorption data and the two-dimensional van der Waals equation, Ross and Olivier [2, Chapter VII] were able to convincingly demonstrate that a virtually single electric field strength could accurately explain the isotherms and thermodynamic properties (particularly the entropies of rotation and vibration) of a wide variety of adsorptives on graphite monolayers, and that the surface field

of several dissimilar adsorbents, both conductors and insulators, all fell in the range $1.0 - 2.0 \times 10^5$ esu/cm².

In this paper, we explore the quantitative application of surface field theory to adsorption on graphite in the context of modern non-local density functional theory.

Theoretical Background

Here, as in previous work [4], we model the adsorbent as a free, flat homogeneous surface of infinite extent. Similarly, the solid-fluid and fluid-fluid dispersion potentials are taken as described by the appropriate summations of the Lennard-Jones pairwise potential function and the free energy functionals are as given by the prescriptions of Tarazona [6]. For this study, we additionally endow the surface with a uniform surface dipole distribution, producing a net electrostatic field, E , directed normal to the surface. For now, we assume that the usual Lennard-Jones parameters are unaffected by the field. (Note: cgs units are used throughout.) Such a dipolar field decays with distance z from the center of the surface dipole according to

$$E(z) = 2pnq \ln(1 + d/z) \quad (2)$$

where n and q are the area density of dipoles and their charge, and d is the dipole length.

In addition to this surface dipole field imposed by the boundary of the solid, the graphene layers of the graphite basal plane are quadrupolar in nature because of their pi electron structure and produce an opposing but shorter -ranged field given by

$$E(z) = -2pnq \ln(z/\sqrt{(z+d)(z-d)}) \quad (3)$$

The quantities n , q and d in equations 2 and 3 have the same meaning, but may have different values.

$$\text{Equation (1) now becomes } \mathbf{m}(z) = E(z)\mathbf{x} \quad (1a)$$

where the surface field is given by Equation (2) or Equation (2 and 3.) as appropriate.

From Coulomb's law, the energy of pairwise interaction of coplanar parallel oriented dipoles is $U = 2\mathbf{m}^2/3s^3$ where s is their separation. In three dimensions,

$$U(z, z') = -2\mathbf{m}(z)\mathbf{m}(z') \left(\frac{1 - (4/3)\cos(\theta)^2}{s^3} \right) \quad (4)$$

where θ is the angle between the s-vector and the z plane. We see that the electrostatic potential is longer ranged than the Lennard-Jones dispersion potential. Equation (4) also tells us that for $\theta \geq 30^\circ$, the interaction energy becomes attractive, as oriented parallel dipoles become more vertically aligned.

Following usual procedures for numerical integration, we express the induced dipole contribution to the chemical potential by a vector along the z-axis, each element being the integral in polar coordinates over x, θ of the plane at z' having density $\rho(z')$ and multiplied by the density vector $\rho(z)$.

$$U_{ff}^{ID}(z) = -8p^2 n_0^2 q_0^2 \mathbf{x}^2 \mathbf{r}(z) \ln[1 + d/z] \sum_{z'} \ln[1 + d/z'] \mathbf{r}(z') \frac{\Delta z^2 - 3l_0^2}{9(l_0^2 + \Delta z^2)^{3/2}} \quad (5)$$

In Equation (5), $l_0 = s_{ff} \cos q$ for $\Delta z \leq 1$ and $l_0 = 0$ for $\Delta z > 1$

Equation (5) accounts for the electric field effects on fluid-fluid interactions.

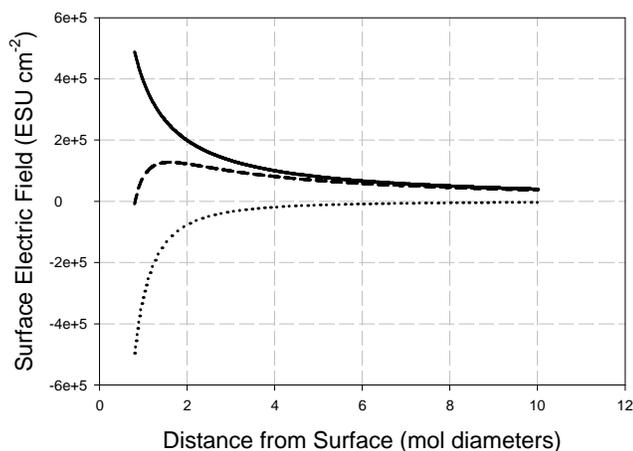


Fig. 1 Plots of the surface electric field near a graphite surface according to Equations 2 and 3: Solid line- surface dipole field, dotted line- quadrupole field, dashed line- net surface field.

There is also a significant contribution to the external wall potential produced by the interaction of the field induced dipoles with their surface mirror. This term is always attractive and is given by

$$U^{elec}(z) = -\frac{1}{2} \mathbf{E}^2(z) \mathbf{x} \quad (6)$$

The total (integral) contribution to the energy of adsorption is then given by

$$U^{elec} = \sum_z \mathbf{r}(z) U^{elec}(z) \quad (7)$$

For fields of the magnitude discussed here, U^{elec} contributes about 1kJ/mole to the energy of adsorption.

The iterative solution of the DFT expression for the equilibrium density profile is carried out as usual.

Results and Conclusions

We will demonstrate that the inclusion of the induced dipole interactions and the mirror potential predicted by surface field theory into the NLDFT formalism as mean-field-like, electrostatic contributions to the chemical potential produces a superior fit to the experimental data for argon adsorbed on Sterling FT G(2700) graphite.

References

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