Model of Meniscus Shape and Disjoining Pressure of Thin Liquid Films on Nanostructured Surfaces with Electrostatic Interactions

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ABSTRACT: The effect of electrostatic interactions on the stability of thin liquid films on nanostructured surfaces is important in lubrication, wetting, and phase change but is poorly understood. In this study, a general, closed-form model is developed to account for both the effects of electrostatic and van der Waals interactions on meniscus shape and disjoining pressure for thin liquid films on nanostructured surfaces based on the minimization of free energy, the Derjaguin approximation, and the disjoining pressure theory for flat surfaces. The model is verified using the molecular dynamics (MD) simulations for a water–alumina system with both triangular and square nanostructures of varying depth and film thickness. Good agreement is obtained between MD results and model predictions, demonstrating the robustness of the analytical model. The results show that the electrostatic interactions enhance the disjoining pressure, thereby making the meniscus more conformal to the nanostructured surfaces. In addition, the electrostatic disjoining pressure is shown to increase with the nanostructure depth but decrease with the thin film thickness.

1. INTRODUCTION

The stability of thin liquid films is important in lubrication, wetting and spreading, condensation, evaporation, and boiling, as well as solidification and melting, since the rupture of the thin films can lead to dramatic changes in their desired properties. For instance, the rupture of thin films can cause several orders of magnitude decrease in heat flux in thin film evaporation. In recent years, nanostructures have been introduced as a means to control the stability of these thin films. For example, superhydrophobic nanostructured surfaces have been shown to enhance the continuous delivery of liquid to the thin film region and thus achieving high evaporative heat fluxes in cooling high power electronics and lasers.

The disjoining pressure is the excess pressure required to evaporate liquid molecules due to the presence of solid–liquid intermolecular forces, and it ultimately governs the stability of the thin film. Classical theory predicts that the van der Waals contribution to the disjoining pressure, \( \Pi_{vdW} \), as a function of the film thickness, is

\[
\Pi_{vdW} = \frac{A}{6\pi\delta_0^3},
\]

where \( A \) is the Hamaker constant and \( \delta_0 \) is the liquid film thickness. However, the classic disjoining pressure theory assumes atomically smooth surfaces and is not capable of capturing the effect of small-scale surface topologies on disjoining pressure. In order to better predict the ability of nanostructured surfaces to increase the stability of thin liquid films, we have recently developed a general, closed-form model to predict the effect of nanostructures on the disjoining pressure. Through comparisons with molecular dynamics simulations of a water–gold system with triangular and square nanostructures of varying depth and film thickness, our analytical model is shown to be accurate and robust. However, our previous model assumes van der Waals forces as the dominant solid–liquid interactions and is thus inadequate in describing the effect of electrostatic interactions between a polar liquid (e.g., water) and an ionic compound surface.

Recently, nanoporous alumina, CuO nanostructures, and Si/SiO\(_2\) biporous wicks have been used to create superhydrophobic surfaces in order to enhance the liquid delivery to the thin film regions where high heat fluxes occur. In such cases, the electrostatic interactions between the nanostructured surfaces and the polar liquid (e.g., water) play an important role in determining the disjoining pressure. For an atomically flat surface, the electrostatic contribution to the disjoining pressure of a thin liquid film is given by

\[
\Pi_e = 2\epsilon(\frac{k_B T}{ze})^2 K^2
\]

where \( k_B \) is the Boltzmann constant, \( \epsilon \) is the relative permittivity, \( \epsilon_0 \) is the vacuum permittivity, \( \epsilon \) is the electron charge, \( z \) is the valence, \( T \) is the temperature, and \( K \) is related to the surface charge density \( \sigma \) with electroneutrality following \( k_B T \tan (K\delta_0)/(ze) = -\sigma/(\epsilon_0\epsilon) \).

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demonstrated that the electrostatic interactions are able to extend the meniscus of an evaporating thin film in nanopores by conducting a force analysis taking into account the electrostatic disjoining pressure of a thin film on a flat surface using a simplified form of eq 2 at the limit of $\delta_0 \to \infty$. However, the effect of electrostatic interactions between the thin film and nanostructured surfaces on the disjoining pressure and meniscus shape, especially for cases where the thin film thickness is comparable to the pore size so that the nanostructure can no longer be assumed flat, is poorly understood.

Molecular dynamics (MD) simulations are a powerful tool for investigating the role of nanoscale effects on the disjoining pressure and liquids. In previous MD studies, we have shown that electrostatic interactions between water and induced charges on gold surfaces enhance the disjoining pressure. However, atomistic simulations are limited by the specific material systems used and geometries studied, which results in a need for a general model that can describe the meniscus shape and disjoining pressure of a thin liquid film on a nanostructured surface in the presence of electrostatic interactions.

In the present work, a general, closed-form model of the meniscus shape and disjoining pressure for a thin film on nanostructured surface accounting for both van der Waals and electrostatic interactions between liquid and solid is developed based on the minimization of system free energy, Derjaguin approximation, and the disjoining pressure theory for flat surfaces. Molecular dynamics simulations are performed for a water–alumina system to validate the proposed model. The model is demonstrated for 2D periodic nanostructured surfaces of triangular and square shapes, and the results are compared quantitatively with molecular dynamics simulations of a water film on an alumina surface based on well-calibrated potentials. The effects of film thickness, nanostructure depth, and electrostatic forces on the meniscus shape and disjoining pressure are examined. Finally, the effect of nanostructures on the strength of electrostatic interactions is also explored with MD simulations.

2. METHOD

2.1. Model Development of Meniscus Shape and Disjoining Pressure. In this section, a theoretical model is developed to predict the meniscus shape and disjoining pressure of thin liquid films on nanostructured surfaces with both van der Waals and electrostatic interactions between solid and liquid. The schematics of a thin liquid film of thickness $\delta_0$ on 2D periodic nanostructured surfaces of wavelength $L$, depth $D$, and triangular and square shapes are shown in Figure 1a and 1b, respectively. The basic assumptions are

(i) The liquid film is in contact with its own vapor, and the vapor near the thin film is assumed to behave as an ideal gas; and

(ii) The meniscus shape, $\zeta_{\text{lm}}$, is periodic with the same wavelength $L$ as that of the substrate surface $\zeta_c$.

For a thin liquid film on a curved surface in equilibrium with its own vapor, the vapor pressure, $P_v$, near the thin film is affected by both the disjoining pressure and the curvature of the liquid meniscus following:

$$P_C + \Pi_{\text{rough}} = -\rho kT \ln \left( \frac{P_v}{P_{\text{sat}}} \right)$$

(3)

where $P_C$ is the capillary pressure of the liquid film, $\Pi_{\text{rough}}$ is the disjoining pressure on a curved surface, $\rho$ is the liquid density, and $P_{\text{sat}}$ is the saturation pressure at temperature $T$. The disjoining pressure $\Pi_{\text{rough}}$ includes both the van der Waals and electrostatic contributions. For a flat surface, $\Pi_{\text{flat}} = \Pi_{\text{vdW}} + \Pi_{\text{e}}$, where $\Pi_{\text{vdW}}$ and $\Pi_{\text{e}}$ are determined by eqs 1 and 2, respectively. In the limit of $\delta_0 \to 0$, eq 2 reduces to $\Pi_{\text{e}} = -\frac{2kT}{\varepsilon_0} \delta_0$, and at $\delta_0 \to \infty$, it yields $\Pi_{\text{e}} = \frac{\varepsilon_0}{2\delta_0} \frac{kT}{\varepsilon_0} \delta_0^2$.

As shown in Hu et al. the meniscus shape of a thin film on a nanostructured surface, as a result of the competition between the capillary pressure and disjoining pressure, can be characterized by a scaled healing length, $\xi/D$, where $\xi = \gamma / (d\Pi_{\text{vdW}}/d\delta_0)^{1/2}$ and $D$ the nanostructure depth. When only van der Waals interactions are considered between the solid and liquid, the scaled healing length takes the form of $\xi = \delta_0^2 (\rho / (2\gamma))^{1/2}$. When electrostatic interactions are taken into consideration, $\Pi_{\text{flat}} = \Pi_{\text{vdW}} + \Pi_{\text{e}}$, the scaled healing length becomes

$$\frac{\xi}{D} = \frac{\sqrt{\gamma}}{D} \left( \frac{A}{2\delta_0^2} + \frac{\varepsilon_0}{\delta_0} \delta_0 T \frac{\varepsilon_0^2}{2\pi^2} \right)$$

(4)

Here, the electrostatic contribution $\Pi_{\text{e}}$ uses the expression of $\delta_0 \to \infty$ for simplicity.

Without loss of generality, we represent the meniscus shape $\zeta(x)$, using the following (Fourier) cosine series:

$$\zeta(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos \left( \frac{2\pi n x}{L} \right)$$

(5)

where $a_0 = 2\delta_0$. For nanostructured surfaces, it is convenient to introduce a modified film thickness $\delta^*(x)$ as the shortest distance between the meniscus profile and structured solid surface as $\delta^*(x) = \delta(x) / r$, where $r = (1/L) \int_{-L/2}^{L/2} (1 + (\zeta^2)^{1/2}) \, dx$ is the Wenzel roughness ratio between the actual and flat surface areas. The modified film thickness has more utility in this model than the traditional definition of film thickness $\delta(x)$,
which is the vertical thickness $\delta(x)$ defined as the difference between the solid and liquid surface at a point $x$: $\delta(x) = \zeta_l(x) - \zeta_s(x)$. 

The total free energy of the system, $W_{\text{total}}$, consists of the surface excess energy $W_{\text{sur}}$, the van der Waals interaction energy $W_{\text{vdW}}$, and the electrostatic interaction energy $W_{\text{el}}$. The surface excess energy is given as $W_{\text{sur}} = \gamma \alpha_{\text{L-V}}$, where $\gamma$ is the surface tension of the liquid, and $\alpha_{\text{L-V}}$ is the liquid–vapor interfacial area. For a 2D meniscus, the liquid–vapor interfacial area is calculated as $\alpha_{\text{L-V}} = \int \zeta_l(x) \, dx$, where $\zeta_l(x)$ is the local slope of the liquid–vapor surface and is given as $\zeta_l(x) = -\sum_{n=0}^\infty (2\pi n a_n/L) \sin((2\pi n a_n/L) x)$ by using eq 5. The surface excess energy can be expressed as

$$ W_{\text{sur}} = \int_{-L/2}^{L/2} \left[ 1 + \left( \zeta_l(x) \right)^2 \right]^{1/2} \, dx $$

(6)

Minimizing the total free energy of the system by setting $\partial W_{\text{total}} / \partial \zeta_l + (\partial W_{\text{vdW}} / \partial \zeta_l) \delta \zeta_l + (\partial W_{\text{el}} / \partial \zeta_l) \delta \zeta_l = 0$, yields

$$ \frac{\partial W_{\text{sur}}}{\partial \zeta_l} + \left( \frac{\partial W_{\text{vdW}}}{\partial \zeta_l} \right) \delta \zeta_l + \left( \frac{\partial W_{\text{el}}}{\partial \zeta_l} \right) \delta \zeta_l = 0 $$

(7)

where $\partial W_{\text{vdW}} / \partial \zeta_l = (\partial W_{\text{vdW}} / \partial \delta^*) (\partial \delta^*/\partial \zeta_l) = (\partial W_{\text{vdW}} / \partial \delta^*) / r$ and $\partial W_{\text{el}} / \partial \zeta_l = (\partial W_{\text{el}} / \partial \delta^*) (\partial \delta^*/\partial \zeta_l) / (\partial \delta^*/\partial \zeta_l) = (\partial W_{\text{el}} / \partial \delta^*) / r$. By definition, the disjoining pressure is the integral of the free energy due to solid–liquid interactions with respect to film thickness $\delta$, i.e., $\partial W_{\text{vdW}} + W_{\text{el}} / \partial \delta^* = \Pi_{\text{vdW}}(\delta^*) + \Pi_{\text{el}}(\delta^*)$. Therefore,

$$ \frac{\partial W_{\text{vdW}}}{\partial \zeta_l} + \left( \frac{\partial W_{\text{vdW}}}{\partial \zeta_l} \right) \delta \zeta_l + \left( \frac{\partial W_{\text{el}}}{\partial \zeta_l} \right) \delta \zeta_l = 0 $$

(8)

Substituting eqs 1, 2, 5, 6, and 8 into eq 7, it follows

$$ \int_{-L/2}^{L/2} \pi \frac{\pi}{L} \sin \left( \frac{2\pi n a_n}{L} x \right) \sum_{m=1}^\infty a_m \frac{2\pi m}{L} \sin \left( \frac{2\pi m}{L} x \right) \, dx $$

$$ + \left[ \sum_{m=1}^\infty a_m \frac{2\pi m}{L} \sin \left( \frac{2\pi m}{L} x \right) \right]^2 \int_{-L/2}^{L/2} \pi \delta = 0 $$

(9)

where $K$ is related with the surface charge density $\sigma$ by $2k_B T \sigma / \zeta_s (K \delta^*) / (ze) = -\sigma / (\varepsilon_0 k_B T)$. The closed-form relation given in eq 9 predicts the wave amplitudes, i.e., $a_n (n = 1, 2, \ldots, \infty)$, and hence the meniscus shape of a thin liquid film of thickness $\delta_0$ on a nanostructured surface with a prescribed profile $\zeta_s(x)$.

Applying the Derjaguin approximation, the local disjoining pressure of a curved surface is approximated by the disjoining pressure of a flat substrate of the same local film thickness, and averaging the total disjoining pressure along $x$ give the following mean disjoining pressure on a nanostructured surface

$$ \bar{\Pi}_{\text{rough}} = \frac{A \sigma^3}{6\pi L} \int_{-L/2}^{L/2} \left[ \sum_{n=1}^\infty a_n \cos \left( \frac{2\pi n a_n}{L} x \right) \right] \, dx $$

$$ + 2\varepsilon_0 \pi \frac{k_B T}{ze} \int_{-L/2}^{L/2} K^2 \, dx $$

(10)

Averaging both sides of eq 3 along $x$ and substituting eq 10, it yields

$$ \frac{P_c}{P_{\text{sat}}} = \exp \left\{ -\frac{A \pi}{6\pi L \rho k_B T} \int_{-L/2}^{L/2} \sum_{n=1}^\infty a_n \cos \left( \frac{2\pi n a_n}{L} x \right) \, dx \right\} $$

$$ - \delta_0 - \zeta_s(x) \right\}^3 $$

$$ - \left\{ \frac{2\varepsilon_0 \pi k_B T}{ze} \int_{-L/2}^{L/2} K^2 \, dx \right\} $$

(11)

where the capillary pressure, $P_c$, is canceled out due to symmetry. Equation 11 gives a closed-form relation for the vapor pressure of a thin film of thickness $\delta_0$ on a nanostructured surface with profile $\zeta_s(x)$ using Fourier coefficients $a_n$, calculated from eq 9. In the limit of $\zeta_s = \text{constant}$ (i.e., a flat solid surface), the roughness ratio $r = 1$, the Fourier coefficients $a_n = 0$ for $n = 1, 2, 3, \ldots$, and eq 11 reduces to

$$ \frac{P_c}{P_{\text{sat}}} = \exp \left\{ -\frac{A}{6\pi \rho k_B T} \sigma / (2\varepsilon_0 \pi k_B T / ze) \right\} $$

(12)

where the first term and second term in the bracket of the right-hand side of eq 12 denote the van der Waals contribution and electrostatic contribution to disjoining pressure, respectively. In the limit of $\delta_0 \to 0$, eq 12 can be further simplified to

$$ \frac{P_c}{P_{\text{sat}}} = \exp \left\{ -\frac{A}{6\pi \rho k_B T} \sigma / (2\varepsilon_0 \pi k_B T / ze) \right\} $$

(13)

In the limit of $\delta_0 \to \infty$, eq 12 is simplified to

$$ \frac{P_c}{P_{\text{sat}}} = \exp \left\{ -\frac{A}{6\pi \rho k_B T} \sigma / (2\varepsilon_0 \pi k_B T / ze) \right\} $$

(14)

2.2. Molecular Dynamics Simulations. MD simulations were performed for water thin films on flat and nanostructured alumina surfaces to validate the proposed model. All simulations were performed using LAMMPS, and the CLAYFF potential was used to describe the intermolecular interactions in the water-alumina system. The $\alpha$-alumina (0001) surface, the most energetically favorable surface of crystalline alumina in nature, and the amorphous alumina, the common structure of nanoporous alumina, were simulated in the present work. The $\alpha$-alumina (0001) surface was generated by cleaving bulk crystalline $\alpha$-alumina, while the amorphous alumina surface was generated through a melt-quenching method. In the melt-quenching method, a bulk crystalline $\alpha$-alumina substrate was first equilibrated at 300 K, heated to 3500 K in 1 ns in an NVT ensemble where the pressure is controlled isotropically at 1 atm, held at 3500 K for 1 ns, and then quenched to 300 K in 1 ns. Two free surfaces were then cleaved from the bulk alumina and a subsequent NVT equilibration was performed at 300 K for 1 ns. The resulting amorphous alumina surface reveals an average roughness of 0.4 nm. Triangular and square nanostructured amorphous alumina surfaces were then generated by cleaving the flat amorphous alumina surfaces with a subsequent NVT equilibration at 300 K for 1 ns.

Figures 1c, 1d, and 1e show the simulation setup of a water film of thickness $\delta_0$ on flat, triangular, and square nano-
structured amorphous alumina surfaces, respectively. In each setup, two water films are separated 20 nm apart. Periodic boundary conditions are applied in all directions and the alumina substrate is frozen at each end of the z direction. The wavelength of the nanostructure, \( L \), is fixed at 24.32 nm for both triangular and square nanostructured amorphous alumina surfaces. For both triangular and square nanostructured amorphous alumina surfaces, the depth of the nanostructure, \( D \), is varied from 3.04 to 6.08 nm so that the aspect ratios of the nanostructures (2D/L) are 1:4 and 1:2, respectively. Thin water films with different thicknesses (i.e., 1.25, 2.48, and 3.72 nm at 300 K) are considered. The meniscus shape of water thin films were simulated on triangular and square nanostructured amorphous alumina surfaces at 300 K. The MD simulations for water thin films on flat crystalline and amorphous alumina surfaces, and on triangular and square nanostructured amorphous alumina surfaces were equilibrated in an NVT ensemble at 400 K for 1 ns, and the vapor pressure was calculated from averaging the data between 200 ps to 1 ns. It is noted that the model developed in Section 2.1 can be applied at any temperature as long as the assumption of ideal gas holds true. The simulation temperature of 400 K was selected to reduce fluctuations in vapor pressure calculations from MD simulations while keeping the ideal gas assumption valid.

In order to investigate how the nanostructures affect the strength of the intermolecular forces, MD simulations were performed to determine the interaction energy per unit actual area for water thin films on flat and triangular nanostructured amorphous alumina surfaces, compared with that of water thin films on flat and triangular nanostructured gold surfaces where van der Waals interactions are the only dominant force. The interaction energy per actual area of the solid–liquid interface can be calculated using

\[
W = \left( E_S + E_L - E_{\text{total}} \right) / A
\]

(15)

where \( A \) is the actual area of the solid–liquid interface (i.e., \( A = \left( 4D^2 + L^2 \right)^{1/2} \) for triangular nanostructured surface), \( E_{\text{total}} \) is the equilibrium total energy of the solid and liquid in contact, \( E_S \) and \( E_L \) are total energy of solid and liquid in vacuum, respectively. In the present simulations, the \( E_S, E_L, \) and \( E_{\text{total}} \) are evaluated using three separate NVT ensembles at 300 K.

In order to examine the effect of electrostatic interactions on meniscus shape, the water film with a thickness of 2.48 nm on a triangular nanostructured amorphous alumina surface with depth of 6.08 nm is simulated with and without electrostatic interactions between water and alumina. The case without electrostatic interactions is set up by turning off the Coulombic potential between water and alumina. Table 1 summarizes all MD cases simulated in this study.

3.3. Determination of the Hamaker constant and surface charge. The model developed in Section 2.1 is a general model for an arbitrary material system where both van der Waals and electrostatic interactions are dominant. In order to compare the model predictions with MD simulations for the water–alumina system described in Section 2.2, the material-dependent Hamaker constant \( A \) that characterizes the strength of van der Waals interactions and the surface charge density \( \sigma \) that affects the short-range electrostatic interactions are needed. Following the Lifshitz theory, the Hamaker constant between water and alumina can be calculated using

\[
A = \frac{3}{4} k_b T \left( \frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right)^2 \left( \frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right)^2 + \frac{3 h \nu_s}{8 \pi^2} \left( \frac{\sigma_1^2 - \sigma_3^2}{\sigma_1^2 + \sigma_3^2} \right)^2 \left( \frac{1}{n_1^2} + \frac{1}{n_3^2} \right)^{3/2} \left[ \left( n_1^2 + n_3^2 \right)^{3/2} \left( n_1^2 + n_3^2 \right)^{3/2} + \left( n_2^2 + n_3^2 \right)^{3/2} \right]
\]

(16)

where \( n \) is the refractive index, \( h \) is Planck’s constant, \( \nu_s \) is the adsorption frequency of water, and the subscripts 1, 2, and 3 represent alumina, water liquid, and water vapor, respectively. The tabulated parameters are given as \( n_1 = 1.75, n_2 = 1.333, n_3 = 1.0002, \epsilon_1 = 11.6, \epsilon_2 = 80, \epsilon_3 = 100, \) and \( \nu_s = 3.0 \times 10^{-14} \) s. The Hamaker constant for the alumina–water–vapor system calculated using eq 16 yields \( A = 3.49 \times 10^{-20} \) J.

The surface charge density \( \sigma \) was calculated using the charge density profile of a water thin film on an alumina surface from the MD simulations. The charge density profile of water thin films on \( \alpha \)-alumina(0001) surface was first calculated and verified against Argyris et al. with less than 2% relative error. For a water thin film on a crystalline alumina surface, the charge density profile shows alternative positive and negative charge layers of water near alumina. The surface charge density calculated based on the total charge of the first charge layer of water per surface area is 0.34C/m² for a crystalline \( \alpha \)-alumina(0001) surface. However, amorphous alumina surfaces have a roughness of \( \sim 0.4 \) nm. For such cases, the surface charge density was calculated using the 3D grid method, where the simulation domain was divided into 0.3 × 0.3 × 0.3 A³ grids and the mass and charge densities were calculated for each grid. Using the mass density profile to identify the 3D solid–liquid interface, the surface charge density of water on an amorphous alumina surface was calculated to be 0.31 C/m² based on the total charge of the first charge layer per surface area of the 3D solid–liquid interface. It is noted that the calculated difference in disjoining pressure, based on surface charge density of 0.34C/m² and 0.31C/m², is within 2%.

3. RESULTS AND DISCUSSION

3.1. Effect of Electrostatic Interactions on Disjoining Pressure. Figure 2 shows the comparison between the MD calculated (symbols) and model predicted (lines) scaled vapor pressure as a function of the film thickness for water thin films of varying thickness on flat crystalline and amorphous alumina surfaces at 400 K. The black line represents the prediction of

"Table 1. Summary of MD Cases Simulated in This Study of Thin Water Films on Solid Surfaces"

<table>
<thead>
<tr>
<th>solid substrate</th>
<th>( D ) (nm)</th>
<th>( L ) (nm)</th>
<th>( \delta_i ) (nm)</th>
<th>S–L interaction</th>
<th>( T ) (K)</th>
<th>results</th>
</tr>
</thead>
<tbody>
<tr>
<td>flat ( \alpha )-alumina (0001)</td>
<td>0</td>
<td>24.32</td>
<td>0.7, 0.95, 1.55, 3.15, 4.67, 6.25</td>
<td>vdW + electrostatic</td>
<td>400</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>flat amorphous alumina</td>
<td>0</td>
<td>24.32</td>
<td>0.7, 0.95, 1.55, 3.15</td>
<td>vdW + electrostatic</td>
<td>400</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>triangular nanostructured amorphous alumina</td>
<td>3.04, 6.08</td>
<td>24.32</td>
<td>1.25, 2.48, 3.72</td>
<td>vdW + electrostatic</td>
<td>300, 400</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>triangular nanostructured amorphous alumina</td>
<td>6.08</td>
<td>24.32</td>
<td>2.48</td>
<td>vdW</td>
<td>300</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>square nanostructured amorphous alumina</td>
<td>3.04, 6.08</td>
<td>24.32</td>
<td>1.25, 2.48, 3.72</td>
<td>vdW + electrostatic</td>
<td>300, 400</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>flat gold</td>
<td>0</td>
<td>22.84</td>
<td>2.48</td>
<td>vdW</td>
<td>300</td>
<td>( \sigma )</td>
</tr>
<tr>
<td>triangular nanostructured gold</td>
<td>2.85, 3.81, 5.71, 11.42</td>
<td>22.84</td>
<td>2.48</td>
<td>vdW</td>
<td>300</td>
<td>( \sigma )</td>
</tr>
</tbody>
</table>
the classical theory, and the red line represents the prediction with electrostatic interactions accounted for following eq 12. The circles and triangles represent MD results for water thin films on crystalline α-alumina (0001) surface and on amorphous alumina, respectively. As shown in Figure 2, the discrepancy between the scaled vapor pressure of the α-alumina (0001) surface and the amorphous alumina surface is within the error bars, indicating that the crystalline structure does not significantly affect the disjoining pressure. Furthermore, the vapor pressure from MD simulations agrees well with the prediction of eq 12, which verifies the validity of our MD results for a flat surface. Classical theory that neglects electrostatic interactions overestimates the scaled vapor pressure (or underestimates the disjoining pressure) as compared with the MD results and eq 12, demonstrating that the electrostatic interactions enhance the disjoining pressure. The blue and green dashed lines represent the prediction of eq 13 (i.e., simplified eq 12 in the limit of \( \delta_0 \to 0 \)) and eq 14 (i.e., simplified eq 12 in the limit of \( \delta_0 \to \infty \)), respectively. As shown in Figure 2, eq 13 agrees well with eq 12 for \( \delta_0 > 0.5 \) nm, while eq 14 overestimates the electrostatic contribution to the disjoining pressure. For \( \delta_0 > 3 \) nm, eq 14 agrees well with eq 12 indicating that it is safe to use \( \delta_0 \to \infty \) when the water film thickness is larger than 3 nm, while eq 13 greatly overestimates the disjoining pressure. For a water film with thickness between 0.5 and 3 nm, both eqs 13 and 14 overestimate the disjoining pressure.

### 3.2. Meniscus Shape and Disjoining Pressure of Triangular Nanostructures

Figure 3a shows the snapshots of MD calculated meniscus shapes for equilibrated water films of thickness \( \delta_0 = 1.25, 2.48, \) and 3.72 nm on triangular nanostructured amorphous alumina surfaces of depth \( D = 3.04 \) and 6.08 nm at 300 K. As \( \delta_0 \) decreases or increases, the meniscus becomes more conformal to the solid surface. To better quantify the meniscus shape, the scaled wave amplitude, \( A_m/A_{m,max} \), as a function of the scaled healing length \( \zeta/D \) is plotted in Figure 3b for both model predictions (lines) and MD results (symbols) at 300 K. Here, the wave amplitude \( A_m \), i.e., the largest distance between the curved and flat menisci, is defined as \( A_m = L_m(0) - \delta_0 \) = \( \sum_{i=1}^{n} a_{0i} \) and \( A_{m,max} = D/2 \). As shown in Figure 3b, the MD results agree well with the closed-form solutions of eq 9, demonstrating that our model accounting for the electrostatic interactions is adequate to predict the meniscus shape of a thin film on a nanostructured substrate. As the scaled healing length increases, the surface tension force becomes stronger than the solid–liquid intermolecular forces, which leads to a smaller wave amplitude (or a more flat meniscus).

In order to investigate the effect of electrostatic interactions on the meniscus shape, Figure 4a compares the first 20 Fourier coefficients obtained from the model and MD simulations for a water film of thickness \( \delta_0 = 2.48 \) nm on a triangular nanostructure of \( D = 6.08 \) nm with and without electrostatic interactions between alumina and water. The Fourier coefficients are calculated by solving eq 9 numerically in conjunction with the electroneutrality condition, i.e., \( 2k_BT \tan(K\delta_0)/(ze) = -\sigma/(\varepsilon\varepsilon_0) \). It is noted that, for a flat surface, both the film thickness \( \delta^* \) and \( K \) are constant along \( x \). For a nanostructured surface, however, \( \delta^* \) and \( K \) vary along \( x \). Approximating \( \tan(K\delta_0^*)/(ze) = -\sigma/(\varepsilon\varepsilon_0) \), which is used to determine the model-predicted Fourier coefficients shown in Figure 4a. Good agreements are obtained between the closed-form model and MD results for simulations that both include and neglect electrostatic interactions between alumina and water. When the electrostatic interactions are turned off, the leading order coefficient \( a_1 \) of the meniscus wave amplitude decreases by 33%, indicating a more flat meniscus without electrostatic interactions. Figure 4b shows the comparison between the model predicted and MD simulated meniscus shapes of a water film on a triangular nanostructure with and without electrostatic interactions, where the average relative discrepancy is 4% for the case without electrostatic interactions and 3% for with electrostatics. Consistent with the effect of electrostatic interactions on a flat surface, the electrostatic interactions also enhance the disjoining pressure...
of a nanostructured surface, which in turn makes the meniscus shape more conformal as shown in Figure 4b.

The scaled vapor pressure, $P_v/P_{sat}$, as a function of the water film thickness, $\delta_0$, for triangular nanostructures of depth $D = 0, 3.04, 6.08$ nm at 400 K is plotted in Figure 5. The MD results (symbols) are presented against closed-form solution, eq 11 (line). It can be seen from Figure 5 that, for triangular nanostructured surfaces, the MD results agree well with the closed-form model. The vapor pressure decreases with the nanostructure depth, indicating that the disjoining pressure enhances with $D$. As the film thickness increases, the scaled vapor pressure $P_v/P_{sat}$ is close to 1.0 for all nanostructures investigated. The change in vapor pressure due to nanostructures becomes smaller (or disjoining pressure attenuates) as the thickness of the liquid film increases.

### 3.3. Meniscus Shape and Disjoining Pressure of Square Nanostructure

Figure 6a shows the snapshots of MD-calculated meniscus shapes for equilibrated water films of thickness $\delta_0 = 1.25, 2.48,$ and $3.72$ nm on square alumina nanostructures of depth $D = 3.04$ and $6.08$ nm at 300 K. For both nanostructure depths, as $\delta_0$ decreases, the meniscus shape changes from flat to conformal to the solid surface. Moreover, as $D$ increases, the meniscus also becomes more conformal. As a result, for the case of $\delta_0 = 1.25$ nm and $D = 6.08$ nm, the strong disjoining pressure finally causes the meniscus to break up. Figure 6b shows the scaled wave amplitude as a function of the scaled healing length on square nanostructures. Error bars are calculated using three separate NVT simulations with different velocity seeds used to initialize the temperature.
increasing $D$ leads to smaller scaled wave amplitudes for all film thicknesses.

Figure 7a shows the comparison of the first 20 Fourier coefficients for a water film of thickness $\delta_0 = 1.25$ nm on a square nanostructure of $D = 3.04$ nm. Good agreement is reached between the model and MD results, indicating that the model is capable of accurately predicting the meniscus shapes on nanostructures with sudden profile changes. Figure 7b shows the corresponding meniscus shapes, where the averaged relative discrepancy is 4% between from MD results and model predictions.

Figure 8 shows the scaled vapor pressure as a function of the film thickness for water films on flat and square nanostructures of depths $D = 3.04$ and $6.08$ nm. The black line represents the classic theory, the blue and red lines are for the closed-form model of eq 11, and the symbols are MD results that show good agreement with the models. Similar to the cases of triangular nanostructures, the effect of disjoining pressure enhances with increasing nanostructure depth $D$ for the square nanostructures, but weakens with increasing liquid film thickness. Note that, due to numerical instability while calculating the Fourier coefficients, the model predictions stop at $\delta_0 = 0.9$ and 1.9 nm for $D = 3.04$ and $6.08$ nm, respectively. In reality, there may exist a critical film thickness, for a given nanostructured surface, below which the meniscus breaks up. Although our present model, which assumes a continuous meniscus, cannot capture such breakup events, it provides an upper bound of the critical film thickness. In other words, liquid film with thickness above 0.9 nm will be stable on a square nanostructure of depth $D = 3.04$ nm.

3.4. The Effect of Nanostructures on the Strength of Electrostatic Interactions. Figure 9 shows the MD calculated interaction energy per actual solid–liquid interfacial area as a function of the aspect ratio of the nanostructures for water thin films on triangular nanostructured gold and amorphous alumina surfaces. Error bars are calculated using three different random velocity seeds for temperature initialization.

Figure 9. Interaction energy per actual solid–liquid interfacial area as a function of the aspect ratio of the nanostructures for water thin films on triangular nanostructured gold and amorphous alumina surfaces. Error bars are calculated using three different random velocity seeds for temperature initialization.

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Figure 9. Interaction energy per actual solid–liquid interfacial area as a function of the aspect ratio of the nanostructures for water thin films on triangular nanostructured gold and amorphous alumina surfaces. Error bars are calculated using three different random velocity seeds for temperature initialization.
the van der Waals interactions between the side walls of the nanostructures can be negligible because their distance is much larger than local film thickness and van der Waals forces are weak for such a long distance.20 However, the electrostatic interactions are longer range forces whose contribution between side walls may not be negligible. Since both side walls of the nanostructured alumina surfaces carry the same charges, their interactions are repulsive. As the nanostructure aspect ratio increases, the repulsive forces between the side walls increase, leading to a decrease in electrostatic strength. It is noted that the interaction energy per actual surface area decreases by less than 10% when the nanostructure aspect ratio increases from 0 to 1.0. Due to this week effect of nanostructures on electrostatic strength, the model developed in Section 2.1 for constant electrostatic interaction strength still gives good predictions of meniscus shape and disjoining pressure as compared to the MD results.

4. CONCLUSION

In this paper, a closed-form model is derived to accurately predict the meniscus shape and disjoining pressure of a thin liquid film on a nanostructured surface accounting for both van der Waals and electrostatic interactions between a solid and a thin liquid film. Molecular dynamics simulations of water thin films on triangular and square amorphous alumina nanostructures are performed to verify the model. Good agreements are obtained between MD results and model predictions for thin films of varying thickness on nanostructured surfaces of varying depth. The results show that electrostatic interactions enhance the disjoining pressure and make the meniscus more conformal to the nanostructured surface. The electrostatic contribution to the disjoining pressure increases with nanostructure depth and decreases with film thickness. For a given nanostructure, the wave amplitude of the meniscus increases with decreasing thin film thickness. Furthermore, the strength of electrostatic interactions for thin liquid films on nanostructured surfaces decreases with increasing nanostructure aspect ratio.

The model developed here will enable more accurate prediction of heat fluxes in thin film evaporation utilizing a variety of nanostructured surfaces and better nanostructure designs for enhanced thin film stability. Future work will focus on a better understanding of the evaporating thin film region that is away from equilibrium.

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Notes
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