Effect of Nanostructures on the Meniscus Shape and Disjoining Pressure of Ultrathin Liquid Film

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Supporting Information

ABSTRACT: The stability of thin liquid films on nanostructured surfaces is important but poorly understood. Here, we develop a general model of the meniscus shape and disjoining pressure for thin liquid films on nanostructured surfaces based on the minimization of the free energy and the Derjaguin approximation. This model is then compared with molecular dynamics simulations for a water–gold system with triangular and square nanostructures of varying depth and film thickness, demonstrating the robustness of the analytical model.

KEYWORDS: Disjoining pressure, meniscus shape, surface tension, molecular dynamics

Thin liquid films on solid surfaces are ubiquitous in nature, e.g., as lubricant on the cornea of our eyes, as a premelting layer giving rise to frost heave, between emulsion droplets and bubbles in emulsions and foams, among many others. The stability of these thin liquid films is critically important in lubrication, wetting and spreading, condensation, evaporation, and boiling, as well as solidification and melting, since the break up of the thin films due to instabilities can result in 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. Thus, it is of critical importance to understand the properties of thin liquid films and control or engineer their stability.

In recent years, nanostructures have been introduced as a means to control the stability of these thin films. For example, superhydrophilic nanostructured surfaces are used to enhance the continuous delivery of liquid to the thin film region to achieve high heat fluxes in thin film evaporation for cooling high power electronics and lasers. Lyophobic nanostructured surfaces have also been used to control local intermolecular interactions for patterning liquid films in flexible electronics and microfluidic devices. Despite their proven success, current configurations of nanostructured surfaces designed for thin film stability enhancement rely highly on empirical experiments that are costly and time-consuming. There is still a fundamental lack of understanding regarding the stability of thin liquid films, which depends strongly on the disjoining pressure, and its relationship to the nanostructured surface upon which it resides.

The disjoining pressure, i.e., the excess pressure required to evaporate liquid molecules due to the presence of solid–liquid intermolecular forces, determines the stability of the thin film. Classic theory predicts the disjoining pressure, $\Pi$, as a function of the film thickness given by

$$\Pi_{\text{flat}} = \frac{A}{6\pi\delta_0^3}$$

where $A$ is the Hamaker constant and $\delta_0$ is the liquid film thickness. Equation 1 is based on the assumption of atomically smooth surfaces and is inadequate in describing the effect of small-scale topology on the disjoining pressure. Thus, several attempts have been made to examine the effect of nanostructures on disjoining pressure. Ojha et al. accounted for such effect by experimentally correlating an equivalent Hamaker constant with surface roughness. Robbins et al. developed a generalized model of the disjoining pressure and meniscus profile for an arbitrary, nanostructured surface with prior knowledge of the vapor pressure near the thin film. However, such vapor pressure is difficult to measure in practice. Alternatively, molecular dynamics (MD) simulations have proven to be a powerful tool in investigating the role of nanoscale effects on the disjoining pressure. However, atomistic model results can be limited by the specific potentials used and geometries studied, resulting in a need for a general model that can describe the meniscus shape and disjoining pressure of a thin film on a nanostructured surface.

In this letter, we develop a general, closed-form model of the disjoining pressure and meniscus shape for a thin film on nanostructured surfaces based on the minimization of system free energy and the Derjaguin approximation, i.e., approximating the local disjoining pressure of a curved surface by a planar meniscus of the same local film thickness. The scaled healing length $\xi/D$ ($D$ the nanostructure depth) is introduced to represent the competition between the liquid surface tension and...
and the solid–liquid intermolecular force, both important in small scales. 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 a gold surface based on well-calibrated potentials. The effects of film thickness, nanostructure depth, and temperature on meniscus shape and disjoining pressure are examined. The results presented here will be used to guide nanostructured surface designs for improved thin film property in lieu of trial and error experiments.

The schematics of a thin liquid film of thickness $\delta_0$ on 2D periodic nanostructured surfaces of wavelength $L$ and triangular and square shapes are shown in Figure 1a,b, respectively. The disjoining pressure on a curved surface, $\Pi = \gamma \frac{\partial \sigma}{\partial h}$, where $\gamma$ is the interfacial tension, $\sigma$ the surface energy, and $h$ the height of the liquid film.

Figure 1. (a,b) Schematic of a thin liquid film on (a) a triangular nanostructure and (b) a square nanostructure. (c–e) Molecular dynamics simulation setups for water films on (c) a flat gold surface, (d) a triangular gold nanostructure, and (e) a square gold nanostructure.

and square shapes are shown in Figure 1a,b, respectively. The basic assumptions of the model are

i) the van der Waals interactions are the dominating intermolecular interactions between the liquid film and the nanostructured surface;

ii) the vapor near the thin film is assumed to behave as ideal gas;

iii) the meniscus shape, $\zeta(x)$, is periodic with the same wavelength $L$ as that of the substrate surface $\zeta_0$.

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

$$P_C + \Pi_{rough} = -\rho k_B T \ln \left( \frac{P}{P_{sat}} \right)$$

(2)

where $P_C$ is the capillary pressure of the liquid film, $\Pi_{rough}$ the disjoining pressure on a curved surface, $\rho$ the liquid density, $k_B$ the Boltzmann constant, and $P_{sat}$ the saturation pressure at temperature $T$.

Two mechanisms within a liquid film determine the shape of the meniscus profile. The capillary pressure, resulting from the surface tension force, tends to keep the meniscus flat, while the disjoining pressure makes the film conformal to the substrate. At equilibrium, the meniscus shape is a result of the competition between the capillary pressure and disjoining pressure, characterized by a healing length $\xi = \delta_0^2/(A/2\pi)$. Here, we scale the healing length with the nanostructure depth $D$, following

$$\xi = \frac{\delta_0^2}{D} \frac{\delta_0}{\sqrt{A/2\pi D}}$$

(3)

where $(\xi/D)^2 = (\gamma/D)/(d\Pi_{sat}/d\delta_0)$ represents the ratio of surface tension over disjoining pressure. As $\xi/D \to 0$, the solid–liquid intermolecular interactions dominate, and when $\xi/D \to \infty$, the surface tension dominates.

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

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

(4)

where $a_0 = 2\delta_0$. Traditionally, the film thickness $\delta(x)$ is defined as the vertical thickness of the film, and the mean film thickness is $\delta_0$. For systems where the substrates are structured, a modified film thickness $\delta(x)$ is introduced to denote the shortest distance between the meniscus profile and solid surface following $\delta(x) = \delta(x)/r$, where $r = (1/L)\int_{-L/2}^{L/2}(1 + (\zeta_L(x))^2)\,dx$ is the Wenzel roughness ratio between the actual and flat surface areas. This gives rise to a mean modified film thickness $\delta_0 = (1/L)\int_{-L/2}^{L/2}\delta(x)\,dx = \delta_0/r$.

The total free energy of the system consists of two contributions, namely, the surface excess energy, $W_s = \gamma \int_{-L/2}^{L/2} (1 + \zeta_L(x))^2)\,dx$, and the van der Waals interaction energy, $W_{vdW} = (A/12\pi)\int_{-L/2}^{L/2}(1/\delta^4)\,dx$. Minimizing the total energy of the system by setting $dW_{total} = (dW_{total}/d\zeta_L)\,d\zeta_L = 0$, it yields

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

$$- \frac{A\delta_0^2}{\delta_0} \int_{-L/2}^{L/2} \cos \left( \frac{2\pi n x}{L} \right) \,dx$$

$$= \frac{A\delta_0^2}{\delta_0} \left[ \sum_{n=1}^{\infty} a_n \frac{2\pi n x}{L} \cos \left( \frac{2\pi n x}{L} \right) \right]$$

$$= \frac{A\delta_0^2}{\delta_0} \left[ \sum_{n=1}^{\infty} a_n \frac{2\pi n x}{L} \cos \left( \frac{2\pi n x}{L} \right) \right]$$

(5)

This closed-form relation 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 $\zeta_L(x)$.

In the limit of $|\zeta_L(x)| << 1$ and $|\delta(x) - \delta_0| >> \delta_0$, which corresponds to small wave amplitudes and nanostructured depths, eq 5 reduces to the following relation between $a_n$ and the scaled healing length $\xi/D$.

$$a_n = \frac{\pi}{L} \int_{-L/2}^{L/2} \cos \left( \frac{2\pi n x}{L} \right) \zeta_L(x) \,dx$$

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

(6)

The detailed derivation of eqs 5 and 6 are shown in the Supporting Information.

Applying the Derjaguin approximation, where the local disjoining pressure is approximated by the disjoining pressure of a flat substrate, $\Pi_{sat}$, with the local film thickness $\delta(x)$, it
follows \( \Pi_{\text{rough}}^{p(x)} \cong \Pi_{\text{flat}}^{p(x)} = A / \left[ 6 \pi \delta^2 (x)^3 \right] \). Averaging \( \Pi_{\text{rough}}^{p(x)} \) along \( x \) gives the following mean disjoining pressure on a nanostructured surface

\[
\Pi_{\text{rough}} = \frac{A}{6 \pi L} \int_{-L/2}^{L/2} \sum_{n=1}^{\infty} a_n \cos \left( \frac{2\pi n}{L} x \right) + \delta_0 - \zeta_0(x) \right]^{-3} r \, dx
\]

(7)

Averaging both sides of eq 2 along \( x \) and substituting eq 7, it yields

\[
\frac{P_c}{P_{\text{sat}}} = \exp \left[ -\frac{A}{6 \pi L \rho k_b T} \int_{-L/2}^{L/2} \left( \sum_{n=1}^{\infty} \frac{a_n^2 + \frac{1}{L} \int_{-L/2}^{L/2} a_n \cos \left( \frac{2\pi n}{L} x \right) \zeta_0(x) \, dx \right) \right]
\]

(8)

where the capillary pressure, \( P_c \), is canceled out due to symmetry. Equation 8 gives a closed-form relation for the vapor pressure of a thin film of thickness \( \delta_0 \) on a nanostructured surface with profile \( \zeta_0(x) \) using Fourier coefficients \( a_n \) calculated from eq 5. In the limit of \( b(x) - \delta_0 \ll \delta_0 \), eq 8 reduces to

\[
\frac{P_c}{P_{\text{sat}}} = \exp \left[ -\frac{A}{6 \pi L k_b T} \int_{-L/2}^{L/2} \zeta_0(x)^3 \right]
\]

(9)

Now consider a nanostructured surface with depth \( D \) and triangular profile \( \zeta_0(x) = -(D/2) x \mid x \in [-L/2, L/2] \) as shown in Figure 1a. For this specific nanostructure, as \( \xi / D \to 0 \), eq 6 predicts \( l_{t_1} \) to be about 9 and 25 times as large as \( l_{a_1} \) and \( l_{a_0} \), respectively, and hence, the meniscus shape can be approximated using \( \zeta_0(x) = a_1 \cos \left( \pi L x \right) + \delta_0 \). Note that for a thin film with a flat meniscus, \( l_{a_1} = 0 \), while \( l_{a_0} \) is maximized for a perfectly conformal film. Substituting \( r = 1 / \cos \theta \) (\( \theta \) the angle of the nanostructure) into eq 5 and considering only the first order cosine wave, the mean disjoining pressure for a thin liquid film on a triangular nanostructure can be approximated as

\[
\frac{P_c}{P_{\text{sat}}} = \exp \left[-\frac{A}{6 \pi L k_b T} \cos^3 \theta \int_{-L/2}^{L/2} a_1 \cos \left( \frac{2\pi n}{L} x \right) + \delta_0 - \zeta_0(x) \right]^{-3} \, dx
\]

(12)

In the limit of \( b(x) - \delta_0 \ll \delta_0 \), eq 12 can be further reduced to

\[
\frac{P_c}{P_{\text{sat}}} = \exp \left[-\frac{A}{6 \pi L k_b T} \cos^3 \theta \int_{-L/2}^{L/2} a_1 \cos \left( \frac{2\pi n}{L} x \right) + \delta_0 - \zeta_0(x) \right]^{-3} \, dx
\]

(13)

In order to test the robustness of the model, a thin film on a square nanostructure of profile \( \zeta_0(x) = -(D/2) x \mid x \in [-L/2, L/2] \) is considered at \( L/2 \) with \( (D/2) \), \( (L/4) \), or \( L \) is the distance of the gold substrate. The TIP4P-Ew water model was used for water interactions were validated against recent studies.31 In our previous work,25,30 All simulations were performed using LAMMPS31 in an NVT (N the number of atoms, V the volume, and T the temperature) ensemble. The wavelength of the nanostructure, \( L \), is fixed at 22.84 nm. The depth of the nanostructure, \( D \), is varied from 2.85, 3.81, and 5.71 nm to 11.42 nm, so that the aspect ratios of the nanostructures (2D/L) are 1:4, 1:3, 1:2, and 1:1, respectively. Thin water films with different thicknesses (i.e., 1.25, 2.48, and 4.73 nm at 300 K) were simulated on these nanostructured surfaces. The TIP4P-Ew water model gives the surface tension of water \( \gamma \) to be 65.2 mJ/m² at 300 K and 46.5 mJ/m² at 400 K.32 The Hamaker
constant is calculated based on the Lennard-Jones potential for water–gold interactions from $\lambda = 4\varepsilon \rho_l \rho_f \sigma_{A_u/O}^6 \varepsilon_{A_u/O}^{25}$ where $\rho_l$ and $\rho_f$ are the densities of water and gold, respectively.

The simulation system was first equilibrated in an NVT ensemble at 300 K for 1 ns (or until the meniscus shape no longer changes with time) to investigate the effect of nanostructures on meniscus shape at room temperature. The meniscus shape $\zeta(x)$ was analyzed using a grid method, where the simulation domain is divided into grids of 0.3 Å in size, and the density of each grid is calculated to generate a density profile in the $x$–$z$ plane. The density profile exhibits a liquid–vapor interfacial region where the local density gradually reduces from the liquid density $\rho_l$ to the vapor density $\rho_f$. Following Carey and Wemhofer, the interface location is at the grids with the local density equal to $(\rho_l + \rho_f)/2$, and the grids are connected to form the meniscus profile $\zeta(x)$ based on averaging over 400 ps in equilibrium. The simulation system was also equilibrated in an NVT ensemble at 400 K for 1 ns to investigate the effect of nanostructures on meniscus shape and disjoining pressure where evaporation and condensation occur.

The local pressure tensor is calculated with contributions of kinetic motion of molecules and contributions of the intermolecular forces. The vapor pressure $P_v$ is calculated by summing up the local pressure tensor in the vapor region and averaged from 200 ps to 1 ns.

Figure 2a shows the snapshots of MD-calculated meniscus shapes for equilibrated water films of thickness $\delta_0 = 1.25, 2.48$, and 4.75 nm on triangular nanostructured gold surfaces of depth $D = 2.85, 3.81, 5.71$, and 11.42 nm at 300 K. As $\delta_0$ decreases or $D$ increases, the meniscus becomes more conformal with the solid surface. To better quantify the meniscus shape, the scaled amplitude, $l(a_l)/\alpha_{l,\text{max}}$, as a function of the scaled healing length $\xi/D$, is plotted in Figure 2b for both model predictions (lines) and MD results (symbols) at 300 and 400 K. The solid lines are obtained based on the closed-form solutions using eq 10, and the dashed lines are for the simplified expression, eq 11, in the limit of $l(a_l) \ll L$ and $\delta_0(x) - \delta_j \ll \delta_0$. As shown in Figure 2b, the MD results agree well with the closed-form solutions, demonstrating that our model, eq 10, is adequate to predict the meniscus shape of a thin film on a nanostructured substrate when the van der Waals interactions are the dominating solid–liquid intermolecular interactions. As the scaled healing length increases, the surface tension force becomes stronger than the solid–liquid intermolecular force, which leads to a smaller wave amplitude (or a more flat meniscus). The deviation between the closed-form (solid line) and simplified (dashed line) models is insignificant for a small nanostructure depth (e.g., $D = 2.85, 3.81$, and 5.71 nm), but becomes obvious for a large nanostructure depth (e.g., $D = 11.42$ nm) when the assumption of $\delta(x) - \delta_j \ll \delta_0$ breaks down. Note that $\delta(x) - \delta_j \ll \delta_0$ varies with $x$ and ranges between 0 and $D/2\delta_0$. Thus, as $D$ increases, $\delta(x) - \delta_j \ll \delta_0$ increases, and at $D = 11.42$ nm, $\delta(x) - \delta_j/\delta_0 \approx 0.8$, deviating from $\delta(x) - \delta_j \ll \delta_0$. For convenience, we use the upper bound $D/2\delta_0 \ll 1$ instead of $\delta(x) - \delta_j \ll \delta_0$ for the validity criterion of the simplified model.

As shown in Figure 2b, the resulting differences in meniscus shape at 300 K (open symbols) and 400 K (filled symbols) are within computational errors. As temperature increases, the liquid density decreases, which leads to an increase in $\delta_0$ (roughly following $\delta_0 \propto \rho_l^{-1}$) and further weakens the disjoining pressure. However, the surface tension $\gamma$ decreases with temperature, resulting in a decreasing capillary pressure. For example, for a water thin film, when $\delta_0$ changes from 1.25, 2.48, and 4.75 nm at 300 K to 1.31, 2.61, and 5.11 nm at 400 K, respectively, the surface tension of water is reduced from 65.2 to 47.5 mJ/m² at 300 K to 400 K. On the basis of eq 3, the scaled healing length $\xi/D$ scales with $\delta_0/\sqrt{\gamma}$ and decreases only by $\sim 4\%$ as temperature increases from 300 to 400 K.

In order to justify the simplification of the meniscus shape to a cosine wave for the triangular nanostructured surface, Figure 3a shows 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 $D = 5.71$ nm. Figure 3a shows good agreements between the closed-form model and MD results, whereas discrepancies exist between the simplified model and MD results. The leading order coefficient $a_1$ from both the closed-form model and MD simulations is about 10 times that of $a_2$ and much larger than other higher order coefficients, so it is appropriate to simplify the meniscus to a cosine wave function. To more directly compare the model and MD simulations, Figure 3b shows the comparison between the model-predicted and MD simulated meniscus shapes. The average relative discrepancy is $3\%$ between the closed-form model and MD results, and $7\%$ between the simplified model and MD. For $\delta_0 = 2.48$ nm and $D = 5.71$ nm, $D/2\delta_0 \lesssim 1$, the validity of the simplified model starts to fail, which explains large discrepancies between the simplified model and MD results for both the Fourier coefficients and the resulted meniscus shape.
The scaled vapor pressure, $P_s/P_{sat}$ as a function of the water film thickness, $\delta_0$, for different nanostructure depths, $D$, at 400 K is plotted in Figure 4. The MD results (symbols) are presented against both closed-form solution, eq 12 (solid line), and the simplified expression, eq 13 (dashed line). As shown in previous MD work,25,34 for thin films on flat surfaces, the MD-calculated vapor pressure of thin water films agrees well with the classic disjoining pressure theory. It can be seen from Figure 4, for nanostructured surfaces, the MD results agree well with both the closed-form and simplified models. The vapor pressure decreases with the nanostructure depth, indicating that the disjoining pressure is enhanced with increasing nanostructure depth. The deviation between the closed-form and simplified models is small for $D = 2.85$, 3.81, and 5.71 nm and becomes relatively large for $D = 11.42$ nm but still within the error bar of the MD results. Therefore, for the conditions considered, the simplified model is adequate to predict the disjoining pressure of thin liquid films on a nanostructured substrate. Note that, statistical fluctuations of the MD results may lead to calculation errors, as in the case of $\delta_0 = 5.11$ nm. As the film thickness increases, the scaled vapor pressure $P_s/P_{sat}$ 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. For example, for cases of $\delta_0 = 1.31$ and 5.11 nm, the differences in $P_s/P_{sat}$ between flat and nanostructured substrate of $D = 11.42$ nm are 0.178 and 0.019, respectively.

Figure 5a shows the snapshots of MD-calculated meniscus shapes for equilibrated water films of thickness $\delta_0 = 1.25, 2.48, 3.72$, and 4.75 nm on square gold nanostructures of depth $D = 2.85$ and 5.71 nm at 300 K. For both nanostructure depths, as $\delta_0$ decreases, the meniscus shape changes from flat, to \textquotedblleft funnellike\textquotedblright, and finally becomes more and more conformal to the square nanostructures. Moreover, as $D$ increases, the meniscus also becomes more conformal to the solid surface. As a result, for the case of $\delta_0 = 1.25$ nm and $D = 5.71$ nm, the strong disjoining pressure finally causes the meniscus to break up. Figure 5b,c shows the comparison of model predicted (back lines) and MD-calculated (blue, red, green, and pink lines) meniscus shapes for water film of different thicknesses on square nanostructures with depth $D = 2.85$ and 5.71 nm, respectively. Good agreements are reached between model predictions and MD results for all cases.

To quantitatively compare the MD results with model predictions, the Fourier coefficients of the meniscus shape obtained from the model are compared with those from MD simulations for water thin films on square gold nanostructures. Figure 6a shows the comparison for the first 20 Fourier coefficients of water film of thickness $\delta_0 = 1.25$ nm on a square nanostructure of $D = 2.85$ 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. Unlike the triangular nanostructured surface, the Fourier coefficients for $n > 1$ are not trivial such that the meniscus shape on the square nanostructure cannot be simplified as a cosine wave. Nevertheless, as shown in Figure 6a, the leading order coefficient $a_1$ is still at least three times larger than other Fourier coefficients, and hence, $a_1$ plays an important role in determining the wave amplitude of the meniscus. Here, the wave amplitude $A_m$, i.e., the largest distance between the curved and flat menisci, is given as $A_m = \zeta_n(0) = \sum_{m}a_m$. Figure 6b shows the scaled wave amplitude as a function of scaled healing length for a meniscus on square nanostructures, where lines represent the model prediction and symbols represent MD results at 300 K. Good agreement is achieved between the model and MD results. For each nanostructure depth $D$, the scaled wave amplitude, $2A_m/D$ (or $A_m/L_{m,\text{max}}$), increases monotonically with decreasing scaled
healing length, $\xi/D$. This is because a thinner liquid film thickness (or a smaller scaled healing length) results in a stronger disjoining pressure and therefore a more conformal film of a larger wave amplitude. When $\xi/D \to 0$, the scaled wave amplitude converges to $2A_{\text{max}}/D = 1.0$, corresponding to a conformal film whose wave amplitude equals $D/2$. In addition, for the same $\xi/D$, increasing $D$ leads to smaller scaled wave amplitudes for all film thicknesses. Note that, because of the numerical instability while calculating the Fourier coefficients, the model predictions stop at $\xi/D = 0.2830$ (corresponding to $\delta_0 = 1.1$ nm) for $D = 2.85$ nm and $\xi/D = 0.4222$ (corresponding to $\delta_0 = 1.9$ nm) for $D = 5.71$ nm. It is noted that the interactions between the side walls may play a role in determining the meniscus shape if the sidewall spacing is comparable or smaller than the local film thickness. In the present work, the sidewall spacing is $L/2 = 11.42$ nm, much larger than the local thin film thickness, so that its effect is negligible.

Figure 5. (a) Meniscus shape of water films of varying thickness on square gold nanostructures with different depths at 300 K. (b,c) Comparison of MD simulation and model prediction for meniscus shape on square nanostructures with (b) depth of 2.85 nm and (c) depth of 5.71 nm. The blue, red, green, and pink lines represent the menisci of MD simulations for film thickness of 1.25, 2.48, 3.72, and 4.75 nm, respectively. The black solid line represents the solid surface, and the black dashed lines are based on the closed-form model.

Figure 6. (a) Comparison of MD simulation and model prediction for the first 20 Fourier coefficients of the meniscus shape for water film of thickness $\delta_0 = 1.25$ nm on a square nanostructure of depth $D = 2.85$ nm. (b) Comparison of MD simulation and model prediction for scaled wave amplitude as a function of the scaled healing length on square nanostructures of depth $D = 2.85$ and 5.71 nm.
thickness above 1.1 nm will be stable on a square nanostructure of depth $D = 2.85$ nm.

In this letter, a novel closed-form model is derived to accurately predict the meniscus shape and disjoining pressure of a thin liquid film on a general, nanostructured surface based on minimizing the system free energy and the Derjaguin approximation. Molecular dynamics simulations of water thin films on two representative surfaces, i.e., triangular and square gold nanostructures, are performed to verify the model. Good agreements are obtained between MD results and model predictions for thin films of varying thickness above 1.1 nm will be stable on a square nanostructure.

The model predictions for scaled vapor pressure for square nanostructures, are performed to verify the model. Good agreements are obtained between MD results and model predictions for thin films of varying thickness above 1.1 nm will be stable on a square nanostructure.

The authors declare no competing financial interest.

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**REFERENCES**

(24) Please see the Supporting Information.

**ASSOCIATED CONTENT**

- **Supporting Information**
  Derivation details of the closed-form model for meniscus shape of a thin film on a nanostructured surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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