The intrinsic viscosity of dilute solutions of stiff polymers*

U. M. Titulaer† and J. M. Deutch‡

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 9 July 1975)

The intrinsic viscosity of a dilute polymer solution is studied for a polymer model with rigid constraints on some quantities, such as bond lengths and bond angles. The constraints are introduced via a harmonic constraining potential; the strength of this potential is taken to infinity at the end of the calculation. Expressions for the frequency dependent intrinsic viscosity are obtained with the correlation function formalism. The limiting form for the case in which the constraints become rigid is obtained via a systematic expansion procedure. In the limit we obtain a contracted description in terms of the unconstrained variables only. We discuss the form of the polymer diffusion equation and various expressions for the stress tensor that may be used in the context of such a contracted description, as well as expressions for both the frequency dependent and the frequency independent part of the intrinsic viscosity. We compare our results with those of other authors. Complete agreement is found with the results of Fixman and Kovac, and with the corrected version of the theory of Erpenbeck and Kirkwood. Discrepancies are found with results of Doi, Nakajima, and Wada, and of Hassager. The origin of these discrepancies is explained.

I. INTRODUCTION

Recently considerable attention has been given to the dynamics of stiff polymer chains. In particular a number of alternative formalisms[1–4] have been presented for determining the frequency dependent intrinsic viscosity $[\eta(\omega)]$ for dilute polymer solutions. We have advocated[5] the correlation function method as an attractive procedure for determining $[\eta(\omega)]$. The purpose of this paper is to demonstrate how the correlation function method provides a direct way of determining $[\eta(\omega)]$ for a model polymer with constraints. We will treat the constraints by a method adopted earlier by Fraenkel[6] for a simpler model: we introduce a harmonic potential, characterized by a force constant κ, that keeps the constrained quantities close to their equilibrium values. After evaluation of the correlation functions we pass to the rigid limit $\kappa \to \infty$. We will also compare our results with those of alternative formalisms in order to clarify the relationship of the different approaches. The alternative approaches we consider are those due to Fixman and Kovac (FK),[1] Doi, Nakajima, and Wada (DNW),[2] and Hassager (H),[3] as well as the classical work of Erpenbeck and Kirkwood.[4]

The correlation function expression for the intrinsic viscosity[5] is

$$[\eta(\omega)] = \frac{N_A\beta}{M\eta_0}\int_0^\infty \exp[-i\omega t]\langle J_{xy}\exp[\mathfrak{D}^\dagger t]J_{xy}\rangle\, dt\ , \tag{1.1}$$

where N_A is Avogadro's number, M the polymer molecular weight, η_0 the solvent viscosity, and J_{xy} the appropriate expression for the xy component of the stress tensor. For a single polymer composed of N beads:

$$J_{xy} = -\sum_{n=1}^{N} x_n \frac{\partial U}{\partial y_n}\ , \tag{1.2}$$

where x_n (y_n) denotes the x (y) coordinate of the nth bead and U is the potential energy of interaction between the beads. In Eq. (1.1) the angular bracket denotes an average over the equilibrium distribution function $P_{\text{eq}} \propto \exp[-\beta U]$ and $\mathfrak{D}^\dagger$ is the adjoint of the Smoluchowski diffusion operator for the polymer; in $3N$ vector notation

$$\mathfrak{D}^\dagger = \nabla_{\mathbf{R}}^T \cdot \mathbf{D} \cdot \nabla_{\mathbf{R}} - \beta(\nabla_{\mathbf{R}} U)^T \cdot \mathbf{D} \cdot \nabla_{\mathbf{R}}\ , \tag{1.3}$$

where $\mathbf{R} \equiv (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and the diffusion tensor $\mathbf{D}$ is given by the $3N\times 3N$ matrix with 3×3 submatrices between $\mathbf{r}_n$ and $\mathbf{r}_m$ equal to

$$\mathbf{D}_{nm} = \beta^{-1}[\zeta_n^{-1}\mathbf{I}\,\delta_{nm} + \mathbf{T}_{nm}]\ , \tag{1.4}$$

where ζ_n is the bead friction constant and $\mathbf{T}_{nm}$ is the Oseen hydrodynamic interaction tensor with argument $\mathbf{r}_n - \mathbf{r}_m$.

In terms of the eigenvalues and eigenfunctions of $\mathfrak{D}^\dagger$, defined by the equation

$$\mathfrak{D}^\dagger f_m = -\lambda_m f_m\ , \tag{1.5}$$

we may write the expression (1.1) for $[\eta(\omega)]$ as

$$[\eta(\omega)] = \frac{N_A\beta}{M\eta_0}\sum_m \frac{|\langle J_{xy}|f_m\rangle|^2}{i\omega + \lambda_m}\ . \tag{1.6}$$

The scalar product $\langle A|B\rangle$ is defined as

$$\langle A|B\rangle = \int A^*(\mathbf{q})\,B(\mathbf{q})\,P_{\text{eq}}(\mathbf{q})\,J(\mathbf{q})\,d^{3N}\mathbf{q}\ , \tag{1.7}$$

with $\mathbf{q} \equiv (q_1, \ldots, q_{3N})$ a convenient set of coordinates and $J(\mathbf{q})$ the Jacobian of the transformation from $\mathbf{R}$ to $\mathbf{q}$.

The central task in the correlation function method is the determination of the eigenfunctions f_m and the associated eigenvalues λ_m. To determine these quantities for the case of a stiff polymer chain it is convenient to choose the system of coordinates in such a way that the first h of them, $Q_1 \ldots, Q_\alpha, \ldots, Q_h$, are the quantities, such as bond lengths and possibly bond angles, that are kept constant in the rigid limit. These coordinates are referred to as hard coordinates. They are supplemented by $3N$-h other coordinates, $q_{h+1}, \ldots, q_\alpha, \ldots, q_{3N}$, which will be referred to as soft coordinates.

Since the system of coordinates just described will in general be nonorthogonal it will be necessary to adopt tensor notation. For the reader's convenience we will state the few facts and definitions used in this paper: One distinguishes contravariant and covariant basis vectors,

$$\mathbf{e}_i \equiv \frac{\partial q_i}{\partial \mathbf{R}} \quad \text{and} \quad \mathbf{e}^i \equiv \frac{\partial \mathbf{R}}{\partial q_i} \; ; \tag{1.8}$$

with these one forms contravariant and covariant components of vectors and tensors, e.g.

$$A_i \equiv \mathbf{A} \cdot \mathbf{e}_i \quad \text{and} \quad B^{ij} \equiv \mathbf{e}^i \cdot \mathbf{B} \cdot \mathbf{e}^j \; . \tag{1.9}$$

The basic vector differential operators are given by

$$(\nabla f)^i = \frac{\partial f}{\partial q_i} \quad \text{and} \quad \nabla \cdot \mathbf{A} = J^{-1} \sum_{i=1}^{3N} \frac{\partial}{\partial q_i} J A_i \; , \tag{1.10}$$

where the Jacobian J equals

$$J = \left| \det(\mathbf{e}^i \cdot \mathbf{e}^j) \right|^{1/2} . \tag{1.11}$$

Finally, we will use the Einstein summation convention throughout the following discussion: every index that occurs both as a covariant and as a contravariant index is summed over its entire range, with the understanding that a "hard" index (a, b, c) runs from 1 to h, a "soft" index (α, β, γ) runs from $h+1$ to $3N$, and a "general" index (i, j, k) runs from 1 to $3N$. This means that summation signs such as the one in Eq. (1.10) will henceforth be omitted. No knowledge of tensor theory beyond what is recapitulated in this paragraph is needed to understand the theory presented in this paper.

As stated earlier, we will adopt Fraenkel's method[6,5] to describe the rigid constraints that are present in our polymer model. This implies that the potential energy of interaction U is the sum of a "soft" part $U^{(s)}$ and a potential that is harmonic in the deviations of the hard coordinates Q_a from their equilibrium values ${}^0Q_a$:

$$U = U^{(s)} + \tfrac{1}{2}\kappa\, G^{ab}(Q_a - {}^0Q_a)(Q_b - {}^0Q_b) \; , \tag{1.12}$$

where G^{ab} is an arbitrary, positive definite matrix, which may be a function of the configuration of the system. Eventually we will consider the rigid limit, in which the force constant becomes arbitrarily large.

When we substitute the form (1.12) for the potential and rewrite Eq. (1.3) in the coordinate system just described, using Eq. (1.10), we obtain

$$\mathfrak{D}^\dagger = J^{-1} \frac{\partial}{\partial q_i} J D_{ij} \frac{\partial}{\partial q_j} - \beta \left(\frac{\partial U^{(s)}}{\partial q_i} \right) D_{ij} \frac{\partial}{\partial q_j} - \beta\kappa\, G^{ab}(Q_b - {}^0Q_b) D_{aj} \frac{\partial}{\partial q_j} \; . \tag{1.13}$$

The equilibrium distribution function is

$$P_{\mathrm{eq}}(\mathbf{q}) = \mathfrak{N} \left| \det G \right|^{1/2} \kappa^{h/2} \times \exp[-\beta U^{(s)} - \tfrac{1}{2}\beta\kappa\, G^{ab}(Q_a - {}^0Q_a)(Q_b - {}^0Q_b)] \; , \tag{1.14}$$

where $\mathfrak{N}$ is a normalization constant chosen such that

$$\int P_{\mathrm{eq}}(\mathbf{q}) J(\mathbf{q})\, d^{3N}\mathbf{q} = 1 \; . \tag{1.15}$$

II. DETERMINATION OF THE EIGENFUNCTIONS

In order to determine the eigenfunctions in the limit when κ becomes large we separate the operator $\mathfrak{D}^\dagger$ into a sum of terms selected according to their order in $\kappa^{-1/2}$

$$\mathfrak{D}^\dagger = \mathfrak{D}^{(-2)} + \mathfrak{D}^{(-1)} + \mathfrak{D}^{(0)} + \dots \; . \tag{2.1}$$

In this evaluation $(Q_a - {}^0Q_a)$ is considered a quantity of order $\kappa^{-1/2}$ and $\partial/\partial Q_a$ is considered a quantity of order $\kappa^{1/2}$ when it is able to remove a factor $(Q_a - {}^0Q_a)$. Clearly the leading term in the above expansion is

$$\mathfrak{D}^{(-2)} = {}^0D_{ab} \frac{\partial}{\partial Q_a} \frac{\partial}{\partial Q_b} - \beta\kappa\, {}^0G^{ab}\, {}^0D_{bc} (Q_a - {}^0Q_a) \frac{\partial}{\partial Q_c} \; , \tag{2.2}$$

where the left superscript zero on any function of $\mathbf{q}$ denotes that the hard coordinates are replaced by their equilibrium values ${}^0Q_a$. The explicit expressions for $\mathfrak{D}^{(-1)}$ and $\mathfrak{D}^{(0)}$ are lengthy and accordingly relegated to Appendix A.

In order to determine the eigenvalues and eigenfunctions of $\mathfrak{D}^\dagger$ we write the eigenfunctions as a sum of contributions $f^{(j)}$ of order $\kappa^{-j/2}$:

$$f = f^{(0)} + f^{(1)} + f^{(2)} + \dots \; , \tag{2.3}$$

and similarly the eigenvalues; these depend analytically on κ and are therefore of the form

$$\lambda = \lambda^{(-2)} + \lambda^{(0)} + \lambda^{(2)} + \dots \; . \tag{2.4}$$

Substitution of Eqs. (2.1), (2.3), and (2.4) into the eigenvalue equation, Eq. (1.5), and equating terms of the same order in $\kappa^{-1/2}$, leads to the relations

$$\mathfrak{D}^{(-2)} f^{(0)} = -\lambda^{(-2)} f^{(0)} \; , \tag{2.5a}$$

$$\mathfrak{D}^{(-1)} f^{(0)} + \mathfrak{D}^{(-2)} f^{(1)} = -\lambda^{(-2)} f^{(1)} \; , \tag{2.5b}$$

$$\mathfrak{D}^{(0)} f^{(0)} + \mathfrak{D}^{(-1)} f^{(1)} + \mathfrak{D}^{(-2)} f^{(0)} = -\lambda^{(0)} f^{(0)} - \lambda^{(-2)} f^{(2)} \; . \tag{2.5c}$$

The solution of Eq. (2.5a) proceeds by the standard method.[7] We first determine the right eigenvector $P^a_{(l)}$ of the nonsymmetric matrix ${}^0G^{ab}\, {}^0D_{bc}$, which obey the relations

$${}^0G^{ab}\, {}^0D_{bc} P^c_{(l)} = \mu_{(l)} P^a_{(l)} \, ; \; P^a_{(l)}\, {}^0D_{ab} P^b_{(m)} = \delta_{lm} \; . \tag{2.6}$$

When we define the quantity

$$Q'_{(l)} = P^a_{(l)}(Q_a - {}^0Q_a) \; , \tag{2.7}$$

then the eigenvalues and eigenfunctions of Eq. (2.5a) may be written as

$$\lambda^{(-2)}(n_1, \dots, n_h) = -\beta\kappa \sum_{l=1}^{h} n_l\, \mu_{(l)} \; , \tag{2.8a}$$

$$f^{(0)}(n_1, \dots, n_h) = C(n_1, \dots, n_h) \prod_l H_{n_l}[(\beta\kappa\,\mu_{(l)})^{1/2} Q'_{(l)}] \; , \tag{2.8b}$$

where $n_1, \dots, n_h$ are nonnegative integers, $H_n(x)$ denotes the nth Hermite polynomial, and $C(n_1, \dots, n_h)$ is an as yet arbitrary function of the soft coordinates, subject to the normalization requirement that

$$\int |f^{(0)}|^2 P_{\mathrm{eq}} J\, d^{3N}\mathbf{q} = 1 \; . \tag{2.9}$$

For those eigenfunctions for which the parameter $\hat{n} = \sum_l n_l$ does not vanish it will not be necessary to proceed further. For convenience we denote eigenfunctions from this set by the symbol h. For those eigenfunctions for which the parameter is zero, $\lambda^{(-2)}$ vanishes and $f^{(0)}$ is a function of the soft coordinates only. We denote eigenfunctions from the set $\hat{n} = 0$ by the symbol g. As we shall see later, eigenfunctions h with $\hat{n} = 1$, which are linear combinations of $(Q_a - {}^0Q_a)$, contribute to the high frequency limiting viscosity, while eigenfunctions g, with $\hat{n} = 0$, contribute to the frequency dependent part of the viscosity. It is necessary to consider these latter eigenfunctions in more detail.

For this purpose we expand the function g according to Eq. (2.3) and arrive at the set of equations

$$\mathfrak{D}^{(-2)} g^{(0)} = 0 \;, \tag{2.10a}$$

$$\mathfrak{D}^{(-1)} g^{(0)} + \mathfrak{D}^{(-2)} g^{(1)} = 0 \;, \tag{2.10b}$$

$$\mathfrak{D}^{(0)} g^{(0)} + \mathfrak{D}^{(-1)} g^{(1)} + \mathfrak{D}^{(-2)} g^{(2)} = -\lambda^{(0)} g^{(0)} \;. \tag{2.10c}$$

Equation (2.10a) is obeyed by an function of the soft coordinates only. As shown in Appendix A, we can solve

$$g^{(1)} = -[{}^0D^{-1}_{(h)}]^{ab}\, {}^0D_{b\alpha}(Q_a - {}^0Q_a) \frac{\partial}{\partial q_\alpha} g^{(0)} \;, \tag{2.11}$$

where $D_{(h)}$ denotes the restriction of **D** to the hard subspace. Next, evaluation of the first two terms on the lhs of Eq. (2.10c) leads to the result

$$\begin{aligned}\mathfrak{D}^{(0)} g^{(0)} + \mathfrak{D}^{(-1)} g^{(1)} = \Bigg[& {}^0J^{-1} \frac{\partial}{\partial q_\alpha}\, {}^0J \tilde{D}_{\alpha\beta} \frac{\partial}{\partial q_\beta} \\ & - \beta \left(\frac{\partial U^{(s)}}{\partial q_\alpha} \right) \tilde{D}_{\alpha\beta} \frac{\partial}{\partial q_\beta} \Bigg] g^{(0)} \\ & + \beta\kappa E^{ab}_\alpha [(Q_a - {}^0Q_a)(Q_b - {}^0Q_b) \\ & - (\beta\kappa)^{-1} ({}^0G^{-1})_{ab}] \frac{\partial}{\partial q_\alpha} g^{(0)} \;, \end{aligned} \tag{2.12}$$

with the definitions

$$\tilde{D}_{\alpha\beta} = {}^0D_{\alpha\beta} - {}^0D_{\alpha a} ({}^0D^{-1}_{(h)})^{ab}\, {}^0D_{b\beta} \;, \tag{2.13}$$

$$E^{ab}_\alpha = {}^0G^{ac} \left[{}^0D_{c\beta} \frac{\partial}{\partial q_\beta} ({}^0D^{-1}_{(h)})^{bd}\, {}^0D_{d\alpha} - {}^0D'^{\,b}_{c\alpha} + {}^0D'^{\,b}_{cd} ({}^0D^{-1}_{(h)})^{de}\, {}^0D_{e\alpha} \right] , \tag{2.14}$$

and

$${}^0A'^{\,a} = \left(\frac{\partial}{\partial Q_a} A \right)_{\mathbf{Q}={}^0\mathbf{Q}} \;. \tag{2.15}$$

The structure of the last term in Eq. (2.12) is exactly that of the eigenfunctions h of the operator $\mathfrak{D}^{(-2)}$ with $\hat{n} = 2$. Accordingly it is possible, as is shown in Appendix A, to choose $g^{(2)}$ in such a way that $\mathfrak{D}^{(-2)} g^{(2)}$ cancels this term. The resulting eigenvalue equation for $g^{(0)}$ is

$$\left[{}^0J^{-1} \frac{\partial}{\partial q_\alpha}\, {}^0J \tilde{D}_{\alpha\beta} \frac{\partial}{\partial q_\beta} - \beta \left(\frac{\partial U^{(s)}}{\partial q_\alpha} \right) \tilde{D}_{\alpha\beta} \frac{\partial}{\partial q_\beta} \right] g^{(0)} = -\lambda^{(0)} g^{(0)} \;, \tag{2.16}$$

with $\tilde{D}_{\alpha\beta}$ given by Eq. (2.13). Notice that one may extend the definition Eq. (2.13) to all coordinates; whenever one of the indices assumes a "hard" value, the matrix element will vanish. We may therefore replace the indices (α, β) in Eq. (2.13) by (i, j) without altering the physical consequences of the equation.

III. CALCULATION OF THE INTRINSIC VISCOSITY

The next step in our development consists of calculating the matrix elements $\langle J_{xy} | f_m \rangle$. The stress tensor J_{xy}, Eq. (1.2), may be expressed in Cartesian coordinates as

$$J_{xy} = \mathbf{I}^T \cdot \nabla_{\mathbf{R}} U \;, \tag{3.1}$$

where I is a $3N$-dimensional vector whose only nonvanishing components are those on the site y_n, which equal x_n. In the general coordinate system

$$J_{xy} = I_i \frac{\partial U}{\partial q_i} \;. \tag{3.2}$$

The operator J_{xy} is the sum of a "soft" part $J^{(s)}_{xy}$ containing $U^{(s)}$ and a "hard" part $J^{(h)}_{xy}$,

$$J^{(h)}_{xy} = -\kappa I_a G^{ab}(Q_b - {}^0Q_b) \;; \tag{3.3}$$

the explicit form of I_i is

$$I_i = \sum_n \frac{\partial q_i}{\partial q_n} x_n \;. \tag{3.4}$$

When we inspect Eq. (1.6) for the intrinsic viscosity $[\eta(\omega)]$, we see that eigenfunctions of type h and type g contribute in a different fashion to $[\eta(\omega)]$. For an eigenfunction of type h the eigenvalue λ_m is of order κ and we may neglect $i\omega$ in the denominator in the rigid limit. This means that such eigenfunctions contribute to the limiting high frequency viscosity. Moreover one needs only consider the part of $\langle J_{xy} | h_m \rangle$ that is of order $\kappa^{1/2}$. Such a contribution can only arise from $J^{(h)}_{xy}$. According to Eq. (3.3) the dominant part of $J^{(h)}_{xy}$ is a linear combination of eigenfunctions of type h with $\hat{n} = 1$; therefore it follows from the known properties of Hermite polynomials that only eigenfunctions with $\hat{n} = 1$ can give contributions of order $\kappa^{1/2}$ to the matrix elements $\langle J^{(h)}_{xy} | f_m \rangle$. For eigenfunctions of type g the eigenvalue λ_m is of order unity, and the term $i\omega$ in the denominator can no longer be neglected; such eigenfunctions therefore contribute to the frequency dependent part of $[\eta(\omega)]$. Moreover we have to determine $\langle J_{xy} | g_m \rangle$ up to terms of order unity (terms of order $\kappa^{1/2}$ are absent in this case).

A. Limiting high frequency viscosity

The limiting high frequency viscosity may be written as

$$[\eta_\infty] = \lim_{\omega\to\infty} \lim_{\kappa\to\infty} \frac{N_A \beta}{M\eta_0} \sum_m{}' \frac{\langle J_{xy} | h_m \rangle \langle h_m | J_{xy} \rangle}{i\omega + \lambda_m} \;, \tag{3.5}$$

where the prime on the sum indicates restriction to eigenfunctions of type h with $\hat{n} = 1$. As κ increases the term $(i\omega)$ in the denominator may be neglected.

Moreover, as we just saw, only the dominant part of $J^{(h)}_{xy}$ must be retained in Eq. (3.5). This dominant part of the stress tensor, denoted as $J^{(-1)}_{xy}$, is

$$J^{(-1)}_{xy} = -\kappa\, {}^0G^{ab}\, {}^0I_a(Q_b - {}^0Q_b) \equiv \kappa r^b (Q_b - {}^0Q_b) \;, \tag{3.6}$$

where the vector r^b,

$$r^b = -{}^0G^{ab}\, {}^0I_a \;, \tag{3.7}$$

is introduced for convenience.

Since the expression

$$-\sum_m{}' |h_m\rangle \lambda_m^{-1} \langle h_m|$$

is exactly the inverse of the operator $\mathfrak{D}^\dagger$ restricted to the space spanned by eigenfunctions of type h with $\hat{n} = 1$, and since $J^{(-1)}_{xy}$ lies in that same space, Eq. (3.5) may be written as

$$[\eta_\infty] = \frac{N_A \beta}{M\eta_0} \kappa^2 \langle r^b (Q_b - {}^0Q_b) | [\mathfrak{D}^{(-2)}]^{-1} | r^a (Q_a - {}^0Q_a) \rangle \;, \tag{3.8}$$

where $\mathfrak{D}^\dagger$ has been replaced by its leading term $\mathfrak{D}^{(-2)}$. This matrix element is evaluated by noting that

$$\mathfrak{D}^{(-2)}\, r^a(Q_a - {}^0Q_a) = -\beta\kappa\, {}^0G^{ab}\, {}^0D_{bc}\, r^c(Q_a - {}^0Q_a)\ , \tag{3.9}$$

as may be verified by direct substitution. Accordingly

$$[\mathfrak{D}^{(-2)}]^{-1}\, r^a(Q_a - {}^0Q_a) = -(\beta\kappa)^{-1}[{}^0D^{-1}_{(h)}]^{ab}({}^0G^{-1})_{bc}\, r^c(Q_a - {}^0Q_a)\ . \tag{3.10}$$

Substitution of Eq. (3.10) into Eq. (3.8) leads to

$$[\eta_\infty] = \frac{N_A\kappa}{M\eta_0}\langle r^b(Q_b - {}^0Q_b)\,|\,[{}^0D^{-1}_{(h)}]^{ad}({}^0G^{-1})_{dc}\, r^c(Q_a - {}^0Q_a)\rangle\ . \tag{3.11}$$

Integration over the hard coordinates replaces $(Q_b - {}^0Q_b) \times (Q_a - {}^0Q_a)$ in the rigid limit by $(\beta\kappa)^{-1}({}^0G^{-1})_{ba}$, and employing Eq. (3.7) one arrives at the result

$$[\eta_\infty] = \frac{N_A}{M\eta_0\beta}\langle\langle {}^0I_a[{}^0D^{-1}_{(h)}]^{ab}\, {}^0I_b\rangle\rangle\ , \tag{3.12}$$

where $\langle\langle\ldots\rangle\rangle$ denotes an equilibrium average over soft coordinates:

$$\langle\langle A\rangle\rangle = \int A(q_\alpha)\, P^{(s)}_{\mathrm{eq}}(q_\alpha)\, {}^0J(q_\alpha)\, d^{3N-h}q_\alpha \tag{3.13}$$

with

$$P^{(s)}_{\mathrm{eq}} = \mathfrak{N}\exp[-\beta\, {}^0U^{(s)}]\ . \tag{3.14}$$

B. Intrinsic viscosity at arbitrary frequency

In order to evaluate the matrix element $\langle J_{xy}|g_m\rangle$ to the required order in κ we insert the expansion Eq. (2.3) for g_m and the analogous one for J_{xy},

$$J_{xy} = J^{(-1)}_{xy} + J^{(0)}_{xy} + \cdots\ , \tag{3.15}$$

with $J^{(-1)}_{xy}$ given by Eq. (3.6) and

$$J^{(0)}_{xy} = -{}^0I_i\, {}^0\!\left[\frac{\partial U^{(s)}}{\partial q_i}\right] - \kappa\, {}^0(I_aG^{ab})^{,c}(Q_b - {}^0Q_b)(Q_c - {}^0Q_c)\ . \tag{3.16}$$

These substitutions lead to the expression

$$\langle J_{xy}|g_m\rangle = \langle J^{(-1)}_{xy}|g^{(0)}_m\rangle + \langle J^{(-1)}_{xy}|g^{(1)}_m\rangle + \langle J^{(0)}_{xy}|g^{(0)}_m\rangle + \cdots\ . \tag{3.17}$$

All matrix elements in Eq. (3.17) have to be evaluated up to order unity. In the second and third term this may be done by replacing the quantities $U^{(s)}$, G^{ab}, and J in the definition (1.7) of the matrix elements [with the expression (1.14) for $P_{\mathrm{eq}}(\mathbf{q})$] by their equilibrium values, and performing the Gaussian integrations. A similar procedure applied to the first term in Eq. (3.17) gives zero, since the integrand is odd in $(Q_a - {}^0Q_a)$. However, a nonvanishing contribution of order unity is obtained when one includes corrections of order $\kappa^{-1/2}$ to P_{eq} and J, which which arise from the dependence of $U^{(s)}$, G^{ab}, and J on the hard coordinates. As shown in more detail in Appendix B, this leads to an expression for the matrix element (3.17) of the form

$$\langle J_{xy}|g_m\rangle^{(0)} = \langle\langle \tilde{J}_{xy}\, g^{(0)}_m\rangle\rangle \tag{3.18}$$

with the average $\langle\langle\ldots\rangle\rangle$ defined by Eq. (3.13) and

$$\tilde{J}_{xy} = -{}^0I_\alpha\frac{\partial\, {}^0U^{(s)}}{\partial q_\alpha} - \beta^{-1}\, {}^0I_a^{,a} - \beta^{-1}\, {}^0J^{-1}\, {}^0I_a\, {}^0J^{,a} + \beta^{-1}\, {}^0I_a[{}^0D^{-1}_{(h)}]^{ab}\, {}^0D_{b\alpha}\frac{\partial}{\partial q_\alpha}\ , \tag{3.19}$$

where the operation $\partial/\partial q_\alpha$ in the last term acts on the function $g^{(0)}_m$ in the rhs of Eq. (3.18).

In order to facilitate the comparison with alternative formalisms in the next section we present a few equivalent forms for the expression (3.19). First we note that the second and third term on the rhs of Eq. (3.19) may be combined to give

$$-\beta^{-1}\, {}^0\!\left(J^{-1}\frac{\partial}{\partial Q_a}J I_a\right)\ . \tag{3.20}$$

A comparison with Eq. (1.10) shows that the expression in brackets is exactly the "hard" part of div I. From the representation of I in Cartesian coordinates, given after Eq. (3.1), it is easy to see that div I vanishes identically. Therefore we may replace the "hard" part of div I by minus its "soft" part; when this is done Eq. (3.19) becomes

$$\tilde{J}_{xy} = -{}^0I_\alpha\frac{\partial\, {}^0U^{(s)}}{\partial q_\alpha} + \beta^{-1}\, {}^0I_\alpha^{,\alpha} + \beta^{-1}\, {}^0J^{-1}\, {}^0I_\alpha\, {}^0J^{,\alpha} + \beta^{-1}\, {}^0I_a[{}^0D^{-1}_{(h)}]^{ab}\, {}^0D_{b\alpha}\frac{\partial}{\partial q_\alpha}\ . \tag{3.21}$$

The quantity $\tilde{J}_{xy}$ always occurs in the matrix element on the rhs of Eq. (3.18). When the average $\langle\langle\ldots\rangle\rangle$ is written out explicitly according to Eq. (3.13) one checks easily, by means of an integration by parts, that the first three terms on the rhs of Eq. (3.21) may be replaced by $-\beta^{-1}I_\alpha(\partial/\partial q_\alpha)$. This allows one to rewrite Eq. (3.21) in the compact form

$$\tilde{J}_{xy} = -\beta^{-1}\tilde{I}_\alpha\frac{\partial}{\partial q_\alpha}\ , \tag{3.22}$$

with

$$\tilde{I}_\alpha = {}^0I_\alpha - {}^0D_{\alpha b}[{}^0D^{-1}_{(h)}]^{ba}\, {}^0I_a\ . \tag{3.23}$$

In order to make the meaning of the operation $\partial/\partial q_\alpha$ in Eq. (3.22) more explicit one may replace the operator from (3.22) by

$$\tilde{J}_{xy} = -\beta^{-1}\tilde{I}_\alpha[\partial\log g^{(0)}_m/\partial q_\alpha]\ . \tag{3.24}$$

Starting from the form (3.24) for $\tilde{J}_{xy}$ it is easy to make contact with a description using the concept of "diffusion force" or "entropic force." The latter is usually given as

$$F^i_{\mathrm{ent}} = -\beta^{-1}[\partial\log P/\partial q_i]\ , \tag{3.25}$$

where P is the nonequilibrium distribution function of the polymer. For our case we must choose $P = P_m$ with

$$P_m = g^{(0)}_m P^{(s)}_{\mathrm{eq}}\ , \tag{3.26}$$

and $P^{(s)}_{\mathrm{eq}}$ defined by Eq. (3.14). It is now easy to verify that $\tilde{J}_{xy}$ can also be written as

$$\tilde{J}_{xy} = -\tilde{I}_\alpha\left[\frac{\partial\, {}^0U^{(s)}}{\partial q_\alpha} - F^\alpha_{\mathrm{ent}}\right]\ , \tag{3.27}$$

where $\tilde{I}_\alpha$ and F^α_{ent} are defined by Eqs. (3.23) and (3.25).

We wish to stress that the entropic force enters into Eq. (3.27) as a derived quantity; it is merely a convenient way of expressing a part of the contribution of the "hard" forces to the part of the stress tensor that contributes to the frequency dependent part of $[\eta(\omega)]$. Our starting expression for J_{xy}, Eq. (1.2), contains no contributions from "entropic forces." Further comments on this point will be made in Sec. IV.

C. An alternative form for the stress tensor

When the hydrodynamic interaction is neglected, or replaced by a preaveraged expression,[8] the matrix $\mathbf{D}_{nm}$, Eq. (1.4), is replaced by the unit matrix multiplied by a number $\hat{D}_{nm}$, that does not depend on the chain configuration. In this case it is possible to circumvent the laborious evaluation of $\langle J_{xy} | g_m \rangle$ described in the preceding subsection. For this purpose we consider the quantity

$$E_{xy} = \sum_{n,m=1}^{N} [\hat{\mathbf{D}}^{-1}]_{nm} x_n y_m \quad , \tag{3.28}$$

where $\hat{\mathbf{D}}$ is the $N \times N$ matrix formed by the $\hat{D}_{nm}$ and x_n and y_n are the x and y coordinates of the nth bead. Using the form (1.3) for $\mathfrak{D}^\dagger$ one easily verifies

$$\mathfrak{D}^\dagger E_{xy} = -\beta(J_{xy} + J_{yx}) = -2\beta J_{xy} \quad . \tag{3.29}$$

By employing the self-adjointness of $\mathfrak{D}^\dagger$ with respect to the scalar product $\langle A | B \rangle$ we find

$$\langle J_{xy} | f_m \rangle = -2\beta\lambda_m \langle E_{xy} | f_m \rangle \quad . \tag{3.30}$$

Since E_{xy} contains no contributions of negative order in $\kappa^{-1/2}$, the zeroth order contribution to the matrix element with an eigenfunction of type $g(\hat{n} = 0)$ is

$$\langle J_{xy} | g_m \rangle = -2\beta\lambda_m \langle\langle E_{xy} g_m^{(0)} \rangle\rangle \quad , \tag{3.31}$$

with $\langle\langle \dots \rangle\rangle$ defined by Eq. (3.18). Using Eq. (3.31) we may rewrite the expression (1.6) for $[\eta(\omega)]$ in the form

$$[\eta(\omega)] = [\eta_\infty] + \frac{N_A}{4M\eta_0\beta} \sum_m \frac{\lambda_m^2 | \langle\langle E_{xy} g_m^{(0)} \rangle\rangle |^2}{i\omega + \lambda_m} \quad , \tag{3.32}$$

or equivalently, by using the identity $\lambda_m^2 = \lambda_m[(i\omega + \lambda_m) - i\omega]$,

$$[\eta(\omega)] = [\eta(0)] - \frac{i\omega N_A}{4M\eta_0\beta} \sum_m \frac{\lambda_m | \langle\langle E_{xy} g_m^{(0)} \rangle\rangle |^2}{i\omega + \lambda_m} \quad . \tag{3.33}$$

This second form may be convenient, since a simple form for $[\eta(0)]$ is available[9] for the case where the hydrodynamic interaction is neglected or preaveraged.

IV. COMPARISON WITH OTHER THEORIES

Our theory differs from earlier ones in two important aspects: in the use of the correlation function method and in the treatment of the rigid constraints.

The choice of the correlation function method, rather than the method employing the average of the stress tensor in the presence of an externally imposed velocity gradient (a method used in all papers discussed in this section except those by Doi, Nakajima, and Wada[2] and by Doi and Okano)[10] was made as a matter of convenience. This choice allows us to confine our attention to the expression for the diffusion operator $\mathfrak{D}^\dagger$ and the stress tensor J_{xy} in the absence of any external flow, which are considerably simpler than the corresponding expressions in the presence of an externally imposed flow field. Moreover, we feel that any ambiguities that may have existed with respect to the correlation function method have been resolved in recent discussions.[5,11] However, the two formalisms are equivalent as long as one neglects non-Newtonian effects, which we do throughout this paper, and as long as one remains in the full configuration space of the polymer, including both hard and soft coordinates. Any differences between our results and those of earlier treatments must therefore be ascribed to a different treatment of the rigid constraints.

In the following survey we concentrate our attention on the way other workers treat the rigid constraints. In addition we will compare their results to the ones we presented in the preceding two sections, especially the effective diffusion operator that enters into the eigenvalue equation for the $g_m^{(0)}$, Eq. (2.16); the expression for the limiting high frequency viscosity, Eq. (3.12); and the expression for the "effective stress tensor" $\tilde{J}_{xy}$, for which various forms were found in the last half of Sec. III. B.

A. Comparison with the work of Fixman and Kovac

Fixman and Kovac (FK)[1] eliminate the "hard" forces from their formalism in an early stage of their calculations by postulating that their effect is the exact cancellation of any force component that would lead to a change in any of the constrained quantities when substituted in an expression of the type

$$\frac{\partial}{\partial t}\mathrm{R} = \mathbf{D} \cdot \mathbf{F} \quad . \tag{4.1}$$

In this equation $\mathbf{D}$ is the diffusion matrix, Eq. (1.3), and $\mathbf{F}$ is the sum of a soft force and an entropic contribution:

$$\mathbf{F} = -\nabla_{\mathrm{R}} U^{(s)} + \mathbf{F}_{\mathrm{ent}} \quad , \tag{4.2}$$

with $\mathbf{F}_{\mathrm{ent}}$ given by Eq. (3.25).

FK show that the effect of the cancellation of terms in $\mathbf{F}$ that would lead to change in any constrained quantity is to replace $\mathbf{D}$($-\mathbf{B}$ in the notation of FK) by a matrix $\mathscr{G}$ [Eq. (FK 4.22), see also FK Sec. III]. When we choose as hard coordinates $\frac{1}{2} | \mathbf{r}_n - \mathbf{r}_{n+1} |^2$ for a constrained bond length and $(\mathbf{r}_{n-1} - \mathbf{r}_n) \cdot (\mathbf{r}_n - \mathbf{r}_{n+1})$ for a constrained bond angle, then this matrix may be expressed as

$$\mathscr{G} = {}^0\mathbf{D} - {}^0\mathbf{D} \cdot {}^0\mathbf{e}_a [{}^0D_{(h)}^{-1}]^{ab} \, {}^0\mathbf{e}_b \cdot {}^0\mathbf{D} \quad , \tag{4.3}$$

with

$${}^0D_{(h)cd} = {}^0\mathbf{e}_c \cdot {}^0\mathbf{D} \cdot {}^0\mathbf{e}_d \quad . \tag{4.4}$$

The quantity (4.3) is the extension of our matrix $\tilde{D}_{\alpha\beta}$, Eq. (2.13), to the full configuration space (cf. the remark at the end of Sec. II), written in Cartesian coordinates. Actually the quantities used by FK are not exactly equal to ours, since FK first eliminated the center of mass coordinates. This difference, on which we will comment later in this subsection, is inessential for the argument just given and for the comparisons to follow.

Once the identification (4.3) has been made it is easy to see that the eigenvalue equation (FK 4.27) becomes identical to our Eq. (2.16) after elimination of the factor Ψ_e. This in turn implies that the expression (FK 6.23) for the frequency dependent intrinsic viscosity, in the case where the hydrodynamic interaction is preaveraged or neglected, becomes identical to our Eq. (3.33), after the requisite rescaling of units (Ref. 1b, Table I). The expression for $[\eta_\infty]$ derived from Eq. (FK 5.10) is identical to our Eq. (3.12). Finally, the expression (FK 4.30) for the stress tensor with substitution of Eq. (FK 4.34) reduces to our Eq. (3.18), with J_{xy} given by Eq. (3.24), when all terms associated with externally imposed velocity fields in Eq. (FK 4.34) are omitted. In order to arrive at their result FK have to include an entropic force contribution in their starting expression for the stress tensor; this term has been the subject of some controversy, and our approach allows us to sidestep the issue. In Ref. 5 we showed that inclusion or omission of the entropic force term is immaterial as long as one stays in the complete configuration space of hard and soft coordinates; this was shown by means of an integration by parts. This proof no longer applies, however, when the FK projection operator M, (FK 3.25) or (FK 3.26), is inserted. The inclusion of an entropic force term is necessary in the FK formalism.

A minor difference between our theory and that of FK concerns the treatment of the center-of-mass coordinates, which FK eliminate at the beginning. As long as the potential energy does not depend on the position of the center-of-mass, any derivative with respect to the center-of-mass coordinates commutes with $\mathfrak{D}^\dagger$ and we may choose all eigenfunctions of $\mathfrak{D}^\dagger$ to be plane waves with respect to the center-of-mass coordinates. Moreover, since J_{xy} does not depend on the center-of-mass position, only eigenfunctions with wavevector zero contribute to the intrinsic viscosity. Therefore it would have been possible in our treatment to eliminate the center-of-mass coordinates for the outset, and to reduce the dimension of our configuration space accordingly.

The results obtained by FK are confirmed by our analysis. Our procedure, which employs an explicit model for the constraining forces is straightforward and proceeds without great cost in terms of the simplicity of the derivations. Finally, our treatment makes it possible, at least in principle, to determine corrections for the case in which the constraints are not completely rigid.

B. Comparison with work of the University of Tokyo group

The two papers discussed in this subsection, one by Doi, Nakajima, and Wada (DNW)[2] and one by Doi and Okano (DO),[10] provide an approach which is in many aspects very close to ours. In Ref. 10 and in Appendix II of Ref. 2 the intrinsic viscosity is determined by the correlation function method and the constraints are effectuated by a harmonic potential, whose strength approaches infinity in the rigid limit. In some respects their treatment is less complete than ours; they consistently neglect hydrodynamic interactions and they do not derive any explicit expression for the diffusion operator $\mathfrak{D}^\dagger$, except for the case of a dumbbell. On the other hand, Ref. 2 contains a very clear and extensive discussion of the limiting high frequency viscosity, which goes beyond the scope of the present paper.

The expression (DNW 13) for the high frequency viscosity is identical in content to our Eq. (3.12), when we substitute the expression for $\mathbf{D}$ in the absence of hydrodynamic interaction,

$$D_{ij} = (\beta\zeta)^{-1}\mathbf{e}_i \cdot \mathbf{e}_j \equiv (\beta\zeta)^{-1} C_{ij} \quad . \tag{4.5}$$

With this identification our $D_{(h)ab}$ becomes identical with the A_{ij} of Eq. (DNW 9). The I_i of (DNW 11) is equal to our I_a.

The expression (DNW II.6) for the part of the stress tensor that contributes to the frequency dependent part of the intrinsic viscosity differs from our $\tilde{J}_{xy}$; the expression (DNW II.9) is exactly equal to the first two terms in Eq. (3.19), as is easily seen by evaluation of the Gaussian average $\langle f_i f_j \rangle_f$ in Eq. (DNW II.6). The third term in Eq. (3.19) is caused by the dependence of the Jacobian on the hard coordinates. Its absence in Ref. 2 is probably due to an oversight; Eq. (DNW II.6) is not used any further in Ref. 2, and the corresponding expressions in Ref. 10, e.g., Eqs. (DO 52) and (DO 68), do contain such contributions from the Jacobian.

The absence of the fourth term in Eq. (3.19) from Eq. (DNW II.6), and also from Eq. (DO 68), is, however, due to a basic flaw of the method employed by DNW and DO. These authors argue that the oscillations in hard and soft coordinates take place on such different time scales that any quantity used to describe low-frequency behavior can be preaveraged over the hard coordinates. This description has been criticized[12] as "overly coarse grained." While the preaveraging can be justified in simple cases [in fact Eq. (DO 52) yields the correct viscosity for a solution of dumbbells], it leads to errors when the hard and soft coordinates are coupled to one another by means of the hydrodynamic interaction, or by means of the metric tensor $\mathbf{e}_i \cdot \mathbf{e}_j$ that occurs in the formula for D_{ij} in the absence of hydrodynamic interactions, Eq. (4.5). Inspection of the fourth term in Eq. (3.19) shows that the existence of nonvanishing elements in D_{ij} between hard and soft coordinates is indeed needed to obtain a contribution from this term.

The coupling between hard and soft coordinates will cause a forced low-frequency vibration of some hard coordinates whenever certain soft coordinates are excited. While the amplitude of these forced oscillations is indeed very small (of order $\kappa^{-1/2}$), the presence of a factor κ in front of the $(Q_b - {}^0Q_b)$ in the basic expression for $J_{xy}^{(h)}$, Eq. (3.3), cuases them to contribute a term of order unity to the matrix element of J_{xy} that occurs in the expression for the frequency dependent part of the intrinsic viscosity.

The fact that hydrodynamic interactions couple hard and soft coordinates was already recognized by Erpenbeck and Kirkwood[4]; the fact that such couplings also occur through the metric tensor was long ignored, and stressed only rather recently in a paper by Fixman.[13] Once alert to the possibility one easily sees that such couplings occur in the bond vector description of any chain of more than two particles, which was used, e.g., by DO in Ref. 10 and by Hassager in some of the work discussed in the next subsection.

C. Comparison with Hassager's formalism

In Ref. 3 Hassager (H) discusses the intrinsic viscosity of various models for polymer solutions, using a formalism that treats the constrained coordinates as absolutely fixed quantities, and considers only processes in the $3N$-h dimensional configuration space with soft coordinates only. For a comparison of the basic diffusion equations, Eq. (H 7) and our Eq. (2.16), it is useful to remark that our matrix $\tilde{D}$, Eq. (2.13), may be obtained by first restricting the inverse matrix $\mathbf{D}^{-1}$ to the space of the soft coordinates and inverting the resulting $(3N\text{-}h)\times(3N\text{-}h)$ matrix:

$$\tilde{D}_{\alpha\beta}=[(D^{-1})^{-1}_{(s)}]_{\alpha\beta} \quad , \tag{4.6}$$

as is easily proved by use of the formula

$$(D^{-1})^{\alpha\beta} D_{\beta i}=\delta^{\alpha}_{i}-(D^{-1})^{\alpha a} D_{a i} \quad . \tag{4.7}$$

Hassager neglects the hydrodynamic interaction, so his $(D^{-1})^{\alpha\beta}$ is $\beta\zeta$ times the restriction of the covariant metric tensor $\mathbf{e}^i\cdot\mathbf{e}^j\equiv C^{ij}$ to the soft subspace. The matrix $[C^{-1}]_{st}$ in Eq. (H 7) is therefore equal to our $\tilde{D}_{\alpha\beta}$, apart from a factor $\beta\zeta m$, where m is the mass of a polymer bead, which Hassager includes in his definition of C^{ij}. However, the operator in Eq. (H 7) does not reduce to the adjoint of the one in our Eq. (2.16) when the external-flow terms are omitted, since Eq. (H 7) contains the "restricted" Jacobian $|\det C^{\alpha\beta}|^{1/2}$, while our Eq. (2.16) contains the full Jacobian $|\det C^{ij}|^{1/2}$.

The same difference occurs in the expressions for the equilibrium probability distributions. Hassager's equilibrium distributions, e.g., Eq. (H 31) for a flexible chain of three beads, differ from our $P^{(s)}_{\text{eq}}$, Eq. (3.14), by a factor $[(\det C^{\alpha\beta})/(\det C^{ij})]^{1/2}$. For a flexible chain of two beads this factor is proportional to $(1-\frac{1}{4}\cos^2\chi)^{1/2}$, with χ the angle between the two bonds. Expressions for longer flexible chains have been derived by Fixman.[13]

The two equilibrium ensembles have a simple physical interpretation. Hassager's equilibrium distribution, which was proposed earlier by Kramers,[14] corresponds to a probability density concentrated on the sharp hypersurface $\mathbf{Q}={}^0\mathbf{Q}$ with surface density $\exp[-\beta U^{(s)}]$. Our equilibrium distribution, Eq. (1.14) corresponds to a probability density proportional to $|\det G|^{1/2}(\beta\kappa)^{h/2}\times\exp[-\beta U^{(s)}]$ within a shell of equivalent thickness $[\beta\kappa\mu_{(l)}]^{-1/2}$ in the direction $Q'_{(l)}$, where $\mu_{(l)}$ and $Q'_{(l)}$ are defined in Eq. (2.6) and (2.7), respectively. From Eq. (2.6) we see that

$$\prod_{l=1}^{h}[\beta\kappa\mu_{(l)}]^{-1/2}=(\beta\kappa)^{-h/2}\,|\det({}^0G^{ab}\,{}^0D_{bc})|^{-1/2}$$
$$=(\beta\kappa)^{-h/2}\,|\det{}^0D|^{-1/2}|\det{}^0G|^{-1/2} \quad . \tag{4.8}$$

In order to convert this into a thickness in terms of $\mathbf{R}$ rather than $Q'_{(l)}$ we must multiply Eq. (4.8) with the Jacobian of the corresponding transformation, which is the product of that from $Q'_{(l)}$ to Q_a, with Jacobian $|\det D|^{1/2}$ as a consequence of Eq. (2.6), and that from q_i to $\mathbf{R}$ with Jacobian $J=|C^{ij}|^{1/2}$. We conclude that the total amount of probability density in an area with soft coordinates between q_α and $q_\alpha+dq_\alpha$ is proportional to

$$|\det{}^0G|^{1/2}(\beta\kappa)^{h/2}\exp[-\beta\,{}^0U^{(s)}]$$
$$\cdot\,(\beta\kappa)^{-h/2}\,|\det{}^0D|^{-1/2}|\det{}^0G|^{-1/2}$$
$$\times|\det{}^0D|^{1/2}\,|C^{ij}|^{1/2}\prod_{\alpha=h+1}^{3N}dq_\alpha \quad . \tag{4.9}$$

If we want to express this in terms of a surface probability density $\sigma(\mathbf{q}_\alpha)$ we must divide this by the surface volume element $|C^{\alpha\beta}|^{1/2}\Pi^{3N}_{\alpha=h+1}dq_\alpha$; thus we obtain for $\sigma(\mathbf{q}_\alpha)$

$$\sigma(\mathbf{q}_\alpha)=|C^{ij}|^{1/2}|C^{\alpha\beta}|^{-1/2}\exp[-\beta\,{}^0U^{(s)}]$$
$$\equiv\sigma_0(\mathbf{q}_\alpha)\exp[-\beta\,{}^0U^{(s)}] \quad . \tag{4.10}$$

An alternative form for $\sigma_0(\mathbf{q}_\omega)$ can be obtained by considering the covariant matrix F_{ij} defined as

$$F_{i\alpha}=\tilde{C}_{i\alpha}\,;\quad F_{ia}=C_{ia} \quad . \tag{4.11}$$

Since F_{ij} can be obtained from C_{ij} by subtracting some linear combinations of the "soft" rows from each of the "hard" rows we see that $\det F_{ij}=\det C_{ij}=(\det C^{ij})^{-1}$. On the other hand $\det F_{ij}=(\det\tilde{C}_{\alpha\beta})(\det C_{ab})$. Therefore we see that

$$\sigma_0(\mathbf{q}_\alpha)=|\det C_{ab}|^{-1/2} \quad . \tag{4.12}$$

In particular for the case of a single hard variable the factor (4.12) becomes $|\nabla_{\mathbf{R}}Q|^{-1/2}$. In this form the expression is familiar from the theory of the microcanonical ensemble in statistical mechanics,[15] where the surface probability density on the energy surface $\mathcal{H}=E_0$ is put equal to $|\text{grad}\,\mathcal{H}|^{-1/2}$ in order to account for the variable thickness of the shell enclosed between the surface $\mathcal{H}=E_0$ and $\mathcal{H}=E_0+\Delta E$.

In some earlier discussions[13,16] it is shown that the two ensembles can be obtained from two different expressions for the joint equilibrium distribution function for coordinates and momenta of the polymer beads. The two expressions differ in the treatment of the momenta conjugate to the hard variables. Putting them identically equal to zero, while allowing the soft momenta to assume a Maxwell distribution, results in Kramers' ensemble, used in Ref. 3, while allowing all coordinates to assume a Maxwell distribution results in an ensemble equal to the one we used, after integration over all momenta. Since the momenta do not play any further role in a theory based on a Smoluchowski equation, we slightly prefer the explanation given earlier.

In his calculation of the intrinsic viscosity Hassager uses the Giesekus[17] expression for the stress tensor, which reduces to the one we discussed in Sec. III. C in the absence of an imposed flow field. As we saw there, the expression obtained by that formalism for $[\eta(\omega)]$ does not contain any terms that depend explicitly on the coupling between hard and soft coordinates, and the only differences between Hassager's results and ours are due to the difference in the Jacobian. The close agreement between the results obtained for a flexible chain of three beads by Hassager and by FK suggest that these differences, while theoretically interesting, are numerically insignificant.[1b,3b]

D. Comparison with the work of Erpenbeck and Kirkwood

Kirkwood and his collaborators have presented a number of versions of the theory of the intrinsic viscosity of polymer solutions for a model polymer with constraints. All theories provide a description in the space spanned by the soft covariant basis vectors $\mathbf{e}^\alpha = \partial \mathbf{R}/\partial q_\alpha$; this space is called "chain space" in Kirkwood's formulation. In the earlier papers[18] all couplings between hard and soft coordinates were neglected, but the errors thus introduced were corrected, first only in part in the paper by Erpenbeck and Kirkwood (EK),[4a] and later almost completely in an erratum to that paper (EKC).[4b] A remaining inaccuracy is the assertion in Ref. 4a, after Eq. (EK 2), that the metric tensor consists of two blocks, one for "chain space" and one for the complementary space. As pointed out by Fixman,[13] this assumption is in general not correct. In this subsection we will compare the results of the corrected version of the EK theory with those obtained in this paper.

From the definition (EKC 1), which is identical in content with our Eq. (4.6) it follows that their $D_{\alpha\beta}$, is equal to $\tilde{D}_{\alpha\beta}$. to the diffusion operator on the lhs of Eq. (EKC 2) is the adjoint of the one appearing in Eq. (2.16). In particular the quantity $g^{1/2}$ is the full Jacobian, rather than the restricted Jacobian that appears in Hassager's equation and in earlier versions of Kirkwood's theory. The quantity G in (EKC 5) corresponds to $M\eta_0\zeta[\eta(\omega)]/N_A$ in our formulation, while the average $\langle\cdots\rangle_0$ in Eq. (EKC 5) is exactly our $\langle\langle\cdots\rangle\rangle$. The terms $H^{(0)}$ and $H^{(1)}$ give the high frequency limiting viscosity, and $H^{(2)}$ gives the frequency dependent part. EK introduce the eigenvalues $\beta\zeta\sigma_j$ and eigenvectors ϕ_j of the diffusion matrix $\mathbf{D}$,

$$\mathbf{D}\cdot\phi_j = \beta\zeta\sigma_j\phi_j \quad . \tag{4.13}$$

When the dyadic $\sum_j \phi_j\sigma_j^{-1}\phi_j$ is recognized as $(\beta\zeta)^{-1}\mathbf{D}^{-1}$, and when the x and y axes in the EK description are interchanged (EK consider J_{yx} instead of J_{xy}) then the contribution of the first two terms in (EKC 5) to the viscosity becomes, in the notation of our paper,

$$[\eta_\infty] = \frac{N_A\beta}{M\eta_0}\langle\langle {}^0\mathrm{I}\cdot[{}^0\mathbf{D}^{-1} - {}^0\mathbf{D}^{-1}\cdot{}^0\mathbf{e}^\alpha\tilde{D}_{\alpha\beta}\,{}^0\mathbf{e}^\beta\cdot{}^0\mathbf{D}^{-1}]\cdot{}^0\mathrm{I}\rangle\rangle. \tag{4.14}$$

A comparison with the forms (4.3) and (4.6) for $\tilde{D}_{\alpha\beta}$ shows that the matrix in brackets in (4.14) is the Cartesian representation of the extension of the matrix $[D^{-1}_{(h)}]^{ab}$ to the full configuration space, made by putting zeros for any element with at least one soft index. Consequently Eq. (4.14) is identical with our result (3.12). The matrix element in the term $H^{(2)}$ in Eq. (EKC 5), which contributes to the frequency dependent part of $[\eta(\omega)]$, may be written in our notation as

$$\left\langle\left\langle g_m^{(0)}\,{}^0J^{-1}\frac{\partial}{\partial q_\beta}\,{}^0J\,\tilde{D}_{\beta\alpha}\,{}^0\mathbf{e}^\alpha\cdot\mathbf{D}^{-1}\cdot\mathrm{I}\right\rangle\right\rangle \;. \tag{4.15}$$

[Notice that the eigenfunctions $\psi_\lambda(\mathbf{q})$, Eq. (EK 17), correspond to our $[P^{(s)}_{\mathrm{eq}}]^{1/2}g_m^{(0)}$; see also the equation following Eq. (EK 19)]. Via a formal extension of $\tilde{D}$ to the full space and use of Eqs. (2.13) and (3.23) we obtain

$$\tilde{D}_{\beta i}({}^0D^{-1})^{ij}\,{}^0\mathrm{I}_j = \{\delta^j_\beta - {}^0D_{\beta a}[{}^0D^{-1}_{(h)}]^{ab}\,\delta^b_j\}\,{}^0I_j = \tilde{I}_\beta \quad . \tag{4.16}$$

Therefore Eq. (4.15) has the form of Eq. (3.18) with $\tilde{J}_{xy}$ given by

$$\tilde{J}_{xy} = {}^0J^{-1}\frac{\partial}{\partial q_\alpha}\,{}^0J\tilde{I}_\alpha \quad . \tag{4.17}$$

By a partial integration, similar to the one that leads from Eq. (3.21) to Eq. (3.27), we may rewrite this as

$$\tilde{J}_{xy} = \tilde{I}_\alpha F^\alpha_{\mathrm{ent}} \quad , \tag{4.18}$$

with the entropic force F^α_{ent} given by Eq. (3.25). Equation (4.18) is exactly equal to Eq. (3.27) for the case in which $U^{(s)}$ vanishes; the result (EKC 5) is only valid for the case of vanishing $U^{(s)}$, since this assumption is made in deriving Eq. (EK 28).

The analysis in this subsection shows that the results of the corrected version of the Erpenbeck–Kirkwood theory agree with those of our theory and that of Fixman and Kovac. This is true in spite of the unwarranted assumption in EK about the form of the metric tensor. Actually, when the corrections from EKC are made, all references to the metric tensor disappear from the results of EK.

V. CONCLUDING REMARKS

In this paper we presented a theory of the intrinsic viscosity of dilute solutions of stiff polymers.

Constrained quantities, such as bond lengths and possibly bond angles, are treated as classical dynamical variables, subject to a strong, harmonic, but otherwise arbitrary potential. The advantage of this approach is that it allows us to start from well-established basic equations, formulated in the Cartesian coordinate system. The asymptotic forms for the case in which the constraints become rigid are then established by means of a straightforward expansion procedure.

Our expressions for the intrinsic viscosity are obtained by the correlation function method; this permits a simple analysis in terms of the diffusive motion of a polymer in the absence of any imposed velocity field. Of course the correlation function method also restricts us to the linear response regime. However, our treatment of constraints can surely be extended to the nonlinear regime.

In Sec. IV we showed that our results are in complete agreement with those obtained by Fixman and Kovac[1] and by Erpenbeck and Kirkwood.[4] Discrepancies are found with the results of Doi *et al.*[2,10] and Hassager.[3] In the case of Doi *et al.* the discrepancy can be attributed to a premature averaging over the constrained coordinates; in Hassager's case it is related to a different choice of the equilibrium ensemble and the use of a different Jacobian in the divergence operation.[19] The difference in ensembles is discussed in Sec. IV. C and Ref. 13. The most striking difference is the presence in Hassager's ensemble, which was originally proposed by Kramers,[14] of correlations in the orientation of different bond vectors, even in the absence of any potential depending on those relative orientations; we will call such correlations "Kramers correlations" in the remainder of this section.

In Sec. X of Ref. 3 Hassager reports a further discrepancy between the two ensembles, the result obtained with his model for the first non-Newtonian correction to the static viscosity of a three-bead flexible chain differs from the expression obtained by Bird, Johnson, and Curtiss[20] with a model of the kind discussed in this paper.

In Ref. 3 it is suggested that Kramers' ensemble is the appropriate one when the hard variables are treated quantum-mechanically rather than classically. Although the resolution of this question must await a quantum treatment of the entire polymer–solvent system, we will briefly state our reasons for doubting this conjecture.

One might try to include some quantum effects by replacing the classical probability distribution for the normal coordinates $Q'_{(i)}$ of Eq. (2.7) by the probability distribution derived from the quantum vibrational partition function. The latter is a Gaussian with width $\frac{1}{2}\hbar\omega \times\coth(\frac{1}{2}\beta\hbar\omega)$ rather than β^{-1}, with ω the frequency of the oscillator.[21] After integration over the hard coordinates this probability distribution leads to our $P_{\text{eq}}^{(s)}$, Eq. (3.14), rather than to Kramers' ensemble.

Another indication is obtained by considering the Schrödinger equation for a model polymer molecule in vacuum. This sytem is simply a vibrating (and rotating) molecule, described by a Hamilton operator whose structure is similar to $\mathfrak{D}^\dagger$ in the free draining limit.[22] This system is discussed in a rather qualitative was by Gō and Scheraga.[16] We wish to point out that a much more explicit procedure to pass to the rigid limit in the Schrödinger equation for such a molecule, very similar to the one we employed in Sec. II, is given by Flügge and Weiguny.[23] When their procedure is adapted to a freely jointed chain molecule, an effective Schrödinger operator results for the soft coordinates only, that is of the form (2.16) without soft potential. In particular the divergence operation contains the full Jacobian, and the ground state does not show any Kramers correlations. When the soft degrees of freedom are treated classically one obtains an equilibrium distribution of the type described in the preceding paragraph, and not Kramers' ensemble, as claimed in Ref. 16.

For the reasons outlined above we prefer the freely jointed chain model, used in this paper and, e.g., in Refs. 1, 2, and 4, to Kramers' model. While the latter is internally consistent,[13] it is unlikely to be obtainable from any model in which the constraints are described by means of a realistic potential.

ACKNOWLEDGMENTS

We thank Dr. Jeffrey Kovac, Dr. Marshall Fixman, and Dr. Ole Hassager for very helpful discussions and comments.

APPENDIX A

The operator $\mathfrak{D}^{(-1)}$ is given by

$$\mathfrak{D}^{(-1)} = -\beta\kappa\, {}^0G^{ab}(Q_b - {}^0Q_b)\, {}^0D_{a\alpha}\frac{\partial}{\partial q_\alpha} + {}^0J^{-1}\frac{\partial}{\partial q_\alpha}\, {}^0J\, {}^0D_{\alpha a}\frac{\partial}{\partial Q_a} - \beta\, {}^0\!\left[\frac{\partial U^{(s)}}{\partial q_\alpha}\right]{}^0D_{\alpha a}\frac{\partial}{\partial Q_\alpha} + {}^0D_{\alpha a}\frac{\partial^2}{\partial q_\alpha \partial Q_a} - \beta\, {}^0[U^{(s)}]^{,a} D_{ab}\frac{\partial}{\partial Q_b}$$
$$- \beta\kappa\, {}^0G^{ab,c}(Q_a - {}^0Q_a)(Q_, - {}^0Q_c)\, {}^0D_{bd}\frac{\partial}{\partial Q_d} - \beta\kappa\, {}^0G^{ab}(Q_b - {}^0Q_b)\, {}^0D_{ac}^{,d}(Q_d - {}^0Q_d)\frac{\partial}{\partial Q_c} + {}^0J^{-1}\, {}^0(JD_{ab})^{,a}$$
$$+ {}^0(J^{-1})^{,a}(Q_a - {}^0Q_a)\, {}^0J\, {}^0D_{bc}\frac{\partial^2}{\partial Q_b\, \partial Q_c} \quad . \tag{A1}$$

When $\mathfrak{D}^{(-1)}$ operates on $g^{(0)}$, only the first term contributes and it is then easy to verify by substitution that Eq. (2.11) is a solution of Eq. (2.10b), when the latter is used to determine $g^{(1)}$.

In order to evaluate Eq. (2.12) we need only those parts of $\mathfrak{D}^{(0)}$ that do not vanish when operating on $g^{(0)}$, i.e., those terminating in a $\partial/\partial q_\alpha$. This part of $\mathfrak{D}^{(0)}$, denoted by $\mathfrak{D}_g^{(0)}$, is given by

$$\mathfrak{D}_g^{(0)} = {}^0J^{-1}\frac{\partial}{\partial q_\alpha}\, {}^0J\, {}^0D_{\alpha\beta}\frac{\partial}{\partial q_\beta} - \beta\frac{\partial\, {}^0U^{(s)}}{\partial q_\alpha}\, {}^0D_{\alpha\beta}\frac{\partial}{\partial q_\beta} - \beta\, {}^0[U^{(s)}]^{,a}\, {}^0D_{a\alpha}\frac{\partial}{\partial q_\alpha} - \beta\kappa\, {}^0G^{ab,c}(Q_b - {}^0Q_b)(Q_c - {}^0Q_c)\, {}^0D_{a\alpha}\frac{\partial}{\partial Q_\alpha}$$
$$- \beta\kappa\, {}^0G^{ab}(Q_b - {}^0Q_b)\, {}^0D_{a\alpha}^{,c}(Q_c - {}^0Q_c)\frac{\partial}{\partial q_\alpha} + {}^0J^{-1}\, {}^0(JD_{a\alpha})^{,a}\frac{\partial}{\partial q_\alpha} \quad . \tag{A2}$$

When Eq. (A1) is applied to $g^{(1)}$, all terms except the last one contribute to the result. The second and third terms in $\mathfrak{D}^{(-1)}g^{(1)}$ combine with the first two terms in $\mathfrak{D}_g^{(0)}g^{(0)}$ to give the expression containing $\tilde{D}_{\alpha\beta}$ in Eq. (2.12). The terms containing hard derivatives of the quantities $U^{(s)}$, G^{ab}, and J cancel exactly, and the remaining terms combine into the expression containing $[Q_a - {}^0Q_a)(Q_b - {}^0Q_b) - (\beta\kappa)^{-1}(G^{-1})_{ab}]$, when use is made of the relation $(G^{-1})_{ab}G^{bc} = \delta_a^c$, where δ_a^c is the unit tensor in the hard indices: $\delta_a^c A^a = A^c$; $\delta_a^c A_c = A_a$. The choice for $g^{(2)}$ that leads to cancellation of the E_α^{ab} term in Eq. (2.12) is

$$g^{(2} = \tfrac{1}{2}[{}^0D_{(h)}^{-1}]^{ab}({}^0G^{-1})_{bc}E_\alpha^{cd}[Q_a - {}^0Q_a)(Q_d - {}^0Q_d) - (\beta\kappa)^{-1}({}^0G^{-1})_{ad}]\frac{\partial}{\partial q_\alpha}q^{(0)} \; ; \tag{A3}$$

when we apply $\mathfrak{D}^{(-2)}$ to Eq. (A3) we obtain exactly minus the E_α^{ab} term of Eq. (2.12).

APPENDIX B

When one evaluates Eq. (3.17), substitution of Eq. (2.11) for $g_m^{(1)}$ in the second term on the rhs leads immediately to the fourth term on the rhs of Eq. (3.19. To evaluate the first term in Eq. (3.17) we must expand the weight factor $P_{\mathrm{eq}}(\mathbf{q})\,J(\mathbf{q})$ in Eq. (1.7):

$$P_{\mathrm{eq}}(\mathbf{q})\,J(\mathbf{q}) = P_{\mathrm{eq}}^{(0)}\,{}^0J(1 + p_{\mathrm{eq}}^{(1)} + \cdots) \ , \tag{B1}$$

with [cf. Eq. (1.14)]

$$P_{\mathrm{eq}}^{(0)} = \mathfrak{N}\left|\det{}^0G\right|^{1/2}\kappa^{h/2} \times \exp[-\beta\,{}^0U^{(s)} - \tfrac{1}{2}\beta\kappa\,{}^0G^{ab}(Q_a - {}^0Q_a)\,(Q_b - {}^0Q_b)] \ , \tag{B2}$$

$$p_{\mathrm{eq}}^{(1)} = \{{}^0J^{-1}\,{}^0J^{,a} + \tfrac{1}{2}\left|{}^0\det G\right|^{-1}\,{}^0(\det G)^{,a} - \beta\,{}^0[U^{(s)}]^{,a} - \tfrac{1}{2}\beta\kappa\,{}^0G^{bc,a}(Q_b - {}^0Q_b)\,(Q_c - {}^0Q_c)\}\,(Q_a - {}^0Q_a) \ . \tag{B3}$$

After substitution of Eq. (3.6) for $J_{xy}^{(-1)}$ one sees that only the term with $p_{\mathrm{eq}}^{(1)}$ in Eq. (B1) contrubutes to the matrix element $\langle J_{xy}^{(-1)}|g_m^{(0)}\rangle$; after evaluation of the Gaussian integrals we collect the following contributions to $\tilde{J}_{xy}$:

$$-\beta^{-1}\,{}^0J^{-1}\,{}^0I_a\,{}^0J^{,a} - \tfrac{1}{2}\beta^{-1}I_a\left|\det{}^0G\right|^{-1}(\det G)^{,a} + {}^0I_a^0[U^{(s)}]^{,a} + \beta^{-1}\,{}^0I_a\,{}^0G^{ab,c}({}^0G^{-1})_{bc} + \tfrac{1}{2}\beta^{-1}I_a\,{}^0G^{bc,a}({}^0G^{-1})_{bc} \ . \tag{B4}$$

Since the coefficient of G^{bc} in $\det G$ is exactly $|\det G|G_{bc}^{-1}$, the second and the last term cancel one another. Next we evaluate $\langle J_{xy}^{(0)}|g_m^0\rangle$ by substitution of Eq. (3.16) for $J_{xy}^{(0)}$. In this case we may replace $P_{\mathrm{eq}}J$ by $P_{\mathrm{eq}}^{(0)}\,{}^0J$, and the Gaussian integral gives the following contributions to $\tilde{J}_{xy}$:

$$-{}^0I_i\,{}^0\!\left[\frac{\partial U^{(s)}}{\partial q_i}\right] - \beta^{-1}\,{}^0I_a^{,a} - \beta^{-1}\,{}^0I_a\,{}^0G^{ab,c}({}^0G^{-1})_{bc} \ . \tag{B5}$$

Adding the contributions (B4) and (B5) gives

$$-\beta^{-1}\,{}^0J^{-1}\,{}^0I_a\,{}^0J^{,a} - {}^0I_\alpha\,\frac{\partial\,{}^0U^{(s)}}{\partial q_\alpha} - \beta^{-1}\,{}^0I_a^{,a} \ . \tag{B6}$$

These are exactly the first three terms on the rhs of Eq. (3.19). This concludes our derivation of the exexpression (3.19) for J_{xy}.

---

*Supported in part by the National Science Foundation.

†Present address: Institut für Theoretische Physik A, RWTH Aachen, 5100 Aachen, Germany.

‡John Simon Guggenheim Memorial Fellow 1974–75.

[1] M. Fixman and J. Kovac, J. Chem. Phys. **61**, 4939 (a) and 4950(b), (1974). Equations in the first paper are cited as (FK 1.1) etc.

[2] M. Doi, H. Nakajima, and Y. Wada, "Theory of the High-frequency Limiting Viscosity of a Dilute Polymer Solution I," submitted in Colloid and Polymer Science. Equations are cited as (DNW 1) etc. A preliminary report appeared in Rept. Prog. Polym. Phys. Jpn. **16**, 91 (1973).

[3] O. Hassager, J. Chem. Phys. **60**, 2111(a) and 4001(b) (1974). Equations in the first paper are cited as (H 1) etc.

[4] J. J. Erpenbeck and J. G. Kirkwood, J. Chem. Phys. **29**, 909 (1958); Erratum, J. Chem. Phys. **38**, 1023 (1963). Equation from the paper and the erratum are cited as (EKC 1) etc., respectively.

[5] B. U. Felderhof, J. M. Deutch, and U. M. Titulaer, J. Chem. Phys. **63**, 740 (1975).

[6] G. K. Fraenkel, J. Chem. Phys. **20**, 42 (1952).

[7] e.g. H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, 1950), Chap. 10.

[8] E.g. H. Yamakawa, *Modern of Polymer Solutions* (Harper and Row, New York, 1971), Sec. 31.

[9] Yu. Ya. Gotlib and Yu. Ye. Svetlov, Polymer Sci. USSR **8**, 1670 (1966); see also P. Debye, J. Chem. Phys. **14**, 636 (1946); and Ref. 14.

[10] M. Doi and K. Okano, Polymer J. **5**, 216 (1973). Equations are cited as (DO.1) etc.

[11] W. H. Stockmeyer, G. Wilemski, H. Yamakawa, and G. Tanaka, J. Chem. Phys. **63**, 1039 (1975).

[12] H. Yamakawa, G. Tanaka, and W. H. Stockmayer, J. Chem. Phys. **61**, 4535 (1974).

[13] M. Fixman, Proc. Natl. Acad. Sci. USA **71**, 3050 (1974).

[14] H. A. Kramers, Physica **11**, 1 (1944), translated in J. Chem. Phys. **14**, 415 (1946).

[15] D. ter Haar, *Elements of Thermostatics*, 2nd ed. (Holt, Rinehart, and Winston, New York, 1966), p. 159.

[16] N. Go and H. A. Scheraga, J. Chem. Phys. **51**, 4751 (1969).

[17] H. Giesekus, Rheol. Acta **5**, 29 (1966).

[18] J. G. Kirkwood, Rec. Trav. Chim. Pays Bas **68**, 649 (1949), J. Polym. Sci. **12**, 1 (1954); J. A. Riseman, and J. G. Kirkwood, in *Rheology*, edited by F. R. Eirich (Academic, New York, 1956), Vol. I, Chap. 113.

[19] The two differences are related; for the self-adjointness of $\mathfrak{D}^\dagger$ it is necessary that the Jacobians in the divergence operation and in the weighting factor of the integration are the same.

[20] R. B. Bird, M. W. Johnson, Jr., and C. F. Curtiss, J. Chem. Phys. **51**, 3023 (1969).

[21] A. Messiah, *Quantum Mechanics* (North Holland, Amsterdam, 1970), Vol. I, Sec. XII.12.

[22] The immediate analog of the Hamilton operator is not $\mathfrak{D}^\dagger$ but the operator L, introduced in Ref. 4, Eq. (EK.15). It is related to $\mathfrak{D}^\dagger$ by the identity

$$\mathfrak{D}^\dagger f = [P_{\mathrm{eq}}^{(s)}]^{-1/2}\,L\,[P_{\mathrm{eq}}^{(s)}]^{1/2} f.$$

[23] S. Flügge and A. Weiguny, Z. Phys. (Leipz). **162**, (1961), see also H. Diehl, S. Flügge, U. Schröder, A. Völkel, and A. Weiguny, *ibid*. **162**, 1 (1961). We wish to thank Dr. James Kinsey for bringing this work to our attentiona and for a helpful discussion on the subject.