The Viscosity Increment for a Dilute Suspension of Triaxial Ellipsoids in Dominant Brownian Motion

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Using a model first introduced by Simha (*J. Phys. Chem.* **44**, 25 (1940)), an explicit expression for the viscosity increment of a dilute suspension of general triaxial ellipsoidal particles is derived assuming that Brownian motion is dominant and that the particles are on average at rest in the referential frame. By comparison with a recently published numerical procedure (Rallison, *J. Fluid Mech.* **84**, 237 (1978)) it is shown that this latter assumption leads to no significant errors for "globular" particles (axial ratios < 3) and to only very small errors ($\sim 1\%$) for the worst case. The use of the viscosity increment, together with other hydrodynamic parameters, for estimation of unique values for the three principle axes of globular particles is briefly discussed.

INTRODUCTION

One way in which the biologist hopes to use theoretical results from the rheology of suspensions is in trying to infer the shape of biological macromolecules from experiments on suspensions of the molecules. In contrast with the detailed picture of molecular structure that emerges from X-ray studies of the crystalline state, such an approach can hope to do little more than select the best approximation to the gross structure from a limited range of simple shapes such as rods, disks, and ellipsoids. Nevertheless the study has considerable importance since the conformation of the molecule in its crystalline state may differ significantly from its conformation *in vivo* where it is surrounded by fluid.

Within the class of ellipsoidal models only ellipsoids of revolution have been used hitherto, and although the advent of the modern high-speed computer has rendered possible the use of the general ellipsoidal model, it seems to have been widely considered that no great gain would be obtained from doing so. Obviously the structure of some molecules is such that no ellipsoid can remotely approximate even their hydrated shape, but many biological macromolecules, in particular, globular proteins, will be well modeled by an ellipsoid, and it seems likely to us that the extra degree of freedom available in a general ellipsoidal model would lead to more useful results.

To obtain an estimate of shape for an assumed model requires a number of different types of measurements to be carried out on the suspension (3)—experiments on translational diffusion, sedimentation, viscosity, and electric birefringence, for example. Small and Isenberg (4) have recently tabulated the Perrin equations (5) for diffusion in the case of general ellipsoidal particles by computation, and in this paper we derive an explicit formula (Eq. [9]) for the viscosity increment of a dilute suspension of rigid ellipsoidal particles subject to overwhelming Brownian motion which generalizes the widely used classical formula for ellipsoids of revolution first proposed by Simha (1). Although the derivation of this formula involves an approximation, no difference at levels likely to be experimentally significant for the range of axial ratios in question

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is noted from values yielded by a general numerical procedure recently published by Rallison (2). We are able to restrict our investigation to dilute suspensions and to the very simplest flows since, for the applications in which we are concerned, the dilution will be within the control of the experimenter while the flows of interest will be the simple viscometric ones such as Couette or Poiseuille flow. Indeed, in practice, the experiments are conducted so that the results may be extrapolated to infinite dilution and zero shear rate.

BROWNIAN MOTION

Although the forces and torques exerted upon a suspended particle by a viscous fluid are all ultimately of molecular origin, it is convenient to distinguish those that can be explained by continuum hydrodynamics from those, due to molecular fluctuations, that give rise to Brownian motion. If we first completely neglect the Brownian motion, it is clear that, once a steady state has been attained, suspended particles free of any external impressed forces must move in such a way as to make the hydrodynamic force and torque acting upon them zero.

Let us consider a steady, simple-shearing flow. The motion of the fluid in the neighborhood of any point can be decomposed into three components: a translational velocity which varies from point to point, an angular velocity which for this type of flow is the same at all points, and a pure straining motion which again is the same at all points. If now a single neutrally buoyant, rigid ellipsoidal particle is introduced the flow will be disturbed, although at large distances from the ellipsoid the disturbance will tend to zero. We shall assume that the motion of the ellipsoid and of the fluid is such that the Reynolds number is very small. Then it is possible on the basis of the work of Oberbeck (6) and Jeffrey (7) to say what the hydrodynamic forces and torques acting on the particle are. In particular it is known that the force will be zero when the translational velocity of the particle is the same as the translational velocity of the point in the undisturbed flow at which the particle is suspended. The situation for angular velocity is more complicated since two factors come into play: one gives a torque if the angular velocity of the particle differs from the angular velocity defined by the undisturbed flow (or, equivalently, by the actual flow at infinity), while the other gives a torque if the principal axes of the ellipsoid have a different orientation from the principal axes of the straining motion defined by the undisturbed flow. Taken together these mean that the angular motion of the particle under zero torque conditions is very complicated (7, 8) and a complete solution for it is not known.

Turning to the Brownian motion which is in the nature of a fluctuation the simplest question we can ask is, what is the average velocity and the average angular velocity of the particle? By the average we mean in the first instance the time average, although in practice this will be assumed equal to a volume average taken over an ensemble of a very large number of particles suspended in unit volume (see (9) for a detailed discussion of various methods of averaging). Ignoring for the moment the hydrodynamic forces, we can answer the question by saying that on average the particle is at rest in the local frame of reference defined by the undisturbed flow. In other words it is on average moving with the translational velocity of the point in the undisturbed flow at which it is suspended and with the angular velocity defined by the undisturbed flow.

When we come to consider the combined effect of the hydrodynamic forces and the Brownian motion no problem arises with the translational motion of the particle since both effects tend in the same direction—motion with the translational velocity of the flow. But for the angular motion the situation is less simple, the two effects do not have the same tendency, and we must consider a range of possibilities depending upon the relative strengths of the two. We shall only be considering the case of overwhelming Brownian motion in which the hydrodynamic effects are completely negligible compared with the Brownian motion effects. Thus we shall take it that on average the particles are rotating with the local angular velocity of the ambient flow. This latter condition has been proved for axisymmetric particles (10–14). We here make the assumption that it will be true to an adequate approximation for general ellipsoids of low axial ratios (a/b 1.0 → 3.0, b/c 1.0 → 3.0)—i.e., for a typical globular protein. As will be apparent later (see Discussion) the magnitude of the uncertainty introduced by this assumption can be ascertained by comparison of values from our formula with those of Rallison's numerical procedure (2). We may additionally assume that the orientation of the particles will be random. This last fact would not be so if hydrodynamic forces and torques were not negligible for they introduce systematic motions and hence preferred orientations.

THE SIMHA MODEL OF OVERWHELMING BROWNIAN MOTION

We consider a homogeneous dilute suspension of identical rigid ellipsoids randomly oriented in an incompressible Newtonian fluid in which they are neutrally buoyant. The ambient flow is taken to be a slow simple-shearing flow, while the suspended particles are taken to be moving with the velocity and the angular velocity of the ambient flow appropriate to the point at which each is suspended. Near each particle this ambient flow is disturbed but is taken still to be a slow (low Reynolds number) flow so that we may apply the classical results of Jeffrey (7). This model, which is taken to be appropriate for the case of overwhelming Brownian motion, derives from Simha (1), although in his original work doubt is left about whether or not the particles are rotating with the local angular velocity of the fluid.

The key simplifying feature of the model introduced by Simha is that it eliminates the complicated statistical problem presented by the Brownian motion by substituting an assembly of particles all moving with the average motion. This, together with the assumptions of diluteness and random orientation, allows us to compute the effect of the suspended particles by simply summing their individual effects. The symmetry of the particle distribution in the model means that non-Newtonian behavior will not appear, and also allows us to use the energy dissipation method of computing the viscosity (9, 15).

The simplifications of the model are achieved, however, at a price. Non-Newtonian and concentration-dependent effects, which to the theoretical rheologist are of the greatest interest, have been deliberately discarded; and the model can say nothing about lesser degrees of Brownian motion. In effect we shall be calculating only the first term of a series; nevertheless even this is of great value to the experimental biochemist. In applications, of course, one must distinguish the question of what results follow from the model from the question of the conditions under which the model is applicable.

THE VISCOSITY INCREMENT

We let μ^* be the viscosity measured in an experiment on a dilute suspension of particles in a fluid of viscosity μ. If c is the concentration—the total volume of the particles in a unit volume of the suspension—then the viscosity increment, ν, is defined by

$$\mu^*/\mu = 1 + \nu c, \qquad [1]$$

where, when ν is independent of c, the linear dependence of μ^*/μ upon c gives the empirical characterization of a dilute suspension. From the theoretical point of view, however, a dilute suspension is one in which there are no hydrodynamic interactions between the particles and thus in which

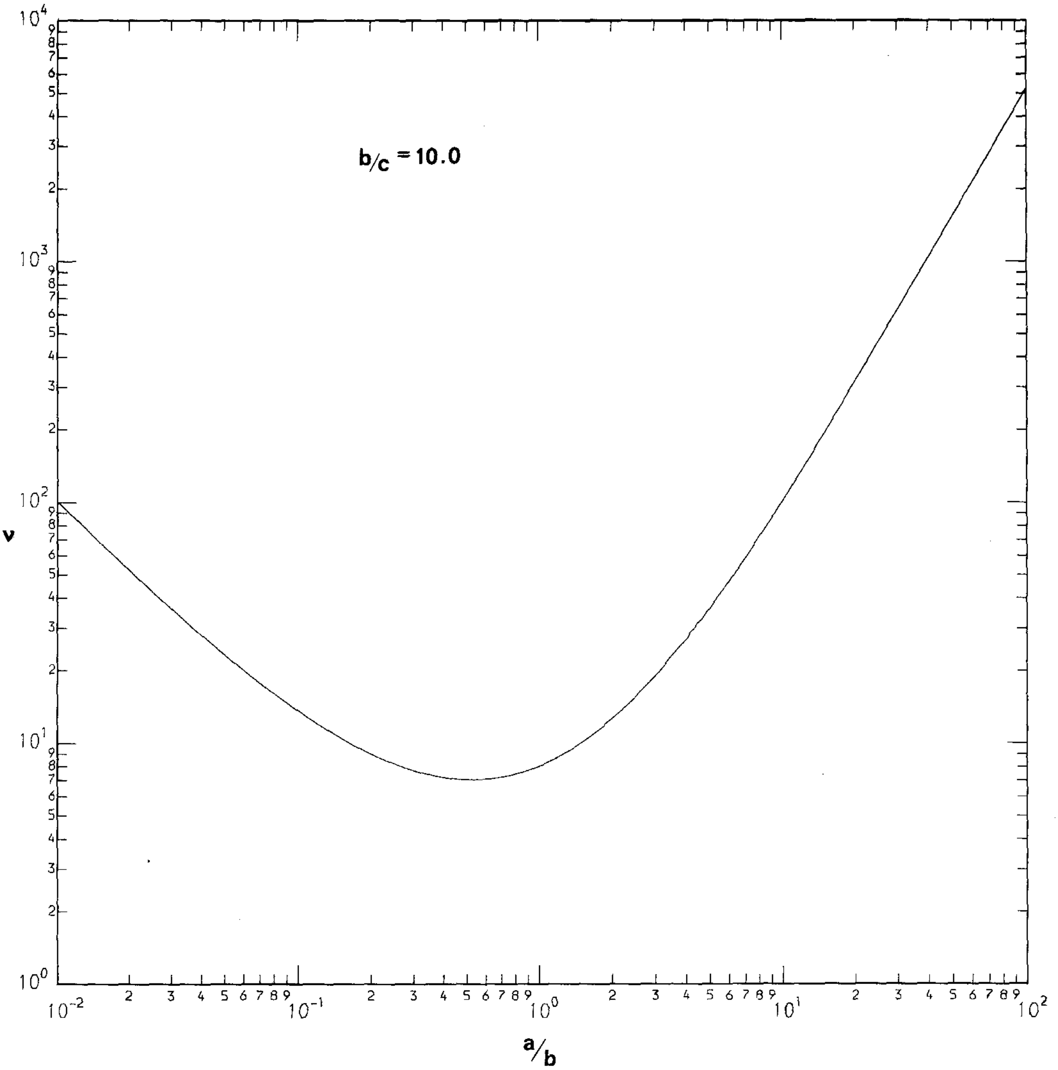

FIG. 1. A plot of ν as a function of a/b when $b/c = 10.0$ ($a > b > c$). This agrees closely to that given by Rallison (2, Fig. 7). (N.B., Rallison has $c > a > b$.)

each particle independently contributes to the viscosity the same amount it would were it alone present. This contribution for a general ellipsoidal particle was first calculated by Jeffrey (7) using considerations of energy dissipation, and it is a straightforward matter to extend his results to cover the case of ellipsoids rotating with the local angular velocity of the ambient flow as required by our model.

Taking a rectangular Cartesian coordinate system (x_i) with origin at the center of the ellipsoid and aligned along its principal axes, the velocity field of the fluid far from the particle is given up to terms of order r^{-3} by

$$u_i = d_{ij}x_j - 4A_{jk}x_jx_kx_ir^{-5} - (4/3)(A_{ij} - A_{ji})x_jr^{-3}, \quad [2]$$

where (d_{ij}) are the components of the velocity gradient tensor of the ambient flow and

TABLE I

Values of ν as a Function of $(a:b:c)$ for a General Triaxial Ellipsoid $(a > b > c)$[a]

Oblate ellipsoid a/b	Prolate ellipsoid b/c										
	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
1.0	2.500	2.507	2.524	2.550	2.583	2.620	2.661	2.706	2.753	2.803	2.854
1.1	2.507	2.520	2.544	2.576	2.614	2.656	2.702	2.751	2.803	2.857	2.913
1.2	2.525	2.545	2.575	2.612	2.655	2.703	2.754	2.808	2.865	2.923	2.983
1.3	2.553	2.579	2.615	2.658	2.706	2.759	2.815	2.874	2.935	2.998	3.063
1.4	2.588	2.621	2.662	2.711	2.764	2.822	2.883	2.947	3.013	3.081	3.151
1.5	2.630	2.668	2.716	2.770	2.829	2.892	2.958	3.027	3.098	3.171	3.245
1.6	2.677	2.722	2.775	2.834	2.899	2.967	3.039	3.113	3.189	3.267	3.346
1.7	2.729	2.779	2.839	2.904	2.974	3.047	3.124	3.204	3.285	3.368	3.453
1.8	2.785	2.842	2.907	2.978	3.053	3.132	3.215	3.300	3.386	3.475	3.565
1.9	2.844	2.908	2.978	3.055	3.137	3.222	3.310	3.400	3.492	3.586	3.681
2.0	2.908	2.977	3.054	3.137	3.224	3.315	3.408	3.504	3.602	3.702	3.803

[a] On the basis of Eq. [9].

(A_{ij}) are coefficients independent of position but depending upon the (d_{ij}) and the angular velocity of the particle (see (7, Eqs. 25, 26), noting A_{11} is Jeffrey's A, A_{12} is his H, A_{21} his H', etc.); the usual summation convention is used in our equations. The additional rate of dissipation of energy, Δ, due to the presence of the particle is found to be

$$\Delta = (32/3)\pi\mu A_{ij}d_{ij}, \qquad [3]$$

(compare (7, Eq. 58)). For the particular case of a particle rotating with the fluid the (A_{ij}) are homogeneous linear functions of the (d_{ij}),

$$A_{ij} = C_{ikjl}d_{kl}, \qquad [4]$$

where the coefficients (C_{ikjl}) can be read off from Jeffrey's formulas. For a simple-shearing flow of the suspension there will be orthogonal unit vectors (n_i), (m_i) such that

$$d_{ij} = \kappa n_i m_j, \qquad [5]$$

where κ is the shear rate, the components of these vectors being time dependent since the coordinate system we are using is rotating in space. Thus we obtain

$$\Delta = (32/3)\pi\mu\kappa^2 n_i n_j C_{ijkl} m_k m_l. \qquad [6]$$

At any given instant the components of (n_i) and (m_i) will differ according to which particle of the suspension we consider, but, subject only to the condition that the two vectors be orthogonal, all directions will be equally likely by our assumption on the Brownian motion. We thus calculate the total rate of dissipation of energy by all the particles in unit volume by taking the volume average of [6] over all directions (n_i), (m_i) subject to the restriction of orthogonality. This calculation is straightforward and gives

$$\Delta_{\text{tot}} = (32/3)\pi\mu\kappa^2 NZ, \qquad [7]$$

where N is the number density of suspended particles, and where

$$Z = \frac{1}{30}\left\{\frac{\alpha_0'' + \beta_0'' + \gamma_0''}{\beta_0''\gamma_0'' + \gamma_0''\alpha_0'' + \alpha_0''\beta_0''}\right\} + \frac{1}{40}\left\{\frac{\beta_0 + \gamma_0}{\alpha_0'(b^2\beta_0 + c^2\gamma_0)} + \frac{\gamma_0 + \alpha_0}{\beta_0'(c^2\gamma_0 + a^2\alpha_0)} + \frac{\alpha_0 + \beta_0}{\gamma_0'(a^2\alpha_0 + b^2\beta_0)}\right\}, \qquad [8]$$

where a, b, c are the semiaxes of the ellipsoid, and where α_0 etc. which depend on a, b, c are defined by certain elliptic integrals given by Jeffrey (7). Equating Δ_{tot} with

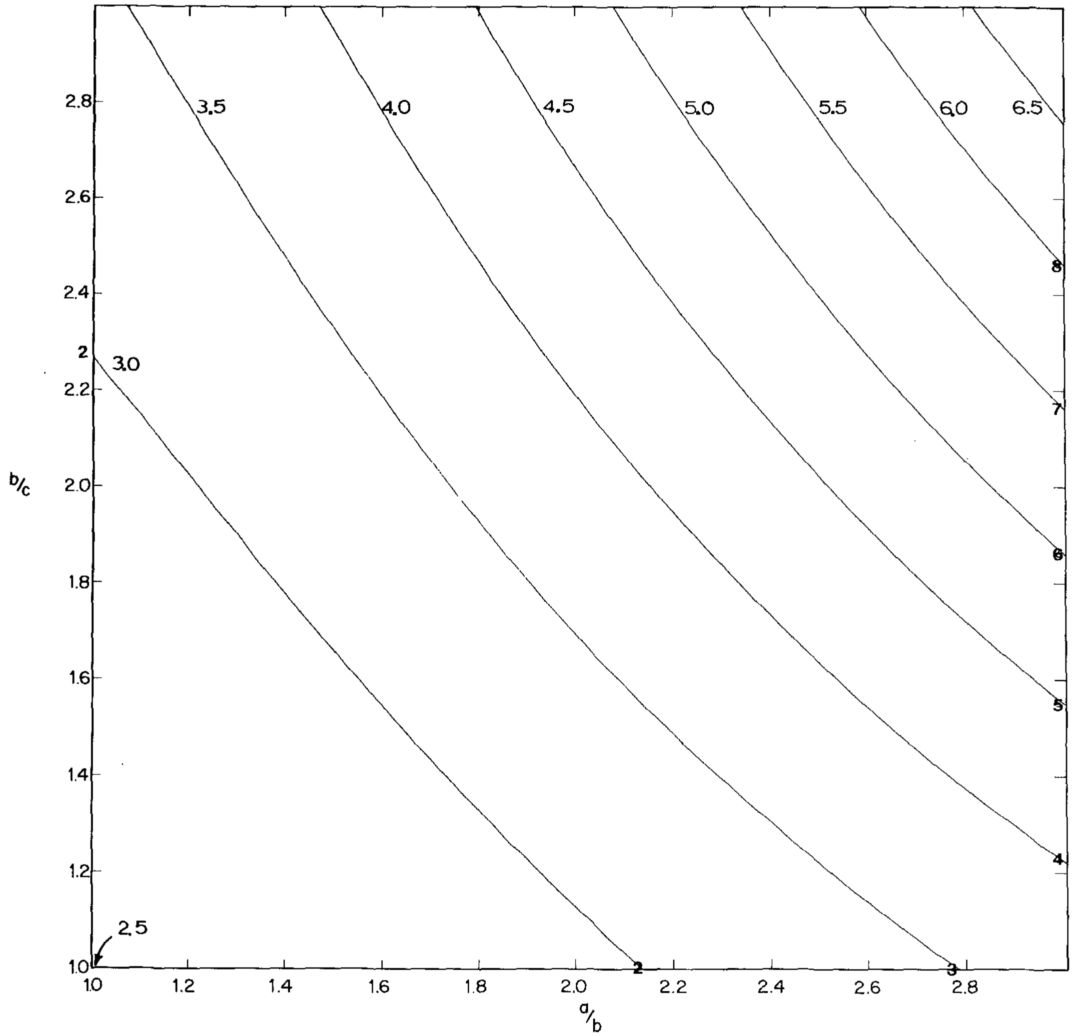

FIG. 2. Contour diagram showing curves of constant ν as a function of the semiaxial ratios a/b, b/c, on the basis of Eq. [9].

$(\mu^* - \mu)\kappa^2$ gives the result

$$\nu = \frac{1}{abc}\left\{\frac{4(\alpha_0'' + \beta_0'' + \gamma_0'')}{15(\beta_0''\gamma_0'' + \gamma_0''\alpha_0'' + \alpha_0''\beta_0'')} + \frac{1}{5}\left[\frac{\beta_0 + \gamma_0}{\alpha_0'(b^2\beta_0 + c^2\gamma_0)} + \frac{\gamma_0 + \alpha_0}{\beta_0'(c^2\gamma_0 + a^2\alpha_0)} + \frac{\alpha_0 + \beta_0}{\gamma_0'(a^2\alpha_0 + b^2\beta_0)}\right]\right\}. \quad [9]$$

When $b = c$ this formula reduces to the classical equation first derived by Simha (1), and when $a = b = c$ it reduces to the value $\nu = 2 \cdot 5$ derived by Einstein (16, 17). Had Simha really been considering a model in which the ellipsoids had zero rotation as his words may have suggested, the formula should have reduced in the case of a sphere to $\nu = 4$ as shown by Brenner (18). That it in fact gives $2 \cdot 5$ is sufficient to rule out that interpretation although indeed it has been known since the work of Saito (12) that the classical formula held only on the assumption that overwhelming Brownian motion implied that the particles were rotating with the local angular velocity of the fluid.

DISCUSSION

A general analysis using the full statistical treatment of the angular motion has recently been given by Rallison (2). His results for the case of overwhelming Brownian motion show that to first order in the shear rate, the non-Newtonian stress effects vanish which is consistent with our assumption of Newtonian behavior for very low shear rates. He also gives an expression for ν correct to first order in the shear rate, although not in the form of a simple formula like [9], but by using numerical methods Rallison is able to give a plot of ν for various axial ratios. The results are clearly very close to those obtained from [9]; compare our Fig. 1 with Rallison's Fig. 7.

However, an exact comparison (J. M. Rallison, personal communication) shows a very slight discrepancy between values from our formula and from Rallison's procedure, although this discrepancy is not apparent within four significant figures for the range of asymmetry which we are considering (Table I). The values given in Table I are therefore definitive. It has been indicated to us (J. M. Rallison, H. Brenner, private communications of unpublished work) that our formula requires the addition of a small extra term related to the deviation from our assumed condition of particles rotating on average with the local angular velocity of the fluid. The numerical results show our approximation to be extremely accurate for "globular" particles, as noted above, but for certain particles of higher asymmetry calculations suggest that deviations of up to 1% in ν can arise.

For the determination of shape parameters for globular particles, the extension to the general ellipsoidal case by using Eq. [9] should provide a much more powerful approach, but is not without difficulty since a given value of ν does not uniquely fix the two independent axial ratios of the ellipsoid. This is illustrated in Table I and Fig. 2. We are investigating the possibilities of applying our newly derived relationship to macromolecular suspensions using computer-based numerical inversion techniques treating the two axial ratios and the molecular volume as parameters to be simultaneously determined from experimental data obtained from a range of techniques, including viscosity. The results of these investigations have been encouraging and will be described elsewhere (3).

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REFERENCES

1. Simha, R., *J. Phys. Chem.* **44,** 25 (1940).
2. Rallison, J. M., *J. Fluid Mech.* **84,** 237 (1978).
3. Harding, S. E., and Rowe, A. J., in preparation.
4. Small, E. W., and Isenberg, I., *Biopolymers* **16,** 1907 (1977).
5. Perrin, F., *J. Phys. Radium* **7,** 1 (1936).
6. Oberbeck, A., *J. Reine Angew. Math.* **81,** 62 (1876).
7. Jeffrey, G. B., *Proc. Roy. Soc. London Ser. A* **102,** 161 (1922).
8. Chwang, A. T., *J. Fluid Mech.* **72,** 17 (1975).
9. Batchelor, G. W., *J. Fluid Mech.* **41,** 545 (1970).
10. Kuhn, W., and Kuhn, H., *Helv. Chim. Acta* **38,** 97 (1945).
11. Brinkman, H. C., *et al. in* "Proc. Int. Rheol. Congr., Schveningen, 1949," Vol. II, p. 77.
12. Saito, N., *J. Phys. Soc. Japan* **6,** 297 (1951).
13. Scheraga, H. A., *J. Chem. Phys.* **23,** 1526 (1955).
14. Brenner, H., *Chem. Eng. Sci.* **27,** 1069 (1972).
15. Brenner, H., *Progr. Heat Mass Transfer* **5,** 93 (1972).
16. Einstein, A., *Ann. Phys.* **19,** 289 (1906).
17. Einstein, A., *Ann. Phys.* **34,** 591 (1911).
18. Brenner, H., *J. Colloid Interface Sci.* **32,** 141 (1970).