# Direct Measurement of Infinitesimal Depletion Force in a Colloid-Polymer Mixture by Laser Radiation Pressure

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It is widely believed that depletion force causes formation of colloidal crystal or flocculation in the stable colloidal suspension mixed with nonadsorbing polymers. This force works between a colloidal particle and plane, which can be regarded as a sphere with infinite radius. We report a novel technique that enables us to measure the depletion force working between a colloidal particle and a glass surface using laser radiation pressure. We found that the observed force almost coincides with the predicted one. [S0031-9007(97)03137-2]

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When electrolyte composition surrounding latex particle is altered properly, e.g., reduction of the ionic strength by dialysis, latex particles form ordered phase [1]. In this case, it is widely believed that the crystal formation is due to the interparticle repulsive force and counted as one of the examples of Alder phase transition [1,2]. By adding adequate amounts of nonadsorbing polymers [3] (or smaller latex particles [4]), the system also undergoes phase separation or flocculation and forms dense ordered phase as well as dilute disordered phase.

This phenomenon is not based on an interaction between latex particle and polymer such as *bridging* where polymers role like glue, but is caused by a new interparticle attractive force called "depletion" force. This hypothesis [5] has been investigated theoretically [6] or experimentally [3–7] by many groups from some angle and technique. A brief outline of this effect—*depletion effect*—is mentioned in the following sentences.

In dilute solution, polymers behave like hard sphere and refuse to interpenetrate each other. In the mixture of such polymers and latex particles, there exist the regions where the center of mass of the polymer cannot get into and is referred to depletion region (see Fig. 1). These regions exist surrounding each latex particle as well as along the hard wall. The thickness of the layer of depletion region is equal to the effective radius of polymer that may coincide with the hard-sphere radius of polymer described above. When a latex particle approaches another latex particle or hard wall, the depletion regions overlap each other. Then, the total volume of the depletion region in the system decreases as much as the overlapped volume. As a result, the entropy of polymer solution increases and free energy decreases. This discussion suggests that the entropic attractive force—depletion force—is generated between particles as well as between particle and plane such as the internal wall of the cell.

The increase of free energy $\Delta F$ is written as $-Nk_BT \ln[(V + \Delta V)/V]$, where $N$ is the total number of polymers, $k_B$ the Boltzmann constant, $T$ the absolute temperature, $V$ the original free volume for the center of mass of the polymers, and $\Delta V$ is the volume of the overlapped depletion region. Here we have assumed that dilute polymer solution is an ideal solution [8]. As $\Delta V$ is a function of the gap $d$ between two particles (or the distance between particle and wall), depletion force $f$ is given as $f = -\partial\Delta F/\partial d = (Nk_BT/V)(\partial\Delta V/\partial d)$. Here we have assumed that $\Delta V/V \ll 1$. Then, $f$ can be written as

$$f = \frac{Nk_BT}{V} S_{\text{osm}} = \Pi S_{\text{osm}} . \tag{1}$$

In fact, $Nk_BT/V$ is equal to the osmotic pressure $\Pi$ of polymer solution. We define $\partial\Delta V/\partial d$ as the area $S_{\text{osm}}$ on which osmotic pressure presses, and this equation suggests that depletion force is analogous to osmotic pressure. $S_{\text{osm}}$ is the area of the cross circle of two surfaces of depletion regions represented in Fig. 1.

The measurement of such microscopic interparticle force has been almost impossible due to the difficulty of

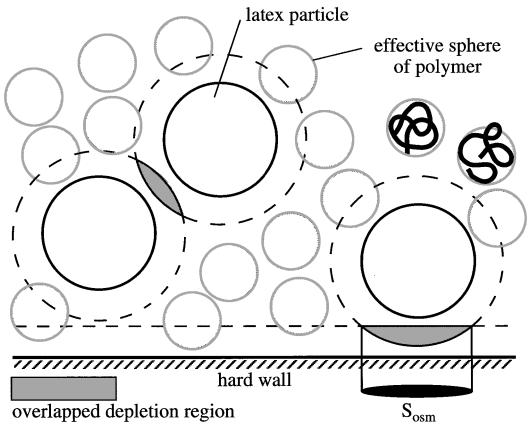


FIG. 1. Illustration of depletion effect. See the third and fourth paragraphs of text.

  

control of the particle position as well as the extremely weak strength of the force but few examples [9]. We have taken notice of radiation pressure—the pressing force given by light to object—and have succeeded in applying it to the direct measurement of depletion force. It is of importance to point out that milliwatts of focused laser light can exert sufficient radiation pressure force on micrometer sized particles [10].

Because of a few technical problems, we investigated depletion force not between two latex particles but between latex particle and wall of cell in this study. As described above, depletion force is generated where depletion region exists, e.g., between sphere and plane, and provides us a good estimation of depletion force between latex particles (see Fig. 1).

Figure 2 shows schematic representation of experimental setup and technique (see the figure caption for details of method of measurement). We investigated the system that consists of poly (ethylene oxide) (PEO) and few polystyrene latex particles in water. We set the number concentration of latex particles about 1 particle/$(50\ \mu\text{m})^3$. Polystyrene latex (1.0 $\mu$m in diameter) was obtained from Sekisui Chemical Co., Ltd. PEO ($M_w = 2 \times 10^6$ and $1 \times 10^6$) with the inhibitor BHT were obtained from

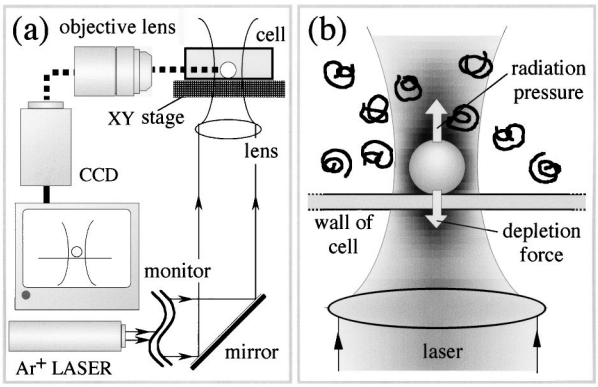


FIG. 2. (a) Schematic diagram of basic apparatus. (b) A latex particle irradiated by a focused laser in the sample cell; the sample cell was placed on a *XY* stage. Internal cell bottom surface was observed through objective lens by a CCD camera. By moving the optical cell using the *XY* stage, the latex particle trapped on the wall of the cell was detected using the focused and attenuated Ar ion laser beam as an illumination. At this moment, we were able to detect two-dimensional Brownian motion of the particle as the fluctuation of the scattered light from the particle. This Brownian motion was easily overcome by the slight increase of the laser intensity that trapped the particle at the center of the beam axis; since the force that radiation pressure gives on the particle has the components toward as well as along the center of the beam axis [10]. Then, increasing the laser power gradually (under computer control), when the power amounted to the certain value, the trapped particle on the internal wall of the cell by the depletion force was torn off and blown away in solution by radiation pressure. The value of laser intensity at that moment was regarded as a measure of the strength of the force working between the particle and wall, that is, depletion force.

Aldrich Chemical Company Inc. We chose the PEO with inhibitor because PEO has a tendency to react with $O_2$ from the air to form colored material [11]. We have used the value of radius of gyration, $R_g$, of PEO using $M_w$ dependence determined by J. C. Selser *et al.* [12] ($R_g = 0.101\ \mu$m for $M_w = 2 \times 10^6$ and $R_g = 0.0677\ \mu$m for $M_w = 1 \times 10^6$). We have performed the measurement for each $M_w$ of PEO and found essentially the same results if scaled to $M_w$ properly. Here, only the result for $M_w = 2 \times 10^6$ is shown in this report due to the limitation of space.

After a given amount of PEO was added to this dilute latex solution, the sample solution was transferred into the optical cell on the experimental setup and was kept for one hour before the measurement to reduce the convection in the cell. Optical cell was constructed of normal micro slide glass (MATSUNAMI GLASS Ind., Ltd. S-1112) and was disposed after each experiment. In the water, this glass surface carries faint same negative charge as latex particle [13]. All measurements were performed at the room temperature.

It is important to study the trapping energy in comparison with the thermal energy $k_BT$. In case of flat wall and spherical particle, we have $\Delta F_{\max} = -(k_BTN/V)\pi[4r_{\text{lat}}r_{\text{pol}}^2 + (4/3)r_{\text{pol}}^3]$, where $r_{\text{lat}}$ is the radius of the latex particle and $r_{\text{pol}}$ is the effective radius of the polymer. We have used the radius of gyration $R_g$ as $r_{\text{pol}}$ in this report. From these simple estimations, we can calculate the concentration at which $\Delta F_{\max}$ goes beyond $k_BT$ and it is found to be 0.0241 $\mu M$. It was indeed very hard to detect trapped particles below and just above this concentration. In addition, no trapped particle was found at all for concentration of PEO = 0.

Figure 3 represents the raw data of the concentration dependence of the minimum laser intensity required to blow the particle off the wall of the cell (in short, *blow intensity*). Here, each circle represents one latex particle studied. Since we can draw only a rough tendency as it is, distributions of blow intensity on each concentration were plotted, e.g., in the Fig. 3 inset. We find that most of such a histogram have a clear maximum or specific cutoff value. Rather large variance (around the mode value) may be partially due to the fact that $\Delta F_{\max}$ on a given range of concentration is $\sim 1-3$ times of $k_BT$ as well as due to the condition of the glass surface being not so flat for the micrometer sized particle (maximum unevenness of the surface is 0.9 $\mu$m) [13].

We found that laser output of 1 mW gave radiation pressure force of $0.0395 \pm 0.0023$ pN for a latex particle on a glass surface (see [14] for details). Mode or cutoff values of the intensity are plotted in Fig. 4. As clearly seen here, these bars are fairly proportional to the polymer concentration up to the certain concentration $c^\dagger$. Making an analogy between depletion force and osmotic pressure, this part of the result is easily understood. See Eq. (1). $S_{\text{osm}}$ is defined above as the area of cross circle of two

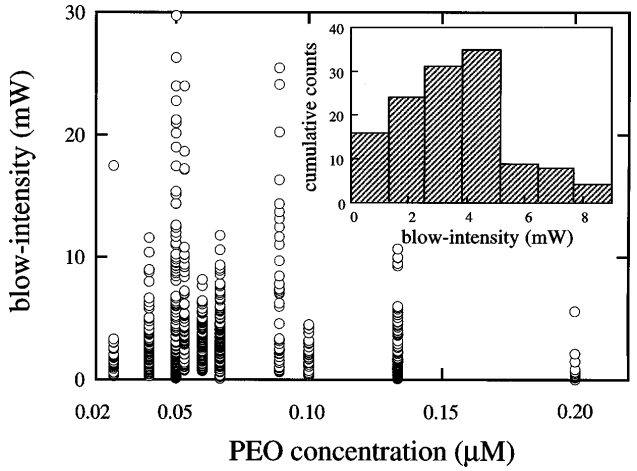


FIG. 3. Dependencies of the minimum laser intensity required to blow the particle away (in short, *blow intensity*) on PEO concentration. Each circle represents the result of one measurement. Over 97% of the events are plotted in this figure. The number of the data is about 100 on each concentration. Inset: typical histogram of the blow intensity at 0.0667 $\mu M$ with clear maximum.

surfaces of depletion regions and corresponds to the area under osmotic pressure. In the case of a spherical particle and flat wall, we found that $S_{\rm osm}$ can be written as

$$S_{\rm osm} = 4\pi r_{\rm lat} r_{\rm pol} \qquad (2)$$

and is constant as far as $r_{\rm lat}$ and $r_{\rm pol}$ are constant. Theoretical strength of the depletion force predicted by Eqs. (1) and (2) are presented by dotted lines as 1.55(pN) per $(\mu M)$ in Fig. 4. Solid line is obtained by the least squares method for the center of vertical bars up to $c^{\dagger}$.

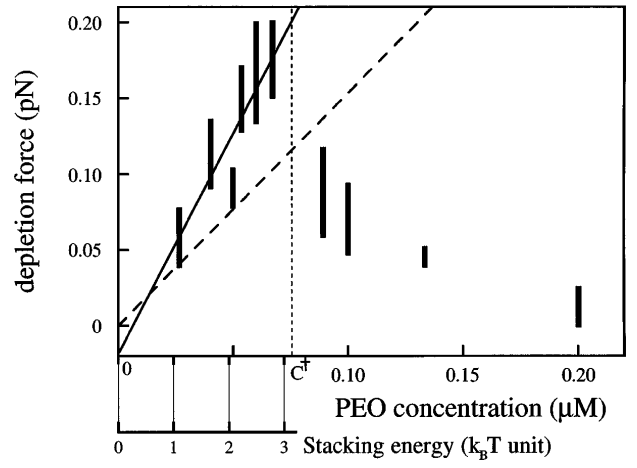


FIG. 4. Concentration dependencies of the depletion force. The length of each vertical bar corresponds to the width of the bar of mode or cutoff value in each histogram (see Fig. 3 inset). The scale of the horizontal subaxis is defined as the unit that corresponds to the concentration where stacking energy of the depletion force is equal to $k_B T$. $C^{\dagger}$ shows the maximum concentration up to where the depletion force is proportional to polymer concentration.

Small nonzero (negative) intersection of the solid line and ordinate might suggest the existence of Coulombic repulsive force between glass plate and latex particles. However, we also studied the system with 1 and 2 $mM$ of salt (NaCl) and obtained similar results within the experimental errors. Thus, this nonzero intersection might be due to a systematic error associated with the measurement of very weak forces. As the observed force depends strongly on the polymer concentration but not on the ionic strength up to 2 m$M$, we can conclude that we have observed the depletion force. It might be of interest to point out here that, above 5 $mM$ of NaCl, we found strongly stuck particles to the glass surface that indicated the van der Waals interaction.

The ratio of slope of observed force (solid line) to predicted force (dotted line) $p$ is 1.88. (We found that $p$ is 1.77 for $M_w = 1 \times 10^6$.) This discrepancy might be due to the following possibilities.

(I) The error of the estimation of depletion region (is equivalent to that of effective radius, $r_{\rm lat}$ or $r_{\rm pol}$). (i) The repulsive interaction between glass wall and PEO (or between latex particle and PEO) that might increase the thickness of the layers of depletion region along the glass wall and, as a result, increase the depletion force. (ii) In the estimation of depletion force we have used $R_g$ as $r_{\rm pol}$. It is important to point out that $R_g$ might not always coincide to $r_{\rm pol}$ [7], since $r_{\rm pol}$ should be the radius when polymer behaves like hard sphere. (iii) Physisorption of the polymers to the latex particle that might increase $r_{\rm lat}$.

(II) If the bottom part of the latex sphere that is pressed to the glass wall by the depletion force becomes flat and the vertical height becomes 5% less than the original diameter, $S_{\rm osm}$ increases as much as 20%. Such deformation of shape of latex particle also increases apparent depletion force.

(III) Another attractive force *depending on* the PEO concentration exists. Despite this discrepancy, we would like to stress the fact that the observed strength of depletion force almost coincides with the predicted one.

The remaining problem is the sudden decrease of the depletion force above $c^{\dagger}$. To understand these results, it is very important to point out that polymer solution has a characteristic length scale called correlation length $\xi$. $\xi$ is equal to hydrodynamic radius and proportional to $r_{\rm pol}$ and $R_g$ for the dilute solution where polymer is independent of each other. However, above certain concentration, the polymer starts to overlap each other. Such concentration is referred to as $c^*$ that gives the boundary between dilute solution and semidilute solution [8]. For semidilute solution, because of the physical interpolymer entanglement, each polymer is divided into smaller units called blobs. The size of these blobs determines the characteristic length scale of the solution. In other words, polymer behaves as the sphere with a radius of $\xi$. Thus, $r_{\rm pol}$ in Eq. (2) must be replaced with correlation length $\xi$.

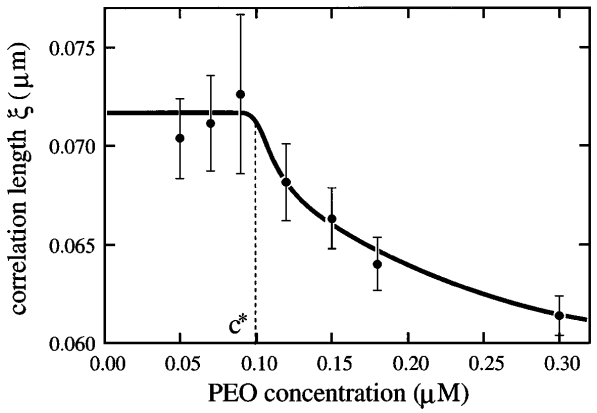


FIG. 5. Dependencies of the correlation length $\xi$ of PEO on concentration. These plots are obtained by quasielastic light scattering spectroscopy. Measurements were done at $1/|\vec{k}_s| = 0.1291\ \mu$m. The concentration where $\xi$ begins to decrease gives us $c^*$ of polymer solution where polymers start to overlap.

Figure 5 represents the observed $\xi$ of the polymer solution. As clearly seen here, sudden decrease of $\xi$ occurs at about 0.1 $\mu M$. This concentration corresponds to $c^*$ for this system. Above $c^*$, $\Pi$ might increase but the $S_{\text{osm}}$ decrease resulted in the decrease of the depletion force. It is of great importance to point out that $c^\dagger$ where depletion force begins to decrease suddenly is in good agreement with $c^*$ where polymers start to overlap.

These results clearly show that the force which traps latex particles onto the glass surface is *mainly* the depletion force. Moreover, this conclusion provides us with strong evidence that depletion force causes the formation of colloidal crystal or flocculation in the stable colloidal suspension mixed with water-soluble polymer. Here we want to emphasize that the force working to micrometer sized particle is measured directly and the observed value almost coincides with the predicted one.

This technique that makes the measurement of various infinitesimal forces on a particle possible can be applied to the studies of interaction between charged particle and surfaces. For example, by using antibody coated latex particles and antigen coated surfaces, this technique can be available to the study of antigen antibody interactions.

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[14] The common method of obtaining the conversion factor $\alpha$ of the laser intensity to force was decided by the measurement of the terminal velocity of the same latex particle illuminated by the same laser beam in water using the Stokes' law. However, $\alpha$ is *not* applicable to the particle next to the glass wall. Because the refractive indices of glass of the cell (1.523) and latex particle ($\sim$1.6) are very close compared to that of water (1.33); radiation pressure force for latex particle on a glass wall might be smaller than the force observed in water. To correct this effect, we performed the following experiment. In experimental setup represented in Fig. 2(a), we set another laser beam irradiated from above as well as beneath the particle on the glass plane in aqueous solution without polymers. The laser beam from above had the role to trap the particle instead of the depletion force and had fixed output. Slightly increasing the output of laser from beneath, we measured the point that the force from beneath exceeded the force from above. From the ratio $\beta$ of these two radiation pressure forces, we were able to get real conversion factor $\alpha/(\beta + 1)$. This is calculated on the assumption that the reflection from the particle surface next to the glass surface can be neglected (largest conversion factor is $\alpha/\beta$). As a result, we found that laser output of 1 mW gave radiation pressure force of $0.0395 \pm 0.0023$ pN for a latex particle on glass surface.