Entropic Attraction and Repulsion in Binary Colloids Probed with a Line Optical Tweezer

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The long-range entropic forces that arise between two micrometer-sized colloidal spheres in a fluid of much smaller colloidal spheres were directly measured using a line-scanned optical tweezer. This new technique allowed us to measure the functional form of the potential with sub-$k_BT$ energy and 15 nm spatial resolution. At the lowest small sphere concentrations, the potential was monotonically attractive, while at higher concentrations an oscillatory potential was observed, due to the liquid structure of the small spheres. Surprisingly, the large spheres came together only rarely at the higher concentrations, suggesting a new means for stabilizing suspensions using entropy alone. [S0031-9007(99)09246-7]

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Entropic forces between macromolecules in suspension are often produced by the addition of smaller particles to the background solvent [1–11]. These forces have considerable technological importance ranging from protein crystallization to the reversible aggregation of industrial suspensions. At low concentrations of the small species, the forces are traditionally described by the depletion model of Asakura and Oosawa [1], which predicts a monotonically attractive potential, with a range given by the small species diameter. When the smaller particles are concentrated, however, their liquid-structural correlations can dramatically change the interaction to include a repulsive or even oscillatory component [3].

We present the first direct measurement of these effects between two colloidal particles in suspension. Our experiments reveal depletion attraction and repulsion, and exhibit an unexpected slowing down of the aggregation kinetics as the small spheres are made more concentrated. We measured the interaction potential between an isolated pair of 1100 ± 15 nm diameter PMMA (polymethylmethacrylate) spheres (Bangs Labs, Inc) induced by a background of smaller, 83 nm diameter PS (polystyrene) spheres (Seradyn, Inc). We varied the volume fraction of the small spheres, $\phi_S$, by diluting the $\phi_S = 0.42$ stock solution (as measured by viscometry [12]) with a buffer of 5 mM NaCl and 5 mM SDS surfactant, which prevents colloidal aggregation. The bare interactions between the individual large or small spheres are expected to be a screened electrostatic repulsion [13] with a 3 nm screening length. Since this length is so small compared to the particle diameters, we can treat the bare interaction as effectively hard spherelike. However, this electrostatic repulsion does cause the small spheres’ effective radius to be slightly larger than their actual radius [10].

The entropic interactions between a pair of the larger spheres were measured by threading the larger spheres on a rod of light, i.e., a line-scanned optical tweezer [14,15]. In this trap, colloidal spheres are free to diffuse in one dimension, along the scan direction, while being strongly confined in the two perpendicular directions. The system’s own thermal fluctuations then allow us to map out the pair interaction. Specifically, we trap two large spheres in the line tweezer and measure the probability of finding them at a given separation using digital video microscopy. The measured equilibrium probability $P(r)$ of finding the spheres with separation $r$ is given by the Boltzmann equation, $P(r) \propto \exp[-F(r)/k_BT]$, where $F(r)$ is the system’s Helmholtz free energy.

The measured large sphere pair potentials are presented in Fig. 1 for seven values of $\phi_S$ ranging from 0.04 to 0.42, as well as a control measurement with $\phi_S = 0$. The most prominent feature is a strong attraction at short range. An explanation of this attractive depletion force was first provided by the Asakura-Oosawa [1] (AO) theory, which assumes that the small spheres behave as an ideal gas. Around each large sphere there is a thin shell, or “depletion zone” (Fig. 2a), into which the centers of the small spheres cannot penetrate. When two large spheres approach each other, their depletion zones overlap, increasing the total volume accessible to the small spheres, increasing their entropy, and decreasing the system’s free energy.

To quantitatively test the AO model, we fit the low concentration data (after subtracting the weak attraction of the $\phi_S = 0$ curve) with a modified AO form:

$$F_{AO}(r) = \frac{k_BT \phi_S^*}{(2a_S^*)^3} (2a_S^* + 2a_L - r)^2 \times \left( 2a_S^* + 2a_L + \frac{r}{2} \right),$$

where $a_S^* = a_S + \delta a_S$ and $\phi_S^* = \phi_S(1 + \delta a_S/a_S)^3$ are the effective small sphere radius and volume fraction corrected to include the typical small sphere electrostatic interaction range $2\delta a_S$, and where $a_S, a_L$ are the small and large spheres’ bare radii. We model the effect of our 15 nm instrumental resolution by first converting $F_{AO}(r)$ to a probability distribution $P(r)$ via the Boltzmann relation, then smoothing $P(r)$ with a Gaussian kernel with a half-width of 15 nm, and then finally converting $P(r)$ back to a potential by a natural logarithm. The curves shown in
FIG. 1. The entropic interaction potentials measured with small sphere volume fractions ranging from $\phi_S = 0$ to 0.42 (the large sphere volume fraction was less than 0.2). At the lowest volume fractions [curves (b), (c)] the potential is monotonically attractive, resembling the Asakura-Oosawa depletion model [1]. As more spheres are added, a repulsive barrier forms [(d), (e)], before becoming fully oscillatory [(f), (g)]. The spheres for curve (h) never reached the primary depletion minimum. Each curve had to be shifted [16] a small amount horizontally to register their primary minima, due to the roughly 15 nm sphere polydispersity. The weak attraction seen in the $\phi_S = 0$ case is presumably due to van der Waals attraction [17,18].

Fig. 3 are typical fits with $\delta a_S = 7 \pm 3$ nm and $a_L$ taken as free parameters. Models with $\delta a_S = 0$ typically underestimate the well depth by 30%–50%.

Our measurements also convincingly show that, when $\phi_S > 0.1$, there is a substantial depletion repulsion [3] at separations of about one small sphere diameter from contact. This repulsion, which is not predicted by the AO model, can be qualitatively explained by realizing that the small spheres will tend to form layers around the large spheres (Fig. 2b). When the gap between the spheres is commensurate with these layers, the free energy is lower; when incommensurate, the energy is higher. For $\phi_S \geq 0.25$, the effect of the higher order shells becomes significant, making the potential oscillatory (Fig. 1). The oscillation wavelength decreases monotonically as the concentration is increased, and is comparable to the mean spacing in the small sphere fluid, in qualitative agreement with recent calculations by Dickman et al. [3].

In addition to information regarding the two spheres’ energetics, our measurements also provide dynamical information. The most interesting feature we observe is a dramatic slowing of the two spheres’ relative Brownian motion as $\phi_S$ was increased. Briefly, we counted the number of times the two large spheres thermally activated into the primary depletion minimum during each one hour measurement. For the $\phi_S = 0.21$ run, the beads came together more than 200 times, and for the $\phi_S = 0.34$ case, only 3 times. Since the corresponding depletion repulsion barriers are superficially the same and the measured large sphere diffusivities are within a factor of 2, this slowing is completely unexpected.

To fall into the primary minimum, the large spheres must first squeeze out the dense monolayer of small spheres between them. It seems likely that the anomalous slowing could be due to the peculiar hydrodynamics,
phase behavior, or collective motion of that quasi-two-
dimensional layer. It is also possible that there exists a
very high (and very narrow) energetic barrier which merely
appears small due to our finite resolution. Understanding
this barrier will likely require new theoretical insight,
perhaps by simulations which include particle dynamics,
unlike the earlier work [3].

Whatever their exact cause, our observations suggest
that it may be possible to “entropically stabilize” colloids,
which would otherwise aggregate, simply by adding an
inert smaller species. Similar effects might significantly
slow reaction rates in crowded macromolecular solutions,
and introduce a multitude of metastable states in depletion-
induced colloidal crystals. It also seems likely that the
smaller than expected energy scales seen in earlier deple-
tion experiments [6] carried out at large $\phi_S$ could be ex-
plained if this effect allowed the spheres to probe only the
higher order, and thus weaker minima.

These data were collected with the microscope and op-
tical tweezer system represented schematically in Fig. 2c.
Optical tweezers exploit optical gradient forces to trap di-
electric particles in three dimensions near the waist of a
strongly focused laser beam [14]. We scan the laser fo-
cus from side to side, rapidly enough that a particle cannot
follow the trap but responds instead to the time-averaged
optical field. A pair of trapped spheres will then undergo
Brownian diffusion along the line, while strongly confined
in the two perpendicular directions [15]. They act as if
threaded on a frictionless rod. Two properties of the line
tweezer are essential to our potential measurement. First,
the tweezer-induced forces along the line of the sphere cen-
ters are weak enough to be easily subtracted from the mea-
sured free energy. Second, the tweezer serves to strongly
confine both spheres to the microscope’s focal plane, al-
lowing us to equate the in-plane separation measured from
a video image and the spheres’ actual three-dimensional
separation.

We seal about 20 $\mu l$ of the binary suspension between
a microscope slide and cover glass with a 120 $\mu m$ thick
Parafilm spacer. We then trap a single pair of 1.1 $\mu m
PMMA spheres on the line focus, about 1.5 $\mu m$ above con-
tact with the cover glass. Control measurements indicate
no wall-induced effects at this separation — more than 400
screening lengths or 15 small bead diameters. This dis-
tance also gives the best optical trapping and thus spatial
resolution for the measured potential. We typically video-
tape the two spheres for one hour, which yields $2 \times 10^5$
separation measurements.

Accurately measuring the separation of the two spheres
was complicated by the overlap of their diffraction-
broadened images. On top of the roughly 15 nm random
error caused by camera noise and the small out of plane
motion, overlap effects cause a systematic overestimation
of the sphere separation. At contact, the apparent distance
between the two image centroids [19] was typically
100 nm larger than the actual center-center separation.
We applied a correction procedure which assumes that the
individual sphere images overlap via linear superposition
of brightness. For instance, when finding the centroid of
the right sphere, we must first subtract the contribution of
the left sphere from the image. We used a mirror-reversed
copy of the left sphere’s isolated left-hand side as a model
for its overlapping right-hand side. We estimate that
the residual overlap error is less than 30 nm at contact,
and the resulting spatial warping of our data to be less
than 10%.

The optical tweezer induces two types of forces on the
spheres, which were subtracted from the data using the pro-
cedure shown in Fig. 4. If the scan rate of the tweezer is
not completely uniform, the particles will migrate along the
line to regions where the scan rate is slowest (i.e., where
the time-averaged electric field is greatest). We used a nonuni-
form scan waveform such that the two spheres shared a
one-dimensional, roughly harmonic potential well. This
external force field speeds data collection for small separa-
rations and causes the fictitious attraction observed at long
range. At slow scan rates, the tweezer can “kick” the
beads [15] in the scan direction. For our fast bidirectional
scanning any small kicks cancel each other, leaving unbi-
sased Brownian motion.

We also observe and correct for a gentle repulsion at in-
termediate distance, indicated in Fig. 4. This repul-
sion is present even when $\phi_S = 0$. Its strength depends on
both the laser power and polarization, and its range is
comparable to the width of our laser focus. This repul-
sion is likely caused by the dipole-dipole interaction [20]
between the optical-frequency electric dipole moments induced when both spheres are in the laser focus.

Our measurements of depletion forces and kinetics provide detailed information about the structure and rheology of the background suspension—in this case details that are too small to be studied with ordinary microscopy or light scattering. In addition to the monodisperse hard spheres used in this study, we can measure the depletion effects due to soft polymer coils \([7,11]\), rodlike colloids, or polydisperse spheres. Such research should provide substantial insight into the properties of these interesting suspensions as well as their biological analogs.

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[12] The weight fraction of small spheres \(\phi_w\) in each sample was determined by weighing the dried sample. This was then converted to a volume fraction \(\phi_v\) by \(\phi_v = (1.28 \pm 0.04)\phi_w\). The factor 1.28 was determined by measuring the viscosity of dilute small sphere suspensions and fitting the data to \(\nu = \nu_0 (1 + 2.5\phi_v)\), and accounts for any small sphere porosity and swelling in contact with water.
[16] The contact separation used to shift Fig. 1, curve \((h)\), was found by forcing the two spheres into the primary minimum (not shown) using the laser tweezer. Since for curve \((g)\) the spheres explored only the primary minimum 3 times during the one hour experiment, the depth of the minimum could be roughly \(1k_BT\) in error.