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Kinetics of Phase Separation in Polydisperse Polymer Mixtures

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ABSTRACT: The linearized theory of spinodal decomposition of binary (AB) mixtures is extended to a polymer mixture where both the A chains and the B chains may be polydisperse. The treatment is based on a dynamic generalization of the Flory–Huggins lattice model including vacancies (that model "free volume"), considering the limit where the vacancy concentration is small and the system is brought to a state close to the spinodal curve. It is shown that in this case the amplification factor $R(q)$ of the fluctuations with wavevector q has the same behavior as in the monodisperse mixture; only the prefactors get renormalized by certain combinations of moments over the molecular weight distribution. Experimental consequences of these results are briefly discussed as well as the related case of unmixing of a monodisperse three-component system (polymer A, polymer B_1, and polymer B_2).

1. Introduction

The kinetics of phase separation of fluid binary polymer mixtures triggered by the spontaneous growth of concentration fluctuations ("spinodal decomposition"[1-6]) has found much recent attention, both experimentally[7-20] and theoretically.[21-29] There are two reasons that the study of spinodal decomposition in polymer mixtures is particularly rewarding:

(i) For large molecular weights, unmixing proceeds so slowly that the initial stages where the concentration inhomogeneities are still small are rather conveniently observed,[14-16] and a meaningful comparison with the "linearized" theory describing these initial stages then should be possible,[21-24,26,29] unlike fluid mixtures of small molecules,[6] where one practically always probes the coarsening behavior occurring at the later stages of unmixing.[3,4]

(ii) Due to the mean-field character[23,24,30,31] of the unmixing transition in polymer mixtures, there is a well-defined initial time regime in polymer mixtures where the linear theory should actually be quantitatively valid,[23,24] unlike fluid mixtures of small molecules or solid alloys where nonlinear behavior of the concentration fluctuations is predicted[5] and found[3,4] already during the earliest stages.

Thus, a quantitative comparison between theory[21-29] and experiment[7-20] would be very desirable: first, a significant experimental check of the theory would show whether our current theoretical understanding of the problem is fairly complete; second, fitting the theory to the experimental data then would yield several interesting microscopic parameters characterizing the mixture.

Unfortunately, such an approach is still hampered by the fact that the theory[21-29] always has considered the idealized case of monodisperse polymers only, while in practice polydispersity of the chains[32] must always be accounted for. The polydispersity changes the parameters describing the static scattering in the one-phase region[33] and the spinodal curve and may have a drastic effect on the equilibrium phase diagram, as given by the "coexistence curve" (binodal) of the mixture.[34-36] The present paper now describes an attempt to fill this gap and study the effect of polydispersity on the kinetic factors entering the theory of spinodal decomposition.

For monodisperse binary mixtures of A chains (consisting of N_A "Kuhn segments" of size σ_A) and B chains (consisting of N_B segments of size σ_B), it was predicted that in the initial stages the relaxation of concentration fluctuations at wavevector q is described by the "amplification factor" $R(q)$ described by

$$R(q) = -q^2 \Lambda(q) \frac{1}{S_T^{\text{coll}}(q)} \tag{1}$$

where $S_T^{\text{coll}}(q)$ is a scattering function describing the collective concentration fluctuations of the mixture and $\Lambda(q)$ is an effective Onsager coefficient describing the interdiffusion of the chains. Denoting the volume fraction of the A segments as ϕ and that of the B segments as $1 - \phi$ (neglecting "free volume", the mixture is treated as incompressible), one finds for long wavelengths (q^{-1} exceeding the radii of both A coils and B coils)[21-23,37,38]

$$\frac{1}{S_T^{\text{coll}}(q)} = \frac{1}{\phi N_A} + \frac{1}{(1-\phi)N_B} - 2\chi + \frac{1}{18}\left(\frac{\sigma_A^2}{\phi} + \frac{\sigma_B^2}{1-\phi}\right)q^2 \tag{2}$$

Here χ is the Flory–Huggins parameter,[35,38,39] and 2χ is defined as the second derivative of the enthalpy with respect to ϕ, normalized per volume of a Flory–Huggins

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lattice cell (which we take as unity to simplify our notation). Corrections to the gradient energy term (proportional to q^2 in eq 2) due to chain interactions[23] are neglected. The kinetic factor $\Lambda(q)$ in the long-wavelength limit has been obtained as[23,40]

$$\Lambda^{-1}(0) = [N_A \phi D_A^*]^{-1} + [N_B(1-\phi)D_B^*]^{-1} \tag{3}$$

where D_A^* is the tracer diffusion coefficient of an A chain in a B environment and D_B^* the tracer diffusion coefficient of a B chain in an A environment. We note that the equation of the spinodal curve is given by

$$\chi = \chi_{sp}(\phi) = \frac{1}{2}\left(\frac{1}{\phi N_A} + \frac{1}{(1-\phi)N_B}\right) \tag{4}$$

hence $[S_T^{coll}(q)]^{-1} < 0$ in the unstable region inside of the spinodal curve for small enough q, and the amplification factor $R(q)$ in eq 1 is positive, leading to an initial exponential growth of concentration fluctuations.

Now the static scattering function of polydisperse polymer mixtures has already been obtained by Joanny[33] as

$$\frac{1}{S_T^{coll}(q)} = \frac{1}{\phi \overline{N_A}^w} + \frac{1}{(1-\phi)\overline{N_B}^w} - 2\chi + \frac{q^2}{18}\left[\frac{\overline{N_A}^z}{\overline{N_A}^w}\frac{\sigma_A^2}{\phi} + \frac{\overline{N_B}^z}{\overline{N_B}^w}\frac{\sigma_B^2}{1-\phi}\right] \tag{5}$$

where the averages $\overline{N^w}$ and $\overline{N^z}$ over the chain-length distribution are defined in the standard way as[32]

$$\overline{N^w} = \overline{N^2}/\overline{N^1},\ \overline{N^z} = \overline{N^3}/\overline{N^2} \tag{6}$$

and the (unnormalized) moments $\overline{N^k}$, k integer, are defined in terms of the number n_{N_i} of chains of length N_i in the system

$$\overline{N^k} = \sum_i n_{N_i} N_i^k \tag{7}$$

The questions to be asked in the present paper hence are the following: does the separation of $R(q)$ into a static part $[S_T^{coll}(q)]^{-1}$ and a dynamic part $q^2\Lambda(q)$ in eq 1 hold also in the polydisperse case? If so, what is the generalization of eq 3 to the polydisperse case?

To answer these questions, we formulate in section 2 the generalized diffusion equation for a polydisperse polymer mixture. Section 3 discusses the time-dependent structure factor for quenches leading to the vicinity of the spinodal curve. Section 4 discusses a simplified example, where one species is assumed to be monodisperse and the other species is assumed to be a mixture of two monodisperse fractions. Section 5 discusses the application of our results to typical experimental cases and summarizes our conclusions.

2. Diffusion in the Flory–Huggins Lattice Model of Polydisperse Polymer Mixtures

Following Flory[39] and Lacombe and Sanchez[39] we assume a lattice model where each cell can be taken by either one polymer segment or a vacancy, described by a free energy per cell volume (k_B is Boltzmann's constant, T is temperature)

$$f/k_BT = \sum_{i=1}^{m_A}\frac{\phi_i^A}{N_i^A}\ln\phi_i^A + \sum_{i=1}^{m_B}\frac{\phi_i^B}{N_i^B}\ln\phi_i^B + \phi_V\ln\phi_V + \chi_{AB}\phi_A\phi_B + \chi_{AV}\phi_A\phi_V + \chi_{BV}\phi_B\phi_V$$

$$\phi_A \equiv \sum_{i=1}^{m_A}\phi_i^A, \qquad \phi_B \equiv \sum_{i=1}^{m_B}\phi_i^B, \qquad \phi_A + \phi_B + \phi_V = 1 \tag{8}$$

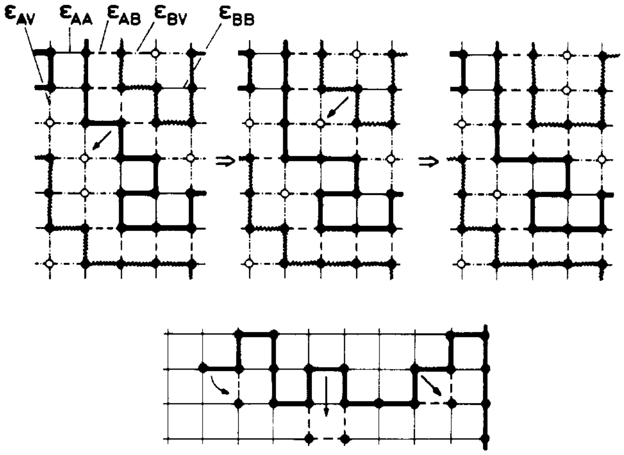

Figure 1. Schematic illustration of the dynamic Flory–Huggins lattice model of a polymer mixture as it is used, for instance, in Monte Carlo simulations.[42] Lattice sites taken by segments are indicated by full dots; lattice sites taken by vacancies are denoted by empty circles. A chains are denoted by thick bonds between the segments and B chains by wavy bonds. Nearest-neighbor interaction energies between segments of the same kind (ϵ_{AA} and ϵ_{BB}) are denoted by full straight lines and between segments of different kinds (ϵ_{AB}) by broken lines [note that $\chi_{AB} = z/2(\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB})/k_BT$, z being the coordination number]. Interactions between segments and vacancies (ϵ_{AV} and ϵ_{BV}) are denoted by dashed–dotted lines. Dynamics is introduced into this model by random motion of single bonds (at the chain ends), by "crankshaft" motions of three neighboring bonds, and by random exchange of two neighboring bonds which form an angle of 90°, as indicated in the lower part of the figure. These motions must obey the excluded volume principle that each site can be taken by a single segment only, and the energies ϵ_{AA}, ϵ_{AB}, ϵ_{BB}, ϵ_{AV}, and ϵ_{BV} must be taken into account by suitable transition probabilities satisfying the detailed balance principle with the canonic probability distribution in order to guarantee approach toward thermal equilibrium. The upper part of the figure illustrates that by suitable succession of these random motions a lattice site previously taken by an A segment later may be taken by a B segment.

Here $\phi_i^{A(B)}$ is the volume fraction of the i-th fraction of polymer A (B) of chain length N_i^A (N_i^B), we assume there are m_A (m_B) such fractions, and we assume a volume fraction ϕ_V of vacancies and allow for *three* Flory–Huggins parameters χ_{AB}, χ_{AV}, and χ_{BV} (i.e., we assume that the interaction energies do not depend on the chain lengths and hence are the same for all fractions of a species). The vacancies are needed in this context to allow for a dynamics in terms of random local motions of the chains;[41,42] see, e.g., Figure 1. Since we wish to consider how concentration inhomogenities relax, we must allow our volume fractions $\vec{\phi} \equiv (\phi_1^A, ..., \phi_{m_A}^A, \phi_1^B, ..., \phi_{m_B}^B, \phi_V)$ to depend on the position $\mathbf{r}$ in the lattice, and we must add gradient energy terms in the free energy functional $\mathcal{F}$, in addition to the integral of eq 8 over the whole volume

$$\mathcal{F}/k_BT = \int d\mathbf{r}\, \{f(\vec{\phi}(\mathbf{r}))/k_BT + \sum_{i=1}^{m_A} a_i^2(\vec{\phi}) \times [\nabla\phi_i^A(\mathbf{r})]^2 + \sum_{i=1}^{m_B} b_i^2(\vec{\phi})[\nabla\phi_j^B(\mathbf{r})]^2\} \tag{9}$$

Here the characteristic lengths $a_i(\vec{\phi})$ and $b_i(\vec{\phi})$ must be chosen as[43]

$$a_i(\vec{\phi}) = \sigma_A/(6(\phi_i^A)^{1/2}), \quad b_i(\vec{\phi}) = \sigma_B/(6(\phi_i^B)^{1/2}), \quad \text{for } \phi_V \rightarrow 0 \tag{10}$$

in order that eq 9 is consistent with eq 5.

Since the total number of chains for each fraction of A and B chains and the number of vacancies[44] in the model are conserved, we have continuity equations

$$\frac{\partial \phi_i^{\mathrm{A}}(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{J}_i^{\mathrm{A}}(\mathbf{r},t) = 0, \qquad i = 1, ..., m_{\mathrm{A}} \quad (11a)$$

$$\frac{\partial \phi_i^{\mathrm{B}}(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{J}_i^{\mathrm{B}}(\mathbf{r},t) = 0 \qquad i = 1, ..., m_{\mathrm{B}} \quad (11b)$$

$$\frac{\partial \phi_{\mathrm{V}}(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{J}_{\mathrm{V}}(\mathbf{r},t) = 0 \quad (11c)$$

The current densities of the i-th fraction of polymer A (B) are denoted as $\mathbf{J}_i^{\mathrm{A(B)}}(\mathbf{r},t)$, respectively. The current density of the vacancies $\mathbf{J}_{\mathrm{V}}(\mathbf{r},t)$ can be eliminated by using the relation

$$\mathbf{J}_{\mathrm{V}}(\mathbf{r},t) = -\sum_{i=1}^{m_{\mathrm{A}}} \mathbf{J}_i^{\mathrm{A}}(\mathbf{r},t) - \sum_{i=1}^{m_{\mathrm{B}}} \mathbf{J}_i^{\mathrm{B}}(\mathbf{r},t) \quad (12)$$

Consistent with the microscopic picture, Figure 1, that there is only direct interchange possible between either A segments and vacancies or B segments and vacancies, we assume that the driving force for $\mathbf{J}_i^{\mathrm{A}}(\mathbf{r},t)$ $[\mathbf{J}_i^{\mathrm{B}}(\mathbf{r},t)]$ is the chemical potential difference between the respective polymer fraction and the vacancies

$$\mathbf{J}_i^{\mathrm{A}}(\mathbf{r},t) = -\frac{\lambda_i^{\mathrm{A}}(\vec{\phi}(\mathbf{r},t))}{k_{\mathrm{B}}T} \nabla[\mu_i^{\mathrm{A}}(\mathbf{r},t) - \mu_{\mathrm{V}}(\mathbf{r},t)], \qquad i = 1, ..., m_{\mathrm{A}} \quad (13a)$$

$$\mathbf{J}_i^{\mathrm{B}}(\mathbf{r},t) = -\frac{\lambda_i^{\mathrm{B}}(\vec{\phi}(\mathbf{r},t))}{k_{\mathrm{B}}T} \nabla[\mu_i^{\mathrm{B}}(\mathbf{r},t) - \mu_{\mathrm{V}}(\mathbf{r},t)], \qquad i = 1, ..., m_{\mathrm{b}} \quad (13b)$$

the λ_i^{A} and λ_i^{B} being suitable Onsager coefficients that will be discussed below. Now in homogeneous equilibrium the chemical potentials μ_i^{A}, μ_i^{B}, and μ_{V} are simply expressed in terms of partial derivatives of f in eq 8

$$\mu_i^{\mathrm{A}} = f + \sum_{j=1}^{m_{\mathrm{A}}} \frac{\partial f}{\partial \phi_j^{\mathrm{A}}}(\delta_{ij} - \phi_j^{\mathrm{A}}) - \sum_{j=1}^{m_{\mathrm{B}}} \frac{\partial f}{\partial \phi_i^{\mathrm{B}}}\phi_j^{\mathrm{B}} - \frac{\partial f}{\partial \phi_{\mathrm{V}}}\phi_{\mathrm{V}} \quad (14a)$$

$$\mu_i^{\mathrm{B}} = f - \sum_{j=1}^{m_{\mathrm{A}}} \frac{\partial f}{\partial \phi_j^{\mathrm{A}}}\phi_j^{\mathrm{A}} + \sum_{j=1}^{m_{\mathrm{B}}} \frac{\partial f}{\partial \phi_j^{\mathrm{B}}}(\delta_{ij} - \phi_j^{\mathrm{B}}) - \frac{\partial f}{\partial \phi_{\mathrm{V}}}\phi_{\mathrm{V}} \quad (14b)$$

$$\mu_{\mathrm{V}} = f - \sum_{j=1}^{m_{\mathrm{A}}} \frac{\partial f}{\partial \phi_j^{\mathrm{A}}}\phi_j^{\mathrm{A}} - \sum_{j=1}^{m_{\mathrm{B}}} \frac{\partial f}{\partial \phi_j^{\mathrm{B}}}\phi_j^{\mathrm{B}} + \frac{\partial f}{\partial \phi_{\mathrm{V}}}(1 - \phi_{\mathrm{V}}) \quad (14c)$$

and hence

$$\mu_i^{\mathrm{A}} - \mu_{\mathrm{V}} = \frac{\partial f}{\partial \phi_i^{\mathrm{A}}} - \frac{\partial f}{\partial \phi_{\mathrm{V}}}, \qquad i = 1, ..., m_{\mathrm{A}} \quad (15a)$$

$$\mu_i^{\mathrm{B}} - \mu_{\mathrm{V}} = \frac{\partial f}{\partial \phi_i^{\mathrm{B}}} - \frac{\partial f}{\partial \phi_{\mathrm{V}}} \; ... \; i = 1, ..., m_{\mathrm{B}} \quad (15b)$$

In the inhomogeneous case, the partial derivatives $\partial f/\partial \phi$ are to be replaced by functional derivatives $\delta \mathcal{F}/\delta \phi$. Thus eq 15 gets complemented by terms due to the gradient energies in eq 9

$$\mu_i^{\mathrm{A}}(\mathbf{r},t) - \mu_{\mathrm{V}}(\mathbf{r},t) = \frac{\partial f(\vec{\phi}(\mathbf{r},t))}{\partial \phi_i^{\mathrm{A}}(\mathbf{r},t)} - \frac{\partial f(\vec{\phi}(\mathbf{r},t))}{\partial \phi_{\mathrm{V}}(\mathbf{r},t)} - 2k_{\mathrm{B}}Ta_i^2(\vec{\phi})\nabla^2\phi_i^{\mathrm{A}}(\mathbf{r},t) \quad (16a)$$

$$\mu_i^{\mathrm{B}}(\mathbf{r},t) - \mu_{\mathrm{V}}(\mathbf{r},t) = \frac{\partial f(\vec{\phi}(\mathbf{r},t))}{\partial \phi_i^{\mathrm{B}}(\mathbf{r},t)} - \frac{\partial f(\vec{\phi}(\mathbf{r},t))}{\partial \phi_{\mathrm{V}}(\mathbf{r},t)} - 2k_{\mathrm{B}}Tb_i^2(\vec{\phi})\nabla^2\phi_i^{\mathrm{B}}(\mathbf{r},t) \quad (16b)$$

where terms nonlinear in $\nabla\phi$ have been neglected since we wish to consider small deviations from equilibrium only. In this limit, we linearize all derivatives $\partial f/\partial \phi$ as follows $(\bar{\vec{\phi}}(=\overline{\phi_1^{\mathrm{A}}}, ..., \overline{\phi_{m_{\mathrm{A}}}^{\mathrm{A}}}, \overline{\phi_1^{\mathrm{B}}}, ..., \overline{\phi_{m_{\mathrm{B}}}^{\mathrm{B}}}, \bar{\phi}_{\mathrm{V}})$ describes the equilibrium volume fractions):

$$\frac{\partial f(\vec{\phi}(\mathbf{r},t))}{\partial \phi_i^{\mathrm{A}}(\mathbf{r},t)} = \left.\frac{\partial f(\vec{\phi})}{\partial \phi_i^{\mathrm{A}}}\right|_{\bar{\vec{\phi}}} + \sum_{j=1}^{m_{\mathrm{A}}} \left.\frac{\partial^2 f(\vec{\phi})}{\partial \phi_i^{\mathrm{A}} \partial \phi_j^{\mathrm{A}}}\right|_{\bar{\vec{\phi}}} [\phi_j^{\mathrm{A}}(\mathbf{r},t) - \overline{\phi_j^{\mathrm{A}}}] + \sum_{j=1}^{m_{\mathrm{B}}} \left.\frac{\partial^2 f(\vec{\phi})}{\partial \phi_i^{\mathrm{A}} \partial \phi_j^{\mathrm{B}}}\right|_{\bar{\vec{\phi}}} [\phi_j^{\mathrm{B}}(\mathbf{r},t) - \overline{\phi_j^{\mathrm{B}}}] + \left.\frac{\partial^2 f(\vec{\phi})}{\partial \phi_i^{\mathrm{A}} \partial \phi_{\mathrm{V}}}\right|_{\bar{\vec{\phi}}} [\phi_{\mathrm{V}}(\mathbf{r},t) - \bar{\phi}_{\mathrm{V}}] \quad (17)$$

and similarly for all other derivatives. Inserting eq 16 and 17 into the set of differential equations following from eq 11 and 13

$$\frac{\partial \phi_i^{\mathrm{A}}(\mathbf{r},t)}{\partial t} = \frac{\lambda_i^{\mathrm{A}}(\bar{\vec{\phi}})}{k_{\mathrm{B}}T} \nabla^2[\mu_i^{\mathrm{A}}(\mathbf{r},t) - \mu_{\mathrm{V}}(\mathbf{r},t)], \qquad i = 1, ..., m_{\mathrm{A}} \quad (18a)$$

$$\frac{\partial \phi_i^{\mathrm{B}}(\mathbf{r},t)}{\partial t} = \frac{\lambda_i^{\mathrm{B}}(\bar{\vec{\phi}})}{k_{\mathrm{B}}T} \nabla^2[\mu_i^{\mathrm{B}}(\mathbf{r},t) - \mu_{\mathrm{V}}(\mathbf{r},t)], \qquad i = 1, ..., m_{\mathrm{B}} \quad (18b)$$

one obtains a set of $m_{\mathrm{A}} + m_{\mathrm{B}}$ coupled diffusion equations. Introduction of spatial Fourier transforms $\phi_{iq}^{\mathrm{A}}(t)$ and $\phi_{iq}^{\mathrm{B}}(t)$ of the volume fraction deviations $\phi_i^{\mathrm{A}}(\mathbf{r},t) - \overline{\phi_i^{\mathrm{A}}}$ and $\phi_i^{\mathrm{B}}(\mathbf{r},t) - \overline{\phi_i^{\mathrm{B}}}$ reduces this set of coupled diffusion equations to the following set of coupled ordinary differential equations[43] $\{\phi_{iq}^{\mathrm{A}}(t) \equiv (\mathrm{volume})^{-1/2} \int \exp(-i\mathbf{q}\cdot\mathbf{r})[\phi_i^{\mathrm{A}}(\mathbf{r},t) - \overline{\phi_i^{\mathrm{A}}}]\, \mathrm{d}\mathbf{r}\}$

$$\frac{\partial \phi_{iq}^{\mathrm{A}}(t)}{\partial t} = -\lambda_i^{\mathrm{A}}(\bar{\vec{\phi}})q^2\{\sum_{j=1}^{m_{\mathrm{A}}} M_{ij}^{\mathrm{AA}}\phi_{jq}^{\mathrm{A}}(t) + \sum_{j=1}^{m_{\mathrm{B}}} M_{ij}^{\mathrm{AB}}\phi_{jq}^{\mathrm{B}}(t) + 2a_i^2(\bar{\vec{\phi}})q^2\phi_{iq}^{\mathrm{A}}(t)\} \quad (19a)$$

$$\frac{\partial \phi_{iq}^{\mathrm{B}}(t)}{\partial t} = -\lambda_i^{\mathrm{B}}(\bar{\vec{\phi}})q^2\{\sum_{j=1}^{m_{\mathrm{A}}} M_{ij}^{\mathrm{BA}}\phi_{jq}^{\mathrm{A}}(t) + \sum_{j=1}^{m_{\mathrm{B}}} M_{ij}^{\mathrm{BB}}\phi_{jq}^{\mathrm{B}}(t) + 2b_i^2(\bar{\vec{\phi}})q^2\phi_{iq}^{\mathrm{B}}(t)\} \quad (19b)$$

and the M_{ij}^{AA}, M_{ij}^{AB}, M_{ij}^{BA}, and M_{ij}^{BB} are matrix elements of a $(m_{\mathrm{A}} + m_{\mathrm{B}}) \times (m_{\mathrm{A}} + m_{\mathrm{B}})$ matrix, defined as follows:

$$\boldsymbol{M} = \begin{pmatrix} \boldsymbol{M}^{\mathrm{AA}} & \boldsymbol{M}^{\mathrm{AB}} \\ \boldsymbol{M}_{\mathrm{BA}} & \boldsymbol{M}^{\mathrm{BB}} \end{pmatrix} \quad (20)$$

with

$$M_{ij}^{\mathrm{AA}} = \frac{\delta_{ij}}{N_i^{\mathrm{A}}\overline{\phi_i^{\mathrm{A}}}} + \frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{AV}} \quad (21a)$$

$$M_{ij}^{\mathrm{AB}} = \frac{1}{\bar{\phi}_{\mathrm{V}}} + \chi_{\mathrm{AB}} - (\chi_{\mathrm{AV}} + \chi_{\mathrm{BV}}) = M_{ij}^{\mathrm{BA}} \quad (21b)$$

$$M_{ij}^{\mathrm{BB}} = \frac{\delta_{ij}}{N_i^{\mathrm{B}}\overline{\phi_i^{\mathrm{B}}}} + \frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{BV}} \quad (21c)$$

We now look for solutions of the type $\phi_{iq}^{\mathrm{A}}(t) = \tilde{\phi}_{iq}^{\mathrm{A}} \exp(-Dq^2t)$ and $\phi_{iq}^{\mathrm{B}}(t) = \tilde{\phi}_{iq}^{\mathrm{B}} \exp(-Dq^2t)$. In terms of the $(m_{\mathrm{A}} + m_{\mathrm{B}})$-dimensional vector $\tilde{\vec{\phi}}_q \equiv (\tilde{\phi}_{1q}^{\mathrm{A}}, ..., \tilde{\phi}_{m_{\mathrm{A}}q}^{\mathrm{A}}, \tilde{\phi}_{1q}^{\mathrm{B}}, ..., \tilde{\phi}_{m_{\mathrm{B}}q}^{\mathrm{B}})$ this problem amounts to the solution of the equation

$$\boldsymbol{M}_D \cdot \tilde{\vec{\phi}}_q = \mathbf{0}$$

$$\boldsymbol{M}_D = \begin{pmatrix} \boldsymbol{M}^{\mathrm{AA}} - \boldsymbol{I}^{\mathrm{A}} & \boldsymbol{M}^{\mathrm{AB}} \\ \boldsymbol{M}^{\mathrm{BA}} & \boldsymbol{M}^{\mathrm{BB}} - \boldsymbol{I}^{\mathrm{B}} \end{pmatrix} \quad (22)$$

where the $\boldsymbol{I}^{\mathrm{A}}$ and $\boldsymbol{I}^{\mathrm{B}}$ are diagonal matrices with the elements

$$I_{ij}^{\mathrm{A}} = \delta_{ij}[D/\lambda_i^{\mathrm{A}}(\vec{\bar{\phi}}) - 2q^2a_i^2(\vec{\bar{\phi}})]$$

$$I_{ij}^{\mathrm{B}} = \delta_{ij}[D/\lambda_i^{\mathrm{B}}(\vec{\bar{\phi}}) - 2q^2b_i^2(\vec{\bar{\phi}})] \qquad (23)$$

Hence the possible solutions for the diffusion constant D follow from the eigenvalue problem

$$\mathrm{Det}\, \boldsymbol{M}_D = 0 \qquad (24)$$

A general and explicit discussion of this problem is possible in the limit $\phi_{\mathrm{V}} \to 0$ (incompressible polymer mixture). First we look for a solution of eq 24 with $D = 0$. This yields, for $q = 0$

$$\frac{1}{\sum_{i=1}^{m_{\mathrm{A}}} N_i^{\mathrm{A}}\overline{\phi_i^{\mathrm{A}}}} + \frac{1}{\sum_{i=1}^{m_{\mathrm{B}}} N_i^{\mathrm{B}}\overline{\phi_i^{\mathrm{B}}}} - 2\chi_{\mathrm{AB}} = 0 \qquad (25)$$

Since in terms of the distribution functions $n_{N_i^{\mathrm{A}}}$ and $n_{N_i^{\mathrm{B}}}$ of chain lengths N_i^{A} and N_i^{B} we have (V being the total volume of the system)

$$\overline{\phi_i^{\mathrm{A}}} = n_{N_i^{\mathrm{A}}}N_i^{\mathrm{A}}/V, \qquad \overline{\phi_i^{\mathrm{B}}} = n_{N_i^{\mathrm{B}}}N_i^{\mathrm{B}}/V \qquad (26)$$

and (cf eq 7)

$$\overline{\phi^{\mathrm{A}}} = \sum_{i=1}^{m_{\mathrm{A}}}\overline{\phi_i^{\mathrm{A}}} = \frac{1}{V}\sum_{i=1}^{m_{\mathrm{A}}} n_{N_i^{\mathrm{A}}}N_i^{\mathrm{A}} = \overline{N_{\mathrm{A}}^1}/V, \qquad \overline{\phi^{\mathrm{B}}} = \overline{N_{\mathrm{B}}^1}/V \qquad (27)$$

Thus eq 25 can be written as

$$\frac{1}{\overline{\phi^{\mathrm{A}}}\,\overline{N_{\mathrm{A}}^2}/\overline{N_{\mathrm{A}}^1}} + \frac{1}{\overline{\phi^{\mathrm{B}}}\,\overline{N_{\mathrm{B}}^2}/\overline{N_{\mathrm{B}}^1}} - 2\chi_{\mathrm{AB}} = 0 \qquad (28)$$

This is the condition for the spinodal curve, consistent with eq 5 (remember eq 6 and $\overline{\phi^{\mathrm{B}}} = 1 - \overline{\phi^{\mathrm{A}}}$ if $\phi_{\mathrm{V}} = 0$). The vanishing of D at the spinodal curve expresses standard critical slowing down; inside the spinodal region a negative solution for D will yield the amplification rate $R(q \to 0)$ mentioned in eq 1, thus describing spinodal decomposition. In the next section, we discuss the eigenvalue spectrum that follows from eq 24.

3. Interdiffusion and Spinodal Decomposition near the Spinodal Curve

Since $\boldsymbol{M}_D$ in eq 22 is a $(m_{\mathrm{A}} + m_{\mathrm{B}}) \times (m_{\mathrm{A}} + m_{\mathrm{B}})$ matrix, the eigenvalue problem eq 24 in general yields $m_{\mathrm{A}} + m_{\mathrm{B}}$ (real[43]) solutions for D. We now discuss the physical meaning of these solutions, in the limit $\bar{\phi}_{\mathrm{V}} \to 0$ where

$$\lambda_i^{\mathrm{A}}(\vec{\bar{\phi}}) = \Gamma_i^{\mathrm{A}}\bar{\phi}_{\mathrm{V}}, \qquad \lambda_i^{\mathrm{B}}(\vec{\bar{\phi}}) = \Gamma_i^{\mathrm{B}}\bar{\phi}_{\mathrm{V}} \qquad (29)$$

As is obvious from Figure 1, polymer motions are frozen out in the limit $\bar{\phi}_{\mathrm{V}} \to 0$ and hence it is reasonable to assume that the Onsager coefficients vanish linearly as $\bar{\phi}_{\mathrm{V}} \to 0$. If we now expand

$$D = D_0 + D_1\bar{\phi}_{\mathrm{V}} \qquad (30)$$

we find by expanding eq 24 in a Taylor series in $\bar{\phi}_{\mathrm{V}}$ that there is a single solution for D that has $D_0 \neq 0$, given by

$$D_0 = \sum_{i=1}^{m_{\mathrm{A}}}\Gamma_i^{\mathrm{A}} + \sum_{i=1}^{m_{\mathrm{B}}}\Gamma_i^{\mathrm{B}} \qquad (31)$$

while all other $(m_{\mathrm{A}} + m_{\mathrm{B}} - 1)$ solutions for D have $D_0 = 0$. Now a consideration of the resulting eigenvector shows that eq 31 is the rate of the density mode (diffusion of vacancies against diffusion of polymers irrespective of their kind). This mode is of no interest to us here. Disregarding this solution, we find that D_1 is obtained as the solution of the following equation:

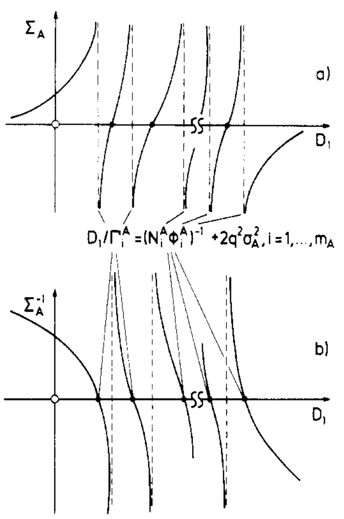

Figure 2. Schematic plot of the function $\sum_{\mathrm{A}}$ (a) and its inverse $\sum_{\mathrm{A}}^{-1}$ (b) as a function of D_1. The origin of the coordinate system is indicated by an open circle. Zeros of the functions $\sum_{\mathrm{A}}$ and $\sum_{\mathrm{A}}^{-1}$ are indicated by dots and poles by broken straight lines. For both $\sum_{\mathrm{A}}$ and $\sum_{\mathrm{A}}^{-1}$ only the part near the coordinate origin and the part near the largest zero are shown, as $\sum_{\mathrm{A}}$ has m_{A} poles in total.

$$\prod_{j=1}^{m_{\mathrm{B}}}\left[\frac{1}{N_j^{\mathrm{B}}\overline{\phi_j^{\mathrm{B}}}} + 2q^2b_i^2(\vec{\bar{\phi}}) - \frac{D_1}{\Gamma_j^{\mathrm{B}}}\right) \Bigg/ \sum_{i=1}^{m_{\mathrm{B}}}\prod_{j\neq i}\left[\frac{1}{N_j^{\mathrm{B}}\overline{\phi_j^{\mathrm{B}}}} + 2q^2b_i^2(\vec{\bar{\phi}}) - \frac{D_1}{\Gamma_j^{\mathrm{B}}}\right] + \prod_{j=1}^{m_{\mathrm{A}}}\left[\frac{1}{N_j^{\mathrm{A}}\overline{\phi_j^{\mathrm{A}}}} + 2q^2a_i^2(\vec{\bar{\phi}}) - \frac{D_1}{\Gamma_j^{\mathrm{A}}}\right] \Bigg/ \sum_{i=1}^{m_{\mathrm{A}}}\prod_{j\neq i}\left[\frac{1}{N_j^{\mathrm{A}}\overline{\phi_j^{\mathrm{A}}}} + 2q^2a_i^2(\vec{\bar{\phi}}) - \frac{D_1}{\Gamma_j^{\mathrm{A}}}\right] - 2\chi_{\mathrm{AB}} = 0 \qquad (32)$$

Note that in the limit $\bar{\phi}_{\mathrm{V}} \to 0$, which we have invoked to derive eq 32, there are $m_{\mathrm{A}} + m_{\mathrm{B}} - 1$ interdiffusion modes $D = D_1\bar{\phi}_{\mathrm{V}}$ following from this equation, which hence are well separated from the density mode, eq 31.

For the moment, we assume that $D_1/\Gamma_j^{\mathrm{A}} \neq (N_j^{\mathrm{A}}\overline{\phi_j^{\mathrm{A}}})^{-1} + 2q^2a_i^2(\vec{\bar{\phi}})$, for all $j = 1, \ldots, m_{\mathrm{A}}$, and also $D_1/\Gamma_j^{\mathrm{B}} \neq (N_j^{\mathrm{B}}\overline{\phi_j^{\mathrm{B}}})^{-1} + 2q^2b_i^2(\vec{\bar{\phi}})$, for all $j = 1, \ldots, m_{\mathrm{B}}$. Then eq 32 can be rewritten as, using eq 10

$$f(D_1) \equiv \left[\sum_{i=1}^{m_{\mathrm{B}}}\left[\frac{1}{N_i^{\mathrm{B}}\overline{\phi_i^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\phi_i^{\mathrm{B}}}} - \frac{D_1}{\Gamma_i^{\mathrm{B}}}\right]^{-1}\right]^{-1} + \left[\sum_{i=1}^{m_{\mathrm{A}}}\left[\frac{1}{N_i^{\mathrm{A}}\overline{\phi_i^{\mathrm{A}}}} + \frac{q^2\sigma_{\mathrm{A}}^2}{18\overline{\phi_i^{\mathrm{A}}}} - \frac{D_1}{\Gamma_i^{\mathrm{A}}}\right]^{-1}\right]^{-1} = 2\chi_{\mathrm{AB}} \qquad (33)$$

We now discuss the right-hand side of eq 33, $f(D_1)$ as function of D_1. The sum $\sum_{\mathrm{A}} \equiv \sum_{i=1}^{m_{\mathrm{A}}}[(N_i^{\mathrm{A}}\overline{\phi_i^{\mathrm{A}}})^{-1} + q^2\sigma_{\mathrm{A}}^2/(18\overline{\phi_i^{\mathrm{A}}}) - D_1/\Gamma_i^{\mathrm{A}}]^{-1}$ has poles at the points $D_1/\Gamma_i^{\mathrm{A}} = (N_i^{\mathrm{A}}\overline{\phi_i^{\mathrm{A}}})^{-1} + q^2\sigma_{\mathrm{A}}^2/(18\overline{\phi_i^{\mathrm{A}}})$, $i = 1, \ldots, m_{\mathrm{A}}$, and changes there from $+\infty$ to $-\infty$ as D_1 increases. All these poles are at positive values of D_1. In between each pair of poles there must be one zero of $\sum_{\mathrm{A}}$ (Figure 2a). When the inverse of $\sum_{\mathrm{A}}$ is taken, the role of poles and zeros simply becomes interchanged (Figure 2b). The same argument holds for $\sum_{\mathrm{B}} \equiv \sum_{i=1}^{m_{\mathrm{B}}}[(N_i^{\mathrm{B}}\overline{\phi_i^{\mathrm{B}}})^{-1} + q^2\sigma_{\mathrm{B}}^2/(18\overline{\phi_i^{\mathrm{B}}}) - D_1/\Gamma_i^{\mathrm{B}}]^{-1}$ and its inverse. Therefore the function $f(D_1) = \sum_{\mathrm{A}}^{-1} + \sum_{\mathrm{B}}^{-1}$ has the same qualitative form as $\sum_{\mathrm{A}}^{-1}$ has, Figure 2b, only the number of poles and zeros has correspondingly increased. Now the essential point is that there is a single branch of $f(D_1)$ at negative D_1 until the first pole of $f(D_1)$ which occurs at positive D_1. This implies that eq 33 admits a single solution which can change its sign as χ_{AB} increases: this is the interdiffusion solution that we are interested in, with the sign change corresponding to the vanishing of D at the spinodal curve, considered in eq 25–28. This point can actually be proven[43] by a consideration of the eigenvectors resulting from eq 22 as solutions for $\bar{\phi}_q$ when the eigenvalue D is inserted in eq 22 and 23. For these eigenvectors, again a systematic expansion in powers of $\bar{\phi}_V$ can be made. It turns out that the eigenvector of the density mode is of order $\overline{\phi_V{}^1}$, and hence density relaxation makes a negligible contribution to the relaxation of the structure factor, which is physically perfectly reasonable. The solution of eq 33 for $\chi_{AB} > 0$ with the smallest D_1, which is the solution changing its sign at the spinodal, corresponds to interdiffusion where the currents of all A fractions are parallel to each other and antiparallel to the currents of all B fractions. The other interdiffusion solutions (none of which become unstable as the spinodal is crossed) correspond to motions where interdiffusion also occurs within one species of polymers (e.g., large A chains diffuse against short A chains and similarly for the B chains).

Since eq 33 is a highly nonlinear equation for D_1, it is not possible to derive its solutions analytically in the general case. Very close to the spinodal curve, however, the smallest solution $D_1^{(1)}$ becomes very small, unlike the other solutions, which stay nonzero at the spinodal and in general are not small there. This implies that $D_1^{(1)}$ near the spinodal can be found by linearizing eq 33 in D_1, which yields

$$D_1^{(1)} = \left\{ \frac{\sum_{i=1}^{m_A} (\Gamma_i^A)^{-1}[(N_i^A\overline{\phi_i^A})^{-1} + q^2\sigma_A^2/(18\overline{\phi_i^A})]^{-2}}{[\sum_{i=1}^{m_A}[(N_i^A\overline{\phi_i^A})^{-1} + q^2\sigma_A^2/(18\overline{\phi_i^A})]^{-1}]^2} + \frac{\sum_{i=1}^{m_B} (\Gamma_i^B)^{-1}[(N_i^B\overline{\phi_i^B})^{-1} + q^2\sigma_B^2/(18\overline{\phi_i^B})]^{-2}}{[\sum_{i=1}^{m_B} [(N_i^B\overline{\phi_i^B})^{-1} + q^2\sigma_B^2/(18\overline{\phi_i^B})]^{-1}]^2} \right\}^{-1} \times \{[\sum_{i=1}^{m_A} [(N_i^A\overline{\phi_i^A})^{-1} + q^2\sigma_A^2/(18\overline{\phi_i^A})]^{-1}]^{-1} + [\sum_{i=1}^{m_B} [(N_i^B\overline{\phi_i^B})^{-1} + q^2\sigma_B^2/(18\overline{\phi_i^B})]^{-1}]^{-1} - 2\chi_{AB}\} \quad (34)$$

From this equation we see that near the spinodal a separation of the amplification rate $R(q) = -q^2\bar{\phi}_V D_1$ in a static part $1/S_T^{\mathrm{coll}}(\mathbf{q})$ and a dynamic part $\Lambda(q)$ indeed holds: the second expression in braces agrees with eq 5 when we expand it to first order in q^2. In fact, our treatment is valid only to this order in q^2 but not to higher order in q^2, due to the use of the gradient square approximation in eq 9. In this order, one cannot study the q dependence of $\Lambda(q)$ in a consistent way yet; omitting the q^2 corrections in the first expression in braces of eq 34, we hence obtain $\Lambda(0)$ as

$$\Lambda^{-1}(0) = \bar{\phi}_V^{-1}\left\{ \frac{\sum_{i=1}^{m_A} (\Gamma_i^A)^{-1}(N_i^A\overline{\phi_i^A})^2}{[\sum_{i=1}^{m_A} (N_i^A\overline{\phi_i^A})]^2} + \frac{\sum_{i=1}^{m_B} (\Gamma_i^B)^{-1}(N_i^B\overline{\phi_i^B})^2}{[\sum_{i=1}^{m_B} (N_i^B\overline{\phi_i^B})]^2} \right\} \quad (35)$$

A physically reasonable limit requires that Γ_i^A vanishes when $\overline{\phi_i^A} \rightarrow 0$, since otherwise eq 13a would yield a nonvanishing current $\mathbf{J}_i^A$ in this limit, which is physically unreasonable. Actually, this consideration suggests a linear relationship between Γ_i^A and $\overline{\phi_i^A}$ and similarly between Γ_i^B and $\overline{\phi_i^B}$

$$\Gamma_i^A = \gamma_i^A\overline{\phi_i^A}, \qquad \Gamma_i^B = \gamma_i^B\overline{\phi_i^B}, \qquad \overline{\phi_i^A} \rightarrow 0, \quad \overline{\phi_i^B} \rightarrow 0 \quad (36)$$

where γ_i^A and γ_i^B are constants staying finite and nonzero in this limit. This implies further

$$\Lambda^{-1}(0) = \bar{\phi}_V^{-1}\left\{ \frac{\sum_{i=1}^{m_A} (\gamma_i^A)^{-1}\overline{\phi_i^A}(N_i^A)^2}{[\sum_{i=1}^{m_A} (\overline{\phi_i^A}N_i^A)]^2} + \frac{\sum_{i=1}^{m_B} (\gamma_i^B)^{-1}\overline{\phi_i^B}(N_i^B)^2}{[\sum_{i=1}^{m_B} (\overline{\phi_i^B}N_i^B)]^2} \right\} \quad (37)$$

and using eq 26, 27, 6, and 7, we find

$$\Lambda^{-1}(0) = \bar{\phi}_V^{-1}\left\{ \sum_{i=1}^{m_A} (\gamma_i^A)^{-1}\frac{n_{N_i^A}(N_i^A)^3\overline{N_A{}^1}}{(\overline{N_A{}^2})^2\bar{\phi}_A} + \sum_{i=1}^{m_B} (\gamma_i^B)^{-1}\frac{n_{N_i^B}(N_i^B)^3\overline{N_B{}^1}}{(\overline{N_B{}^2})^2\bar{\phi}_B} \right\} \quad (38)$$

In order to proceed further, assumptions have to be made on the molecular weight dependence of the effective friction coefficients γ_i^A and γ_i^B. If all chains are sufficiently short, the dynamics can be described by the Rouse model.[45] Then the tracer diffusion constants vary inversely with the molecular weight; i.e., the friction coefficients are independent of molecular weight

$$\gamma_i^A \equiv \gamma_A, \qquad \gamma_i^B \equiv \gamma_B, \qquad \text{independent of } i \text{ (Rouse model)} \quad (39)$$

Then eq 38 reduces to

$$\Lambda^{-1}(0) = \bar{\phi}_V^{-1}\left\{ \gamma_A^{-1}\frac{\overline{N_A{}^z}}{\overline{N_A{}^w}\bar{\phi}_A} + \gamma_B^{-1}\frac{\overline{N_B{}^z}}{\overline{N_B{}^w}\bar{\phi}_B} \right\} \quad (40)$$

In comparison with the monodisperse case, eq 3, where $D_A{}^* = \phi_V\gamma_A/N_A$ and $D_B{}^* = \phi_V\gamma_B/N_B$, we recognize that monodisperse and polydisperse cases have the same qualitative structure: only the friction coefficients γ_A and γ_B are "renormalized" by the factors $\overline{N_A{}^w}/\overline{N_B{}^z}$ and $\overline{N_B{}^w}/\overline{N_B{}^z}$, which typically are of order unity.

A similar simple structure results if all the chains are so long that the reptation model[46] applies to all the fractions. Then the tracer diffusion constants vary inversely with the square of the molecular weight. This behavior implies that the friction coefficients vary inverse proportionally with the molecular weight

$$\gamma_i^A = \gamma_A{}'\frac{d_A{}^2}{\sigma_A{}^2N_i^A}, \quad \gamma_i^B = \gamma_B{}'\frac{d_B{}^2}{\sigma_B{}^2N_i^B}, \qquad \text{reptation model} \quad (41)$$

where $\gamma_A{}'$ and $\gamma_B{}'$ are effective friction constants and d_A and d_B effective "tube diameters". If one would choose $\gamma_A{}' = \gamma_A$ and $\gamma_B{}' = \gamma_B$, then the crossover between eq 40 and 41 would occur exactly for such chain lengths where the end-to-end distances R_i^A and R_i^B are equal to the tube diameters, since $R_i^A = \sigma_A(N_i^A)^{1/2}$ and $R_i^B = \sigma_B(N_i^B)^{1/2}$. Of course, near this crossover region the precise behavior of

γ_i^{A} and γ_i^{B} is described neither by eq 40 nor by eq 41, and then eq 38 cannot be easily evaluated. Only if the molecular weights are large enough that eq 41 holds for all i do we get again a simple expression, namely

$$[\Lambda(0)]^{-1} = \bar{\phi}_{\mathrm{V}}^{-1}\left\{\frac{\sigma_{\mathrm{A}}^2}{\gamma_{\mathrm{A}}' d_{\mathrm{A}}^2 \bar{\phi}_{\mathrm{A}}} \frac{\overline{N_{\mathrm{A}}^4}/\overline{N_{\mathrm{A}}^1}}{(\overline{N_{\mathrm{A}}^{\mathrm{w}}})^2} + \frac{\sigma_{\mathrm{B}}^2}{\gamma_{\mathrm{B}}' d_{\mathrm{B}}^2 \bar{\phi}_{\mathrm{B}}} \frac{\overline{N_{\mathrm{B}}^4}/\overline{N_{\mathrm{B}}^1}}{(\overline{N_{\mathrm{B}}^{\mathrm{w}}})^2}\right\} \qquad (42)$$

Again the factors that appear in the monodisperse case {namely $\sigma_{\mathrm{A}}^2 N_{\mathrm{A}}/(\gamma_{\mathrm{A}}' d_{\mathrm{A}}^2 \bar{\phi}_{\mathrm{A}})$ and $\sigma_{\mathrm{B}}^2 N_{\mathrm{B}}/(\gamma_{\mathrm{B}}' d_{\mathrm{B}}^2 \bar{\phi}_{\mathrm{B}})$} are only changed by ratios of the moments of the molecular weight distribution, i.e., constants of order unity. A discussion of quantitative examples for these effects is deferred to section 5.

Here we return to the description of the relaxation of the volume fractions $\phi_{iq}^{\mathrm{A}}(t)$ and $\phi_{iq}^{\mathrm{B}}(t)$ and emphasize that this results in a description of spinodal decomposition on the Cahn[2] level: thermal fluctuations in the state at temperature T to which the quenching experiment leads are neglected; one only considers the amplification of fluctuations existing at temperature T_0 where the quench was started (Figure 3). Since often there temperatures are not very different from each other (it is also possible that $T_0 < T$, if one has a system with a lower critical consolution point), this Cahn level of the theory is often not realistic.

Following Cook[47] it now is standard procedure[23,29] to account for fluctuations by adding a random force $\Theta_{iq}^{\mathrm{A}}(t)$ and $\Theta_{iq}^{\mathrm{B}}(t)$ to the right-hand side of eq 19. This random force satisfies the relations

$$\langle \Theta_{iq}^{\mathrm{A}}(t)\rangle_{\mathrm{T}} = 0, \qquad \langle \Theta_{iq}^{\mathrm{B}}(t)\rangle_{T} = 0 \qquad (43a)$$

$$\langle \Theta_{iq}^{\mathrm{A}}(t)\Theta_{jq}^{\mathrm{A}}(t')\rangle_T = \langle|\Theta_{iq}^{\mathrm{A}}|^2\rangle_T \delta_{ij}\delta(t-t') \qquad (43b)$$

$$\langle \Theta_{iq}^{\mathrm{B}}(t)\Theta_{jq}^{\mathrm{B}}(t')\rangle_T = \langle|\Theta_{iq}^{\mathrm{B}}|^2\rangle_T \delta_{ij}\delta(t-t') \qquad (43c)$$

and mixed correlations $\langle \Theta_{iq}^{\mathrm{A}}(t)\Theta_{jq}^{\mathrm{B}}(t')\rangle_T$ are also assumed to vanish. The strength of these random forces is determined by the conditions

$$\langle|\Theta_{iq}^{\mathrm{A}}|^2\rangle_T = 2\lambda_i^{\mathrm{A}}(\bar{\vec{\phi}})q^2, \qquad \langle|\Theta_{iq}^{\mathrm{B}}|^2\rangle_T = 2\lambda_i^{\mathrm{B}}(\bar{\vec{\phi}})q^2 \qquad (44)$$

(Comparing eq 44 to the monodisperse case [eq 2.14 of ref 23], one should note that in eq 2.14 of ref 23 a factor of 2 was erroneously omitted.) The choice eq 44 ensures that eq 19 supplemented with the random force terms is consistent with the correct static equilibrium, as described by the structure factor $S_{\mathrm{T}}^{\mathrm{coll}}(q)$, eq 5. If we calculate now dynamic structure factors $\langle|\phi_q^{\mathrm{A}}(t)|^2\rangle_T = \sum_{i,j}\langle|\phi_{iq}^{\mathrm{A}}(t)\phi_{jq}^{\mathrm{A}}(t)|^2\rangle_T$, which describe the time evolution of the scattering intensity observed after the quenching experiments sketched in Figure 3, we find one term relaxing proportional to $\exp(-2q^2\bar{\phi}_{\mathrm{V}}D_1^{(1)}t)$ analogous to the interdiffusion term considered in the monodisperse case,[23,29] but in addition there are also terms relaxing with the other eigenvalues $D_1^{(\nu)}$, the spectrum following from eq 33, such as $\exp[-q^2\bar{\phi}_{\mathrm{V}}(D_1^{(\nu)} + D_1^{(\nu')})t]$. For a quantitative description of the structure factor, also the eigenvectors belonging to the eigenvalues $D_1^{(\nu)}$ and $D_1^{(\nu')}$ would be needed, which we have not been able to calculate explicitly. Again, however, we can make the point that for quenches leading in the close vicinity of the spinodal curve the rate of the interdiffusion term, $2|D_1^{(1)}|$, is very much smaller than any other rate $D_1^{(\nu)} + D_1^{(\nu')}$, where either $\nu \neq 1$ or $\nu' \neq 1$. Consequently on the time scale of interest, where $2q^2\bar{\phi}_{\mathrm{V}}|D_1^{(1)}|t$ is of order unity, all other relaxation has died out, and we recover a single-exponential relaxation again. In this spirit, it makes sense to restrict the discussion to the interdiffusion mode $D_1^{(1)}$ in eq 34 and use eq 38–42 for describing the relaxation also when fluctuations are being taken into account.

4. Special Cases: A Monodisperse Polymer Mixture with an Arbitrary Fraction of Vacancies and a Polymer Mixture where A is Monodisperse and B Contains Only Two Fractions

From the preceding section it is evident that even within the framework of the (certainly oversimplified[48,49]) dynamic version of the Flory–Huggins lattice model interdiffusion and spinodal decomposition can be treated only in rather restrictive limits: the vacancy concentration must nearly vanish, $\bar{\phi}_{\mathrm{V}} \to 0$, and also we can consider only the close vicinity of the spinodal curve. On the other hand, due to fluctuations neglected in mean-field theories, the Flory–Huggins[39] approach is not accurate in the very close vicinity of the spinodal curve (in a region of width proportional to $N^{-1/3}$ in a symmetric polymer mixture where $N_{\mathrm{A}} = N_{\mathrm{B}}$);[23,24] in particular, the linearization eq 17 is not valid there.

Thus it is of interest to consider special cases where these restrictive limits can be relaxed. The simplest case is a monodisperse polymer mixture containing an arbitrary fraction of vacancies. It turns out that this case is fully analogous to eq 19: rather than the sums $\sum_{j=1}^{m_{\mathrm{A}}}$ and $\sum_{j=1}^{m_{\mathrm{B}}}$, we now have single terms; i.e., the matrices $\boldsymbol{M}^{\mathrm{AA}}$, $\boldsymbol{M}^{\mathrm{AB}}$, $\boldsymbol{M}^{\mathrm{BA}}$, and $\boldsymbol{M}^{\mathrm{BB}}$ reduce to scalars. The explicit form of eq 19 then is

$$\frac{\partial\phi_q^{\mathrm{A}}(t)}{\partial t} = -\lambda^{\mathrm{A}}(\bar{\vec{\phi}})q^2\left\{\left(\frac{1}{\bar{\phi}_{\mathrm{A}}N_{\mathrm{A}}} + \frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{AV}}\right)\phi_q^{\mathrm{A}}(t) + \left[\frac{1}{\bar{\phi}_{\mathrm{V}}} + \chi_{\mathrm{AB}} - (\chi_{\mathrm{AV}} + \chi_{\mathrm{BV}})\right]\phi_q^{\mathrm{B}}(t) + \frac{\sigma_{\mathrm{A}}^2 q^2}{18\bar{\phi}_{\mathrm{A}}}\phi_q^{\mathrm{A}}(t)\right\} \qquad (45a)$$

$$\frac{\partial\phi_q^{\mathrm{B}}(t)}{\partial t} = -\lambda^{\mathrm{B}}(\bar{\vec{\phi}})q^2\left\{\left[\frac{1}{\bar{\phi}_{\mathrm{V}}} + \chi_{\mathrm{AB}} - (\chi_{\mathrm{AV}} + \chi_{\mathrm{BV}})\right]\phi_q^{\mathrm{A}}(t) + \left(\frac{1}{\bar{\phi}_{\mathrm{B}}N_{\mathrm{B}}} + \frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{BV}}\right)\phi_q^{\mathrm{B}}(t) + \frac{\sigma_{\mathrm{B}}^2 q^2}{18\bar{\phi}_{\mathrm{B}}}\phi_q^{\mathrm{B}}(t)\right\} \qquad (45b)$$

When $\phi_q^{\mathrm{A}}(t) = \varphi_q^{\mathrm{A}} \exp(-Dq^2t)$ and $\phi_q^{\mathrm{B}}(t) = \varphi_q^{\mathrm{B}} \exp(-Dq^2t)$ is written, eq 45 yields a quadratic equation for D, which is solved by

$$D = \frac{1}{2}\left\{\lambda_{\mathrm{A}}(\bar{\vec{\phi}})\left(\frac{1}{\bar{\phi}_{\mathrm{A}}N_{\mathrm{A}}} + \frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{AV}} + \frac{\sigma_{\mathrm{A}}^2q^2}{18\bar{\phi}_{\mathrm{A}}}\right) + \lambda_{\mathrm{B}}(\bar{\vec{\phi}})\left(\frac{1}{\bar{\phi}_{\mathrm{B}}N_{\mathrm{B}}} + \frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{BV}} + \frac{\sigma_{\mathrm{B}}^2q^2}{18\bar{\phi}_{\mathrm{B}}}\right)\right\} \pm \frac{1}{2}\left[\left\{\lambda_{\mathrm{A}}(\bar{\vec{\phi}})\left(\frac{1}{\bar{\phi}_{\mathrm{A}}N_{\mathrm{A}}} + \frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{AV}} + \frac{\sigma_{\mathrm{A}}^2q^2}{18\bar{\phi}_{\mathrm{A}}}\right) - \lambda_{\mathrm{B}}(\bar{\vec{\phi}})\left[\frac{1}{\bar{\phi}_{\mathrm{B}}N_{\mathrm{B}}} + \frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{BV}} + \frac{\sigma_{\mathrm{B}}^2q^2}{18\bar{\phi}_{\mathrm{B}}}\right]\right\}^2 + 4\lambda_{\mathrm{A}}(\bar{\vec{\phi}})\lambda_{\mathrm{B}}(\bar{\vec{\phi}})\left[\frac{1}{\bar{\phi}_{\mathrm{V}}} + \chi_{\mathrm{AB}} - \chi_{\mathrm{AV}} - \chi_{\mathrm{BV}}\right]^2\right]^{1/2} \qquad (46)$$

Now for

$$\bar{\phi}_{\mathrm{A}} \gg \bar{\phi}_{\mathrm{V}}/N_{\mathrm{A}}, \qquad \bar{\phi}_{\mathrm{B}} \gg \bar{\phi}_{\mathrm{V}}/N_{\mathrm{B}} \qquad (47)$$

the two solutions of eq 46 simply become

$$D_+ \cong [\lambda_{\mathrm{A}}(\bar{\vec{\phi}}) + \lambda_{\mathrm{B}}(\bar{\vec{\phi}})]/\bar{\phi}_{\mathrm{V}} \tag{48a}$$

$$D_- \cong [\lambda_{\mathrm{A}}^{-1}(\bar{\vec{\phi}}) + \lambda_{\mathrm{B}}^{-1}(\bar{\vec{\phi}})]^{-1}\left\{\frac{1}{\bar{\phi}_{\mathrm{A}}N_{\mathrm{A}}} + \frac{1}{\bar{\phi}_{\mathrm{B}}N_{\mathrm{B}}} - 2\chi_{\mathrm{AB}} + \frac{\sigma_{\mathrm{A}}^2q^2}{18\bar{\phi}_{\mathrm{A}}} + \frac{\sigma_{\mathrm{B}}^2q^2}{18\bar{\phi}_{\mathrm{B}}}\right\} \tag{48b}$$

Since eq 45 implies that the ratio $\varphi_q^{\mathrm{B}}/\varphi_q^{\mathrm{A}}$ is given by

$$\varphi_q^{\mathrm{B}}/\varphi_q^{\mathrm{A}} = \left\{D - \lambda_{\mathrm{A}}(\bar{\vec{\phi}})\left[\frac{1}{\bar{\phi}_{\mathrm{A}}N_{\mathrm{A}}} + \frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{AV}} + \frac{\sigma_{\mathrm{A}}^2q^2}{18\bar{\phi}_{\mathrm{A}}}\right]\right\} \Big/ \left\{\lambda_{\mathrm{A}}(\bar{\vec{\phi}})\left[\frac{1}{\bar{\phi}_{\mathrm{V}}} + \chi_{\mathrm{AB}} - \chi_{\mathrm{AV}} - \chi_{\mathrm{BV}}\right]\right\} \tag{49}$$

we find from eq 48 that for $D = D_+$ we have $\varphi_q^{\mathrm{B}}/\varphi_q^{\mathrm{A}} \approx \lambda_{\mathrm{B}}/\lambda_{\mathrm{A}} > 0$ while for $D = D_-$ we have $\varphi_q^{\mathrm{B}}/\varphi_q^{\mathrm{A}} \approx -1$. As expected, D_+ is the density mode already identified also in the polydisperse case [cf. eq 29 and 31], and D_- is the interdiffusion mode $\bar{\phi}_{\mathrm{V}}D_1^{(1)}$ identified in eq 34–42. While in the polydisperse case we have needed $\bar{\phi}_i^{\mathrm{A}} \gg \bar{\phi}_{\mathrm{V}}/N_{\mathrm{A}}^i$ and $\bar{\phi}_i^{\mathrm{B}} \gg \bar{\phi}_{\mathrm{V}}/N_{\mathrm{B}}^i$ to derive eq 34–42 and hence the limit $\bar{\phi}_{\mathrm{V}} \to 0$ needed to be invoked, eq 48 needs only the much less stringent condition eq 47, which for large N_{A} and N_{B} is always true, except for $\bar{\phi}_{\mathrm{A}} \to 0$ or $\bar{\phi}_{\mathrm{B}} \to 0$. Equation 48 has been anticipated in earlier work.[23] Using eq 29 and 36, we find that eq 48 can also be written in terms of the friction coefficients γ_{A} and γ_{B}

$$D_- = \bar{\phi}_{\mathrm{V}}\left[\frac{1}{\bar{\phi}_{\mathrm{A}}\gamma_{\mathrm{A}}} + \frac{1}{\bar{\phi}_{\mathrm{B}}\gamma_{\mathrm{B}}}\right]^{-1}\left\{\frac{1}{\bar{\phi}_{\mathrm{A}}N_{\mathrm{A}}} + \frac{1}{\bar{\phi}_{\mathrm{B}}N_{\mathrm{B}}} - 2\chi_{\mathrm{AB}} + \frac{\sigma_{\mathrm{A}}^2q^2}{18\bar{\phi}_{\mathrm{A}}} + \frac{\sigma_{\mathrm{B}}^2q^2}{18\bar{\phi}_{\mathrm{B}}}\right\} \tag{50}$$

We emphasize that eq 46–50 do not imply that we consider states very close to the spinodal.

Next we consider the case where A is still monodisperse but B contains two fractions, B_1 and B_2. Now D is obtained as a solution of the cubic equation

$$\left\{\frac{1}{N_{\mathrm{A}}\bar{\phi}_{\mathrm{A}}} + \frac{q^2\sigma_{\mathrm{A}}^2}{18\bar{\phi}_{\mathrm{A}}} + \frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{AV}} - \frac{D}{\lambda_{\mathrm{A}}(\bar{\vec{\phi}})}\right\}\left\{\frac{1}{N_1^{\mathrm{B}}\overline{\bar{\phi}_1^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\bar{\phi}_1^{\mathrm{B}}}} - \frac{D}{\lambda_1^{\mathrm{B}}(\bar{\vec{\phi}})}\right\}\left\{\frac{1}{N_2^{\mathrm{B}}\overline{\bar{\phi}_2^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\bar{\phi}_2^{\mathrm{B}}}} - \frac{D}{\lambda_2^{\mathrm{B}}(\bar{\vec{\phi}})}\right\} + \left\{\frac{1}{N_1^{\mathrm{B}}\overline{\bar{\phi}_1^{\mathrm{B}}}} + \frac{1}{N_2^{\mathrm{B}}\overline{\bar{\phi}_2^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\bar{\phi}_1^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\bar{\phi}_2^{\mathrm{B}}}} - \frac{D}{\lambda_1^{\mathrm{B}}(\bar{\vec{\phi}})} - \frac{D}{\lambda_2^{\mathrm{B}}(\bar{\vec{\phi}})}\right\} \times \left\{\left(\frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{AV}}\right)\left(\frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{BV}}\right) - \left(\frac{1}{\bar{\phi}_{\mathrm{V}}} + \chi_{\mathrm{AB}} - \chi_{\mathrm{AV}} - \chi_{\mathrm{BV}}\right)^2 + \left(\frac{1}{\bar{\phi}_{\mathrm{V}}} - 2\chi_{\mathrm{BV}}\right)\left[\frac{1}{N_{\mathrm{A}}\bar{\phi}_{\mathrm{A}}} + \frac{q^2\sigma_{\mathrm{A}}^2}{18\bar{\phi}_{\mathrm{A}}} - \frac{D}{\lambda_{\mathrm{A}}(\bar{\vec{\phi}})}\right]\right\} = 0 \tag{51}$$

For the generalization of eq 47, namely, $\bar{\phi}_{\mathrm{A}} \gg \bar{\phi}_{\mathrm{V}}/N_{\mathrm{A}}$, $\overline{\bar{\phi}_1^{\mathrm{B}}} \gg \bar{\phi}_{\mathrm{V}}/N_1^{\mathrm{B}}$, and $\overline{\bar{\phi}_2^{\mathrm{B}}} \gg \bar{\phi}_{\mathrm{V}}/N_2^{\mathrm{B}}$, we may express the eigenvalue spectrum resulting from eq 51 as follows: $D = D_0$ or $D = \bar{\phi}_{\mathrm{V}}D_1$, with

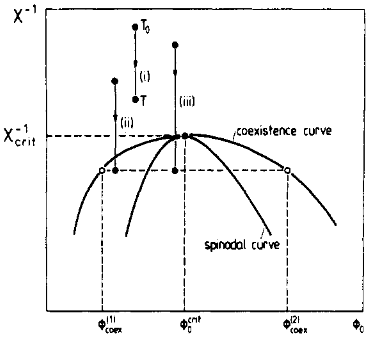

Figure 3. Schematic phase diagram of a polymer mixture with a critical point of unmixing occurring at a volume fraction ϕ_0^{crit} and the value χ_{crit} of the (temperature-dependent) effective interaction parameter χ. Also, three types of quenching experiments (i), (ii), and (iii) from an initial state at temperature T_0 to other states at a temperature T are indicated.

$$D_0 = \Gamma^{\mathrm{A}} + \Gamma_1^{\mathrm{B}} + \Gamma_2^{\mathrm{B}} \tag{52a}$$

$$D_1^{(1,2)} = \frac{1}{2(\Gamma^{\mathrm{A}} + \Gamma_1^{\mathrm{B}} + \Gamma_2^{\mathrm{B}})}[S_1 \mp (S_1^2 - 4S_2(\Gamma^{\mathrm{A}} + \Gamma_1^{\mathrm{B}} + \Gamma_2^{\mathrm{B}}))^{1/2}] \tag{52b}$$

where we have defined the abbreviations S_1 and S_2

$$S_1 = \Gamma^{\mathrm{A}}(\Gamma_1^{\mathrm{B}} + \Gamma_1^{\mathrm{B}})\left(\frac{1}{N_{\mathrm{A}}\bar{\phi}_{\mathrm{A}}} + \frac{\sigma_{\mathrm{A}}^2q^2}{18\bar{\phi}_{\mathrm{A}}} - 2\chi_{\mathrm{AB}}\right) + \Gamma_1^{\mathrm{B}}(\Gamma_{\mathrm{A}} + \Gamma_2^{\mathrm{B}})\left(\frac{1}{N_1^{\mathrm{B}}\overline{\bar{\phi}_1^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\bar{\phi}_1^{\mathrm{B}}}}\right) + \Gamma_2^{\mathrm{B}}(\Gamma_{\mathrm{A}} + \Gamma_1^{\mathrm{B}})\left(\frac{1}{N_2^{\mathrm{B}}\overline{\bar{\phi}_2^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\bar{\phi}_2^{\mathrm{B}}}}\right) \tag{53a}$$

$$S_2 = \Gamma_{\mathrm{A}}\Gamma_1^{\mathrm{B}}\Gamma_2^{\mathrm{B}}\left(\frac{1}{N_1\overline{\bar{\phi}_1^{\mathrm{B}}}} + \frac{1}{N_2\overline{\bar{\phi}_2^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\bar{\phi}_1^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\bar{\phi}_2^{\mathrm{B}}}}\right)\left\{\frac{1}{N_{\mathrm{A}}\bar{\phi}_{\mathrm{A}}} + \frac{\sigma_{\mathrm{A}}^2q^2}{18\bar{\phi}_{\mathrm{A}}} - 2\chi_{\mathrm{AB}} + \left[\left(\frac{1}{N_1\overline{\bar{\phi}_1^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\bar{\phi}_1^{\mathrm{B}}}}\right)^{-1} + \left(\frac{1}{N_2\overline{\bar{\phi}_2^{\mathrm{B}}}} + \frac{q^2\sigma_{\mathrm{B}}^2}{18\overline{\bar{\phi}_2^{\mathrm{B}}}}\right)^{-1}\right]^{-1}\right\} \tag{53b}$$

The brace in S_2 is positive in the one-phase region and for $q = 0$ changes sign at the spinodal. It is easy to see that only the smaller of the two solutions of eq 52b, $D_1^{(1)}$, changes sign there, while $D_1^{(2)}$ always is positive, in conformity with the general considerations of the previous section. When χ_{AB} is sufficiently large, i.e., for deep quenches far below the spinodal, also S_1 becomes negative, and hence the interference term in the structure factor, relaxing with a factor $\exp[-q^2\bar{\phi}_{\mathrm{V}}(D_1^{(1)} + D_1^{(2)})t] = \exp[-q^2\bar{\phi}_{\mathrm{V}}S_1t/(\Gamma^{\mathrm{A}} + \Gamma_1^{\mathrm{B}} + \Gamma_2^{\mathrm{B}})]$, then is an exponentially growing term. This behavior is qualitatively different from the monodisperse case, where we have always a single-exponential growing term only. Note, however, that the theory described here is valid only if q^2_{crit}, where $1/S_{\mathrm{T}}^{\mathrm{coll}}(q)$ in eq 2 and 5 changes sign, satisfies the conditions $q^2_{\mathrm{crit}}\sigma_{\mathrm{A}}^2N_{\mathrm{A}} \lesssim 1$, $q^2_{\mathrm{crit}}\sigma_{\mathrm{B}}^2N_1^{\mathrm{B}} \lesssim 1$, and $q^2_{\mathrm{crit}}\sigma_{\mathrm{B}}^2N_2^{\mathrm{B}} \lesssim 1$: if these conditions are no longer satisfied, corrections to the gradient square approximation in eq 9 are important.[33] This fact prevents the application of the present theory to very deep quenches.

In the present example, it is also straightforward to determine the eigenvectors that belong to the three eigenvalues of D, namely D^0, $\bar{\phi}_V D_1^{(1)}$, and $\bar{\phi}_V D_1^{(2)}$ (eq 52), and to verify[43] the comments given about this problem in section 3. In particular, the eigenvector belonging to $D_1^{(2)}$ indeed corresponds to relaxation of concentration between the two fractions B_1 and B_2, together with relaxation between A and B.

5. Application to Experiment and Concluding Remarks

In most real systems the distribution of the polymerization index N_m (number of monomers per chain) can be well approximated by continuous distributions such as the "lognormal distribution"[32]

$$n_m(N_m) = \frac{1}{(2\pi)^{1/2}\sigma N_M}\left(\frac{N_m}{N_M}\right)^A \exp\left\{-\frac{[\ln (N_m/N_M)]^2}{2\sigma^2}\right\} \bigg/ Y \quad (54)$$

where N_M is the median of the distribution, σ characterizes its width, Y is determined from the normalization condition $\int_0^\infty n_m(N_m)\, dN_m = 1$, and A is a parameter. Practical examples show that typically the choice $A = 0$ {where $Y = \exp(\sigma^2/2)$}, the so-called "Lansing–Krämer distribution", is appropriate.[43,50]

In the previous sections, however, we have considered a subdivision of the chains into N subunits (Kuhn segments) of size σ rather than into the N_m monomers (of size b). Since each subunit contains n_s monomers and the end-to-end distance satisfies the relation

$$\langle R^2 \rangle = N\sigma^2 = N_m b^2 C \quad (55)$$

where C is a constant depending on the detailed structure of the polymer, we can conclude

$$N = N_m/n_s, \qquad \sigma^2 = n_s b^2 C \quad (56)$$

Thus each (integer) value of N actually corresponds to n_s polymerization indices N_m in the interval from $n_s N - n_s/2$ to $n_s N + n_s/2 - 1$. For reasonably smooth distributions $n_m(N_m)$ such as eq 54 we may neglect the variation of n_m inside such an interval and take all these n_s values equal to $n_m(N_m)$. As a consequence, the chain-length distribution n_N considered in eq 7 and 26 is obtained in terms of the distribution $n_m(N_m)$ of the polymerization index as

$$n_N = n_s n_m(N_m) \quad (57a)$$

which implies the relation for the moments (using eq 56)

$$\overline{N^k} = \frac{1}{n_s^{\,k}}\overline{N_m^{\,k}} \quad (57b)$$

From eq 57b and 56 it is easy to see that the "kinetic prefactor" of the diffusion coefficient neither in the case of the Rouse model (eq 40) nor in the case of the reptation model (eq 42) depends on the number n_s of the monomers per subunit: we have

$$\overline{N^z}/\overline{N^w} = \overline{N_m^{\,z}}/\overline{N_m^{\,w}} \quad (58a)$$

$$\frac{\sigma^2}{d^2}\,\frac{\overline{N^4}/\overline{N^1}}{(\overline{N^w})^2} = \frac{b^2 C}{d^2}\,\frac{\overline{N_m^{\,4}}/\overline{N_m^{\,1}}}{(\overline{N_m^{\,w}})^2} \quad (58b)$$

This result is physically reasonable, since the choice of subunits in the Flory–Huggins theory contains some arbitrariness; by the help of eq 58 the Onsager coefficient $\Lambda(0)$ can always be expressed directly in terms of physically meaningful well-defined quantities.

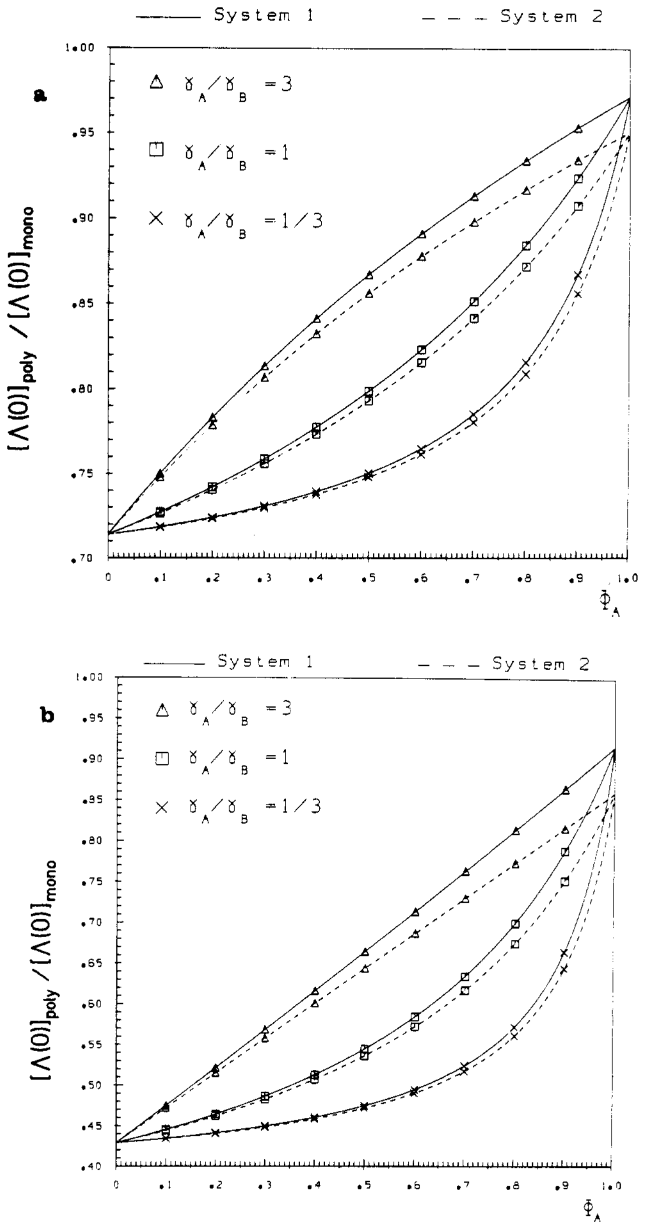

Figure 4. Concentration dependence of the ratio between the Onsager coefficient $\Lambda(0)$ for the polydisperse case (eq 40, for the Rouse model, and eq 42, for the reptation model) and the Onsager coefficient in the monodisperse case (eq 3). Full and broken curves refer to two samples of PSD as described in the text. Case (a) refers to the use of the Rouse model and case (b) to the use of the reptation model. Note that the different symbols denoting the concentrations at which eq 40 and 42 were evaluated only serve to distinguish the various ratios of γ_A/γ_B.

As an example, Figure 4 shows the ratio $[\Lambda(0)]_{poly}/[\Lambda(0)]_{mono}$, using three choices of the ratio γ_A/γ_B or γ_A'/γ_B', respectively, and data for the moments are chosen from fits of eq 54 to a measured sample[51] of poly(vinyl methyl ether) (PVME) representing polymer A and two different samples[51] of deuteriated polystyrene (PSD) as polymer B. These samples could be well fitted by the parameters $N_M = 390.7$ and $\sigma = 1.18$ (PVME), $N_M = 585$ and $\sigma = 0.17$ (PSD, sample 1), and $N_M = 1725.4$ and $\sigma = 0.22$ (PSD, sample 2) in the Lansing–Krämer distribution. It is seen that this ratio of the Onsager coefficients is always less than unity; on the PSD-rich side this reduction is about a factor of 2, since the PVME sample is very polydisperse, while on the PVME-rich side the reduction is only a few percent. Note that in this figure we have neglected any intrinsic concentration dependence of the friction parameters γ_A and γ_B, of course; in real systems such concentration dependences often cannot be neglected, however.

For example, usually the glass transition temperatures of the two partners of a polymer mixture may differ substantially, and thus a concentration dependence of the glass transition temperature $T_g(\phi)$ arises. Now the intrinsic bead mobilities and hence the friction coefficients depend very strongly on the temperature distance from the glass transition temperature.[52,53] These effects may be much more important than the concentration dependences resulting from polydispersity, as analyzed in the present work. Therefore, the experimental study of the concentration dependence of the interdiffusion coefficient is still somewhat controversial.[52-54] The theoretical situation is not completely clear either, because one may have doubts on the conditions under which the present vacancy model is applicable to polymer mixtures,[44,48,49] and other assumptions[41,44,55]—which seem hard to prove also, however—lead to different results. Note, however, that all other theoretical work on interdiffusion has only considered monodisperse polymer mixtures so far, and hence a quantitative comparison of the results of ref 41 and 55 to most real data is doubtful already for that reason. For an experimental check on the foundations of the present theory it would be most useful to use a system where monomeric mobilities are independent of concentration[53] and to characterize the system very carefully such that effects due to the concentration and temperature dependences of χ_{AB} could be corrected for. A most stringent test of the theory is provided,[56] if measurements on the rate $R(q)$ at constant temperature and constant distance from the spinodal $\chi_{\mathrm{AB}} - \chi_{\mathrm{AB}}{}^{\mathrm{sp}}$ are made for variable ratio $\overline{N_{\mathrm{m}}{}^{\mathrm{z}}}/\overline{N_{\mathrm{m}}{}^{\mathrm{w}}}$. This seems possible in principle by working with "tailored" molecular weight distributions produced by suitable mixing of fractions such that $\overline{N_{\mathrm{m}}{}^{\mathrm{w}}}$ stays fixed; cf. eq 5.

More definite are our conclusions on the effect of polydispersity on q^2_{crit}, i.e., the wavevector where $R(q)$ in eq 1 changes sign. Defining an effective Flory–Huggins parameter χ' relating to a monomer instead of $\chi = \chi_{\mathrm{AB}}$ in eq 5 relating to a segment, we have to choose $\chi' = \chi/n_{\mathrm{s}}$; hence in terms of moments over the molecular weight distribution $\overline{N_{\mathrm{Am}}{}^{\mathrm{z}}}$, $\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}$, $\overline{N_{\mathrm{Bm}}{}^{\mathrm{z}}}$, and $\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}$ we obtain

$$q^2_{\mathrm{crit}} = 18\left[2\chi' - \frac{1}{\phi\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}} - \frac{1}{(1-\phi)\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}}\right] \Bigg/ \left[\frac{\overline{N_{\mathrm{Am}}{}^{\mathrm{z}}}}{\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}}\frac{b_{\mathrm{A}}{}^2C_{\mathrm{A}}}{\phi} + \frac{\overline{N_{\mathrm{Bm}}{}^{\mathrm{z}}}b_{\mathrm{B}}{}^2C_{\mathrm{B}}}{\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}(1-\phi)}\right] \tag{59}$$

where in eq 55 we have allowed for different constants b_{A}, b_{B}, C_{A}, and C_{B} for the two types of chain but have chosen n_{s} the same for both chains. Figure 5 shows a plot of $(q^2_{\mathrm{crit}})_{\mathrm{polydisperse}}/(q^2_{\mathrm{crit}})_{\mathrm{monodisperse}}$ vs. $\bar{\phi}_{\mathrm{A}}$, where the molecular weights of the monodisperse case were chosen to match the weight averages of the polydisperse case, $N_{\mathrm{Am}} = \overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}$ and $N_{\mathrm{Bm}} = \overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}$, so that the thermodynamic factor $2\chi' - (\phi\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}})^{-1} - [(1-\phi)\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}]^{-1}$ is exactly the same as the corresponding factor in the monodisperse case. Of course, Figure 5 makes sense only for this region of ϕ where this thermodynamic factor is positive (i.e., inside the spinodal). Again the same data on PVME and PSD as in Figure 4 have been used. It is seen that polydispersity has the effect of reducing the characteristic wavevectors somewhat and needs to be taken into account if one wishes to quantitatively analyze experimental data on q^2_{crit}, such as provided in recent work.[15,16,57]

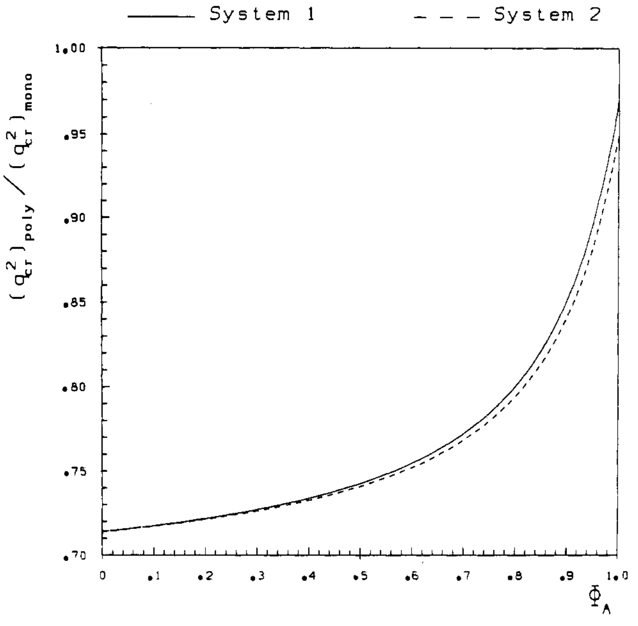

Figure 5. Plot of $(q^2_{\mathrm{crit}})_{\mathrm{polydisperse}}/(q^2_{\mathrm{crit}})_{\mathrm{monodisperse}}$ vs. ϕ_{A}. The full curve refers to PSD sample 1 and the broken curve to PSD sample 2, as described in the text.

As a practical example, let us discuss the recent experiment by Hashimoto et al.,[57] where a mixture of PS and PVME was studied, with molecular weights $M_{\mathrm{n}}^{\mathrm{PS}} = 2.0 \times 10^5$ $\{M_{\mathrm{w}}/M_{\mathrm{n}} = 1.05\}$ and $M_{\mathrm{n}}^{\mathrm{PVME}} = 4.7 \times 10^4$ $\{M_{\mathrm{w}}/M_{\mathrm{n}} = 1.5\}$ at $\phi_{\mathrm{A}} = \phi_{\mathrm{PVME}} = 0.8$. Hashimoto et al. quote that $R_{\mathrm{gyr}}^{\mathrm{PVME}} = (b_{\mathrm{A}}{}^2C_{\mathrm{A}}\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}/6)^{1/2} = 97$ Å and $R_{\mathrm{gyr}}^{\mathrm{PS}} = (b_{\mathrm{B}}{}^2C_{\mathrm{B}}\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}/6)^{1/2} = 129$ Å. Hashimoto et al.[57] measure $q_{\mathrm{m}}{}^2$ the position of maximum growth rate, for several quench depths, and compare their data to theoretical predictions[21] for a symmetrical monodisperse mixture. They observe that typically the experimental q_{m} is a factor of about 2.2–2.6 smaller than the theoretical one. Since $q_{\mathrm{m}}{}^2 = (^1/_2)q^2_{\mathrm{crit}}$, eq 59 implies in terms of the gyration radii

$$q_{\mathrm{m}}{}^2 = 3\left[\chi' - \frac{1}{2\phi\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}} - \frac{1}{2(1-\phi)\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}}\right]\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}} \Bigg/ \left[\frac{\overline{N_{\mathrm{Am}}{}^{\mathrm{z}}}}{\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}}\frac{1}{\phi}(R_{\mathrm{gyr}}^{\mathrm{A}})^2 + \frac{\overline{N_{\mathrm{Bm}}{}^{\mathrm{z}}}}{\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}}\frac{\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}}{\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}}\frac{1}{(1-\phi)}(R_{\mathrm{gyr}}^{\mathrm{B}})^2\right] \tag{60}$$

Since the value of χ' where the bracket in the numerator of eq 60 vanishes defines the spinodal χ_{s}', we can rewrite eq 60 as

$$(q_{\mathrm{m}}R_{\mathrm{gyr}}^{\mathrm{A}})^2 = 3\frac{\chi' - \chi_{\mathrm{s}}'}{\chi_{\mathrm{s}}'}\left[\frac{1}{2\phi} + \frac{1}{2(1-\phi)}\frac{\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}}{\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}}\right] \Bigg/ \left[\frac{1}{\phi}\frac{\overline{N_{\mathrm{Am}}{}^{\mathrm{z}}}}{\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}} + \frac{1}{(1-\phi)}\frac{\overline{N_{\mathrm{Bm}}{}^{\mathrm{z}}}}{\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}}\frac{\overline{N_{\mathrm{Am}}{}^{\mathrm{w}}}}{\overline{N_{\mathrm{Bm}}{}^{\mathrm{w}}}}\left(\frac{R_{\mathrm{gyr}}^{\mathrm{B}}}{R_{\mathrm{gyr}}^{\mathrm{A}}}\right)^2\right] \tag{61}$$

For a symmetrical monodisperse mixture, we have for a critical quench $\phi = 1 - \phi = {}^1/_2$, and we would obtain from eq 61 the standard result[21]

$$(q_{\mathrm{m}}R_{\mathrm{gyr}})^2 = \frac{3}{2}\,\frac{\chi' - \chi_{\mathrm{s}}'}{\chi_{\mathrm{s}}'} \tag{62}$$

However, using the data quoted by Hashimoto et al.[57] and the molecular weights of the PVME monomer[32] (58) and the PS monomer[32] (104) to find $\overline{N_{\mathrm{PVMEm}}^{\mathrm{n}}} \cong 811$, $\overline{N_{\mathrm{PSm}}^{\mathrm{n}}} \cong 1924$, we can evaluate the right-hand side of eq 61 if we make the further assumption that eq 54 holds for the samples, since then $\overline{N^z}/\overline{N^w} = M_w/M_n$ {this assumption should be checked experimentally, if a very accurate comparison between theory and experiment is desired}. In the present example, eq 61 then yields

$$(q_m R_{gyr}^{A})^2 = \frac{3}{2}\,\frac{\chi' - \chi_s'}{\chi_s'} \bigg/ (1.32)^2 \qquad (63)$$

which implies that the actual q_m should be a factor of 1.32 smaller than the symmetrical one. Since Hashimoto et al.[57] normalize q_m with an arbitrarily chosen R_0 = 110 Å instead of R_{gyr}^{PVME}, the factor in between the actual normalized q_m and the symmetrical one should be 1.17, in disagreement with the observation.

However, in contrast to the suggestion of Hashimoto et al.,[57] we feel that it is not clear whether their experiment does point toward any serious deficiency of the theory for the initial stages of phase separation. One should also keep in mind that further uncertainties are involved in estimating the quantity $(\chi' - \chi_s')/\chi_s'$, since in this mixture the temperature and concentration dependence of χ' is difficult to understand.[58] In fact, the value of χ_s' implied by eq 60, $\chi_s' \approx 0.00207$, is not in agreement with the expression $\chi' = 0.05125 - 21.27/T$ quoted by Hashimoto et al.,[57] who state that the temperature of the spinodal is T_s = 427 K, which would imply $\chi_s' = 0.0015$.

Finally, we emphasize that the present discussion of polydispersity effects on phase separation was strictly restricted to the very early stages where the linearized theory of spinodal decomposition can be applied. Clearly, a study of polydispersity effects on nucleation phenomena and on the late stages of phase separation is very interesting[57,59] but is beyond the scope of the present work. It is already quite clear that the present dynamic Flory–Huggins model due to its neglect of hydrodynamical effects would not be applicable to the late stages of spinodal decomposition in polymer blends; careful experimental work will be required to decide whether the present theory can account for the early stages quantitatively and to settle the various theoretical questions on the appropriate modeling of interdiffusion in polymer mixtures. Last, we also draw attention to polydispersity effects on viscosity and self-diffusion coefficients in pure one-component systems rather than mixtures, which are nontrivial to understand particularly for the reptation model.[60]

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Nonlinear Viscoelasticity of Semidilute Polystyrene Solutions. Effect of Molecular Weight Distribution

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ABSTRACT: The nonlinear viscoelasticity of an entangled polymer may be represented by a function $h(t,\gamma) = G(t,\gamma)/G(t,0)$, where $G(t,\gamma)$ is the relaxation modulus at the magnitude of shear γ. The function $h(t,\gamma)$ is unity at $t = 0$, decreases with time, and levels off at a time τ_k independent of γ to a value $h(\gamma)$, which is well compared with the prediction of the tube model theory for polymers with sharp molecular weight distributions. Here we measured the function $h(t,\gamma)$ for semidilute polystyrene solutions containing polymers with molecular weights M_S and M_L ($>M_S$) by mass concentrations c_S and c_L, respectively; $10^{-4}M_L = 842$ or 448; $20 \le 10^{-4}M_S \le 289$; $c_L = 0.038$ g cm^{-3} and $1 \le c_S/c_L \le 2.6$. When $M_L \ge 4.7M_S$ the characteristic time τ_k was determined by M_L and the total concentration, $c_S + c_L$, and was independent of M_S or c_L/c_S. This result may be consistent with the prediction of the tube model theory. When M_S was smaller than the entanglement molecular weight corresponding to the total concentration, the nonlinear function $h(\gamma)$ was equal to that of monodisperse polymers. When M_S was larger, $h(\gamma)$ was larger than expected. The result may imply that the short chains have more effect than retarding the overall motion of long chains even at times much longer than the relaxation time of the short chains.

Introduction

The effect of molecular weight distribution (MWD) has long been one of the difficult problems in the study of polymer viscoelasticity.[1] Recent development in the theory of polymer chain entanglement based on the tube model[2-4] has given a big impact on this problem and the effect of MWD on linear viscoelasticity is now studied in connection with the molecular motion in entangled systems.[5-13] It is hoped that studies of polymers with a bimodal MWD (i.e., a blend of two samples with different molecular weights) may be used to assess the assumptions of the theoretical model of entangled polymer and to attain a better understanding of molecular motion. As for the nonlinear viscoelasticity, the tube model theory gives a simple description of the effect of varying strain on the relaxation modulus based on the molecular motion after an instantaneous deformation of the entangled polymer.[3,4] There are a few attempts to modify the theory to include the effect of MWD.[14,15] On the other hand, experimental studies have mostly been concerned with the flow properties at a constant rate of shear.[16] Even the result of elaborate studies on polymers with a bimodal MWD[17,18] is not very convenient for analysis under light of the new theory of entanglement. The purpose of the present study is to provide data of the strain-dependent relaxation modulus for solutions of polymers with a bimodal MWD. The strain-dependent relaxation modulus, $G(t,\gamma)$, is the ratio of the shear stress to the magnitude of shear, γ, applied to the material at time $t = 0$. The limit at $t \to 0$ of $G(t,\gamma)$ is the linear relaxation modulus, $G(t)$. We define two functions to represent the nonlinear behavior

$$h(t,\gamma) = G(t,\gamma)/G(t) \tag{1}$$

$$h(\gamma) = \lim_{t\to\infty} h(t,\gamma) \tag{2}$$

According to the tube model theory,[2-4] the gross shape of a polymer chain varies in two processes, the equilibration process of the fluctuation of chain contour length and the reptation process. The characteristic times, τ_B and τ_C, of the respective processes vary with the number of entanglement per chain, N, as follows:[2-4,19,20]

$$\tau_B \propto \tau_A N^2 \tag{3}$$

$$\tau_C \propto \tau_A N^{3.5} \tag{4}$$

where τ_A is the relaxation time of an entangled strand. In most cases, τ_C is much larger than τ_B. On application of a large strain to the material,[3,4] the chain is elongated and oriented to a certain direction on average. The tensile force along the chain relaxes as the contour length equilibrates and accordingly a large portion of stress relaxes with the characteristic time τ_B. At times sufficiently longer than τ_B, the relaxation modulus is predicted to be factored as

$$G(t,\gamma) = G(t)h(\gamma) \qquad (t \gg \tau_B) \tag{5}$$

The succeeding relaxation is caused by the reptation, or the disengagement of the chain from the oriented tube region, with the characteristic time τ_C. The function $h(\gamma)$ can be calculated from the increase of chain contour length on deformation of the material and is independent of the material. The predicitions are in good accord with the observation for polymer solutions with sharp MWD,[21-26] as explained below.

A typical example of $G(t,\gamma)$ is shown in Figure 1 for a solution in Aroclor 1248 of a polystyrene with sharp MWD: $M = 2.89 \times 10^6$ and $c = 0.076$g cm^{-3} at 30 °C. The curves at the bottom represent the function $h(t,\gamma)$. The $G(t)$ values in the long-time range marked C can be fitted with an asymptotic equation

$$G(t) = G_1 \exp(-t/\tau_1) \tag{6}$$

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