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Microscopic Theory of Viscoelasticity in Binary Polymer Mixtures

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ABSTRACT: A general microscopic theory of viscoelasticity for a binary mixture of two species is developed by using projection operator formalism. The theory is applicable to binary polymer blends, binary mixtures of nonpolymeric fluids, and solutions of homopolymers in a solvent of small molecules. Particular attention is given to the effect of viscoelasticity on the spectrum of quasi-elastic light (QEL) scattering from semidilute and concentrated polymer solutions. The results are compared with those previously obtained by Wang using the linearized hydrodynamic description of binary fluids which predict that the viscoelastic effect on the QEL spectrum will vanish when the specific volumes of the polymer and the solvent molecules are equal. We find that there is an additional contribution to the viscosity, not present in Wang's theory, that can account for the viscoelastic effect experimentally observed by Brown and Stepanek in semidilute solutions near Θ condition even when the specific volumes are matched.

Introduction

Quasi-elastic light (QEL) scattering from polymer solutions in the semidilute concentration regime is of experimental and theoretical interest. It has been found experimentally that the spectrum of the scattered light, particularly in poor semidilute solutions near Θ condition, is multimodal, with relaxation times spanning 7–8 decades in the time scale.[1,2] The relaxation time distribution typically displays a narrow peak for short times with a relaxation frequency proportional to q^2, where q is the scattering wavenumber. This fast diffusive mode is attributed to collective motions in the cross-linked network on time scales shorter than the characteristic lifetime of the entanglements. The relaxation time distribution also displays a very broad q-independent peak at large relaxation times. These nondiffusive slow modes are attributed to the viscoelastic effects in the transient network and are believed to represent the relaxation of concentration fluctuations in a viscous solvent on time scales longer than the characteristic entanglement times in which chains can disentangle.[3,4] Various models, such as the transient gel and "blob" diffusion models,[1-3] have been proposed and enjoyed limited success in the qualitative description of the QEL scattering spectrum from semidilute polymer solutions. They have recently been reviewed by Brown and Stepanek.[1]

Recently, a more detailed description of the viscoelastic effects on dynamic light scattering spectra from polymer solutions has been provided by Wang.[5,6] In this work, Wang extended the linearized hydrodynamic description of binary fluids previously developed by Bearman and Kirkwood[7] in the 1950s to polymer solutions consisting of a polymer component in a small molecular solvent. In Wang's work, the term representing the coupling between the concentration fluctuations and viscoelastic relaxation is found to be proportional to the difference between the specific volumes of monomers and solvent molecules. Hence, it is predicted that the contribution of the viscoelasticity to the QEL scattering spectrum vanishes when the specific volumes are equal. On the other hand, it has been observed experimentally by Brown and Stepanek[8] that the viscoelastic mode is still present in the spectrum even when the specific volumes are matched by properly adjusting experimental conditions. This apparent disagreement between the theory and experiment has motivated us to develop a general microscopic theory of viscoelasticity for a binary mixture of two polymer species A and B, in which one or both of the components can be solvents, in order to explain the origin of the observed discrepancy between the experiment and Wang's theory. We show that there is indeed an additional term in the viscosity kernel that remains finite when the specific volumes are equal.

Our approach is based on the Zwanzig–Mori[9,10] projection operator formalism. This formalism was implemented in 1970 by Akcasu and Daniels[11] to incorporate viscoelasticity in the linear hydrodynamic description of simple liquids by including the nonconserved part of the pressure tensor as one of the dynamical variables characterizing a macroscopic state of a liquid. The same formalism was used in 1972 by Desai[12] to extend the theory of light scattering from binary liquids as developed by Mountain and Deutch[13] in 1969. Desai's work implicitly included the linear viscoelasticity in binary fluid mixtures even though its emphasis was primarily on the analysis of Rayleigh–Brillouin scattering. In 1988 Hess and Akcasu[14] used a similar formalism to study the interdiffusion process in binary polymer mixtures by choosing the density and concentration fluctuations and their currents as state variables. In this paper, we implement the Zwanzig–Mori[9,10] formalism by using the same set of dynamical variables as in Desai's work but excluding the temperature fluctuations (isothermal limit), with the primary purpose of studying the effect of viscoelasticity on the light scattering from binary polymer mixtures. The present work is essentially an extension of the work by Hess and Akcasu[14] to incorporate a detailed description of viscoelasticity.

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Description of the Theory

We consider a mixture of two species (or components) A and B each consisting of n_α identical polymer chains with polymerization indices p_α, $\alpha = \mathrm{A,B}$. The total number of monomers or segments in each component is denoted by $N_\alpha = p_\alpha n_\alpha$. For the case of the polymer solution with one component to be a nonpolymeric molecular solvent, we set the solvent component to A with $p_\mathrm{A} = 1$ and $N_\mathrm{A} = n_\mathrm{A}$ and the polymer component to B. The fluctuations in the mass densities in the Fourier space are

$$\rho_\alpha(\mathbf{q},t) = \sum_{j=1}^{N_\alpha} m_\alpha\left[\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}_j^\alpha} - \frac{1}{V}\delta(\mathbf{k})\right] \tag{1}$$

where m_α and $\mathbf{r}_j^\alpha$ denote the mass and the position vector of the jth monomer belonging to the component α, respectively, V is the volume of the system, and $\delta(\mathbf{k})$ is the Kronecker delta. We construct a density vector as

$$\xi = \begin{bmatrix}\xi_+\\ \xi_-\end{bmatrix} \tag{2}$$

with elements

$$\xi_+ = \frac{1}{\rho_0}(\rho_\mathrm{A} + \rho_\mathrm{B}) \tag{3a}$$

$$\xi_- = \frac{\rho_\mathrm{A}}{\rho_\mathrm{A0}} - \frac{\rho_\mathrm{B}}{\rho_\mathrm{B0}} \tag{3b}$$

where $\rho_{\alpha0}$ are the equilibrium mass densities of the components, and $\rho_0 = \rho_\mathrm{A0} + \rho_\mathrm{B0}$ is the total mass density of the binary mixture. The variable $\xi_+(\mathbf{q},t)$ denotes the fluctuation in the total mass density, whereas $\xi_-(\mathbf{q},t)$ denotes the fluctuation in the concentration (or composition). The reason for transforming from partial mass densities ρ_A and ρ_B to the variables ξ_+ and ξ_- is that the latter represent respectively the sound mode and the interdiffusion mode, which relax on very different time scale. In contrast, the relaxation of the partial densities ρ_A and ρ_B involves both of these relaxation modes. The transformation in eq 3 can be written as $\boldsymbol{\xi} = \mathbf{R}\rho$ with $\rho = [\rho_\mathrm{A},\rho_\mathrm{B}]^\mathrm{T}$ and

$$\mathbf{R} = \begin{bmatrix}\dfrac{1}{\rho_\mathrm{o}} & \dfrac{1}{\rho_\mathrm{o}}\\[2mm] \dfrac{1}{\rho_\mathrm{Ao}} & -\dfrac{1}{\rho_\mathrm{Bo}}\end{bmatrix} \tag{4}$$

The longitudinal current density vector $\mathbf{J}(\mathbf{q},t)$ associated with the variables ξ_+ and ξ_- is defined by

$$\dot{\boldsymbol{\xi}} = ik\mathbf{J} \tag{5}$$

with components

$$J_+ = \frac{1}{\rho_0}(j_\mathrm{A} + j_\mathrm{B}) \tag{6a}$$

and

$$J_- = \frac{j_\mathrm{A}}{\rho_\mathrm{A0}} - \frac{j_\mathrm{B}}{\rho_\mathrm{B0}} \tag{6b}$$

In eq 6, $j_\alpha(\mathbf{q},t)$ denotes the longitudinal momentum densities of component α and is defined by $\dot\rho_\alpha = ikj_\alpha$. Explicitly,

$$j_\alpha = \sum_{j=1}^{N_\alpha}\hat{\mathbf{k}}\cdot\mathbf{p}_j^\alpha\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}_j^\alpha} \tag{7}$$

where $\hat{\mathbf{k}} = \mathbf{k}/k$, and $\mathbf{p}_j^\alpha = m_\alpha\mathbf{v}_j^\alpha$ is the momentum of the jth monomer of component α. Equation 6 can be written in a compact way as $\mathbf{J} = \mathbf{Rj}$ with $\mathbf{j} = [j_\mathrm{A},j_\mathrm{B}]^\mathrm{T}$.

We now implement the Zwanzig–Mori formalism with the set of dynamic variables $\mathbf{A} = [\xi_+,\xi_-,J_+,J_-]^\mathrm{T}$. The resulting Langevin equations for $\boldsymbol{\xi}(\mathbf{q},t)$ are the conservation relations already presented in eq 5. The Langevin equation for $\mathbf{J}(\mathbf{q},t)$ is obtained with the projection operator technique:

$$\dot{\boldsymbol{\xi}}(t) = ik\mathbf{J}(t) \tag{8a}$$

$$\dot{\mathbf{J}}(t) = ik\langle\mathbf{J}\mathbf{J}^\dagger\rangle\cdot\langle\boldsymbol{\xi}\boldsymbol{\xi}^\dagger\rangle\cdot\boldsymbol{\xi}(t) - \int_0^t \mathrm{d}u\ \varphi(t-u)\cdot\mathbf{J}(u) + \mathbf{F}(t) \tag{8b}$$

where the dots above $\boldsymbol{\xi}$ and $\mathbf{J}$ denote time derivatives, and the broken brackets imply equilibrium averages. The formal definitions of the random Langevin force $\mathbf{F}(t)$ and the memory matrix $\varphi(t)$ in terms of the modified propagator $\exp[t(1-\hat{P})iL]$ and projection operator $\hat{P}$, which is defined by its action on an arbitrary phase spacer vector $\mathbf{G}$ as $\hat{P}\cdot\mathbf{G} = \langle\mathbf{G}\mathbf{A}^\dagger\rangle\cdot\langle\mathbf{A}\mathbf{A}^\dagger\rangle^{-1}\cdot\mathbf{A}(0)$, are[10]

$$\mathbf{F}(t) = \mathrm{e}^{t(1-\hat{P})iL}(1-\hat{P})\dot{\mathbf{J}}(0) \tag{9}$$

$$\varphi(t) = \langle\mathrm{e}^{t(1-\hat{P})iL}(1-\hat{P})\dot{\mathbf{J}},\dot{\mathbf{J}}^\dagger\rangle\cdot\langle\mathbf{J}\mathbf{J}^\dagger\rangle^{-1} \tag{10}$$

The explicit calculation of the time evolution of $\varphi(t)$ in terms of the modified propagator is in general impossible. However, its initial value $\varphi(0)$ can be calculated explicitly by expressing it in terms of the equilibrium correlation functions given by:

$$\varphi(0) = \langle\dot{\mathbf{J}}\dot{\mathbf{J}}^\dagger\rangle\cdot\langle\mathbf{J}\mathbf{J}^\dagger\rangle^{-1} - k^2\langle\mathbf{J}\mathbf{J}^\dagger\rangle\cdot\langle\boldsymbol{\xi}\boldsymbol{\xi}^\dagger\rangle^{-1} \tag{11}$$

The equilibrium correlation functions can then in turn be expressed in terms of the interparticle potentials and the equilibrium distribution function.[11,12,14] Hence, in principle $\varphi(0)$ can be calculated once the interaction potentials are specified. It is therefore convenient to write $\varphi(t)$ as

$$\varphi(t) = \mathbf{L}(t)\ \varphi(0) \tag{12a}$$

with $\mathbf{L}(0) = \mathbf{I}$, where $\mathbf{I}$ is the identity matrix. The formal definition of the normalized memory function $\mathbf{L}(t)$ follows from eqs 10 and 12a as

$$\mathbf{L}(t) = \langle\mathrm{e}^{t(1-\hat{P})iL}(1-\hat{P})\dot{\mathbf{J}},\dot{\mathbf{J}}^\dagger\rangle\cdot\langle(1-\hat{P})\dot{\mathbf{J}},\dot{\mathbf{J}}^\dagger\rangle^{-1} \tag{12b}$$

More will be said about $\mathbf{L}(t)$ later.

In the study of interdiffusion processes, as discussed in ref 14, the small-k limit of $\varphi(k,0)$ plays an important role. This small-k limit is also crucial in the discussion of viscoelasticity as will be apparent below. Therefore, we study $\varphi(k\rightarrow0,0)$ using eq 11 in some detail. Since the second term in the latter is already proportional to k^2, we consider only the first term, which can be written as:

$$\varphi(k\rightarrow0,0) = \mathbf{R}\cdot\langle\dot{\mathbf{j}}\dot{\mathbf{j}}^\dagger\rangle\cdot\langle\mathbf{j}\mathbf{j}^\dagger\rangle^{-1}\cdot\mathbf{R}^\mathrm{T} \tag{13a}$$

where we have used $\mathbf{J} = \mathbf{Rj}$ and $\dot{\mathbf{J}} = \mathbf{R}\dot{\mathbf{j}}$. The matrix element $\langle j_\alpha j_\beta^*\rangle$ is calculated using eq 7 as $\langle j_\alpha j_\beta^*\rangle = VK_\mathrm{B}T\rho_{\alpha0}\delta_{\alpha\beta}$. The $\dot{j}_\alpha = \mathrm{d}j_\alpha/\mathrm{d}t$ is obtained from eq 7 as

$$\dot{j}_\alpha = \sum_{j=1}^{N_\alpha}\left[f_j^\alpha + ik\frac{1}{m_\alpha}p_j^\alpha p_j^\alpha\right]\mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}_j^\alpha} \tag{13b}$$

where $f_j^\alpha = \mathrm{d}p_j^\alpha/\mathrm{d}t$ denotes the longitudinal component of the force exerted on the jth monomer of the species α by all the other particles in both components. We see from eq 13b that in the small-k limit

$$\dot{j}_\alpha(k \to 0) = \sum_{j=1}^{N_\alpha} f_j^\alpha = F_\alpha \tag{13c}$$

where F_α is the total force along $\hat{\mathbf{k}}$ on the αth component. Since the sum of the internal forces of both components vanishes, we find

$$\dot{j}_\mathrm{A}(k \to 0) = F_\mathrm{AB}$$

$$\dot{j}_\mathrm{B}(k \to 0) = -F_\mathrm{AB} \tag{14}$$

where F_AB denotes the total force exerted on component A by all particles of component B. The expression of $\varphi(k \to 0,0)$ is obtained by substituting eq 14 into eq 13a and performing the indicated matrix multiplications. The result is presented as the first term in eq 17.

In order to obtain the expression of $\varphi(k,0)$ for finite k, we write $\dot{j}_\alpha$ when $k \neq 0$ as

$$\dot{j}_\mathrm{A} = F_\mathrm{AB} + ik\tilde{\pi}_\mathrm{A} \tag{15a}$$

$$\dot{j}_\mathrm{B} = -F_\mathrm{AB} + ik\tilde{\pi}_\mathrm{B} \tag{15b}$$

where the microscopic expressions of $\tilde{\pi}_\mathrm{A}$ and $\tilde{\pi}_\mathrm{B}$ are obtained from eq 13b as

$$\tilde{\pi}_\alpha = \sum_{j=1}^{N_\alpha} \left[f_j^\alpha \frac{1 - \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}_j^\alpha}}{ik} + \frac{1}{m_\alpha} p_j^\alpha p_j^\alpha \right] \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}_j^\alpha} \tag{16}$$

The physical implication of the separation in eq 15 is that the linear momentum for a given component alone is not conserved in a multicomponent mixture. It would therefore by misleading to express $\dot{j}_\alpha$ as $\dot{j}_\alpha = ik\pi_\alpha$, as was done in ref 12, which would imply $\dot{j}_\alpha(k \to 0) = 0$, in contrast to the result in eq 14. In the paper by Bearman–Kirkwood,[7] the separation in eq 15 is implemented approximately and somewhat inconsistently in the sense that part of $ik\tilde{\pi}_\mathrm{A}$ is included in F_AB.

We now substitute eq 15 into eq 11 and obtain, after some algebra,

$$\varphi(k,0) = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \frac{M}{m_\mathrm{A} m_\mathrm{B}} \zeta(0) + k^2 \eta(k,0) \tag{17}$$

where M is the total mass of all components in the system, i.e., $M = N_\mathrm{A} m_\mathrm{A} + N_\mathrm{B} m_\mathrm{B}$, and

$$\zeta(0) = \frac{1}{K_\mathrm{B} T} \frac{1}{N_\mathrm{A} N_\mathrm{B}} \langle F_\mathrm{AB} F_\mathrm{AB} \rangle \tag{18}$$

which denotes the initial value of the force–force correlation function, normalized to a pair of A and B particles. The expression of $\eta(k,0)$ in eq 17 is found as

$$\eta(k,0) = \langle \boldsymbol{\pi}\boldsymbol{\pi}^\dagger \rangle \cdot \langle \mathbf{J}\mathbf{J}^\dagger \rangle^{-1} - \langle \mathbf{J}\mathbf{J}^\dagger \rangle \cdot \langle \boldsymbol{\xi}\boldsymbol{\xi}^\dagger \rangle^{-1} + \frac{1}{ik\mu_0} [\mathbf{e} \langle F_\mathrm{AB} \boldsymbol{\pi}^\dagger \rangle - \langle \boldsymbol{\pi} F_\mathrm{AB}^* \rangle \mathbf{e}^\mathrm{T}] \cdot \langle \mathbf{J}\mathbf{J}^\dagger \rangle^{-1} \tag{19}$$

where we have introduced

$$\pi^\mathrm{T} = [\pi_+, \pi_-] \tag{20a}$$

with

$$\pi_+ = \frac{1}{\rho_0} [\tilde{\pi}_\mathrm{A} + \tilde{\pi}_\mathrm{B}] \tag{20b}$$

$$\pi_- = \frac{1}{\rho_\mathrm{A0}} \tilde{\pi}_\mathrm{A} - \frac{1}{\rho_\mathrm{B0}} \tilde{\pi}_\mathrm{B} \tag{20c}$$

$\tilde{\pi}_\mathrm{A}$ and $\tilde{\pi}_\mathrm{B}$ are the longitudinal partial pressure tensors, whereas π_+ and π_- can be interpreted as the longitudinal total pressure tensor and longitudinal diffusion pressure tensor, respectively. If one introduces $\tilde{\pi} = \mathrm{column}[\tilde{\pi}_\mathrm{A}, \tilde{\pi}_\mathrm{B}]$, then eq 20 can be compressed as

$$\pi = \mathbf{R}\tilde{\pi} \tag{21}$$

In the last term of eq 19, we have also introduced $\mathbf{e} = [0,1]^\mathrm{T}$ and

$$\frac{1}{\mu_0} = \frac{1}{\rho_\mathrm{A0}} + \frac{1}{\rho_\mathrm{B0}} \tag{22}$$

One can show that the limit of $\eta(k,0)$ as $k \to 0$ is finite even though ik appears in the denominator in eq 19.

With the above definitions, the Langevin equations (8) read as

$$\dot{\boldsymbol{\xi}}(t) = ik\mathbf{J}(t) \tag{23a}$$

$$\dot{\mathbf{J}}(t) = ik \langle \mathbf{J}\mathbf{J}^\dagger \rangle \cdot \langle \boldsymbol{\xi}\boldsymbol{\xi}^\dagger \rangle \cdot \boldsymbol{\xi}(t) - \int_0^t \mathrm{d}u \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \frac{M}{m_\mathrm{A} m_\mathrm{B}} \zeta(t-u) \cdot \mathbf{J}(u) - k^2 \int_0^t \mathrm{d}u\, \eta(t-u) \cdot \mathbf{J}(u) + \mathbf{F}(t) \tag{23b}$$

According to eq 12a, the time dependence $\eta(k,t)$ is given by

$$\eta(k,t) = \mathbf{L}(t)\, \eta(k,0) \tag{24}$$

where the time evolution of $\mathbf{L}(t)$ is governed by the modified propagator given in eq 12b, and $\zeta(t)$ is expressed as

$$\zeta(t) = \frac{1}{K_\mathrm{B} T} \frac{1}{N_\mathrm{A} N_\mathrm{B}} \langle \mathrm{e}^{t(1-\hat{P})iL} F_\mathrm{AB}(0), F_\mathrm{AB}(0) \rangle \tag{25}$$

which can be demonstrated by substituting the small-k limit of $\dot{\mathbf{J}}(\mathbf{k},0)$ directly into eq 10. The time evolution of $\eta(k,t)$ can also be expressed explicitly in terms of the modified propagator. However, the expression in eq 24 lends itself better to approximations as the following discussions will indicate.

In eq 23 all the equilibrium averages are either calculable directly, e.g., $\langle \mathbf{J}\mathbf{J} \rangle$, or expressible in terms of thermodynamic derivatives in the limit $k \to 0$.[11,12] Only $\mathbf{L}(k,t)$ cannot be calculated explicitly because its time evolution is governed by the modified propagator. An implementation of the memory function formalism with the extended set of dynamical variables that includes also the time derivatives of the nonconserved parts of the pressure tensor (see Appendix A) shows that the Laplace transform of $\mathbf{L}(t)$ can be expressed as

$$\tilde{\mathbf{L}}(s) = [s\mathbf{I} + \tilde{\boldsymbol{\Phi}}(s)]^{-1} \tag{26}$$

where $\tilde{\boldsymbol{\Phi}}(k,s)$ denotes the 2×2 memory matrix in the above extended description. In the Markov limit, which corresponds to replacing $\tilde{\boldsymbol{\Phi}}(k,s)$ by $\tilde{\boldsymbol{\Phi}}(k,0)$, $\mathbf{L}(t)$ can be written as

$$\mathbf{L}(t) = \mathrm{e}^{-t\mathbf{W}} \tag{27}$$

where $\mathbf{W}(k) = \tilde{\boldsymbol{\Phi}}(k,0)$. In this limit, only the relaxation matrix $\mathbf{W}$ has to be modeled. The eigenvalues of $\mathbf{W}$ yield the relaxation frequencies of the viscoelastic modes.

We can eliminate $\mathbf{J}(t)$ in eq 23 to obtain an equation for $\boldsymbol{\xi}(t)$:

$$\ddot{\boldsymbol{\xi}}(t) = -k^2\langle \mathbf{J}\mathbf{J}^\dagger\rangle\cdot\langle \boldsymbol{\xi}\boldsymbol{\xi}^\dagger\rangle^{-1}\cdot\boldsymbol{\xi}(t) - \int_0^t \mathrm{d}u \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \frac{M}{m_\mathrm{A}m_\mathrm{B}}\zeta(t-u)\cdot\dot{\boldsymbol{\xi}}(u) - k^2\int_0^t \mathrm{d}u\ \eta(t-u)\cdot\dot{\boldsymbol{\xi}}(u) + ik\mathbf{F}(t) \quad (28)$$

This equation was previously obtained by Hess and Akcasu[14] with a slightly different normalization in their study of the interdiffusion process in polymer mixtures by neglecting the second integral term which accounts for the viscoelastic effects. In this paper, we focus our attention on the effect of viscoelasticity on dynamic light scattering and the retention of this term is very important.

By multiplying eq 28 by $\boldsymbol{\xi}^\dagger(0)$ and taking the equilibrium average, we obtain an equation for the dynamic scattering matrix $\mathbf{S}(k,t) = \langle\boldsymbol{\xi}(t)\ \boldsymbol{\xi}^\dagger(0)\rangle$. The contribution of the random Langevin force, $\langle \mathbf{F}(t)\ \boldsymbol{\xi}^\dagger(0)\rangle$, vanishes exactly by virtue of $(1 - \mathrm{P})\boldsymbol{\xi}^\dagger(0) = 0$ (cf. eq 9). The resulting equation reads

$$\ddot{\mathbf{S}}(t) = -\mathrm{k}^2\langle \mathbf{J}\mathbf{J}^\dagger\rangle\cdot\langle \boldsymbol{\xi}\boldsymbol{\xi}^\dagger\rangle\cdot\mathbf{S}(t) - \int_0^t \mathrm{d}u \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} \frac{M}{m_\mathrm{A}m_\mathrm{B}}\zeta(t-u)\cdot\dot{\mathbf{S}}(u) - k^2\int_0^t \mathrm{d}u\ \eta(t-u)\cdot\dot{\mathbf{S}}(u) \quad (29)$$

which can be solved for $\mathbf{S}(k,t)$ with the Laplace transform technique. Although this equation is exact, it does not display explicitly the coupling between the density and concentration fluctuations. Therefore, we explicitly investigate in the following section the equations for the components $\xi_+(t)$ and $\xi_-(t)$ and introduce approximations appropriate to light scattering experiments. We also compare our results with those by Wang.[5,6]

Connection with Wang's Work

We start by writing eq 28 in component form. Verifying first that $\langle \mathrm{J}_+\mathrm{J}_+^*\rangle = k_\mathrm{B}TV/\rho_0$, $\langle J_-J_-^*\rangle = k_\mathrm{B}TV/\mu_0$ and $\langle \mathrm{J}_+\mathrm{J}_-^*\rangle = 0$, we find

$$\ddot{\xi}_+(t) = -k^2\frac{k_\mathrm{B}T}{\rho_0}V\frac{\langle\xi_-\xi_-^*\rangle}{\Delta}\left[\xi_+(t) - \frac{\langle\xi_+\xi_-^*\rangle}{\langle\xi_-\xi_-^*\rangle}\xi_-(t)\right] - k^2\int_0^t \mathrm{d}u\ [\eta_{++}(t-u)\ \dot{\xi}_+(u) + \eta_{+\,-}(t-u)\ \dot{\xi}_-(u)] + F_+(t) \quad (30a)$$

$$\ddot{\xi}_-(t) = -k^2\frac{k_\mathrm{B}T}{\mu_0}\frac{V}{\Delta}[\langle\xi_+\xi_+^*\rangle\xi_-(t) - \langle\xi_-\xi_+^*\rangle\xi_+(t)] - \frac{M}{m_\mathrm{A}m_\mathrm{B}}\int_0^t \mathrm{d}u\ \zeta(t-u)\ \dot{\xi}_-(u) - k^2\int_0^t \mathrm{d}u\ [\eta_{-\,+}(t-u)\ \dot{\xi}_+(u) + \eta_{-\,-}(t-u)\ \dot{\xi}_-(u)] + F_-(t) \quad (30b)$$

where

$$\Delta = \langle\xi_-\xi_-^*\rangle\langle\xi_+\xi_+^*\rangle - |\langle\xi_+\xi_-^*\rangle|^2 \quad (31)$$

We note that the friction term $\zeta(t)$ appears only in eq 30b, which describes an interdiffusion process including viscoelastic effects.

The next task is to identify the equilibrium averages $\langle\xi_\alpha\xi_\beta^*\rangle$ in terms of thermodynamic quantities appearing in the macroscopic hydrodynamic theory. To this end, we introduce the following linear transformation from ξ_+ and ξ_- to ξ and ξ_1:

$$\xi = \xi_+ - \frac{\langle\xi_+\xi_-^*\rangle}{\langle\xi_-\xi_-^*\rangle}\xi_- \quad (32a)$$

$$\xi_1 = \xi_- \quad (32b)$$

The reason for this transformation is that the variables ξ and ξ_1 were used by Desai[12] in his description of binary fluid mixtures, and their static correlations were related to thermodynamic quantities. The variables ξ and ξ_1 are orthogonal to each other in the sense that $\langle\xi_1\xi^*\rangle = 0$. The variable ξ can be expressed directly in terms of the mass densities ρ_A and ρ_B:

$$\xi = \bar{v}_\mathrm{A}\rho_\mathrm{A} + \xi v_\mathrm{B}\rho_\mathrm{B} \quad (33)$$

where $\bar{v}_\mathrm{A}$ and $\bar{v}_\mathrm{B}$ are the partial specific volumes of components A and B, respectively. They are given by Desai[12] as

$$\bar{v}_\mathrm{A} = -\frac{\langle\rho_\mathrm{B}\xi_-^*\rangle}{\langle\xi_-\xi_-^*\rangle}\frac{1}{\rho_\mathrm{A0}\rho_\mathrm{B0}} \quad (34a)$$

$$\bar{v}_\mathrm{B} = \frac{\langle\rho_\mathrm{A}\xi_-^*\rangle}{\langle\xi_-\xi_-^*\rangle}\frac{1}{\rho_\mathrm{A0}\rho_\mathrm{B0}} \quad (34b)$$

$$\bar{v}_\mathrm{BA} = \bar{v}_\mathrm{B} - \bar{v}_\mathrm{A} = \frac{1}{\mu_0}\frac{\langle\xi_+\xi_-^*\rangle}{\langle\xi_-\xi_-^*\rangle} \quad (34c)$$

In the limit of $k \to 0$, $\bar{v}_\mathrm{A}$, $\bar{v}_\mathrm{B}$, and $\bar{v}_\mathrm{AB}$ are expressed in terms of thermodynamic derivatives of chemical potentials. Desai[12] also showed that in the limit of $k \to 0$

$$\frac{1}{V}\langle\xi\xi^*\rangle = k_\mathrm{B}T\chi_\mathrm{T} \quad (35a)$$

$$\frac{1}{V}\langle\xi_-\xi_-^*\rangle = \frac{k_\mathrm{B}T}{\mu_0^2}\left[\frac{1}{\rho_0}\left(\frac{\partial\mu}{\partial c}\right)_{P,T}\right]^{-1} \quad (35b)$$

where χ_T is the isothermal compressibility. The remaining task is to identify Δ and $\langle\xi_+\xi_+^*\rangle/\Delta$ in eq 30 in terms of $\langle\xi\xi^*\rangle$ and $\langle\xi_-\xi_-^*\rangle$ which have already been identified above. This can be done conveniently by writing the transformation in eq 32 in matrix form as $\boldsymbol{\xi}' = \mathbf{Z}\boldsymbol{\xi}$ where $\xi' = \mathrm{column}[\xi,\xi_1]$,

$$\mathbf{Z} = \begin{bmatrix} 1 & \mu_\mathrm{o}\bar{v}_\mathrm{AB} \\ 0 & 1 \end{bmatrix} \quad (36)$$

and, as before, $\xi = \mathrm{column}[\xi_+,\xi_-]$. Then

$$\langle\boldsymbol{\xi}'\boldsymbol{\xi}'^\dagger\rangle = \mathbf{Z}\{\boldsymbol{\xi}\boldsymbol{\xi}^\dagger\rangle\mathbf{Z}^\mathrm{T} \quad (37)$$

Since $|\mathbf{Z}| = 1$, from eq 31 we find $\Delta = |\langle\boldsymbol{\xi}\boldsymbol{\xi}^\dagger\rangle|$ or

$$\Delta = \langle\xi\xi^\dagger\rangle\langle\xi_-\xi_-^{\ \dagger}\rangle \quad (38)$$

This result leads to the following identification in eq 30a:

$$\frac{k_\mathrm{B}T}{\rho_0}\frac{\langle\xi_-\xi_-^*\rangle}{\Delta/V} = \frac{1}{\rho_0\chi_\mathrm{T}} = C_\mathrm{L}^{\ 2} \quad (39)$$

where C_L is the longitudinal isothermal speed of sound.

The identification of $\langle\xi_+\xi_+^*\rangle/\Delta$ appearing in eq 30b is made by first writing eq 37 as

$$\langle\boldsymbol{\xi}\boldsymbol{\xi}^\dagger\rangle^{-1} = \mathbf{Z}^\mathrm{T}\langle\boldsymbol{\xi}'\boldsymbol{\xi}'^\dagger\rangle^{-1}\mathbf{Z}$$

and then calculating the 2–2 element of both sides. The result is

$$\frac{\langle \xi_+\xi_+^* \rangle}{\Delta} = \frac{{\mu_0}^2 {\bar{v}_{AB}}^2}{\langle \xi\xi^* \rangle} + \frac{1}{\langle \xi_-\xi_-^* \rangle} \tag{40}$$

where $\langle \xi\xi^* \rangle$ and $\langle \xi_-\xi_-^* \rangle$ have already been identified in eq 35.

In order to display the connection between the above microscopic theory and Wang's macroscopic approach written in terms of the total mass density $\rho = \rho_A + \rho_B$ and the mass density of the polymer component, ρ_B, we now express eq 30, written for ξ_+ and ξ_-, in terms of $\rho(t)$ and $\rho_B(t)$. Noting that $\rho(t) = \rho_0\xi_+(t)$ and

$$\rho_B(t) = \mu_0\left[\frac{\rho_0}{\rho_{A0}}\xi_+(t) - \xi_-(t)\right] \tag{41}$$

which follows from the definition of ξ_- in eq 3b, we find for the mean of $\rho(t)$

$$\ddot{\rho}(t) = -k^2{C_L}^2[\rho_0\bar{v}_A\rho(t) + \rho_0\bar{v}_{AB}\rho_B(t)] - \rho_0 k^2\sigma_+(t) \tag{42}$$

where $\sigma_+(t)$ denotes the memory term in eq 30a expressed in terms of $\rho(t)$ and $\rho_B(t)$, i.e.,

$$\sigma_+(t) = \int_0^t \mathrm{d}u \left\{\left[\frac{1}{\rho_0}\eta_{+\,+}(t-u) + \frac{1}{\rho_{A0}}\eta_{+\,-}(t-u)\right]\dot{\rho}(u) - \frac{1}{\mu_0}\eta_{+\,-}(t-u)\dot{\rho}_B(u)\right\} \tag{43}$$

We note that eq 42 is exact except for the neglect of the average of the random force, which implies linearization. It differs from the corresponding equation derived by Wang (eq 10 in ref 5) in two respects: The first term in eq 42 corresponds to the total pressure P owing to the fact that

$$\nabla P = {C_L}^2\rho_0\bar{v}_A\nabla\rho + \left(\frac{\partial P}{\partial \rho_B}\right)_{T,\rho}\nabla\rho_B \tag{44}$$

The factor $\rho_0\bar{v}_A$ in the first term of eq 44 is not present in eq 9 of ref 5. The second discrepancy between eq 42 and the corresponding eq 10 of ref 5 lies in the way the effect of the viscoelastic modes on the total density fluctuation is taken into account. This effect is represented in eq 42 by $\sigma_+(t)$ and by the second term on the right-hand side of eq 10 of ref 5. Whereas the latter involves only the derivative of the total density $\dot{\rho}(t)$, $\sigma_+(t)$ in eq 42 contains also a contribution from $\dot{\rho}_B(t)$ through the kernel $\eta_{+\,-}(t)$.

The equation satisfied by $\rho_B(t)$ can be obtained by differentiating eq 41 with respect to time twice and using eq 30. We shall present the result in the isobaric limit only, which is reached after the total pressure equilibrates in time scales shorter than the relaxation times of the concentration and viscoelastic modes. In this limit, we first solve eq 30a for $\xi_+(t)$, treating $\xi_-(t)$ as stationary, and obtain its asymptotic form as

$$\xi_+(t) \rightarrow \frac{\langle \xi_+\xi_-^* \rangle}{\langle \xi_-\xi_-^* \rangle}\xi_-(t) \tag{45}$$

We then solve eq 30b for $\xi_-(t)$ by eliminating $\xi_+(t)$ using its asymptotic value in eq 45. This procedure corresponds to the adiabatic elimination of a fast variable.

The relaxation of $\xi_+(t)$ to its asymptotic value is described by eq 30a with $\dot{\xi}_-(t) = 0$:

$$\ddot{\xi}_+(t) + k^2\tilde{\eta}_{+\,+}(0)\dot{\xi}_+(t) + k^2{C_L}^2\xi_+(t) = k^2{C_L}^2\mu_0\bar{v}_{AB}\xi_-(t) \tag{46}$$

where $\tilde{\eta}_{+\,+}(s)$ denotes the Laplace transform of $\eta_{+\,+}(t)$. In obtaining eq 46 from eq 30a, we assumed that $\eta_{+\,+}(t)$ decays faster than $\dot{\xi}_+(t)$. This simplification facilitates the interpretation of eq 46 as an equation that describes sound waves in a viscous medium. When the oscillations are underdamped, its solution reads

$$\xi_+(t) = \mu_0\bar{v}_{AB}\xi_-(t) + C_1\mathrm{e}^{-\gamma t}\cos(\omega t + \theta) \tag{47a}$$

where C_1 and θ are constants of integration, and

$$\gamma = \frac{1}{2}k^2\tilde{\eta}_{+\,+}(0)$$

$$\omega = kC_L\left(1 - \frac{\gamma^2}{k^2{C_L}^2}\right)^{1/2}$$

Equation 47a shows that $\tilde{\eta}_{+\,+}(0)$ is responsible for the damping of the sound waves in the mixture. When the oscillations are overdamped, the relaxation of $\xi_+(t)$ is described by

$$\xi_+(t) = \mu_0\bar{v}_{AB}\xi_-(t) + C_1\mathrm{e}^{-\gamma t} \tag{47b}$$

with $\gamma \approx {C_L}^2/\tilde{\eta}_{+\,+}(0)$.

The relationship between $\xi_+(t)$ and $\xi_-(t)$ in eq 45, which will be used to eliminate $\xi_+(t)$ in solving eq 30b for $\xi_-(t)$, is equivalent to assuming that the pressure gradient is zero at all times, i.e., the isobaric limit. Equation 45 can also be expressed in terms of the other variables as

$$\bar{v}_A\rho_A(t) + \bar{v}_B\rho_B(t) = 0 \tag{48a}$$

$$\rho(t) = \frac{\bar{v}_B}{\bar{v}_A}\rho_B(t) \tag{48b}$$

Since $\bar{v}_A\rho_A(t)$ and $\bar{v}_B\rho_B(t)$ denote the fluctuations in the volume fractions of the components, eq 48a is a statement of local incompressibility. It also implies $\xi_+(t) = (\bar{v}_{AB}/\rho_0\bar{v}_A)\rho_B(t)$ when eq 48b is used in $\xi_+(t) = \rho(t)/\rho_0$ and $\xi_-(t) = \rho_B(t)/\rho_{A0}\rho_{B0}\bar{v}_A$ when eq 48a is substituted in eq 3b. Thus, in the isobaric limit, both $\xi_+(t)$ and $\xi_-(t)$ are proportional either to $\rho_B(t)$ or to $\rho_A(t)$.

The time evolution of the mean of $\xi_-(t)$ in the isobaric limit is obtained from eq 30b by eliminating $\xi_+(t)$ using eq 45 as

$$\ddot{\xi}_-(t) = -k^2\frac{k_BT}{\mu_0}\frac{V}{\langle \xi_-\xi_-^* \rangle}\xi_-(t) - \frac{M}{m_Am_B}\tilde{\zeta}(0)\,\dot{\xi}_-(t) - k^2\int_0^t \mathrm{d}u\,\eta(t-u)\,\dot{\xi}_-(u) \tag{49}$$

where we have introduced

$$\eta(t) = \frac{\langle \xi_+\xi_-^* \rangle}{\langle \xi_-\xi_-^* \rangle}\eta_{-\,+}(t) + \eta_{-\,-}(t) \tag{50a}$$

which can also be written in terms of the thermodynamic quantities using the identifications made in eq 34 as

$$\eta(t) = \mu_0\bar{v}_{BA}\eta_{-\,+}(t) + \eta_{-\,-}(t) \tag{50b}$$

In obtaining eq 49 we used the Markov limit of the friction term and introduced $\tilde{\zeta}(0)$, where $\tilde{\zeta}(s)$ is the Laplace transform of $\zeta(t)$. In Appendix B we present the details of the Markov limit to show why it affects only the friction term. Since $\xi_{-}(t)$ is proportional to $\rho_{\mathrm{B}}(t)$, eq 49 leads to

$$\ddot{\rho}_{\mathrm{B}}(t) = -k^2\frac{\mu_0}{\rho_0}\left(\frac{\partial\mu}{\partial c}\right)_{T,\rho}\rho_{\mathrm{B}}(t) - \frac{M}{m_{\mathrm{A}}m_{\mathrm{B}}}\tilde{\zeta}(0)\,\dot{\rho}_{\mathrm{B}}(t) - k^2\int_0^t \mathrm{d}u\;\eta(t-u)\,\dot{\rho}_{\mathrm{B}}(u) \qquad (51)$$

This equation has exactly the same form as eq 26 in ref 5, which is written for the density of the polymer component in the binary mixture. There is however an important difference in the terms representing the viscoelastic effects, i.e., the last term in eq 51. The second term $\eta_{--}(t)$ in the expression of the viscosity kernel $\eta(t)$ in eq 50b is not present in Wang's work. Since the latter contains only the first term, which is proportional to $\bar{v}_{\mathrm{A}} - \bar{v}_{\mathrm{B}}$, it predicts the viscoelastic effects to vanish when $\bar{v}_{\mathrm{A}} = \bar{v}_{\mathrm{B}}$ (when the factor $\beta = 0$ in Wang's notation). Hence, the effect of viscoelasticity on the QEL spectrum observed by Brown and Stepanek[8] in semidilute polymer solutions in poor solvents can be attributed to this additional term. The conclusion that $\eta(t)$ does not vanish when $\bar{v}_{\mathrm{A}} = \bar{v}_{\mathrm{A}}$ is one of the main contributions of this paper.

Time Dependence of $\eta(t)$

In this section we discuss the time dependence of $\eta(t)$ in eq 51. The time dependence of the viscosity tensor $\eta(t)$ is given in the Markov limit by eqs 24b and 27 as

$$\eta(t) = \mathrm{e}^{-\mathbf{W}t}\eta(0) \qquad (52\mathrm{a})$$

where the microscopic expression of $\eta(0)$ was given in eq 19. We expand $\exp[-\mathbf{W}t]$ as

$$\mathrm{e}^{-\mathbf{W}t} = \mathrm{e}^{-\lambda_1 t}\mathbf{E}_1 + \mathrm{e}^{-\lambda_2 t}\mathbf{E}_2 \qquad (52\mathrm{b})$$

where λ_1 and λ_2 are the eigenvalues of the 2 × 2 relaxation frequency matrix $\mathbf{W}$, and $\mathbf{E}_1$ and $\mathbf{E}_2$ are the idempotent matrices with the property $\mathbf{E}_i\mathbf{E}_j = \mathbf{E}_i\delta_{ij}$. $\mathbf{E}_1$ and $\mathbf{E}_2$ can be expressed in terms of the right and left eigenvectors of $\mathbf{W}$,[15] but these expressions will not be needed in the following derivations. Using eq 52, one can show after some algebra that

$$\eta_{-+}(t) = \mathrm{e}^{-\lambda_1 t}a_{-+} + \mathrm{e}^{-\lambda_2 t}b_{-+}$$

$$\eta_{--}(t) = \mathrm{e}^{-\lambda_1 t}\mathrm{a}_{--} + \mathrm{e}^{-\lambda_2 t}\mathrm{b}_{--}$$

where a_{ij}; $= [\mathbf{E}_1\eta(0)]_{ij}$ and $b_{ij} = [\mathbf{E}_2\eta(0)]_{ij}$. Substitution of these results into eq 50b yields

$$\eta(t) = [\mu_0\bar{v}_{\mathrm{BA}}a_{-+} + a_{--}]\mathrm{e}^{-\lambda_1 t} + [\mu_0\bar{v}_{\mathrm{BA}}b_{-+} + b_{--}]\mathrm{e}^{-\lambda_2 t} \qquad (53)$$

Since the relaxation matrix $\mathbf{W}(k) = \tilde{\mathbf{\Phi}}(k,0)$, wher $\tilde{\mathbf{\Phi}}(k,s)$ is the Laplace transform of the memory matrix in the six-component description (see Appendix A), its eigenvalues and eigenvectors cannot be calculated explicitly. Hence, both λ_1 and λ_2, as well as a_{ij} and b_{ij} have to be modeled, even though the elements of $\eta(0)$ can be calculated at least in principle in terms of the equilibrium correlation functions.[11,12] Therefore, eq 53 is presented only to display the structure of the time dependence of $\eta(t)$. The fact that the relaxation of the latter is described by two exponentials is a consequence of the use of the Markov approximation in the six-component description. The representation of the exact time dependence of $\eta(t)$ requires an infinite set of exponential functions, or nonexponential functions, e.g., stretched exponentials. One of the consequences of eq 53 is that $\eta(t)$ decays with two relaxation frequencies even in the case of $\bar{v}_{\mathrm{A}} = \bar{v}_{\mathrm{B}}$. In the interpretion of light scattering experiments a single-exponential representation $\eta(t)$ may be sufficient to analyze the data in concentrated homopolymer solutions.[16]

Calculation of $S(k,t)$

The dynamic scattering function $S(k,t) = \langle\rho_{\mathrm{B}}(\mathbf{k},t)\,\rho_{\mathrm{B}}(-\mathbf{k},0)\rangle$ is obtained from eq 51 by taking its Laplace transform with the initial conditions $S(k) = \langle|\rho_{\mathrm{B}}(\mathbf{k})\rangle|^2\rangle$ and $\langle\dot{\rho}_{\mathrm{B}}(\mathbf{k},0)\,\rho_{\mathrm{B}}(-\mathbf{k},0)\rangle = 0$ as

$$\tilde{S}(k,s) = \frac{f(s)}{\Delta(s)}S(k) \qquad (54)$$

with

$$f(s) = s + f + k^2\tilde{\eta}(s)$$

$$\Delta(s) = sf(s) + k^2E_{\mathrm{os}}$$

$$E_{\mathrm{os}} = (\mu_0/\rho_0)/(\partial\mu/\partial c)_{T,\rho}$$

$$f = (M/m_{\mathrm{A}}m_{\mathrm{B}})\tilde{\zeta}(0)$$

where E_{os} and f denote the osmotic modulus and friction coefficient, respectively, as introduced by Brochard and de Gennes.[1,3] When $\eta(t)$ is represented by a sum of exponentials as in eq 53, $S(k,t)$ is also expressed as a sum of exponentials:

$$S(k,t) = S(k)\sum_j R_j\mathrm{e}^{-\Gamma_j t} \qquad (55)$$

where $-\Gamma_j$ are the poles of $\tilde{S}(k,s)$, i.e., the roots of the denominator in eq 54 so that $\Delta(-\Gamma_j) = 0$, and R_j are the residues of $\tilde{S}(k,s)$ at these poles which we assume to be simple. The R_j are calculated as

$$R_j = f(-\Gamma_j)/\Delta'(-\Gamma_j)$$

where $\Delta'(s) = \mathrm{d}\Delta(s)/\mathrm{d}s$ provided $f(s)$ is analytic at $s = -\Gamma_j$. Because of the normalization of $S(k,t)$ in eq 55, $\sum_j R_j = 1$. There are four terms in eq 55 when $\eta(t)$ is represented by two exponentials as the six-component description implies in Markov limit. When the second-order time derivative of $\rho_{\mathrm{B}}(t)$ in eq 51 is neglected in the small frequency limit $\omega \ll f$, which is consistent with the Markov limit (see Appendix B), there remains only three exponentials in eq 55, $f(s)$ reduces to $f(s) = f + k^2\tilde{\eta}(s)$, and $\Delta(s)$ becomes a third-order polynomial in s. It is interesting to point out that, in this limit, the first cumulant of $S(k,t)$ can be calculated from eq 54 by using the final value theorem, which states $\lim_{t\to 0} h(t) = \lim_{s\to\infty}\tilde{h}(s)$ where $\tilde{h}(s)$ is the Laplace transform of $h(t)$, provided both limits exist. Using the definition of the first cumulant as $\Omega = -\lim_{t\to 0}\mathrm{d}\ln S(k,t)/\mathrm{d}t$ and the final value theorem, we find

$$\Omega(k) = -\lim_{s\to\infty}\left[s^2\frac{f(s)}{\Delta(s)} - s\right] \qquad (56)$$

which yields $\Omega(k) = k^2D_{\mathrm{c}}$ where $D_{\mathrm{c}} = E_{\mathrm{os}}/f$, the collective diffusion coefficient. This is an interesting result because it implies that the first cumulant is not affected by the viscoelasticity. If we had retained the second-order time derivative of $\rho_{\mathrm{B}}(t)$ in eq 51, the initial slope of $S(k,t)$ would be zero, as one can verify by using eq 55.

In the earlier models of viscoelasticity reviewed in ref 1, $\eta(t)$ is represented by a single exponential as

$$\eta(t) = E_g e^{-t/T_r}$$

where E_g is the longitudinal bulk modulus, and the relaxation time T_r is taken to be the characteristic lifetime of the entanglements in the transient network.[1,3] In this case, $\Delta(s)$ is quadratic in s, and $S(k,t)$ is represented by a bimodal distribution with relaxation frequencies Γ_1 and Γ_2, which satisfy $\Gamma_1\Gamma_2 = k^2D_c/T_r$ and $\Gamma_1 + \Gamma_2 = T_r^{-1} + k^2D_g$, where $D_g = (E_{os} + E_g)/f$, pseudo gel diffusion coefficient.[1,3] The amplitudes of the modes R_1 and $R_2 = 1 - R_1$ in this case can be obtained explicitly using $R_1 + R_2 = 1$ and $\Gamma_1R_1 + \Gamma_2R_2 = \Omega(k)$ as

$$R_1 = \frac{\Omega(k) - \Gamma_2}{\Gamma_1 - \Gamma_2} \tag{57}$$

In the absence of viscoelasticity, i.e., when $E_g = 0$, $D_c = D_g$, $\Gamma_1 = k^2D_c = \Omega(k)$, which represents the collective diffusion, and $\Gamma_2 = T_r^{-1}$. The amplitude, R_2, of the mode corresponding to Γ_2 is zero in this case, and there is only one exponential term in the spectrum of the scattered light, because $R_1 = 1$ according to eq 57. When the coupling between the collective diffusion and viscoelastic mode is taken into account, i.e., $E_g \neq 0$, the relaxation frequencies can be approximated as $\Gamma_1 \approx k^2D_g$ and $\Gamma_2 \approx T_r^{-1}(D_c/D_g)$, provided $k^2D_g \gg T_r^{-1}$. As is observed experimentally, the relaxation frequency Γ_2 of the slow mode is independent of k. The coupling to the viscoelastic mode alters the diffusion coefficient D_g of the fast diffusive mode. Since $D_g > D_c$, the collective diffusion is enhanced in the presence of viscoelasticity. The bimodal representation of the light scattering was used earlier by Adam and Delsanti[16] to interpret the scattering data. The general properties of the relaxation frequencies when $\eta(t)$ is represented by more than two exponentials have been studied recently by Genz.[17]

Concluding Remarks

We have developed a microscopic theory of viscoelasticity for a mixture of two species. The theory is general and applicable to binary polymer blends, binary mixtures of nonpolymeric fluids, and a solution of homopolymers in a solvent of small molecules. We have demonstrated that, in the small k (wavenumber) limit, the microscopic theory reproduces the hydrodynamic description of binary mixtures with microscopic expressions for the various thermodynamic quantities, such as the isothermal compressibility, specific volumes, etc., and have compared the resulting hydrodynamic equations with those used by Wang.[5] We have found that, in the viscosity kernel $\eta(t)$, which describes the coupling between the viscoelastic modes and the concentration fluctuation, there is an additional term which is not present in Wang's theory. This term does not vanish when the specific volumes of the components $\bar{v}_A$ and $\bar{v}_B$ are matched. Thus, the effect of viscoelasticity experimentally observed by Brown and Stepanek[8] under the experimental condition of $\bar{v}_A = \bar{v}_B$ cannot be ruled out a priori. Although one may be able to interpret light scattering experiments under various experimental conditions using the present theory and by properly modeling the viscosity kernel $\eta(t)$, the theory still does not explicitly display the effect of the solvent quality, the molecular weight, and entanglement of the chains on the viscoelastic modes. This detailed information is implicit in the formal expressions of $\eta(t)$ and the other thermodynamic quantities in the theory, and its extraction from these definitions requires a detailed study of interactions between the monomer and monomer–solvent and solvent–solvent molecules. Such a study is considered to be outside of the scope of this paper.

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Appendix A. Six-Component Description

In this appendix we compare the four- and six-component descriptions to justify eq 26 in the text. The dynamical variables in the extended six-component description of a binary mixture are chosen as $\mathbf{A} = [\xi,\mathbf{J},\sigma]^T$, where ξ and $\mathbf{J}$ were defined in eqs 2–5 in the text. The additional variable σ is defined through

$$\dot{\mathbf{J}}(t) = \langle \dot{\mathbf{J}}\xi^\dagger\rangle \cdot \langle \xi\xi^\dagger\rangle^{-1} \cdot \xi(t) + \sigma(t) \tag{A1}$$

It is clear from its definition in eq A1 that σ is orthogonal to ξ, i.e., $\langle \sigma(0)\ \xi^*(0)\rangle = 0$. Its orthogonality to $\mathbf{J}$ follows from odd–even parity cosnideration. The physical meaning of $\sigma(t)$ follows from its definition as the nonconserved part of the pressure tensor. It represents the viscous stress tensor. Implementation of the memory function formalism with a projection operator projecting onto the initial values ξ, $\mathbf{J}$, and σ yields the following Langevin equation in addition to the conservation equations $\dot{\xi}(t) = ik\mathbf{J}(t)$ and eq A1:

$$\dot{\sigma}(t) = \langle \dot{\sigma}\mathbf{J}^\dagger\rangle \cdot \langle \mathbf{J}\mathbf{J}^\dagger\rangle \cdot \mathbf{J}(t) - \int_0^t \mathbf{\Phi}(t-u) \cdot \sigma(u) + \mathbf{F}_\sigma(t) \tag{A2}$$

Since the average of the Langevin force over the initial distribution vanishes in the linear approximation, eq A2 represents, when averaged over the initial distribution, the microscopic version of the linear constitutive equation relating the mean values of the viscosity stress tensor to the rate of strain tensor. Since $\langle \mathbf{F}_\sigma(t)\ \mathbf{J}^\dagger(0)\rangle = 0$, we can calculate the time correlation function $\langle \sigma(t)\ \mathbf{J}^\dagger(0)\rangle$ exactly from eq A2. Denoting the Laplace transform of $\sigma(t)$ by $\tilde{\sigma}(s)$, we find

$$\langle \tilde{\sigma}(s)\ \mathbf{J}^\dagger\rangle = [s\mathbf{I} + \tilde{\mathbf{\Phi}}(s)]^{-1} \cdot \langle \dot{\sigma}\mathbf{J}^+\rangle \cdot \langle \mathbf{J}\mathbf{J}^\dagger\rangle^{-1} \cdot \langle \tilde{\mathbf{J}}(s)\ \mathbf{J}^\dagger\rangle \tag{A3}$$

We now compare the six- and four-component descriptions by inspecting the expression of $\dot{\mathbf{J}}(t)$ in these descriptions, i.e., eqs A1 and 8b in the text, respectively. Since $\langle \dot{\mathbf{J}}\xi^\dagger\rangle = ik\langle \mathbf{J}\mathbf{J}^\dagger\rangle$, the first terms on the right-hand side in these equations are identical. Hence, we obtain

$$\sigma(t) = -\int_0^t du\ \varphi(t-u) \cdot \mathbf{J}(u) + \mathbf{F}(t) \tag{A4}$$

By multiplying both sides of eq A4 by $\mathbf{J}^\dagger(0)$, taking the equilibrium average and the Laplace transform of the resulting equation, we find

$$\langle \tilde{\sigma}(s)\mathbf{J}^\dagger(0)\rangle = -\tilde{\varphi}(s) \cdot \langle \mathbf{J}(s)\ \mathbf{J}^\dagger\rangle \tag{A5}$$

Comparison of eqs A3 and A5 yields

$$\tilde{\varphi}(s) = -[s\mathbf{I} + \tilde{\mathbf{\Phi}}(s)]^{-1} \cdot \langle \dot{\sigma}\mathbf{J}^\dagger\rangle \cdot \langle \mathbf{J}\mathbf{J}^\dagger\rangle^{-1} \tag{A6}$$

which relates the memory functions in the four- and six-component descriptions. We now show that eq A6 can be written as

$$\tilde{\varphi}(s) = [s\mathbf{I} + \tilde{\mathbf{\Phi}}(s)]^{-1}\cdot\varphi(0) \qquad \text{(A7)}$$

where $\varphi(0)$ is given in eq 11 in the text. To do this, we first verify that $-\langle\dot{\sigma}\mathbf{J}^{\dagger}\rangle = \langle\sigma\dot{\mathbf{J}}^{\dagger}\rangle$ and then substitute into the latter $\sigma(0)$ from eq A1. The result is

$$-\langle\dot{\sigma}\mathbf{J}^{\dagger}\rangle = \langle\dot{\mathbf{J}}\dot{\mathbf{J}}^{\dagger}\rangle - \langle\dot{\mathbf{J}}\xi^{\dagger}\rangle\cdot\langle\xi\xi^{\dagger}\rangle^{-1}\cdot\langle\xi\dot{\mathbf{J}}^{\dagger}\rangle \qquad \text{(A8)}$$

Since $\langle\dot{\mathbf{J}}\xi^{\dagger}\rangle = ik\langle\mathbf{J}\mathbf{J}^{\dagger}\rangle$ and $\langle\xi\dot{\mathbf{J}}^{\dagger}\rangle = -ik\langle\mathbf{J}\mathbf{J}^{\dagger}\rangle$, eq A8 can be written as

$$-\langle\dot{\sigma}\mathbf{J}^{\dagger}\rangle = \langle\dot{\mathbf{J}}\dot{\mathbf{J}}^{\dagger}\rangle - k^2\langle\mathbf{J}\mathbf{J}^{\dagger}\rangle\cdot\langle\xi\xi^{\dagger}\rangle^{-1}\cdot\langle\mathbf{J}\mathbf{J}^{\dagger}\rangle \qquad \text{(A9)}$$

Multiplying both sides of eq A9 by $\langle\mathbf{J}\mathbf{J}^{\dagger}\rangle^{-1}$ from the right, we recapture the expression of $\varphi(0)$ as given in eq 11, thus proving eq A7. The latter expression is just the continued fraction expansion of $\tilde{\varphi}(s)$ and was used to obtain eq 26 in the text.

Appendix B. Implementation of the Markov Limit in Equation 49

Equation 49 has the following generic form before the Markov limit is implemented:

$$\ddot{S}(k,t) = -k^2aS(q,t) - b\int_0^t \mathrm{d}u\ \zeta(u)\ \dot{S}(k,t-u) - k^2\int_0^t \mathrm{d}u\ \eta(u)\ \dot{S}(k,t-u) \qquad \text{(B1)}$$

where a and b are constants independent of k. The Markov limit implies $k \rightarrow 0$ and $t \rightarrow \infty$, keeping $k^2t = \tau$ fixed. Changing t to τ, denoting $S(k,\tau/k^2)$ by $S(\tau)$, and noting that $\dot{S}(k,\tau/k^2) = k^2\dot{S}(\tau)$, one gets

$$k^2\ddot{S}(\tau) = -aS(\tau) - b\int_0^{\tau/k^2} \mathrm{d}u\ \zeta(u)\ \dot{S}(\tau-uk^2) - \int_0^{\tau} \mathrm{d}v\ \eta(v)\ \dot{S}(\tau-v) \qquad \text{(B2)}$$

In the last term of eq B2, we substituted $u = v/k^2$. We now take the limit $k \rightarrow 0$ and obtain

$$0 = -aS(\tau) - b\dot{S}(\tau)\ \tilde{\zeta}(0) - \int_0^{\tau} \mathrm{d}v\ \eta(v)\ \dot{S}(\tau-v) \qquad \text{(B3)}$$

When eq B3 is written in the original variables t and k, one obtains eq 49 in the text. We note that the second derivative of $S(k,t)$ in eq B1 vanishes in the Markov limit. We kept it in eq 49 for comparison with the phenomenological theory.

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