Monitoring particle adsorption by use of laser reflectometry near the critical angle

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We investigate the use of laser reflectometry near the critical angle to monitor particle adsorption onto a flat glass surface. Experimental results show that positive particles are adsorbed onto the glass surface and that their adsorption kinetics depend strongly on the volume fraction occupied by the particles in suspension but not appreciably on the particle size. The reflectance near the critical angle is dominated by the particles on the surface, with the contribution of the particles in suspension being very low. We compare the reflectance change near the critical angle with the change in reflectance near the Brewster angle when particles are adsorbed onto the glass surface. We find that reflectometry near the critical angle is 3000 times more sensitive than it is near the Brewster angle. Some optical images are presented to validate our results. © 2004 Optical Society of America

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1. Introduction

The study of adsorption of particles onto surfaces is relevant to colloid science and biophysics, and it is related to a variety of practical problems such as chemisorption, catalysis, and biopolymer immobilization. Particle adsorption at the solid–liquid interface refers to a process that leads to an increase in the particle concentration in the region adjacent to the solid interface. In the absence of a chemical reaction and of convective fluxes, adsorption is driven by van der Waals and electrostatic forces and is modulated by Brownian motion and hydrodynamic interactions. Particle adsorption depends on the bulk concentration near the surface, the form of the particles, and the forces involved in the interaction among particles and between the particles and the surface. At present, particle adsorption cannot be described by a general theory, and it is, in fact, a complex problem. Random sequential adsorption (RSA) is the simplest model used to describe this process. It transforms the physical problem into a statistical one that describes the particle adsorption as a random process. This model consists of placing the particles on the surface, one by one, under the following two conditions: (i) once a particle is adsorbed, its position is permanently fixed and (ii) two particles do not overlap in the range of their interaction. These conditions are satisfied when the particle–surface interaction is dominant and when there is no diffusion of the particles onto the surface. The RSA model implicitly assumes that the particles are adsorbed in a monolayer. This model has been applied to the adsorption of biological and colloidal particles onto a flat surface ever since it was experimentally observed that these systems are irreversibly adsorbed in monolayer form onto the surface. When the interaction among particles is due only to particle volume, RSA is able to predict the maximum surface coverage \( \theta_{\text{max}} \), also called the jamming limit, of 0.547 for this adsorption process.  

Interacting particles can be studied with this same formalism by definition of an effective interaction range. A particle adsorbed onto the surface produces an exclusion volume, defined by the interaction with other particles, that can be greater than its own volume. Adsorption kinetics is also an important topic. A generalized Langmuir equation has been proposed to
describe this process.\textsuperscript{1,10} The solution of this equation depends strongly on the surface exclusion effect [condition (ii) above]. In the simplest case, the RSA approach, the dependence of the surface coverage ($\theta$) on time yields the power law $\theta_{\text{max}} - \theta = t^{-1/2}$ near the jamming limit.\textsuperscript{11,12}

RSA is a special case of particle adsorption, but other physical situations can be present. Particle adsorption can be limited by the diffusive process of particles from the solution to the surface.\textsuperscript{12} Furthermore, particle diffusion on the surface can be faster than particle adsorption, allowing a thermodynamic equilibrium of the particle on the surface.\textsuperscript{12,13} In both cases maximum adsorption and kinetic behaviour are different from those in the RSA model. Indeed, the behavior of multilayers formed by particles of different charges\textsuperscript{14} should be different from that predicted by the RSA model. To validate the use of the models to solve a variety of problems associated with particle adsorption, we require experimental techniques that measure the surface coverage fraction in real time with a minimum perturbation to the system.

Optical methods have shown a good performance in this type of study. Experiments can be carried out \textit{in situ} without any special preparation, and data acquisition can be relatively fast. Therefore optical methods may allow the determination of not only the final state of the film but also the kinetics of the adsorption process. Optical microscopy has been previously used to study the particle distribution on a surface covered by large particles (>1 $\mu$m) under the influence of gravity,\textsuperscript{15} as well as adsorption in the presence of convective forces.\textsuperscript{16} Optical reflectometry\textsuperscript{17} and ellipsometry\textsuperscript{18} have also been used to study particle adsorption. One advantage of these techniques is that they can be used to study the adsorption of small particles (<1 $\mu$m). However, it is not a trivial task to analyse the adsorption of particles that form layers on a surface by use of reflectometry and ellipsometry. Analysis of the experimental data obtained with these techniques requires the use of models for interpretation.\textsuperscript{18}

A simple technique for real-time monitoring of an adsorption process that may offer high sensitivity is the use of laser reflectometry near the critical angle (LRCA). Basically one needs a prism that is in contact with a suspension of particles and that measures the reflectance of a laser beam incident near the critical angle on the prism side. This technique has already been used to measure variations in the effective index of refraction of a suspension of particles,\textsuperscript{19} in which it was observed that particle adsorption onto the prism interface produced strong changes in reflectance.

The purpose of the present study is to establish the applicability of LRCA to monitoring in real time the adsorption of particles onto a flat interface and to evaluate this technique's sensitivity. To this end, we prepared water suspensions of electrically charged latex particles and placed them in contact with an optical prism while measuring the reflectance of a laser beam near the critical angle as a function of time. Positive and negative particles were used in this study. The volume fraction of particles was kept low so that the measured signals were due mainly to the particles adsorbed onto the interface. The adsorption of particles forming a monolayer on the glass interface was confirmed by optical microscopy. Sequential injections of positive and negative particles were also carried out in this study.

2. Experiments

A. Latex Particles and Cleaning Process

Latex particles were made of poly(styrene) by surfactant-free emulsion polymerization. Positive and negative particles were synthesized by use of 2-2’-azobis(2-methylpropionamidine) dihydrochloride and persulfate of potassium, respectively, and the following recipe: water, 18.0 ml; styrene (monomer), 1.0 ml; and different initiator amounts depending on the electrical charge and size of the particle. The synthesis was carried out at 70 °C and 750 rpm for 24 h; details of the polymerization for negative particles are given in Ref. 20. The synthesis produced monodisperse particles from 100 to 450 nm in diameter. Particle size was measured by dynamic light scattering and verified by atomic force microscopy (AFM, Nanoscope II). AFM images of some of the positive and negative particles used in this study are shown in Fig. 1. The polydispersity of these particles is estimated to be less than 4% for negative particles and less than 10% for positive particles from the dynamic light-scattering measurements. A summary of the particle diameter, the electrical charge, and the volume fractions used in the experiments is presented in Table 1. The particle refraction index of the poly(styrene) particles is 1.59.

In this study we used a cylindrical prism (BK7 glass, CIO, Guanajuato, Mexico) for the laser reflectance measurements and glass slabs (Corning, Marlborough, Massachusetts) with an area of 1 cm × 6 cm as additional probes during the experiments. These glasses were extensively cleaned before use in the reflectance experiments. They were immersed in a 50%–50% solution of hydrogen peroxide (H$_2$O$_2$) and sulfuric acid for 60 min. The glasses were then rinsed with millipore water and immersed in a detergent solution (Micro, Burlington, New Jersey) of 1%
volume at 80 °C for 20 min. Finally they were rinsed many times with millipore water. Glasses were used immediately after this cleaning process.

B. LRCA Technique

We used the experimental setup depicted in Fig. 2, consisting of a half-cylinder prism (n1 = 1.51) inserted laterally on a cylindrical container made of Teflon. The inner volume of the container was ~15 ml. The prism was placed on top of a high-precision goniometer (Newport, Irvine, California; 1 arc min as minimum scale). The base of the prism was a wall of the container. There was enough room in the container to place glass slabs as additional probes for particle adsorption. A linearly polarized He–Ne (Coherent, Santa Clara, California) laser beam (λ = 0.638 μm) of Gaussian cross section with a diameter of ~0.85 mm was reflected from the base of the prism. The system was aligned so that the point of the laser reflection on the base of the prism was along the axis of rotation of the goniometer, and the laser tube was rotated to yield TM polarization upon reflectance. Then the angle of incidence was adjusted by rotating the goniometer. Thus the laser remained fixed in this arrangement. The reflected laser beam was redirected into a silicon photodetector (PD1). The photodetector generated a current signal, which was amplified and converted into a voltage signal. To remove laser-induced drifts and noise, we divided the signal voltage from PD1 by using a reference voltage that is proportional to the output power of the laser. We obtained the reference voltage by using a beam splitter to divide the laser beam before it entered the half-cylinder prism and by measuring the optical power of the reference beam with a second photodetector (PD2). The output signal was taken as the ratio of the signal and reference voltages. The output signal was measured with a 6-digit voltmeter. During the experiments in this study, the output voltage was read and registered by a computer every second. Each reading corresponded to the average of the output voltage over a fraction of a second, and we refer to each measurement as the dc voltage of the output signal.

In the experiments performed in this study, we fixed the angle of incidence at the critical angle, \( \theta_c \), for the prism interface when the external medium is water. The critical angle is obtained from Snell’s law as \( \sin(\theta_c) = n_2/n_1 \), where \( n_1 \) and \( n_2 \) are the refraction indices of the cylindrical prism and water, respectively. To locate the critical angle in a precise and reproducible way in our experiments, we incorporated into our experimental system the possibility of modulating in real time the angle of incidence. This is accomplished by reflecting the laser beam before it enters the prism, using a piezoelectric driven mirror (M1) controlled with a function generator. By adding a small sinusoidal modulation to the angle of incidence, we can measure the reflectivity and its angle differential in a very precise way. In this case the signal of the photodetector consists of an ac signal superposed to a dc signal. At a given angle of incidence, the dc signal is proportional to the reflectivity, whereas the amplitude or the rms value of the ac signal is proportional to the angular derivative of the reflectivity. In our experiment the bulk volume fraction was low, and the critical angle determined for water was not strongly modified by the presence of particles in suspension.

When particles are adsorbed at the base of the prism, the reflectance at the critical angle decreases as a function of the surface coverage fraction owing to scattering of light from the particles. Light incident on the particles, either as propagating or evanescent waves, is scattered in all directions, and therefore optical power is removed from the reflected beam. The reduction of the reflected power for a given coverage fraction is described as a function of the particle size. For spherical particles, the scattering of light by the particles is dictated by Mie theory. In this paper we do not attempt to model theoretically the experimental curves. We first aim to demonstrate the applicability of the technique to obtain qualitative information about the adsorption process.

C. Sample Preparation and Measurement Procedure

Particle injection was carried out in a setup shown schematically in Fig. 3. Particle adsorption occurred on the base of the half-cylinder prism and on some probes introduced into the cell. A 20-ml liquid
sample was injected into the container, and the suspension flowed by gravitational force into the cylindrical container. The level of the liquid sample in the cylindrical container was controlled by the level of the hose used to drain the cell. The angle of incidence was fixed at the critical angle. This angle was determined by modulation of the angle of incidence and by location of the angular position for which the ac signal in the photodetector is maximum. Once the angle of incidence was fixed, the modulator was turned off. Then, the particles in suspension were injected by adding the particle suspension to container A and by draining the water from the cylindrical container. The reflectance was recorded a few minutes before particle injection to monitor the entire adsorption process. For sequential injection of positive and negative particles, positive particles were displaced with water and negative particles were injected. This process was repeated with the positive and negative particles in alternate roles. All the experiments were carried out at room temperature.

D. Optical Microscopy Images

During the experiments the glass probes were removed from the container at different times along the particle adsorption process. These probes served to inspect the state of the particle adsorption at the corresponding times by optical microscopy. We used an inverted microscope (Olympus, Model IX71), the differential-interference-contrast–Nomasky technique, and an aprochromatic objective of 100:1 magnification to improve the contrast. Images were digitalized with a CCD camera (Hitachi, KP-161) and sent to a computer for analysis. Surface coverage was determined by use of software in the public domain.21

3. Results and Discussion

A. Particle Adsorption

Adsorption of positive and negative particles on bare glass surface was studied through independent experiments, the results of which are reported in Figs. 4 and 5. In these experiments the reflectance signal (dc voltage) for an angle of incidence near the critical angle was monitored as a function of time. We observed different signal behaviors, depending on the charge of the latex particles. The results shown in Fig. 4 correspond to positive particles of 258-nm diameter at a volume fraction of 0.1% denoted as (250 nm, 10%). The first arrow indicates when the particles were injected. After injection the reflectance signal started to decrease with time, implying that particle adsorption was in progress. Particle adsorption is expected for the positive particles because the glass surface is negatively charged. A cleaning process, which consists of gently rubbing a soft piece of cotton on the base of the prism, resets the adsorption process. Two cleaning processes, denoted by arrows, are shown in Fig. 4 at 734 and 1738 s. After cleaning, the signal returned to its original value, indicating a reversible process. A similar experiment was conducted for slightly smaller negative particles at the same volume fraction (250 nm, 0.1%), and adsorption is not observed. The reflectance signal at the critical angle versus time is plotted in Fig. 5. The first arrow indicates when the particles were injected; the second, when the cleaning process was practiced. Between these two arrows, the dc signal does not change, indicating that negative particles

Fig. 3. Schematic representation of the injection system and the homemade flux cell.

Fig. 4. Reflectance signal as a function of time for positive particles (diameter, 258 nm; volume fraction, 0.1%). The first arrow indicates when the particles are injected. The second and third arrows indicate when the film of particles adsorbed onto the surface is cleaned.

Fig. 5. Reflectance signal as a function of time for negative particles (diameter, 250 nm; volume fraction, 0.1%). The second arrow indicates when the surface is cleaned. The signal is constant between these two arrows, indicating that there was no adsorption.
are not adsorbed, as expected, and that negative particles are repelled by the negative glass surface. The dc signal remains stable and is modified only during the cleaning process conducted at approximately 697 s.

We can deduce from these experiments that electrical forces drive particle adsorption on the glass surface. Positive particles are adsorbed efficiently onto the surface and produce a variation in the intensity of the light reflected. Negative particles can be localized near the surface, forming a structure near the surface; however, particles do not get close enough to the surface to scatter light efficiently. Particle adsorption onto a bare glass surface is therefore referred to as adsorption of positive particles. It is interesting to observe the dependence of the adsorption kinetics on the volume fraction of the particles in suspension and on their size. The effect of the suspension volume fraction can be seen from the curves shown in Fig. 6. We followed the adsorption process at three different volume fractions, 0.023%, 0.07%, and 0.14% with particles of 129-nm diameter. We observe a clear difference between the curves. For example, at the 0.14% volume fraction, the adsorption stopped after 1400 s, whereas, for the 0.023% volume fraction, it takes 10 times longer for the adsorption process to stop, which is at ~14,000 s.

Although we do not expect a linear relation between the change in the reflected signal and the surface coverage fraction, we can define adsorption time ($\tau$) as the time it takes the reflected intensity to decrease to $e^{-1} = 37\%$ of its initial value. At this time, the light intensity has decreased appreciably and the signal is close to the plateau, where maximum adsorption occurs and an equilibrium is reached. The adsorption times obtained from the curves in Fig. 6 are 561, 1660, and 7257 s for volume fractions of 0.14%, 0.07%, and 0.023%, respectively. This dependence is easily confirmed because the curves reach the same plateau independently of the suspension volume fraction. This constant plateau also implies that the final reflectance near the critical angle is basically independent of the volume fraction of the suspended particles used in our experiments. Therefore the change in reflectance caused by the adsorbed particles on the surface is more important than the change in reflectance that is due to particles suspended in water.

Figure 7 shows the effect of the particle size on the particle adsorption process for particle diameters of 248 and 542 nm at 0.14% volume fraction. The effect of the particle size on the adsorption process is less evident in these experiments because reflectance curves depend on the particle size and because the plateau has a different value for each particle size. This difference could be due to the final surface density of adsorbed particles, but it could also be due to the difference in light scattered by particles of different sizes. The latter effect is probably the case, because $\tau$ for the two particles is comparable (233 and 337 s for particles of 129- and 271-nm diameter, respectively) and because the plateau decreases with particle size. Therefore the adsorption kinetics depend much less strongly on particle size than on the bulk volume density of the particles.

We designed a simple experiment to obtain progressive images of the adsorption process. Particles of 300 nm at a volume fraction of 0.14% were monitored, and three probes were removed at different times during the process. The images of these probes are shown in Fig. 8, in which we can observe the adsorbed particles at 900, 1800, and 3600 s in Figs. 8(a), 8(b), and 8(c), respectively. The coverage fractions for these images are determined to be 9%, 22%, and 37%, respectively. An image of the prism is also shown in Fig. 8(d). We can observe that the surface coverage is greater (47%) in the image and that the structure of particles is similar to that observed in the probes. These images allow us to make an important observation: Particles are adsorbed in the form of a monolayer on the glass surface. This indicates that changes in the reflectance...
are due only to an increase in the surface coverage that occurs during the adsorption process. From the image analysis we can also observe that the coverage fractions are lower than that predicted by the RSA approach. This result is due to the repulsive electrostatic forces that exist among particles and that limit a high surface coverage.

The reflectance variations reported above are due to two contributions: (i) from the particles dispersed in the solution (bulk contribution) and (ii) from particles adsorbed on the surface (surface contribution). It is clear that only the second contribution plays a role in the experiment with the negative particles discussed above, whereas both contributions are factors in the case of the positive particles. We have already observed that the surface contribution contributes mainly to the change in reflectance. Therefore an additional experiment should confirm this result. An adsorption curve for particles of 300 nm in diameter and 0.14% in bulk volume fraction is shown in Fig. 9. We stopped the adsorption process by injecting pure water to the container at 1323 s. We can observe a slight variation in the reflectance signal after the water was injected. This provides definitive evidence that reflectance at the critical angle is dominated by the surface contribution under the present experimental conditions.

A theoretical model is necessary to analyze quantitatively the adsorption curves presented in this study. Any proposed model has to address two main problems. The first involves correctly interpreting the reflectance variations and their relation to the surface coverage fraction of the adsorbed particles and their size (optical problem). The second one entails understanding the adsorption mechanisms that drive particle adsorption on the surface (physicochemical problem). Use of the LRCA technique for further investigation of the adsorption of particles requires our solving the first problem in order to study the adsorption process and to validate an adsorption model.

B. Sequential Adsorption of Positive and Negative Particles

The adsorption of particles for alternate injections of positive and negative particles was investigated by LRCA as well. The results are presented in Fig. 10. At the beginning of the experiment, when positive particles were injected, the reflectance signal decreased, indicating particle adsorption. Adsorption was
stopped by injecting water into the cell before the signal plateau had been reached. We note that after the water rinsing, the signal is constant. When the negative suspension injection is followed by a water rinsing, no changes in the reflectance signal can be observed. A second injection of positive particles again induces particle adsorption, which is stopped and stabilized by water rinsing. A second injection of negative particles is then administered, which is followed by particle adsorption that finally is stopped by an injection of water. This process could indicate multilayer buildup, which may be plausible in the present system. From the adsorption curve in this experiment, it is not possible to elucidate the structure formed by the adsorbed particles; however, it is clear that this LRAC technique was capable of following the alternate adsorption process. An optical microscopy image reveals that we produced agglomerates of positive–negative particles on the surface during this process. Figure 11 shows how the monolayer of the first positive particles is destroyed by negative particles that form agglomerates. Thus the fabrication of multilayers with these particles is not evident under the present experimental conditions.

C. Brewster Angle Versus Critical Angle

A comparison between the sensitivity of reflectometry near the critical angle and at the Brewster angle to particle adsorption yields interesting results. Reflectometry at the Brewster angle is currently used in the study of particle adsorption in a liquid–solid interface. Unlike the LRAC technique in which the reflectance has a maximum, the Brewster angle has a minimum reflectance $R_{\text{Brewster}}$ in the TM mode, as in the case of our experiments near the critical angle. For this comparison, we prepared a batch of particles of 430-nm diameter and at 0.14%. The adsorption curves obtained by reflection near the critical angle and near the Brewster angle are shown in Fig. 12. The reflectance signal was monitored as a function of time in both cases. We can see that the change in reflectance near the critical angle is greater than that at the Brewster angle. The sensitivity of these methods can be compared from the slope of the curves. A simple calculation yields an average slope between 0 and 3000 s of
9.63 \times 10^{-4} \text{ V/s} \text{ near the critical angle and } 2.6 \times 10^{-7} \text{ V/s} \text{ for the Brewster angle. The slope for LRCA is approximately 3000 times larger than that for the Brewster angle. This is an important difference in sensitivity. The rms value of the noise in both curves, estimated from the raw data, was found to be approximately the same. Therefore the increase in sensitivity implies an improvement in resolution under the same experimental conditions.}

4. Conclusions

The present study shows that LRCA may be a powerful tool in the study of particle adsorption. LRCA was proposed as a simple, high-sensitivity technique for the study of particle adsorption onto a flat surface. In this study we used electrically charged polystyrene latex particles. Experimental results showed that forces of electrical origin drive particle adsorption. Positive particles are adsorbed onto a negatively charged glass surface, whereas negative particles are not adsorbed onto this surface. A sequential adsorption experiment, which utilized positive and negative particles, was also investigated. With the help of optical microscopy, we found that adsorbed positive particles formed monolayers on the glass surface and that the maximum surface coverage was less than 47%. However, for sequential adsorption, the monolayer formed for positive particles is destroyed by the negative particles that form agglomerates on the glass surface. We have estimated the adsorption time of positive particles with diameters in the range of a few hundred nanometers at low concentrations (volume fractions from 0.023% to 0.14%) to be of the order of minutes. We found experimentally that the change in reflectance near the critical angle is dominated by scattering from particles adsorbed onto the surface rather than from particles suspended in the solution and that LRCA is considerably more sensitive than reflectometry at the Brewster angle under the same experimental conditions. We expect that our experimental results will lead to the development of theoretical models for analyzing LRCA curves.

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