functionality from the single amine-cured epoxies might account for the gross difference in the deformation behavior. The amount of the elongation along the amine direction exceeds the macroscopic strain slightly. The amine chain occupies only part of the specimen volume, and the other part of the volume is occupied by the epoxy chains which is too rigid to be stretched. The scattering intensity of the first peak is enhanced along the stretch direction, an indication of the alignment of the amine chains along the stretch axis. After the deformation, the second peak remains unchanged in its position as well as its intensity. Neither reorientation nor elongation takes place along the epoxy linkages. It is noteworthy that the network structure of the epoxy cured with a mixture of two amines has not been completely resolved so far, let alone the mechanism of the network formation process. The interpretation regarding the possible formation of D-230 gel particles is rather speculative. Nevertheless, the deformation result demonstrates once again the deformability of the amine chains and the rigidity of the epoxy linkages.

Another phenomenon commonly observed in most of the scattering results of the deformed samples was a decrease in the small-angle intensity in the stretch direction. Since there is no detailed molecular model available for the deformation process in epoxies or any highly cross-linked polymers, no interpretation can be attached to this finding.

In summary, the epoxies cured with di- or triamines with a narrow molecular weight distribution display an interesting deformation behavior; the flexible amine chains are preferentially aligned in the stretch direction without a significant increase in the length of the chains between the cross-links. The evidence supporting the chain alignment comes from the enhancement of the peak intensity in the stretch direction and the presence of the birefringence. For these samples containing the D-2000 diamine, the evidence of the alignment of the amine chain in the stretch direction is apparent; the changes in the intensity and the position of the scattering maximum all occurred at the q region corresponding to the average end to end distance of the amine chains. When the SANS results between the swollen sample and the solid-state deformed ones are compared the unfolding mechanism seems to operate in the later case; this is contrary to what the unfolding mechanism was originally proposed for. However, more data from other measuring techniques such as NMR are definitely needed before a definite model can be built.

All of the deformations were conducted at a temperature below the glass transition temperature of the samples. However, annealing above the glass transition temperature had no effect on the conformation of the chains in the deformed sample as judged by the scattering results.

The neutron scattering result of the swollen D-2000 cured epoxy clearly demonstrates the deformability of the flexible amine chains within the epoxy network. Furthermore, the scattering result of the cured epoxy sample made from mixed long and short amines suggest the importance of the topological connectivity on the deformation behavior for epoxies and possibly for other cross-linked polymers.

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Registry No. (DGEBA)(D-2000) (copolymer), 110302-44-8; (DGEBA)(T-403) (copolymer), 70548-69-5; neutron, 12586-31-1.

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On the Theory of Dynamic Screening in Macroparticle Solutions

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ABSTRACT: An analysis is presented of hydrodynamic screening in a suspension of mobile Brownian particles. It is shown that screening is a transient phenomenon which vanishes for stationary flows unless the particles interact so strongly that they form a rigid network of immobilized obstacles.

1. Introduction

In two earlier papers[1,2] we have analyzed the screening of hydrodynamic interactions in gels and porous media. The nonfluid parts of these systems were modeled as randomly distributed collections of interaction sites which scattered the flow of the solvent and thereby dissipated its energy. Because of the immobility of the matrix material the locations of the sites were permanently fixed.

It is natural to wonder whether similar screening effects will occur when the interaction sites are mobile, as are the solute particles in polymeric and macromolecular solutions and in concentrated suspensions. This problem has been addressed previously by a number of authors[3-13] but not in ways that we judge to be satisfactory. Although it is not our intention to present a systematic critique of these earlier studies, we do advise readers who peruse this literature to be wary of heuristic arguments which in different papers have led to diametrically opposed conclusions.

Several of the previous investigators[10-13] share the opinion that screening occurs for steady flows of solutions containing mobile particles, provided that the spatial inhomogeneities fall within specified ranges (characterized by certain values of the wave vector $\mathbf{q}$). In the present paper we analyze hydrodynamic screening for a simple model of a suspension. Our conclusion is that when the solute particles (hydrodynamic scattering sites) are mobile, screening is a transient phenomenon which ceases as the flow tends to stationarity.

The following section contains the mathematical details of our analysis. The third and final section is a brief discussion of results.

2. Theory of Dynamic Screening

We begin with an equilibrium system consisting of Brownian solute particles uniformly dispersed throughout an incompressible Newtonian fluid. At the time $t = 0$ an external field with force density $\mathbf{f}(\mathbf{r};t)$ is turned on. What we wish to determine is the effect of the solute particles on the flow generated by the action of this external field. For simplicity the Brownian particles will be treated as interacting material points which exert point frictional forces on the surrounding fluid.

The external force density is assumed to be of the form

$$\mathbf{f}(\mathbf{r};t) = \mathbf{F}(t)\delta(\mathbf{r} - \mathbf{R}_0) \tag{2.1}$$

with $\mathbf{R}_0$ a fixed point that does not coincide with the location of any solute particle. The motions of the Brownian particles ($i = 1, 2, ..., N$) are governed by the stochastic Langevin equations

$$M\ddot{\mathbf{R}}_i = \sum_j \mathbf{F}_{ij}(\mathbf{R}_i - \mathbf{R}_j) + \mathbf{K}_i(\dot{\mathbf{R}}_i,\mathbf{R}_i;t) + \mathbf{S}(\mathbf{R}_i;t) + \mathbf{E}(\mathbf{R}_i;t) \tag{2.2}$$

with M denoting the mass and $\mathbf{R}_i$ and $\dot{\mathbf{R}}_i$ the position and velocity of solute particle i. $\mathbf{F}_{ij}$ is the force on particle i due to its interaction with particle j, $\mathbf{E}(\mathbf{R}_i;t) = -\partial\phi(\mathbf{R}_i;t)/\partial\boldsymbol{R}_i$ is the force on i due to an external conservative field with potential ϕ and $\mathbf{S}$ is the "random" force which ensures that at equilibrium the solute particles and the solvent will share a common temperature. Finally, $\mathbf{K}_i$ is a frictional force,

$$\mathbf{K}_i(\dot{\mathbf{R}}_i,\mathbf{R}_i;t) = -\xi[\dot{\mathbf{R}}_i(t) - \mathbf{w}^*(\mathbf{R}_i(t);t)] \tag{2.3}$$

proportional to the phenomenological coefficient ξ. The symbol $\mathbf{w}^*(\mathbf{R}_i;t)$ appearing here is the "virtual" velocity of the fluid, that is, the flow velocity at the location of particle i calculated as if that one particle were absent but all others were placed at their instantaneous locations. This virtual flow field is determined by the expression

$$\mathbf{w}^*(\mathbf{R}_i,t) = \int_0^t \mathrm{d}t' \int \mathrm{d}\mathbf{r}'\ \boldsymbol{T}(\mathbf{R}_i-\mathbf{r}';t-t')\cdot [\mathbf{f}(\mathbf{r}';t') - \sum_{j\neq i}^{N} \mathbf{K}_j(\dot{\mathbf{R}}_j,\mathbf{R}_j;t')\delta[\mathbf{r}' - \mathbf{R}_j(t')]] \tag{2.4}$$

with $\boldsymbol{T}(\mathbf{r};t)$ denoting the time-dependent generalization of the Oseen tensor[1,9,14] which characterizes the flow of the solvent in response to an imposed force.

We now introduce

$$\hat{n}_i(\mathbf{r},t) = \delta[\mathbf{r} - \mathbf{R}_i(t)] \tag{2.5}$$

and

$$\hat{\mathbf{j}}_i(\mathbf{r},t) = \dot{\mathbf{R}}_i(t)\delta[\mathbf{r} - \mathbf{R}_i(t)] \tag{2.6}$$

the microscopic density and current of an individual Brownian particle. The total microscopic solute density and current are then

$$\hat{n}(\mathbf{r};t) = \sum_{i=1}^{N} \hat{n}_i(\mathbf{r};t) \tag{2.7}$$

and

$$\hat{\mathbf{j}}(\mathbf{r};t) = \sum_{i=1}^{N} \hat{\mathbf{j}}_i(\mathbf{r};t) \tag{2.8}$$

respectively. By combining (2.3) and (2.4) and using the definitions (2.5) and (2.6), we obtain the set of coupled equations

$$\hat{\mathbf{k}}_i(\mathbf{r};t) = -\xi\hat{\mathbf{j}}_i(\mathbf{r};t) + \xi\int_0^t \mathrm{d}t' \int \mathrm{d}\mathbf{r}'\ \boldsymbol{T}(\mathbf{r}-\mathbf{r}';t-t')\cdot [\mathbf{f}(\mathbf{r}';t') - \sum_{j\neq i}^{N} \hat{\mathbf{k}}_j(\mathbf{r}';t')]\hat{n}_i(\mathbf{r};t) \tag{2.9}$$

for the microscopic friction force densities,

$$\hat{\mathbf{k}}_i(\mathbf{r};t) \equiv \hat{n}_i(\mathbf{r};t)\mathbf{K}_i(\dot{\mathbf{R}}_i,\mathbf{R}_i;t) \tag{2.10}$$

The fluid velocity field generated by the external force density $\mathbf{f}(\mathbf{r};t)$ is related to these friction force densities by the formula

$$\hat{\mathbf{w}}(\mathbf{r};t) = \int_0^t \mathrm{d}t' \int \mathrm{d}\mathbf{r}'\ \boldsymbol{T}(\mathbf{r}-\mathbf{r}';t-t')\cdot[\mathbf{f}(\mathbf{r}';t') - \sum_{i=1}^{N} \hat{\mathbf{k}}_i(\mathbf{r}';t')] \tag{2.11}$$

This velocity field is a functional of the random force $\mathbf{S}$ which, in turn, depends on the positions and velocities of all the Brownian particles. These quantities are known only in a statistical sense, namely, in terms of appropriate probability distributions. Thus, our real concern is with the *average* response of the fluid to the external force, characterized by the average velocity field

$$\mathbf{W}(\mathbf{r};t) \equiv \langle\hat{\mathbf{w}}(\mathbf{r};t)\rangle = \int_0^t \mathrm{d}t' \int \mathrm{d}\mathbf{r}'\ \boldsymbol{T}(\mathbf{r}-\mathbf{r}';t-t')\cdot[\mathbf{f}(\mathbf{r}';t') - \sum_{i=1}^{N} \langle\hat{\mathbf{k}}_i(\mathbf{r}';t')\rangle] \tag{2.12}$$

The bracket $\langle\cdot\cdot\rangle$ appearing here indicates an average over all random variables related to the motion of the Brownian solute particles.

In order to compute the average flow field from formula 2.12 we must express the average frictional forces as functionals of the external force density. According to (2.9) these average forces are related to the force–density correlation functions by the formulas

$$\langle\hat{\mathbf{k}}_i(\mathbf{r};t)\rangle = -\xi\langle\hat{\mathbf{j}}_i(\mathbf{r};t)\rangle + \xi\int_0^t \mathrm{d}t' \int \mathrm{d}\mathbf{r}'\ \boldsymbol{T}(\mathbf{r}-\mathbf{r}';t-t')\cdot [\mathbf{f}(\mathbf{r}';t')\langle\hat{n}_i(\mathbf{r};t)\rangle - \sum_{j\neq i}^{N} \langle\hat{\mathbf{k}}_j(\mathbf{r}';t')\hat{n}_i(\mathbf{r};t)\rangle] \tag{2.13}$$

Equations 2.13 are the lowest order members of a hierarchy that can be generated by averaging (2.9) with products of single-particle microscopic densities.

To transform relationships 2.13 into a closed set of equations for the specific friction force densities, we introduce the simple mean-field approximation

$$\langle\hat{\mathbf{k}}_j(\mathbf{r}';t')\hat{n}_i(\mathbf{r};t)\rangle \doteq \langle\hat{\mathbf{k}}_j(\mathbf{r}';t')\rangle\langle\hat{n}_i(\mathbf{r};t)\rangle \tag{2.14}$$

and then linearize about the initial, uniform state of equilibrium. This linearization of the averaged fields is indicated as follows

$$\begin{aligned}\langle \hat{n}_i(\mathbf{r};t)\rangle &= V^{-1} + \delta n_i(\mathbf{r};t)\\ \langle \hat{\mathbf{j}}_i(\mathbf{r};t)\rangle &= \mathbf{0} + \delta\mathbf{j}_i(\mathbf{r};t)\\ \langle \hat{\mathbf{k}}_i(\mathbf{r};t)\rangle &= \mathbf{0} + \delta\mathbf{k}_i(\mathbf{r};t)\end{aligned} \tag{2.15}$$

with V denoting the volume of the system and δn_i, $\delta\mathbf{j}_i$, and $\delta\mathbf{k}_i$ the averaged distortions produced by the external force $\mathbf{f}(\mathbf{r};t)$. The mean-field approximation and linearization lead from (2.13) to the equations

$$\delta\mathbf{k}_i(\mathbf{r};t) = -\xi\delta\mathbf{j}_i(\mathbf{r};t) + \xi V^{-1}\int_0^t \mathrm{d}t' \int \mathrm{d}\mathbf{r}'\ \boldsymbol{T}(\mathbf{r}-\mathbf{r}';t-t')\cdot \left[\mathbf{f}(\mathbf{r}';t') - \sum_{j\neq i}^{N} \delta\mathbf{k}_j(\mathbf{r}';t')\right] \tag{2.16}$$

It is the total frictional force density,

$$\delta\mathbf{k}(\mathbf{r};t) = \sum_{i=1}^{N} \delta\mathbf{k}_i(\mathbf{r};t) \tag{2.17}$$

that is needed in eq 2.12. According to (2.16) this quantity satisfies the linear integral equation

$$\delta\mathbf{k}(\mathbf{r},t) = -\xi\delta\mathbf{j}(\mathbf{r},t) + \xi c\int_0^t \mathrm{d}t' \int \mathrm{d}\mathbf{r}'\ \boldsymbol{T}(\mathbf{r}-\mathbf{r}';t-t')\cdot [\mathbf{f}(\mathbf{r}';t') - (1 - 1/N)\delta\mathbf{k}(\mathbf{r}';t')] \tag{2.18}$$

wherein $\delta\mathbf{j}(\mathbf{r},t) = \sum_{i=1}^{N}\delta\mathbf{j}_i(\mathbf{r};t)$ and $c = N/V$. Because the number of Brownian solute particles is much greater than one, the integrand factor $(1 - 1/N)$ differs insignificantly from unity.

It is both convenient and natural to introduce the Fourier–Laplace transforms of $\delta\mathbf{k}(\mathbf{r};t)$ and $\mathbf{W}(\mathbf{r};t)$ and of the functions $\mathbf{f}(\mathbf{r};t)$ and $\boldsymbol{T}(\mathbf{r};t)$ to which they are related by eq 2.12 and 2.18. These integral transforms are defined as follows

$$\delta\tilde{\mathbf{k}}(\mathbf{q},\omega) = \int_0^\infty \mathrm{d}t\ e^{-i\omega t}\int \mathrm{d}\mathbf{r}\ e^{-i\mathbf{q}\cdot\mathbf{r}}\delta\mathbf{k}(\mathbf{r};t) \tag{2.19}$$

and the transforms of (2.18) and (2.12) are

$$\delta\tilde{\mathbf{k}}(\mathbf{q},\omega) = -\xi\delta\tilde{\mathbf{j}}(\mathbf{q};\omega) + \xi c\tilde{\boldsymbol{T}}(\mathbf{q};\omega)\cdot[\tilde{\mathbf{f}}(\mathbf{q},\omega) - \delta\tilde{\mathbf{k}}(\mathbf{q},\omega)] \tag{2.20}$$

and

$$\tilde{\mathbf{W}}(\mathbf{q},\omega) = \tilde{\boldsymbol{T}}(\mathbf{q},\omega)\cdot[\tilde{\mathbf{f}}(\mathbf{q},\omega) - \delta\tilde{\mathbf{k}}(\mathbf{q},\omega)] \tag{2.21}$$

respectively, with[1,9,14]

$$\tilde{\boldsymbol{T}}(\mathbf{q},\omega) = [\rho_0(i\omega + \nu_0 q^2)]^{-1}[\boldsymbol{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}] \tag{2.22}$$

Here ρ_0 is the mass density of the solvent, $\nu_0 = \eta_0/\rho_0$ its kinematic viscosity, and $\hat{\mathbf{q}} \equiv \mathbf{q}/q$.

It follows from (2.20) that

$$\delta\tilde{\mathbf{k}}(\mathbf{q},\omega) = -\xi\delta\tilde{\mathbf{j}}(\mathbf{q},\omega) + \frac{\xi c/\rho_0}{i\omega + \nu_0 q^2 + \xi c/\rho_0}[\boldsymbol{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}]\cdot [\tilde{\mathbf{f}}(\mathbf{q},\omega) + \xi\delta\tilde{\mathbf{j}}(\mathbf{q},\omega)] \tag{2.23}$$

Consequently, the averaged flow velocity can be written in the form

$$\tilde{\mathbf{W}}(\mathbf{q};\omega) = \tilde{\boldsymbol{T}}_{\mathrm{SC}}(\mathbf{q};\omega)\cdot[\tilde{\mathbf{f}}(\mathbf{q},\omega) + \xi\delta\tilde{\mathbf{j}}(\mathbf{q};\omega)] \tag{2.24}$$

with

$$\tilde{\mathbf{T}}_{\mathrm{SC}}(\mathbf{q},\omega) = [i\rho_0\omega + \eta_0 q^2 + \xi c]^{-1}[\boldsymbol{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}] \tag{2.25}$$

denoting the Fourier–Laplace transform of the screened (SC) Oseen tensor. This tensor is the response function of the Navier–Stokes–Brinkman[1-3] equation for flow through porous media.

The averaged total solute current $\delta\tilde{\mathbf{j}}(\mathbf{q},\omega)$ which appears in (2.24) is itself a functional of the external force density $\tilde{\mathbf{f}}(\mathbf{q},\omega)$. To determine this functional relationship an equation of motion must be constructed for the current of the Brownian solute particles. This we do by returning to the equations of motion, (2.2), from which it follows that

$$M\partial_t\hat{\mathbf{j}}(\mathbf{r};t) + \nabla_{\mathbf{r}}\cdot\hat{\sigma}(\mathbf{r};t) = \hat{\mathbf{s}}(\mathbf{r},t) + \hat{\mathbf{k}}(\mathbf{r},t) + \hat{\mathbf{e}}(\mathbf{r},t) \tag{2.26}$$

Here $\hat{\mathbf{k}}(\mathbf{r},t)$ is the total friction force density defined by (2.17). The quantities

$$\hat{\mathbf{s}}(\mathbf{r},t) = \mathbf{S}(\mathbf{r};t)\hat{n}(\mathbf{r},t) \tag{2.27a}$$

and

$$\hat{\mathbf{e}}(\mathbf{r},t) = \mathbf{E}(\mathbf{r};t)\hat{n}(\mathbf{r},t) \tag{2.27b}$$

are the densities of the random and external forces, respectively. Finally, the microscopic osmotic stress tensor $\hat{\sigma}$ is the sum of a kinetic part

$$\hat{\sigma}_{\mathrm{kin}}(\mathbf{r},t) = M\sum_{i=1}^{N} \dot{\mathbf{R}}_i(t)\dot{\mathbf{R}}_i(t)\delta[\mathbf{r} - \mathbf{R}_i(t)] \tag{2.28}$$

and a potential part

$$\hat{\sigma}_{\mathrm{pot}}(\mathbf{r},t) = -\tfrac{1}{2}\int \mathrm{d}\mathbf{r}'\ \frac{(\mathbf{r} - \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}F(|\mathbf{r} - \mathbf{r}'|)\hat{n}(\mathbf{r};t)\hat{n}(\mathbf{r}';t) \tag{2.29}$$

wherein $F(|\mathbf{r} - \mathbf{r}'|)$ denotes the magnitude of the two-body, central force $\mathbf{F}(\mathbf{r},\mathbf{r}') = \mathbf{F}(\mathbf{r}-\mathbf{r}')$.

The Fourier–Laplace transform of the average of eq 2.26 is

$$Mi\omega\delta\tilde{\mathbf{j}}(\mathbf{q},\omega) + i\mathbf{q}\cdot\tilde{\sigma}(\mathbf{q},\omega) = \delta\tilde{\mathbf{k}}(\mathbf{q},\omega) + \delta\tilde{\mathbf{e}}(\mathbf{q},\omega) \tag{2.30}$$

with

$$\delta\tilde{\mathbf{e}}(\mathbf{q},\omega) = c\tilde{\mathbf{E}}(\mathbf{q},\omega) = -ic\mathbf{q}\tilde{\phi}(\mathbf{q},\omega) \tag{2.31}$$

denoting the Fourier–Laplace transform of the linearized form (cf. eq 2.15) of $\mathbf{e}(\mathbf{r},t) = \mathbf{E}(\mathbf{r};t)[c + \delta n(\mathbf{r},t)]$. To obtain eq 2.30 we also have set the average of the random force density equal to zero (viz., $\tilde{\mathbf{s}}(\mathbf{q},\omega) = \langle\hat{\mathbf{s}}(\mathbf{q},\omega)\rangle = 0$) and used the symbol $\tilde{\sigma}$ for the transform,

$$\tilde{\sigma}(\mathbf{q},\omega) = \langle\hat{\sigma}(\mathbf{q},\omega)\rangle \tag{2.32}$$

of the averaged osmotic stress tensor. In the remainder of this paper it is assumed that this average stress tensor can be represented by the Newtonian form

$$\sigma(\mathbf{r};t) = \boldsymbol{I}\pi(\mathbf{r};t) - M\nu_{\mathrm{B}}[\nabla_{\mathbf{r}}\delta\mathbf{j}(\mathbf{r};t) + (\nabla_{\mathbf{r}}\delta\mathbf{j}(\mathbf{r};t))^T - \tfrac{2}{3}\boldsymbol{I}\nabla_{\mathbf{r}}\cdot\delta\mathbf{j}(\mathbf{r};t)] \tag{2.33}$$

with $\pi(\mathbf{r};t)$ a nonequilibrium analogue of the osmotic pressure that depends only on the solute concentration $c = c(\mathbf{r},t)$ [so that $\nabla_{\mathbf{r}}\pi = (\partial\pi/\partial c)\nabla_{\mathbf{r}}c$] and $\nu_{\mathrm{B}} = \eta_{\mathrm{B}}/Mc$ a kinematic viscosity characteristic of the Brownian (B) solute particles. According to the ansatz (2.33) the symmetric second-rank tensor $\tilde{\sigma}(\mathbf{q},\omega)$ is represented by the sum of two terms, one the isotropic tensor $\boldsymbol{I}\tilde{\pi}(\mathbf{q},\omega)$, with $\tilde{\pi}$ a function of $\tilde{c} = \tilde{c}(\mathbf{q},\omega)$, and the other proportional to the symmetric and traceless part of $\mathbf{q}\delta\tilde{\mathbf{j}}(\mathbf{q},\omega)$. This seems quite reasonable in the long-wavelength limit but it surely is inadequate for large values of $\mathbf{q}$. Thus, we cannot expect predictions based upon (2.33) to be reliable in the short-wavelength limit. It also should be recognized that the mean-field approximation (2.14) will produce errors that are likely to be large in the short-wavelength regime. Although it is obvious from these comments that one should not place too much trust in the predictions of our theory for short wavelengths, approximations similar to or even more restrictive than ours have been used by other investigators (e.g., ref 10 and 12) who then argued for the existence of static screening.

The result of substituting the Fourier–Laplace transform of the constitutive formula (2.33) into eq 2.30 is the relationship

$$Mi\omega\delta\tilde{\mathbf{j}}(\mathbf{q},\omega) + i\mathbf{q}\tilde{\pi}(\mathbf{q},\omega) + M\nu_{\mathrm{B}}q^2[\delta\tilde{\mathbf{j}}(\mathbf{q},\omega) + {}^1\!/_3\hat{\mathbf{q}}\hat{\mathbf{q}}\cdot\delta\tilde{\mathbf{j}}(\mathbf{q},\omega)] = \delta\tilde{\mathbf{k}}(\mathbf{q},\omega) + \delta\tilde{\mathbf{e}}(\mathbf{q},\omega) \tag{2.34}$$

Then with $\delta\tilde{\mathbf{k}}$ given by (2.23) we obtain for $\delta\tilde{\mathbf{j}}$ the sum of tranverse and longitudinal components

$$\delta\tilde{\mathbf{j}}_{\perp}(\mathbf{q},\omega) = (\xi c/\rho_0)M^{-1}[(i\omega + \nu_{\mathrm{B}}q^2) \times (i\omega + \nu_0 q^2 + \xi c/\rho_0) + (\xi/M)(i\omega + \nu_0 q^2)]^{-1}[\boldsymbol{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}]\cdot\tilde{\mathbf{f}}(\mathbf{q},\omega) \tag{2.35}$$

and

$$\delta\tilde{\mathbf{j}}_{\parallel}(\mathbf{q},\omega) = M^{-1}[i\omega + {}^4\!/_3\nu_{\mathrm{B}}q^2 + \xi/M]^{-1}[-i\mathbf{q}\tilde{\pi}(\mathbf{q},\omega) + c\tilde{\mathbf{E}}(\mathbf{q},\omega)] \tag{2.36}$$

The second of these can be rewritten in the form

$$\delta\tilde{\mathbf{j}}_{\parallel}(\mathbf{q},\omega) = -\tilde{D}(\mathbf{q},\omega)i\mathbf{q}\tilde{c} + \tilde{K}(\mathbf{q},\omega)\tilde{\mathbf{E}}(\mathbf{q},\omega) \tag{2.37}$$

with $\tilde{K} = M^{-1}[i\omega + {}^4/_3\nu_{\mathrm{B}}q^2 + \xi/M]^{-1}$ and $\tilde{D} = \tilde{K}(\partial\pi/\partial c)$ identified as the solute mobility and self-diffusion coefficient, respectively. In the low-frequency, long-wavelength hydrodynamic limit $\tilde{K} \rightarrow K = \xi^{-1}$ and $\tilde{D} \rightarrow D = \xi^{-1}(\partial\pi/\partial c)$.

Because the tensor $\tilde{\boldsymbol{T}}_{\mathrm{SC}}(\mathbf{q},\omega)$ [and $\tilde{\boldsymbol{T}}(\mathbf{q},\omega)$ as well] is transverse, only the corresponding transverse projection of the current $\delta\tilde{\mathbf{j}}$ contributes to the flow velocity $\tilde{\mathbf{W}}(\mathbf{q},\omega)$ given by (2.24). Therefore, from (2.24) and (2.35) we conclude that

$$\tilde{\mathbf{W}}(\mathbf{q},\omega) = \tilde{\boldsymbol{T}}^{\mathrm{EFF}}(\mathbf{q},\omega)\cdot\tilde{\mathbf{f}}(\mathbf{q},\omega) \tag{2.38}$$

The response tensor appearing here is related to the unscreened Oseen tensor of (2.22) by the formula

$$\tilde{\boldsymbol{T}}^{\mathrm{EFF}}(\mathbf{q},\omega) = \tilde{\boldsymbol{T}}_{\mathrm{SC}}(\mathbf{q},\omega)\tilde{\chi}(\mathbf{q},\omega) \tag{2.39}$$

with

$$\tilde{\chi}(q,\omega) = [(M/\xi)(i\omega + \nu_{\mathrm{B}}q^2) + 1][(M/\xi) \times (i\omega + \nu_{\mathrm{B}}q^2) + (i\omega + \nu_0 q^2)(i\omega + \nu_0 q^2 + \xi c/\rho_0)^{-1}]^{-1} \tag{2.40}$$

The function $\tilde{\chi}(\mathbf{q},\omega)$ determines the influence of the particle mobility on the effective hydrodynamic interaction, which otherwise would be given by the screened Oseen tensor $\tilde{\boldsymbol{T}}_{\mathrm{SC}}(\mathbf{q},\omega)$.

The characteristic frequency of the perturbing force $\tilde{\mathbf{f}}(\mathbf{q},\omega)$ fixes the value of ω. Thus, in the low-frequency (or long-time) limit, the tensor $\tilde{\boldsymbol{T}}^{\mathrm{EFF}}(\mathbf{q},\omega)$ assumes a stationary value

$$\lim_{\omega\to 0} \tilde{\boldsymbol{T}}^{\mathrm{EFF}}(\mathbf{q},\omega) = [q^2\eta^{\mathrm{EFF}}(q)]^{-1}[\boldsymbol{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}] \tag{2.41}$$

dependent upon an effective viscosity $\eta^{\mathrm{EFF}}(q)$ defined by the formula

$$\eta^{\mathrm{EFF}}(q) = \eta_0[1 + (M/\xi)\nu_{\mathrm{B}}q^2]^{-1}[1 + (M/\xi)\nu_{\mathrm{B}}q^2 + Mc\nu_{\mathrm{B}}/\eta_0] \tag{2.42}$$

When the "solute viscosity" ν_{B} is set equal to zero, $\eta^{\mathrm{EFF}}(q) \rightarrow \eta_0$ and expression 2.41 reduces to the familiar formula for the low-frequency limit of the Oseen tensor. There clearly is no screening in this case. However, if the solute fluid is viscous ($\nu_{\mathrm{B}} \neq 0$), there are two different low-frequency limits of $\tilde{\boldsymbol{T}}^{\mathrm{EFF}}$, depending on the value of wavenumber q or, equivalently, on the distance separating a point within the fluid from the location at which the perturbing force $\mathbf{f}$ is applied. In the large wave vector regime defined by $(M/\xi)\nu_{\mathrm{B}}q^2 \gg 1 + Mc\nu_{\mathrm{B}}/\eta_0$ one finds that

$$\lim_{q\to\infty} \eta^{\mathrm{EFF}}(q) = \eta_0 \tag{2.43}$$

Thus, close to the source of the perturbation the effective viscosity is that of the solvent, and since so few solute particles can interfere with the solvent flow, there is no hydrodynamic screening.

For small values of q (or at large distances from the source) the effective viscosity reduces to the sum of the solvent and solute viscosities, viz.,

$$\lim_{q\to 0} \eta^{\mathrm{EFF}}(q) = \eta_0 + cM\nu_{\mathrm{B}} \tag{2.44}$$

Again, there is no screening.

By rewriting (2.42) in the form

$$\eta^{\mathrm{EFF}}(q) = \eta_0\left[1 + (\xi c/\eta_0 q^2)\left(1 + \frac{1}{(M/\xi)\nu_{\mathrm{B}}q^2}\right)^{-1}\right] \tag{2.45}$$

we see that the low-frequency limit of $\tilde{\boldsymbol{T}}^{\mathrm{EFF}}(\mathbf{q},\omega)$ given by (2.41) will exhibit screening only if the value of $(M/\xi)\nu_{\mathrm{B}}q^2$ is much larger than unity. To illustrate how this might come about let us introduce

$$\tau_{\mathrm{B}} = M/\xi \tag{2.46}$$

the momentum relaxation time of a Brownian particle, and

$$\tau_{\mathrm{B}}{}^{\mathrm{VIS}} = l^2/\nu_{\mathrm{B}} \tag{2.47}$$

the shear wave relaxation time associated with the Brownian solute fluid. The latter of these is the time required for a solute–fluid shear wave to move a distance $l = c^{-1/3}$, equal to the average spacing between solute particles. The value of τ_{B} is about 10^{-6} s for macroparticle suspensions[15] and falls in the range from 10^{-14} to 10^{-12} s for polymers with molecular weights of 10^4–10^6.

In terms of these characteristic times $(M/\xi)\nu_{\mathrm{B}}q^2 = (\tau_{\mathrm{B}}/\tau_{\mathrm{B}}{}^{\mathrm{VIS}})(lq)^2$ and so, provided that lq remains finite,

$$\lim_{\tau_{\mathrm{B}}/\tau_{\mathrm{B}}{}^{\mathrm{VIS}}\to\infty} \eta^{\mathrm{EFF}}(q) = \eta_0 + \xi c/q^2 \tag{2.48}$$

and

$$\lim_{\tau_{\mathrm{B}}/\tau_{\mathrm{B}}{}^{\mathrm{VIS}}\to\infty} \tilde{\boldsymbol{T}}^{\mathrm{EFF}}(\mathbf{q},\omega{=}0) = \tilde{\boldsymbol{T}}_{\mathrm{SC}}(\mathbf{q},\omega{=}0) \equiv (\eta_0 q^2 + \xi c)^{-1}(\boldsymbol{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}) \tag{2.49}$$

In the limit $\tau_{\mathrm{B}}/\tau_{\mathrm{B}}{}^{\mathrm{VIS}} \rightarrow \infty$, the solute particles are unable to move regardless of the magnitude of the applied force, either because they are so massive ($M \rightarrow \infty$) or because their mutual interactions are so strong ($\nu_{\mathrm{B}} \rightarrow \infty$). This is the situation which prevails in a gel and it is well-known[1] that in this case the screening due to the randomly distributed obstacles (gel blobs) is given by $\tilde{\boldsymbol{T}}_{\mathrm{SC}}(\mathbf{q},\omega{=}0)$ of (2.49).

When the frequency of the perturbing force is finite the function $\tilde{\chi}(\mathbf{q},\omega)$ will depend on two additional characteristic times

$$\tau_0{}^{\mathrm{VIS}} = l^2/\nu_0 \tag{2.50}$$

and

$$\tau_{\mathrm{SC}} = \rho_0/c\xi \tag{2.51}$$

There are two situations for which screening obviously occurs. The first arises when the frequency of the perturbing force, $\tilde{\mathbf{f}}(\mathbf{q},\omega)$, is greater than any of the characteristic frequencies, $\tau_{\mathrm{B}}{}^{-1}$, $(\tau_{\mathrm{B}}{}^{\mathrm{VIS}})^{-1}$, $(\tau_0{}^{\mathrm{VIS}})^{-1}$, and $\tau_{\mathrm{SC}}{}^{-1}$. Then, provided that lq remains finite it follows that

$$\lim_{\omega\to\infty} \tilde{\varphi}(\mathbf{q},\omega) = 1 \tag{2.52}$$

and there is screening because the particles are unable to follow the rapidly changing directions of the solvent flow.

The second situation is characterized by particles so massive that their motions are unaffected by the flow of the solvent. In this case $\tau_B \to \infty$ and

$$\lim_{\tau_B\to\infty} \tilde{\chi}(\mathbf{q},\omega) = 1 \tag{2.53}$$

The screening that results is identical with that produced by the fixed obstacles which constitute a randomly distributed "porous medium".

3. Closing Comments

The principal conclusion of our analysis is that hydrodynamic screening occurs only as a transient phenomenon in solutions containing interacting, mobile solute particles. Screening is absent when the flow is steady. This conclusion is supported by the following phenomenological argument: hydrodynamic screening is evidence of (or a consequence of) a process that weakens the fluid flow by an irreversible dissipation of its energy. In our model the mechanism for this irreversible process is the interaction between the fluid and the point centers of friction. The flow exerts forces on the mobile sites which, unless constrained, accelerate until the drag vanishes and along with it the attendant hydrodynamic screening. Consequently, no hydrodynamic screening is to be expected when the flow is steady and the solute particles are mobile.

While our considerations have been specific to a suspension of identical, structureless particles, we believe that similar conclusions are applicable to polymers modeled as aggregates of Brownian particles bound to one another either by springs or rigid rods. To treat these more complicated systems one must, of course, modify the theory of section 2 to take account of the differences between the interactions of particles bound to one another and those which are not. However, the physical picture associated with hydrodynamic screening remains unchanged—polymer molecules immersed in a steadily flowing solvent will translate, rotate, and alter their shapes until the total frictional force and torque vanish. Once these adjustments have occurred, the motions of the polymers will be steady (unaccelerated) and free from hydrodynamic screening.

Some authors (e.g., ref 16) have suggested that hydrodynamic screening is produced by entanglements among polymer chains. As far as we can tell there is little direct evidence in support of this conjecture. However, it is quite possible that at polymer concentrations so high that the mean separation between segments (blobs or beads) belonging to different chains becomes comparable to the range of the excluded-volume interactions, the mobilities of the individual Brownian particles will be greatly diminished. In this event the solution will exhibit a gel-like behavior so that the model developed in our previous paper[1] becomes applicable. This corresponds to the $\nu_B \to \infty$, $\tilde{\chi} \to 1$ limit of the two-fluid model of the present paper, although we do not expect that this simple mean-field theory can provide an accurate description of concentrated gels or gel-like solutions.

In addition to the argument presented in the first paragraph of this section, there is a second, very fundamental objection to the existence of hydrodynamic screening in homogeneous solutions. According to the principle of Galilean invariance the form of the linear equations of motion of the effective medium (composite of solvent and solute) should be unchanged when the velocity is everywhere increased by an additive constant. This principle would be violated if the equations included a uniformly distributed frictional force. This difficulty has been recognized by some of the very same people who are advocates of hydrodynamic screening in systems containing mobile solute particles. In particular, de Gennes[10] has contended that although there is no screening for small values of the wavenumber q, it will occur for larger values of q. According to his argument, when q is large enough, different parts of a polymer coil experience oppositely directed flows so that the polymer as a whole will behave as a porous body permeated by a uniformly flowing fluid. Although this argument seems plausible enough, it is not supported by the equation he derived, namely, eq II-9 of ref 10. The proposed mechanism should be represented mathematically by some novel q-dependent frictional term and not by the conventional Darcy-like homogeneous frictional force that appears in the de Gennes theory. Then too, the more we think about it the less reasonable does it seem that there should be screening for a range of wavenumbers (or distances from the source of fluid disturbances) intermediate between the small values of q, for which (almost) everyone agrees there is no screening, and the very large values of q, which correspond to locations so near the source of disturbance that screening is impossible.

It is important to recognize that the two-fluid model used in the present paper is closely analogous to that of de Gennes,[10] with ours being somewhat more specific because of its reliance upon a definite equation of motion, (2.34), for the Brownian solute fluid. Also the Fourier transforms have been properly performed here. However, aside from these minor differences, there is a term-for-term correspondence between the expression

$$c^{-1}\delta\tilde{\mathbf{j}}_\perp(\mathbf{q},\omega) = M^{-1}(i\omega + \nu_B q^2 + \xi/M)^{-1}[\xi^{-1}\tilde{\mathbf{E}}(\mathbf{q},\omega) + \tilde{\mathbf{w}}^*(\mathbf{q},\omega)] \tag{3.1}$$

which follows directly from (2.3), (2.31), and (2.34) and de Gennes's eq II-5, with his symbols $\dot{\mathbf{r}}$, $M(\mathbf{k})$, $\tilde{B}$, $\mathbf{f}$, and $\mathbf{u}$ appearing in place of our $c^{-1}\delta\tilde{\mathbf{j}}_\perp$, $\mathrm{M}^{-1}(i\omega + \nu_B q^2 + \xi/M)^{-1}$, ξ^{-1}, $\tilde{\mathbf{E}}$, and $\tilde{\mathbf{w}}^*$, respectively. de Gennes uses the symbol $\mathbf{k}$ for the wave vector whereas we have used $\mathbf{q}$. The reason that his $\mathbf{u}$ appears in place of our $\tilde{\mathbf{w}}^*$ is that he does not distinguish between the virtual velocity (our $\mathbf{w}^*$) and the averaged velocity (our $\mathbf{W}$) of the solvent. It is even more remarkable that our $M^{-1}(i\omega + \nu_B q^2 + \xi/M)^{-1}$ evaluated at $\omega = 0$ exhibits precisely the same limiting values for $k \to 0$ and $k \to \infty$ as were assumed by de Gennes, who restricted his considerations to "slow motions (far below acoustic frequencies)". In this regard the solute viscosity ν_B is essential.

The reason why we do not find the screening at large q which de Gennes has reported is because of the incorrect way the high-q limit was treated in his paper. Instead of looking at the high-q limit of the complete expression (2.39) for $\boldsymbol{T}^{\mathrm{EFF}}(\mathbf{q},\omega=0)$, de Gennes only examined a factor corresponding to our $\tilde{\chi}(\mathbf{q},\omega=0)$, thereby disregarding the wavenumber dependence of $\tilde{\boldsymbol{T}}_{\mathrm{SC}}(\mathbf{q},\omega=0)$. As a consequence of this the conclusions reached in part 1 of his section II are incorrect.

Results somewhat similar to those of de Gennes were reported in one recent study by Muthukumar and Edwards[12] and another by Odijk.[13] However, so far as we have been able to determine, neither of these studies provides a truly compelling mathemathical demonstration that screening actually occurs in stationary flows for high or moderately high values of q.

Muthukumar[11] recently has identified several deficiencies of the Freed–Edwards theory of polymer solution dynamics and then used their multiple scattering technique to show that there is no hydrodynamic screening in infinitely dilute polymer solutions. Identical findings have been reported by Freed and Perico[16] who based their analysis on the model of phantom polymer chains. The conclusions of these two independent studies, although effectively limited in their applicability to very dilute solutions, are in agreement with ours. An advantage of our approach is a simpler formalism which is less prone to the incorporation of unphysical approximations such as those due to the deficiencies of the original Freed–Edwards theory and into which the effects of nonideality can be more easily introduced, e.g., by the introduction of the solute viscosity ν_B. Of course, the mean-field approximation used here is almost certainly too crude to predict the correct concentration dependence of the effective transport coefficients. In order to go beyond this simple approximation additional information is needed about the statistics of the solution (see, for example, ref 1).

It also must be remembered that quasi-hydrodynamic theories of macroparticle solution dynamics are apt to be unreliable in the high-q (short wavelength) regime. This is because the linearized Navier–Stokes equation used to describe the solvent is valid only for long wavelengths. A similar criticism applies to the Newtonian stress tensor we have used to describe the dynamics of the solute. However, one must bear in mind that the definitions of "small" and "large" wavenumbers involve length scales which may be different for the two fluids. A proper theory, using a more fundamental statistical mechanical approach, hasn't yet been reported. All of the previous theories to which references have been made throughout this paper are based on similar assumptions and therefore share common deficiencies.

Finally, in a recent series of papers Richter et al.[17-19] have used the term "incomplete hydrodynamic screening" to describe a heuristic approximation obtained by replacing the solvent viscosity on the Oseen tensor with an effective, distance-dependent viscosity according to the relation

$$\eta_{\text{eff}}^{-1}(r) = [\eta_0^{-1} - \eta^{-1}(c)] \exp(-r/l(c)) + \eta^{-1}(c)$$

The quantity $l(c)$ appearing here is called by the authors a hydrodynamic screening length and $\eta(c)$ is the concentration-dependent viscosity of the polymer solution. Based on our calculations, we can find no justification for their "incompletely screened hydrodynamic model", which apparently was inspired by an analogy with electrostatic relations.

The experimental results on the wavevector dependence and on the time dependence of coherent scattering function presented by these authors[18] do show, for dense polymer fluids, the "Rouse-like" behavior expected if screening were to occur. In our opinion, there is still no clear explanation of these results.

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