

Supplementary Information for: The role of surface topography on the self-assembly of polymeric surfactants[†]

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1 The “locally-spherical” approximation

As discussed in the main text, in [*Phase separation of mixed polymer brushes on surfaces with nonuniform curvature*, J. Chem. Phys. 139(19), 2013], Tung and Cacciuto not only make a local density approximation but also assume that the brush behaves as it would on a spherical surface with the same average mean curvature. This is an approximation and does not hold exactly for a locally cylindrical surface, as the result deviates from the exact calculation that can be performed in this case, see Eqs.17 and 18 in the main text. Notice that, however, the difference is only quantitative but not qualitative, in the sense that the prediction of phase stability is not affected. Importantly, with this additional approximation one could treat more general surfaces where the curvature varies along more than a single direction, which can be done by simply replacing $R(\vec{r}) = 1/c_{\text{mean}}(\vec{r})$ in the definition of the scaled variable y in the equation reported below (see the main text for more details and the exact definition of y).

Thus, for reference and potential future studies, we report here the results we would obtain if such a “locally-spherical” surface approximation was made, which can be simply derived from functional minimisation of the free-energy density procedure, leading to the following self-consistent equations:

$$\phi_{\text{Sph}}(\vec{r}) = \frac{1}{e^{f_{\text{Sph}}(\phi_L, \mu)} + 1} \quad (1)$$

$$\begin{aligned} f_{\text{Sph}}(\phi_L, \mu) = & 2\chi(1 - 2\phi_L) \\ & + \frac{3}{2}\gamma\phi_L^{\frac{1}{2}}\frac{v}{y} \log \left[\frac{1 + \left(\frac{y}{v}\right) \left(1 + \alpha\phi_L^{\frac{1-v}{2v}}\right)}{1 + \left(\frac{y}{v}\right)} \right] \\ & + \frac{\frac{1-v}{2v}\alpha\gamma\phi_L^{\frac{1}{2v}}}{1 + \left(\frac{y}{v}\right) \left(1 + \alpha\phi_L^{\frac{1-v}{2v}}\right)} + \mu, \end{aligned} \quad (2)$$

where we remind both ϕ_L and y are functions of the point \vec{r} on the surface.

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2 Understanding the limitations of our model: the local approximation

When treating surfaces of spatially varying curvature, we make a local density approximation. In practice, this means the polymer experience an environment that is consistent with what would be felt if it was on a surface of uniform curvature, with the value of this effective curvature being the one measured at the polymer grafting point. In this way, the local curvature at the grafting point is all that is necessary to write down our free-energy functional.

This approximation is expected to fail for “long brushes”, more precisely, brushes for which the brush height is larger than the length-scale on which the curvature varies appreciably, λ_0 in our system in the main text. For short brushes, the position of the whole polymer backbone is strongly correlated with the grafting point but this is not the case anymore for long brushes, where points on the polymer backbone far enough from the grafting point lose any spatial correlation with it and the chain explores environments that could be consistent with grafting points with a different curvature, see Figure 1 below.

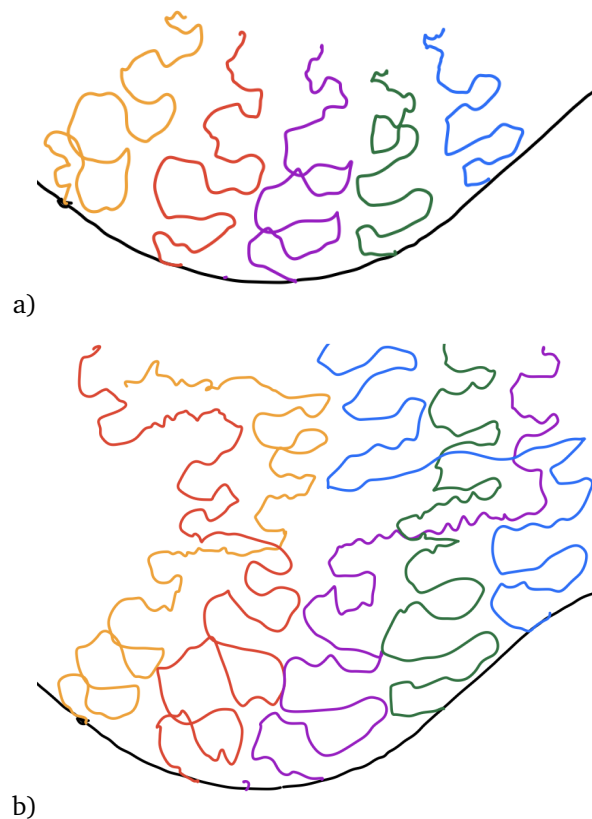


Figure 1: a) Short brush, where a local density approximation holds because the whole polymer is strongly spatially correlated with the grafting point. b) For long enough brushes, far away from the grafting point the polymer backbone is uncorrelated with the grafting point and explores environments that could be consistent with a different surface curvature.

3 Height profile & curvature for our sinusoidally-modulated surface

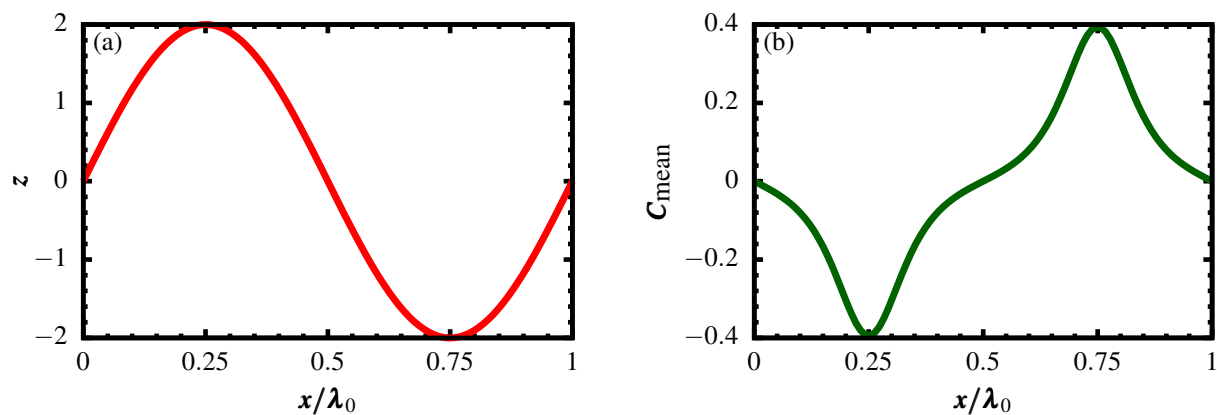


Figure 2: a) Height profile of a repeating unit of the sinusoidally modulated surface used in our simulations, together with b) its corresponding curvature, for $(a, \lambda) = (2.0, 10)$. The point $x/\lambda = 1/2$, represents the boundary between negative and positive curvatures in our system.

4 Self-assembly on generic surfaces with curvature varying along 2 dimensions

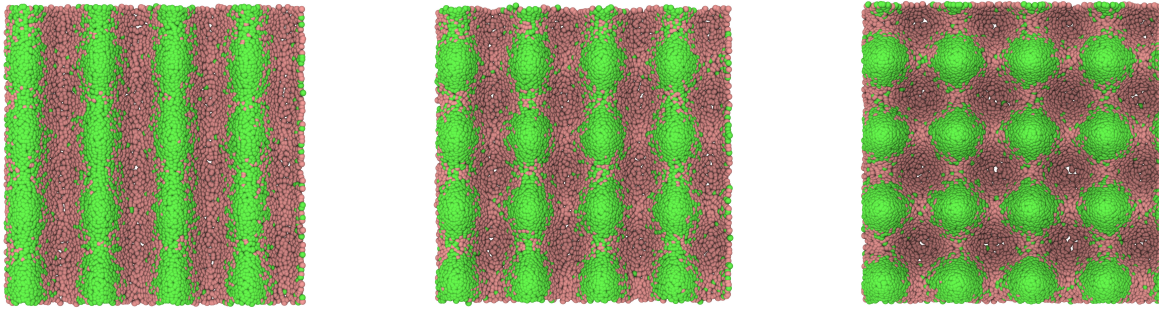
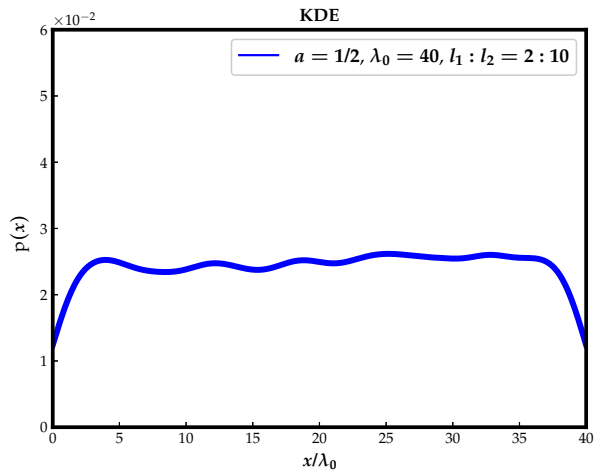
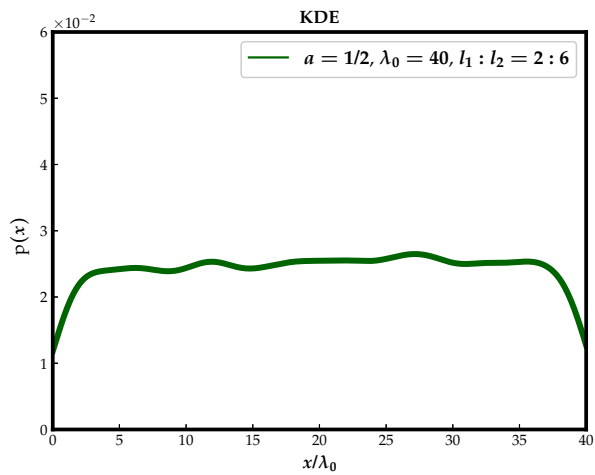
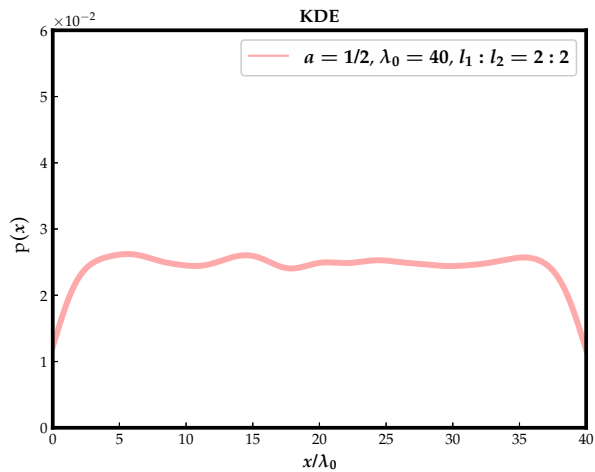
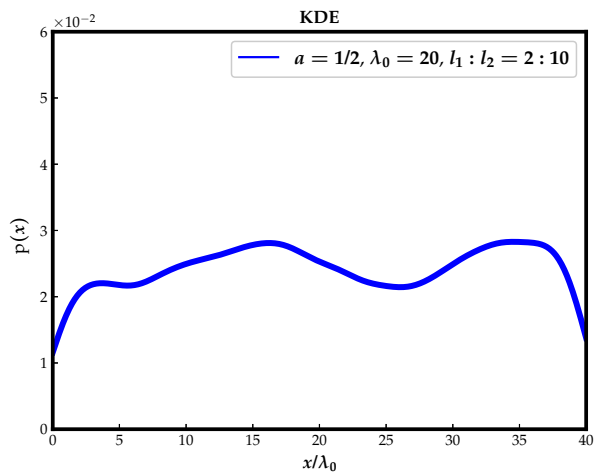
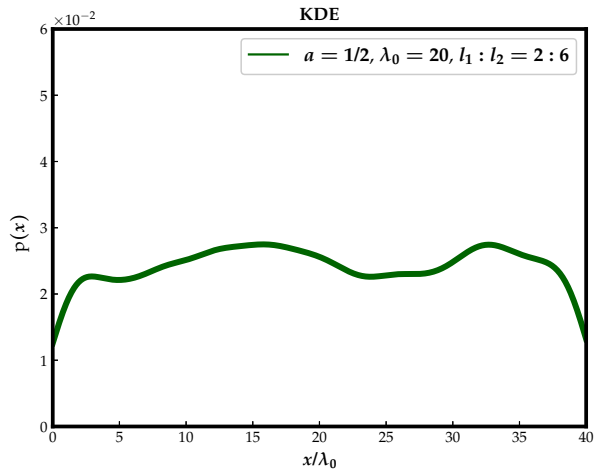
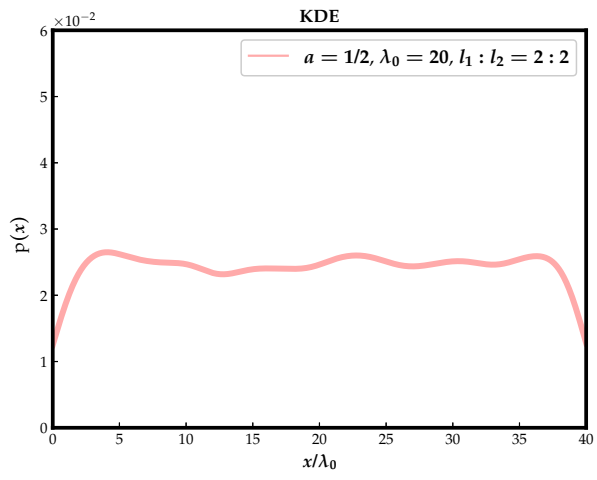
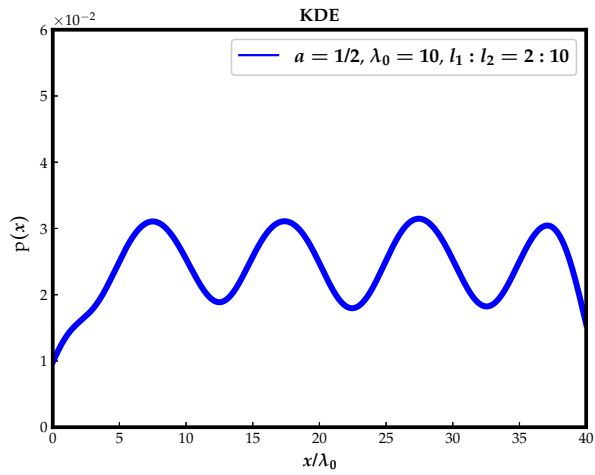
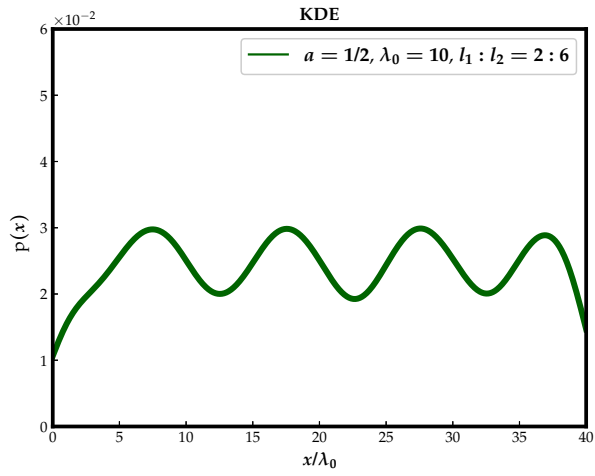
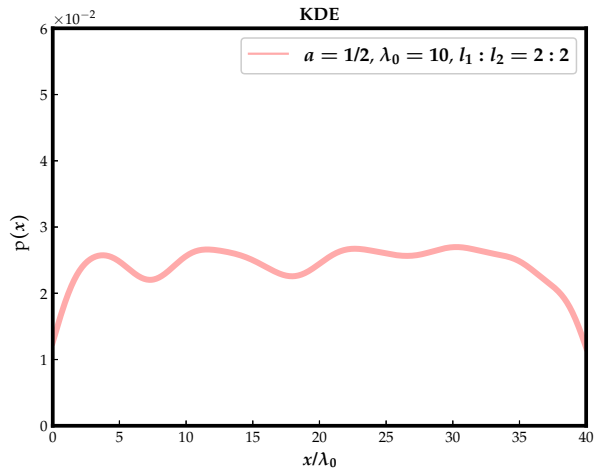


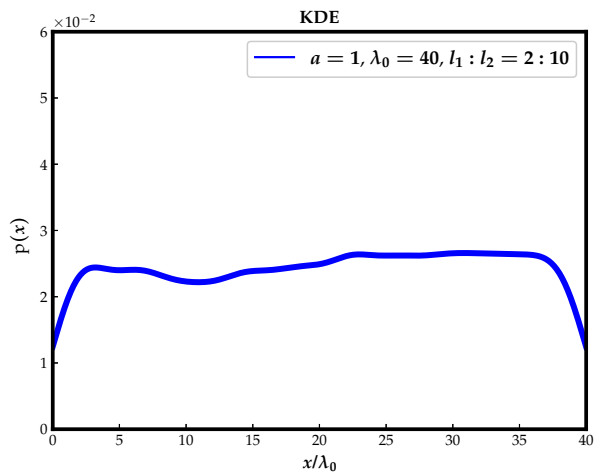
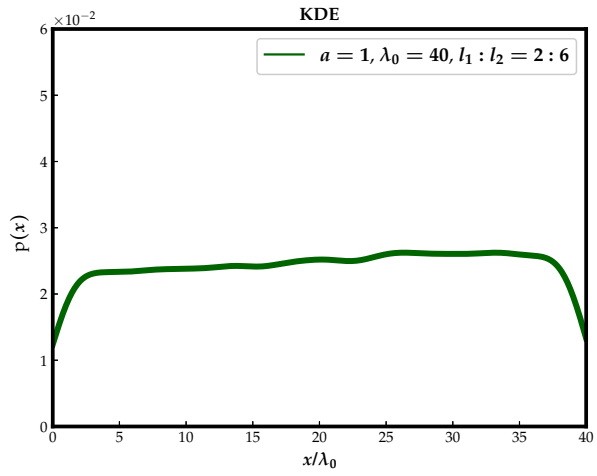
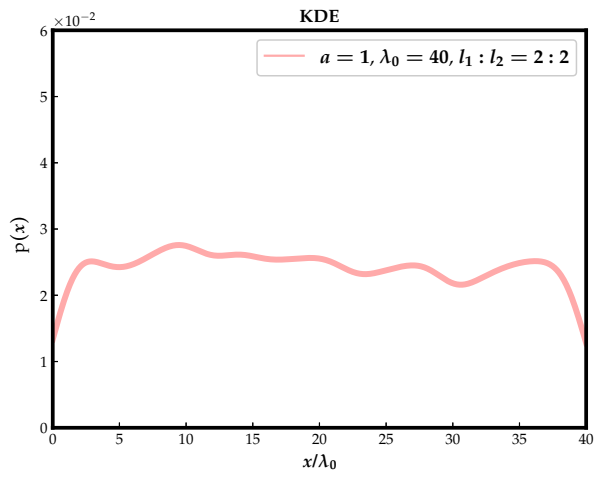
Figure 3: Representative snapshots of equilibrium patterns, viewed from the top perpendicularly to the x-y plane, for different combination of surface topographic parameters (a, λ_a) and (b, λ_b) for a surface varying as $z = a \sin(x/\lambda_a) + b \sin(y/\lambda_b)$. Moving from left to right, the modulation along the y-direction changes as $b = 0.5, 1.0, 2.0$ whereas the other values are fixed to $a = 2.0, \lambda_a = 10$ and $\lambda_b = 10$ (all length-scales are provided in reduced units, see the main text). As it can be clearly observed, even when the curvature varies both along x and y , the qualitative behaviour remains the same as when curvature varies along a single dimension only, as discussed in the main text, with long surfactants segregating in positive curvature regions and short surfactants in the negative curvature regions. Notice that surfaces whose curvature varies along more than 1 spatial dimension (i.e., without cylindrical symmetry), can be studied using the additional “locally-spherical” approximation, see the discussion and the equation in the first section of the Supplementary Information. The asymmetry parameter used for this plot is $\alpha = 3$, the polymeric surfactants are, like in the main text, perfectly miscible, and described by a repulsive potential between beads which is the same independently from their type (here, $a_{11} = a_{22} = a_{12} = 18.75k_B T$). The head beads of short surfactants are depicted in red, whereas in green those for the long surfactants (tails not shown for clarity).

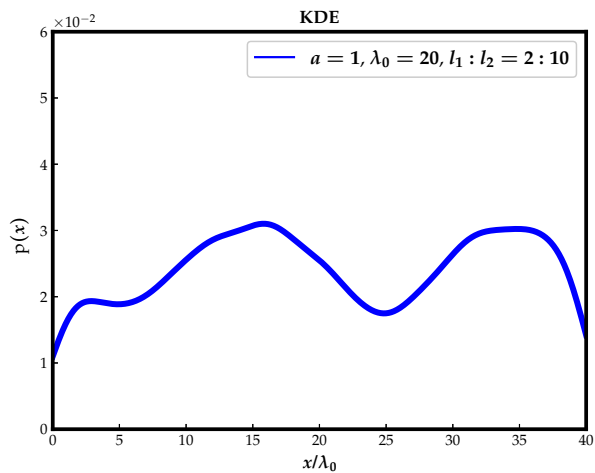
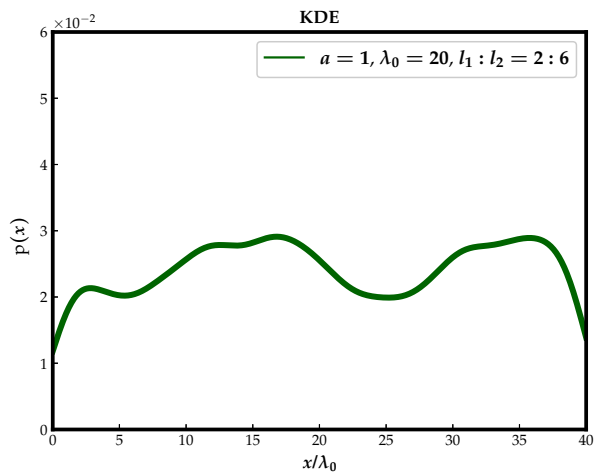
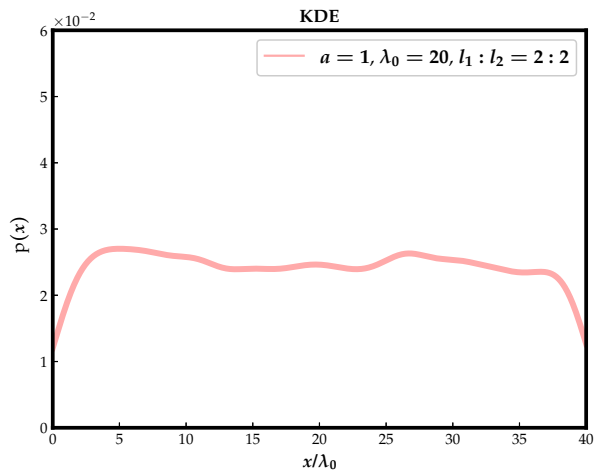
5 Surface densities

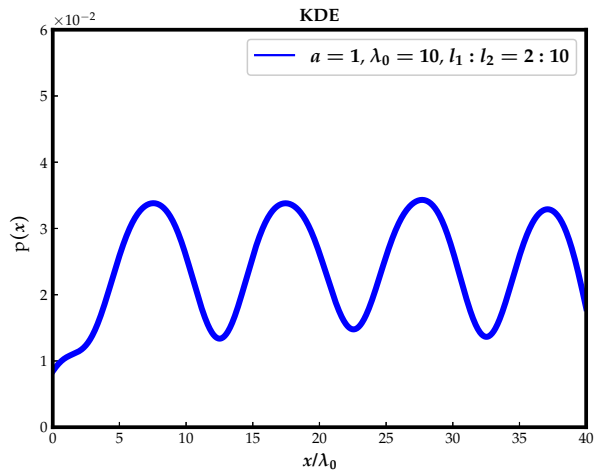
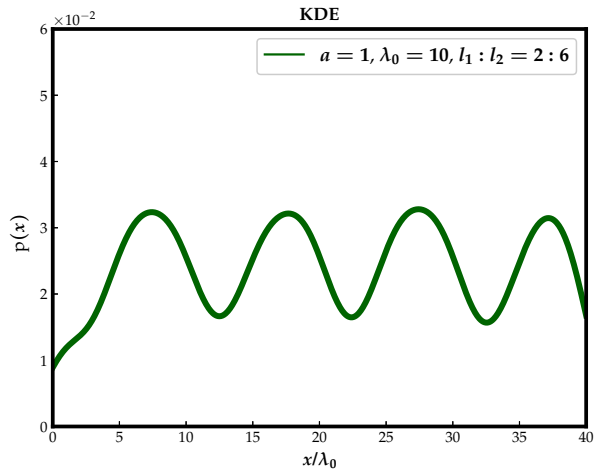
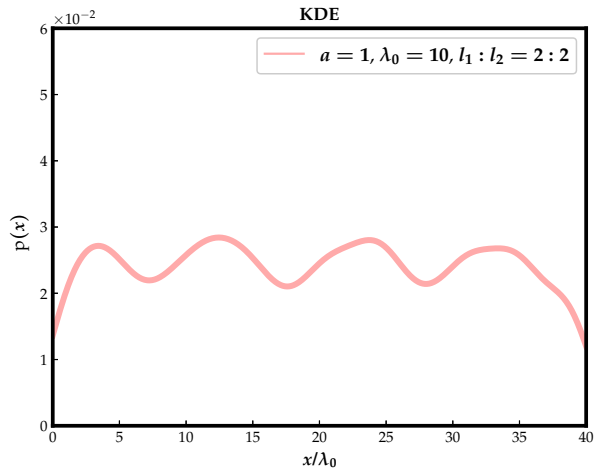


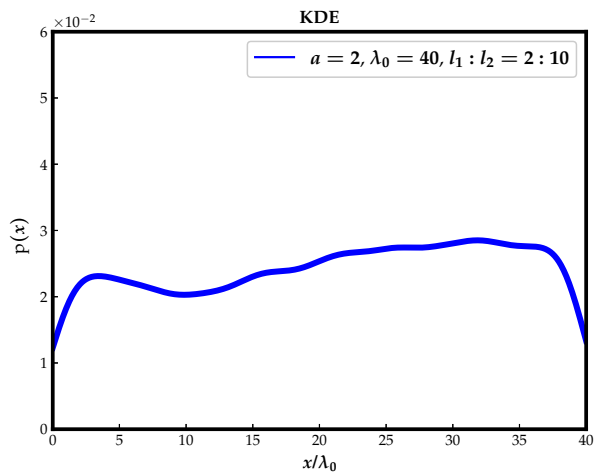
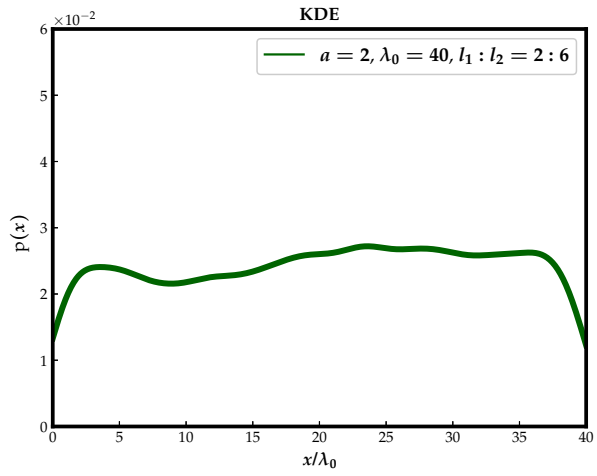
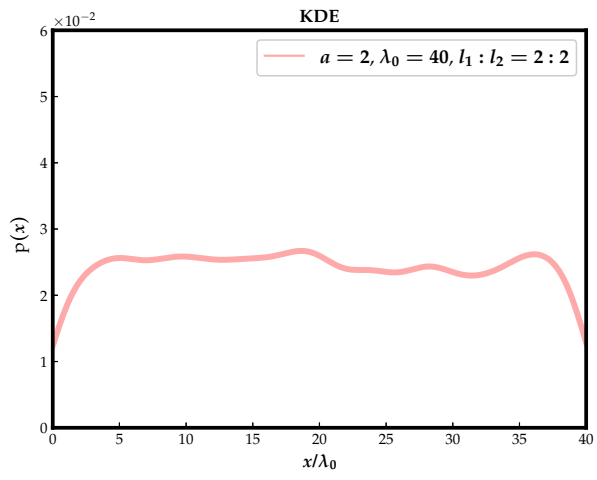


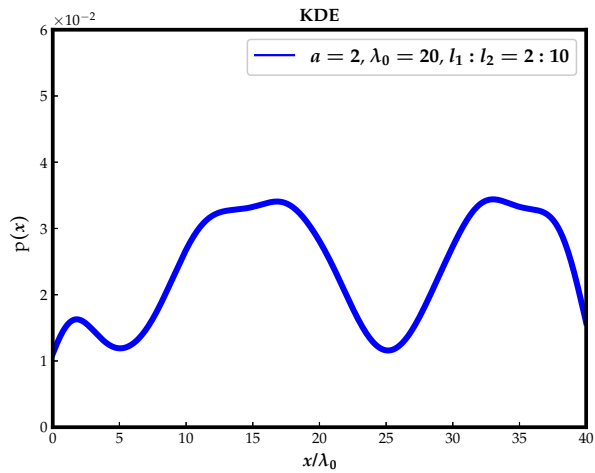
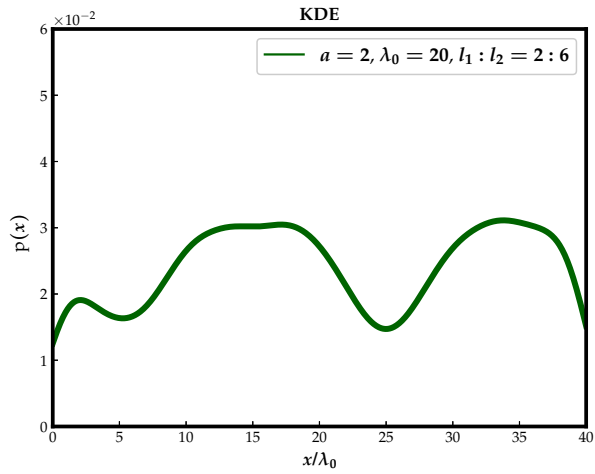
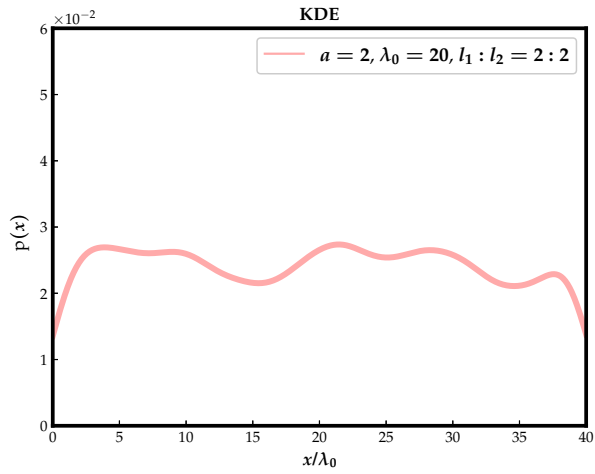












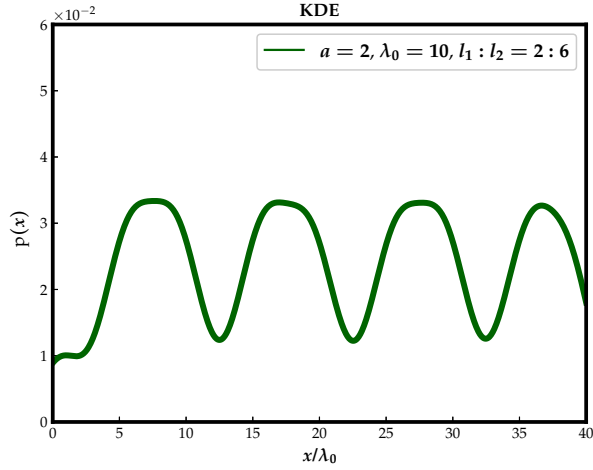
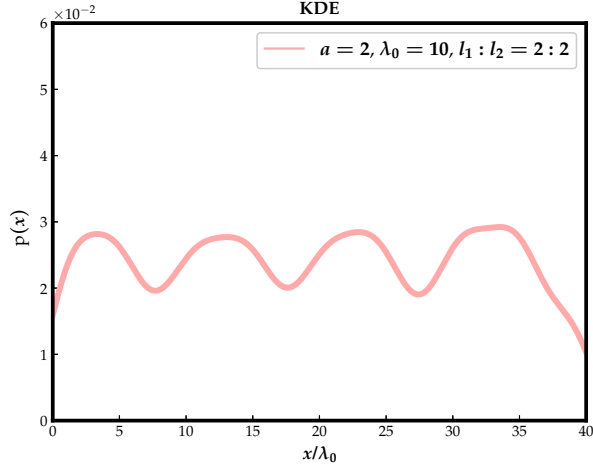


Figure 4: (color online). Local density (calculated via a kernel density estimations) corresponding to the studies of Table 1, for different combination of surface topographic parameters a and λ_0 , and different surfactant lengths ratio $l_1 : l_2$ for an otherwise perfectly miscible system where the repulsive potential between beads is the same independently from their type. Note that the ratio of $l_1 : l_2 = 2 : 2$ are always depicted in pink, the ratio of $l_1 : l_2 = 2 : 6$ are always depicted in green, whereas in blue those for the the ratio of $l_1 : l_2 = 2 : 10$. A Gaussian kernel is adopted for the density estimation, with a width of 1.5σ in our studies, where σ is the size of a bead in our DPD description (see the main text for details).