Φ for monodisperse polystyrene in cyclohexane at 34.5 °C is

$$\Phi = (2.5_5 \pm 0.1) \times 10^{23}\ \mathrm{mol}^{-1}$$

where the value 0.1 represents a rough estimate of the total uncertainty associated with our measurements and data analysis. This final value is smaller than the three theoretical values quoted at the beginning of this paper. The disagreement can no longer be attributed to the polydispersity effect. It is our great pleasure to quote Flory's statement[13] that, "the true value (of Φ) probably is about 2.5×10^{21} in the previously given units" (which corresponds to $2.5 \times 10^{23}\ \mathrm{mol}^{-1}$).

The absolute value of our Φ depends on the literature values chosen for Rayleigh's ratio for pure benzene and the specific refractive index increment of aqueous KCl in calibrating our photogoniometer and differential refractometer, respectively. We simply accepted them as correct, since in no case of our previous studies on a variety of polymer + solvent systems had we met any significant and systematic disagreement between the M_w values determined by light scattering with these literature data and those by sedimentation equilibrium.

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Chain Molecule Hydrodynamics by the Monte-Carlo Method and the Validity of the Kirkwood–Riseman Approximation

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ABSTRACT: A preaveraged hydrodynamic interaction between chain segments was introduced by Kirkwood and Riseman in their well-known 1948 paper on sedimentation and viscosity, but its degree of correctness for chain molecules has never been well established. In this paper we avoid the approximation by creating a number of randomly generated chain configurations on a computer, solving the Burgers–Oseen interaction problem for each configuration, and finally averaging the results, thus getting rid of the preaveraging approximation. A chain model of beads with Gaussianly distributed spacing was used. Two thousand Gaussianly distributed interbead vectors were created by a pseudo-random-number generator, and these were strung together end-to-end in various ways into chains of up to 50 vectors per chain. Each 50-vector chain required the solution of 157 simultaneous equations. The results for the 50-vector chain show that the Kirkwood–Riseman (KR) sedimentation coefficient is about 13% too high, the KR intrinsic viscosity is about 12% too high, and the molecular weight calculated by the Flory–Scheraga–Mandelkern formula from the combination of sedimentation and viscosity is about 25% too low. Comparison of chains with 5, 10, 25, and 50 vectors suggests that a chain with an infinite number of beads would not give results much different from the 50-vector case.

We consider the effects of two approximations introduced into the theory of the hydrodynamic properties of chain molecules by Kirkwood and Riseman[1] and by Kirkwood.[2] The first of these approximations consisted of preaveraging the hydrodynamic interactions between the segments of the chain and the second of approximating the inverse of the diffusion tensor by the tensor composed of the inverses of the elements of the original tensor. These approximations have been discussed, and improved or removed in some special cases, by subsequent authors.[3-7] Here we shall attempt to assess by numerical "Monte-Carlo" methods the effects of these approximations on the sedimentation coefficient and on the viscosity number (intrinsic viscosity). Another objective is to improve the determination of the molecular weight by the Flory–Scheraga–Mandelkern method from viscosity and sedimentation.

The model is a random-flights chain constructed from N vectors of random length and direction joined end to end. As usual, the vectors connect $N + 1$ segments each with Stokes radius a. A number of such chains with different conformations are generated, and the hydrodynamic problem is solved for each chain; the results are then averaged. In this way the preaveraging of the Kirkwood–Riseman (KR) approximation is avoided; at the same time the inverses are taken in the correct order.

Methods

We replace the real system of flexible chain molecules by an ensemble of rigid, randomly selected models of chains. While this procedure appears to be a drastic oversimplification, we attempt to show below that it is valid as long as Brownian motion is overwhelming.

Consider an ensemble of molecules in a certain steady state with applied external forces or external flows. In steady state the system is translating (in sedimentation) or rotating (in laminar flow) at a constant rate, while the distribution of internal coordinates (exclusive of orientation

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in the shear case) is constant in time, any motions produced in these internal coordinates being balanced by equal and opposite flows produced by diffusion. In general, one could describe such an ensemble by the use of a generalized diffusion equation,[2,8] but if we restrict ourselves to small perturbations from equilibrium and consider only effects linear in the perturbation (sedimenting force or shear rate), then H. A. Kramers[9] showed how to simplify the problem. Specifically, he demonstrated that, if the flow is irrotational, and in so far as terms linear in the externally applied force or flow are concerned, it is sufficient to average over forces and conformations using the probability distribution function of the molecule in the system at rest. (The forces, of course, are not those of the molecule at rest.) This, together with the fact that the distribution of internal coordinates is constant in time, implies that the properties of molecules in flow can be calculated as if the molecules were holding their internal conformations fixed, whether they are actually flexible or not, as far as the terms linear in applied force or flow are concerned. The corollary is that one can calculate the average instantaneous forces on any conformation of such molecules, flexible or not, as if the molecules were rigid. (This simplification was exploited by Kramers himself[9] and by Kirkwood and Riseman,[1] for example.) Therefore in the following we shall proceed as if the molecules were rigid.

The problem of the rotation of the molecules has to be considered separately. Kramers (loc. cit.) showed that the rotational component of laminar flow can be subtracted out and only the remaining irrotational flow considered in so far as the calculation of the intrinsic viscosity goes. We demonstrate in Appendix A by extending Kramers' argument that in sedimentation one component does have to be retained, however; this is rotation around the direction of sedimentation, here taken to be the z axis of a left-handed Cartesian set. This component, Ω_z, is illustrated by the rotation of the rotor of a helicopter, or of a falling leaf; it spontaneously accompanies the sedimentation of most asymmetric models. Therefore we shall calculate Ω_z explicitly when we calculate sedimentation rates.

(The above argument is too brief to do justice to a subtle problem. See also the Addendum section at the end of this paper. Until the subject has had further study, therefore, we must consider our results on the viscosity number to be provisional.)

The segments of each chain interact with the fluid flow in the usual way through direct friction and through hydrodynamic interaction with each other. The hydrodynamic problem without the KR approximations is the same one that has been treated several times recently by Yamakawa and co-workers for rods and rings[10] and by McCammon and Deutch[11] and de la Torre and Bloomfield for various models of viruses and similar structures.[12] However, because our models lack symmetry and because we wish to treat the viscosity number as well as sedimentation, we have to arrange our formulas somewhat differently. We therefore give a brief derivation of them.

Fundamental Equations. Let $\mathbf{R}_i$ be the location of the ith segment, $\mathbf{F}_i$ be the frictional force exerted by the segment on the fluid, $\mathbf{u}_i$ be the velocity of the segment, and $\mathbf{v}_i$ be the velocity that the fluid would have at $\mathbf{R}_i$ if that segment were absent. By Stokes' law,

$$\mathbf{F}_i = \rho(\mathbf{u}_i - \mathbf{v}_i) \tag{1}$$

where $\rho = 6\pi\eta a$, and a is the effective radius of the segment. The Oseen–Burgers interaction tensor $\mathbf{T}_{ij}$ gives the fluid flow at the location $\mathbf{R}_i$ produced by the force $\mathbf{F}_j$ at $\mathbf{R}_j$. The total flow at $\mathbf{R}_i$ is then

$$\mathbf{v}_i = \sum_{i\neq j}\mathbf{T}_{ij}\mathbf{F}_j + \mathbf{v}_{0i} \tag{2}$$

where $\mathbf{v}_{0i}$ is any externally imposed flow that the fluid would have in the same experiment but with the chain removed. We can combine eq 1 and 2 to get

$$(1/\rho)\mathbf{F}_i + \sum_{i\neq j}\mathbf{T}_{ij}\mathbf{F}_j - \mathbf{u}_i = -\mathbf{v}_{0i} \tag{3}$$

In steady state at low flow rates, as discussed above, all the $\mathbf{u}_i$ must be those of a rigid body. If the velocity of a local origin moving with the body is $\mathbf{u}$ and the rate of rotation about the z axis is Ω_z, the rigid-body formulas are:

$$u_{ix} = u_x - y_i\Omega_z \tag{4a}$$

$$u_{iy} = u_y + x_i\Omega_z \tag{4b}$$

$$u_{iz} = u_z \tag{4c}$$

where x_i, y_i, z_i are components of the vector from the local origin to the ith segment in a left-handed coordinate system.

When eq 4 are substituted into eq 3 we have a set of $3(N + 1)$ equations with $3(N + 1) + 4$ unknowns, the latter being the $3(N + 1)$ components of the forces $\mathbf{F}_i$ together with u_x, u_y, u_z, and Ω_z. Moreover, the total force, $\mathbf{F}$, externally imposed on the molecule is known (it is the sedimenting force in sedimentation and is zero in the case of the viscosity experiment), so that we have three more equations for its three components:

$$\sum_i \mathbf{F}_i = \mathbf{F} \tag{5}$$

Finally, we have one condition on the rotation Ω_z; in the case of the viscosity problem Ω_z is zero, while in the case of sedimentation the total torque around the z axis is zero, since there are no external forces in the x or y directions to generate such a torque. This last condition gives us one more equation, which is

$$\Omega_z = 0 \tag{6a}$$

(viscosity), or

$$\sum_i (y_iF_{ix} - x_iF_{iy}) = 0 \tag{6b}$$

(sedimentation). Thus there are in all $3(N + 1) + 4$ equations for the $3(N + 1) + 4$ unknowns.

Some differences between these equations and those of de la Torre and Bloomfield call for comment. If one considers $\mathbf{u}$ to be a known quantity and $\mathbf{F}$ an unknown, as can be done in the case of sedimentation, then one can solve eq 3 for the $\mathbf{F}_i$ and get $\mathbf{F}$ from eq 5. This method would have the advantage of requiring only $3N + 3$ unknowns, but unfortunately it does not seem to be applicable to the viscosity problem, since here $\mathbf{u}$, the velocity of the local origin, is not known at the outset. However, de la Torre and Bloomfield used a variant of this method for their sedimentation problems. Instead of evaluating the $\mathbf{F}_i$ explicitly, they, following Yamakawa and Tanaka,[10] evaluated the six independent components of the tensors $\mathbf{G}_i$ relating the $\mathbf{F}_i$ to $\mathbf{u}$,

$$\mathbf{F}_i = \mathbf{G}_i{:}\mathbf{u} \tag{7}$$

which are components of the inverse of the matrix of eq 3. Unfortunately, in this version the method seems to require $6(N + 1)$ unknowns, unless a coordinate system can be found that simultaneously diagonalizes the tensors $\mathbf{G}_i$, which is possible only in some simple cases.[10,12] For these reasons we have used the method set forth in the preceding paragraph, which is essentially that of McCammon and Deutch[11] generalized to include translation–rotation coupling.

The set of simultaneous equations 3 through 6 were solved twice with different vectors on the right-hand side. In the first case, corresponding to sedimentation with a force along the z axis, all the elements on the right-hand side of eq 3 were set to zero, while the z component of the total sedimenting force $\mathbf{F}$ was set equal to $N + 1$, equivalent to unit force in the z direction on each of the $N + 1$ segments. The value found for the z component of $\mathbf{u}$ in this way is the desired sedimentation velocity. (The other components of $\mathbf{u}$ represent the sideways motions produced by the sedimentation of the randomly oriented asymmetric particles.)

In the second case the viscosity problem was treated. Here the total force $\mathbf{F}$ was set equal to zero. Following Kramers[9] again, the right-hand elements of eq 3 were set up to represent the irrotational part of the simple laminar flow,

$$\nu_{0ix} = \kappa z_i \qquad \nu_{0iy} = \nu_{0iz} = 0 \tag{8}$$

The irrotational part of this flow is

$$\nu_{0ix} = (\kappa/2)z_i \qquad \nu_{0iy} = 0 \qquad \nu_{0iz} = (\kappa/2)x_i \tag{9}$$

Hence the elements of the right-hand side of eq 3 were $(\kappa/2)z_i$, 0, and $(\kappa/2)x_i$, in succession for i from 0 to N. (In the actual numerical calculation we set κ equal to 2.)

The Stokes Radius and the Hydrodynamic Interaction Tensor. The choice of the Stokes radius, a, and the representation of the tensors $\mathbf{T}_{ij}$ posed some problems. The original Oseen–Burgers form of $\mathbf{T}_{ij}$, which is proportional to $1/R_{ij}$, is correct only if $\mathbf{R}_{ij}$ does not become too small, otherwise the equations become singular.[13,14] One way to avoid the difficulty would be to represent the segments by spheres, to use the correct form of $\mathbf{T}_{ij}$ for spheres,[14] and to avoid those unphysical conformations in which $\mathbf{R}_{ij}$ was less than the diameter of the spheres. This, however, would give us chains with excluded volume, whereas we would like to be able to treat chains either with or without excluded volume (e.g., in Flory Θ solvents). Furthermore, a sphere is not a realistic representation of a Gaussian chain segment. Two Gaussian segments, unlike two solid spheres, can mutually interpenetrate without their hydrodynamic interactions becoming singular. Therefore we have adopted the following approximate, but we hope not unrealistic, scheme. Since the Oseen–Burgers

$$\mathbf{T}_{ij} = (1/8\pi\eta R_{ij})(\mathbf{I} + \mathbf{R}_{ij}\mathbf{R}_{ij}/R_{ij}^2) \tag{10}$$

form[15] is always correct at large distances, we use this form for all $\mathbf{R}_{ij}$ greater than a crossover value, call it R_c, to be selected. For $\mathbf{R}_{ij}$ less than R_c we hold $\mathbf{T}_{ij}$ constant at its value, averaged over orientations, at the crossover radius, R_c. This avoids having large values of $\mathbf{T}_{ij}$ at small $\mathbf{R}_{ij}$ and minimizes the chances of eq 3 becoming singular. We then assume that this constant value of $\mathbf{T}_{ij}$ is such that the friction coefficient of two overlapping segments ($R_{ij} < R_c$) is the same as the Kirkwood–Riseman value of the friction coefficient of two random-coil segments of unit length joined at their centers to form a cross. The latter was calculated by Stockmayer and Fixman.[16] The details are given in Appendix B. The result for the crossover radius is

$$R_c = a/(2 - \sqrt{2}) \tag{11a}$$

and the corresponding value of $\mathbf{T}_{ij}$ for $R_{ij} \leq R_c$ is

$$\mathbf{T}_{ij} = 1/[6\pi\eta(1 + 1/\sqrt{2})a] \tag{11b}$$

The Stokes radius, a, was chosen so that the friction coefficient, ρ, is equal to the KR value of a nondraining random coil of root mean square length b (which we take to be unity in the actual calculation), our model for the segment. This value is[1]

$$a = 9\pi^{1/2}/(4 \times 6^{3/2}) = 0.27135b \tag{12}$$

The approximations inherent in the above scheme should have only a small effect on the final results for long chains, for two reasons. First, as the number of segments gets larger the results depend less and less on the values of $\mathbf{T}_{ij}$ at small distances, less and less on the friction coefficient ρ, and more and more on the values of $\mathbf{T}_{ij}$ at large distances $\mathbf{R}_{ij}$, since the number of terms in eq 3 near the diagonal increases as N, while the numbers of the others, corresponding mainly to large $\mathbf{R}_{ij}$, increase as N^2. Second, we are interested in the effects of the Kirkwood–Riseman approximations, and these should be relatively independent of the exact form chosen for ρ and for $\mathbf{T}_{ij}$, as long as exactly the same forms are used both with and without the Kirkwood–Riseman approximations.

In the actual solution of the equations the viscosity η was replaced by unity. Thus the quantity $\mathbf{u}$ represents numerically the sedimentation velocity in a solvent of unit viscosity with unit sedimenting force acting on each bead. Correspondingly, in the calculation of $[\eta]$ the forces $\mathbf{F}$ represent the forces in a system with $\eta = 1$ and with $\kappa = 2$.

The Sedimentation Coefficient and the Viscosity Number. To proceed from our solutions to the conventional sedimentation coefficient and viscosity number we go through the following steps. The $\mathbf{u}$ that we calculate is the sedimentation velocity of a molecule with unit root mean square segment length, b, in a solvent of unit viscosity with unit sedimenting force on each segment. In general the velocity in a solvent of viscosity η and with a force g on each segment would be

$$\mathbf{u}' = (g/\eta b)u \tag{13}$$

In the case of centrifugation with centrifuge angular velocity w, rotor radius r, chain molecular weight M, and Archimedes factor $(1 - \bar{v}\rho')$, we would have

$$(N + 1)g = M(1 - \bar{v}\rho')w^2r/N'' \tag{14}$$

where N'' is Avogadro's number. The sedimentation coefficient is defined as

$$s = (u'/w^2r) \times 10^{13} \tag{15}$$

From these we can get the relation between the sedimentation coefficient and our solution for the vertical component of $\mathbf{u}$, u_z, as

$$s \times 10^{-13} = \frac{M(1 - \bar{v}\rho')u_z}{N''(N + 1)\eta b} \tag{16}$$

Equation 16 contains too many extraneous factors to be useful. However, by dimensional considerations we know that the sedimentation velocity u_z should be proportional to the sedimenting force divided by a frictional factor, which latter is proportional to a distance. This leads us to define a dimensionless factor, P,

$$P = (N + 1)b/(\sqrt{6}Ru_z) \tag{17}$$

where R is the root-mean-square "central radius of gyration" of the chain,

$$R^2 = \sum r_i^2/(N + 1) \tag{18}$$

where r_i is the distance of the ith segment from the center of mass of the chain. This definition of P is, in fact, equivalent to that of P. J. Flory,[17] who put

$$P = f/(\sqrt{6}R\eta) \tag{19}$$

with f, the frictional coefficient, defined by the Svedberg equation,

$$f = M(1 - \bar{v}\rho')/[N''(s \times 10^{-13})] \tag{20}$$

With eq 16 these also give eq 17. The root mean square radius R is, of course, evaluated on the same sample of chains to which eq 3 through 6 are applied. (In our terms $f = (N + 1)g/u_z'$.) The factor P can thus be used to measure the effects of the KR approximations on the sedimentation rate without regard to the trivial factors of amount of sedimenting force and chain extension.

Similar considerations apply to the viscosity. The viscosity number, $[\eta]$, in units of cm^3/g, is usually[1,15] given as

$$[\eta] = N''(\textstyle\sum z_i F_{ix})/(M\eta\kappa) \tag{21}$$

To reduce statistical fluctuations we found it useful to average $z_i\mathbf{F}_{ix}$ with $x_i\mathbf{F}_{iz}$, since both quantities should have the same ensemble averages with the irrotational flow of eq 9, and both are available from the solutions of eq 3 through 6. Also, we set κ equal to the number 2 and η equal to unity in the numerical calculation, and we measured lengths in units of the root mean square segment length, b. Hence the actual equation used for $[\eta]$ was

$$[\eta] = N''(N + 1)b^3E/2M \tag{22}$$

where E, the dimensionless number actually computed by the program, is:

$$E = \textstyle\sum(z_iF_{ix} + x_iF_{iz})/[(N + 1)\kappa\eta b^3] = \textstyle\sum(z_iF_{ix} + x_iF_{iz})/[2(N + 1)] \tag{23}$$

Again, to remove trivial effects of chain size we follow Flory[17] and define a factor Φ:

$$\Phi = [\eta]M/(\sqrt{6}R)^3 \tag{24}$$

From 22 and 24 we find

$$\Phi/N'' = (N + 1)b^3E/[2(\sqrt{6}R)^3] \tag{25}$$

Mandelkern, Flory, and Scheraga[18,19] introduced a factor, β, by eliminating the radius R from a combination of P and Φ:

$$\beta = \left(\frac{N''}{M^{2/3}}\right)\left(\frac{\eta s \times 10^{-13}}{1 - \bar{v}\rho'}\right)\left(\frac{[\eta]}{100}\right)^{1/3} \tag{26}$$

We are interested in the use of this factor to determine the molecular weight M from sedimentation and viscosity by means of eq 26. Introducing eq 16 and 22, we get

$$\beta^3 = N''u_z{}^3E/[200(N + 1)^2] \tag{27}$$

It is simpler for the purpose of determining M to define a related quantity, B, such that

$$M = BN''[\eta]^{1/2}[s\eta/(1 - \bar{v}\rho')]^{3/2} \tag{28}$$

By substitution we can show that

$$B = (N''\beta^{-3} \times 10^{-41})^{1/2} \tag{29}$$

and

$$B = (N + 1)(2/E)^{1/2}u_z{}^{-3/2} \times 10^{-39/2} \tag{30}$$

Thus we can evaluate β and B, as well as P and Φ/N'', for our model from the solutions of eq 3 through 6.

Solution of the Equations. The maximum number of simultaneous equations that can be solved is limited by the amount of computer time available, so it is important that the method of solution be as efficient as possible. Since the matrix of the equations is symmetric, factorization of the matrix into upper and lower triangular matrices by the so-called Cholesky method[20] is advantageous. It was necessary to modify the standard program published by Martin et al.[21] to avoid dividing by the diagonal elements, since four of these are zero, but the modifications turned out to be easy and effective for the matrices encountered here. The result was a program that solved the equations for both the sedimentation and viscosity cases at once, using on the order of $(3N)^3/6$ multiplications and $(3N)^2/2$ storage locations.

Iterative methods, of the type used by de la Torre and Bloomfield,[12] were tried but did not seem to offer any advantages for the type of random matrices encountered here.

The efficiency of the program and possible effects of round-off errors were checked by solving several sets of 156 equations (eq 3 and 5 with $N = 50$) by both the modified Cholesky method and by a program of successive elimination of unknowns used as a standard method by the UCSD computer center. (This latter is used because it is applicable to any type of matrix, symmetric or not, but it requires $(3N)^3/3$ multiplications and uses $(3N)^2$ storage locations.) The cost of the Cholesky-type program was less than half as much, and the results were identical in so far as the numbers recorded in the output, that is, to within one part of 10 000 for sedimentation and viscosity.

The size of the chain that could be handled in this way and still allow a reasonable sample size was about 50 vectors. Since the overall expense of solving one chain goes approximately as the product of the time and the amount of storage required, that is, as N^5, even large increases in computer power would not allow this size to be much extended. Exact modeling of real chains with thousands of monomer units is therefore not feasible in general by the method described.

Our approach is therefore somewhat different. It is the hydrodynamic interactions, $\mathbf{T}_{ij}$, of the chain elements which are of interest to us; these interactions become more and more important as N increases, leading finally to a completely interacting, or "nondraining", chain[1] where the diagonal elements of eq 3 can be neglected. Real chains, which of course consist of contiguous, not separated, segments, are very near, or at, the nondraining limit.[22] Fortunately, even at $N = 50$ the solutions of the KR equations are close to their nondraining limits, and by taking a series of increasing values of N, up to 50, with and without the KR approximations, we can even make reasonable extrapolations toward the limits.

This scheme was implemented in the following way. Five-hundred random three-dimensional vectors, with a Gaussian distribution of lengths, but unit root mean square length, were generated by a standard routine.[23] These were then strung end to end in chains to make four sets of random-flight chains, one set with 100 chains of 5 vectors each, one with 50 chains of 10 vectors each, one with 20 chains of 25 vectors each, and one with 10 chains of 50 vectors each. The root mean square radius $\mathbf{R}$ was evaluated on each chain, and eq 3 through 6 were solved. The resulting values of R^2, the sedimentation velocity, u_z, and the moments of the forces in shear flow, E, were averaged over all chains for each value of N. Finally P and Φ, β, and B were calculated from the average for each set of chains of a given N. The use of the same 500 vectors for all four sets of chains was designed to reduce the statistical fluctuations and to allow the effects of N to be more easily isolated.

The whole process was repeated four times with independent sets of 500 random vectors so the results could be examined for systematic biases arising from nonrandomness in the pseudorandom numbers (none were found). Finally, all the results for each value of N were averaged.

The calculation was programmed in ALGOL. Numerical operations were carried out by a Burroughs B6700 computer in the UCSD Computer Center.

The Kirkwood–Riseman, Diagonal, and Free-Draining Approximations. For proper comparison we need the results of the KR and free-draining approximations applied to the same sample of model chains used in the more exact calculation described above, and in the KR case based on the same interaction tensor. This is very simple to do with sedimentation. Kirkwood's later method,[2] which was thought to lead to the same results as those in the earlier Kirkwood–Riseman paper,[1] uses the sum of all the coefficients in the first two terms on the left-hand side of eq 3. The formula (remembering that we have unit sedimenting force on each segment) is

$$u_{z,\mathrm{kr}} = 1/\rho + \sum_i \sum_{i \neq j} T_{ij,zz}/(N+1) \tag{31}$$

This quantity was evaluated for each individual chain that was generated.

The calculation of the KR approximation to E, which is proportional to $[\eta]$, was likewise carried out for each individual chain. The original KR procedure[1] can be simplified somewhat (without changing the results);[25,26] it then amounts to solving eq 3 and 5 with the $\mathbf{T}_{ij}$ replaced by their preaveraged values. The preaveraged $\mathbf{T}_{ij}$ tensors have vanishing xy, yz, and xz components, and their xx, yy, and zz components are identical, so eq 3 and 5 reduce to three independent sets of equations identical with each other on the left-hand sides. We solved the x and z sets of these by using eq 9 for the right-hand sides. The resulting forces were then used in eq 23 to produce E_{kr} for comparison with E from the "exact" calculation.

The preaveraged interaction tensor elements, $\langle \mathbf{T}_{ij} \rangle$, had to be calculated by using the modified Oseen–Burgers form described above in eq 10 and in the sentences following that. These elements are

$$\langle \mathbf{T}_{ij} \rangle = \int_0^{R_c} t(R_c) g_{ij}(r)\,\mathrm{d}r + \int_{R_c}^{\infty} t(r) g_{ij}(r)\,\mathrm{d}r \tag{32}$$

where R_c is the crossover radius defined above, $t(r)$ is the orientational average of the diagonal elements of $\mathbf{T}_{ij}$,

$$t(r) = 1/(6\pi\eta r) \tag{33}$$

and $g_{ij}(r)$ is the usual Gaussian intersegment distance distribution function,

$$g_{ij}(r) = \left(\frac{3}{2\pi^2 |i-j| b^2} \right)^{3/2} \exp\left(\frac{-3r^2}{2|i-j|b^2} \right) \tag{34}$$

These integrals can be evaluated in terms of the error function, erf, to yield finally

$$\langle \mathbf{T}_{ij} \rangle = \frac{1}{6\pi\eta R_c} \left[\mathrm{erf}(q) - 2q\frac{e^{-q^2}}{\sqrt{\pi}} \right] + \frac{e^{-q^2}}{(6\pi^3|i-j|)^{1/2}\eta b} \tag{35}$$

with

$$q = [3/(2|i-j|)]^{1/2} R_c/b \tag{36}$$

This approaches the usual KR form, $(1/6\pi\eta b)(6/\pi|i-j|)^{1/2}$, when R_c is made to approach zero.

The KR approximation can also be employed in the traditional way by using the theoretically expected average segment positions. We need results of this kind on chains of the same size as used in our other calculations; by comparison we can assess the magnitude of sampling errors in the Monte-Carlo procedure.

There are actually several possible versions of this form of the KR approximations. For sedimentation the simplest is to use eq 31, but with the preaveraged tensor elements from eq 35 in place of the $T_{ij,zz}$ calculated for each individual chain, no further averaging is then necessary. This was the formula proposed by Kirkwood in his 1953 paper;[2] we call it the "preaveraged matrix-sum method". Another version originally proposed by Kirkwood and Riseman in 1948[1] amounted to solving eq 3 and 5 with the preaveraged tensor elements from eq 35; in our notation, it amounts to putting eq 3 in the following form:

$$(1/\rho)F_{iz} + \sum_{j \neq i} \langle \mathbf{T}_{ij} \rangle F_{jz} = u_{z,\mathrm{KR}} \tag{37}$$

We shall refer to this as the method of "inversion of the preaveraged matrix". (In the literature matters were confused by the approximate procedure employed by Kirkwood and Riseman to solve this eq 37. Their procedure used a Fourier series of suspect convergence and accidentally gave a result identical with that of the preaveraged matrix-sum method.) Actually the matrix-sum method amounts to *assuming* that the solutions of eq 37, the $\mathbf{F}_i$, are all equal to unity; in fact, they are not. When eq 37 is correctly inverted, the results are different from those of the preaveraged matrix-sum method, as we shall see.

For the viscosity problem things are simpler in that there is nothing equivalent to the matrix-sum method. One either uses the preaveraged $\langle \mathbf{T}_{ij} \rangle$ elements on individual chains and then averages the results, as was discussed above, or one applies the preaveraged $\langle \mathbf{T}_{ij} \rangle$ to preaveraged chain conformations, thus eliminating the sampling errors. We now proceed to do the latter. We follow the procedure described in ref 26, that is, we invert the matrix of the $\langle \mathbf{T}_{ij} \rangle$ and use the inverse matrix to generate the sum, $\sum z_i F_{ix}$, which is needed for $[\eta]$. The formula can be derived as follows:

$$E_{\mathrm{KR}} = \frac{\sum_i \langle z_i F_{ix} \rangle}{(N+1)\eta\kappa b^3} = \frac{\sum_i \langle z_i \sum_j [(\rho H_{ij}^{-1})\nu_{ix}] \rangle}{(N+1)\eta\kappa b^3} \tag{38a}$$

$$E_{\mathrm{KR}} = \frac{\rho}{2(N+1)\eta b^3} \sum_i \sum_j H_{ij}^{-1} \langle z_i z_j \rangle \tag{38b}$$

where the matrix $\mathbf{H}$ has the following elements:

$$H_{ij} = 1 \qquad H_{ij} = \rho \langle \mathbf{T}_{ij} \rangle \tag{39}$$

The preaveraged quantities $\langle z_i z_j \rangle$ are readily calculated by the methods of ref 24; they are

$$\frac{\langle z_i z_j \rangle}{b^2} = \frac{(2N+3)(N+2)}{18(N+1)} - \frac{(i+1)(N+1-i) + (j+1)(N+1-j)}{6(N+1)} - \frac{|i-j|}{6} \tag{40}$$

We remind the reader that the calculations of the last two paragraphs give the KR results in the traditional way, with no Monte-Carlo contribution at all, but for finite N and with the modified interaction tensor. In contrast, the methods of the first two paragraphs of this section give the KR results for the specific sample of chains generated by the random-number program. Differences among the results are a measure of the statistical fluctuations resulting from finite sample size. In addition we can expect to see differences between the 1948 and 1953 versions of the KR approximations.

Table I
Ten Individual Chains of 50 Vectors Each

no.	R^2 [a]	h^2 [a]	u_z [b]	$u_{z,\mathrm{kr}}$ [c]	$u_{z,\mathrm{dg}}$ [d]	u_{hor} [e]	E [b]	E_{kr} [c]	E_{fd} [f]
1	11.724	45.617	0.9967	1.0677	1.009	0.0333	7.9012	8.3765	17.5937
2	8.088	94.032	1.1191	1.3037	1.135	0.0811	6.8755	7.3343	13.7129
3	13.868	107.537	1.0674	1.1569	1.079	0.0833	10.5749	10.5913	23.6751
4	8.456	61.027	1.1595	1.2615	1.174	0.0743	6.6908	7.1276	14.4428
5	3.698	10.043	1.3850	1.5699	1.402	0.1468	2.9552	3.3984	5.1180
6	6.452	22.165	1.1992	1.3158	1.225	0.0029	5.3670	6.0164	12.4431
7	5.949	37.064	1.2824	1.5349	1.312	0.0671	1.7046	2.1806	2.7724
8	5.054	25.000	1.3233	1.6277	1.334	0.0896	4.2116	5.5467	11.5053
9	2.816	16.370	1.4962	1.7830	1.530	0.0212	2.1900	3.0990	4.8287
10	16.289	58.171	1.0975	1.1846	1.110	0.0686	12.5683	14.2343	37.0871
mean	8.239	47.704	1.2126	1.3806	1.2311	0.0770	6.044	6.7905	14.3179
st dev	±4.2	±31	±0.15	±0.22	±0.16	±0.04	±3.3	±3.7	±10.2

[a] R^2 is the mean square central radius of gyration; h^2 is the mean square end-to-end distance. [b] Results from the solution of eq 3, 5, and 6. [c] From Kirkwood-Riseman expressions. [d] From "diagonal approximation". [e] $u_{\mathrm{hor}}^2 = u_x^2 + u_y^2$. [f] From free-draining approximation.

de la Torre and Bloomfield[12] have introduced a "diagonal approximation", which consists of dropping the *xy*, *xz*, and *yz* elements of $\mathbf{T}_{ij}$. We have experimented with this approximation in the sedimentation problem, where it offers substantial advantages. Since the tensor becomes diagonal in 3-space, only the *z* components enter the sedimentation problem, and the number of equations to be solved is thereby reduced by about a factor of 3. The resulting system has the form of eq 37, but with $T_{ij,zz}$ replacing $\langle \mathbf{T}_{ij} \rangle$, and, of course, $u_{z,\mathrm{dg}}$ on the right-hand side representing the sedimentation velocity. These equations were solved numerically for each chain generated by the random-number program.

The free-draining approximation simply neglects the $\mathbf{T}_{ij}$ terms completely. In this case we find that u_z is independent of the number of segments, *N*, and is, with $g = 1$,

$$u_{z,\mathrm{fd}} = 1/\rho \tag{41}$$

The corresponding viscosity quantity *E* from eq 3, 9, and 23 is, with η and *b* equal to 1,

$$E_{\mathrm{fd}} = \rho \sum (x_i^2 + z_i^2)/[2(N + 1)] \tag{42}$$

Results

In Table I are shown the results of these calculations on the first ten individual chains of 50 vectors each; these were the first ten of such chains generated by the random-number program. The averages in the second and third columns can be compared to the expected mean squares of the central radii of gyration and of the end-to-end distances, which are obtained from the formulas

$$R^2 = N(N + 2)/(6N + 6) \tag{43}$$

$$h^2 = N \tag{44}$$

Equation 44 is familiar; eq 43, which includes terms of importance when *N* is small, can be easily derived by standard methods.[24] The resulting numbers, which are reported in the first lines of Table II, are in quite good agreement with the average results in Table I. We conclude that this sample of ten chains is reasonably representative.

Turning now to the main goal of this paper, the comparison of the rigorous solutions of the hydrodynamic equations with the results of the KR approximations, we find the relevant quantities in Table I in columns four, five, eight, and nine. We recall that u_z is proportional to the sedimentation coefficient and *E* to $[\eta]$. We see immediately that while the actual numbers vary widely from one chain to another, the KR results are always higher than the rigorous ones. The tentative conclusion is that the KR method consistently overestimates both the sedimentation rate and the viscosity.

Table II
Predicted Values

	N				
	5	10	25	50	∞
h^2	5	10	25	50	
R^2	0.9722	1.8182	4.3269	8.4967	
$u_{z,\mathrm{fd}}$	0.1955	0.1955	0.1955	0.1955	
E_{fd}	1.6576	3.1001	7.3775	14.4871	
E_{kr}, eq 38b	1.9153	2.8889	4.7912	6.8914	
Φ_{kr}/N''	0.4078	0.4410	0.4709	0.4828	0.4741[a]
	From Eq 31				
$u_{z,\mathrm{kr}}$	0.4455	0.6081	0.9497	1.3454	
P_{kr}	5.5764	5.4767	5.3731	5.3091	5.1148[b]
$\beta_{\mathrm{kr}} \times 10^{-6}$	2.4197	2.5288	2.6346	2.6886	2.7740
$B_{\mathrm{kr}} \times 10^{19}$	6.5209	6.1032	5.7395	5.5674	5.3122
	From Eq 37				
$u_{z,\mathrm{kr}}$	0.4429	0.6023	0.9366	1.3243	
P_{kr}	5.6091	5.5295	5.4482	5.3937	5.2019[c]
$\beta_{\mathrm{kr}} \times 10^{-6}$	2.4056	2.5047	2.5983	2.6465	2.7275
$B_{\mathrm{kr}} \times 10^{19}$	6.5783	6.1917	5.8602	5.7009	5.4488

[a] Calculated from Yoshizaki and Yamakawa, ref 27. [b] $(3\pi)^{3/2}/2^{5/2}$, ref 1 and 2. [c] $\Gamma(1/2)\Gamma(3/4)/8^{1/2}\pi\Gamma(5/4)$, from Auer and Gardner, as quoted in ref 28.

This conclusion is reinforced by the results on the whole ensemble of chains summarized in Table III, where the results on chains of smaller size are also included. The KR results consistently differ from the rigorous results, and always in the same direction. It is perhaps easiest to look at the reduced quantities, *P*, Φ, β, and *B*, where the direct effects of chain length have been removed. The factor *P*, defined by eq 17 or 19, is a reduced translational friction coefficient, while Φ, eq 24 or 25, is a reduced viscosity number. The averaged KR frictional coefficients are always low, and the averaged KR viscosity numbers are always high.

In Table III we can see that the diagonal approximation of de la Torre and Bloomfield[12] is quite good; though not in perfect agreement with the rigorous results, it is much better than the KR approximation.

Precision. In the discussion of the significance of these effects close attention must be paid to the question of precision, which is limited, as in most Monte-Carlo calculations, by the finite size of the sample. The computer was programmed to report the standard deviation of most of the primary quantities calculated. As a measure of the precision of the average values we list in Table III the

Table III
Monte-Carlo Values

	N			
	5	10	25	50
no. of chains in sample	400	200	80	40
h^2	5.1720 ± 0.2[a]	11.2074 ± 0.6	26.0539 ± 2	50.6177 ± 5
R^2	1.0062 ± 0.03[a]	1.9867 ± 0.07	4.6698 ± 0.2	8.9227 ± 0.6
u_z	0.4249 ± 0.002[a]	0.5611 ± 0.005	0.8454 ± 0.01	1.1827 ± 0.02
$u_{z,\mathrm{kr}}$	0.4433 ± 0.002[a]	0.5996 ± 0.006	0.9367 ± 0.02	1.3394 ± 0.03
$u_{z,\mathrm{dg}}$	0.4301 ± 0.002[a]	0.5669 ± 0.005	0.8581 ± 0.01	1.2011 ± 0.02
$u_{\mathrm{kr}} - u$	0.0184 ± 0.0006[a]	0.0385 ± 0.002	0.0884 ± 0.005	0.1568 ± 0.01
E	1.7713 ± 0.05[a]	2.7139 ± 0.09	4.5978 ± 0.3	6.5945 ± 0.5
E_{kr}	1.9870 ± 0.08[b]	3.0984 ± 0.1	5.1810 ± 0.3	7.4034 ± 0.4
E_{fd}	1.7245 ± 0.07[b]	3.3712 ± 0.13	8.1602 ± 0.7	15.7599 ± 1
$E_{\mathrm{kr}} - E$	0.2157 ± 0.01[a]	0.3844 ± 0.02	0.5831 ± 0.06	0.8089 ± 0.1
P	5.7471 ± 0.06[b]	5.7041 ± 0.03	5.8101 ± 0.2	5.8935 ± 0.2
P_{kr}	5.5085 ± 0.05[b]	5.3378 ± 0.03	5.2438 ± 0.1	5.2040 ± 0.1
$P - P_{\mathrm{kr}}$	0.2386 ± 0.008[b]	0.3663 ± 0.006	0.5663 ± 0.03	0.6895 ± 0.07
P_{dg}	5.6776 ± 0.06[b]	5.6457 ± 0.03	5.7241 ± 0.2	5.8032 ± 0.2
Φ/N''	0.3582 ± 0.006[b]	0.3677 ± 0.009	0.4030 ± 0.01	0.4293 ± 0.03
Φ_{kr}/N''	0.4019 ± 0.007[b]	0.4198 ± 0.01	0.4541 ± 0.01	0.4819 ± 0.03
$(\Phi_{\mathrm{kr}} - \Phi)/N''$	0.0437 ± 0.002[b]	0.0521 ± 0.004	0.0511 ± 0.006	0.0526 ± 0.006
$\beta \times 10^{-6}$	2.2485 ± 0.05[b]	2.2853 ± 0.05	2.3132 ± 0.1	2.3290 ± 0.07
$\beta_{\mathrm{kr}} \times 10^{-6}$	2.4376 ± 0.06[b]	2.5524 ± 0.07	2.6671 ± 0.1	2.7412 ± 0.06
$B \times 10^{19}$	7.2795 ± 0.1[b]	7.1045 ± 0.1	6.9763 ± 0.2	6.9053 ± 0.1
$B_{\mathrm{kr}} \times 10^{19}$	6.4490 ± 0.1[b]	6.0190 ± 0.1	5.6350 ± 0.2	5.4079 ± 0.1

[a] Standard deviation of the mean = (standard deviation in the sample)/(square root of the number of chains).[c] [b] Standard deviation of the mean = (standard deviation among the means of the four subsamples)/2.[c] [c] Each of the above notes applies to all the standard deviations in the corresponding line, not just to the first column.

standard deviations divided by the square root of the number of chains in the sample. This is strictly valid as a measure of the precision of the average only when the population is normally distributed, but the latter is at least approximately true of the quantities of interest here. But where two quantities are being compared and their fluctuations are strongly correlated, as in the case of sedimentation rate with and without the KR approximation, for example, then the standard deviations of the individual quantities do not tell the whole story. For that reason we also had the program report the standard deviation of the difference in such cases. From these standard deviations we can see that the differences are highly significant.

Determination of the precision of the derived quantities, P, Φ, β, and B, involves more problems. All of these are the ratios or products of the averages of several quantities, such as E and R^2, whose values are more or less correlated in the population. Therefore one cannot use the usual propagation-of-error formulas. On the other hand, it would be meaningless to calculate β, for example, for each individual chain and average the results, since β is defined as a combination of average sedimentation rate, average mean square radius and average viscosity number, these being the quantities measured in experiments. What we actually did was to calculate separate values of β from the averaged u_z, $[\eta]$, and R^2 from each of the four subsamples corresponding to the four different sets of 500 random vectors. The standard deviation of this population of four quantities divided by $4^{1/2} = 2$ then served as a measure of the precision of the "global" value of β, which itself had to be calculated from u_z, $[\eta]$, and R^2, each averaged over the whole sample of 2000 vectors. (This global value of β was not exactly equal to the average of the β's of the four subsets because β is not related to the other quantities by a linear formula.) Exactly the same procedure was used for P, Φ, and B.

Analytical KR Calculations. In Table II are reported the results of the completely analytical calculations of the Kirkwood–Riseman type from eq 31 through 38. Comparison of these with the results in Table III gives an independent measure of the sampling errors. Looking at the first lines of the tables, we see that the Monte-Carlo values of h^2 and R^2 are consistently high, although the maximum difference from the analytical values is barely more than two standard deviations. Apparently the mean extension of the particular set of 2000 vectors that was generated was toward the high side of the expected range.

Consistent with the above is the finding that the Monte-Carlo sedimentation velocities are all low, as compared with the results of eq 31, though all within two standard deviations. Correspondingly, the viscosity quantities are all high, though again within two standard deviations. Comparing the reduced sedimentation velocities P_{kr} and P_{KR}, we see that the Monte-Carlo results are low, like the actual velocities; apparently the fluctuations in u and R do not entirely compensate each other, although the effects of changing N are largely eliminated. On the other hand, the viscosity quantities Φ show good compensation of the fluctuations of E and R. The Monte-Carlo value of the Flory–Mandelkern–Scheraga parameter B_{kr} is well within two standard deviations of the analytical value, B_{KR}.

The sedimentation rates from eq 37, the improved KR equation, are a step in the direction of the rigorous results, but only a small step.

Discussion and Conclusions

Fluctuations. Our scheme of first creating 500 random vectors and then combining them into sets of chains of various lengths was designed to reduce fluctuations when comparing one length with another. However, the results did not show that this design was notably more successful than a completely random selection would have been. The fluctuations with change of N within each set of quantities, such as R^2, Φ, and B, were not significantly less than the corresponding fluctuations between the sets.

Considering now the fluctuations within the one ensemble of ten chains displayed in Table I, the nature of these deserves comment. The large relative fluctuations in R^2 and h^2 are to be expected from the well-known distribution formulas for these quantities with Gaussian chains.[27,28] Likewise the free-draining viscosity number, as measured by E_{fd}, which by eq 42 is seen to be simply a component of R^2, should have a large fluctuation, as is observed, and it is hardly surprising that the "exact" and KR viscosity numbers behave similarly. In fact, the rank orders of the exact and the free-draining viscosities are the same except for one inconsequential inversion. Also to be expected is the fact that the rank ordering of the sedimentation velocities is nearly the inverse of the rank ordering of R^2, that is, the fastest sedimenting molecules are those that are folded most compactly. What is perhaps less expected is the relatively small fluctuation of the sedimentation velocity compared to the fluctuation in the other quantities; in fact, the percent standard deviation of the sedimentation velocity u is less than one quarter of that of R^2 or of E. That is, while the more compact molecules do sediment faster than the more extended ones, the magnitude of the difference is not great. This insensitivity to overall chain conformation probably comes from the inverse-distance character of the hydrodynamic interaction which causes short intersegment distances to be emphasized in sedimentation, in contrast to R^2, where linear dependence on R_{ij}^2 emphasizes the large distances; since there are fewer large distances, the statistical fluctuations are greater.

These fluctuations in the rate of sedimentation, and corresponding fluctuations in the rate of sideways motion, u_{hor}, change with time for individual molecules and should produce a series of random-flight excursions that should simulate ordinary diffusion.[29] However a numerical calculation using the velocities actually found in this work and estimates of the conformational relaxation times showed that the effect is at least a million times smaller than ordinary diffusion with random coils of molecular weights less than 10^8 in centrifugal fields found in present centrifuges.

Implications for Real Chains. We must warn against any attempt to apply our results on, say, the 51-segment chain to any real chain of 51 monomer units. The segments in our model are an abstraction, and the model with a given number of segments is not intended to represent literally some real chain since we have not taken accurate account of the hydrodynamic interaction within segments or between overlapping segments. We believe, however, that this model and real flexible chains of a variety of structures all approach a similar limit, the so-called "nondraining" limit, as the number of segments becomes indefinitely large,[22] and what we are attempting to do is to see how the properties of the model behave as the limit is approached. The current work deals specifically with Gaussian chains in Θ solvents, since we have not imposed on the segments either limited flexibility or excluded volume.

With these remarks in mind we present Figure 1, where we have plotted some of our results as functions of the number of intersegment vectors, N. In the KR approximation P, Φ, and B become linear functions of $N^{-1/2}$ as N approaches infinity, hence the choice of $N^{-1/2}$ as abscissa. What appear are consistent and almost linear trends of the three quantities, which show the deviations of the "exact" from the KR quantities getting larger as N becomes larger. The forms of the curves suggest a linear extrapolation to infinite N. Very tentatively we make this extrapolation and add the results to the analytical KR values in Table II; the results are given in Table IV. With more confidence we can at least take the values in Figure 1 at $N = 50$ as lower limits to the values at infinite N; these give the minimum estimates also recorded in Table IV. (The latter is omitted for Φ, since here the dependence on N is so small.)

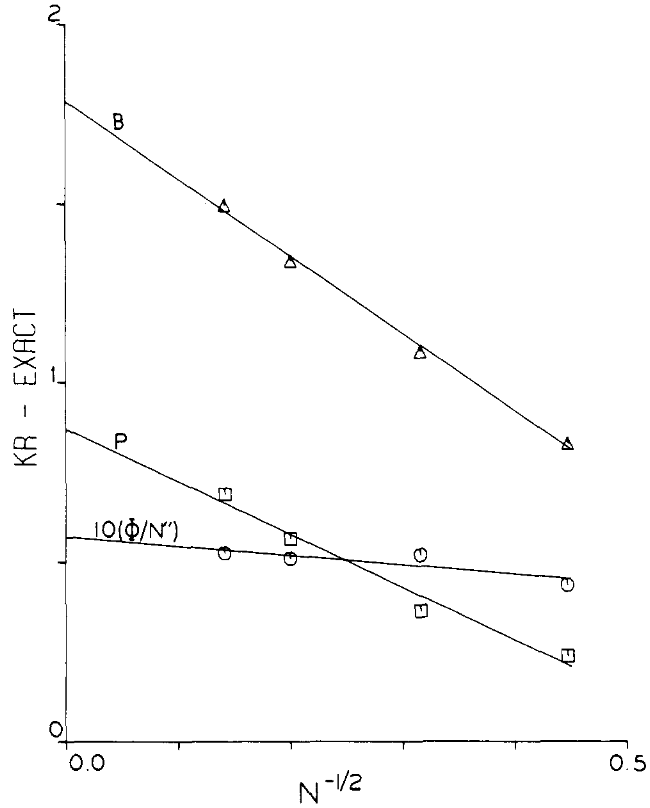

Figure 1. The differences, $(\Phi_{kr} - \Phi)/N''$, $P - P_{kr}$, and $(B - B_{kr}) \times 10^{19}$ are plotted as functions of the reciprocal of the square root of the number of intersegment vectors, N.

Table IV
Estimates of Hydrodynamic Parameters at Infinite N

quantity	minimum	extrapolated
P	5.80	5.99
Φ/N''		0.417
Φ		2.51×10^{23}
β	2.35×10^{6}	2.29×10^{6}
B	6.81×10^{-19}	7.10×10^{-19} [a]
B		7.18×10^{-19} [b]

[a] By linear extrapolation of $B - B_{kr}$. [b] From the values of $P - P_{kr}$ and $(\Phi_{kr} - \Phi)/N''$ extrapolated separately.

It is pleasing to note that the value of Φ, 2.51×10^{23}, is in fair agreement with Pyun and Fixman's estimate[7] of 2.66×10^{23} obtained from the first two orders of a perturbation scheme.

The conclusion is clear; the KR approximation overestimates the sedimentation rate of a long Gaussian chain by at least 13%, and it also overestimates the viscosity number by at least 12%. That both quantities are overestimated is somewhat surprising, since one is a mobility and the other a resistance, but such is the case.

As a result, the two ways of calculating the constant, B, in the Flory-Mandelkern-Scheraga formula differ by nearly 30%, with the exact value being higher, that is, leading to higher molecular weights.

General Remarks. We have tested the Kirkwood-Riseman approximations on a random sample of model polymer chains and have found that these approximations do indeed lead to some inaccuracy in the sedimentation coefficient and in the viscosity number. However, it is this author's feeling that the approximations work surprisingly well, certainly well enough to justify the widespread use to which they have been put in the three decades since they were originally published. The inaccuracy that results from their use is about the same as the usual precision of the corresponding experimental quantities, considering that three measurements, of a hydrodynamic quantity, of a molecular weight, and of a radius of gyration, must be combined for any meaningful comparison. For critical applications, however, the corrections obtained in this paper should be applied, incomplete though they may be.

The methods used herein obviously have wider application. It would be easy to modify the program to generate chains of various types, such as chains containing excluded volume or wormlike character, for example, and also to calculate other quantities, such as rotational diffusion coefficients. Some work on the last problem by Dr. Paul Hagerman is in progress, and the author has carried out some preliminary studies of the effect of excluded volume. The author would be glad to supply copies of the ALGOL program to anyone who is interested.

One serious difficulty that limits the use of the Monte-Carlo method requires attention. As mentioned at the end of the section on methods, the growth of the number of operations and of the number of storage locations is so rapid with increasing N as to set an effective ceiling on N near 100 for any presently conceivable computing machine, unless some new method is introduced. The diagonal approximation of de la Torre and Bloomfield is a useful step in this direction, but some even more drastic simplification seems to be needed to make the treatment of an accurate model of a real molecule possible.

Addendum. Dr. Marshal Fixman has pointed out in private discussion that the viscosity can be calculated for a flow pattern with an axis of cylindrical symmetry (so-called elongational flow[30]). In this case the arguments of Appendix A apply, and just as in sedimentation, Ω_z is not zero, but must be treated as an unknown, while we must set the torque around the z axis equal to zero. Equation 9 for the flow in this case becomes

$$v_{0ix} = (\kappa/2)x_i \qquad v_{0iy} = (\kappa/2)y_i \qquad v_{0iz} = -\kappa z_i \tag{45}$$

and eq 23 for E is replaced[31] by

$$E = \sum(-x_iF_{ix} - y_iF_{iy} + 2z_iF_{iz})/[3(N+1)\kappa\eta b^3] \tag{46}$$

Here the z axis is the axis of cylindrical symmetry.

In order to see what the actual numerical effects of the rotation about the cylindrical axis were, we carried out a calculation both with $\Omega_z = 0$ and with Ω_z as an unknown, and for both sedimentation and viscosity, on the first 500 random vectors. The averaged results are shown in Table V. The values of Ω_z shown are root mean squares. The sedimentation part of the calculation with Ω_z as an unknown is identical with that of Table I; the viscosity part differs only because of the different flow pattern.

It can be seen that while the rotation rates themselves are appreciable, their effects on sedimentation and viscosity are negligibly small. A fundamental problem is raised by this result, however. The viscosity is a coefficient in a linear relation between the stress tensor and the velocity gradient tensor. The flow pattern of eq 45 is a linear superposition of two patterns of the type of eq 9. If the viscosity is to be a constant coefficient, we should solve eq 45 under the same conditions, $\Omega_z = 0$, that we used with eq 9. But for the flow pattern of eq 45 we deduced that we should properly use the condition that Ω_z is a variable and the total torque about the z axis is zero. We have just seen that the results under these two conditions are not the same, although the difference is very small. Hence the viscosity appears not to be a constant, which is paradoxical.

Table V
Effect of Rotation Around the Axis of Cylindrical Symmetry

	N			
	5	10	25	50
no. of chains in sample	100	50	20	10
	$\Omega_z = 0$			
u_z	0.4275	0.5651	0.8717	1.2126
E	1.6448	2.6196	4.6808	6.9911
	Ω_z Variable			
u_z	0.4277	0.5653	0.8720	1.2130
Ω_z(sed.)	0.0102	0.0069	0.0075	0.0073
E	1.6441	2.6189	4.6799	6.9888
Ω_z(visc.)	0.0419	0.0330	0.0286	0.0421

A discussion of the validity of the Kramers rigid-body postulate, but for the case of the preaveraged KR tensor, has been given by Gotlib and Svetlov.[32]

Acknowledgment. I would like to thank Walter H. Stockmayer for informing me of some unpublished work bearing on the rotation problem by Wilemski, Tanaka, and himself, and I would like to thank him and Marshal Fixman for long-distance discussions of that subject. Dr. Fixman also graciously sent me a preliminary copy of a manuscript in which he further studies the matter.

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Appendix A: Rotation and Brownian Motion

Rotation of a molecule in sedimentation or in the irrotational shear flow of eq 9 can be induced by hydrodynamic interaction with the flow. To the extent that these rotations tend to disturb the orientational distribution of the molecule, they will be opposed by Brownian motion and their effects will be minimized. However continuous steady rotation in one direction cannot disturb the orientational distribution if the latter is already symmetrical. Therefore the crucial question is whether the induced rotation is continuous and steady, or whether it varies with the angle of rotation.

To make these ideas quantitative we introduce an angle of rotation, θ, measured about some axis of interest. The orientational probability distribution function of this angle is $\psi(\theta)$. The current of rotational flow in the ensemble is, of course, $\psi(\theta)\dot{\theta}$. This current is composed of a part, $\psi\dot{\theta}_h$, induced by the externally imposed force or flow and a Brownian-motion part, proportional to minus the gradient of ψ times a diffusion coefficient, Θ. In the steady state the divergence, that is, the derivative with respect to θ, of the total current must be zero:

$$\partial(\psi\dot{\theta})/\partial\theta = \partial(\psi\dot{\theta}_h)/\partial\theta - \Theta\,\partial^2\psi/\partial\theta^2 = 0 \tag{A1}$$

This current is, of course, the average current in the ensemble. But since the hydrodynamic equations, eq 3–6, are linear in the rotation rate, Ω, the averaging commutes with solving the equations, and it is valid to use an average current in the equations.

Upon integrating eq A1 from 0 to 2π we find,

$$\psi\dot{\theta} = \psi\dot{\theta}_h - \Theta\,\partial\psi/\partial\theta = \text{constant} \tag{A2}$$

And if we integrate again, we find,

$$\int \psi\dot{\theta}\,d\theta = 2\pi\psi\dot{\theta} = \int \psi\dot{\theta}_h\,d\theta - \Theta[\psi(2\pi) - \psi(0)] \tag{A3}$$

But ψ must be single valued, so the last term vanishes. Also, at low flow rates ψ has changed very little from its equilibrium constant value of $1/2\pi$ so it may be factored out of the integral, and we finally get

$$\dot{\theta} = \frac{1}{2\pi}\int_0^{2\pi} \dot{\theta}_h \, d\theta \tag{A4}$$

Thus the ensemble-averaged net rotation rate, $\dot{\theta}$, at any angle θ is a constant equal to just the average around the rotation axis of the hydrodynamically induced part of this rotation, as long as the perturbations resulting from the flow are small.

We can now show that in many cases $\dot{\theta}_h$ varies with θ in such a way that its average, the integral in eq A4, is zero. To do this, for example, for the rotation about the x axis of a molecule sedimenting in the z direction, we recognize that $\dot{\theta}_h$ would in this case be just Ω_x in the set of eq 4 and 5, but generalized to include Ω_x as well as Ω_z. We can easily show from these equations that Ω_x must oscillate symmetrically about zero as θ goes from 0 to 2π. We simply rotate the molecule about the x axis by π radians without changing its shape; thereby x remains the same, but the values of y and z are replaced by their negatives. Each coefficient in the equations either remains the same or changes sign; consequently each variable must do one or the other. The total force $\mathbf{F}$ does not change sign, so none of the individual forces $\mathbf{F}_i$ can change. Examination of the equations in detail then easily shows that Ω_x must change sign in this rotation. Hence its integral over the domain 0 to 2π vanishes. Remembering that we have left Brownian motion out of account, we can identify Ω_x here with $\dot{\theta}_h$. However, from eq A4 we see that the true $\dot{\theta}$, with Brownian motion included, must vanish. In effect, Brownian motion imposes a constraint on the system such that the average rate of rotation around the x axis is zero. Hence in solving the equations with Brownian motion considered we must set $\Omega_x = 0$.

We can make the same argument for Ω_y in the same situation, but the argument fails for Ω_z. In fact, since the z axis is the symmetry axis of the external force, it is obvious that rotating the molecule around it does not change the distribution function ψ, also that there can be no diffusion current around it, and finally that Ω_z is constant for all θ. The result, from eq A4, is that

$$\dot{\theta} = \dot{\theta}_h = \Omega_z \tag{A5}$$

Hence Ω_z is an unknown that must be obtained by solving eq 4, 5, and 6, with the external torque set equal to zero.

The same argument can be applied to Ω_x and Ω_z for a molecule in the irrotational shear flow of eq 9. Both Ω_x and Ω_z are zero in this case when Brownian motion is taken into account. For Ω_y the argument has to be changed slightly, using a rotation of $\pi/2$ about the y axis instead of π, but the conclusion is that $\Omega_y = 0$ also.

Thus the effects of Brownian motion on rotation appear as certain constraints in the hydrodynamic equations. In some cases these constraints are imposed on the components of the rotation rates, Ω, and in others on the components of the external torque.

Appendix B

This section describes the determination of the crossover radius, R_c. This is the radius at which the angular average of the translational friction coefficient, f, of two interpenetrating segments becomes equal to f of the branched chain formed by joining the two segments at their centers. The friction coefficient of the latter was calculated by Stockmayer and Fixman;[16] it is $2/(3(2^{1/2}) - 2)$ times f of the linear chain formed by joining two segments end to end. The latter in the KR approximation is $2^{1/2}$ times the f of one segment, so we get that f of the branched chain is

$$f_{\mathrm{br}} = 2\rho/(3 - 2^{1/2}) \tag{B1}$$

ρ being the friction coefficient of one segment.

To get the friction coefficient of two overlapping segments, numbers 1 and 2, with an interaction tensor of T (T actually a scalar in this case), we must solve the special case of eq 3 and 5 (eq 6 is identically satisfied with two segments):

$$(1/\rho)F_1 + TF_2 - u = 0 \tag{B2a}$$

$$TF_1 + (1/\rho)F_2 - u = 0 \tag{B2b}$$

$$F_1 + F_2 = 2 \tag{B2c}$$

from which we find that $u = 1/\rho + T$. (For simplicity we have left the x and y components out of the calculation; F_1, F_2, and u refer to the z component only.) The friction coefficient is the ratio of the total force, 2, to u, so that for two overlapping segments,

$$f_{\mathrm{ov}} = 2/(1/\rho + T) \tag{B3}$$

Equating eq B1 and B3, and using $\rho = 6\pi\eta a$, we find

$$T = (2 - 2^{1/2})/(6\pi\eta a) \tag{B4}$$

To determine the crossover radius, R_c, we require that this be equal to the orientational average of $\mathbf{T}_{ij}$ at $R_{ij} = R_c$, the average of which is the scalar $1/(6\pi\eta R_c)$. So the result is

$$R_c = a/(2 - 2^{1/2}) \tag{B5}$$

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Investigation of Local Motions in Polymers by the Method of Molecular Dynamics

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ABSTRACT: The main features of local motions in linear polymer chains and in cross-linked macromolecules were studied by the method of molecular dynamics. The chain model consists of particles connected by rigid bonds and interacting with each other and with solvent particles with Lennard-Jones potential forces. Chains with various numbers of units were considered at various concentrations and temperatures. The characteristics of local motions (translational and rotational mobility), normal modes, and cooperative motions and the effect of cross-linking on local chain mobility were investigated. The results of numerical experiments (NE) are compared with analytical results for a viscoelastic Hearst–Harris (H–H) model. It is shown that the characteristics of both local motions and normal modes are close to those of viscoelastic models. The dependence of the characteristic relaxation times of normal modes on the wavenumber virtually coincides with that for the H–H model. The present study suggests that in cross-linked systems the translational and rotational mobility of the cross-link and the adjoining chain elements are greatly hindered. The relationship between the characteristic times obtained in NE and experimental results on dielectric relaxation and polarized luminescence is discussed.

The molecular theory of equilibrium properties of polymers in solution, in the melt and in bulk, is based on the principles and methods of conformational statistics of macromolecules developed by Flory and co-workers,[2] Volkenstein,[3a] Ptitsyn and Birshtein,[3b] and others. This theory started from simple models of a polymer chain describing qualitatively the observed relationships. Models of real chains as developed at present permit the determination of numerical values of physical parameters. In contrast, in the molecular theory of the nonequilibrium relaxation process in polymers we are only at the beginning of our path. The dynamic theory of polymers uses mainly semiphenomenological viscoelastic models that describe the average motion of chain segments containing many units. The transition to models in which the kinetic element is represented by a rigid link or a monomer unit rather than by a flexible subchain is difficult, because their analytical description involves substantial mathematical difficulties. These difficulties increase on passing from the description of the motion of a single chain in a continuous viscous medium to a more detailed description in which the interactions of polymer particles with each other and the solvent are explicitly taken into account.

Computer simulation of molecular motion is the most suitable method for solving these problems. According to the degree of precision desired, different models and corresponding methods of motion simulation may be used. In lattice chain models, motion occurs as a result of random local rearrangements of chain elements. The mechanism of local mobility (various types of elementary jumps) is postulated and its manifestations in various dynamic chain characteristics are considered. Monte-Carlo methods are used for computer simulation of the motion of such models.[4-8]

The method of Brownian dynamics[9-12] consists of numerical solution of Langevin equations. This method makes it possible to take into account rigid bonds, valence angles, and the potential energy of internal rotation.[11] Ceperley and co-workers[12] take into account also the spatial interactions of chain particles separated from each other along the chain contour. Just as for viscoelastic models, the medium surrounding the macromolecule is described as a continuous viscous liquid which is also a source of random Brownian forces affecting chain elements.

The method of molecular dynamics (MD) provides an even more detailed description; it takes into account explicitly both the interactions between chain units and the interactions with solvent particles. During the last two decades this method has been widely used in the physics of liquids.[13-15] It was developed for polymer chains by Balabaev, Grivtsov, and Shnol[16-18] and applied to the investigation of relaxation properties of polymers by the present authors.[19,20] The MD method seems to be the most suitable for describing highly condensed systems, for which it is doubtful whether the medium surrounding a given macromolecule can be described as a continuous liquid. Because computer time is limited, a combination of these complementary methods probably offers the best solution. The results obtained by a more detailed method may provide the basis for a more "grain-coarsed" description.

The present work deals with some results of a study of local mobility in macromolecules in the liquid phase (in solution and in the melt) by the MD method. The study was carried out with the simplest model for a polymer chain: a chain of point-like particles with mass m bonded by rigid bonds and interacting with each other and with similar solvent particles with Lennard-Jones potential forces. This model is a polymeric analogue of a model widely used for studying the properties of simple liquids by the MD method.[14] Recently works of other authors dealing with the MD of oligomers and polymers have also appeared.[21-23] They consider mainly the mathematical

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