

Frictional properties of dilute polymer solutions. II. The effect of preaveraging

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Our development of the Debye-Bueche theory for the frictional properties of dilute polymer solutions is continued. A simplified version of the mean field theory is introduced that involves a preangular average (PAA) of the hydrodynamic interaction. A comparison is made between the exact mean field theory and the simplified PAA theory for the case of a uniform sphere and of an infinitesimal shell segment distribution.

I. INTRODUCTION

This is the second paper in a series dealing with the frictional properties of dilute polymer solutions. The theory is developed from the physical ideas of Debye and Bueche¹ and is put forth as an attractive alternative to the Kirkwood-Riseman (KR) theory.² Our approach³ is applicable to cross-linked polymers and does not require "preaveraging" of the hydrodynamic interaction.

The preaveraging approximation was introduced in the KR theory for computational convenience, and it consists of replacing the Oseen hydrodynamic interaction tensor by a scalar quantity. The consequences of this preaveraging in KR theory have not been sufficiently explored. A similar approximation can be made in our theory, and in the present article we investigate the resulting *simplified theory*.

A detailed comparison is made between the results of the exact and the simplified theories for the case of a uniform sphere and that of a spherical shell segment distribution. It turns out that the preangular average (PAA) yields surprisingly accurate results for the translational drag coefficient f_d and fair results for the intrinsic viscosity $[\eta]$. On the other hand for the rotational friction coefficient f_r , the PAA is somewhat poorer.

For the rotational friction coefficient the exact analysis³ is no more complicated than the simplified theory, and hence the former is to be preferred. However, for translational drag and intrinsic viscosity the exact theory, to be presented in following papers,^{4,5} is rather involved owing to the vector character of the equations. Thus for the latter two transport coefficients the simplified theory is an attractive route for the quick derivation of results, which presumably are accurate for a wide variety of spherically symmetric segment distributions.

II. THE PRAVERAGING APPROXIMATION

The microscopic theory is based on the equations describing the hydrodynamic interactions between polymer segments. The fluid in which the polymer is immersed is assumed to satisfy the linear Navier-Stokes equations for incompressible steady flow. The forces exerted by the n polymer segments on the fluid are related by the

set of equations

$$\mathbf{F}_j = \zeta[\mathbf{u}(\mathbf{r}_j) - \mathbf{v}_0(\mathbf{r}_j)] - \zeta \sum_{\substack{k=1 \\ (k \neq j)}}^n \mathbf{T}_{jk} \cdot \mathbf{F}_k \quad (j=1, \dots, n), \quad (2.1)$$

where $\mathbf{v}_0(\mathbf{r})$ is the unperturbed velocity field, i.e., the flow of the fluid if the polymer were absent, $\mathbf{u}(\mathbf{r}_j)$ in the velocity of segment j as given by the rigid body motion of the polymer, ζ is the friction coefficient of the segment, and \mathbf{T}_{jk} is the Oseen hydrodynamic interaction tensor

$$\mathbf{T}_{jk} = \mathbf{T}(\mathbf{r}_j - \mathbf{r}_k), \quad \mathbf{T}(\mathbf{R}) = \frac{1}{8\pi\eta_0} \left[\frac{\mathbf{1}}{R} + \frac{\mathbf{R}\mathbf{R}}{R^3} \right], \quad (2.2)$$

where η_0 is the solvent viscosity.

The microscopic equations (2.1) depend parametrically on the locations of the polymer segments, and in order to make progress a statistical average must be performed over the distribution of polymer conformations. In the conventional KR theory² the Oseen tensor in (2.1) is preaveraged over equilibrium configurations before further handling of the equations. Thus \mathbf{T}_{jk} is replaced by

$$\langle \mathbf{T}_{jk} \rangle = (1/6\pi\eta_0) \langle 1/r_{jk} \rangle \mathbf{1} \quad (2.3)$$

directly in (2.1), where it has been assumed that the distribution of $\mathbf{r}_j - \mathbf{r}_k$ is spherically symmetric. The replacement (2.3) is a rather severe "approximation" that introduces both an isotropy and a positional averaging of the interaction that is not present in the physical picture underlying the model.

In our theory,³ as presented in I, we first average the continuum analogue of the microscopic Eqs. (2.1) and then employ a mean field approximation. Thus we arrive at an equation for the average force density $\mathbf{F}(\mathbf{r})$,

$$\mathbf{F}(\mathbf{r}) = \zeta\rho(\mathbf{r})[\mathbf{u}(\mathbf{r}) - \mathbf{v}_0(\mathbf{r})] - \zeta\rho(\mathbf{r}) \int \mathbf{T}(\mathbf{r} - \mathbf{r}') \cdot \mathbf{F}(\mathbf{r}') d\mathbf{r}', \quad (2.4)$$

where $\rho(\mathbf{r})$ is the average segment density. This can be written in the abbreviated form

$$\mathbf{F}(\mathbf{r}) = \zeta\rho(\mathbf{r})[\mathbf{u}(\mathbf{r}) - \mathbf{V}(\mathbf{r})], \quad (2.5)$$

where $\mathbf{V}(\mathbf{r})$ is the average fluid flow velocity, which from (2.4) satisfies the integral equation

$$\mathbf{V}(\mathbf{r}) = \mathbf{v}_0(\mathbf{r}) - \zeta \int \mathbf{T}(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') [\mathbf{V}(\mathbf{r}') - \mathbf{u}(\mathbf{r}')] d\mathbf{r}' \quad (2.6)$$

In addition, one finds by averaging the microscopic Oseen equations for the pressure

$$P(\mathbf{r}) = p_0(\mathbf{r}) + \frac{1}{4\pi} \int \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3} \cdot \mathbf{F}(\mathbf{r}') d\mathbf{r}' \quad (2.7)$$

where $P(\mathbf{r})$ is the average pressure, and $p_0(\mathbf{r})$ is the fluid pressure in the absence of the polymer. It has been shown in I that (2.6) and (2.7) are equivalent to the equations

$$\eta_0 \nabla^2 \mathbf{V}(\mathbf{r}) - \zeta \rho(\mathbf{r}) [\mathbf{V}(\mathbf{r}) - \mathbf{u}(\mathbf{r})] - \nabla P(\mathbf{r}) = 0; \nabla \cdot \mathbf{V} = 0 \quad (2.8)$$

These are the starting equations of the Debye-Bueche theory,¹ and they amount to linear Navier-Stokes equations for an incompressible fluid with added terms for the friction between polymer and fluid.

In the simplified version of our theory we replace the Oseen tensor $\mathbf{T}(\mathbf{R})$ appearing in (2.4) and (2.6) by its angular average

$$\mathbf{T}(\mathbf{R}) \rightarrow \frac{1}{4\pi} \int \mathbf{T}(\mathbf{R}) d\Omega = \frac{\mathbf{1}}{6\pi\eta_0 R} \quad (2.9)$$

We shall refer to this (unjustified) simplification as the PAA (preangular average). The equation for the average force density becomes

$$\mathbf{F}(\mathbf{r}) = \zeta \rho(\mathbf{r}) [\mathbf{u}(\mathbf{r}) - \mathbf{v}_0(\mathbf{r})] - \frac{\zeta}{6\pi\eta_0} \rho(\mathbf{r}) \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \mathbf{F}(\mathbf{r}') d\mathbf{r}' \quad (2.10)$$

while the equation for the average fluid flow velocity becomes

$$\mathbf{V}(\mathbf{r}) = \mathbf{v}_0(\mathbf{r}) - \frac{\zeta}{6\pi\eta_0} \int \frac{1}{|\mathbf{r} - \mathbf{r}'|} \rho(\mathbf{r}') [\mathbf{V}(\mathbf{r}') - \mathbf{u}(\mathbf{r}')] d\mathbf{r}' \quad (2.11)$$

The relation (2.5) between \mathbf{F} and \mathbf{V} is still valid. The PAA is only a part of the preaveraging introduced in KR theory; the interaction is made spatially isotropic but the averaging over the segment statistical distribution is not prematurely applied.

III. THE SIMPLIFIED THEORY

The basic equations of the simplified theory are Eq. (2.11) for the fluid flow velocity $\mathbf{V}(\mathbf{r})$, and Eq. (2.5) relating \mathbf{V} to the force density $\mathbf{F}(\mathbf{r})$. The PAA is a severe approximation as follows immediately from the observation that the condition of incompressible flow, $\nabla \cdot \mathbf{V} = 0$, in general is violated. On the other hand, it has the advantage that the vector character of the equations is simplified, and as we shall show it leads to surprisingly accurate results for the transport coefficients of translational drag and intrinsic viscosity.

Applying the Laplacian ∇^2 to both sides of (2.11) and using the identity

$$\nabla_r^2 |\mathbf{r} - \mathbf{r}'|^{-1} = -4\pi \delta(\mathbf{r} - \mathbf{r}') \quad (3.1)$$

one finds for $\mathbf{V}(\mathbf{r})$

$$\nabla^2 \mathbf{V}(\mathbf{r}) - \frac{2}{3} \kappa^2(\mathbf{r}) [\mathbf{V}(\mathbf{r}) - \mathbf{u}(\mathbf{r})] = \nabla^2 \mathbf{v}_0 \quad (3.2)$$

where $\kappa^2(\mathbf{r}) = \zeta \rho(\mathbf{r}) / \eta_0$.

The right-hand side of (3.2) equals $\eta_0^{-1} \nabla p_0$ and in the applications we shall treat this is actually zero. The difference between (3.2) and (2.8) is the occurrence of the extra factor $\frac{2}{3}$ and the absence of the pressure term in (3.2). The condition of incompressibility is dropped and hence in the simplified theory the pressure plays no role.

We now specialize to the flow situations for the three transport coefficients of interest, viz. translational and rotational drag, and intrinsic viscosity. It is convenient to choose a coordinate frame in which the polymer is at rest with center of mass at the origin so that $\mathbf{u}(\mathbf{r}) = 0$. Also we consider only spherically symmetric segment distribution $\rho(r)$. For translational drag one has $\mathbf{v}_0(\mathbf{r}) = \mathbf{v}_0$ constant. For rotational drag $\mathbf{V}_0(\mathbf{r}) = \boldsymbol{\omega} \times \mathbf{r}$, where $\boldsymbol{\omega}$ is a constant vector. For viscosity the unperturbed flow is chosen as.⁶

$$\mathbf{v}_0(\mathbf{r}) = \mathbf{g} : \mathbf{r} \quad (3.3)$$

where \mathbf{g} is a constant, symmetric, traceless tensor. In all three cases $\nabla^2 \mathbf{v}_0 = 0$, as mentioned before. The vector equation (3.2) can now be reduced to a scalar equation by the substitution

$$\mathbf{V}(\mathbf{r}) = \psi(r) \mathbf{v}_0(\mathbf{r}) \quad (3.4)$$

where $\psi(r)$ depends only on the radial distance. This leads to

$$\mathbf{v}_0 \nabla^2 \psi + 2(\nabla \psi \cdot \nabla) \mathbf{v}_0 - \frac{2}{3} \kappa^2(r) \psi \mathbf{v}_0 = 0 \quad (3.5)$$

For translational drag the second term vanishes and one obtains the radial equation

$$\psi_0'' + \frac{2}{r} \psi_0' - \frac{2}{3} \kappa^2(r) \psi_0 = 0 \quad (3.6)$$

where a prime indicates differentiation with respect to r , and we have inserted a subscript 0. For both rotational drag and viscosity one finds from (3.5)

$$\psi_1'' = \frac{4}{r} \psi_1' - \frac{2}{3} \kappa^2(r) \psi_1 = 0 \quad (3.7)$$

where we have inserted a subscript 1. Note that (3.6) is precisely the radial Schrödinger equation for threshold low energy s -wave scattering from a repulsive spherical potential, while (3.7) with the substitution $\psi_1 = \phi(r)/r$ is the radial equation for p -wave scattering. This analogy has motivated our use of the subscripts 0 and 1.

The differential equations (3.6) and (3.7) must be solved with the boundary conditions that $\psi_0(r)$ and $\psi_1(r)$ be regular at the origin and tend to unity at infinity.

The asymptotic behavior of the two functions is given by

$$\psi_0(r) \approx 1 - a_0/r$$

and

$$\psi_1(r) \approx 1 - a_1^3/r^3 \text{ as } r \rightarrow \infty \quad (3.8)$$

with effective radii a_0 and a_1 . In the quantum mechanical analogy a_0 represents the scattering length for s -wave scattering.

It is useful to find the integral equations corresponding

to the differential equations (3.6) and (3.7) by substituting the ansatz (3.4) directly into the integral equation (2.11) for $\mathbf{V}(\mathbf{r})$. Using the identity

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{4\pi}{2l+1} \frac{r_{<}^l}{r_{>}^{l+1}} Y_{lm}(\Omega) Y_{lm}^*(\Omega') \quad (3.9)$$

where $r_{<}(r_{>})$ is the lesser (larger) of r and r' , and using the properties of the spherical harmonics Y_{lm} one finds for $\psi_0(r)$

$$\psi_0(r) = 1 - \frac{2}{3} \frac{\xi}{\eta_0} \int_0^{\infty} \frac{1}{r_{>}} \psi_0(r') \rho(r') (r')^2 dr' \quad (3.10)$$

Similarly for $\psi_1(r)$,

$$\psi_1(r) = 1 - \frac{2}{9} \frac{\xi}{\eta_0} \int_0^{\infty} \frac{r_{<}}{rr_{>}} \psi_1(r') \rho(r') (r')^3 dr' \quad (3.11)$$

Comparing the integral equations with the asymptotic behavior (3.8) one finds for the effective radii

$$\begin{aligned} a_0 &= \frac{2}{3} \frac{\xi}{\eta_0} \int_0^{\infty} \psi_0(r) \rho(r) r^2 dr, \\ a_1 &= \frac{2}{9} \frac{\xi}{\eta_0} \int_0^{\infty} \psi_1(r) \rho(r) r^4 dr. \end{aligned} \quad (3.12)$$

IV. TRANSPORT COEFFICIENTS

The transport coefficients can be expressed in terms of the effective radii. The translational friction coefficient f_d is defined by⁷

$$\mathcal{F} = \int \mathbf{F}(\mathbf{r}) d\mathbf{r} = -f_d \mathbf{v}_0, \quad (4.1)$$

where \mathbf{v}_0 is the constant unperturbed flow and the polymer is taken at rest ($\mathbf{u}=0$). Hence the PAA expression for the translational friction coefficient f_d is

$$\begin{aligned} f_d &= 4\pi\xi \int_0^{\infty} \psi_0(r) \rho(r) r^2 dr \\ &= 6\pi\eta_0 a_0, \quad (\text{PAA}) \end{aligned} \quad (4.2)$$

which is precisely of the Stokes form.

The rotational friction coefficient f_r is defined by⁷

$$\mathcal{T} = \int \mathbf{r} \times \mathbf{F}(\mathbf{r}) d\mathbf{r} = -f_r \boldsymbol{\omega} \quad (4.3)$$

for the unperturbed flow $\mathbf{v}_0(\mathbf{r}) = \boldsymbol{\omega} \times \mathbf{r}$. Hence the PAA expression for f_r is

$$\begin{aligned} f_r &= \frac{8\pi}{3} \xi \int_0^{\infty} \psi_1(r) \rho(r) r^4 dr \\ &= 12\pi\eta_0 a_1^2, \quad (\text{PAA}) \end{aligned} \quad (4.4)$$

which is to be compared with the Stokes expression for a hard sphere $f_r = 8\pi\eta_0 R^3$, where R is the sphere radius. Note that the first equality in (4.4) is identical to the expression (I. 3.14) of the exact mean field theory³ with $\phi(r)$ replaced by $\psi_1(r)$. In the free draining limit both $\phi(r) = 1$ and $\psi_1(r) = 1$, so that in this limit the exact and the simplified theory lead to the same result. The second equality in (4.4) must be compared³ with (I. 3.7) $f_r = 8\pi\eta_0 a^3$. In the hard sphere limit both a and a_1 tend to the sphere radius R , so that in this limit the simplified theory predicts a rotational friction coefficient which is a factor $\frac{3}{2}$ too large.

For viscosity the unperturbed flow pattern is given by (3.3) by comparing the stress tensor of the unperturbed flow with the stress tensor in the presence of ρ_p polymers per unit volume one finds for the change in viscosity^{5,7} $\Delta\eta = \eta - \eta_0$.

$$\Delta\eta = -\rho_p \int F_{\alpha}(\mathbf{r}) X_{\beta} d\mathbf{r} / 2g_{\alpha\beta} \quad (4.5)$$

where the integral is calculated for a single polymer with center of mass at the origin and $g_{\alpha\beta}$ is a nonvanishing component of \mathbf{g} . Conventionally the intrinsic viscosity $[\eta]$ is defined⁷ by

$$[\eta] = \Delta\eta / \eta_0 c = N_A \Delta\eta / M\eta_0 \rho_p \quad (4.6)$$

where c is the solute concentration (g/cm³), N_A is Avogadro's number, and M is the molecular weight of the polymer.

Substituting (2.5) and (3.4) in (4.5) one finds

$$\begin{aligned} \Delta\eta &= \frac{2\pi}{3} \rho_p \xi \int_0^{\infty} \psi_1(r) \rho(r) r^4 dr \\ &= 3\pi\rho_p \eta_0 a_1^2. \quad (\text{PAA}) \end{aligned} \quad (4.7)$$

Comparison of (4.4) and (4.7) yields the relation

$$\Delta\eta = \frac{1}{4} \rho_p f_r \quad (\text{PAA}) \quad (4.8)$$

for any spherically symmetric segment distribution. This relation also holds in the KR theory,⁸ but it is not valid in the exact mean field theory, where the PAA is not introduced.

In Eqs. (4.2), (4.4), and (4.7) we have for each of the transport coefficients two alternative expressions. The coefficients can be calculated either by determining the functions $\psi_{0,1}(r)$ and performing the integrals or by determining the effective radii a_0 and a_1 from the asymptotic behavior Eq. (3.8).

In the following section we evaluate the transport coefficients explicitly for some simple segment distributions.

V. EXPLICIT SOLUTIONS FOR UNIFORM SPHERE AND SPHERICAL SHELL

For the *uniform density sphere* where n segments are distributed uniformly throughout a sphere of radius R we have

$$\begin{aligned} \rho(r) &= \rho = n \left[\frac{4}{3} \pi R^3 \right]^{-1} \quad \text{for } 0 \leq r < R \\ &= 0 \quad \text{for } R < r < \infty, \end{aligned} \quad (5.1)$$

and correspondingly $\kappa^2(r) = \kappa^2$ for $r < R$ with $\kappa^2 = \xi\rho/\eta_0$. The solution of (3.6) which is regular at the origin and satisfies the boundary condition at infinity is

$$\begin{aligned} \psi_0(r) &= B_0 \sinh(\sqrt{\frac{2}{3}} \kappa r) / (\sqrt{\frac{2}{3}} \kappa r) \quad \text{for } 0 \leq r < R \\ &= 1 - A_0/r \quad \text{for } R < r < \infty \end{aligned} \quad (5.2)$$

where the constants A_0 and B_0 are to be determined by the condition that ψ_0 and ψ_0' be continuous at $r=R$. One has $a_0 = A_0$ and one easily finds that

$$a_0 = R S_0(\sqrt{\frac{2}{3}} \kappa R) \quad (5.3)$$

where

$$G_0(x) = 1 - \frac{\tanh x}{x} \quad (5.4)$$

Thus the translational drag for the uniform density sphere in the PAA theory is given by

$$f_d = 6\pi\eta_0 R G_0(\sqrt{\frac{2}{3}} \kappa R) \quad (\text{PAA, sphere}) \quad (5.5)$$

which should be compared to the exact mean field result^{1,4}

$$f_d = 6\pi\eta_0 R \frac{S_0(\kappa R)}{1 + \frac{1}{2} G_0(\kappa R)/(\kappa R)^2} \quad (\text{exact, sphere}) \quad (5.6)$$

The solution of (3.7) which is regular at the origin and satisfies the boundary condition at infinity is

$$\psi_1(r) = \frac{B_1}{r^2} \left[\cosh(\sqrt{\frac{2}{3}} \kappa r) - \frac{\sinh(\sqrt{\frac{2}{3}} \kappa r)}{\sqrt{\frac{2}{3}} \kappa r} \right] \quad 0 \leq r < R$$

$$= 1 - A_1/r^3 \quad R < r < \infty \quad (5.7)$$

Note that the solution ψ_0, ψ_1 for the interior region $r < R$ are closely related to the modified Bessel functions of the first kind $I_{l+1/2}(\kappa r \sqrt{\frac{2}{3}})$ for $l=0, 1$. The constants A_1 and B_1 in (5.7) must be determined by the condition that ψ_1 and ψ_1' be continuous at $r=R$. One has $a_1^2 = A_1$ and easily finds

$$a_1^2 = R^3 G_1(\sqrt{\frac{2}{3}} \kappa R) \quad (5.8)$$

where

$$G_1(x) = 1 + 3/x^2 - 3 \coth x/x \quad (5.9)$$

Thus according to (4.4)

$$f_r = 12\pi\eta_0 R^3 G_1(\sqrt{\frac{2}{3}} \kappa R) \quad (\text{PAA, sphere}) \quad (5.10)$$

which should be compared to the exact mean field result³

$$f_r = 8\pi\eta_0 R^3 G_1(\kappa R) \quad (\text{exact, sphere}) \quad (5.11)$$

For the viscosity one finds from (4.8)

$$\Delta\eta/\eta_0 = \frac{9}{4} \rho_p \mathcal{V} G_1(\sqrt{\frac{2}{3}} \kappa R) \quad (\text{PAA, sphere}) \quad (5.12)$$

where $\mathcal{V} = \frac{4}{3}\pi R^3$ is the volume of the polymer sphere. This should be compared to the exact mean field result^{1,5}

$$\frac{\Delta\eta}{\eta_0} = \frac{5}{2} \rho_p \mathcal{V} \frac{S_1(\kappa R)}{1 + 10 G_1(\kappa R)/(\kappa R)^2} \quad (\text{exact, sphere}) \quad (5.13)$$

We also consider the case of a *spherical shell* of infinitesimal thickness with n segments distributed uniformly over the shell at $r=R$; thus

$$\rho(r) = (n/4\pi R^2) \delta(r-R) \quad (5.14)$$

The differential equation (3.6) for $\psi_0(r)$ with $\kappa^2(r)=0$ in the regions $r < R$ and $r > R$ now has the solution

$$\psi_0(r) = B_0 \quad 0 \leq r < R$$

$$= 1 - A_0/r \quad R < r < \infty \quad (5.15)$$

The constants A_0 and B_0 are determined by the conditions that $\psi_0(r)$ be continuous at $r=R$, and that $\psi_0'(r)$ have a jump discontinuity given by

$$\psi_0'(R_+) - \psi_0'(R_-) = (n\xi/6\pi\eta_0 R^2) \psi_0(R) \quad (5.16)$$

Defining the constant κ by $\kappa^2 = 3n\xi/4\pi\eta_0 R^3$, as for the

uniform sphere, one easily finds for the translational drag

$$f_d = 6\pi\eta_0 R (\kappa R)^2 / [\frac{3}{2} + (\kappa R)^2], \quad (\text{PAA exact, shell}) \quad (5.17)$$

which is identical to that obtained in the exact mean field theory.⁴ This is the only case investigated where the results of the PAA and exact theories are identical.

The differential equation (3.7) for $\psi_1(r)$ now has the solution

$$\psi_1(r) = B_1 \quad 0 \leq r < R$$

$$= 1 - A_1/r^3 \quad R < r < \infty \quad (5.18)$$

The constants A_1 and B_1 are again determined by the condition that $\psi_1(r)$ is continuous and that $\psi_1'(r)$ has the same jump discontinuity as given for $\psi_0'(r)$ in (5.16). Hence one finds for the rotational drag

$$f_r = 8\pi\eta_0 R^3 (\kappa R)^2 / [9 + \frac{2}{3} (\kappa R)^2], \quad (\text{PAA, shell}) \quad (5.19)$$

which should be compared to the exact mean field result³

$$f_r = 8\pi\eta_0 R^3 (\kappa R)^2 / [9 + (\kappa R)^2] \quad (\text{exact, shell}) \quad (5.20)$$

For the viscosity one finds

$$\Delta\eta/\eta_0 = \frac{5}{2} \rho_p \mathcal{V} (\kappa R)^2 / [15 + \frac{10}{3} (\kappa R)^2], \quad (\text{PAA, shell}) \quad (5.21)$$

which should be compared to the exact mean field result⁵

$$\Delta\eta/\eta_0 = \frac{5}{2} \rho_p \mathcal{V} (\kappa R)^2 / [15 + (\kappa R)^2] \quad (\text{exact, shell}) \quad (5.22)$$

Note that the rotational friction coefficient is predicted in the simplified theory as larger than in the exact mean field theory, while the viscosity is predicted smaller.

This concludes our discussion of the simplified PAA theory for f_d, f_r , and $\Delta\eta$. Explicit results have been presented for the uniform sphere and the spherical shell. In Sec. VII we compare the results of the exact and simplified theory in more detail in order to examine the consequences of the preaveraging that is introduced in the simplified version of the theory.

VI. VARIATION PRINCIPLES

Variational principles and perturbation procedures may be developed for the PAA theory as has been done for the exact theory³⁻⁵ for the calculation of frictional properties when the segment density $\rho(r)$ has a more complicated form, e.g., Gaussian. For the sake of comparison we list here the variational principles of PAA theory.

For translational drag the differential equation (3.6) can be written in the form $L_0 \psi_0 = 0$ with L_0 defined by

$$L_0 = r^2 \frac{d^2}{dr^2} + 2r \frac{d}{dr} - \frac{2}{3} r^2 \kappa^2(r) \quad (6.1)$$

One can now look for trial functions $\psi_{0,t}(r)$ which are regular at the origin and have asymptotic behavior

$$\psi_{0,t}(r) \approx 1 - a_{0,t}/r \quad \text{as } r \rightarrow \infty \quad (6.2)$$

The variation principle then reads

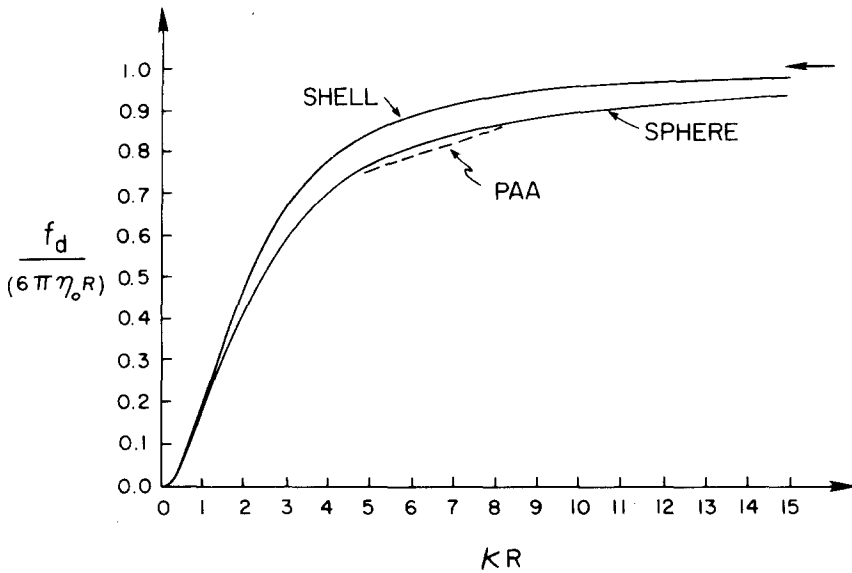


FIG. 1. The reduced translational friction coefficient for the sphere and the shell versus (κR) . For the shell the mean field and PAA theories give identical results. For the sphere, the minor difference between the mean field and PAA theories are exaggerated.

$$a_0 \leq a_{0,t} - \int_0^\infty \psi_{0,t}(L_0 \psi_{0,t}) dr \quad (6.3)$$

or alternatively

$$a_0 \leq \int_0^\infty [(\psi'_{0,t})^2 + \frac{2}{3} \kappa^2(r) \psi_{0,t}^2] r^2 dr. \quad (6.4)$$

For rotational friction and viscosity we can immediately copy the variational principle derived in I, since the differential equation (3.7) differs only by the factor $\frac{2}{3}$ from the corresponding Eq. (I. 3.4). Hence we define the linear operator L_1 by

$$L_1 = r^2 \frac{d^2}{dr^2} + 4r \frac{d}{dr} - \frac{2}{3} r^2 \kappa^2(r). \quad (6.5)$$

For trial functions $\psi_{1,t}(r)$ which are regular at the origin and have asymptotic behavior

$$\psi_{1,t}(r) \sim 1 - a_{1,t}^3 / r^3 \quad \text{as } r \rightarrow \infty, \quad (6.6)$$

one then has the variational principle

$$a_1^3 \leq a_{1,t}^3 - \frac{1}{3} \int_0^\infty \psi_{1,t}(L_1 \psi_{1,t}) r^2 dr \quad (6.7)$$

or alternatively

$$a_1^3 \leq \frac{1}{3} \int_0^\infty [(\psi'_{1,t})^2 + \frac{2}{3} \kappa^2(r) \psi_{1,t}^2] r^4 dr. \quad (6.8)$$

VII. COMPARISON OF RESULTS

The apparently mild simplification of the PAA may lead to both qualitative and quantitative differences with the exact theory. We have already noted that in the simplified theory the condition of incompressible flow, $\nabla \cdot \mathbf{V} = 0$, is violated. Moreover, as shown in (3.4), for the external flows $\mathbf{v}_0(\mathbf{r})$ under consideration the flow pattern $\mathbf{V}(\mathbf{r})$ will always be parallel to the external flow $\mathbf{v}_0(\mathbf{r})$, and therefore will be vastly different from the exact flow pattern. Hence it is surprising that at least for the transport coefficients of translational drag and viscosity the simplified theory actually gives rather accurate results.

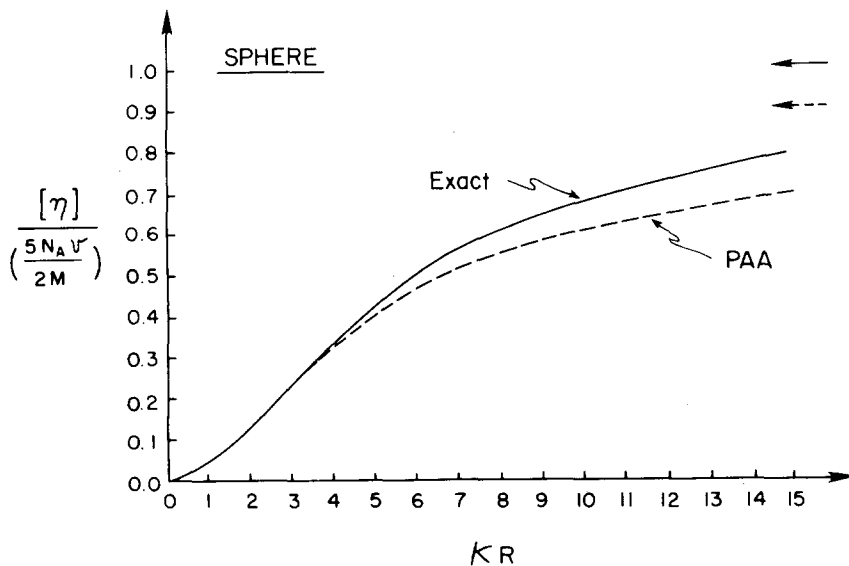


FIG. 2. The reduced intrinsic viscosity for the sphere versus (κR) according to the mean field (—) and PAA (---) theories. The asymptotic values for large (κR) are indicated by arrows.

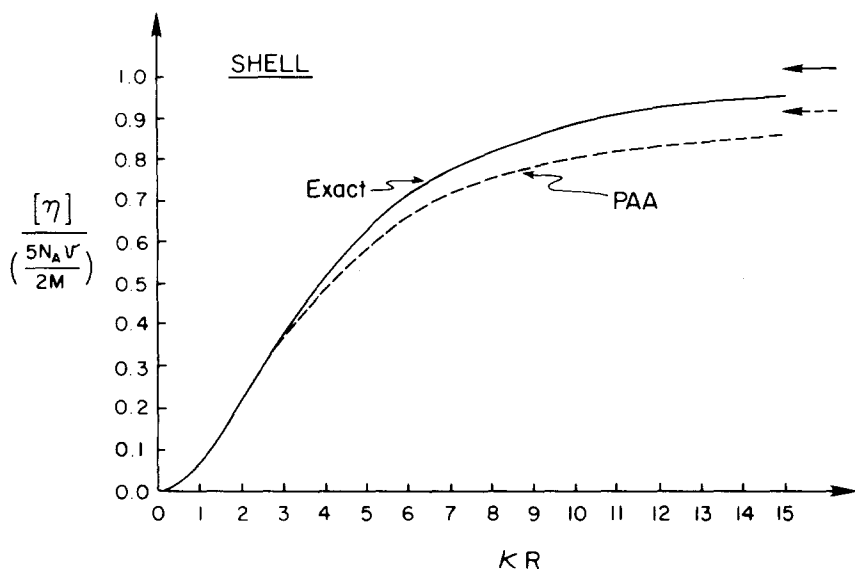


FIG. 3. The reduced intrinsic viscosity for the shell versus (κR) according to the mean field (—) and PAA(---) theories. The asymptotic values for large (κR) are indicated by arrows.

One example of the qualitative difference between the theories concerns the relation $\Delta\eta = (1/4)\rho_p f_r$, which we have found in the PAA theory, Eq. (4.8). The relation also holds in the KR theory,⁸ but is not valid in the exact mean field theory. For example, in the case of the uniform density sphere one finds from Eqs. (5.11) and (5.13)

$$\Delta\eta = \frac{5}{12} \rho_p f_r [1 + \frac{5}{3} f_r / \eta_0 v (\kappa R)^2]^{-1} \quad (7.1)$$

Thus despite conventional wisdom the combination of intrinsic viscosity and rotatory friction coefficient measurements (from flow birefringence experiments⁹) potentially may elucidate the shape and/or structure of the polymer in solution.

The quantitative differences that may arise between the exact mean field theory and the simplified PAA theory can be illustrated by comparing the results for the sphere and the shell. Different frictional properties may reflect the differences in the two theories in different ways because each transport coefficient is related to a different integral over the flow. In addition the differences will depend on the particular segment distribution under consideration.

In Fig. (1) the translational friction coefficient is plotted versus the dimensionless ratio κR . This ratio is roughly proportional to $(nb/R)^{1/2}$, where b is the length associated with a segment and R the radius of the sphere

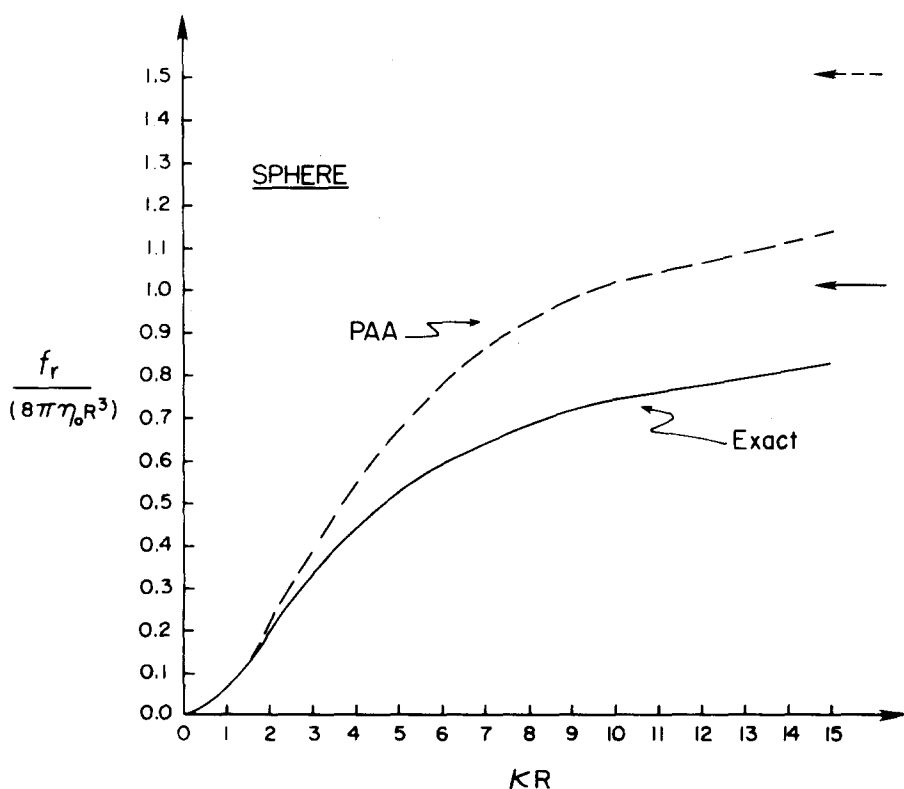


FIG. 4. The reduced rotatory friction coefficient for the sphere versus (κR) according to the mean field (—) and PAA (---) theories. The asymptotic values for large (κR) are indicated by arrows.

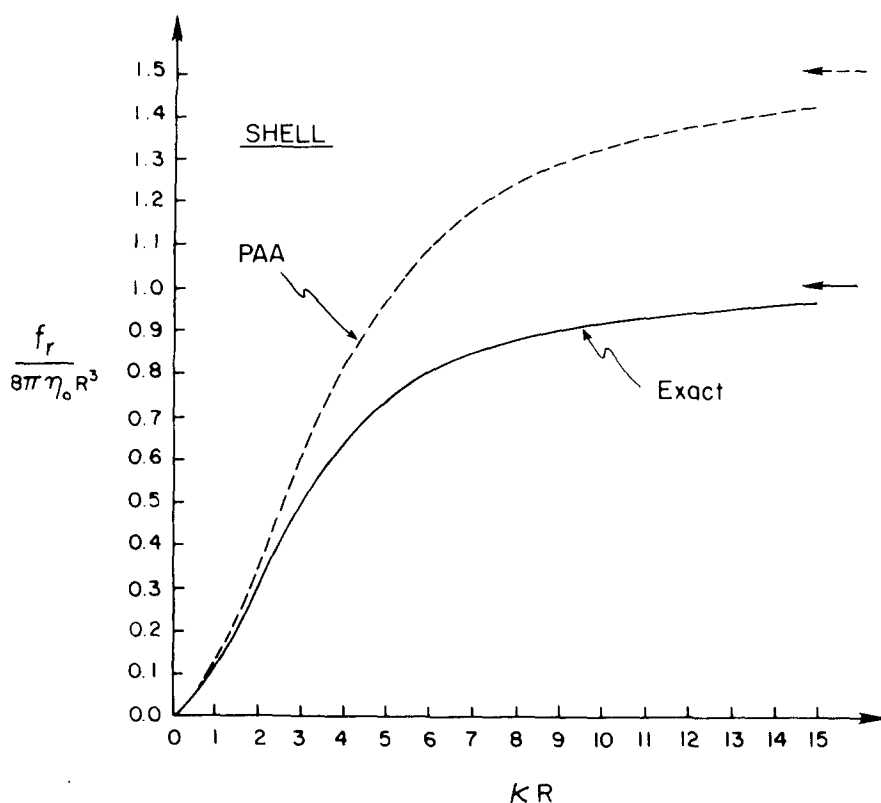


FIG. 5. The reduced rotatory friction coefficient for the shell versus (κR) according to the mean field (—) and PAA (---) theories. The asymptotic values for large (κR) are indicated by arrows.

or shell. For f_d the PAA and exact theories give very similar results. In the case of the shell both theories give the same answer. In the case of the sphere the correction factors in (5.5) and (5.6), despite a different functional dependence on the parameter κR , agree within 1% over the range $0 < \kappa R < 16$ considered. In Figs. 2 and 3 results are presented for $[\eta]$ versus κR for the case of the sphere and shell, respectively. Note that the limiting value approached for large κR is different for the two theories, in the case of the sphere and the shell $\{[\eta](\text{PAA})/[\eta](\text{exact})\} = 0.9$ at $\kappa R = \infty$. Finally in Figs. 4 and 5 results are presented for the rotatory friction coefficient f_r versus κR for the case of the sphere and shell, respectively. Here one finds the greatest quantitative differences between the two theories; for example, $[f_r(\text{PAA})/f_r(\text{exact})] = 1.5$ at $\kappa R = \infty$ for both the sphere and the shell. For all these frictional properties there is of course agreement between the two theories in the free-draining $(\kappa R) \rightarrow 0$ limit.

The results presented here for the sphere and shell already permit one to examine problems of chemical interest. For example Bloomfield *et al.*¹⁰ have undertaken a numerical study of the translational friction coefficient of multisubunit structures that are intended to serve as models for proteins and viruses. A particular model they consider is a spherical shell of radius R composed of identical and spherical particles of radius b that are uniformly spread over the shell. They numerically investigate within the framework of the KR theory, the dependence of the translational friction coefficient f_d on $\beta = (b/r)$, the ratio of the subunit radius to the shell radius, and on ξ the fraction of subunits that are randomly removed from the shell. This problem may be studied

analytically in our theory. For small β the maximum number of subunits that can fit on the shell is

$$n_{\max} = (\pi/2\sqrt{3})(4\pi R^2/\pi b^2) = 2\pi/(\beta^2\sqrt{3}), \quad (7.2)$$

where the numerical factor arises because of the triangular close packing of spheres on the surface. A particular surface density $\tau = [n/(4\pi R^2)]$ is related to n_{\max} by

$$\tau = (1 - \xi)n_{\max}/(4\pi R^2), \quad (7.3)$$

where $\xi = [(n_{\max} - n)/n_{\max}]$ is the fraction of spheres removed. Hence one finds a value of (κR^2) given by

$$(\kappa R)^2 = (\sqrt{3}\xi/2\eta_0\beta^2R)(1 - \xi) = (3^{3/2}\pi/\beta)(1 - \xi), \quad (7.4)$$

where in the last relation we have employed Stokes' law for each segment $\xi = 6\pi\eta_0 b$. Consequently according to Eq. (5.17) our theory predicts

$$f_d = 6\pi\eta_0 R \frac{1 - \xi}{(1 - \xi) + (\beta\sqrt{3}/2\pi)}. \quad (7.5)$$

For $\xi = 0$ this result shows a decrease of the friction coefficient as $\beta = (b/r)$ increases owing to the increase in the size of the gaps between the spheres. One finds

$$f_d/6\pi\eta_0 R = 1/(1 + 0.276\beta) \quad (7.6)$$

in contrast to the numerical result obtained by Bloomfield *et al.* [Ref. (10); Eq. (25)] who on the basis of the Kirkwood approximation¹¹ predict a linear increase with β :

$$f_d/6\pi\eta_0 R = 1 + 0.25\beta. \quad (7.7)$$

At present we have no explanation for this discrepancy.

Perhaps the most interesting result of the Bloomfield *et al.* numerical analysis is the weak dependence of $(f_d/6\pi\eta_0R)$ on ξ for low values of β . The values of ξ must be surprisingly large before this ratio declines appreciably from unity. Our analytic result Eq. (7.5) is consistent with this important effect. For example if $\beta=0.1$ and $(1-\xi)=0.2$ we find $(f_d/6\pi\eta_0R)=0.88$ which is within the scatter of the numerical result for this case if 80% of the spheres removed.

Future work will be directed toward (a) obtaining numerical results for frictional properties with more realistic segment densities for both the exact mean field and simplified PAA theories; (b) application to problems of chemical interest; and (c) investigation of the effects of correlations on the mean field results.

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