Hence, the glassy *state* surely cannot be described by only one ξ parameter; the glass *transition*, however, being characterized by a T_g from an extrapolation method, can be represented approximately by the one-parameter model, at least in the case of atactic PS.

These aspects allow a new interpretation of the findings of McKinney and Simha for PVAC. Apparently the hole fraction h does not freeze-in completely at T_g but only a part of it. At lower temperatures the remaining holes take their equilibrium values under certain restraint conditions. In ref 33 Goldbach and Rehage propose the following molecular interpretation for the glass transition of PS: The interaction forces between neighbored phenyl groups of different polystyrene molecules work as fluctuating physical cross-links. Above T_g the frequency of the interchange of places is very high allowing the polymer chains to take their equilibrium positions within the time scale. At T_g a critical frequency of place interchanging is attained preventing the chains to glide off each other, the substance vitrifies. At lower temperatures only a part of the phenyl groups can move freely, under restraint conditions. At T_β all remaining phenyl groups loose their mobility causing a further restriction of the chain mobility. A correlation of the chain mobility to the hole fraction h of the Simha theory shows that h must not be constant at T_g.

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Possible Role of the Inertia of the Liquid in the Intrinsic Viscosity of Rodlike Particles

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ABSTRACT: In Burgers' formulation a suspended particle contributes to the viscosity of the suspension through the forces which the particle exerts on the liquid. For bodies in the form of a rod, it is convenient to distinguish between the radial forces (in the direction of the axis of the rod) and the tangential forces (perpendicular to the axis). The radial force is determined entirely by the velocity gradient, and its Fourier time transform has negligible high-frequency components. It is found that the radial contribution to the viscosity is not affected by the inertia of the liquid. The tangential force, however, is determined also by the rapidly fluctuating rotational Brownian motion, the Fourier time transform of which does contain components of quite high frequency. In these rapidly changing velocities and forces the inertia of the liquid plays an important role. The analysis is made for a rigid dumbbell, and although no explicit final answers for the intrinsic viscosity are obtained, the results in the limit of low and of high frequencies suggest that the tangential contribution to the viscosity is substantially reduced by the inertia of the liquid.

As early as 1938 Huggins[1] published a theory of the intrinsic viscosity of rigid rods, and it seems appropriate in a paper which pays tribute to his numerous contributions to science to discuss the possible effect of the inertia of the liquid. The model used by Huggins was a linear array of beads, used also in theories by Kuhn[2] and, later, by Kirkwood;[3–6] the rigid

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dumbbell is the simplest form of this model. In these theories, the inertia of the liquid is ignored because it is generally believed that accelerations are damped out so rapidly that their effect is negligible. In fact, until recently, the role of inertia in the transport properties of solutions and suspensions has been almost completely neglected. It has been known for more than a hundred years that the frictional resistance for a particle that moves through a liquid with time-dependent velocity is not proportional to this velocity but contains, in addition, terms which depend on the density of the liquid and the history of previous accelerations. The same is true for rotational motion, but the possible consequences for the transport phenomena in suspensions have scarcely been investigated, except for the phenomenon of Brownian motion the theory of which has recently been reconsidered by numerous authors;[7-17] a review can be found in ref 18.

Similar remarks can be made in connection with hydrodynamic interaction, which has almost always been treated as though the distance between the interacting particles remained constant and the flow field were steady. As early as 1938, Burgers[19] derived an equation from Oseen's results to describe the effect of a time-dependent force acting on a liquid at a fixed point. Szu and Hermans[20] considered the more general case of a time-dependent force acting at a position which changes with time, but applications of these results are scarce. Reference is made to Chang and Mazo,[21] who discussed high-frequency motions of polymer segments in a solution, and also to Chow and Hermans,[22] who considered the hydrodynamic interaction of two Brownian particles.

Szu and Hermans[23] discussed the effect of inertia on the intrinsic viscosity of elastic dumbbells but neglected the hydrodynamic interaction. As will be explained later, this amounts to saying that their theory makes use of the "high-frequency approximation", i.e., in the Fourier time transforms of velocities and forces, the high frequencies are assumed to play the predominant role.

The present article is concerned with rigid dumbbells. These have been the subject of extensive studies by Bird and co-workers.[24,25] To bring out the important points more clearly, the motion of our dumbbell is restricted to a plane, but the hydrodynamic equations used are three dimensional. The extension to three-dimensional motion in section VI is simple and can be kept very concise. A few aspects of the extension to rods are discussed in section VII.

To estimate the hydrodynamic interaction, the forces exerted on the liquid by the two ends of the dumbbell are replaced by point forces. Yamakawa[26-28] and Fujita[29] have developed more refined methods in which the beads are replaced by a distribution of forces over their surfaces. Mention may be made also of work by Wakiya[30,31] on the motion of two spheres separated by a very small distance, and of recent work by Wolynes and Deutch[32] who question the applicability of the nonslip condition when the distance between the interacting particles becomes very small. However, in view of the complications introduced by inertia effects, refinements of this kind will not be considered.

(I) Outline of the Method

Two spherical beads of radius a are situated at positions 1 and 2 indicated in Figure 1. They are connected by a rigid, frictionless rod. The undisturbed velocity of the liquid is

$$\mathbf{v}^0 = qy\,\mathbf{e}_x \qquad (I.1)$$

where $\mathbf{e}_x$ is the unit vector in the direction of the x axis. The center of the dumbbell is at the origin and moves with a velocity equal to the velocity in (I.1) of the liquid at that point.

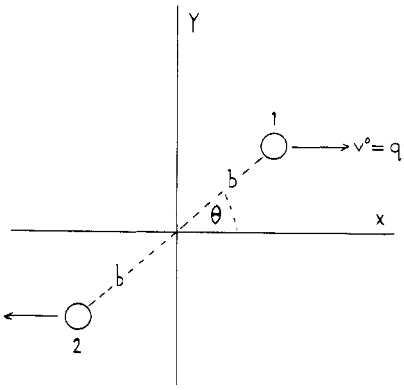

Figure 1. Rigid dumbbell consisting of two beads 1 and 2 in a velocity gradient, $\mathbf{v}^0 = qy\,\mathbf{e}_x$.

The contribution of the dumbbell to the viscosity of the suspension will be calculated from the forces which the two beads exert on the liquid, using the method advocated by Burgers;[19] see also Kramers.[33] Burgers considered two equal but opposite forces $\mathbf{F}$ and $-\mathbf{F}$, where $\mathbf{F}$ has the components X, Y, and Z, say. these forces act at the points (x, y, z) and $(-x, -y, -z)$, respectively. Their contribution to the viscosity was found to be given by

$$q\,\delta\mu = -2\langle Xy\rangle \qquad (I.2)$$

where the angular brackets denote an average over a stationary ensemble. In Burgers' case the force F was in the radial direction, i.e., the components X, Y, and Z were proportional to x, y, and z, respectively. It is easy to show, however, by a simple extension of Burgers' reasoning, that the result in (I.2) remains valid for arbitrary direction of the force F.

It will be convenient to consider the viscosity contribution as the sum of two terms, one due to the radial and the other to the tangential component of the force. At the position of bead No. 1 the undisturbed velocity in (I.1) has a radial and a tangential component

$$v_r^0 = qy\cos\theta = qb\sin\theta\cos\theta; \qquad v_\theta^0 = -qy\sin\theta = -qb\sin^2\theta \qquad (I.3)$$

The force exerted on the liquid by bead No. 2 results in an additional velocity field which, at the position of bead No. 1, has the components δv_r and δv_θ, say. The total velocity of the liquid at the position of bead No. 1 has components

$$v_r = v_r^0 + \delta v_r;\; v_\theta = v_\theta^0 + \delta v_\theta \qquad (I.4)$$

The velocity of the bead itself has the components

$$u_r = 0;\; u_\theta = b\dot\theta \qquad (I.5)$$

where the dot denotes differentiation with respect to time. We relate the forces which the beads exert on the liquid to the velocities $\mathbf{u}$ and $\mathbf{v}$ and eliminate $\delta\mathbf{v}$ by means of Oseen's equations. The result for the radial force depends only on the undisturbed velocity $\mathbf{v}^0$ and can be used immediately to find the corresponding value of $\langle Xy\rangle$ in eq I.2. The result for the tangential force contains also the tangential bead velocity $b\dot\theta$. Our method to find the corresponding average of Xy will be based on the appropriate Langevin equation for the tangential motion.

The averaging is done over a staionary ensemble of particles, i.e., an ensemble in which the particles have been exposed to the constant shear-rate q for a sufficient length of time to neglect the effect of initial conditions. Averages in such an ensemble are time independent.

(II) Result in the Absence of Inertia

When steady state equations are used, we find for the force which bead No. 1 exerts on the liquid

$$F_{\mathrm{r}} = -\zeta_0(v_{\mathrm{r}}{}^0 + \delta v_{\mathrm{r}});\ F_\theta = \zeta_0(b\dot{\theta} - v_\theta{}^0 - \delta v_\theta) \qquad \text{(II.1)}$$

while $\delta\mathbf{v}$ is determined by Oseen's equations (explained in more detail in section III)

$$\delta v_{\mathrm{r}} = -\frac{2F_{\mathrm{r}}}{8\pi\mu}\frac{1}{2b};\ \delta v_\theta = -\frac{F_\theta}{8\pi\mu}\frac{1}{2b}$$

Eliminating $\delta\mathbf{v}$ and using eq II.3, we get

$$F_{\mathrm{r}} = \frac{-\zeta_0 qb \sin\theta\cos\theta}{1-2\beta};\ F_\theta = \frac{\zeta_0 b(\dot{\theta} + q\sin^2\theta)}{1-\beta} \qquad \text{(II.2)}$$

Here

$$\beta = \zeta_0/16\pi\mu b \qquad \text{(II.3)}$$

$$\zeta_0 = 6\pi\mu a \qquad \text{(II.4)}$$

μ being the viscosity of the solvent. The frictional coefficient ζ_0 has been equated to Stokes' result for solid spheres with stick boundary conditions, but in reality its precise value need not be specified. The x component of F_{r} is $F_{\mathrm{r}}\cos\theta$, so that the radial contribution $(\delta\mu)_{\mathrm{r}}$ to the viscosity is found from

$$q(\delta\mu)_{\mathrm{r}} = \frac{2\zeta_0 qb^2}{1-2\beta}\langle\sin^2\theta\cos^2\theta\rangle = \frac{1}{8}\frac{2\zeta_0 qb^2}{1-2\beta} + 0(\geq q^2) \qquad \text{(II.5)}$$

The symbol $0(\geq q^n)$ indicates proportionality to a power of q that is at least n but could be larger.

The tangential contribution to the viscosity is found by considering the Langevin equation

$$I\ddot{\theta} + \frac{2\zeta_0 b^2}{1-\beta}(\dot{\theta} + q\sin^2\theta) = M \qquad \text{(II.6)}$$

where I is the moment of inertia of the dumbbell and M is the random torque acting on it. Note that by averaging over the ensemble we find immediately

$$\langle\dot{\theta}\rangle = -q/2 + 0(\geq q^2) \qquad \text{(II.7)}$$

The force on the liquid is $2\zeta_0 b(1-\beta)^{-1}(\dot{\theta} + q\sin^2\theta)$ and its x component is $\sin\theta$ times as large. Consequently we find $(\delta\mu)_\theta$ from

$$q(\delta\mu)_\theta = 2\zeta_0 b^2(1-\beta)^{-1}\langle\dot{\theta}\sin^2\theta + q\sin^4\theta\rangle \qquad \text{(II.8)}$$

Here

$$\begin{aligned}\langle\dot{\theta}\sin^2\theta\rangle &= {}^1\!/_2\langle\dot{\theta}\rangle - {}^1\!/_2\langle\dot{\theta}\cos 2\theta\rangle \\ &= {}^1\!/_2\langle\dot{\theta}\rangle - {}^1\!/_4\,(\mathrm{d}/\mathrm{d}t)\langle\sin 2\theta\rangle = {}^1\!/_2\langle\dot{\theta}\rangle \qquad \text{(II.9)}\end{aligned}$$

because the average of a periodic function in a stationary ensemble is independent of time. Taking into account eq II.7 and the fact that $\langle\sin^4\theta\rangle = {}^3\!/_8 + 0(\geq q)$ we find from (II.8)

$$q(\delta\mu)_\theta = \frac{1}{8}\frac{2\zeta_0 qb^2}{1-\beta} + 0(\geq q^2) \qquad \text{(II.10)}$$

These results are for motion in a plane, but the extension to three-dimensional motion is straightforward (see also section VI) and gives for the total viscosity contribution

$$\delta\mu^{\mathrm{III}} = \frac{\zeta_0 b^2}{3(1-\beta)(1-2\beta)}(1 - {}^8\!/_5\beta) + 0(\geq q^2) \qquad \text{(II.11)}$$

This result agrees with that of Bird et al.[24,25] in the limit of small q and with the answer found for an oscillatory shear by the "correlation function method" in the limit of zero frequency.[34–38]

In the subsequent sections it will be taken into account that the velocities and forces are, in reality, functions of time. In particular, the angular velocity $\dot{\theta}$ is of large magnitude and changes very rapidly with time. Its average (eq II.7) is very small because there are almost as many positive as negative contributions. In fact, the nonzero average may be considered as caused by (a) the angular velocity due to the velocity gradient and (b) the diffusive flux which counteracts the orientation that would result from this gradient in the absence of diffusion.

The use of a "diffusion force" in the calculation of intrinsic viscosity has been discussed in some detail by Stockmayer et al.[39] This discussion was triggered by recent work based on linear response theory which uses the momentum correlation function for fluctuations at equilibrium (i.e., in the absence of a gradient) and which has shown that in this approach the diffusion force plays no role; the viscosity is determined by the forces within the molecule.[38] Now, the diffusive flux counteracting the orientation in the presence of a gradient is, of course, a somewhat different matter,[39] but it is explicitly pointed out that our own calculation has no need of a diffusive force anyway. All we are concerned with is the force acting on the liquid; the average effect of this force on the viscosity is derived from the Langevin equation without resorting to an orientational distribution function.

One could still raise the question whether the intramolecular force which the correlation function approach shows to be responsible for the viscosity must indeed be considered as varying rapidly with time, thus requiring a treatment which takes time dependence into account. The answer to this question is perhaps best given by the following argument.

The Langevin equation for a bead might have been formulated in terms of Cartesian coordinates (either two or three dimensions)

$$m\ddot{\mathbf{r}} + \zeta_0\dot{\mathbf{r}} + H\mathbf{r} = \mathbf{F} \qquad \text{(II.12)}$$

where m is the mass of a bead, $\mathbf{r}$ is its position, $\mathbf{F}$ is the random force, and $H\mathbf{r}$ is the force which holds the two beads together (the equation ignores the hydrodynamic interaction because it is not needed to make our point). As the force $H\mathbf{r}$ preserves the length of the dumbbell, it must vary with time in such a manner that $\mathbf{r}\cdot\dot{\mathbf{r}} = 0$ and hence $\mathbf{r}\cdot\ddot{\mathbf{r}} = -\dot{r}^2$. It therefore follows immediately from eq II.12 that

$$Hr^2 = \mathbf{F}\cdot\mathbf{r} + m\dot{r}^2$$

showing that H varies with time as rapidly as the random force F.

(III) The Inertia of the Liquid is Taken Into Account

The force of the liquid exerted by a sphere which moves with time-dependent velocity $\mathbf{u}$ in an incompressible Newtonian liquid that itself has a time-dependent velocity $\mathbf{v}$ has been calculated by Mazur and Bedeaux;[40] see also Felderhof.[41] Its Fourier time transform is

$$\mathbf{F}(\omega) = \zeta(\omega)\mathbf{u}(\omega) - \zeta_0\{(1 + \alpha a)\overline{\mathbf{v}(\omega)^{\mathrm{S}}} + {}^1\!/_3\alpha^2 a^2\overline{\mathbf{v}(\omega)^{\Omega}}\} \qquad \text{(III.1)}$$

where

$$\alpha = (-\mathrm{i}\omega/\nu)^{1/2} \qquad \text{(III.2)}$$

$$\zeta(\omega) = \zeta_0(1 + \alpha a + {}^1\!/_9\alpha^2 a^2) \qquad \text{(III.3)}$$

a is the radius of the sphere, $\overline{\mathbf{v}(\omega)^{\mathrm{S}}}$ is the velocity of the liquid averaged over the surface of the sphere, and $\overline{\mathbf{v}(\omega)^{\Omega}}$ is the velocity of the liquid averaged over its volume; μ is the viscosity and $\nu = \mu/\rho_0$ is the kinematic viscosity, ρ_0 being the density of the liquid. The restriction to point forces implies that we replace $\overline{\mathbf{v}(\omega)^{\mathrm{S}}}$ and $\overline{\mathbf{v}(\omega)^{\Omega}}$ by the velocity which the liquid would have had at the center of the bead, hence

$$\mathbf{F}(\omega) = \zeta(\omega)\mathbf{u}(\omega) - \bar{\zeta}(\omega)[\mathbf{v}^0(\omega) + \delta\mathbf{v}(\omega)] \qquad \text{(III.4)}$$

$$\bar{\zeta}(\omega) = \zeta_0(1 + \alpha a + {}^1\!/_3\alpha^2 a^2) \qquad \text{(III.5)}$$

Having defined the forces in relation to the velocities, we turn to the hydrodynamic interaction between the two beads. Here it is important to remember that the angular velocities relative to the liquid are due to Brownian motion, and this has a consequence which introduces a considerable simplification in the theory. The relaxation time for the rotational Brownian motion is of the order I/B, where I is the moment of inertia of the particle and B is its frictional coefficient, i.e., the frictional torque per unit angular velocity. As explained in earlier work[22,42] I/B is so small that the angular displacement during a relaxation time is negligible and, for this reason, the hydrodynamic interaction between two beads in the dumbbell is essentially that between two beads at fixed positions.

To proceed, we note first that the velocity $\delta\mathbf{v}$ at the position of bead 1 caused by the presence of bead 2 is a result of the force which bead No. 2 exerts on the liquid. We write

$$\delta\mathbf{v}_1 = \mathbf{S}\cdot\mathbf{F}_2 \qquad \text{(III.6)}$$

where $-\mathbf{F}_2$ is the force on bead No. 2 and $\mathbf{S}$ is a tensor (Oseen tensor) the form of which is discussed later. Likewise we find, for bead No. 2,

$$\delta\mathbf{v}_2 = \mathbf{S}\cdot\mathbf{F}_1$$

where $-\mathbf{F}_1$ is the force on bead No. 1.

Due to the antisymmetric nature of the problem, not only the velocities $\mathbf{u}_1$ and $\mathbf{u}_2$ of the two beads are at all times equal in magnitude but opposite in sign, but this is true also for the forces $\mathbf{F}_1$ and $\mathbf{F}_2$ and, therefore, for the disturbances $\delta\mathbf{v}_1$ and $\delta\mathbf{v}_2$. This is a consequence of the fact that also $\mathbf{v}_1{}^0$ and $\mathbf{v}_2{}^0$ are equal but opposite in sign for all times. For this reason it is sufficient to consider only bead No. 1. We drop the subscript 1 and write eq III.6

$$\delta\mathbf{v} = -\mathbf{S}\cdot\mathbf{F} \qquad \text{(III.7)}$$

Taking the Fourier time transform,

$$\delta\mathbf{v}(\omega) = -\mathbf{S}(\omega)\mathbf{F}(\omega) \qquad \text{(III.8)}$$

where $\mathbf{S}(\omega)$ is the Fourier transform of the operator $\mathbf{S}$.

Due to the fact that the hydrodynamic interaction may be calculated for beads at fixed positions, we may use the result given by Burgers[19] for a time-dependent force acting at a fixed point. This has the important consequence that the radial velocity δv_r depends only on the radial force F_r and the tangential component δv_θ is determined by the tangential force F_θ. In other words, in the coodinates (r,θ) the tensor $\mathbf{S}$ is diagonal.

Indeed, if we introduce a Cartesian coordinate system (ξ, η, ζ), the application of Burgers' formula shows that the components δv_ξ, δv_η of the velocity produced at the position of bead No. 1 by a force $X(t)$ in the ξ direction at the position of bead No. 2 are

$$\delta v_\xi = (8\pi\mu)^{-1}\int_{-\infty}^{t}\mathrm{d}\tau X(\tau)\left(\nabla^2 - \frac{\partial^2}{\partial\xi^2}\right)\psi(t-\tau);$$

$$\delta v_\eta = -(8\pi\mu)^{-1}\int_{-\infty}^{t}\mathrm{d}\tau X(\tau)\frac{\partial^2}{\partial\xi\partial\eta}\psi(t-\tau) \qquad \text{(III.9)}$$

where

$$\psi(t) = 2(\nu/\pi)^{1/2}r^{-1}\int_0^r \mathrm{d}s t^{-1/2}[1-\exp(-s^2/4\nu t)] \qquad \text{(III.10)}$$

∇^2, $\partial^2/\partial\xi^2$, and $\partial^2/\partial\xi\partial\eta$ operate with respect to the distance $r = r(\xi, \eta, \zeta)$ between the two beads.

To apply this to a radial force, take the ξ axis in radial and the η axis in tangential direction, putting $X = F_\mathrm{r}$. After performing all the operations indicated, we substitute $\xi = 2b$, $\eta = 0$, $\zeta = 0$. This leads to

$$\delta v_\xi(=\delta v_\mathrm{r}) = -S_\mathrm{r}(\omega)F_\mathrm{r}(\omega);\ \delta v_\xi(=\delta v_\theta) = 0$$

where

$$S_\mathrm{r}(\omega) = -(16\pi\mathrm{i}\omega\rho_0 b^3)^{-1}[1-(1+2\alpha b)\exp(-2\alpha b)] \qquad \text{(III.11)}$$

For the application of eq III.9 to a tangential force, we need only take the ξ axis in tangential and the η axis in radial direction and put $X = F_\theta$. Then, at the end of the operations, we substitute $\xi = 0$, $\eta = 2b$, $\zeta = 0$. It is then found that

$$\delta v_\xi(=\delta v_\theta) = -S_\theta(\omega)F_\theta(\omega);\ \delta v_\eta(=\delta v_\mathrm{r}) = 0$$

where

$$S_\theta(\omega) = -(32\pi\mathrm{i}\rho_0\omega b^3)^{-1}[1-(1+2\alpha b)^2\exp(-2\alpha b)] \qquad \text{(III.12)}$$

Substituting in eq III.4 and eliminating $\delta\mathbf{v}$,

$$F_\mathrm{r}(\omega) = \frac{\zeta(\omega)u_\mathrm{r}(\omega) - \bar{\zeta}(\omega)v_\mathrm{r}{}^0(\omega)}{1-\bar{\zeta}(\omega)S_\mathrm{r}(\omega)};$$

$$F_\theta(\omega) = \frac{\zeta(\omega)u_\theta(\omega) - \bar{\zeta}(\omega)v_\theta{}^0(\omega)}{1-\bar{\zeta}(\omega)S_\theta(\omega)} \qquad \text{(III.13)}$$

(IV) Low-Frequency Approximation

From eq III.11 and III.12 it is clear that a series expansion in powers of ω requires that $\alpha b = (-\mathrm{i}\omega/\nu)^{1/2}b$ is of small magnitude. In the ω spectrum we will doubtless find very low frequencies of the order of the velocity gradient q, but a role will be played also by frequencies of the order of the reciprocal relaxation time for rotational Brownian motion. These are of order B/I, where B is the rotational frictional coefficient for the dumbbell and I its moment of inertia. We may expect B to be of the order of $\zeta_0 b^2 = 6\pi\mu a b^2$, whereas I is of order $(4/3)\pi a^3\rho b^2$ if ρ is the density of the beads. Assuming that ρ is of the same order of magnitude as the density ρ_0 of the liquid, we can estimate the reciprocal relaxation time as roughly of the order of ν/a^2, and this would make αb of order b/a, which is larger than unity. It is clear therefore that an expansion in powers of ω can do no more than predict the order of magnitude of the role of inertia. In the case of rodlike particles we are at the other extreme: $|\alpha b| \gg 1$, which is discussed later.

Based on the expressions III.3 and III.5, III.11 and III.12, the series expansion of (III.13) is straightforward. Taking into account that $u_\mathrm{r} = 0$:

$$F_\mathrm{r}(\omega) = \frac{-\zeta_0}{1-2\beta}\left[1 - A_\mathrm{r}\frac{b^2}{\nu}\mathrm{i}\omega + 0(\omega^{3/2})\right]v_\mathrm{r}{}^0(\omega) \qquad \text{(IV.1)}$$

$$F_\theta(\omega) = \frac{\zeta_0}{1-\beta}\left[1 - A_0\frac{b^2}{\nu}\mathrm{i}\omega + 0(\omega^{3/2})\right]u_\theta(\omega) - \frac{\zeta_0}{1-\beta}\left[1 - B_\theta\frac{b^2}{\nu}\mathrm{i}\omega + 0(\omega^{3/2})\right]v_\theta{}^0(\omega) \qquad \text{(IV.2)}$$

where

$$\beta = \frac{\zeta_0}{16\pi\mu b} = \frac{3a}{8b} \qquad \text{(IV.3)}$$

$$A_\mathrm{r} = (1-2\beta)^{-1}(a/b)(3/4 - 2a/3b) \qquad \text{(IV.4)}$$

$$A_\theta = (1-\beta)^{-1}(a/b)(9/8 - 8a/9b + a^2/12b^2) \qquad \text{(IV.5)}$$

$$B_\theta = (1-\beta)^{-1}(a/b)(9/8 - a/6b) \qquad \text{(IV.6)}$$

Note that neither (IV.1) nor (IV.2) contains terms proportional to $\omega^{1/2}$; these are completely eliminated by the hydrodynamic interaction, as observed already by Szu and Hermans[42] in a different context. If now we omit $\omega^{3/2}$ and higher powers of ω, it follows from (IV.1) and (IV.2) that

$$F_\mathrm{r} = \frac{-\zeta_0 b}{1-2\beta}\left(1 + A_\mathrm{r}\frac{b^2}{\nu}\frac{\mathrm{d}}{\mathrm{d}t}\right)q\sin\theta\cos\theta \qquad \text{(IV.7)}$$

$$F_\theta = \frac{\zeta_0 b}{1-\beta}\left\{\left(1 + A_\theta\frac{b^2}{\nu}\frac{\mathrm{d}}{\mathrm{d}t}\right)\dot{\theta} + \left(1 + B_\theta\frac{b^2}{\nu}\frac{\mathrm{d}}{\mathrm{d}t}\right)q\sin^2\theta\right\} \qquad \text{(IV.8)}$$

The radial contribution to the viscosity is not affected by inertia, because $\langle \sin\theta \cos\theta (\mathrm{d}/\mathrm{d}t) \sin\theta \cos\theta \rangle$ in a stationary ensemble is zero. Thus we recover the result (II.5) for $(\delta\mu)_r$. A comparison of (IV.8) with (II.2) shows that the tangential force on the liquid is increased by the amount $\zeta_0 b(1-\beta)^{-1}(b^2/\nu)[A_\theta\ddot{\theta} + B_\theta q\, \mathrm{d}(\sin^2\theta)/\mathrm{d}t]$, which will contribute to $q(\delta\mu)_\theta$ an amount

$$q(\delta\mu)_\theta{}' = 2\zeta_0 b^2(1-\beta)^{-1}(b^2/\nu)A_\theta\langle\ddot{\theta}\sin^2\theta\rangle \qquad \text{(IV.9)}$$

because the average of $\sin^2\theta\, \mathrm{d}(\sin^2\theta)/\mathrm{d}t$ is zero. Now, the Langevin equation for the tangential motion becomes, instead of (II.6),

$$I^*\ddot{\theta} + \frac{2\zeta_0 b^2}{1-\beta}\left\{\dot{\theta} + \left(1 + B_\theta\frac{b^2}{\nu}\frac{\mathrm{d}}{\mathrm{d}t}\right)q\sin^2\theta\right\} = M \qquad \text{(IV.10)}$$

where

$$I^* = I + \frac{2\zeta_0 b^2}{1-\beta}A_\theta\frac{b^2}{\nu} = I + I' \qquad \text{(IV.11)}$$

Here I^* plays the role of an "apparent" moment of inertia. We now make use of the well-known fact[8,12,18] that the autocorrelation function $K(t) = \langle M(t_0)M(t_0+t)\rangle$ is related to the frictional coefficient B by the fluctuation-dissipation theorem: $K(\omega) = 2kT(\mathrm{Re})B(\omega)$. In the present case $B(\omega) = c_1 + \omega i c_2$ where c_1 and c_2 are constants, both real. This means that $K(\omega) = 2kTc_1$, i.e., $K(t)$ is a delta function. In other words, the omission of powers $\omega^{3/2}$ and higher implies that the process, notwithstanding the inertia, is Markovian. As a result, $M(t)$ is not correlated with $\theta(t')$ at times $t' \le t$.

Averaging eq IV.10 we find that eq II.7 remains valid and for this reason also (II.9) remains valid. For $\langle\dot{\theta}\sin^2\theta + q\sin^4\theta\rangle$ we find again the value $q/8$, but to obtain $q(\delta\mu)_\theta$ we must now add the result (IV.9). Multiplying eq IV.10 by $\sin^2\theta$ and averaging:

$$I^*\langle\ddot{\theta}\sin^2\theta\rangle = -\frac{2\zeta_0 b^2}{1-\beta}\langle\dot{\theta}\sin^2\theta + q\sin^4\theta\rangle$$

and this leads immediately to

$$(\delta\mu)_\theta = (\delta\mu)_\theta{}^0\frac{I}{I+I'} \qquad \text{(IV.12)}$$

where $(\delta\mu)_\theta{}^0$ is the contribution in the absence of inertia effects. This result predicts a quite substantial reduction in $(\delta\mu)_\theta$. For the special case in which the two beads in the dumbbell touch each other, i.e., $b = 2a$, one would find

$$\delta\mu_\theta/\delta\mu_\theta{}^0 = (1 + 12\rho_0/\rho)^{-1} \qquad \text{(IV.13)}$$

which would predict the very large reduction of about 85% in $\delta\mu_\theta$ when $\rho = 2\rho_0$. We must remember that this is based on the low-frequency approximation and does not say anything about the contributions from higher frequencies in the Fourier transform. In the next section, however, it will be found that very high frequencies may likewise lead to a considerable reduction.

A simple physical explanation of the effect of inertia in the low-frequency limit is as follows. The viscosity contribution is derived from the force exerted on the liquid. In the absence of inertia the tangential component of this force is proportional to the tangential velocity of the bead relative to the liquid. When inertia is included we must add to this force a term proportional to the angular acceleration and (as can be seen from the Langevin equation) this acceleration tends to be negative when the angular velocity is positive, and vice versa. In other words, positive velocities are more often accompanied by negative than by positive accelerations, i.e., the force on the liquid is more often reduced than increased by the effect of inertia. Similar reasoning can give a qualitative explanation of the role of inertia in the high-frequency limit.

(V) High-Frequency Approximation

It has already been pointed out at the beginning of section IV that many of the frequencies that contribute to the Fourier time transforms are probably of order ν/a^2, which makes $2\alpha b$ a rather large number.

We need not consider the high-frequency limit in the radial contribution to the viscosity, because this is determined by the velocity of the liquid alone. Although at the position of a bead this is time dependent because θ changes with time, the rate of change is very small, namely proportional to the gradient q, so that the Fourier transform has negligible high-frequency components.

For the high frequencies considered, the tensor component S_θ in eq III.12 is very small: the hydrodynamic interaction becomes negligible. Consequently we find from eq III.13 that

$$F_\theta \simeq \zeta_{0\mathrm{p}}b\dot{\theta} + \bar{\zeta}_{0\mathrm{p}}qb\sin^2\theta$$

where $\zeta_{0\mathrm{p}}$ and $\bar{\zeta}_{0\mathrm{p}}$ are determined by their Fourier transforms (III.3) and (III.5), respectively. The Langevin equation for the tangential motion will now become

$$I\ddot{\theta} + 2b^2(\zeta_{0\mathrm{p}}\dot{\theta} + q\bar{\zeta}_{0\mathrm{p}}\sin^2\theta) = M \qquad \text{(V.1)}$$

and the process is no longer Markovian. Due to the $\sin^2\theta$ term, it is also nonlinear, and we have not been able to find a solution for this problem. Although isolated attempts to solve nonlinear stochastic processes have been reported,[43,44] the theory can still be said to be in its infancy. All we are able to do is to make a tentative estimate of the order of magnitude of inertia effects. To this end we consider in ζ and $\bar{\zeta}$ only the term of order $\omega^{1/2}$. This means that we take

$$\zeta_{0\mathrm{p}} = \bar{\zeta}_{0\mathrm{p}} = \zeta_0\left\{1 + a(\pi\nu)^{-1/2}\int_{-\infty}^{t}\mathrm{d}s(t-s)^{-1/2}\,\mathrm{d}/\mathrm{d}s\right\} \qquad \text{(V.2)}$$

If we abbreviate

$$\lambda = \sin^2\theta \qquad \text{(V.3)}$$

the Langevin equation in the absence of inertia effects is

$$I\ddot{\theta} + 2b^2\zeta_0(\dot{\theta} + q\lambda) = M \qquad \text{(V.4)}$$

and the process is Markovian. As shown before, we then have $\langle\dot{\theta}\lambda\rangle = -q/4 + 0(\ge q^2)$, and we can therefore conclude from eq V.4 that

$$\langle\ddot{\theta}\lambda\rangle = -2b^2\zeta_0 q/8I + 0(\ge q^2) \qquad \text{(V.5)}$$

When eq V.2 is used, the force on the liquid, which was $\zeta_0 b(\dot{\theta} + q\lambda)$ in the absence of inertia, will now be

$$\zeta_0 b\left\{\dot{\theta} + a(\pi\nu)^{-1/2}\int_{-\infty}^{t}\mathrm{d}s(t-s)^{-1/2}\ddot{\theta}(s) + q\lambda\right\}$$

where the correction for inertia in front of the term $q\lambda$ has been omitted, because this term has negligible high-frequency components in its Fourier transform. We are thus led to consider the following correction to the tangential viscosity contribution:[46]

$$q(\delta\mu)_\theta{}' = 2\zeta_0 b^2 a(\pi\nu)^{-1/2}\left\langle\lambda(t)\int_{-\infty}^{t}\mathrm{d}s(t-s)^{-1/2}\ddot{\theta}(\mathrm{s})\right\rangle \qquad \text{(V.6)}$$

For a rough estimate we replace the lower integration limit by $t - \tau$, where τ is of the order of the relaxation time for Brownian motion,

$$\tau \simeq m/\zeta_0 \qquad \text{(V.7)}$$

m being the mass of a dumbbell bead. We know also that λ

changes very little in a time of order τ, which means that eq V.6 may be replaced by

$$q(\delta\mu)_\theta' = 2\zeta_0 b^2 a(\pi\nu)^{-1/2} \int_{t-\tau}^{t} \mathrm{d}s(t-s)^{-1/2}\langle\lambda(s)\ddot{\theta}(s)\rangle \tag{V.8}$$

As a first approximation we use the correlation (V.5) for the inertia-free process and find

$$q(\delta\mu)_\theta' = -2\zeta_0 b^2 a(\pi\nu)^{-1/2}(2b^2\zeta_0 q/8I)2(m/\zeta_0)^{1/2} \tag{V.9}$$

This would mean that the relative correction for inertia in $(\delta\mu)_\theta$ is of order

$$-\frac{2a}{(\pi\nu)^{1/2}}\left(\frac{m}{\zeta_0}\right)^{1/2}\frac{2\zeta_0 b^2}{I} = -\frac{2a}{(\pi\nu)^{1/2}}\left(\frac{\zeta_0}{m}\right)^{1/2} \tag{V.10}$$

If we use Stokes' expression for ζ_0 this is $-6(2\pi\rho/\rho_0)^{-1/2}$ where ρ is the density of the beads and ρ_0 that of the liquid. The magnitude of this relative effect could easily become larger than unity, which shows that our procedure overestimates it. It is clearly not permissible to consider the effect as a "perturbation" of the inertia-free problem. Moreover, the high frequencies considered are of the same order of magnitude as or even larger than the ratio c/a, where c is the velocity of sound and a the bead radius. For such frequencies the liquid may no longer be treated as incompressible[13,45] and the friction becomes smaller than that given in eq III.1. For these frequencies, therefore, the entire theory should be reconsidered, but this would introduce mathematical difficulties which appear to be insurmountable at the present time. All we can say is that our estimate suggests the existence of a relatively large effect of the inertia on the tangential contribution to the viscosity of the suspension. In other words, we cannot solve the problem quantitatively but we can at least say that there *exists* a serious problem.

(VI) Dumbbell in Three-Dimensional Motion

For the problem in hand, polar coordinates r, θ, ϕ are most conveniently defined by

$$x = r\cos\theta,\ y = r\sin\theta\cos\phi,\ z = r\sin\theta\sin\phi \tag{VI.1}$$

This choice has the advantage that velocities and forces along the ϕ coordinate have no x component so that, according to eq I.2, they do not contribute to the viscosity of the suspension. Thus there will be only contributions $(\delta\mu)_\mathrm{r}$ and $(\delta\mu)_\theta$.

The undisturbed velocity of the liquid has the components

$$v_\mathrm{r}{}^0 = qr\sin\theta\cos\theta\cos\phi,\ v_\theta{}^0 = -qr\sin^2\theta\cos\phi,\ v_\phi = 0 \tag{VI.2}$$

The hydrodynamic interaction can be accounted for as previously. For the special case of negligible inertia effects, reference can be made to the work of Bird.[24,25] The Oseen tensor for this problem is diagonal in the coordinates r, θ, ϕ, and the two contributions to the viscosity are found to be

$$(\delta\mu)_\mathrm{r}{}^0 = \frac{2\zeta_0 b^2}{15(1-2\beta)} + 0(\geq q);\ (\delta\mu)_\theta{}^0 = \frac{\zeta^0 b^2}{5(1-\beta)} + 0(\geq q) \tag{VI.3}$$

As mentioned already in section II, the sum $(\delta\mu)_\mathrm{r}{}^0 + (\delta\mu)_\theta{}^0$ agrees also with the result of linear response theory.

Even when inertia is taken into account, the Oseen tensor remains diagonal as a result of the fact that angular displacements during the relaxation time for rotatory Brownian movement are negligibly small, so that the interaction is essentially that between two beads at fixed positions; this was explained in section III.

As regards the radial force, its Fourier time transform has negligible high-frequency components. Considering the low-frequency approximation as in section IV, one can easily show that also for three-dimensional motion the radial contribution to the viscosity is not affected by inertia.

The influence of inertia on $(\delta\mu)_\theta$ is of the same nature as in the case of two-dimensional motion. This is not developed in detail because, just as in the two-dimensional case, the results are restricted to estimates of the order of magnitude at the two limits of low and high frequences. As found also in sections IV and V, the theory predicts that the reduction in $(\delta\mu)_\theta$ may become quite appreciable.

(VII) Rod-Shaped Particles

The extension to rods can be made on the basis of a model which replaces the rod by a linear array of beads (Huggins, ref 1). The hydrodynamic interaction between the beads using the steady state Oseen tensor was discussed by Kirkwood and co-workers.[3-6] For the radial forces on the beads the results of Kirkwood's procedure can be used without modification. For the tangential forces, however, the calculation must be modified, because it is clear from what was said at the beginning of section IV that the "low-frequency approximation" loses all meaning when the distance between two beads becomes much more than their diameter. For such beads, at high frequencies, the hydrodynamic interaction is negligible and we will have to resort to considerations such as those developed in section V.

Nevertheless, even at high frequencies, there will be hydrodynamic interaction between neighbors. This reduces the frictional force. It can also be shown that it reduces the relative effect of inertia by a factor of about 2, thus reducing the estimate of the role of inertia that was made in section V, bringing it down closer to a more realistic value.

(VIII) Conclusion

Our study of the time dependence of rotational velocities and the resulting forces exerted on the liquid suggests that the contribution of these forces to the viscosity of the suspension is reduced by inertia effects. The theory assumes the solvent to be Newtonian and incompressible. Due to mathematical difficulties, a complete theory has not been worked out, but a consideration of the two limits of low and high frequency indicates that the effect of inertia on the contribution from rotation may be considerable. It is not anticipated that the mathematical difficulties will be fully overcome in the very near future, because they are made considerably worse by the fact that at high frequencies the compressibility of the liquid cannot be neglected. In addition, the theory may have to consider the effect of slip conditions and possible other complications arising from hydrodynamic interaction at short distances.

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(46) The result eq V.6 might seem to be time dependent, but this is only apparently so. In a stationary ensemble $\langle \lambda(t)\dot{\theta}(s)\rangle$ is a function of the difference $t - s$, say $f(t - s)$, and the integral may therefore be written $\int_0^\infty dz z^{-1/2} f(z)$, which is independent of t.

Conformational Studies of Oligopeptides Containing Proline and Glycine[1]

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ABSTRACT: Nuclear magnetic resonance, infrared, and circular dichroism methods were used to study the conformational properties of N-acetyl-N'-ethylprolineamide (*blocked* Pro single residue), N-acetyl-N'-methylglycineamide (*blocked* Gly single residue), N-acetyl-N'-methylglycylprolineamide (*blocked* Gly-Pro), and N-acetyl-N'-methylprolylglycineamide (*blocked* Pro-Gly) in various solvents. It was found that all four peptide molecules exist in solution at 29 °C as an ensemble of several conformations. In the blocked Pro single residue, the acetyl-Pro peptide bond was found to exist in both the cis and the trans forms, with $\Delta G°_{\text{trans}\rightarrow\text{cis}} \approx 0.7$ kcal/mol in CD_2Cl_2 and $\approx$0.4 kcal/mol in DMSO at 29 °C. In the trans form, the hydrogen-bonded conformation (C_7^{eq}, with $\psi_{\text{Pro}} \approx 80°$) and nonhydrogen-bonded conformations (with ψ_{Pro} being unidentified) coexist. The blocked Gly single residue was found to exist as a flexible molecule, with the C_7 and other conformations present; no cis–trans isomerism was observed. Blocked Gly-Pro showed cis–trans isomerism about the Gly-Pro peptide bond with $\Delta G°_{\text{trans}\rightarrow\text{cis}} \approx 0.7$ kcal/mol in DMSO and $\approx$1.5 kcal/mol in CD_2Cl_2 at 29 °C. The Gly residue in blocked Gly-Pro was found to exist, to a large extent, in the fully extended (C_5) structure, with the Pro residue in Gly-Pro assuming the C_7^{eq} conformation as well as other (nonhydrogen-bonded) conformations. No evidence for large amounts of β bend was detected in Gly-Pro. The temperature dependence of the NMR and CD data of blocked Gly-Pro in water was found to be similar to that of poly(Gly-Pro), indicating that the conformational properties of the polymer can be attributed to local interactions (i.e., those within the dipeptide unit). The predominant conformations of blocked Pro-Gly were found to contain a 4→1 hydrogen bond; the molecules also showed restricted segmental motion of the Gly residue. These observations indicate the presence of β bends (along with other conformations). The experimentally determined properties of the four peptide molecules were compared with those determined from previous theoretical studies using empirical conformational energy calculations and, with some exceptions, were found to be in good agreement.

The hypothesis has been presented[3,4] that the conformation of a given sequence of amino acids in a protein is determined largely, but not exclusively, by intra-residue interactions. If this hypothesis is correct, a short sequence of amino acid residues in a globular protein should exist in a conformation similar to one or more of the stable structures of the same amino acid sequence in an oligomer in solution. This is the basis for using random copolymers for determining the tendency of single amino acid residues to adopt the α-helical conformation[5] and for studying short peptides to determine their tendency toward formation of chain reversal (bend) conformations in proteins.[6–13] In this paper, we examine oligopeptides (specifically, *blocked* single residues and *blocked* dipeptides) containing proline and glycine. The α-amino and α-carboxyl groups are blocked to eliminate charge effects and to simulate the environment of the *poly*peptide chain. Earlier studies[14–16] have treated *unblocked* oligopeptides of proline and glycine, where the peptide molecules are ionizable. The proline and glycine residues are of interest in protein structure because they are found frequently in β-bend conformations, Pro-Gly having a high propensity for forming a bend but Gly-Pro having a very low one.[13,17,18] Proline is of special interest because cis conformations have been observed in peptide bonds preceding Pro in small molecules[14–16,19–25] and in proteins.[26]

The purposes of this paper are to employ proton nuclear magnetic resonance (NMR), infrared (IR), and circular dichroism (CD) methods to: (a) determine the preferred conformations (including possible cis and trans peptide forms) of the N-acetyl-N'-ethylamide of Pro and the N-acetyl-N'-methylamides of Gly, Gly-Pro, and Pro-Gly; (b) compare the calculated structures of the N-acetyl-N'-methylamides of Gly,[27] Pro,[27] Gly-Pro,[28,29] and Pro-Gly[28,29] with those observed experimentally; (c) determine the influence of solvent