

Feature Article

DIRECT MEASUREMENT OF WEAK DEPLETION FORCE BETWEEN TWO SURFACES*

Xiang-jun Gong^b, Xiao-chen Xing^a, Xiao-ling Wei^a and To Ngai^{a**}

^a Department of Chemistry, the Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China

^b Department of Physics, the Chinese University of Hong Kong, Shatin, N.T., Hong Kong, China

Abstract In a mixture of colloidal particles and polymer molecules, the particles may experience an attractive “depletion force” if the size of the polymer molecule is larger than the interparticle separation. This is because individual polymer molecules experience less conformational entropy if they stay between the particles than they escape the inter-particle space, which results in an osmotic pressure imbalance inside and outside the gap and leads to interparticle attraction. This depletion force has been the subject of several studies since the 1980s, but the direct measurement of this force is still experimentally challenging as it requires the detection of energy variations of the order of $k_B T$ and beyond. We present here our results for applying total internal reflection microscopy (TIRM) to directly measure the interaction between a free-moving particle and a flat surface in solutions consisting of small water-soluble organic molecules or polymeric surfactants. Our results indicate that stable nanobubbles (*ca.* 150 nm) exist free in the above aqueous solutions. More importantly, the existence of such nanobubbles induces an attraction between the spherical particle and flat surface. Using TIRM, we are able to directly measure such weak interaction with a range up to 100 nm. Furthermore, we demonstrate that by employing thermo-sensitive microgel particles as a depleting agent, we are able to quantitatively measure and reversibly control $k_B T$ -scale depletion attraction as function of solution pH.

Keywords: Depletion interaction; Total internal reflection microscopy (TIRM); Nanobubbles; Microgel particles.

INTRODUCTION

In a mixture of micron colloidal particles and nonadsorbed nano-particles (often known as depletants), as far as the surfaces of two micron particles approach within the diameter d of the nanoscale particles, a so called entropic depletion effect appears: those nano-particles are excluded from the gap between the two larger particles and thereby create an attractive force between the two larger particles due to an imbalance osmotic pressure (Π) inside and outside the gap region^[1]. The entropic depletion force plays an important role in many industrial processes^[2], biological interactions^[3–5] and in the formation of special material structures^[6–10]. For examples, it was used and explored specially in the self-assembly of different shaped forms, either forming stacks or on surfaces^[11–13]. An outstanding advantage in using depletion forces for control and assembly is that the interaction potentials are easily controlled in the weak-attraction regime, namely, $1–5 k_B T$.

Both theoretical and experimental studies on depletion problem have been published over the past several

* This work was financially supported by the Hong Kong Special Administration Region (HKSAR) General Research Fund (CUHK 402809, 2160387) and the Direct Grant for Research 2008/09 of the Chinese University of Hong Kong (CUHK 2060371).

** Corresponding author: To Ngai, E-mail: tongai@cuhk.edu.hk

Invited lecture presented at the International Symposium on Polymer Physics, 2010, Jinan, China

Received June 17, 2010; Revised June 30, 2010; Accepted July 9, 2010

doi: 10.1007/s10118-010-1012-8

decades. Asakura and Oosawa (AO)^[14] and Vrij^[15] independently calculated the depletion potential between two colloidal particles in dilute polymer solutions. In their model, the colloidal particles were treated as hard spheres and a simple depletion potential with a range of the radius of gyration of polymer (R_g) and strength proportional to the concentration of polymers was obtained. Despite its simplicity, AO theory gives the length scale and magnitude of the depletion force in agreement with simulations and experiments. On the other hand, the experimental measurements of depletion interactions have been carried out in the presence of nanoparticle suspensions^[16], surfactant micellar solutions^[17, 18], polymer solutions^[19, 20] and charged polyelectrolytes^[21, 22]. However, direct detection of depletion interactions is still in challenge, if not impossible, because the depletion potential variations are in the order of $k_B T$, which can be easily masked by the thermal fluctuation^[23]. So it's unsurprising that depletion was first measured directly only 17 years ago using the surface force apparatus (SFA)^[17]. Measurements have recently done by techniques such as optical tweezers (OT)^[24–26], atomic force microscopy (AFM)^[27, 28] and total internal reflection microscopy (TIRM)^[29–31]. In particular, TIRM is an extremely sensitive noninvasive technique that has been used to measure the weak depletion force acting on a free-moving particle in the presence of neutral polymer^[32], and charged colloidal rods^[33].

Recently, we have accidentally found that stable nanobubbles with size range around hundred nanometers can exist free in solutions consisting of small organic molecules^[34] or polymeric surfactants such as Pluronic copolymers^[35]. Note that previously, these “bulk-free” nanobubbles are frequently related to the large supermolecules made of water and organic molecules^[36]. Herein, we present the study to investigate the effects of presence or absence of these bulk-free nanobubbles on the interaction between a free-moving colloidal particle and a flat surface in aqueous solutions. It is found that the existence of nanobubbles in the aqueous solution, like the nonadsorbing polymers and micelles, can induce attraction between the particle and the flat surface. Using total internal reflection microscopy (TIRM), we are able to directly measure such weak interaction with a range up to 100 nm. Furthermore, by employing poly(*N*-isopropylacrylamide-*co*-methacrylic) (PNIPAM-*co*-MAA) microgel particles as a depleting agent^[37], we found that the depletion interactions can be easily triggered by changing the pH values of the solution and thus provide a new way of using depletion forces to direct the assembly of colloidal particles.

EXPERIMENTAL

Total Internal Reflection Microscopy (TIRM)

TIRM is a sensitive technique that it can detect the interaction potential profiles between a micron particle and a flat surface. This technique has been described elsewhere^[29, 30]. Briefly, in a TIRM measurement, an evanescent wave, which decays exponentially with the distance from the interface, is generated at the solid/liquid interface by a total internally reflection within the glass slide. Any particle located close enough to the surface of the glass slide will scatter the incident evanescent wave. The scattered intensity depends on the distance between the sphere particle and the surface of the glass slide as^[29]

$$I(h) = I_0 \exp(-\beta h) \quad (1)$$

where h is the distance from the spherical particle to the slide surface, I_0 is the “stuck” particle intensity, when $h = 0$, and β^{-1} is the characteristic penetration length. Measuring the scattered intensity over a long period provides a histogram of the separation distance, $p(h)$, which can be related to the total potential energy, $\Phi(h)$, at that point through a Boltzmann relationship^[29]

$$p(h) = A \exp\left[-\frac{\Phi(h)}{k_B T}\right] \quad (2)$$

where A is a constant normalizing the integrated distribution to unity. The potential energy profile is obtained by inverting the distribution.

In our typical TIRM experiment, a diluted micron polystyrene (PS) latex dispersion was initially pumped into a carbonized PTFE frame sandwiched between two cleaned silica microscopy slides. The evanescent wave

with a penetration depth of 110.4 nm was produced by use of a 28 mW HeNe laser operating at 632.8 nm, which was calculated via $\beta = 4\pi/\lambda((n_1 \sin \theta)^2 - n_2^2)^{1/2}$, where the incident angle $\theta = 70^\circ$, λ is the wavelength of incident light beam, and $n_1 = 1.330$ and $n_2 = 1.515$ are the refractive indices of the water and the glass, respectively. Then a PS particle of average brightness was selected and held in place with optical tweezers generated by a solid-state Nd:YAG laser (output 300 mW at wavelength 532 nm), while the rest of the particles were washed from the cell with the solvent. After that, the interaction between the single free-moving PS particle and glass surface in the desired solution was recorded. The intensity measurements were collected through single photon counting by a photomultiplier tube (PMT Hamamatsu H7155).

RESULTS AND DISCUSSION

Depletion Attraction Induced by Nanobubbles

Recently, stable nanobubbles with size range around hundred nanometers have been reported to exist free in different aqueous solutions, including surfactant-water, alcohol-water, sugar-water and other water-soluble organic molecule aqueous solution^[36]. Further studies suggest that these bulk-free nanobubbles are negatively charged because the hydroxyl ions (OH^-) from the dissociation-association of water molecules prefer to stay at the gas-water interface^[37, 38]. In addition, they can be reversibly removed by repeated filtration and regenerated by air injection. Therefore, we conduct the first study to investigate the effects of presence or absence of the bulk-free nanobubbles on the interaction between a free-moving colloidal particle and a flat surface in an aqueous solution of α -cyclodextrin (CD)^[34].

We use the total internal reflection microscopy (TIRM) to quantitatively measure the interaction between a free-moving polystyrene (PS) colloidal particle and a hydrophilic glass surface, both with the presence or absence of these nanobubbles in an alkaline α -CD solution. The experimental setup of TIRM is shown in Fig. 1 and details could be found in our previous work^[34]. It should be noted that to remove the spontaneously formed bulk-free nanobubbles in α -CD solution, the particle was held with optical tweezers coupled in TIRM, and then the solution was repeatedly filtrated by circulating to pass a Nylon-filter (Millipore 0.45 μm) in the line 2.

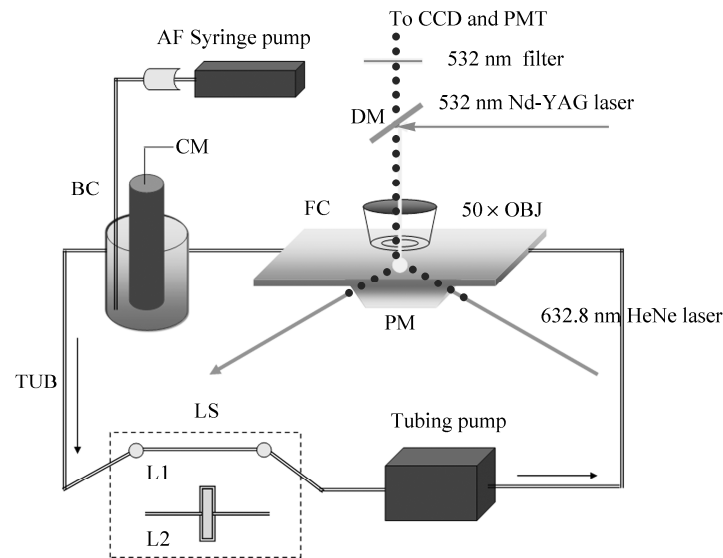


Fig. 1 The TIRM experimental setup to conduct the measurement of interaction between single PS particle and flat surface with the presence or absence of bulk-free nanobubbles in α -CD aqueous solution

AF = air filter (including a Nylon-0.2 μm filter and a wash bottle of saturated NaOH aqueous solution); CM = conductivity meter; BC = buffer cell; LS = line selector; L1 = line 1; L2 = line 2 (including a nylon-0.45 μm filter); FC = flow cell; PM = prism; OBJ = objective; TUB = tefton tube; DM = dichroic mirror; F = 532 nm optic filter; Black arrows present the direction of flow when the tubing pump is run.

Previously, we have indicated that repeated filtration can effectively remove the bulk-free nanobubbles in the aqueous solution without change the α -CD concentration^[36]. On the other hand, the reintroduction of nanobubbles to the solution can simply be achieved by injecting air (*ca.* 200 mL) to the buffer cell (BC) with a syringe pump and then circulated the system to the flow cell in a closed loop. Therefore, using a combination of optical tweezers and the tubing flex pump, we can measure the interaction between a PS particle and a hydrophilic surface both with the presence or absence of the bulk-free nanobubbles in a reproducible and reversible way. More importantly, we are able to use the same single particle and the hydrophilic glass surface to obtain a complete set of interaction potentials under the conditions with or without existence of bulk-free nanobubbles, which not only significantly facilitates us to compare between the measured potential profiles, but also minimizes the effects of particle and surface variation.

Figure 2 shows the total seven measurements of the interaction potentials between the particle and flat surface under different conditions. In order to distinguish different measurements shown in Fig. 2, the subscripts Pr and Ab were used to denote the measured potential ($\Phi_{Pr}(h)$ or $\Phi_{Ab}(h)$) with presence or absence of nanobubbles, respectively. Meanwhile, a conductivity meter (Jenway) was used to monitor the bulk conductivity of the aqueous solution in buffer cell (BC) during the measurements as shown in Fig. 1. It nearly remained constant (*ca.* $(21 \pm 0.3) \mu\text{Scm}^{-1}$) during the whole seven measurements, indicating that repeatedly filtration or reintroduction nanobubbles has no effect on it. In other words, the ionic strength (Debye length) was kept unchanged during the measurements so that we can ensure that the only difference in the aqueous environment is the existence of the bulk-free nanobubbles or not.

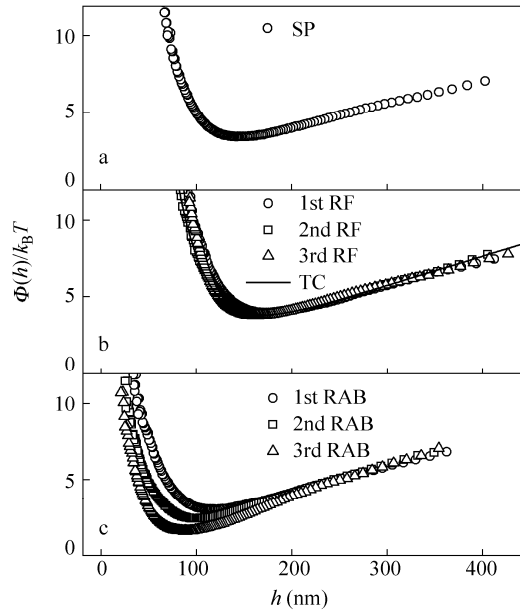


Fig. 2 TIRM measured interaction potential profiles ($\Phi(h)/k_B T$) between the PS particle and glass surface under different solution conditions

SP is solution with spontaneously dissolved α -CD molecules; RF means that the solution after repeatedly filtrated while RAB presents the solution after the air bubbles were reintroduced. 1st, 2nd and 3rd present the corresponding ordinal number; TC is a theoretical curve from Eq. (3) with $\kappa^{-1} = 30 \text{ nm}$ and $G = 70 \text{ fN}$.

Figure 2(a) shows the typical interaction potential profile between the PS particle and flat surface with spontaneously dissolved α -CD ($c_{\alpha\text{-CD}} = 7.90 \times 10^{-3} \text{ g/mL}$) in NaOH aqueous solution ($\text{pH} = 10.0$). It is worth to mention again that nanobubbles can be spontaneously formed in the α -CD aqueous solution so that the interaction between the PS particle and flat surface is under the conditions of existence of the bulk-free

nanobubbles. However, Fig. 2(b) clearly shows that after nanobubbles were removed by repeatedly filtration (RF), the measured potential profiles $\Phi_{Ab}(h)$ shifted far away from the flat surface. Moreover, the measured $\Phi_{Ab}(h)$ in three different cycles collapse to a single theoretical curve (TC), which can be well described by the superposition of a gravitational contribution and an electrostatic term^[15, 16, 18]

$$\frac{\Phi(h)}{k_B T} = B \exp(-\kappa h) + \frac{G}{k_B T} h \equiv \frac{\Phi_{Ab}(h)}{k_B T} \quad (3)$$

where $G = (\rho_p - \rho_w)Vg$ is the weight of the particle with ρ_p and ρ_w being the density of the particle and water respectively, V the volume of the particle and g the acceleration of gravity. B is a function of the surface potential between the surface and particle, which is difficult to determine independently and κ^{-1} is Debye length. In other words, without the existence of bulk-free nanobubbles, there are only two contributions to the particle-surface interaction; namely, the electrostatic double layer repulsion and gravity. The fitting gives $G = (72 \pm 2)$ fN and $\kappa^{-1} = (30 \pm 2)$ nm, which agree well to the theoretical values ($G = 70$ fN, $\kappa^{-1} = 30$ nm) as calculated using known size and density (1.055 g cm^{-3}) of the PS particle and the used electrolyte concentration, respectively. This agreement also shows that the presence of the free α -CD molecules in the aqueous solutions has little effect on the interaction between the particle and surface.

On the other hand, when nanobubbles were presented in the aqueous solution by reintroducing the air bubbles (RAB), the measured potential profiles $\Phi_{Pr}(h)$ became deeper and shifted gradually closer to the flat surface. Supposedly, there exists an attractive force between the particle and glass surface. Besides, by comparison with the interaction potential of the spontaneously dissolved α -CD solutions shown in Fig. 2(a), the measured $\Phi_{Pr}(h)$ under the conditions of RAB moves closer and deeper because more bulk-free nanobubbles are expected to be generated in aqueous solution by directly air injection. Interestingly, $\Phi_{Pr}(h)$ moves closer and closer after each cycle of RAB, indicating that the regeneration of the bulk-free nanobubbles, especially their concentrations and size distribution could not be well controlled in this experiment. However, because the nanobubbles can be deliberately removed and regenerated, the measured total interactions $\Phi(h)$ here can be reversibly tuned between $\Phi_{Ab}(h)$ and $\Phi_{Pr}(h)$ by simple varying the aqueous solutions with the existence of nanobubbles or not, which can never observe in the conventional mixture of colloid and nonabsorbing polymers.

In order to have a better understanding the effects of the presence of nanobubbles on the interaction between the particle and flat surface, each measured $\Phi_{Pr}(h)$ was subtracted by $\Phi_{Ab}(h)$ so that the net interaction, $\Phi_{Dep}(h)$ ($\Phi_{Dep}(h) = \Phi_{Pr}(h) - \Phi_{Ab}(h)$) was obtained and plotted in Fig. 3. It clearly shows that with the existence of nanobubbles, there has an attraction, which is continuous and with the measurable distance up to *ca.* 200 nm. The attractive interaction is weaker in the spontaneously dissolved α -CD process, but those by reintroduction of

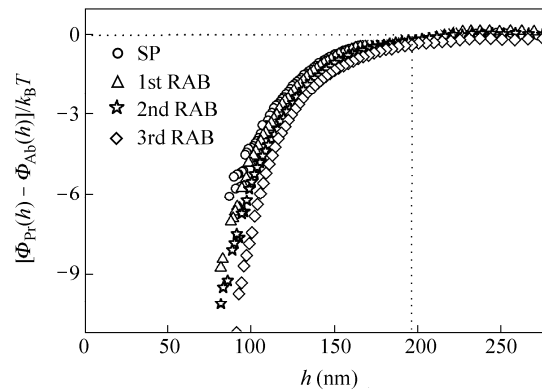


Fig. 3 Depletion potential ($\Phi_{Dep}(h) = \Phi_{Pr}(h) - \Phi_{Ab}(h)$) between the PS particle and glass surface with the presence of bulk-free nanobubbles (Reproduced with permission from the literature [34])
1st, 2nd and 3rd present the corresponding ordinal number in subtraction; The dot line is a guiding line to show the range of the attraction.

the nanobubbles under three different cycles are similar, revealing that the range of the interaction between the particle and flat surface is nanobubble concentration dependent as more nanobubbles can be generated by direct air injection. Note that such long-range attraction is quite weak if we compare it with the interaction induced by bridging of interfacial nanobubbles^[34]. What is the nature of such long-range attractive interaction? As we have mentioned above, nanobubbles free in aqueous solution are negatively charged. Moreover, the negatively charged PS particle and the hydrophilic glass surface were used in the TIRM measurements. Therefore, we can reasonably assume that charged nanobubbles might not adsorb to both the particle and glass surface. In this way, we conjecture that the measured attraction may be the depletion attraction caused by the exclusion or depletion the charged nanobubbles from the gap between the PS particle and glass surface.

In order to confirm our hypothesis, we applied a classical depletion potential function to fit the measured profiles shown in Fig. 3, namely

$$\begin{aligned} \Phi_{\text{Dep}}(h) &= -\pi\Gamma[(a+\Delta)(h-2\Delta)^2 + \frac{1}{3}(h-2\Delta)^3] & \text{for } 0 < h < 2\Delta \\ &= 0 & \text{for } h > 2\Delta \end{aligned} \quad (4)$$

where Γ is the osmotic pressure of the bulk solution, a is the radius of the colloidal particle (here $a = 3.2 \mu\text{m}$) and 2Δ is the depletion region^[39]. The fitting gives the depletion region (2Δ) and osmotic pressure (Γ) as $(190 \pm 10) \text{ nm}$ and $0.2\text{--}0.3 \text{ Pa}$, respectively. The fitted depletion region almost equals to the diameter of nanobubbles ($2R_b$) and thickness of the nanobubbles's double layer (κ^{-1}), i.e., $2\Delta \sim 2R_b + \kappa^{-1}$, indicating that our experimental results are in good agreement with the theoretical values predicated by Eq. (4). Therefore, we conclude that the origin of the measured weak attraction is induced by the depletion of negatively charged nanobubbles from the gap between particle and glass surface. Under this condition, there will be a solvent-rich region between the PS particles and flat surface that is surrounding by a bulk fluid of the nanobubbles. Fig. 4 has schematically showed that this can lead to an imbalance osmotic pressure inside and outside the gap and results in a net attractive

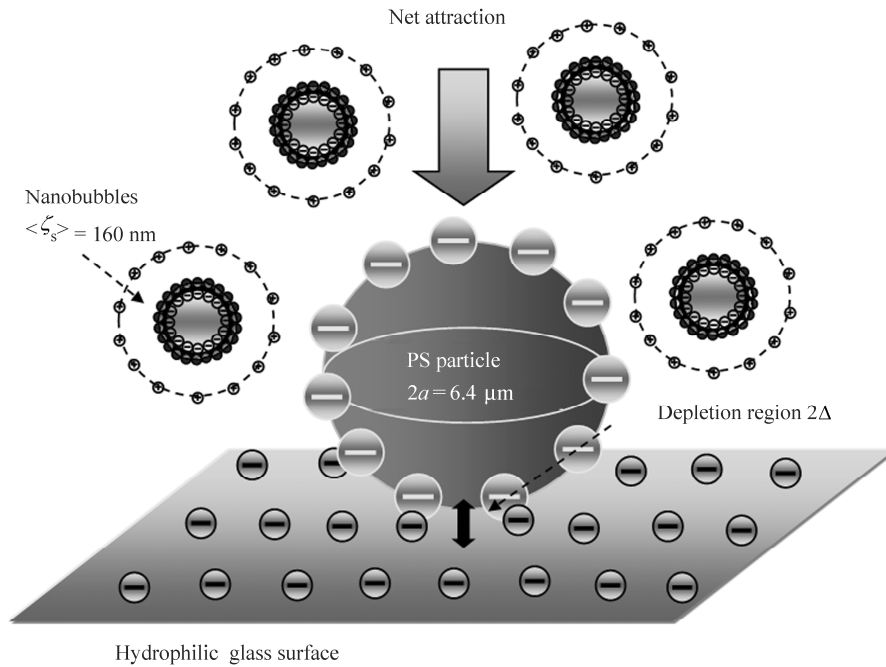


Fig. 4 Schematic shows the long-range depletion attraction induced by bulk-free nanobubbles in α -CD aqueous solutions (Reproduced with permission from the literature [34])

“−” Presents negative charge; “+” Presents counterion (not in a proportional scale).

osmotic force that pushes the PS particle to the surface.

Because of the obtained values of Π , we further tried to estimate the number density of the bulk-free nanobubbles (n_b) by following equation^[40, 41]

$$\Pi = k_B T (n_b + \frac{Z^2 n_s^2}{4n_s}) \quad \text{for } n_s > Zn_b \quad (5)$$

where Z is the total charge number of a nanobubble and n_s is the number density of counterions. Note that for α -CD in 0.1 mmol/L NaOH solution, where $n_s \approx 6 \times 10^4 \mu\text{m}^{-3}$ and zeta-potential of a nanobubble was found as -40 mV, the total charge number and surface charge density in a nanobubble can be estimated as $Z \approx 3 \times 10^3$ and *ca.* 0.02 e nm^{-2} , respectively. In this way, n_b can be determined as $1.2\text{--}1.4 \mu\text{m}^{-3}$, which is relatively low in the aqueous solution. However, the corresponding induced osmotic pressure is high because the osmotic pressure can be dramatically enhanced (*ca.* 50 times) by the presence of counterions around the nanobubbles. Importantly, it is worth to point out that the found value is still much lower than the osmotic pressure attributed by the dissolved gas. This might provide one explanation why it is always no easy to completely remove the nanobubbles by degassing either surfactant-water or colloidal dispersions.

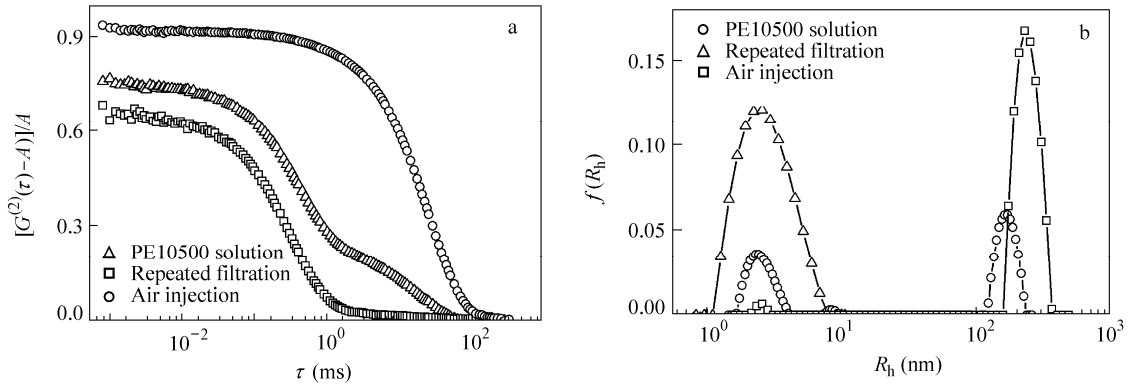


Fig. 5 Normalized intensity-intensity time correlation functions ($[G^{(2)}(\tau) - A]/A$) and their corresponding average hydrodynamic radius ($\langle R_h \rangle$) of PE10500 triblock copolymer in 0.2 mmol/L NaCl solution before and after 200 times filtration as well as directly air injection (Reproduced with permission from the literature [35])

In another similar study based on Pluronic PE10500 copolymer system, we use TIRM to directly measure the interactions between a $6.0 \mu\text{m}$ PS sphere and a hydrophilic silica plate in the presence of Pluronic PE10500 triblock copolymer aqueous solution^[35]. The existence of nanobubbles in PE10500 triblock copolymer solution was proved by laser light scattering (LLS) measurements through repeated filtration and air injection (Fig. 5). Figure 5 shows that the measured normalized intensity-intensity time correlation functions and their corresponding average hydrodynamic radius ($\langle R_h \rangle$) of PE10500 triblock copolymer in 0.2 mmol/L NaCl solution contain more than one relaxation modes. The average hydrodynamic radius R_h of the fastest mode is *ca.* 2.7 nm, which is the size of free individual PE10500 molecules in the aqueous solution, and an intermediate peak of *ca.* 7.0 nm is due to the formation of micelles^[42, 43]. On the other hand, there is a slow mode with an average hydrodynamic radius of *ca.* 166 nm, and they may be those nanobubbles freely in the aqueous solution. The direct evidence is the slow mode can be successfully removed after repeated filtration by using a tubing flex pump. In a repeated filtration, the solution was circulated to pass through a $0.45 \mu\text{m}$ hydrophilic filter with no significant effect on the PE10500 copolymer concentration as PE10500 is a relatively small molecule. The slow mode did not reappear in the solution after its removal; however, it comes back after injecting fresh air into the slow-mode-free solution, as shown in Fig. 5. The peak related to this new slow mode is generally larger and broader than those spontaneously dissolved PE10500 solution because that the formation of nanobubbles is hard to be fully controlled. As a consequence, we conclude that the slow mode observed in the spontaneously

dissolved PE10500 copolymer solution in 0.2 mmol/L NaCl solution is related to free nanobubbles which has size larger than 100 nm. The stabilization of these nanobubbles free in solution can be attributed to the existence of these small amphiphilic PE10500 triblock copolymer in the bulk and on the interface.

Figure 6 shows that in the absence of PE10500 triblock copolymer, there are just two contributions to the interactions between the PS particle and flat surface in 0.2 mmol/L NaCl aqueous solution, namely, the electrostatic double layer repulsion on the left side of the minimum and gravitational energy on the right side of the minimum, which can be described by Eq. (3). After pumping the spontaneously dissolved PE10500 copolymer in 0.2 mmol/L NaCl solution through the sample cell and waited for *ca.* 12 h, it is observed that the measured potential profile is deeper and shifts closer to the flat surface, indicating that the addition of PE10500 copolymer solution has induced an attraction. On the other hand, after rinsing the sample cell again with 0.2 mmol/L NaCl solution, the measured potential profile moved to larger separation. In other words, the induced attractive force disappears. As the nanobubbles free in PE10500 aqueous solution have just been shown to be negatively charged and we have used sulfonated PS particle and the hydrophilic glass surface (both are negatively charged) in the TIRM measurements, we can reasonably assume that charged nanobubbles will not preferentially absorb to both the particle and glass surface^[35]. In this way, we conjecture that the measured attraction shown in Fig. 6 may be the depletion attraction caused by the exclusion or depletion the large charged nanobubbles from the gap between the PS particle and glass surface as the separation distance between the particle-surface (*ca.* 133 nm) is smaller than the physical size of the charged nanobubbles (*ca.* 166 nm) under the condition of 0.2 mmol/L NaCl aqueous solution^[36]. By consideration that PEO-PPO-PEO is the most commonly used industrial stabilizer, our above results thus shed light on the stability of application of colloid-polymer mixtures in the industry.

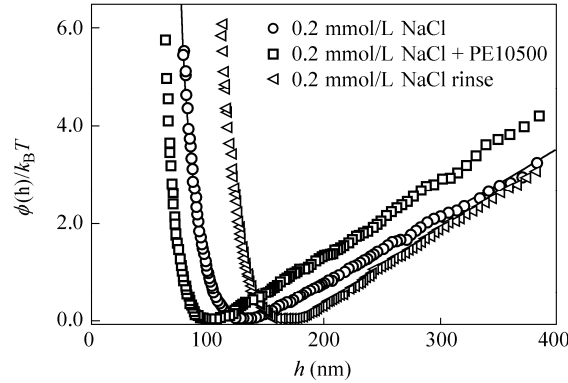


Fig. 6 The measured interaction potentials ($\Phi(h)/k_B T$) between a PS particle and a glass surface under different conditions (Reproduced with permission from the literature [35])

$\Phi_A(h)/k_B T$: the interaction potential between the bare PS particle and surface in 0.2 mmol/L NaCl solution; $\Phi_B(h)/k_B T$: the interaction potential between the PS particle and surface after pumping the spontaneously dissolved PE10500 triblock copolymer in 0.2 mmol/L NaCl solution; $\Phi_C(h)/k_B T$: the interaction potential between the PS particle and surface after rinse with 0.2 mmol/L NaCl solution; The solid line is a theoretical fitted curve from Eq. (3).

Depletion Attraction Induced by pH-sensitive Microgels

Despite the nanobubble-induced depletion attraction has been thoroughly discussed, however, since the size and concentration of nanobubbles were not under a well-controlled manner by spontaneously formation, the range and strength of depletion force could not be finely tuned. Inspired by these limitations, we have synthesized the microgel particles, poly(*N*-isopropylacrylamide-*co*-methacrylic) (PNIPAM-*co*-MAA) to mediate the depletion interaction. One advantage of using PNIPAM-*co*-MAA microgel particles as the depleting agents lies in the fact that PNIPAM-based microgels exhibit an extreme response to changes in pH, which can lead to dramatic changes in particle size. TIRM was then applied to directly measure the pH-triggered depletion interaction acting on a sphere immersed in the solution of such microgels close to a flat glass surface^[37].

Figure 7 shows that the interaction potentials between the PS sphere and surface in the presence of swollen microgels are significantly changed. Note that the contribution of gravity has been subtracted from all potentials since the same PS sphere was used. It clearly shows that the addition of swollen microgels induces a long-range attractive force occurring at separation distances ranging from 150 nm to 250 nm, which may be contributed to either bridging or depletion. This attractive force is seen to increase with increasing swollen microgel concentration, while the separation distance decreases. Moreover, at higher swollen microgel volume fractions, the attractive well becomes narrow and steep as well as acting over smaller separation distances. It is expected that the microgels at pH 9.43 are negatively charged due to the dissociation of $-\text{COOH}$ on the network chains. The selected PS sphere and the hydrophilic glass surface are also negatively charged during the measurements. Thus, we can reasonably assume that microgels will not preferentially absorb to either the PS sphere or glass surface and exclude the bridging effect. Meanwhile, the alternation of the electrostatic interaction between the PS sphere and the flat surface after introducing the microgels is ignorable which is confirmed by comparing the electrostatic parameter B according to Eq. (3) of the electrostatic part of the interaction before and after introducing the microgels, where the conductivities are kept to be the same. To confirm the hypothesized pH dependence, we rinsed the sample cell with a large amount of deionized water and then pumped the microgels with solution pH 4.51. Figure 7 shows that the measured long-range attractive force disappears and leaves only the electrostatic repulsion. We related this effect to the collapsed microgels, with the hydrodynamic diameter smaller than the sphere-surface distance, which are able to move into the gap region. The imbalance in osmotic pressure inside and outside the region will disappear as will the depletion attractive force. Note that this attractive force can be regenerated by reintroduction of microgels at high pH condition, and the process is reversible, indicating that microgel-triggered depletion attractive force is pH dependent. The fitting of the net attraction induced by microgel solution at pH = 9.43 using Eq. (4) gives 2Δ *ca.* 250 nm and Π *ca.* 0.4 Pa. Note that the fitted depletion region can be compared to the hydrodynamic diameter of the swollen microgels, suggesting that our experimental results are in good agreement with the theoretical values predicted by Eq. (4).

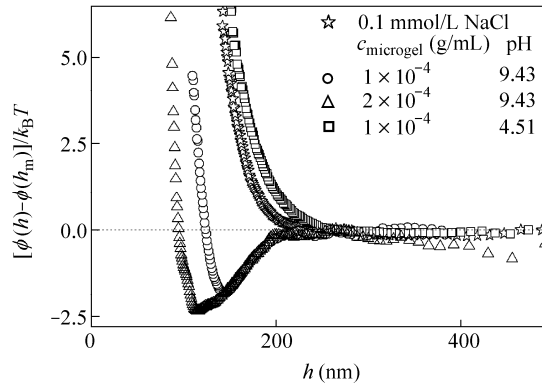


Fig. 7 The measured interaction potentials ($\Phi(h)/k_B T$) between the polystyrene sphere and flat surface under different environmental conditions (Reproduced with permission from the literature [37])

CONCLUSIONS

In summary, by using single-particle force microscopy, TIRM, we have directly measured the interactions between a free-moving particle and a flat surface with the presence or absence of the nanobubbles in a controllable way. The thickness of the depletion region was measured, and the results are consistent with theoretical predication. Moreover, it is shown that nanobubble induced depletion attraction are very weak, but the measurable distance can be up to 200 nm. The origin of such attraction supposedly comes from exclusion or depletion of the charged nanobubbles from the gap between particle and flat surface. By considering that the formation of bulk-free nanobubbles in various aqueous solutions, including surfactant-water, colloids and

emulsions, is a spontaneous process, our results thereby provides the first experimental evidence to the ongoing controversial debates over the unexpected emulsification and stability of oil emulsion in highly degassed water. Moreover, we report the first direct measurement of the pH-triggered depletion interaction potentials between a polystyrene sphere and a flat substrate as mediated by PNIPAM-*co*-MAA microgels. When the solution pH of the microgel dispersion was high, an attractive force occurring at separation distance of 150–250 nm was observed and increased in magnitude with increasing microgel concentrations. However, this depletion force disappeared as soon as changing the microgel dispersion to a low pH solution. The current study demonstrates the ability to quantitatively measure and reversibly control $k_B T$ -scale depletion attraction as a function of solution pH. Therefore, it offers a promising route to use such tunable depletion forces in the formation of complex colloidal assemblies.

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