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Depletion versus stabilization induced by polymers and nanoparticles: The state of the art

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ABSTRACT

The entropic depletion interaction has been the subject of several studies over the past decade because it plays an important role in many industrial applications and also involves in controlling biological interactions. In this short review, we discuss recent developments associated with using nonintrusive optical techniques for directly measuring k_BT-scale depletion interaction. In particular, we limit the scope of this review to the use of total internal reflection microscopy (TIRM) for quantitative measurements of interactions between a single, colloidal particle and a flat surface mediated by the presence of neutral polymers, polyelectrolytes, and charged nanoparticles with different softness based on our recent works. Finally, we conclude with some perspectives on future research efforts in this field.

1. Introduction

Colloidal suspensions are widely used in food industry, medical treatments, petroleum exploitations, and manufacturing industries [1–3] so that they have been received broad attentions for many decades. The stability, or so-called phase behaviors, plays an essential role for those applications. The simplest case of a colloidal suspension is one-component system: colloids with a uniform size are suspended in an aqueous environment. The phase behavior of one-component system can be readily appreciated and predicted using the theory that was developed by Derjaguin, Landau, Verwey, and Overbeek (DLVO) [3–5], in which the repulsion arising from the overlap of double-layers in a colloidal pair and the ubiquitous attraction from van der Waals are counted to predict whether the system could stay at a single phase (stable) or would phase separate (unstable). In real situation, however, multi-components systems are often met, where the system contains two or more colloidal components that possess distinctive physical or chemical properties. Aside from the specific interactions might arising from those different components, DLVO theory is not sufficient to predict the phase behavior because adding another component or more components to a one-component system will lead to an additive interaction, the so-called exclusion effect, arising from the entropy of mixture. A well-known example is binary mixture of two colloids with distinctive size, where the colloids with larger size will be depleted to squeeze more volume for those smaller colloids, resulting in increase of the entropy of mixture. This additive interaction or smaller colloids usually is termed depletion or depletants. More practical example is the adding nonadsorbing polymers leads to the creaming and phase separation of natural rubber [6].

Asakura and Oosawa [7] have theoretically quantified the depletions in 1950s by means of an argument based on asymmetrical osmotic pressures. They argued that in a mixture consisting of large particles and nonadsorbing small pieces, if the depletion zones of large particles overlap, the concentration gradient of small ones takes place between inside and outside of the overlap layers. Consequently, the imbalance of osmotic pressure causing by the concentration gradient induces a net attractive force to pull the large particles close to each other. In AO model, the depletion interaction between large spheres is described as

$$\frac{\phi_{\mathrm{dep}}(h)}{k_{\mathrm{B}}T}=\begin{cases}-2\pi n_p a R^2\left(1-\dfrac{h}{2R}\right)^2, & \& \ 0\le h\le 2R\\ 0, \quad \& \ h\ge 2R\end{cases}$$

where a is the radius of large particles, and n_p and R are the number density and the radius of the depletant, respectively. Here, the depletant is considered as ideal hard spheres, and $a \gg R$. In 1970s, Vrij [8] proposed to treat the polymer depletants as penetrable hard spheres (PHS), which subsequently was found to be better for describing ideal polymer chains. On the other hand, many properties of the depletant, such as concentration [9,10], charge [11,12], shape [13,14], and softness [15,16], were independently taken account into the calculation of depletion interaction.

Experimentally, it is rather difficult to directly measure the depletion force since this interaction is very weak, in the scale of several kT. A few techniques such as surface force apparatus (SFA) [17,18], atom force microscopy (AFM) [19], optical tweezers (OT) [20], magnetic chaining technique [21], and total internal reflection micocopy (TIRM) [22–24] have been applied to measure the depletion interaction. Most studies

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have firstly focused on measuring the depletion interaction induced by charged [17] or concentrated depletants [19] because the magnitude of the weak depletion interaction could be enhanced under these conditions. Neutral polymer chains were later applied as depletants but the adsorption in the system became a matter of debate [20,25,26•,27]. Recently, various depletants such as supramolecular polymers [28], nanoparticles [29,30], and microgel [31,32] were also used to investigate the depletion interaction. Meanwhile, the charge, shape [33], and polydispersity [22] of depletants were also extensively discussed in the experiments. Therefore, the studies have shifted from the measurements of depletion forces or the critical conditions to induce depletion interaction to control the depletion interaction.

In this short review, we discuss recent experimental explorations in the use of TIRM to nonintrusively measure the depletion interaction. This review is organized as follows: we first provide a brief introduction of TIRM since this is the main method used in our group to study colloidal interactions. We then review recent development in using of TIRM for measuring the particle–surface interactions mediated by the presence of different kinds of depletants, including neutral polymer chains, charged polymers, and charged nanoparticles with different softness based on our recent work. Finally, we provide a summary and some perspectives on future research efforts in this field.

2. Total internal reflection microscopy (TIRM)

TIRM is a technique used to measure directly the mean potential of the interaction between a microscopic colloidal particle and a glass plate. The details regarding to TIRM and its application in measuring different colloidal, surfaces, and external forces can be found in several reviews [34••,35]. Briefly, in TIRM, a laser beam is totally reflected from a surface, but an extremely small amount of light, called as an evanescent light, diffuses into the interface. Its intensity exponentially decreases as the distance away from the interface increases. When a particle is close to the interface, it scatters this light. By measuring the scattering intensity, we can monitor how far the particle is away from the interface. The particle can be controlled by optical tweezers or an electromagnetic force. In this way, TIRM can probe the force that levitates a Brownian particle above a glass substrate (the interface). In equilibrium, the particle elevations are distributed according to Boltzmann statistics; so a histogram of the heights can be used to map the potential energy profile of the particle

3. Depletion induced by neutral and charged polymers

3.1. Neutral polymers

As a popular model polymer, polyethylene oxide (PEO) is well soluble in aqueous and organic solvent, such that the interactions between colloids mediated by the PEO polymers were directly measured in past decades [26•,36•]. However, the interaction resulted from the existing of PEO polymer appeared to vary significantly from study to study. For example, Bechinger et al. [36•] performed measurements on the interactions between a charged polystyrene (PS) particle and a glass surface in dilute PEO solutions with TIRM, and they concluded the occurrence of depletion force induced by free PEO chains in bulk solution. However, depletion interaction was not found by Kleschanok et al. [26•] in the same system using TIRM. Conversely, a steric repulsion due to the formation of a brushlike PEO layer on the PS particle and the glass surface was proposed. Recently, we have used TIRM to systematically measure the interaction between a free-moving PS sphere and a flat hydrophilic glass surface in the solution contain PEO polymer with a broad range of concentrations [37]. Our results revealed that the particle–surface interactions are highly dependent on polymer concentration. As shown in Fig. 1, when the PEO concentration is $C/C^* < 0.51$, the interactions between the particle and surface are still dominated by repulsive forces, originating from double layer repulsion, in line with the classical DLVO theory. When the PEO concentration was increased to $0.51 < C/C^* < 0.85$, a long-range depletion was detected and the magnitude increased as concentration increased. However, this depletion was not well described by simple AO model. The reasons may be attributed to the fact that the size of the polymer chain can no longer be used to represent the characteristic length of this system as concentration increases, and the polydispersity as well as the soft nature of the polymer chains that are not included in the simple AO models. When the PEO concentration was further increased above C^* ($1.7 < C/C^* < 2.56$), the mesh size of the PEO decreased from 67.4 to 49.6 nm, and we found that the attractive depletion became weaker and disappeared finally as the correlation length of PEO decreases in the overlap region so that the polymers can get into the gap between the probe particle and the glass surface. At much higher PEO concentration, $C/C^* \sim 3.40$ and the mesh size of PEO was reduced ~40.0 nm, and oscillatory structural force was found. This systematic study clearly indicated how PEO concentration can affect the interactions of aqueous colloidal systems, and this displaced promise for further design and monitoring of the interactions between surfaces coated with nonionic polymers.

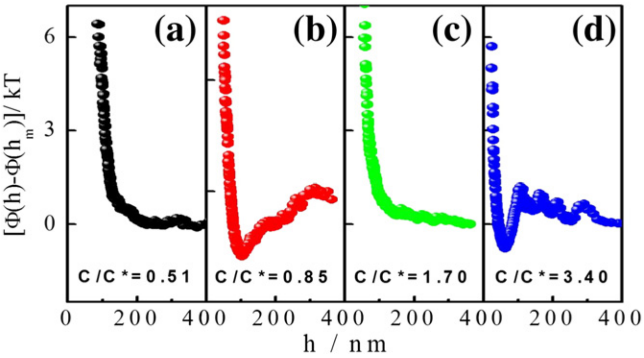

Fig. 1. Potential profiles between the PS latex and the glass slide in PEO aqueous solution with increasing PEO concentrations from (a) to (d) where the gravity part have been all removed [37•]. At low polymer concentration shown in (a), the interaction between two surfaces in the presence of PEO is mainly dominated by repulsive forces, originating from diffuse layer overlap. As polymer concentration increases, a long-range depletion attraction sets in as shown in (b). However, when the concentration continues to increase, the depletion attraction greatly decreases as (c). At very high concentration, oscillatory structural force is detected as shown in (d).

3.2. Charged polymers

Charged polymers such as polyelectrolytes also have been widely applied in industrial applications such as wastewater treatment, paper making, and formulation of foods, paints, or cosmetics [38–41]. The measurements of interactions related to polyelectrolytes in colloidal systems give important guidance on further applications of polyelectrolytes. Recently, we used TIRM to measure the interaction forces between surfaces in the presence of unadsorbed cationic poly(ethylenimine) (PEI) chains, which have been widely used to tune the stability of colloidal suspensions and have also gained importance as gene carriers in biomedical applications [42•]. Fig. 2 illustrates both the salt and free PEI concentration dependence of the induced interaction at low ionic strength solutions. The results showed a reproducible long-ranged attraction (appeared at $h > 60$ nm, ~1.5 to 2.0 k_BT) induced by the addition of free PEI chains at PEI concentrations as low as 10 ppm. Moreover, this attractive force increases with increasing polyelectrolyte concentration and increasing background electrolyte ionic strength. Since the adsorbed PEI layers on PS sphere and glass slide surface are very thin (~4–6 nm) compared to the separation distance (>60 nm), the presence of steric forces, direct bridging forces or midplane crossing bridging forces is highly unlikely. We suspect that this attractive force might originate from depletion. However, the single PEI free chain typically has a size around 4 nm; it is hard to imagine how such small polyelectrolytes