Distribution analyses are performed at low concentrations. Besides, for PS–CH $\mu_1(0)$ was found to be little different from ν_1, like $\bar{\mu}^{215}$ from $\bar{\nu}^{215}$. This will be true for most polymer–solvent systems. Coefficients for the linear and second-order pressure effects may therefore be considered which do not include a pressure-dependent thermodynamic interaction or, alternatively, are given a value calculated for the weight average of $M^{1/2}$ for the distribution investigated.

A stronger effect of pressure on the excluded volume may be expected to occur for a polymer–solvent pair for which the total volume undergoes a larger change on mixing. In the event of contraction a rise in the pressure will cause the chain molecules to expand. Thus the discontinuous state of the solution with respect to the segments is diminished and a further reduction in the volume of the solution is achieved. Contraction, therefore, goes with a pressure effect which increases with M and w_0. Hence a more rapid increase of μ_1 with M and w will occur for PS in butanone than in CH. In butanone at 0.5 segment fraction of polymer, Flory and Höcker[38] observed a volume decrease 6 times larger than they found for PS in CH. However, since PS–butanone is athermal, a linkage of the pressure and temperature dependence as suggested by eq 51 and 61 cannot be made.

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Supplementary Material Available: Appendix 1, where eq 40 is derived, and Appendix 2, where $d\Theta/dp$ (eq 53) is discussed (8 pages). Ordering information is given on any current masthead page.

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Screened Hydrodynamic Interactions in a Semidilute Solution of Rodlike Macromolecules

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ABSTRACT: We have extended the theory of Doi and Edwards for a semidilute solution of rodlike molecules by including the effects of hydrodynamic interactions into the expression for the stress tensor. This is done by using the solution of the Kirkwood–Riseman equation, modified for the semidilute regime by the inclusion of a screened hydrodynamic interaction tensor, as derived by Freed and Edwards. When hydrodynamic interactions are neglected, our result for the shear dependence of the normalized viscosity reduces to the extended version of the Doi and Edwards theory due to Jain and Cohen. Inclusion of hydrodynamic interactions gives excellent agreement with experimental results.

Introduction

Kirkwood was the first to formulate a logically consistent theory of the contributions of hydrodynamic interactions to the dynamics of polymeric solutions. This theory, based on the Oseen tensor, was successfully applied to dilute solutions of rodlike molecules as early as 1950.[1] It produced significant improvements over earlier theories of rods which had ignored the hydrodynamic interactions.

There is substantial experimental and theoretical evidence that at sufficiently high concentrations screening totally obliterates the effects of hydrodynamic interactions. However, there is an intermediate range of number con-

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centrations, $c \gtrsim L^{-3}$ (with L the length of a rod), in which these interactions are expected to be of considerable importance. A straightforward extension of Kirkwood's method to these higher concentrations necessarily involves consideration of all rods at once, thus making the problem very difficult to handle. Fortunately, the remarkable theoretical advances that Freed and Edwards[2] have made during the past decade make it possible to write a "Kirkwood–Riseman (KR) equation" involving a *single* polymer molecule, thus retaining the essential simplicity of Kirkwood's dilute solution theory at much higher concentrations. This is managed by introducing an effective, concentration-dependent hydrodynamic interaction tensor in place of the Oseen tensor of the original KR theory. We make use of an averaged form of this interaction tensor in the following development.

Recently, Doi and Edwards[3] considered the problem of the shear dependence of the viscosity of a semidilute solution of rodlike polymers within the concentration range $1/L^3 \ll c \ll 1/dL^2$, with $d \ll L$ denoting the width of a rod. They determined the diffusive properties and the rod orientational distribution function on the basis of plausible geometric arguments. We shall incorporate their results into our solution of the KR equation. To determine rheological properties Doi and Edwards worked with a very approximate form of the stress tensor and consequently were led to an unrealistic prediction of the shear dependence of viscosity. Jain and Cohen,[4] who recently reconsidered this same problem by taking account of a term in the stress tensor that had been discarded by Doi and Edwards, obtained considerably better agreement with experiment. The purpose of the present paper is to resolve the remaining discrepancies with experiment by properly taking account of the modification of the stress tensor due to hydrodynamic interactions.

Theory

We consider Kirkwood's "shish kabob" model of a rod of $N + 1$ beads evenly spaced at positions $\vec{R}_i = a(i - N/2)\hat{e}_r$ with $i = 0, 1, ..., N$. The (preaveraged) KR equation has the form

$$\vec{F}_i + \zeta\sum_{j\neq i}\langle T_{ij}\rangle\vec{F}_j = -\zeta(\vec{v}_i^{\,0} - \vec{u}_i) \tag{1}$$

where $\langle T_{ij}\rangle$ is the modulus of an effective, concentration-dependent hydrodynamic interaction tensor,[2] averaged over all possible orientations of the rodlike polymers. The equations defining $\langle T_{ij}\rangle$ will be given below. $-\vec{F}_i$ is the force on the ith bead, ζ is a bead friction coefficient, $\vec{v}_i^{\,0} = g(\vec{R}_i\cdot\hat{e}_z)\hat{e}_x$ is the unperturbed solvent velocity at the position of the ith bead, and

$$\vec{u}_i = (\vec{v}_i^{\,0}\cdot\hat{e}_\theta)\hat{e}_\theta + (\vec{v}_i^{\,0}\cdot\hat{e}_\phi)\hat{e}_\phi - a\left(i - \frac{N}{2}\right)\left[D^{\theta\theta}\frac{\partial \ln P(\theta,\phi)}{\partial\theta}\hat{e}_\theta + D^{\phi\phi}\sin\theta\frac{\partial \ln P(\theta,\phi)}{\partial\phi}\hat{e}_\phi\right] \tag{2}$$

is the velocity of the ith bead.[5] Here $P(\theta,\phi)$ is the orientational distribution function of the rods. In Kirkwood's theory the components of the diffusion tensor, $D^{\theta\theta}$ and $D^{\phi\phi}$, are functionals of the hydrodynamic interaction tensor. For the sake of simplicity we shall use the rotational diffusion coefficient D_r obtained by Doi and Edwards,[3] setting $D^{\theta\theta} = D_\mathrm{r}$ and $D^{\phi\phi} = D^{\theta\theta}/\sin^2\theta = D_\mathrm{r}/\sin^2\theta$ in eq 2. In addition to the simplifications that it produces, this replacement also allows us to make direct contact with the stress tensor formulas used in ref 3 and 4. The issue of consistency involved in this replacement will be considered in a separate paper.

An equation for $\langle(\vec{F}_i\cdot\hat{e}_x)(\vec{R}_j\cdot\hat{e}_z)\rangle$ can be obtained from (1) and (2) as follows:

$$\langle(\vec{F}_i\cdot\hat{e}_x)(\vec{R}_j\cdot\hat{e}_z)\rangle + \zeta\sum_{k\neq i}\langle T_{ik}\rangle\langle(\vec{F}_k\cdot\hat{e}_x)(\vec{R}_j\cdot\hat{e}_z)\rangle = -\zeta a^2\left(i - \frac{N}{2}\right)\left(j - \frac{N}{2}\right)\left[g\langle(\hat{e}_r\cdot\hat{e}_z)^2(\hat{e}_x\cdot\hat{e}_r)^2\rangle + D_\mathrm{r}\left\langle\frac{\partial \ln P}{\partial\theta}(\hat{e}_\theta\cdot\hat{e}_x)(\hat{e}_r\cdot\hat{e}_z) + D_\mathrm{r}\frac{1}{\sin\theta}\,\frac{\partial \ln P}{\partial\phi}(\hat{e}_\phi\cdot\hat{e}_x)(\hat{e}_r\cdot\hat{e}_z)\right\rangle\right] \tag{3}$$

After a partial integration[6] this takes the form

$$\langle(\vec{F}_i\cdot\hat{e}_x)(\vec{R}_j\cdot\hat{e}_z)\rangle + \zeta\sum_{k\neq i}\langle T_{ik}\rangle\langle(\vec{F}_k\cdot\hat{e}_x)(\vec{R}_j\cdot\hat{e}_z)\rangle = -(\zeta a^2 D_\mathrm{r})\left(i - \frac{N}{2}\right)\left(j - \frac{N}{2}\right)\left[3\langle u_x u_z\rangle + \frac{g}{D_\mathrm{r}}\langle u_x^{\,2}u_z^{\,2}\rangle\right] \tag{4}$$

where $u_x \equiv (\hat{e}_r\cdot\hat{e}_x)$ and $u_z \equiv (\hat{e}_r\cdot\hat{e}_z)$. In terms of $\phi_{ij} = -(4/N^2)(1/\zeta a^2 D_\mathrm{r})\langle(\vec{F}_i\cdot\hat{e}_x)(\vec{R}_j\cdot\hat{e}_z)\rangle$ and $f_{ij} = (2/N)(i - N/2)(2/N)(j - N/2)Y(g/D_\mathrm{r})$, with $Y(g/D_\mathrm{r}) = [3\langle u_x u_z\rangle + (g/D_\mathrm{r})\langle u_x^{\,2}u_z^{\,2}\rangle]$, eq 4 becomes

$$\phi_{ij} + \zeta\sum_{k\neq i}\langle T_{ik}\rangle\phi_{kj} = f_{ij} \tag{5}$$

Then, by defining $\hat{T}_{ik} \equiv (N/2)6\pi\eta_\mathrm{s}a\langle T_{ik}\rangle$, with η_s the solvent viscosity, and introducing the continuous indices $x = (i - N/2)/(N/2)$ and $y = (j - N/2)/(N/2)$, we can write the KR equation as

$$\phi(x,y) + \lambda_0\int_{\substack{-1\\|x-z|>2/N}}^{1}\hat{T}(x,z)\phi(z,y)\,\mathrm{d}z = xyY(g/D_\mathrm{r}) \tag{6}$$

Here $\lambda_0 = \zeta/6\pi\eta_\mathrm{s}a \equiv b/a$, the ratio of bead radius to segment length, is the so-called hydrodynamic strength parameter.

The viscosity increment $\delta\eta \equiv \eta - \eta_\mathrm{s}$ is given[1] by

$$\delta\eta = -\frac{c}{g}\sum_j\langle(\vec{F}_j\cdot\hat{e}_x)(\vec{R}_j\cdot\hat{e}_z)\rangle = \frac{N^3c(\zeta a^2D_\mathrm{r})}{8g}\int_{-1}^{1}\phi(x,x)\,\mathrm{d}x \tag{7}$$

where $\phi(x,x)$ is obtained by solving the KR equation (6). By using Kirkwood's standard approximation procedure for solving equations of this type, we obtain the formula

$$\delta\eta = \frac{N^3c(\zeta a^2D_\mathrm{r})}{12}\,\frac{1}{g}Y(g/D_\mathrm{r})F(g/D_\mathrm{r},c) \tag{8}$$

where

$$F(g/D_\mathrm{r},c) = \frac{6}{\pi^2}\sum_{p=1}^{\infty}\frac{1}{p^2}\,\frac{1}{1 + \lambda_0\hat{T}_p} \tag{9}$$

and

$$\hat{T}_p = \frac{1}{2}\int_{\substack{-1\\\{|x-z|>2/N\}}}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}z\;e^{i\pi p(z-x)}\hat{T}(x,z) \tag{10}$$

These are still formal expressions since the objects $\hat{T}_p$ have not yet been fully specified. If the hydrodynamic interactions could be completely ignored, then all of these functions would equal zero and the shear dependence of $\eta - \eta_\mathrm{s}$ would be determined exclusively by the function

$$Y(g/D_\mathrm{r}) = 3\langle u_x u_z\rangle + \frac{g}{D_\mathrm{r}}\langle u_x^{\,2}u_z^{\,2}\rangle \tag{11}$$

Doi and Edwards[3] retained only the first (diffusive) term of (11). Jain and Cohen[4] included the quartic (streaming) term as well and found results that were in markedly better, but still imperfect, agreement with experiment. We shall see that the factor $F(g/D_\mathrm{r},c)$ in eq 8 is just what is needed to obtain excellent agreement with experiment.

In contrast to the situation for dilute solutions, no simple analytical expression currently is available for the effective hydrodynamic interaction $\hat{T}(x,y)$ appropriate to a concentrated solution. However, the theory of Freed and Edwards does provide the following set of coupled equations (see eq 8.5.71 and 8.5.76 and the comments that follow them in ref 2 or eq 24–27 of ref 7) for the quantities $\hat{T}_p$:

$$\hat{T}_p = \left(\frac{1}{3}\right)\left(\frac{N}{2}\right)(6\pi\eta_s a)\int \frac{\mathrm{d}^3k}{(2\pi)^3}\,\frac{[g_p(k) - \tilde{g}_p(k)]}{\eta_s k^2 - \Sigma_0(k)} \tag{12}$$

$$\Sigma_0(k) = -\frac{Nc}{4}\zeta\sum_{p=-\infty}^{\infty}\frac{g_p(k)}{1 + \lambda_0\hat{T}_p} \tag{13}$$

Here

$$g_p(k) = \int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y\; e^{i\pi p(x-y)}S_k(x,y) \tag{14a}$$

$$\tilde{g}_p(k) = \underset{\{|x-y|>2/N\}}{\int_{-1}^{1}\mathrm{d}x\int_{-1}^{1}\mathrm{d}y}\; e^{i\pi p(x-y)}S_k(x,y) \tag{14b}$$

and

$$S_k(x,y) \equiv \langle e^{i\vec{k}\cdot\hat{e}_r(Na/2)(x-y)}\rangle = \sum_{\substack{l=0\\(l\text{ even})}}^{\infty}(-)^{l/2}\pi^{1/2}b_{l0}2(2l+1)^{1/2}j_l\left(\frac{kaN}{2}|x-y|\right) \tag{15}$$

where j_l is a spherical Bessel function. The averaging indicated in eq 15 has been performed by using the orientational distribution function

$$P(\theta,\phi) = \sum_{\substack{l=0\\(l\text{ even})}}^{\infty}\sum_{m=0}^{l} b_{lm}|lm) \tag{16}$$

with

$$|lm) = Y_l^m(\theta,\phi) \qquad \text{for } m = 0$$

$$|l\mathrm{m}) = \frac{1}{2^{1/2}}[Y_l^m(\theta,\phi) + (-)^m Y_l^{-m}(\theta,\phi)] \qquad \text{for } m > 0$$

and coefficients b_{lm} determined by the equations[3]

$$l(l+1)b_{lm} + (g/\bar{D}_r)\sum_{\substack{l'=0\\(l'\text{ even})}}^{\infty}\sum_{m'=0}^{l'}(lm|\Gamma|l'm')b_{l'm'} = 0 \tag{17}$$

These involve matrix elements $(lm|\Gamma|l'm')$ that have been evaluated in ref 3 and a parameter $g/\bar{D}_r$, which is connected to g/D_r of eq 4 by the relationship

$$(g/D_r) = (g/\bar{D}_r)[Q(g/\bar{D}_r)]^{-2} \tag{18}$$

wherein Q is a function given in ref 3.

Approximate solutions of the equations (17) are obtained by selecting a numerical value for $g/\bar{D}_r$ and truncating the l' sum at an appropriately chosen integer $l'_{\max}$ (as was done in ref 3 and 4). Then, by using eq 18, one obtains the coefficients b_{lm} as functions of g/D_r. This permits theoretical predictions to be compared with experimental results, which are plotted as functions of g/D_r.

Numerical Results

The set of equations (12) and (13) can be solved iteratively. One begins by substituting for $\hat{T}_p$ in eq 13 the expression

$$\hat{T}_p(0) = \left(\frac{1}{3}\right)\left(\frac{N}{2}\right)(6\pi\eta_s a)\int \frac{\mathrm{d}^3k}{(2\pi)^3}\,\frac{[g_p(k) - \tilde{g}_p(k)]}{\eta_s k^2}$$

appropriate to the limit of an infinitely dilute solution. This produces a first approximation to $\Sigma_0(k)$, which then can be inserted into (13) to yield second iterates of the $\hat{T}_p$. Five or six such iterations usually were required in order to determine the function $F(g/D_r,c)$ to two significant figures. This tolerance was selected as a compromise between numerical accuracy and the expense of the calculations. To achieve this accuracy the computations usually required the evaluation of the set of $\hat{T}_p$'s with $p = 1, ..., 20$. A value of $\eta_s = 1$ cP was used throughout these calculations. This same iterative procedure recently was used by Perico and Cuniberti[7] to determine the $\hat{T}_p$'s for a flexible Gaussian chain at zero shear.

Table I
Values of $F(g/D_r,c)$ for Various Values of g/D_r and cL^3

	cL^3							
g/D_r	0	5	10	50	100	150	200	230
0	0.70	0.71	0.72	0.76	0.80	0.82	0.84	0.84
1	0.70	0.71	0.72	0.76	0.80	0.82	0.83	0.84
3	0.69	0.69	0.70	0.74	0.77	0.80	0.81	0.82
6	0.67	0.67	0.68	0.71	0.74	0.76	0.78	0.79
10.35	0.64	0.65	0.65	0.68	0.71	0.73	0.74	0.75
21.31	0.61	0.61	0.62	0.64	0.66	0.67	0.69	0.70
56.18	0.57	0.57	0.57	0.58	0.59	0.60	0.61	0.62
118.63	0.53	0.53	0.53	0.53	0.54	0.54	0.55	0.55

Table II
Values of the Ratio $F(g/D_r,c)/F(0,c)$ for Various Values of g/D_r and cL^3

	cL^3							
g/D_r	0	5	10	50	100	150	200	230
1	1	1	1	1	1	1	1	1
3	0.98	0.98	0.98	0.97	0.97	0.97	0.97	0.97
6	0.95	0.95	0.94	0.93	0.93	0.93	0.93	0.93
10.35	0.92	0.91	0.91	0.89	0.89	0.89	0.89	0.89
21.31	0.87	0.86	0.86	0.83	0.82	0.82	0.82	0.82
56.18	0.81	0.80	0.79	0.76	0.74	0.73	0.73	0.73
118.63	0.76	0.75	0.74	0.69	0.67	0.66	0.66	0.65

Table I contains values of $F(g/D_r,c)$ for various values of g/D_r and cL^3. The entries in Table II are of $F(g/D_r,c)/F(0,c)$. This ratio is found to be relatively insensitive to concentration throughout the range $L^{-3} \ll c \ll (dL^2)^{-1}$. [For the parameter values $L = 1000$ Å, $a = 20$ Å, $d = b = \lambda_0 a = (0.2)(20\text{ Å}) = 4$ Å, this range is $1 \ll cL^3 \ll 250$.] Thus, to a good approximation $\Phi(g/D_r) \equiv F(g/D_r,c)/F(0,c)$ is a function of g/D_r alone. Consequently, the ratio of viscosity increments at finite and zero shear is (cf. eq 8) given by

$$\delta\eta(g)/\delta\eta(0) = [\delta\eta(g)/\delta\eta(0)]_{\mathrm{JC}}\Phi(g/D_r) \tag{19}$$

where $[\delta\eta(g)/\delta\eta(0)]_{\mathrm{JC}}$ refers to the value of this ratio calculated by Jain and Cohen in ref 4. Our predictions of the shear viscosity, including the factor $\Phi(g/D_r)$, are presented in Figure 1. The curve labeled FD has been drawn with the entries from Table II specific to $cL^3 = 50$. However, as we previously have remarked, its position is only weakly dependent on concentration. This behavior is entirely in accord with the experimental observation that data for different concentrations fall on a single master curve over a wide range of g/D_r values.[4,8] The predictions of eq 19 are in quite good agreement with the experimental data presented in ref 4, some of which are included here as the circles and squares appearing in Figure 1. Although data from different sources are not in complete agreement, these differences are small and could be due to a number of effects such as polydispersity, bending motions, and translational–rotational coupling, which are disregarded by all the theories considered here. The curves labeled DE

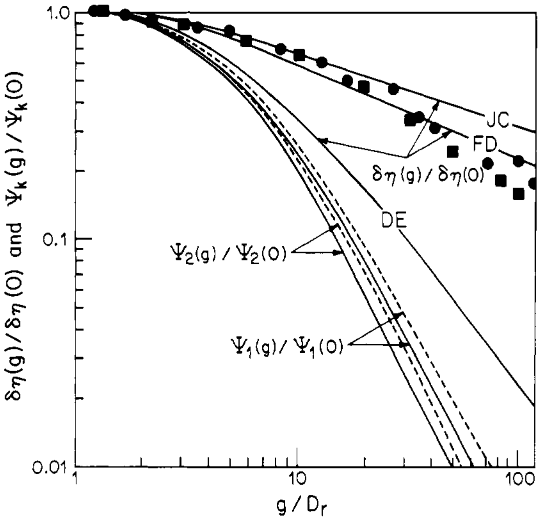

Figure 1. The three uppermost curves are ratios of the viscosity increments $[\delta\eta(g)/\delta\eta(0)] = (\eta(g) - \eta_s)/(\eta(0) - \eta_s)]$ at finite shear to those at zero shear plotted vs. the dimensionless rate of shear g/D_r. The labels DE, JC, and FD, respectively, refer to the predictions of the Doi–Edwards theory, the theory of Jain and Cohen, and of our eq 19 with $cL^3 = 50$. The circles and squares indicate experimental results (for PBLG in *m*-cresol) taken from Figures 5 and 7, respectively, of ref 4. Finally, the pairs of curves labeled $\psi_k(g)/\psi_k(0)$ show how the normal stress coefficients vary with the shear rate. The dashed curves were computed according to the theory of Doi and Edwards and the solid curves are the predictions of the present theory for $cL^3 = 50$.

and JC were calculated by using the theories of Doi and Edwards and of Jain and Cohen, respectively.

Finally, we have included in Figure 1 theoretical predictions of the two coefficients $\psi_1(g)$ and $\psi_2(g)$, which are related to the normal stresses by the formulas

$$N_1 = \sigma_{zz} - \sigma_{xx} \equiv \psi_1(g)g^2$$

$$N_2 = \sigma_{yy} - \sigma_{zz} \equiv \psi_2(g)g^2 \qquad (20)$$

According to our theory

$$\psi_k(g) = \frac{1}{12}N^3c(\zeta a^2 D_r)\frac{1}{g^2}Y_k(g/D_r)F(g/D_r,c) \qquad (21)$$

with F defined by eq 9 and where $Y_1(g/D_r) = 3\langle u_z^2 - u_x^2\rangle$ and $Y_2(g/D_r) = 3\langle u_y^2 - u_z^2\rangle$. Here there are no contributions from the quartic (streaming) terms and so the ratio of a normal stress coefficient to its value at zero shear can be written as

$$\psi_k(g)/\psi_k(0) = [\psi_k(g)/\psi_k(0)]_{\mathrm{DE}}\Phi(g/D_r) \qquad (22)$$

with $[\psi_k(g)/\psi_k(0)]_{\mathrm{DE}}$ denoting the value of this ratio that is predicted by the theory of Doi and Edwards. The effects of hydrodynamic screening on these normal stresses can be extracted from the entries in Table II or seen by comparing the pairs of curves in Figure 1.

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Sedimentation of Asymmetric Elastic Dumbbells and the Rigid-Body Approximation in the Hydrodynamics of Chains

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ABSTRACT: The "rigid-body approximation", which has been used in much previous work on the hydrodynamics of flexible-chain molecules, is studied by the complete working out of a test case. The model used is that of the familiar elastic dumbbell, but here with the two beads having different Stokes radii. The diffusion equation of the internal coordinates of this model is solved numerically, and the coefficients of sedimentation and diffusion of the center of mass are calculated. It is found that the motions of the internal and external coordinates are coupled and that a circulation, similar to a vortex ring, occurs in the internal coordinates when translational forces are applied to the whole molecule. Thus the motion is not perfectly described as that of an ensemble of rigid bodies, although the deviations from this simplified description are small.

Introduction

The steady-state hydrodynamic behavior of long-chain molecules is an area in which outstanding unsolved problems remain in spite of some spectacular successes. A common model is the bead–spring chain with hydrodynamic interaction expressed by the Burgers–Oseen tensor; with this model hydrodynamic problems such as sedimentation or viscosity can be formulated rigorously as diffusion problems in the multidimensional space of the chain. The difficulty comes in solving the diffusion equation, since in this equation every coordinate is coupled to every other by hydrodynamic interaction if not by direct spring connections. The problem can be solved in closed form only after preaveraging the elements of the Burgers–Oseen tensor, an approximation originally introduced by Kirkwood and Riseman;[1] then a transformation to

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