with the theoretical picture of the rare-earth crystal field that has been built up in recent years.[17,18] Certainly they are consistent with the idea that overlap and covalency give the dominant contributions to both the $n=4$ and $n=6$ parameters.

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[18] M. M. Ellis and D. J. Newman, J. Chem. Phys. **49,** 4037 (1968).

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Potential Flows of Dilute Polymer Solutions by Kramers' Method

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Kramers' method for describing the hydrodynamic behavior of a dilute solution of polymer molecules has been extended to include the "bead–spring" models. The connection between previous results of Kramers (for the bead–rod model), and of Rouse and Zimm (for the bead–spring model) is established. Finally, an expression is obtained for the elongational viscosity; it is found that the elongational viscosity increases with elongational rate, as was found earlier by Lodge (for a network theory) and by Roscoe (for a theory of suspensions).

I. MOLECULAR MODELS AND COORDINATE SYSTEMS

For this discussion a polymer molecule is idealized as a set of N beads interconnected by $N-1$ Hookean springs. Let L be the distance between the centers of two beads when there are no forces acting, and H be the Hooke-law constant of the springs. The special case of $H=\infty$ and $L\neq 0$ corresponds to infinitely stiff springs (i.e., rigid rods), as considered by Kramers[1] in his study of zero-shear-rate viscosity and flow birefringence; the same model was considered by Rivlin[2] in his comparison between a molecular and a continuum model. The special case of $H\neq\infty$ and $L=0$ corresponds to the model used by Rouse[3] and Zimm[4] in their studies of the complex viscosity. Initially we consider the more general case of $H\neq\infty$ and $L\neq 0$ so as to be able to obtain both limiting cases as well as intermediate ones.

Let the coordinates of the center of the ith bead, referred to a laboratory-fixed coordinate system, be x_i, y_i, z_i (the coordinates used by Zimm); let X_i, Y_i, Z_i be the coordinates of the $(i+1)$th bead with respect to the ith bead (the coordinates used by Rouse). Further, let the coordinates of the center of gravity of the bead–spring system be X_0, Y_0, Z_0. We then have

$$X_0=(1/N)\sum_{i=1}^{N}x_i,$$

$$X_p=x_{p+1}-x_p,\qquad p=1,2,\cdots,N-1 \tag{1}$$

or

$$x_i=X_0+(1/N)\sum_{p=1}^{N-1}G_{ip}X_p\qquad i=1,2,\cdots,N, \tag{2}$$

in which

$$G_{ip}=p,\qquad \text{if } p<i,$$

$$G_{ip}=-(N-p),\qquad \text{if } p\geq i. \tag{3}$$

Note that $\sum_i G_{ip}=0$ and that $N^{-1}\sum_i G_{ip}G_{iq}=g_{pq}$, where

$$g_{pq}=p(N-q),\qquad \text{if } p\leq q,$$

$$g_{pq}=q(N-p),\qquad \text{if } q\leq p. \tag{4}$$

With these relations it follows from Eq. (2) that

$$\sum_{i=1}^{N}x_i^2=NX_0^2+(1/N)\sum_{p=1}^{N-1}\sum_{q=1}^{N-1}g_{pq}X_pX_q. \tag{5}$$

In addition, the trace of the matrix of the g_{pq} can be shown to be[1]

$$\sum_p g_{pp}=\tfrac{1}{6}(N+1)(N)(N-1). \tag{6}$$

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[1] H. A. Kramers, Physica **11,** 1 (1944).
[2] R. S. Rivlin, Trans. Faraday Soc. **45,** 739 (1949).
[3] P. E. Rouse, Jr., J. Chem. Phys. **21,** 1272 (1953).
[4] B. H. Zimm, J. Chem. Phys. **24,** 269 (1956).

The eigenvalues[5] of the matrix of the g_{pq} are $\lambda_p = N/(4\sin^2 p\pi/2N)$. Here and elsewhere we adopt the convention that summations on the indices i, j, go from 1 to N, whereas those on p, q, go from 1 to $N-1$.

II. KRAMERS' METHOD AS EXTENDED TO THE BEAD-SPRING MODEL

We now idealize a dilute polymer solution as a suspension of bead–spring systems in a Newtonian solvent of viscosity η_s. The bead–spring systems are so widely separated that they do not interfere with each other's motions; that is, no "entanglements" are considered. The forces acting on the beads are: (1) The random forces associated with Brownian motion, (2) the systematic hydrodynamic drag, and (3) the forces exerted by neighboring beads through the connecting springs.

The solvent is taken to be in a state of potential flow, and the flow field is homogeneous, so that the rate of deformation tensor $\dot{\gamma}_{mn} = \partial v_n/\partial x_m + \partial v_m/\partial x_n$ is the same at all positions. Furthermore, we consider only flow systems for which it is possible to choose the coordinate system so that the solvent velocity at the origin is zero.

To find out how the solute molecules change the viscosity of the solution, we consider the effect of a single bead–spring system whose center of gravity is at the origin. It is assumed that the center of gravity stays at the origin (the "no-drift assumption"). The effect of all the solvent molecules is obtained by adding up the contributions of all the individual molecules.

The x component of the equation of motion for the ith bead in the bead–spring system is

$$m\ddot{x}_i = -\zeta(\dot{x}_i - v_{xi}) + B_{xi} + kT(\partial \ln\psi_L/\partial x_i). \quad (7)$$

Here v_{xi} is the x component of the fluid velocity at the ith bead, and B_{xi} is the x component of the Brownian motion force. Also ψ_L is defined by

$$\ln\psi_L = -(H/2kT) \sum_p (R_p - L)^2, \quad (8)$$

where

$$R_p^2 = (x_{p+1} - x_p)^2 + (y_{p+1} - y_p)^2 + (z_{p+1} - z_p)^2. \quad (9)$$

The quantity ζ is the friction constant, equal to $6\pi\eta_s r_b$, where η_s is the solvent viscosity and r_b is the radius of the spherical bead. Since the flow field is derived from a velocity potential Φ, the fluid velocity is given by $\mathbf{v} = -\nabla\Phi$. If we now define, following Kramers,

$$U = \zeta \sum_i \Phi(\mathbf{r}_i), \quad (10)$$

then the equation of motion for the bead may be re written as

$$m\ddot{x}_i = -\zeta\dot{x}_i + B_{xi} - (\partial/\partial x_i)(U - kT \ln\psi_L), \quad (11)$$

This is just the same as the equation of motion for a bead in a fluid at rest, but acted on by an external force derivable from a potential, $U - kT\ln\psi_L$. This is the essential point in Kramers' theory. *One replaces a non-equilibrium problem by an equivalent fictitious problem involving a system at equilibrium.* The use of this analogy allows the molecular distribution function to be written down immediately from equilibrium statistical mechanics as

$$W = \text{const}\,\delta(X_0)\delta(Y_0)\delta(Z_0) \exp\Big[-(m/2kT) \sum_i (\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2) + (U - kT\ln\psi_L)/kT\Big]. \quad (12)$$

The inclusion of the delta functions ensures that the molecule will not "drift" from the origin. Equation (12) differs from the expression presented by Kramers in the inclusion of the term containing ψ_L, which accounts for the spring forces. Averages with respect to this distribution function will be indicated by the notation $\langle\ \rangle_{\text{Av}}$.

For the bead–spring model, the contributions of one polymer molecule to the components of the stress tensor τ_{ij} are, according to Kramers,[1]

$$\delta\tau_{xx} = \sum_i \langle(\partial U/\partial x_i)x_i\rangle_{\text{Av}},$$
$$\delta\tau_{xy} = \sum_i \langle(\partial U/\partial x_i)y_i\rangle_{\text{Av}}, \text{ etc.} \quad (13)$$

Hence the stress tensor for the solution is $\tau_{ij} = \tau_{ij,s} + n_0\delta\tau_{ij}$, where $\tau_{ij,s}$ is the solvent contribution and n_0 is the number density of the polymer molecules.

III. COMPARISON OF THE RESULTS OF KRAMERS AND ZIMM FOR ZERO-SHEAR-RATE VISCOSITY

We now consider the homogeneous flow field used by Kramers, namely that for which the velocity potential is $\Phi = -\frac{1}{2}\kappa xy$; hence $\partial v_x/\partial y + \partial v_y/\partial x = \kappa$ everwhere in the flow field and for very slow flow $\tau_{yx} = -\eta_0\kappa$. Equations (10), (12), and (13) then lead to

$$\delta\tau_{xy} = -\tfrac{1}{2}\zeta\kappa \sum_i \langle y_i^2\rangle_{\text{Av}}$$

$$= -\tfrac{1}{2}\zeta\kappa \frac{\displaystyle\int\cdots\int \Big(\sum_i y_i^2\Big) \exp\left(\frac{\zeta\kappa}{2kT}\sum_i x_i y_i\right) \exp\left[-\frac{H}{2kT}\sum_p (R_p - L)^2\right] \delta(X_0)\delta(Y_0)\delta(Z_0)\,dx_1\cdots dz_N}{\displaystyle\int\cdots\int \exp\left(\frac{\zeta\kappa}{2kT}\sum_i x_i y_i\right) \exp\left[-\frac{H}{2kT}\sum_p (R_p - L)^2\right] \delta(X_0)\delta(Y_0)\delta(Z_0)\,dx_1\cdots dz_N}. \quad (14)$$

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[5] R. B. Bird, M. W. Johnson, and J. F. Stevenson, "Molecular Theories of Elongational Viscosity," Proc. Intern. Congr. Rheology 5th Kyōto, Japan, 1968.

Note that if the exponent containing κ is expanded in powers of κ, the first term is all we need to obtain the zero-shear-rate viscosity of the fluid. This is the approximation considered by Kramers, Rouse, Zimm, etc. We begin by considering the same level of approximation. Equation (14) may be rewritten in terms of the relative coordinates of Eq. (1) and the g_{pq} of Eq. (4); in so doing we use the fact that the Jacobian of transformation is unity,

$$\delta\tau_{xy}=-\tfrac{1}{2}\zeta\kappa\frac{\int\cdots\int[N^{-1}\sum_p\sum_q g_{pq}Y_pY_q]\exp\left(-\frac{H}{2kT}\sum_p(R_p-L)^2\right)dX_1\cdots dZ_{N-1}}{\int\cdots\int\exp\left[-\frac{H}{2kT}\sum_p(R_p-L)^2\right]dX_1\cdots dZ_{N-1}}. \qquad (15)$$

The center-of-gravity coordinates X_0, Y_0, Z_0 have now disappeared in the integration. Changing to polar coordinates ($X_p=R_p\sin\theta_p\cos\phi_p$, $Y_p=R_p\sin\theta_p\sin\phi_p$, $Z_p=R_p\cos\theta_p$), and performing the angular integration, gives a factor of $\frac{1}{3}$,

$$\delta\tau_{xy}=-\tfrac{1}{6}\zeta\kappa\frac{N^{-1}\sum_q g_{qq}\int\cdots\int R_q^2\exp\left[-\frac{H}{2kT}\sum_p(R_p-L)^2\right]R_1^2dR_1\cdots R_{N-1}^2dR_{N-1}}{\int\cdots\int\exp\left[-\frac{H}{2kT}\sum_p(R_p-L)^2\right]R_1^2dR_1\cdots R_{N-1}^2dR_{N-1}}, \qquad (16)$$

In the sum on q, all the integrals involving R_q^2 are identical so that the summation and integrations may be performed separately to give

$$\delta\tau_{xy}=-\tfrac{1}{6}\zeta\kappa[(N+1)(N)(N-1)/6N](L^{(4)}/L^{(2)}), \qquad (17)$$

where

$$L^{(s)}=\int_0^\infty(R_p)^s\exp\left[-\frac{H}{2kT}(R_p-L)^2\right]dR_p. \qquad (18)$$

Hence finally, the increase in the zero-shear-rate viscosity, η_0, due to the presence of one polymer molecule will be

$$\delta\eta_0=[\zeta(N+1)(N-1)/36](L^{(4)}/L^{(2)}). \qquad (19)$$

The two limiting cases studied earlier are (for large N)

(i) $H=\infty$ (Kramers' bead–rod model)

$$\delta\eta_0=\zeta N^2L^2/36 \quad\text{or}\quad \eta_0=\eta_s+n_0(\zeta N^2L^2/36); \qquad (20)$$

(ii) $L=0$ (Rouse and Zimm's bead–spring model with Hookean springs)

$$\delta\eta_0=(\zeta N^2/36)(3kT/H) \quad\text{or}\quad \eta_0=\eta_s+n_0(\zeta N^2b^2/36). \qquad (21)$$

Here, the Hooke spring constant H is related to Zimm's b by $H=3kT/b^2$ (see, e.g., Treloar[6]), where b^2 is the mean-square end-to-end distance of Rouse's "submolecule." It is thus clear that the two limiting models lead to formally similar results, as noted (but not explained as above) by Zimm.[4] The more general result in Eq. (19), with $L\neq0$, could be used to take into account empirically the nonzero value of the mean end-to-end distance of the "submolecule" resulting from the fact that in a real polymer molecule the bonds are not freely rotating.

If, now, we return to Eq. (14) and do not omit the exponential factors containing κ, then for $L=0$ this leads to

$$\delta\tau_{xy}=(\tfrac{1}{2}\zeta\kappa)\left(\frac{HkT}{N}\right)\sum_{p=1}^{N-1}\frac{\lambda_p}{(\zeta\kappa\lambda_p/2N)^2-H^2}, \qquad (22)$$

$$\delta\tau_{xx}=\delta\tau_{yy}=(\tfrac{1}{2}\zeta\kappa)^2\left(\frac{kT}{N^2}\right)\sum_{p=1}^{N-1}\frac{\lambda_p^2}{(\zeta\kappa\lambda_p/2N)^2-H^2}, \qquad (23)$$

$$\delta\tau_{zz}=0. \qquad (24)$$

In the limit as $\kappa\rightarrow0$, Eq. (22), simplifies to Eq. (21) since $\sum\lambda_p=\operatorname{tr}(g_{pq})$.

IV. ELONGATIONAL FLOW OF A SUSPENSION OF BEAD–SPRING SYSTEMS

Next we consider elongational flow[7] with the velocity potential $\Phi=\frac{1}{4}\bar{\kappa}(x^2+y^2-2z^2)$. The velocity distribution is then $v_x=-\frac{1}{2}\bar{\kappa}x$, $v_y=-\frac{1}{2}\bar{\kappa}y$, $v_z=\bar{\kappa}z$. This flow has been studied from a continuum mechanics point of view by Coleman and Noll,[8] who found that, when inertial effects are included, surface forces have to be supplied to maintain the flow.

When Kramers' method[1] is applied to this problem for $L=0$, we get

$$\delta\tau_{zz}=\frac{\zeta\bar{\kappa}}{N}\sum_p\frac{\lambda_pkT}{(\zeta\bar{\kappa}\lambda_p/N)-H}, \qquad (25)$$

$$\delta\tau_{xx}=\delta\tau_{yy}=\frac{\zeta\bar{\kappa}}{N}\sum_p\frac{\lambda_pkT}{(\bar{\kappa}\zeta\lambda_p/N)+2H}. \qquad (26)$$

The elongational viscosity[7] then becomes

$$\begin{aligned}\bar{\eta}&=3\eta_s[1+(n_0/3\eta_s\bar{\kappa})(\delta\tau_{xx}-\delta\tau_{zz})]\\&=3\eta_s\left[1+\frac{n_0kT}{\eta_s}\sum_p\frac{\tau_p}{(1-2\tau_p\bar{\kappa})(1+\tau_p\bar{\kappa})}\right],\end{aligned} \qquad (27)$$

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[6] L. R. G. Treloar, *The Physics of Rubber Elasticity* (Oxford University Press, Cambridge, 1958), Chap. 3.

[7] A. S. Lodge, *Elastic Liquids* (Academic Press Inc., New York, 1964), pp. 114–120.

[8] B. D. Coleman and W. Noll, Phys. Fluids **5**, 840 (1962).

where the $\tau_p = \zeta\lambda_p/2NH$ are the Rouse relaxation times[3] (the λ_p being the eigenvalues of the Kramers' $\mathbf{g}$ matrix). Exactly the same result[5] may be obtained from the Rouse–Zimm theory, even though the initial formulation of the problem is quite different. In the limit of small elongational rates, the above expression leads to the following limiting expression:

$$\bar{\eta}_0 = 3\eta_s\{1 + (n_0/\eta_s)[(\zeta N^2/36)(3kT/H)]\}. \quad (28)$$

Comparison of this result with Eq. (21) shows that $\bar{\eta}_0 = 3\eta_0$ as it should.

It should be noted that as $\bar{\kappa}$ increases, $\bar{\eta}$ eventually becomes infinite. Similar predictions have resulted from a network theory of polymers,[7] from a theory of suspensions,[9] and from an empirical continuum model.[10] In the case of the bead–spring model the reason for the infinity which arises in Eq. (27) is that the Hookean springs are capable of infinite extension; real molecules can be stretched only to a finite length, and hence the infinite result in Eq. (27) is doubtless unreasonable.[5] The elongational viscosity for the bead–rod model with $N = 2$ has been computed,[5] and it was found that $\bar{\eta}$ increases slowly to an asymptotic value.

V. CONCLUSIONS

The Kramers method (originally formulated for bead–rod systems) has been extended to provide a description of the potential flows of suspensions of bead–spring systems. It is shown that the molecular model employed here can be used to get the bead–rod and bead–spring results for polymer-solution viscosities as limiting cases. Elongational viscosity is calculated for the bead–spring (or Rouse) model, but it is believed that the results are unrealistic because of a fundamental inadequacy in the model. The analytical expression for elongational viscosity is identical to that obtained by solving the "diffusion equation" for the distribution function in configuration space (the Rouse–Zimm approach).

VI. NOTATION

$\mathbf{B}_i$	Brownian motion force [Eq. (7)]
G_{ip}	Coefficients in Eq. (2)
g_{pq}	Coefficients in Eq. (5)
H	Hooke spring constant
k	Boltzmann's constant
L	Length of spring in absence of force
m	Mass of bead
N	Number of beads
n_0	Number density of macromolecules
T	Absolute temperature
U	Quantity defined in Eq. (10)
v_x	x component of velocity
x, y, z	Laboratory coordinates
X_p, Y_p, Z_p	Internal coordinates
X_0, Y_0, Z_0	Coordinates of center of gravity
η	Viscosity
η_0	Zero-shear-rate viscosity
η_s	Solvent viscosity
$\bar{\eta}$	Elongational viscosity
$\bar{\eta}_0$	Elongational viscosity at $\bar{\kappa} = 0$
κ	Shear rate
$\bar{\kappa}$	Elongation rate
λ_p	Eigenvalues of $\mathbf{g}$ matrix
τ_{ij}	Stress-tensor components
Φ	Velocity potential
ψ_L	Quantity defined in Eq. (8)

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[9] R. Roscoe, J. Fluid Mech. **28**, 273 (1967).

[10] R. B. Bird and T. W. Spriggs, Phys. Fluids **8**, 1390 (1965).