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Do We Understand the Collective Short-Time Dynamics in Multicomponent Polymer Melts?

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Phase separation in multicomponent polymer melts is a ubiquitous process in polymer engineering and consequently has also attracted abiding interest from simulation and theory. Whereas the equilibrium thermodynamics of macrophase separation and microphase separation in homopolymer blends and copolymers can be rather quantitatively described by Self-Consistent Field Theory (SCFT) or extensions that capture fluctuations, the kinetics of structure evolution poses challenges for a theoretical description. Examining simple, prototypical examples, we highlight the role of internal modes and indicate how Dynamic Self-Consistent Field Theory (D-SCFT) can be generalised to include the consequences of the subdiffusive single-chain dynamics for the collective kinetics on times comparable to the Rouse-relaxation time.

1 Introduction

Structure formation – macrophase separation or self-assembly into spatially modulated phases – in multicomponent polymer melts is ubiquitously employed in technical applications such as plastics toys made of rubber-toughened/high-impact polystyrene or soles of shoes and tire treads using poly(styrene-butadiene-styrene) (SBS) triblock copolymers. Blending two different polymers, one fabricates a composite with improved materials characteristics. By virtue of chain connectivity, long macromolecules have a small entropy of mixing, and a minuscule repulsion between the monomeric repeating units of different polymer species gives rise to domain formation. In these spatial regions, monomeric repeating units of one species are enriched and they are separated by interfaces from the domains of the other monomer species. The phase behaviour in equilibrium, the properties of interfaces between domains, and the self-assembly of block copolymers, where the two monomer species are covalently linked together into a macromolecule and macroscopic phase separation is avoided, are rather well understood. Since the long macromolecules in a melt strongly interdigitate, one molecule interacts with many neighbours and the equilibrium behaviour can be accurately described by SCFT.

In practical applications, however, thermodynamic equilibrium often is not achieved. For instance, in rubber-toughened polystyrene the hard, brittle polystyrene and the soft, deformable rubber do not macroscopically phase separate but rather form an assembly of interfaces with a characteristic domain size of micrometers. It is exactly this nonequilibrium morphology that gives rise to the improved impact resistance. Likewise, copolymers almost never form an ideal crystalline arrangement of domains. Instead, without external guiding fields, the morphology is riddled with defects and the perfecting of order is protracted.

Therefore it is important to understand the kinetics of structure formation in order to predict and tailor the structure evolution. The accurate knowledge of the equilibrium thermodynamics and the free energy of a phase-separated morphology is an excellent starting point. In the following, we consider an incompressible, two-component polymer melt, where $\phi_A(\mathbf{r},t)$ and $\phi_B(\mathbf{r},t) = 1 - \phi_A(\mathbf{r},t)$ denote the normalised number densities of monomer species, A and B. SCFT provides for each morphology, ϕ_A, an accurate value of the free energy, $\mathcal{F}[\phi_A]$, and of the exchange chemical potential, μ, assuming that the molecular conformations are in equilibrium with the instantaneous value of the density, $\phi_A(\mathbf{r},t)$. In a nonequilibrium situation, the chemical potential varies in space and its gradient gives rise to a current. Since the density is locally conserved, we obtain a model-B time evolution[1–3]

$$\frac{\partial \phi_{\mathbf{q},A}(t)}{\partial t} = -\mathbf{q}^2 \Lambda_{\mathbf{q}} \frac{\mu_{\mathbf{q}}[\phi_A]}{k_{\mathrm{B}}T} \tag{1}$$

where $\Lambda_{\mathbf{q}}$ denotes the Onsager coefficient that relates the gradient of the chemical potential to a current of the density. The wavevector-dependence of $\Lambda_{\mathbf{q}}$ signals the spatial nonlocality of the relation between chemical potential and current that stems from the chain connectivity. This kinetic equation forms the basis of D-SCFT.[4–12]

Consider an ideal mixture of two structurally and dynamically symmetric homopolymers with no repulsion between the two monomer species, $\chi_{\mathrm{FH}}N = 0$. Here, χ_{FH} and N denote the Flory-Huggins parameter and the chain length, respectively. Initially, at time $t = 0$, there is a small-amplitude, sinusoidal density modulation with wavevector $\mathbf{q}$. Within linear-response approximation, the chemical potential is linearly related to the amplitude of the density modulation, $\frac{\mu_{\mathbf{q}}}{k_{\mathrm{B}}T} = \frac{N}{S_{\mathbf{q}}}\phi_{\mathbf{q},A}$, where $S_{\mathbf{q}}$ denotes the static, collective structure factor. Inserting this expression into Eq. 1, we simply obtain

$$\phi_{\mathbf{q},A}(t) = \phi_{\mathbf{q},A}(0) \exp\left(-\mathbf{q}^2 \Lambda_{\mathbf{q}} \frac{N}{S_{\mathbf{q}}} t\right) \tag{2}$$

i. e. the density modulation exponentially decays with a wavevector-dependent relaxation time. By the same token, Eq. 1 also predicts that the collective, dynamic structure factor, $S_{\mathbf{q}}(t) \sim \langle \phi_{\mathbf{q},A}(t)\phi_{\mathbf{q},A}(0)\rangle$ decays exponentially in time at fixed $\mathbf{q}$.

On the other hand, since the mixture is ideal, the collective dynamic structure factor, $S_{\mathbf{q}}(t)$, is proportional to the dynamic form factor, $S^{(0)}_{\mathbf{q}}(t)$, of a single chain. Indeed, $S^{(0)}_{\mathbf{q}}(t)$ decays exponentially in time for $(\mathbf{q}R_{\mathrm{e}})^2 \to 0$ (with R_{e} being the root mean-squared end-to-end distance). In the opposite limit, $(\mathbf{q}R_{\mathrm{e}})^2 \gg 1$ and times, t, smaller than the Rouse time, τ_{R}, however, the subdiffusive behaviour of the monomer mean-squared displacement, $g_1(t)$, alters the decay. Qualitatively, one obtains[2]

$$\ln\frac{\phi_{\mathbf{q},A}(t)}{\phi_{\mathbf{q},A}(0)} = \ln\frac{S^{(0)}_{\mathbf{q}}(t)}{S^{(0)}_{\mathbf{q}}} \sim \mathbf{q}^2 g_1(t) \sim (\mathbf{q}R_{\mathrm{e}})^2\sqrt{\frac{t}{\tau_{\mathrm{R}}}} \qquad \text{for} \quad t \ll \tau_{\mathrm{R}} \tag{3}$$

In Fig. 1 we present our simulation data using a dense melt, $\sqrt{\bar{\mathcal{N}}} = 51\,200$, of finely discretised Gaussian chains, $N = 256$, within our soft, coarse-grained model.[14, 15] The simulations were performed with our parallel, GPU-accelerated program, SOMA.[16] Due to the softness of the potentials, macromolecular contours can cross each other in the course of their motion, and the single-chain dynamics is quantitatively described by the Rouse model.[17] Unlike Eq. 1, the simulations include thermal fluctuations but their effect is rather small because of the large invariant degree of polymerisation, $\bar{\mathcal{N}}$. Also the simulations do

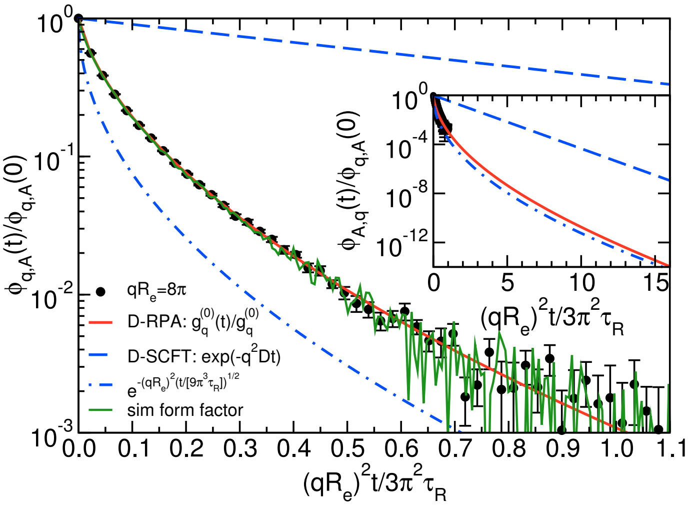

Figure 1. Relaxation of a density modulation with amplitude $\phi_{\mathbf{q},A}(t)$ at $qR_\mathrm{e} = 8\pi$ in a symmetric homopolymer blend at $\chi_\mathrm{FH}N = 0$. The decay of the amplitude in the simulation, (black circles), is compared with the dynamic, single-chain form factor, $S_\mathbf{q}^{(0)}(t)$ (red line – Rouse prediction, green line – simulation), and its limiting behaviours for long and short times (dashed and dashed-dotted blue lines, respectively). The inset illustrates the decay of the amplitude on longer time scales. Adapted from Ref. 13

not invoke the Random-Phase Approximation (RPA) approximation of a linear relation between density modulation and chemical potential.

The decay of the amplitude agrees quantitatively with the decay of the dynamic, single-chain form factor, and the semilogarithmic representation of the data highlights the nonexponential decay in time.

Thus, D-SCFT fails to account for the qualitative features of the collective kinetics of structure formation on short time scales. These scales, however, are important for a variety of processes and computational techniques:

- After a quench of a multicomponent melt from the homogeneous state deep into a (micro)phase-separated phase, initially, density fluctuations are strongly amplified, and the morphology obtained after this spinodal phase-separation dictates the subsequent ordering kinetics. The importance of the early-time dynamics holds, *a fortiori*, in the case that the structure formation is directed by external guiding fields, *e. g.* surface-directed spinodal decomposition or Directed Self Assembly (DSA).

- Process-Directed Self Assembly (PDSA) of copolymers tailors changes of thermodynamic control parameters, *e. g.* pressure or temperature, to reproducibly fabricate well-defined unstable states. The thermodynamic process is constructed such that this so-constructed unstable state relaxes into a new, metastable state with desired properties, *e. g.* a bicontinuous network morphology.[18, 19] This relaxation typically requires changes of density on the scale of the unit cell of the spatially modulated phase. Since the periodicity is on the order R_{e}, the concomitant time scale is on the order of the Rouse time, τ_{R}.

- Advancements in parallel computing enable the investigation of ever larger systems, however, relevant problems of larger systems often also entail longer time scales. Thus, computational techniques to extend the time scale of particle-based simulations have attracted abiding interest. For instance, the Heterogeneous Multiscale Method (HMM)[20–22] aims at predicting the time evolution by parameterising a dynamic continuum model on-the-fly, using *e. g.* a description similar to D-SCFT. In order to project the short-time kinetics into the future, the dynamic continuum model must be able to accurately describe both, the short-time and the long-time collective kinetics.

In the following, we outline a generalisation of Eq. 1 that accounts for the subdiffusive, single-chain dynamics by an Onsager coefficient that not only depends on the wavevector but, additionally, on the frequency, ω. This is equivalent to introducing memory effects into Eq. 1, which are qualitatively expected when coarse-graining a microscopic particle-based model into a continuum description that only retains the slow, locally conserved density fields.

2 Generalised Model-B Dynamics

The strong bonded forces do not only give rise to a wavevector-dependence of $\Lambda_{\mathbf{q}}$ in Eq. 1 but, additionally, result in a subdiffusive single-chain dynamics according to the Rouse model.[17] In order to account for the single-chain dynamics in the collective kinetics, Semenov[23] proposed the following generalisation of Eq. 1

$$\frac{\partial \phi_{\mathbf{q},A}(t)}{\partial t} = -\mathbf{q}^2 \int_{-\infty}^{t} \mathrm{d}\tau \; \Lambda_{\mathbf{q}}(t-\tau) \frac{\mu_{\mathbf{q}}[\phi_{\mathbf{q},A}(\tau)]}{k_{\mathrm{B}}T} \tag{4}$$

with a time-dependent Onsager coefficient, $\Lambda_{\mathbf{q}}(t)$. Recently, using the Dynamic Random-Phase Approximation (D-RPA),[2, 23–25] we have derived an explicit expression for the Fourier-Laplace transform, $\tilde{\Lambda}_{\mathbf{q}}(\omega)$ of this generalised Onsager coefficient,[13]

$$\frac{i\omega}{\mathbf{q}^2 N \tilde{\Lambda}_{\mathbf{q}}(\omega)} = \frac{\tilde{\chi}_{\mathbf{q},AA} + 2\tilde{\chi}_{\mathbf{q},AB} + \tilde{\chi}_{\mathbf{q},BB}}{\tilde{\chi}_{\mathbf{q},AA}\tilde{\chi}_{\mathbf{q},BB} - (\tilde{\chi}_{\mathbf{q},AB})^2} - \frac{1}{S_{\mathbf{q}}} \tag{5}$$

in terms of the dynamic susceptibilities

$$\tilde{\chi}_{\mathbf{q},\alpha\beta}(\omega) \equiv -\int_{0}^{\infty} \mathrm{d}t \; \frac{\partial S^{(0)}_{\mathbf{q},\alpha\beta}(t)}{\partial t} e^{-i\omega t} = S^{(0)}_{\mathbf{q},\alpha\beta}(0) - i\omega \tilde{S}^{(0)}_{\mathbf{q},\alpha\beta}(\omega) \tag{6}$$

with $S^{(0)}_{\mathbf{q},\alpha\beta}(t)$ being the concentration-weighted, dynamic, single-chain form factors of monomer species, α and β. $S_{\mathbf{q}}$ is the static, collective structure factor at $\chi_{\mathrm{FH}}N = 0$.

Notably, this Onsager coefficient does not depend on the strength of the pairwise interaction, $\chi_{\mathrm{FH}}N$. Thus, Eq. 4 conserves the separation between the thermodynamic force, $\nabla\mu$, and the kinetic coefficient that relates this thermodynamic force to a current.

To illustrate the consequences of the time-dependence of the Onsager coefficient, we consider an ideal, symmetric homopolymer blend with $\chi_{\rm FH}N = 0$. Eq. 5 simplifies to

$$\tilde{\Lambda}_{\mathbf{q}}(\omega) = \bar{\phi}_A(1-\bar{\phi}_A)\frac{g_{\mathbf{q},1}}{\mathbf{q}^2}\left[\frac{g_{\mathbf{q},1}}{\tilde{g}_{\mathbf{q},1}(\omega)} - i\omega\right] = \frac{S_{\mathbf{q}}}{N\mathbf{q}^2\tau_{\rm R}}\left[\frac{g_{\mathbf{q},1}\tau_{\rm R}}{\tilde{g}_{\mathbf{q},1}(\omega)} - i\omega\tau_{\rm R}\right] \tag{7}$$

where $g_{\mathbf{q},f}$ and $\tilde{g}_{\mathbf{q},f}(\omega)$ denote the Debye function that characterises the static, single-chain form factor of the fraction, f, of a Gaussian chain and the Laplace transform of the dynamic, single-chain form factor, respectively. $S_{\mathbf{q}} = \bar{\phi}_A(1-\bar{\phi}_A)Ng_{\mathbf{q},1}$ is the collective structure factor of a symmetric blend at $\chi_{\rm FH}N = 0$.

Inserting this frequency-dependent Onsager coefficient in the Laplace transform of Eq. 4,

$$i\omega\tilde{\phi}_{\mathbf{q},A}(\omega) - \phi_{\mathbf{q},A}(0) = -\mathbf{q}^2\tilde{\Lambda}_{\mathbf{q}}\frac{\tilde{\mu}_{\mathbf{q}}}{k_{\rm B}T} \tag{8}$$

where $\phi_{\mathbf{q},A}(0)$ denotes the starting morphology at $t = 0$, we obtain

$$\phi_{\mathbf{q},A}(0) = \frac{g_{\mathbf{q},1}}{\tilde{g}_{\mathbf{q},1}(\omega)}\tilde{\phi}_{\mathbf{q},A} \qquad \text{or} \qquad \phi_{\mathbf{q},A}(t) = \phi_{\mathbf{q},A}(0)\frac{g_{\mathbf{q},1}(t)}{g_{\mathbf{q},1}} = \phi_{\mathbf{q},A}(0)\frac{S^{(0)}_{\mathbf{q}}(t)}{S^{(0)}_{\mathbf{q}}} \tag{9}$$

in accord with Eq. 3 and the simulation data in Fig. 1.

In the case that the generalised Onsager coefficient, $\tilde{\Lambda}_{\mathbf{q}}(\omega)$, does not depend on ω, we recover Eq. 1. To this end, the following sequence of approximations is often employed:

1. We define $\varphi_{\mathbf{q},\alpha\beta}(t) \equiv S^{(0)}_{\mathbf{q},\alpha\beta}(t)/S^{(0)}_{\mathbf{q},\alpha\beta}(0)$ in order to separate the equilibrium thermodynamic properties, characterised by the static, single-chain form factor, $S^{(0)}_{\mathbf{q},\alpha\beta}(0)$, from the dynamics. $\varphi_{\mathbf{q},\alpha\beta}(0) = 1$ and $\varphi_{\mathbf{q},\alpha\beta}(t) \to 0$ for $t \to \infty$.

2. Ignoring the details of the temporal relaxation, we can crudely approximate

   $$\varphi_{\mathbf{q},\alpha\beta}(t) \approx e^{-t/\tau_{\mathbf{q},\alpha\beta}} \quad \text{and} \quad \tilde{\chi}_{\mathbf{q},\alpha\beta} \approx \frac{S^{(0)}_{\mathbf{q},\alpha\beta}}{1 + i\omega\tau_{\mathbf{q},\alpha\beta}} \tag{10}$$

   by an exponential decay with a wavevector-dependent timescale, $\tau_{\mathbf{q},\alpha\beta}$. Such an approximation is appropriate for symmetric homopolymer blends on large length scales, but it fails for copolymers (as shown below), and it is inappropriate for short length scales, *c.f.* Fig. 1.

3. Assuming that the relaxation times of the different dynamic, single-chain form factors were identical, $\tau_{\mathbf{q},\alpha\beta} \approx \tau_{\mathbf{q}}$, which is *e. g.* appropriate for symmetric homopolymer blends or the scale-free Porod limit, $(\mathbf{q}R_{\rm e})^2 \gg 1$ and $t \ll \tau_{\rm R}$, in symmetric copolymers, we obtain a frequency-independent Onsager coefficient

   $$\tilde{\Lambda}_{\mathbf{q}}(\omega) \approx \frac{S_{\mathbf{q}}}{N\mathbf{q}^2\tau_{\mathbf{q}}} \tag{11}$$

   where $S_{\mathbf{q}}$ is the collective structure factor of the ideal mixture, $\chi_{\rm FH}N = 0$. This gives rise to an Onsager coefficient, $\Lambda_{\mathbf{q}}(t) \approx \frac{S_{\mathbf{q}}}{N\mathbf{q}^2\tau_{\mathbf{q}}}\delta(t)$, that is local in time.

4. Assuming a diffusive relaxation, $\tau_{\mathbf{q}} \approx \frac{3\pi^2}{(\mathbf{q}R_{\mathrm{e}})^2}\tau_{\mathrm{R}} = \frac{1}{\mathbf{q}^2 D}$ with $D = \frac{R_{\mathrm{e}}^2}{3\pi^2\tau_{\mathrm{R}}}$ within the Rouse model being the single-chain self-diffusion coefficient, one arrives at the Onsager coefficient of D-SCFT,

$$\Lambda_{\mathbf{q}}^{\mathrm{D-SCFT}} \approx \frac{S_{\mathbf{q}}}{N} D \tag{12}$$

Specifically, for an ideal mixture – homopolymer blend or diblock copolymer melt – with $\chi_{\mathrm{FH}}N = 0$, small-amplitude density modulations give rise to $\frac{\mu_{\mathbf{q}}}{k_{\mathrm{B}}T} = \frac{N}{S_{\mathbf{q}}}\phi_{\mathbf{q},A}$. Thus Eqs. 1 and 12 yield the simple, general D-SCFT prediction

$$\phi_{\mathbf{q},A}(t) = \phi_{\mathbf{q},A}(0)\exp(-\mathbf{q}^2 Dt) \qquad \text{for} \quad \chi_{\mathrm{FH}}N = 0 \tag{13}$$

i. e. density modulations decay *via* the diffusion of the macromolecules' centre of mass. This prediction agrees with the decay of the dynamic, single-chain form factor on large scales but fails to describe the simulation data for $(\mathbf{q}R_{\mathrm{e}})^2 \gg 1$, as demonstrated in Fig. 1.

Using extensive computer simulations on JUWELS through the NIC, we can validate each of these approximations, illustrate their consequences, and quantify to what extent the generalised model-B dynamics, Eq. 4, improves the description of structure evolution.

3 Validation: Decay of a Large-Scale Density Modulation in a Symmetric Copolymer Melt

For a symmetric copolymer melt at $\chi_{\mathrm{FH}}N = 0$, the Onsager coefficient of D-SCFT takes the simple form $\Lambda_{\mathbf{q}}^{\mathrm{D-SCFT}} = \left(g_{\mathbf{q},1/2} - \frac{1}{4}g_{\mathbf{q},1}\right) D$, and D-SCFT predicts that density modulations, $\phi_{\mathbf{q},A}(t)$, exponentially decay in time with the relaxation time $\tau_{\mathbf{q}} = \frac{1}{\mathbf{q}^2 D}$, *i. e.* the larger the scale of the density modulation the slower is its temporal decay.

In Fig. 2 we present the simulation data for the decay of a density modulation in a melt of symmetric diblock copolymers with $\chi_{\mathrm{FH}}N = 0$. Two wavevectors, $qR_{\mathrm{e}} = 2\pi/3$ and $2\pi/6$, are considered. The data are compared to the predictions of D-SCFT and two marked discrepancies are observed: (i) The decay of the density modulation in the particle-based simulation is much faster than predicted by D-SCFT, and (ii) the relaxation time in the simulation is largely independent from the wavevector.

We again expect that the density modulation decays like the dynamic, collective structure factor, $S_{\mathbf{q}}(t)$, that can be expressed in terms of dynamic, single-chain form factors by D-RPA. For $\chi_{\mathrm{FH}}N = 0$ we obtain

$$\frac{\phi_{\mathbf{q},A}(t)}{\phi_{\mathbf{q},A}(0)} = \frac{S_{\mathbf{q}}(t)}{S_{\mathbf{q}}} \overset{\text{D-RPA}}{\approx} \frac{g_{\mathbf{q},1/2}(t) - \frac{1}{4}g_{\mathbf{q},1}(t)}{g_{\mathbf{q},1/2} - \frac{1}{4}g_{\mathbf{q},1}} \tag{14}$$

To make progress, we note that, on large length scales, $(\mathbf{q}R_{\mathrm{e}})^2 \ll 1$, the dynamic form factor, $g_{\mathbf{q},f}(t)$, of a fraction, f, of a Rouse chain takes the form

$$g_{\mathbf{q},f}(t) \approx g_{\mathbf{q},f}e^{-\mathbf{q}^2 Dt - (\mathbf{q}R_{\mathrm{e}})^2 h_f(t)} \tag{15}$$

where the function $h_f(t)$ characterises the deviation from the diffusive relaxation due to internal modes for $t \ll \tau_{\mathrm{R}}$. $h_f(t)$ monotonically increases from $h_f(0) = 0$ to a plateau value,

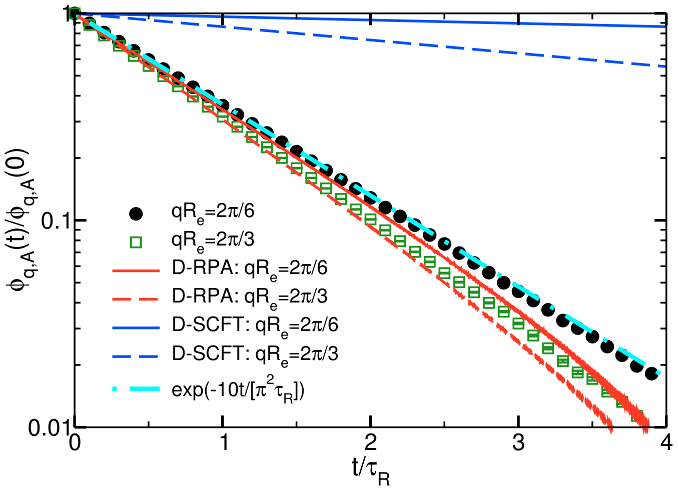

Figure 2. Relaxation of large-wavelength density fluctuation with $qR_\mathrm{e} = 2\pi/6$ and $2\pi/3$ in a disordered symmetric copolymer melt, $\chi_\mathrm{FH} = 0$. The simulation data (circles, squares) are compared to the prediction of D-RPA (red lines), D-SCFT (blue lines), and the approximation of the generalised model B (cyan line) according to Eq. 19 for $(\mathbf{q}R_\mathrm{e})^2 \to 0$ and $\omega\tau_\mathrm{R} \to 0$. Adapted from Ref. 13.

$h_f(\infty)$, for $t \gg \tau_\mathrm{R}$. Note that this function identically vanishes, when we consider an entire Rouse chain, *i. e.* $h_1(t) \equiv 0$, and $h_{1/2}(t)$ tends to its plateau value, $h_{1/2}(\infty) = 1/36$, on the time scale τ_R. Using Eq. 15 in Eq. 14, we obtain[13]

$$\frac{\phi_{\mathbf{q},A}(t)}{\phi_{\mathbf{q},A}(0)} \approx \left[1 - \frac{h_{1/2}(t)}{h_{1/2}(\infty)}\right] e^{-\mathbf{q}^2 Dt} + \mathcal{O}\left((\mathbf{q}R_\mathrm{e})^2\right) \tag{16}$$

Thus, the decay of the large-scale density modulation arises from the first factor, which approaches zero on the time scale, τ_R, that is independent from the wavevector, $\mathbf{q}$ – in agreement with the simulation data in Fig. 2.

In the case of symmetric copolymer melts, Eq. 5, adopts the simple form

$$\tilde{\Lambda}_\mathbf{q}(\omega) = \left(g_{\mathbf{q},1/2} - \frac{1}{4}g_{\mathbf{q},1}\right) \frac{1}{\mathbf{q}^2\tau_\mathrm{R}} \left[\frac{\left(g_{\mathbf{q},1/2} - \frac{1}{4}g_{\mathbf{q},1}\right)\tau_\mathrm{R}}{\tilde{g}_{\mathbf{q},1/2}(\omega) - \frac{1}{4}\tilde{g}_{\mathbf{q},1}(\omega)} - i\omega\tau_\mathrm{R}\right] \tag{17}$$

On large length scales, $g_{\mathbf{q},1/2} - \frac{1}{4}g_{\mathbf{q},1} = \frac{(\mathbf{q}R_\mathrm{e})^2}{144} + \mathcal{O}\left((\mathbf{q}R_\mathrm{e})^4\right)$ and, in the same limit, we use the Rouse model to compute

$$\tilde{g}_{\mathbf{q},1/2}(\omega) - \frac{1}{4}\tilde{g}_{\mathbf{q},1}(\omega) \approx \frac{2(\mathbf{q}R_\mathrm{e})^2}{3\pi^4} \sum_{p \text{ odd}} \frac{1}{p^4(\mathbf{q}^2 D + \frac{p^2}{\tau_\mathrm{R}} + i\omega)} \tag{18}$$

and obtain the frequency-dependent Onsager coefficient

$$\tilde{\Lambda}_{\mathbf{q}}(\omega) \approx \frac{\pi^6 D}{4608}\left[\frac{1}{\sum_{p\ \mathrm{odd}} \frac{1}{p^4(\mathbf{q}^2 D\tau_{\mathrm{R}}+p^2+i\omega\tau_{\mathrm{R}})}} - i\omega\tau_{\mathrm{R}}\right] \tag{19}$$

In marked contrast to $\Lambda_{\mathbf{q}}^{\mathrm{D-SCFT}}$, this generalised Onsager coefficient remains finite for $(\mathbf{q}R)^2 \to 0$, indicating that the relaxation stems from internal modes.[24, 25] Specifically, for $(\mathbf{q}R_{\mathrm{e}})^2 \to 0$ and $\omega\tau_{\mathrm{R}} \to 0$, we find $\tilde{\Lambda}_{\mathbf{q}}(\omega) \to 5D/24$, corresponding to a time-independent Onsager coefficient, $\Lambda_{\mathbf{q}} \to 5D/24$, that qualitatively differs from the D-SCFT prediction. This approximate Onsager coefficient yields a single-exponential decay, $\phi_{\mathbf{q},A}(t) = \phi_{\mathbf{q},A}(0)\exp(-10t/[\pi^2\tau_{\mathrm{R}}])$ that is in excellent agreement with the simulation data, see Fig. 2.

4 Concluding Remarks

Using computer simulations of a soft, coarse-grained model[14, 15] in conjunction with the parallel, GPU-accelerated program SOMA,[16] we have investigated the short-time dynamics of multicomponent polymer melts.[13] Even for the most basic kinetic process – the decay of a density modulation in an ideally miscible system, $\chi_{\mathrm{FH}}N = 0$ – we have found significant deviations from D-SCFT.[4–12] In the case of a miscible homopolymer blend, we observed that the amplitude of a short-scale density modulation does not exponentially decay in time and is much faster than predicted by D-SCFT. We trace this failure of D-SCFT back to the subdiffusive mean-squared monomer displacement for times smaller than τ_{R}. Likewise, for the temporal decay of a large-scale density modulation in symmetric diblock copolymers, we observe that the relaxation time scale is independent from the wavevector in the limit $(\mathbf{q}R_{\mathrm{e}})^2 \to 0$, whereas D-SCFT predicts $\tau_{\mathbf{q}} = 1/(\mathbf{q}^2 D)$.

We have demonstrated that these deviations can be accounted for by a generalised model B with a wavevector- and frequency-dependent Onsager coefficient.[23] Using D-RPA, we have obtained an explicit expression for the Onsager coefficient in terms of the dynamic, single-chain form factors.[13] Thereby a direct connection between the nontrivial single-chain dynamics and the generalised Onsager coefficient is established.

Combining this generalised Onsager coefficient with the accurate chemical potential of SCFT we expect that our approach can also be extended to the nonlinear regime, where D-RPA breaks down but SCFT still provides an accurate estimate for the chemical potential.

Our present validation of the generalised model B has been limited to all but the simplest, prototypical cases. For practical applications, multicomponent systems with a repulsion between different monomer species, $\chi_{\mathrm{FH}}N > 0$, are important as well as systems with structural and dynamic asymmetries. Moreover, our studies have been restricted to unentangled polymers because our soft, coarse-grained particle-based model does not enforce noncrossability of molecular contours and analytic predictions for the dynamic, single-chain form factors are available within the Rouse model.[17] Additionally, it is interesting to investigate more complex chain architectures, such as *e. g.* multiblock copolymers, star or branched polymers, and multicomponent polymer networks. In these examples the regime of subdiffusive dynamics is significantly more extended in time.

Given that the phase separation and self-assembly of complex multicomponent molecules have attracted abiding interest and that experimentally observed structures do not always correspond to equilibrium phases but, instead, are dictated by the kinetics of structure formation, we expect that the outlined techniques will find ample applications to explore the kinetics of structure formation in these fascinating materials.

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