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J. B. Sokoloff

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Compression and lubrication of salt free polyelectrolyte microgel particles in highly compressed suspensions by counterion osmotic pressure

J. B. Sokoloff

Department of Physics and Center for Interdisciplinary Research on Complex Systems,
 Northeastern University, Boston, Massachusetts 02115, USA

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The compression of polyelectrolyte microgel particles in a salt-free highly compressed colloid due to osmotic pressure outside of the particles due to counterions located there is studied for a model based on a quasi-analytic solution of the Poisson-Boltzmann equation and a model for the gel elasticity based on counterion osmotic pressure inside the particles and polymer elasticity (of entropic origin). It is found that for particles of radius of the order of a tenth of a micron, the counterion osmotic pressure should play a significant role in the compression of the particles, especially particles which do not have a corona (i.e., nonlinked polymer chains attached to their surface). The presence of a corona of monomer density smaller than that of the core of the microgel reduces the contribution of the osmotic pressure due to counterions outside of the microgel. It is also demonstrated that counterion osmotic pressure outside the particles can provide a significant contribution to the lubrication of the interface between the particles and a surface along which the compressed colloid is made to slide, for sufficiently slow velocities. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922325>]

I. INTRODUCTION

Borrega *et al.*¹ found that polyelectrolyte microgel colloid suspensions in a salt-free solution exhibit a much more gradual dependence of viscosity on volume fraction than hard sphere suspensions, if the radius of one of the microgel particles in the suspension, when swollen with fluid, is of the order of 100 nm, even for volume fractions comparable to one. They attributed this behavior to the softness of the microgel particles, which allows them to shrink in size, by expelling fluid, as they are packed together. They attributed the compression of the particles at high volume fraction to osmotic pressure due to counterions residing outside of the particles. They presented estimates of the degree of swelling of the microgel particles as a function of the fraction of counterions residing outside of the gel particles. The fraction of counterions lying outside to the particles was determined using a screening length for screening of the electrostatic interaction between the microgel particles that appear in a theory for the interaction between microgel particles based on the random phase approximation,³ an approximation commonly used in many body theory of electrons in metals to treat the screening of the electrostatic interaction between the electrons. This approximation is based on lowest order perturbation theory in the interaction potential. Romeo *et al.*² have shown by light scattering experiments and numerical estimates that for salt free suspensions of micron size polyelectrolyte microgels, the particles also compress at high volume fraction, but the compression can be accounted for by steric interaction alone. Their numerical estimates based on Denton's theory³ show that this is to be expected because the fraction of the counterions found outside the microgel particles is very small. In Refs. 4 and 5, it was shown that when two polyelectrolyte hydrogels with flat surfaces in a salt-free solution are pressed together, they tend to maintain a thin

fluid layer between them, as a result of osmotic pressure due to counterions that have diffused into the interface between the two gels. This result is based on a quasi-analytic solution of the Poisson-Boltzmann equation and a model for the elastic behavior of polyelectrolyte brushes due to Pincus.⁶ In Secs. II and III, this result will be applied to the microgel particles of Refs. 1 and 2. A discussion about the role played by counterion osmotic pressure on the lubrication of microgel colloid flow will be given in Sec. IV.

II. CALCULATION OF VERSUS FOR MICROGELS WITHOUT A CORONA

The role of osmotic pressure due to counterions outside of the microgels on their compression as the microgels in a colloid of microgels are pressed against each other is explored. Here, a model for the role of counterions on the compression of the gels will be explored in order to determine the conditions under which effects of counterions are important.

If we treat the microgels as spheres, when their concentration reaches the point at which the volume available to each microgel, n_g^{-1} , where n_g is the number of microgel particles per unit volume, is comparable to v_0 , the volume of a single microgel when fully swollen in the dilute solution limit, the gels will no longer be spherical. Rather, they might take on the shape of a spherical figure with randomly placed flat surfaces on which the microgel is in contact with other microgels. Assuming that the particles have a reasonably narrow distribution in sizes, however, it is reasonable to assume that the cells formed by the planes of contact of a particle with its neighbors (which are in contact with it) will have a volume comparable to the volume of a regular rhombic dodecahedron (the volume of a Wigner-Seitz unit cell of a face centered cubic lattice, which is a periodic close packed lattice of particles

which are compressed together). While there can be some fairly flat low volume cells in this distribution, most of the cells should have a volume comparable to that of the regular dodecahedron unit cell, whose volume is equal to the total volume of the colloid divided by the number of particles. Still, to be accurate, this is probably an upper boundary on the volume per particle. The volume fraction is defined as the ratio of the volume of a swollen particle to the volume available per particles, which in this approximation is the volume of a rhombic dodecahedron. The dodecahedron volume is shown in a problem in Ashcroft and Mermins solid state physics book to be $3(2)^{1/2}/\pi = 1.35$ times the volume of a sphere inscribed in the dodecahedron, which is comparable to the volume of one of the particles when it is compressed. There is no point in obtaining a more accurate value for the volume fraction when the experimental data are analyzed by modeling the compressed particles by spheres,² when they are actually flattened at the places in which they are in contact with neighboring particles. In Ref. 5, it is shown that when two hydrogels with flat surfaces in a salt-free solution are pressed together, the thickness of the thin interface region can be determined by solving the Poisson-Boltzmann equation for a salt-free solution,

$$\frac{d^2\phi(z)}{dz^2} = 2k_0^2 e^{\phi(z)} + K_0^2 [\theta(-z - \Delta\ell) + \theta(z - \Delta\ell)], \quad (1)$$

where $\phi(z) = \ell_B \psi(z)/e^2$, where $\psi(z)$ is the electrostatic potential, a distance z from the center of the interface, $\ell_B = e^2/\epsilon k_B T$ (where e is the electron charge, ϵ is the dielectric constant of water, and $k_B T$ is the product of Boltzmann's constant, the temperature) is the Bjerrum length, $k_0^2 = 2\pi\ell_B n_0$, where n_0 is the counterion concentration at the midpoint of the interface between two gels in contact and $K_0^2 = 4\pi\ell_B n_f$ where n_f is the number of electronic fixed charges per unit volume inside of a microgel. Equation (1) can be partially integrated by multiplying the equation by $d\phi/dz$ and integrating to yield the equation⁵

$$2k_0(z + \Delta\ell) = \int_{\phi(-\Delta\ell)}^{\phi(z)} \frac{d\phi}{[e^{-\phi} - 1 + r(\phi - \phi(-\Delta\ell))]^{1/2}}, \quad (2)$$

where $r = n_f/n_0$. It is shown in Ref. 5 that when $KH \gg 1$, where H is the gel thickness, the solution of the Poisson-Boltzmann equation can be found to a good approximation by determining the values of the parameters for which the plots of the functions $e^{-\phi} - 1$ and $r(\phi(-\Delta\ell) - \phi)$ versus ϕ are nearly tangent to each other at the point where $\phi = \phi(-D/2)$, where $z = -D/2$ is the location of the surface of the lower gel opposite the interface. Then, equating these two functions (which is shown in Ref. 5 to be the condition for charge neutrality) and their derivatives (the condition for their being tangent to each other) at $\phi = \phi(-D/2)$, we obtain

$$e^{-\phi(-D/2)} = r, \quad (3a)$$

$$r(\phi(-\Delta\ell) - \phi(-D/2)) = e^{-\phi(-D/2)} - 1, \quad (3b)$$

whose solution is

$$\phi(-\Delta\ell) = 2\ln[\cos(k_0\Delta\ell)] = \frac{r-1}{r} - \ln(r). \quad (4)$$

The solution for $\Delta\ell$ is

$$\cos(k_0\Delta\ell) = \frac{1}{r^{1/2}} \exp\left[\frac{1}{2}\left(1 - \frac{1}{r}\right)\right], \quad (5)$$

$$\Delta\ell = k_0^{-1} \arccos[r^{-1/2} \exp((1 - r^{-1})/2)], \quad (6a)$$

where $r = n_f/n_0$, $k_0 = (2\pi\ell_B n_0)^{1/2}$. Since the thickness of the interface is much greater than the width of a facet, we expect that the small $\Delta\ell$ limit of Eq. (6a) should give a reasonably good approximation for $\Delta\ell$. In the limit of $k_0\Delta\ell \ll 1$, Eq. (6a) reduces to

$$2^{1/2} k_0 \Delta\ell = r - 1. \quad (6b)$$

Using as a model for a polyelectrolyte hydrogel, a mechanism used by Pincus to model the stiffness of polyelectrolyte polymer brushes,⁶ it was shown that the pressure that results when such a gel is compressed is given by⁵

$$k_B T (n_f - n_{f0}^2/n_f). \quad (7)$$

This expression was derived in Ref. 5 assuming a hydrogel with a flat surface. It is correct to use this expression in this problem in the highly compressed gel limit because in the limit in which $\Delta\ell$ is much smaller than the width of the facet, it should be valid right under the facet, provided that n_f and n_{f0} represent their values just under a facet. Setting this expression equal to the net force acting across the interface, which is equal to counterion osmotic pressure at the center of the interface region $k_B T n_0$ plus the van der Waals attraction per unit area acting across the interface $-A_H/(6\pi\Delta\ell^3)$, where A_H is the Hamaker constant, we obtain

$$r^{-1} = 1 - (n_{f0}/n_f)^2 + A_H/(6\pi n_f \Delta\ell^3). \quad (8)$$

As we shall see in Sec. IV, because the Hamaker constant for two hydrogels is very small (i.e., about 10^{-23} J), the effects of the van der Waals interaction are very small, until $\Delta\ell$ is quite small. Therefore, let us first neglect the van der Waals attraction, with the understanding that the results that we will obtain will not be valid below a value of $\Delta\ell$ of the order of a nanometer, as we shall see in Sec. IV. If we write $k_0 = r^{-1/2}(n_f/n_{f0})^{1/2} k_{f0}$, where $k_{f0} = (2\pi\ell_B n_{f0})^{1/2}$, Eq. (6b) can be written as

$$k_{f0} \Delta\ell = 2^{-1/2} (n_{f0}/n_f)^{1/2} (r^{3/2} - r^{1/2}). \quad (9)$$

If we take n_f and n_{f0} to represent average values of these quantities over the particle (instead of their values near a facet, as assumed above), Eq. (7) is not valid because the polymer elasticity term in Eq. (7) (the second term) is only valid if the compression of the gel only occurs below a single facet. Since the particle is also compressed well below each facet, however, the compression closer to the center of the particle, and away from any of the individual facets, will be better described by a compression that is spherically symmetric about the center of the particle, which would be better described by an expression for compression of the gel similar to the one proposed by Flory to describe swelling of a hydrogel.⁷ This is discussed in the Appendix, where an approximate expression midway between the expression in Eq. (2) and a Flory-like expression is proposed. The expression for the elasticity proposed in the Appendix is Eq. (A8),

$$k_B T n_{f0}^{2/(1+\alpha)} n_f^{(2\alpha-1)/(1+2\alpha)},$$

where α is a parameter whose value lies between 0 and 1. If it is 0, this expression reduces to the one for the elasticity in Eq. (7), and if it is 1, it reduces to the Flory expression. Since

$$\Delta\ell = 2^{-1/2} k_{f0}^{-1/2} (n_{f0}/n_f)^{1/2} [(1 - n_{f0}^{2/(1+2\alpha)} / n_f^{2/(1+2\alpha)})^{-3/2} - (1 - n_{f0}^{2/(1+2\alpha)} / n_f^{2/(1+2\alpha)})^{-1/2}], \quad (10)$$

using Eq. (A11) to substitute for r . The volume per microgel when the microgels are compressed, including the water surrounding it, which is the average volume of the dodecahedra defined earlier, representing the volume available per compressed particle, is then given approximately by

$$4 \cdot 2^{1/2} (R_i + \Delta\ell)^3 \approx 4 \cdot 2^{1/2} [R_i^3 + 4\pi R_i^2 \Delta\ell], \quad (11)$$

where R_i is the mean perpendicular distance from the center of the compressed microgel to one of its facets. Although a compressed particle is no longer spherical, let us define an average radius for it is denoted by R by setting $(4\pi/3)R^3$ equal to the volume available per particle. (We will choose to calculate $R/R_0 = (n_{f0}/n_f)^{1/3}$, rather than n_{f0}/n_f because Ref. 2 presents its data in terms of a particle radius, rather than a density, even though the highly compressed particles are not spherical.)

most of the polymers in the particle are closer to the center than to one of the facets, we will use that expression with $\alpha = 2/3$ in the calculations performed in this section, which should give reasonable estimate of the quantities that will be calculated. With this assumption, Eq. (9) becomes

Then, $n_f = N_f / [(4\pi/3)R^3]$, where N_f is the number of monomers per particle. It is easily shown that since the volume available per particle is equal to the volume of one dodecahedron, $4 \cdot 2^{1/2} R_i^3$ that $R_i = \gamma R$, where $\gamma = 2^{-1/6}(\pi/3)^{1/3} = 0.904$.⁸ At this point R can be taken to represent the core of the microgel, and we will assume that the polymers sticking out of the microgel surface have been completely compressed, or alternatively, we can take R to represent a mean radius. Then, the ratio of the volume of a swollen microgel v_0 to the volume available to each microgel n_g^{-1} is given by

$$\xi = n_g v_0 = \frac{(4\pi/3)R_0^3}{4 \cdot 2^{1/2} [R_i^3 + 4\pi R_i^2 \Delta\ell]}, \quad (12)$$

where R_0 is the radius of the swollen microgel, and hence, from Eqs. (8)–(12), we obtain

$$\xi = [\gamma^3 \bar{r} + (3/2^{1/2}) \gamma^2 (k_{f0} R_0)^{-1} \bar{r}^{7/6} ((1 - \bar{r}^{2/(1+2\alpha)})^{-3/2} - (1 - \bar{r}^{2/(1+2\alpha)})^{-1/2})]^{-1}, \quad (13)$$

where $\bar{r} = \bar{n}_{f0}/n_f = R^3/R_0^3$. Using Eq. (13) and the numerical values of the various parameters given in the paper by Romeo, *et al.*,² we plot R/R_0 vs. ξ in the middle curve in Fig. 1. The upper curve is a plot of $\xi^{-1/3}$, which is what one would get if the compression due to counterions outside the microgels was neglected. The reason that the dependence of R/R_0 on ξ is reasonably well approximated by what one would get if there were no counterions outside the microgels might be because $k_{f0} R_0 = 109$, since $k_{f0} = (2\pi\ell_B n_{f0})^{1/2} = 13.6 \times 10^7 \text{ m}^{-1}$, with $\ell_B = 7.1 \times 10^{-10} \text{ m}$ and $n_{f0} = N_f / (4\pi R_0^3/3) = 4.12 \times 10^{24} \text{ m}^{-3}$ and $R_0 = 8 \times 10^{-7} \text{ m}$.² We can see that in order to make the effects of counterions more observable, it is necessary to study microgels in which n_{f0} is smaller, or to do the experiment on microgels of smaller radius. For example, Borrega *et al.*, use gels with a swollen gel radius of the order of $2.2 \times 10^{-7} \text{ m}$, so that $k_{f0} R_0 = 29.7$, assuming that the microgels discussed in Ref. 1 have the same value of n_{f0} as those discussed in Ref. 2. We repeated the above plot for this radius and obtained the result shown in the lowest curve in Fig. 1. By comparing the lower two curves in Fig. 1, we see that in both curves, the compression of the particles occurs before ξ is larger than one, but it is more pronounced for the smaller microgel particles of Ref. 1.

III. CALCULATION OF R_0/R VERSUS ξ WITH A CORONA ON THE MICROGELS

We now assume that each microgel has a swollen and unswollen core of radii R_0 and R , respectively. The cores of the microgels are also assumed to be surrounded by a swollen microgel corona of thickness q_0 and an unswollen microgel corona of thickness q made up of polymers attached at one end to the core, which are not linked to each other, respectively, and that $q_0 \ll R_0$ and $q \ll R$, respectively. Then, the volume of these coronas can be approximated by $4\pi R_0^2 q_0$ and $4\pi R^2 q$, respectively. Let N_f and N'_f represent the number of counterions inside the core and corona, respectively, and therefore, the unswollen gel number density of counterions in the core is given by $n_f = N_f / (4\pi R^3/3)$ and the number density of counterions inside the corona is given by $n'_f = N'_f / (4\pi R^2 q)$. The swollen gel counterion number densities for the core and corona are n_{f0} and n'_{f0} , respectively. From Refs. 4–6, we know that compressional stress of both the corona and core given respectively by

$$k_B T (n'_f - n_{f0}^2/n'_f) \quad (14)$$

and Eq. (14) with the second term replaced by Eq. (A8) (treating the corona as a polyelectrolyte polymer brush) must

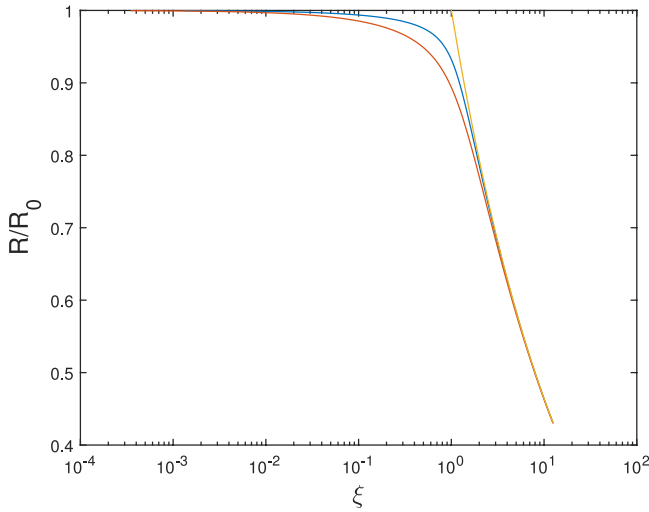


FIG. 1. The lowest curve is a plot of R/R_0 versus ξ for $k_{f0}R_0 = 29.9$. The middle curve is a plot of R/R_0 versus ξ for $k_{f0}R_0 = 109$. The upper curve is a plot of $R_0/R = \xi^{-1/3}$, which is what one would get if the compression due to counterions outside the microgels was neglected.

both be equal to the counterion osmotic pressure just outside the corona, $k_B T n_0$, in equilibrium. The expression for the elasticity given in Eq. (7) is valid for the corona because all of the polymers in the corona lie right near a facet. Then, setting these two expressions for the compressional strain equal to each other, we obtain

$$n'_f(1 - n_{f0}^2/n_f^2) = n_f[1 - (n_{f0}/n_f)^{2/(1+2\alpha)}]. \quad (15)$$

Using the above expressions for n'_f and n_f , Eq. (15) becomes

$$[N'_f/(3R^2q')](1 - q'^2R^4/q_0^2R_0^4) = (N_f/R^3)[1 - (R/R_0)^{6/(1+2\alpha)}], \quad (16)$$

where q' is chosen so that

$$4(2^{1/2})[(R_i + q)^3 - R_i^3] \approx 12(2^{1/2})R_i^2q \\ = (4\pi/3)[(R + q')^3 - R^3] \approx 4\pi R^2q',$$

where the left hand side is the difference between the total dodecahedron volume, including the corona, and the dodecahedron volume of the core, which gives $q = \gamma q' = 0.904q'$.

That is, q' is chosen so that $(4\pi/3)(R + q')^3$ is the total volume inside a particle and its corona. Setting $\bar{r} = (R/R_0)^3$ and $\delta = N_f/N'_f$, Eq. (16) becomes

$$1 - (q'^2/q_0^2)\bar{r}^{4/3} = 3(q'/R)\delta(1 - \bar{r}^{2/(1+2\alpha)}) \quad (17)$$

whose solution for q'/q_0 is

$$q'/q_0 = [(3\delta\gamma/2\bar{r}^{5/3})^2(q_0/R_0)^2(1 - \bar{r}^{2/(1+2\alpha)})^2 + \bar{r}^{-4/3}]^{1/2} \\ - (3\delta\gamma/2\bar{r}^{5/3})(q_0/R_0)(1 - \bar{r}^{2/(1+2\alpha)}). \quad (18)$$

Using Eq. (6b), we find that

$$2^{1/2}k_0\Delta\ell = 2^{1/2}r^{-1/2}(n'_f/n'_{f0})^{1/2}k_{f0}\Delta\ell = r - 1, \quad (19)$$

where in this case, r is given by Eq. (8) with n_f and n_{f0} replaced by n'_f and n'_{f0} defined above Eq. (14). Then, using Eqs. (17)–(19), we find that ξ , the ratio of the volume of an swollen microgel to the volume of the fluid available to it is, to a reasonable approximation,

$$\xi = \frac{(4\pi/3)(R_0 + q_0)^3}{(4)(2^{1/2})[(\gamma R + q)^3 + 4\pi(\gamma R + q)\Delta\ell]}, \quad (20)$$

which can be written as

$$\xi = \frac{(1 + Q_0)^3}{(\gamma\bar{r}^{1/3} + Q_0/Q')^3 + 3(\gamma\bar{r}^{1/3} + Q_0/Q')^2\Delta\ell/R_0}, \quad (21)$$

where $Q' = q_0/q$ and $Q_0 = q_0/R_0$. Equation (21) relates \bar{r} to ξ . The left hand graph in Fig. 2 shows plots made using Eq. (21) of $R/R_0 = \bar{r}^{1/3}$ versus ξ for $\delta = 10$, $Q_0 = 0.1$, corresponding to $n'_{f0}/n_{f0} = (3Q_0\delta)^{-1} = 1/3$, for $k_{f0}R_0 = 29.9$ and $k_{f0}R_0 = 109$. The right hand graph shows the same plots with δ changed from the value 10 to the value 30, which corresponds the ratio $n'_{f0}/n_{f0} = (3Q_0\delta)^{-1} = 1/9$. A plot of $(R + q)/(R_0 + q_0)$, the ratio of the total microgel radii (i.e., including the width of the corona) is identical to the plot of R/R_0 shown in Fig. 2. Comparing this figure to Fig. 1, we see that the presence of the corona reduces the compression of the microgel for $\xi < 1$ because it reduces $\Delta\ell$ for a given compression of the gel, because the corona is more easily compressed than the core of the microgel particle because of its lower density. The fact that the right hand graph in Fig. 2, which was made with a lower monomer density than the left hand plot, shows a greater

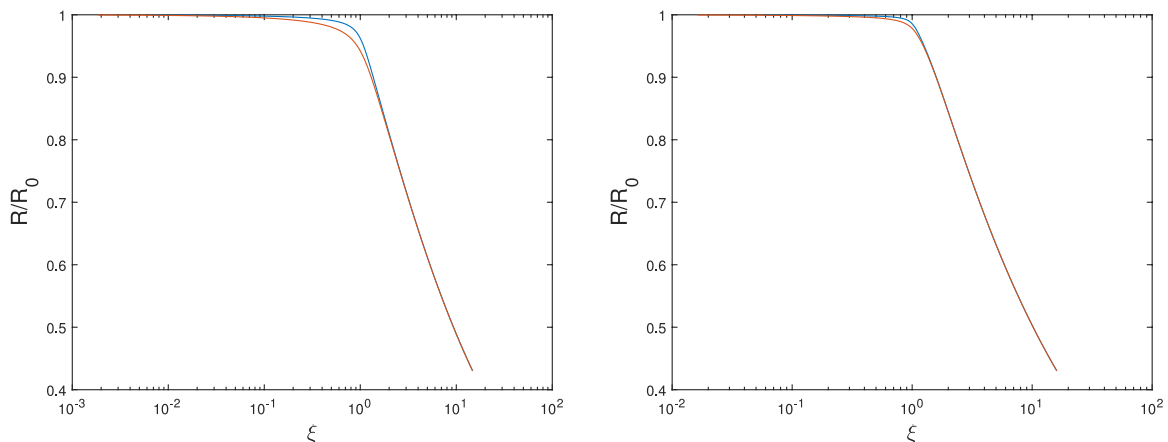


FIG. 2. The figure on the left shows plots made using Eq. (16) of $R/R_0 = \bar{r}$ versus ξ for $\delta = 10$ and $Q_0 = 0.1$. The lower curve is for $k_{f0}R_0 = 29.9$ and the upper curve is for $k_{f0}R_0 = 109$. The figure on the right shows the same plots for $\delta = 30$ and $Q_0 = 0.1$.

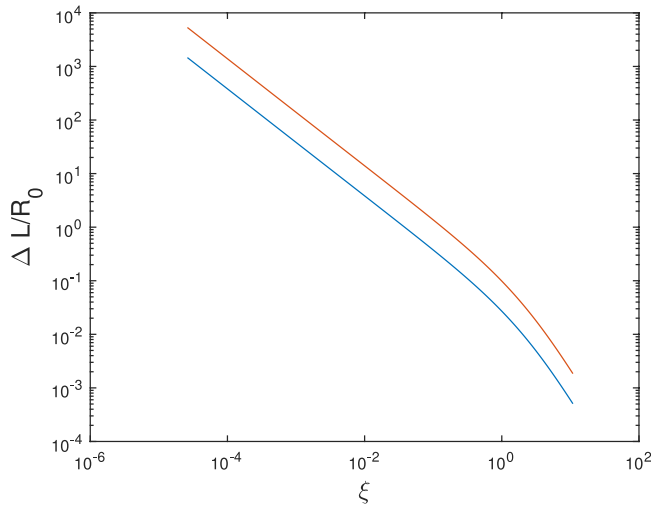


FIG. 3. The above figures are plots made using Eq. (16) of $\Delta\ell$ versus ξ with $\delta = 10$, $Q_0 = 0.1$. The upper curve is for $k_{f0}R_0 = 29.9$ and the lower curve is for $k_{f0}R_0 = 109$.

reduction of the compression of the microgel for $\xi < 1$ is consistent with this conclusion. As a consequence, the plot of R/R_0 looks more like the results of Ref. 2, in which the plot of R/R_0 looks like the behavior that we would expect if there was no counterion osmotic pressure outside of the microgel particles. In Fig. 3, a log-log plot of $\Delta\ell$ versus ξ is shown for both $k_{f0}R_0 = 29$ and 109.

IV. EFFECTS OF COUNTERION OSMOTIC PRESSURE ON MICROGEL COLLOID FRICTION

In Ref. 1, it was found that polyelectrolyte microgel colloids in salt free solution exhibit a much more gradual dependence of viscosity on volume fraction than hard sphere suspensions, which the authors attribute to effects of counterions outside of the particles. Although in order to try to understand this, the theoretical problem that should be studied is the shearing of colloid glasses; let us first consider the simpler problem of the friction that occurs when such colloid glasses are forced to move parallel to a smooth surface.⁹ In the latter paper, the experimental results are interpreted in terms of elasto-hydrodynamic lubrication theory in which a liquid lubricating film is maintained at the interface between a microgel particle and the surface with respect to which the particle is sliding by hydrodynamic forces. The thickness of that layer is found from a scaling treatment of the Navier-Stokes equation, applied to the geometry of this problem (essentially the standard treatment of elasto-hydrodynamic lubrication¹¹). The thickness of that lubricating layer is found to be of the order of $(\eta_s VR/G_p)^{1/2}$, where η_s is the viscosity of water, V is the sliding velocity, R , is the radius of the particle, and G_p is Young's modulus of the particle, and the resulting frictional stress is found to be of the order of

$$(\eta_s V/R)^{1/2} (G_0^4/G_p)^{1/6}, \quad (22)$$

where G_0 is the shear modulus of the particle. Substituting $\eta_s = 0.001$ Pa s, $V = 0.2 \times 10^{-3}$ m/s, $R = 2.2 \times 10^{-7}$ m, and $G_p = 10^4$, the values given in Ref. 9, we obtain for the frictional

stress of the particle 11.1 Pa. On the other hand, in Ref. 5, it was proposed that even at zero sliding velocity, a lubricating film can be maintained at the interface by counterion osmotic pressure. As can be seen in Figs. 2 and 3, once R is compressed to about $0.5R_0$, $\Delta\ell/R_0$ is reduced to about 10^{-2} , which in the experiments in Ref. 9 corresponds to $\Delta\ell \approx 2$ nm, but the water will be sheared over a penetration distance into the gel of the order of the mesh size, which could be about 50 nm.⁵ Then, on the basis of this picture, the frictional stress will be given by

$$\eta_s V/d, \quad (23)$$

where $d \approx 50$ nm is the distance over which the film is sheared, which gives a shear stress of 3.99 Pa, for the above value for V , indicating that the elasto-hydrodynamic lubrication mechanism dominates for this sliding speed. (Actually, if the frictional stress is defined as the friction force divided by R^2 , as was done in Ref. 9, it will be a tenth of this value or 0.4 Pa.) Therefore, it appears that if the mechanism that of Ref. 5 for polyelectrolyte microgels operates, at much slower sliding speeds, the frictional stress should switch from the square root dependence on velocity of the elasto-hydrodynamic mechanism to a linear dependence at slower sliding velocities, which was reported in a latter paper.¹⁰ Another question that we might ask is why is the liquid in the lubricating liquid film between the microgel particles and the wall does not appear to be sheared over a penetration distance comparable to the gel mesh size into the microgels as predicted in Ref. 5, which could make the frictional stress considerably smaller than the estimates in Meeker, *et al.*, which assume that it is sheared only over the thickness of the lubricating layer. One possibility is that the microgel particles are pressed against each other with sufficient force to cause them to expel some of the liquid with which they are swollen. For example, the mesh size in the direction perpendicular to the microgel surface would then be reduced to about 12.5% of its swollen gel value for $R_0/R = 2$, since $n_f/n_{f0} = (R_0/R)^3 = 8$; this would reduce d in Eq. (23) to 3.5 nm, which increases the frictional stress given by Eq. (23) to 5.7 Pa.

In Ref. 10, a more detailed theoretical treatment of the friction acting on microgel colloids when they slide relative to their confining walls is given, which includes in addition to elasto-hydrodynamic forces, van der Waals forces, forces due to ion osmotic pressure, and steric interactions. Using the usual method of determining the Hamaker constant for the van der Waals force acting between two solids separated by a third medium (in this case a liquid), the effective Hamaker constant for the van der Waals interaction between a microgel particle and a solid surface is given by¹³

$$A = [(A_{mm})^{1/2} - (A_{ww})^{1/2}][(A_{ss})^{1/2} - (A_{ww})^{1/2}], \quad (24)$$

where A_{mm} is the Hamaker constant for the interaction of two microgel particles, A_{ss} is for two solids that the walls are made from, and A_{ww} is the Hamaker constant for water. For $A_{mm} = 3.78 \times 10^{-20}$ J, $A_{ss} = 6 \times 10^{-20}$ J, and $A_{ww} = 3.73 \times 10^{-20}$ J, we obtain from Eq. (24), $A = 6.68 \times 10^{-23}$ J. With this Hamaker constant, we obtain for the van der Waals force per unit area for a spacing of the microgel particle's surface from a wall of $d = 2$ nm of

$$-\frac{A}{6\pi d^3} = 4.43 \times 10^2 \text{ Pa}. \quad (25)$$

The osmotic pressure due to counterions residing outside the microgel particle is given by $k_B T n_0$. For the wall-gel interface, n_0 is the counterion density at the wall.¹² The largest value of n_0 is the value at which all fluids are expelled from a hydrogel. It is⁵ $n_f = n_{f0}(R_0/R)^3 = 3.30 \times 10^{25} \text{ m}^{-3}$ for $R_0/R = 2$ given above and $n_{f0} = 4.12 \times 10^{24} \text{ m}^{-3}$. Then, the resulting counterion osmotic pressure is $1.32 \times 10^5 \text{ Pa}$, which dominates over the van der Waals force for this value of R_0/R . For $R_0/R = 2.5$, however, the van der Waals force already dominates over the counterion osmotic pressure.

Let us now study the relative effects of counterion osmotic pressure and van der Waals interaction between a microgel and a wall in more detail. We will follow the treatment of this problem in Ref. 12. When we have both counterion osmotic pressure and van der Waals interaction, the net repulsive or attractive force per unit area acting across the interface is

$$P = k_B T n_0 - \frac{A_H}{6\pi\Delta\ell^3}, \quad (26)$$

which can be written in dimensionless variables as

$$\bar{P} = \frac{P}{k_B T n_{f0}} = (\bar{r}r)^{-1} - \frac{A}{y^3}, \quad (27)$$

where $\bar{r} = (1 - r^{-1})^{7/6}$ from its definition under Eq. (13) and from Eq. (A11) with $\alpha = 2/3$, $A = A_H k_{f0}^2 / (6\pi k_B T n_{f0})$, and $y = k_{f0} \Delta\ell$. (The factor \bar{r} in the first term on the right hand side of Eq. (27) is a modification of the treatment in Ref. 12.) A plot of both Eq. (27) and the first term on the right hand side of Eq. (27) (i.e., the osmotic pressure alone), using the values of A_H and n_{f0} given above, is shown in Fig. 4. From the plot of the right hand side of Eq. (27) in Fig. 4, we can determine that the maximum value of $P = 2.5 k_B T n_{f0} = 4.82 \times 10^4 \text{ Pa}$, which occurs at $\Delta\ell = 0.661 \text{ nm}$. For y larger than 0.2, which is for the above value of n_{f0} corresponds to $\Delta\ell = 1.47 \text{ nm}$, the van der Waals interaction has a negligible effect.

Let us now consider possible effects of surface roughness of both the microgel and the wall surface on the relative dominance of counterion osmotic pressure and the van der Waals force acting between a microgel particle and a surface

with which it is in contact. Any surface will have hills or asperities, and on the interface between each pair of asperities belonging to the two surfaces in contact, we expect there to be smaller asperities in contact. This process should continue for self-affine surfaces as we look on smaller and smaller length scales, until we get to the smallest length scale in the problem, which in this case is the gel mesh size.^{5,12} On the smallest length scale asperities in contact, the normal stress can potentially be quite large, because these smallest length scale asperities must provide all of the normal load that acts between the two surfaces. Once the normal stress on a pair of smallest length scale asperities in contact exceeds the maximum value of P given by Eq. (27), the thickness of the interface liquid layer $\Delta\ell$ separating these two asperities in contact will decrease to zero.¹² Persson's multiscale contact mechanics theory¹⁴ provides a convenient way to estimate effects of multiscale roughness, for self-affine surfaces. In Ref. 5, it was shown on the basis of this theory that the probability of the maximum of P (P_{max}) being exceeded at an n th length scale asperity is

$$e^{-P_{max}^2/P_n^2}, \quad (28)$$

where p_n is the root mean square normal stress acting at the n th length scale asperity. On the basis of Persson's theory,

$$p_n \approx (\pi/2) \frac{h_0 E^*}{L_0} \left[\frac{\pi H}{1-H} \right]^{1/2} \left[\frac{L_0}{L_n} \right]^{1-H}, \quad (29)$$

where L_n is the n th length scale, h_0 is the root mean square height variation of a surface, $E^* = E/(1 - \nu^2)$, where E is Young's modulus and ν is Poisson's ratio, and H is the Hurst index. The Hurst index is defined as follows: If L'_n is the n th length scale normal to the surface and L_n is the n th length scale along the surface, $(L'_n/L'_{n-1}) = (L_n/L_{n-1})^H$, the reduction in heights as we go from length scale L_{n-1} to L_n . We will choose $h_0/L_0 = 0.01$ and $H = 0.8$, which is a reasonable value for self-affine surfaces. The minimum L_n is the mesh size, which is approximately 10^{-8} m , and the maximum length scale is $R = 2.2 \times 10^{-7} \text{ m}$. Substituting these numbers, we get $p_n \approx 0.11 E^*$. For a hydrogel, $E^* \approx k_B T n_{f0} = 1.32 \times 10^5 \text{ Pa}$, using the value of n_{f0} given under Eq. (25). Then, $p_n \approx 1.45 \times 10^4 \text{ Pa}$. From Eq. (28), we get 1.59×10^{-5} for the probability of the van der Waals force dominating over the counterion osmotic pressure, but because of the uncertainty in the numbers used and the uncertainty in the applicability of a multiscale contact mechanics theory to a situation in which there are not that many length scales, we cannot say for certain that in all cases, the counterion osmotic pressure will dominate in the slow sliding speed limit.

V. CONCLUSIONS

The compression of polyelectrolyte microgels in a salt-free highly compressed colloid due to osmotic pressure outside of the particles due to counterions located there is studied for a model based on a quasi-analytic solution of the Poisson-Boltzmann equation and a model for the gel elasticity based on counterion osmotic pressure inside the particles and polymer elasticity. It is found that for particles of radius of

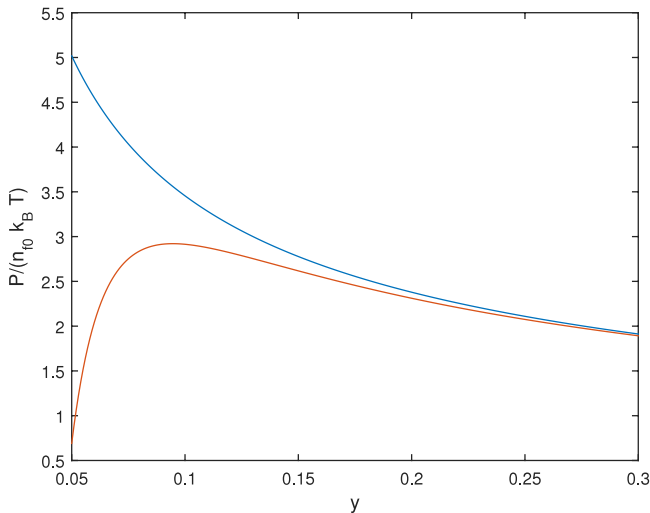


FIG. 4. The above figure is a plot of Eq. (27) (the lower curve) and the first term on the right hand side of Eq. (27) (the upper curve) versus y .

about 0.2 μm , the counterion osmotic pressure should play a significant role in the compression of the particles at high volume fractions. For particles which have a corona (i.e., polymer chains attached to their surface) of lower monomer density than that of the core of the microgel particles, it plays a less significant role. It is also demonstrated that counterion osmotic pressure outside the particles will provide the major contribution to the lubrication of the interface between the particles and a surface along which the compressed colloid is made to slide, for sufficiently slow sliding velocities.

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APPENDIX: DERIVATION OF A FORMULA FOR THE MICROGEL ELASTICITY

At points inside a microgel particle which are not too far away from a facet, the compression of the gel will be primarily normal to that facet, and hence, it is reasonable to assume that

$$n_f \sim \frac{fN}{LL_{\parallel}^2}, \quad (\text{A1})$$

where L is of the order of a mean mesh spacing normal to the facet, L_{\parallel} is a mean mesh spacing parallel to the facet, N is the number of monomers between two links, and f is the number of electron charges e per monomer. It is reasonable to assume that during compression, as L is reduced below L_0 , the mean mesh spacing for a swollen particle, L_{\parallel} remains $\approx L_0$, and we can assume that

$$n_{f0} \sim \frac{fN}{L_0^3}. \quad (\text{A2})$$

On the other hand, it is reasonable to assume that close to the center of a compressed particle, we may assume that, since the compression is closer to being spherically symmetric about the particle's center,

$$n_f \sim \frac{fN}{L^3}. \quad (\text{A3})$$

This is the form proposed by Flory for homogeneously compressed gels.⁷ For an average position inside a microgel particle, we expect n_f to lie between the forms given in Eqs. (A1) and (A3). Then, let us assume that $L_{\parallel} \approx L_0(L/L_0)^{\alpha} = L^{\alpha}L_0^{1-\alpha}$, where α has a value between 0 and 1, so that for $\alpha = 0$, n_f is given by Eq. (A1) with $L_{\parallel} = L_0$ and for $\alpha = 1$, n_f is given by Eq. (A3). Then,

$$n_f \approx \frac{fN}{L^{1+2\alpha}L_0^{2(1-\alpha)}}. \quad (\text{A4})$$

Then, the polymer elasticity of the gel is given by

$$\frac{P_{\text{elast}}}{k_B T} = \frac{L}{Na^2 L_{\parallel}^2} = \frac{1}{Na^2 L^{2\alpha-1} L_0^{2(1-\alpha)}}. \quad (\text{A5})$$

We solve Eq. (A4) for L as a function of n_f and substitute in Eq. (A5), giving

$$\frac{P_{\text{elast}}}{k_B T} = \frac{n_f^{(2\alpha-1)/(1+2\alpha)}}{a^2 N^{4\alpha/(1+2\alpha)} L_0^{4(1-\alpha)/(1+2\alpha)} f^{(2\alpha-1)/(1+2\alpha)}}. \quad (\text{A6})$$

Let us use the equilibrium condition,

$$k_B T n_0 = k_B T n_f - P_{\text{elast}}, \quad (\text{A7})$$

to obtain an expression for L_0 , by using the fact that when no force is applied to the surface of the particle (i.e., when $n_0 = 0$), $L = L_0$, and hence, $n_f = n_{f0}$. Then, setting $n_0 = 0$ in Eq. (A7), setting $L = L_0$ in Eq. (A6), and then substituting the resulting expression for P_{elast} in Eq. (A7), we obtain $L_0 = f^{1/2} Na$ for all values of α . Substituting this value for L_0 in Eq. (A6), Eq. (A6) becomes

$$\frac{P_{\text{elast}}}{k_B T} = n_{f0}^{2/(1+2\alpha)} n_f^{(2\alpha-1)/(1+2\alpha)}. \quad (\text{A8})$$

For $\alpha = 0$, we obtain

$$\frac{P_{\text{elast}}}{k_B T} = n_{f0}^2 / n_f, \quad (\text{A9})$$

the value used in Refs. 4, 5, and 12. When $\alpha = 1$, we obtain

$$\frac{P_{\text{elast}}}{k_B T} = n_{f0}^{2/3} n_f^{1/3}. \quad (\text{A10})$$

Then, from Eq. (A8), we find that

$$r^{-1} = n_0/n_f = [1 - (n_{f0}/n_f)^{2/(1+2\alpha)}], \quad (\text{A11})$$

from Eqs. (A7) and (A8), which is the expression for r used in Sec. II.

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