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Translational diffusion of chain polymers. II. Effect of internal friction[a)]

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The translational diffusion constant $D_0(\lambda)$ of chain polymers has been evaluated for models that contain internal friction measured by a strength parameter λ. $D_0(\lambda)$ is an upper bound to the true diffusion constant $D(\lambda)$. The method of evaluation is based on the facts that the power series expansion of $D_0(\lambda)$ in λ is a series of Stieltjes, and the coefficients in this power series permit a rapid evaluation from equilibrium simulations. Convergent Padé approximants are therefore available. Results are reported for theta point chains with N beads, including Gaussian and lattice models, with $N \leqslant 1792$. In the limit $\lambda \to \infty$, $D_0(\lambda)$ approaches the translational diffusion constant of a chain that diffuses as a rigid body, and this diffusion constant $D_0(\infty)$ is known to be a lower bound to $D(\lambda)$. The two main findings are these: First, $D_0(\infty)$ is approached very closely by $D_0(\lambda)$ for fairly modest values of λ, comparable in size to ordinary bead friction constants. Second, the ratio R_G/R_H of radius of gyration to hydrodynamic radius, which is the same as $D_0(\lambda)/D_0(0)$, seems to have a limit at $N \to \infty$ which depends on the backbone model, and probably depends on the bead friction constant. That is, as a result of fluctuations in hydrodynamic interaction the translational diffusion constant fails to satisfy universality. The deviations seem to be rather small for this transport property, on the order of 5%.

I. INTRODUCTION

The simpler transport coefficients of chain polymers, such as the translational and rotational diffusion constant and the intrinsic vicosity, are generally held to be independent of detailed structural properties and conformational relaxation rates, in the long chain, nondraining limit. In this limit the specified transport coefficients are believed to be determined entirely by the radius of gyration of the chain and the viscosity of the solvent. Here a contrary view is inferred from simulations that include "internal friction." It seems quite improbable, in view of the simulations, that the proportionality constants connecting the radius of gyration and the hydrodynamic radii for the various transport coefficients are related by universal proportionality constants, independent of local structure, local relaxation rates, and polymer species.

The first doubts about the conventional view resulted from dynamical simulations[1] of the translational diffusion constant D and intrinsic viscosity, and were strengthened by equilibrium simulations[2] of D. In the present work internal friction between beads nearby along the backbone is introduced into the model, which previously allowed for fluctuating hydrodynamic interaction, and quite dramatic effects on translational diffusion are found.

The model may be summarized in the equation of motion

$$\mathbf{F}_i^T = -\mathbf{F}_i^H + \mathbf{F}_i^I + \mathbf{P}_i + \mathbf{S}_i, \tag{1.1}$$

$$\mathbf{F}_i^H \equiv \beta(\mathbf{V}_i - \mathbf{V}_i'), \tag{1.2}$$

where $\mathbf{F}_i^T$ is the total force on a bead i. The total force is set to zero in the approximation of vanishing inertia.

The ordinary frictional resistance to motion of a bead through the solvent is given by the first term on the right-hand side of Eq. (1.1); β is a friction constant, $\mathbf{V}_i$ is the velocity of the bead, and $\mathbf{V}_i'$ is the perturbed solvent velocity. The latter has a long ranged part given by the Oseen interaction.

The internal friction force $\mathbf{F}_i^I$ is in general proportional to some linear combination of the components of relative velocity, such as $(\mathbf{V}_j - \mathbf{V}_k)$. The restricted form that has been used will be discussed below. We note, however, that we have not been constrained by the designation "internal" to use only the most limited possible forms of $\mathbf{F}_i^I$. Rates of crossing rotational barriers will depend on the solvent and may be proportional to solvent viscosity, the resistance to small group rotations may not be given accurately by the chosen form of hydrodynamic interaction; one or both such effects may be the physical basis[3,4] of $\mathbf{F}_i^I$. The main distinction between $\mathbf{F}_i^H$ and $\mathbf{F}_i^I$ is that the former force is supposed to act with equal magnitude and opposite sign on the polymer bead and the solvent, and therefore produces a long ranged perturbation of solvent flow. The work produced by $\mathbf{F}_i^I$, on the other hand, is presumed to be dissipated promptly as heat at or near the point of application. For physical consistency, therefore, it must be supposed that $\mathbf{F}_i^I$ is a short ranged force. It is in addition supposed here that $\mathbf{F}_i^I$ depends only on the velocity and position of other beads j such that $|i - j|$ is small.

The potential force $\mathbf{P}_i$ includes an external force that drives the sedimentation or diffusion process, and a backbone force that holds the chain together. No excluded volume forces between beads far apart along the backbone were included in the simulations. Finally $\mathbf{S}_i$ is the random or entropic force $-k_B T \nabla_i \ln \Psi$, where Ψ is the probability density for chain configurations.

In outline the work is as follows. In Sec. II the bead velocities and diffusion constant are formally evaluated. It is found that the only modification caused by the introduction of internal friction is to replace the usual HI matrix H by $(H^{-1} + \lambda Q)^{-1}$, where Q enters as the proportionality ma-

trix connecting the array F^I to the array of bead velocities V, $F^I = -\lambda QV$. λ is a number introduced to measure the strength of internal friction. (The effect of internal friction on the viscosity problem, or on other problems for which the unperturbed fluid velocity is nonvanishing, is more complicated.)

In Sec. III the previous bounds[5-7] on transport coefficients, which are here applied only to translational diffusion, are considered for the modified diffusion matrix. It is found that Zimm's algorithm[8] for D, which involves the assumption or rigid body motion and was later determined to yield a lower bound[7] D_{LB}, is entirely unaffected by the introduction of internal friction. The focus of the calculation is therefore on upper bounds D_{UB}. One such upper bound $D_0(\lambda)$ is evaluated by simulations. If internal friction is sufficiently strong that the polymer molecule is limited to rigid body motion, one expects that $D(\lambda) \rightarrow D_{LB}$, because D_{LB} is a calculated diffusion constant for a chain undergoing rigid body motion. It seems also that $D_0(\lambda)$ approaches $D(\lambda)$ or D_{LB} under the same condition of strong internal friction, but this is mainly an empirical observation. To show that such a convergence must occur involves a limiting process that is only briefly considered in Sec. III.

In Sec. IV a technical feature of the modified diffusion matrix is exploited in order to make the simulations feasible for long chains. It turns out that the upper bound to the diffusion constant expanded in powers of λ is in fact a series of Stieltjes.[9] Therefore Padé approximants formed from the coefficients of the series have known and favorable convergence properties. The coefficients may be calculated much more rapidly than the analytically summed series, since the latter requires matrix inversions and the former requires only matrix multiplications of a column matrix. And the Padé approximants give D as a function of λ, while the matrix inversions would have to be repeated for each value of λ.

The results are considered in Sec. V. The surprising finding is that the upper and lower bounds for linear polymer chains are brought into near coincidence by a very small amount of internal friction of the specified local nature. The magnitude of internal friction required to produce quasirigid motion, and reduce D to values close to the lower bound, need only be comparable with the magnitude of ordinary frictional forces. Planar rings of beads behave rather differently. As the number of beads and the radius of the ring increase, with a constant separation between neighboring beads, the strength of internal friction required to obtain rigid body behavior steadily increases. Probably the effect seen for rings is due to the decreasing resistance to long wavelength, out of plane motions, as the ring grows larger. These motions are difficult to control with short range interactions, as is now well known to bridge designers.

The physical origin of the observed failure of universality remains to be discovered. It may be that the picture of a porous but rigid sphere should be replaced by that of an oil drop, within which a certain amount of flow can occur, depending on the relative viscosities of the drop and the surrounding medium.[10] Alternative possibilities involve slipping of the solvent in the outer regions of a polymer coil, or large fluctuations of configuration which allow solvent pene-

tration at any chain length. It may be significant that the conventional diffusion matrix H has elements which are individually associated with two body hydrodynamic interactions, whereas the modifications due to internal friction in effect introduce many body interactions. In any event, no modification of H_{ij} which restricts the configurational dependence of H_{ij} to R_{ij} and which retains the long ranged Oseen form seems capable of showing the observed effects.

II. EQUATIONS OF MOTION

A. Introduction of internal friction

The total force F_i^T on a bead i, $i = 1,...,N$, has been decomposed in Eq. (1.1) into forces of varied physical origin. The determination of bead velocities still requires an expression for the perturbed solvent velocities V_i'. These are given by

$$V' = V^0 + TF^H, \tag{2.1}$$

where V^0 is the unperturbed solvent velocity and T is a matrix of hydrodynamic interaction (HI) dyadics T_{ij}. In general, an array is indicated by the suppression of subscripts that refer to individual beads. It follows from Eqs. (1.2) and (2.1) that

$$F^H = H^{-1}(V - V^0), \tag{2.2}$$

where

$$H \equiv \beta^{-1} + T. \tag{2.3}$$

The diffusion matrix H is presumed to be positive definite. The H_{ij} calculated by Rotne and Prager[5] have been used here, and possess the required property.

The force of internal friction is assumed to have the form

$$F_i^I = -\lambda \sum_j q_{ij} \cdot (V_i - V_j) \tag{2.4}$$

or

$$F^I = -\lambda QV, \tag{2.5}$$

where λ is a nonnegative ordering parameter that measures the strength of internal friction, and the dyadics q_{ij} are functions of configuration that remain to be specified. The required properties of these dyadics will be considered below. Substitution from Eqs. (2.2) and (2.4) into Eq. (1.1) gives

$$V = G[H^{-1}V^0 + P + S], \tag{2.6}$$

where

$$G \equiv (H^{-1} + \lambda Q)^{-1}. \tag{2.7}$$

Thus the matrices for hydrodynamic friction and internal friction add to give the total friction matrix G^{-1}. For the translational diffusion problem being considered, the motion is presumed to be induced by an external force which is included in P, and V^0 may be suppressed:

$$V = G(P + S). \tag{2.8}$$

Thus the bead velocities are given by similar formulas for chains with or without internal friction, if V^0 is suppressed. The effects of internal friction are fully expressed by the change in the diffusion matrix from H to G. This fact will be useful in applying previous results. If V^0 represents uniform

motion, for which QV^0 vanishes, a similar simplification applies to the formula for $V - V^0$.

B. Properties of internal friction

It is essential on both mathematical and physical grounds that Q be chosen a nonnegative matrix, i.e., that the energy dissipation

$$\lambda V^T Q V \equiv \lambda \sum \sum \mathbf{V}_i \cdot \mathbf{Q}_{ij} \cdot \mathbf{V}_j \qquad (2.9)$$

is nonnegative for any V. V^T is the transpose of V. It suffices to restrict q_{ij} in Eq. (2.4) to symmetric nonnegative dyadics, because then each term in the double sum

$$V^T Q V = \frac{1}{2} \sum \sum \mathbf{V}_{ij} \cdot \mathbf{q}_{ij} \cdot \mathbf{V}_{ij}, \qquad (2.10)$$

where

$$\mathbf{V}_{ij} \equiv \mathbf{V}_j - \mathbf{V}_i$$

is individually nonnegative.

It is perhaps desirable that energy dissipation due to internal friction should vanish for rigid body motion of the polymer. If the dissipation does not vanish, it is not entirely appropriate to refer to λQV as internal friction. Any dissipation due to rigid body motion would have to be ascribed to relative motion of the polymer framework and other degrees of freedom in the solvent or polymer. But this is mainly a question of nomenclature. The important physical distinction between F^H and F^I, both of which are frictional forces, is that stated in the Introduction; the former force acts directly between the solvent and polymer and produces long ranged perturbations in the solvent velocity, and a reactive force $-F^H$ on the polymer, while F^I is presumed to give no long ranged velocity perturbations. The microscopic source of F^I might well lie in motions, such as the rotation of small groups or passage over rotational energy barriers, that dissipate energy in proportion to the solvent viscosity. In that event the complete friction matrix $(H^{-1} + \lambda Q)$ will remain proportional to the solvent viscosity, which is of course not an internal property of the chain.

In practice it is clear from Eq. (2.10) that translational motion of the polymer results in no energy dissipation from (the given) internal friction. For pure rotation with angular velocity ω, $\mathbf{V}_{ij} = \omega \times \mathbf{R}_{ij}$, Eq. (2.10) shows that energy dissipation might occur unless the dyadic q_{ij} is highly restricted. The present calculations were based on

$$\mathbf{q}_{ij} = q(|i - j|)(\mathbf{1} + \mathbf{e}_{ij}\mathbf{e}_{ij}),$$

$$q(m) = \begin{Bmatrix} 1 \text{ if } m < m_{max} \\ 0 \text{ if } m > m_{max} \end{Bmatrix}, \qquad (2.11)$$

where $\mathbf{e}_{ij}$ is a unit vector along $\mathbf{R}_{ij}$. The $\mathbf{e}_{ij}\mathbf{e}_{ij}$ part of the dyadic does not produce energy dissipation in rotational motion, but the unit dyadic does produce a small amount of dissipation. The amount is proportional to N, on the average, according to Eq. (2.10). The total frictional dissipation for rotation of long chains[11] is proportional to N^2 in the absence of HI, and to $N^{3/2}$ in the presence of strong HI, so the introduction of internal friction does not lead to a direct dissipation of energy comparable to that caused by F^H for overall

motions of the chain. The indirect effects will be seen to be more significant. We might add that preliminary studies with the unit dyadic suppressed in Eq. (2.11) indicate no qualitative changes, although the effects are smaller.

C. Translational diffusion constant

As was seen above, if V^0 vanishes the only effect of internal friction is to replace H by G in the expression (2.8) for bead drift velocities. Consequently the various formulas previously derived[7] for the translational diffusion constant D may be used with that minor change. We put

$$D(\lambda) = D_0(\lambda) - D_1(\lambda), \qquad (2.12)$$

where

$$ND_0(\lambda) \equiv \langle A^T G A \rangle_e \qquad (2.13)$$

and

$$A_i \equiv \mathbf{e}_z. \qquad (2.14)$$

$\langle \ \rangle_e$ designates an equilibrium average over configurations, and $\mathbf{e}_z$ is a unit vector along the z axis. D is defined here as the ratio of the center-of-mass velocity to the external force per bead (rather than to the total force). $D_0(\lambda)$ reduces to the Kirkwood formula[11] if $\lambda = 0$. The correction to D_0 is given by[7]

$$ND_1(\lambda) = k_B T \langle f^D \mathcal{M}^{-1} f^D \rangle_e, \qquad (2.15)$$

where

$$f^D \equiv \Psi_e^{-1} \nabla^T (\Psi_e U), \qquad (2.16)$$

$$U \equiv G A, \qquad (2.17)$$

and $\mathcal{M}$ is a positive definite diffusion operator. $\mathcal{M}$ is given by the previous expression[7] with H replaced by G. Ψ_e is the equilibrium distribution function. Previous expressions that give upper and lower bounds for $D_1(\lambda)$ will be considered below.

III. UPPER AND LOWER BOUNDS ON DIFFUSION CONSTANT

A. Lower bound on D(λ)

Zimm's rigid body hypothesis has been shown[7] to provide an upper bound to D_1, which therefore yields a lower bound on $D = D_0 - D_1$. This lower bound can be shown as follows to be entirely unchanged by the incorporation of internal friction.

The upper bound on $D_1(\lambda)$ has the form[7]

$$ND_1(\lambda) \equiv \langle (U - V^a)^T G^{-1} (U - V^a) \rangle_e, \qquad (3.1)$$

where V^a is a trial set of bead velocities that is subject to certain restrictions. Rigid body translation and rigid body rotation around the direction $\mathbf{e}_z$ of the external force satisfy the restrictions, and are the most general motions for which simulations have been performed. V^a may actually be restricted to rigid body translation because the restricted rotational motion does not correlate with U in Eq. (3.1).

Substitution of U from Eq. (2.17), i.e., $U = GA$, into Eq. (3.1) gives

$$ND_1(\lambda) = \langle A^T G A - 2A^T V^a + V^{aT} G^{-1} V^a \rangle_e \qquad (3.2)$$

and combination with D_0 from Eq. (2.13) gives

$$ND_{LB}(\lambda) = \langle 2A^T V^a - V^a G^{-1} V^a \rangle_e. \qquad (3.3)$$

Since Eq. (2.7) for G gives

$$G^{-1} V^a = H^{-1} V^a + Q V^a = H^{-1} V^a \qquad (3.4)$$

and because $Q V^a$ vanishes if V^a represents rigid body translation, the lower bound to $D(\lambda)$ provided by Eq. (3.3) is unchanged by the incorporation of internal friction.

B. Upper bound on $D(\lambda)$

The crudest upper bound on $D(\lambda)$ follows from the observation that $D_1(\lambda)$ is positive, and therefore $D_0(\lambda)$ is itself an upper bound on $D(\lambda)$. The bound $D_0(\lambda)$ is computed in the simulations. It will be seen in the discussion of results, Sec. V, that $D_0(\lambda)$ decreases sharply as λ increases from 0.

A brief discussion of $D_1(\lambda)$ is appropriate. Extensive simulations[2] on variational lower bounds to $D_1(0)$ have been performed, with the rather curious results which motivated the present work on internal friction. It was found that the contribution of gross distortions of the chain to $D_1(0)$ were quite small; i.e., they were comparable with the estimate $D_1(0) = 0.016\,73 D_0(0)$ obtained for preaveraged HI.[1,8,11] The main contribution to $D_1(0)$ seen in the variational work was due to small scale (and therefore rapidly relaxing) distortions, just as had earlier been inferred from dynamical simulations.[1] It is not *a priori* clear what the effect on $D_1(\lambda)$ will be as λ is increased from zero, because two opposing effects in the expression (2.15) for $D_1(\lambda)$ come into play.

First, internal friction slows up the relaxation of local distortions and should decrease the eigenvalues of the operator $\mathscr{M}$. This effect would cause $D_1(\lambda)$ to increase. However, rigid body rotation is negligibly affected by internal friction, and should therefore provide a relaxation mechanism that limits the magnitude of this effect.

Second, increased internal friction should decrease f^D in Eq. (2.15). The vector U in Eqs. (2.16) and (2.17) is a product of the diffusion matrix G into the external force. Therefore, U gives the instantaneous velocities of the beads in response to the external force, in the absence of any potential forces. As internal friction increases, these velocities must reduce to those available to a rigid body. For such motion $U \nabla^T \Psi_e$ vanishes, and f^D will vanish if $\nabla^T U = 0$. The velocities due to center-of-mass motion, say U_C, will certainly give $\nabla^T U_C = 0$, and the average angular velocity of chains and the instantaneous angular velocity of rings will vanish, so probably f^D will become very small as internal friction increases. The condition earlier imposed,[7] that the divergence of the diffusion matrix vanishes, would make $\nabla^T U$ vanish, but this condition was not in fact used in any essential way in the derivation of bounds, and has not been imposed here.

Despite the absence of a proof, the simulations indicate that the dominant effect of increasing λ is a sharp decrease in f^D and $D_1(\lambda)$, and in fact that $D_1(\lambda)$ vanishes as $\lambda \to \infty$. This behavior is inferred from the observed approach of $D_0(\lambda)$ to rigid body results.[12]

IV. THE SERIES OF STIELTJES

The pratical evaluation of $D_0(\lambda)$ from Eqs. (2.13) and (2.7) is greatly facilitated by the observation that the power series expansion of $D_0(\lambda)$ in λ is a series of Stieltjes. Therefore Padé approximants formed from the coefficients in that series form useful bounds on $D_0(\lambda)$. Moreover, the fact that $D_0(\lambda)$ cannot decrease below the bound for rigid body motion as $\lambda \to \infty$ suggests that the Padé approximants ought to converge very well, and they do. The coefficients themselves are evaluated from the products of square matrices into column matrices, as opposed to the much slower process of matrix inversion required by a direct evaluation of $D_0(\lambda)$.

The demonstration that $D_0(\lambda)$ generates a series of Stieltjes mimics standard proofs that a positive definite matrix H and a symmetric matrix Q, which here is also nonnegative, can be simultaneously diagonalized. Let $E_1, E_1^{-1} = E_1^T$ be the orthogonal transformation that diagonalizes H:

$$E_1^{-1} H E_1 = H_1, \qquad (4.1)$$

where H_1 is diagonal. Then Eqs. (2.7) and (2.13) give

$$ND_0(\lambda) = \langle A_1^T (H_1^{-1} + \lambda Q_1)^{-1} A_1 \rangle_e, \qquad (4.2)$$

where

$$A_1 \equiv E_1^{-1} A,$$
$$Q_1 \equiv E_1^{-1} Q E_1 = E_1^T Q E_1. \qquad (4.3)$$

Because $E_1^{-1} = E_1^T$, Q_1 as well as Q is nonnegative. Next let E_2 be the square root of H_1; H_1 and E_2 are both diagonal. A stretching transformation with E_2 gives

$$ND_0(\lambda) = \langle A_2^T (1 + \lambda Q_2)^{-1} A_2 \rangle_e, \qquad (4.4)$$

where

$$A_2 \equiv E_2 A_1,$$
$$Q_2 \equiv E_2 Q_2 E_2. \qquad (4.5)$$

Finally, suppose that the symmetric matrix Q_2 is diagonalized by the orthogonal transformation E_3:

$$ND_0(\lambda) = \langle A_3^T (1 + \lambda Q_3)^{-1} A_3 \rangle_e, \qquad (4.6)$$

where

$$A_3 \equiv E_3^{-1} A_2,$$
$$Q_3 \equiv E_3^{-1} Q_2 E_3 = E_3^T Q E_3, \qquad (4.7)$$

and Q_3 is diagonal and nonnegative. With $Q_3(i)$ the ith term along the diagonal of Q_3,

$$ND_0(\lambda) = K \sum_{j=0}^{\infty} (-\lambda)^j \langle [Q_3(i)]^j \rangle_A, \qquad (4.8)$$

where

$$K \equiv \left\langle \sum_{i=1}^{3N} [A_3(i)]^2 \right\rangle_e \qquad (4.9)$$

and $\langle ... \rangle_A$ is an average over the continuous set of configurations and over the integer labels $i = 1,...,3N$, with (positive) weight $[A_3(i)]^2 \Psi_e$. Equation (4.8) constitutes the required form of a series of Stieltjes.

It follows that the $[d,n]$ Padé approximant to $D_0(\lambda)$, where d is the degree of the denominator polynomial in λ and n is the degree of the numerator polynomial, has certain

useful properties.[9] The $[d,d]$ approximant is an upper bound to $D_0(\lambda)$ and $[d,d-1]$ is a lower bound. The upper bounds turn out to converge quite rapidly with increasing d, the lower bounds more slowly. Since $D_0(\lambda)$ is itself an upper bound to $D(\lambda)$, the $[d,d]$ approximants are upper bounds to $D(\lambda)$ itself, and are altogether more useful, therefore, than other approximants.

In practice the series expansion is computed directly from Eqs. (2.7) and (2.13):

$$ND_0(\lambda) = \sum_{j=0}^{\infty} (-\lambda)^j c_j, \qquad (4.10)$$

where

$$c_0 = \langle A^T HA \rangle_e = ND_0(0) \qquad (4.11)$$

and

$$c_j = \langle (HA)^T Q (HQ)^{j-1} (HA) \rangle_e, \quad j > 0. \qquad (4.12)$$

The assumption is made here that the $[d,d]$ Padé approximant is carried to convergence with respect to d, and need not be distinguished from $D_0(\lambda)$. The results on linear chains show such convergence rather clearly for d in the range 8–16. The ring data for very large λ would have benefitted from somewhat larger d.

V. RESULTS

With the assumed convergence of $[d,d]$ Padé approximants to $D_0(\lambda)$, the following inequality relates the translational diffusion constant to the available bounds:

$$D_0(\lambda) \geqslant D(\lambda) \geqslant D_{LB}. \qquad (5.1)$$

The strength parameter λ for internal friction is the only explicit argument, but obviously the results will depend also on the functional form used for internal friction and on the integer parameter m_{max} of Eq. (2.11). The lower bound D_{LB} is indepenent of all aspects of internal friction. No simulation results for D_{LB} will be displayed. The simulations concern the upper bound $D_0(\lambda)$ obtained from Eqs. (4.10)–(4.12). However, the preliminary report[12] of this work showed good agreement betwen $D_0(\infty)$ and D_{LB} for Gaussian chains.

The results are expressed in terms of the quantity $D_0(\lambda)/D_0(0)$. The Padé approximant to the simulation results gives values of $D_0(\lambda)$ for all λ, including specifically the denominator $D_0(0)$. This value was in excellent agreement with analytical values, where they were known.

In terms of the ratio $\rho \equiv R_G/R_H$, where R_G is the radius of gyration and R_H is a hydrodynamic radius (defined in terms of the Stokes–Einstein expression for the diffusion constant),

$$D_0(\lambda)/D_0(0) = \rho(\lambda)/\rho(0). \qquad (5.2)$$

The quantity $\rho(0)$ represents Kirkwood's approximation for the diffusion constant, and for chains $\rho(0)$ approaches 1.5045 in the infinite chain limit. $\rho(\lambda)$ is, like $D_0(\lambda)$, an upper bound to the value formed from the exact diffusion constant for the given model. In other words, the true decrease in $\rho(\lambda)/\rho(0)$ below unity must be greater than the values which have been calculated for a given model.

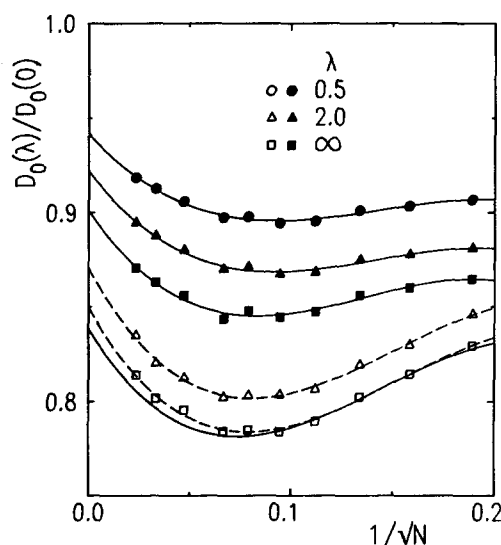The implied unit of length is always the bond length or

FIG. 1. The points are $D_0(\lambda)/D_0(0)$ for $28 < N < 1792$. The curves are least square fits of cubic polynomials in $1/\sqrt{N}$ to the points. Solid markers refer to Gaussian chains with bead diameter $d = 1$, and open markers refer to the cubic lattice model with $d = 1.5$. $m_{max} = 3$ except for the solid curve at the bottom, which refers to the cubic lattice model with $\lambda \to \infty$ and $m_{max} = 12$.

root mean square bond length, as is appropriate to the system being studied. Bead friction constants are specified by the Stokes diameter d expressed in this unit of length. Numerical values of λ are always expressed as ratios to the bead friction constant used for the particular calculation. Rotne–Prager HI was used except for the ring simulations, where the Oseen approximation was used.

Figure 1 includes the data shown before,[12] except for omission of the curve showing D_{LB}, and adds new points for $N = 1796$ and the curve for $m_{max} = 12$. The four choice cubic lattice model has relative weights 0.5, 1, and 2 for the
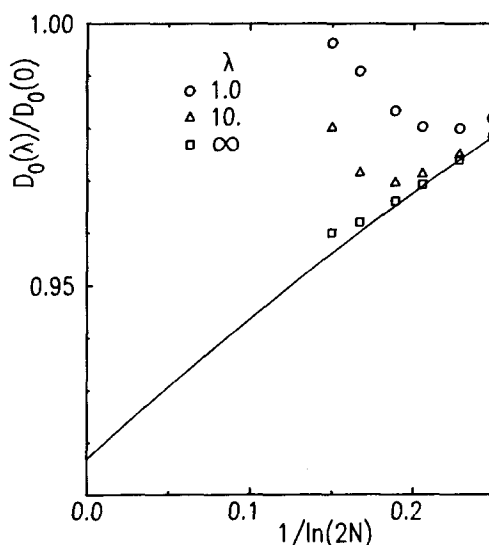

FIG. 2. Data for regular polygonal arrays of N beads with Oseen hydrodynamic interaction, $d = 0.9$, and $m_{max} = 3$. $N = (28, 40, 65, 100, 200, 400)$. The markers are simulation results and the curve shows exact results for a rigid array of beads.
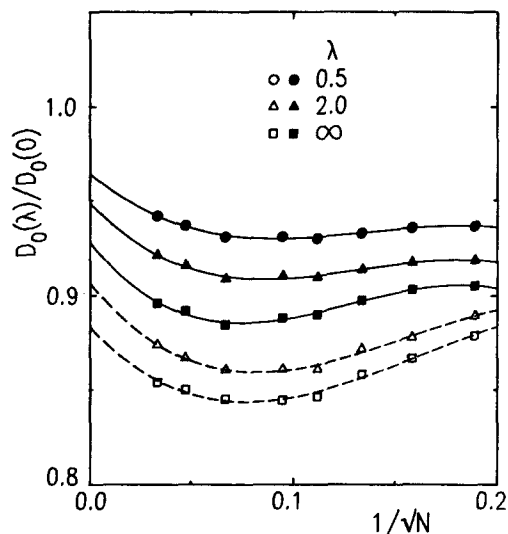
FIG. 3. Same notation as Fig. 1, except that $28 < N < 896$ and the bead diameter is $d = 0.5$ for the Gaussian and cubic lattice chains.

from 3 to 12 lowers the point for $N = 400$ from 0.960 to 0.958, still slightly removed from the exact 0.956. A possible physical origin of this difficulty in obtaining rigid ring limits was offered in the Introduction.

Figure 3 shows results similar to Fig. 1. The parameters differ only in the use of $d = 0.5$ for both Gaussian and lattice models.

Since the values of $D_0(\lambda)$ are upper bounds, while $D_0(\infty)$ seems to be in reasonably good agreement with D_{LB}, the specification of a moderate value such as $\lambda = 2$ in Figs. 1 or 3 would establish that $D(2)$ lies in the band between the two lowest curves appropriate to a given model, either Gaussian or lattice chains. A comparison between the Gaussian band in Fig. 3 and the lattice band in Fig. 1 indicates that the limiting values for $N \to \infty$ must lie more than 5% apart, unless there is an unexpected change in shape of the curves that is not predictable from data with $N < 1792$. Barring that change in shape, one is obliged to conclude that R_G/R_H is not a universal number in the infinite chain limit.

trans, gauche, and cis conformations, respectively; cis configurations were favored because the preceding work[2] showed larger effects of fluctuating HI for more compact configurations. The small difference between the two bottom curves is due entirely to the change in m_{max} from 3 (dashed curve and open markers) to 12 (solid curve). We assume that the diffusion constant for $\lambda \to \infty$ should be the same for any range of internal friction, i.e., for any m_{max}, and therefore ascribe the difference between the two curves to a residual difference between $D_0(\lambda)$ and the possibly larger value of the Padé approximant, which is what is actually calculated. The larger is m_{max} the faster is the convergence of the approximants with respect to order.

Rather different behavior with respect to λ is shown for regular polygonal arrays of N beads in Fig. 2. $N < 400$. The curves for different λ do not run parallel to each other with changing N, as they did for linear chain polymers. Instead, there is a strong tendency for the curves to diverge as N increases. The difference between the markers for $\lambda \to \infty$ and the exact[13,14] curve is again ascribed to a slight lack of convergence in the Padé approximants. An increase in m_{max}

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