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Dynamics of Polydisperse Polymer Mixtures

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ABSTRACT: We develop a general analysis of the diffusive dynamics of polydisperse polymers in the presence of chemical potential gradients, within the context of the tube model (with all species entangled). We obtain a set of coupled dynamical equations for the time evolution of the polymeric densities in a form proposed phenomenologically in recent work by Clarke, but with explicitly derived coefficients. For the case of chemical polydispersity (a set of chains that are identical except for having a continuous spectrum of enthalpic interaction strengths) the coupled equations can be fully solved in certain cases. For these, we study the linearized mode spectrum following a quench through the spinodal, with and without a passive (polymeric) solvent. We also study the more conventional case of length polydisperse chains in a poor solvent. Here the mode structure is more complicated and exact analysis difficult, but enough progress can still be made to gain some qualitative insight. We briefly discuss the modifications required to allow for the presence of unentangled, low molecular weight species in the system.

1. Introduction

There has been significant recent progress in the study of polydisperse polymers under equilibrium conditions. This includes work on static phase coexistence (reviewed in ref 1) and on interfacial thermodynamics in situations of spatial inhomogeneity.[2] Much of this work has been based on exploiting the fact that, within a standard Flory−Huggins picture of the polymeric systems involved, the excess free energy depends only on a small number of moments of the distribution of polymer lengths or, if the chains are polydisperse not in length but in some other feature, moments of the distribution of that feature. An example of the latter is chemical polydispersity, where chains have, in effect, a continuous distribution of χ parameters[1] but are otherwise identical; see also ref 3. (This can be realized experimentally by having a random copolymer in which the fraction of each type of monomer varies from chain to chain.) This moment structure carries over into the nonlocal excess free energy for inhomogeneous states, at least in limiting cases;[2] the moments become local moment density fields which depend nonlocally on the number densities of the individual polymeric species.

Much less is understood about the dynamics of polydisperse systems. Consider, for example, the early stages of spinodal decomposition following a quench into the unstable regime. For length polydispersity this has been studied in recent papers by Clarke[4] and by Warren,[5] but even the qualitative picture remains far from clear. One complicating factor behind this is that, for the normal case of length polydispersity, the simplifications brought about by the moment structure in the excess free energy do not lead to any obvious simplification of the dynamical equations: the natural coordinates for dynamics are not the moment densities, but the species monomer densities. (See ref 6 for a related discussion, in the context of colloids, addressed there via a perturbation theory in the narrowness of the size distribution.) Previous treatments of length polydispersity mapped the polydisperse situation into that of a mixture with a finite set of components by matching the lowest moments of the distribution.[7] For chemical polydispersity, however, there is significantly more carryover of the simplifications in the excess free energy to dynamics. The basic reason for this is that such chains are all dynamically degenerate (they have the same mobilities and structures) even though they are subject to different thermodynamic forces. Hence they can, in effect, be linearly recombined into moment densities, which diagonalize the thermodynamics. This is not possible for length polydispersity where the mobilities (and also the structure factors) of the polymeric species vary from one chain to another; in general, there is then no practical way to simultaneously diagonalize the thermodynamic and the mobility-related factors in the diffusion matrix.

In this paper, we develop a general formalism which includes, in principle, both chemical and length polydispersity (among others). In part, this formalism resembles that of Clarke,[4] but it is more general and supplements his phenomenological equations with explicit calculation of the coefficients from a microscopic model based on the tube dynamics. The latter approach was developed previously in a similar context (but without polydispersity) by Brochard.[8] These developments are presented in sections 2 and 3. In section 4, we present the free energy functional employed thereafter, and in section 5, we address in some detail the case of chemically polydisperse chains. These are considered in the melt and also in the presence of a passive solvent (one that does not have any direct enthalpic preference between the chemically polydisperse species). For the first case, the dynamical equations can be solved in detail; in the second case, we find a relatively simple mode structure requiring a two-by-two diagonalization whose details involve the shape of the polydisperse distribution in the homogeneous (parent) phase. This simplifies further for the case of a symmetric parent.

These results are then contrasted with those in the literature for the case of length polydispersity, which

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is studied further in section 6. Although, for the reasons stated above, the same level of progress cannot be made in this case, the formal structure of the problem (which involves, for example, a coupling to negative moments of the length distribution) is rather interesting. We are able to make some indicative progress by using a truncation scheme along the lines suggested by Warren,[5] and indicate avenues for further analysis. Section 7 contains our conclusions.

2. System and Basic Dynamics

We consider a polydisperse mixture of polymers. Each species is characterized by the chain number density $\rho_i(\mathbf{r})$. (We use a discrete notation, but the continuum limit can be taken finally, as required.) The corresponding monomer density is written as $\phi_i(\mathbf{r}) = N_i\rho_i(\mathbf{r})$, where N_i is the polymerization index of species i; note that this neglects terms $O(\nabla^2)$ terms; see section 4. Depending on the kind of polydispersity, N_i may be the same for different species. When dealing with polydisperse mixtures, the chain number density is the natural density to work with (as opposed to monomer density), because it characterizes the overall motion of the chain.

The continuity equation for polymer species i is

$$\frac{\partial \rho_i}{\partial t} = -\nabla\cdot(\rho_i \mathbf{v}_i) \tag{1}$$

where $\mathbf{v}_i$ is the mean velocity of species i, and $\rho_i\mathbf{v}_i = \mathbf{J}_i^{\mathrm{t}}$ is the total flux of that species. We can rewrite this equation explicitly as a diffusion equation by introducing the barycentric velocity as a reference velocity. The barycentric velocity $\mathbf{v}^{\mathrm{m}}$ is defined as

$$\mathbf{v}^{\mathrm{m}} = \sum_i \phi_i \mathbf{v}_i \tag{2}$$

Since the polymer mixture is assumed to be incompressible, we have that at every point $\sum_i\phi_i = 1$. (So far this does not exclude the possibility of a low molecular weight "solvent" among the species i.) This mass conservation property implies that $\mathbf{v}^{\mathrm{m}}$ is solenoidal, i.e., $\nabla\cdot\mathbf{v}^{\mathrm{m}} = 0$. If we introduce the following time derivative

$$\frac{\mathrm{d}}{\mathrm{d}t} \equiv \frac{\partial}{\partial t} + \mathbf{v}^{\mathrm{m}}\cdot\nabla \tag{3}$$

then the continuity equation, eq 1, can be rewritten as

$$\frac{d\rho_i}{\mathrm{d}t} = -\nabla\cdot\mathbf{J}_i \tag{4}$$

which has the form of a diffusion equation, expressed in terms of the diffusive flux $\mathbf{J}_i$ of species i, which coincides with the total flux only when measured in the barycentric frame of reference:

$$\mathbf{J}_i \equiv \mathbf{J}_i^{\mathrm{t}} - \rho_i\mathbf{v}^{\mathrm{m}} = \rho_i(\mathbf{v}_i - \mathbf{v}^{\mathrm{m}}) \tag{5}$$

We could, of course, have chosen any other reference velocity in place of $\mathbf{v}^{\mathrm{m}}$, although in that case the continuity equation does not have the convenient form of eq 4. An exception is the special case of mechanical equilibrium ($\nabla p = 0$); for this situation, the diffusive flux can be defined with respect to any reference velocity leading to the same expression for it. However, in general, concentration gradients in our system will induce pressure gradients and thence fluid flow, which is handled by use of the barycentric frame.

2.1. Phenomenological Model. Following Clarke's phenomenological model,[4] we can start from the diffusive (Cahn–Hilliard) dynamics expressed in eq 4 and *assume* that the diffusive flux of species i has the expression

$$\mathbf{J}_i = \frac{M_i^0}{N_i}\nabla\mu_i + \rho_i\mathbf{v}^r \tag{6}$$

where μ_i is the chemical potential of species i, and M_i^0 is a phenomenological mobility coefficient, and $\mathbf{v}^r$ is an unknown reference velocity that is common to all polymer species. We can use the incompressibility condition (local conservation of mass) to fix this reference velocity because $\sum_i N_i\mathbf{J}_i = 0$. The diffusive flux then simplifies to

$$\mathbf{J}_i = \sum_k M_{ik}\nabla\mu_k \tag{7}$$

where we identify the mobility matrix

$$M_{ik} = \frac{M_i^0}{N_i}\delta_{ik} - \rho_i M_k^0 \tag{8}$$

This model does not provide explicit expressions for the mobilities M_i^0. It seems reasonable to assume that they are proportional to the density, suggesting the more general form

$$M_{ik} = A_i\rho_i\delta_{ik} - \rho_i\rho_k B_{ik} \tag{9}$$

where for length polydispersity A_i and B_{ik} will depend on N_i. In general, they might also depend on any other polydisperse feature such as the fraction of monomers of given chemical type on chain of species i. In the next section, we develop a particular microscopic model in which the only dependences enter through the N_i (so that the case of chemical polydispersity becomes especially simple). We will show that we can recover the generic form for the diffusive fluxes, eq 7, although now with explicit expressions for the mobility coefficients.

3. Microscopic Model (Following Brochard)

For a dense mixture of long chains, we will use the tube model to describe polymer dynamics, as applied to interdiffusion by Brochard.[8] We assume that all the chains are dynamically similar in all respects apart from their lengths: that is, we ignore the effect of chemical species on entanglement length, mobility, etc. According to classical reptation theory (which assumes that each polymer moves through a tube made of the network),[9] the center of mass velocity $\mathbf{v}_i$ of polymer species i, is related to its curvilinear velocity w_i (which determines its motion through the tube), as follows:

$$\mathbf{v}_i = w_i\frac{\mathbf{h}_i}{L_i} \tag{10}$$

where L_i is the contour length of the tube and $\mathbf{h}_i$ is the end-to-end polymer vector. Under near-equilibrium conditions, these are related by

$$L_i^2 = \frac{N_i}{N_e}\langle h_i^2\rangle \tag{11}$$

where the entanglement parameter N_e is related to the tube diameter.[9] Note that N_e should be smaller than N_i for all species present; for length polydispersity, this restricts the applicability of the present model to the case where all species, including any “solvent”, are fully entangled.

In using eq 11, we assume that the polymer conformation is not significantly distorted from its equilibrium counterpart. Hence, the dynamics we will describe below will hold only for chemical potential gradients weak enough that one does not enter the non-Newtonian flow regime, where the flow response to pressure gradients becomes nonlinear. Using the previous expression, the curvilinear and center-of-mass velocities *measured relative to a static network* are then related through

$$|\mathbf{v}_i|^2 = \frac{N_e}{N_i}w_i^2 \tag{12}$$

In practice, the network of entanglements is common to all the polymers, but need not be static. If the system moves under the action of an external field, this network will be characterized by a common velocity, $\mathbf{v}_t$, or “tube velocity” . Equation 12 should then be generalized to

$$|\mathbf{v}_i - \mathbf{v}_t|^2 = \frac{N_e}{N_i}w_i^2 \tag{13}$$

Following Doi and Onuki,[10] we may now deduce the (linearized) equations of motion by minimizing the energy dissipation rate of the system. This has two contributions: one related to the free energy variation and the second to the energy dissipation due to the friction between the polymers and the tube. We analyze the two terms in turn.

3.1. Free Energy Rate Contribution. Generically, the free energy of a polydisperse polymer mixture can be expressed as the sum of an ideal and an excess contribution:

$$F = \int d\mathbf{r}\, f[\{\rho_i(\mathbf{r})\}] = \int d\mathbf{r}\, \{k_B T\sum_i \rho_i(\mathbf{r}) \log \rho_i(\mathbf{r}) + f^{ex}[\rho_i(\mathbf{r})]\} \tag{14}$$

where f^{ex} is in general a nonlocal function of the chain-number density. The free energy rate (which we define as the contribution to the dissipation of the system due to work done against thermodynamic gradients) can then be written as

$$\frac{\partial F}{\partial t} = \int \frac{\partial f(\mathbf{r})}{\partial t}\, d\mathbf{r} = -\int \mu_i(\mathbf{r})\nabla\cdot(\mathbf{v}_i\rho_i)\, d\mathbf{r} \tag{15}$$

where the chemical potential is defined in general as $\mu_i(\mathbf{r}) = \delta F/\delta\rho_i(\mathbf{r})$ and where use has been made of mass conservation, eq 1. This result is general, although in section 4 we will discuss specific examples for the free energy of polymer mixtures, expressed in terms of moments of the chain number densities.

3.2. Tube Dissipation Rate. The tube dissipation rate arises from the friction of the polymer against the network during its motion. Hence the relevant polymer velocity is the curvilinear one, w_i. The dissipation is then assumed to be proportional to its square, and to the number of monomers of each polymer species. If we denote by ξ_{0i} the microscopic friction constant of species i, we can write the tube dissipation rate as

$$W = \int d\mathbf{r}\sum_i \frac{1}{2}\phi_i\xi_{0i}w_i^2 = \int d\mathbf{r}\sum_i \frac{1}{2}\xi_i|\mathbf{v}_i - \mathbf{v}_t|^2 \tag{16}$$

where we have used the equilibrium relation between the curvilinear and the center of mass velocity for polymer species i, eq 13, and introduced the polymer friction coefficient

$$\xi_i = \xi_0\frac{N_i}{N_e}\phi_i = \xi_0\frac{N_i^2}{N_e}\rho_i \tag{17}$$

Since ξ_{0i} is a microscopic friction coefficient, related to the interaction between a given monomer and the network, we assume it is the same for all the species; i.e., $\xi_{0i} = \xi_0$. While true for pure length polydispersity, when chemical polydispersity is present this will not be strictly correct. (The resulting errors should, however, be quantitative not qualitative in nature, especially, for example, when the chemical differences involve only deuteration.)

Brochard’s picture has allowed us to obtain explicit expression for the friction coefficients, derived from a bem microscopic model. In particular, it predicts a quadratic dependence of the friction coefficient on the polymerization index N_i of species i. Within our assumption of constant ξ_{0i}, it is only for length polydispersity that the mobility contributions will depend on polydispersity. For other situations such as chemical polydispersity, its influence on the diffusion coefficients will enter only through the thermodynamics of the system.

Following Brochard,[8] the tube velocity is now determined by requiring that the friction force acting on the network should balance. Such a force can be obtained from the dissipation rate W taking its derivative with respect to the tube velocity. Requiring $\delta W/\delta\mathbf{v}_t = 0$ determines the tube velocity

$$\mathbf{v}_t = \frac{\sum_i \xi_i\mathbf{v}_i}{\sum_i \xi_i} \tag{18}$$

Note that, except for the important case of length polydispersity, the tube velocity always coincides with the barycentric velocity in our model. This coincidence is very useful to analyze the diffusion, because under these circumstances $\rho_i(\mathbf{v}_i - \mathbf{v}_t)$ is already the diffusive flux of species i (and we obtain below an explicit expression for $\mathbf{v}_i - \mathbf{v}_t$). In this respect, length polydispersity plays a distinctive role from the dynamical point of view.

3.3. Total Dissipation Rate. The total dissipation rate (essentially the entropy production rate) for our polymer mixture is now written as

$$R = \int d\mathbf{r}\left\{\sum_i\left[\frac{1}{2}\xi_i\left|\mathbf{v}_i - \mathbf{v}_t\right|^2 - \mu_i\nabla\cdot(\rho_i\mathbf{v}_i)\right] - p\nabla\cdot\sum_i\phi_i\mathbf{v}_i\right\} \tag{19}$$

where the third term is introduced to enforce incompressibility (cf. eq 4). Here p, the associated Lagrange multiplier, corresponds to the pressure.

The polymer velocities are derived by minimizing R. Imposing $\delta R/\delta \mathbf{v}_i = 0$, we get

$$\xi_i(\mathbf{v}_i - \mathbf{v}_\mathrm{t}) + \rho_i \nabla \mu_i + \phi_i \nabla p = 0 \tag{20}$$

Summing over all components (and imposing incompressibility, i.e., $\sum_i \phi_i(\mathbf{r}) = 1$), we recover

$$\nabla p = -\sum_i \rho_i \nabla \mu_i \tag{21}$$

which is simply the Gibbs−Duhem equation (this shows that the Lagrange multiplier p corresponds indeed to the thermodynamic pressure). Using this explicit expression, the velocity of polymer i has the form

$$\mathbf{v}_i = \mathbf{v}_\mathrm{t} - \frac{\rho_i}{\xi_i}\nabla \mu_i + \frac{\phi_i}{\xi_i}\sum_k \rho_k \nabla \mu_k \tag{22}$$

From this we can write the diffusive flux of species i as

$$\mathbf{J}_i = \rho_i \left(\mathbf{v}_\mathrm{t} - \mathbf{v}^\mathrm{m} - \frac{\rho_i}{\xi_i}\nabla \mu_i + \frac{\phi_i}{\xi_i}\sum_k \rho_k \nabla \mu_k\right) \tag{23}$$

We can again use the incompressibility condition to obtain an explicit expression for $\mathbf{v}_\mathrm{t} - \mathbf{v}^\mathrm{m}$; imposing $\sum N_i \mathbf{J}_i = 0$ leads in this case to

$$\mathbf{v}_\mathrm{t} - \mathbf{v}^\mathrm{m} = \sum_i \left\{\frac{\rho_i \phi_i}{\xi_i} - \rho_i \sum_k \frac{{\phi_k}^2}{\xi_k}\right\} \nabla \mu_i \tag{24}$$

which shows that these two velocities are not independent of each other, and that their difference is proportional to the chemical potential gradients, but not simply to the pressure gradient (hence this difference is not caused by a departure from mechanical equilibrium).

As we have already mentioned, in the absence of length polydispersity, $\mathbf{v}_\mathrm{t} - \mathbf{v}^\mathrm{m}$ is zero within our model, because we assume $\xi_i \propto \phi_i N_i$. In the remaining case of length polydispersity, the difference can be expressed as

$$\mathbf{v}_\mathrm{t} - \mathbf{v}^\mathrm{m} = \frac{1}{\alpha}\sum_i \left\{\frac{1}{N_i} - \rho\right\} \rho_i \nabla \mu_i \tag{25}$$

where $\rho = \sum_i \rho_i$ is the overall local chain density and $\alpha \equiv \xi_0/N_\mathrm{e}$.

3.4. Result for the Mobility Matrix. Substituting eq 24 into the expression for the diffusive flux, eq 23, we get

$$\mathbf{J}_i = \sum_k \left\{-\frac{\rho_i}{\xi_i}\delta_{ik} + \rho_k\left(\frac{\phi_i}{\xi_i} + \frac{\phi_k}{\xi_k}\right) - \rho_k \sum_j \frac{{\phi_j}^2}{\xi_j}\right\} \rho_i \nabla \mu_k \tag{26}$$

This diffusive flux is proportional to the chemical potential gradients. It has the form of eq 7, with the generalized mobility matrix, eq 9. However, in this case, we have obtained an explicit expression for the mobility coefficients. As had been hypothesized, the mobility is proportional to the chain number density. However, for this model we have derived the dependence on the polymer length (which enters through the friction coefficients and which turns out to be nontrivial). We can rewrite eq 26 in the same form as eq 9, with the following choice of the mobility matrix:

$$M_{ik} = -\frac{\rho_i \rho_i}{\xi_i}\delta_{ik} + \rho_i \rho_k \left(\frac{\phi_i}{\xi_i} + \frac{\phi_k}{\xi_k}\right) - \rho_i \rho_k \sum_j \frac{{\phi_j}^2}{\xi_j} \tag{27}$$

This shows that the phenomenological model recovers the correct functional dependence for the diffusive flux.

Comparing with the expression introduced in eq 9, our analysis based on the physical hypotheses of Brochard's picture,[8] yields

$$A = -\frac{\rho_i}{\xi_i}, \quad B = -\frac{\phi_i}{\xi_i} + \frac{\phi_k}{\xi_k} + \sum_j \frac{{\phi_j}^2}{\xi_j} \tag{28}$$

In the subsequent sections, we analyze in detail several applications of this result, for different forms of the polydisperse polymer free energy.

As mentioned previously, our expression for the diffusive flux, eq 26, has the same general form as that obtained by Clarke[4] for the case of length polydispersity. The main conceptual difference is that, while Clarke expresses diffusive fluxes as gradients of the polymer chemical potential (relative to the solvent chemical potential) plus a global convective contribution with respect to an unspecified common velocity, in our case we define diffusive fluxes with respect to the barycentric velocity. (We will come back to this comparison in section 6.) So far, in fact, we have not introduced any explicit solvent, although the model as presented above does permit one to enter it as one of the species i, so long as this "solvent" is itself made of chains that are long enough to be entangled. We will return to the issue of solvent dynamics in the following sections.

4. Free Energy Functional

We now discuss the common structure of the free energy functional for all the systems we address below. For definiteness, we consider polymer free energies that are derived from a specific nonlocal free energy functional proposed in ref 2. It has the form (setting $k_\mathrm{B}T = 1$)

$$\mathscr{F} = \int \mathrm{d}\mathbf{r}\, \{\sum_k \rho_k(\mathbf{r})(\log(\rho_k(\mathbf{r})) - 1) + F^\mathrm{ex}[\{m_n(\mathbf{r})\}]\} \tag{29}$$

where the excess free energy depends on a finite set of moments. These moments are locally varying quantities that depend nonlocally on the associated chain number densities through

$$m_n(\mathbf{r}) = \sum_k \omega_{nk} \int N_k \tilde{w}_k(\mathbf{r} - \mathbf{r}')\rho_k(\mathbf{r}')\, \mathrm{d}\mathbf{r} \tag{30}$$

where $\tilde{w}_k(\mathbf{r} - \mathbf{r}')$ is related to the structure factor of a polymer chain of species k in a specific way.[11] The quantity ω_{nk} defines the nth moment in terms of the polydisperse variable; in all cases of interest here it is a simple power (e.g., $\omega_{nk} = {N_k}^n$ in the case of length polydispersity).

The use of this functional, which contains the information on the internal structure of the chains, will allow us to address issues such as the dependence of the initial unstable modes on the wave vector, in the case of a system undergoing spinodal decomposition. For small wavevectors the nonlocal kernel $\tilde{\omega}_k$ appropriate to a Gaussian chain is well approximated by the following gradient expansion[2]

$$\tilde{w}_k(\mathbf{r}-\mathbf{r}') = \left(1 + \frac{N_k}{24}\nabla^2\right)\delta(\mathbf{r}-\mathbf{r}') \equiv W_{0k}\delta(\mathbf{r}-\mathbf{r}') \quad (31)$$

where the additional subscript 0 denotes the small wavevector limit. The operator W_{0k} will be used in subsequent sections. Note that the chosen normalization, $\int \tilde{w}_k(\mathbf{r})\, d\mathbf{r} = 1$, means that factors N_k appears beside it in eq 30. Thus, in the case of length polydispersity, the zeroth nonlocal moment $m_0(\mathbf{r})$ (which corresponds to choosing $\omega_{0k} = N_k{}^0 = 1$) in fact describes the local monomer concentration. For chemical polydispersity it is again the local monomer concentration, with no discrimination between monomers of different chemical species. (In the absence of a solvent species $m_0(\mathbf{r})$ is unity everywhere because of incompressibility.)

Note that although we use a specific form, eq 29, for the nonlocal contributions to the polymer free energy, it is chosen so as to reduce to a standard Flory–Huggins theory, in the limit of zero wavenumber. This requirement fixes the form of the term $F^{\text{ex}}[\{m_n(\mathbf{r})\}]$ in eq 29. Moreover, once the gradient expansion eq 31 is adopted, the nonlocality we choose has a wider justification than the underlying model defined by eq 30. In particular, the same form for the gradients could be obtained by the random phase approximation.[2] A nonlocal free energy functional will in principle require, for consistency, a nonlocal expression for the mobility matrix. Such effects have been considered previously in the literature.[12] However, for simplicity, we will make in this paper the assumption that the mobility coefficients can be regarded as local, as is normal practice.[3,4,10]

5. Chemical Polydispersity

Chemical polydispersity describes a set of polymers all with the same length, but a continuously varying interaction parameter. The normal example is a melt of random copolymers of equal length made of two monomers, e.g., deuterated and hydrogenated, that differ slightly in their enthalpic interaction. Within the model outlined above, we assume that this is the bem only difference. Each chain is then described by a polydisperse quantity f_i obeying $-1 \le f_i \le 1$ which controls the proportion of the different monomers present along it; they have no correlation other than this, and within a mean field approximation the presence of variable f_i is equivalent to a spectrum of χ parameters affecting different chains.[13] The moment densities $m_n(\mathbf{r})$ are then defined by the choice $\omega_{nk} = f_k{}^n$; and within Flory–Huggins theory, the excess free energy is simply $F^{\text{ex}} = -\chi m_1{}^2$.[1] Here χ is the Flory parameter controlling the interaction between the two different monomers.

Next we treat this case of the chemically polydisperse melt. However, we also allow for a solvent to be present. Technically, this is already included in the preceding formalism so long as the solvent is considered as “just another species” within our incompressible mixture of many polymers. Indeed there would be nothing to prevent us developing the general formalism to address this case without singling the solvent out for any special treatment at all. But the fact that its length and chemistry will usually be different from all the remaining polymers implies that the solvent will have a distinct dynamical behavior, which it is convenient to handle separately. Moreover, because of incompressibility, both the thermodynamics and the dynamics of the solvent are subservient to the remaining species and this will allow us to focus on the dynamics of the moments $m_n(\mathbf{r})$ of the chemically polydisperse chains alone. These dynamics will, of course, be different according to whether a solvent is present or not.

Note that this treatment of the solvent does not release us from the assumptions of the tube model made in our earlier derivation of the diffusive fluxes. In particular, this means that the solvent itself must consist of chains long enough to be fully entangled (though, in the cases addressed below, much shorter than the remaining, chemically polydisperse, chains of primary interest). However, as we will discuss in section 6, we can later on use the general form of the equations for the diffusive fluxes to guess how these may behave for an unentangled solution.

As discussed in section 3 above, a key simplifying feature for chemical polydispersity is that (within the approximations we have taken) the structure factors and mobilities of the chains are independent of the polydisperse feature f_i. In fact, many of the results described below for this case will also hold for any other kind of polydispersity with the same attribute, even if the structure of the excess free energy is not that corresponding to chemical polydispersity. We will point out, below, where the number of moments appearing in the excess free energy plays a role in the results we obtain.

5.1. Chemically Polydisperse Polymer Melt. The diffusive flux for this system is specially simple. The mobility coefficients in eq 28 reduce to

$$A = -\frac{1}{\alpha N_{\text{p}}{}^2} \quad (32)$$

$$B = -\frac{1}{\alpha N_{\text{p}}} \quad (33)$$

With our assumptions, this is true for any melt when all polymers have the same length $N = N_{\text{p}}$.

We will focus on polymer melts whose excess free energy depends only on a finite set of moments. With chemical polydispersity, Flory–Huggins theory states that only the first moment of the chemical composition is involved:[1]

$$F^{\text{ex}}[m_n(\mathbf{r})] = -\chi m_1{}^2 \quad (34)$$

Correspondingly, the chemical potential gradients simplify to

$$\nabla\mu_k = \frac{1}{\rho_k}\nabla\rho_k - 2\chi N_{\text{p}}\omega_{1k}\left[1 + \frac{N_{\text{p}}}{24}\nabla^2\right]\nabla m_1 \quad (35)$$

Note that in this case the function $W_0 \equiv 1 + N_{\text{p}}/24\ \nabla^2$ does not depend on the polymer species. Since all polymers have the same length, we have (to second order in gradients),

$$N_{\text{p}}\sum_k \omega_{nk}\rho_k(\mathbf{r}) = \left[1 - \frac{N_{\text{p}}}{24}\nabla^2\right] m_n(\mathbf{r}) = W_0{}^{-1} m_n(\mathbf{r}) \quad (36)$$

where W_0^{-1} is the inverse operator of W_0, likewise expanded to second order in gradients. Making use of this relation, the evolution equation for the species reads

$$\frac{d\rho_i}{dt} = -\frac{1}{\alpha N_p}\sum_k \nabla\cdot\left(-\frac{\delta_{ik}}{N_p} + \rho_i\right)\rho_k \nabla\mu_k = -\frac{1}{\alpha N_p}\nabla\cdot\left\{-\frac{1}{N_p}\nabla\rho_i + 2\chi[\omega_{1i}\rho_i - W_0^{-1}m_1\rho_i]W_0\nabla m_1\right\} \quad (37)$$

where due to incompressibility, $\nabla m_0 = 0$. This equation holds to leading nontrivial order in *separate* gradient expansions in the thermodynamics and in the relationships between fluxes and chemical potentials.[12] This is the normal procedure in Cahn–Hilliard approaches to polymer dynamics and is the simplest theory able to predict a nontrivial wavevector dependence for the growth rates in spinodal decomposition.[3,4,10]

The evolution equation of the moment densities $m_i(\mathbf{r})$ can in turn be written, within the same order of approximation, as

$$\frac{dm_n}{dt} = D_0\{\nabla^2 m_n + 2\chi N_p W_0 \nabla\cdot[(W_0^{-1}m_1)(W_0^{-1}m_n) - (W_0^{-1}m_{n+1})]W_0\nabla m_1\} \quad (38)$$

with $D_0 \equiv 1/(\alpha N_p^2)$. The diffusion coefficient D_0 sets the time scale, which, as expected, decreases proportionally to the increase of the friction coefficient.

This equation for the moment dynamics can be easily generalized to the case in which the excess free energy is a function of any finite set of moments. One gets in that case

$$\frac{dm_n}{dt} = D_0\{\nabla^2 m_n + N_p W_0 \nabla\cdot\sum_{\alpha\beta} F^{\text{ex}''}_{\alpha\beta}\,((W_0^{-1}m_{\alpha+n}) - (W_0^{-1}m_\alpha)(W_0^{-1}m_n))\,W_0\nabla m_\beta\} \quad (39)$$

Note that for generic free energies this expression involves a linearization in moment gradients (which was not required for an excess free energy quadratic in m_1 as considered above). Apart from this, eqs 38 and 39 have the same structure. Each moment relaxes proportional to its own density deviation with a relaxation rate D_0 but is also coupled to all other species through the various moments that appear in the excess free energy of the model.

Note also that the mobility does not play a major role; it only defines a characteristic time scale (which we will call the fast scale) $\tau_f(q) = 1/D_0q^2$ where q is the wavenumber. In contrast, the coefficients $F^{\text{ex}''}_{\alpha\beta}$ are related to the location of any phase transitions and/or spinodals. Proximity to these will control the form of any slow modes present. As a result, for an excess free energy with n moments there are n potential slow modes related to the thermodynamic forces of the system. This implies that, even if there is an hierarchy of kinetic time scales, it will be finite. (The situation will be quite different for length polydispersity, where there is no clear factorization of the moment evolution equations—see section 6 below.)

For the chemically polydisperse melt there is only one moment appearing in the excess free energy (m_1). The eigenfunctions of the diffusion[14] then have a very simple structure. In fact, all moments with $n > 1$ are eigenvectors with the same eigenvalue $\lambda_n = -q^2D_0$ [15] with no wave vector dependence other than the usual diffusive one. On the other hand, when we linearize the evolution eq 38 at wavenumber q, we find the one remaining eigenvalue

$$\lambda_1 = -q^2D_0\,[1 - 2\chi N_p(\tilde{m}_2 - \tilde{m}_1^2)W_0^2(q)] = -D_0q^2\left[1 - \frac{\chi}{\chi_s}\left(1 - \frac{N_p}{12}q^2\right)\right] \quad (40)$$

where the tildes denote values in the homogeneous parent state about which the linearization is performed. We have also used that the interaction strength at the spinodal is given by $N_p\chi_s = 1/(2(\tilde{m}_2 - \tilde{m}_1^2))$. As expected, λ_1 changes sign at the spinodal, and defines a slow mode in its vicinity (slow relative to all higher eigenmodes $\lambda_{n>1}$) that will control the early-stage kinetics of the phase separation process. During the initial stages of phase separation, all moments $n > 1$ will relax fast toward their corresponding local equilibrium values; but these values are controlled by λ_1 which evolves on a slower time scale. Note that this slow mode is not simply the first moment m_1 but a linear combination of all moments.

These results for the chemically polydisperse melt contrast strongly with those given in the previous literature for length polydispersity[5,4] as discussed further in section 6 below.

Specifically, since there is only one relevant moment, there is no distinction between a quenched and an annealed spinodal that can define different kinetic scenarios as described by Warren[5] for length polydisperse solutions. Moreover, the slowest mode (which is the unstable one) is the only mode that involves the first moment. All moments of the distribution, except for the first one, will accommodate rapidly to the mean local composition, governed by the slow relaxation mode involving m_1. Finally, the wave vector dependence of the unstable mode is independent of polydispersity, and the same as in a monodisperse system. Only the overall amplitude (determined by the thermodynamics) is modified by polydispersity.

5.2. Chemically Polydisperse Polymers in a Passive Solvent. In this case, unlike the melt, the mobility plays a role beyond that of a simple scale factor in the dynamics. As explained previously, it is convenient to single out the solvent for special treatment en route to deriving dynamical equations for the moments m_n. For definiteness (and a clearer separation of time scales) we treat the case where the solvent has length $N_s \ll N_p$, although we continue to assume that all species are entangled. The ratio of the two lengths is defined as $r \equiv N_p/N_s$.

The generic expression for the diffusive flux and the free energy will both depend now on the solvent number density. We first rewrite the relevant expressions in terms of polymer densities alone. These expressions will be valid both for this model and for length polydispersity addressed in section 6. Because of incompressibility, the solvent number density is related to the monomer concentration (m_0) through

$$\rho_s = \frac{1 - m_0}{N_s} \quad (41)$$

where we have disregarded the internal structure of the solvent in writing this as a local relation. This is a good approximation at large r when the solvent is much smaller than the remaining polymers. In what follows, we treat r as a large parameter and are mainly concerned with the leading behavior in that limit, but where subleading corrections are calculated, this is done without correcting eq 41.

We can now single out the solvent contribution both to the diffusive fluxes and the chemical potential gradients. For what we will call a "passive" solvent, its contribution to the free energy, eq 29 is simply to add a local entropic term $\rho_s(\ln \rho_s - 1)$. Then

$$\rho_s \nabla \mu_s = -\frac{1}{N_s} \nabla m_0 \tag{42}$$

Note that for symmetric distributions in a passive solvent there is no tendency for the chemically polydisperse polymers to separate collectively from the solvent; the only tendency toward phase separation is within the polydisperse distribution itself. This ceases to apply for an asymmetric distribution of solute species. Note also that a more general solvent would introduce (as well as ignorable linear terms) terms in $m_0 m_1$ into the excess free energy, leading to somewhat more complicated phase behavior[1] and dynamics.

Using the fact that ρ_s depends only on the overall monomer concentration, the diffusive flux for the polymer species, given by eq 7, can now be expressed as a function of polymer variables only:

$$\mathbf{J}_i = \sum_k{}' \left\{ -\frac{\delta_{ik}}{\xi_i} + \frac{\phi_i}{\xi_i} + \frac{\phi_k}{\xi_k} - \left(\sum_j{}' \frac{{\phi_j}^2}{\xi_j} + \frac{(1-m_0)^2}{\xi_s} \right) \right\} \rho_k \rho_i \nabla \mu_k - \left[\frac{\phi_i}{\xi_i} + \frac{\phi_s}{\xi_s} - \sum_j{}' \frac{{\phi_j}^2}{\xi_j} - \frac{(1-m_0)^2}{\xi_s} \right] \frac{\rho_i}{N_s} \nabla m_0 \tag{43}$$

where the prime means that the sums run only over the solute polymer species.

For a solution of chemically polydisperse polymers, the excess free energy for a passive solvent may again be written within Flory−Huggins theory as

$$F^{\mathrm{ex}} = -\chi {m_1}^2 \tag{44}$$

where the interaction amplitude of interest (around the spinodal) obeys $\chi N_p \simeq 1$. The chemical potential gradient is again given by eq 35. We can now derive expressions for the diffusive fluxes of each polymer species, following the same kind of derivation as for the melt. We take advantage of the fact that the friction coefficients for all species is the same (see eq 17) to arrive at

$$\mathbf{J}_i = D_0 \rho_i \sum_k{}' \{ -\delta_{ik} + N_p \rho_k \} \nabla \mu_k - D_0 \rho_i \{ N_p (1-m_0) \times (r-1) \sum_k{}' \rho_k \nabla \mu_k + r(1 + m_0(r-1)) \nabla m_0 \} \tag{45}$$

The first line coincides with the expression of the diffusive flux of a species in the melt. The presence of a passive solvent has two effects in the polymer dynamics, which correspond to the two terms appearing in the second line of eq 45. Gradients in the local monomer concentration generate a flux of each species of polymers, but in addition, the local presence of a solvent allows global polymer rearrangements according to

$$\sum_k{}' \rho_k \nabla \mu_k = \frac{1}{N_p} {W_0}^{-1} \nabla m_0 - 2\chi({W_0}^{-1} m_1) W_0 \nabla m_1 \tag{46}$$

The analysis is very different from the melt case because now gradients in the local overall monomer concentration do not vanish.

Introducing the diffusive fluxes of the moment densities

$$\mathbf{j}_n \equiv N_p \sum_k \omega_{nk} W_0 \mathbf{J}_k \tag{47}$$

and then using eq 45, these read

$$\mathbf{j}_n = D_0 \{ -\nabla m_n + 2\chi N_p W_0 [({W_0}^{-1} m_{n+1}) - ({W_0}^{-1} m_{n+1})({W_0}^{-1} m_1)] W_0 \nabla m_1 + 2\chi N_p W_0 (1-m_0)(r-1)({W_0}^{-1} m_n)({W_0}^{-1} m_1) W_0 \nabla m_1 + W_0 ({W_0}^{-1} m_n)[-r(1 - m_0 + m_0 r) + (2 - m_0 - r(1-m_0)){W_0}^{-1}] \nabla m_0 \} \tag{48}$$

leading to

$$\mathbf{j}_n = D_0 \{ -\nabla m_n + 2\chi N_p [\tilde{m}_{n+1} - \tilde{m}_n \tilde{m}_1] {W_0}^2 \nabla m_1 + 2\chi N_p (1-\tilde{m}_0)(r-1)\tilde{m}_n \tilde{m}_1 {W_0}^2 \nabla m_1 + \tilde{m}_n [2 - \tilde{m}_0 - r(1-\tilde{m}_0) - r(1 - \tilde{m}_0 + \tilde{m}_0 r) W_0] \nabla m_0 \} \tag{49}$$

where we have now linearized the fluxes, as appropriate for studying the structure factor during the early stages of phase separation. As in eq 40, the tilde refers to values of the moments evaluated at the reference state, instead of being dynamical quantities.

Again, the first line in the previous expression is the contribution that we obtained for the melt. The second line requires the presence of a solvent and corresponds to a correlated flow of all the species that avoids segregation. Finally, the third line corresponds to the diffusive flux of a given species induced by solvent gradients.

In terms of these moment fluxes, the evolution equation for the moments read

$$\frac{\mathrm{d} m_n}{\mathrm{d} t} = -\nabla \cdot \mathbf{j}_n \tag{50}$$

which yields the final results for the linearized dynamic equations of the moment densities themselves

$$\frac{\mathrm{d} m_n}{\mathrm{d} t} = D_0 \{ \nabla^2 m_n - 2\chi N_p [m_{n+1} - \tilde{m}_n \tilde{m}_1 (1 - (r-1) \times (1 - \tilde{m}_0))] {W_0}^2 \nabla^2 m_1 - \tilde{m}_n [1 - (1-\tilde{m}_0)(r-1) - r(1 + \tilde{m}_0(r-1)) W_0] \nabla^2 m_0 \} \tag{51}$$

Although these equations are more complicated than for the case of a melt (eq 38), they do retain a relatively simple quasi-triangular form[16] that allows us to analyze in some detail the structure of the eigenvalues. The fact that all moments only couple to the first two moments (m_0 and m_1) imply that, except for these two, the rest are degenerate eigenfunctions. Hence we may set $\lambda_n = -D_0 q^2$ for $n = 2, 3, \ldots$. The interesting dynamical behavior lies then in the remaining two eigenmodes, which are the only ones that involve m_0 and m_1.

5.2.1. Dependence on Solvent Size Ratio. In general the expressions for the two eigenvalues is quite involved, but given our assumptions so far, they can be found for arbitrary r. However, the derivation was subject to eq 41, which itself is valid for large r only. Hence, we relegate the general expressions to Appendix A.

In the limiting case of very large polymers (i.e., $r \gg 1$), the two eigenvalues simplify to

$$\lambda_0 = -q^2 D_0 r^2 \tilde{m}_0^{\,2} W_0(q) \tag{52}$$

$$\lambda_1 = -q^2 D_0\left[1 - \frac{\chi}{\chi_s} W_0(q)^2\right] \tag{53}$$

where $\chi_s = \tilde{m}_0/(2(\tilde{m}_0\tilde{m}_2 - \tilde{m}_1^2))$ is the spinodal value of the interaction parameter (to leading order in large r). For the particular case of a symmetric parent (i.e., a symmetric distribution of the polydisperse species in the homogeneous phase prior to the quench) the expressions for the eigenvalues are particularly simple. In this case $\tilde{m}_1 = 0$ in the initial state and the eigenmodes that involve m_0 and m_1 do not mix them; their eigenvalues (exact to order q^4) are

$$\lambda_0 = -D_0 q^2[1 - \tilde{m}_0\{1 - (1 - \tilde{m}_0)(r - 1) - r[1 + \tilde{m}_0(r - 1)]W_0(q)\}] \tag{54}$$

$$\lambda_1 = -D_0 q^2(1 - 2\chi\tilde{m}_2 W_0(q)^2) = -D_0 q^2\left(1 - \frac{\chi}{\chi_s} W_0(q)^2\right) \tag{55}$$

with $\chi_s = 1/(2\tilde{m}_2)$ the spinodal value of the interaction parameter for a symmetric parent. Note that eqs 53 and 55 have the same form as the relevant eigenvalue in the melt case, eq 40. The only difference is the location of the spinodal; it is through the thermodynamic sector only that the solvent, and likewise the polydispersity, can enter. This shows that in the limit of high size ratio ($r \gg 1$) the main features of mode structure are, within our model, universal.

Likewise, if we look at the wave vector dependence of the eigenvalues λ_0 and λ_1, we see that it does not depend directly on polydispersity. This behavior is again analogous to that of the melt and can be attributed to the absence of coupling of the unstable mode to all the rest of the modes. This is contrary to what happens for length polydispersity, as we discuss in section 6.

For both symmetric and asymmetric parents, in the limit $r \gg 1$, the two eigenvalues scale asymptotically as

$$\lambda_0 \sim -\frac{q^2\tilde{m}_0^{\,2}}{\alpha N_s^{\,2}} \tag{56}$$

$$\lambda_1 \sim -\frac{q^2}{\alpha N_p^{\,2}}\left[1 - \frac{\chi}{\chi_s}\right] \tag{57}$$

but the convergence to this limit as r is increased strongly depends on parental asymmetry. In Figure 1 we show the wave vector dependence of the unstable eigenmode, λ_1 for an exponential parent ($\rho_n \sim \exp(af_n)$) as a function of the size ratio r for different values of a. When the asymmetry parameter a is increased, the wavevector dependence becomes more sensitive to the size ratio r (in fact, for $a = 0$ there is no dependence on r; cf. eq 55). The dependence on size ratio becomes also more relevant as the polymer dilution increases. For high asymmetry and dilution (Figure 1c), the convergence to infinite aspect ratio becomes much slower and it is not monotonic for intermediate values of r. In Figure 2, we show the wave vector dependence of the stable mode, λ_0, for two disparate values of the asymmetry at high dilution. The dependence on q is monotonic as anticipated. In all cases the curves converge in the limit of large aspect ratios (note that because of the different scaling of the two eigenvalues λ_0 and λ_1 we have scaled here λ_0 by r^2). For large asymmetry (Figure 2b), also for this stable mode the convergence to the high aspect ratio limit becomes slower and it is nonmonotonic for intermediate r values.

5.2.2. Qualitative Behavior at Large Size Ratio. The above analysis shows that, for large size ratios between solute and solvent ($r \gg 1$), λ_0 is much larger than the rest of the eigenvalues. This means that the mode connected with λ_0 (which, for a symmetric parent only, does not involve m_1) will grow or decay much faster than all the rest of the modes, whose rates scale with the inverse of the solute polymer length N_p, defining for $n > 1$ a common time scale $\tau_f(q) = 1/D_0q^2$. The latter was already identified as the fast time scale in the melt case. The corresponding modes remain fast relative not to the solvent mode (which is faster) but to a single slow mode. This is governed by λ_1, which splits off from this family of modes with a time scale that diverges on the spinodal.

This means that during the early stages of phase separation (or during the decay of an external perturbation within the stable region of the phase diagram), the overall monomer density is first equilibrated (if necessary); on this time scale the remaining moments are effectively quenched. In a second stage, the chemical composition will relax toward its equilibrium distribution (with the monomer density slaved to this). Close to the spinodal this chemical relaxation can, just as in the melt case, be separated into two stages. These entail relatively rapid equilibration of the higher moments to a state of local equilibrium set by the slow evolution of the mean composition variable m_1 (which is the local excess of A over B monomers in the case of a random copolymer system). It is notable that, for an asymmetric parent, the two relevant modes include nontrivial linear combination of m_0 and m_1, while for a symmetric parent these two moments appear separately in the corresponding eigenfunctions. This is because of the thermodynamic coupling which, for an asymmetric parent, requires chemical separation to be accompanied by changes in the overall monomer density.

This picture is somewhat analogous to one described by Warren for the case of length polydisperse polymers undergoing phase separation from an incompatible solvent.[5] Warren developed a picture in which there were two separate spinodal curves: the equilibrium one and, within it, a quenched one to describe the dynamics of a hypothetical system whose overall monomer density could change but where the relative prevalence of different chain lengths could not change locally. Between these two spinodals, the kinetics were argued to be controlled by the slow sorting out of the polydisperse species.

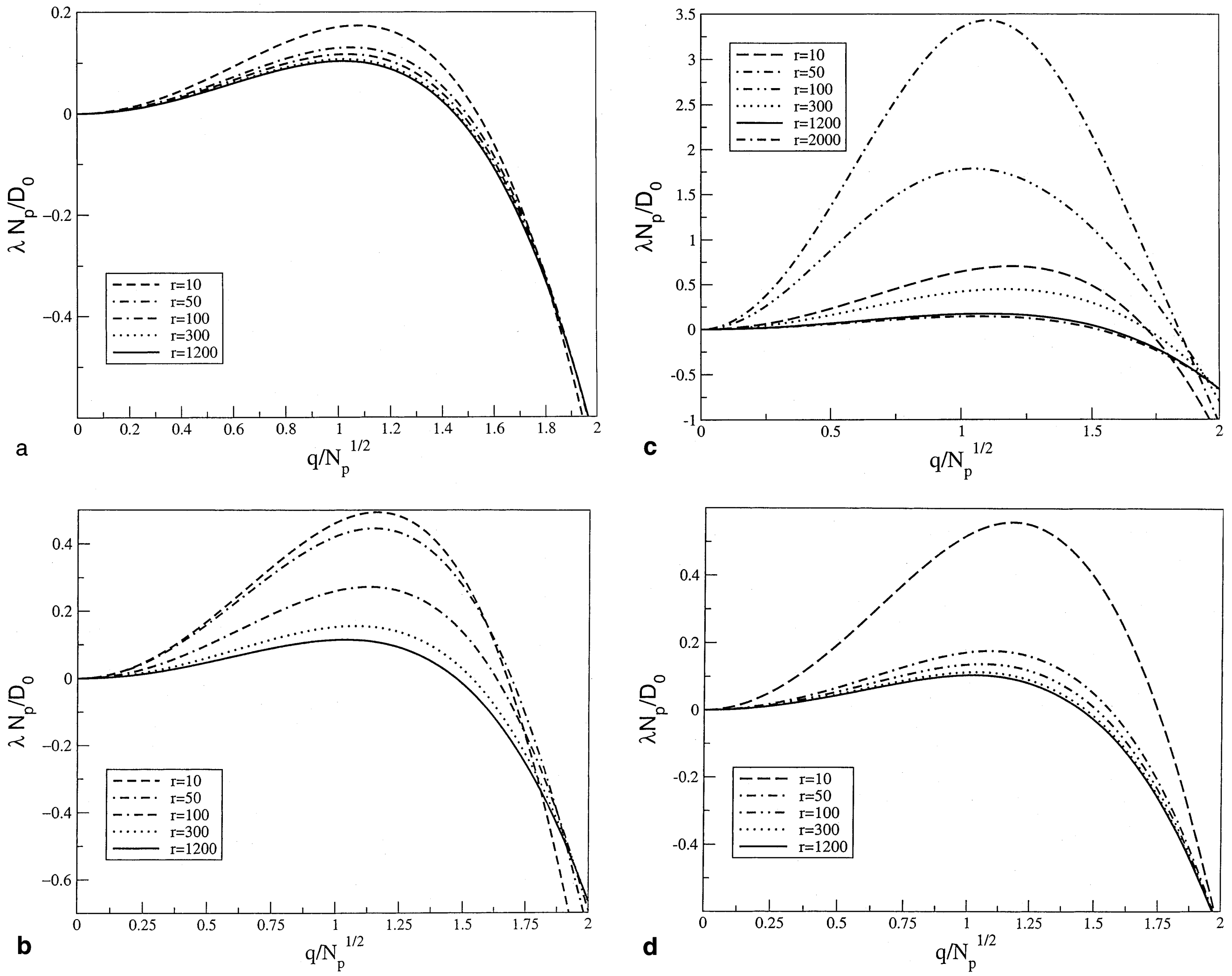

Figure 1. Wavevector dependence of the unstable eigenmode $\lambda_1 N_p/D_0$ for an exponential parent $\rho_n \sim \exp(af_n)$ at $\chi = 1.2\chi_s$. The wave vector q is measured in units of $N_p^{-1/2}$. In all the plots, we show the eigenmodes for four different size ratios $r = 10, 50, 100, 300$, and 1200. In the different plots we change the degree of asymmetry of the chemical distribution (increasing with increasing a), and compare dense and dilute suspensions: (a) $a = 2$, $\tilde{m}_0 = 0.15$; (b) $a = 5$, $\tilde{m}_0 = 0.15$; (c) $a = 10$, $\tilde{m}_0 = 0.15$; (d) $a = 10$, $\tilde{m}_0 = 0.8$.

For chemically polydisperse chains in a solvent, a similar scenario can arise. However, for the passive solvent considered here, this can only happen for an asymmetric parent since otherwise the phase separation is toward two states of equal solvent density; this density coincides with that in the initial state. Accordingly there is no driving force for phase separation in a symmetric system on the time scale of the fast (solvent) mode as may be confirmed by constructing the relevant free energy with quenched $\langle f\rangle = \tilde{m}_1/\tilde{m}_0$. If we consider a fully quenched situation where all higher moments are slave to m_0, (i.e. higher moments evolve as $m_n = \langle f^n\rangle m_0$), its linearized evolution equation is

$$\frac{\mathrm{d}m_0}{\mathrm{d}t} = D_0\{1 - 2\chi\tilde{m}_0\langle f\rangle^2(1 - \tilde{m}_0)[1 + \tilde{m}_0(r - 1)]W_0^{\,2} + \tilde{m}_0[-1 + (1 - \tilde{m}_0)(r - 1) + r(1 + (r - 1)\tilde{m}_0)W_0]\}\nabla^2 m_0 \quad (58)$$

which for large r will give a relaxation rate scaling with the fastest mode of the system. This leads to a rapid growth of fluctuations, but only inside a region where the quenched system is unstable; such a region is present only for an asymmetric parent.

In Figure 3, we show the quenched and annealed spinodals for a chemically polydisperse mixture with an exponential parent shape ($\rho_n \sim \exp(af_n)$) for different values of the parameter a (which controls the degree of asymmetry of the mixture) and of the size ratio r. One can see that in the regime where polymers are much larger than the solvent, the two spinodals are far apart. There is thus a broad region, between the two spinodals, where the density relaxation will take place only through a slow sorting of the chemical species. The slowest process will then control the initial steps of the phase separation process, determining the relevant time scale.

6. Length Polydispersity

6.1. Structure of Equations. Before analyzing the effect of length polydispersity in detail, it is instructive to compare the structure of eq 26 with the analogous one derived by Clarke.[4] He obtained diffusive fluxes for the monomer concentrations, disregarding (as we do) the internal structure of the chains when constructing the relation between fluxes and chemical potential gradients. (The internal structure enters only when calculating these gradients.) We may rewrite our results

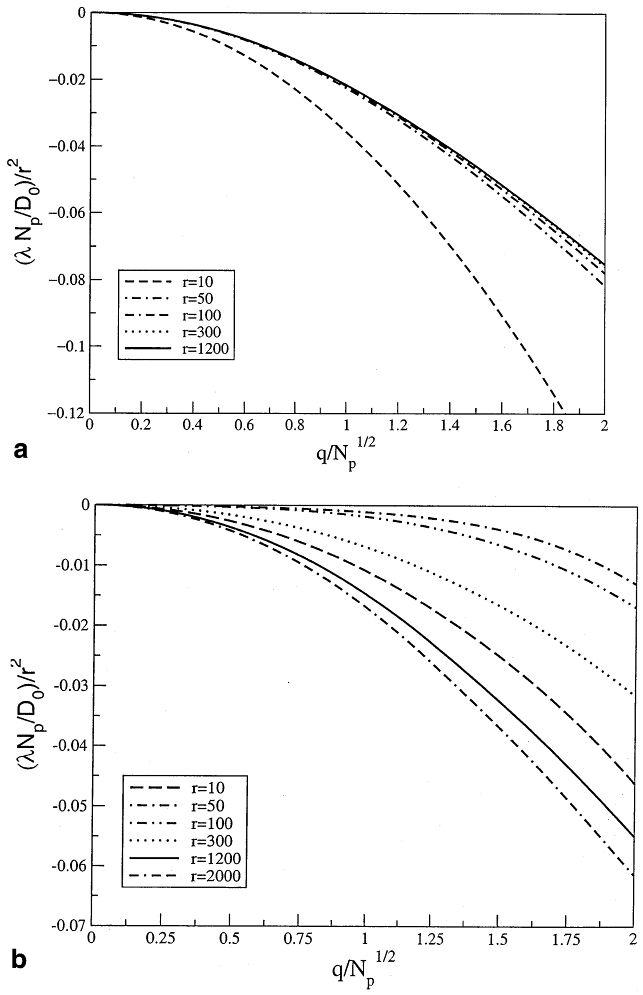

Figure 2. Wavevector dependence of the stable eigenmode $\lambda_0 N_p/D_0$ for an exponential parent $\rho_n \sim \exp(af_n)$ at high dilution $m_0 = 0.15$ and $\chi = 1.2\chi_s$. The wave vector q is measured in units of $N_p^{-1/2}$: (a) $a = 2$; (b) $a = 10$.

in terms of the *monomeric* flux of each species i (that we will call $\tilde{\mathbf{J}}_i$) starting from eq 26. We get

$$\tilde{\mathbf{J}}_i = \sum_k \left\{ -\frac{\delta_{ik}}{\xi_i} + \left(\frac{\phi_i}{\xi_i} + \frac{\phi_k}{\xi_k}\right) - \sum_j \frac{\phi_j^2}{\xi_j} \right\} \phi_i \phi_k \nabla\tilde{\mu}_k \equiv \sum_j \Lambda_{ij} \nabla\tilde{\mu}_j \tag{59}$$

where $\tilde{\mu}_k$ is the monomeric chemical potential of species k, i.e., $\tilde{\mu}_k = \delta F/\delta\phi_k$. The mobility matrix Λ_{ij} coincides with the one derived by Clarke (cf. eq 22 of ref 4), if we identified the phenomenological coefficients $\tilde{\lambda}_i$[17] introduced in that paper as

$$\tilde{\lambda}_i \equiv \frac{\phi_i^2}{\xi_i} \tag{60}$$

The basic differences between Clarke's approach and ours is then that while he considered diffusive fluxes referred to a common velocity fixed through incompressibility, in our case the diffusive fluxes are defined with respect to the barycentric velocity. In this way, we get diffusive fluxes that are strictly proportional to the chemical potential gradients of each species.

Nonetheless this comparison is suggestive, because the phenomenological model of Clarke is claimed to apply both to entangled and unentangled mixtures. In the former case he suggests that $\tilde{\lambda}_i$ should scale as the inverse of the polymer length, $\tilde{\lambda}_i \sim 1/N_i$. We have derived this result in section 3. Brochard's theory (which was our own starting point in section 3), and also Kramer's theory[18] (on which Clarke based some of his reasoning) both assume that the diffusion is controlled by the fastest species (they are accordingly referred to as "fast mode theories").[19] Hence, it is not surprising that we get mobility coefficients that concur with those posited by Clarke on the basis of Kramer's model.

For the unentangled case, Clarke argues that, because of the different scaling of the self-diffusion coefficient with polymerization (Rouse model[9]) one can assume that in this situation $\tilde{\lambda}_i$ is a constant instead. Although we have derived the expressions for the diffusive fluxes within the context of the tube model, if we assume, following Clarke, that their overall functional form is the same in the unentangled case we can use our results in both situations simply by changing the dependence of the friction coefficients on the polymer lengths. For chemical polydispersity as discussed above, this means modifying only one or two global parameters (solvent and solute chain mobilities) of the theory; for length polydispersity the effect is more complicated and discussed in section 6.4 below.

6.2. Length-Polydisperse Chains in a Solvent. For length-polydisperse chains in a solvent, treated within Flory−Huggins theory, the free energy is written as

$$\mathcal{F} = \int d\mathbf{r}\{\sum_k \rho_k(\mathbf{r})(\ln \rho_k(\mathbf{r}) - 1) + \chi m_0(\mathbf{r})(1 - m_0(\mathbf{r}))\} \tag{61}$$

where we have initially chosen the sum over species to bem include the solvent chains, while the moments are the linear nonlocal combinations of the polymer number densities defined in eq 30 with $\omega_{nk} = N_k^n$, and the solvent chains bem *excluded*. Note that, as described following eq 30, m_0 is the total volume fraction occupied by solute monomers. The chemical potentials of the species are accordingly

$$\mu_k = \log \rho_k + \chi N_k - 2\chi N_k \int \tilde{w}_k(\mathbf{r} - \mathbf{r}')m_0(\mathbf{r}')\, d\mathbf{r}' \tag{62}$$

$$\mu_s = \log \rho_s = \log\left(\frac{1 - m_0}{N_s}\right) \tag{63}$$

where we again neglect the spatial extent of the solvent chains, presuming them small compared to the typical size of the solute polymers.

As we did for chemical polydispersity, we now choose to treat the solvent as a separate species and derive equations for the diffusive fluxes of the solute polymers with the solvent coupling eliminated (statically and dynamically) via the incompressibility constraint, eq 41. Using this relation, and the fact that $W_{0i} - 1$ is linear in species length,[20] the diffusive flux of species i can now be found to second order in gradients. The full result is given in Appendix B and is quite complicated. Truncat-

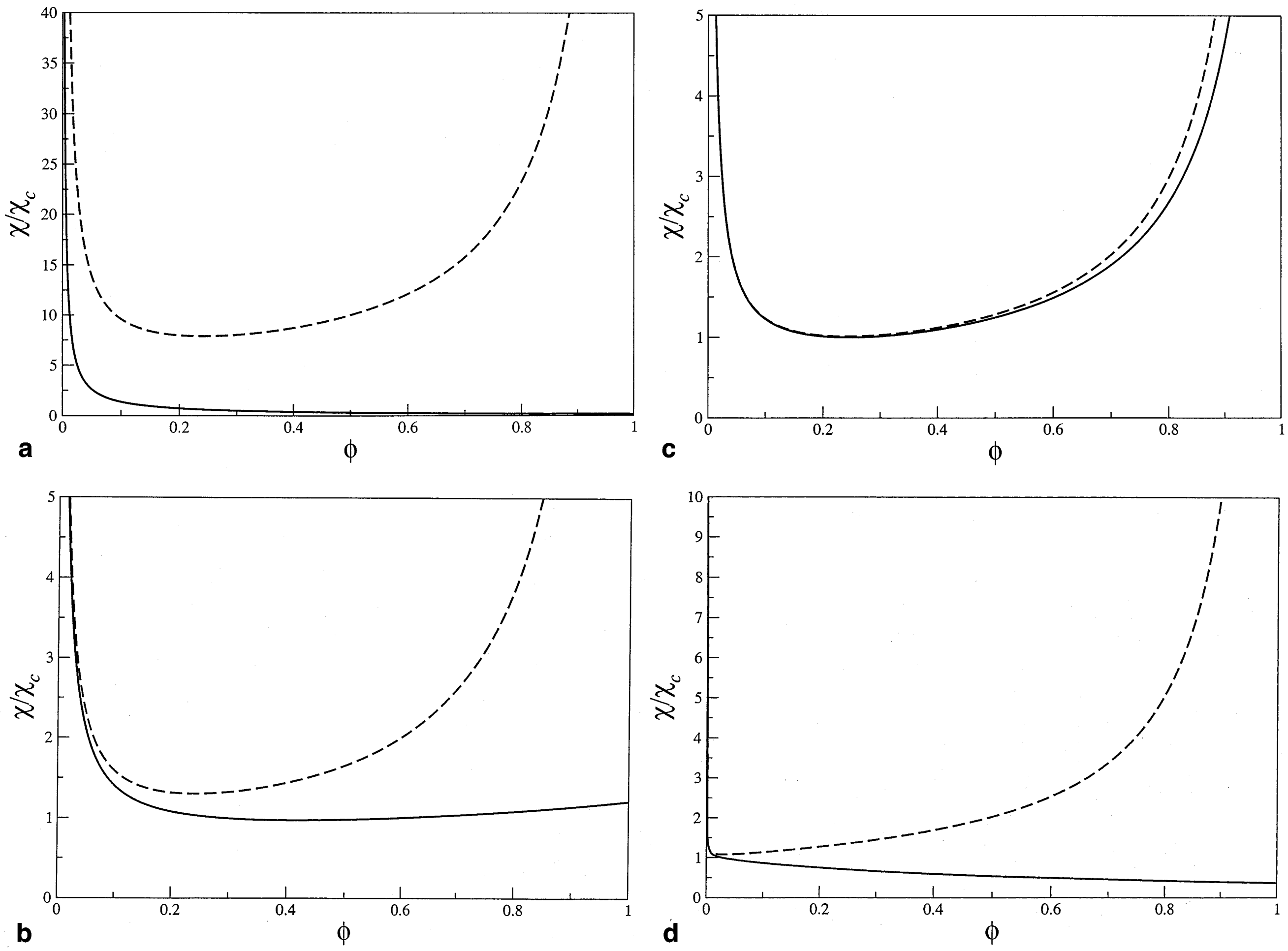

Figure 3. Quenched (long-dashed) and annealed (continuous) spinodals for a chemically polydisperse mixture with an exponential parent shape $\rho_n \sim \exp(af_n)$ as a function of monomer concentration for various degrees of asymmetry a and size ratio r. The interaction strength χ is normalized by its value at the critical point, χ_c, for the corresponding set of parameters r and a: (a) $a = 1$, $r = 10$; (b) $a = 5$, $r = 10$; (c) $a = 20$, $r = 10$; (d) $a = 20$, $r = 1000$.

ing further to first order in gradients, the fluxes obey (with $\alpha = \xi_0/N_e$)

$$\alpha \mathbf{J}_i = -\frac{1}{N_i^2}\nabla\rho_i + \rho_i\nabla m_{-2} + \left[\frac{\rho_i}{N_i} - \rho_i\left(m_{-1} + \frac{1-m_0}{N_s}\right)\right]\nabla m_{-1} + \rho_i\left[2\chi(1-m_0) - \frac{1}{N_s}\right]\left(\frac{1}{N_i} - \mathrm{m}_{-1} + \frac{m_0}{N_s}\right)\nabla m_0 \quad (64)$$

The completely different appearance of this expression from the one obtained previously for chemical polydispersity arises because the friction factor ξ in eq 26 depends explicitly on polymerization index N_i, which is now the polydisperse variable and not the same for all solute chains. Because of the factor N_k arising in the definition of the moments, eq 30, the overall number density of solute chains is m_{-1}. Since in addition the friction appears as a denominator in eq 26, two negative moments appear in the above equation.

Rewriting this in terms of diffusive fluxes $\mathbf{j}_n$ for the moment densities $m_n(\mathbf{r})$, we obtain in the linearized regime

$$\alpha \mathbf{j}_n = -\nabla m_{n-2} + \tilde{m}_n\nabla m_{-2} + \left[\tilde{m}_{n-1} + \tilde{m}_n\tilde{m}_{-1} - \tilde{m}_n\frac{1-\tilde{m}_0}{N_s}\right]\nabla m_{-1} + \left[2\chi(1-\tilde{m}_0) - \frac{1}{N_s}\right]\left(\tilde{m}_{n-1} - \tilde{m}_n\tilde{m}_{-1} + \frac{\tilde{m}_0\tilde{m}_n}{N_s}\right)\nabla m_0 \quad (65)$$

In Appendix B, we provide the corresponding expression to second order in gradients, which can be used, in principle, to study the wavevector dependence of the relaxation modes.

But even in the long wavelength limit, the set of equations is no longer at all tractable: moment m_n is coupled to m_{n-2}, and all moments are coupled to m_0, m_{-1}, and m_{-2}. The higher moments are no longer simple eigenfunctions. Also, there is the additional complication that moments of negative powers of the chain length have entered the description. Since we know that the set of functions $\omega_i(N) = N^i$ form a basis for $i = 0, 1, \ldots$, we can in fact express each negative moment as a linear combination involving only moments with positive index. In doing so, though, we reach an expression for the diffusive fluxes of positive moments which couple to gradients of *all* the other positive moments. It is clear that the diffusion matrix is no longer truncatable and an infinite hierarchy of dynamical modes can be expected. Note that this hierarchy remains compatible with a gross separation into two basic time scales when solvent and solute chains are very different in length. One can still expect a single mode scaling with the inverse solvent size, with the remainder involving the solute chain sizes instead; the hierarchy controls the details of how the solute chains segregate by size.

6.3. Approximate Truncation of the Dynamics. Following Warren,[5] we can try to analyze in more detail the structure of the dynamic modes for length polydispersity by considering the dynamical equations of a finite subset of moments created by simply truncating the diffusion matrix. Thus, we assume that the flux of any species is only coupled to spatial gradients of a finite set of moments. A priori, there is no guarantee that such a process will preserve the character of the modes; we will attempt to verify, a posteriori, that this procedure is in fact sensible.

Let us consider a two-moment description and assume that the two relevant modes are the volume fraction, m_0, and the chain number density, m_{-1}. According to eq 65, their fluxes are coupled to gradients of other moments. However, the assumption that only m_0 and m_{-1} are relevant allows us to express other moments by the corresponding projection into the subspace spanned by the retained moments. To be precise, the weight functions ω_k with k different from 0 and -1 will be approximated as a linear combination of those two weight functions, using the shape of the parent. In this way, we can write

$$\omega_{-k} = \frac{\langle N^{-k}\rangle\langle N^{-2}\rangle - \langle N^{-k-1}\rangle\langle N^{-1}\rangle}{\langle N^{-2}\rangle - \langle N^{-1}\rangle^2}\omega_0 + \frac{\langle N^{-k-1}\rangle - \langle N^{-k}\rangle\langle N^{-1}\rangle}{\langle N^{-2}\rangle - \langle N^{-1}\rangle^2}\omega_{-1} \quad (66)$$

where $\langle ...\rangle$ means an average over the chain length distribution in the parent. With this choice we ensure that the average of ω_{-k} and $\omega_{-k}N^{-1}$ over the parent remains correct.

We can now approximate the two additional moments (m_{-2} and m_{-3}) appearing in the evolution equations of the monomer and chain number densities as linear combination of the retained quantities. In this way, we disregard the coupling of all moments except for m_0 and m_{-1}, getting a closed set of equations. The required projection of moments m_{-3} and m_{-2} read

$$m_{-3} = \frac{\langle N^{-3}\rangle\langle N^{-2}\rangle - \langle N^{-4}\rangle\langle N^{-1}\rangle}{\langle N^{-2}\rangle - \langle N^{-1}\rangle^2}m_0 + \frac{\langle N^{-4}\rangle - \langle N^{-3}\rangle\langle N^{-1}\rangle}{\langle N^{-2}\rangle - \langle N^{-1}\rangle^2}m_{-1} \equiv \beta_{\bar{3}\bar{1}}m_{-1} + \beta_{\bar{3}\bar{0}}m_0$$

$$m_{-2} = \frac{\langle N^{-2}\rangle^2 - \langle N^{-3}\rangle\langle N^{-1}\rangle}{\langle N^{-2}\rangle - \langle N^{-1}\rangle^2}m_0 + \frac{\langle N^{-3}\rangle - \langle N^{-2}\rangle\langle N^{-1}\rangle}{\langle N^{-2}\rangle - \langle N^{-1}\rangle^2}m_{-1} \equiv \beta_{\bar{2}\bar{1}}m_{-1} + \beta_{\bar{2}\bar{0}}m_0 \quad (67)$$

The averages $\langle ...\rangle$ can be expressed in terms of the moments of the parent (which are constants, not dynamical variables) through $\langle N^n\rangle = \tilde{m}_{n-1}/\tilde{m}_{-1}$.

The diffusive fluxes for the retained moments then reduce to

$$\alpha\mathbf{j}_{-1} = \left[-\beta_{\bar{3}\bar{1}} + \beta_{\bar{2}\bar{1}}m_{-1} + m_{-2} - m_{-1}^{\ 2} - (1 - m_0)\frac{m_{-1}}{N_s}\right]\nabla m_{-1} + \left\{-\beta_{\bar{3}0} + \beta_{\bar{2}0}m_{-1} + 2\chi(1 - m_0)\left[m_{-2} - m_{-1}^{\ 2} + \frac{m_{-1}m_0}{N_s}\right] \quad (68)\right.$$

$$\left. + \frac{1}{N_s}\left(m_{-1}^{\ 2} - m_{-2} - \frac{m_{-1}m_0}{N_s}\right)\right\}\nabla m_0 \quad (69)$$

$$\alpha\mathbf{j}_0 = (1 - m_0)\left[-\beta_{\bar{2}\bar{1}} + m_{-1} - \frac{m_0}{N_s}\right]\nabla m_{-1} + (1 - m_0)\left\{-\beta_{\bar{2}0} + 2\chi\left[m_{-1}(1 - m_0) + \frac{m_0^{\ 2}}{N_s}\right] - \frac{m_{-1}}{N_s} - \frac{m_0^{\ 2}}{(1 - m_0)N_s^{\ 2}}\right\}\nabla m_0 \quad (70)$$

In the linearized regime, each of the factors preceding the gradient operator can be evaluated using the parent, in which $\tilde{m}_k = \tilde{m}_0 \langle N^{k+1}\rangle/\langle N\rangle$. Using also the size ratio $r = \langle N\rangle/N_s$, the linearized equations read then

$$\alpha\mathbf{j}_{-1} = [-\langle N\rangle^2\beta_{\bar{3}\bar{1}} + \langle N\rangle\beta_{\bar{2}\bar{1}}\tilde{m}_0 + \tilde{m}_0(\langle N^{-1}\rangle\langle N\rangle - \tilde{m}_0 - r(1 - \tilde{m}_0))]\frac{1}{\langle N\rangle^2}\nabla m_{-1} + \{-\langle N\rangle^3\beta_{\bar{3}\bar{0}} + \langle N\rangle^2\beta_{\bar{2}\bar{0}}\tilde{m}_0 - 2\chi\langle N\rangle(1 - \tilde{m}_0)\tilde{m}_0\,[\langle N^{-1}\rangle\langle N\rangle + \tilde{m}_0(r - 1)] - r\tilde{m}_0(\tilde{m}_0(r - 1) + \langle N^{-1}\rangle\langle N\rangle)\}\frac{\nabla m_0}{\langle N\rangle^3}$$

$$\alpha\mathbf{j}_0 = (1 - \tilde{m}_0)\,[-\langle N\rangle\beta_{\bar{2}\bar{1}} + (1 - r)\tilde{m}_0]\,\frac{1}{\langle N\rangle}\nabla m_{-1} + (1 - \tilde{m}_0)\left[-\langle N\rangle^2\beta_{\bar{2}\bar{0}} + 2\chi\langle N\rangle\tilde{m}_0(1 + \tilde{m}_0(r - 1)) - \tilde{m}_0 r\left(1 + \frac{\tilde{m}_0 r}{1 - \tilde{m}_0}\right)\right]\frac{1}{\langle N\rangle^2}\nabla m_0 \quad (71)$$

These expressions remain fairly cumbersome. To proceed further and gain explicit expressions for the eigenvalues, we will consider only one specific example, where the parent has a uniform distribution with mean length $\langle N\rangle$ and half-width Δ. We will work with the preceding expressions which are lowest order in the gradient expansion. To simplify things further we will consider the limit of a narrow parent ($\langle N\rangle \gg \Delta$) and large size ratio ($r \gg 1$). To the lowest order, the two eigenvalues then simplify to

$$
\begin{aligned}
\lambda_0 &= -D_m q^2 \Biggl\{ [1 + \tilde{m}_0(r-1)]^2 \left(1 - \frac{\chi}{\chi_s}\right) + \\
&\qquad \frac{(1-\tilde{m}_0)(1+\tilde{m}_0 r)\left[1 + \left(1 - \frac{\chi}{\chi_s}\right)(3 + 2\tilde{m}_0 r)\right]}{3\left[1 - \left(1 - \frac{\chi}{\chi_s}\right)(1+\tilde{m}_0 r)^2\right]} \left(\frac{\Delta}{2\langle N\rangle}\right)^2 \Biggr\} \\
&\simeq -\frac{q^2 \tilde{m}_0{}^2}{N_s{}^2}\left(1 - \frac{\chi}{\chi_s}\right) - \frac{2q^2}{3\langle N\rangle^2}(1-\tilde{m}_0)\left(\frac{\Delta}{2\langle N\rangle}\right)^2 \\
\lambda_1 &= -D_m q^2 \Biggl\{ 1 + \Biggl[63 + 5\tilde{m}_0 r - 5\tilde{m}_0{}^2 r - \left(1 - \frac{\chi}{\chi_s}\right) \times \\
&\qquad (1+\tilde{m}_0 r)(43 + 48\tilde{m}_0 r)/15 \left[1 - \left(1 - \frac{\chi}{\chi_s}\right) \times \right. \\
&\qquad\qquad \left. (1+\tilde{m}_0 r)^2\right]\Biggr] \left(\frac{\Delta}{2\langle N\rangle}\right)^2 \Biggr\} \\
&\simeq -\frac{q^2}{\langle N\rangle^2}\left[1 + \frac{16}{5}\left(\frac{\Delta}{2\langle N\rangle}\right)^2\right] \qquad (72)
\end{aligned}
$$

where $D_m \equiv 1/\alpha\langle N\rangle^2$ is a characteristic diffusion coefficient for the polymer solution and where the value of the spinodal strength χ_s coincides with its monodisperse counterpart to the order of validity of the previous expressions.

We see that (at least in the low q limit studied here) the two modes show a structure analogous to, but crucially different from, that described before for chemical polydispersity. The generic tendency at large size ratio r is for λ_0 to greatly exceed λ_1, with the former defining a fast time scale and the latter a slow one. But this tendency is reversed close enough to the spinodal, where λ_0 now vanishes (not λ_1 as in the chemically polydisperse case). The difference arises because for chemical polydispersity the excess free energy involves the first moment of the polymer species, while here it involves the monomer concentration (zeroth moment). The nominally "fast" mode is the thermodynamically unstable one; this was anticipated in Warren's original proposal.[5] Between the quenched and the annealed spinodals, the phase separation can only proceed initially via species sorting, whereas beyond the quenched spinodal, the fast mode (λ_0) will drive the phase separation process from the outset.

To see if the assumption that only two moments matter is too crude, we have repeated the analysis assuming that the relevant moments are the three to which all the other moments are coupled, i.e., m_{-2}, m_{-1}, m_0. For the linearized regime we give the expressions for the corresponding fluxes in Appendix C. In the limit of a narrow parent and large asymmetry the qualitative behavior of the three eigenmodes, found numerically, is the same as the one discussed with the previous approximation, in the sense that in both cases one eigenvalue (λ_0) is generically larger than the rest (since it scales with the inverse solvent size) but crosses over to become smaller than the others in a narrow region as the spinodal is reached.[21]

6.4. Unentangled Solution of Length-Polydisperse Chains. As we have discussed previously, if we follow Clarke,[4] we can assume that the expressions for the diffusive fluxes derived for an entangled mixture in eq 26 keep their general form for an unentangled solution. The only difference is that in this case the friction coefficients are proportional solely to the monomer concentrations, $\xi_i \equiv \alpha\phi_i$, and beyond this have no explicit dependence on polymer length. In this case, the diffusive fluxes of species, eq 26, reduce to

$$
\mathbf{J}_i = \frac{1}{\alpha}\left\{ \sum_k{}' \left[-\frac{\delta_{ik}}{N_i} + \rho_k \right] \rho_i \nabla\mu_k + \rho_i \rho_s \nabla\mu_s \right\} \qquad (73)
$$

and those of the moment densities become

$$
\begin{aligned}
\mathbf{j}_n = \frac{1}{\alpha}\Biggl\{ &-\nabla m_{n-1} + m_n \nabla m_{-1} + \Biggl[2\chi\Bigl[m_n(1 - m_0) + \\
&\frac{1}{24}(m_{n+1}\nabla^2 + m_n \nabla^2 m_1 - m_n m_1 \nabla^2)\Bigr] - \\
&\frac{m_n}{N_s} - \frac{1}{24} m_n \nabla^2 \Biggr] \nabla m_0 \Biggr\} \qquad (74)
\end{aligned}
$$

where we have related local moments of chain number densities to local moments of monomer concentrations.[20]

To analyze the onset of phase separation, we can linearize the previous expression to give

$$
\begin{aligned}
\mathbf{j}_n = \frac{1}{\alpha}\Biggl\{ &-\nabla m_{n-1} + \tilde{m}_n \nabla m_{-1} + \\
&\tilde{m}_n [2\chi\langle N\rangle(1 - \tilde{m}_0) - r] \frac{\nabla m_0}{\langle N\rangle} \Biggr\} \qquad (75)
\end{aligned}
$$

If we assume that we can isolate the dynamics of m_0 and m_{-1} by closing their dynamic equations as was done in the previous section, we obtain for a parent with narrow uniform distribution, in the limit of a narrow distribution (i.e., $\Delta\langle 1$)

$$
\begin{aligned}
\lambda_0 &= -\hat{D}_m q^2 \Biggl[(1 + \tilde{m}_0(r-1))\left(1 - \frac{\chi}{\chi_s}\right) + \\
&\qquad \frac{(1-\tilde{m}_0)\Delta^2}{3\left[-1 + \left(1 - \frac{\chi}{\chi_s}\right)(1 + \tilde{m}_0(r-1))\right]} \Biggr] \\
\lambda_1 &= -\hat{D}_m q^2 \Biggl\{ 1 + \Delta^2 \Biggl[\frac{22}{15} - \\
&\qquad \frac{1 - \tilde{m}_0}{15\left[-1 + \left(1 - \frac{\chi}{\chi_s}\right)(1 + \tilde{m}_0(r-1))\right]} \Biggr] \Biggr\} \qquad (76)
\end{aligned}
$$

where, as before, $\hat{D}_m \equiv 1/\alpha\langle N\rangle$ is a characteristic diffusion coefficient for the polymer solution. Again, we have kept only the dominant contribution in r. The value of χ_s is the same as for the entangled solution, and deviations from its monodisperse value are also negligible in the narrow limit examined.

The eigenmodes here are thus essentially equivalent to the situation described above for the entangled solution. We again observe the appearance of a "fast" mode which nonetheless becomes slow very close to (and then unstable at) the spinodal. Away from there, the generic ratio between the two eigenmodes in this case is not as big as for the entangled case, because the dependence of the friction coefficients on polymerization is not as strong here.

Incidentally, note that in the hypothetical case that the friction coefficient would have been proportional to the chain number density, and then all moments would have coupled to themselves and to m_0, m_1, and m_2. In this case, the only nontrivial eigenmodes would have been the three involving these three moments. A simple picture in terms of the moments is hence recovered exactly in that case.

7. Conclusions

In this paper, we have analyzed the dynamics of polydisperse polymeric materials. Polydispersity affects both the thermodynamics and the mobilities of the system. For a polymeric dense solution, for any polydispersity other than length polydispersity, the mobilities are the same for all species. In such a case, the moment structure of the excess free energy carries over to the dynamics of the system, and it is possible to obtain a simple picture in terms of the moments that appear in the excess free energy. Those are the relevant ones in the linearized dynamic regime, and we have analyzed their implications for the particular case of chemical polydispersity.

The moment structure of the equations of motion makes it possible to map the polydisperse system into an effective binary mixture with a judicious choice of "effective" species. These fictitious species are linear combinations of chain densities such as the monomer concentration and the mean chemical composition. Previous work has not exploited this choice but instead used a small number of discrete values of the polydisperse variable to impersonate the case of continuous polydispersity.[7]

We have seen that this finite moment structure implies in turn that there exists a finite hierarchy of relevant modes in the system. These modes define a fast and a slow time scale that will affect how kinetics takes place depending on the position in the phase diagram. Hence, there will be situations where the fast separation of the overall density will be dominant at short times (and only later the local chemical composition will rearrange on a slower time scale), but in certain instances, it will be the chemical sorting of species that will control the kinetics from the beginning.

The difficulties in the treatment of length polydispersity come from the interplay of dynamics and thermodynamics. In the approach of Warren,[5] such a coupling is not accounted for. Were no such coupling present, our analysis could follow that for chemical polydispersity; we might even be tempted to average (over the parent) the diffusion matrix and the chemical potential gradients separately. However, our analysis suggests that this constitutes a poor description of the true dynamics.

The dependence of mobility on polymer length makes the treatment of length polydispersity more complicated due to the interplay between free energy changes and mobility couplings. Starting from a fast mode theory, we have derived the equations of motions for the moments. By keeping both positive and negative powers of the length, we arrived at a set of dynamical equations that, while more complicated than for chemical polydispersity, retain a relatively simple structure. In fact, the evolution of a given moment is only coupled to gradients of three other moments (whereas in terms of the species, all species are coupled to gradients of all the other species). The fact that we have to keep negative powers of N_i stems from the fact that we are dealing with a fast mode theory. If we re-express those powers in terms of positive powers of N_i, then the dynamics of the remaining moments couple to gradients of all the others. This shows that a judicious choice of moments (including negative ones where appropriate) is central to the simplification of the dynamics.

The study of the linear dynamics shows also the appearance of a fast a a slow time scales (as was the case for chemical polydispersity),although in this case the role of the fast and slow modes are inverted. A detailed analysis of the modes deserves further work to elucidate the structure of the slow time scale.

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Appendix A. Eigenvalues for Chemical Polydispersity

For a chemically polydisperse solution in the presence of a passive solvent, the two relevant eigenvalues in the linearized regime are obtained from eq 51. The only coupled moments are m_0 and m_1. Therefore, the relevant linear system of equations is then defined by the matrix shown in eq 77.

$$\begin{pmatrix} -q^2D_0\{1-\tilde{m}_0\,[1-(1-\tilde{m}_0)(r-1)-r\,[1+\tilde{m}_0(r-1)]W_0(q)]\} & 2\chi D_0N_{\rm p}\tilde{m}_1(1-\tilde{m}_0)\,\{1+\tilde{m}_0(r-1)\}\,W_0(q)^2q^2 \\ q^2D_0\tilde{m}_1\,\{1-(1-\tilde{m}_0)(r-1)-r\,[1+\tilde{m}_0(r-1)]W_0(q)\} & -q^2D_0\,\{1-2\chi N_{\rm p}\,[\tilde{m}_2-\tilde{m}_1{}^2(1-(r-1)(1-\tilde{m}_0))]\,W_0(q)^2 \end{pmatrix} \tag{77}$$

Using Mathematica, we get its corresponding eigenvalues

$$\lambda_0 = \frac{D_0q^2}{2}\{-1-(1+\tilde{m}_0(r-1))^2+2\chi[\tilde{m}_2+\tilde{m}_1{}^2(-1+(1-\tilde{m}_0)(r-1))]+\Delta\}+\frac{D_0q^4}{48}\{4\chi(-\tilde{m}_2+\tilde{m}_1{}^2(2+\tilde{m}_0(-1+r)-r))+\tilde{m}_0(1+\tilde{m}_0(-1+r))r\}+\frac{D_0q^4}{48\Delta}\{\tilde{m}_0{}^2(1+\tilde{m}_0(-1+r))(2+\tilde{m}_0(-1+r))(-1+r)r+8\chi^2(\tilde{m}_2+\tilde{m}_1{}^2(-2+\tilde{m}_0+r-\tilde{m}_0r))^2+2\chi(-4+5r+\tilde{m}_0(-1+r)(-2+3r))(\tilde{m}_0\tilde{m}_2+\tilde{m}_1{}^2(-2+\tilde{m}_0(2-\tilde{m}_0+(-1+\tilde{m}_0)r)))\} \tag{78}$$

$$\lambda_1 = \frac{D_0q^2}{2}\{-1-(1+\tilde{m}_0(r-1))^2+2\chi[\tilde{m}_1{}^2(r-1)(1-\tilde{m}_0)+\tilde{m}_2-\tilde{m}_1{}^2]-\Delta\}+\frac{D_0q^4}{48}\{4\chi(-\tilde{m}_2+\tilde{m}_1{}^2(2+\tilde{m}_0(-1+r)-r))+\tilde{m}_0(1+\tilde{m}_0(-1+r))r\}+\frac{D_0q^4}{48\Delta}\{(\tilde{m}_0{}^2(1+\tilde{m}_0(-1+r))(2+\tilde{m}_0(-1+r))(-1+r)r)-8\chi^2(\tilde{m}_2+\tilde{m}_1{}^2(-2+\tilde{m}_0+r-\tilde{m}_0r))^2+-2\chi(-4+5r+\tilde{m}_0(-1+r)(-2+3r))(\tilde{m}_0\tilde{m}_2+\tilde{m}_1{}^2(-2+\tilde{m}_0(2-\tilde{m}_0+(-1+\tilde{m}_0)r)))\} \tag{79}$$

where the quantity Δ can be expressed as

$$\Delta \equiv \{(1+(1+\tilde{m}_0(r-1))^2+2\chi\,[-\tilde{m}_2+\tilde{m}_1{}^2-\tilde{m}_1{}^2(r-1)(1-\tilde{m}_0)])^2+4(1+\tilde{m}_0(r-1))(-1-\tilde{m}_0(r-1)+2\chi[\tilde{m}_2(1+\tilde{m}_0(r-1))-\tilde{m}_1{}^2r])\}^{1/2} \tag{80}$$

Appendix B. General Expression for Fluxes in Length-Polydisperse Case

In the main text, we have given only the expressions for the diffusive fluxes in the linearized case because the generic expressions become quite lengthy, and display them here instead. The generic expressions for the diffusive flux of species i can be expressed as

$$\alpha\mathbf{J}_i = -\frac{1}{N_i{}^2}\nabla\rho_i+\rho_i\nabla m_{-2}+\rho_i\Big[\frac{1}{N_i}-\Big(m_{-1}+\frac{1-m_0}{N_\mathrm{s}}\Big)-\frac{1}{24}\nabla^2+\frac{1}{24}\nabla^2m_0\Big]\nabla m_{-1}+\Big\{2\rho_i\chi\Big[\frac{W_{0i}}{N_i}-\frac{1}{N_i}\Big(m_0-\frac{1}{24}\nabla^2m_1+\frac{1}{24}m_1\nabla^2\Big)-m_{-1}+\frac{1}{24}\nabla^2m_0-\frac{1}{24}m_0\nabla^2+\Big(m_{-1}-\frac{1}{24}\nabla^2m_0+\frac{1-m_0}{N_\mathrm{s}}\Big)\Big(m_0-\frac{1}{24}\nabla^2m_1+\frac{1}{24}m_1\nabla^2\Big)\Big]+\rho_i\Big[-\frac{1}{24N_i}\nabla^2+\Big(m_{-1}+\frac{1-m_0}{N_\mathrm{s}}\Big)\frac{1}{24}\nabla^2-\frac{1}{N_\mathrm{s}}\Big(\frac{1}{N_i}+\frac{m_0}{N_\mathrm{s}}-m_{-1}+\frac{1}{24}\nabla^2m_0\Big)\Big]\Big]\Big\}\nabla m_0 \tag{81}$$

while the corresponding fluxes for the moments can be expressed as

$$\mathbf{j}_n = -\nabla m_{n-2}+m_n\nabla m_{-2}+\Big[m_{n-1}-m_nm_{-1}-\frac{m_n(1-m_0)}{N_\mathrm{s}}+\frac{1}{24}m_n(\nabla^2m_0-\nabla^2)\Big]\nabla m_{-1}+\Big\{2\chi\Big[(1-m_0)\Big(m_{n-1}-m_nm_{-1}+\frac{m_nm_0}{N_\mathrm{s}}\Big)+\frac{1}{24}\Big[\nabla^2m_n+m_n((1-m_0)\nabla^2m_0-m_0\nabla^2)+\Big(m_nm_{-1}+\frac{m_n(1-m_0)}{N_\mathrm{s}}-m_{n-1}\Big)(m_1\nabla^2-\nabla^2m_1)\Big]\Big]-\frac{m_{n-1}-m_n(m_{-1}-m_0/N_\mathrm{s})}{N_\mathrm{s}}+\frac{1}{24}\Big(-m_{n-1}+m_nm_{-1}+\frac{m_n(1-m_0)}{N_\mathrm{s}}\Big)\nabla^2-\frac{m_n}{24N_\mathrm{s}}\nabla^2m_0\Big\}\nabla m_0 \tag{82}$$

Appendix C. Diffusive Fluxes after Dynamical Projection

We provide here the expression for the diffusive fluxes of the moments m_{-2}, m_{-1}, and m_0, when we have derived a closed set of equation for their dynamics. These expressions were used to obtain numerically the three corresponding eigenmodes, and can be written down as

$$\mathbf{j}_{-2} = (-\langle N\rangle^2\gamma_{\bar{4}\bar{2}}+\tilde{m}_0\langle N\rangle\langle N^{-1}\rangle)\,\frac{1}{\langle N\rangle^2}\nabla m_{-2}+[-\gamma_{\bar{4}\bar{1}}\langle N\rangle^3+\tilde{m}_0\langle N^{-2}\rangle\langle N\rangle^2-\tilde{m}_0\langle N^{-1}\rangle\langle N\rangle(r(1-\tilde{m}_0)+\tilde{m}_0)]\,\frac{\nabla m_{-1}}{\langle N\rangle^3}+[-\langle N\rangle^4\gamma_{\bar{4}0}+\tilde{m}_0(2\chi\langle N\rangle(1-\tilde{m}_0)-r)(\langle N^{-2}\rangle\langle N\rangle^2+\tilde{m}_0(r-1)\langle N^{-1}\rangle\langle N\rangle)]\,\frac{\nabla m_0}{\langle N\rangle^4}$$

$$\mathbf{j}_{-1} = (-\langle N\rangle\gamma_{\bar{3}\bar{2}}+\tilde{m}_0)\frac{1}{\langle N\rangle}\nabla m_{-2}+(-\langle N\rangle^2\gamma_{\bar{3}\bar{2}}+\tilde{m}_0\langle N^{-1}\rangle\langle N\rangle-\tilde{m}_0((1-\tilde{m}_0)r+\tilde{m}_0))\frac{1}{\langle N\rangle^2}\nabla m_{-1}+[-\langle N\rangle^3\gamma_{\bar{3}0}+2\chi\langle N\rangle\tilde{m}_0(1-\tilde{m}_0)(\langle N^{-1}\rangle\langle N\rangle+\tilde{m}_0(r-1))-r\tilde{m}_0(\langle N^{-1}\rangle\langle N\rangle+\tilde{m}_0(r-1))]\,\frac{1}{\langle N\rangle^3}\nabla m_0$$

$$\mathbf{j}_0 = -(1-\tilde{m}_0)\nabla m_{-2}-\tilde{m}_0(1-\tilde{m}_0)(r-1)\frac{\nabla m_{-1}}{\langle N\rangle}+m_0[2\chi\langle N\rangle(1-\tilde{m}_0)(1+\tilde{m}_0(r-1))-r(1+\tilde{m}_0(r-1))]\frac{\nabla m_0}{\langle N\rangle^2} \tag{83}$$

The coefficients $\gamma_{\bar{i}\bar{j}}$ with $i = 4, 3$ and $j = 2, 1, 0$ are the equivalent of the coefficients $\beta_{\bar{i}\bar{j}}$ in eqs 67 when we project the moments m_{-4} and m_{-3} into the subspace spanned by the moments m_{-2}, m_{-1}, and m_0. The values of these coefficients are functions of the subspace chosen.

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(10) Doi, M.; Onuki, A. *J. Phys. II* **1992**, *2*, 1631.
(11) The weight function is related to the square root of the Debye function. For a polymer of length N_i, one has $\omega(q) = N_i g(q)^{1/2.}$ In the text, we are interested in the low q expansion of the Debye function $g(q)$; see ref 2. $g(q)$ also depends on the polymer length through the gyration radius.
(12) In the present formulation, the determination of the diffusive flux is done neglecting the spatial extent of the polymeric chains, and this is introduced only in this section to describe the thermodynamics. This description follows in spirit what is done in ref 4, and in Cahn−Hilliard theory for polymeric systems generally. However, a more systematic approach would be to consider the nonlocal relation between the monomer and the chain density when deriving the diffusion fluxes (see, e.g.: Pincus, P. *J. Chem. Phys.* **1981**, *75*, 1996). The nonlocal dependence derived in this reference for the blend mobility suggests that to leading order in the wave vector the results we report will not be affected, while the subsequent dependence in wave vector will have modified amplitudes; however, we do not expect that the general trends of our results will be affected by the disregarded nonlocal effects in the mobility matrix.
(13) The use of dynamical mean field theory (variable effective χ) in treating random copolymers requires that the monomeric interactions are sufficiently weak that these do not present barriers to the diffusion of any individual chain. See, e.g. Bouchaud, J.-P.; Cates, M. E. *J. Phys. (Paris) II* **1993**, *3*, 1171.
(14) The diffusion matrix D_{ij} is defined by writing eq 38 as $\dot{m}_i(q) = D_{ij}(q)m_j(q)$ in Fourier space.
(15) Note that the eigenvalues λ_i are rates that control the initial growth of the moments. They are then characteristic frequencies defined by $\delta m_n(t) = \delta m_n(0)\ \exp(\lambda_n t)$.
(16) Except for the fact that m_0 depends on m_1, the matrix of coefficients that defines the linear dynamics of this system is lower triangular.
(17) What we call $\tilde{\lambda}_i$ (with i being a species) corresponds to the coefficients λ_i in ref 4. We have introduced the tilde to avoid confusion with the growth rates, which are referred to as λ_n (with n being a moment).
(18) Kramer, E. J.; Green, P.; Palstrom, C. J. *Polymer* **1984**, *25*, 473.
(19) The fact that Brochard's model is a fast mode theory can be appreciated in the expressions for the diffusive fluxes, eq 26. The contribution of species j to the flux of species i is inverserly proportional to its friction coefficient (which in turn is proportional to its polymerization length). Hence, the longer the chain the smaller the cooresponding contribution to the diffusive flux of the rest of the species.
(20) This in turn means that $\sum_k \omega_{nk} N_k \rho_k(\mathbf{r}) = m_n(\mathbf{r}) - {}^1/_{24}\nabla^2 m_{n+1}(\mathbf{r})$.
(21) The perturbative analysis around the monodisperse limit should be analyzed carefully, since it has a singular character depending how it is performed. Moreover, an incomplete treatment of the dynamics based on a finite subset of moments may give rise to spurious oscillatory modes. We thank M. R. L. Evans for an enlightening discussion of this point.

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