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THE POTENTIAL ENERGY OF A PAIR OF POLYSTYRENE SPHERES IN ALTERNATING ELECTRIC FIELDS

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INTRODUCTION

The drastic change in the viscosity of electrorheological (ER) fluids when an external electric field is applied has intrigued scientists from many different fields including engineering, chemistry, and physics for over half a century. It has been generally understood that the microscopic attractive forces between induced dipole moments of the suspended particles have important effects on macroscopic fluid properties. Great effort has been given recently to maximizing the strength of the attractive forces between the particles in ER fluids to achieve practical fluids, and important progress has been made. Many questions, however, need to be investigated further. For example, it has been known that the addition of a small amount of water, that is, the addition of mobile charge carriers to an ER fluid, increases the ER effect, although the exact role that the mobile charges play in strengthening the induced dipole moments of the suspended particles is still not very well understood.¹ It has also been shown in recent work on the stress response of ER fluids to transient electric fields that the relaxation process of an ER fluid is more complicated than just a simple fluid-particle dielectric mismatch model, and the surface conductivity of impurities adsorbed on particle surfaces seems to be a contributing factor.²

In the preliminary work presented here, we focus on trying to understand the strength of the microscopic interactions between colloidal particles in alternating electric fields. The system used is a model system of aqueous suspensions of monodisperse polystyrene spheres. By using digital microscopy techniques^{3,4} to measure the inter-particle separations between two spheres at thousands of different times and at several different field strengths, we have been able to determine the probability density function $P(r)$ for the separation distance r between the two particle centers.

Under equilibrium statistical mechanics, the probability density function is related to the pair potential $U(r)$ by

$$P(r) = Ce^{-U(r)/kT}, \quad (1)$$

where C is a normalization constant. From this, we can quantitatively deduce the mutual interaction potential energy of the particles and have found qualitative agreement between our observations and theoretical predictions. This agreement seems to validate the experimental approach here as being of use for studying inter-particle interactions in colloidal suspensions.

Even though an aqueous suspension is not a conventional ER fluid (where one normally uses a non-conducting suspension), there are several advantages. Firstly, because of the monodispersity of the polystyrene particles, the strengths of the interactions between different pairs of particles are more uniform compared to a polydisperse system, and this makes interpretation of our experimental results more straightforward. Secondly, since we are interested in general in studying the role of mobile charges in a suspension, having an aqueous suspension is not a disadvantage. However, as will be explained below, in this preliminary experiment, we operate at a frequency of the applied field where the effect of the mobile charges is minimized and the polarization of the particles is dominated by the dielectric mismatch between the particles and the suspending fluid. We expect that under these conditions the polystyrene/water system is equivalent to a non-conducting suspension. Therefore, the significance of the experimental results presented here, as well as the usefulness of our experimental technique, are not limited to just this model system, but may also apply to the typical ER suspension of non-conducting particles and solvent.

We begin this paper with a theoretical discussion in which the contributions of electrostatic repulsion, electric-field-induced dipole interaction, and van der Waals attraction to the pair potential are first considered. A probability density function for the distance between a pair of particles is then obtained from the pair potential using equilibrium statistical mechanics. The theoretical discussion is followed by a detailed description of the experimental apparatus — one that allows us to isolate pairs of polystyrene spheres in an essentially two-dimensional geometry by restricting the particles to a narrow gap between parallel glass plates. Finally, we examine the results of our experiments and compare our findings with theoretical predictions.

THEORY

Double Layer Repulsion

To calculate the total mutual potential energy of a pair of charged spheres in our experiment, we first consider the electrostatic interaction in the absence of an external electric field, known as double layer repulsion. The charges originate from the polystyrene sulfonate particles losing positive surface ions into the water, leaving the particles with a negative surface charge. Positive free ions are then attracted to the spheres and form a positively charged layer around each sphere, which screens the repulsive force. The layer of free positive ions around a colloidal particle and the negative surface charge on the colloidal particle together comprise the electric double layer. The thickness of the free ions screening the repulsion between colloidal particles is the Debye screening length, κ^{-1} , and for water at room temperature,^{5,6}

$$\kappa^{-1} = \left(\frac{\epsilon_0 \epsilon'_{rw} kT}{\sum_i Z_i^2 e^2 n_{i0}} \right)^{\frac{1}{2}} \approx \frac{3\text{\AA}}{\sqrt{I}}, \quad (2)$$

where ϵ'_{rw} is the real part of the relative dielectric constant of water and I is the molar ionic strength of the solution. The sum here is over different types of ions, each with its own valence Z_i and its own numerical density n_{i0} .

Proceeding from the assumption that the average concentration of free ions at a given point can be calculated from the average value of the electric potential at the same point, one can use the Poisson-Boltzmann equation for the electric potential in the vicinity of a colloidal particle. One can get approximate analytical solutions of the Poisson-Boltzmann equation only in certain limiting situations.⁵ One of these situations — of relevance to our experiment — occurs when the diameter of the spheres is both much greater than the Debye screening length and also much greater than the separation $r - d$ between the surfaces of the spheres. In this limit, the double layer repulsive energy between a pair of particles is

$$U_d(r) = \pi \epsilon_0 \epsilon'_w d V_s^2 \exp(-\kappa(r - d)), \quad (3)$$

where V_s is the surface potential of the sphere. For our experiments, with $d = 2.16 \mu\text{m}$, $V_s \sim 30\text{mV}$,⁷ $I = 0.1 \text{ mM}$, $\kappa d = 42 (\gg 1)$, and $0 < (r - d)/d < 0.3$, the repulsive energy reaches a peak of $\sim 1000kT$ when two particles touch each other.

Electric Dipole Attraction

There are three contributing factors to the induced dipole moment of a particle. One is due to the mobile charges in the double layer, which we will call double layer polarization. The second and third are due to the dielectric and conductivity mismatch between the particle and the suspending fluid, which are called dielectric and Maxwell-Wagner polarization, respectively. The field-induced attraction between particles arises from this field-induced polarization of the colloids. A *single* dielectric sphere immersed in a conducting solvent distorts a uniformly applied electric field in such a way that the field outside the sphere can be described as the superposition of the undistorted field and the field due to a point dipole located at the center of the sphere with moment $\mu = \alpha K E$, where E is the applied electric field, $\alpha \equiv 4\pi\epsilon_0\epsilon'_w$, and $K \equiv [(\epsilon_p - \epsilon_w)/(\epsilon_p + 2\epsilon_w)](d/2)^3$,⁸ where ϵ_p and ϵ_w are the complex dielectric constants of the particle and water, respectively.

Double layer polarization arises from the fact that the applied electric field affects the distribution of the positive mobile charges in the double layer of a polystyrene sphere. At low frequencies, the particle can be thought of as having a thin conducting layer on its surface, and in this case, the effective particle dielectric constant ϵ_p is greater than that of the water. The applied electric field polarizes the double layer and creates a dipole moment in the direction of the applied electric field, since $K > 0$. However, at high frequencies, when the field alternates faster than the double layer can follow, there will be no induced dipole moment in the double layer, and only the dielectric polarization of the polystyrene sphere remains. In this limit, one thinks of the particle as being a neutral plastic sphere immersed in water, because the charges in the double layer no longer respond to the rapidly alternating field. Since polystyrene has a dielectric constant much less than that of water, the particle behaves as a dielectric hole, and $K < 0$. The cutoff frequency for the crossover from double layer to dielectric polarization is approximately the inverse of the time for the ions to diffuse a distance equal to the radius of the sphere: $\omega_c = D/a^2$, with D the ion diffusion constant. For $1 \mu\text{m}$ spheres, this occurs at about 10 kHz. We have observed this crossover between the two forms of polarization by constructing electrodes which produce a large gradient in the electric field. In this case, there is a net force on the field-induced dipoles, and the spheres move in the field. Dielectric holes ($K < 0$) are repelled from the high-field region, but dielectric inclusions ($K > 0$) are attracted to the high field. Through observation of the motion of spheres in the field gradient, we experimentally observe ω_c to be $\sim 30 \text{ kHz}$ for the spheres in our study.

A single sphere in a uniform electric field is exactly equivalent to a single dipole, with no other multipoles of higher order. However, a second sphere in the vicinity of the first experiences a non-uniform field, which is the sum of the external field and the dipolar field of the first sphere. Thus the induced dipole moment is different from that of a single sphere in a uniform electric field. One could argue that higher order multipole moments should also be considered, but computer simulations show that as long as $K < 0.5$, which is the case for the dielectric constants of polystyrene and water at high frequencies, the error due to ignoring the higher order moments is less than a few percent.⁹ Because of this, we ignore higher order moments and only consider dielectric dipole interactions between polystyrene spheres here.

The frequency of the applied electric field used in this experiment is 360 kHz — high enough for us to neglect the double layer polarization and consider only the dielectric dipole interaction between two polystyrene spheres. We consider two particles positioned such that the relative position vector connecting their centers has magnitude r and is oriented at an angle θ relative to the direction of the applied electric field. To calculate the strength of the induced dipole moment of each sphere, both the strength of the applied electric field and the field created by the dipole moment of the neighboring particle are considered. Because of the symmetry of the dipolar potential, the potential energy of two induced dipoles can be solved exactly, accounting for the mutual polarization of the two spheres:

$$U_p(r, \theta) = \frac{\alpha}{r^3} \left| \frac{K|E_0|}{1 + \frac{K}{r^3}} \right|^2 \left\{ 1 - \left[2 \left| \frac{\frac{3K}{r^3}}{1 - \frac{2K}{r^3}} \right| + 4 \operatorname{Re} \left(\frac{\frac{3K}{r^3}}{1 - \frac{2K}{r^3}} \right) + 3 \right] \cos^2 \theta \right\}. \quad (4)$$

Van der Waals Attraction

Van der Waals forces also play an important role in the interactions between colloidal particles.⁵ The energy of the non-retarded van der Waals attraction between two spheres is^{5,6}

$$U_v(r) = -\frac{A}{12} \left\{ \frac{1}{\left(\frac{r}{d}\right)^2 - 1} + \frac{1}{\left(\frac{r}{d}\right)^2} + 2 \ln \left[\frac{\left(\frac{r}{d}\right)^2 - 1}{\left(\frac{r}{d}\right)^2} \right] \right\}, \quad (5)$$

where A is the Hamaker constant, determined by the composition of the colloidal particles. For polystyrene, the Hamaker constant is about $1.0 \times 10^{-21} \text{J}$.¹⁰ The energy of the van der Waals attraction diverges as two spheres approach each other and r approaches d . In our experiment, however, the van der Waals attraction is a very small effect, because double layer repulsion prevents the particles from approaching too close to each other, and this results in the induced dipole-dipole attraction being dominant over the range of distances where our measurements are done.

Total Potential

In our model of polystyrene spheres interacting in a uniform electric field, the total potential energy is a combination of double layer repulsive energy, dipole-dipole attractive energy, and the van der Waals attractive energy:

$$U_t(r, \theta) = U_d(r) + U_p(r, \theta) + U_v(r). \quad (6)$$

The double layer repulsion creates an energy barrier of about $1000kT$ for $(r - d)/d \approx 0.01$. If two particles bump into each other and break through this energy barrier, the two particles will be permanently bound by the van der Waals attraction, and thermal energy usually cannot break them apart. Outside this barrier is the induced dipole-dipole attractive potential well created by the applied electric field. In our experiment, this well can be

Figure 1. The pair potential energy in units of kT due to double layer repulsion ($U_d(r)$), van der Waals attraction ($U_v(r)$), and the dipole-dipole electric field-induced attraction, evaluated at $\theta=0$ ($U_p(r,0)$), as well as the total potential ($U(r,0)$) for a pair of $2.16 \mu\text{m}$ diameter polystyrene spheres, are plotted as a function of the fractional separation of the surfaces ($r/d - 1$) of the two spheres. The high-frequency electric field has RMS amplitudes of (a) 51 V/mm, (b) 63 V/mm, (c) 95 V/mm, and (d) 126 V/mm, respectively.

as deep as $1180kT$. (See Figure 1.) It should be mentioned here that glass is also negatively charged in water, so that there is double layer repulsion between the polystyrene spheres and the surface of the glass, as well. This helps to confine the polystyrene spheres to the mid-plane between the two glass plates. Once it has broken through the double layer repulsive energy barrier, a polystyrene sphere can become permanently bound to the glass surface.

In Figure 2, $P(r)$ is plotted against r . $P(r)$ is obtained by numerically evaluating the following expression:

$$P(r) = \frac{\int_0^{2\pi} e^{-U_t/kT} d\theta}{\int_0^{2\pi} \int_{1.01d}^R e^{-U_t/kT} r' dr' d\theta} \quad (7)$$

Here R is the upper limit of r in the experiment, and this distribution is normalized so that¹²

$$\int_{1.01d}^R P(r) r dr = 1. \quad (8)$$

Figure 2. Normalized probability density function $P(r)$ of the separations of a pair of charged $2.16 \mu\text{m}$ diameter polystyrene spheres as a function of the fractional separation of the sphere surfaces, $r/d - 1$. The probability density functions are calculated from the theoretical pair-potential energy shown in Fig. 1. The RMS value of the applied electric field and the minimum of the pair potential for each curve are also indicated.

EXPERIMENTAL DETAILS

The Cell

The cell used in this experiment is shown in Figure 3. It consists of parallel glass plates clamped between two aluminum holders. An O-ring serves both as a seal for the sample cell and also as a compliant spacer for adjusting the gap between the glass plates. The bottom glass plate has a coating of indium-tin-oxide (ITO), a transparent conductor. Two parallel electrodes have been etched onto the ITO surface, providing a uniform electric field between the electrodes when connected to a power supply. The distance between the electrodes is 0.560 mm in this experiment. The samples used in this experiment are comprised of $2.16 \mu\text{m}$ -diameter polystyrene spheres¹¹ suspended in a 0.1 mM NaCl aqueous solution, and are injected into the cell through one of the syringes. The other syringe keeps the pressure inside the sealed space the same as outside.

Data Acquisition

The cell is placed under an Olympus microscope with a $50\times$ long working distance objective lens. The images are first acquired using a CCD camera and recorded by a SVHS Sony tape recorder. The even-fields of the recorded images are then analyzed by a Macintosh computer that has an 8-bit, 480×640 digitizing board.

We adjust the microscope to have the centers of the spheres appear brighter than the background. By setting a threshold above the background and below the light intensity around the centers of the spheres, the spheres can be identified as bright clusters of pixels with intensities above the threshold. The computer finds the centers of the bright clusters and

Figure 3. Illustration of a side view of the cell placed under an optical microscope.

records them as the coordinates of the spheres. The distance calibration is done with a stage micrometer with 10- μm scales. Both x and y directions are calibrated before the experiment.

We analyze 8,000 images for each of four different RMS field strengths (51V/mm, 63V/mm, 95V/mm, and 126V/mm) at 360 kHz. When the pair breaks up, *i.e.*, when the distance between the two spheres is so great that the binding energy is less than kT , the two particles can diffuse away from each other and do not recombine, and the data taking has to stop. This break-up prevents us from taking data below about 50 V/mm.

RESULTS

The measured pair distance as a function of image frame number is shown for each field strength in Figure 4. We can see that the fluctuation of the pair distance decreases as the electric field becomes stronger.

In Figure 5, we show $P(r)$ vs. $r/d - 1$ for our experiment. Here $P(r)$ is defined as:

$$P(r)\Delta r = \frac{1}{r} \frac{\text{counts in } [r, r + \Delta r]}{\text{counts in } [1.01d, 1.25d]}. \quad (9)$$

Here r is restricted to lie between $1.01d$ and $1.25d$, and the distribution is normalized so that¹²

$$\int_{1.01d}^{1.25d} P(r)rdr = 1. \quad (10)$$

The finite resolution of the optics system and electronic noise in the imaging system in the experiment lead to some uncertainty in the measurement of the distance between two spheres. When a pair of spheres has surmounted the double layer repulsive energy barrier and has

Figure 4. Experimental measurements of the fractional separation, $r/d - 1$, of the surfaces of a pair of charged $2.16 \mu\text{m}$ diameter polystyrene spheres. 1000 measurements were taken at a rate of 10/sec. The measured RMS value of the applied electric field and the calculated minimum of the pair potential for each curve are also indicated.

Figure 5. Measured probability density function of the separation of a pair of polystyrene spheres as a function of the fractional separation of the sphere surfaces. The probability density functions are obtained by integration of the displacement data shown in Fig. 4. The measured field amplitudes and the calculated minima in the corresponding pair-potential are indicated in the figure.

Figure 6. The theoretical probability function of the fractional separation between the surfaces of a pair of spheres, shown in Fig. 2, is convolved with the experimental point-spread function for the four experimental values of the applied field. Reasonable qualitative agreement between the theory (Fig. 6) and experiment (Fig. 5) is evident.

become permanently bound by a van der Waals attraction to the surface of a glass plate, the distance between the spheres does not change with time, and the probability density function $P(r)$ should be a delta function. Instead of this, however, the measured $P(r)$ has a Gaussian distribution with a finite width (point-spread function). Therefore, to compare experimental

results with predictions from our model, we have to take the effects of this uncertainty into account by performing a convolution of the theoretical results with the experimental point-spread function, which is shown in Figure 6.

As we can see from Figures 5 and 6, our experimental results agree qualitatively with the predictions from the simple model proposed in this paper, but it is obvious that a more sophisticated model is needed to explain the long tails of the experimental probability distribution function.

The results of this preliminary experiment also show that the digital image microscopy technique is a useful tool for quantitatively measuring the pair potential between a pair of colloidal particles under the influence of a uniform alternating electric field. We should emphasize that an aqueous suspension of polystyrene particles is only one of the systems that can be studied by this technique. Based on the positive results of this work, we plan to investigate many other systems to study the interactions between colloidal particles in electric fields and thereby advance our understanding of ER on a microscopic level.

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