Collective Diffusion in Polymer Solutions

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ABSTRACT: The decay of concentration fluctuations in polymer solutions is investigated. Starting from a microscopic basis, a theoretical framework is developed to describe so-called memory effects leading to additional slow modes. The theory is formulated for a multicomponent system. These general results are applied to a homopolymer–solvent system. With respect to the interpretation of dynamic light scattering the behavior at small scattering vectors q is relevant. In this case, an approximately diffusive decay mode and slower, approximately q-independent modes related to viscoelastic properties are predicted at higher polymer concentrations. The relation to typical experimental results and to the theory recently presented by Wang is discussed.

1. Introduction

Dynamic light scattering offers the possibility of studying the dynamics of polymer solutions over many decades in time. The result is commonly interpreted in terms of the dynamic scattering intensity $I(q,t)$, which is proportional to the field correlation function of the scattered light and depends on time t and scattering vector q. It coincides with the static scattering intensity $I(q)$ at $t = 0$ and decays for $t > 0$. The behavior at small scattering vectors q relevant for the interpretation of dynamic light scattering results is considered. In the case of a monodisperse, dilute polymer solution, the decay of $I(q,t)$ is single exponential and is characterized by a rate $\Gamma = q^2 D_0$, which determines the translational diffusion coefficient D_0 of a practically isolated chain. Over a limited concentration regime, the decay remains still single exponential, but the rate $\Gamma = q^2 D_{\text{coll}}$ is characterized by the collective diffusion coefficient D_{coll}. Because the compressibility of the polymer subsystem decreases with increasing concentration, the decay of concentration fluctuations is enhanced, thus D_{coll} increases. This is at least qualitatively understood and is sufficient for the interpretation of data on monodisperse polymers in good solvents at dilute to semidilute concentrations.[1–3]

In recent years, several experiments on polymer solutions at higher concentrations have been performed,[3–9] and additional slow, nondiffusive modes have been observed. In the limiting case of a polymer melt, a broad distribution of q-independent rates is quite typical, while the diffusive decay mentioned above is not visible. In the case of a polymer solution, a decrease in solvent quality or in temperature leads to the occurrence of additional slow contributions in the decay of the dynamic scattering intensity. By varying temperature or polymer concentration, a gradual change from a regime governed by a diffusive behavior to a regime more similar to the case of a melt has been observed.[6–8]

Several explanations have been proposed: The dependence on molecular weight led to the assumption that these slow contributions are due to self-diffusion of the chains.[4] Self-diffusion is indeed significantly slower than the collective process mentioned above and becomes slower with increasing polymer concentration because the single particle motion is hindered by surrounding polymers. To test this assumption, results from pulsed-field-gradient NMR[5] and forced Rayleigh scattering[10] both measuring self-diffusion have been compared to the slow rate found from dynamic light scattering. The data differed strongly from each other and outruled such an explanation.

An alternative interpretation is the existence of large clusters or strongly entangled regions.[3] Such contributions are expected to be diffusive if q^{-1} is larger than the cluster size. Therefore, clusters have to be very large to cause nondiffusive modes. Alternative experiments, which are sensitive to the presence of clusters, are necessary to solidify such an explanation.

A third type of interpretation originates from the analogy to a melt. Within a hydrodynamic description, a coupling between the decay of density fluctuations in a melt and longitudinal viscoelasticity has been predicted.[11] Typical times of slow modes in polymer solutions observed in dynamic light scattering are indeed quite similar to slow mechanical times[6] and support such an idea. These observations led to the concept that the fast process is due to concentration fluctuations of the polymer subsystem, while viscoelastic modes originate from density fluctuations of the entire system.[8] A strong objection against this concept is the fact that density fluctuations may relax by the much faster motion of solvent molecules. However, if partial specific volumes of solvent and polymer differ, a fluctuation in total density created by a fluctuation in polymer density may not fully relax by the fast motion of solvent molecules alone. This has been taken into account by Wang[12,13] on the basis of a hydrodynamic description due to Bearman and Kirkwood[14] treating a multicomponent fluid system. Wang predicts a viscoelastic influence on the decay of concentration fluctuations of the polymer component if the coupling parameter $\beta \propto (\partial\rho/\partial\rho_2)_{p,T}$, where ρ is the total density, ρ_2 the polymer density, p the pressure, and T the temperature, is nonvanishing. Doi and Onuki[15] also investigated the coupling between concentration fluctuations and viscoelasticity. They assumed a constitutive equation for the stress which involves the average polymer velocity and not the average velocity of the entire system. Because of this ad hoc assumption, viscoelasticity has a direct influence on concentration fluctuations, thus it is also present for $(\partial\rho/\partial\rho_2)_{p,T} = 0$. Very recently, Akcasu, Klein, and Wang[16] found that there is indeed an additional term, which is not present in Wang's original theory, causing viscoelastic effects on the decay of concentration fluctuations of the polymer component even if the specific volumes of these components are identical. Also very recently, an experimental study by Brown and Stepanek[17] confirmed the existence of slow viscoelastic modes for $(\partial\rho/\partial\rho_2)_{p,T} = 0$.

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From these considerations it is evident that a microscopic description may contribute to the clarification of the controversial points of view. Within the Mori–Zwanzig projection operator formalism, Desai[18] already predicted a coupling of concentration fluctuations to the stress in a mixture of two fluids. In the case considered here, a strong asymmetry between the time scales of motion for solvent molecules and the motion of polymer chains is a dominant dynamical feature. To take this into account, the solvent is regarded as an inert background adjusting very fast to the motion of statistical chain segments. The Liouville equation is employed to study the slow motion of the chains. As it is known from molecular liquids[19] and colloids,[20] generalized transport functions determined from memory equations have to be introduced when considering long-time effects. Standard methods of statistical mechanics are employed to derive their formal expressions. When the time scale of the dynamics of solvent molecules and internal motion inside statistical segments is well separated from the chain motion, high-frequency processes can be introduced by a friction constant, or a time independent mobility function. Thus, in the "short" time limit, the segments are considered as Brownian particles, which leads to the typical behavior known for the fast decay rate. At longer times, interactions among polymer chains are known to slow down self-diffusion of polymers considerably, but the consequences on collective diffusion as observed by dynamic light scattering are not at all obvious. To establish a theoretical framework for the treatment of this complicated time regime is the main aim of this paper. A relation between the slowing down of internal motion of individual chains and the decay of concentration fluctuations is found. The internal motion of individual polymers is known to create viscoelastic effects.[21] This finally provides the link between collective diffusion and viscoelasticity on a microscopic basis.

The general theory is formulated for a multicomponent polymer system in a solvent. Besides being more general, it shows the relation to theories considering the coupling of different decay modes due to the presence of various species. This type of approach has been established by Akcasu et al.[22] Section 2 briefly repeats some results valid for short times. Generalized transport functions are introduced in section 3. In section 4, consequences for a system containing one type of homopolymer are investigated. Section 4.1 simplifies the results in order to obtain a tractable description for this important case, while section 4.2 elucidates the role of internal relaxation in individual polymers. From the experimental point of view, the relation to viscoelastic properties is of great importance. This aspect is considered in section 5. While representing the longitudinal viscoelastic response by a sum of Debye-like contributions, general trends are discussed in section 5.1. Section 5.2 shows numerical examples, and section 5.3 presents further results on the time dependence of the dynamic scattering intensity. This also offers the opportunity for a comparison to Wang's result and the consideration of the gel limit. Appendix A contains the mathematical procedure to obtain the results of section 3, and Appendix B gives the explicit formulas leading to the numerical results in section 5.2.

2. Short-Time Behavior

In the presentation of the general theory, a multicomponent system is considered. It is composed of s polymeric components, and Greek indices refer to the various polymer species. If the system contains homopolymers, these components refer to chains differing in the type of monomers or in the degree of polymerization. Diblock copolymers have to be regarded as a two-component system in this context.[24] In addition to the polymers, a homogeneous solvent providing a continuous background as well as a heat bath may be present. If the total system—polymer and solvent—is incompressible, it is not necessary to take into account the solvent explicitly as a distinct species.[23] In this case, the microscopic properties of the polymer segments have to be considered as renormalized quantities influenced by the properties of the solvent.

Dynamic partial intensities $I_{\alpha\beta}(q,t)$ are commonly introduced as correlation functions of the Fourier transforms of partial segment densities refering to species α and β. The partial densities are given by

$$\rho_{\alpha}(\mathbf{q},t) = V^{-1/2}\sum_{i}^{n_\alpha}\sum_{l}^{N_\alpha} \exp[-i\mathbf{q}\cdot\mathbf{r}_{il}^{(\alpha)}(t)] \qquad (1)$$

where $\mathbf{r}_{il}^{(\alpha)}(t)$ denotes the position of segment l on polymer i at time t, and V is the scattering volume. The summation in eq 1 is performed over all N_α segments on all n_α polymers belonging to species α. For a shorter notation, a column vector $\rho(\mathbf{q})$ having elements $\rho_\alpha(\mathbf{q})$, $\alpha = 1, \ldots s$, and the corresponding transposed and complex conjugated vector $\rho^{+}(\mathbf{q}) = (\rho_1(-\mathbf{q}), \ldots, \rho_s(-\mathbf{q}))$ is introduced. Within this notation, the $s \times s$ matrix of partial intensities can be expressed as

$$\mathbf{I}(q,t) = \langle \rho(\mathbf{q},t{=}0)\rho^{+}(\mathbf{q},t)\rangle \qquad (2)$$

where $\langle \ldots \rangle$ refers to the equilibrium average. For $t = 0$, eq 2 gives the matrix of static partial intensities $\mathbf{I}(q)$.

The dynamic behavior of the scattering intensities has been discussed in terms of a cumulant expansion[22] which is briefly sketched. The short-time limit of the first time derivative of $I_{\alpha\beta}(q,t)$ determines the mobility matrix $\mathbf{M}(q)$ having the elements

$$M_{\alpha\beta}(q) = -\frac{1}{q^2}\frac{\partial I_{\alpha\beta}(q,t)}{\partial t}\Big|_{t\to 0} \qquad (3)$$

The limit $t \to 0$ refers to a time domain on which statistical segments are regarded as Brownian particles. Many collisions with solvent molecules as well as internal relaxations due to the various additional degrees of freedom inside a single segment give rise to Brownian motion over short distances compared to typical segment separations. Such a time regime is implied in eq 3.

When considering polymers with segmental friction coefficients ξ_α in the absence of hydrodynamic interaction, the mobility matrix is diagonal and independent of q,

$$M_{\alpha\beta} = \delta_{\alpha\beta}\, c_\alpha \frac{k_B T}{\xi_\alpha} \qquad (4)$$

where $c_\alpha = n_\alpha N_\alpha / V$ gives the segment density of species α and $\delta_{\alpha\beta}$ is the Kronecker symbol. Hydrodynamic interaction leads to off-diagonal components of the mobility tensor defined in eq 3 and a dependence on the scattering vector q.

For short times, the equation of motion for the partial intensities is assumed to take the form

$$\frac{\partial}{\partial t}\mathbf{I}(q,t) = -\boldsymbol{\Omega}(q)\cdot\mathbf{I}(q,t) \qquad (5)$$

This result may be obtained by using the Kirkwood–Riseman or Smoluchowski operator while neglecting memory terms.[22,23] The assumption behind eq 5 is that the corresponding time scale, on which such a description is applicable, exists. The frequency matrix $\mathbf{\Omega}(q)$ can be obtained from eq 3 as

$$\mathbf{\Omega}(q) = q^2\, \mathbf{M}(q)\cdot\mathbf{I}^{-1}(q) \qquad (6)$$

The $(s \times s)$ matrix $\mathbf{\Omega}(q)$ has s eigenvalues $\Gamma_i(q)$, and the solution of eq 5 is a superposition of exponential decays

$$I_{\alpha\beta}(q,t) = \sum_{i=1}^{s} a_{\alpha\beta}^{(i)}(q)\, \exp[-\Gamma_i(q)t] \qquad (7)$$

with amplitudes $a_{\alpha\beta}^{(i)}(q)$. The measured scattering intensity is a linear combination of partial intensities weighted with appropriate scattering lengths. It is evident from eq 7 that also this quantity can be expressed as a sum of exponential decays having the same rates $\Gamma_i(q)$ as the partial intensities, while the amplitudes depend on the scattering lengths as well. If only one type of polymer is present, $s = 1$, eq 7 predicts a single exponential decay. The mathematical technique to treat eq 5 is well-known and is elucidated in refs 25 or 26.

To consider the dynamics at arbitrary times, eq 5 is insufficient, and so-called memory effects may contribute. To treat this more complicated case, eq 5 has to be replaced by a more general equation of motion. This is the topic of the following section.

3. Dynamics at Arbitrary Times

To treat dynamical properties at arbitrary times, generalized transport functions are introduced. A straightforward generalization of eq 5 leads to the definition of a generalized time-dependent "frequency matrix" $\mathbf{\Omega}(q,t)$ by

$$\frac{\partial}{\partial t}\mathbf{I}(q,t) = -\mathbf{\Omega}(q,t)\cdot\mathbf{I}(q,t) \qquad (8)$$

If the matrix $\mathbf{\Omega}(q,t)$ is approximately constant over a certain range of time, the mathematical procedure mentioned in the preceding section can be used to evaluate the decay rates relevant for this specific time domain. This is of special importance in the short-time or in the long-time limit. If only one polymeric species is present, the corresponding scalar function $\Omega(q,t)$ can be obtained directly from the time derivative of the logarithm of the scattering intensity. Therefore, the unconventional definition in eq 8 introduced earlier by Akcasu[27] has some appealing features.

From the theoretical point of view, it is more convenient to consider equations of motion in Laplace space. This leads to the definition of a generalized diffusion matrix by

$$z\tilde{\mathbf{I}}(q,z) - \mathbf{I}(q) = -q^2\tilde{\mathbf{D}}(q,z)\cdot\tilde{\mathbf{I}}(q,z) \qquad (9)$$

where $\tilde{f}(z)$ denotes the Laplace transform of a time dependent function, or matrix, $f(t)$. Equation 9 corresponds to a memory equation for the intensity matrix. An additional equation describes the time development of the generalized diffusion matrix and defines a generalized friction matrix $\tilde{\mathbf{\Xi}}(q,z)$ by

$$z\, \tilde{\mathbf{D}}(q,z) - \mathbf{D}(q,t{=}0) = -\tilde{\mathbf{\Xi}}(q,z)\cdot\mathbf{m}^{-1}\cdot\tilde{\mathbf{D}}(q,z) \qquad (10)$$

where the diagonal matrix of masses $\mathbf{m}$ has elements $m_{\alpha\beta} = m_\alpha\delta_{\alpha\beta}$ and m_α denotes the mass of a segment belonging to species α. Equations 9 and 10 are mere definitions, and their meaning in terms of microscopic quantities can be derived by standard techniques of statistical mechanics[19,20] as shown in Appendix A.

When treating a colloidal system, Hess and Klein[20] described the time evolution of the macromolecules by a Fokker–Planck operator, which had been derived earlier on the basis of a Liouville description for a system of spherical macromolecules much larger than the solvent molecules.[28] A corresponding derivation has not been accomplished for a polymer–solvent system, and it may in fact be impossible to carry out in a rigorous way because a separation in fast and slow variables may only apply approximately. Therefore, the dynamics are described by the Liouville operator $\mathcal{L}$ here, and assumptions on the separation of time scales, which are hidden when applying the Fokker–Planck operator, are stated explicitly. This procedure makes it more transparent at which stages such assumptions play a role.

The intensity matrix can formally be expressed as

$$\mathbf{I}(q,t) = \langle \rho(\mathbf{q}) \exp[-\mathcal{L}t]\rho^+(\mathbf{q})\rangle \qquad (11)$$

and a vector of longitudinal currents is introduced by a continuity equation

$$\mathrm{i}q\mathbf{j}^+(\mathbf{q}) = \frac{\partial}{\partial t}\rho^+(\mathbf{q}) = -\mathcal{L}\rho^+(\mathbf{q}) \qquad (12)$$

Its components are given by

$$j_\alpha(\mathbf{q}) = V^{-1/2}\sum_{i}^{n_\alpha}\sum_{l}^{N_\alpha}\hat{\mathbf{q}}\cdot\frac{\mathbf{p}_{il}^{(\alpha)}}{m_\alpha}\exp[-\mathrm{i}\mathbf{q}\cdot\mathbf{r}_{il}^{(\alpha)}] \qquad (13)$$

where $\hat{\mathbf{q}}$ denotes the unit vector in $\mathbf{q}$ direction and $\mathbf{p}_{il}^{(\alpha)}$ is the momentum of segment l on polymer i of species α.

Correlations of the longitudinal currents specify the generalized diffusion matrix $\tilde{\mathbf{D}}(q,z)$

$$\tilde{\mathbf{D}}(q,z) = \langle \mathbf{j}(\mathbf{q})[z + \mathcal{L}Q_c]^{-1}\, \mathbf{j}^+(\mathbf{q})\rangle\langle\rho(\mathbf{q})\rho^+(\mathbf{q})\rangle^{-1} \qquad (14)$$

Q_c is orthogonal to the projector P_c, eq A.5, on the partial densities. Because the partial densities $\rho_\alpha(\mathbf{q})$ are conserved quantities, the resolvent operator $[z + \mathcal{L}Q_c]^{-1}$ may be replaced by $[z + \mathcal{L}]^{-1}$ in the small $\mathbf{q}$ limit, and eq 14 reduces to the familiar Kubo relation then. From eq 14 it is evident that $\mathbf{D}(q,t{=}0)$ can be calculated from static correlation functions alone, and the result is given in eq A.10.

The formal expression for the generalized friction matrix is given by

$$\tilde{\Xi}_{\alpha,\beta}(q,z) = \frac{1}{k_BTc_\beta}\frac{m_\beta}{m_\alpha}\langle \mathcal{F}_{\alpha,tot}(\mathbf{q})Q_cQ_j[z + \mathcal{L}Q_cQ_j]^{-1}\, Q_cQ_j\mathcal{F}^*_{\beta,tot}(\mathbf{q})\rangle \qquad (15)$$

where

$$\mathcal{F}^*_{\alpha,tot}(\mathbf{q}) = m_\alpha\frac{\partial}{\partial t}j^*_\alpha(\mathbf{q}) = V^{-1/2}\sum_{i}^{n_\alpha}\sum_{l}^{N_\alpha}\hat{\mathbf{q}}\cdot\mathbf{F}_{il,tot}^{(\alpha)} + \mathrm{i}q\, V^{-1/2}\sum_{i}^{n_\alpha}\sum_{l}^{N_\alpha}\left(\hat{\mathbf{q}}\cdot\mathbf{F}_{il,tot}^{(\alpha)}\,\frac{\exp[\mathrm{i}\mathbf{q}\cdot\mathbf{r}_{il}^{(\alpha)}] - 1}{\mathrm{i}q} + \frac{1}{m_\alpha}(\hat{\mathbf{q}}\cdot\mathbf{p}_{il}^{(\alpha)})^2\exp[\mathrm{i}\mathbf{q}\cdot\mathbf{r}_{il}^{(\alpha)}]\right) \qquad (16)$$

P_j is the projector on the longitudinal currents, eq A.12, and $Q_j = 1 - P_j$ is its orthogonal counterpart. $\mathbf{F}_{il,tot}^{(\alpha)}$ is the total force exerted on segment (il) due to the solvent as well as interactions with other polymer segments. Whereas $\rho^+(\mathbf{q})$ follows a continuity equation, eq 12, this is not the case for $\mathbf{j}^+(\mathbf{q})$ because the partial currents are not conserved. The first term in eq 16 for the time evolution of $j_\alpha^*(\mathbf{q})$ is related to the total forces exerted on species α, and the second term contains the longitudinal component of a $\mathbf{q}$-dependent stress. Therefore, $\tilde{\Xi}(q,z)$ involves correlations of the total forces exerted on species α as well as correlations of a generalized longitudinal stress. The latter creates a coupling to viscoelasticity.

In the long-time limit, a relation between $\Omega(q,t\rightarrow\infty)$, providing information on the relevant decay rates, and $\tilde{\Xi}(q,z\rightarrow 0)$ can be established within the Markov approximation

$$\Omega_{\alpha\beta}(q,t\rightarrow\infty) = q^2 k_B T m_\alpha \sum_\gamma^s \frac{c_\gamma}{m_\gamma}[\tilde{\Xi}^{-1}(q,z\rightarrow 0)]_{\alpha\gamma}[\mathbf{I}^{-1}(q)]_{\gamma\beta} \tag{17}$$

When comparing this result to eqs 4 and 6, one may notice that the term $(\delta_{\alpha\beta}/\xi_\alpha)$ relevant for the short-time behavior is replaced by $[\tilde{\Xi}^{-1}(q,z\rightarrow 0)]_{\alpha,\beta}$ in the long-time limit. This may be understood by the following reasoning: Forces between polymer segments lead to additional energy dissipation. While the influence at intermediate times may be quite complicated, the behavior at long times can be described by an additional friction. In general, slowing down of motion is expected.

To discuss the consequences on the dynamic scattering intensity, more specific approximations have to be introduced. Several consequences in case of a homopolymer–solvent system containing only one type of polymer are discussed in the following sections.

4. Homopolymer–Solvent System

To elucidate some general tendencies, a system containing one type of polymer is considered. For the interpretation of light scattering data, the limit of small scattering vectors q is relevant. This case is investigated. The various $(s \times s)$ matrices introduced in the preceding sections for the multicomponent case reduce to scalar functions for $s = 1$. Greek indices, which are necessary to distinguish between the various species in the preceding sections, are omitted in the following. Equations 9 and 10 provide the relation between the dynamic intensity, $I(q,t)$, and the generalized friction function, $\Xi(q,t)$, in Laplace space. In order to obtain results on the time development of $I(q,t)$, suitable approximations for $\Xi(q,t)$ have to be made. This is done in section 4.1. Section 4.2 relates these findings to the dynamics of individual polymers.

4.1. Generalized Friction Function. Equations 15 and 16 determine the generalized friction function. For vanishing $\mathbf{q}$, $\mathcal{F}^*$ is determined by the total force acting on all segments, see eq 16, and is independent of interactions among polymer segments because such terms cancel pairwise in the summation. As an approximation, the forces due to the solvent molecules are assumed to relax on a quite fast time scale, and their correlations are approximated by their $z \rightarrow 0$ result. When neglecting correlations of these rapidly fluctuating forces on different polymer segments, a constant segmental friction coefficient is defined from

$$\tilde{\Xi}(q\rightarrow 0,z\rightarrow 0) = \xi \tag{18}$$

Correlations of forces exerted by the solvent on different segments correspond to hydrodynamic interaction, and eq 18 has to be modified.

An approximatively z-independent value of $\tilde{\Xi}(q\rightarrow 0,z)$ implies an exponential decay of the dynamic intensity in the overdamped limit governed by the rate $q^2(k_BT/\xi)(c/I(0))$. This result means the following: Even if the diffusion of individual chains is slowed down considerably—as it is in the case of an "entangled" system—the global motion of the polymer subsystem observed at $q \rightarrow 0$ remains unaffected because slowing down of individual chains is exactly balanced by the higher cooperativity of the motion. Corresponding results have been obtained by alternative methods[29,30] in the case of Brownian spheres.

In the following, the contribution to the generalized friction function in the order of q^2 is considered. Forces between polymer segments are assumed to provide the dominant, and also slowly relaxing, contribution to the stress, which leads to the approximation

$$\Xi(t) = \xi\delta(t) + \frac{q^2}{ck_\mathrm{B}TV}\langle\sigma_{zz}Q_jQ_c \exp[Q_cQ_j\mathcal{L}Q_cQ_jt]Q_jQ_c\sigma_{zz}\rangle + 0(q^4) \tag{19}$$

where

$$\sigma_{zz} = \sum_i^n\sum_l^N \hat{\mathbf{q}}\cdot\mathbf{F}_{il}\hat{\mathbf{q}}\cdot\mathbf{r}_{il} \tag{20}$$

is the contribution to the stress tensor due to interactions among the polymers only. $\mathbf{F}_{il}$ denotes the interaction force on segment (il) due to other polymer segments. As the system is isotropic, $\mathbf{q}$ is deliberately chosen in z-direction.

The time development in eq 19 is governed by the projected Liouville operator. If the projector would project on conserved variables, it could be replaced by $\mathcal{L}$ in the small q limit. Here, straightforward algebra leads to

$$\lim_{\mathbf{q}\rightarrow 0} Q_cQ_j\mathcal{L}Q_cQ_j = \mathcal{L} + \frac{1}{k_BTnN}[\hat{\mathbf{q}}\cdot\mathbf{F}_{pol}\rangle\langle\hat{\mathbf{q}}\cdot\mathbf{v}_{pol} - \hat{\mathbf{q}}\cdot\mathbf{v}_{pol}\rangle\langle\hat{\mathbf{q}}\cdot\mathbf{F}_{pol}] \tag{21}$$

where

$$\mathbf{F}_{pol} = \sum_i^n\sum_l^N \mathbf{F}_{il,tot} \tag{22}$$

is the total force acting between polymers and solvent, and

$$\mathbf{v}_{pol} = \sum_i^n\sum_l^N \frac{\mathbf{p}_{il}}{m} \tag{23}$$

is the velocity of the polymer subsystem. For $\mathbf{F}_{pol} \propto \mathbf{v}_{pol}$, as it is the case on a coarse-grained Brownian time scale, the second term in eq 21 vanishes. Here, the projected Liouville operator is replaced by $\mathcal{L}$ as an approximation. A very similar simplification is commonly done in the context of mode–mode coupling approximations[19] even for all values of $\mathbf{q}$. It rigorously holds when expanding $\Xi(t)$, eq 19, to first order in time, and also in the weak coupling limit partly neglecting polymer–solvent interactions.

Because

$$\lim_{q\to 0} Q_c Q_j \sigma_{zz} = \lim_{q\to 0} Q_c \sigma_{zz} \to \sigma_{zz} \tag{24}$$

holds, the friction function is given by

$$\Xi(t) = \xi\delta(t) + \frac{q^2}{ck_{\mathrm{B}}TV}\langle \sigma_{zz}(0)\sigma_{zz}(t)\rangle + 0(q^4) = \xi\delta(t) + \frac{q^2}{c}\eta_{\|}(t) + 0(q^4) \tag{25}$$

where $\eta_{\|}(t)$ is the contribution to the longitudinal viscosity due to interactions among polymers. A strong, and also slowly decaying, contribution arises from forces connecting individual chains. It is well-known from experiments that the presence of polymers in solution drastically increase the viscosity of the fluid system while creating viscoelastic relaxations much slower than relaxations in the pure solvent. Keeping only these terms leads to

$$\Xi(q,t) = \xi\delta(t) + q^2\frac{1}{Nk_BT}\sum_{l,m}^{N}\langle f_l^z(0)z_l(0)\, f_m^z(t)z_m(t)\rangle + 0(q^4) \tag{26}$$

where f_l^z denotes the z-component of the force $\mathbf{f}_l$ connecting segments on one chain, and z_l gives the z-coordinate of the segment position.

The result of this analysis may be expressed in the following way: Collective diffusion is directly coupled to the longitudinal viscosity arising from the presence of polymers, as can be seen from eq 25. This longitudinal viscosity is essentially due to forces connecting the chains, eq 26, and therefore relaxes on a time scale typical for internal relaxations of individual chains. This relates collective diffusion and internal chain motion.

From this microscopic derivation it is evident that viscoelasticity arising from the presence of polymers has a direct influence on Ξ and thus on the decay of concentration fluctuations. No additional coupling parameter β depending on the difference of specific volumes of polymer and solvent, as it has been suggested by Wang,[12,13] is involved. This agrees with the considerations by Doi and Onuki[15] and is supported by experiments.[17] Akcasu, Klein, and Wang[16] have recently undertaken a calculation using the Mori–Zwanzig technique while choosing the dynamic variables in a specific way. Their new results show that—besides the contribution proportional to β already reported by Wang—an additional term independent of the coupling parameter β has to be taken into account as well. Only this term is present here, because the interactions among polymers are considered to provide the dominant contribution to the stress, while neglecting all other terms when simplifying the general expressions.

Equations 25 and 26 indicate two alternative ways to procede further: One possibility consists in an investigation of the single polymer behavior and establishes a relation to the microscopic properties of the polymers. This aspect is considered in section 4.2. The second possibility is a closer investigation of the relation between viscoelasticity and the dynamic scattering intensity and provides an experimental test of the underlying assumptions. This is the topic of section 5.

4.2. Relation to Single Polymer Dynamics. Equation 26 relates the additional contribution to the generalized friction function to the time correlation function of position and forces inside an individual polymer chain. With further assumptions on the single chain dynamics this expression can be evaluated.

The intramolecular forces connecting the chains are modeled by entropic spring forces between next neighbors. In a continuum description, these can be expressed as

$$\mathbf{f}_l = K\frac{\partial^2 \mathbf{r}_l}{\partial l^2} \tag{27}$$

where $K = 3k_BT/\sigma^2$ is the spring constant and σ^2 is the mean squared distance between subsequent statistical segments. The space coordinates $z_l(t)$ are expressed by normal coordinates $Z_p(t)$[32]

$$Z_p(t) = \frac{1}{N}\int_0^N dl\, z_l(t)\cos(p\pi lN) \qquad \text{for } p = 1, 2, ..., N \tag{28}$$

It is further assumed that the relaxations of different normal modes are uncorrelated, $\langle Z_p(0)Z'_p(t)\rangle \propto \delta_{pp'}$, and can be characterized by a typical time τ_p. Inserting eqs 27 and 28 in eq 26 leads to a sum of time correlation functions involving a product of four normal coordinates. After employing Wick's theorem to factorize the four-point correlation function into a sum of two-point correlations, the result for $\Xi(q,t)$ can be expressed in terms of the normalized correlation functions related to the internal modes, $p \geq 1$

$$C_p(t) = \frac{\langle Z_p(0)Z_p(t)\rangle}{\langle Z_p(0)Z_p(0)\rangle} = \frac{N\sigma^2}{6\pi^2p^2}\langle Z_p(0)Z_p(t)\rangle \simeq \exp[-t/\tau_p] \tag{29}$$

The value for the static correlation function $\langle Z_p(0)Z_p(0)\rangle$ is independent of the chain dynamics and is a consequence of Gaussian chain statistics, which is consistent with the presentation of the intramolecular forces in eq 27. When neglecting hydrodynamic interaction, the result

$$\tilde{\Xi}(q,z\to 0) = \xi + q^2k_BT\frac{1}{N}\sum_{p=1}^{N}\tau_p = \xi + q^2k_BT\bar{\tau}(c,N) \tag{30}$$

can be obtained by straightforward algebra. So the additional friction depends on the mean relaxation time $\bar{\tau}(c,N)$ of the internal polymer modes. Obviously, long times, or small p, contribute most to the average.

When describing single chain dynamics within the Rouse model, the contribution to the friction function in order q^2 is given by $(\xi(qR_G)^2/3)$, where the radius of gyration is $R_G = \sigma(N/6)^{1/2}$. Such a term is clearly of minor importance. In the framework of reptation theory, the time $\bar{\tau}(c,N)$ scales as N^3, which then leads to a much larger additional term in the order of $(\xi(qR_G)^2N^2)$. Experiments for long chains indicate even a stronger dependence of $\bar{\tau}(c,N)$ on N. Thus, appreciable effects are expected especially for longer chains, which cannot be described within the Rouse model.

The dynamic intensity can be obtained from eqs 9, 10, and A.10 as

$$\tilde{I}(q,z) = I(q)\left[z + q^2\frac{k_BT}{\tilde{\Xi}(q,z)}\frac{c}{I(q)}\right]^{-1} \tag{31}$$

where the overdamped limit, $\tilde{\Xi}/m \gg z$, is considered. This limit is already implicitly assumed in theoretical treatments on short-time behavior, so it is very well justified at longer times. In general, eq 31 is a complicated expression in Laplace space and leads to a decay of the dynamic intensity, which cannot easily be expressed as a superposition of a few exponential decay modes. It seems more appropriate to express the result as

$$I(q,t) = I(q)\exp[-\Gamma(t)t] \tag{32}$$

The short-time limit of $\Gamma(t)$ is the first cumulant, Γ_0, and is related to the static scattering intensity $I(q)$ by

$$\Gamma(t\rightarrow 0) = \Omega(q,t\rightarrow 0) = \Gamma_0(q) = q^2\frac{k_BT}{\xi}\frac{c}{I(q)} \tag{33}$$

when hydrodynamic interaction is neglected. Because $I(q)$ approaches a constant value for scattering vectors characteristic for light scattering, this initial decay is diffusive. The long time behavior in the Markov limit is characterized by

$$\Gamma(t\rightarrow\infty) = \Omega(q,t\rightarrow\infty) = \Gamma_\infty(q) = q^2\frac{k_BT}{\tilde{\Xi}(q,z\rightarrow 0)}\frac{c}{I(q)} \tag{34}$$

Thus, the friction coefficient ξ is replaced by the larger generalized friction function $\tilde{\Xi}(q,z\rightarrow 0)$. If the contribution in the order of q^2 dominates the result for $\tilde{\Xi}(q,z\rightarrow 0)$ in eq 30, the limiting rate Γ_∞, eq 34, is approximately independent of the scattering vector q. The ratio of the short-time and the long-time limit of $\Gamma(t)$ can be expressed as

$$\frac{\Gamma_0(q)}{\Gamma_\infty(q)} = \frac{\tilde{\Xi}(q,z\rightarrow 0)}{\tilde{\Xi}(q,z\rightarrow\infty)} = 1 + q^2\frac{k_BT}{\xi}\bar{\tau}(c,N) \tag{35}$$

and may serve as a measure of the importance of memory effects. A large difference between $\Gamma_0(q)$ and $\Gamma_\infty(q)$ implies a strong deviation from a single exponential decay of the dynamic scattering intensity $I(q,t)$ and is expected if the mean relaxation time $\bar{\tau}(c,N)$ for the internal modes of individual chains is very long. The presence of neighboring polymers and entanglements slows down the motion considerably and enhances such a long-time effect. Qualitatively, this may explain the observation that slow modes become slower with increasing concentration or increasing chain length.[4-6]

Some remarks on the interpretation of these results are in order: The physical origin of the slowing down in the decay of concentration fluctuations stems from the fact that a decay of such fluctuations involves internal motion of individual chains as well. With decreasing wavelength of fluctuations a stronger deformation of single chains becomes necessary. For small, but nonvanishing q this may lead to apparently nondiffusive modes.

5. Relation to Viscoelastic Behavior

Equation 25 also serves as the starting point to discuss the relation between viscoelasticity and the decay of the dynamic scattering intensity. It contains only those contributions to the longitudinal viscosity, which are related to the forces connecting the chain segments. The longitudinal viscosity of a real system is influenced by many other mechanisms as well. So $\eta_\parallel(t)$ in eq 25 cannot be regarded as the total, measurable viscosity. Nevertheless, if the forces along the chain relax quite slowly as compared to other relevant processes, $\eta_\parallel(t)$ may be estimated from the low-frequency part of the mechanical response. For simplicity, only these slow relaxations are considered in the following. In Section 5.1, the longitudinal modulus is modeled as a sum of Debye-like contributions. Section 5.2 gives an illustration of the result for a simplified model. Section 5.3 establishes the link to Wang's theoretical predictions which provide further insight into the behavior of the dynamic scattering intensity.

5.1. General Results. The longitudinal modulus, which depends on the frequency ω, is written in the general form

$$\tilde{\mathcal{G}}(\omega) = \mathrm{i}\omega\sum_i\frac{G_i}{\Gamma_i^{(G)} + \mathrm{i}\omega} = \mathrm{i}\omega\,\tilde{\eta}_\parallel(\omega) \tag{36}$$

and is related to a frequency dependent viscosity. The corresponding time dependent viscosity can be expressed as

$$\eta_\parallel(t) = \sum_i G_i\exp[-\Gamma_i^{(G)}t] \tag{37}$$

Combining eqs 25, 31, and 37 leads to

$$\frac{\tilde{I}(q,z)}{I(q)} = \frac{1}{\Gamma_0}\left[\hat{z} + \left\{1 + \sum_i\frac{g_i}{\hat{z} + \Gamma_i^{(G)}/\Gamma_0}\right\}^{-1}\right]^{-1} \tag{38}$$

where $\hat{z} = z/\Gamma_0$ and the dimensionless quantities g_i are given by

$$g_i = \left(\frac{G_i}{ck_BT}\right)\frac{I(q)}{c} \tag{39}$$

The relations eqs 38 and 39 contain only quantities, which can be estimated from experimental results.

If the viscoelastic contribution in eq 38 is unimportant, a single exponential decay with the rate Γ_0 is expected. If, instead, the viscoelastic contribution is important, a slowing down of the decay of the dynamic intensity is expected with increasing time. In this case, the long-time limiting rate

$$\Gamma_\infty(q) = \frac{\Gamma_0(q)}{1 + \Gamma_0(q)\sum g_i/\Gamma_i^{(G)}} \tag{40}$$

becomes significantly slower than $\Gamma_0(q)$ and is approximately independent of the scattering vector. For a further illustration of the trends, a very simple model for the viscoelastic relaxation is studied.

5.2. Numerical Results. Based on eq 38 a simple example is considered. The viscoelastic response is assumed to consist of two Debye-like relaxations with rates $\Gamma_1^{(G)}$ and $\Gamma_2^{(G)}$ and dimensionless strength $g_1 = g_2 = g$, which are related to the modulus by eq 39. Assuming two rates is the easiest way of introducing a certain amount of broadening in the mechanical response. It simplifies the mathematical treatment considerably and contains essential features expected for more realistic models. In this special case, the inverse Laplace transform of $\tilde{I}(q,z)$, eq 38, can be calculated analytically. The dynamic intensity is obtained as a sum of three exponential contributions

$$\frac{I(q,t)}{I(q)} = \sum_{i=1}^{3}A_i\exp[-\gamma_i^{(DLS)}t] \tag{41}$$

The decay rates $\gamma_i^{(DLS)}$ and the amplitudes A_i are given in Appendix B. In the numerical examples of this section, the (arbitrary) units of the various rates are omitted, because results only depend on the ratio of the rates, see eq 38. Obviously, numerical values of the time t then refer to the corresponding inverse units.

When assuming that the first cumulant Γ_0 scales as q^2, tendencies for different values of the scattering vector can be studied. This is illustrated in Figure 1. Different

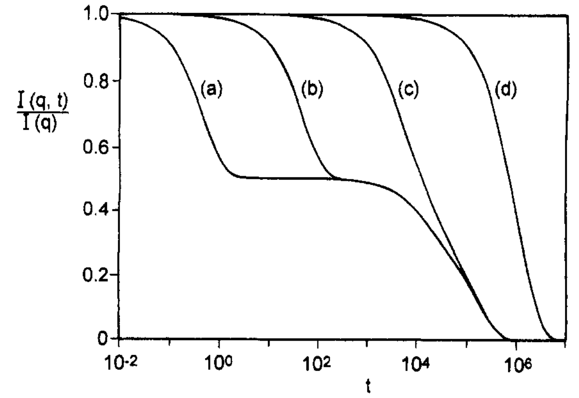

Figure 1. The normalized dynamic scattering intensity $I(q,t)/I(q)$ is shown as a function of time t. The parameters are $g_1 = g_2 = 0.5$, $\Gamma_1^{(G)} = 10^{-4}$, and $\Gamma_2^{(G)} = 10^{-5}$. Different curves refer to different values of the first cumulant $\Gamma_0 \propto q^2$: (a) $\Gamma_0 = 1$, (b) $\Gamma_0 = 0.01$, (c) $\Gamma_0 = 10^{-4}$, and (d) $\Gamma_0 = 10^{-6}$.

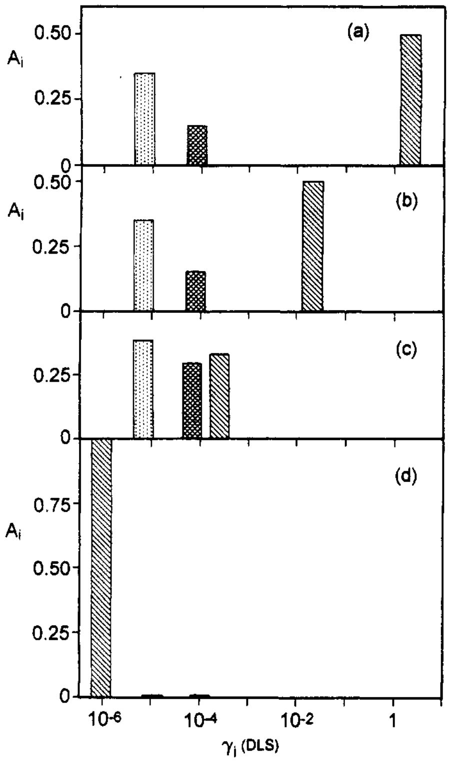

Figure 2. The amplitudes A_i are shown as a function of the decay rates $\gamma_i^{(DLS)}$ for the system considered in Figure 1. Different plots refer to different values of Γ_0, and different fillings refer to the diffusive rate and to the two viscoelastic rates, respectively. $\Gamma_0 = 1$ in Figure 2a, $\Gamma_0 = 0.01$ in Figure 2b, $\Gamma_0 = 10^{-4}$ in Figure 2c, and $\Gamma_0 = 10^{-6}$ in Figure 2d.

curves in Figure 1 refer to different values of Γ_0, thus to different scattering vectors. For small scattering vectors, a nearly single exponential decay is obtained, while for larger q^2 a plateau at intermediate times is visible, which is followed by a much slower decay essentially determined by typical viscoelastic times.

More insight is obtained when presenting the amplitudes A_i as a function of the decay rates $\gamma_i^{(DLS)}$. This presentation in Figure 2a–d shows the distribution of relaxation rates. For each value of Γ_0, or q^2, three rates $\gamma_i^{(DLS)}$ are obtained. Two of these rates are in the order of magnitude of $\Gamma_1^{(G)}$ and $\Gamma_2^{(G)}$, respectively, and are hardly influenced by q^2 or Γ_0. In the following, these are called the "viscoelastic modes". A third mode is strongly dependent on q^2 and is in the order of magnitude of Γ_0. Therefore, it approximately scales as q^2 and is called the "diffusive mode" here. Three different cases can be distinguished: For $\Gamma_0 \ll \Gamma_i^{(G)}$, or small q, a single exponential decay with a diffusive rate Γ_0 is expected, while the amplitudes related to the viscoelastic contributions are neglible. This can be seen in Figure 2d. For $\Gamma_0 \simeq \Gamma_i^{(G)}$, the three rates $\gamma_i^{(DLS)}$ are in the same order of magnitude, thus the decay appears broader than single exponential. This is illustrated in Figure 2c and in curve c of Figure 1. When diffusive and viscoelastic rates have amplitudes of the same magnitude and are encountered in the same time regime as illustrated in Figure 2c, the dynamic intensity obtained experimentally may be difficult to analyze in terms of q-dependent and q-independent modes. If $\Gamma_0 \gg \Gamma_i^{(G)}$ the spectrum clearly separates into a part which is approximately independent of the scattering vector and a faster diffusive part. This situation is shown in Figure 2a,b.

From this simple example, several conclusions can be drawn: The fasted rate which can be measured is the "diffusive" rate in the order of magnitude of the first cumulant. This also applies in the case $\Gamma_0 < \Gamma_i^{(G)}$, because only the diffusive contribution has an appreciable amplitude then and causes an approximately single exponential decay. With increasing q^2, or increasing Γ_0, a separation into a viscoelastic part and a diffusive part of the relaxation rates is expected if typical viscoelastic contributions slower than Γ_0 are present. Such a separation has been observed in many experiments.[3,6,8,7]

Finally, the dependence on the parameters g_i, eq 39, is discussed. Figure 3 shows the amplitudes and rates for various choices of $g = g_1 = g_2$. If the low-frequency viscoelastic contribution is negligible, $g \ll 1$, a single exponential decay with a diffusive decay rate Γ_0 is expected. This is shown in Figure 3a and refers to the case of small interaction effects or low polymer concentration or short chains. With increasing g, the amplitudes of the viscoelastic contributions increase. For values in the order of unity, see Figure 3b, the viscoelastic and the diffusive part have comparable amplitudes, thus both are visible. In the case of large g shown in Figure 3c the amplitudes of the viscoelastic modes increase, and the fast, approximately diffusive rate becomes difficult to detect. When considering the decay of $I(q,t)/I(q)$ as a function of t, an intermediate plateau regime close to unity is expected. Therefore, an essentially q-independent decay is seen. This is similar to the behavior in polymer melts. From Figure 3a–c also a shift of the diffusive rate away from Γ_0 to higher values is observed. This feature is explained in section 5.3.

Nicolai et al.[6] made an extensive comparison between light scattering data and mechanical measurements. They found strong analogies with respect to the typical times. These analogies can be understood from the simple example given here. They observed that a change in temperature barely influenced the mechanical properties in the polystyrene–DOP system under investigation, while the amplitudes of slow modes increased strongly with decreasing temperature. Simultaneously, the static scattering intensity increased, which was explained by a deterioration in solvent quality. Equation 39 relates the model parameter g_i to the static scattering intensity. An increase of $I(q)$ implies an increase of g_i and therefore an increase of amplitudes for the viscoelastic modes, which is in keeping with the experimental observation.

5.3. Comparison to Wang's Theory. The recent series of publications by Wang[9,12,13] provided new impulses on the interpretation of slow modes observed by dynamic light scattering and initiated further experimental studies. To clarify this still controversial topic, a comparison

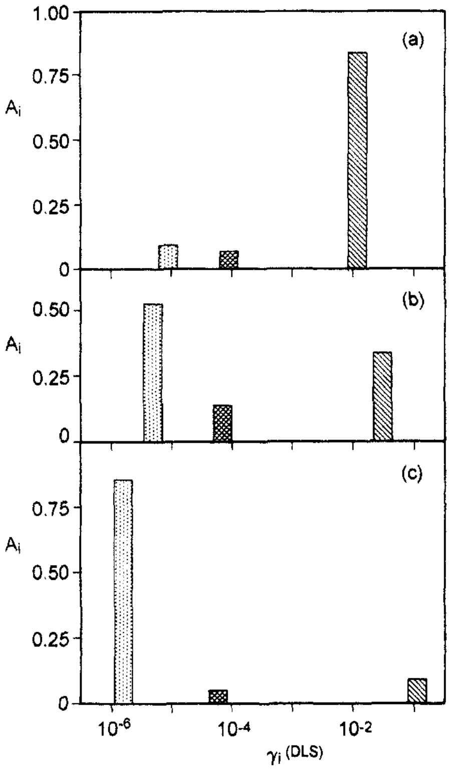

Figure 3. The influence of the parameter $g = g_1 = g_2$ on the distribution of relaxation rates is shown. The parameters are $\Gamma_0 = 10^{-2}$, $\Gamma_1^{(G)} = 10^{-4}$, and $\Gamma_2^{(G)} = 10^{-5}$. Different plots refer to different values of g, and different fillings refer to the diffusive rate and to the two viscoelastic rates, respectively. $g = 0.1$ in Figure 2a, $g = 1$ in Figure 2b, and $g = 5$ in Figure 2c.

between Wang's results and my work is helpful. In the course of this comparison, some additional useful relations concerning the time dependence of $I(q,t)$ are presented. Finally, it is illustrated how the gel limit considered by Adam and Delsanti[34] can be obtained within the framework of this paper. To facilitate the comparison, eq 38 is written as

$$\frac{\tilde{I}(q,z)}{I(q)} = \frac{1+\sum_{j=1}^{n}\frac{B_j}{z+\Gamma_j^{(G)}}}{z\left(1+\sum_{j=1}^{n}\frac{B_j}{z+\Gamma_j^{(G)}}\right)+q^2D_\pi} \tag{42}$$

The q-dependent constants in eq 42 are given by

$$q^2D_\pi = q^2\frac{k_BTc}{\xi I(q)} = \Gamma_0(q) \tag{43}$$

$$B_j = q^2\frac{G_j}{\xi c} \tag{44}$$

In analogy to Wang's definitions, the quantity

$$q^2D_c = q^2D_\pi + \sum_{j=1}^{n}B_j \tag{45}$$

is introduced.

Wang considers the one-sided Fourier transform of the normalized dynamic intensity, $S(q,t) = I(q,t)/I(q)$, and obtains the result

$$\tilde{S}(q,\omega) = \frac{1+\sum_{j=1}^{n}\frac{B_j^{(W)}}{i\omega+\Gamma_j^{(G)}}}{i\omega\left(1+\sum_{j=1}^{n}\frac{B_j^{(W)}}{i\omega+\Gamma_j^{(G)}}\right)+q^2D_\pi^{(W)}} \tag{46}$$

The real part of $\tilde{S}(q,\omega)$ is the dynamic structure factor which determines the spectrum of the scattered light. The constants in eqs 46 are given by

$$q^2D_\pi^{(W)} = q^2\frac{\phi_1}{\xi}\left(\frac{\partial\pi}{\partial\rho_2}\right)_{p,T} \tag{47}$$

$$B_j^{(W)} = q^2\frac{\beta M_j^{(W)}}{\xi\rho_2^0} \tag{48}$$

and

$$q^2D_c^{(W)} = q^2D_\pi^{(W)} + \sum_{j=1}^{n}B_j^{(W)} \tag{49}$$

is introduced. In eqs 47–49, the index 1 refers to the solvent and 2 to the polymer. ρ_i gives the density of species i, and ϕ_i the corresponding volume fraction. ρ refers to the total density and π denotes the osmotic pressure. In this notation, $[\phi_1(\partial\pi/\partial\rho_2)_{p,T}/\xi]$ represents the diffusion coefficient due to osmotic pressure fluctuations and corresponds to the term $[ck_BT/(\xi I(q))]$ in the notation of the preceding sections. Note that $I(q\rightarrow 0)$ is proportional to the compressibility of the polymer subsystem. Wang obtained eqs 46–49 by representing the total viscoelastic modulus as a sum of Debye-like contributions with amplitudes M_j and rates $\Gamma_j^{(G)}$ in analogy to eq 36. Note that eq 36 introducing the moduli G_j only refers to contributions arising from the polymer chains. A coupling parameter $\beta = (\rho_2^0/\rho_0)(\partial\rho/\partial\rho_2)_{p,T}$, where the index '0' refers to the equilibrium values of the respective densities, appears as a prefactor in the viscoelastic term in eq 48. This is a consequence of the hydrodynamic equations employed by Wang. As it has already been mentioned in section 4.1, very recent results by Akcasu, Klein, and Wang[16] lead to a modification of the value of $B_j^{(W)}$, which should not influence the q-dependence.

As can be seen from a comparison of eqs 43–45 to 47–49, the mathematical structures of eqs 42 and 46 are identical. This becomes evident when realizing that the Laplace transform and the one-sided Fourier transform are related to each other simply by replacing the Laplace variable z by the Fourier variable $i\omega$. Therefore, when formulating the results for $I(q,t)$ in terms of either q^2D_π, q^2D_c, and B_j or $q^2D_\pi^{(W)}$, $q^2D_c^{(W)}$, and $B_j^{(W)}$, respectively, the formal expressions have to be identical.

For a further investigation of the time dependence of the dynamic intensity, eq 42 is written in the form

$$\frac{\tilde{I}(q,z)}{I(q)} = \frac{F(z)}{G(z)} \tag{50}$$

where

$$F(z) = \prod_{l=1}^{n}(z+\Gamma_l^{(G)}) + \sum_{j=1}^{n}B_j\prod_{l\neq j}^{n}(z+\Gamma_l^{(G)}) \tag{51}$$

and

$$G(z) = (z + q^2D_\pi)\prod_{l=1}^{n}(z + \Gamma_l^{(G)}) + z\sum_{j=1}^{n}B_j\prod_{l\neq j}^{n}(z + \Gamma_l^{(G)}) \qquad (52)$$

The denominator of eq 50, $G(z)$, is a polynomial in the Laplace variable z of order $(n + 1)$. Therefore, it can be expressed as

$$G(z) = \prod_{k=1}^{n+1}(z + \gamma_k^{(DLS)}) \qquad (53)$$

where the rates $\gamma_k^{(DLS)}$ can be obtained from eq 52 by solving $G(z) = 0$ for z. Because of eq 53, eq 50 can be written in the form

$$\frac{\tilde{I}(q,z)}{I(q)} = \sum_{k=1}^{n+1}\frac{A_k}{z + \gamma_k^{(DLS)}} \qquad (54)$$

where A_k are amplitudes related to the decay rates $\gamma_k^{(DLS)}$.

Inverse Laplace transform of eq 54 then predicts the dynamical intensity as a sum of $(n + 1)$ exponential decays weighted with amplitudes A_k

$$I(q,t) = I(q)\sum_{k=1}^{n+1}A_k\exp[-\gamma_k^{(DLS)}t] \qquad (55)$$

A convenient sum rule is obtained when comparing the coefficients of z^n in eqs 52 and 53, which leads to

$$\sum_{k=1}^{n+1}\gamma_k^{(DLS)} = \sum_{k=1}^{n}\Gamma_k^{(G)} + q^2D_c \qquad (56)$$

where the definition 45 has been inserted. From the exact relation 56 it can be seen that in the special case $\gamma_k^{(DLS)} \simeq \Gamma_k^{(G)}$, $k = 1, ..., n$, the rate $\gamma_{n+1}^{(DLS)}$ has to be in the order of q^2D_c. To test the applicability of such a guess guided by physical intuition, $G(z)$ is written as

$$G(z) = (z + q^2D_c)\prod_{l=1}^{n}(z + \Gamma_l^{(G)}) - \sum_{j=1}^{n}B_j\Gamma_j^{(G)}\prod_{l\neq j}^{n}(z + \Gamma_l^{(G)}) \qquad (57)$$

If all viscoelastic rates $\Gamma_l^{(G)}$ are very small quantities, the second term of eq 57 is less important than the first contribution. In this case, one may approximate

$$G(z) \simeq (z + q^2D_c)\prod_{l=1}^{n}(z + \Gamma_l^{(G)}) \qquad (58)$$

which is strictly valid only in the limit $\Gamma_l^{(G)} \rightarrow 0$.

When comparing eq 58 to 53, the rates relevant for dynamic light scattering are obtained as

$$\gamma_k^{(DLS)} \simeq \Gamma_k^{(G)}, \qquad k = 1, ..., n$$

$$\gamma_{n+1}^{(DLS)} \simeq q^2D_c > q^2D_\pi \qquad (59)$$

In section 5.2, numerical results for the case $n = 2$ are considered. Two of the rates obtained for the decay of the dynamic scattering intensity are indeed in the order of magnitude of the two viscoelastic rates. The third, diffusive rate shows a tendency to be enhanced as compared to the first cumulant $\Gamma_0 = q^2D_\pi$. This enhancement of the diffusive rate as compared to the first cumulant q^2D_π increases with increasing viscoelastic modulus, which can be seen from a comparison of Figure 3a–c. This is in qualitative agreement with eq 59. In Figures 2a–c, similar tendencies are observed, but in Figure 2d, which refers to the case $\Gamma_k^{(G)} > q^2D_\pi$, $k = 1, ..., n$, the diffusive rate is simply given by $q^2D_\pi = \Gamma_0$. So the approximate prediction in eq 59 for the rates applies at least semiquantitatively if the rates $\Gamma_k^{(G)}$ are small compared to the first cumulant q^2D_π.

The amplitudes are obtained from the comparison of eqs 50 and 54. Within the approximation 58, they are determined as

$$A_k = \frac{B_k}{q^2D_c - \Gamma_k^{(G)}} \simeq \frac{B_k}{q^2D_c} \qquad k = 1, ..., n \qquad (60)$$

and

$$A_{n+1} = 1 - \sum_{l=1}^{n}A_k \simeq \frac{D_\pi}{D_c} \qquad (61)$$

Equation 60 predicts that the amplitudes A_k, $k = 1, ..., n$, are proportional to the moduli $G_k \propto B_k$. This may be compared to the mathematically exact results of section 5.2. In each of the Figures 2a–d and 3a–c, the moduli $g_1 \propto G_1 \propto B_1$ and $g_2 \propto G_2 \propto B_2$ have the same value. Whereas eq 60 predicts equal amplitudes of the viscoelastic rates in these cases, the two amplitudes obtained from the exact solution may differ significantly from this approximative prediction. This is pronounced in Figure 3c and indicates the limitations of the approximation.

When assuming eqs 59–61 to be valid, the dynamic intensity can be written as

$$I(q,t) \simeq I(q)\left(\frac{D_\pi}{D_c}\exp[-q^2D_ct] + \sum_{l=1}^{n}\frac{B_l}{q^2D_c}\exp[-\Gamma_l^{(G)}t]\right) \qquad (62)$$

When inserting Wang's expression $D_\pi^{(W)}$, $D_c^{(W)}$, and $B_l^{(W)}$ for the corresponding parameters in eq 62, this leads to his predictions on the dynamic intensity. As pointed out in the comparison to the exact solutions in section 5.2, this approximation gives a reasonable guideline for the understanding, but has its limitations especially with respect to the predictions on the amplitudes or when considering viscoelastic contributions which are not slow as compared to q^2D_π. In the case $D_c \gg D_\pi$, the amplitude of the rate q^2D_c as predicted by eq 62 is very small. For this reason, the fastest rate which can be *measured* by dynamic light scattering is expected to be somewhat larger than the first cumulant q^2D_π but still remains roughly in this order of magnitude.

Already Brochard and de Gennes[33] discussed whether viscoelastic modes due to the rubber elasticity of a transient polymer network can be observed in light scattering. For small q, they arrived at the conclusion that only the diffusive mode is visible. As explained in the beginning of section 4.1 about the limiting behavior for $q \rightarrow 0$, the decay rate in this case is q^2D_π, in keeping with considerations by Brochard and de Gennes. Equation 62 does not apply in this case because $\Gamma_l^{(G)} \ll q^2D_\pi$ has been assumed for its derivation. For viscoelastic rates much slower than q^2D_π, Brochard and de Gennes predicted a vanishing amplitude for the fast component. In this case, the amplitude can be approximately calculated from eq

62 and is given by D_π/D_c. This value is strongly determined by the amplitudes G_i of the modulus, or, more precisely, by the value of the coupling parameter g_i, as can be seen from eqs 43–45 and 39. Therefore, if the moduli G_i are very small, their effect on the scattering is also very small irrespective of the related times. This was not considered by Brochard and de Gennes. For large coupling parameters g_i, or for high moduli G_i, the amplitude of the fast component is small, which then is in keeping with the prediction by Brochard and de Gennes.

As pointed out in the derivation of eq 62, this result is mathematically exact in the limit of vanishing rates $\Gamma_l^{(G)}$. In this case, the dynamic intensity does not vanish at long times and is given by

$$I(q,t) \simeq I(q)\left(\frac{D_\pi}{D_c}\exp[-q^2D_ct] + \frac{D_c - D_\pi}{D_c}\right) \qquad (63)$$

In such a gel limit, the relaxation rate is indeed given by q^2D_c and corresponds to the prediction by Adam and Delsanti[34] for the gel region. It is not at all trivial to recover their result from a limiting case of this approach. The memory function in Adam and Delsanti's work is proportional to the modulus, whereas the memory function obtained here—and in Wang's work—is proportional to the viscosity. For small q, $D_\pi \simeq D_\pi(q\rightarrow 0)$, the plateau value of $I(q,t)/I(q)$ at long times is predicted to be independent from the scattering vector.

From this considerations it is evident that the mathematical structure of the approach presented here is identical to Wang's predictions when presenting the viscoelastic modulus by a sum of Debye relaxations. Whereas the sum rule in eq 56 is an exact consequence of this model, eq 62 is an approximative result which, because of its simplicity, may be very useful in understanding various tendencies. Within this approximation, q^2D_c is the fastest rate expected to contribute to dynamic light scattering, whereas the first cumulant q^2D_π is influenced by all decay rates. In typical experimental results, the frequency dependence of the modulus and the decay observed by dynamic light scattering are often represented more efficiently by algebraic functions of frequency or a Kohlrausch–Williams–Watts behavior. Further studies to incorporate such a behavior may facilitate the interpretation of experimental data.

6. Discussion

The decay of concentration fluctuations in a polymer solution has been investigated with special emphasis on long-time effects. All processes considered here originate from the diffusive motion of chain segments. In this sense, the q-independent modes are only apparently nondiffusive because of the additional influence of interactions or steric hinderances. An essential ingredient is the assumption about a separation of time scales related to molecular processes—as collisions with solvent molecules or motion inside a statistical segment—and the motion on the level of statistical segments, which involves much slower relaxations. Such an assumption is also present in the Rouse model[32] or in theories starting from cumulant expansions.[23] In the latter type of theories, dynamical properties are represented entirely by the friction coefficient ξ or the mobility $M(q)$. When considering a polymer melt, Hess and Akcasu[35] described the dynamics entirely in terms of correlation functions of forces between segments. Therefore, additional fast processes are not included. The theory presented here forms a link between the case of a melt as considered by Hess and Akcasu and current theories based on the short-time behavior in polymer solutions. This will become more obvious when a system containing two polymeric species is considered. In this more complicated case, the dynamics of both polymeric components include slow processes and additional, explicitly time dependent effects due to forces between the polymer species arise. This leads to a contribution to the generalized friction matrix in the order of q^0, which cannot simply be treated as a constant term represented by segmental friction coefficients and implies a qualitatively different behavior.

The relation between viscoelasticity and the dynamic scattering has been discussed. Essentially, two conditions have to be satisfied for the observation of slow modes: Viscoelastic relaxations slower than the initial, diffusive decay rate must be present in the system, and their contribution to the modulus has to be large enough, or, more precisely, the sum of the parameters $g_i = (G_i/k_BT)(I(q)/c)$ has to be of order unity. This part of the work was especially aimed at the possibilities for an interpretation of experimental results. It relates quite complicated material properties. But it does not provide an underlying microscopic understanding. For a deeper insight, an additional theory on the single polymer dynamics in the presence of neighboring polymers is necessary. Schweizer[31] developed a theory on the dynamics of individual polymers within a surrounding polymer matrix. In a similar way as it was done here for a polymer solution, he related the collective dynamics of the polymer melt to the individual polymer motion and realized the importance of mutual influence, which should be treated in a self-consistent way. Here, it is shown how the collective behavior is influenced by the dynamics of individual polymers in the case of a polymer solution. Combining such approaches may lead to a better theoretical understanding.

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Appendix A. Derivation of the Friction Matrix

Aim of this section is to elucidate the derivation of the generalized diffusion matrix, eq 14, and the generalized friction matrix, eq 15. The procedure closely parallels the treatment by Hess and Klein[20] for a system of Brownian spheres within a Fokker–Planck description. In order to consider the dynamics of polymer segments, the Liouville operator $\mathcal{L}$ is decomposed in a term involving the partial derivatives with respect to the coordinates of polymer segments, which have to be regarded as generalized coordinates here, and an additional contribution $\mathcal{L}_R$

$$\mathcal{L} = -\sum_{\alpha}^{s}\sum_{i}^{n_\alpha}\sum_{l}^{N_\alpha}\left(\frac{\mathbf{p}_{il}^{(\alpha)}}{m_\alpha}\cdot\frac{\partial}{\partial \mathbf{r}_{il}^{(\alpha)}} + \mathbf{F}_{il,tot}^{(\alpha)}\cdot\frac{\partial}{\partial \mathbf{p}_{il}^{(\alpha)}}\right) + \mathcal{L}_R \qquad (A.1)$$

By virtue of this construction, $\mathcal{L}_Rf$ vanishes if the phase space function f depends only on positions and momenta of polymer segments. A phase space variable f develops with the adjoint of $\mathcal{L}$

$$\frac{\partial}{\partial t}f = -\mathcal{L}f \qquad (A.2)$$

Taking the time derivative of the formal expression for the intensity matrix, eq 11, leads after Laplace transformation to

$$z\tilde{\mathbf{I}}(q,z) - \mathbf{I}(q) = -\langle \rho(\mathbf{q})\mathcal{L}[z + \mathcal{L}]^{-1}\rho^{+}(\mathbf{q})\rangle \quad \text{(A.3)}$$

The operator identity

$$[z + \mathcal{L}]^{-1} = [z + \mathcal{L}Q]^{-1}\,(1 - \mathcal{L}P[z + \mathcal{L}]^{-1}) \quad \text{(A.4)}$$

is valid for any projector P and its orthogonal projector $Q = 1 - P$, which may easily be seen when multiplying this identity with the operator $[z + \mathcal{L}]$ from the right. The projector

$$P_c\ldots = \rho^{+}\cdot\langle\rho\rho^{+}\rangle^{-1}\cdot\langle\rho\ldots\rangle = \sum_{\alpha\beta}^{s}\rho_{\alpha}^{*}(\mathbf{q})[\mathbf{I}^{-1}(q)]_{\alpha\beta}\langle\rho_{\beta}(\mathbf{q})\ldots\rangle \quad \text{(A.5)}$$

projects on the partial densities and $Q_c = 1 - P_c$. For simplicity, the argument $\mathbf{q}$ is omitted. The operator identity A.4 for $P = P_c$, eq A.5, is inserted in eq A.3. According to the form of A.4, a sum of two terms results. In the first contribution, A, the resolvent operator is expanded in $(\mathcal{L}Q_c/z)$, which leads to

$$A = -\langle\rho\mathcal{L}[z + \mathcal{L}Q_c]^{-1}\rho^{+}\rangle = \frac{1}{z}\langle\rho\mathcal{L}\rho^{+}\rangle - \frac{1}{z}\sum_{l=1}^{\infty}\left\langle\rho\mathcal{L}\left(\frac{-\mathcal{L}Q_c}{z}\right)^{l}\rho^{+}\right\rangle = 0 \quad \text{(A.6)}$$

$(-\mathcal{L}\rho^{+})$ gives the longitudinal current $\mathbf{j}^{+}$ defined in eq 12 and is orthogonal to the density. Therefore, the first term of eq A.6 vanishes. The second term of this expression vanishes as well because $Q_c\rho^{+} = 0$, thus $A = 0$. So eq A.3 can be written as

$$z\tilde{\mathbf{I}}(q,z) - \mathbf{I}(q) = \langle\rho\mathcal{L}[z + \mathcal{L}Q_c]^{-1}\mathcal{L}\rho^{+}\rangle\cdot\langle\rho\rho^{+}\rangle^{-1}\cdot\langle\rho[z + \mathcal{L}]^{-1}\rho^{+}\rangle \quad \text{(A.7)}$$

The last factor in eq A.7 is the formal expression for the Laplace transform of the dynamic intensity matrix $\tilde{\mathbf{I}}(q,z)$, see eq 11. So eq A.7 has the form of eq 9 defining the generalized diffusion matrix. $\langle\rho\mathcal{L}\ldots\rangle$ can be replaced by $-\langle(\mathcal{L}\rho)\ldots\rangle$, because $-\mathcal{L}$ is the adjoint of $\mathcal{L}$ with respect to this scalar product. Expressing eq A.7 in terms of the longitudinal currents $\mathbf{j}$ defined in eq 12 and comparing the result to eq 9 gives eq 14. After inverse Laplace transformation this leads to

$$\mathbf{D}(q,t) = \langle\mathbf{j}\exp[-\mathcal{L}Q_c t]\mathbf{j}^{+}\rangle\cdot\mathbf{I}^{-1}(q) \quad \text{(A.8)}$$

To obtain the value for $t = 0$, the static correlation function of longitudinal currents is calculated from the equipartition theorem of energy as

$$\langle j_{\alpha}j_{\beta}^{*}\rangle = k_B T\delta_{\alpha\beta}\frac{c_{\alpha}}{m_{\alpha}} \quad \text{(A.9)}$$

which leads to

$$D_{\alpha\beta}(q,t=0) = \frac{k_B T}{m_{\alpha}}c_{\alpha}[\mathbf{I}^{-1}(q)]_{\alpha\beta} \quad \text{(A.10)}$$

Next, the formal expression for the generalized friction matrix is considered. Taking the time derivative of eq A.8 gives after Laplace transformation

$$z\tilde{\mathbf{D}}(q,z) - \mathbf{D}(t=0) = -\langle\mathbf{j}\mathcal{L}Q_c[z + \mathcal{L}Q_c]^{-1}\mathbf{j}^{+}\rangle\cdot\langle\rho\rho^{+}\rangle^{-1} \quad \text{(A.11)}$$

The projector on the longitudinal currents is introduced by

$$P_j\ldots = \mathbf{j}^{+}\langle\mathbf{j}\mathbf{j}^{+}\rangle^{-1}\langle\mathbf{j}\ldots\rangle = \sum_{\alpha}^{s}j_{\alpha}^{*}(\mathbf{q})\frac{m_{\alpha}}{c_{\alpha}k_B T}\langle j_{\alpha}\ldots\rangle \quad \text{(A.12)}$$

and its orthogonal counterpart is $Q_j = 1 - P_j$. The unit operator $1 = P_j + Q_j$ is now inserted in front of the resolvent operator in eq A.11. This leads to

$$z\tilde{\mathbf{D}}(q,z) - \mathbf{D}(t=0) = -\langle\mathbf{j}\mathcal{L}Q_c\mathbf{j}^{+}\rangle\cdot\langle\mathbf{j}\mathbf{j}^{+}\rangle^{-1}\tilde{\mathbf{D}}(q,z) - \langle\mathbf{j}\mathcal{L}Q_cQ_j[z + \mathcal{L}Q_c]^{-1}\mathbf{j}^{+}\rangle\cdot\langle\rho\rho^{+}\rangle^{-1} \quad \text{(A.13)}$$

The factor $\langle\mathbf{j}\mathcal{L}Q_c\mathbf{j}^{+}\rangle$ in the first term of eq A.13 vanishes. This may be seen from the following arguments $Q_c\mathbf{j}^{+} = \mathbf{j}^{+}$, because the longitudinal current $\mathbf{j}^{+}$ is orthogonal to the density ρ. $\mathcal{L}\mathbf{j}^{+}$ is proportional to the longitudinal "forces" $\mathcal{F}_{tot}$ introduced in eq 16. The factor under consideration is thus proportional to the static correlation function $\langle\mathbf{j}\mathcal{F}_{tot}\rangle$, which vanishes because it is a mean value of a phase space function odd in the particle momenta. To evaluate the resolvent operator in the remaining term of eq A.13, the operator identity, eq A.4, for the projector P_j, eq A.12, is inserted, which leads to

$$z\tilde{\mathbf{D}}(q,z) - \mathbf{D}(t=0) = -\langle\mathbf{j}\mathcal{L}Q_cQ_j[z + \mathcal{L}Q_cQ_j]^{-1}\mathbf{j}^{+}\rangle\cdot\langle\rho\rho^{+}\rangle^{-1} + \langle\mathbf{j}\mathcal{L}Q_cQ_j[z + \mathcal{L}Q_cQ_j]^{-1}\mathcal{L}Q_cP_j[z + \mathcal{L}Q_c]^{-1}\mathbf{j}^{+}\rangle\cdot\langle\rho\rho^{+}\rangle^{-1} \quad \text{(A.14)}$$

The first term of this expression vanishes because $Q_j\mathbf{j}^{+} = 0$. In the second term of eq A.14, the explicit form for P_j given in eq A.12 is inserted. When employing eq 14, this leads to

$$z\tilde{\mathbf{D}}(q,z) - \mathbf{D}(t=0) = -\langle(\mathcal{L}\mathbf{j})Q_cQ_j[z + \mathcal{L}Q_cQ_j]^{-1}\mathcal{L}Q_c\mathbf{j}^{+}\rangle\cdot\langle\mathbf{j}\mathbf{j}^{+}\rangle^{-1}\cdot\tilde{\mathbf{D}}(q,z) \quad \text{(A.15)}$$

This has the form of eq 10, which defines the generalized friction matrix. Using $Q_c\mathbf{j}^{+} = \mathbf{j}^{+}$, and the fact that also the product Q_cQ_j is a projector because of $P_jP_c = 0$, inserting the definition of the longitudinal forces $\mathcal{F}_{tot}$, eq 16, and comparing to eq 10 leads to eq 15.

Appendix B. Rates and Amplitudes

The decay rates relevant for the simple example of section 5.2 are obtained by determining the three poles of $\tilde{I}(q,z)$, eq 38, in the special case of two Debye-like viscoelastic contributions. These poles are situated on the negative real axis and determine the decay rates

$$\begin{aligned}\gamma_1^{(DLS)} &= \left(-2|p|^{1/2}\cos\left(\frac{\phi}{3}\right) + a\right)\Gamma_0\\ \gamma_2^{(DLS)} &= \left(2|p|^{1/2}\cos\left(\frac{\phi-\pi}{3}\right) + a\right)\Gamma_0\\ \gamma_3^{(DLS)} &= \left(2|p|^{1/2}\cos\left(\frac{\phi+\pi}{3}\right) + a\right)\Gamma_0\end{aligned} \quad \text{(B.1)}$$

where

$$a = \frac{1}{3}\left(\frac{\Gamma_1^{(G)}}{\Gamma_0} + \frac{\Gamma_2^{(G)}}{\Gamma_0} + g_1 + g_2 + 1\right)$$

$$p = a^2(b-1)$$

$$b = \frac{\Gamma_1^{(G)}\Gamma_2^{(G)}}{\Gamma_0^2} + (g_1+1)\frac{\Gamma_2^{(G)}}{\Gamma_0} + (g_2+1)\frac{\Gamma_1^{(G)}}{\Gamma_0}$$

$$\cos(\phi) = -\frac{2a^3 - ab + \Gamma_1^{(G)}\Gamma_2^{(G)}/\Gamma_0^{(2)}}{2|p|^{3/2}} \tag{B.2}$$

When the poles are determined, $\tilde{I}(q,z)$ in eq 38 can be written as

$$\frac{\tilde{I}(q,z)}{I(q)} = \sum_{i=1}^{3} \frac{A_i}{z + \gamma_i^{(DLS)}} \tag{B.3}$$

where the amplitudes A_i are given by

$$A_1 = \frac{c-d}{(\gamma_3^{(DLS)} - \gamma_1^{(DLS)})(\gamma_2^{(DLS)} - \gamma_1^{(DLS)})}$$

$$A_2 = \frac{e - A_1(\gamma_3^{(DLS)} - \gamma_1^{(DLS)})}{\gamma_3^{(DLS)} - \gamma_2^{(DLS)}}$$

$$A_3 = 1 - A_1 - A_2 \tag{B.4}$$

with

$$c = \Gamma_1^{(G)}\Gamma_2^{(G)} + g_1\Gamma_2^{(G)}\Gamma_0 + g_2\Gamma_1^{(G)}\Gamma_0$$

$$d = \gamma_1^{(DLS)}(\Gamma_1^{(G)} + \Gamma_2^{(G)} + g_1\Gamma_0 + g_2\Gamma_0 - \gamma_1^{(DLS)})$$

$$e = \Gamma_1^{(G)} + \Gamma_2^{(G)} + g_1\Gamma_0 + g_2\Gamma_0 - \gamma_1^{(DLS)} - \gamma_2^{(DLS)} \tag{B.5}$$

After inverse Laplace transformation of eq B.3, eq 41 is obtained.

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