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Viscosity of polymer solutions

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Abstract. A cluster expansion theory is developed for the shear viscosity of solutions of linear polymers in the steady-state limit as a virial series in concentration. By assuming the chains to be rigid with respect to the translational diffusion of the centres of mass and the rotational motion of the chains, the Kirkwood–Riseman results for the translational and rotational friction coefficients are recovered at infinite dilution. The intrinsic viscosity is the same as that of Kirkwood and Riseman if the angular velocity of any segment of a chain is replaced by the configurationally averaged angular velocity of the chain. The multiple scattering technique and the conventional pre-averaging approximation are utilised in the analysis. Within these approximations, there is no hydrodynamic screening at infinite dilution in contrast with the results of Freed and Edwards. Every virial coefficient in the present formulation for the viscosity is convergent so that the viscosity can be directly determined to any desired order in concentration. The cluster expansion for viscosity has been converted to a set of coupled equations similar to the one obtained by Freed and Edwards but with different structure.

1. Introduction

Although the literature on the theoretical study of the frictional properties of polymers in infinitely dilute solution is rich (see e.g. Yamakawa 1971, Stockmayer 1976), there is only one theory, due to Freed and Edwards (1974, 1975a, b), to discuss the transport coefficients of polymers in solutions at non-zero concentrations. By incorporating both the intramolecular and intermolecular hydrodynamic interactions, these authors provided a multiple scattering theory and showed how Zimm and Rouse limits follow at very low and very high polymer concentrations, respectively. The Rouse limit emerges because of the screening of hydrodynamic interactions among the various segments of any given chain by all other chains. Despite its success in giving the concentration dependence of relaxation lifetimes of polymer modes in dilute solutions (Muthukumar and Freed 1977, 1978) and other related properties (Metiu and Freed 1977), the Freed–Edwards theory suffers from the following deficiencies.

(i) The net force acting on a single polymer chain in the absence of any external forces does not vanish in this theory, thus violating the conservation laws (see equation (8.5.9) of Freed (1978)).

(ii) The intrinsic viscosity $[\eta]$ calculated using this theory is higher than the experimental value by a factor of about two and is exactly twice the value obtained by Kirkwood and Riseman (1948) in the steady-state limit. In addition, the theoretical

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Huggins coefficient is smaller by a factor of two than the experimental value. (The calculation of the Huggins coefficient for linear polymers in θ solvents by Freed and Edwards (1975a) contains a numerical error and the value is actually 0.3787. In addition, their value of $[\eta]$ is a factor of two larger than their reported result.)

(iii) The rotary motion and the translational diffusion of the polymer chains are not explicitly taken into account. This leads to a hydrodynamic screening even for an infinitely dilute solution. This screening is equivalent to that of Darcy flow through a stationary suspension of spheres (Freed and Muthukumar 1978) and is to be contrasted with the absence of hydrodynamic screening for a mobile suspension of hard spheres at low concentrations (Muthukumar and Freed 1980).

In this paper, we present a general multiple scattering theory free from the above deficiencies. The translational diffusion and the rotary motion of the various polymer chains are incorporated explicitly by assuming that the chains are rigid with respect to these degrees of freedom. The formal mathematical treatment is presented in § 2 and we obtain a set of equations for the combined polymer–fluid system. In order to make the concepts and techniques of multiple scattering clear, we first study the case of one polymer chain present in a solvent. Restricting ourselves to the steady-state limit we begin with the set of equations derived above to obtain the velocity field. The formal theory is presented in § 3. In the infinite dilution limit, we calculate the intrinsic viscosity, translational and rotational friction coefficients within the framework of the pre-averaging approximation and these are shown to be the same as the Kirkwood–Riseman results. Section 4 contains the details of these calculations. The hydrodynamic screening is also evaluated in this section. A cluster expansion for the specific viscosity η_{sp} of the polymer solution as a function of concentration is developed in § 5 and the results are discussed in the last section.

2. Mathematical formulation

For conservative dynamical systems, the equations of motion can be derived by varying the time integral of the Lagrangian \mathcal{L}

$$\delta \int dt \mathcal{L}[q, \dot{q}, \dots] = 0 \quad (2.1)$$

where q is a generalised coordinate. When frictional forces are present, Rayleigh's dissipation function $\mathcal{F}[\dot{q}]$ (Whittaker 1937) should be constructed and the Rayleighian, $\mathcal{R} = \mathcal{L} + \mathcal{F}$, is varied to obtain the equations of motion

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{q}} - \frac{\partial \mathcal{L}}{\partial q} + \frac{\partial \mathcal{F}}{\partial \dot{q}} = 0. \quad (2.2)$$

We now derive the equations of motion for the combined polymer–fluid system. The solvent alone is assumed to satisfy the linearised Navier–Stokes equation

$$\rho_0 \frac{\partial \mathbf{v}(\mathbf{r}, t)}{\partial t} - \eta_0 \nabla^2 \mathbf{v}(\mathbf{r}, t) + \nabla P(\mathbf{r}, t) = 0. \quad (2.3)$$

Here $\mathbf{v}(\mathbf{r}, t)$ is the velocity field at any space point \mathbf{r} and time t , P is the pressure, η_0 is the shear viscosity of the solvent and ρ_0 is the mass density of the solvent. The polymer is taken to be a chain of n beads which are assumed to be point friction sources, each with

mass m . The molecular weight of the chain, M , is nm . In general, the polymer chain obeys an equation of the form

$$\tau \frac{\partial \mathbf{R}_{\alpha i}(t)}{\partial t} + \Delta_{\alpha i} \mathbf{R}_{\alpha i} = \mathbf{f}_{\alpha i} \quad (2.4)$$

where $\mathbf{R}_{\alpha i}$ is the position vector of the i th bead of the chain α and τ is the hopping time given by Verdier and Stockmayer (1962) and Edwards and Goodyear (1972). The second term of (2.4) is to be interpreted as an operator expression and describes any desired model dynamics of the chain. We now assume that the chain can undergo rigid body rotation when a torque is applied. The velocity of the i th bead is therefore given by

$$\dot{\mathbf{R}}_{\alpha i} = \dot{\mathbf{R}}_{\alpha}^0 + \boldsymbol{\omega}_{\alpha} \times \mathbf{S}_{\alpha i} \quad (2.5)$$

where $\dot{\mathbf{R}}_{\alpha}^0$ is the translational velocity of the centre of mass of α , $\boldsymbol{\omega}_{\alpha}$ is the angular velocity of α , and $\mathbf{S}_{\alpha i}$ is the position vector of the i th bead with respect to the centre of mass of α , $\mathbf{S}_{\alpha i} = \mathbf{R}_{\alpha i} - \mathbf{R}_{\alpha}^0$.

The dynamics of the fluid and the chains are coupled by hydrodynamic boundary conditions. For simplicity we use the no-slip boundary condition,

$$\mathbf{v}(\mathbf{R}_{\alpha i}) = \dot{\mathbf{R}}_{\alpha i}. \quad (2.6)$$

The Rayleighian appropriate to the combined polymer–fluid system containing N chains is then

$$\mathcal{R} = \mathcal{L}_s + \mathcal{F}_s + \mathcal{L}_p + \mathcal{F}_p + \mathcal{F}_{sp} \quad (2.7)$$

where

$$\begin{aligned} \mathcal{L}_s &= \frac{\rho_0}{2} \int d\mathbf{r} dt v^2(\mathbf{r}, t) + \int d\mathbf{r} dt \Phi_s(\mathbf{r}, t) \\ \mathcal{F}_s &= -\frac{1}{2}\eta_0 \int d\mathbf{r} dt [\nabla \mathbf{v}(\mathbf{r}, t)]^2 + \int d\mathbf{r} dt P(\mathbf{r}, t) \nabla \cdot \mathbf{v}(\mathbf{r}, t) \\ \mathcal{L}_p &= \frac{1}{2}m \sum_{\alpha=1}^N \sum_{i=1}^n \dot{\mathbf{R}}_{\alpha i}^2(t) + \sum_{\alpha i} \int dt \Phi_p(\mathbf{R}_{\alpha i}(t), t) \\ \mathcal{F}_p &= \frac{1}{2}\tau \sum_{\alpha i} \int dt \dot{\mathbf{R}}_{\alpha i}^2(t) \\ \mathcal{F}_{sp} &= \sum_{\alpha i} \int dt \boldsymbol{\sigma}_{\alpha i}(t) \cdot \left[\dot{\mathbf{R}}_{\alpha i}(t) - \mathbf{v} \left(\mathbf{R}_{\alpha i}(0) + \int_0^t dt' \dot{\mathbf{R}}_{\alpha i}(t'), t \right) \right]. \end{aligned}$$

Here $\boldsymbol{\sigma}_{\alpha i}$ are Lagrange multipliers to ensure the no-slip boundary condition. Φ_s and Φ_p are any net potential fields present in the solvent and polymer, respectively. When the rigid body rotation condition (2.5) is included we obtain

$$\begin{aligned} \mathcal{L}_p &= \frac{1}{2}M \sum_{\alpha} \int dt \dot{\mathbf{R}}_{\alpha}^2(t) + \frac{1}{2} \sum_{\alpha} \int dt \boldsymbol{\omega}_{\alpha} \cdot \mathbf{I}_{\alpha} \cdot \boldsymbol{\omega}_{\alpha} + \sum_{\alpha i} \int dt \Phi_p(\mathbf{R}_{\alpha i}(t), t) \\ &= \frac{1}{2}M \sum_{\alpha} \int dt \dot{\mathbf{R}}_{\alpha}^2(t) + \frac{1}{2} \sum_{\alpha} \int dt (I_{\alpha x} \omega_{\alpha x}^2 + I_{\alpha y} \omega_{\alpha y}^2 + I_{\alpha z} \omega_{\alpha z}^2) \\ &\quad + \sum_{\alpha i} \int dt \Phi_p(\mathbf{R}_{\alpha i}(t), t) \end{aligned} \quad (2.8)$$

$$\mathcal{F}_p = \frac{1}{2}n\tau \sum_{\alpha} \int dt \dot{\mathbf{R}}_{\alpha}^2(t) + \frac{1}{2} \frac{\tau}{m} \sum_{\alpha} \int dt (I_{\alpha x} \omega_{\alpha x}^2 + I_{\alpha y} \omega_{\alpha y}^2 + I_{\alpha z} \omega_{\alpha z}^2)$$

$$\mathcal{F}_{sp} = \sum_{\alpha i} \int dt \boldsymbol{\sigma}_{\alpha i}(t) \cdot \left\{ \dot{\mathbf{R}}_{\alpha}^0(t) + \boldsymbol{\omega}_{\alpha} \times \mathbf{S}_{\alpha i}(t) - \mathbf{v} \left[\mathbf{R}_{\alpha i}(0) + \int_0^t dt' (\dot{\mathbf{R}}_{\alpha}^0(t') + \boldsymbol{\omega}_{\alpha} \times \mathbf{S}_{\alpha i}(t')), t \right] \right\}.$$

In these equations \mathbf{I}_{α} is the inertia tensor of α and x, y and z are the principal axes in which \mathbf{I} is diagonal. Introducing a field $\mathbf{X}(\mathbf{r}, t)$ where $\partial \mathbf{X}(\mathbf{r}, t) / \partial t \equiv \mathbf{v}(\mathbf{r}, t)$, the equation of motion for the fluid is given by

$$\begin{aligned} \frac{d}{dt} \frac{\partial \mathcal{L}_s}{\partial \dot{\mathbf{X}}} - \frac{\partial \mathcal{L}_s}{\partial \mathbf{X}} + \frac{\partial}{\partial \mathbf{X}} (\mathcal{F}_s + \mathcal{F}_{sp}) &= 0 \\ \rho_0 \frac{\partial}{\partial t} \mathbf{v}(\mathbf{r}, t) - \eta_0 \nabla^2 \mathbf{v}(\mathbf{r}, t) + \nabla P(\mathbf{r}, t) &= \mathbf{F}(\mathbf{r}, t) + \sum_{\alpha i} \delta(\mathbf{r} - \mathbf{R}_{\alpha i}(t)) \boldsymbol{\sigma}_{\alpha i}(t) \quad (2.9) \\ \mathbf{F}(\mathbf{r}, t) &= -\partial \Phi_s / \partial \mathbf{X} \end{aligned}$$

where $\delta(\mathbf{r})$ is the Dirac delta function.

The equation of motion for the centre of mass of α is given by

$$\begin{aligned} \frac{\partial}{\partial t} \frac{\partial \mathcal{L}_p}{\partial \dot{\mathbf{R}}_{\alpha}^0} - \frac{\partial \mathcal{L}_p}{\partial \mathbf{R}_{\alpha}^0} + \frac{\partial}{\partial \mathbf{R}_{\alpha}^0} (\mathcal{F}_p + \mathcal{F}_{sp}) &= 0 \\ M \ddot{\mathbf{R}}_{\alpha}^0 + n\tau \dot{\mathbf{R}}_{\alpha}^0 &= -\sum_i \boldsymbol{\sigma}_{\alpha i} + \mathbf{f}_{\alpha} \quad (2.10) \\ \mathbf{f}_{\alpha} &= -\partial \Phi_p / \partial \mathbf{R}_{\alpha}^0. \end{aligned}$$

Equations (2.10) specify three degrees of freedom for the rigid chain. The other three degrees of freedom are obtained by considering the rotary motion of the chain in terms of the three Euler angles θ, ϕ and ψ . These are related to the components of $\boldsymbol{\omega}$ along the principal axes as (Whittaker 1937)

$$\begin{aligned} \omega_x &= \dot{\phi} \sin \theta \sin \psi + \dot{\theta} \cos \psi \\ \omega_y &= \dot{\phi} \sin \theta \cos \psi - \dot{\theta} \sin \psi \\ \omega_z &= \dot{\phi} \cos \theta + \dot{\psi}. \end{aligned} \quad (2.11)$$

Out of the three generalised forces corresponding to θ, ϕ and ψ , only one, namely, $-\partial \Phi_p / \partial \psi$, gives the torque along one of the principal axes (z axis) N_z . Therefore taking ψ as the generalised coordinate we get

$$\frac{\partial}{\partial t} \frac{\partial \mathcal{L}_p}{\partial \dot{\psi}} - \frac{\partial \mathcal{L}_p}{\partial \psi} + \frac{\partial}{\partial \psi} (\mathcal{F}_p + \mathcal{F}_{sp}) = 0 \quad (2.12)$$

$$I_{\alpha z} \dot{\omega}_{\alpha z} - \omega_{\alpha x} \omega_{\alpha y} (I_{\alpha x} - I_{\alpha y}) + (\tau / m) I_{\alpha z} \omega_{\alpha z} - \sum_i (\sigma_{\alpha i x} r_{\alpha i y} - \sigma_{\alpha i y} r_{\alpha i x}) = N_{\alpha z}. \quad (2.13)$$

The equations for torque along other principal axes of α are obtained by permuting the indices in (2.13). Since the frictional terms dominate over the inertial terms in this problem, the latter can be safely ignored. In the static limit, we obtain from (2.5), (2.6),

(2.9), (2.10) and (2.13)

$$-\eta_0 \nabla^2 \mathbf{v}(\mathbf{r}) + \nabla P(\mathbf{r}) = \mathbf{F}(\mathbf{r}) + \sum_{\alpha} \sum_i \delta(\mathbf{r} - \mathbf{R}_{\alpha i}) \boldsymbol{\sigma}_{\alpha i} \quad (2.14a)$$

$$\sum_i \boldsymbol{\sigma}_{\alpha i} = \mathbf{f}_{\alpha} \quad (2.14b)$$

$$-\sum_i \boldsymbol{\sigma}_{\alpha i} \times \mathbf{S}_{\alpha i} = \mathbf{N}_{\alpha} \quad (2.14c)$$

$$\mathbf{v}(\mathbf{R}_{\alpha i}) = \dot{\mathbf{R}}_{\alpha i} = \dot{\mathbf{R}}_{\alpha}^0 + \boldsymbol{\omega}_{\alpha} \times \mathbf{S}_{\alpha i} \equiv \mathbf{u}_{\alpha} + \boldsymbol{\omega}_{\alpha} \times \mathbf{S}_{\alpha i}. \quad (2.14d)$$

Since the Lagrange multiplier $\boldsymbol{\sigma}_{\alpha i}$ possesses a simple physical interpretation of force exerted by the i th bead of chain α on the fluid, (2.14) are intuitively obvious.

3. Infinite dilution limit

In this section we consider the change in shear viscosity of the solvent due to the presence of one polymer chain (say α) in the static limit. When the inertial terms are ignored the equations of motion for the combined polymer–fluid system are given by (2.14). Since there is now only one chain, (2.14a) reads as

$$-\eta_0 \nabla^2 \mathbf{v}(\mathbf{r}) + \nabla P(\mathbf{r}) = \mathbf{F}(\mathbf{r}) + \sum_{i=1}^n \delta(\mathbf{r} - \mathbf{R}_{\alpha i}) \boldsymbol{\sigma}_{\alpha i}. \quad (3.1)$$

Now we seek to obtain an expression for the velocity field $\mathbf{v}(\mathbf{r})$ from (3.1) by eliminating the unknown $\{\boldsymbol{\sigma}_{\alpha i}\}$. The formal solution of (3.1) is

$$\mathbf{v}(\mathbf{r}) = \int d\mathbf{r}' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \left(\mathbf{F}(\mathbf{r}') + \sum_{i=1}^n \delta(\mathbf{r}' - \mathbf{R}_{\alpha i}) \boldsymbol{\sigma}_{\alpha i} \right) \quad (3.2)$$

where $\mathbf{G}(\mathbf{r})$ is the familiar Oseen tensor

$$\mathbf{G}(\mathbf{r}) = (1/8\pi\eta_0|\mathbf{r}|) \left(\mathbf{I} + \frac{\mathbf{r}\mathbf{r}}{|\mathbf{r}|^2} \right). \quad (3.3)$$

Substitution of (3.2) into (2.14d) yields

$$\mathbf{u}_{\alpha} + \boldsymbol{\omega}_{\alpha} \times \mathbf{S}_{\alpha p} = \int d\mathbf{r}' \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \sum_{j=1}^n \mathbf{K}_{\alpha}(\mathbf{S}_{\alpha p} - \mathbf{S}_{\alpha j}) \cdot \boldsymbol{\sigma}_{\alpha j} \quad (3.4)$$

where

$$\mathbf{K}_{\alpha}(\mathbf{S}_{\alpha p} - \mathbf{S}_{\alpha j}) \equiv \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{R}_{\alpha j}). \quad (3.5)$$

We now define an inverse operator \mathbf{K}_{α}^{-1} as

$$\sum_{p=1}^n \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \cdot \mathbf{K}_{\alpha}(\mathbf{S}_{\alpha p} - \mathbf{S}_{\alpha j}) = \mathbf{I} \delta_{ij}. \quad (3.6)$$

Multiplying (3.4) by $\mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p})$ and summing over p , we obtain an expression for $\boldsymbol{\sigma}_{\alpha i}$,

$$\boldsymbol{\sigma}_{\alpha i} = - \sum_{p=1}^n \int d\mathbf{r}' \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \cdot \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \sum_{p=1}^n \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \cdot (\mathbf{u}_{\alpha} + \boldsymbol{\omega}_{\alpha} \times \mathbf{S}_{\alpha p}). \quad (3.7)$$

A closed expression for $\sigma_{\alpha i}$ can be obtained by eliminating u_α and ω_α by the use of (2.14). The insertion of (3.7) into (2.14) yields

$$\begin{pmatrix} f_\alpha \\ N_\alpha \end{pmatrix} = \begin{pmatrix} \sum_{ij} K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) & -\sum_{ij} K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) \times S_{\alpha j} \\ \sum_{ij} S_{\alpha i} \times K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) & -\sum_{ij} S_{\alpha i} \times K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) \times S_{\alpha j} \end{pmatrix} \begin{pmatrix} u_\alpha \\ \omega_\alpha \end{pmatrix} - \sum_{ij} \int dr' \begin{pmatrix} K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) \cdot G(R_{\alpha j} - r') \cdot F(r') \\ S_{\alpha i} \times K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) \cdot G(R_{\alpha j} - r') \cdot F(r') \end{pmatrix}. \quad (3.8)$$

This equation possesses a simple physical interpretation. The 2×2 matrix appearing in the first term on the right-hand side of (3.8) is the microscopic friction tensor matrix. When an average over the distribution of the beads i and j of the chain is performed, the elements of this matrix provide the polymer friction coefficients. The translational friction coefficient, f_t , and the rotational friction coefficient, f_r , are given by the diagonal elements,

$$\begin{aligned} f_t &= \left\langle \sum_{ij} K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) \right\rangle \equiv \langle g_t \rangle \\ f_r &= - \left\langle \sum_{ij} S_{\alpha i} \times K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) \times S_{\alpha j} \right\rangle \equiv \langle g_r \rangle \end{aligned} \quad (3.9)$$

where the angular brackets denote the averaging over the distributions of i and j . f_t and f_r are explicitly evaluated in the next section within the pre-averaging approximation. The cross friction coefficients given by the off-diagonal elements of the 2×2 matrix vanish within the pre-averaging scheme. Therefore, we ignore these cross translational-rotational friction terms in the following derivation for notational convenience, but keep them in the general derivation presented in § 5.

When the external forces and torques vanish, $f_\alpha = 0 = N_\alpha$, (3.8) and (3.9) give

$$\begin{aligned} u_\alpha &= g_t^{-1} \cdot \sum_{ij} \int dr' K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) \cdot G(R_{\alpha j} - r') \cdot F(r') \\ \omega_\alpha &= g_r^{-1} \cdot \sum_{ij} \int dr' S_{\alpha i} \times K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) \cdot G(R_{\alpha j} - r') \cdot F(r') \end{aligned} \quad (3.10)$$

where

$$g_t \cdot g_t^{-1} = I \quad \text{and} \quad g_r \cdot g_r^{-1} = I. \quad (3.11)$$

Substituting (3.10) into (3.7) gives

$$\begin{aligned} \sigma_{\alpha i} &= - \sum_j \int dr' \left(K_\alpha^{-1}(S_{\alpha i}, S_{\alpha j}) - \sum_{pp'} K_\alpha^{-1}(S_{\alpha i}, S_{\alpha p}) \cdot g_t^{-1} \cdot K_\alpha^{-1}(S_{\alpha p}, S_{\alpha j}) \right. \\ &\quad \left. + \sum_{pp'} K_\alpha^{-1}(S_{\alpha i}, S_{\alpha p}) \times S_{\alpha p} \cdot g_r^{-1} \cdot S_{\alpha p'} \times K_\alpha^{-1}(S_{\alpha p'}, S_{\alpha j}) \right) \cdot G(R_{\alpha j} - r') \cdot F(r'). \end{aligned} \quad (3.12)$$

Inserting (3.12) into (3.2), we obtain an expression for the velocity field $v(r)$,

$$v(r) = \int dr' G(r - r') \cdot F(r') + \int dr' dr'' dr''' G(r - r') \cdot T_\alpha(r', r'') \cdot G(r'', r''') \cdot F(r''')$$

where

$$\begin{aligned} \mathbf{T}_\alpha(\mathbf{r}, \mathbf{r}') = & -\sum_{ij} \delta(\mathbf{r} - \mathbf{R}_{\alpha i}) \left(\mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) - \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \cdot \mathbf{g}_t^{-1} \cdot \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) \right. \\ & \left. + \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \times \mathbf{S}_{\alpha p} \cdot \mathbf{g}_r^{-1} \cdot \mathbf{S}_{\alpha p'} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) \right) \delta(\mathbf{r}' - \mathbf{R}_{\alpha j}). \end{aligned} \quad (3.13)$$

This is the equation we set out to derive.

Now we proceed to evaluate the change in shear velocity due to the added chain as follows. Upon averaging (3.13) with respect to the random distribution of \mathbf{R}_α^0 we obtain

$$\begin{aligned} \mathbf{V}(\mathbf{r}) = \langle \mathbf{v}(\mathbf{r}) \rangle = & \int d\mathbf{r}' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') \\ & + \int d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \langle \mathbf{T}_\alpha(\mathbf{r}', \mathbf{r}'') \rangle \cdot \mathbf{G}(\mathbf{r}'' - \mathbf{r}''') \cdot \mathbf{F}(\mathbf{r}'''). \end{aligned} \quad (3.14)$$

Alternatively we can write an equivalent expression for $\langle \mathbf{v}(\mathbf{r}) \rangle$ by performing this average on (3.1) directly. This yields

$$-\eta_0 \nabla^2 \mathbf{V}(\mathbf{r}) + \nabla \langle P(\mathbf{r}) \rangle - \int d\mathbf{r}' \boldsymbol{\Sigma}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{V}(\mathbf{r}') = \mathbf{F}(\mathbf{r}) \quad (3.15)$$

where

$$\int d\mathbf{r}' \boldsymbol{\Sigma}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{V}(\mathbf{r}') = \left\langle \sum_{i=1}^n \delta(\mathbf{r} - \mathbf{R}_{\alpha i}) \boldsymbol{\sigma}_{\alpha i} \right\rangle. \quad (3.16)$$

Thus all the contribution of the chain α to the dissipation mechanism of the fluid is contained in (3.16). This is actually the average contribution of chain α to the divergence of the stress tensor for the fluid. The formal solution of (3.15) is now

$$\mathbf{V}(\mathbf{r}) = \int d\mathbf{r}' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \int d\mathbf{r}' d\mathbf{r}'' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \boldsymbol{\Sigma}(\mathbf{r}' - \mathbf{r}'') \cdot \mathbf{V}(\mathbf{r}''). \quad (3.17)$$

This is an integral equation that can be iterated indefinitely,

$$\mathbf{V}(\mathbf{r}) = \int d\mathbf{r}' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \int \mathbf{G} \cdot \boldsymbol{\Sigma} \cdot \mathbf{G} \cdot \mathbf{F} + \dots \quad (3.18)$$

Since we are interested in very dilute solutions we truncate the series in (3.18) at the second term and a comparison with (3.14) gives an expression for the unknown $\boldsymbol{\Sigma}$,

$$\boldsymbol{\Sigma}(\mathbf{r} - \mathbf{r}') = \langle \mathbf{T}_\alpha(\mathbf{r} - \mathbf{r}') \rangle. \quad (3.19)$$

Defining the Fourier transform as

$$\mathbf{F}(\mathbf{k}) = \int d\mathbf{r} \mathbf{F}(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \quad (3.20)$$

where \mathbf{k} is the Fourier variable conjugate to the position variable \mathbf{r} , (3.15) becomes

$$[\mathbf{I}\eta_0 k^2 - \boldsymbol{\Sigma}(\mathbf{k})] \cdot \mathbf{V}(\mathbf{k}) + i\mathbf{k}P(\mathbf{k}) = \mathbf{F}(\mathbf{k}). \quad (3.21)$$

Thus clearly the change in shear viscosity of the fluid, $\delta\eta$, due to the added polymer chain is given by $-\boldsymbol{\Sigma}_{k^2}$, the k^2 term of $-\boldsymbol{\Sigma}(\mathbf{k})$. Therefore the intrinsic viscosity is given by

$$\delta\eta/\eta_0 c = [\eta] = -N \boldsymbol{\Sigma}_{k^2} / \eta_0 c k^2 \quad (3.22)$$

where N is the total number of polymer chains (assumed in this section to be non-interacting) present in the solution and c is the polymer concentration. The explicit evaluation of $[\eta]$ according to (3.22) is presented in the next section. From the structure of equation (3.21), the hydrodynamic screening is given by $\Sigma(k=0)$ and its value is presented below.

4. Calculation of f_t , f_r and $[\eta]$

In this section, we present the algebraic details for the calculation of these frictional coefficients. Here we assume that the chain possesses Gaussian statistics. Further we employ the simple and convenient pre-averaging approximation. These approximations may be lifted if desired without any new conceptual difficulties.

4.1. Translational friction coefficient

Converting the summations in (3.9) to integrals with the changes of variables $x = 2i/n - 1$ and $y = 2j/n - 1$, we obtain

$$f_t = \frac{n^2}{4} \int_{-1}^1 dx \int_{-1}^1 dy \langle K^{-1}(x, y) \rangle \quad (4.1)$$

where the angular brackets indicate the average over the Gaussian distribution for the various polymer segments. Expanding $\langle K^{-1}(x, y) \rangle$ in double Fourier series

$$\langle K^{-1}(x, y) \rangle = \sum_{\mu=-\infty}^{\infty} \sum_{\mu'=-\infty}^{\infty} K_{\mu\mu'}^{-1} \exp(i\pi\mu x - i\pi\mu' y)$$

with

$$K_{\mu\mu'}^{-1} = \frac{1}{4} \int_{-1}^1 dx \int_{-1}^1 dy \langle K^{-1}(x, y) \rangle \exp(-i\pi\mu x + i\pi\mu' y) \quad (4.2)$$

f_t is readily given by

$$f_t = n^2 K_{00}^{-1}. \quad (4.3)$$

Using the pre-averaging approximation we get from (3.6)

$$K_{\mu\mu}^{-1} = n^{-2} (K_{\mu\mu})^{-1} \quad (4.4)$$

where

$$K_{\mu\mu'} = \frac{1}{4} \int_{-1}^1 dx \int_{-1}^1 dy \langle K(x, y) \rangle \exp(-i\pi\mu x + i\pi\mu' y) \quad (4.5)$$

$$\langle K(x, y) \rangle = \sum_{\mu, \mu'=-\infty}^{\infty} K_{\mu\mu'} \exp(i\pi\mu x - i\pi\mu' y).$$

For a Gaussian chain

$$\begin{aligned} \langle K(\mathbf{S}_i - \mathbf{S}_j) \rangle &= (1/6\pi\eta_0) \langle 1/|\mathbf{S}_i - \mathbf{S}_j| \rangle \\ &= (1/6\pi\eta_0 l) (6/\pi |i - j|)^{1/2} \end{aligned} \quad (4.6)$$

where l is Kuhn step length. Therefore, substituting

$$\langle K(x, y) \rangle = (1/6\pi\eta_0 l)(12/\pi n|x-y|)^{1/2} \tag{4.7}$$

into (4.5), we obtain

$$\begin{aligned} K_{00} &= \frac{1}{2\eta_0 l} \int_{-1}^1 dx \int_{-1}^1 dy (12\pi^3 n|x-y|)^{-1/2} \\ &= \frac{8\sqrt{2}}{3} h \end{aligned} \tag{4.8}$$

where

$$h = 1/\eta_0 l(12\pi^3 n)^{1/2}.$$

Combining (4.3), (4.4) and (4.8), the translational friction coefficient readily reduces to the familiar Kirkwood–Riseman result for the non-free-draining limit

$$f_t = 3/8h\sqrt{2}. \tag{4.9}$$

4.2. Rotary friction coefficient

Utilising the pre-averaging approximation in (3.9), the rotary friction coefficient becomes

$$f_r = \frac{2}{3} \sum_{i,j=1}^n \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \langle \mathbf{K}_{ij}^{-1} \rangle. \tag{4.10}$$

Changes of variables, $x = 2i/n - 1$, readily yield, for a Gaussian chain,

$$f_r = \frac{n^2}{6} \int_{-1}^1 dx \int_{-1}^1 dy f(x, y) \langle \mathbf{K}^{-1}(x, y) \rangle \tag{4.11}$$

where

$$f(x, y) = (nl^2/24)[3(x^2 + y^2) - 6|x-y| + 2].$$

Expanding $f(x, y)$ in double Fourier series,

$$f(x, y) = \sum_{\lambda\lambda'} f_{\lambda\lambda'} \exp(-i\pi\lambda x + i\pi\lambda' y) \tag{4.12}$$

$$f_{\lambda\lambda'} = \frac{1}{4} \int_{-1}^1 dx \int_{-1}^1 dy f(x, y) \exp(i\pi\lambda x - i\pi\lambda' y)$$

and using (4.2) in (4.11), we obtain

$$f_r = \frac{2}{3} n^2 \sum_{\mu\mu'} f_{\mu\mu'} K_{\mu\mu'}^{-1}. \tag{4.13}$$

From (4.5) and (4.7), $K_{\mu\mu'}$ is given as

$$\begin{aligned} K_{\mu\mu'} &= \frac{1}{2} h \int_{-1}^1 dx \int_{-1}^1 dy |x-y|^{-1/2} \exp(-i\pi\mu x + i\pi\mu' y) \\ &= \begin{cases} 8\sqrt{2}h/3 & \mu = 0 = \mu' \\ h\delta_{\mu\mu'}(2/|\mu|)^{1/2} & \mu \neq 0. \end{cases} \end{aligned} \tag{4.14}$$

In obtaining (4.14) we have employed the Kirkwood–Riseman approximation of taking the asymptotic result for large $|\mu|$ and $|\mu'|$ of the integral appearing in (4.14).

Now from (4.14) and (4.12), for $\mu \neq 0$,

$$\begin{aligned} f_{\mu\mu} &= (nl^2/96) \int_{-1}^1 dx \int_{-1}^1 dy [3(x^2 + y^2) - 6|x - y| + 2] \exp[i\pi\mu(x - y)] \\ &= (nl^2/6) \int_{-1}^1 dx [(3/4\pi^2\mu^2) + (-1)^\mu (3ix/4\pi\mu) \exp(i\pi\mu x)] \\ &= (nl^2/2\pi^2\mu^2). \end{aligned} \quad (4.15)$$

Since f_{00} vanishes, substitution of (4.4), (4.14) and (4.15) into (4.13) yields

$$f_r = (2nl^2/3\pi^2) \sum_{\mu=1}^{\infty} [1/h2^{1/2}\mu^{3/2}]. \quad (4.16)$$

By a similar argument, it can easily be shown that the cross translational–rotational friction coefficients vanish.

4.3. Intrinsic viscosity

From (3.19) and (3.13)

$$\begin{aligned} \Sigma(\mathbf{k}) &= \int d(\mathbf{r} - \mathbf{r}') \langle \mathbf{T}_\alpha(\mathbf{r} - \mathbf{r}') \rangle \exp[-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] \\ &= -\frac{1}{V} \int d(\mathbf{r} - \mathbf{r}') \int d\mathbf{R}_\alpha^0 \exp[-i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] \delta(\mathbf{r}' - \mathbf{R}_\alpha^0 - \mathbf{S}_{\alpha i}) \delta(\mathbf{r}' - \mathbf{R}_\alpha^0 - \mathbf{S}_{\alpha j}) \\ &\quad \times \left[\mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) - \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \cdot \mathbf{g}_t^{-1} \cdot \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) + \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \right. \\ &\quad \left. \times \mathbf{S}_{\alpha p} \cdot \mathbf{g}_r^{-1} \cdot \mathbf{S}_{\alpha p'} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) \right] \\ &= -\frac{1}{V} \sum_{ij} \exp[-i\mathbf{k} \cdot (\mathbf{S}_{\alpha i} - \mathbf{S}_{\alpha j})] \left[\mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \right. \\ &\quad \left. - \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \cdot \mathbf{g}_t^{-1} \cdot \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) \right. \\ &\quad \left. + \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \times \mathbf{S}_{\alpha p} \cdot \mathbf{g}_r^{-1} \cdot \mathbf{S}_{\alpha p'} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) \right] \end{aligned} \quad (4.17)$$

where V is the total volume of the system. Therefore the k^2 component of $\Sigma(\mathbf{k})$ is given exactly by

$$\begin{aligned} -V\Sigma_{k^2} &= \sum_{ij} (\mathbf{k} \cdot \mathbf{S}_{\alpha i})(\mathbf{k} \cdot \mathbf{S}_{\alpha j}) \left[\mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) - \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \cdot \mathbf{g}_t^{-1} \cdot \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) \right. \\ &\quad \left. + \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \times \mathbf{S}_{\alpha p} \cdot \mathbf{g}_r^{-1} \cdot \mathbf{S}_{\alpha p'} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) \right]. \end{aligned} \quad (4.18)$$

The first term on the right-hand side yields, upon pre-averaging,

$$\begin{aligned} \left\langle \sum_{ij} (\mathbf{k} \cdot \mathbf{S}_{\alpha i})(\mathbf{k} \cdot \mathbf{S}_{\alpha j}) \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \right\rangle &= \frac{1}{3} k^2 \sum_{ij} \langle \mathbf{S}_{\alpha i} \cdot \mathbf{S}_{\alpha j} \rangle \langle \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \rangle \\ &= (nl^2 k^2 / 3\pi^2) \sum_{\mu=1}^{\infty} \mu^{-3/2} / \sqrt{2} h \end{aligned} \quad (4.19)$$

where (4.10) and (4.16) are utilised. The second term on the right-hand side of (4.18) gives, when pre-averaged,

$$\begin{aligned} - \left\langle \sum_{iipp'} (\mathbf{k} \cdot \mathbf{S}_i)(\mathbf{k} \cdot \mathbf{S}_j) \mathbf{K}^{-1}(\mathbf{S}_i, \mathbf{S}_p) \cdot \mathbf{g}_t^{-1} \cdot \mathbf{K}^{-1}(\mathbf{S}_p, \mathbf{S}_j) \right\rangle \\ = -\frac{1}{3} (k^2 / f_t) \sum_{iipp'} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \langle \mathbf{K}_{ip}^{-1} \rangle \langle \mathbf{K}_{p'j}^{-1} \rangle. \end{aligned} \quad (4.20)$$

Converting these sums into integrals and expanding $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$, $\langle \mathbf{K}_{ip}^{-1} \rangle$ and $\langle \mathbf{K}_{p'j}^{-1} \rangle$ in double Fourier series we readily get a value of $-k^2 f_{00} / 3K_{00} K_{00}$ for (4.20). This vanishes since $f_{00} = 0$.

In the evaluation of the third term on the right-hand side of (4.18), we further assume that the angular velocity of a bead is the same as the configuration averaged angular velocity of the chain. This then yields upon pre-averaging

$$\begin{aligned} \left\langle \sum_{iipp'} (\mathbf{k} \cdot \mathbf{S}_i)(\mathbf{k} \cdot \mathbf{S}_j) \mathbf{K}^{-1}(\mathbf{S}_i, \mathbf{S}_p) \times \mathbf{S}_p \cdot \mathbf{g}_r^{-1} \cdot \mathbf{S}_p \times \mathbf{K}^{-1}(\mathbf{S}_p, \mathbf{S}_j) \right\rangle \\ = -\frac{1}{9} f_r^{-1} k^2 (\mathbf{I} - k^{-2} \mathbf{k} \mathbf{k}) \sum_{iipp'} \langle \mathbf{S}_i \cdot \mathbf{S}_p \rangle \langle \mathbf{S}_p \cdot \mathbf{S}_j \rangle \langle \mathbf{K}_{ip}^{-1} \rangle \langle \mathbf{K}_{p'j}^{-1} \rangle. \end{aligned} \quad (4.21)$$

Transforming the sums into integrals and expanding the various averages appearing in (4.21) in double Fourier series, and combining with (4.10) and (4.16), (4.21) becomes

$$-(nl^2 / 6\pi^2) k^2 (\mathbf{I} - k^{-2} \mathbf{k} \mathbf{k}) \sum_{\mu=1}^{\infty} \mu^{-3/2} / \sqrt{2} h. \quad (4.22)$$

Since we are interested in the shear viscosity, combining (4.22), (3.22), (4.18), (4.19), (4.20) and (4.22), we obtain for $[\eta]$

$$\begin{aligned} [\eta] &= (Nnl^2 / 6\eta_0 c V\pi^2) \sum_{\mu=1}^{\infty} \mu^{-3/2} / \sqrt{2} h \\ &= (N_A nl^2 / 6\eta_0 M\pi^2) \sum_{\mu=1}^{\infty} \mu^{-3/2} / \sqrt{2} h \end{aligned} \quad (4.23)$$

where we have used the identity $c = NM / N_A V$, where N_A is Avogadro's number. Equation (4.23) is identical to the result of Kirkwood and Riseman (1948) for the non-free-draining limit.

4.4. Hydrodynamic screening

From (3.13), (3.19) and (3.20), $\Sigma(k=0)$ becomes, upon pre-averaging, for N chains

$$\begin{aligned} \frac{V}{N} \Sigma(k=0) &= \sum_{ij} \langle \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \rangle - \frac{1}{f_t} \sum_{iipp'} \langle \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \rangle \langle \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) \rangle \\ &\quad + \frac{1}{f_r} \sum_{iipp'} \langle \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \times \mathbf{S}_{\alpha p} \rangle \langle \mathbf{S}_{\alpha p'} \times \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) \rangle. \end{aligned} \quad (4.24)$$

From (4.1), we see that the first and second terms on the right-hand side of (4.24) are f_t and $-f_t$, respectively. The third term vanishes. Therefore there is no hydrodynamic screening.

5. Cluster theory for shear viscosity

In this section we consider a suspension of N polymer chains each with n beads. Here we incorporate the inter-chain hydrodynamic interactions explicitly. Except for this additional feature, the derivation is identical to the one presented in § 2.

5.1. Formal velocity field

The equation of motion for the fluid containing N chains is

$$-\eta_0 \nabla^2 \mathbf{v}(\mathbf{r}) + \nabla P(\mathbf{r}) = \mathbf{F}(\mathbf{r}) + \sum_{\alpha=1}^N \sum_{i=1}^n \delta(\mathbf{r} - \mathbf{R}_{\alpha i}) \boldsymbol{\sigma}_{\alpha i}. \quad (5.1)$$

The formal solution of (5.1) is

$$\mathbf{v}(\mathbf{r}) = \int d\mathbf{r}' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \left[\mathbf{F}(\mathbf{r}') + \sum_{\alpha i} \delta(\mathbf{r}' - \mathbf{R}_{\alpha i}) \boldsymbol{\sigma}_{\alpha i} \right]. \quad (5.2)$$

Combining (5.2) and (2.14d) yields

$$\begin{aligned} \mathbf{u}_{\alpha} + \boldsymbol{\omega}_{\alpha} \times \mathbf{S}_{\alpha p} &= \int d\mathbf{r}' \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \sum_{j=1}^n \mathbf{K}_{\alpha}(\mathbf{S}_{\alpha p} - \mathbf{S}_{\alpha j}) \cdot \boldsymbol{\sigma}_{\alpha j} \\ &\quad + \sum_{\beta \neq \alpha} \sum_{j=1}^n \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{R}_{\beta j}) \cdot \boldsymbol{\sigma}_{\beta j}. \end{aligned} \quad (5.3)$$

Use of (3.6) gives

$$\begin{aligned} \boldsymbol{\sigma}_{\alpha i} &= \sum_{p=1}^n \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \cdot (\mathbf{u}_{\alpha} + \boldsymbol{\omega}_{\alpha} \times \mathbf{S}_{\alpha p}) - \sum_p \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \\ &\quad \cdot \left(\int d\mathbf{r}' \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \sum_{\beta \neq \alpha} \sum_j \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{R}_{\beta j}) \cdot \boldsymbol{\sigma}_{\beta j} \right). \end{aligned} \quad (5.4)$$

Inserting (5.4) into (2.14b) and (2.14c) and ignoring external forces and torques we obtain

$$\begin{aligned} \sum_{i,j=1}^n \begin{pmatrix} \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) & -\mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \times \mathbf{S}_{\alpha j} \\ \mathbf{S}_{\alpha i} \times \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) & -\mathbf{S}_{\alpha i} \times \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \times \mathbf{S}_{\alpha j} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{u}_{\alpha} \\ \boldsymbol{\omega}_{\alpha} \end{pmatrix} &= \sum_{i,j=1}^n \begin{pmatrix} \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \\ \mathbf{S}_{\alpha i} \times \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \end{pmatrix} \\ &\quad \cdot \left(\int d\mathbf{r}' \mathbf{G}(\mathbf{R}_{\alpha j} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \sum_{\beta \neq \alpha} \sum_{p=1}^n \mathbf{G}(\mathbf{R}_{\alpha j} - \mathbf{R}_{\beta p}) \cdot \boldsymbol{\sigma}_{\beta p} \right). \end{aligned} \quad (5.5)$$

Rewriting (5.5), \mathbf{u}_{α} and $\boldsymbol{\omega}_{\alpha}$ are given by

$$\begin{aligned} \mathbf{u}_{\alpha} &= \sum_{j,p} [\mathbf{g}_{\tau}^{-1} \cdot \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha j}, \mathbf{S}_{\alpha p}) + \mathbf{g}_{\tau}^{-1} \cdot \mathbf{S}_{\alpha j} \times \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha j}, \mathbf{S}_{\alpha p})] \\ &\quad \times \left(\int d\mathbf{r}' \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \sum_{\beta \neq \alpha} \sum_{p'} \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{R}_{\beta p'}) \cdot \boldsymbol{\sigma}_{\beta p'} \right) \end{aligned}$$

$$\omega_\alpha = \sum_{jp} [\mathbf{g}_{rt}^{-1} \cdot \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha j}, \mathbf{S}_{\alpha p}) + \mathbf{g}_r^{-1} \cdot \mathbf{S}_{\alpha j} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha j}, \mathbf{S}_{\alpha p})] \times \left(\int d\mathbf{r}' \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \sum_{\beta \neq \alpha} \sum_{p'} \mathbf{G}(\mathbf{R}_{\alpha p} - \mathbf{R}_{\beta p'}) \cdot \boldsymbol{\sigma}_{\beta p'} \right) \quad (5.6)$$

where \mathbf{g}^{-1} are given by

$$\sum_{ij} \begin{pmatrix} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) & -\mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \times \mathbf{S}_{\alpha j} \\ \mathbf{S}_{\alpha i} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) & -\mathbf{S}_{\alpha i} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \times \mathbf{S}_{\alpha j} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{g}_t^{-1} & \mathbf{g}_{tr}^{-1} \\ \mathbf{g}_{rt}^{-1} & \mathbf{g}_r^{-1} \end{pmatrix} = \mathbf{I}. \quad (5.7)$$

Insertion of (5.6) for \mathbf{u}_α and ω_α into (5.4) yields

$$\begin{aligned} \sigma_{\alpha i} = & - \sum_{j=1}^n \left(\mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) - \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \cdot [\mathbf{g}_t^{-1} \cdot \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) \right. \\ & + \mathbf{g}_{tr}^{-1} \cdot \mathbf{S}_{\alpha p'} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j})] + \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \times \mathbf{S}_{\alpha p} \\ & \cdot [\mathbf{g}_{rt}^{-1} \cdot \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) + \mathbf{g}_r^{-1} \cdot \mathbf{S}_{\alpha p'} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j})] \Big) \\ & \cdot \left(\int d\mathbf{r}' \mathbf{G}(\mathbf{R}_{\alpha j} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \sum_{\beta \neq \alpha} \sum_{p''} \mathbf{G}(\mathbf{R}_{\alpha j} - \mathbf{R}_{\beta p''}) \cdot \boldsymbol{\sigma}_{\beta p''} \right). \end{aligned} \quad (5.8)$$

Iterating (5.8) indefinitely and then substituting the resulting expression for $\sigma_{\alpha i}$ into (5.1), we obtain a general multiple scattering expression for the velocity field,

$$\mathbf{v}(\mathbf{r}) = \sum_{n=0}^{\infty} \mathbf{v}^{(n)}(\mathbf{r}) \quad (5.9a)$$

$$\mathbf{v}^{(0)}(\mathbf{r}) = \int d\mathbf{r}' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') \quad (5.9b)$$

$$\mathbf{v}^{(1)}(\mathbf{r}) = \sum_{\alpha=1}^N \int d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{T}_\alpha(\mathbf{r}' - \mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}'' - \mathbf{r}''') \cdot \mathbf{F}(\mathbf{r}''') \quad (5.9c)$$

$$\begin{aligned} \mathbf{v}^{(2)}(\mathbf{r}) = & \sum_{\alpha} \sum_{\beta \neq \alpha} \int d\mathbf{r}' \cdots d\mathbf{r}^v \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{T}_\alpha(\mathbf{r}' - \mathbf{r}'') \\ & \cdot \mathbf{G}(\mathbf{r}'' - \mathbf{r}''') \cdot \mathbf{T}_\beta(\mathbf{r}''' - \mathbf{r}^{iv}) \cdot \mathbf{G}(\mathbf{r}^{iv} - \mathbf{r}^v) \cdot \mathbf{F}(\mathbf{r}^v) \end{aligned} \quad (5.9d)$$

$$\begin{aligned} \mathbf{v}^{(n)}(\mathbf{r}) = & \sum_{\alpha_1} \sum_{\alpha_2 \neq \alpha_1} \cdots \sum_{\alpha_n \neq \alpha_{n-1}} \int \prod_{i=1}^{2n+1} d\mathbf{r}_i \mathbf{G}(\mathbf{r} - \mathbf{r}_1) \cdot \mathbf{T}_{\alpha_1}(\mathbf{r}_1 - \mathbf{r}_2) \\ & \cdot \mathbf{G}(\mathbf{r}_2 - \mathbf{r}_3) \cdot \mathbf{T}_{\alpha_2}(\mathbf{r}_3 - \mathbf{r}_4) \cdots \mathbf{T}_{\alpha_n}(\mathbf{r}_{2n-1} - \mathbf{r}_{2n}) \cdot \mathbf{G}(\mathbf{r}_{2n} - \mathbf{r}_{2n+1}) \cdot \mathbf{F}(\mathbf{r}_{2n+1}) \end{aligned} \quad (5.9e)$$

where \mathbf{T}_α is

$$\begin{aligned} \mathbf{T}_\alpha(\mathbf{r} - \mathbf{r}') = & - \sum_{i,j=1}^n \delta(\mathbf{r} - \mathbf{R}_{\alpha i}) \left(\mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) - \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \right. \\ & \cdot [\mathbf{g}_t^{-1} \cdot \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) + \mathbf{g}_{tr}^{-1} \cdot \mathbf{S}_{\alpha p'} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j})] + \sum_{pp'} \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \times \mathbf{S}_{\alpha p} \\ & \left. \cdot [\mathbf{g}_{rt}^{-1} \cdot \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) + \mathbf{g}_r^{-1} \cdot \mathbf{S}_{\alpha p'} \times \mathbf{K}_\alpha^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j})] \right) \delta(\mathbf{r}' - \mathbf{R}_{\alpha j}). \end{aligned} \quad (5.10)$$

Note that the single chain operator $\mathbf{T}_\alpha(\mathbf{r} - \mathbf{r}')$ depends on the centre of mass of the chain α through $\mathbf{R}_{\alpha i}(=\mathbf{R}_\alpha^0 + \mathbf{S}_{\alpha i})$ and $\mathbf{R}_{\alpha j}$.

5.2. Average velocity field

As in § 3, we write an effective Navier–Stokes equation for the average velocity field in the whole polymer solution,

$$-\eta_0 \nabla^2 \mathbf{V}(\mathbf{r}) + \nabla \langle P(\mathbf{r}) \rangle - \int d\mathbf{r}' \boldsymbol{\Sigma}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{V}(\mathbf{r}') = \mathbf{F}(\mathbf{r}')$$

where

$$\int d\mathbf{r}' \boldsymbol{\Sigma}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{V}(\mathbf{r}') = \left\langle \sum_{\alpha=1}^N \sum_{i=1}^n \delta(\mathbf{r} - \mathbf{R}_{\alpha i}) \boldsymbol{\sigma}_{\alpha i} \right\rangle. \quad (5.11)$$

This term corresponds to the contributions of all the chains to the divergence of the stress tensor for the fluid. Here the angular brackets indicate an ensemble average with respect to the distribution of all the centres of mass of the chains. The configurational average for any individual chain is implicitly present in the derivation and is explicitly expressed only in the algebraic calculations of the final steps. Similar to (3.18), we can write an expression for the average velocity field with the new definition of $\boldsymbol{\Sigma}$ for N chains, (5.11), as

$$\begin{aligned} \langle \mathbf{v}(\mathbf{r}) \rangle &= \mathbf{V}(\mathbf{r}) \\ &= \int d\mathbf{r}' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') + \int d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \boldsymbol{\Sigma}(\mathbf{r}' - \mathbf{r}'') \\ &\quad \cdot \mathbf{G}(\mathbf{r}'' - \mathbf{r}''') \cdot \mathbf{F}(\mathbf{r}''') + \int d\mathbf{r}' d\mathbf{r}'' d\mathbf{r}''' d\mathbf{r}^{iv} d\mathbf{r}^v \mathbf{G}(\mathbf{r} - \mathbf{r}') \cdot \boldsymbol{\Sigma}(\mathbf{r}' - \mathbf{r}'') \\ &\quad \cdot \mathbf{G}(\mathbf{r}'' - \mathbf{r}''') \cdot \boldsymbol{\Sigma}(\mathbf{r}''' - \mathbf{r}^{iv}) \cdot \mathbf{G}(\mathbf{r}^{iv} - \mathbf{r}^v) \cdot \mathbf{F}(\mathbf{r}^v) + \dots \end{aligned} \quad (5.12)$$

Since $\boldsymbol{\Sigma}$ is the net effect of all the multiple scattering disturbances of the velocity field involving all N chains, it is convenient to define it as

$$\boldsymbol{\Sigma}(\mathbf{r} - \mathbf{r}') = \sum_{j=1}^{\infty} \boldsymbol{\Sigma}_{(j)}(\mathbf{r} - \mathbf{r}') \quad (5.13)$$

where $\boldsymbol{\Sigma}_{(j)}$ represents a multiple scattering sequence with j factors of $T_{(\alpha)}$. By substituting (5.9) for $\mathbf{v}(\mathbf{r})$ in (5.12) and then combining with (5.13) it follows that

$$\begin{aligned} \boldsymbol{\Sigma}_{(1)}(\mathbf{r} - \mathbf{r}') &= \left\langle \sum_{\alpha=1}^N \mathbf{T}_\alpha(\mathbf{r} - \mathbf{r}') \right\rangle \\ \boldsymbol{\Sigma}_{(2)}(\mathbf{r} - \mathbf{r}') &= \sum_{\alpha=1}^N \sum_{\beta \neq \alpha} \int d\mathbf{r}'' d\mathbf{r}''' \langle \mathbf{T}_\alpha(\mathbf{r} - \mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}'' - \mathbf{r}''') \cdot \mathbf{T}_\beta(\mathbf{r}''' - \mathbf{r}') \rangle \\ &\quad - \sum_{\alpha} \sum_{\beta} \int d\mathbf{r}'' d\mathbf{r}''' \langle \mathbf{T}_\alpha(\mathbf{r} - \mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}'' - \mathbf{r}''') \cdot \langle \mathbf{T}_\beta(\mathbf{r}''' - \mathbf{r}') \rangle \end{aligned}$$

$$\begin{aligned}
\Sigma_{(3)}(\mathbf{r}-\mathbf{r}') = & \int d\mathbf{r}'' d\mathbf{r}''' d\mathbf{r}^{iv} d\mathbf{r}^v \left[\sum_{\substack{\alpha \\ \beta \neq \alpha \\ \gamma \neq \beta}} \langle \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \right. \\
& \cdot \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}^{iv}) \cdot \mathbf{G}(\mathbf{r}^{iv}-\mathbf{r}^v) \cdot \mathbf{T}_\gamma(\mathbf{r}^v-\mathbf{r}') \rangle \\
& - \sum_{\substack{\alpha, \beta \\ \gamma \neq \beta}} \langle \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \cdot \langle \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}^{iv}) \cdot \mathbf{G}(\mathbf{r}^{iv}-\mathbf{r}^v) \cdot \mathbf{T}_\gamma(\mathbf{r}^v-\mathbf{r}') \rangle \rangle \\
& - \sum_{\substack{\alpha, \gamma \\ \beta \neq \alpha}} \langle \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \cdot \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}^{iv}) \rangle \cdot \mathbf{G}(\mathbf{r}^{iv}-\mathbf{r}^v) \cdot \langle \mathbf{T}_\gamma(\mathbf{r}^v-\mathbf{r}') \rangle \rangle \\
& \left. + \sum_{\alpha\beta\gamma} \langle \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \cdot \langle \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}^{iv}) \rangle \cdot \mathbf{G}(\mathbf{r}^{iv}-\mathbf{r}^v) \cdot \langle \mathbf{T}_\gamma(\mathbf{r}^v-\mathbf{r}') \rangle \right]. \tag{5.14}
\end{aligned}$$

Note that although $\Sigma_{(3)}$ represents a sequence of three scattering events, one of such sequences can involve only two chains, e.g. when $\gamma = \alpha$. Therefore it is convenient to rearrange the various terms in the infinite series (5.14) so as to yield a virial expansion for Σ in the number of distinct chains participating in a scattering sequence

$$\Sigma(\mathbf{r}-\mathbf{r}') = \sum_{i=1}^N \Sigma_i(\mathbf{r}-\mathbf{r}') \tag{5.15}$$

where Σ_i depicts the contribution arising from all the multiple scattering events taking place among any set of i distinct polymer chains. Except for $\Sigma_1(\mathbf{r}-\mathbf{r}')$, every Σ_i is an infinite multiple scattering series. The leading terms of a few of these are

$$\begin{aligned}
\Sigma_1(\mathbf{r}-\mathbf{r}') = & \left\langle \sum_{\alpha=1}^N \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}') \right\rangle \\
\Sigma_2(\mathbf{r}-\mathbf{r}') = & \int d\mathbf{r}'' d\mathbf{r}''' \left[\sum_{\alpha=1}^N \sum_{\beta \neq \alpha} \langle \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \cdot \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}') \rangle \right. \\
& \left. - \sum_{\alpha} \sum_{\beta} \langle \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \rangle \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \cdot \langle \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}') \rangle \right] \\
& + \int d\mathbf{r}'' d\mathbf{r}''' d\mathbf{r}^{iv} d\mathbf{r}^v \left[\sum_{\substack{\alpha \\ \beta \neq \alpha}} \langle \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \right. \\
& \cdot \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}^{iv}) \cdot \mathbf{G}(\mathbf{r}^{iv}-\mathbf{r}^v) \cdot \mathbf{T}_\alpha(\mathbf{r}^v-\mathbf{r}') \rangle \\
& - \sum_{\substack{\alpha \\ \beta \neq \alpha}} \langle \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \rangle \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \cdot \langle \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}^{iv}) \rangle \cdot \mathbf{G}(\mathbf{r}^{iv}-\mathbf{r}^v) \cdot \langle \mathbf{T}_\alpha(\mathbf{r}^v-\mathbf{r}') \rangle \rangle \\
& - \sum_{\substack{\alpha \\ \beta \neq \alpha}} \langle \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \cdot \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}^{iv}) \rangle \cdot \mathbf{G}(\mathbf{r}^{iv}-\mathbf{r}^v) \cdot \langle \mathbf{T}_\alpha(\mathbf{r}^v-\mathbf{r}') \rangle \rangle \\
& \left. + \sum_{\alpha\beta} \langle \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \rangle \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \cdot \langle \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}^{iv}) \rangle \cdot \mathbf{G}(\mathbf{r}^{iv}-\mathbf{r}^v) \cdot \langle \mathbf{T}_\alpha(\mathbf{r}^v-\mathbf{r}') \rangle \right] \\
& + \dots
\end{aligned}$$

$$\Sigma_3 = \left[\sum_{\substack{\alpha \\ \beta \neq \alpha \\ \alpha \neq \gamma \neq \beta}} \langle \mathbf{T}_\alpha \cdot \mathbf{G} \cdot \mathbf{T}_\beta \cdot \mathbf{G} \cdot \mathbf{T}_\gamma \rangle - \sum_{\substack{\alpha, \beta \\ \alpha \neq \gamma \neq \beta}} \langle \mathbf{T}_\alpha \rangle \cdot \mathbf{G} \cdot \langle \mathbf{T}_\beta \cdot \mathbf{G} \cdot \mathbf{T}_\gamma \rangle \right. \\ \left. - \sum_{\substack{\alpha \\ \beta \neq \alpha \\ \gamma \neq \alpha}} \langle \mathbf{T}_\alpha \cdot \mathbf{G} \cdot \mathbf{T}_\beta \rangle \cdot \mathbf{G} \cdot \langle \mathbf{T}_\gamma \rangle + \sum_{\substack{\alpha \beta \\ \gamma \neq \alpha}} \langle \mathbf{T}_\alpha \rangle \cdot \mathbf{G} \cdot \langle \mathbf{T}_\beta \rangle \cdot \mathbf{G} \cdot \langle \mathbf{T}_\gamma \rangle \right] + \dots \tag{5.16}$$

Thus (5.15) is a cluster expansion in increasing order of concentration. This, when substituted into (3.22), yields a virial expansion in concentration for the specific viscosity of the polymer solution. The ensemble averages of the various terms present in Σ_i of (5.16) can, in principle, develop concentration dependencies owing to the concentration dependence of distribution functions so care must be exercised in collecting the various virial coefficients.

It is convenient to employ a pictorial representation for the terms in (5.16). Each factor of \mathbf{T} is represented by a single broken line and each G is depicted by a single horizontal line. The presence of an average over the centres of mass of the chains is represented by a single bubble. The broken lines, associated with a given chain, are joined together at the bubble. When t distinct chains are involved in a term in (5.16), then in the corresponding diagram there are t distinct points along the contour of the bubble at which broken lines intersect it. In writing these diagrams the exclusion condition, requiring that no two successive broken lines are associated with the same chain, should be borne in mind. Using this nomenclature, (5.16) is diagrammatically presented in figure 1.

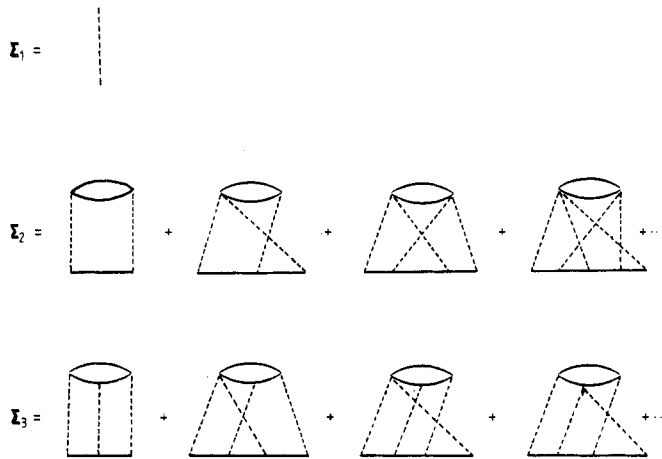


Figure 1. Diagrammatic representation of equation (5.16) for the general case.

The averaging with respect to the centres of mass, the integrations over all spatial positions and the summations over the chains are understood to be taken in these diagrams. Also, a diagram involving x chains and y scattering operators includes all the terms in (5.16) with x chains and y scattering operators. For example, the first diagram for Σ_3 in figure 1 represents the square bracket on the right-hand side of Σ_3 in (5.16).

5.3. Specific viscosity in ideal solutions

Under θ conditions, the average polymer–polymer interaction and polymer–solvent interaction cancel each other so the effective potential energy of interaction of the chains can be taken to be zero. Now, (5.16) simplifies to

$$\begin{aligned} \Sigma_1(\mathbf{r}-\mathbf{r}') &= \frac{N}{V} \int d\mathbf{R}_\alpha^0 \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}') \\ \Sigma_2(\mathbf{r}-\mathbf{r}') &= \left(\frac{N}{V}\right)^2 \int d\mathbf{R}_\alpha^0 d\mathbf{R}_\beta^0 d\mathbf{r}'' d\mathbf{r}''' d\mathbf{r}^{iv} d\mathbf{r}^v \mathbf{T}_\alpha(\mathbf{r}-\mathbf{r}'') \cdot \mathbf{G}(\mathbf{r}''-\mathbf{r}''') \\ &\quad \cdot \mathbf{T}_\beta(\mathbf{r}'''-\mathbf{r}^{iv}) \cdot \mathbf{G}(\mathbf{r}^{iv}-\mathbf{r}^v) \cdot \mathbf{T}_\alpha(\mathbf{r}^v-\mathbf{r}') + \dots \end{aligned} \tag{5.17}$$

etc. The multiple scattering series given by (5.17) for θ solutions is diagrammatically represented in figure 2. The broken lines which are connected at the top correspond to terms involving fluid scattering by the same chain.

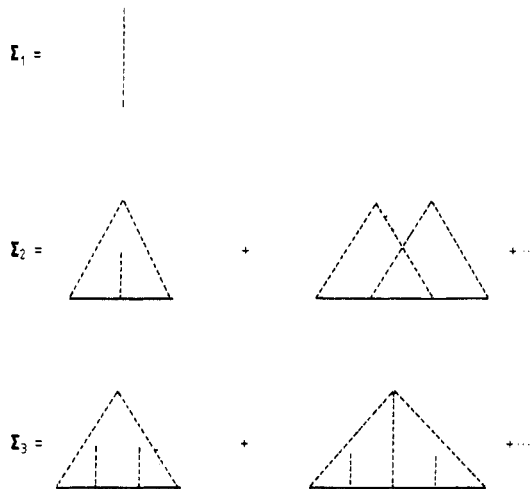


Figure 2. Diagrammatic representation of equation (5.17) for ideal solutions.

As explained in § 3, the k^2 term of $\Sigma(\mathbf{k})$ defined by

$$\Sigma(\mathbf{k}) = \int d\mathbf{r} \Sigma(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \tag{5.18}$$

gives the change, $\delta\eta$, in shear viscosity of the polymer solution as

$$\frac{\delta\eta}{\eta_0 c} (\mathbf{I} - k^{-2} \mathbf{k}\mathbf{k}) = -(1/\eta_0 c k^2) (\mathbf{I} - k^{-2} \mathbf{k}\mathbf{k}) \cdot \Sigma_{k^2}. \tag{5.19}$$

Explicit evaluation of the terms in (5.17) and then combining with (5.15), (5.18) and (5.19) gives the specific viscosity as a function of concentration to any desired order in concentration.

6. Discussion

The formal solution of (5.11) for the average velocity field can be expressed as

$$\mathbf{V}(\mathbf{r}) = \int d\mathbf{r}' \hat{\mathbf{G}}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') \quad (6.1)$$

where $\hat{\mathbf{G}}(\mathbf{r} - \mathbf{r}')$ represents the average hydrodynamic interaction between any two spatial points \mathbf{r} and \mathbf{r}' in the *whole* polymer solution. All the complexities and the dynamic consequences arising from the various multiple scattering sequences between the chains are implicitly present in $\hat{\mathbf{G}}$. Comparison of (6.1) with (5.11) readily yields

$$\hat{\mathbf{G}}(\mathbf{r} - \mathbf{r}') = \int \frac{d^3k}{(2\pi)^3} \frac{(\mathbf{I} - k^{-2}\mathbf{k}\mathbf{k})}{[\eta_0 k^2 \mathbf{I} - \boldsymbol{\Sigma}(\mathbf{k})]} \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}')] \quad (6.2)$$

where $\boldsymbol{\Sigma}(\mathbf{k})$ is given by (5.18), (5.15) and (5.16) for θ solutions. Summarising, we have the coupled equations

$$\hat{\mathbf{K}}_\alpha(\mathbf{S}_{\alpha i} - \mathbf{S}_{\alpha j}) \equiv \hat{\mathbf{G}}(\mathbf{S}_{\alpha i} - \mathbf{S}_{\alpha j}) = \int \frac{d^3k}{(2\pi)^3} \frac{(\mathbf{I} - k^{-2}\mathbf{k}\mathbf{k})}{[\eta_0 k^2 \mathbf{I} - \boldsymbol{\Sigma}(\mathbf{k})]} \exp[i\mathbf{k} \cdot (\mathbf{S}_{\alpha i} - \mathbf{S}_{\alpha j})] \quad (6.3a)$$

$$\boldsymbol{\Sigma}(\mathbf{k}) = \sum_{i=1}^N \int d\mathbf{r} \boldsymbol{\Sigma}_i(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \quad (6.3b)$$

where $\boldsymbol{\Sigma}_i$ are given by (5.16). For ideal solutions, $\boldsymbol{\Sigma}_i$ should be obtained from (5.17). When the rotational and cross translational-rotational terms are suppressed in the various integrals of (5.17), the set of coupled equations of (6.3) is identical to the one given by Freed and Edwards.

Now, the Huggins coefficient, k_H , defined by

$$(\eta - \eta_0)/\eta_0 c = [\eta] + k_H [\eta]^2 c + \dots \quad (6.4)$$

can be calculated by two methods. The first method is an iterative one and involves the following steps. Determine \mathbf{K}_α from (6.3a) in the infinite dilution limit, when $\boldsymbol{\Sigma}(\mathbf{k})$ is absent. Truncate the series in (6.3b) at $i = 1$. Substitute infinite dilution value of \mathbf{K}_α in the expression for $\boldsymbol{\Sigma}_1$ according to (5.16). Use this in (6.3b). This gives $\boldsymbol{\Sigma}^{(1)}(\mathbf{k})$ proportional to concentration. (This determines the intrinsic viscosity.) Insert this $\boldsymbol{\Sigma}^{(1)}$ in (6.3a) to obtain the concentration-dependent $\hat{\mathbf{K}}_\alpha^{(1)}$. When this is utilised in (6.3b) we get $\boldsymbol{\Sigma}^{(2)}(\mathbf{k})$ up to order c^2 . From (5.19), k_H can be calculated.

The second method is a more direct one. As outlined in § 5, we already have a virial expansion for the specific viscosity. For the determination of k_H we need to consider all the diagrams in figure 1 which contain two distinct chains only. Restricting ourselves only to the leading diagram, $\boldsymbol{\Sigma}_2^1$, namely, the first on the right-hand side of $\boldsymbol{\Sigma}_2$ in figure 2, we get from (5.17) and (5.10)

$$\begin{aligned} \boldsymbol{\Sigma}_2^1(\mathbf{r} - \mathbf{r}') = & \left(\frac{N}{V}\right)^2 \sum_{ijmm'pp'} \int d\mathbf{R}_\alpha^0 d\mathbf{R}_\beta^0 \delta(\mathbf{r} - \mathbf{R}_\alpha^0 - \mathbf{S}_{\alpha i}) \bar{\mathbf{T}}_\alpha(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \\ & \cdot \mathbf{G}(\mathbf{R}_\alpha^0 + \mathbf{S}_{\alpha j} - \mathbf{R}_\beta^0 - \mathbf{S}_{\beta p}) \cdot \bar{\mathbf{T}}_\beta(\mathbf{S}_{\beta p}, \mathbf{S}_{\beta p'}) \cdot \mathbf{G}(\mathbf{R}_\beta^0 + \mathbf{S}_{\beta p'} - \mathbf{R}_\alpha^0 - \mathbf{S}_{\alpha m}) \\ & \cdot \bar{\mathbf{T}}_\alpha(\mathbf{S}_{\alpha m}, \mathbf{S}_{\alpha m'}) \delta(\mathbf{r}' - \mathbf{R}_\alpha^0 - \mathbf{S}_{\alpha m'}) \end{aligned} \quad (6.5)$$

where

$$\begin{aligned} \bar{\mathbf{T}}_{\alpha}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) &= \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) - \sum_{pp'} \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \\ &\quad \cdot [\mathbf{g}_{\text{tr}}^{-1} \cdot \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) + \mathbf{g}_{\text{tr}}^{-1} \cdot \mathbf{S}_{\alpha p'} \times \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j})] \\ &\quad + \sum_{pp'} \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha p}) \times \mathbf{S}_{\alpha p} \cdot [\mathbf{g}_{\text{tr}}^{-1} \cdot \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j}) + \mathbf{g}_{\text{tr}}^{-1} \cdot \mathbf{S}_{\alpha p'} \times \mathbf{K}_{\alpha}^{-1}(\mathbf{S}_{\alpha p'}, \mathbf{S}_{\alpha j})]. \end{aligned} \quad (6.6)$$

Using the Fourier representations of the delta functions and the Oseen tensor \mathbf{G} , the Fourier transform of (6.5) yields

$$\begin{aligned} \Sigma_2^1(\mathbf{k}) &= \left(\frac{N}{V}\right)^2 \sum \int \frac{d^3 k'}{(2\pi)^3} \exp[-i\mathbf{k} \cdot (\mathbf{S}_{\alpha i} - \mathbf{S}_{\alpha m'}) + i\mathbf{k}' \cdot (\mathbf{S}_{\alpha j} - \mathbf{S}_{\beta p} + \mathbf{S}_{\beta p'} - \mathbf{S}_{\alpha m})] \\ &\quad \times \bar{\mathbf{T}}_{\alpha}(\mathbf{S}_{\alpha i}, \mathbf{S}_{\alpha j}) \cdot \mathbf{G}(\mathbf{k}') \cdot \bar{\mathbf{T}}_{\beta}(\mathbf{S}_{\beta p}, \mathbf{S}_{\beta p'}) \cdot \mathbf{G}(\mathbf{k}') \cdot \bar{\mathbf{T}}_{\alpha}(\mathbf{S}_{\alpha m}, \mathbf{S}_{\alpha m'}) \end{aligned} \quad (6.7)$$

where

$$\mathbf{G}(\mathbf{k}) = (1/\eta_0 k^2)(\mathbf{I} - k^{-2} \mathbf{k}\mathbf{k}). \quad (6.8)$$

Explicit evaluation of k_H using (6.7) and the iterative procedure given in the previous paragraph and the comparison of the results will be discussed in a later paper.

As shown in § 4, when the translational diffusion of the centre of mass of the chain and the rotational motion of the chain are included, we get the same intrinsic viscosity as obtained by Kirkwood and Riseman. In addition, we find for dilute solutions that there is no hydrodynamic screening within the pre-averaging approximation, when the angular velocity of a chain for a particular configuration is replaced by the average angular velocity. This result is in sharp contrast to the one obtained by Freed and Edwards.

As the concentration of the polymer solution increases, the translational diffusion of the centres of mass of the chains and their rotational motion become increasingly suppressed. Consequently the hydrodynamic screening grows as the concentration increases and eventually the hydrodynamic interaction is fully screened to give the Rouse behaviour. The concentration dependence of the translational and rotational diffusion coefficients in semidilute solutions is to be investigated in order to understand the hydrodynamic screening fully and thus the transition from Zimm-like behaviour to Rouse-like behaviour. We hope to return to these points in a later paper.

The virial expansion presented in this paper provides a natural method to treat the excluded volume effect on the intrinsic viscosity and the Huggins coefficient. The diagrams on the right-hand side of Σ_2 in figure 1 can, in principle, be evaluated from a knowledge of the radial distribution function for any given strength of excluded volume interaction. This then provides specific viscosity as a function of the goodness of the solution.

We now summarise the important results derived in this paper.

(i) We have derived a multiple scattering theory for a solution of rigid polymers to obtain a cluster expansion in polymer concentration for the shear viscosity of the solution. Convergent and explicit expressions are obtained for the leading virial coefficients for the viscosity.

(ii) At infinite dilution, we recover the well known results of Kirkwood and Riseman for the intrinsic viscosity and the translational and rotational friction coefficients. On the other hand the $[\eta]$ obtained from the Freed-Edwards theory for the static limit is a factor of two larger than the Kirkwood-Riseman result.

(iii) We demonstrate that there is no hydrodynamic screening at infinite dilution again in contrast with the Freed–Edwards theory. This is an important result as it refers to the symmetry of the equation of motion. In other words, our result shows that the fluid flow present in an infinitely dilute polymer solution obeys the Navier–Stokes equation. On the other hand the presence of hydrodynamic screening in the formulation of Freed and Edwards indicates that there is Darcy flow even in dilute solutions. Thus, the hydrodynamic screening at higher concentrations obtained by Freed and Edwards arises from the assumed Darcy flow. Although such a Darcy flow is intuitively obvious at very high polymer concentrations, it does not arise at lower concentrations thus making the Freed–Edwards theory invalid.

(iv) At non-zero concentrations, diagrammatic expressions are obtained for the various virial coefficients for the viscosity, specifically an explicit expression is obtained for the Huggins coefficient.

Thus the treatment presented here forms a firmer basis for the calculation of the transport coefficients in dilute polymer solutions than the Freed–Edwards theory and offers a natural extension for higher concentrations. Also it suggests that there is an onset of the hydrodynamic screening through the transition from the fluid flow at infinitely low polymer concentrations to Darcy flow at high concentrations. In general, the hydrodynamic screening length depends on the concentration-dependent translational diffusion coefficient and viscosity. Therefore the calculations of k_H and the Huggins coefficient analogues for the translational and rotational friction coefficients are important to understand the hydrodynamic screening at low but non-zero concentrations. We plan to calculate these in the near future.

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