Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A qualitative model based on surface accumulation

In the channel with the total volume V_c, two regions can be identified: (i) the region of surface accumulation and (ii) the bulk region. As shown in Fig. S1, the former is located near the proximal wall and has the volume V_s^0. The rod concentration in this region is ϕ_s^0. The latter is located in the center of the channel and has the volume V_b. The rod concentration in this region can be reasonably assumed as the rod concentration in the reservoir ϕ_r. Evidently, one has $V_c = 2V_s^0 + V_b$. Because of surface accumulation, the condition $\phi_s^0 > \phi_r$ is assumed.

The rod concentration in the channel can be expressed as

$$\phi_c = (2\phi_s^0 V_s^0 + \phi_r V_b) / V_c. \tag{1}$$

The partition ratio is given by

$$\Psi = \phi_c / \phi_r = (\phi_s^0/\phi_r)(2V_s^0/V_c) + (V_b/V_c)$$
$$= (\phi_s^0/\phi_r)\alpha_s + \alpha_b, \tag{2}$$

where the volume ratios of the two regions are defined as $\alpha_s = (2V_s^0/V_c) < 1$ and $\alpha_b = (V_b/V_c) < 1$, and certainly $\alpha_s + \alpha_b = 1$. Because the contribution from the region of surface accumulation is $\phi_s^0/\phi_r > 1$, one can conclude from Eq. (2) that $\Psi > 1$ as long as $\alpha_b > 0$ ($V_b > 0$). That is, the partition ratio is always greater than unity as the regions of surface accumulation do not overlap each other, i.e., $H \geq 2$.

As the regions of surface accumulation are just in contact, the bulk region vanishes and one has $\alpha_b = 0$ ($V_b = 0$). According to Eq. (2), the maximum partition ratio appears as

$$\Psi_{max} = (\phi_s^0/\phi_r) > 1. \tag{3}$$

In the absence of the bulk region, the regions of surface accumulation overlap with each other and the excluded volume effect comes into play. Therefore, one expects that as the channel width (H) is further reduced, the rod concentration in the region of surface accumulation (ϕ_s) decreases and one has $\phi_s < \phi_s^0$. This fact leads to the decrease of ϕ_c which is dominated by the decrement of ϕ_s and the rapid decay of Ψ.

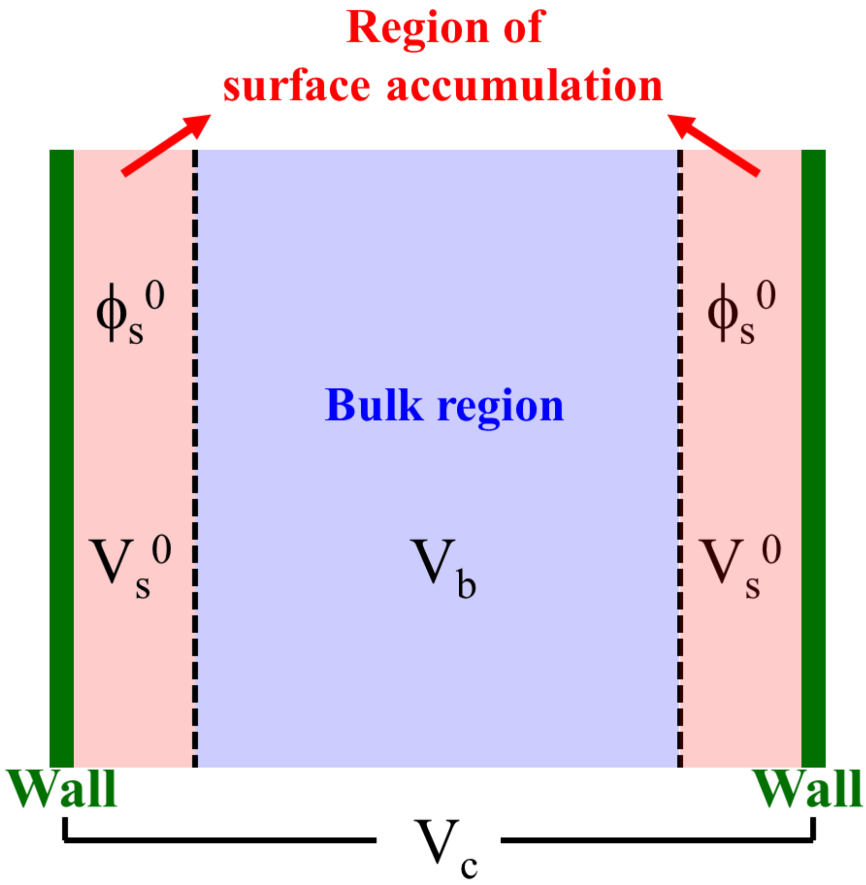

Figure S1. Two regions in the channel.

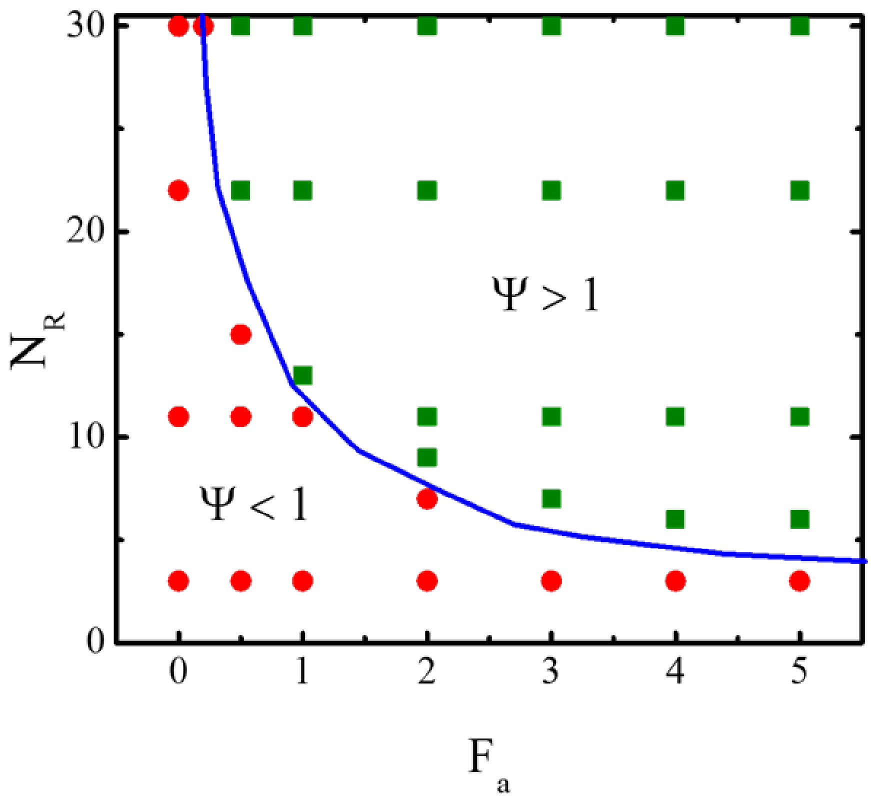

Figure S2. The 2d phase diagram $\Psi(N_R, F_a)$ for $H = 2.5$ and $\phi_r = 5 \times 10^{-3}$.