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Kinetic crossover of rough surface growth in a colloidal system

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The scaling behavior of the surface of polystyrene colloidal particles depositing on the contact line between the colloidal latex film and the glass substrate is studied. We analyzed the morphology of the formed surface and the scaling exponents α and β, defining the surface width $w(L,t) \sim L^{\alpha} f(t/L^{\alpha/\beta})$. The value of roughness exponent α changes from 0.5 in a time regime to 0.71 at later times of the depositing process. To our knowledge, this is the first experimental evidence of a crossover phenomenon of rough surface growth in a colloidal system. The underlying physical reason for this phenomenon is suggested. [S1063-651X(96)10410-4]

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I. INTRODUCTION

Stochastic growth phenomena observed in a wide variety of natural and industrial dynamic processes such as crystal growth, vapor deposition, electroplating, etc., lead to the formation of rough surfaces and interfaces [1]. Understanding the dynamics of the formation and growth kinetics of rough surfaces is one of the most challenging problems in surface science. Recently, it has been realized that stochastically growing surfaces exhibit nontrivial scaling behavior and evolve naturally to steady state having no characteristic time and spatial scales. So, the general scaling theory has been employed to describe and understand such surfaces [2]. Particularly, the fluctuation on surface can be described by the function $h(x,t)$, which gives the height of the surface at position x and time t from the original flat surface. In the case where the surface cannot be expressed by a single value function of x, the function $h(x,t)$ gives the maximum height of the surface at x. The surface width on length scale L at time t is defined as the standard deviation, $w(L,t) \equiv (\langle h^2\rangle - \langle h\rangle^2)^{1/2}$, and is expected to obey the scaling law

$$w(L,t) = L^{\alpha} f(t/L^{\alpha/\beta}), \tag{1}$$

where α and β are the dynamic exponents, and the scaling function

$$f(x) \sim \begin{cases} x^{\beta} & \text{for} \quad x \ll 1 \\ \text{const} & \text{for} \quad x \gg 1. \end{cases} \tag{2}$$

Initially, the surface width grows with time due to the build-up of fluctuations according to $w(L,t) \sim t^{\beta}$. After some time, the surface reaches a steady state, and the width obeys a power law $w(L,t) \sim L^{\alpha}$. A considerable number of computer simulation and theoretical studies [1–7] have been carried out, but there is far less experimental evidence [8].

The colloidal system is a good model system for the study of the dynamics of crystallization and aggregation [9], due to the slow growth rate of colloidal crystals and easy observation with visible light. Motivated by the rapidly increasing interest in rough surface growth and far-from-equilibrium phenomena, we use a colloidal system as a model of molecular level surface growth.

Here we present experiments in which polystyrene colloidal spheres deposit to the solution wedge close to the contact line between the colloidal latex thin film and the glass slide. In these experiments the colloidal particles form a rough surface. The analysis of the surface profile and the exponents obtained support the scaling theory. The experimental results indicate the presence of two regimes of scaling behavior during the rough surface growth process. Initially, the growth can be described by the standard EW model [3]. The roughness exponent α maintains 0.5 for a period of time before a crossover to $\alpha = 0.71$ sets in.

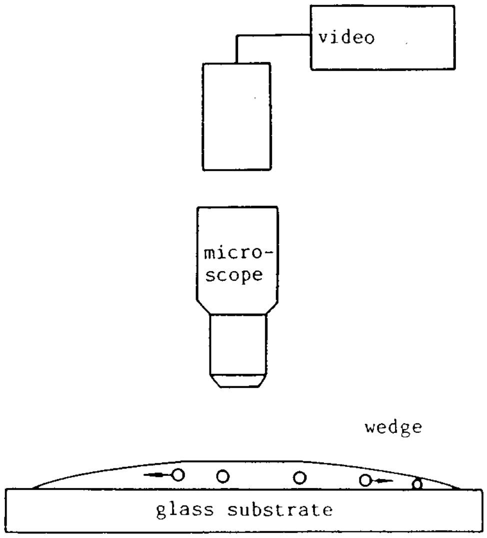

FIG. 1. Experimental setup of rough surface growth, the colloidal spheres deposit to the liquid contact wedge and form a rough surface.

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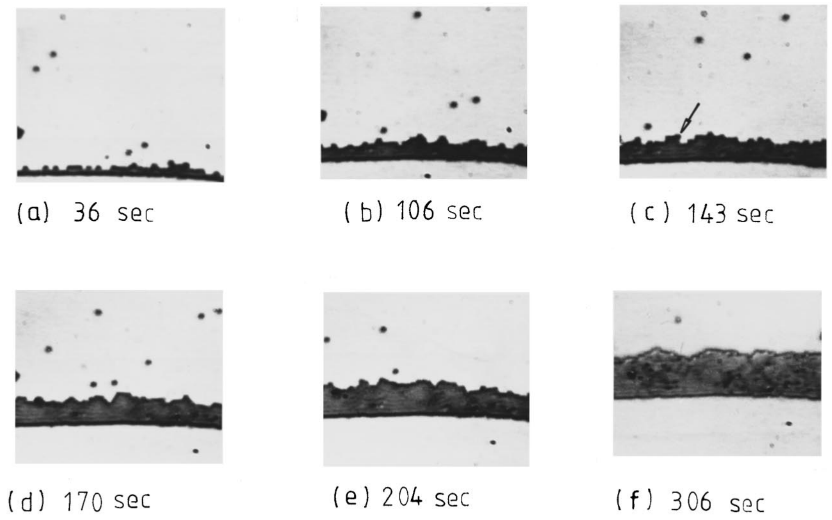

FIG. 2. Snapshots of depositing process forming a rough surface, the arrow in (c) shows where surface diffusion takes place.

II. EXPERIMENTAL SETUP

The polystyrene latex spheres of ~0.8 μm diameter, which we used in our experiments, are synthesized by emulsion polymerization. The polydispersity is better than 2%, which is stable due to the double charge layers on the surfaces of colloidal particles. The particles will not aggregate in the usual case. Before experiments, the latex is purified [10] to remove impurities such as free emulsifying, inorganic salts, various by-products, etc.

The experiments are performed on a colloidal solution thin film mounted on a glass slide (see Fig. 1). The glass slide is well cleaned so that the solution wets on it to form a very thin film. The colloidal spheres deposit to the liquid contact wedge once the thin film is formed. The process is observed *in situ* through an optical microscope equipped with a video system for imaging processing.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Direct observations show that once the colloidal thin film is formed, the colloidal particles begin to rain into the contact wedge. The thickness at the center of the film is measured to be about 100 μm, whereas near the edge of the film it is much thinner. The volume concentration (particle number density) is controlled to be about 5%. The deposited spheres form a two-dimensional colloidal crystal along the contact wedge. The typical surface in a deposition process is shown in Fig. 2, from which it can be seen that the particles move from top to bottom and deposit in the wedge forming a close-packed two-dimensional crystal. The surface we study in this paper is the up surface of the crystal. It is not clear now what mechanism makes the colloidal particles aggregate near the contact wedge. We also observed the phenomenon that particles landing on the peaks [as indicated by the arrow in Fig. 2(c)] would tend to roll down to valleys, which means that the valleys may receive more particles. We think that this phenomenon is expected to lead to a smoother overall surface just like the gravity smoothening effect in the EW model. At the beginning of the deposition process, the surface is being driven through the colloidal solution film so fluently that there are no severe pinning events. After a period of time (about 200 sec), the surface is advancing slowly. The monomers still are driven into the surface, instead of random ballistic deposition, the particles transport trajectories now are Brownian.

The video pictures are digitized with a resolution of 512×512 pixels. The surface is defined as the set of the highest positions in columns of the occupied pixels from a straight reference line. The exponent β was obtained by determining the standard deviation of the surface heights versus time. Figure 3 shows that the surface width grows with time. From the power law fitted to the data we get the value of β. The scaling exponent $\beta = 0.26 \pm 0.03$, averaging over five different samples.

To extract the roughness exponent α, we investigated the length scale dependence of the rms width $w(L)$ of the saturated surface where, in the experiments at hand, L is the length of line segment under examination, smaller than the straight contact line to avoid boundary effects. Figure 4 shows the plots of saturation width as a function of length scale at different times. Figure 5 depicts that during the whole deposition process, the value of α changes with time. The results for different samples are the same.

From the results obtained above, it can be seen that the

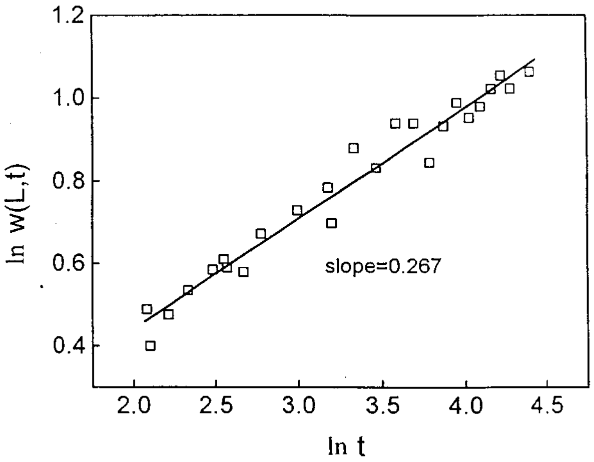

FIG. 3. ln-ln plot of the surface width versus time t for one sample. The line fit of the data is the value of β, $\beta = 0.267$ for this typical case.

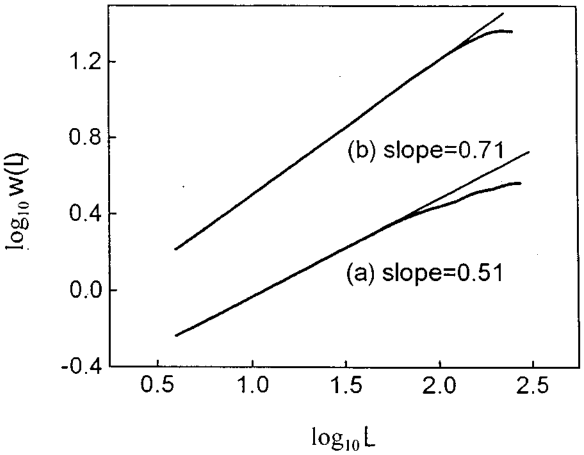

FIG. 4. Double $\log_{10}$ plot of $w(l)$ and l. The roughness exponent α describing the scaling of the surface is determined from the slope of the straight line to the data. (a) $\alpha = 0.51$ at $t = 100$ sec; (b) $\alpha = 0.71$ at $t = 300$ sec.

rough surface growth in the colloidal particle deposition process obeys the scaling law [Eq. (1)]. What surprises us is that the roughness exponent changes from 0.5 to 0.71.

A physically reasonable model for describing the evolution of the profile in the surface growth was first proposed by Edwards and Wilkinson [3],

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + \eta(x,t), \tag{3}$$

where $h(x,t)$ is the height of a growing surface in d dimension space, ν is the relaxation coefficient, and η is the stochastic noise driving the growth. The above EW equation includes both random deposition process and surface relaxation, by including the diffusion term. Employing Fourier transformations, calculating $w(L,t)$ yields that

$$\alpha = (3-d)/2, \quad \beta = (3-d)/4. \tag{4}$$

In our case $d = 2$, $\beta = 0.25$, and $\alpha = 0.5$. KPZ theory gives the same results. It can be seen that the exponents obtained at earlier times in our experiments are approximately equal to the theoretical results, which shows that the EW (or KPZ) model captures the essential physics of the random deposition process with the finite surface diffusion. Unfortunately, the scaling behavior at later times cannot be explained by the EW (or KPZ) theory.

Motivated by the fact that in later times of our experiments the particles move to the surface with Brownian trajectories and some pinning events are observed at the growing surface, we try the following EW equation subject to quenched noise [11,12]:

$$\frac{\partial h}{\partial t} = \nu \nabla^2 h + \eta(x,h) + F \tag{5}$$

with

$$\langle \eta(x,h)\eta(x',h')\rangle = \delta(x-x')\delta(h-h'). \tag{6}$$

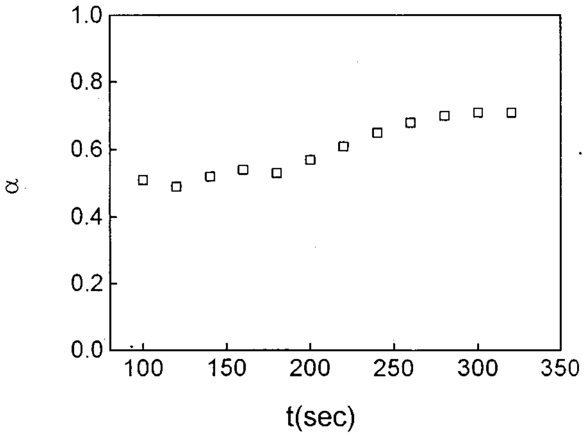

FIG. 5. The variation of the α with time during the depositing process. A crossover of α from 0.51 to 0.71 is evident.

Here, F is the driving force, which may be originated from the water flow from the center of the solution film to the contact wedge. F decreases with time in the whole depositing process. In earlier times, the advancing surface is strongly pushed by the driving force, $F \gg \langle \eta^2 \rangle$. Here, we can write $h = \tilde{h} + Ft$, so Eq. (5) becomes $\partial \tilde{h}/\partial t = \nu \nabla^2 \tilde{h} + \eta(x,Ft)$ [13]. In this regime the surface is being driven quickly and fluently; the particles randomly deposit to the surface with ballistic trajectories. Equation (5) reduces to the usual EW scenario with uncorrelated stochastic noise [Eq. (3)], with the standard EW (or KPZ) saturation width exponent $\alpha = 0.5$. After a period of time, the driving force decreases noticeably. So once the advancing surface encounters an obstacle, it becomes temporarily pinned at a particular site. At the same time, nearby opposing segments of the surface continue advancing and will pinch off the pin, effectively generating the lateral growth mechanism associated with the $(\nabla h)^2$ term. In this growth regime, the height-height correlation of the surface becomes stronger. So the roughness exponent α becomes larger. In numerical studies based on Eq. (5) [12] the calculated exponent α is close to the value 0.71 which we found experimentally.

IV. CONCLUSION

We present a colloidal system which displays a rough surface growth process. *In situ* observation shows that the surface growth can be separated into two regimes. In the earlier times, the random deposition and the surface smoothing effect due to the surface diffusion are two characteristics of the growth. In this regime, the scaling exponents α and β are calculated to be 0.5 and 0.26, respectively, which is in agreement with the ordinary EW model. In the later period of time, the surface is being driven through the colloidal solution film and there are some pinning events. This feature leads to lateral growth mechanism in the surface. In this situation, α is 0.71.

In order to explain the crossover phenomenon between these two dynamic scaling behaviors, we apply Eq. (5) to describe the growth. The scaling behavior of $\alpha = 0.5$ can be considered as in the extreme limit of strong driving, i.e., $F \gg \langle \eta^2 \rangle^{1/2}$. But the stochastic type of noise $\eta(x,h)$ is not always dominant. As time goes on, F decreases and couples with $(\nabla h)^2$ and $\eta(x,h)$, so the value of α increases to be 0.71. The experimental results are in general agreement with the numerical results based on Eq. (5).

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