Solvation Effects in Self-Assembled Systems

Laura J. Douglas Frink
Materials Simulation Science Dept.,
Sandia National Laboratories, Albuquerque, New Mexico 87185-1111

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I. INTRODUCTION

Many types of self-assembly can be found in nature. They include crystallization, the formation of micelles, and the folding of proteins. Recently there has been much interest in pursuing nano-to-microscopically engineered materials by way of self-assembly on imprinted or templated surfaces. This process has been called soft lithography \[1\]. In all of these diverse cases, wetting plays a critical role in the assembly process. Wetting involves the interactions of the substrate or amphiphilic molecule or macromolecule with a solvent. In many self-assembled systems we find that the critical feature of the system is a substrate or macromolecule with a dual (both hydrophilic and hydrophobic) nature. In this paper we discuss the wetting properties of a striped surface where the stripes represent alternating chemical characteristics. We show how the chemical heterogeneity affects the wetting properties of the surface (e.g. the static contact angle), and discuss the length scale limitations on the soft lithography approach.

In this paper, the wetting of a chemically heterogeneous surface \[2,3\] is studied using a nonlocal Density Functional Theory (DFT). The results for the heterogeneous surface model we discuss have immediate implications for soft-lithography by self-assembly. It also lends fundamental insight into the mechanisms controlling self-assembly of macromolecules.

In both macroscopic \[4,5\] and statistical mechanical studies \[6-8\] of fluid-solid interfaces, the attraction of a fluid for a surface is often quantified by a contact angle, $\theta$. When $\theta = 180^\circ$, the fluid-surface interaction is non-wetting, and liquid will be displaced from such a surface by an intervening vapor film. When $\theta = 0^\circ$, the interaction is completely wetting, and a liquid film will form on the surface when the bulk fluid is vapor. The contact angle may be calculated from

$$
\cos \theta = \frac{\Omega_{SV}^f - \Omega_{SL}^f}{\Omega_{LV}^f}
$$

since the surface free energies for solid-liquid, $\Omega_{SL}^f$, solid-vapor, $\Omega_{SV}^f$ and liquid-vapor, $\Omega_{LV}^f$ interfaces can be calculated with the DFT we apply.

II. MODEL/THEORY

The heterogeneous surface model we have used is sketched in Fig.1. The planar surface is split into stripes that alternate between type I (hydrophobic) and type II (hydrophilic). Each surface type is defined by its extent, $l$, and the magnitude of the interaction energy parameter with the fluid, $\varepsilon_{wf}$. Density distributions are assumed to be uniform in $z$ since the surface properties are uniform in this dimension.

The underlying molecular model describing fluid-fluid interactions is the cut and shifted 12-6 Lennard-Jones (LJ) potential, $u(r) = u_{LJ}(r) - u_{LJ}(r_c)$. Wall-fluid interactions are found by integrating the 12-6 potential over the surface of interest. The characteristic interaction length for all calculations is the solvent particle diameter, $\sigma$. 
FIG. 1. A diagram of a chemically heterogeneous surface model. The surface is composed of stripes of alternating surface chemistry defined by the wall-fluid interaction potential parameters, $\epsilon_{wf}$ and $\sigma_{wf}^2$ and the extent of each stripe, $l'$ and $l''$. The length of the computational domain perpendicular to the surface is $L_x$ and parallel to the surface is $L_y$. The origin of the computational domain is located inside the surface such that the fluid-surface interface is found at $x = 0.5\sigma$.

In this paper, $l'$, $l''$, and $l'''$ are varied while the other parameters are fixed. Specifically, $kT/\varepsilon = 0.8$ (k is the Boltzmann constant), $\rho_s \sigma^3 = 1$, $\epsilon_{wf} = 0.5\varepsilon$, and $\sigma_{wf}^2 = \sigma_{wf}^3 = \sigma$. The cutoffs are varied from $r_{c,wf} = r_c = 2.5\sigma$ to $10\sigma$. The bulk liquid and vapor coexistence densities are $\rho^L \sigma^3 = 0.709$ and $\rho^L \sigma^3 = 0.0114$ for $r_c = 2.5\sigma$.

The nonlocal DFT we apply here is the fundamental measures DFT of Rosenfeld [9]. Attraction are treated with a strict mean field approximation. Briefly, DFT is based on the functional minimization of the grand potential $\Omega$ with respect to the fluid density distribution, $\rho(r)$, $\delta \Omega / \delta \rho(r) = 0$.

Given the equilibrium density distribution, the grand potential, $\Omega$, as well as the surface free energy, $\Omega^f = \Omega - \Omega_b$, may be calculated immediately. The grand potential of the bulk solution is $\Omega_b = -pV$ where $p$ is the pressure in the bulk fluid and $V$ is the volume of the system. Eq.1 may then be used to calculate the contact angle.

III. RESULTS

In order to calculate contact angles, the surface free energy, $\Omega^f$ must be calculated for solid-liquid (SL), solid-vapor (SV), and liquid-vapor (LV) interfaces (see Eq.1). The LV need only be calculated once, but SL and SV profiles are needed for each value of the surface parameters. Fig.2 shows one example of a SV density distribution where the surface-fluid interaction parameter is particularly strong.

Fig.2 shows a condensed phase of nanoscopic extent near the hydrophilic portions of the surface. There is ordering in the condensed nanophase both parallel and perpendicular to the surface. The perpendicular ordering is due to the presence of the solid while the parallel ordering arises from the presence of a vapor interface perpendicular to the surface.
FIG. 2. The fluid density distribution, $\rho \sigma^{-1}(x,y)$ near a surface with $\epsilon_{wf}^{II} = 6.32$ and $l^{II} = 5\sigma$ when the bulk is a vapor.

In the case displayed in Fig.2, the magnitude of the peaks in the first layer is as high as $\rho \sigma^3 = 20$. This phase is more like a condensed crystal than a condensed liquid. For larger $\epsilon_{wf}^{II}$, convergence becomes difficult due to the steepness of the density distributions. This numerical difficulty suggests that the system might prefer to break the symmetry in $z$ and form a nanoscopic crystal. In order to verify this hypothesis, 3D-DFT or molecular simulations must be performed.

In Fig.2, $\epsilon_{wf}^I = 0.1\epsilon$ and $\epsilon_{wf}^{II} = 3.16\epsilon$. A homogeneous surface with $\epsilon_{wf} = 3.16\epsilon$ would be completely wetting with $\cos \theta = 1$; however a homogeneous surface with $\epsilon_{wf} = (\epsilon_{wf}^{II} + \epsilon_{wf}^I)/2 = 1.63\epsilon$ would be partially wetting with $\cos \theta \approx 0.6$. For the chemically heterogeneous surfaces, the contact angle depends on the extent of the inhomogeneity, $l^I$ and $l^{II}$.

In order to systematically study wetting for the chemically heterogeneous surfaces, DFT calculations were performed for $0.2\sigma \leq l^{II} = l^I \leq 30\sigma$ varying $\epsilon_{wf}^{II}$ through the complete range of contact angles. The values of $\cos \theta$ were calculated from Eq.1, and the results for cases with $l^{II} > 1$ are shown in Fig.3.

Fig.3 shows that it becomes more difficult to reach complete wetting as $l^{II}$ increases. A negative deviation from the homogeneous surface is found for $l^{II} > 2\sigma$. For the cases $l^{II} = 5\sigma$ and $l^{II} = 30\sigma$, the curves stop at the points where convergence became difficult due to ordering in the nanoscopic condensed region (see Fig.2).

Fig.3 demonstrates that the presence of chemical inhomogeneity on a surface can have a profound effect on the wetting transition where a thick liquid film forms at a solid-vapor interface (i.e. where $\cos \theta = 1$). A more complete
FIG. 3. The cosine of the contact angle ($\cos \theta$) as a function of the mean wall-fluid interaction parameter, $<\epsilon_{wf}> = 0.5 \cdot (\epsilon_{wf}^{I'} + \epsilon_{wf}^{I''})$, for the case $l'' = l'^{I''}$. The various curves here are: $l'^{I''} = 1.5 \sigma$ (solid line), $l'^{I''} = 2 \sigma$ (dotted line), $l'^{I''} = 3 \sigma$ (dashed line), $l'^{I''} = 5 \sigma$ (dashed-dotted line), and $l'^{I''} = 30 \sigma$ (+). The homogeneous case (see Fig.2) is indicated by the ●.

search of phase space indicates that a complex phase diagram controls the state of the adsorbed fluid at the surface. This phase diagram is shown in Fig.4.

The phase transitions in Fig.4 include local layering and global wetting transitions. In addition we have included (in dashed lines) the lines of numerical instability due to ordering in the nanoscopic condensed region. There are two lines of numerical instability for the wall-liquid profiles. The upper curve is related to a local ordering near the hydrophilic parts of the surface. The lower curve is related to ordering along the entire surface.

IV. CONCLUSIONS

In this paper, we have presented the results of nonlocal 2D DFT calculations on the wetting properties of chemically heterogeneous surfaces. These calculations showed complex density distributions and phase behavior as a result of the heterogeneity.

The location of the wetting transition was found to be strongly dependent on the nature (extent and strength) of the heterogeneity, and complete wetting was suppressed altogether if the hydrophobic parts of the surface were large enough. In these cases, the condensed nanophase may crystallize if the hydrophilic surface-fluid interactions are strong enough. By exploring the phase space including strength of hydrophilic interactions and extent of chemical heterogeneity, an operational phase diagram was established that could be used for designing nanoscopically tailored devices and materials.
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