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Steps wandering on the lysozyme and KDP crystals during growth in solution

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Abstract

We have applied atomic force microscopy for the study in solution of time evolution of step roughness on the crystal faces with high (pottasium dihydrophosphate: KDP) and low (lysozyme) density of kinks. It was found that the roughness increases with time revealing the time dependence as $t^{1/4}$. Step velocity does not depend upon distance between steps, that is why the experimental data were interpreted on the basis of Voronkov theory, which assume, that the attachment and detachment of building units in the kinks is major limitation for crystal growth. In the frame of this theoretical model the calculation of material parameters is performed. © 2001 Published by Elsevier Science B.V.

Keywords: Atomic force microscopy; Crystallization; Step formation and bunching; Biological molecules – proteins; Stepped single crystal surfaces; Solid–liquid interfaces

Steps fluctuations during crystal growth in solutions practically are not yet studied. We know only one study (ferritin protein crystallization [1]) where the time dependence of step roughness was measured. At the same time the crystallization from gases at high temperatures is described previously in various experimental and theoretical papers. On one part, this is directly connected with the fact that the achievement of high space resolution in condensed matter meets experimental problems. On another part, the theoretical interpretation of the obtained data is much more complicated due to the unknown energetics of crystal growth in solution and its dissolution. Important and not yet solved problem connected with growth of water-soluble crystals (and all others also) is the achievement of high quality crystal materials. The influence of fluctuations on the impurity distribution in the crystal and the lost of morphology stability by the growing surface, which leads to capture of impurities from the solution and the appearance of striations, are not well. The aim of the present study is to find the rate of step fluctuations and its dependence upon time for two well-known water-soluble crystals of different nature—potassium dihydrophosphate (KDP) and high molecular mass protein—lysozyme (orthorhombic modification). This information is strongly necessary for the calculation of material parameters of growing crystal and for estimation of the influence of fluctuations on the crystal quality.

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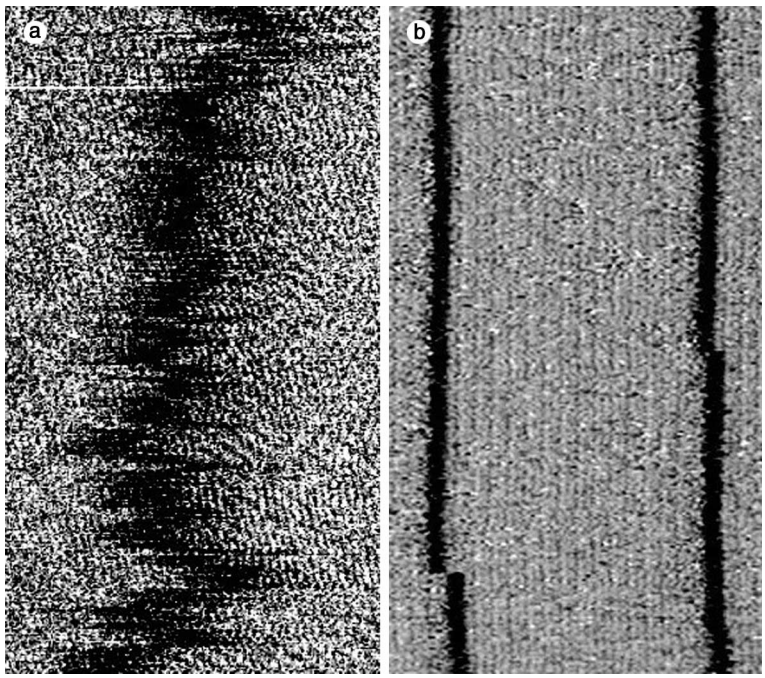

Fig. 1. AFM images of steps on the growing faces of crystals. (a) (1 0 1) face of KDP. The sizes of elementary unit: $a = b = 0.745$, $c = 0.695$ nm. Step height 0.52 nm, its velocity ~0.2 nm/s. Image size 22×40 nm^2 obtained at tip scanning frequency 61 Hz with 512 scans. (b) (0 1 0) face of orthorhombic lysozyme. The size of elementary unit cell: $a = 5.65$, $b = 7.45$, $c = 3.05$ nm. The steps move at the velocity ~0.2 nm/s. Image size 255×320 nm^2 obtained at tip scanning frequency 10 Hz with 512 scans.

Fig. 1 shows atomic force microscopy (AFM) images of steps on the growing faces of these crystals. For KDP crystal the step is strongly corrugated and the kink density is so high that straight lines between them are not seen. It can be regarded that every second place is occupied by a kink. The following arguments are necessary to prove, that the obtained AFM image correspond to the real step fluctuations process: (1) the step corrugation does not depend neither upon AFM tip velocity nor upon the interaction force between the tip and the surface (velocity and applied force were changed in the range of one order); (2) the control measurements with nonsoluble in water graphite and lithium niobate crystals revealed no step fluctuations while performing measurements in water, and this is quite reasonable, because there must be no fluctuations at room temperatures for these systems. The steps on the lysozyme face are parallel to the molecular rows and contain a few kinks well established in the images. These images are obtained only when the applied force between AFM tip and sample is less than 10^{-9}, otherwise clearly observed in AFM images damage of crystal surface occurs.

The measured average distance between kinks on the (1 1 0) face of lysozyme is equal to 35 nm while the standard deviation is 28 nm. We have measured the distance between 88 kinks, kink depth was equal to the size of lattice unit cell in [0 0 1] direction, $d = 9.29$ nm, in 55% of all the cases. Half of this value $(1/2d)$ corresponds to 28% of kinks, 14% of kinks reveal depth equal to $1.5d$ and $2d$. One kink has a depth corresponding to $2.5d$, four kinks—$3d$. The appearance of kinks with not whole values of its depth may be the result of tip interaction. The distribution of the distance between kinks reveal random form [2]. The reasons for this may and also for the presence of kinks with different depth may be the impurities: if the kink is stopped by the impurity the neighbor kink catches up this one.

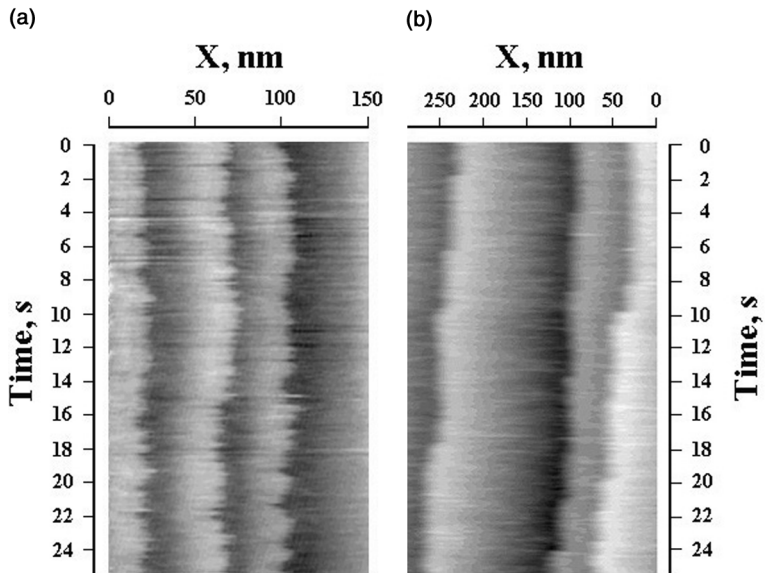

Fig. 2. The image of the step when slow tip scanning is disabled. 512 scans, 20.3 Hz. (a) (1 0 1) face of KDP. Step fluctuations on the (1 0 0) face during growth and dissolution are observed in Ref. [3]. (b) (1 1 0) face of lysozyme.

Fluctuations were studied using AFM while the tip scanning in low speed direction was switched off. The changes of step position versus time (KDP) or time interval between the appearance of two consequent kinks, its depth and sign (lysozyme) were measured. Typical images of steps observed in this mode are shown in Fig. 2.

During the observation of lysozyme crystal steps the attachments of building units were in 79% of the cases, detachment −21% of the cases. The ratio of these values must be equal to the ratio between real and equilibrium concentration of solution, in our case −1.74. The reason for this phenomena, also found in Ref. [1], is not yet known.

Time dependencies of step coordinates $x(t)$ are shown in Fig. 3. More than 1000 coordinates is measured for KDP, and for lysozyme the time for arrival of 190 kinks were measured. These data (Fig. 3) was used for the composition of autocorrelation function:

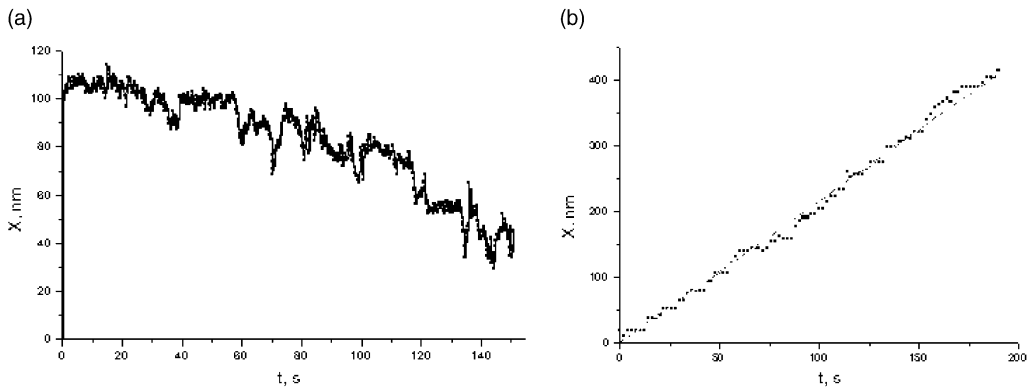

Fig. 3. Coordinate of step region versus time. (a) KDP; (b) lysozyme.

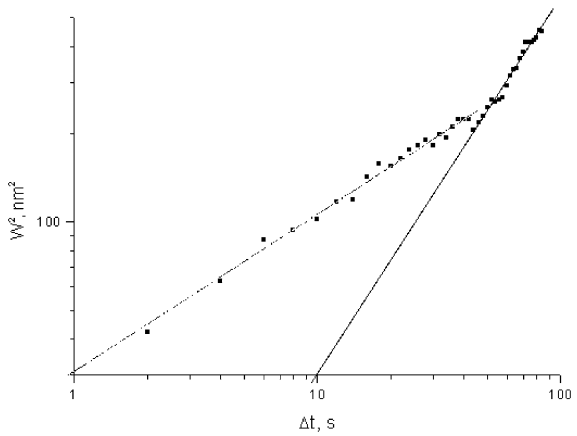

Fig. 4. Autocorrelation function for lysozyme (according to curve in Fig. 3(b)). Curve slopes: 0.53 ± 0.02 for the first region, 1.26 ± 0.04 for the second region.

$$W^2 = \langle [x(t + \Delta t) - x(t)]^2 \rangle$$

the averaging is performed for every time t for constant time interval Δt. W characterizes step fluctuations (its roughness) and its growing during the interval Δt. We use only small value $\Delta t \sim 5$ s for KDP, because for large values of Δt the movement of the step as a whole influence the calculations. In the case of lysozyme the step shift determined by mean step velocity ($V = 2.16 \pm 0.01$ nm/s) was extracted from the coordinate $x(t)$. The dependence of $W^2(\Delta t)$ for lysozyme is shown in logarithmic scale in Fig. 4.

The initial region of these curves ($0.2 < \Delta t < 5$ s for KDP and $2 < \Delta t < 40$ s for lysozyme) may be linearized when x-coordinate on the drawing corresponds to $\Delta t^{1/2}$. A second region is seen for lysozyme where $W^2 \sim \Delta t^{5/4}$ ($40 < \Delta t < 85$ s). There is still no interpretation for this region. Linearized curves are shown in Fig. 5.

In early 80s Voronkov had developed a theory for fluctuations of growing step [4,5] assuming that supersaturation near the kinks is constant and the same as it is in bulk solution. This means, that process of growth is limited by the acts near the kink: attachment and detachment of building units. This theory was applied for the data interpretation, because the performed measurements has shown, that steps velocities for KDP and lysozyme were independent upon distance between steps. The distance varied 10 times in our experiments. This gives the evidence, that the diffusion fields of concentrations of building units approaching the steps do not coincide. So it is reasonable to assume, that the supply of soluble matter exceeds its consumption. It is worth noting also, that supersaturation near the surface is the same as in the volume while step velocity is low and velocity dependence upon supersaturation is nonlinear. The dependencies obtained by Voronkov are the following:

$$W^2 = (\chi t)^{1/2},$$

$$\chi = 2(\beta/\alpha_e)kTac/\pi = 2a^4\omega^-(c\rho)^2/\pi, \quad (1)$$

$$\beta = a(c\rho)\omega^- \quad (2)$$

$$\alpha_e = kTc/(c\rho)a^2, \quad (3)$$

where β is the step kinetics coefficient, $\alpha_e = \alpha + d^2\alpha/d\varphi^2$, the step stiffness corresponding to the

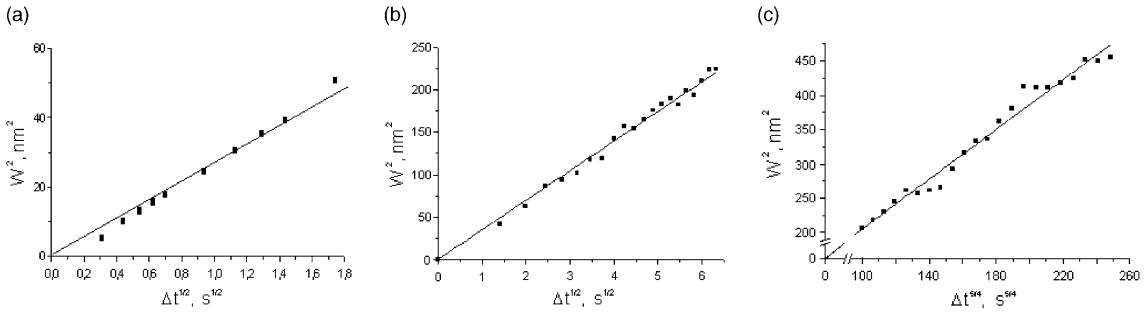

Fig. 5. Linearized autocorrelation functions. (a) KDP, $W^2/t^{1/2} = 27$ m^2/s$^{1/2}$. (b) Lysozyme—first region, $W^2/t^{1/2} = 35.0 \pm 0.3$ nm^2/s$^{1/2}$. (c) Lysozyme—second region, $W^2/t^{5/4} = 1.81 \pm 0.01$ nm^2/s$^{5/4}$.

Table 1
Parameters characterizing step fluctuations

Parameters	KDP(1 0 1), step ∥ [1 1 1]	Lysozyme (1 1 0), step ∥ [0 0 1]	Au(1 1 0), 565 K, data from Ref. [7]
χ, cm^4/s	0.73×10^{-25}	$(1.22 \pm 0.02) \times 10^{-25}$	2.75×10^{-30}
a, cm	6.78×10^{-8}	9.29×10^{-7}	4.07×10^{-8}
c, cm	12.63×10^{-8}	3.05×10^{-7}	2.88×10^{-8}
h, cm	5.2×10^{-8}	4.48×10^{-7}	2.88×10^{-8}
$\omega^-(c\rho)^2$, s^{-1}	5.4×10^4	0.26	1.57
β/α_e, cm^2/erg s	330	16.1	0.048
$c\rho$	0.5	0.087	0.0156
ω^-, s^{-1}	6.0×10^4	34	6.5×10^3
β, cm/s	0.74×10^{-3}	2.8×10^{-6}	4.1×10^{-6}
α_e, erg/cm	2.25×10^{-6}	1.71×10^{-7}	8.57×10^{-5}
α_e/h, erg/cm^2	43	0.38	~3000

increase of free linear energy (α) during step inclination from straightforward form to the angle φ, the derivative is calculated for $\varphi = 0$. At high kink density (ρ) the free energy of the step riser may be regarded to be equal to $\alpha_e/h = \alpha/h$, where h corresponds to step height. The value $c\rho$ corresponds to the rate of step coverage by kinks (the probability to find a kink in a definite place of a step) and provides more information while comparing two different substances than the kink density. ω^-, the frequency of particle detachment from the kink (in equilibrium is equal to the frequency of attachment), a, the distance between the rows of closely packed building units, which form the step, c, the distance between the building units in one row, k, the Boltzman constant, T, the temperature.

The linear dependence between W and $t^{1/4}$ is observed in Voronkov model even for small times, when the neighbor regions of step are correlated. Before this moment as also for Brownian motion $W \sim t^{1/2}$. Similar phenomenon is observed in Ref. [6] in computer experiments for random particle attachment with surface relaxation.

It is worth noting, that the measurements of step fluctuation on the (1 1 0) face of crystal gold, growing in gaseous phase at much higher temperatures reveal that W^2 is also proportional to $t^{1/2}$. The coefficient in this proportion has a linear dependence on ρ when $T = \text{const}$. For $\rho = \text{const}$ this coefficient as it must for ω^-, was in exponential dependence upon temperature [7,8]. All this in a good agreement with Voronkov theory. Note, that for the first time the linear dependence of fluctuation amplitude was proportional to $t^{1/4}$ for the case fluctuations of polymer chains according to the theory developed in Ref. [9].

Our experimental data for KDP and lysozyme (for small Δt) reveal the same appearance $W(t)$, so it is possible to calculate the main parameters in Voronkov equation. These parameters are shown in Table 1. For comparison the same parameters are shown for gold (our estimation for the results from Ref. [8]). Step height was measured experimentally. Parameter a and c for KDP are calculated from cell sizes, because it is still unknown what can be regarded as building unit here, and the kinks are not observed. The kink depth (a) for lysozyme is regarded to be equal to unit cell size, though two times smaller kinks are also observed. The parameters ω^-, $(c\rho)^2$ and β/α_e are calculated from experimental value of χ. Values of $c\rho$ are obtained in experiments, and the value of ω^-, β and α_e are calculated using Eqs. (1)–(3).

Parameters calculated in this way are different from those obtained in different methods. The kinetics coefficient for KDP defined by interferometric measurements was six times higher [10] and the surface energy is two times smaller. The kinetics coefficient for lysozyme may be found while dividing the mean value of the step velocity (2.16 nm/s) by the supersaturation of solution (0.74 in our experiment). This value $\beta = 2.9 \times 10^{-7}$ cm/s is one order smaller than that shown in Table 1.

Consequently, ω^- will be also one order smaller. The possible reason for the discrepancy may be due to the following two circumstances. First of all, the theory does not take into account the role of impurities. Also the main question about the building unit and mechanism of kink formation is not clear: what attach to the crystal—individual ions, molecules or its clusters. Thus the value of kink depth is not clear. Nevertheless, the values of χ are of some independent interest. If it becomes possible to learn in some future, what building unit is, and its size will be established, then the parameters in Eqs. (1)–(3) can be easily recalculated.

The value of χ is defined by ω^- and ρ (and also by the size of building unit). This parameters in their our turn depends upon the binding energy of particles in crystal: the lower the energy—the higher the kink density and the detachment of particles from the kinks becomes easier. However for the crystallization in solution in contrary to gases the enthalpy of phase transition depends not only upon the energy of crystal lattice but also on the interaction with the environment due to hydration of particles and processes of water restructure. Particularly, the equilibrium flow of the particles into the kink (and equal to it flow ω^-) is as higher as the solubility [11]. That is why there is no direct relationship in between ω^- and $c\rho$ so that it is not possible to predict the step fluctuations during crystal growth.

Knowing χ it is possible to estimate the role of fluctuations on the morphological stability of the surface and the uniformity of the whole crystal. A step, moving at mean velocity V, at the same time experiences fluctuations. That is why a step segment is delayed on one place for some time, periodically leaving it. Step segment will certainly move forward only after time interval τ_f, which can be found from the equation $(\chi\tau_f)^{1/4} \approx V\tau_f$. This results in $\tau_f \approx (\chi/V^4)^{1/3}$. If the fluctuation shift during the time interval τ_f is equal to the half distance between the steps, then the steps may coagulate. This shift is equal to $V\tau_f \approx (\chi/V)^{1/3}$. For lysozyme V is about 1 nm/s, such a shift is possible when the distance between the steps is about 20 nm.

It was mentioned above, that the uniformity of distribution of incorporated by the crystal impurities to much extent depends upon the rate of fluctuations. Let's write τ as a time for desorbtion of impurity from the first surface layer of the crystal. If the time duration of the fluctuation near the impurity captured by the previous monolayer is higher than its desorbtion time ($\tau_f > \tau$), then the capture of the impurity will go in equilibrium conditions, and the impurity will be uniformly distributed in the volume of the crystal. In opposite case the crystal will be not uniform.

Thus we have shown, that steps on the face of growing KDP crystal intensively fluctuates. The increase of fluctuations in time for KDP and lysozyme follows one and the same behavioral pattern, which can be derived from the assumption that the supersaturation near the kink is constant.

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