

# A Sphere Buoyant in a Dilute Polymer Solution

S. GRISAFI, *P. O. Box 230086, Brooklyn, New York 11223-0003*

## Synopsis

The density and pressure fields of a dilute polymer solution are nonuniform at the surface of a small sphere even when there is no fluid motion. The polymer solution is modeled by an ensemble of Hookean dumbbells. A hard core potential is assumed as the only interaction between the sphere and the macromolecules. The pressure field about the sphere is transversely isotropic. The perpendicular component of the pressure at the interface is greater than the isotropic pressure in the bulk of the fluid. The parallel component of the pressure at the interface is less than the bulk isotropic pressure. The surface adsorption (cf., surface pressure) and the film thickness vary with a parameter that is the ratio of the sphere radius,  $a$ , to the root mean square extension of the dumbbells,  $R_0$ . The spherical results coincide with the plane wall results for  $a/R_0$  greater than approximately 100.

## INTRODUCTION

Dispersions of solid particles in polymer solutions find application in many technologies. The stability of the dispersions depends upon the interaction between the particles and the polymer.<sup>1</sup> It is well known that the presence of a solid surface can modify the rheological properties of a polymer solution.<sup>2</sup> For the sake of analysis the dispersed particles can be considered to be spheres. Previous investigations of the interface addressed a plane surface.<sup>3</sup> Our present concern is the interface between a sphere and a dilute polymer solution containing macromolecules of a size comparable to that of the sphere. Our objective is to demonstrate by a theoretical analysis the nonuniformity of the density and pressure fields about the sphere. We supplement this demonstration with a prediction of the surface adsorption and the film thickness of the interface. We choose these two quantities since they can be measured experimentally and therefore enable experimental verification of the theoretical predictions.

One consequence of the nonuniformity of the polymer solution density and pressure fields at the interface is the apparent slip of the fluid at the solid surface. This has been observed for the flow of dilute polymer solutions in capillaries.<sup>4</sup> One hypothesis for the occurrence of apparent slip is steric hindrance. The steric hindrance hypothesis differs from the others<sup>4</sup> in that only it predicts different interfacial properties when the fluid is at rest.<sup>5</sup> The possibility of nonuniform interfacial properties about a spherical particle immersed in a polymer solution at rest has implications for the stability of dispersions in quiescent media. That is, the sedimentation rates of the particles may be affected by the nonuniform interfacial properties. Our analysis assumes the fluid to be at rest about the sphere because a particle in dispersion is in a quasi-static suspension. A departure from this quasi-static condition results in the

sedimentation of the dispersed particles. Hence, our analysis should be considered as providing the initial conditions for analyses of colloidal stability.

We apply the steric hindrance hypothesis to the interface between a sphere and a dilute polymer solution. The macromolecules are modeled by an ensemble of Hookean dumbbells. The molecular weight distribution for the polymer is the Dirac delta distribution. We assume that the macromolecules do not interact with one another. Hence, the analysis is applicable only to solutions at infinite dilution. The hard core potential is assumed to be the only interaction between the macromolecules and the sphere. This choice of wall potential alters the polymer density and pressure fields about the sphere by causing a depletion of polymer within the interface. We evaluate these changes and show how they relate to the experimentally observable surface adsorption and film thickness.

### FORMULATION OF THE PROBLEM

The number density of dumbbells is defined as<sup>5</sup>

$$n(\mathbf{r}) = \int d\mathbf{r}_2 \Psi(\mathbf{r}_1 = \mathbf{r}, \mathbf{r}_2) \quad (1)$$

The configuration space distribution (CSD),  $\Psi$ , is a function of the position of the beads of the dumbbell,  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . The integration is over all permissible coordinates for the position vector of bead 2 while holding bead 1 at any point in space. To visualize the volume of permissible orientations, one may consider a point source of light to shine from bead location  $\mathbf{r}_1$ . The integration volume is then the volume that is illuminated. The zone of forbidden orientations is that which is cast in the shadow of the sphere.

To evaluate the polymer density field about a sphere of radius  $a$ , we place the origin of a spherical-polar coordinate system at the center of the sphere. Applying the spherical coordinate system yields

$$n(\mathbf{r}) = 2\pi \int_a^\infty dr_2 r_2^2 \int_0^{\theta_s} d\theta_2 \sin \theta_2 \Psi(\mathbf{r}_1 = \mathbf{r}, \mathbf{r}_2) \quad (2)$$

where  $\theta_2$  is the angle measured from the initial ray  $\mathbf{r}_2$ .  $\theta_s$  defines the boundary of the shadow region,

$$\theta_s = \text{Arc cos}(a/r) + \text{Arc cos}(a/r_2) \quad (3a)$$

For the fluid at rest about the sphere, the CSD is given by

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = (3/2\pi)^{3/2} n_\infty \exp(-3/2(r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta_2)/R_0^2) \quad (3b)$$

where  $n_\infty$  is the polymer number density far from the sphere. The root mean square (rms) extension of the macromolecules is designated by  $R_0$ . Note that  $R_0$  serves as a measure of the polymer molecular weight.

Performing the integration yields

$$\begin{aligned}
 n(r) = n_\infty & (1 + \operatorname{erf}((3/2)^{1/2}(r - a)/R_0) \\
 & + (r^2 - a^2)^{1/2}/r \operatorname{erfc}((3/2(r^2 - a^2))^{1/2}/R_0))/2 \\
 & + 1/(6\pi)^{1/2}R_0/r(\exp(-3/2(r - a)^2/R_0^2) - \exp(-3/2(r^2 - a^2)/R_0^2)) \quad (4a)
 \end{aligned}$$

where erf denotes the error function and erfc denotes its complement. When we equate the distance from the wall  $z$  with  $(r - a)/R_0$ , for large values of  $a/R_0$  we expect the density field to approach that adjacent to a plane wall,

$$n(r) = n_\infty (1 + \operatorname{erf}((3/2)^{1/2}z))/2 \quad (4b)$$

The polymer density field is usually not directly observable. The adsorbance at a spherical surface should be observable via ellipsometry. The theoretical quantity corresponding to the ellipsometric adsorbance is the surface adsorption,  $\Gamma$ . The surface adsorption is related to the density field by<sup>3</sup>

$$\Gamma = \int_a^\infty drn(r) - n_\infty \quad (5a)$$

The surface adsorption is related to the surface pressure,  $P^{(s)}$ , by

$$P^{(s)} = \Gamma/(kT) \quad (5b)$$

where  $k$  is Boltzmann's constant and  $T$  is the absolute temperature.

To describe the thickness of the interface, we adopt the concept of an equivalent homogeneous film.<sup>6</sup> This device employs a boundary layer of a constant density throughout the interface. The thickness of this boundary layer,  $\delta$ , is given by

$$\delta = \left( \int_a^\infty drn(r) - n_\infty \right)^2 / \int_a^\infty dr(n(r) - n_\infty)^2 \quad (6a)$$

The constant polymer density,  $n_f$ , existing within this interface can be expressed in terms of the surface adsorption and the film thickness<sup>6</sup>

$$\delta(n_f - n_\infty) = \Gamma \quad (6b)$$

Hence, the surface adsorption and the film thickness serve to define completely the equivalent homogeneous interface.

For the fluid at rest about the sphere there exist no shear stresses within the fluid, only normal stresses or pressure. The total stress in the fluid about the sphere is the sum of the polymer and solvent contributions. The solvent contribution is the familiar isotropic pressure. The polymer contribution consists of a kinetic contribution and an intramolecular contribution. The intramolecular contribution,  $\sigma^{(c)}$ , results from the tension in the Hookean spring of the dumbbell. The kinetic contribution is isotropic,  $\sigma^{(k)}\delta$ , where  $\delta$  is the unit tensor. The kinetic contribution is given by<sup>7</sup>

$$\sigma^{(k)} = -2nkT \quad (7)$$

To evaluate the intramolecular contribution we center our coordinate system at a position  $\mathbf{r}$  along the spring of the dumbbell. Doing so enables us to be certain that the orientations we include contribute to the polymer stress. The intramolecular contribution is expressed as<sup>5</sup>

$$\sigma^{(c)} = H \int d^3\mathbf{R} \int_0^1 d\alpha \Psi(\mathbf{r} - \alpha\mathbf{R}, \mathbf{r} + (1 - \alpha)\mathbf{R}) \quad (8a)$$

where  $\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1$ . Applying the spherical coordinate system at  $\mathbf{r}$  yields

$$\begin{aligned} \sigma^{(c)} = 2\pi H \int_0^\infty dR R^2 \int_V d\theta \sin \theta \int_0^1 d\alpha R^2 (\cos^2\theta \delta_\perp \delta_\perp + \sin^2\theta \delta_\parallel \delta_\parallel) \\ \times \Psi(-\alpha\mathbf{R}, (1 - \alpha)\mathbf{R}) \quad (8b) \end{aligned}$$

where  $\delta_\perp$  is the unit vector normal to the surface of the sphere and  $\delta_\parallel$  is a unit vector parallel to the surface. The angle  $\theta$  is measured from the initial ray  $\mathbf{r}$ . The integration for  $\theta$  is over the domain  $V$  consisting of all permissible orientations.

The symmetry condition

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \Psi(\mathbf{r}_2, \mathbf{r}_1) \quad (9)$$

permits us to limit  $\theta \leq \frac{1}{2}\pi$  radians. With the origin at  $\mathbf{r}$  the angle between the beads of the dumbbell is always  $\pi$  radians. To evaluate the limits for  $\theta$  we consider the spherical obstacle. The easiest route to take is to perform the required integrations over all space then subtract out the orientations blocked by the sphere. Breaking up the intramolecular contribution into its components yields

$$\begin{aligned} \sigma_\perp^{(c)} = n_\infty kT \left( 1 - 3 \int_0^{\theta_c} d\theta \sin \theta \cos^2\theta (\operatorname{erfc}((3/2)^{1/2}\beta/R_0) \right. \\ \left. + (2/(3\pi))^{1/2}\beta/R_0 \exp(-3/2\beta^2/R_0^2)) \right) \quad (10a) \end{aligned}$$

$$\begin{aligned} \sigma_\parallel^{(c)} = n_\infty kT \left( 2 - 3 \int_0^{\theta_c} d\theta \sin^3\theta (\operatorname{erfc}((3/2)^{1/2}\beta/R_0) \right. \\ \left. + (2/(3\pi))^{1/2}\beta/R_0 \exp(-3/2\beta^2/R_0^2)) \right) \quad (10b) \end{aligned}$$

where  $\theta_c$  is given by

$$\sin \theta_c = a/r \quad (10c)$$

and  $\beta$  is given by

$$\beta = r \cos \theta - (a^2 - r^2 \sin^2 \theta)^{1/2} \quad (10d)$$

Note that the parallel component is the sum of the colatitude,  $\delta_\theta \delta_\theta$ , and azimuthal,  $\delta_\phi \delta_\phi$ , contributions where  $\phi$  is the azimuthal angle. The polymer contribution to the pressure is therefore transversely isotropic. The perpendicular component of the total pressure is

$$P_\perp = P_s + 2nkT - \sigma_\perp \quad (11a)$$

and the parallel component is

$$P_\parallel = P_s + 2nkT - \frac{1}{2}\sigma_\parallel \quad (11b)$$

where  $P_s$  is the solvent contribution to the pressure.

## RESULTS AND DISCUSSION

The polymer density field about the sphere is presented in dimensionless form in Figure 1. The choice of abscissa  $(r - a)/R_0$  permits direct comparison of the density profile for each value of the parameter  $a/R_0$ . It also shows how the profiles converge to a limiting profile as  $a/R_0$  increases. This limiting profile is the planar limit. The density profile about the sphere reaches the density profile adjacent to a plane wall at approximately  $a/R_0 = 100$ . Hence, for particles of a size two orders of magnitude or more greater than the size of the macromolecules, the curvature of the particle's surface can be neglected. The polymer

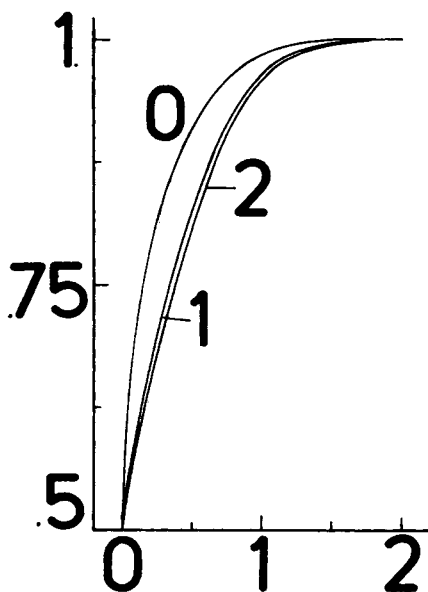


Fig. 1. Polymer density about a sphere of radius  $a$ . The abscissa is  $(r - a)/R_0$ . The ordinate is  $n/n_\infty$ . The curves are marked by the logarithm of their value for  $a/R_0$ .

density reaches to within 99% of its unbounded value at approximately  $(r - a)/R_0 = 1.5$ . The value of the polymer density at the surface of the sphere is  $\frac{1}{2}n_\infty$  for all values of  $a/R_0$ .

The thickness of an equivalent homogeneous film and its corresponding surface adsorption are shown in Figure 2 as a function of the parameter  $a/R_0$ . For the choice of the hard core potential as the only interaction between the sphere and the macromolecules, the surface adsorption is negative for all values of  $a/R_0$ . This signifies that there is a depletion of polymer within the interface, as can also be seen from the density profiles. The surface adsorption approaches its planar limit of  $\Gamma/(n_\infty R_0) = -1/(6\pi)^{1/2}$  with increasing values of  $a/R_0$ . The surface adsorption reaches to within 1% of its planar limit at approximately  $a/R_0 = 20$ . The film thickness approaches to within 1% its planar limit of  $\delta/R_0 = .786$  also at approximately  $a/R_0 = 20$ . At the planar limit, the density within this equivalent homogeneous film is 71% of the bulk polymer density.

The perpendicular contribution to the polymer pressure is presented in dimensionless form in Figure 3. The choice of the abscissa  $(r - a)/R_0$  has the same advantages for the pressure field as it does for the density field. The polymer contribution to the perpendicular pressure within the interface is greater than the polymer pressure in the bulk of the fluid. With increasing values of  $a/R_0$  the perpendicular pressure approaches the uniform profile of the planar limit. In the planar limit the perpendicular pressure has its unbounded value right up to the surface. As can be seen in Fig. 3, the perpendicular pressure has nearly reached its planar limit at  $a/R_0 = 100$ .

Figure 4 presents the polymer contribution to the parallel pressure. The polymer contribution to the parallel pressure within the interface is less than

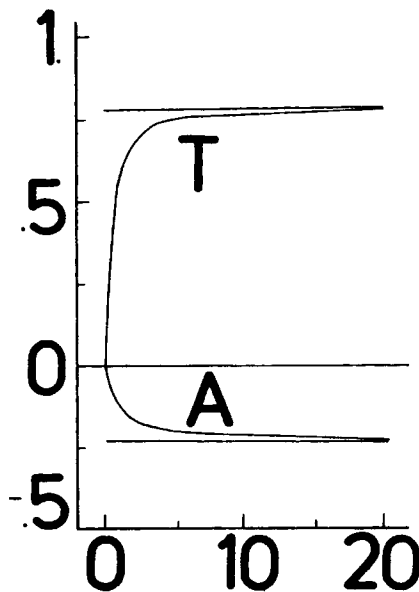


Fig. 2. The dimensionless surface adsorption,  $\Gamma/(n_\infty R_0)$ , or surface pressure,  $P^{(s)}/(n_\infty kTR_0)$ , is the curved marked by A. The boundary layer thickness of an equivalent homogeneous film,  $\delta/R_0$ , is the curve marked by T. The abscissa is  $a/R_0$ . The planar limit for each quantity is indicated by the horizontal asymptote for each curve.

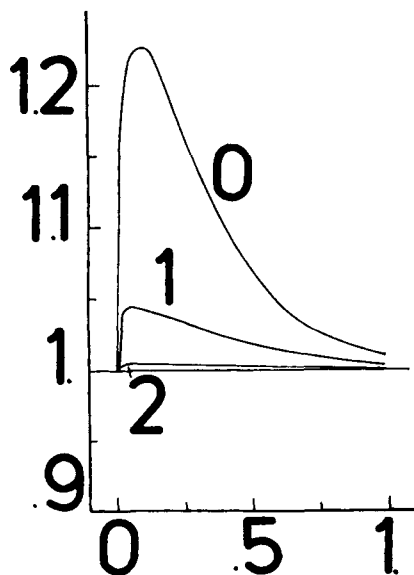


Fig. 3. Perpendicular polymer pressure at the interface. The abscissa is  $(r - a)/R_0$ . The ordinate is  $(P_{\perp} - P_s)/(n_{\infty}kT)$ . The curves are marked by the logarithm of their value for  $a/R_0$ .

the polymer pressure in the bulk of the fluid. The parallel pressure reaches its planar limit at approximately  $a/R_0 = 100$ . Its planar limit shows a spatial variation that has been discussed before.<sup>5</sup> The perpendicular and parallel pressures satisfy the equation of motion for this geometry

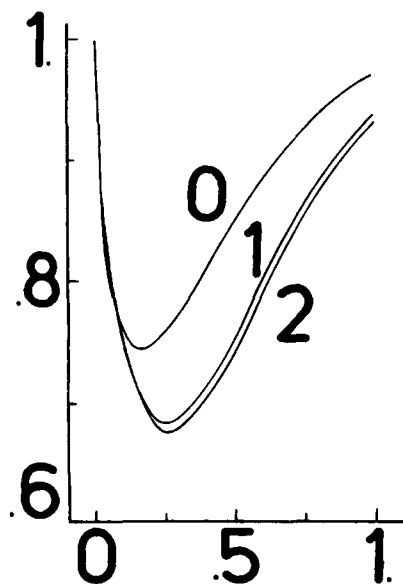


Fig. 4. Parallel polymer pressure at the interface. The abscissa is  $(r - a)/R_0$ . The ordinate is  $(P_{\parallel} - P_s)/(n_{\infty}kT)$ . The curves are marked by the logarithm of their value for  $a/R_0$ .

$$dP_{\perp}/dr + 2/r(P_{\perp} - P_{\parallel}) = 0 \quad (12)$$

The equation of motion does not tell us whether or not the parallel pressure varies with  $r$ . This could only be found from kinetic theory.

## CONCLUSIONS

Both the polymer density and pressure fields in the immediate vicinity of a sphere immersed in a dilute polymer solution differ from what we assume the sphere to experience. The surface of the sphere experiences a transversely isotropic pressure contributed by the polymer. The perpendicular component of the polymer pressure at the interface is greater than the isotropic pressure in the bulk of the fluid. The parallel component at the interface is less than the isotropic pressure in the bulk. For particles of a size two or more orders of magnitude larger than the size of the macromolecules, the particle surface can be modeled as a plane wall.

An interface with rheological properties different from the bulk may affect the rate of sedimentation of particles in polymer solutions. It seems prudent to consider the difference between the interfacial and bulk properties when we consider the stability of dispersions of solid particles. The difference in the properties of the interface will depend upon the chemistry of the interaction between the particle and polymer. The trends predicted by the hard core potential will not agree with situations in which a positive net adsorption of polymer occurs at the interface. However, in those cases the interfacial properties will also differ from that of the bulk. The magnitude of some of the other observable phenomena that the steric hindrance hypothesis can predict, such as the apparent slip of dilute polymer solutions in capillaries, suggests that the nonuniform interfacial properties should be taken into account. We suggest that analyses of colloidal stability include the nonuniformity of the density and pressure fields about the dispersed particles.

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