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A microscopic treatment of the friction tensor of a polymer in dilute solution

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Abstract. Mode coupling techniques are used to derive, from the exact equation of motion, an expression for the diffusion tensor, and hence the friction tensor, of a polymer chain in dilute solution. This theory allows one to analyse the approximations needed to obtain an expression for the friction tensor similar to the usual hydrodynamic results, and provides a framework in which non-hydrodynamic contributions can be discussed.

1. Introduction

In the early theories of polymer dynamics the solvent was treated as a hydrodynamic continuum and most modern theories (see, for instance, Yamakawa 1971) also make use of a similar description of the solvent. In order to understand the basis of these hydrodynamic theories from a more microscopic point of view, several workers have considered the derivation of the Kirkwood diffusion equation from the exact equations of motion (Yamakawa *et al* 1974, Curtiss *et al* 1976). There have also been several recent attempts to understand the relationship between the Kirkwood diffusion equation and the Rouse–Zimm equations (Bixon 1973, Zwanzig 1974, Altenberger 1975, Akcasu and Gurol 1976).

An alternative approach for investigating the microscopic basis of these hydrodynamic approaches is through mode coupling theory. In a previous paper (Kapral *et al* 1976) we showed how Kirkwood's expression for the diffusion coefficient of a polymer could be derived by considering the coupling of the local total monomer density to a bilinear variable involving the local momentum density of the fluid. In this calculation the coupling of the polymer to the fluid modes occurs naturally and does not require imposing a boundary condition. Such calculations are useful not only in terms of understanding the basis of hydrodynamic theories but also provide a framework in which one can extend these theories to a non-hydrodynamic regime (Duzy and Kapral 1977).

In this paper we show how similar techniques can be used to derive expressions for the average diffusion tensor, and hence the friction tensor, of the polymer chain. In contrast to our earlier work, we focus on the dynamics of the individual monomers rather than on the dynamic structure factor of the entire polymer.

2. Mode coupling calculation of the friction coefficient

We consider a single polymer chain composed of n monomers with mass m in a solvent. If the momentum of the jth monomer unit is $\boldsymbol{p}_j (j = 1, \ldots, n)$ (we will henceforth use Latin indices to denote monomer units) then the generalised average friction tensor of the polymer chain, $\zeta(z)$, can be defined by the relation

$$\langle \boldsymbol{p}(z)\boldsymbol{p}^{\dagger}\rangle\langle \boldsymbol{p}\boldsymbol{p}^{\dagger}\rangle^{-1} \equiv \boldsymbol{D}(z)/mk_{\mathrm{B}}T = (z + \boldsymbol{\zeta}(z)/m)^{-1} \qquad (2.1)$$

where $\boldsymbol{D}(z)$ is the average diffusion tensor. Here $\boldsymbol{p}^{\dagger} = (\boldsymbol{p}_1, \boldsymbol{p}_2, \ldots, \boldsymbol{p}_n)$, an argument z denotes the Laplace transform of the corresponding time-dependent variable and the angle brackets denote an equilibrium average in the canonical ensemble over all solvent and polymer phase space variables.

In general the friction tensor consists of both microscopic and hydrodynamic contributions which arise from interactions between monomer units which occur via the solvent. Expressions for the zero frequency solvent averaged friction tensor which are based on calculations in which the solvent is described by hydrodynamic equations are well known. For example, in Kirkwood's theory the configuration averaged friction tensor is

$$\boldsymbol{\zeta}(z = 0) = \langle \zeta(\boldsymbol{1} + \zeta\boldsymbol{T})^{-1}\rangle_{\mathrm{P}} \qquad (2.2)$$

where $\langle \ldots \rangle_{\mathrm{P}}$ denotes an average over all configurations of the polymer chain and $\boldsymbol{T}$ is the Oseen tensor:

$$\boldsymbol{T}_{ij} = (8\pi\eta_0 R_{ij})^{-1}(1 + \hat{\boldsymbol{R}}_{ij}\hat{\boldsymbol{R}}_{ij}), \qquad (2.3)$$

with $\boldsymbol{R}_{ij} = \boldsymbol{R}_i - \boldsymbol{R}_j$ ($\boldsymbol{R}_i$ is the position of the ith monomer) and η_0 the solvent viscosity. In equation (2.2) the microscopic monomer friction is ζ.

In this section we show how an expression for the friction tensor can be derived from the exact equations of motion using mode coupling techniques. The expression we obtain is similar to that in equation (2.2) but the Oseen tensor appears in a pre-averaged form. One can extract the hydrodynamic contribution to the friction tensor by investigating the coupling between the monomer momenta and the hydrodynamic modes of the system. Since the hydrodynamic interactions between the monomers depend primarily on the viscous modes of the fluid (Kapral *et al* 1976), we wish to consider the coupling between the monomer momenta and the total momentum density of the fluid (solvent plus polymer), $\boldsymbol{g}_q$:

$$\boldsymbol{g}_q = \rho_0^{-1} \sum_{\mu=1}^{N} \boldsymbol{p}_{\mu} \, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\mu}} \qquad (2.4)$$

where the sum on the Greek index μ runs over all particles in the system $N = n + N_{\mathrm{s}}$, where N_{s} is the number of solvent molecules, ρ_0 is the total equilibrium mass density of the system, and $\boldsymbol{r}_{\mu}$ is the position of the μth particle. Since the coupling of the $\boldsymbol{p}_j$ to $\boldsymbol{g}_q$ vanishes in the thermodynamic limit the simplest coupling of a monomer variable to a conserved fluid mode is through a nonlinear term. In contrast to our earlier work we consider a more microscopic description of the polymer chain and hence focus on the coupling to the bilinear variables $\boldsymbol{g}_q n_{-q}^{l}$, where n_q^l is the Fourier transform of the local density of the lth monomer

$$n_q^l = \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_l}. \qquad (2.5)$$

This bilinear variable represents the fluid momentum density relative to the position of the kth monomer.

A treatment of the friction can be carried out which only includes the coupling of the momenta to these bilinear variables; this will be described in § 3. The structure of equation (2.2) suggests that it is appropriate to consider a description where the force which the jth monomer exerts on the fluid, $\boldsymbol{F}_j$, is explicitly included. Hence, we consider a description based on the set of suitably orthogonalised variables,

$$\{\boldsymbol{p}_j, \boldsymbol{F}_j, \boldsymbol{B}_q^j\} \qquad (j = 1, \ldots, n), \tag{2.6}$$

with

$$\boldsymbol{B}_q^j = \boldsymbol{g}_q n_{-q}^j - \rho_0^{-1} \sum_{i=1}^{n} \chi_{ji}(q) \boldsymbol{p}_i, \tag{2.7}$$

where

$$\chi_{ji}(q) = \langle \exp[\mathrm{i}\boldsymbol{q} \cdot (\boldsymbol{R}_i - \boldsymbol{R}_j)] \rangle_{\mathrm{P}}. \tag{2.8}$$

In order to derive generalised Langevin equations we construct a Mori projection operator, $\mathscr{P}$, which projects an arbitrary dynamical variable, θ, onto these variables

$$\mathscr{P}\theta = \sum_{i=1}^{n} \frac{\langle \theta \boldsymbol{p}_i \rangle}{m k_{\mathrm{B}} T} \cdot \boldsymbol{p}_i + \sum_{i,j=1}^{n} \langle \theta \boldsymbol{F}_i \rangle \cdot (\langle \boldsymbol{F}\boldsymbol{F}^{\dagger} \rangle^{-1})_{ij} \cdot \boldsymbol{F}_j + \frac{\rho_0}{k_{\mathrm{B}} T V} \sum_{i,j=1}^{n} \sum_{\boldsymbol{q}}{}' \langle \theta \boldsymbol{B}_{-q}^{i} \rangle (\chi^{-1}(q))_{ij} \cdot \boldsymbol{B}_q^j, \tag{2.9}$$

where $\boldsymbol{F} = \dot{\boldsymbol{p}}$. The random forces corresponding to the variables in equation (2.6) are

$$\boldsymbol{f}_j^p = (1 - \mathscr{P}) \mathrm{i} L \boldsymbol{p}_j = 0$$

$$\boldsymbol{f}_j^F = \dot{\boldsymbol{F}}_j + \sum_{i=1}^{n} \frac{\langle \boldsymbol{F}_j \boldsymbol{F}_i \rangle}{m k_{\mathrm{B}} T} \cdot \boldsymbol{p}_i - \frac{\rho_0}{k_{\mathrm{B}} T V} \sum_{i,l=1}^{n} \sum_{\boldsymbol{q}}{}' \langle (\mathrm{i} L \boldsymbol{F}_j) \boldsymbol{B}_{-q}^{i} \rangle (\chi(q)^{-1})_{il} \cdot \boldsymbol{B}_q^l \tag{2.10}$$

$$\boldsymbol{f}_j^B(\boldsymbol{q}) = \dot{\boldsymbol{B}}_q^j - \sum_{i,l=1}^{n} \langle (\mathrm{i} L \boldsymbol{B}_q^j) \boldsymbol{F}_i \rangle \cdot (\langle \boldsymbol{F}\boldsymbol{F}^{\dagger} \rangle^{-1})_{il} \cdot \boldsymbol{F}_l.$$

In equations (2.10) L is the Liouville operator of the entire system. The generalised Langevin equations follow from the application of the operator identity $(A+B)^{-1} = A^{-1} + (A+B)^{-1} B A^{-1}$ with $A = z + (1 - \mathscr{P})\mathrm{i}L$ and $B = \mathscr{P}\mathrm{i}L$ to the random forces in equation (2.10) (Kapral *et al* 1976). We obtain

$$z\boldsymbol{p}(z) - \boldsymbol{p} = \boldsymbol{F}(z) \tag{2.11}$$

$$z\boldsymbol{F}(z) - \boldsymbol{F} = -\boldsymbol{\phi}^F(z) \cdot \boldsymbol{F}(z) - (m k_{\mathrm{B}} T)^{-1} \langle \boldsymbol{F}\boldsymbol{F}^{\dagger} \rangle \cdot \boldsymbol{p}(z) + V^{-1} \sum_{\boldsymbol{q}}{}' \boldsymbol{V}^{FB}(\boldsymbol{q}) \cdot \boldsymbol{B}_q(z) + \boldsymbol{f}^F(z), \tag{2.12}$$

$$z\boldsymbol{B}_q(z) - \boldsymbol{B}_q = -\boldsymbol{\phi}^B(\boldsymbol{q}, z) \cdot \boldsymbol{B}_q(z) + V^{BF}(\boldsymbol{q}) \cdot \boldsymbol{F}(z) + \boldsymbol{f}^B(\boldsymbol{q}, z). \tag{2.13}$$

In these equations the damping matrix element $\boldsymbol{\phi}^F$ is

$$\boldsymbol{\phi}^F(z) = \langle \boldsymbol{f}^F(z) \boldsymbol{f}^{F\dagger} \rangle \cdot \langle \boldsymbol{F}\boldsymbol{F}^{\dagger} \rangle^{-1}. \tag{2.14}$$

For a dilute polymer solution (dropping terms $\mathrm{O}(n/N)$)

$$\boldsymbol{\phi}^B(\boldsymbol{q}, z) \simeq \langle \boldsymbol{f}^B(\boldsymbol{q}, z) \boldsymbol{f}^B(\boldsymbol{q})^{\dagger} \rangle \cdot \chi(q)^{-1} \frac{\rho_0}{k_{\mathrm{B}} T V} \tag{2.15}$$

where we have in addition made the factorisation assumption $\langle \boldsymbol{g}_q^{\mathrm{s}} n_{-q}^{i} \boldsymbol{g}_{-q'}^{\mathrm{s}} n_{q'}^{j}\rangle \simeq \langle \boldsymbol{g}_q^{\mathrm{s}} \boldsymbol{g}_{-q'}^{\mathrm{s}}\rangle\langle n_{-q}^{i} n_{q'}^{j}\rangle$, where $\boldsymbol{g}_q^{\mathrm{s}}$ is the momentum density of the solvent. It is this approximation which makes $\boldsymbol{\phi}^B$ diagonal in $\boldsymbol{q}$. The non-linear streaming terms are defined by

$$\boldsymbol{V}^{FB}(\boldsymbol{q}) = \frac{\rho_0}{k_{\mathrm{B}}T}\langle(\mathrm{i}L\boldsymbol{F})\boldsymbol{B}_q^{\dagger}\rangle \cdot \boldsymbol{\chi}(q)^{-1}, \tag{2.16}$$

and

$$\boldsymbol{V}^{BF}(\boldsymbol{q}) = \langle(\mathrm{i}L\boldsymbol{B}_q)\boldsymbol{F}^{\dagger}\rangle \cdot \langle \boldsymbol{F}\boldsymbol{F}^{\dagger}\rangle^{-1}. \tag{2.17}$$

In order to calculate the $\langle \boldsymbol{p}(z)\boldsymbol{p}^{\dagger}\rangle$ correlation function and hence the friction from equation (2.11) we need to compute $\langle \boldsymbol{F}(z)\boldsymbol{p}^{\dagger}\rangle$. Postmultiplying equations (2.12) and (2.13) by $\boldsymbol{p}^{\dagger}$ and averaging yields

$$z\langle \boldsymbol{F}(z)\boldsymbol{p}^{\dagger}\rangle = -\boldsymbol{\phi}^F(z) \cdot \langle \boldsymbol{F}(z)\boldsymbol{p}^{\dagger}\rangle - \frac{\langle \boldsymbol{F}\boldsymbol{F}^{\dagger}\rangle}{mk_{\mathrm{B}}T} \cdot \langle \boldsymbol{p}(z)\boldsymbol{p}^{\dagger}\rangle$$
$$+ V^{-1}\sum_{\boldsymbol{q}}{}' \boldsymbol{V}^{FB}(\boldsymbol{q}) \cdot (z + \boldsymbol{\phi}^B(\boldsymbol{q}, z))^{-1} \cdot \boldsymbol{V}^{BF}(\boldsymbol{q}) \cdot \langle \boldsymbol{F}(z)\boldsymbol{p}^{\dagger}\rangle. \tag{2.18}$$

Postmultiplying equation (2.13) by $\boldsymbol{B}_q^{\dagger}$, averaging and substituting into equation (2.18) gives

$$\langle \boldsymbol{F}(z)\boldsymbol{p}^{\dagger}\rangle = -\left(z + \boldsymbol{\phi}^F(z) - V^{-1}\int_0^{\infty} \mathrm{d}t\, \mathrm{e}^{-zt} \sum_{\boldsymbol{q}}{}' \boldsymbol{V}^{FB}(\boldsymbol{q}) \cdot \langle \boldsymbol{B}_q(t)\boldsymbol{B}_q^{\dagger}\rangle \cdot \langle \boldsymbol{B}_q\boldsymbol{B}_q^{\dagger}\rangle^{-1} \cdot \boldsymbol{V}^{BF}(\boldsymbol{q})\right)^{-1}$$
$$\cdot \frac{\langle \boldsymbol{F}\boldsymbol{F}^{\dagger}\rangle}{mk_{\mathrm{B}}T} \cdot \langle \boldsymbol{p}(z)\boldsymbol{p}^{\dagger}\rangle. \tag{2.19}$$

Again for the dilute polymer solution considered here we may approximate

$$\langle \boldsymbol{B}_q(t)\boldsymbol{B}_q^{\dagger}\rangle \cdot \langle \boldsymbol{B}_q\boldsymbol{B}_q^{\dagger}\rangle^{-1} \simeq \langle \boldsymbol{g}_q^{\mathrm{s}}(t)\boldsymbol{n}_{-q}(t)\boldsymbol{g}_{-q}^{\mathrm{s}}\boldsymbol{n}_q\rangle \cdot \boldsymbol{\chi}(q)^{-1}\frac{\rho_0}{k_{\mathrm{B}}TV}. \tag{2.20}$$

If we now make a dynamical factorisation approximation on the correlation function appearing in equation (2.20) we obtain

$$\langle \boldsymbol{B}_q(t)\boldsymbol{B}_q^{\dagger}\rangle \cdot \langle \boldsymbol{B}_q\boldsymbol{B}_q^{\dagger}\rangle^{-1} \simeq \boldsymbol{G}_q^{g}(t)\boldsymbol{G}_{-q}^{n}(t), \tag{2.21}$$

where the propagators are defined by

$$\boldsymbol{G}_q^{g}(t) = \langle \boldsymbol{g}_q^{\mathrm{s}}(t)\boldsymbol{g}_{-q}^{\mathrm{s}}\rangle\rho_0/k_{\mathrm{B}}TV \tag{2.22}$$

and

$$\boldsymbol{G}_q^{n}(t) = \langle \boldsymbol{n}_q(t)\boldsymbol{n}_q^{\dagger}\rangle \cdot \boldsymbol{\chi}(q)^{-1}. \tag{2.23}$$

Using equation (2.21) in equation (2.19), keeping only the transverse part of the propagator $\boldsymbol{G}_q^{g}$, and inserting the resulting expression for $\langle \boldsymbol{F}(z)\boldsymbol{p}^{\dagger}\rangle$ into equation (2.11) after averaging with $\boldsymbol{p}^{\dagger}$ we find

$$\langle \boldsymbol{p}(z)\boldsymbol{p}^{\dagger}\rangle \cdot \langle \boldsymbol{p}\boldsymbol{p}^{\dagger}\rangle^{-1}$$
$$= \Bigg[z + \Bigg(z + \boldsymbol{\phi}^F(z) - \int_0^{\infty} \mathrm{d}t\, \mathrm{e}^{-zt} V^{-1} \sum_{\boldsymbol{q}}{}'$$
$$\times \sum_{\lambda=1}^{2} \boldsymbol{V}^{FB}(\boldsymbol{q}) \cdot \hat{\boldsymbol{\epsilon}}^{\lambda}(\hat{\boldsymbol{\epsilon}}^{\lambda} \cdot \boldsymbol{G}_q^{g}(t) \cdot \hat{\boldsymbol{\epsilon}}^{\lambda})G_q^{n}(t)\hat{\boldsymbol{\epsilon}}^{\lambda} \cdot \boldsymbol{V}^{BF}(\boldsymbol{q})\Bigg)^{-1} \cdot \frac{\langle \boldsymbol{F}\boldsymbol{F}^{\dagger}\rangle}{mk_{\mathrm{B}}T}\Bigg]^{-1}. \tag{2.24}$$

Here $\hat{\boldsymbol{\epsilon}}^{\lambda}$ is a member of an orthogonal set of unit vectors with $\hat{\boldsymbol{\epsilon}}^{3}$ along $\boldsymbol{q}$. Comparison with equation (2.1) yields an expression for the generalised friction tensor, $\boldsymbol{\zeta}(z)$. If the mode coupling contribution in equation (2.24) is dropped then we sdefine the resulting 'bare' friction as

$$\boldsymbol{\zeta}^{*}(z) \equiv (z + \boldsymbol{\phi}^{F}(z))^{-1} \cdot \langle \boldsymbol{F}\boldsymbol{F}^{\dagger} \rangle / k_{\mathrm{B}}T. \tag{2.25}$$

Using this definition the full friction which follows from equation (2.24) can be written in the form

$$\boldsymbol{\zeta}(z) = (\mathbf{1} + \boldsymbol{\zeta}^{*}(z) \cdot \boldsymbol{\tau}(z))^{-1} \cdot \boldsymbol{\zeta}^{*}(z), \tag{2.26}$$

where

$$\boldsymbol{\tau}(z) = -\langle \boldsymbol{F}\boldsymbol{F}^{\dagger} \rangle^{-1} \cdot \frac{k_{\mathrm{B}}T}{V} \int_{0}^{\infty} \mathrm{d}t\, \mathrm{e}^{-zt} \sum_{\boldsymbol{q}}{}' \sum_{\lambda=1}^{2} \boldsymbol{V}^{FB}(\boldsymbol{q}) \cdot \hat{\boldsymbol{\epsilon}}^{\lambda} (\hat{\boldsymbol{\epsilon}}^{\lambda} \cdot \boldsymbol{G}_{q}^{g}(t) \cdot \hat{\boldsymbol{\epsilon}}^{\lambda}) G_{q}^{n}(t) \hat{\boldsymbol{\epsilon}}^{\lambda} \cdot \boldsymbol{V}^{BF}(\boldsymbol{q}). \tag{2.27}$$

Note that in the zero-frequency limit equation (2.26) has a structure similar to that of equation (2.2) where $\boldsymbol{\zeta}^{*}(0)$ corresponds to the monomer friction. We shall show that $\boldsymbol{\tau}(0)$ is, in a certain approximation, equal to the pre-averaged Oseen tensor. In order to carry out this analysis we shall consider the structure of the streaming terms, $\boldsymbol{V}^{FB}$ and $\boldsymbol{V}^{BF}$. Inserting equation (2.7) into equation (2.16) we obtain

$$\boldsymbol{V}^{FB}(\boldsymbol{q}) = (k_{\mathrm{B}}T)^{-1} \langle \boldsymbol{F}\boldsymbol{F}^{\dagger} \rangle - \frac{\rho_0}{k_{\mathrm{B}}T} \langle \boldsymbol{F} (\mathrm{i}L \boldsymbol{g}_q \boldsymbol{n}_{-q})^{\dagger} \rangle \boldsymbol{\chi}(q)^{-1}. \tag{2.28}$$

The first term does not depend on q and the second term is at least of order q^2 since $\boldsymbol{g}_q \boldsymbol{n}_{-q}$ is conserved and $\langle \boldsymbol{F}(\mathrm{i}L\boldsymbol{g}_q\boldsymbol{n}_{-q})^{\dagger} \rangle$ is even under the parity operation. If the matrix elements are scaled by a, the diameter of a monomer, we see that the second term contains factors $\mathrm{O}((qa)^2)$ and higher compared to the first. Since the sum on $\boldsymbol{q}$ in equation (2.27) is restricted to values $\boldsymbol{q} \leqslant \boldsymbol{q}_0$, where $\boldsymbol{q}_0$ is a macroscopic wavevector, the product $q_0 a \ll 1$ and hence the contribution of the second term in equation (2.28) relative to that of the first will be small. Thus, if we only retain the first term in equation (2.28) and use a similar approximation for $\boldsymbol{V}^{BF}$ we find

$$\boldsymbol{\tau}(z) = \frac{1}{\rho_0 V} \int_{0}^{\infty} \mathrm{d}t\, \mathrm{e}^{-zt} \sum_{\boldsymbol{q}}{}' \sum_{\lambda=1}^{2} \hat{\boldsymbol{\epsilon}}^{\lambda} \hat{\boldsymbol{\epsilon}}^{\lambda} (\hat{\boldsymbol{\epsilon}}^{\lambda} \cdot \boldsymbol{G}_{q}^{g}(t) \cdot \hat{\boldsymbol{\epsilon}}^{\lambda}) \boldsymbol{G}_{q}^{n}(t) \boldsymbol{\chi}(q). \tag{2.29}$$

To reduce equation (2.29) further we assume that the propagators can be evaluated in the hydrodynamic limit:

$$(\hat{\boldsymbol{\epsilon}}^{\lambda} \cdot \boldsymbol{G}_{q}^{g}(t) \cdot \hat{\boldsymbol{\epsilon}}^{\lambda}) \boldsymbol{G}_{q}^{n}(t) \simeq \exp[-q^2(\nu_0 \mathbf{1} + \boldsymbol{D})t] \simeq \exp(-q^2 \nu_0 t)\mathbf{1}, \tag{2.30}$$

where ν_0 is the kinematic viscosity of the solvent, $\nu_0 = \eta_0/\rho_0$, $\boldsymbol{D}$ is the diffusion tensor and $\mathbf{1}$ is a unit tensor. The last approximation makes use of the fact that the viscous modes decay much more rapidly than the diffusive modes. Since the diagonal elements of $\boldsymbol{\chi}(q)$ are unity, the diagonal part of $\boldsymbol{\tau}(z)$ will depend strongly on $\boldsymbol{q}_0$. However, for most models of a flexible polymer chain the off-diagonal elements of $\boldsymbol{\chi}(q)$ decay sufficiently rapidly so that the dependence on $\boldsymbol{q}_0$ is negligible. Hence, $\boldsymbol{\tau}(z)$ can be written as

$$\boldsymbol{\tau}(z) = (3\pi^2\eta_0)^{-1}[q_0 - \alpha \tan^{-1}(q_0/\alpha)]\mathbf{1} + \langle \boldsymbol{T}(z) \rangle_{\mathrm{P}} \equiv M(q_0)\mathbf{1} + \langle \boldsymbol{T}(z) \rangle_{\mathrm{P}}, \tag{2.31}$$

with $\alpha^2 = z/\nu_0$, where the frequency-dependent Oseen tensor is given by

$$\boldsymbol{T}_{ij}(z) = (4\pi\eta_0 R_{ij})^{-1}[(\mathrm{e}^{-\alpha R_{ij}} + Q(\alpha R_{ij}))\mathbf{1} - (\mathrm{e}^{-\alpha R_{ij}} + 3Q(\alpha R_{ij}))\hat{\boldsymbol{R}}_{ij}\hat{\boldsymbol{R}}_{ij}], \tag{2.32}$$

where

$$Q(X) = X^{-2}[\mathrm{e}^{-X}(1+X) - 1].$$

We have therefore written $\boldsymbol{\tau}(z)$ as the sum of a hydrodynamic contribution to the monomer friction and a term involving the Oseen interactions between the monomers. Because of the choice of projection operator, $\boldsymbol{\zeta}^*(z)$ in equation (2.25) did not contain the hydrodynamic contribution to the monomer friction. If we now define an effective monomer friction, $\boldsymbol{\zeta}_{\mathrm{m}}(z)$, as

$$\boldsymbol{\zeta}_{\mathrm{m}}(z) = \left(z + \boldsymbol{\phi}^F(z) + M(q_0)\frac{\langle \boldsymbol{F}\boldsymbol{F}^\dagger\rangle}{k_{\mathrm{B}}T}\right)^{-1} \cdot \frac{\langle \boldsymbol{F}\boldsymbol{F}^\dagger\rangle}{k_{\mathrm{B}}T}, \tag{2.33}$$

equation (2.26) takes the form

$$\boldsymbol{\zeta}(z) = (\mathbf{1} + \boldsymbol{\zeta}_{\mathrm{m}}(z) \cdot \langle \boldsymbol{T}(z)\rangle_{\mathrm{P}})^{-1} \cdot \boldsymbol{\zeta}_{\mathrm{m}}(z). \tag{2.34}$$

It is clear that this equation is of the same form as equation (2.2). $\boldsymbol{\zeta}_{\mathrm{m}}(z)$ is the microscopic friction tensor and contains a mode coupling contribution. This contribution depends on the cut-off wavevector which is proportional to the inverse size of the monomer units. Equation (2.34) is in one sense more general than equation (2.2) in that the full frequency dependence of the hydrodynamic interactions is taken into account. However, the Oseen tensor appears in a pre-averaged form.

3. Alternative calculation of the friction

The calculation described in § 2 differs from most mode coupling calculations of single-particle properties in that the coupling of the forces to momenta are explicitly included. On the basis of these earlier calculations one would expect that the calculation could be carried out by considering only the direct coupling of the monomer momenta to $\boldsymbol{B}_q$. Although such a calculation can be performed, there are interesting differences from that described in the previous section. The technically interesting difference is that the coupling matrix elements are frequency dependent rather than equal-time correlation functions. This makes the analysis of the coupling matrix elements more complex and a simple approximation, analogous to that adopted in the previous section, leads to a result for $\boldsymbol{\zeta}(z)$ which corresponds to the first term in the expansion of the matrix inverse in equation (2.34).

Considering the variable $\{\boldsymbol{p}, \boldsymbol{B}_q\}$ and the projection operator

$$\mathscr{P}\theta = \frac{\langle \theta \boldsymbol{p}^\dagger\rangle}{mk_{\mathrm{B}}T} \cdot \boldsymbol{p} + \frac{\rho_0}{k_{\mathrm{B}}TV}\sum_{q}{}' \langle \theta \boldsymbol{B}_q^\dagger\rangle \boldsymbol{\chi}(q)^{-1} \cdot \boldsymbol{B}_q \tag{3.1}$$

and carrying out a calculation similar to that described in § 2 we find

$$\langle \boldsymbol{p}(z)\boldsymbol{p}^\dagger\rangle \cdot \langle \boldsymbol{p}\boldsymbol{p}^\dagger\rangle^{-1} = \left(z + \frac{\boldsymbol{\zeta}_0(z)}{m} + \frac{\delta\boldsymbol{\zeta}(z)}{m}\right)^{-1}, \tag{3.2}$$

where the bare friction tensor $\boldsymbol{\zeta}_0(z)$ is

$$\boldsymbol{\zeta}_0(z) = \langle\{[z + (1-\mathscr{P})\mathrm{i}L]^{-1}\boldsymbol{F}\}\boldsymbol{F}^\dagger\rangle / k_{\mathrm{B}}T, \tag{3.3}$$

and the mode coupling contribution $\delta\boldsymbol{\zeta}(z)$ is

$$\delta\boldsymbol{\zeta}(z)=-V^{-1}\sum_{\boldsymbol{q}}{}'\sum_{\lambda=1}^{2}\boldsymbol{\Lambda}^{pB}(\boldsymbol{q},z)\cdot\hat{\boldsymbol{\epsilon}}^{\lambda}\int_{0}^{\infty}\mathrm{d}t\,\mathrm{e}^{-zt}(\hat{\boldsymbol{\epsilon}}^{\lambda}\cdot\boldsymbol{G}_{q}^{g}(t)\cdot\hat{\boldsymbol{\epsilon}}^{\lambda})\boldsymbol{G}_{q}^{n}(t)\hat{\boldsymbol{\epsilon}}^{\lambda}\cdot\boldsymbol{\Lambda}^{Bp}(\boldsymbol{q},z). \tag{3.4}$$

The dynamical coupling matrix elements are defined by

$$\boldsymbol{\Lambda}^{pB}(\boldsymbol{q},z)=\langle\{[z+(1-\mathscr{P})\mathrm{i}L]^{-1}\boldsymbol{F}\}\dot{\boldsymbol{B}}_{q}^{\dagger}\rangle\chi(q)^{-1}\frac{\rho_0}{k_{\mathrm{B}}T} \tag{3.5}$$

and

$$\boldsymbol{\Lambda}^{Bp}(\boldsymbol{q},z)=\langle\{[z+(1-\mathscr{P})\mathrm{i}L]^{-1}\dot{\boldsymbol{B}}_{q}\}\boldsymbol{F}^{\dagger}\rangle/k_{\mathrm{B}}T. \tag{3.6}$$

A comparison of equations (3.2) and (2.24) shows that in the present calculation the mode coupling contribution is to the friction itself, while in the earlier calculation the mode coupling contribution appears as a term in the inverse friction. An explicit calculation of the friction using equation (3.4) requires an analysis of the dynamical coupling matrix elements $\boldsymbol{\Lambda}^{pB}$ and $\boldsymbol{\Lambda}^{Bp}$. As in § 2, we use equation (2.7) to write

$$\boldsymbol{\Lambda}^{pB}(\boldsymbol{q},z)=-\boldsymbol{\zeta}_0(z)+\langle\{[z+(1-\mathscr{P})\mathrm{i}L]^{-1}\boldsymbol{F}\}(\mathrm{i}L\boldsymbol{g}_{q}\boldsymbol{n}_{-q})^{\dagger}\rangle\cdot\chi(q)^{-1}\frac{\rho_0}{k_{\mathrm{B}}T} \tag{3.7}$$

with an analogous expression for $\boldsymbol{\Lambda}^{Bp}(\boldsymbol{q},z)$. Once again using parity one can show that the second term in equation (3.7) is $O((aq)^2)$ and can be neglected in comparison with the first. Following § 2 we finally obtain

$$\delta\boldsymbol{\zeta}(z)=-\boldsymbol{\zeta}_0(z)\cdot(\boldsymbol{M}(q_0)+\langle\boldsymbol{T}(z)\rangle_{\mathrm{P}})\cdot\boldsymbol{\zeta}_0(z), \tag{3.8}$$

and

$$\boldsymbol{\zeta}(z)=\boldsymbol{\zeta}_0^*(z)-\boldsymbol{\zeta}_0(z)\cdot\langle\boldsymbol{T}(z)\rangle_{\mathrm{P}}\cdot\boldsymbol{\zeta}_0(z), \tag{3.9}$$

with

$$\boldsymbol{\zeta}_0^*(z)=\boldsymbol{\zeta}_0(z)-\boldsymbol{M}(q_0)\boldsymbol{\zeta}_0(z)\cdot\boldsymbol{\zeta}_0(z). \tag{3.10}$$

The resulting expression for $\boldsymbol{\zeta}(z)$ has a structure similar to an expanded form of equation (2.34). However, because of the difference in the projection operators in the two calculations the second mode coupling calculation does not provide as complete a separation of the hydrodynamic and microscopic contributions.

4. Concluding remarks

The aim of the present work has been the derivation, from a microscopic point of view, of the friction tensor of a polymer chain. Standard calculations (Yamakawa 1971) take a macroscopic point of view. The solvent is treated as a continuum and the interactions between the monomers and the solvent molecules are accounted for by boundary conditions. When the monomers are small and comparable in size to the solvent molecules it is not clear that such a description is appropriate. However, since the resulting expression for the friction tensor (equation (2.2)) has a wide range of applicability, it is of interest to examine how such a form can be obtained from a microscopic theory and to provide a framework for extensions of this result. The calculations presented in this paper begin such a programme.

It is useful to compare our result for the friction tensor (equation (2.34)) with that in equation (2.2). Since equation (2.2) gives the zero-frequency friction tensor we first consider this limit. Our expression for $\boldsymbol{\zeta}(z=0)$ differs from that in equation (2.2) in two respects. First, as noted earlier, we obtain a result in which the Oseen tensor appears in a pre-averaged form. We will return to a discussion of this point below. Second, we obtain a much more general form for the microscopic friction $\boldsymbol{\zeta}_{\mathrm{m}}(z=0)$. In the usual description the microscopic friction tensor is taken to be diagonal with elements $\zeta\delta_{ij}$, where $\zeta = 6\pi\eta_0(a/2)$ for stick boundary conditions. Our result for $\boldsymbol{\zeta}_{\mathrm{m}}(0)$ has the form

$$\boldsymbol{\zeta}_{\mathrm{m}}(0) = [\boldsymbol{\zeta}^*(0)^{-1} + (3\pi^2\eta_0)^{-1}q_0\mathbf{1}]^{-1},$$

where $\boldsymbol{\zeta}^*(0)$ is the 'bare' friction defined in equation (2.25). If the 'bare' friction is dropped in this equation we have $\boldsymbol{\zeta}_{\mathrm{m}}(0) \simeq 6\pi\eta_0(\pi/2q_0)$, a result similar to the hydrodynamic result with an effective radius equal to $\pi/2q_0$. In a more complete theory the solvent–monomer collision dynamics will provide a natural cut-off in the theory and remove the explicit dependence on q_0. However, for small monomer units the microscopic friction may be dominated by the 'bare' part as is evidenced by the utility of the Enskog binary collision approximation for the transport properties of dense fluids. In addition, as can be seen from equation (2.25), $\boldsymbol{\zeta}^*$ also includes the direct interactions (i.e. non-hydrodynamic) between the monomer units and therefore incorporates the full internal dynamics of the chain. The explicit calculation of $\boldsymbol{\zeta}^*$ is difficult but can be carried out for simple models.

The full frequency dependence of $\boldsymbol{\zeta}(z)$ given in equation (2.34) will manifest itself only at rather high frequencies. For example, the frequency dependence of $\langle \boldsymbol{T}_{ij}(z)\rangle_{\mathrm{P}}$ will be important for $z \sim \nu_0/|i-j|l^2$, where l is the bond length. For typical values of the kinematic viscosity and polymer size this yields frequencies in the range 10^{13}–$10^9\ \mathrm{s}^{-1}$. In equation (2.34) the microscopic friction tensor is also frequency dependent, but this frequency dependence will be important only in the higher portion of the frequency range given above. We note that although the hydrodynamic contribution (proportional to $M(q_0)$) depends explicitly on the cut-off wavevector, for small a/q_0 this contribution has a structure similar to the frequency-dependent friction in a hydrodynamic calculation (Landau and Lifshitz 1966). Thus, for many applications the zero-frequency approximation will be adequate, but the frequency dependence may be detectable in certain scattering experiments.

Another aspect of the present calculation is the framework it provides for more refined calculations of the friction tensor. One such example can be seen from a consideration of equation (2.29). In the reduction of equation (2.29) to the pre-averaged Oseen tensor in equation (2.31) hydrodynamic forms for the propagators $\boldsymbol{G}_q^{\mathrm{s}}(t)$ and $\boldsymbol{G}_q^{\eta}(t)$ have been used. For a Gaussian chain $\chi_{ij}(q)$ has the form $\chi_{ij}(q) = \exp(-\frac{1}{6}l^2q^2|i-j|)$. Thus, for small $|i-j|$ the significant values of $\boldsymbol{q}$ in the sum in equation (2.29) can be as large as $10^8\ \mathrm{cm}^{-1}$. For these large wavevectors the above mentioned hydrodynamic forms for the propagators are not adequate. Other approximations for the propagators which take fuller account of the solvent properties and are valid for larger $\boldsymbol{q}$ can be used in equation (2.29) and will lead to an improved description.

We have mentioned earlier that the present result involves the Oseen tensor in a pre-averaged form. Since the projection operator formalism is in principle exact, this approximate form is probably related to our use of the factorisation approximation in evaluating certain correlation functions. One possible way of avoiding this difficulty is to make use of a different projection operator which involves a full phase space description of the polymer in both the linear and non-linear variables. This will lead to a generalised Fokker–Planck equation.

Finally we note that using equations (2.1) and (2.34) it is easy to calculate the diffusion coefficient of the centre of mass of the polymer and the result is identical to that obtained earlier (Kapral *et al* 1976). However, it is important to notice that the present calculation is more microscopic and amounts to giving two further orders in a continued fraction expansion (Mori 1965).

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