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Dynamic coupling between stress and composition in polymer solutions and blends

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Abstract. — Phenomenological hydrodynamic equations are proposed for entangled polymer blends as generalization of those for polymer solutions. They can describe coupling between macroscopic flow and relative diffusion. The key concept we use is the "tube velocity" introduced by Brochard in the problem of mutual diffusion in polymer blends. As applications, (i) we give a general expression for the time-correlation function of the polymer concentration around equilibrium and examine its relaxation in some typical cases. It can be strongly influenced by the viscoelastic effect when the two polymers have different lengths. Our expression can also be used for gelling solutions and explains previous dynamic light scattering experiments at the sol-gel transition. (ii) Detailed calculations are performed for the case of a single rheological relaxation time (the Maxwell model). The steady state structure factor is obtained to linear order in macroscopic flow. (iii) We predict that composition inhomogeneity is created in mixtures of long and short polymers undergoing nonuniform flow. Its origin is that the longer chains support stress more than the shorter ones and the resultant imbalance of stress causes relative motion of the two polymers. These results are applicable both to solutions and blends.

1. Introduction.

In the usual treatment of flow in polymeric liquids, the polymer composition is assumed to be uniform in space. However, it has been suggested that the composition should not be uniform under nonuniform velocity gradients [1, 2]. An early argument for the effect was based on consideration of the elastic free energy. That is, chains in spatial region with higher velocity gradients are more deformed than those in regions with lower velocity gradients, and have larger values of the chemical potential. As a result, they will migrate toward regions with lower velocity gradients in order to reduce the total free energy of the system. However, this argument has recently been criticized as it uses the principle of minimizing the free energy in nonequilibrium states [3, 4].

Experimental studies of the flow-induced polymer migration are still not abundant [5], although the effect has been discussed in a broad range of problems such as the polymer retention in flow through porous media [2], the anomalous size effect of the viscosity in polymer solutions through narrow tubes [2], and the shear-induced phase separation [6, 7]. Unfortunately, most of these experiments have not been decisive enough to establish the effect and the existence of the effect itself has often been questioned [8].

However, we should mention experiments by Zimm and his coworkers reported in biological journals [9, 10], which clearly evidenced the effect. They found that, when a DNA solution is sheared between two cones, DNA molecules migrate toward the center and longer ones move faster than shorter ones. This effect has been utilized as a DNA separator [10]. Zimm *et al.* also showed, using a bead spring model for DNA molecules, that the migration can take place due to the normal stress effect [11], although detailed comparison between their theory and experiments has not been made furthermore.

Very recently interest toward the problem has revived in connection with the shear-induced phase separation, which is now being observed by dramatic light scattering experiments [12-14]. Theoretically, Helfand and Fredrickson [3], and Onuki [4] criticized the early theory based on the free energy principle, and proposed new kinetic equations in the presence of flow near the consolute point. Doi [15] proposed a two fluid model and predicted macroscopic concentration gradient induced in entangled polymer solutions under nonuniform flow. Although controversy existed on the form of kinetic equations at an early stage, it has now settled, and the kinetic approach has converged to a common framework [15-17].

The kinetic equations developed so far are those for polymer solutions consisting of polymer and solvent, the latter having a low molecular weight. It is naturally expected that analogous effects should also exist in polymer melts consisting of two kinds of polymers with different molecular weights, M_L and M_S. In the extreme limit, $M_S << M_L$, the mixture should behave like a polymer solution and composition inhomogeneity should be induced by shear in the same manner. Indeed it has been reported that in polymer blends phase separation can be triggered by shear [18]. A question then arises : how can the kinetic equations for polymer solutions be generalized for mixtures of polymer melts with general M_S and M_L? The purpose of this paper is to give such a generalization on the basis of two early works; one is the two fluid model for polymer solutions [15], and the other is Brochard's theory [19] on mutual diffusion in polymer melts. Since these theories were published both in conference proceedings, we shall first review them in some detail in sections 2 and 3 and then generalize the ideas to derive kinetic equations for polymer melts in section 4. The theory will be applied to examine the viscoelastic effect on dynamic scattering in section 5, the steady state structure factor in weak shear for the Maxwell model in section 6, and compositional inhomogeneity in the cone-and-plate rheometer in section 7.

2. Two fluid model for polymer solutions.

2.1 RAYLEIGH'S VARIATIONAL PRINCIPLE. — Let us consider a polymer solution in which bulk flow and diffusion are taking place simultaneously, where the polymer velocity differs from the solvent velocity. Let $v_p(r, t)$ and $v_s(r, t)$ be the average velocities of polymer and solvent, respectively, and $\phi(r, t)$ be the volume fraction of polymer at point r and time t. We assume that the solvent and polymer have the same specific volume, so that the polymer mass density ρ_p divided by ϕ is equal to the solvent mass density ρ_s divided by $1 - \phi$. It follows from the conservation law that

$$\frac{\partial \phi}{\partial t} = - \nabla \cdot (\phi v_p) = \nabla \cdot [(1 - \phi) v_s] \tag{2.1}$$

The volume average velocity v is given by

$$v = \phi v_{\mathrm{p}} + (1 - \phi)v_{\mathrm{s}} \qquad (2.2)$$

It follows from (2.1) that

$$\nabla \cdot v = 0 \qquad (2.3)$$

To determine v_{p} and v_{s}, we shall use Rayleigh's variational principle [20, 21]. This is simply a variational statement for the following kinetic equation for thermodynamic quantities x_i ($i = 1, 2, \cdots n$),

$$\frac{\mathrm{d}x_i}{\mathrm{d}t} = -\Sigma L_{ij}(\{x\})\frac{\partial F(\{x\})}{\partial x_j} \qquad (2.4)$$

where F is the thermodynamic free energy and L_{ij} the kinetic coefficients; the matrix made of L_{ij} is positive-definite. Let M_{ij} be the inverse matrix of L_{ij},

$$\Sigma_j M_{ij}L_{jk} = \delta_{ik} \quad , \qquad (2.5)$$

then equation (2.4) can be written as

$$\Sigma_j M_{ij}\frac{\mathrm{d}x_j}{\mathrm{d}t} = -\frac{\partial F}{\partial x_i} \qquad (2.6)$$

Equation (2.6) can be stated in a variational principle that the following function, which we shall call Rayleighian,

$$R = \frac{1}{2}\sum_{i,j} M_{ij}\dot{x}_i\dot{x}_j + \sum_i \frac{\partial F}{\partial x_i}\dot{x}_i \quad , \qquad (2.7)$$

be minimized with respect to $\dot{x}_i$ with x_i held fixed. We shall call

$$W = \sum_{i,j} M_{ij}\dot{x}_i\dot{x}_j \qquad (2.8)$$

the dissipation function since it represents the energy dissipation for given $\dot{x}_i$. The second term in (2.7)

$$\dot{F} = \sum_i \frac{\partial F}{\partial x_i}\dot{x}_i \qquad (2.9)$$

denotes the free energy change due to $\dot{x}_i$.

In the present problem, $\dot{x}_i$ correspond to $v_{\mathrm{p}}(r, t)$ and $v_{\mathrm{s}}(r, t)$, and the dissipation function is written as

$$W = \int \mathrm{d}r\left[\zeta(v_{\mathrm{p}} - v_{\mathrm{s}})^2 + \eta_{\mathrm{s}}(\nabla v_{\mathrm{s}} \cdot \nabla v_{\mathrm{s}})\right] \qquad (2.10)$$

The first term is the energy dissipation caused by relative motion between polymer and solvent, and the second term represents the energy dissipation caused by solvent velocity gradients. Here η_{s} is the solvent viscosity and ζ stands for the friction constant per unit volume and is of order $\eta_{\mathrm{s}}\zeta_{\mathrm{b}}^{-2}$, ξ_{b} being the so-called blob size [22]. In entangled polymer systems, the second term is much smaller than the first and will be dropped in the following discussion.

It must be noted that (2.10) does not represent the whole energy dissipation taking place in the system. Equation (2.10) represents only the part of the energy dissipation which is directly coupled with the velocities v_{p} and v_{s}. The total energy dissipation involves other terms which arises from the local motion of polymer segments, but it does not affect the equations for v_{p} and v_{s} such as (2.16) and (2.17) to follow. Hence we can use (2.10) to generate kinetic equations, but we have to remember that W does not represent the whole energy dissipation.

The free energy of the system consists of two terms; one is the mixing free energy F_{mix}, and the other is the elastic free energy F_{el} associated with the conformational entropy of polymer chains. Their explicit forms will be given in the subsequent sections.

2.2 DIFFUSION NEAR EQUILIBRIUM. — If the polymer conformation is in equilibrium, the free energy consists of F_{mix} only, which is written as

$$F_{\text{mix}} = \int dr f(\phi(r)) \quad , \tag{2.11}$$

where $f(\phi)$ is the free energy per unit volume of a solution with polymer concentration ϕ. For simplicity we have neglected the gradient free energy ($\propto |\nabla \phi|^2$) arising from inhomogeneity of $\phi(r)$. The time derivative of (2.11) can be written as

$$\dot{F}_{\text{mix}} = \int \frac{\partial f}{\partial \phi} \dot{\phi} dr = - \int \frac{\partial f}{\partial \phi} \nabla \cdot (\phi v_{\text{p}}) dr \tag{2.12}$$

Thus the Rayleighian to be minimized is

$$R = \int \left[\frac{1}{2} \zeta(\phi)(v_{\text{p}} - v_{\text{s}})^2 - \frac{\partial f}{\partial \phi} \nabla \cdot (\phi v_{\text{p}}) \right] dr \tag{2.13}$$

This has to be minimized under the incompressible condition,

$$\nabla \cdot [v_{\text{p}} \phi + v_{\text{s}}(1 - \phi)] = 0 \tag{2.14}$$

which is accounted for by adding the term,

$$\int dr p(r,t) \nabla \cdot [v_{\text{p}} \phi + v_{\text{s}}(1 - \phi)] \quad , \tag{2.15}$$

to the Rayleighian (2.13). The condition that the functional derivative of the Rayleighian with respect to v_{p} and v_{s} be zero gives

$$\zeta(v_{\text{p}} - v_{\text{s}}) + \phi \nabla \frac{\partial f}{\partial \phi} - \phi \nabla p = 0 \quad , \tag{2.16}$$

$$\zeta(v_{\text{s}} - v_{\text{p}}) - (1 - \phi) \nabla p = 0 \tag{2.17}$$

Elimination of ∇p yields

$$v_{\text{p}} - v_{\text{s}} = -\frac{1}{\zeta} \phi(1 - \phi) \nabla \frac{\partial f}{\partial \phi} \tag{2.18}$$

The right hand side of (2.18) can be rewritten in terms of the osmotic pressure

$$\pi(\phi) = \phi \frac{\partial f}{\partial \phi} - f \tag{2.19}$$

as

$$v_{\text{p}} - v_{\text{s}} = -\frac{1 - \phi}{\zeta} \nabla \pi \tag{2.20}$$

This is the formula used in the theory of the concentration fluctuation in polymer solutions [22].

2.3 BULK FLOW IN POLYMER SOLUTIONS. — If the polymer conformation is not in equilibrium, we have to account for the elastic free energy. To see how this effect enters in the above formulation, let us consider a homogeneous system in which v_p and v_s are equal to v as in the conventional theory of polymer rheology.

It is generally accepted in polymer rheology that stress in polymeric liquids originates from the conformational entropy of polymer chains and that there exists a free energy F_{el} associated with the chain conformation. The F_{el} is a functional of the past history of deformations, and is related to the stress tensor $\sigma_{\alpha\beta}$ as follows. Suppose that a small deformation is applied to a polymeric liquid in a very short time and that each point in the system is displaced as $r \to r' = r + u(r)$; then, the change of F_{el} for arbitrary $u(r)$ is given by

$$\delta F_{el} = \int \sigma_{\alpha\beta} \frac{\partial u_\alpha}{\partial r_\beta} dr \tag{2.21}$$

Equation (2.21) implies that the change of the free energy for the velocity $v(r)$ is written as

$$\dot{F}_{el} = \int \sigma_{\alpha\beta} \frac{\partial v_\alpha}{\partial r_\beta} dr \tag{2.22}$$

Hence the Rayleighian is given by

$$R = \int \boldsymbol{\sigma} : \nabla v dr - \int p \nabla \cdot v dr \tag{2.23}$$

(Notice that the term W of the dissipation function is zero in this case.) Thus the variational principle gives the force balance equation,

$$\nabla \cdot (\boldsymbol{\sigma} - p\mathbf{I}) = 0 \tag{2.24}$$

To obtain $v(r,t)$ for given boundary conditions, we need a constitutive equation which determines the stress tensor $\boldsymbol{\sigma}$ for a given velocity gradient ∇v. A classical example is the following upper convective Maxwell model [26],

$$\frac{D\boldsymbol{\sigma}}{Dt} - (\nabla v)^{\dagger} \cdot \boldsymbol{\sigma} - \boldsymbol{\sigma} \cdot \nabla v + \frac{1}{\tau}(\boldsymbol{\sigma} - G_e\mathbf{I}) = 0 \tag{2.25}$$

where $D/Dt \equiv \partial/\partial t + v \cdot \nabla$ is the convective time derivative, τ is the rheological relaxation time, and G_e is the shear modulus. The zero-frequency viscosity η in this model is equal to $G_e\tau$. More accurate and elaborate constitutive equations are known as described in detail in the literature [24, 26, 27]. Given some constitutive equation, the force balance equation (2.24) and the incompressible condition $\nabla \cdot v = 0$ determine $v(r,t)$ and $p(r,t)$.

2.4 VISCOELASTIC EFFECT ON DIFFUSION. — If v_p and v_s are not equal, the above story has to be modified. It is clear that v in (2.22) should be replaced by v_p since it is the deformation of the polymer which causes the change of the free energy. Hence $\dot{F}_{el}$ is given by

$$\dot{F}_{el} = \int \boldsymbol{\sigma}^{(n)} \cdot \nabla v_p dr \tag{2.26}$$

Here $\boldsymbol{\sigma}$ has been replaced by $\boldsymbol{\sigma}^{(n)}$ in order to emphasize their difference. The $\boldsymbol{\sigma}^{(n)}$ will be called the network stress and the distinction will be explained later. Therefore, the Rayleighian to be minimized with respect to v_p and v_s is

$$R = \int \left[\frac{1}{2}\zeta(v_p - v_s)^2 - \frac{\partial f}{\partial \phi} \nabla \cdot (\phi v_p) + \boldsymbol{\sigma}^{(n)} \cdot \nabla v_p - p \nabla \cdot (\phi v_p + (1 - \phi)v_s) \right] dr \quad , \tag{2.27}$$

which gives

$$\zeta(v_p - v_s) + \nabla \pi - \nabla \cdot \sigma^{(n)} + \phi \nabla p = 0 \quad, \tag{2.28}$$

$$\zeta(v_s - v_p) + (1 - \phi) \nabla p = 0 \tag{2.29}$$

Thus, we obtain

$$v_p - v_s = -\frac{1}{\zeta}(1 - \phi) \nabla \cdot \left[\pi \mathbf{I} - \sigma^{(n)} \right] \quad, \tag{2.30}$$

$$\nabla \cdot (\sigma^{(n)} - (\pi + p)\mathbf{I}) = 0 \quad, \tag{2.31}$$

which are the basic equations derived in reference [15].

Equation (2.30) shows that the motion of polymers relative to the solvent is driven by not only the gradient of the osmotic pressure π, but also the gradient of the elastic stress $\sigma^{(n)}$. Indeed several authors pointed out that the elastic stress should contribute to the diffusion of polymers. Tanaka and Filmore [28] proposed that the swelling speed of gels is driven by the elastic stress and the osmotic pressure. Brochard and de Gennes argued that the same effect should exists in entangled polymer solutions, and discussed its consequences on relaxation of the concentration fluctuations in semidilute solutions with theta solvent [29, 30] and on diffusion kinetics [31]. The physics underlying these theories is that the stress in the entangled polymer systems is supported by chains and thus, if there is a gradient in the stress, it creates a net force on the chains resulting in their migration relative to the solvent.

In these early theories, however, attention was focused on diffusion in quiescent states and the convective motion was not examined. On the other hand, above theory accounts for both the polymer and solvent velocities explicitly and, consequently, it can describe the coupling between convection and diffusion.

In the two fluid model, the bulk flow is determined by the second equation (2.31) which represents a force balance. Hence the tensor,

$$\sigma = \sigma^{(n)} - (\pi + p)\mathbf{I} \quad, \tag{2.32}$$

represents the total stress tensor. Now the distinction between the network stress $\sigma^{(n)}$ and the mechanical stress σ is explained. The network stress $\sigma^{(n)}$ differs from the mechanical stress by the isotropic tensor $(\pi + p)\mathbf{I}$. For incompressible fluids with homogeneous composition this distinction has no significance since the isotropic term $p\mathbf{I}$ is determined by the incompressible condition $\nabla \cdot v = 0$. However, if the diffusion is taking place, the isotropic term matters since it appears in the driving force for v_p, the divergence of which generally remains.

To determine $\sigma^{(n)}$, a new constitutive equation is needed. Conventional rheological constitutive equations can be used for the deviatopic part of the tensor $\sigma^{(n)}$, i.e., $\sigma^{(n)} - (\mathbf{I}/3)\mathrm{Tr}\sigma^{(n)}$, which is equal to that of the mechanical stress tensor σ. On the other hand, very little is known on the isotropic part $(\mathbf{I}/3)\mathrm{Tr}\sigma^{(n)}$. In reference [15], it was assumed that $\mathrm{Tr}\sigma^{(n)}$ vanishes. This assumption is justified for a certain molecular model. Indeed, for the reptation model, it can be shown that $\mathrm{Tr}\sigma^{(n)}$ is zero if the length of the polymer along the tube is equal to the equilibrium value. Since no precise information is available on $\mathrm{Tr}\sigma^{(n)}$, we proceed assuming that $\mathrm{Tr}\sigma^{(n)}$ is zero. Thus from (2.35) we have

$$\sigma^{(n)} = \sigma - \frac{1}{3}(\mathrm{Tr}\sigma)\mathbf{I} \tag{2.33}$$

Therefore, in polymer solutions, if the rheological constitutive equation for σ and the osmotic pressure $\pi(\phi)$ are known, v_p and v_s are determined by (2.30) and (2.31). On the other hand,

in polymer gels the diagonal part $\frac{1}{3}(\mathrm{Tr}\boldsymbol{\sigma})\mathbf{I}$ gives rise to an important contribution to the total osmotic pressure. (In Ref. [32] it is included into the definition of π).

Note that, since $\sigma^{(n)}$ arises from network deformations, it should be determined by the gradient of v_p. For example, in the linear response regime $\boldsymbol{\sigma}^{(n)}$ is generally written as [15]

$$\sigma_{ij}^{(n)} = \int_{-\infty}^{t} \mathrm{d}t' G(t-t')\kappa_{ij}^{(\mathrm{p})}(t') \tag{2.34}$$

where

$$\kappa_{ij}^{(\mathrm{p})} = \frac{\partial}{\partial x_i}v_{\mathrm{p}j} + \frac{\partial}{\partial x_j}v_{\mathrm{p}i} - \frac{2}{3}(\nabla \cdot v_\mathrm{p})\delta_{ij} \tag{2.35}$$

The $G(t)$ is the stress relaxation function related to the complex shear viscosity $\eta^*(\omega)$ by

$$\eta^*(\omega) = \int_0^\infty \mathrm{d}t e^{-i\omega t}G(t) \tag{2.36}$$

Here ∇v_p is used in the place of ∇v in the conventional rheological equation. We claim that ∇v_p should be used when $v_\mathrm{p} \neq v$. This point has very important implications as it will be discussed later.

With (2.30) ϕ obeys the following diffusive equation,

$$\frac{\partial}{\partial t}\phi = -\nabla \cdot(\phi v) + \nabla \cdot \left[\frac{1}{\zeta}\phi(1-\phi)^2\right]\left[\phi \nabla \frac{\partial}{\partial \phi}f - \nabla \cdot \boldsymbol{\sigma}^{(n)}\right] \tag{2.37}$$

This form of the equation was first proposed in reference [3] for the Rouse model and rederived in references [16] and [17] for the entangled case. The gradient free energy can be taken into account if $\partial f/\partial\phi$ in the above equation is replaced by $\delta F/\delta\phi$, F being the total free energy for ϕ.

3. Brochard's theory for mutual diffusion in polymer blends.

3.1 ENERGY DISSIPATION FUNCTION IN THE REPTATION THEORY. — To introduce another key concept, we shall describe Brochard's theory for mutual diffusion in entangled polymer melts in the framework of the Rayleighian formalism. Consider a mixture of long (L) and short (S) polymers, each having degree of polymerization, N_L and N_S, with $N_\mathrm{L} > N_\mathrm{S} > N_\mathrm{e}$, where N_e is the degree of polymerization corresponding to the entanglement molecular weight.

Let v_L and v_S be their average velocities. As in the previous section, we assume that the volume fraction ϕ_L and ϕ_S satisfy

$$\frac{\partial \phi_i}{\partial t} = -\nabla \cdot(v_i\phi_i) \quad \text{and} \quad \sum_i \phi_i = 1 \;, \tag{3.1}$$

where i stands for L or S.

To determine v_i, let us first suppose the situation in which the polymers L and S are moving through a fixed network. This is the case treated in the classical reptation theory [33], which assumes that each polymer moves through a tube made of the network. If a polymer moves with a curvilinear velocity w_i along the tube, its center of mass moves with the velocity

$$v_i = \frac{1}{L_i}w_i h_i \qquad (i = \mathrm{L}, \mathrm{S}) \;, \tag{3.2}$$

where L_i is the contour length of the tube, and h_i is the end-to-end vector of the polymer. At equilibrium, L_i is related to the square average of h_i as

$$L_i^2 = \frac{N_i}{N_e}\overline{h_i^2} \tag{3.3}$$

Taking the square of the average of (3.2) and using (3.3), we have

$$v_i^2 = \frac{N_e}{N_i}w_i^2 \tag{3.4}$$

Here we have assumed that the polymer conformation is not significantly altered from that in equilibrium. This assumption is not valid in the non-Newtonian regime where rheological responses become non linear. However, the main point of the present theory is to elucidate the coupling between stress and diffusion in the simplest manner, so we will neglect this effect.

Now the energy dissipation W in this system is caused by the relative motion between polymers and networks, and is proportional to the square of the curvilinear velocity w_i. Let ζ_{0i} be the microscopic friction constant of the polymer i; then, the energy dissipation function is written as

$$W = \int \mathrm{d}r \sum_i \phi_i \zeta_{0i} w_i^2 \tag{3.5}$$

Using (3.4), this can be rewritten as

$$W = \int \mathrm{d}r \sum_i \phi_i \frac{N_i}{N_e}\zeta_{0i} v_i^2 = \int \mathrm{d}r \sum_i \zeta_i v_i^2 \ , \tag{3.6}$$

where

$$\zeta_i = \phi_i \frac{N_i}{N_e}\zeta_{0i} \tag{3.7}$$

For simplicity we shall assume that the microscopic friction is common to both species and write $\zeta_0 = \zeta_{0L} = \zeta_{0S}$. This dependence of ζ_i on ϕ_i and N_i will be crucial in the following discussions. We note that it can also be found from more straightforward considerations on dynamics given in the last part of section 4 below.

3.2 ENERGY DISSIPATION IN A MOVING NETWORK. — Now let us come back to the diffusion problem in polymer-polymer mixtures. Brochard assumed that the topological constraints imposed on each polymer can be modeled by a molecular field represented by a network. The network is common to all polymers and moves with a certain velocity v_T, which she called the tube velocity. If the network moves with v_T, (3.2) should be modified as

$$v_i - v_T = \frac{1}{L_i}w_i h_i \tag{3.8}$$

Hence the dissipation function is of the form,

$$W = \int \mathrm{d}r \sum_i \phi_i \frac{N_i}{N_e}\zeta_{0i}(v_i - v_T)^2 = \int \mathrm{d}r \sum_i \zeta_i(v_i - v_T)^2 \tag{3.9}$$

Brochard determined the tube velocity v_T from the condition that the frictional force acting on the network should balance. Since the force in unit volume is $(1/2)\delta W/\delta v_T$, the force balance equation is written as

$$\sum_i \zeta_i(v_i - v_T) = 0 \ , \tag{3.10}$$

which gives v_T in linear combination of v_L and v_S as

$$v_T = \frac{1}{\zeta_L + \zeta_S}(\zeta_L v_L + \zeta_S v_S) \tag{3.11}$$

From (3.9) and (3.11) the dissipation function is expressed as

$$W = \int dr \zeta (v_L - v_S)^2 \ , \tag{3.12}$$

where

$$\zeta = \frac{\zeta_L \zeta_S}{\zeta_L + \zeta_S} \quad \text{or} \quad \frac{1}{\zeta} = \frac{1}{\zeta_L} + \frac{1}{\zeta_S} \tag{3.13}$$

3.3 MUTUAL DIFFUSION COEFFICIENT. — Given the form of the dissipation function, the subsequent development is straightforward. Following Brochard, we shall consider the case in which the elastic energy of polymers is negligible. Hence $\dot{F}_{mix}$ is given by

$$\dot{F}_{mix} = -\int dr \frac{\partial f}{\partial \phi_L} \nabla \cdot (\phi_L v_L) = -\int dr \mu \nabla \cdot (\phi_L v_L) \tag{3.14}$$

where $\mu = \partial f / \partial \phi_L$ is equal to the difference in the monomeric chemical potentials $(\mu = \mu_L - \mu_S)$. Thus the Rayleighian becomes

$$R = \int dr \left[\frac{1}{2}\zeta(v_L - v_S)^2 - \mu \nabla \cdot (\phi_L v_L) - p \nabla \cdot \sum_i (\phi_i v_i) \right] \ , \tag{3.15}$$

from which we find

$$\zeta(v_L - v_S) + \phi_L \nabla \mu + \phi_L \nabla p = 0 \ , \tag{3.16}$$

$$\zeta(v_S - v_L) + \phi_S \nabla p = 0 \tag{3.17}$$

Addition of these equations leads to

$$\nabla p + \phi_L \nabla \mu = 0 \ , \tag{3.18}$$

and elimination of ∇p yields

$$v_L - v_S = -\frac{1}{\zeta}\phi_S \phi_L \nabla \mu \tag{3.19}$$

Equation (3.19) can be written using the volume average velocity,

$$v = \phi_L v_L + \phi_S v_S \ , \tag{3.20}$$

as

$$v_L - v = -\frac{1}{\zeta}\phi_S^2 \phi_L \nabla \mu \tag{3.21}$$

Thus the flux of the long polymer in the reference frame moving with v is

$$J_L = \phi_L(v_L - v) = -\frac{1}{\zeta}\phi_S^2 \phi_L^2 \nabla \mu$$

$$= -\frac{N_e}{\zeta_0}\left[\frac{1}{N_S \phi_S} + \frac{1}{N_L \phi_L}\right]\phi_S^2 \phi_L^2 \frac{\partial^2 f}{\partial \phi_L^2} \nabla \phi_L \tag{3.22}$$

The mutual diffusion constant D_m is defined by

$$J_L = -D_m \nabla \phi_L \quad , \tag{3.23}$$

so it follows Brochard's result [19],

$$D_m = \frac{N_e}{\zeta_0} \left[\frac{1}{N_S \phi_S} + \frac{1}{N_L \phi_L} \right] \phi_S^2 \phi_L^2 \frac{\partial^2 f}{\partial \phi_L^2} \tag{3.24}$$

This expression was already presented by Kramer *et al.* [34] and Silescu [35], and has been confirmed by experiments [36, 34]. It interpolates the diffusion constants in the dilute limit,

$$D_i = \lim_{\phi_i \to 0} D_m \propto N_e / N_i^2 \quad , \tag{3.25}$$

where $i = L$ or S and use has been made of the relation $\partial^2 f / \partial \phi_L^2 \propto 1/\phi_i N_i$ as $\phi_i \to 0$. However, it should be noted that Brochard's theory derives (3.24) for the incompressible polymer model, whereas the other theories [34, 35] are based on the compressibility of polymer melts. We believe that the compressibility assumption is not necessary to reach (3.24).

4. Two fluid model for polymer blends.

4.1 GENERALIZED BROCHARD'S THEORY. — Having described the basic physics, we shall now make a generalization of Brochard's theory. It is straightforward to account for the stress gradient in her diffusion equation. A natural way of doing this is to assume that $\dot{F} = \dot{F}_{mix} + \dot{F}_{e\ell}$ is given by

$$\dot{F} = \int dr \left[-\mu \nabla \cdot (\phi_L v_L) + \sigma^{(n)} \cdot \nabla v_T \right] \tag{4.1}$$

Notice that ∇v_p in equation (2.27) has been replaced by ∇v_T. This is consistent with the reptation theory for viscoelasticity. According to Doi and Edwards [23], macroscopic deformation changes conformation of the tube and causes stress, so it is natural to assume that the network stress $\sigma^{(n)}$ acts on the tube. Substitution of (3.11) into (4.1) gives

$$\dot{F} = \int dr \left[-\mu \nabla \cdot (\phi_L v_L) + \sigma^{(n)} \cdot \nabla (\zeta_L + \zeta_S)^{-1} (\zeta_L v_L + \zeta_S v_S) \right] \tag{4.2}$$

Following the same procedure as in subsection (2.4) we can determine v_L and v_S as

$$\zeta(v_L - v_S) + \phi_L \nabla \mu + \phi_L \nabla p - \frac{\zeta_L}{\zeta_L + \zeta_S} \nabla \cdot \sigma^{(n)} = 0 \quad , \tag{4.3}$$

$$\zeta(v_S - v_L) + \phi_S \nabla p - \frac{\zeta_S}{\zeta_L + \zeta_S} \nabla \cdot \sigma^{(n)} = 0 \tag{4.4}$$

Hence the counterparts of (3.18) and (3.19) are

$$\phi_L \nabla \mu + \nabla p - \nabla \cdot \sigma^{(n)} = 0 \quad , \tag{4.5}$$

$$v_L - v_S = \frac{1}{\zeta} \phi_L \phi_S [-\nabla \mu + \alpha \nabla \cdot \sigma^{(n)}] \quad , \tag{4.6}$$

where α in (4.6) is the following dimensionless coefficient,

$$\alpha = \frac{1}{\zeta_L + \zeta_S}\left(\frac{1}{\phi_L}\zeta_L - \frac{1}{\phi_S}\zeta_S\right)$$
$$= (N_L - N_S)/(\phi_L N_L + \phi_S N_S) \tag{4.7}$$

On the second line of (4.7) use has been made of (3.7) and the assumption $\zeta_{0L} = \zeta_{0S} = \zeta_0$. The α tends to $1/\phi_L$ in the polymer + solvent limit, $N_L \gg N_S$ and $\phi_L N_L \gg \phi_S N_S$, so that (4.6) reduces to (2.30). It vanishes for $N_L = N_S$, as ought to be the case, where the two species of polymers undergo the same deformations. We can also check that the tube velocity v_T given by (3.11) may be expressed in terms of α in the form,

$$v_T = v + \phi_L\phi_S\alpha(v_L - v_S) \tag{4.8}$$

For $N_L = N_S$ we simply have $v_T = v$ even in the presence of diffusion.

As in the previous sections, (4.5) represents the force balance equation. If the osmotic pressure π is introduced by

$$\pi = \phi_L\frac{\partial f}{\partial \phi_L} - f \quad, \tag{4.9}$$

(4.5) is written as

$$\nabla \cdot [\sigma^{(n)} - (\pi + p)\mathbf{I}] = 0 \tag{4.10}$$

Thus the total stress is given by

$$\sigma = \sigma^{(n)} - (\pi + p)\mathbf{I} \tag{4.11}$$

On the other hand, (4.6) represents the diffusion driven by the chemical potential and the network stress.

Equation (4.6) is the main result of our generalization of the previous two theories reviewed in sections 2 and 3. In fact, we can check the following. i) Without $\nabla \cdot \sigma^{(n)}$, (4.6) reduces to Brochard's result for mutual diffusion. ii) For $N_L \gg N_S$ and $\phi_L N_L \gg \phi_S N_S$ it reduces to (2.30) if $1/\zeta \cong N_e/\zeta_0 N_S$ in the melt case is identified with $1/\zeta$ in (2.30) for solutions.

4.2 EFFECT OF ACCELERATION. — So far we have completely neglected the inertia force in the previous formulation. The acceleration of the velocities can be accounted for if we start from the Lagrangean formalism with dissipation [20]. As a result we should obtain, instead of (4.3) and (4.4),

$$\rho_L\frac{Dv_L}{Dt} = -\zeta(v_L - v_S) - \phi_L\nabla\mu - \phi_L\nabla p + \frac{\zeta_L}{\zeta_L + \zeta_S}\nabla\cdot\sigma^{(n)} \quad, \tag{4.12}$$

$$\rho_S\frac{Dv_S}{Dt} = -\zeta(v_S - v_L) - \phi_S\nabla p + \frac{\zeta_S}{\zeta_L + \zeta_S}\nabla\cdot\sigma^{(n)} \quad, \tag{4.13}$$

where ρ_L and ρ_S are the mass densities of the two polymers. Here we are assuming $\rho_L/\phi_L = \rho_S/\phi_S = \rho$ are constants as in section 3, and $Dv_i/Dt = \partial v_i/\partial t + (v_i \cdot \nabla)v_i \cong \partial v_i/\partial t$ for $i = L, S$. In terms of $v = \phi_L v_L + \phi_S v_S$ and the relative velocity w defined by

$$w = v_L - v_S \quad, \tag{4.14}$$

(4.12) and (4.13) can be rewritten as

$$\rho\frac{\partial v}{\partial t} + \left(\rho\frac{\partial}{\partial t}\phi_{\mathrm{L}}\right)w = \boldsymbol{\nabla}\cdot\left[\boldsymbol{\sigma}^{(n)} - (p+\pi)\mathbf{I}\right] \quad , \tag{4.15}$$

$$\frac{\partial w}{\partial t} = -\frac{1}{\rho}\,\boldsymbol{\nabla}\,\mu + \frac{1}{\rho}\alpha\,\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}^{(n)} - \left(\frac{1}{\rho_{\mathrm{L}}} + \frac{1}{\rho_{\mathrm{S}}}\right)\zeta w \quad , \tag{4.16}$$

α being defined by (4.7). In most cases the second term on the left hand side of (4.15) and the left hand side of (4.16) are much smaller than the other terms in the equations. If they are neglected, we obtain the usual equation of motion for bulk flow,

$$\rho\frac{Dv}{Dt} = \boldsymbol{\nabla}\cdot\left[\boldsymbol{\sigma}^{(n)} - (p+\pi)\mathbf{I}\right] \quad , \tag{4.17}$$

and (4.6) for the relative velocity $w = v_{\mathrm{L}} - v_{\mathrm{S}}$. We may set $Dv/Dt \cong \partial v/\partial t$ here. For completeness, we write down the diffusion equation for ϕ_{L} using (3.1) and $v_{\mathrm{L}} = v + \phi_{\mathrm{S}}w$ in the form,

$$\frac{\partial}{\partial t}\phi_{\mathrm{L}} = -\boldsymbol{\nabla}\cdot(\phi_{\mathrm{L}}v) + \boldsymbol{\nabla}\left(\frac{1}{\zeta}\phi_{\mathrm{L}}^2\phi_{\mathrm{S}}^2\right)\cdot[\boldsymbol{\nabla}\,\frac{\partial f}{\partial\phi_{\mathrm{L}}} - \alpha\boldsymbol{\nabla}\cdot\boldsymbol{\sigma}^{(n)}] \tag{4.18}$$

Replacement of $\partial f/\partial\phi_{\mathrm{L}}$ by $\delta F/\delta\phi_{\mathrm{L}}$ should be made to account for the gradient free energy as discussed below (2.37).

We notice that the first terms on the right hand sides of (4.12) and (4.13) may be rewritten as

$$-\zeta(v_{\mathrm{L}} - v_{\mathrm{S}}) = -\zeta_{\mathrm{L}}(v_{\mathrm{L}} - v_{\mathrm{T}}) \quad , \tag{4.19}$$

$$-\zeta(v_{\mathrm{S}} - v_{\mathrm{L}}) = -\zeta_{\mathrm{S}}(v_{\mathrm{S}} - v_{\mathrm{T}}) \quad , \tag{4.20}$$

where the tube velocity v_{T} is given by (3.11) and the friction coefficients ζ_{L} and ζ_{S} are defined by (3.7). These terms can hence be interpreted as the friction terms between the polymers and the tubes, the latters being common to the two species of polymers and playing the role of mean field constraints, in accord with the discussion in section 3. It is then natural that ζ_i are linearly dependent on ϕ_i as (3.7). Their molecular weight dependence ($\propto N_i/N_{\mathrm{e}}$) can simply be derived from the requirement that the equation for ϕ_{L} or ϕ_{S} should tend to the diffusion equation $\partial\phi_i/\partial t = D_i\nabla^2\phi_i$ with $D_i \propto N_{\mathrm{e}}/N_i^2$ in the dilute limit $\phi_i \to 0$ (see (3.25)).

In the polymer + solvent case we have claimed in subsection 2.4 that the network stress is created by ∇v_{p}. In the melt case v_{p} should be replaced by the tube velocity v_{T}, so that in the linear response regime the counter part of (2.34) is

$$\sigma_{ij}^{(n)} = \int_{-\infty}^{t} \mathrm{d}t'\,G(t-t')\kappa_{ij}^{(\mathrm{T})}(t') \quad , \tag{4.21}$$

where

$$\kappa_{ij}^{(\mathrm{T})} = \frac{\partial}{\partial x_i}v_{\mathrm{T}j} + \frac{\partial}{\partial x_j}v_{\mathrm{T}i} - \frac{2}{3}(\boldsymbol{\nabla}\cdot v_{\mathrm{T}})\delta_{ij}$$

$$= \left[\frac{\partial}{\partial x_i}v_j + \frac{\partial}{\partial x_i}v_j\right] + \phi_{\mathrm{L}}\phi_{\mathrm{S}}\alpha\left[\frac{\partial}{\partial x_i}w_i + \frac{\partial}{\partial x_j}w_j - \frac{2}{3}(\boldsymbol{\nabla}\cdot w)\delta_{ij}\right] \tag{4.22}$$

On the second line of (4.22), use has been made of (4.8) and $\boldsymbol{\nabla}\cdot v = 0$. The second term on the right hand side ($\propto \nabla w$) will be crucial in section 5.

We also note that the Rayleighan formalism used here is essentially the same as the usual principle of positive entropy production. We may construct another theoretical scheme to reach (4.12) and (4.13) by introducing conformation tensors for the two polymers as in references [16] and [17]. If these tensors are convected by v_L and v_S but are both rotated by the same ∇v_T in their convective equations, the network force $\nabla \cdot \sigma^{(n)}$ turns out to be divided as (4.12) and (4.13) between the two polymers.

5. Viscoelastic effect on diffusion near equilibrium.

5.1 RELAXATION OF SMALL DEVIATIONS. — We here examine the effect of the coupling between stress and diffusion around equilibrium. We may treat both polymer solutions and polymer blends by the same equations with general coupling constant α. We assume that there is no macroscopic flow and all the deviations from equilibrium depend on space and time as $\exp(iq \cdot r + i\omega t)$. Then (4.18) may be linearized as

$$i\omega\delta\phi_L = -L_0\left[q^2\left(\frac{\partial^2 f}{\partial\phi_L^2}\right)\delta\phi_L + \alpha Z\right] \quad , \tag{5.1}$$

where

$$Z = \nabla\nabla : \sigma^{(n)} = \sum_{i,j}\frac{\partial^2}{\partial x_i\partial x_j}\sigma_{ij}^{(n)} \tag{5.2}$$

The L_0 is the kinetic coefficient given by

$$L_0 = \frac{1}{\zeta}(\phi_L\phi_S)^2 \tag{5.3}$$

The network stress is expressed as (4.21) together with (4.22) in the linear regime, leading to

$$Z = -\frac{4}{3}[\phi_L\phi_S\alpha\eta^*(\omega)q^2]iq \cdot w \quad , \tag{5.4}$$

where $\eta^*(\omega)$ is the complex shear viscosity defined by (2.37). Further using

$$i\omega\delta\phi_L = -(\phi_L\phi_S)iq \cdot w \quad , \tag{5.5}$$

we may express Z in terms of $\delta\phi_L$ and rewrite (5.1) as

$$\left[i\omega + L_0q^2\left(\frac{\partial^2 f}{\partial\phi_L^2} + \frac{4}{3}i\omega\alpha^2\eta^*(\omega)\right)\right]\delta\phi_L = 0 \tag{5.6}$$

This result is consistent with Brochard and de Gennes' theory for the case of polymer solution (where $\alpha = 1/\phi$) [29, 30]. They assumed that $\delta\phi$ follows the same relaxation as (5.6). This is because the decay rate should tend to that of gels [37], $\Gamma_{gel} = \zeta^{-1}q^2(\phi^2\partial^2 f/\partial\phi^2 + \frac{4}{3}G_e)$, in the high frequency limit, $\omega\tau >> 1$, and to that of fluids in the low frequency limit, $\omega\tau << 1$, where G_e is the shear modulus and τ is the rheological relaxation time. The viscoelastic correction can be important for θ solvents, whereas it is very small for good solvents. This is because $\phi^2(\partial^2 f/\partial\phi^2)/G_e$ is of order 1 in θ solvents but is very large ($\sim 10^2$) in good solvents [38].

However, it has not been stated that the viscoelastic effect can be important even at very low frequencies, $\omega\tau \ll 1$, if we are interested in physical processes on spatial scales shorter than a characteristic length $\xi_{\rm ve}$. By setting $\eta^*(\omega) \cong \eta^*(0) = \eta$ for $\omega\tau \ll 1$ in (5.6), we define $\xi_{\rm ve}$ by

$$\xi_{\rm ve}^2 = \frac{4}{3}L_0\alpha^2\eta \tag{5.7}$$

Then, on time scales longer than τ, $\delta\phi_{\rm L}(r,t)$ in the real space obeys a modified diffusion equation,

$$(1 - \xi_{\rm ve}^2\nabla^2)\frac{\partial}{\partial t}\delta\phi_{\rm L} = D_{\rm m}\nabla^2\delta\phi_{\rm L} \quad, \tag{5.8}$$

where $D_{\rm m}$ is defined by (3.24). It is important that $\xi_{\rm ve}$ can be much longer than the gyration radius of chains or the thermal correlation length. To see this, let us rewrite (5.7) more explicitly as

$$\xi_{\rm ve}^2 = \frac{4}{3}(\frac{N_{\rm e}}{\zeta_0})\phi_{\rm L}\phi_{\rm S}\left[(N_{\rm L} - N_{\rm S})^2/N_{\rm L}N_{\rm S}(\phi_{\rm L}N_{\rm L} + \phi_{\rm S}N_{\rm S})\right]\eta \quad, \tag{5.9}$$

where use has been made of (3.7), (4.7), and (5.3). Order estimations will be made in typical cases:

(i) When $N_{\rm L}$ and $N_{\rm S}$ are of the same order (say, $N_{\rm L}/N_{\rm S} = 2$), we find

$$\xi_{\rm ve}^2 \sim \phi_{\rm L}\phi_{\rm S}(1 - \frac{N_{\rm S}}{N_{\rm L}})^2 L_{\rm tube}^2 \quad, \tag{5.10}$$

where $L_{\rm tube}(\propto N_{\rm e}^{-1/2}N_{\rm L} \sim N_{\rm e}^{-1/2}N_{\rm S})$ is the tube length in the reptation theory.

(ii) In the dilute limit $\phi_i \to 0$ ($i = {\rm L}$ or ${\rm S}$),$\xi_{\rm ve}^2$ becomes proportional to ϕ_i as

$$\xi_{\rm ve}^2 \sim \phi_i\frac{1}{N_{\rm L}N_{\rm S}}(N_{\rm L} - N_{\rm S})^2 L_{\rm tube}^2 \quad, \tag{5.11}$$

where $L_{\rm tube}$ is the tube length composed of the host chains. We notice that $\xi_{\rm ve}$ can be very long even for extremely small ϕ_i.

(iii) In the polymer + solvent case we have $L_0 \cong \phi^2/\zeta \sim \eta_{\rm s}^{-1}\phi^2\xi_{\rm b}^2$ and $\alpha = 1/\phi$, where $\eta_{\rm s}$ is the solvent viscosity and $\xi_{\rm b}$ is the blob size (see the last sentence of subSect. 4.1). Therefore,

$$\xi_{\rm ve}^2 \sim \xi_{\rm b}^2\eta/\eta_{\rm s} \tag{5.12}$$

The ratio $\eta/\eta_{\rm s}$ becomes very large in the entangled case, so that $\xi_{\rm ve} \gg \xi_{\rm b}$ there.

In a forthcoming paper we will show that the viscoelastic effect can severely slow down the growth of nucleating droplets in metastable states.

5.2 TIME-CORRELATION FUNCTION. — We then calculate the time-correlation function for the thermal fluctuations of $\phi_{\rm L}$ in equilibrium,

$$S(q,t) = <\phi_q(t)\phi_q(0)^*> \quad, \tag{5.13}$$

where $< \cdot >$ is the equilibrium average and $\phi_q(t)$ is the Fourier component of $\phi_{\rm L}(r,t)$. The equal-time correlation function will be assumed to be of the Ornstein-Zernike form,

$$\begin{aligned}\chi_q &= S(q,0)\\ &= \chi_0/(1 + q^2\xi_{\rm th}^2)\end{aligned} \tag{5.14}$$

The ξ_{th} is the thermal correlation length and grows on approaching to thermodynamic instability points. To account for the q-dependence of χ_q the gradient term ($\propto (\nabla\phi_L)^2$) in the free energy, which has been neglected so far, should be added to the mixing free energy. This generalization simply amounts to replacing $\partial^2 f/\partial\phi_L^2$ in (5.6) etc. by $k_B T/\chi_q$, which obviously indicates

$$\chi_0 = \lim_{q\to 0}\chi_q = k_B T/(\partial^2 f/\partial\phi_L^2) = k_B T\phi_L/(\partial\pi/\partial\phi_L) \tag{5.15}$$

The Laplace transformation (or the one-sided Fourier transformation) with respect to time is written as

$$\widehat{S}(q,\omega) = \int_0^\infty dt e^{-i\omega t} S(q,t) \ , \tag{5.16}$$

which is analytic for Im$\omega < 0$. The so-called dynamic structure factor $S(q,\omega)$ is then given by

$$S(q,\omega) = \int_{-\infty}^\infty dt e^{-i\omega t} S(q,t) = 2\mathrm{Re}[\widehat{S}(q,\omega)] \ , \tag{5.17}$$

where ω is supposed to be real.

In Appendix A, $\widehat{S}(q,\omega)$ is calculated to have the following form,

$$\widehat{S}(q,\omega) = \chi_q[1 + M^*(\omega)q^2]/[i\omega(1 + M^*(\omega)q^2) + \Gamma_q] \ , \tag{5.18}$$

where Γ_q is the usual thermal decay rate without the viscoelastic effect,

$$\begin{aligned}\Gamma_q &= k_B T L_0 q^2/\chi_q\\ &= D_m q^2(1 + \xi_{th}^2 q^2) \ ,\end{aligned} \tag{5.19}$$

where $D_m = L_0(\partial^2 f/\partial\phi_L^2)$ as given by (3.24). In this paper we consider very viscous systems and neglect the mode-coupling contribution to the thermal decay rate [39]. The $M^*(\omega)$ is defined by

$$M^*(\omega) = \frac{4}{3}L_0\alpha^2\eta^*(\omega) = \xi_{ve}^2\eta^*(\omega)/\eta^*(0) \ , \tag{5.20}$$

where ξ_{ve} is defined by (5.7) and is expressed as (5.9). In the real time representation $S(q,t)$ satisfies the following non-Markovian equation,

$$\dot{S}(q,t) + \Gamma_q S(q,t) + (q^2\xi_{ve}^2/\eta)\int_0^t dt' G(t - t')\dot{S}(q,t') = 0 \ , \tag{5.21}$$

where $\dot{S}(q,t) = \partial S(q,t)/\partial t$. This formula seems to be useful for numerical analysis.

We should also note here that our phenomenological equations cannot describe small-scale motions on the scale of the tube radius d_T [23]. Therefore, the wave number q must satisfy

$$q << 1/d_T \tag{5.22}$$

in our theory in this present form. In semidilute solutions this condition is replaced by $q << 1/\xi_b$, where ξ_b is the blob size.

Previously use has been made of the single-relaxation approximation [29, 30, 40], which assumes

$$\eta^*(\omega) = \eta/[1 + i\omega\tau] \tag{5.23}$$

We may obtain $S(q, \omega)$ in these references from (5.18) by using the above form and taking the real part. In this case $S(q, t)$ is a superposition of two exponential functions,

$$S(q, t)/\chi_q = A_s \exp(-\Gamma_s t) + (1 - A_s) \exp(-\Gamma_f t) \tag{5.24}$$

See Appendix B for Γ_s and Γ_f. Amis and Han first reported that $S(q, t)$ consists of rapidly and slowly decaying components [39]. Afterwards Adam and Delsanti analyzed their light scattering data using the above approximation [38]. Now further data analysis is needed on the basis of the general formula (5.18).

We then examine characteristic features in the relaxation of $S(q, t)$ noting that, in an intermediate frequency range, $1/\tau \lesssim \omega \lesssim 1/\tau_e, \eta^*(\omega)$ behaves as

$$\eta^*(\omega)/\eta^*(0) \cong C_0 (i\omega\tau)^{-\beta} \tag{5.25}$$

This implies $G(t) \propto t^{-1+\beta}$ for $\tau_e \lesssim t \lesssim \tau$. Experiments indicate that $\beta = 0.6 \sim 0.8$ and $C_0 \sim 1$ [23, 27]. The reptation theory [23] shows that τ_e is the time of segment diffusion over the distance of the tube radius d_T. Here we are supposing $qd_T \ll 1$ in (5.22) and hence $S(q, t)$ does not decay appreciably for $t \lesssim \tau_e$ [42].

(i) *Slow thermal relaxation.* In the limit $\Gamma_q \to 0$ we have $\widehat{S}(q, \omega) = \chi_q/i\omega$ from (5.18) and find no relaxation of $S(q, t)$. Therefore, for sufficiently small Γ_q, the decay of $S(q, t)$ should be slower than τ and the ω-dependence of $\eta^*(\omega)$ can be neglected, so

$$\widehat{S}(q, \omega) \cong \chi_q/[i\omega + \widetilde{\Gamma}_q] \quad, \tag{5.26}$$

and $S(q, t) \propto \exp(-\widetilde{\Gamma}_q t)$, where the modified decay rate $\widetilde{\Gamma}_q$ is

$$\begin{aligned}
\widetilde{\Gamma}_q &= (1 + \xi_{ve}^2 q^2)^{-1} \Gamma_q \\
&= D_m q^2 (1 + \xi_{th}^2 q^2)/(1 + \xi_{ve}^2 q^2)
\end{aligned} \tag{5.27}$$

This result is consistent with (5.8), where $q\xi_{th} \ll 1$ was assumed. The above expression is valid only when

$$\tau \widetilde{\Gamma}_q \ll 1 \tag{5.28}$$

In semidilute solutions with good solvent, however, we always have $\widetilde{\Gamma}_q \cong \Gamma_q$ under (5.28) because [38]

$$(\xi_{ve} q)^2/\tau\Gamma_q \sim G_e / \left(\phi^2 \frac{\partial^2 f}{\partial \phi^2} \right) \ll 1 \qquad \text{for} \qquad q\xi_b \lesssim 1 \tag{5.29}$$

Namely, the viscoelastic correction is small for good solvents. On the other hand, it can be apparent close to the critical point or the so-called spinodal point, because $\Gamma_q \tau \ll 1$ holds there in a wide region of q. Polymer blends can be suitable to detect the modified exponential relaxation (5.26), because criticality can be approached with the entanglement density held fixed in melts (which it is not possible for polymer + solvent systems).

(ii) *Rapid thermal relaxation and long wavelength.* Next we assume $\tau\Gamma_q \gg 1$. Furthermore, if $\xi_{ve} q$ is sufficiently small, we have $\widehat{S}(q, \omega) \cong \chi_q/[i\omega + \Gamma_q]$ for $\omega \sim \Gamma_q^*$. Using (5.25) the upper bound of $\xi_{ve} q$ for this condition is obtained as

$$\xi_{ve} q \ll (\tau\Gamma_q)^{\beta/2} \tag{5.30}$$

In this case we also find $\widehat{S}(q,\omega) \cong \chi_q(1 + M^*(\omega)q^2)/\Gamma_q$ for $\omega \ll \Gamma_q$. Combining these two results we devise the following approximate expression,

$$S(q,t)/\chi_q \cong \exp(-\Gamma_q t) + (\xi_{\text{ve}}^2 q^2/\Gamma_q \eta)G(t) \quad , \tag{5.31}$$

which is valid under $\tau\Gamma_q \gg 1$ and (5.30). Here the first and second terms represent the short-time and long-time relaxations, respectively. Note that the second term is of order $\xi_{\text{ve}}^2 q^2/\tau\Gamma_q$ at $t \sim \tau$, which is smaller than 1 in the present case. In semidilute solutions this case will be realized in most realistic conditions of light scattering experiments. The second term of (5.31) is of the order of the shear modulus divided by the bulk modulus and again very small in good solvents from (5.29).

(iii) *Rapid thermal relaxation and short wavelength.* When $\tau\Gamma_q \gg 1$ and $\xi_{\text{ve}}q \gg (\tau\Gamma_q)^{\beta/2}$, we have $| M^*(\omega)q^2 | \gg 1$ for most ω of interest. In this case we find

$$\widehat{S}(q,\omega) \cong \chi_q/[i\omega + (\Gamma_q/\xi_{\text{ve}}^2 q^2)\eta^*(0)/\eta^*(\omega)] \tag{5.32}$$

The resultant relaxation of $S(q,t)$ is very complicated. Interestingly, this kind of relaxation functions has been studied extensively in connections with glass transitions [43]. Furthermore, if $\omega\tau \gg 1$, (5.25) indicates

$$\widehat{S}(q,\omega) \cong \chi_q/[i\omega + A(i\omega)^\beta] \quad , \tag{5.33}$$

where $A = \Gamma_q \tau^\beta/(C_0 \xi_{\text{ve}}^2 q^2)$. The initial decay is then of the form,

$$S(q,t)/\chi_q = 1 - \Gamma(2 - \beta)^{-1}At^{1-\beta} + \cdot \quad , \tag{5.34}$$

which is valid for $At^{1-\beta} \lesssim 1$. The above decay looks like that of a stretched exponential function at short times. For $At^{1-\beta} \gtrsim 1$ and $t \lesssim \tau$, we find a power-law decay [43],

$$\begin{aligned} S(q,t)/\chi_q &\cong \Gamma(\beta)^{-1}A^{-1}t^{-(1-\beta)} \\ &\cong (\xi_{\text{ve}}^2 q^2/\Gamma_q \eta)G(t) \quad , \end{aligned} \tag{5.35}$$

which coincides with the second term of (5.31). For very large $t(\gg \tau)$, the decay will be exponential if the pole of the right hand side of (5.32) closest to the real axis is distinctly separated from the others.

Finally we note that the power-law (5.25) holds over a very wide region of ω in gelling solutions at the sol-gel transition [44]. We believe that the general formula (5.18) is still valid even for gelling solutions. In this case (5.31) and (5.35) show $S(q,t) \propto t^{-(1-\beta)}$ over a very wide region of t. This power-law behavior has already been observed by dynamic light scattering [45, 46].

6. Coupled dynamic equations and response to weak shear.

In the previous section we have derived the non-Markovian linear equation (5.6) for $\delta\phi_{\text{L}}$. The origin of the memory is the slow viscoelastic response and the time-correlation function $S(q,t)$ generally exhibits very complicated behavior. In this section we assume that the stress deviation is governed by the Maxwell model (2.25) with single relaxation time τ. We may then clarify the underlying physics in more depth and perform unambiguous calculations, although

the model should be too much simplified. We suppose a macroscopic flow $v(r)$ with small velocity gradients in the Newtonian regime,

$$\dot{\gamma}\tau << 1 \quad , \tag{6.1}$$

where $\dot{\gamma}$ is the shear rate. We are interested in the linear response of the steady state structure factor against the flow, because it can be detected by scattering experiments, and hence we linearize the dynamic equations to follow.

The equation for ϕ_L is given by (4.18) and that for the stress deviation $\delta\sigma$ from the equilibrium value is obtained from (2.25) in the form,

$$\left(\frac{\partial}{\partial t} + v\cdot\nabla\right)\delta\sigma - (\nabla v)^\dagger\cdot\delta\sigma - \delta\sigma\cdot\nabla v = G_e\kappa^{(T)} - \tau^{-1}\delta\sigma \quad , \tag{6.2}$$

where $\kappa^{(T)} = \{\kappa_{ij}^{(T)}\}$ is the velocity gradient tensor for the tube velocity and may be expressed as (4.22). Hereafter we neglect the fluctuations of the mean velocity v and equate it to the macroscopic flow. In steady states without any inhomogeneities, we would have $\delta\sigma = \eta\kappa$ with $\eta = G_e\tau$. If the composition fluctuates, however, G_e and τ deviate from their spatial averages by

$$\delta G_e = \left(\frac{\partial G_e}{\partial \phi_L}\right)\delta\phi_L \quad , \tag{6.3}$$

$$\delta\tau = \left(\frac{\partial \tau}{\partial \phi_L}\right)\delta\phi_L \tag{6.4}$$

Then it is convenient to set up the linearized equation for Z introduced by (5.2),

$$\left(\frac{\partial}{\partial t} + v\cdot\nabla\right)Z = \tau^{-1}(\kappa:\nabla\nabla)\delta\eta - \tau^{-1}Z + \frac{4}{3}G_e\phi_S\phi_L\alpha\nabla^2(\nabla\cdot w) \quad , \tag{6.5}$$

where $\kappa = \{\kappa_{ij}\}$ is the average velocity gradient tensor,

$$\kappa_{ij} = \frac{\partial}{\partial x_i}v_j + \frac{\partial}{\partial x_j}v_i \quad , \tag{6.6}$$

$\kappa:\nabla\nabla = \sum_{i,j}\kappa_{ij}\partial^2/\partial x_i\partial x_j$, and $\delta\eta$ is the viscosity deviation,

$$\delta\eta = G_e\delta\tau + \tau\delta G_e = \left(\frac{\partial}{\partial \phi_L}\eta\right)\delta\phi_L \tag{6.7}$$

Use has been made of the relation,

$$\nabla\nabla: [v\cdot\nabla\delta\sigma - (\nabla v)^T \delta\sigma - \delta\sigma\cdot\nabla v] = (v\cdot\nabla)Z \quad , \tag{6.8}$$

which holds for incompressible flows with homogeneous gradients.

Now, by expressing $\nabla\cdot w$ in terms of $\delta F/\delta\phi_L$ and Z, we obtain the desired coupled equations,

$$\frac{\partial}{\partial t}\delta\phi_L = -(v\cdot\nabla)\delta\phi_L + L_0[\nabla^2\frac{\delta F}{\delta\phi_L} - \alpha Z] \quad , \tag{6.9}$$

$$\frac{\partial}{\partial t}Z = -v\cdot\nabla Z + \tau^{-1}\left(\frac{\partial\eta}{\partial\phi_L}\right)\left(\kappa:\nabla\nabla\right)\delta\phi_L$$
$$- \left(\frac{4}{3}L_0G_e\alpha\right)\nabla^2(\nabla^2\frac{\delta F}{\delta\phi_L} - \alpha Z) - \tau^{-1}Z \quad , \tag{6.10}$$

where L_0 and ξ_{ve} are defined by (5.3) and (5.7), respectively. The first term on the right hand side of (6.9) and the first two terms on the right hand side of (6.10) arise from the macroscopic flow. If these terms are neglected, elimination of Z yields (5.6) with (5.23) after the Fourier transformation in time. In principle, we may calculate the time-evolution of any small deviations of the composition and the stress with these equations.

To calculate the steady state structure factor $I_q = <| \phi_q |^2>$ we should treat (6.9) and (6.10) as Langevin equations by adding random source terms on the right hand sides. They satisfy the fluctuation-dissipation relations and ensure the equilibrium distribution of $\delta\phi_L$ and Z for $v = 0$. In Appendix B the linear deviation of I_q from its equilibrium value χ_q will be calculated to first order in κ_{ij} in the form,

$$I_q/\chi_q - 1 \cong \frac{1}{2\Gamma_q} \left(\sum_{i,j} \kappa_{ij} q_i q_j \right) \left[-\frac{1}{\xi_{th}^{-2} + q^2} + A_{ve}(q)\xi_{ve}^2 \right] \ , \tag{6.11}$$

where Γ_q is the thermal decay rate (5.19), ξ_{th} is the thermal correlation length defined by (5.14), and ξ_{ve} is the viscoelastic length defined by (5.7). For the simple shear flow we have $\sum_{i,j} \kappa_{ij} q_i q_j = 2\dot{\gamma}q_x q_y$. The term proportional to ξ_{ve}^2 arises from the viscoelastic effect and the coefficient is

$$A_{ve}(q) = \left[\frac{-(q\xi_{th})^2}{1 + (q\xi_{th})^2} + \frac{3}{4}(\alpha\eta)^{-1}\frac{\partial\eta}{\partial\phi_L} + 2\tau\tilde{\Gamma}_q \right] \frac{1}{1 + \tau\tilde{\Gamma}_q} \ , \tag{6.12}$$

where $\tilde{\Gamma}_q$ is the modified decay rate (5.27). The $A_{ve}(q)$ is typically of order 1 for any q unless $N_1 \cong N_2$. For example, $A_{ve}(0) \sim 5$ in polymer + solvent systems. Thus, the intensity deviation consists of the usual part, which is well-known for near-critical fluids with low molecular weight [47], and the viscoelastic part ($\propto \xi_{ve}^2$). These two contributions have the different sign and the ratio of their amplitudes is crudely of order ξ_{th}^2/ξ_{ve}^2.

In semidilute solutions with θ solvent we find $\xi_{th}^2/\xi_{ve}^2 \sim \eta_s(T_c - T_s)/\eta(T - T_s)$ from (5.12) and the Flory-Huggins theory [22], where T_c is the critical temperature and T_s is the so-called spinodal temperature. If T is not close to T_s, the viscoelastic contribution can dominate over the usual one giving rise to abnormal scattering patterns as clearly demonstrated by Wu et al [14] in their light scattering experiment in the flow-shear ($q_x - q_y$) plane. Moreover, they have reported two maxima of the intensity in the plane at very small q. However, (6.11) cannot well explain it, and calculations to nonlinear orders seem to be necessary if the maxima are real. On the other hand, the experiments in references [12] and [13] have been performed in the flow-vorticity ($q_x - q_z$) plane, so they have detected nonlinear effects of shear beyond the scope of this section. Very recently two groups have observed transient behavior of the structure factor after changing the shear rate in a step-wise manner in the Newtonian regime [48, 49]. They have shown that its relaxation is governed by the slower decay rat : Γ_s in (5.24) or in (B10) and (B11). Fuller's group has also detected large signals of form bi efringence and dichroism induced by shear [13, 49]. It then seems to be interesting to measure : cattering generally under oscillatory shear. Calculations of such time-dependent responses are straightforward from our model equations (6.9) and (6.10).

We give further supplementary comments in the following. The calculation of I_q has been much facilitated by the assumption of a single relaxation time. We conjecture that, even for general constitutive models, the form of (6.11) still holds with the order of magnitude of $A_{ve}(q)$ unchanged. In particular, we notice that the long wavelength limit $A_{ve}(0) = \lim_{q\to 0} A_{ve}(q)$ is model-independent as calculated in reference [16] for solutions. For $\tau\Gamma_q << 1$ and $q << \xi_{ve}^{-1}$,

the stress relaxes much more rapidly than $\delta\phi_L$, so

$$Z \cong \left(\frac{\partial\eta}{\partial\phi_L}\right)(\boldsymbol{\kappa}:\nabla\mathbf{V})\delta\phi_L \quad, \tag{6.13}$$

Then $\delta\phi_L$ obeys

$$\frac{\partial}{\partial t}\delta\phi_L \cong -v\cdot\nabla\,\delta\phi_L + L_0\left[\nabla^2\frac{\delta F}{\delta\phi_L} - \left(\alpha\frac{\partial\eta}{\partial\phi_L}\right)(\boldsymbol{\kappa}:\nabla\mathbf{V})\delta\phi_L\right] \quad, \tag{6.14}$$

which is of the same form as the equation by Helfand and Fredrickson [3]. Adding the random force term on the right hand side of (6.14), we readily obtain (6.11) with $A_{ve}(q)\xi_{ve}^2$ replaced by

$$A_{ve}(0)\xi_{ve}^2 = \frac{3}{4}(\alpha\eta)^{-1}\frac{\partial\eta}{\partial\phi_L}\xi_{ve}^2 = (N_e/\zeta_0)(\frac{1}{N_S} - \frac{1}{N_L})\phi_L\phi_S\frac{\partial\eta}{\partial\phi_L} \tag{6.15}$$

This result holds irrespectively of the detail of the constitutive equation. The positivity of $A_{ve}(0)$ is assured because η increases with increase of the longer component and $\partial\eta/\partial\phi_L > 0$.

Equation (6.14) shows that the effective diffusion constant is dependent on the direction $\hat{q} = \frac{1}{q}q$ as

$$D_{eff}(\hat{q}) = L_0\left[\frac{\partial^2 f}{\partial\phi_L^2} - \alpha\frac{\partial\eta}{\partial\phi_L}(\boldsymbol{\kappa}:\hat{q}\hat{q})\right] \quad, \tag{6.16}$$

which is minimized in the direction giving the maximum of $\boldsymbol{\kappa}:\hat{q}\hat{q}$. As a result, the viscoelastic contribution in (6.11) turns out to have the sign opposite to that of the usual normal contribution.

Finally we remark that a very analogous effect has recently been observed by small angle neutron scattering from stretched polymer gels with heterogeneities [50-52]. There, the scattering patterns closely resembles those from sheared polymer solutions. The origin is that density variations are induced around heterogeneities in the shear modulus from mechanical equilibrium and they give rise to a structure factor most enhanced in the stretched direction.

7. Compositional gradient induced in cone-and-plate rheometer.

To examine the composition gradient in the cone-and-plate rheometer [15, 16], let us take a spherical coordinate (r,θ,ϕ) with the origin located at the top of the cone and the reference axis for θ being the symmetry axis of the cone. We may assume that the velocity field is almost a simple shear flow; i.e., the velocity is in the direction of increasing ϕ, and the shear plane is normal to the direction of increasing θ. Hence nonvanishing stress components are given by

shear stress $\sigma_{r\theta} = \sigma_{\theta r}$ \hfill (7.1)

first normal stress difference $N_1 = \sigma_{\phi\phi} - \sigma_{\theta\theta}$ \hfill (7.2)

second normal stress difference $N_2 = \sigma_{\theta\theta} - \sigma_{rr}$ \hfill (7.3)

In the cone-and-plate geometry, these components are independent of the position. Thus the the radial component of (4.6) becomes

$$w_r = \frac{N_e}{\zeta}\left[\left(\frac{1}{N_S} - \frac{1}{N_L}\right)\left(2\sigma_{rr} - \sigma_{\theta\theta} - \sigma_{\phi\phi}\right)\frac{1}{r} + \left(\frac{1}{N_S\phi_S} + \frac{1}{N_L\phi_L}\right)\phi_S\phi_L\frac{\partial^2 f}{\partial\phi_L^2}\frac{\partial\phi_L}{\partial r}\right]$$

$$= -D_m\left[\frac{1}{\phi_L}\frac{\partial\phi_L}{\partial r} + g_r\right] \quad, \tag{7.4}$$

where

$$g_r = \frac{\left(\dfrac{1}{N_S} - \dfrac{1}{N_L}\right)\dfrac{\sigma_N}{r}}{\left(\dfrac{1}{N_S\phi_S} + \dfrac{1}{N_L\phi_L}\right)\phi_S\phi_L\dfrac{\partial^2 f}{\partial \phi_L^2}} \tag{7.5}$$

Here

$$\sigma_N = 2\sigma_{rr} - \sigma_{\theta\theta} - \sigma_{\phi\phi} = N_1 + 2N_2 \tag{7.6}$$

is a combination of the normal stress difference. For usual polymeric liquids, $N_1 + 2N_2$ is positive so that g_r is positive. Hence (7.4) indicates that if a homogeneous blend is sheared, the larger polymers migrate toward the center.

The physical origin of the migration is the same as that of the Weissenberg effect. For convenience, we shall explain this for polymer solutions. It is known that, when a polymer solutions is sheared in a cone-and-plate rheometer, a normal stress which tends to push the cone and plate apart is created. In the conventional rheology, this Weissenberg effect has been explained as follows. The shear flow elongates the polymer and creates a "hoop stress", a tensile force acting along the flow line. The hoop stress acts to move the liquid toward the center and tends to push the cone and plate apart. This explanation assumes that the liquid remains homogeneous. If we account for the difference in the velocity of polymer and solvent, the explanation has to be modified slightly. Since the hoop stress is transmitted by polymers, it will cause motion of polymers toward the center. In the usual polymer solutions, however, migration has not been observed. This is because concentration inhomogeneity created by the Weissenberg effect is suppressed by the thermodynamic force, or more specifically the osmotic pressure which opposed the concentration gradient.

The magnitude of the concentration gradient is therefore determined by two factors, one is the normal stress $\sigma_N = N_1 + 2N_2$, and the other is the osmotic compressibility $\partial\pi/\partial\phi$. In usual polymer solutions, $\partial\pi/\partial\phi$ is large (For example in polystyrene in toluene $\partial\pi/\partial\phi$ is of the order of 10^5Pa at $\phi = 0.1$) hence the concentration gradient created by the flow is small. On the other hand, for poor solvents, a significant concentration gradient should be observed.

In the case of polymer melts, strong compositional inhomogeneity is expected to be observed in the steady state because (i) the normal stress σ_N is much larger in polymer melts than in polymer solutions and (ii) $\partial\pi/\partial\phi$ is smaller in melts than in solutions. On the other hand, the time needed to reach the steady state becomes extremely long in polymer melts. The time may be estimated by ℓ^2/D_m, where ℓ is the characteristic length scale and D_m is the mutual diffusion constant. In polymer melts, D_m becomes very small. For polyethylene of molecular weight of 10^4, D_m is about 10^{-8} at 176 °C. Thus for $\ell = 1$ cm, the time can be 10^8 s $\sim$ 3 years! Hence the concentration inhomogeneity is negligible in the usual rheological experiment. On the other hand, since D_m is strongly dependent on temperature, molecular weight and added plasticizers, the effect can be observed by suitably designed experiments. For example, if one uses polyethylene of 10^3, and can measure the concentration difference of $\ell = 1$ mm, the time required would be 10^4 s $\sim$ 3 hours. Furthermore the time can be shortened if the temperature is raised.

8. Concluding remarks.

We have shown that there is a coupling between stress and diffusion in polymer solutions and blends. The origin is that the stress in entangled polymer systems is not acting equally on each component and, if there is an imbalance in stress, relative motion between the longer and

shorter chains takes place. We have proposed a set of phenomenological equations describing the coupling as a generalization of the earlier theories, the two fluid model in polymer solutions and the Brochard theory for mutual diffusion in polymer blends. Our equations include those proposed previously as special cases.

As applications of the present theory, we have studied (i) the viscoelastic effect in the compositional fluctuations near equilibrium, (ii) change in the structure factor under shear flow, and (iii) compositional inhomogeneity produced in the cone-and-plate rheometer. In particular, we stress that our expression for the dynamic structure factor (5.18) is very general and can be used to explain the power-law relaxation at the sol-gel transition as discussed at the end of section 5. In these problems, the effect of the coupling is suppressed if the osmotic rigidity $\partial\pi/\partial\phi_L$ is increased as in semidilute solutions with good solvent. On the other hand, enhanced effects of the coupling exist near the critical point of phase separation in polymer blends, where $\partial\pi/\partial\phi_L$ becomes very small. There, critical slowing-down and entanglements can both play important roles and experiments to elucidate their interplay seem to be challenging, although experiments in blends have to overcome difficulty arising from very slow diffusion.

The present theory is essentially a phenomenological one, and involves various assumptions. Our major assumptions are that the isotropic part of the network stress is zero and that the entanglement network is common to all polymers participating the entanglement and moves with Brochard's tube velocity. They are placed mainly because they provide us the simplest theory consistent with the existing molecular models and the experimental results, but of course their validity has to be checked in future study. At the same time, there are various possibilities of other generalizations, which may be pursued also. The advantage of the present scheme is that all the parameters involved can be determined by independent measurements of diffusion and viscoelasticity. We thus hope that our predictions will be checked experimentally.

Shear-induced phase separation in polymer blends is a future problem to be investigated. It will occur even in homolog polymer blends consisting of chemically equivalent long and short chains as pointed out in reference [16]. This is not surprising if we notice that long and short chains can have tendency of segregation under unequal deformations in shear flow. In such cases the phase separation is of purely mechanical origin. To detect it, informative will be neutron scattering experiments from sheared polymer blends in which one species is deuterated.

Note added in proof.

After this paper has been accepted, we have noticed a theory of dynamic light scattering from polymer solutions : Wang C.H., *J. Chem. Phys.* **95** (1991) 3788. However, his two-fluid model uses ∇v in the constitutive equation leading to results essentially different from ours. We believe that ∇v_p should appear instead of ∇v in the constitutive equation (2.34).

Appendix. A.

Following reference [29] we apply small, fictitious external fields to the polymer blend. The change in the free energy is

$$\delta F_{\text{ext}} = \int dr(\delta\rho_L U_L + \delta\rho_S U_S)$$

$$\cong \int dr\rho(U_L - U_S)\delta\phi_L \ , \tag{A1}$$

where the total density $\rho = \rho_L + \rho_S$ is assumed to be a constant. Then the forces on the long and short polymers are $-\rho_L \nabla U_L$ and $-\rho_S \nabla U_S$, respectively, and they should be added to the right hand sides of (4.12) and (4.13). As a result the expression for $w = v_L - v_S$, (4.6), is modified as

$$w = \frac{1}{\zeta}\phi_L\phi_S[-\nabla \mu + \alpha \nabla \cdot \sigma^{(n)} - \rho \nabla (U_L - U_S)] \tag{A2}$$

We hereafter assume that $U_L - U_S \propto \exp(iq \cdot r + i\omega t)$ in space and time. Using (5.5) we arrive at

$$\left[i\omega + L_0 q^2 \left(\frac{\partial^2 f}{\partial \phi_L^2} + \frac{4}{3}i\omega\alpha^2\eta^*(\omega)\right)\right]\delta\phi_L = -\rho L_0 q^2(U_L - U_S) \tag{A3}$$

On the other hand, the general linear response theory [53] indicates

$$\delta\phi_L = -\left(\frac{\rho}{k_B T}\right)[\chi_q - i\omega\widehat{S}(q,\omega)](U_L - U_S) \ , \tag{A4}$$

where χ_q and $\widehat{S}(q,\omega)$ are given by (5.14) and (5.16). Comparison of (A3) and (A4) yields

$$-i\omega\widehat{S}(q,\omega) + \chi_q = k_B T L_0 q^2/[i\omega + L_0 q^2 k_B T/\chi_q + \frac{4}{3}i\omega\alpha^2\eta^*(\omega)] \tag{A5}$$

Here, $\partial^2 f/\partial\phi_L^2$ has been replaced by $k_B T/\chi_q$ and, as a result, the both hand sides of (A5) tend to χ_q as $\omega \to 0$. Some manipulations readily lead to (5.18). We also notice that taking the imaginary part of (A5) gives a formula for the dynamic structure factor $S(q,\omega)$ used in references [29] and [30].

Appendix. B.

We Fourier-transform (6.9) and (6.10) , add the random source terms, θ_1 and θ_2, and obtain

$$\frac{\partial}{\partial t}\phi_q = a_1 - h_{11}\phi_q - h_{12}Z_q + \theta_1 \ , \tag{B1}$$

$$\frac{\partial}{\partial t}Z_q = a_2 - h_{21}\phi_q - h_{22}Z_q + \theta_2 \ , \tag{B2}$$

where

$$h_{11} = L_0 k_B T q^2/\chi_q = \Gamma_q \ , \tag{B3}$$

$$h_{12} = L_0\alpha \ , \tag{B4}$$

$$h_{21} = \frac{4}{3}G_e\alpha q^2\Gamma_q \ , \tag{B5}$$

$$h_{22} = \tau^{-1}(1 + \xi_{ve}^2 q^2) \tag{B6}$$

The a_1 and a_2 arise from the macroscopic flow. For example, for the simple shear flow, we obtain

$$a_1 = \dot{\gamma} q_x \frac{\partial}{\partial q_y} \phi_q \quad , \tag{B7}$$

$$a_2 = \dot{\gamma} \left[q_x \frac{\partial}{\partial q_y} Z_q - \tau^{-1} \left(\frac{\partial \eta}{\partial \phi_{\rm L}} \right) q_x q_y \phi_q \right] \tag{B8}$$

The vector $\mathbf{x} = (\phi_q, Z_q)$ then obeys in an abbreviated form,

$$\frac{\partial}{\partial t} x_i = a_i - \sum_{j=1}^{2} h_{ij} x_j + \theta_i \tag{B9}$$

There arise two decay rates, $\Gamma_{\rm s}$ and $\Gamma_{\rm f}$, determined as the eigenvalues of the matrix $\mathbf{H} = \{h_{ij}\}$, which appear in (5.24) and satisfy

$$\Gamma_{\rm s} + \Gamma_{\rm f} = {\rm Tr}\mathbf{H} = \Gamma_q + \tau^{-1}(1 + \xi_{\rm ve}^2 q^2) \quad , \tag{B10}$$

$$\Gamma_{\rm s}\Gamma_{\rm f} = {\rm Det}\mathbf{H} = \Gamma_q \tau^{-1} \tag{B11}$$

In particular, for $\Gamma_{\rm s} \ll \Gamma_{\rm f}, \Gamma_{\rm s}$ is obtained in the form,

$$\Gamma_{\rm s} \cong \Gamma_q / [\tau\Gamma_q + 1 + \xi_{\rm ve}^2 q^2] \quad , \tag{B12}$$

In equilibrium (without a_1 and a_2) the distribution of ϕ_q and that of Z_q are independently Gaussian with variances, $<\mid \phi_q \mid^2> = \chi_q$ and $<\mid Z_q \mid^2> = C_q$, where

$$C_q = \frac{4}{3} G q^4 \tag{B13}$$

The above relation (B13) is obtained from the definition (5.2) and from the fact that the deviatopic part of the stress fluctuations has a variance proportional to G. If we rewrite the right hand sides of (B1) and (B2) in terms of the thermodynamic forces, $f_1 = \chi_q^{-1}\phi_q$ and $f_2 = C_q^{-1} Z_q$, the coefficients in front of them (or h_{ij} multiplied by χ_q or C_q) are the so-called Onsager kinetic coefficients L_{ij}. They are

$$L_{11} = \Gamma_q \chi_q = L_0 k_{\rm B} T q^2 \quad , \tag{B14}$$

$$L_{12} = L_{21} = L_0 \alpha C_q \quad , \tag{B15}$$

$$L_{22} = \tau^{-1}(1 + \xi_{\rm ve}^2 q^2) C_q \tag{B16}$$

The reciprocity relation $L_{12} = L_{21}$ holds as ought to be the case. The variances of the noise terms are determined from the fluctuation-dissipation relations,

$$< \theta_i(q,t)\theta_j(q,t')^* > = 2L_{ij}\delta(t - t') \tag{B17}$$

In the presence of a_1 and a_2 in (B9) the variances $I_{ij} = < x_i x_j^* >$ in steady states satisfy $\partial I_{ij}/\partial t = 0$, so that

$$-\sum_{\ell=1}^{2} h_{i\ell} I_{\ell j} - \sum_{\ell=1}^{2} h_{j\ell} I_{\ell i} + 2L_{ij} + A_{ij} = 0 \quad , \tag{B18}$$

where

$$A_{ij} = <a_i x_j^*> + <a_j^* x_i> \tag{B19}$$

In equilibrium $(A_{ij} = 0)$ the above relations are surely satisfied for $I_{11} = \chi_q, I_{22} = C_q$, and $I_{12} = 0$. For $A_{ij} \neq 0$ the deviation δI_{ij} can be obtained in the form,

$$\delta I_{ij} = \frac{1}{2}(\Gamma_s + \Gamma_f)^{-1}[A_{ij} + \Gamma_s\Gamma_f \sum_{\ell,m} h^{i\ell}A_{\ell m}h^{jm}] \ , \tag{B20}$$

where $\mathbf{H}^{-1} = \{h^{ij}\}$ is the inverse matrix of $\mathbf{H}$, and Γ_s and Γ_f are determined by (B10) and (B11). In particular, the deviation $\delta I_q = \delta I_{11}$ of the density fluctuations may be expressed as

$$\delta I_q = \frac{1}{2}(\Gamma_s + \Gamma_f)^{-1}[A_{11} + \frac{1}{\Gamma_s\Gamma_f}(h_{22}^2 A_{11} + h_{12}^2 A_{22} - 2h_{12}h_{22}A_{12})] \tag{B21}$$

We may calculate A_{ij} from (B7) and (B8) and then obtain (6.11) for the simple shear flow. Furthermore it is readily checked that (6.11) still holds for general incompressible, homogeneous flows.

In addition we note that our model readily confirms the general form (5.18) for the time-correlation function as a special case. In fact, from (B9) the time-correlation functions $<x_i(t)x_j(0)^*>$ in equilibrium satisfy

$$\frac{\partial}{\partial t}<x_i(t)x_j(0)^*> = -\sum_\ell h_{i\ell}<x_\ell(t)x_j(0)^*> \tag{B22}$$

The Laplace transformation of (B22) and some manipulations lead to (5.18).

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