The impact of small-scale geometric roughness on wetting behavior

Supporting information

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Substrate Geometry

We work with substrates consisting of regular rectangular-shaped grooves. A schematic of a typical substrate is provided in Figure S1. The features are characterized by their height \( a \), period \( \lambda \), and length scale \( \lambda_s \), which defines the extent to which the solid portion of a feature extends in the lateral direction. The solid fraction \( f_s \) and roughness factor \( r \) are defined in terms of these geometric parameters as denoted in Figure S1.

\[
\begin{align*}
    f_s &= \frac{\lambda_s}{\lambda} \\
    r &= 1 + \frac{2a}{\lambda}
\end{align*}
\]

Figure S1. Illustration of a substrate with rectangular-shaped grooves.
**Substrates**

Within the “cut” model, the substrate is defined by an atomistically-detailed surface only. For the “Ewald” model, the substrate consists of both an atomistically-detailed surface and a structureless half-wall that accounts for long-ranged interactions between fluid particles and the substrate. Figure S2 provides a schematic of the substrate setup.

**Cut Model**

[Diagram of Cut Model]

**Ewald Model**

[Diagram of Ewald Model]

**Figure S2.** Schematic of the substrates used with the cut and Ewald models.

Atomistically-detailed surfaces are extracted from a face-centered cubic (fcc) lattice with a density of $\rho = 0.5786\sigma_{ff}^{-3}$ (the fcc unit cell has an edge length of $1.905\sigma_{ff}$) and the (100) plane exposed to the fluid. Our calculations with the cut model are completed with substrates carved from lattices spanning 30 $\times$ 6 or 32 $\times$ 6 unit cells, while those with the Ewald model are completed with substrates spanning 16 $\times$ 6 or 15 $\times$ 6 unit cells. In all cases, the minimum height of the lattice ($a = 0$ case) is 3 unit cells. We work with rectangular groove geometries that are characterized by periods $\lambda$ that span from 3.8 to 30.4$\sigma_{ff}$ (2 to 16 unit cells).
**Intermolecular Interactions**

The energy of interaction $u_{ij}^{LJ}$ between any two particles separated by a distance $x$ is given by,

$$u_{ij}^{LJ}(x) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{x} \right)^{12} - \left( \frac{\sigma_{ij}}{x} \right)^6 \right]$$

(1)

where $\epsilon_{ij}$ and $\sigma_{ij}$ are energy and size parameters, respectively. The fluid-fluid (ff) and surface-fluid (sf) size parameters are related as $\sigma_{sf}/\sigma_{ff} = 1.10$. As noted in the main document, we work with two model systems, which are differentiated by the manner in which the long-range interparticle interactions are handled. For the cut model, we use a truncated and shifted potential

$$u_{ij}(r) = \begin{cases} 
    u_{ij}^{LJ}(r) - u_{ij}^{LJ}(r^c_{ij}) & r < r^c_{ij} \\
    0 & r > r^c_{ij}
\end{cases}$$

(2)

with cutoff distances of $r^c_{ff} = 2.5\sigma_{ff}$ and $r^c_{sf} = 5.5\sigma_{ff}$ to describe the interactions. For the Ewald model, we use an Ewald summation [J. Phys. Chem. 1989, 93, 7320] to account for the long-ranged fluid-fluid and surface-fluid dispersion interactions. We use an Ewald precision of $5.0 \times 10^{-5}$ and a real-space cutoff of $5.5\sigma_{ff}$. The interaction between fluid particles and the structureless half wall separated by a vertical distance $z$ is given by the Lennard-Jones 9-3 potential,

$$u_{wf}(z) = \frac{2\pi}{3} \rho_w \sigma_{wf}^3 \epsilon_{wf} \left[ \left( \frac{2}{15} \right) \left( \frac{\sigma_{wf}}{z} \right)^9 - \left( \frac{\sigma_{wf}}{z} \right)^3 \right]$$

(3)

with $\sigma_{wf}/\sigma_{ff} = 1.10$, $\rho_w = 0.5786\sigma_{ff}^{-3}$, and variable $\epsilon_{wf} = \epsilon_{sf}$.

**Simulation Details**

Simulations are conducted in a standard grand canonical ensemble where the volume $V = AH$, activity $\xi$, and temperature $T$ are held constant and the particle number $N$ (density) and energy $E$ fluctuate. Grand canonical simulations are completed with a rectangular parallelepiped box with periodic boundary conditions applied in the $x$ and $y$ directions. The system is closed at both ends of the nonperiodic $z$ direction by the substrate of interest and a control wall. We refer the reader to [J. Chem. Phys. 2011, 135, 234102] for details regarding the control wall. The cross-sectional area $A$ of the simulation box is established by the substrate (see above) and the height varies between $H = 40\sigma_{ff}$ and $45\sigma_{ff}$. Calculations with the cut model are completed at a temperature of $T = 0.70\epsilon_{ff}/k_B$, while those for the Ewald model are performed at $T = 0.85\epsilon_{ff}/k_B$. The simulations are completed with the bulk liquid-vapor saturated activity $\xi_b$ at these conditions. Specifically, we use $\ln(\xi_b/\sigma_{ff}^3) = -5.0214$ for the cut model and $\ln(\xi_b/\sigma_{ff}^3) = -4.7800$ for the Ewald model.

When working with the Ewald model we use an algorithm that assumes the system is periodic in each of the three spatial dimensions. To generate a pseudo two-dimensional system, we extend...
the distance in the non-periodic $z$ direction by an additional $30\sigma_{ff}$ and $60\sigma_{ff}$ of vacuum space for spreading and drying calculations, respectively.

Statistical uncertainties were determined by performing four independent sets of simulations. The standard deviation of the results from the four simulation sets was taken as an estimate of the statistical uncertainty.

**Substrate Images**

The figures below contain snapshots of select substrate configurations used in this work.

**Fixed Shape: $r = 3.0$, $f_s = 0.5$**

\begin{align*}
\lambda &= 3.8 \\
\lambda &= 7.6 \\
\lambda &= 30.4
\end{align*}

**Figure S3.** Substrates with a fixed shape and variable periodicity.
Figure S4. Substrates with a relatively small fixed periodicity of $\lambda = 3.8 \sigma_{ff}$ and variable roughness factor.
Figure S5. Substrates with a relatively large fixed periodicity of $\lambda = 15.2 \sigma_{ff}$ and variable roughness factor.