What Kind of Surface Diffusion Might Operate at the Crystal-solution Interface – in Memory of Ichiro Sunagawa

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Surface diffusion over the crystal – vapor versus the crystal – solution interface. a. On the crystal – vapor interface, nearly all adsorption sites are empty. Thus the potential barrier for the adsorbed particle (red) to jump to the neighboring position (arrows) is determined only by the particle – surface interaction and is typically noticeably lower than the evaporation heat. b. On the crystal – solution interface, nearly all adsorption sites are occupied by the solvent molecules (for instance, water) forming partly ordered immobile adsorption layer cooperatively bound with the solid substrate. Thus desolvation of both the next adsorption site and, partly, of the jumping adsorbed molecule (red) is a must and probably difficult. That difficulty may strongly hinder the tangential mobility of the adsorbed species. On the other hand, a solute molecule located above the adsorption layer (yellow particle) and still attached to the surface (though, much weaker) can move easier.

With profound warmth and respect see I how Prof. Katsuo Tsukamoto, bright scientist of his own, cares on the memory of Ichiro Sunagawa, his Teacher, big Scientist and Personality. This care continues Katsuo’s disposition towards Ichiro not only for the years they both worked in Tohoku University but for the years after Ichiro’s retirements. That is how the science continues forever.

For the first time I met Ichiro in 1965 at the international symposium “Adsorption et Croissance Cristalline” organized in Nancy by R. Kern, Among the attendees were F. C. Frank, I. N. Stranski, P. Hartman, G. M. Pound and other bright people in the crystal growth communities emerging in many countries after the World War II. This symposium was one of the first meetings on crystal growth and manifestation of the exploding interest to this field, as reflected by conferences in USSR, Moscow (held in 1956, Proceedings published in 1959), USA, Cooperstown (both the conference and Proceedings in 1958), followed by the 1-st International Conference on Crystal growth (ICCG1) in Cambridge, USA in 1966, ICCG2 in Birmingham (UK) in 1968, ICCG3 and establishing the International Organization for Crystal Growth in 1971 in Marseille (France). Ichiro was the seed around which the Japanese crystal growth community was assembled and hosted ICCG4 in Tokyo in 1974.

Sunagawa’s talk in Nancy was on relations between
growth conditions and crystal morphology – the subject he was working on for decades as mineralogist with geological background. Feeling that the approach of descriptive mineralogy and geometrical crystallography is far not enough to meet practical industrial and geological needs and simply to satisfy his great curiosity Ichiro always expressed keen interest in physical atomistic view. That was the major subject of our scientific discussions – steps and kinks, fluctuations, roughening transition, incorporation barriers, adsorption and diffusion on surfaces, role of impurities – all what constitute current crystal growth science and technology. My interest was always in Ichiro's master-made surface and bulk morphology images, news and liquidation of my ignorance in geology. Meeting with Ichiro reminded me enlightening conversations with my teacher on the side of experimental crystallization, G. G. Lemmelein, also mineralogist by background. Lemmlein discovered spiral growth morphology on silicon carbide in 1945, made the cartoon on how it works but failed to bring in the screw dislocation concept to understand it. The latter step was made by Sir Charles Frank in 1949.

I do not remember numerous specific problems we discussed with Ichiro. Diffusion over the crystal/solution interface should be among them – because both of us were highly interested in solution growth and because of the rather wide spread belief that surface diffusion in solution growth is as essential as in the vapor growth. In reality, however, experiments on room temperature solution growth suggest that direct incorporation of growth units from solution prevails. (Rashkovich, De Yoreo and many others). The same conclusion was made from the brilliant series of experiments on electro crystallization of Ag accomplished in the 60-70's by Bulgarian school (Kaishev, Budevski, Bostanov, Staikov, et al.). Nevertheless, there was (and still is) a big controversy in interpretations of other electrochemical experiments and some on the room temperature solution growth ascribing noticeable role to surface diffusion. Also, there is a contradiction between common physical sense and the classical view on surface diffusion – if directly applied to the solution growth. This classical pictureviews surface diffusion as jumps of species adsorbed on an otherwise clean singular terrace from one surface site to the other (arrows in Fig. a). That view works perfectly for the clean crystal-vapor interface at temperatures allowing sufficiently high frequency of the jumps tangential to the terrace –
relative to desorption frequency. In this pure vapor case, surface diffusion provides dominant flux of material to the growth steps — as compared with the flux of species incorporating directly from the vapor. This happens for two reasons: 1. Number density of the crystallizing species within the atomic size thick adsorbed surface layer at the terrace is many orders of magnitude higher than the density in the bulk vapor; and 2. The (potential barrier/kT) ratio to move the species from one adsorption position to the next does not exceed several units thus allowing surface diffusion to be fast enough.

Both conditions should typically fail at the crystal solution interface: 1. The density of crystallizing species within the adsorption layer is far not as dramatically different from the density in the bulk (solution) as is this difference in case of vapor growth — since the number density of the crystallizing species in solution is typically much larger than the vapor density and 2. Jumps between surface sites require partial dehydration of both the jumping species and the next site occupied by a solvent molecule (e.g., water) — as sketched on the Fig. b. With the hydration energies of \((10 - 20) \text{ kcal/mol}\) (the measured activation energy scale for the aqueous solution growth) the jump barrier seems to be too high to allow high surface diffusivity. The situation resembles the difference between a man once wandering over an empty square early on the morning versus him the trying to wander over same square during the big event when the square is heavily crowded.

The controversy might be a bit lighter if an assumption is made that the species adsorbed from solution are located not immediately on the naked surface terrace but above the first strongly adsorbed solvent layer — still gaining somewhat in the density but allowing also noticeable surface mobility. Recent G. Sazaki’s optical observations on the near-interface wondering of lysozyme molecule may serve as an indirect support for that assumption.

The surface diffusion story provides just a spirit of our conversations with Ichiro. We did have different scientific psychologies as majority of physicists, mineralogists and chemists do. After the WW II, physics took over further crystal growth science development from hands on mineralogy and our discussions with Ichiro reflected mutual wish to learn more from one another and to enrich our scopes. Ichiro was always curious to learn more on physics and shared his knowledge in geology. Ichiro liked minerals, appreciate and deeply understood their beauty and was happy to spread that feeling. He was also a bearer of Japanese culture. He opened my eyes on some features of Japan and added new bright colors to my life.