Kinetics of crystal growth from solution by atomic force microscopy data

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Abstract. The atomic force method (AFM) makes possible a high-resolution *in situ* observation of elementary processes of crystal surface growth. AFM generates three-dimensional images of the surface; however, it does not allow to measure the actual normal growth rate of the crystal face. We have developed a new way to use AFM images to determine the normal growth rate and value of its fluctuation associated with thermodynamic conditions of growth. We worked out a criterion for characterization of the state of the stationary growth. The point when the growing surface reaches the stationary growth is characterized not only by constancy of the normal rate of growth, but also by stability of its dispersion in time.

The AFM-method helps to register the tendency of thin steps to group together and form macrosteps. We have determined that in one of the experiments the real nature of this grouping is kinematical waves of density of steps. We proved that only three out of the nine were actually kinematical waves, and the rest were produced as a consequence.

Evolution of the sodium chloride surface in the process of its growth from the solution under various conditions was studied using *in situ* investigations by the AFM and statistical approach. The growth steps of the face were classified by height. The rate of tangential movement of the step front was approximated by the movement rate of a great number of dots projected through an orienting grid which was overlaid onto each snapshot in sequence. Then, empirical distributions of the tangential rates and distances between the steps were approximated to the curves of normal and logarithmically normal distribution by the least-squares method. The fluctuation of the parameter for each interval was considered as a statistical value of mean-square deviation. Using a great number of histograms of this type, we managed to draw summarized graphs demon–strating the dynamics of the mean tangential rate of the steps and the distances between them during the whole experiment. We marked the fluctuations of these parameters up and down from each point as a confidence interval (fig. 1).

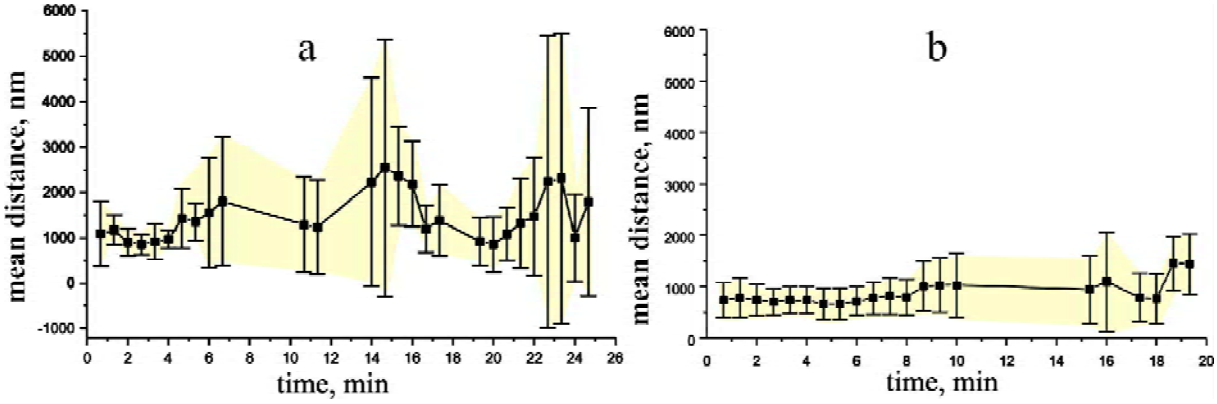


Fig. 1. Examples of fluctuations of the distances between the steps. (a) — experiment with kinematical waves on the surface of growing NaCl (b) — other similar experiment.

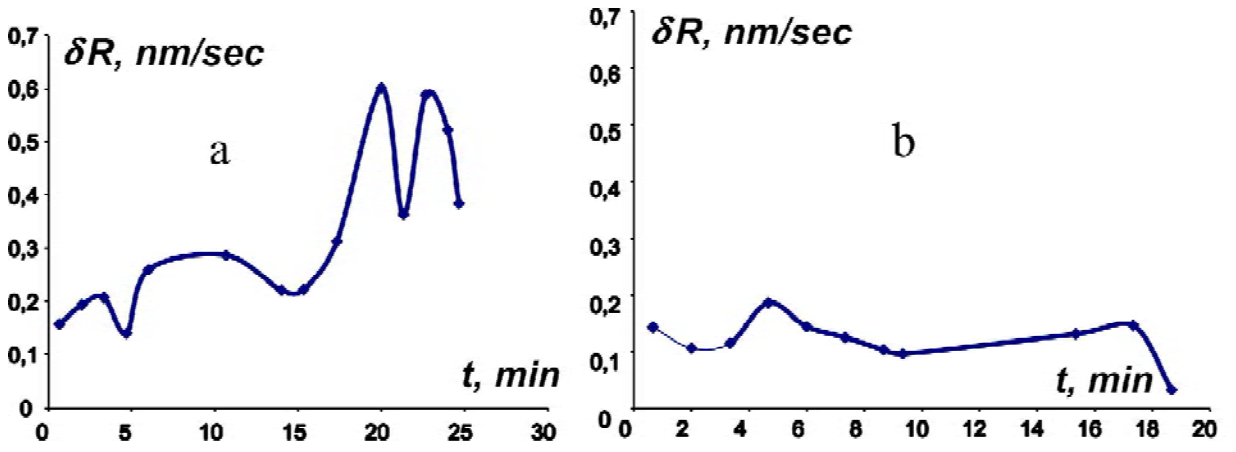


Fig. 2. Fluctuations of normal rate (a) — experiment with kinematical waves, (b) — other similar experiment

The data obtained by this method allows to determine dynamic features of the crystal growth in the process of the surface reaching the state of dynamic equilibrium. We worked out a criterion to characterize the state of dynamic equilibrium (Piskunova, Rakin, 2005). The point when the growing surface reaches the stationary growth is characterized not only by constancy of the normal rate of growth, but also by stability of its dispersion in time. The dispersion of the normal rate of growth is calculated from the sum of the dispersion of tangential rate and the distance between the steps. In this case, the regulations observed through AFM scanning area are fair for all the faces of the growing crystal. The results of the investigation show that the fluctuation value of the normal rate of growth increases nonmonotomically during the experiment (fig. 2a). Thus, in this experiment, the crystal-medium system is rather far from the state of stationary growth compared to the others.

This increase of fluctuation of the normal rate can result from supersaturation increase of solution and from formation of macrostructures on the surface of the crystal. The first explanation is not possible, as the AFM cell did not receive any injections of nutrient solution during the experiment (although the results of another experiment without nutrient injections demon–strated constant normal rate and its dispersion fig. 2b). Fig. 1a shows three peculiar areas character–ized by higher mean values of the parameters and their fluctuations in comparison with the previous period of time. It testifies to the fact that we deal with a new higher qualitative level of surface organization, which can be explained in terms of nonequilibrium thermodynamics (Piskunova, 2006; Prigogin, Kondepudi, 2002). Perhaps these three peculiar areas are visually perceptible in AFM-pictures? During this experiment we could really observe the tendency of thin steps to group together and form macrosteps (fig. 3).

However, we have determined that in the given experiment the real nature of this grouping is kinematical waves of density of steps. Kinematical waves were first described by Kasatkin (1). They present densening and dispersing of growth steps in the echelon.

We made cuts of the 40 AFM-pictures taken from this experiment. Their simple visual comparison allows to see the process of grouping of thin steps. The formed groups have low growth rate, but they eject the lowest thin step that takes high speed across the terrace and joins the next group. This behavior indicates undulatory motion.

In fact, such effect was observed at least nine times during the second experiment. However, we proved that only three out of the nine were actually kinematical waves, and the rest were produced as a consequence.

We transformed the same plane cuts of all images into a digital data file, each profile containing 1500 equally paced dots. The data then underwent FFT (fast Fourier transform), allowing to transfer arbitrary periodic continuous function from the amplitude-time field into the amplitude-frequency form. The moments when multitude of thin steps changes into macrostructure of nonzero amplitude must be recognized against the corresponding Fourier- spectrum. The next step in working out the data was calculating the ratio of maximum amplitude to the area under the Fourier curve. This ratio is shown in fig. 4.

Three peculiar areas marked in fig.4 are characterized by major leaps of the ratio value. The upper curve has a better illustrative effect and presents a derivative from the lower one. These leaps may testify to existence of kinematical waves in the indicated time periods. This occurs from 4th to 7th min, from 14th to 16th min, and from 22nd to 24th min. It is worth noting that these characteristic areas concur with the time intervals, which have sharp changes

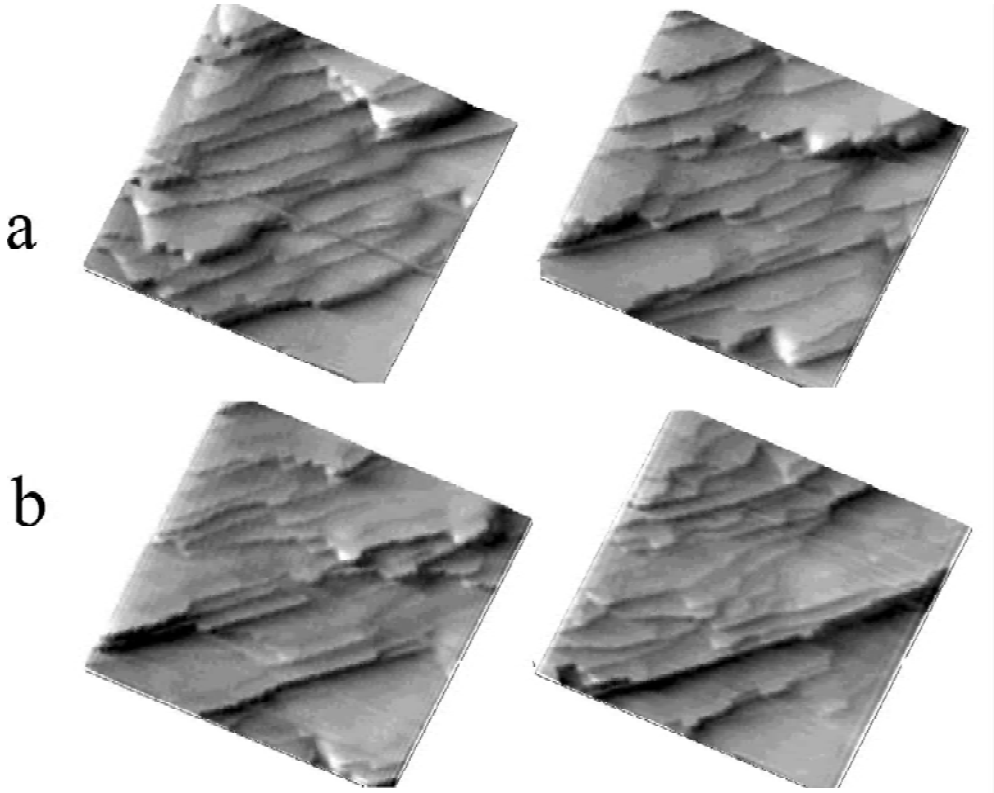


Fig. 3. Grouping of the macrosteps on the growing surface of the crystal NaCl ((a) — 3d and (b) — 14th minute of the experiment). Image size is 7 × 7mkm

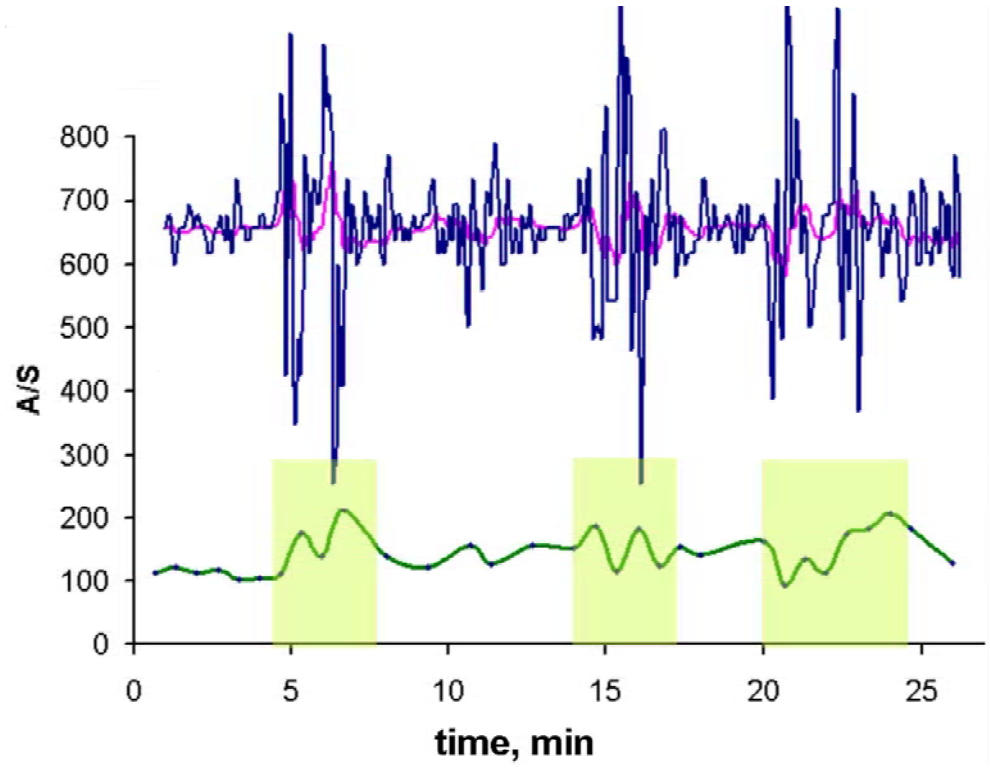


Fig. 4. Kinematical waves of density of steps on the surface of the growing crystal

fluctuation parameters determined by statistical method (fig. 1a).

Thus, we proved that AFM is a unique source of data for performing statistical calculations. Our method allows to do high precision calculations of normal growth rate and its dispersion associated with thermodynamic conditions of crystal growth from solution. The calculations for one of the experiments have shown that the real nature of steps grouping is kinematical waves of density of steps.

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