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Interface repulsion and lamellar structures in thin films of homopolymer blends due to thermal oscillations

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In equilibrium the interface potential that describes the interaction between two AB interfaces in a binary blend of A and B homopolymers is attractive at all distances, resulting in coarsening of the blend morphology even in the absence of interface curvature. We demonstrate that the dissipative assembly in response to a time-periodic variation of the blend incompatibility qualitatively alters this behavior, i.e., for suitable parameters the interface potential exhibits a periodic spatial modulation and AB interfaces adopt a well-defined distance. We explore for which oscillation periods and amplitudes an interface repulsion occurs and demonstrate that we can control the preferred interface distance over a wide range by varying the oscillation period. Using particle-based simulations we explicitly demonstrate that this dissipative assembly of a homopolymer blend results in a lamellar structure with multiple planar interfaces in a thin film geometry.

Dissipative assembly, i.e., the non-equilibrium structure formation due to energy input and concomitant dissipation, is an important mechanism of structure formation in biological and synthetic systems [1–3]. Recently there are efforts to mimic particular aspects of this driven, non-equilibrium assembly in colloidal systems [4–8], and there is an urgent need to understand the underlying design mechanisms [1, 4]. Here we provide an analytical strategy for predicting the dissipative assembly of interfaces and demonstrate that the non-equilibrium structure formation results in a wetting behavior that qualitatively differs from the equilibrium behavior, i.e., the interface interactions switch from attractive to repulsive, giving rise to the dissipative assembly into lamellar morphologies.

The interaction between interfaces is important for wetting and coarsening dynamics [9–13]. The free energy of two planar interfaces per unit area depends on their distance, h , and is given by the interface potential, $g(h)$ [14]. In equilibrium, the interaction between two interfaces in a binary blend is attractive [15], resulting in coarsening even in the absence of interface curvature or collision of interfaces due to thermal motion. In this letter we demonstrate that an oscillatory repulsion between the species qualitatively changes the interface potential, resulting in an interface repulsion and giving rise to a metastable lamellar morphology in a binary blend.

The universal properties of interfaces between the coexisting phases of a binary blend can be described by the Ginzburg-Landau square-gradient theory [9, 16]:

$$\frac{\mathcal{F}[m]}{k_B T \mathcal{N}} = \int d\mathbf{r} \left(-\frac{\alpha}{2} m^2 + \frac{1}{4} m^4 + \frac{1}{2} |\nabla m|^2 \right) \quad (1)$$

where m denotes the order parameter that distinguishes between the two coexisting phases, and \mathcal{N} is a normalization that sets the scale of the free-energy density in units of the thermal energy, $k_B T$. The coefficient α parameterizes the strength of the binary interaction between the constituents of the blend. It is a temperature-like variable that controls the phase behavior, and $\alpha = 0$ corresponds

to the critical point. The square-gradient term penalizes rapid spatial variations of the order parameter and results in a finite width of the interface. The interface profile $m(x) = \sqrt{\alpha} \tanh(x/w)$ with width $w = \sqrt{2/\alpha}$ minimizes the free-energy functional, $\mathcal{F}[m]$, subjected to the boundary conditions $m(x \rightarrow \pm\infty) = \pm\sqrt{\alpha}$ [9]. The interaction between two interfaces is attractive at all distances and decays exponentially with the distance, h . Within Cahn-Hilliard dynamics

$$\frac{\partial m}{\partial t} = \nabla \frac{\Lambda}{k_B T \mathcal{N}} \nabla \frac{\delta \mathcal{F}}{\delta m(\mathbf{r})} \quad (2)$$

this yields to an attractive dynamics of interface distance, $h \frac{dh}{dt} \sim -\exp(-h/w)$ for $\alpha = 1$ [15].

In this letter we consider the case that the incompatibility, α , is a time-periodic function $\alpha = \begin{cases} 1 + \epsilon & \text{for } 0 < t \leq T/2 \\ 1 - \epsilon & \text{for } T/2 < t \leq T \end{cases}$ with period, T , and amplitude, ϵ , of the oscillation. Previous seminal work by Szleifer and co-workers [4, 5] for particle systems demonstrated that oscillations of the interparticle potential with a period that is fast compared to the diffusion timescale of the particles result in an effective interaction that is the time average of the oscillatory potential. The (slow) toggling of interactions also beneficially impacts the crystallization kinetics in colloidal systems [6–8].

In our continuum model, we demonstrate by numerical simulation of the Cahn-Hilliard dynamics, approximate analytical calculations, and simulation of a particle-based model of a symmetric homopolymer blend in a thin film, that an oscillatory incompatibility can qualitatively change the interface potential from attractive to repulsive – a non-equilibrium characteristic that cannot be observed for any averaged (time-independent) value of α . The continued input of energy in this time-periodic non-equilibrium state results in a preferred distance between interfaces and a dissipative assembly of a binary blend into a metastable lamellar configuration, whose lamellar spacing can be controlled by the period, T , of the oscillation of the strength of binary interactions.

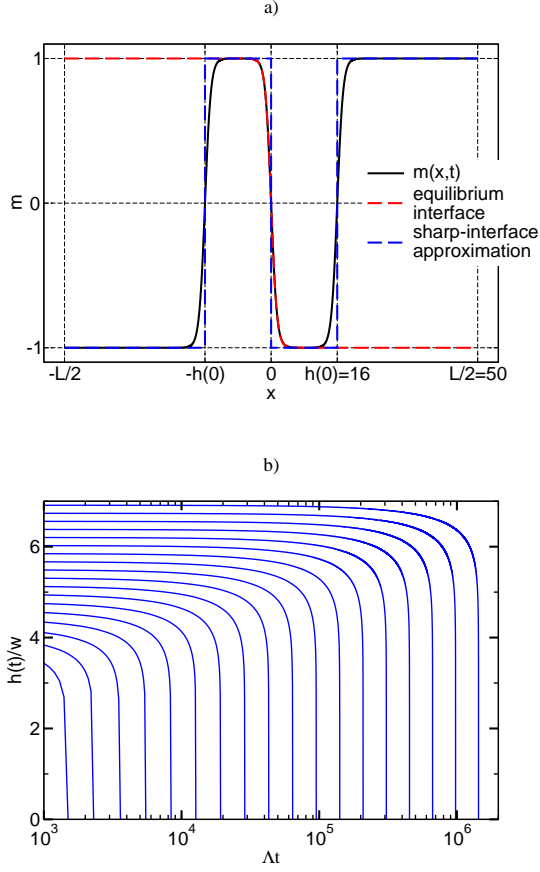


Figure 1: a) Initial interface configuration with an interface distance, $h(0) = 16 \approx 11.3w$, comparison with the equilibrium interface profile for $\alpha \equiv 1$ and the sharp-interface approximation. b) Time evolution towards equilibrium for a constant incompatibility, $\alpha \equiv 1$, *i.e.*, $\epsilon = 0$: interfaces attract each other, their distance $h(t)$ decreases in time, and they annihilate at $h(t^*) = 0$. The concomitant time scale, t^* , increases exponentially with the initial distance, $h(0)$.

First, we study the Cahn-Hilliard dynamics of the Ginzburg-Landau square-gradient functional via a semi-implicit spectral technique, setting $\Lambda = 1$. We consider a one-dimensional system of size $L = 100$. Initially, three interfaces are symmetrically positioned at $-h(0)$, 0 , and $h(0)$ as shown in Figure 1a. Panel b shows the time evolution of the distance, $h(t)$, for constant $\alpha \equiv 1$, *i.e.*, $\epsilon = 0$. As expected [15] the interfaces attract each other and annihilate at a time $\ln \Lambda t^* \sim h(0)$ for $h(0) \gg 1$.

The behavior for oscillating $\alpha(t)$ with amplitude $\epsilon = 0.5$ and period $\Lambda T = 5$ is presented in Figure 2a. If the interfaces are initially closely spaced, $h(0) \lesssim 6w$, they also attract each other and annihilate. For larger initial distances, however, interfaces do not attract. Instead, the interfaces converge toward a well defined, finite sep-

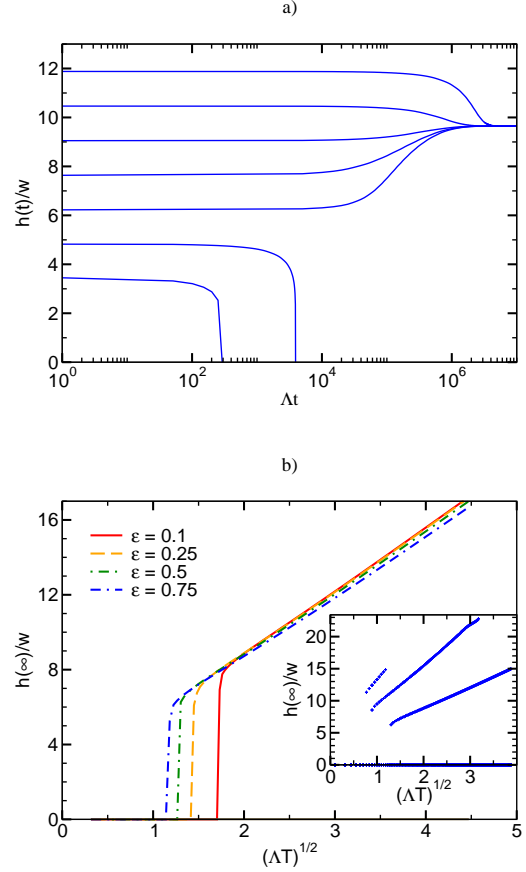


Figure 2: a) Time evolution of the interface distance, $h(t)$, for different starting conditions, $h(0)$, for an oscillatory incompatibility with amplitude $\epsilon = 0.5$ and period $\Lambda T = 5$. b) $h(\infty)$ as a function of the square-root of the oscillation period, T for various amplitudes, ϵ . The inset illustrates further fix-point distances for $\epsilon = 0.5$

aration distance, $h(\infty) \approx 9.6w$.

Figure 2b shows how the fix-point distance, $h(\infty)$, depends on the amplitude, ϵ , and period, ΛT of the oscillation. For very fast oscillations, $T < T^*$, interfaces attract each other and annihilate, *i.e.*, there is no non-trivial fix-point distance, $h(\infty) > 0$; in accord with the prediction of Szleifer and co-workers the driven system behaves similar to an equilibrium system with time-averaged interactions [4, 5]. For slower oscillations, however, there emerges a preferred distance, $h(\infty)$, between the interfaces, and it increases with the period of the oscillations of incompatibility. The amplitude of the oscillations, ϵ , slightly shifts the threshold period, T^* , to smaller values but has only a minor influence on $h(\infty)$ for larger periods. The inset of Figure 2b illustrates that there exist multiple preferred distances for a fixed oscillation period T ; in the following we focus on the smallest non-trivial $h(\infty)$, observed in

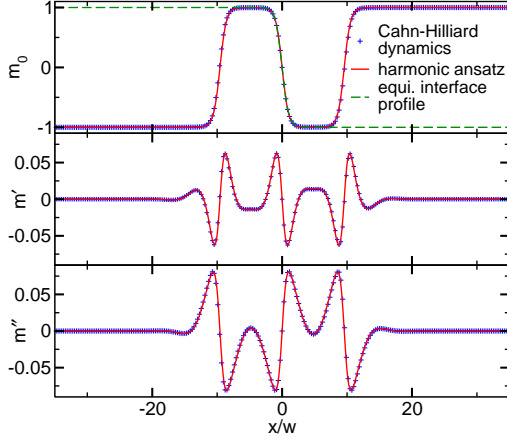


Figure 3: Harmonic analysis of the profile after the fix-point has been approached for $\epsilon = 0.5$ and $\Lambda T = 5$. The upper-panel presents the period-averaged profile, $m_0(x) = \lim_{t \rightarrow \infty} \bar{m}(x, t)$, whereas the lower panels show the in-phase and out-of-phase oscillations. Crosses correspond to the results of the numerical Cahn-Hilliard dynamics whereas the solid lines are the solution of Equation 4.

the numerical Cahn-Hilliard dynamics.

To analyze these findings, we decompose the time-dependent order-parameter profile, $m(x, t)$, in the form

$$m(x, t) \approx m_0(x) + \epsilon [m_1(x)e^{i\omega\Lambda t} + \text{c.c.}] \quad \text{with } \omega = \frac{2\pi}{\Lambda T} \quad (3)$$

after the fix-point distance has been approached. Higher harmonics are ignored. m_0 is the time-averaged profile for $t \rightarrow \infty$, and $m' = -2\epsilon\Im(m_1)$ and $m'' = 2\epsilon\Re(m_1)$ denote the in-phase and out-of-phase oscillations, respectively. Figure 3 shows that m_0 closely resembles the equilibrium profile with the time-averaged $\bar{\alpha} = 1$, whereas the in-phase and out-of-phase contributions exhibit an additional spatial structure that dictates $h(\infty)$.

To make progress, we insert this harmonic ansatz (3) into the kinetic equation (2), approximate $\alpha(t) \approx 1 + \frac{4\epsilon}{\pi} \sin \omega\Lambda t + \dots$, and obtain to leading orders in multiples of the frequency ω

$$0 = -m_0 + m_0^3 - \nabla^2 m_0 + \epsilon^2 \left[\frac{4}{\pi} \Im(m_1) + 6m_0|m_1|^2 \right] \quad (4)$$

$$i\omega m_1 = \nabla^2 \left(\frac{2i}{\pi} m_0 + (3m_0^2 - 1)m_1 - \nabla^2 m_1 \right)$$

where we have twice integrated the first equation with respect to x , using zero-flux boundary conditions and $m(-x) = -m(x)$. The numerical solution of these equations is also shown in Figure 3 as lines, indicating excellent agreement between our ansatz (3) and the long-time, numerical solution of the Cahn-Hilliard dynamics.

In Figure 2 we observe that the convergence of the interface distance, $h(t) \rightarrow h(\infty)$, is much slower than

an oscillation period, T . We exploit this time-scale separation by assuming that the profile, $\bar{m}(x, t) \equiv \frac{1}{T} \int_t^{t+T} dt' m(x, t')$, averaged over one period is dictated by the slow dynamics of $h(t)$, whereas the oscillatory part of the profile rapidly adjusts to $\bar{m}(x, t)$. Thus, we can use Equation 4 with m_0 replaced by \bar{m} to obtain m_1 as a functional of \bar{m} .

Inserting this functional $m_1[\bar{m}]$ into the Cahn-Hilliard equation (2), we obtain an approximation for the slow dynamics of $\bar{m}(x, t)$

$$\frac{\partial \bar{m}}{\partial t} = \nabla \frac{\Lambda}{k_B T N} \nabla (\bar{\mu} + \epsilon^2 \mu_2) \quad (5)$$

$$\text{with } \frac{\bar{\mu}}{k_B T N} = \frac{1}{k_B T N} \frac{\delta \bar{\mathcal{F}}}{\delta \bar{m}} = -\bar{m} + \bar{m}^3 - \nabla^2 \bar{m} \quad (6)$$

$$\frac{\mu_2}{k_B T N} = \frac{4}{\pi} \Im(m_1[\bar{m}]) + 6\bar{m}|m_1[\bar{m}]|^2 \quad (7)$$

where $\bar{\mathcal{F}}$ is the original Ginzburg-Landau free-energy functional (1) with the time-averaged incompatibility $\bar{\alpha} = 1$.

In the Supplementary Information (SI) we show that we can approximate the additional term as the derivative of a Lyapunov functional, $\mu_2 \approx \frac{\delta \mathcal{L}_2}{\delta \bar{m}}$, with

$$\frac{\mathcal{L}_2}{k_B T N} = -\frac{1}{2} \int dx dy \nabla \bar{m}(x) K(x - y) \nabla \bar{m}(y). \quad (8)$$

Thus, the time evolution of the slow period-averaged profile, $\bar{m}(x, t)$, approximately follows a Cahn-Hilliard dynamics with the effective free-energy functional $\mathcal{F}_{\text{eff}}[\bar{m}] = \bar{\mathcal{F}}[\bar{m}] + \epsilon^2 \mathcal{L}_2[\bar{m}]$. In particular, fix-points of the oscillatory dynamics correspond to extrema of $\mathcal{F}_{\text{eff}}[\bar{m}]$. Using a sharp-interface approximation for $\bar{m}(x, t)$, we obtain (see SI)

$$F_{\text{eff}}(h) = \mathcal{F}_{\text{eff}}[\bar{m}] = 2g(h) - g(2h) \quad (9)$$

$$\text{with } g(h) = 4k_B T N \epsilon^2 K(|h|) + \text{const} \quad (10)$$

The kernel, K , in Equation 8 is the sum of two damped, spatially periodic modulations (see SI)

$$K(h) = \Re \left(c_+ e^{-\lambda_+ |h|} + c_- e^{-\lambda_- |h|} \right) \quad \text{with} \quad (11)$$

$$\lambda_{\pm}^2 = 1 \pm \sqrt{1 - i\omega} \quad \text{and} \quad c_{\pm} = \frac{2}{\pi^2 \lambda_{\pm} (1 - \lambda_{\pm}^2)} \quad (12)$$

For slow oscillations, $\omega \ll 1$, we obtain $\lambda_+ \approx 2$ and $\lambda_- \approx \sqrt{i\omega}/2$. Since $1/\Im(\lambda_-)$ sets the characteristic length scale of the spatial modulation of K , this approximation suggest that the fix-point distance scales like $h(\infty) \sim \omega^{-1/2} \sim \sqrt{\Lambda T}$, in qualitative agreement with the numerical data in Figure 2. Additional information about the energy dissipation is provided in the SI.

Lastly, we illustrate the predictions of the Ginzburg-Landau model by particle-based simulations of a symmetric binary polymer blend. Binary polymer blends are well

described by the Ginzburg-Landau free-energy functional [16–18]. Importantly, the parameter α of the Ginzburg-Landau model is related to the distance, $\chi N - 2$, to the critical point of demixing, where N denotes the number of segments per polymer and χ the Flory-Huggins parameter. Thus, minor changes in the pairwise interactions, χ , between segments give rise to pronounced changes in the phase diagram. This sensitivity of the phase behavior of a polymer blend stems from the small translational entropy of the macromolecules and has also been exploited previously in the context of active polymer systems [19]. Moreover, recent experiments by Kriisa and Roth [20] have realized periodic jumps from the one-phase region of the phase diagram into the miscibility gap in polymer blends by subjecting a blend to an oscillating electric field. Additionally, the dynamics of polymers is slow in comparison to that of mixtures of low-molecular weight components and the predicted repulsion between interfaces occurs for moderate and slow oscillations. Thus binary polymer blends are a promising model system to validate our predictions.

The simulations use a soft, coarse-grained model [21] in conjunction with the single-chain-in-mean-field algorithm [22] implemented in the SOMA program [23]. The system of geometry $12 \times 2 \times 2R_{e0}^3$, where R_{e0} denotes the molecules' unperturbed end-to-end distance, is comprised of 61 440 polymers of $N = 16$ segments. There are two hard walls at $x = 0$ and $12R_{e0}$; one boundary attracts the A component of the blend whereas the other wall prefers the B component. The incompatibility toggles between $\chi N = 4 \pm 4$ with a period of $T = 800$ MC-steps [30]. Since we expect that the contribution of the oscillation to the interface potential increases like the square of the oscillation amplitude, we use a large variation of χN . The period, T , roughly corresponds to 0.42 the time a polymer diffuses a distance R_{e0} using Smart MC moves [24] or approximately 10 times the time τ_w a polymer diffuses the intrinsic width, $w_{SSL} \equiv \frac{R_{e0}}{\sqrt{6\chi N}}$ [25] of the interface at $\chi N = 4$. Further details about model and simulation technique are deferred to the SI, which includes Refs. [26, 27].

Figure 4 shows the time evolution of the distance, $h(t)$, for the oscillating χN -parameter and compares the result to that of the equilibrium system with the time-averaged incompatibility $\bar{\chi N} = 4$. In the latter, equilibrium case, the interfaces approach each other and two interfaces annihilate after around 3×10^7 MC-steps or $4 \times 10^5 \tau_w$. In equilibrium there remains only a single interface that fluctuates around the middle of the film (soft-mode phase [13, 28, 29]). In the driven system, where the incompatibility oscillates, there remain three interfaces in the system, and their mutual distances fluctuate around the preferred value, $h(\infty) \approx 3R_{e0} \approx 15w_{SSL}$ in the simulation that are extended to more than 6×10^8 MC-steps or 750 000 oscillation periods, T . The spacing of this lamellar structure of homopolymers, obtained by dissipative

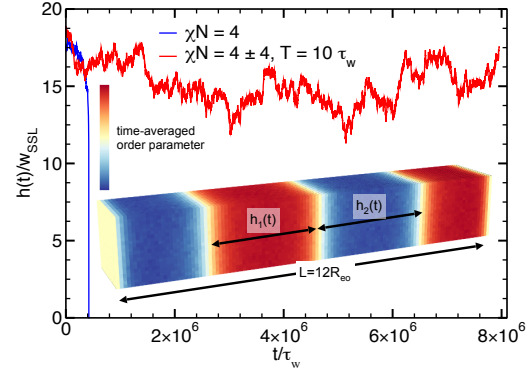


Figure 4: $h(t)$ as observed by particle-based simulations for constant and oscillating incompatibility, $\chi N = 4$ and $\chi N = 4 \pm 4$, respectively. $h(t) = \frac{h_1(t) + h_2(t)}{2}$ is the average of the two interface distances present in the system. Lengths are measured in units of the strong-segregation approximation of the interface width, $w_{SSL} = R_{e0}/\sqrt{6\chi N} \approx 0.2R_{e0}$. Times are measured in units of $t_w = w_{SSL}^2/D$, where D denotes the self-diffusion coefficient in the disordered phase. The inset presents the profile, $m_0(\mathbf{r})$, of the particle-based simulation averaged over the last 100T.

assembly, qualitatively agrees with the predictions of the Ginzburg-Landau model in Figure 2.

In summary we have analytically shown that temporal oscillations of the incompatibility between the species of a blend can qualitatively alter the interface potential from attractive to repulsive. The non-equilibrium phenomena occurs for moderate and slow oscillation periods, T , compared to the time the particles need to diffuse a distance comparable to the interfacial width. This dissipative assembly gives rise to preferred distances, $h(\infty)$, between planar interfaces, and this characteristic spacing of the lamellar morphology of the blend increases with the oscillation period like $h(\infty) \sim \sqrt{\Lambda T}$ for large ΛT , *i.e.*, by varying the periodicity we can tailor the interface spacing without altering the molecular architecture or interactions. Whereas the preferred distances, $h(\infty)$, are rather insensitive to the amplitude of the oscillations, we expect that the strength of the repulsion or the curvature of the interface potential around the preferred distance depends quadratically on the oscillation amplitude. Our particle-based simulations suggest that thin films of polymer blends are ideal model systems to validate our predictions because of the sensitivity of the phase behavior to minuscule changes of segmental interactions and the large time and length scales of polymer materials.

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- [1] M. Fialkowski, K. J. M. Bishop, R. Klajn, S. K. Smoukov, C. J. Campbell, and B. A. Grzybowski, *J. Phys. Chem. B* **110**, 2482 (2006).
- [2] T. D. Seeley, *Biological Bulletin* **202**, 314 (2002).
- [3] G. M. Whitesides and B. Grzybowski, *Science* **295**, 2418 (2002).
- [4] M. Tagliazucchi, E. A. Weiss, and I. Szleifer, *PNAS* **111**, 9751 (2014).
- [5] M. Tagliazucchi and I. Szleifer, *Faraday Discuss.* **186**, 399 (2016).
- [6] J. W. Swan, P. A. Vasquez, P. A. Whitson, E. M. Fincke, K. Wakata, S. H. Magnus, F. D. Winne, M. R. Barratt, J. H. Agui, R. D. Green, et al., *PNAS* **109**, 16023 (2012).
- [7] Z. M. Sherman and J. W. Swan, *ACS Nano* **10**, 5260 (2016).
- [8] Z. M. Sherman and J. W. Swan, *ACS Nano* **13**, 764 (2019).
- [9] J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).
- [10] P. C. Hohenberg and B. I. Halperin, *Rev. Mod. Phys.* **49**, 435 (1977).
- [11] P. G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985).
- [12] A. J. Bray, *Adv. Phys.* **43**, 357 (1994).
- [13] K. Binder, D. Landau, and M. Müller, *J. Stat. Phys.* **110**, 1411 (2003).
- [14] M. Schick, *Liquids at interfaces* **48** (1990).
- [15] K. Kawasaki and T. Ohta, *Physica A* **116**, 573 (1982).
- [16] K. Binder, *Phys. Rev. A* **29**, 341 (1984).
- [17] E. Reister, M. Müller, and K. Binder, *Phys. Rev. E* **64**, 041804 (2001).
- [18] M. Müller and F. Schmid, *Adv. Polym. Sci* **185**, 1 (2005).
- [19] J. Smrek and K. Kremer, *Phys. Rev. Lett.* **118**, 098002 (2017).
- [20] A. Kriisa and C. B. Roth, *ACS Macro Letters* **8**, 188 (2019).
- [21] M. Müller and K. C. Daoulas, *Phys. Rev. Lett.* **107**, 227801 (2011).
- [22] K. C. Daoulas and M. Müller, *J. Chem. Phys.* **125**, 184904 (2006).
- [23] L. Schneider and M. Müller, *Comp. Phys. Comm.* p. in press (2018).
- [24] M. Müller and K. C. Daoulas, *J. Chem. Phys.* **129**, 164906 (2008).
- [25] E. Helfand, *J. Chem. Phys.* **62**, 999 (1975).
- [26] M. Müller and K. Binder, *Macromolecules* **31**, 8323 (1998).
- [27] T. Young, *Philos. Trans. R. Soc. London* **95**, 65 (1805).
- [28] A. O. Parry and R. Evans, *Phys. Rev. Lett.* **64**, 439 (1990).
- [29] M. Müller and K. Binder, *Phys. Rev. E* **63**, 021602 (2001).
- [30] Since the minimal value of the incompatibility is $\chi N = 0$, corresponding to an ideal mixture, the period, T , cannot be made arbitrarily large, *i.e.*, $\Delta T \ll h(0)^2$, in order to retain a spatial modulation of m at all times. We choose this large amplitude in order to increase the strength of the additional contribution to the interface potential.