

A Suspension of Spheres in a Dilute Polymer Solution

S. Grisafi

340 Bushkill St., Easton, Pennsylvania 18042-1856

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ABSTRACT: The Hookean dumbbell model of a macromolecule predicts non-uniform density and pressure fields surrounding a sphere buoyant in a dilute polymer solution when the size of the sphere is of the same order of magnitude as the size of the macromolecules. Using this prediction, the root mean square separation distance of a suspension of spheres buoyant within a dilute polymer solution is found to be inversely proportional to both the square of the radius of a sphere and the density of the polymer solution. The phase space distribution function for an ensemble of spheres immersed at equilibrium within a dilute polymer solution is found and used to

define the magnitude of the ensemble average peculiar acceleration of the spheres. The peculiar acceleration results from changes in direction of the peculiar velocity. It is found to be directly proportional to the temperature, polymer density, and square of the radius of a sphere and inversely proportional to the mass of a sphere. The self-diffusivity of the particles varies directly with the square root of the temperature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2992–2996, 2009

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INTRODUCTION

Colloidal suspensions are ubiquitous in many engineering technologies. The need to understand their stability and dynamic properties motivates both the development of theory and the experimental techniques required to probe distances on the order of the size of molecules. For colloidal dispersions within polymer solutions, the interaction between macromolecule and colloid particle enriches the complexity of the suspension. In a previous study, Grisafi (1990), the Hookean dumbbell model of a macromolecule indicated that within the interfacial region of a sphere buoyant in a dilute polymer solution, whose size is on the same order of magnitude as that of the macromolecules, the density and pressure fields are non-uniform even at equilibrium.¹ The present study addresses the consequences of this phenomenon upon the equilibrium properties of a colloidal dispersion of spheres in a dilute polymer solution.

Most often in the analysis of diffusion of large spherical particles or molecules within liquids use is made of the Stokes–Einstein equation.² This approach for the prediction of the mass diffusivity of a particle within a liquid makes use of the Nernst–Einstein equation.³ The mobility of the particle required for the use of the Nernst–Einstein equation supposes the creeping flow predictions for Newtonian flow about a hard rigid sphere as pro-

vided by Stokes (1850).⁴ Although the use of the Stokes–Einstein equation is ubiquitous in the analysis of particle diffusion in polymer solutions it is clearly inappropriate for those situations in which there is adsorption of the polymer on to the particles. In such situations, the particles become fuzzy and deformable thereby rendering the use of the creeping flow predictions somewhat questionable. It is important to recognize that the Nernst–Einstein equation predicts a direct linear proportionality between the mass diffusion coefficient and the temperature of the liquid suspension. The present analysis is an attempt to provide more realistic diffusion relations for spherical particles immersed in polymer solutions.

In the previous study, the depletion of polymer within the interfacial region results from the steric hindrance of the configurations available to the macromolecules within the confines adjacent to a sphere. This is a passive interaction between macromolecule and particle without any attraction. A comprehensive development of the phase space kinetic theory for polymers with a square well attraction for a solid boundary can be found in Brunn et al.⁵ One effect of an attractive force is to create an adsorbed layer upon the boundary. Beyond the adsorption layer, the passive wall model suffices. When the size of the colloidal particles is smaller than that of the macromolecules, experimental techniques for probing the interface become few and challenging.

A promising new technique for micro-rheology is afforded by the use of laser tweezers as shown by Meyer et al.⁶ This technique uses a colloidal probe

Correspondence to: S. Grisafi (stevegrisafi@aya.yale.edu).

particle possessing an optical index different from the suspended particles, whose optical index must closely match that of the solvent. Particles of a size on the order of 100 nm can be manipulated using the optical trap of the laser tweezers. By establishing a uniform flow past the probe particle, fluid properties within small distances adjacent to the particles can be examined. Since macromolecules can have a length scale significantly greater than 100 nm, this technique holds great promise for the investigation of colloidal dispersions within dilute polymer solutions.

One useful measure of the micro-structure of colloidal suspensions is the concept of the particles' mean free path as indicated by Stickel et al.⁷ This quantity is of a length scale, which can be probed by the laser tweezers. Since uniform flow is equilibrium flow, the laser tweezers can measure the mean free path of the suspension particles or, what is essentially the same thing, the root mean square (RMS) separation distance of the colloidal particles at equilibrium. The non-uniformity of the polymer density and pressure fields surrounding the colloidal particles determines their RMS separation distance. Hence, the present study uses the results found in Grisafi (1990) to evaluate this distance and other properties of a colloid at equilibrium.¹

The pressure field surrounding a colloidal sphere buoyant in a dilute polymer solution was found to be transversely isotropic. There exist two distinct components to the pressure: one perpendicular to the surface of the sphere and one parallel to the surface. The pressure is the sum of contributions from both the polymer and the solvent. Assuming that the colloidal particles are not so small as to be smaller than the solvent molecules, the contribution to the pressure from the solvent is uniform and can be ignored.

In the analysis that follows a phase space kinetic theory of an ensemble of spheres immersed within a dilute polymer solution, modeled using the results of Grisafi (1990), is used to evaluate the RMS separation distance, and other ensemble averages, for the case in which the size of the colloidal particles is much smaller than that of the polymer.¹ Definitive analytical results are available for this case and no recourse to numerical methods is necessary.

DILUTE POLYMER SOLUTION

Let a be the radius of one of N identical spheres immersed within a dilute polymer solution in which they are neutrally buoyant. Let R_0 be the end-to-end distance of the macromolecules at equilibrium. The polymer density and pressure fields surrounding a sphere are given for all values of the ratio a/R_0 in Grisafi (1990).¹ Let P_{\perp} be the component of the pres-

sure normal to the sphere and P_{\parallel} be the component parallel to its surface. Assume that the radius of a colloidal sphere is much smaller than the end-to-end distance of the polymer molecules, but still larger than the solvent molecules. Each sphere within the suspension experiences the pressure field

$$\mathbf{P} = P_{\perp} \delta_{\perp} \delta_{\perp} + P_{\parallel} (\delta - \delta_{\perp} \delta_{\perp}) \quad (1.1)$$

where δ_{\perp} indicates the unit vector normal to the sphere and δ is the unit tensor.

It is assumed that the pressure fields of the particles do not interact with one another. If r measures distance from the center of a sphere and n_{∞} is the uniform bulk number density of the polymer then, in the limit as the ratio a/R_0 goes to zero, the components of the pressure field become

$$\lim_{a/R_0 \rightarrow 0} P_{\perp} / (n_{\infty} k_B T) = 2 - (1 - a^2/r^2)^{3/2} \quad (1.2)$$

$$\lim_{a/R_0 \rightarrow 0} P_{\parallel} / (n_{\infty} k_B T) = 2 - 1/2(1 - a^2/r^2)^{1/2} \times (2 + a^2/r^2) \quad (1.3)$$

where k_B is Boltzmann's constant and T is the absolute temperature. Here, the solvent's contribution to the total pressure is ignored. At the surface of the sphere, the perpendicular component of the pressure equals the parallel component.

DISPERSION OF SPHERES

The colloidal dispersion is modeled in the phase space of an ensemble of N identical spheres. Let ψ denote the phase space distribution (PSD) function. The conservation of the phase space is maintained by Liouville's equation

$$\partial \psi / \partial t = - \sum_{i=1}^N [\partial / \partial \mathbf{r}_i \cdot \psi \dot{\mathbf{r}}_i + \partial / \partial \dot{\mathbf{r}}_i \cdot \psi \ddot{\mathbf{r}}_i] \quad (2.1)$$

where t represents time and the superscript dots signify differentiation with respect to time. Only the conditions at equilibrium are sought from eq. (2.1), therefore, the partial derivative of the distribution function will be set to zero.

For stationary conditions, the partial differential equation governing ψ can be solved explicitly without resorting to any approximate techniques such as the method of moments. The equation must first be fully defined through use of the peculiar velocity field and Newton's second law of mechanics. The velocity $\dot{\mathbf{r}}_i$ of sphere i is decomposed into two parts

$$\dot{\mathbf{r}}_i = \mathbf{u}(\mathbf{r}_i) + \mathbf{v}_i \quad (2.2)$$

where $\mathbf{u}(\mathbf{r}_i)$ is the bulk flow velocity at the location of the sphere and \mathbf{v}_i is its peculiar velocity. Uniform flow is invariant with respect to a Galilean

transformation, hence, it is equivalent to equilibrium. In this case, the bulk flow has the form

$$\mathbf{u} = u\delta_1 \quad (2.3)$$

where u is a constant and δ_1 represents the unit vector in the flow direction. Hence, without loss of generality, the constant u may be set equal to zero.

The acceleration of any sphere i is found using Newton's second law

$$m\ddot{\mathbf{r}}_i = -4\pi a^2 \mathbf{P} \cdot \delta_{\perp i} \delta_{\perp i} \quad (2.4)$$

where m is the mass of any colloidal sphere and $\delta_{\perp i}$ is the unit vector normal to sphere i . Using the expressions for the velocity and acceleration of the spheres in the governing equation for ψ yields

$$\sum_{i=1}^N \mathbf{v}_i \cdot \partial\psi/\partial\mathbf{r}_i - (4\pi a^2)/m \mathbf{P} \cdot \delta_{\perp i} \cdot \partial\psi/\partial v_i = 0 \quad (2.5)$$

where use has been made of the knowledge that the peculiar velocity is a solenoidal field.

The general solution of eq. (2.5) is to be found using the method of characteristics. Along the characteristics of the differential equation, the momentum of the system is a constant. The characteristics are found to be

$$1/2 m \mathbf{v}_i \cdot \mathbf{v}_i + 4\pi a^2 \int^r d\zeta P_{\perp}(\zeta) = C_i \quad (2.6)$$

where the C_i are constants. Using the expression for P_{\perp} from (1.2) to evaluate the required integration along a characteristic yields

$$\int^r d\zeta P_{\perp}(\zeta) = n_{\infty} k_B T [2r/a + 4a/r(1 - a^2/r^2)^{1/2} (1 - a^2/r^2)] \quad (2.7)$$

The general solution to eq. (2.5) possesses only two distinct integration constants. The solution is

$$\psi = \psi_0 \exp \left(\alpha \sum_{i=1}^N [4\pi a^2 n_{\infty} k_B T [2r_i/a + 4a/r_i(1 - a^2/r_i^2)^{1/2} (1 - a^2/r_i^2)] + 1/2 m \mathbf{v}_i \cdot \mathbf{v}_i \right) \quad (2.8)$$

where ψ_0 and α are the integration constants. The constant α is known from the Maxwellian velocity distribution to be

$$\alpha = -1/(k_B T) \quad (2.9)$$

The constant ψ_0 will be used to normalize the distribution.

To facilitate the calculations contract the PSD function to create the configuration space distribution (CSD) function

$$\phi(\{\mathbf{r}_i\}) = \prod_{i=1}^N \int d^3 \mathbf{v}_i \psi(\{\mathbf{r}_i\}, \{\mathbf{v}_i\}) \quad (2.10)$$

where the braces indicate the set of variables contained within. With this definition, the CSD function becomes

$$\phi = \psi_0 ((2\pi k_B T)/m)^{(3N)/2} \exp \left(- \sum_{i=1}^N 4\pi a^2 n_{\infty} [2 r_i/a + 4a/r_i (1 - a^2/r_i^2)^{1/2} (1 - a^2/r_i^2)] \right) \quad (2.11)$$

Define a normalization constant for the CSD such that

$$\phi_0 = \psi_0 ((2\pi k_B T)/m)^{(3N)/2} \quad (2.12)$$

Then the CSD function becomes

$$\phi = \psi_0 \exp \left(- \sum_{i=1}^N 4\pi a^2 n_{\infty} [2 r_i/a + 4a/r_i (1 - a^2/r_i^2)^{1/2} (1 - a^2/r_i^2)] \right) \quad (2.13)$$

with the normalization

$$\phi_0^{-1} = \prod_{k=1}^N 4\pi \int_0^{\infty} dr_k r_k^2 \exp \left(- \sum_{i=1}^N 4\pi a^2 n_{\infty} [2 r_i/a + 4a/r_i (1 - a^2/r_i^2)^{1/2} (1 - a^2/r_i^2)] \right) \quad (2.14)$$

when using spherical coordinates.

ENSEMBLE AVERAGES

Having completely defined the PSD function it can now be used to evaluate ensemble averages of quantities of interest for the system at equilibrium. As mentioned before, the RMS separation distance is a measurable quantity when using advanced techniques such as the laser tweezers. It is defined as

$$\bar{d} = \langle \langle (\mathbf{r}_j - \mathbf{r}_i) \cdot (\mathbf{r}_j - \mathbf{r}_i) \rangle \rangle^{1/2} \quad (3.1)$$

where the angle brackets indicate the ensemble average operation. Written explicitly it becomes

$$\bar{d} = \left[\phi_0 \sum_{j=1}^N \prod_{k=1}^N 4\pi \int_0^{\infty} dr_k r_k^2 (r_j - r_i)^2 \delta_{ij} (1 - \delta_{ij}) \times \exp \left(-\beta \sum_{i=1}^N 2r_i/a + f(r_i) \right) \right]^{1/(2N)} \quad (3.2)$$

where δ_{ij} is Kronecker's delta. The argument of the exponential function contains two quantities meant to simplify the notation. First, there is the parameter β defined as

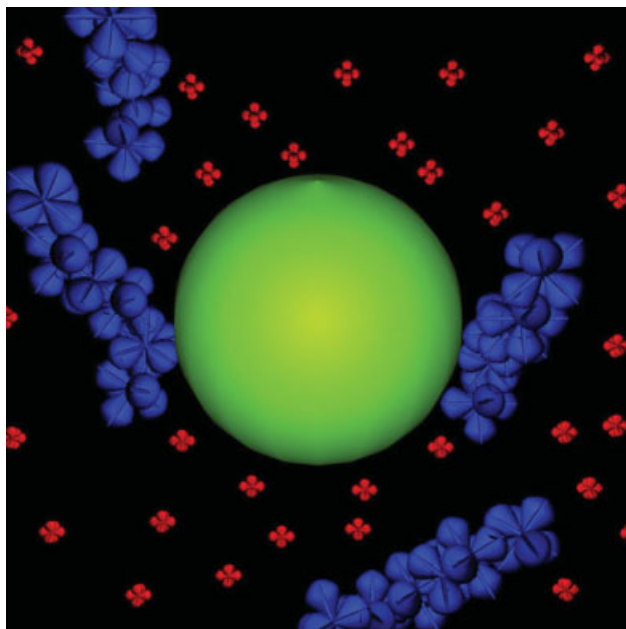


Figure 1 Sphere buoyant in a dilute polymer solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\beta = 4\pi a^2 n_\infty \quad (3.3)$$

Then, there is the function $f(r_i)$, which is defined as

$$f(r_i) = 4a/r_i(1 - a^2/r_i^2)^{1/2}(1 - a^2/r_i^2) \quad (3.4)$$

This function was obtained from the last term on the right side of eq. (2.7).

The required integrations for eq. (3.2) can only be evaluated explicitly for $\beta \ll 1$. This constraint is expected to be met since the polymer solution is dilute and the spheres are much smaller than the macromolecules. Integrating by parts, then retaining only the terms containing β to the highest reciprocal order yields

$$\bar{d} = (\pi 6^{1/2}) / (4a^2 n_\infty) \quad (3.5)$$

This is the average distance one would expect to find between pairs of spheres when the colloid is at equilibrium. For the same condition of $\beta \ll 1$, the CSD normalization constant of eq. (2.14) is found to be

$$\phi_0 = \pi^{2N} (4a^2 n_\infty)^{3N} \quad (3.6)$$

which normalizes the PSD as a probability distribution.

Two other ensemble averages are of interest. The first the author calls the peculiar acceleration, f . It is defined analogously to the centripetal acceleration experienced by a particle in steady rotational motion. This ensemble average is expected to reproduce the magnitude of the average fluctuation changes in the peculiar velocity due to changes in direction. Its definition is

$$f = \langle v^2 / r \rangle \quad (3.7)$$

Evaluating the ensemble average yields

$$f = 8\pi (k_B T) / m a^2 n_\infty \quad (3.8)$$

Last, another ensemble average which is of interest possesses the units of a diffusivity. This could only be interpreted as a mass diffusivity, and not a kinematic viscosity, because the definition of viscosity restricts its use to non-equilibrium situations. The interpretation as a mass diffusivity must also be restricted to that of a self-diffusivity. This is the case in which the erratic path of a particle, identical to all others, but, in some way tagged to make it observable, is traced. The definition of this diffusivity is

$$\mathfrak{D} = (\langle r^2 \overline{v^2} \rangle)^{1/2} \quad (3.9)$$

This quantity evaluates to

$$\mathfrak{D} = \pi / (4a^2 n_\infty) [(6k_B T) / m]^{1/2} \quad (3.10)$$

Notice that the self-diffusivity is directly proportional to the square root of the temperature.

CONCLUSIONS

The RMS separation distance of the particles in suspension is found to be inversely proportional to the concentration of the polymer solution. This prediction is consistent with intuition since one would expect that the more macromolecules there are in solution the closer they will push the colloidal spheres toward one another. The theory also predicts that the RMS separation distance is inversely proportional to the square of the radius of the colloid particles. Thus, the smaller the colloid particles are the greater is their distance from one another. This too is consistent with intuition.

The present study provides predictions for two quantities that are expected to be difficult to distinguish from one another experimentally. The peculiar acceleration is a measure of the collisions undertaken by the particles while the self-diffusivity is a measure of the random walk experienced by the particles. The magnitude of the peculiar acceleration is found to vary in direct linear proportion to changes in temperature. This is identical to the assumption of the Nernst-Einstein equation. However, the diffusivity is found to vary in direct proportion to the square root of the temperature. Intuition provides no insight into why the diffusivity would vary with the square root while the peculiar acceleration varies directly proportional. What is important here is the distinction between the self-diffusivity and the peculiar acceleration. Until now, the peculiar acceleration was an unknown quantity

indistinguishable from the diffusivity. Yet, clearly, there is a distinction between the progression of a random walk and the incidence of collisions. The dependence of the self-diffusivity proportional to the square root of the temperature suggests that a particle requires higher temperatures for an equal progression of a random walk in a polymer solution than for a random walk in a Newtonian solvent. Yet the incidence of collisions for the particle in a polymer solution would have the same linear proportionality with temperature predicted for the diffusivity of the particle in a Newtonian solvent. Thus, it is reasonable to expect that the measurement of mass diffusion coefficients for particles suspended in polymer solutions would be dependent upon the experimental technique.

The deformability of particles with a fuzzy adsorbed polymer layer may cause the temperature dependence of the self-diffusivity to vary neither linearly proportional to the temperature or to vary monotonically with the square root of the temperature. In such cases one might expect local maxima and minima superimposed upon a variation with the square root of the temperature as increasing temperatures cause varying degrees of deformability. When a certain temperature is reached such that no further deformation of the adsorbed polymer layer can occur then one might expect the monotonic variation of the self-diffusivity with increasing temperature to resume.

Interestingly, the theory predicts no dependence of the RMS separation distance upon the temperature of the colloid. The lack of any dependence of the separation distance upon the temperature seems plausible since it is the pressure field, which creates a structure in mechanical equilibrium that determines this distance. The effect of the temperature appears to cancel in the limit where the size of the polymer is much greater than that of the colloidal particles. Perhaps, if there were to be interaction between the pressure fields of individual particles, this prediction might be modified.

While the RMS separation distance depends only upon the size of the colloidal particles and the polymer density, the diffusivity and peculiar acceleration depend also upon the mass of the particles as well as the temperature. The peculiar acceleration is inversely proportional to the mass; while the diffusivity varies inversely with the square root of the mass. Another interesting aspect to the predictions is that the diffusivity varies in a manner similar to that of the RMS separation distance with respect to both the polymer density and the size of the colloidal particles. Yet, the dependence of the peculiar acceleration upon these quantities is inverse to both that of the diffusivity and the RMS separation distance. The peculiar acceleration is enhanced by increases in polymer concentration, but the diffusivity is decreased. They also respond in this same manner to changes in the size of the colloidal particles.

Detection of the variation of colloidal particle separation distances in response to changes in polymer solution concentration ought to be accessible to experimental techniques such as the laser tweezers. Comparison of observation with prediction will help determine the pertinent quantities active in the interfacial regions of colloids. Such knowledge will then enhance our understanding to the stability of colloids. Figure 1 presents an artist's depiction of a nanometer sphere buoyant in a dilute polymer solution.

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