Edward-Wilkinson Behavior of Crystal Surfaces Grown By Sedimentation of SiO_2 Nanospheres

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The surface of the solid structures obtained by natural sedimentation from aqueous solutions of monodisperse SiO_2 spheres is imaged by atomic force microscopy. The dynamic scaling method applied to these images leads to temporal and spatial logarithmic scalings of the surface width that is consistent with the Edward-Wilkinson interface motion equation. It suggests that the interface grows close to equilibrium by the aggregation of SiO_2 spheres which, after reaching the growing surface driven by gravity, relax to minimum potential energy sites without significant attractive particle-particle interactions. [S0031-9007(96)01710-3]

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The understanding of the growth phenomena of technological interest, such as molecular beam epitaxy, chemical vapor deposition, sedimentation, and electrodeposition, is increasingly important from both experimental and theoretical points of view. In particular, continuous and discrete modeling of growth processes have attracted considerable interest [1]. In this sense, the study of the sedimentation of colloidal particles could be useful as they can be regarded as scaled-up atomic systems with charges, sizes, and length scales 10^2–10^5 times larger than atomic species. These particles constitute "ions," and, in the case of aqueous solutions, the interaction between them can be screened by either OH^- or H_3O^+ species [2].

Under adequate gravitational fields, sedimentation occurs leading to crystalline phases which can grow at the expense of the fluid part. The nature of crystal growth is *a priori* not clear, and it can be continuous or proceed via a series of first order surface phase transitions [3]. The mechanism of crystal growth on a flat solid substrate determines the dynamics and structure of the growing interface. The interface evolution can be followed by means of the dynamic scaling theory applied to surface profiles on different time scales [1]. This theory predicts that the root mean square roughness (interface width), $\xi(L,h)$ for length L and average thickness h, scales, when $h \to 0$, as

$$\xi(t) \propto h^{\beta}, \tag{1}$$

whereas, for $h \to \infty$, it scales as

$$\xi(L) \propto L^{\alpha}, \tag{2}$$

with β and α being the dynamic and static surface roughness exponents, respectively.

The growth process should involve local effects such as stochastic noise, site-dependent growth, and surface relaxation. One of the most simple models for phase growth is the random deposition model with surface relaxation [4]. In this model, each particle falls along a randomly selected single column toward the surface until it reaches the top of the interface and then it "diffuses" along the surface to a finite distance, stopping when it reaches the position with the lowest height. This simple model is well described by the Edward-Wilkinson (EW) continuum equation which was derived to understand the particle sedimentation process within a liquid [5]:

$$\partial h/\partial t = V + \nu\nabla^2 h + \eta, \tag{3}$$

where ν is called the "surface tension" term and η is the space- and time-dependent stochastic noise. The constant average velocity, V, of the propagating surface does not affect the scaling properties of the interface. This equation contains the competing effects of gravitational relaxation which tends to smooth the growing surface and the stochastic noise leading to roughening. For a three-dimensional (3D) system, Eq. (3) predicts $\alpha = 0$ and $\beta = 0$. In this case, the correlations decay logarithmically so that, for $1 \ll h \ll L$, it is expected that

$$\xi \propto (\log_{10} h)^{\delta}, \tag{4}$$

and, for $h \gg L \gg 1$,

$$\xi \propto (\log_{10} L)^{\gamma}, \tag{5}$$

with $\gamma = \delta = 0.5$. However, because of the small dependence of ξ on L and h, it is very difficult to determine experimentally the γ and δ exponents [6].

This oversimplified growth model is hardly expected to be applicable to real systems, as it has been shown that the EW equation can be reduced to a perfect equilibrium problem [7], whereas surface growth is typically an irreversible process [8]. Thus, it is not surprising that only a few experimental systems [1] have been reported to obey the logarithmic scaling behavior predicted by the EW equation, and, in many cases, only one of the two characteristic exponents has been measured, making the analysis incomplete [9].

On the other hand, ballistic models have also been proposed to explain the structure of a solid grown by the sedimentation of particles from a colloidal suspension. Particles were added to a flat substrate on randomly selected sites following vertical trajectories, and they stuck in the position with which they first contacted [10]. This model is well described by the Kardar, Parisi, and Zhang (KPZ) [11] interface motion equation which predicts $\alpha \approx 0.40$ and $\beta \approx 0.25$ for 3D. These exponents have been found for several interface growth processes in real systems [8].

In this Letter we report experimental data for the growth of interfaces generated by natural sedimentation of model SiO_2 colloidal particles. The dynamic scaling method applied to atomic force microscopy (AFM) images reveals that the interface properties, for length scales between the silica nanosphere diameter and the average domain size, can be well described by Eq. (3), and suggests that the interface grows close to equilibrium by the aggregation of SiO_2 spheres, driven by gravity, which relax to minimum potential energy sites in the absence of significant attractive particle-particle interactions.

The hydrolysis of Si alkoxide and subsequent polymerization of the Si-O chains at room temperature following the Stöber-Bohn-Fink method [12] was used to obtain amorphous, as confirmed by x-ray diffraction, perfectly spherical SiO_2 particles with a narrow size distribution function. Monodisperse aqueous solutions (pH = 6–7) of SiO_2 spheres (average diameter, $d = 440$ nm, as measured by AFM, transmission electron microscopy, and Bragg diffraction [13]) were used to grow solid structures by natural sedimentation on a $\lambda/10$ polished substrate (polymethyl-methacrylate). We can assume random growth because of the absence of the typical Bragg diffraction patterns present in other self-assembled suspensions [14]. Typical times for the growth of the solid phase are 5–20 days. Following this, the liquid was removed and the solid was dried. The drying process may lead to certain thickness fluctuations on the same sample, being most important for the thinnest samples. The solid surface was imaged using a Nanoscope III (AFM) operating in the tapping mode in ambient conditions. Si cantilevers oscillating at ≈300 kHz were used. 512 × 512 images were taken and analyzed, using the single image dynamic scaling method after fitting the instrument plane and applying a subtracting procedure [15]. Because of the limitation in the scanning range of our microscope, the largest area which can be imaged was close to 40 × 40 μm^2, although, eventually, larger images were taken. Only images taken with sharp tips (i.e., with a tip angle close to the nominal value supplied by the manufacturer) were considered for this study. The image selection was made from the analysis of measured profiles which are the convolution between the tip and the nanosphere geometries.

25 × 25 μm^2 AFM images [Figs. 1(a)–1(c)] of the solid surfaces resulting from the sedimentation of the SiO_2 spheres with three different thicknesses (1, 44, and 750 μm) reveal mainly ordered (111) domains (15–20 μm wide for the thicker samples) with some defects, although small (100) domains have also been observed.

The cross sections of the interfaces with increasing thicknesses (Fig. 2) show profiles consisting of arrays of smooth spheres. Surface roughness results from defects such as steps, vacancies, and domain boundaries. Figure 2 also indicates that the interface does roughen as the thickness increases.

Figure 3 plots the root mean square roughness values (ξ_{AFM}) obtained from the analysis of AFM images versus h. The bottom dashed line indicates the minimum theoretical interface roughness value of a perfect layer of nanospheres with 440 nm of diameter imaged with a sharp tip. It can be seen that, for h values in the range of 5×10^2–5×10^4 nm, ξ increases with h. The continuous curve shows the best fit of the experimental data, for this thickness range, following the $\xi \propto (\log_{10} h)^{0.5}$ dependence predicted by the EW equation for the $L \gg h \gg 1$ limit [5]. Within the experimental error bars, the data are in agreement with this dependence. For $h > 5 \times 10^4$ nm, ξ becomes almost independent of h. This behavior, which implies that $\beta \approx 0$, is consistent with that predicted by the EW model [5].

The single-image dynamic scaling method [16] was used to derive the α values, when $h \gg L \gg 1$, from the equation,

$$\xi(L,h) \propto L^{\alpha}, \tag{6}$$

where L is the length of a segment of the AFM scan of size S measured in the fast scan direction (x). The ξ vs L

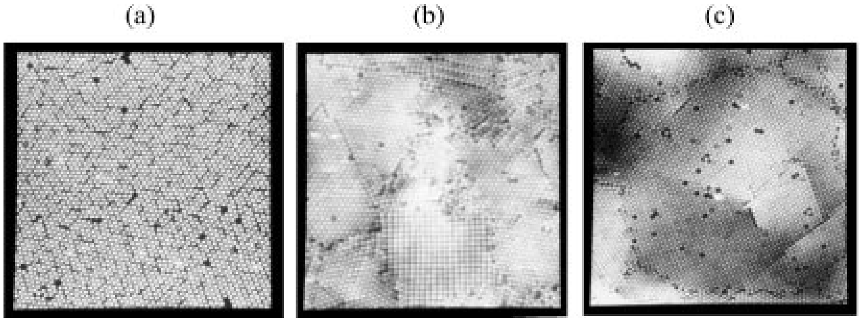

FIG. 1. 25 × 25 μm^2 tapping-mode AFM images of solid surfaces resulting form the sedimentation of the SiO_2 spheres with three different thicknesses: 1 μm (a), 44 μm (b), and 750 μm (c).

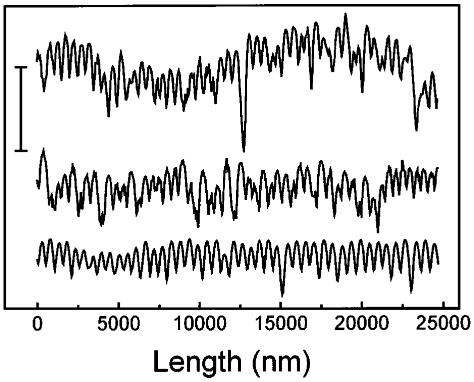

FIG. 2. Surface profiles for the solid surfaces resulting from the sedimentation of the SiO_2 spheres with three different thicknesses: 1 μm (bottom curve), 7 μm, and 750 μm (top profile). The bar indicates 500 nm.

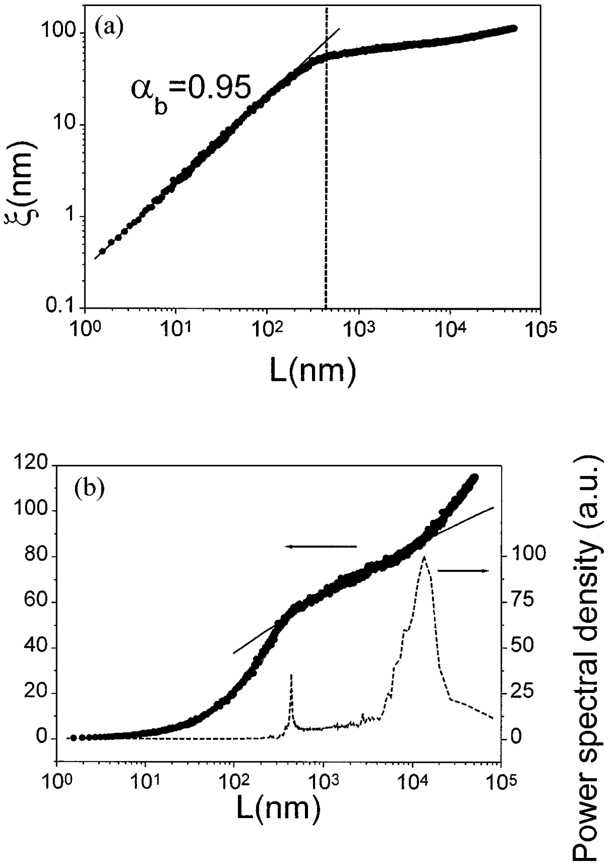

FIG. 4. (a) ξ versus L, logarithmic plot for the 750 μm thick film. The dashed line indicates the average SiO_2 sphere diameter. (b) ξ versus L, semilogarithmic plot for the 750 μm thick film. The continuous line indicates the best $\xi \propto [\log_{10}(L)]^{0.5}$ fit for the $d < L < D$ region covering $\approx$1.5 decades. The dashed curve corresponds to the power spectral density of the same AFM data.

logarithmic plot [Fig. 4(a)] from AFM images of the SiO_2 crystal with $h = 750$ μm shows a linear region with slope $\alpha_b = 0.95 \pm 0.05$ up to $L \approx d$. For $d < L < D$ ($D \approx 15$ μm), a $\xi \propto (\log_{10} L)^{0.5}$ ($\alpha \approx 0$) behavior was observed as is indicated by the continuous curve which shows the best $\xi \propto (\log_{10} L)^{0.5}$ fit of the data for the $d < L < D$ range [Fig. 4(b)]. In Fig. 4(b) is also plotted (dashed curve) the power spectral density of the same AFM data. Two frequencies clearly predominate. The first one, at $L \approx d$, corresponds to the average size of the SiO_2 spheres which introduces the first crossover (lower cutoff) [17]. The second one, at $L \approx D$, is defined by the average domain size, and it corresponds with the second crossover (higher cutoff). Thus the EW scaling would take place for length scales larger than the nanosphere diameter, and less than the average domain size. For $L > D$ the interface roughness is defined by the height fluctuations between different domains.

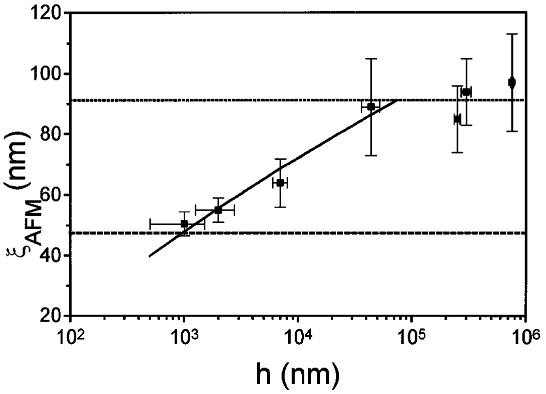

FIG. 3. ξ_{AFM}, corresponding to 40×40 μm^2 AFM images versus h, plot. The bottom dashed line indicates the minimum theoretical ξ value for a perfect layer of nanospheres with a diameter of 440 nm. The top dashed line indicates the ξ average value of the data with $h > 10^5$ nm. The continuous curve shows the best $\xi \propto [\log_{10}(L)]^{0.5}$ fit of the experimental data with film thickness in the range of $5 \times 10^2 < h < 5 \times 10^4$ nm.

The value $\alpha_b \simeq 1$ obtained for $L < d$ is consistent with a smooth surface of the SiO_2 spheres resulting from the polymerization procedure. Two growth mechanisms have been proposed for the sphere growth [18]. In the first one, the sphere would be the result of the aggregation of small particles which could lead to rough fractal surfaces [19]. In the second one, the sphere would be the result of "building units" of (much) smaller size monomers leading to a smoother surface. In our system, each sphere exhibits a Euclidean surface supporting the validity of the second model. In fact, for silica solids grown by the method used in this work, the real area agrees with that expected for solid consisting perfect spheres [18,20].

The $\xi \propto (\log_{10} L)^{0.5}$ behavior for $d < L < D$, when $h \gg L \gg 1$, and the $\xi \propto (\log_{10} h)^{0.5}$ dependence, when $L \gg h \gg 1$, support the validity of the EW interface motion equation to describe the solid surface produced by natural sedimentation of spheres.

It is known that when particle-particle interactions are present in the system they lead to overhangs and void formation. In this case, the system should be described by the KPZ equation, in contrast with our results. Thus, our experimental data show that, for the experimental system studied, the attractive particle-particle interactions are negligible. This fact is in agreement with the silica particles stabilization by a layer of adsorbed water that prevents flocculation, resulting from the reduction in the double layer repulsion [19]. This fact means that the SiO_2 particles would behave as hard spheres which, after reaching the growing surface driven by gravity, relax to the minimum potential energy sites. It results in a close packed lattice with a flat surface, where the surface roughness is mainly associated with steps, vacancies, and domain boundaries.

The validity of the EW equation also indicates that crystal growth by sedimentation of SiO_2 particles can be mapped into a simple equilibrium problem. In fact, the gravitational field G acting at the crystal surface, $G = (\rho - \rho_0)vgd$, where g is the gravitational acceleration, ρ_0 the water density, ρ, v, and d are the density, volume, and diameter, respectively, of the SiO_2 particles, respectively, results in the order of k_bT, the kinetic energy. It means that the growing surface is near the equilibrium, which is consistent with the long times required to grow the solid phase. Particles at "wrong sites" can be removed during the growth process, leading to a close packed ordered surface.

It is well known that there are problems in determining experimentally the EW scaling relations [6]. For instance, in a previous study of the growth of Si-W multilayers, logarithmic behavior has also been observed, but the β value has not been reported for this system either [9]. For our system, and despite its experimental limitations, results are consistent with an EW behavior. Thus, surfaces grown by natural sedimentation of SiO_2 particles seem to be an example of the validity of the EW equation.

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