Supplementary Material

1 Interaction potentials

The net external potential generated by the solid (substrate and pillars) and external perturbative force f_τ has the form

$$U_{net}(x,h) = U_{1s}(x,h) + U_{2s}(x,h) + U_e(x) \tag{S. 1}$$

where $U_{is}(x,h)$ $(i = 1, 2)$ are the potentials due to the ~~test~~ fluid-solid, ~~lubricating~~ fluid-solid interactions, respectively, and $U_e(x) = f_\tau x$ is the potential due to external perturbative force. The zero of the latter potential is selected as the origin.

Due to the ordered geometrical location of the pillars and uniformity of the substrate, the potential is periodic in the x-direction with period L_x (see Fig. 2 in the main text). It can be obtained by integrating the corresponding Lennard-Jones potential (eq 1 in the main text) over the entire volume of the solid and can be written as

$$U_{is}(\mathbf{r}) = \int_{V_s} \rho_s(\mathbf{r}')\phi_{is}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' + \int_{V_p} \rho_s(\mathbf{r}')\phi_{is}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' \tag{S. 2}$$

where V_s is the volume occupied by the substrate, V_p is the volume occupied by the pillars, $\rho_s(\mathbf{r}')$ is the density of the solid. For a uniform solid, $\rho_s(\mathbf{r}') \equiv \rho_s$, and the first integral in eq S. 2 can be calculated analytically

$$\int_{V_s} \rho_s(\mathbf{r}')\phi_{is}(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}' = \frac{2\pi}{3}\epsilon_{is}\rho_s\sigma_{is}^3\Psi(\sigma_{is}, h_p + h)\ . \tag{S. 3}$$

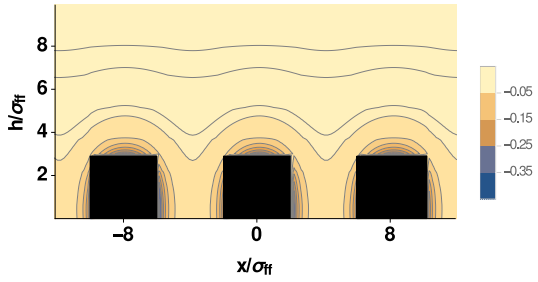

Figure 1: ~~*(fig-potential2d-supplement)~~ Example of the net potential generated by the solid (substrate and pillars). The values of the potential provided on the plot legend are in units of k_BT, where k_B is the Boltzman constant.

where $\Psi(\sigma, H) = \frac{2}{15}\left(\frac{\sigma}{\sigma+H}\right)^9 - \left(\frac{\sigma}{\sigma+H}\right)^3$.

In the second integral in eq S. 2, the integration with respect to y could be performed analytically. Integration with respect of x- and h-coordinate was carried out numerically.

An example of calculated net potential is shown in Figure 1 for the choice of interaction parameters provided in Sec. 2.1.3 of the main text and $f_\tau = 7.8 \times 10^{-16}$N.

2 Euler-Lagrange equations and their solution

The total Helmholtz free energy $F_{tot}[\rho_1(\mathbf{r}), \rho_2(\mathbf{r})]$ can be expressed as the sum of an ideal gas free energy, $F_{id}[\rho_1(\mathbf{r}), \rho_2(\mathbf{r})]$, an excess free energy $F_{ex}[\rho_1(\mathbf{r}), \rho_2(\mathbf{r})]$, and a free energy $F_{1s}[\rho_1(\mathbf{r})] + F_{2s}[\rho_2(\mathbf{r})]$ due to the interactions between fluid and walls. The ideal gas free energy has the form

$$F_{id}[\rho_1(\mathbf{r}), \rho_2(\mathbf{r})] = k_BT \sum_{i=1,2} \int d\mathbf{r}\rho_i(\mathbf{r})\{\log[\Lambda_i^3\rho_i(\mathbf{r})] - 1\} \tag{S. 4}$$

where $\Lambda_i = h_P/(2\pi m_i k_B T)^{1/2}$ is the thermal de Broglie wavelength of the molecules of component i, k_B and h_P are the Boltzmann and Planck constants, respectively, T is the absolute temperature, and m_i is the molecular mass of component i. The excess free energy is composed of a contribution from a reference system of hard spheres $\Phi[\rho_1(\mathbf{r}), \rho_2(\mathbf{r})]$ and a contribution $F_{attr}[\rho_1(\mathbf{r}), \rho_2(\mathbf{r})]$ due to the attractive interactions between the fluid molecules. The former contribution, expressed in Rosenfeld's approximation (Y.Rosenfeld, Phys.Rev.Lett., 1989, **63**, 980.) has the form

$$\Phi[\rho_1(\mathbf{r}), \rho_2(\mathbf{r})]/k_B T = -n_0 \log(1-n_3) + \frac{n_1 n_2 - \mathbf{n}_1 \mathbf{n}_2}{(1-n_3)} + \frac{n_2^2(n_2 - 3\mathbf{n}_1\mathbf{n}_2)}{24\pi(1-n_3)^2} \qquad \text{(S. 5)}$$

where n_α ($\alpha = 0, 1, 2, 3$) and $\mathbf{n}_\alpha$ ($\alpha = 1, 2$) are averaged densities given by

$$n_\alpha(\mathbf{r}) = \sum_{i=1}^{2} \int d\mathbf{r}' \rho_i(\mathbf{r}') \omega_i^{(\alpha)}(\mathbf{r} - \mathbf{r}'), \quad \alpha = 0, 1, 2, 3, \qquad \text{(S. 6)}$$

$$n_\alpha(\mathbf{r}) = \sum_{i=1}^{2} \int d\mathbf{r}' \rho_i(\mathbf{r}') \bar{\omega}_i^{(\alpha)}(\mathbf{r} - \mathbf{r}'), \quad \alpha = 1, 2. \qquad \text{(S. 7)}$$

The scalar, $\omega_i^{(\alpha)}(\mathbf{r} - \mathbf{r}')$, and vector, $\bar{\omega}_i^{(\alpha)}(\mathbf{r} - \mathbf{r}')$, weight functions are provided by R.Roth and S.Dietrich, Phys.Rev.E, 2000, **62**, 6926.

The contribution to the excess free energy due to the attraction between the fluid molecules, calculated in the mean-field approximation, is given by

$$F_{attr}[\rho_1(\mathbf{r}), \rho_2(\mathbf{r})] = \frac{1}{2} \sum_{i,j=1}^{2} \int \int d\mathbf{r} d\mathbf{r}' \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') \phi_{ij}(|\mathbf{r} - \mathbf{r}'|) \qquad \text{(S. 8)}$$

(with $\phi_{ij}(|\mathbf{r} - \mathbf{r}'|) = 0$ for $|\mathbf{r} - \mathbf{r}'| \leq \sigma_{ij}$).

The contribution of the fluid-solid interactions is given by

$$F_{is}[\rho_i(\mathbf{r})] = \int d\mathbf{r}\rho_i(\mathbf{r})\phi_{is}(\mathbf{r}) \ . \tag{S. 9}$$

The Euler-Lagrange equations for the FDDs $\rho_i(x,h)$ $(i=1,2)$ obtained by minimizing the Helmholtz free energy

$$F_{tot}[\rho_1(\mathbf{r}),\rho_2(\mathbf{r})] = F_{id}[\rho_1(\mathbf{r}),\rho_2(\mathbf{r})] + \Phi[\rho_1(\mathbf{r}),\rho_2(\mathbf{r})] + F_{attr}[\rho_1(\mathbf{r}),\rho_2(\mathbf{r})] + \sum_{i=1}^{2} F_{is}[\rho_i(\mathbf{r})] \tag{S. 10}$$

has the following form

$$\log[\Lambda_i^3\rho_i(\mathbf{r})] - Q_i(\mathbf{r}) = \lambda_i/k_BT, \quad (i=1,2) \tag{S. 11}$$

where

$$\begin{aligned} k_BTQ_i(\mathbf{r}) = \ & - \sum_{\alpha=0}^{3}\int d\mathbf{r}'\frac{\partial\Phi}{\partial n_\alpha(\mathbf{r}')}\omega_i^{(\alpha)}(\mathbf{r}-\mathbf{r}') \\ & - \sum_{\alpha=1}^{2}\int d\mathbf{r}'\frac{\partial\Phi}{\partial \mathbf{n}_\alpha(\mathbf{r}')}\bar{\omega}_i^{(\alpha)}(\mathbf{r}-\mathbf{r}') \\ & - \int d\mathbf{r}'[\rho_i(\mathbf{r}')\phi_{ii}(|\mathbf{r}-\mathbf{r}'|) + \rho_j(\mathbf{r}')\phi_{ij}(|\mathbf{r}-\mathbf{r}'|)] - U_{is}(\mathbf{r}), \quad (j\neq i) \end{aligned} \tag{S. 12}$$

and λ_i is a Lagrange multiplier arising because of the constraint of fixed average density of component i in the slit

$$\rho_{i,av} = \frac{1}{V_i}\int_{V_i} d\mathbf{r}\rho_i(\mathbf{r}) \tag{S. 13}$$

where V_i is the volume of the slit accessible to component i. Using eqs S. 11 and S. 13 the Lagrange multipliers can be rewritten in the form

$$\lambda_i = -k_B T \log \left[\frac{1}{\rho_{i,av} V_i \Lambda_i^3} \int_{V_i} d\mathbf{r} e^{Q_i(\mathbf{r})} \right] . \qquad \text{(S. 14)}$$

By eliminating λ_i between eqs S. 11 and S. 14 and perfoming the integration in eq S. 12 with respect to the y-direction, one obtains two integral equations for the FDDs $\rho_1(x,h)$ and $\rho_2(x,h)$ which can be solved by numerical iterations.

The general iteration procedure used in this paper is explained in G.O.Berim and E.Ruckenstein *Nanoscale*, 2015, **7**, 7873. Here we will discuss only the selection of the initial guess which constitutes an important part of the calculations. When the initial guess is selected arbitrarily, usually as a "rectangular" drop at an arbitrary location on the surface, the iterations transform its location and shape toward the location and shape of the stable drop. The required number of iterations depends on how close is the initial guess to the location of the solution of the Euler-Lagrange equation and how quick is the transformation of the intermediate density distribution during iterations. For two-component mixture, the iteration procedure is extremely slow. Hence, the choice of the initial guess has a critical importance in finding the solution in a reasonable time. For the selection of an initial FDD a special approach was developed which is based on the following observation.

Let us suppose that the iterations start with a rectangular initial guess located arbitrarily on the surface of LF (see Figure 2a) and that one keeps track of the difference $\Delta\rho_i^{(k)}(x,h) = \rho_i^{(k+1)}(x,h) - \rho_i^{(k)}(x,h)$ between the density distributions $\rho_i^{(k)}(x,h)$ and

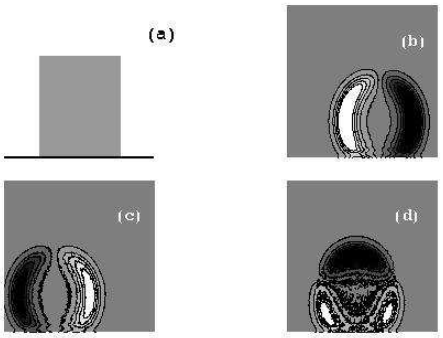

Figure 2: (a) Initial guess for the iteration procedure. (b), (c), and (d) Possible graphs of the differences between two consecutive iterations. Dark areas correspond to negative values of this differences and light areas correspond to positive values.

$\rho_i^{(k+1)}(x,h)$ for component i $(i=1,2)$ provided by two consecutive iterations k and $k+1$. Then, after 50 - 100 iterations this difference as function of x and h has, generally, one of the three shapes presented in Figure 2b, c, and d where the light (dark) areas represent positive (negative) values of $\Delta\rho_i^{(k)}(x,h)$. Figures 2b and c indicate the tendency of the density distribution $\rho_i^{(k)}(x,h)$ to "move" in the direction of the positive part of $\Delta\rho_i^{(k)}(x,h)$, i.e. to the left for Figure 2b and to the right for Figure 2c. Figure 2d indicates the case in which the initial guess is selected almost at the location of the solution of Euler-Lagrange equation.

On the basis of the above observation, we first selected four initial guesses of the same rectangular shape evenly distributed between the middle of the pillars and the the point midway between pillars.

After several iterations (about 100), the differences $\Delta\rho_i^{(k)}(x,h)$ for each initial guess were analyzed. The solution is located between the points where the distributions of

$\Delta\rho_i^{(k)}(x,h)$ "move" towards each other. To determine the location of the solution more precisely, the described procedure was applied to the interval between those specific points found in the previous part of the calculations.

To avoid the divergence of the iteration procedure, the input density profile $\rho_i^{(k),in}(x,h)$ for the $(k+1)$-th iteration $\rho_i^{(k+1)}(x,h)$, generated by the Euler-Lagrange equation, was selected as follows

$$\rho_i^{(k),in}(x,h) = (1-\gamma)\rho_i^{(k-1),in}(x,h) + \gamma\rho_i^{(k)}(x,h) \tag{S. 15}$$

where the constant $\gamma = 0.1$. As a measure of the precision of the iterations the dimensionless quantity

$$\delta = \left| \frac{\lambda_i^{(k+1)} - \lambda_i^{(k)}}{\lambda_i^{(k)}} \right|$$

was employed where $\lambda_i^{(k)}$ is the Lagrange multiplier calculated from eq S. 14 using FDD $\rho_i^{(k)}(x,h)$. The iterations were carried out on a two dimensional grid with a spacing equal to 0.1σ until δ became smaller than 10^{-7}.