5. External-field-driven flow

One of the simplest ways to implement time-dependent boundary conditions in SOMA is to apply a time-dependent external field that is only nonzero close to the boundaries and has the form:

$$E_i(\mathbf{r}, t) = f_i(\mathbf{r}, t)\phi_i(\mathbf{r}, t)\,, \tag{5.1}$$

where $i = \mathrm{A}, \mathrm{B}$ denotes the monomer types. In this section, self-assembled lamellae of diblock-copolymers are moved at constant speed v perpendicular to their orientation using spatially periodic external fields close to the boundaries. In a system that moves along with the external field, each monomer experiences a friction force ζv in the opposite direction, where ζ is obtained from (2.5). The degree of deformation depends on the Péclet number, $P_e \equiv vR_e/D$. For large values $P_e \approx 1$, the chains cannot keep up with the external field movement and the lamellae break. For small $P_e \approx 0$, they have enough time to fully relax to the undeformed shape. In this section, an intermediate regime is investigated to obtain the bending modulus K.

5.1. Reference system

A system of $n = 750$ symmetric diblock-copolymers with $N_A = N_B = N/2 = 16$ and $\chi N = 20$ is used. The box dimensions are $L_x \times L_y \times L_z = 2.5 \times 2.82 \times 1\, R_e^3$, which corresponds to $\sqrt{\bar{N}} = 106$. The spatial discretizations are $\Delta x = 1/16\, R_e$, $\Delta y = 47/800\, R_e$ and $\Delta z = 1\, R_e$. To generate the initial lamellar structure, external fields are applied, as shown in Figure 5.1. The interlayer spacing of $d = 1.41\, R_e$ was found to be stable over the duration of the simulations, but it does not correspond to the equilibrium spacing.

Subsequently, the external fields are switched off everywhere except at a distance less than $b = 0.5\,R_e$ from the boundaries in the x-direction, so the length of the part of the lamellae that is not supported by the external fields is $L = 1.5\,R_e$. Every Δt MCS, the fields are moved by a distance of Δy in the y-direction, so the velocity is $v = 47R_e/(800\Delta t)$. The external fields balance the friction forces at the boundaries and therefore act as bearings for the lamellae. The diffusion constant, D, is obtained from (2.7), where $g_3(t)$ is measured in a system without external fields and $\chi N = 0$.

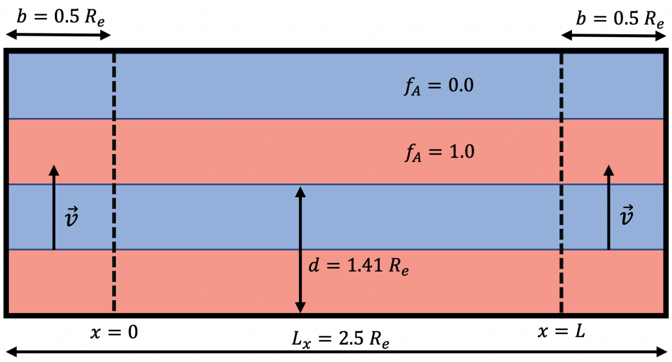


Figure 5.1.: Sketch of the external field $f_A(\mathbf{r}, 0)$. Red domains correspond to $f_A = 1.0$, blue domains to $f_A = 0.0$. $f_B(\mathbf{r}, 0)$ is exactly complementary. Within the region bounded by the dotted lines, the external fields are switched off after the initial lamella structure has been generated.

5.2. Bending modulus

For small deformations, the free energy of a bent lamella is [29]:

$$F_b = \int d\mathbf{r} \left\{ f_0 + \frac{1}{2} K \left(\partial_x^2 u \right)^2 \right\} , \tag{5.2}$$

where f_0 is the free energy per unit volume of the unbent lamella, K is the bending modulus and $u \equiv u(x)$ is the deformation profile of the lamella center of mass. Including the external friction force, and carrying out the integration over y and z, while neglecting the change of volume, the total free energy becomes:

$$\begin{aligned} F &= dL_z \int dx \left\{ f_0 + \frac{1}{2} K \left(\partial_x^2 u \right)^2 - \rho_0 \zeta \frac{P_e D}{R_e} u \right\} \\ &\equiv dL_z \int dx\, f(u, u'') \,. \end{aligned} \tag{5.3}$$

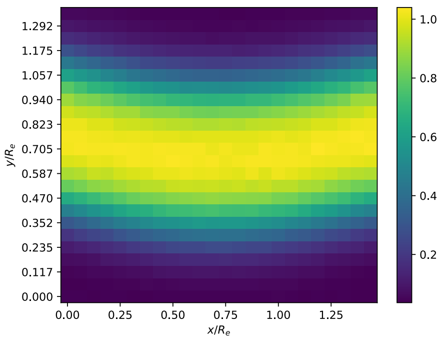
Setting the functional derivative, $\delta F/\delta u$, to zero, leads to the following Euler-Lagrange equation for the deformation profile $u(x)$:

$$\begin{aligned} \frac{\delta F}{\delta u} &= 0 = \frac{\partial f}{\partial u} + \frac{\partial^2}{\partial x^2}\frac{\partial f}{\partial u''} \\ \Longrightarrow K\frac{\partial^4 u}{\partial x^4} &= \rho_0 \zeta \frac{P_e D}{R_e}\,. \end{aligned} \tag{5.4}$$

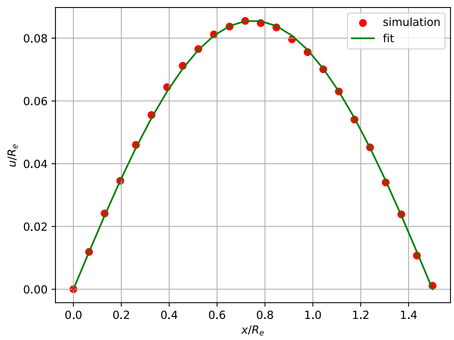
With the boundary conditions $u(0) = u(L) = 0$ and $u''(0) = u''(L) = 0$, one obtains:

$$u(x) = \frac{\rho_0 \zeta P_e D x}{24 K R_e}(L^3 - 2L^2 x + x^3)\,, \tag{5.5}$$

in analogy to a beam bending under a uniform load in the Euler-Bernoulli theory. The resulting lamella profile for $P_e = 0.24$ is shown in Figure 5.2. The fit is in excellent agreement with the simulation data.



(a)



(b)

Figure 5.2.: (a) Heatmap of the steady-state lamella profile in the reference frame that moves with the external field, averaged over all lamellae. (b) Lamella center of mass curve for $P_e = 0.34$. The fit corresponds to (5.5).

The maximum deflection is:

$$u_{max} = u(L/2) = \frac{5\rho_0 \zeta P_e D L^4}{384 K R_e}\,. \tag{5.6}$$

To obtain the bending modulus, u_{max} is measured for various values of P_e, this is shown in Figure 5.3. From (5.6), one obtains $K = 19.98\, k_B T/R_e$. This value is in good agreement with exact SCFT calculations, which give $K = 17.47\, k_B T/R_e$.

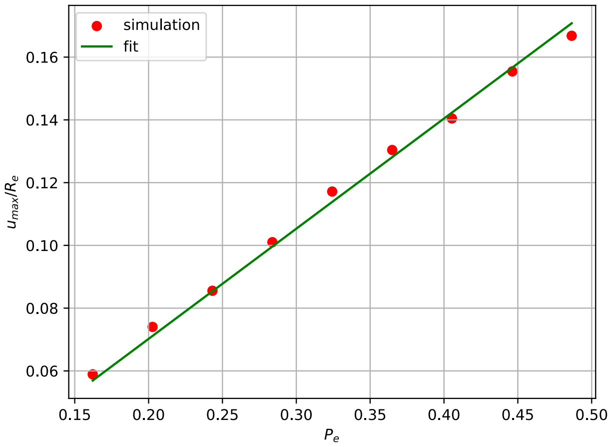


Figure 5.3.: Maximum deflection u_{max} as a function of the Péclet number P_e. The fit corresponds to (5.6).

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