Brownian Dynamics of Polymer Solutions

S. F. Edwards*,[†] and M. Muthukumar[‡]

Institute for Theoretical Physics, University of California, Santa Barbara, California 93106.
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ABSTRACT: The coupled motion of polymers and surrounding fluid is studied in equilibrium under thermal fluctuations. The motion involves the coordinate of single polymers, $\mathbf{R}(s,t)$, s being the monomer label, i.e., the arc distance, $\mathbf{u}(\mathbf{r},t)$ the fluid velocity, and $\rho(\mathbf{r},t)$ the polymer density. The fluid is considered incompressible. The normal modes of the system will on average be the Fourier components $\rho(\mathbf{k},t)$ and $\mathbf{u}(\mathbf{k},t)$, and the Fourier components with respect to s, $\mathbf{R}(q,t)$, of the polymer. The Liouville equation for the whole system is written down, and from it is developed a normal mode equation which amounts to a Fokker–Planck equation in terms of the normal coordinates. This equation then leads to the two-point correlation functions $\langle \mathbf{u}(\mathbf{k},\omega)\mathbf{u}(\mathbf{k}',\omega')\rangle$, $\langle \rho(\mathbf{k},\omega)\rho(\mathbf{k}',\omega')\rangle$, and $\langle \mathbf{R}(q,\omega)\mathbf{R}(q',\omega')\rangle$ in a systematic way. This paper calculates these, and hence the linear transport coefficients below the entanglement transition. It is shown that the hydrodynamic and static screening lengths are related by $\xi_{\mathrm{H}}^{-2} = (\pi/2)cl_1(\xi_{\mathrm{H}}^{-1} + \xi_{\mathrm{s}}^{-1})$, where c is the concentration, l the Kuhn length, and l_1 the swollen Kuhn length.

1. Introduction

The problem of polymer solution dynamics has been much studied, with massive contributions from Stockmayer.[1-3] We feel the time is ripe to make a synthesis of the individual and collective features of this problem, and the simplest area to study is thermal equilibrium since equilibrium properties can be solved in certain cases, and are well outlined in others, and the dynamics associated with these equilibrium situations are also reasonably well sorted out. It appears experimentally that a phase change or something close to it takes place when the polymers reach a certain length, or a certain length density, when a marked rise in viscosity and decreases in diffusivity suggest that entanglements are dominating the motion. Again the dynamics of the system far below and far above this transition are well studied with reasonable success. What we aim to do in this paper is to provide a systematic Brownian dynamics of the coupled system of individual polymers, the polymer density, and the fluid velocity in the solvent. We will display some strikingly analogous structure in the equations for these components and be able to point out how the equations already contain all the entanglement properties and how in the region below the entanglement transition the well-known "preaveraging" approximation is permissible and how above the transition it is not. The paper works out the case below the transition in detail, and a summary of its results is contained in the correlation function table (1.4)–(1.9). The αth polymer has coordinate $\mathbf{R}_\alpha(s_\alpha,t)$, where $s_\alpha = n_\alpha l$, l is the step length, and n_α labels the monomer. The Fourier (Rouse) modes of this polymer are called $\mathbf{R}_\alpha(q,t)$ or in double Fourier transform $\mathbf{R}_\alpha(q,\omega)$. The polymer density $\rho(\mathbf{r},t) = \sum_\alpha \int \mathrm{d}s_\alpha\, \delta[\mathbf{r} - \mathbf{R}_\alpha(s_\alpha,t)]$ with Fourier components $\rho(\mathbf{k},\omega)$ and the fluid velocity is $\mathbf{u}(\mathbf{r},t)$ or $\mathbf{u}(\mathbf{k},\omega)$. The interaction between polymers is characterized by a Flory–Huggins interaction, a pseudopotential w which swells the polymer so that its effective step length becomes l_1

$$\langle [\mathbf{R}(s) - \mathbf{R}(s')]^2 \rangle = l_1|s - s'|$$

Then

$$\langle u^\alpha(\mathbf{k})u^\beta(\mathbf{k}')\rangle = 2k_{\mathrm{B}}T(2\pi)^3(\eta_0 k^2)^{-1}(\delta^{\alpha\beta} - k^\alpha k^\beta/k^2)\delta(\mathbf{k} + \mathbf{k}') \tag{1.1}$$

$$\langle \rho(\mathbf{k})\rho(\mathbf{k}')\rangle = \frac{12c}{l_1}\,\frac{\delta(\mathbf{k} + \mathbf{k}')}{k^2 + \xi_{\mathrm{s}}^{-2}}(2\pi)^3 \tag{1.2}$$

$$\langle e^{i\mathbf{k}\cdot[\mathbf{R}_\alpha(s) - \mathbf{R}_\alpha(s')]}\rangle = e^{-k^2 l_1|s-s'|/6} \tag{1.3}$$

(where ξ_{s} is the static screening length) are equilibrium results.

The dynamic results are given in eq 5.26 to 5.33, where diffusion coefficients for $\mathbf{u}(\mathbf{k})$, the $\mathbf{R}_\alpha$, and $\rho(\mathbf{k})$ are given. The distribution function P is given by

$$\left[\frac{\partial}{\partial t} - \sum_{\mathbf{k}} \frac{\partial}{\partial \mathbf{u}_{\mathbf{k}}} k_{\mathrm{B}}T\eta(\mathbf{k}) \times \left(\frac{\partial}{\partial \mathbf{u}_{-\mathbf{k}}} + \frac{\mathbf{u}_{\mathbf{k}}}{(2\pi)^3 k_{\mathrm{B}}T}\right) - \sum_{\mathbf{k}} \frac{\partial}{\partial \rho_{\mathbf{k}}} D(\mathbf{k}) \left(\frac{\partial}{\partial \rho_{-\mathbf{k}}} + \frac{\Delta_{\mathbf{k}}\rho_{\mathbf{k}}}{(2\pi)^3}\right) - \sum_\alpha \sum_q \frac{\partial}{\partial \mathbf{R}_\alpha(q)} J(q) \left(\frac{\partial}{\partial \mathbf{R}_{\alpha,-q}} + \frac{3q^2 \mathbf{R}_\alpha(q)}{2\pi l_1}\right)\right] P = 0 \tag{1.4}$$

where

$$\eta(k) = \eta_0(k^2 + \xi_{\mathrm{H}}^{-2}), \qquad k > \xi_{\mathrm{H}}^{-1} \tag{1.5}$$

$$= \eta_0 k^2\left(1 + \frac{c}{12\pi} l_1^2 L \xi_{\mathrm{H}}^{-1}\right), \qquad k < \xi_{\mathrm{H}}^{-1} \tag{1.6}$$

$$J(q) = 2/\pi\eta_0 l_1(\xi_{\mathrm{s}}^{-1} + \xi_{\mathrm{H}}^{-1}) \tag{1.7}$$

$$D(\mathbf{k}) = \frac{2k_{\mathrm{B}}Tk^2 c}{\pi\eta_0 l_1}(\xi_{\mathrm{s}}^{-1} + \xi_{\mathrm{H}}^{-1})^{-1} \tag{1.8}$$

and

$$\xi_{\mathrm{H}}^{-2} = \frac{\pi}{2} c l_1(\xi_{\mathrm{s}}^{-1} + \xi_{\mathrm{H}}^{-1}) \tag{1.9}$$

2. Brownian Equations

In a complicated many degrees of freedom problem, a way forward is to look for variables which, in some good approximation, are independent. This is the search for "quasi-particles" in many-body problems, and sometimes this search is successful, sometimes not. However, simple invariance arguments pin down the simplest of these coordinates since, given that however complicated the equations of hydrodynamics may be (raised indices are Cartesian)

$$\langle u^\alpha(\mathbf{r},t)u^\beta(\mathbf{r}',t')\rangle = \mathcal{F}^{\alpha\beta}(\mathbf{r} - \mathbf{r}', t - t') \tag{2.1}$$

$$\langle u^\alpha(\mathbf{k},\omega)u^\beta(\mathbf{k}',\omega')\rangle = (2\pi)^4\left(\delta^{\alpha\beta} - \frac{k^\alpha k^\beta}{k^2}\right) f(\mathbf{k},\omega)\delta(\mathbf{k} + \mathbf{k}')\delta(\omega + \omega') \tag{2.2}$$

the clear hope will be that $\mathbf{u}(\mathbf{k},\omega)$ is a good variable to be studied. The simplest model one can imagine for one of

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[†] Permanent address: Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, England.

[‡] Permanent address: Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003.

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these coordinates is that of the coordinate of a single Brownian particle, a say. Suppose a particle has coordinate $a(t)$ and satisfies the equation of motion

$$\nu\dot{a} + \gamma a = f(t) \tag{2.3}$$

i.e.

$$(i\omega\nu + \gamma)a(\omega) = f(\omega) \tag{2.4}$$

in Fourier transform. If now

$$\langle f(\omega)f(\omega')\rangle = h\delta(\omega + \omega') \tag{2.5}$$

$$\langle a(\omega)a(\omega')\rangle = \frac{h\delta(\omega + \omega')}{\nu\omega^2 + \gamma^2} \tag{2.6}$$

Thus the equilibrium value of a^2 is

$$\frac{1}{2\pi}\int \mathrm{d}\omega \int \mathrm{d}\omega' \,\langle a(\omega)a(\omega')\rangle = h/2\nu\gamma \tag{2.7}$$

In thermal equilibrium this will be calculable from the Boltzmann factor

$$\exp(-\gamma a^2/2k_\mathrm{B}T)$$

i.e.

$$\langle a^2\rangle = k_\mathrm{B}T/\gamma = h/2\nu \tag{2.8}$$

Therefore we identify the Einstein relation

$$k_\mathrm{B}T = h/2\nu \tag{2.9}$$

If we study the probability $P(a,t)$ of finding a, we find that

$$\left[\frac{\partial}{\partial t} + \frac{\partial}{\partial a}\frac{1}{\nu}(-\gamma a + f)\right]P(a,t) = 0 \tag{2.10}$$

The mean probability taken over a Gaussian distribution of $f(\omega)$ is given by

$$\left[\frac{\partial}{\partial t} - \frac{\partial}{\partial a}\left(\frac{k_\mathrm{B}T}{\nu}\right)\left(\frac{\partial}{\partial a} + \frac{\gamma a}{k_\mathrm{B}T}\right)\right]P(a,t) = 0 \tag{2.11}$$

whose equilibrium solution is, of course, the Boltzmann factor and whose complete solution is available in terms of Hermite functions (or in closed form in Mehler's generating function). Let

$$P(a,0) = \sum p_n e^{-\gamma a^2/2k_\mathrm{B}T} He_n(a) \tag{2.12}$$

Then

$$P(a,t) = \sum p_n e^{-n\gamma t/\nu} e^{-\gamma a^2/2k_\mathrm{B}T} He_n(a) \tag{2.13}$$

(so that, as $t \rightarrow \infty$, $P(a,t) \rightarrow p_0$, He_0 being unity). This formalism works for many-component systems if the components are independent; for example, in the Stokes approximation, the equations for the hydrodynamic fluctuations of a liquid of density ρ_f satisfy

$$\rho_f\frac{\partial u^\alpha(k)}{\partial t} + \eta_0 k^2 u^\alpha(k) + ik^\alpha p(k) = f^\alpha(k,t) \tag{2.14}$$

where, since $k^\alpha u^\alpha(k) = 0$, p is given by

$$i\rho_f(f^\alpha(\mathbf{k})k^\alpha)/k^2$$

i.e.

$$\rho_f\frac{\partial u^\alpha(k)}{\partial t} + \eta_0 k^2 u^\alpha(k) = \mathcal{O}_\mathbf{k}{}^{\alpha\beta} f^\beta(\mathbf{k}) \tag{2.15}$$

where $\mathcal{O}_\mathbf{k}$ is the transverse unit tensor

$$\mathcal{O}_\mathbf{k}{}^{\alpha\beta} = \delta^{\alpha\beta} - k^\alpha k^\beta/k^2 \tag{2.16}$$

(Although $\mathcal{O}^{\alpha\beta}$ describes an important physical feature it is just a nuisance in exposition, so we will leave it out, resuscitating it whenever it is important to do so.) So now (2.15) becomes

$$\rho_f\frac{\partial \mathbf{u}(\mathbf{k})}{\partial t} + \eta_0 k^2 \mathbf{u}(\mathbf{k}) = \mathbf{f}(\mathbf{k}) \tag{2.17}$$

and all the previous discussion goes through, with an equilibrium distribution $e^{-H/k_\mathrm{B}T}$ with

$$H = \frac{1}{2}\rho_f\int \mathrm{d}^3r\, \mathbf{u}^2(\mathbf{r}) = \frac{1}{(2\pi)^3}\frac{\rho_f}{2}\int \mathrm{d}^3k\, \mathbf{u}(k)\mathbf{u}(-k) \tag{2.18}$$

and the joint mean probability is now

$$\left[\frac{\partial}{\partial t} - \int \mathrm{d}^3k\, \frac{\partial}{\partial \mathbf{u}(k)}\left(\frac{k_\mathrm{B}T\eta_0 k^2}{\rho_f}\right) \times \left(\frac{\partial}{\partial \mathbf{u}(-k)} + \frac{\rho_f \mathbf{u}(\mathbf{k})}{(2\pi)^3 k_\mathrm{B}T}\right)\right]P = 0 \tag{2.19}$$

where $\partial/\partial\mathbf{u}(\mathbf{k})$ is interpreted as the functional derivative

$$\frac{\partial}{\partial \mathbf{u}(\mathbf{k})}\int \mathrm{d}^3j\, b(\mathrm{j})\mathbf{u}(\mathbf{j}) = \int \mathrm{d}^3j\, b(\mathrm{j})\delta(\mathbf{k} - \mathbf{j}) \tag{2.20}$$

$$= b(\mathbf{k}) \tag{2.21}$$

The first moment of (2.19) with respect to $\mathbf{u}(\mathbf{j},t)$ returns to the mean of (2.17); i.e.

$$\rho_f\frac{\partial\langle \mathbf{u}_\mathbf{j}\rangle}{\partial t} + \eta_0 j^2\langle \mathbf{u}(\mathbf{j})\rangle = 0 \qquad (=\langle \mathbf{f}(\mathbf{j})\rangle) \tag{2.22}$$

A not so trivial example comes in the Rouse dynamics of a single chain.

The probability distribution of a polymer chain which takes up a random flight in space is given in specially simple form in terms of its Fourier components

$$R(q) = \int_0^L \mathrm{d}s\, e^{iqs}R(s) \tag{2.23}$$

$$q = 2\pi p/L \tag{2.24}$$

$$P([R]) = \mathcal{N}\exp\left(-\frac{3}{2lL}\sum q^2|\mathbf{R}(q)|^2\right) \tag{2.25}$$

$\mathcal{N}$ is the appropriate normalization and p is an integer).

Of course, for small distances the structure of the monomer comes into P so this distribution is not valid for large q; but nevertheless it is valuable in terms of notation to use the direct $R(s,t)$ representation

$$P([R]) = \mathcal{N}\exp\left[-\frac{3}{2l}\int_0^L \mathrm{d}s\left(\frac{\partial \mathbf{R}}{\partial s}\right)^2\right] \tag{2.26}$$

In terms of the $R(q)$ one has an entropy

$$S = -\frac{3k_\mathrm{B}}{2lL}\sum q^2|R(q)|^2 \tag{2.27}$$

and hence a free energy $F = -TS$. The equation of motion postulated by Rouse was, in this notation,

$$\nu\dot{\mathbf{R}}(q) + \frac{3k_\mathrm{B}T}{l}q^2\mathbf{R}(q) = \mathbf{f}(q,t) \tag{2.28}$$

which immediately leads to the diffusion equation for the probability for finding the $R(q)$:

$$\left[\frac{\partial}{\partial t} - \int \mathrm{d}q\, \frac{\partial}{\partial \mathbf{R}(q)}\frac{k_\mathrm{B}T}{\nu}\left(\frac{\partial}{\partial \mathbf{R}(q)} + \frac{3q^2}{2\pi l}\mathbf{R}(q)\right)\right]P = 0 \tag{2.29}$$

or in direct coordinates (which are linear but not diagonal)

$$\left[\frac{\partial}{\partial t} - \int \mathrm{d}s \, \frac{\partial}{\partial \mathbf{R}(s)} \frac{k_{\mathrm{B}}T}{\nu}\left(\frac{\partial}{\partial \mathbf{R}(s)} - \frac{3}{l}\frac{\partial^2 R}{\partial s^2}\right)\right] P = 0 \tag{2.30}$$

The Rouse polymer behaves like an assembly of Brownian harmonic oscillators.

The polymer problem contains three sets of variables, $\mathbf{u}(\mathbf{k})$ and $\mathbf{R}(q)$ as above but also $\rho(\mathbf{k})$, the polymer density. Thus the correlation function of a single polymer density is (neglecting end effects)

$$\langle e^{i\mathbf{k}\cdot[\mathbf{R}_\alpha(s,t) - \mathbf{R}_\alpha(s',t')]}\rangle = S_{(\alpha)}(k, t - t', s - s') \tag{2.31}$$

but from this one cannot deduce the full density fluctuation

$$\sum_{\alpha\beta} \int \mathrm{d}s_\alpha \int \mathrm{d}s_\beta \, e^{i\mathbf{k}\cdot[\mathbf{R}_\alpha(s_\alpha,t) - \mathbf{R}_\beta(s_\beta,t)]} = S(\mathbf{k}, t - t') \tag{2.32}$$

(At $t = t'$ define $\Delta_k^{-1} = S(k,0)$)

The X-ray scattering is related to Δ_k^{-1}; the scattering from a chain which alone gives a signal, e.g., one deuterated chain in a medium of others, is

$$S_{\mathbf{k},0,0} = \int \mathrm{d}s_\alpha \int \mathrm{d}s_\alpha' \, S_{(\alpha)}(\mathbf{k},0, s_\alpha - s_\alpha')$$

which is a special value of

$$S_{\mathbf{k},q,\omega} = \int \mathrm{d}s_\alpha \int \mathrm{d}s_\alpha' \int \mathrm{d}t \, e^{iq(s_\alpha - s_\alpha') + i\omega(t-t')} S_{(\alpha)}(k, t - t', s_\alpha - s_\alpha') \tag{2.33}$$

Thus if it is valid to consider these to be our basic quasi-variables, we can aspire to an equation of the type

$$\left[\frac{\partial}{\partial t} - \sum_\alpha \int \mathrm{d}q \, \frac{\partial}{\partial \mathbf{R}_\alpha(q)} J_q \left(\frac{\partial}{\partial \mathbf{R}_\alpha(-q)} + \frac{3q^2}{2\pi l_1}\mathbf{R}_\alpha(q)\right) - \int \mathrm{d}^3k \, \frac{\partial}{\partial \mathbf{u}(\mathbf{k})}\eta_k\left(\frac{\partial}{\partial \mathbf{u}(\mathbf{k})} + \frac{\rho_f \mathbf{u}(\mathbf{k})}{(2\pi)^3 k_{\mathrm{B}}T}\right) - \int \mathrm{d}^3k \, \frac{\partial}{\partial \rho(\mathbf{k})} D_k \left(\frac{\partial}{\partial \rho(-k)} + \frac{\Delta_{\mathbf{k}}\rho(\mathbf{k})}{(2\pi)^3}\right)\right] P = 0 \tag{2.34}$$

whose equilibrium solution is

$$\exp\left[-\frac{3}{2}\sum_\alpha \int_{-\infty}^{\infty} \frac{\mathrm{d}q}{2\pi} \frac{q^2}{l_1(q)} |\mathbf{R}_\alpha(q)|^2 - \frac{\rho_f}{2}\int \frac{\mathrm{d}^3k}{(2\pi)^3} |\mathbf{u}(\mathbf{k})|^2 - \frac{1}{2}\int \frac{\mathrm{d}^3k}{(2\pi)^3} \, \Delta(k) |\rho(\mathbf{k})|^2\right] \tag{2.35}$$

We have not yet specified l_1 or Δ, but in noninteracting cases they will be l and $S_{\mathbf{k},0,0}$ the Debye function

$$S_{\mathbf{k},0,0} = \frac{2c}{\alpha}\left[1 - \frac{1}{\alpha L}(1 - e^{-\alpha L})\right] \tag{2.36}$$

where

$$\alpha = k^2 l/6 \tag{2.37}$$

and c is the concentration of the arc length, i.e., ρ_0. c = (no. of polymers × polymer length)/volume. Our present interest will concentrate on long polymers for which $S_{\mathbf{k},0,0}$ is just $12c/k^2 l$ so that one has a distribution for noninteracting polymers of

$$\exp\left(-\frac{1}{2}\int \frac{\mathrm{d}^3k}{(2\pi)^3}\left(\frac{k^2 l}{12c}\right)|\rho(\mathbf{k})|^2\right)$$

The object of the paper is then to derive $J(q)$, $\eta(\mathbf{k})$, $D(\mathbf{k})$, $l_1(q)$, and $\Delta(\mathbf{k})$, but in practice attention will focus on $J(q)$, $\eta(k)$, and $D(k)$ as the others are equilibrium properties whose derivation does not require a dynamical treatment.

In the next section we write down the Langevin equations for the coupled system and derive the complete but difficult Liouville equation. In sections 4 and 5 this is reduced to the form postulated above.

3. Equations of Motion

The hydrodynamics will always be considered to be at low Reynolds number, and one can either use the Stokes boundary condition

$$\dot{\mathbf{R}}_\alpha = \mathbf{u}(\mathbf{R}_\alpha) \tag{3.1}$$

or allow a slip along the polymer, but not perpendicular to it; i.e., if $\mathbf{t}_\alpha$ is the tangent vector

$$\dot{\mathbf{R}}_\alpha \times \mathbf{t}_\alpha = \mathbf{u}(\mathbf{R}_\alpha) \times \mathbf{t}_\alpha \tag{3.2}$$

Either of these conditions will maintain the impenetrability of one chain to another, but since the Stokes condition is simplest, it will be adopted in the analysis and the results of the more general condition quoted.

An unambiguous way to introduce the boundary condition is to use the Rayleigh friction function,[4-6] or Rayleighian, which takes the place of the Lagrangian in frictional systems. In this method a function $\mathcal{R}$ is defined which is a function of the coordinates x say and the velocity v

$$\mathcal{R} = L([x]) + M([v]) \tag{3.3}$$

and the equations of motion are

$$\frac{\delta}{\delta x}\int L \, \mathrm{d}t + \frac{\delta}{\delta v}\int M \, \mathrm{d}t = 0 \tag{3.4}$$

This formalism readily permits the addition of a Lagrange multiplier for the constraint

$$\dot{\mathbf{R}}_\alpha = \mathbf{u}(\mathbf{R}_\alpha)$$

Introduce $\mathbf{r}(\mathbf{r},t)$ such that

$$\dot{\mathbf{r}}(\mathbf{r},t) = \mathbf{u}(\mathbf{r},t) \tag{3.5}$$

and introduce

$$\mathbf{V}(s,t) = \dot{\mathbf{R}}(s,t) \tag{3.6}$$

Then the Rayleighian contains the Lagrangian part

$$L = \frac{1}{2}\rho_f \int \dot{\mathbf{r}}^2 \, \mathrm{d}^3r + \frac{3k_{\mathrm{B}}T}{2l}\sum_\alpha \int \mathrm{d}s_\alpha \left(\frac{\partial \mathbf{R}_\alpha}{\partial s_\alpha}\right)^2 + \sum_{\alpha,\beta}\int \mathrm{d}s_\alpha \int \mathrm{d}s_\beta \, W[\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\beta(s_\beta)] + \Phi([\mathbf{r}]) \tag{3.7}$$

which is the kinetic energy of the fluid, ρ_f being the density of the fluid, the (free) energy of the polymer including an interaction potential $W(\mathbf{r}) = w\delta(r)$, and any external or random potential present $\Phi([\mathbf{r}])$. The frictional part is

$$M = \frac{1}{2}\eta_0 \int \mathrm{d}^3r \, \frac{\partial u^\alpha}{\partial r^\beta}\frac{\partial u^\alpha}{\partial r^\beta} \tag{3.8}$$

(to which could be added a frictional part

$$\nu \sum_\alpha [(\mathbf{V}_\alpha - \mathbf{u}(\mathbf{R}_\alpha)) \times \mathbf{t}_\alpha]^2 \tag{3.9}$$

if we wished) and the Lagrange multipliers for the boundary condition and incompressibility of the fluid:

$$\sum_\alpha \sigma_\alpha(s_\alpha,t)[\mathbf{V}_\alpha(s_\alpha,t) - \mathbf{u}(\mathbf{R}_\alpha(s_\alpha,t),t)] + \int \mathrm{d}^3r \, p(\mathbf{r})\nabla\cdot\mathbf{u}(\mathbf{r}) \tag{3.10}$$

These give the equations of motion, replacing $\ddot{\mathbf{r}}$ by $\dot{\mathbf{u}}$ and writing **f** for random and external forces:

$$\rho_f \frac{\partial \mathbf{u}}{\partial t} - \eta_0 \nabla^2 \mathbf{u} + \nabla p = \mathbf{f} + \sum_\alpha \int \mathrm{d}s_\alpha\, \delta(\mathbf{r} - \mathbf{R}_\alpha)\sigma_\alpha(s_\alpha) -$$

$$\frac{3k_\mathrm{B}T}{l} R_\alpha'' + k_\mathrm{B}T\nabla_{\mathbf{R}_\alpha} \sum_\beta \int \mathrm{d}s_\beta\, W[\mathbf{R}_\alpha - \mathbf{R}_\beta] = -\sigma_\alpha(s_\alpha) \tag{3.11}$$

Without loss of generality, we put

$$\rho_f = 1$$

and note that p will be determined by div $\mathbf{u} = 0$. Thus

$$\frac{\partial \mathbf{u}}{\partial t} - \eta_0 \nabla^2 \mathbf{u} + \nabla p + \sum_\alpha \int \mathrm{d}s_\alpha\, \delta[\mathbf{r} - \mathbf{R}_\alpha(s_\alpha,t)] \frac{\partial F}{\partial \mathbf{R}_\alpha(s_\alpha)} = \mathbf{f} \tag{3.12}$$

When p is determined by div $\mathbf{u} = 0$ it will result in the transverse tensor of (2.16) appearing in front of all the other terms in the equation. The equation for $\dot{\mathbf{R}}$ follows from $\dot{\mathbf{R}}_\alpha = \mathbf{u}(\mathbf{R}_\alpha)$ so that (3.11), (3.12), and the two conditions

$$\operatorname{div} \mathbf{u} = 0 \tag{3.13a}$$

and

$$\dot{\mathbf{R}}_\alpha = \mathbf{u}(\mathbf{R}_\alpha) \tag{3.13b}$$

complete the equations of motion. But their form is of a continuous field **u** interacting with many polymers $\mathbf{R}_\alpha$. The question arises as to whether the $\mathbf{R}_\alpha$ can be replaced by collective coordinates. It is convenient to write the pseudopotential term in terms of the density coordinates $\rho(\mathbf{k})$ but it is not so simple to write the remaining terms in collective coordinates. One can write part of the free energy for a given ρ in terms of the $\rho(\mathbf{k})$ by invoking the direct integration

$$\exp(-F_\rho/k_\mathrm{B}T) =$$

$$\int \dots \int \prod_{\mathbf{k}} \delta\Big[\rho(\mathbf{k}) - \sum_\alpha \int \mathrm{d}s_\alpha \exp(i\mathbf{k}\cdot\mathbf{R}_\alpha)\Big] \times$$

$$\exp\left\{-\frac{3}{2l}\sum_\alpha \int \mathrm{d}s_\alpha \left(\frac{\partial \mathbf{R}_\alpha}{\partial s_\alpha}\right)^2 - \sum_{\alpha\beta} \int \mathrm{d}s_\alpha \int \mathrm{d}s_\beta\, W[\mathbf{R}_\alpha - \mathbf{R}_\beta]\right\} \tag{3.14}$$

and clearly

$$\int \prod \mathrm{d}\rho(\mathbf{j})\; e^{-F_\rho/k_\mathrm{B}T} = e^{-F/k_\mathrm{B}T} \tag{3.15}$$

where F is the complete free energy without any constraints. The question arising is whether the system defined by the $\mathbf{R}_\alpha$ is defined to the same level of completeness by the $\rho(\mathbf{k})$. It is not, because the $\mathbf{R}(s)$ represent the shape of the polymers and $\rho(\mathbf{r})$ is the scalar density. One can have the polymers changing both their shapes and positions in such a way as to keep the density the same. Thus the $\rho(\mathbf{k})$ are not complete collective coordinates. They are complete in the sense that if we wished to evaluate the equilibrium value of $\langle\rho(\mathbf{k})\rho(\mathbf{k}')\rangle$ it is given exactly by

$$\int \prod \mathrm{d}\rho(\mathbf{j})\; \rho(\mathbf{k})\rho(\mathbf{k}')e^{(F-F_\rho)/k_\mathrm{B}T} \tag{3.16}$$

as this is an identity using (3.14). But the distortion of a molecule by a velocity fluctuation **u** cannot be described by the ρ. Thus if we wish to develop a theory entirely in terms of spatially defined fields like $\mathbf{u}(\mathbf{k})$ and $\rho(\mathbf{k})$ with only "k" indices and not "q" and (α) indices, we need more general collective coordinates such as

$$\mathcal{P}_{\mathbf{k},\mathbf{j}} = \sum_\alpha \int \mathrm{d}s_\alpha\; e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s_\alpha) + i\mathbf{j}\cdot[\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\alpha(0)]} \tag{3.17}$$

where $\mathbf{R}_\alpha(0)$ is an end (without loss of generality). This is not done in the present paper but is an essential ingredient of any coupled hydrodynamic viscoelastic equations for a polymer solution.

This problem can be evaded in the present case of Brownian motion by noting that the fluid velocity can always be decomposed into a gradient and a curl. Thus since the pressure p is eliminated by using the condition div $\mathbf{u} = 0$ the pressure will remove the potential gradient term:

$$\left(\frac{\partial}{\partial t} - \eta_0\nabla^2\right) \operatorname{div} \mathbf{u} - \frac{3k_\mathrm{B}T}{l}\nabla\cdot\sum_\alpha \int \mathrm{d}s_\alpha \frac{\partial^2 \mathbf{R}_\alpha}{\partial {s_\alpha}^2}\delta(\mathbf{r} - \mathbf{R}_\alpha) + \nabla^2 p + k_\mathrm{B}Tw\nabla^2\rho = \operatorname{div} \mathbf{f} \tag{3.18}$$

where $W(r)$ has been replaced by $w\delta(r)$. Therefore

$$p = -k_\mathrm{B}Tw\rho + \frac{3k_\mathrm{B}T}{4\pi l}\sum_\alpha \int \mathrm{d}s_\alpha \frac{1}{|\mathbf{r} - \mathbf{R}_\alpha|} \frac{\partial^2 \mathbf{R}_\alpha}{\partial {s_\alpha}^2} \tag{3.19}$$

so that if

$$\omega = \nabla \times \mathbf{u}$$

$$\frac{\partial \omega}{\partial t} + \eta_0 \nabla^2 \omega - \frac{3k_\mathrm{B}T}{l}\nabla\cdot\sum_\alpha \int \mathrm{d}s_\alpha \frac{\partial^2 \mathbf{R}_\alpha}{\partial {s_\alpha}^2}\delta(\mathbf{r} - \mathbf{R}_\alpha) = \nabla \times \mathbf{f} \tag{3.20}$$

and the potential energy does not affect the fluid velocity except inasmuch as it appears in the equation for **R**.

The equation for ρ can be obtained directly from the $\mathbf{R}_\alpha$ since

$$\partial\rho(\mathbf{k})/\partial t = \sum_\alpha \int \mathrm{d}s_\alpha\, i\mathbf{k}\cdot\dot{\mathbf{R}}_\alpha e^{i\mathbf{k}\cdot\mathbf{R}_\alpha} = i\sum_j \mathbf{k}\cdot\mathbf{u}_\mathbf{j}\rho(\mathbf{k} - \mathbf{j}) \tag{3.21}$$

(The sum sign $\sum_j$ and the integral $\int \mathrm{d}^3 j$ are interchangeable except inasmuch as there is always a special value $j = 0$ present, $\rho_0 = c/l$, the total amount of polymer present, and care must be taken not to lose sight of this term when the integral is used. Another way to put this is that $\rho(\mathbf{k} - \mathbf{j})$ contains the particular value $c\delta(\mathbf{k} - \mathbf{j})$, where c is the arc concentration.)

Since the whole thrust of this paper will be to derive quasi-particle separable equations for the $\mathbf{R}(q)$, $\rho(\mathbf{k})$, and $\mathbf{u}(\mathbf{k})$, one can note at once that for one component alone, when all others are integrated away, F_ρ and F_R must be quadratics

$$\mathcal{N} \int \dots \int \exp\left\{-\frac{3}{2l}\sum_\alpha \int \mathrm{d}s_\alpha \left(\frac{\partial \mathbf{R}}{\partial s_\alpha}\right)^2 - \sum_{\alpha\beta} \int \mathrm{d}s_\alpha \int \mathrm{d}s_\beta\, W[\mathbf{R}_\alpha - \mathbf{R}_\beta]\right\} \prod_{\alpha\neq 1} \prod_{q\neq p} \mathrm{d}\mathbf{R}_\alpha(q) =$$

$$\mathcal{N}_1 \exp(-\,|R_p|^2/g(p)) \qquad (q = 2\pi p/L,\ p \text{ an integer}) \tag{3.22}$$

where $g(q)$ will be $l_1(q)q^{-2}$, l_1 being the swollen step length, about which there is much information: in particular, for a free chain $l_1 \sim q^{-11/5}w^{2/5}$ (modern theories suggest these indices may be out by 1 or 2%)$^{7-10}$ and in a solution where chains overlap, the case studied in this paper, l_1 is a constant, but only returns to l at high concentration or poor solvent. Similarly, F_ρ will have the form $k_\mathrm{B}T\sum_\mathbf{k}\rho_\mathbf{k}\rho_{-\mathbf{k}}\Delta_\mathbf{k}/(2\pi)^3$ so that $\partial F_\rho/\partial\rho_\mathbf{k}$ will be $[k_\mathrm{B}T/(2\pi)^3]\rho_{-\mathbf{k}}\Delta_\mathbf{k}$, where $\Delta_\mathbf{k}$ is the equilibrium value $\langle\rho_\mathbf{k}\rho_\mathbf{j}\rangle = {\Delta_\mathbf{k}}^{-1}\delta(k + j)$. For noninteracting chains $S_k^{(0)}$ is ${\Delta_\mathbf{k}}^{-1}$ at $t = t'$. There remains a tricky point concerning the center of mass motion. If

$$\dot{\mathbf{R}}_\alpha = \mathbf{u}(\mathbf{R}_\alpha,t)$$

defining

$$\mathbf{R}_\mathrm{G} = \frac{1}{L}\int_0^L \mathrm{d}s\ \mathbf{R}(s)$$

$$\dot{\mathbf{R}}_\mathrm{G} = \frac{1}{L}\int_0^L \mathrm{d}s\ \mathbf{u}(\mathbf{R}_\alpha,t)$$

In terms of the Fourier components $R_\alpha(q)$

$$\mathbf{R}_{\alpha,\mathrm{G}} = \mathbf{R}_{\alpha,0}$$

Now in the equation for σ, the free chain part $k_\mathrm{B}Tq^2\mathbf{R}_q$ does not contribute to σ_0 so we can if we wish write the term

$$\sum_\alpha \int \mathrm{d}s_\alpha\ [\delta(\mathbf{r} - \mathbf{R}_\alpha(s_\alpha))]\frac{\partial^2\mathbf{R}_\alpha}{\partial s_\alpha{}^2} \tag{3.23}$$

i.e.

$$\sum_\alpha \int \mathrm{d}s_\alpha\ e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s_\alpha)}\mathbf{R}_\alpha''(s_\alpha) \tag{3.24}$$

as

$$\sum_\alpha \int \left[e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s_\alpha)} - \frac{1}{L}\int \mathrm{d}s'\, e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s')} \right]\mathbf{R}_\alpha''\ \mathrm{d}s_\alpha \tag{3.25}$$

This has the advantage that it explicitly displays the fact that $\mathbf{R}''$ is not coupled to the $k = 0$ mode. One then has

$$\frac{\partial\omega}{\partial t} - \eta_0\nabla^2\omega - \frac{3k_\mathrm{B}T}{l}\sum_\alpha \int \mathrm{d}s_\alpha\ \mathbf{R}_\alpha'' \times \nabla\left[\delta(\mathbf{r} - \mathbf{R}_\alpha(s_\alpha)) - \frac{1}{L}\int \mathrm{d}s'\,\delta(\mathbf{r} - \mathbf{R}_\alpha(s')) \right] = \nabla \times \mathbf{f} \tag{3.26}$$

Now we can write down Liouville's equation in two cases. The first case uses **u** and **R** and the second case uses all three variables.

4. Liouville's Equation for R and u

For the first, one has $P(...\mathbf{u}(\mathbf{k})..., ...[\mathbf{R}_\alpha], ...; t)$

$$\left(\frac{\partial}{\partial t} + \sum_k \frac{\partial}{\partial \mathbf{u}(\mathbf{k})}\cdot\left\{\sum_\alpha \int \mathrm{d}s_\alpha\ e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s_\alpha)}\frac{3k_\mathrm{B}T}{l}R_\alpha''(s_\alpha) - k_\mathrm{B}T\sum_\beta \int \mathrm{d}s_\beta\ \nabla W[\mathbf{R}_\alpha - \mathbf{R}_\beta] - \eta_0k^2\mathbf{u}(\mathbf{k}) + \mathbf{f}(\mathbf{k})\right\} + \sum_\alpha \int \mathrm{d}s_\alpha\ \frac{\partial}{\partial \mathbf{R}_\alpha(s_\alpha)}\cdot\mathbf{u}[\mathbf{R}_\alpha(s_\alpha)] \right)P = 0 \tag{4.1}$$

When **f(k)** is considered as a Brownian random variable it and the viscous term will give rise to a term

$$\frac{\partial}{\partial \mathbf{u}(\mathbf{k})}k_\mathrm{B}T\eta_0k^2\left(\frac{\partial}{\partial \mathbf{u}(-\mathbf{k})} + \frac{\mathbf{u}(\mathbf{k})}{(2\pi)^3k_\mathrm{B}T} \right) \tag{4.2}$$

Thus we can write more briefly

$$\left[\frac{\partial}{\partial t} + \sum_\alpha \int \mathrm{d}s_\alpha\ \frac{\partial}{\partial \mathbf{R}_\alpha(s_\alpha)}\cdot \mathbf{u}[\mathbf{R}_\alpha(s_\alpha)] - \sum_\mathbf{k} \frac{\partial}{\partial \mathbf{u}(\mathbf{k})}\sum_\alpha \int \mathrm{d}s_\alpha\ e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s_\alpha)}\frac{\partial F}{\partial \mathbf{R}_\alpha(s_\alpha)} - \sum_\mathbf{k} \frac{\partial}{\partial \mathbf{u}(\mathbf{k})}\eta_0k^2k_\mathrm{B}T\left(\frac{\partial}{\partial \mathbf{u}(-\mathbf{k})} + \frac{\mathbf{u}(\mathbf{k})}{(2\pi)^3k_\mathrm{B}T} \right) \right]P = 0 \tag{4.3}$$

This has the solution

$$\exp\left[-\frac{1}{2k_\mathrm{B}T}\int \mathrm{d}^3r\ \mathbf{u}^2(r) - \frac{1}{k_\mathrm{B}T}F([R]) \right] \tag{4.4}$$

with $\dot{\mathbf{R}} = \mathbf{u}(\mathbf{R})$ which could be formally incorporated into (4.4) as

$$\prod_\alpha\prod_s \delta(\mathbf{V}_\alpha(s) - \mathbf{u}[\mathbf{R}_\alpha(s)]) \tag{4.5}$$

To reduce this equation to independent components by averaging, we notice first that $F([R])$ depends on all the **R** so we want to average other degrees of freedom away in the pattern $\partial F/\partial \mathbf{R}_\alpha$ (all chains)

average other chains:

$$\frac{\partial F_{(\alpha)}(\mathbf{R}_\alpha)}{\partial \mathbf{R}_\alpha}$$

average all degrees of freedom in chain α except q:

$$\frac{\partial F_{(\alpha)q}(\mathbf{R}_\alpha(q))}{\partial \mathbf{R}_\alpha(q)}$$

where $\partial F_{(\alpha)q}/\partial \mathbf{R}_\alpha(q)$ must be a multiple of $\mathbf{R}_\alpha(q)$. The modeling of F by a quadratic is a purely static problem and has been studied in detail by Muthukumar and Edwards.[11] They use the Fourier transform of the partition function with respect to the density:

$$\exp\left(-\frac{3}{2l}\sum_\alpha \int \mathrm{d}s_\alpha\ R_\alpha'^{\,2} - w\sum_{\alpha,\beta} \int \mathrm{d}s_\alpha \int \mathrm{d}s_\beta\ \delta[\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\beta(s_\beta)] \right) = \mathcal{N}\int ... \int \prod \mathrm{d}\phi_\mathbf{k}\ \exp\left(-\frac{3}{2l}\sum_\alpha \int \mathrm{d}s_\alpha\ R_\alpha'^{\,2} + i\sum_\alpha \int \mathrm{d}s_\alpha\ \phi[\mathbf{R}_\alpha(s_\alpha)] - \frac{1}{2w}\int \mathrm{d}^3r\ \phi^2(r) \right) \tag{4.6}$$

$$\mathcal{N}^{-1} = \int ... \int \prod \mathrm{d}\phi_\mathbf{k}\ \exp\left(-\frac{1}{2w}\int \mathrm{d}^3r\ \phi^2(r) \right) \tag{4.7}$$

and model this with

$$\exp\left(-\frac{3}{2}\sum_\alpha \int \mathrm{d}s_\alpha\ \frac{R_\alpha'^{\,2}}{l_1} - \frac{1}{2}\int \mathrm{d}^3r \int \mathrm{d}^3r'\ \phi(\mathbf{r})\Delta^{-1}(\mathbf{r} - \mathbf{r}')\phi(\mathbf{r}') \right) \tag{4.8}$$

obtaining self-consistent equations for l_1 and Δ. It is well-known that[7,11]

$$\Delta_k = wk^2/(k^2 + \xi_\mathrm{s}^{-2}) \tag{4.9}$$

where ξ_s is the (static) screening length. So $\partial F/\partial \mathbf{R}_\alpha(q)$, when all degrees of freedom except $\mathbf{R}(q)$ itself are averaged away, is, as given by the Appendix,

$$3k_\mathrm{B}T\mathbf{R}(q)\left[\frac{q^2}{l} - \frac{2w}{qL}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \int \frac{\mathrm{d}^3k}{(2\pi)^3} \frac{k^4}{k^2 + \xi_\mathrm{s}^{-2}}e^{-k^2l_1|s-s'|/6}\sin^2\left(\frac{q|s - s'|}{2} \right) \right] \tag{4.10}$$

We are only interested in small q values and have anticipated that the answer is $q^2R(q)/l_1$, so we expand the sine to get

$$\frac{1}{l_1} = \frac{1}{l} - \frac{24w}{\pi^2l_1^3}\int_0^\infty \frac{\mathrm{d}k}{k^2 + \xi_\mathrm{s}^{-2}} \tag{4.11}$$

$$\frac{1}{l_1} = \frac{1}{l} - \frac{\alpha w\xi_\mathrm{s}}{l_1^3} \tag{4.12}$$

where the numerical constant α is $12/\pi$. For the case of $l_1 \gg l$ one has

$$l_1^3 = \alpha w \xi_s l \tag{4.13a}$$

For $l_1 = l + \epsilon$

$$\epsilon = \alpha w \xi_s / l \tag{4.13b}$$

This derivation is a simple averaging and applied to a single chain, where it would be reasonable to associate ξ_s with the size, $(Ll_1)^{1/2}$, of the chain itself, will yield the Flory power

$$\langle [\mathbf{R}(L) - \mathbf{R}(0)]^2 \rangle \propto L^{6/5}$$

This law is not established since more elaborate calculations give a slightly lower index. We must therefore treat the equations (4.13) with caution. However, for high concentrations there is no problem since $\epsilon = \alpha w \xi_s / l$ is a rigorous result in the limit of $c \rightarrow \infty$ or $w \rightarrow 0$.

Returning now to the Liouville equation, which now has a simpler form

$$\left\{ \frac{\partial}{\partial t} + \sum_{\mathbf{k}} \sum_{\alpha} \int \mathrm{d}s_\alpha \, \frac{\partial}{\partial \mathbf{u}(\mathbf{k})} \cdot e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s_\alpha)} \frac{3k_\mathrm{B}T\mathbf{R}_\alpha''}{l_1} - \sum_{\mathbf{k}} \frac{\partial}{\partial \mathbf{u}(\mathbf{k})} \cdot k_\mathrm{B}T\eta_0 k^2 \left(\frac{\partial}{\partial \mathbf{u}(-\mathbf{k})} + \frac{\mathbf{u}(\mathbf{k})}{(2\pi)^3 k_\mathrm{B}T} \right) + \sum_\alpha \int \mathrm{d}s_\alpha \, \frac{\partial}{\partial \mathbf{R}_\alpha(s_\alpha)} \cdot \mathbf{u}[\mathbf{R}_\alpha(s_\alpha)] \right\} P = 0$$

We may now eliminate $\mathbf{u}$ from the $\mathbf{R}$ equation, and $\mathbf{R}$ from the $\mathbf{u}$ equations. Since this whole study is done in thermal equilibrium, one of the pair of coefficients (diffusivity and friction) appearing in each degree of freedom need be calculated; the other follows from the form of equilibrium distribution. Thus the term in $\partial^2/\partial\mathbf{R}_\alpha\partial\mathbf{R}_\beta$ will arise from the iteration of $\partial\mathbf{u}(\mathbf{R}_\alpha)/\partial\mathbf{R}_\alpha$ and will be

$$\frac{\partial}{\partial \mathbf{R}_\alpha} \int \mathrm{d}t \langle \mathbf{u}(\mathbf{R}_\alpha(t),t)\mathbf{u}(\mathbf{R}_\beta(0),0) \rangle \frac{\partial}{\partial \mathbf{R}_\beta}$$

In a systematic derivation the lifetime of the $\mathbf{R}_\alpha$'s will also occur, but we have made the assumption that the fluid propagates motion faster than the movement of the polymers. Hence we can write[12]

$$\langle u^\alpha(\mathbf{R}_\alpha(s_\alpha),t)u^\beta(\mathbf{R}_\beta(s_\beta),t') \rangle = 2k_\mathrm{B}T\delta(t-t') \int \frac{\mathrm{d}^3 j}{(2\pi)^3} \frac{\mathcal{O}_j^{\alpha\beta}}{\eta_0 j^2} \langle e^{i\mathbf{j}\cdot[\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\beta(s_\beta)]} \rangle \tag{4.14}$$

Two difficulties arise with this expression. The effect of having many polymers present will change the effective viscosity from $\eta_0 j^2$ to $\eta(j)$. Should we use $\eta(j)$ in this expression rather than $\eta_0 j^2$? Also the presence of an interaction correlates $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ via the density fluctuation

$$\langle \rho(\mathbf{k})\rho(\mathbf{k}') \rangle = \Delta_\mathbf{k}\delta(\mathbf{k} + \mathbf{k}')$$

which is not easy to obtain within the $\mathbf{R}$ picture alone. One can see the resolution of the first problem easily because we can return to the Langevin equation

$$\frac{\partial \mathbf{u}}{\partial t} - \eta_0 \nabla^2 \mathbf{u} + \nabla p = \mathbf{f} + \sum_\alpha \int \mathrm{d}s_\alpha \, \delta[\mathbf{r} - \mathbf{R}_\alpha(s_\alpha)] \sigma_\alpha(s_\alpha) \tag{4.15}$$

which has the solution

$$u^i = u_0^{\,i} + \sum_\alpha \int \mathrm{d}s_\alpha \int \mathrm{d}t' \, G^{ij}(r, \mathbf{R}_\alpha(s_\alpha); t, t') \sigma_\alpha^{\,j}(s_\alpha, t') \tag{4.16}$$

where G^{ij} is the Oseen tensor and for our present purpose is approximated by the time-independent form using the assumption that the fluid motion is instantaneous.

The velocity $u_0^{\,i}$ is that arising if the polymer is absent, i.e., from $\mathbf{f}$ alone

$$\mathbf{u}(\mathbf{r}) = \mathbf{u}_0(\mathbf{r}) + \frac{3k_\mathrm{B}T}{l_1} \sum_\alpha \int \mathrm{d}s_\alpha \, \mathbf{G}[\mathbf{r} - \mathbf{R}_\alpha(s_\alpha)] \cdot \frac{\partial^2 \mathbf{R}_\alpha(s_\alpha)}{\partial s_\alpha^2} \tag{4.17}$$

and

$$\dot{\mathbf{R}}_\alpha(s_\alpha) = \mathbf{u}_0[\mathbf{R}_\alpha(s_\alpha)] + \frac{3k_\mathrm{B}T}{l_1} \sum_\beta \int \mathrm{d}s_\beta \, \mathbf{G}[\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\beta(s_\beta)] \cdot \frac{\partial^2 \mathbf{R}_\beta(s_\beta)}{\partial s_\beta^2} \tag{4.18}$$

The fluctuations which give rise to the diffusion equation lie in $\mathbf{u}_0$ and the diffusion equation itself immediately follows from (4.14)

$$\left[\frac{\partial}{\partial t} - \sum_{\alpha,\beta} \int \mathrm{d}s_\alpha \int \mathrm{d}s_\beta \, \frac{\partial}{\partial R_\alpha^{\,i}(s_\alpha)} k_\mathrm{B}T G_{\alpha\beta}^{\,ij} \left(\frac{\partial}{\partial R_\beta^{\,j}(s_\beta)} - \frac{3R_\beta''(s_\beta)}{l_1} \right) \right] P = 0 \tag{4.19}$$

where

$$G_{\alpha\beta}^{\,ij} = \int \frac{\mathrm{d}^3 k}{(2\pi)^3} \frac{\delta^{ij} - \dfrac{k^i k^j}{k^2}}{\eta_0 k^2} e^{i\mathbf{k}\cdot[\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\beta(s_\beta)]} \tag{4.20}$$

In this equation the fluid has been eliminated but it still involves all the chains. On the assumption that the fluid is propagating instantaneously the chains behave as if they are fixed. This allows an illuminating approach to be made to (4.19).[6] Recalling the Lagrange multiplies σ_α, if it is assumed that all chains are fixed but one, then

$$\dot{R}_1 = u_{1,0} + G_{11}\sigma_1 + \sum_{\alpha \neq 1} G_{1\alpha}\sigma_\alpha \tag{4.21}$$

$$0 = \mathrm{u}_{\alpha,0} + \sum_{\beta \neq 1} G_{\alpha\beta}\sigma_\beta + G_{\alpha 1}\sigma_1 \tag{4.22}$$

where

$$\mathbf{u}_{\alpha,0} = \mathbf{u}_0(\mathbf{R}_\alpha)$$

and

$$\sigma_1 = \frac{3k_\mathrm{B}T}{l_1}\mathbf{R}_1''$$

If we define a matrix H_{ij} such that

$$\sum_j H_{ij} G_{jl} = \delta_{il}; \qquad i, j, l \neq 1 \tag{4.23}$$

or in full

$$\sum_j \int \mathrm{d}s_j \, \mathbf{H}(\mathbf{R}_i(s_i), \mathbf{R}_j(s_j)) \cdot \mathbf{G}(\mathbf{R}_j(s_j) - \mathbf{R}_l(s_l)) = \mathbf{1}\delta[\mathbf{R}_i(s_i) - \mathbf{R}_l(s_l)] \tag{4.24}$$

$$\dot{R}_1 = u_{1,0} + \frac{3k_\mathrm{B}T}{l_1}\left(G_{11'} - \sum_{\alpha,\beta} G_{1\alpha}H_{\alpha\beta}G_{\beta 1'}\right)R_1'' - \sum_{\alpha,\beta} G_{1\alpha}H_{\alpha\beta}u_{\beta,0} \tag{4.25}$$

It may be noted that the matrix

$$\mathcal{G}(\mathbf{R}_1(s_1), \mathbf{R}_1(s_1')) = G_{11'} - \sum_{\alpha,\beta} G_{1\alpha}H_{\alpha\beta}G_{\beta 1'} \tag{4.26}$$

has the property that it vanishes whenever any $\mathbf{R}_\alpha(s_\alpha)$ equals $\mathbf{R}_1(s_1)$, a consequence of the boundary condition that

$$\mathbf{u}(\mathbf{R}_1) = \dot{\mathbf{R}}_1$$

$$\mathbf{u}(\mathbf{R}_\alpha) = 0$$

so that when $\mathbf{R}_1 = \mathbf{R}_\alpha$

$$\mathbf{u}(\mathbf{R}_1) = \mathbf{u}(\mathbf{R}_\alpha) = 0$$

This now has a good form to average, since one has a single-particle diffusion equation

$$\left[\frac{\partial}{\partial t} - \int \mathrm{d}s_1 \int \mathrm{d}s_1{}' \frac{\partial}{\partial \mathbf{R}(s_1)} k_\mathrm{B} T \mathcal{G}\left(\frac{\partial}{\partial \mathbf{R}(s_1{}')} - \frac{3}{l}\frac{\partial^2 \mathbf{R}(s_1)}{\partial s_1{}^2}\right)\right] P = 0 \quad (4.27)$$

The average of G can be obtained by a series expansion of H about its diagonal terms $G_{\alpha\alpha}$ provided that these are averaged. Thus

$$G_{\alpha\alpha} H_{\alpha\beta} + \sum_{\gamma \neq \beta} G_{\alpha\gamma} H_{\gamma\beta} = \delta_{\alpha\beta} \quad (4.28)$$

Approximate $G_{\alpha\alpha}$ by its average $\mathcal{J}_\alpha$, say

$$\mathcal{J}_\alpha{}^0(q) = \int \mathrm{d}(s_\alpha - s_\alpha{}')\, e^{iq(s_\alpha - s_\alpha{}')} \langle \mathbf{G}[\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\alpha(s_\alpha{}')]\rangle \quad (4.29)$$

$$= \int \mathrm{d}(s - s') \int \frac{\mathrm{d}^3 k}{(2\pi)^3} \frac{1 - \mathbf{kk}/k^2}{\eta_0 k^2} e^{iq(s-s') - k^2 l_1 |s-s'|/6} \quad (4.30)$$

$$= \frac{1}{3\pi^2 \eta_0} \int_0^\infty \mathrm{d}k \frac{k^2 l_1/3}{(k^2 l_1/6)^2 + q^2} \quad (4.31)$$

If the chains are long $G_{\alpha\alpha} - \mathcal{J}_\alpha{}^0$, which shows the effect of the fluctuation of the internal structure of the chain $\mathbf{R}_\alpha$ on the fluid motion, can be neglected and a series developed in the form

$$H_{\alpha\beta} = \frac{\delta_{\alpha\beta}}{\mathcal{J}_\alpha{}^0} - \frac{1}{\mathcal{J}_\alpha{}^0} G_{\alpha\beta} \frac{1}{\mathcal{J}_\beta{}^0} + \frac{1}{\mathcal{J}_\alpha{}^0} G_{\alpha\gamma} \frac{1}{\mathcal{J}_\gamma{}^0} G_{\gamma\beta} \frac{1}{\mathcal{J}_\beta{}^0} - \ldots \quad (4.32)$$

This analysis works also when all the chains are free to move,[4,5] provided their correlation is ignored. This correlation is handled in section 5 since it involves the collective coordinates in terms like the average of

$$G_{\alpha\gamma} G_{\gamma\beta} \quad (4.33)$$

The series can be averaged simply, provided that we ignore the terms like $\alpha = \gamma$ which are permitted in $\sum_{\alpha \neq \beta} \sum_{\beta \neq \gamma}$ and take the summation over $\alpha \neq \beta \neq \gamma \neq \ldots$. Thus this expansion gives

$$\dot{\mathbf{R}}_1 - \frac{3 k_\mathrm{B} T}{l_1}\left(G_{11'} - \sum_\alpha \frac{G_{1\alpha} G_{\alpha 1'}}{\mathcal{J}_\alpha{}^0} + \sum G_{1\alpha} \frac{1}{\mathcal{J}_\alpha{}^0} G_{\alpha\beta} \frac{1}{\mathcal{J}_\beta{}^0} G_{\beta 1'} - \ldots\right) \mathbf{R}_1{}'' = \tilde{\mathbf{u}}_0 \quad (4.34)$$

The kernel in the bracket is in detail

$$\int \frac{\mathrm{d}^3 k}{(2\pi)^3} \frac{(1 - \mathbf{kk}/k^2)}{\eta_0 k^2} e^{i\mathbf{k}\cdot[\mathbf{R}_1(s_1) - \mathbf{R}_1(s_1{}')]} \times \left(1 - c \int_{-\infty}^\infty \frac{\mathrm{d}q}{2\pi} \int \mathrm{d}(s - s') \frac{e^{iq(s-s') - i\mathbf{k}\cdot[\mathbf{R}(s) - \mathbf{R}(s')]}}{\eta_0 k^2 \mathcal{J}^0(q)} + \ldots\right)$$

$$= \int \frac{\mathrm{d}^3 k}{(2\pi)^3} \frac{1 - \mathbf{kk}/k^2}{\eta_0 (k^2 + \xi_\mathrm{H}{}^{-2})} e^{i\mathbf{k}\cdot[\mathbf{R}_1(s_1) - \mathbf{R}_1(s_1{}')]} \quad (4.35)$$

where

$$\xi_\mathrm{H}{}^{-2} = \frac{c}{\eta_0} \int_{-\infty}^\infty \frac{\mathrm{d}q}{2\pi} \int d(s - s') \frac{e^{iq(s-s') - k^2 l_1 |s-s'|/6}}{\mathcal{J}^0(q)} \quad (4.36)$$

$$= \frac{c}{\eta_0} \int_{-\infty}^\infty \frac{\mathrm{d}q}{2\pi} \frac{1}{\mathcal{J}^0(q)} \frac{k^2 l_1/3}{(k^2 l_1/6)^2 + q^2} \quad (4.37)$$

Self-consistently we can replace $\mathcal{J}^0$ by $\mathcal{J}$ using $\eta(k)$:

$$\mathcal{J}(q) = \frac{1}{3\pi^2 c_0} \int_0^\infty \mathrm{d}j \frac{j^2}{j^2 + \xi_\mathrm{H}{}^{-2}} \frac{j^2 l_1/3}{(j^2 l_1/6)^2 + q^2} \quad (4.38)$$

In these expressions one must always regard $\int \mathrm{d}q$ as, strictly speaking, a sum over Fourier coefficients but provided one is concerned with the $\mathbf{k}$ vectors large compared to $2\pi l_1/L$, it is valid to use the integral sign. Under these circumstances we see that q can be ignored in the integral for ξ_H so that

$$\xi_\mathrm{H}{}^{-2} = \frac{\pi}{2} c l_1 \xi_\mathrm{H}{}^{-1} \quad (4.39)$$

and

$$\mathcal{J} = 2\xi_\mathrm{H}/\pi\eta_0 l_1 \quad (4.40)$$

If one worked at low density so that single-chain effects matter, $\xi_\mathrm{H}{}^{-2}$ would not be dominant and one has

$$\mathcal{J}(q) = \frac{2\xi_\mathrm{H}}{\pi\eta_0 l_1} \frac{1 + \left(\dfrac{3q}{l_1}\right)^{1/2} \xi_\mathrm{H}}{1 + \left(\dfrac{12q}{l_1}\right)^{1/2} \xi_\mathrm{H}{}^2 + \dfrac{6q}{l_1} \xi_\mathrm{H}{}^2} \quad (4.41)$$

$$= \frac{2^{1/2}}{\pi\eta_0 (l_1|q|)^{1/2}}, \qquad \xi_\mathrm{H} \to \infty \quad (4.42)$$

However, if one tries a direct solution the equations are very nonlinear and all one can say simply is that for c large

$$\xi_\mathrm{H} = \left(\frac{\pi}{2} c l_1\right)^{-1} \quad (4.43)$$

$$\mathcal{J} = 2\xi_\mathrm{H}/\pi\eta_0 l_1 \quad (4.44)$$

and for c small

$$\mathcal{J} = \frac{2^{1/2}}{\pi\eta_0 (l_1|q|)^{1/2}} \quad (4.45)$$

$$\xi_\mathrm{H} \simeq (\rho k)^{-1/2} \quad (4.46)$$

This value of ξ_H must not be taken seriously, however, since the validity of the geometric series is a high-density theory, and only the equivalent of the Zimm value has validity, $\mathcal{J} = (\pi^2 \eta_0{}^2 l_1 q/2)^{-1/2}$. For chains in an overlapped condition, providing they are not yet in the highly entangled region of high viscosity, the equations (4.37) and (4.38) are valid.

The viscosity of the system is given by the form of $\xi_\mathrm{H}{}^{-2}$ at low $\mathbf{k}$, i.e., k^{-1} of macroscopic size. In this region the summation in (4.37) is precisely the same term as appears in the equation for $\mathbf{u}$ of (3.26); i.e.

$$\eta(k) = \eta_0 k^2 + \delta\eta(k) \quad (4.47)$$

$$\dot{\mathbf{R}}_\alpha - \frac{3 k_\mathrm{B} T}{l} \mathcal{G} \mathbf{R}_\alpha{}'' = \int \delta(\mathbf{r} - \mathbf{R}_\alpha) \mathbf{u}(\mathbf{r})\, \mathrm{d}^3 r \quad (4.48)$$

$$\delta\eta(k) = \frac{3 k_\mathrm{B} T}{l} \int \mathrm{d}s \int \mathrm{d}s' \left(\sum_\alpha e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s)} - \frac{1}{L}\int_0^L \mathrm{d}s_1\, e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s_1)}\right) \mathcal{G}(ss') R_\alpha{}''(s') \quad (4.49)$$

So that, using the Rouse-mode form (remember $\int \mathrm{d}q/q^2 \rightarrow (L/2\pi)\sum_p p^{-2}$)

$$k^2\delta\eta = \frac{c}{2\pi}\sum_p \frac{k^2 l_1/3}{(k^2 l_1/6)^2 + q^2}\,\frac{3k_BTq^2/l_1}{i\omega + 3k_BTq^2J(q)/l_1} \tag{4.50}$$

Note that the effect of removing the center of mass motion (i.e., of using (3.25)) is simply to eliminate the $q = 0$ mode in the sum over q.

For zero frequency and $J \sim \xi_H$

$$k^2\delta\eta = k^2\eta_0 c l_1^2 L/12\pi\xi_H$$

$$\delta\eta = \eta_0 c^2 l_1^3 L/24 \tag{4.51}$$

(for $J \sim q^{-1/2}$ one has the Zimm $L^{1/2}$ law).

The integral for $\eta(k)$ is the same as for ξ_H^{-2}, for they are the same calculation. However, η is normally used for $\mathbf{k}$ macroscopic, whereas in the integral for J and for ξ_H itself, one is in the region

$$Ll > k^{-2} \sim \xi_H^2$$

The results of section 4 are then that the Liouville equation (4.1) can be averaged into the form

$$\left[\frac{\partial}{\partial t} - \sum_{\mathbf{k}}\frac{\partial}{\partial \mathbf{u}_k}\eta(k)\left(\frac{\partial}{\partial \mathbf{u}(k)} + \frac{\mathbf{u}(\mathbf{k})}{(2\pi)^3 k_BT}\right) - \sum_\alpha\sum_q \frac{\partial}{\partial \mathbf{R}_\alpha(q)}J(q)\left(\frac{\partial}{\partial \mathbf{R}_\alpha(q)} + \frac{3q^2}{l_1}\mathbf{R}_\alpha(q)\right)\right]P = 0 \tag{4.52}$$

where

$$\eta(k) = \eta_0 k^2 + \frac{c}{2\pi}\sum_{-\infty}^{\infty}\frac{k^2 l_1/3}{(k^2 l_1/6)^2 + q^2}\,\frac{1}{J(q)} \tag{4.53}$$

$$[= \eta_0(k^2 + \xi_H^{-2}) \qquad \text{when } k\xi_H \sim 1$$

$$= \eta_0\left(1 + \frac{c}{12\pi}l_1^2 L\xi_H^{-1}\right)k^2 \qquad \text{where } k \sim 0] \tag{4.54}$$

and

$$J(q) = \frac{1}{3\pi^2}\int_0^\infty \frac{\mathrm{d}j}{\eta(j)}\,\frac{j^4 l_1/3}{(j^2 l_1/6)^2 + q^2} \tag{4.55}$$

A residual problem is that the correlation between chains reflected in the screening term ξ_s^{-2} in the expected form

$$\langle\rho(\mathbf{k})\rho(\mathbf{j})\rangle = \frac{6c}{ll_1}\,\frac{\delta(\mathbf{k} + \mathbf{j})(2\pi)^3}{k^2 + \xi_s^{-2}} \tag{4.56}$$

does not easily fit into this formalism, where ξ_H appears quite independently. The use of the collective coordinates removes this difficulty.

5. Use of Collective Coordinates in Liouville's Equation

The evolution of ρ can be obtained by direct differentiation as in (3.21).

$$\frac{\partial\rho(\mathbf{k})}{\partial t} = i\mathbf{k}\cdot\sum_\alpha \dot{\mathbf{R}}_\alpha e^{i\mathbf{k}\cdot\mathbf{R}_\alpha} \tag{5.1}$$

One can directly use $\mathbf{u}$

$$\frac{\partial\rho(\mathbf{k})}{\partial t} = \frac{i\mathbf{k}}{(2\pi)^3}\cdot\sum_{\mathbf{j}}\mathbf{u}_{\mathbf{j}}\rho(\mathbf{k} - \mathbf{j}) \tag{5.2}$$

i.e.

$$\frac{\partial\rho}{\partial t} - (\mathbf{u}\cdot\nabla)\rho = 0 \tag{5.3}$$

This gives

$$\left\{\frac{\partial}{\partial t} + \sum_{\mathbf{k}}\frac{\partial}{\partial\rho(\mathbf{k})}\sum_{\mathbf{j}}\frac{(\mathbf{u}\cdot\nabla)_{\mathbf{j}}}{(2\pi)^3}\rho(\mathbf{k} - \mathbf{j}) - \sum_{\mathbf{k}}\frac{\partial}{\partial\mathbf{u}(\mathbf{k})}k_BT\eta_0 k^2\left(\frac{\partial}{\partial\mathbf{u}(-\mathbf{k})} + \frac{\mathbf{u}(\mathbf{k})}{(2\pi)^3 k_BT}\right) - \sum_{\mathbf{k}}\frac{\partial}{\partial\mathbf{u}(\mathbf{k})}\cdot \sum_\alpha\int \mathrm{d}s_\alpha\, e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s_\alpha)}\frac{\partial F}{\partial\mathbf{R}_\alpha(s_\alpha)} + \sum_\alpha\int \mathrm{d}s_\alpha\,\frac{\partial}{\partial\mathbf{R}_\alpha(s_\alpha)}\cdot \mathbf{u}[\mathbf{R}_\alpha(s_\alpha)]\right\}P = 0 \tag{5.4}$$

The obvious awkwardness of this equation lies in the presence of the $\mathbf{R}_\alpha$, whose elimination would require a more general type of collective coordinate which can reflect the vorticity of the fluid. But we can complete the calculation within the present framework by employing the results of the previous section. The simple random phase approximations such as $\langle\rho(\mathbf{k} - \mathbf{m})\rangle$ replacing $\rho(\mathbf{k} - \mathbf{m})$ give zero contribution because of the Oseen tensor. Thus, treating $\mathbf{u}\cdot\nabla\rho$ as a noise and averaging, assuming the $\mathbf{u}$ field decays faster than the ρ field

$$\frac{\partial}{\partial\rho(\mathbf{k})}(\mathbf{u}\cdot\nabla\rho)_{\mathbf{k}} \rightarrow \frac{\partial}{\partial\rho_{\mathbf{k}}}\left\{\int_0^\infty \mathrm{d}\tau\,[\mathbf{u}\cdot\nabla\rho(\tau)]_{\mathbf{k}}[\mathbf{u}\cdot\nabla\rho(0)]_{-\mathbf{k}}\right\}\frac{\partial}{\partial\rho_{-\mathbf{k}}} \tag{5.5}$$

Let

$$D_{\mathbf{k}} = k_BTk^2\int\frac{\mathrm{d}^3m}{(2\pi)^3}\,\mathbf{G}(\mathbf{m})\Delta_{\mathbf{k}-\mathbf{m}}^{-1} \tag{5.6}$$

then, using the usual analysis of fluctuation dissipation theorem one has

$$\left[\frac{\partial}{\partial t} - \sum_{\mathbf{k}}\frac{\partial}{\partial\rho_{\mathbf{k}}}D_{\mathbf{k}}\left(\frac{\partial}{\partial\rho_{-\mathbf{k}}} + \frac{\partial F_\rho}{\partial\rho_{-\mathbf{k}}}\right)\right]P(\rho) = 0 \tag{5.7}$$

the analog of

$$\left[\frac{\partial}{\partial t} - \sum_q\frac{\partial}{\partial\mathbf{R}_q}J(q)\left(\frac{\partial}{\partial\mathbf{R}_{-q}} + \frac{\partial F([R])}{\partial\mathbf{R}_{-q}}\right)\right]P = 0 \tag{5.8}$$

The correlation Δ is a property of equilibrium and will be assumed for the moment (but is indeed well-known[7]) to be given by (4.9). The fluid Green function is the hydrodynamically screened function obtained above, so that

$$D_{\mathbf{k}} = \frac{8k_BTck^2}{\eta_0 l_1}\int\frac{\mathrm{d}^3m}{(2\pi)^3}\,\frac{1}{m^2 + \xi_H^{-2}}\,\frac{1}{(\mathbf{k} - \mathbf{m})^2 + \xi_s^{-2}} \tag{5.9}$$

$$= \frac{2k_BTck^2}{\pi\eta_0 l_1}(\xi_s^{-1} + \xi_H^{-})^{-1} \qquad \text{for small } k \tag{5.10}$$

For small k one has then

$$\left[\frac{\partial}{\partial t} - \sum_{\mathbf{k}}\frac{\partial}{\partial\rho_{\mathbf{k}}}\,\frac{2k_BTck^2}{\pi\eta_0 l_1}(\xi_s^{-1} + \xi_H^{-1})^{-1}\left(\frac{\partial}{\partial\rho_{-\mathbf{k}}} + \frac{\Delta_k\rho_k}{(2\pi)^3}\right)\right]P = 0 \tag{5.11}$$

Finally, we must return to the equation for $\dot{\mathbf{R}}_\alpha$ and include the static correlation between $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$ to produce the final form for $J(q)$. The equation for $\mathbf{R}_\alpha$ is given by

$$\dot{\mathbf{R}}_\alpha - \frac{3k_{\mathrm{B}}T}{l}\sum_\beta \mathbf{G}_{\alpha\beta}\cdot\mathbf{R}_\beta'' + k_{\mathrm{B}}Tw\sum_\beta \mathbf{G}_{\alpha\beta}\cdot\nabla\rho[\mathbf{R}_\beta] = \mathbf{u}_0[\mathbf{R}_\alpha] \tag{5.12}$$

So we need to invert the "matrix" $G_{\alpha\beta}$. The $w\nabla\rho$ term will not enter the subsequent discussion since only its fluctuation is nonvanishing so it will henceforward be omitted. In the earlier discussion the preaveraging approximation replaced $G_{\alpha\beta}$ by $\langle G_{\alpha\alpha}\rangle$ and in the regime where the polymers overlap this is approximately a constant

$$\left\langle \int \frac{\mathrm{d}^3k}{(2\pi)^3}\,\mathbf{G}(k)e^{i\mathbf{k}\cdot[\mathbf{R}_\alpha(s_\alpha)-\mathbf{R}_\alpha(s_\alpha')]}\right\rangle \cong \delta(s_\alpha - s_\alpha')\frac{2}{\pi^2\eta_0 l_1}\int_0^\infty \frac{\mathrm{d}k}{k^2+\xi_{\mathrm{H}}^{-2}} \tag{5.13}$$

$$= \frac{\xi_{\mathrm{H}}}{\pi l_1\eta_0}\delta(s_\alpha - s_\alpha') \tag{5.14}$$

Since $6/k^2l_1$ is the two-body correlation function in the absence of interaction, one can guess that the appropriate generalization will be

$$\frac{1}{\eta_0 l_1}\int_0^\infty \frac{\mathrm{d}^3k}{(2\pi)^3}\,\frac{1-\mathbf{kk}/k^2}{k^2+\xi_{\mathrm{H}}^{-2}}\,\frac{1}{k^2+\xi_{\mathrm{s}}^{-2}} = 1/6\pi\eta_0 l_1(\xi_{\mathrm{H}}^{-1}+\xi_{\mathrm{s}}^{-1}) \tag{5.15}$$

To see this, let us study the solution of an equation like

$$\sum_\beta G_{\alpha\beta}\phi_\beta = \psi_\alpha \tag{5.16}$$

or in full

$$\sum_\beta \int \mathrm{d}s_\beta\, G(\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\beta(s_\beta))\phi(s_\beta) = \psi[\mathbf{R}_\alpha(s_\alpha)] \tag{5.17}$$

A comprehensive treatment of such an equation will require generalized collective coordinates, but a plausible approach is to look for a solution

$$\psi(\mathbf{R}_\alpha(s_\alpha)) = \sum_{\mathbf{p}} e^{i\mathbf{p}\cdot\mathbf{R}_\alpha(s_\alpha)}\psi(\mathbf{p}) \tag{5.18}$$

$$\phi(s_\beta) = \phi[\mathbf{R}_\beta(s_\beta)] = \sum_{\mathbf{m}} e^{i\mathbf{m}\cdot\mathbf{R}_\beta(s_\beta)}\phi_{\mathbf{m}} \tag{5.19}$$

and multiply the whole equation by $\exp(i\mathbf{k}\cdot\mathbf{R}_\alpha(s_\alpha))$ and average. Then

$$\sum_\beta\sum_{n,m} e^{i\mathbf{k}\cdot\mathbf{R}_\alpha(s_\alpha)}\mathbf{G}_n e^{i\mathbf{n}\cdot[\mathbf{R}_\alpha(s_\alpha)-\mathbf{R}_\beta(s_\beta)]}\phi_{\mathbf{m}}e^{i\mathbf{m}\cdot\mathbf{R}_\beta(s_\beta)} = \sum_{\mathbf{p}}\psi_{\mathbf{p}}e^{i(\mathbf{p}+\mathbf{k})\cdot\mathbf{R}_\alpha(s_\alpha)} \tag{5.20}$$

$$\sum_{n,m}\rho_{k+n}\rho_{-n+m}G_n\phi_m = \sum_{\mathbf{p}}\psi_{\mathbf{p}}\rho_{\mathbf{p}+\mathbf{k}} \tag{5.21}$$

Averaging this one has

$$-\mathbf{k} = \mathbf{m} = \mathbf{p}$$

$$\frac{c}{\eta_0 l_1(2\pi)^3}\int \frac{\mathrm{d}^3n}{n^2+\xi_{\mathrm{H}}^{-2}}\,\frac{1-\mathbf{nn}/n^2}{(\mathbf{k}+\mathbf{n})^2+\xi_{\mathrm{s}}^{-2}}\phi_{\mathbf{k}} = c\psi_{\mathbf{k}} \tag{5.22}$$

and consistently neglecting $\mathbf{k}$ in the integral

$$\phi_k = 6\pi\eta_0 l_1\psi_k(\xi_{\mathrm{s}}^{-1}+\xi_{\mathrm{H}}^{-1})$$

The mean matrix to replace $G_{\alpha\beta}$ is then the diagonal constant

$$J = \frac{2}{\pi\eta_0 l_1}(\xi_{\mathrm{s}}^{-1}+\xi_{\mathrm{H}}^{-1})^{-1} \tag{5.23}$$

and the effect of the interaction is then to produce

$$\xi_{\mathrm{H}}^{-2} = \frac{\pi}{2}cl_1(\xi_{\mathrm{H}}^{-1}+\xi_{\mathrm{s}}^{-1}) \tag{5.24}$$

which correctly gives the θ limit when $\xi_{\mathrm{s}} \to \infty$. It is quite straightforward to keep q in the equation when it goes

$$J(q) = \frac{1}{3\pi^2\eta_0}\int_0^\infty \frac{\mathrm{d}k}{k^2+\xi_{\mathrm{H}}^{-2}}\left[\frac{k^4l_1/3}{(k^2l_1/6)^2+q^2} - \frac{\xi_{\mathrm{s}}^{-2}\delta(q)}{l_1(k^2+\xi_{\mathrm{s}}^{-2})}\right] \tag{5.25}$$

The relationship between ξ_{H} and ξ_{s} leads to a revision of the ratio given earlier[13] for the semidilute region, where both are proportional to $(cl_1)^{-1}$. Their ratio is now given by (5.24).

We have now completed the program proposed with the results that the Fokker–Planck equation for the three classes of quasi-excitation will be

$$\left[\frac{\partial}{\partial t} - \sum_{\mathbf{k}}\frac{\partial}{\partial\mathbf{u}(\mathbf{k})}k_{\mathrm{B}}T\eta(\mathbf{k})\left(\frac{\partial}{\partial\mathbf{u}(-\mathbf{k})} + \frac{\mathbf{u}(\mathbf{k})}{(2\pi)^3k_{\mathrm{B}}T}\right) - \sum_{\mathbf{k}}\frac{\partial}{\partial\rho(\mathbf{k})}D(\mathbf{k})\left(\frac{\partial}{\partial\rho(-\mathbf{k})} + \frac{\Delta(\mathbf{k})\rho(\mathbf{k})}{(2\pi)^3}\right) - \sum_\alpha\sum_q\frac{\partial}{\partial\mathbf{R}_\alpha(q)}J(q)\left(\frac{\partial}{\partial\mathbf{R}_\alpha(-q)} + \frac{3q^2\mathbf{R}_\alpha(q)}{2\pi l_1}\right)\right]P = 0 \tag{5.26}$$

where

$$\eta(k) = \eta_0k^2 + \frac{1}{2\pi}\sum_{q\neq0}\frac{S_{\mathbf{k},q,0}}{J(q)} \tag{5.27}$$

$$= \eta_0(k^2+\xi_{\mathrm{H}}^{-2}), \qquad k > \xi_{\mathrm{H}}^{-1}$$

$$= (\eta_0+\delta\eta)k^2, \qquad k < \xi_{\mathrm{H}}^{-1}$$

$$\delta\eta = \frac{c\eta_0}{12\pi}l_1^2L\xi_{\mathrm{H}}^{-1} \tag{5.28}$$

$$J(q) = \int\frac{\mathrm{d}^3j}{(2\pi)^3}\,\frac{S_{j,q,0}}{\eta(j)}(1-\mathbf{jj}/j^2) \tag{5.29}$$

$$= 2/\pi\eta_0 l_1(\xi_{\mathrm{s}}^{-1}+\xi_{\mathrm{H}}^{-1}) \tag{5.30}$$

$$\xi_{\mathrm{H}}^{-2} = \frac{\pi}{2}cl_1(\xi_{\mathrm{H}}^{-1}+\xi_{\mathrm{s}}^{-1}) \tag{5.31}$$

$$D_{\mathbf{k}} = \frac{2k_{\mathrm{B}}Tk^2c}{\pi\eta_0 l_1}(\xi_{\mathrm{s}}^{-1}+\xi_{\mathrm{H}}^{-1})^{-1} \tag{5.32}$$

We have commented that ξ_{s} must have a form proportional to $(cl_1)^{-1}$ in semidilute conditions. An extrapolation formula for ξ_{s} has been given[11]

$$\xi_{\mathrm{s}}^{-2} = \frac{6wc/l_1}{1+\dfrac{27}{8\pi}w\xi_{\mathrm{s}}/l_1^2} \tag{5.33}$$

which with (4.12) completes the relationships.

6. Relationships at Arbitrary Frequencies

The Liouville → Fokker–Planck is an elegant way to show the effects of interactions, both static and dynamic, but it is important to realize that it is not the most general because many of our results can be extended to arbitrary frequencies whereas the Fokker–Planck form always assumes simple exponential decay.

Including frequency in the hydrodynamic response is possible but not very interesting physically since in all practical cases the incompressible fluid propagates much more quickly than any other time scales. However, the frequency dependence of the viscosity is important since it must go over to elasticity at high frequencies. This is, of course, well-known in the Rouse and Zimm equations and in the present work goes much the same way with

$$\eta(k,\omega) = \eta_0 k^2 + \frac{3k_{\mathrm{B}}T}{2\pi l}\sum_{q\neq 0}\frac{q^2}{i\omega + 3k_{\mathrm{B}}TJ(q)q^2/l_1}\,\frac{k^2 l_1/3}{(k^2 l_1/6)^2 + q^2} \tag{6.1}$$

Thus as ω increases, the screening concept is radically changed

$$\eta \rightarrow \eta_0 k^2 + \frac{k_{\mathrm{B}}Tk^2 l_1}{12\pi}\sum_{q\neq 0} J(q)/i\omega \tag{6.2}$$

As one would expect, the subtleties of this work do not arise at high enough frequencies.

Conclusions

It has been shown that the Brownian motion of a solution of interacting polymers can be described by a combination of the density, fluid velocity, and polymer coordinates. The principal result is to improve the equation for the hydrodynamic screening and hence the viscosity in overlapping conditions in which it is proportional to the molecular weight, the Rouse limit, though from the working through of the realistic model rather than the arbitrary friction of the original Rouse treatment. The entanglements of the polymers are fully contained in the unaveraged nonlinear forms but are not in the linearized averages, the hydrodynamic interactions appearing in these linearized forms simply as screening. To study the transition into the high-viscosity regime, where the dynamics will be reptation, requires a nonlinear solution, which is not attempted here.

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Appendix

In this Appendix we derive (4.11). Introducing the Fourier transforms

$$\mathbf{R}_\alpha(q,t) = \int_0^L \mathrm{d}s_\alpha\, e^{-iqs_\alpha}\mathbf{R}_\alpha(s_\alpha,t)$$

$$\mathbf{R}_\alpha(s_\alpha,t) = \int_{-\infty}^{\infty}\frac{\mathrm{d}q}{2\pi}\, e^{iqs_\alpha}\mathbf{R}_\alpha(q,t) \tag{A.1}$$

with $q = 2\pi p/L$ (p is an integer), we get from (3.11)

$$\frac{\partial F}{\partial \mathbf{R}_\alpha(q)} = \frac{3k_{\mathrm{B}}Tq^2}{l}\mathbf{R}_\alpha(q,t) + k_{\mathrm{B}}T\int_0^L \mathrm{d}s_\alpha\, e^{-iqs_\alpha}\nabla_{\mathbf{R}_\alpha(s_\alpha)}\sum_\beta \int_0^L \mathrm{d}s_\beta\, W[\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\beta(s_\beta)] \tag{A.2}$$

We now perform the various averages described by the prescription following (4.5). First, by averaging (A.2) over all other chains, we obtain

$$\begin{aligned}\frac{\partial F}{\partial \mathbf{R}_\alpha(q)} - \frac{3k_{\mathrm{B}}Tq^2}{l}\mathbf{R}_\alpha(q,t) &= k_{\mathrm{B}}T\int_0^L \mathrm{d}s_\alpha\, e^{-iqs_\alpha}\nabla_{\mathbf{R}_\alpha(s_\alpha)}\int_0^L \mathrm{d}s_\alpha{}'\,\Delta[\mathbf{R}_\alpha(s_\alpha) - \mathbf{R}_\alpha(s_\alpha{}')] = \\ &k_{\mathrm{B}}T\int_0^L \mathrm{d}s_\alpha\, e^{-iqs_\alpha}\nabla_{\mathbf{R}_\alpha(s_\alpha)}\int_0^L \mathrm{d}s_\alpha{}'\int\frac{\mathrm{d}^3k}{(2\pi)^3}\,\Delta(k)e^{i\mathbf{k}\cdot[\mathbf{R}_\alpha(s_\alpha)-\mathbf{R}_\alpha(s_\alpha{}')]} = \\ &k_{\mathrm{B}}T\int_0^L \mathrm{d}s_\alpha\int_0^L \mathrm{d}s_\alpha{}'\int\frac{\mathrm{d}^3k}{(2\pi)^3}\, e^{-iqs_\alpha}i\mathbf{k}\Delta(k)e^{i\mathbf{k}\cdot[\mathbf{R}_\alpha(s_\alpha)-\mathbf{R}_\alpha(s_\alpha{}')]} = \\ &k_{\mathrm{B}}T\int_0^L \mathrm{d}s_\alpha\int_0^L \mathrm{d}s_\alpha{}'\int\frac{\mathrm{d}^3k}{(2\pi)^3}\, e^{-iqs_\alpha}\Delta(k)\exp\left\{i\mathbf{k}\cdot\int_{-\infty}^{\infty}\frac{\mathrm{d}q'}{2\pi}\,\mathbf{R}(q')(e^{iq's_\alpha} - e^{iq's_\alpha{}'})\right\} \equiv \mathcal{A}\end{aligned} \tag{A.3}$$

where $\Delta(k)$ is given by (4.9). The equation (A.3) is nonlinear where the dependence of the qth mode on all other modes is given by the term on the right-hand side, $\mathcal{A}$. We now average over all modes except q. This is given explicitly by

$$\mathcal{A} = k_{\mathrm{B}}T\int_0^L \mathrm{d}s_\alpha\int_0^L \mathrm{d}s_\alpha{}'\int\frac{\mathrm{d}^3k}{(2\pi)^3}\, e^{-iqs_\alpha}i\mathbf{k}\Delta(k)\times \left\langle \exp\left\{i\mathbf{k}\cdot\int_{-\infty}^{\infty}\frac{\mathrm{d}q'}{2\pi}\,\mathbf{R}_\alpha(q')(e^{iq's_\alpha} - e^{iq's_\alpha{}'})\right\}\right\rangle_{\{q'\}\neq q} \tag{A.4}$$

where

$$\langle \varkappa\rangle_{\{q'\}\neq q} = \left\{\int\prod_{p'\neq p}\mathrm{d}\mathbf{R}_\alpha(p')\,\varkappa\,\exp\left(-\frac{3}{2L}\,\frac{q'^2\mathbf{R}_\alpha{}^2(q')}{l_1(q')}\right)\right\}\Bigg/ \left\{\int\prod_{p'\neq p}\mathrm{d}\mathbf{R}_\alpha(q')\exp\left(-\frac{3}{2L}\,\frac{q'^2\mathbf{R}_\alpha{}^2(q')}{l_1(q')}\right)\right\} \tag{A.5}$$

We have introduced l_1 in (A.5) because we seek an effective l_1 such that

$$\frac{\partial F}{\partial \mathbf{R}_\alpha(q)} = \frac{3k_{\mathrm{B}}Tq^2}{l_1(q)}\mathbf{R}_\alpha(q,t) \tag{A.6}$$

Substitution of $\mathcal{A}$ from (A.4) into (A.3) and the requirement that the result be (A.6) produces an explicit expression for $l_1(q)$. Expanding of (A.4) as a Taylor series in $\mathbf{R}_\alpha(q,t)$, we get

$$\mathcal{A} = k_{\mathrm{B}}T\int_0^L \mathrm{d}s_\alpha\int_0^L \mathrm{d}s_\alpha{}'\int\frac{\mathrm{d}^3k}{(2\pi)^3}\, e^{-iqs_\alpha}\Delta(k)\left[i\mathbf{k} - \frac{1}{L}(e^{iqs_\alpha} - e^{iqs_\alpha{}'})\mathbf{k}\mathbf{k}\cdot\mathbf{R}_\alpha(q,t) + \text{higher powers of } \mathbf{R}_\alpha(q,t)\right]\times \left\langle \exp\left\{\frac{i\mathbf{k}}{L}\cdot\sum_{\substack{p'=-\infty \\ p'\neq p}}^{\infty}\mathbf{R}_\alpha(p',t)(e^{2\pi ip's_\alpha/L} - e^{2\pi ip's_\alpha{}'/L})\right\}\right\rangle_{\{p'\}\neq p} \tag{A.7}$$

Performing the average given by (A.5) yields

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$$\left\langle \exp\left\langle \frac{i\mathbf{k}}{L} \sum_{\substack{p'=-\infty \\ p'\neq p}}^{\infty} \mathbf{R}_\alpha(p',t)(e^{2\pi i p' s_\alpha/L} - e^{2\pi i p' s_\alpha'/L}) \right\}\right\rangle_{\{p'\}\neq p} = \exp\left\{-\frac{k^2}{3}\int_{-\infty}^{\infty}\frac{\mathrm{d}q}{2\pi}\,\frac{l_1(q)}{q^2}[1 - \cos q|s - s'|]\right\} = \exp(-k^2 l_1|s - s'|/6) \quad \text{(A.8)}$$

We have assumed that l_1 is dependent only on the first mode in obtaining the second equality of (A.8). Substitution of (A.8) into (A.7) gives

$$\mathcal{A} = -\frac{2k_\mathrm{B}T}{3L}\int_0^L \mathrm{d}s_\alpha \int_0^L \mathrm{d}s_\alpha' \int \frac{\mathrm{d}^3k}{(2\pi)^3}\, k^2\Delta(k) \times \sin^2\left(\frac{q|s_\alpha - s_\alpha'|}{2}\right) e^{-k^2 l_1|s_\alpha - s_\alpha'|/6}\mathbf{R}_\alpha(q,t) \quad \text{(A.9)}$$

Combining (A.3), (A.6), and (A.9) yields

$$Lq^2\left(\frac{1}{l} - \frac{1}{l_1}\right) = \frac{2}{9}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \int \frac{\mathrm{d}^3k}{(2\pi)^3}\, k^2\Delta(k) \times \sin^2\left(\frac{q|s - s'|}{2}\right) e^{-k^2 l_1|s - s'|/6} \quad \text{(A.10)}$$

This is exactly the same equation as (4.8a) of ref 11, which was obtained by a different method using a variational procedure. Since we are here interested in the small-q limit only, we expand the sine to get

$$\frac{1}{l} - \frac{1}{l_1} = \frac{w}{18\pi^2 L}\int_0^\infty \mathrm{d}k\, \frac{k^6}{k^2 + \xi_\mathrm{s}^{-2}}\int_0^L \mathrm{d}s \int_0^s \mathrm{d}s'\, (s - s')^2 e^{-k^2 l_1 (s-s')/6} = \frac{24w}{\pi^2 l_1^3}\int_0^\infty \mathrm{d}k\, \frac{1}{k^2 + \xi_\mathrm{s}^{-2}} \quad \text{(A.11)}$$

which is the same as (4.11). Equation 4.9 is used in obtaining the first equality of (A.11).

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Microcalorimetric Study of Poly(ethylene oxide) in Water and in Water–Ethanol Mixed Solvent

Hubert Daoust* and Daniel St-Cyr

Department of Chemistry, Université de Montréal, Montreal, Quebec, Canada H3C 3V1.
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ABSTRACT: Intermediate heats of dilution, heats of mixing, and heat capacities have been measured in the dilute and intermediate concentration ranges for the poly(ethylene oxide) (PEO)–water and PEO–water–ethanol systems. Heats of dilution are exothermic for all systems and pass through a minimum at 50% by weight of ethanol. Heats of fusion of PEO in water and in 50% water–ethanol calculated from the combined heat of dilution and heat of mixing results are 9564 and 10 224 J basemol^{-1}, respectively. Apparent basemolar heat capacity ($C_{p,\phi}$) has been determined for PEO. In water, results show that $C_{p,\phi}$ decreases with increasing concentration and that $C_{p,\phi}$ at infinite dilution decreases with decreasing molecular weight. The value of $C_{p,\phi}$ increases with increasing temperature. Values of $C_{p,\phi}$ in water–ethanol go through a minimum at 30% by weight of ethanol. The results do not support very strongly the existence of an ordered structure for PEO in solution in water. However, they are in very good agreement with the conclusion of a recent light scattering study of the same system assuming that aggregates coexist with molecularly dispersed PEO.

Introduction

Poly(ethylene oxide) (PEO) is a well-known polymer, and its high solubility in water makes it a very interesting industrial material. It is known to be crystalline[1,2] and to have a 7_2-helical conformation in the solid state.[3] Most of the experimental results on PEO solutions lead to the conclusion that the polymer is in its disordered or coiled form in organic solvents.[1,2,4-7] However, the situation is not as clear when water is used as solvent. Some experimental results indicate that PEO in aqueous solutions retains some of its crystalline structure[1] or sees its helical structure changed to a new, less ordered but not completely disordered one.[2] Other experimental results indicate a behavior of PEO molecules in aqueous solution similar to that in organic media, at least for low molecular weight samples.[4,6] The chain expansion of PEO in water is believed to be due to the formation of H bonds between water molecules and oxygen atoms of the chain.[8-10] Experimental results seem to indicate that three water molecules are bound to each PEO oxygen.[1,2,4,10]

Other investigators[11] have assumed a non-free-draining coil model for PEO in aqueous media and they have shown that the chain adopts a more compact conformation as the temperature increases. This is probably due to an increase in the free rotation of chain links accompanied by a weakening of polymer–solvent interactions, leading to a chain contraction. Viscosimetric results[12] support these last observations. Finally, density measurements[13] have shown that the partial molar volume of PEO repeating units in water is the same as for the free monomer. These results indicate that the polymer chain is highly extended, thus giving water molecules free access to the backbone. More recently, a static light scattering study on PEO aqueous solutions leads to the conclusion that aggregates

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