Crystal growth from aqueous solution in the presence of structured impurities

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Appendix A: Adsorbed and solution phase equilibrium

At equilibrium, the chemical potential of the adsorbed and solution phase are equal. Then

$$\mu_{ads} = \mu_{sol}, \tag{1}$$

where μ_{sol} corresponds to the chemical potential of an ideal solution at concentration ρ_I and temperature T. Hence,

$$\beta\mu_{sol} = \beta\mu_0 + \ln\rho_I, \tag{2}$$

where μ_0 is the standard chemical potential and $\beta = 1/k_B T$.

The chemical potential is defined as

$$\mu_0 = -k_B T \ln\left\{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} k_B T\right\}, \tag{3}$$

where h is the Planck constant ($h = 6.6260 \times 10^{-34} J.s$) and m is the mass of the k-mer. Taking into account that the mass of a k-mer is directly proportional to the mass of the monomer unit: $m = k m_0$ with m_0 the mass of the monomer unit. Then, Eq. 2 can be rewritten as:

$$\beta\mu_{sol} = -\frac{3}{2}\ln k - \ln\left\{\left(\frac{2\pi m_0 k_B T}{h^2}\right)^{3/2} k_B T\right\} + \ln\rho_I, \tag{4}$$

and

$$\beta\mu_{sol} = -\frac{3}{2}\ln k + \ln C_I, \tag{5}$$

where $C_I = \rho_I/\rho_I^*$ and $\rho_I^* = \left\{\left(\frac{2\pi m_0 k_B T}{h^2}\right)^{3/2} k_B T\right\}$. This expression relates the chemical potential in solution with the impurity sizes and the concentration in the bulk.

Appendix B: Monte Carlo simulation details

MC simulations were used in order to test the applicability of the new theoretical proposition. The calculations were performed by using L-one-dimensional lattices ($M = L$ sites) and $L \times L$-square lattices ($M = L^2$ sites) with periodic boundary conditions. A linear k-mer is modeled as a group of collinear identical units, each one occupying a single site on the lattice (see Fig. 1). ε_0 is the adsorption energy of a k-mer unit. Then, the corresponding adsorption energies are $\varepsilon_1 = \varepsilon_0$, $\varepsilon_2 = 2\varepsilon_0$, $\varepsilon_3 = 3\varepsilon_0$ and $\varepsilon_4 = 4\varepsilon_0$ for monomers, dimers, trimers and tetramers, respectively.

The crystal surface is in contact with an impurity solution of k-mers with concentration C_I at temperature T. Then, the adsorption process is simulated through a grand canonical ensemble Monte Carlo method. The procedure is as follows. For a given value of the temperature T and concentration C_I, an initial configuration with N_k dimers adsorbed at random positions (on kN_k sites) is generated. Then, an adsorption/desorption process is started, where a linear k-uple of nearest-neighbor sites is randomly chosen, and a random number $\xi \in [0, 1]$ is generated:

1) if the selected entity is a k-uple of empty sites then adsorb a molecule if $\xi \leq W_{ads}$;

2) if the selected entity is a k-uple of sites occupied by atoms belonging to the same molecule then desorb the molecule if $\xi \leq W_{des}$;

3) otherwise, the attempt is rejected.

W_{ads} and W_{des} are the transition probabilities given by the Metropolis rule:

$$W_{ads} = \min\left\{1, C_I \exp\left(-\frac{\Delta E}{k_B T}\right)\right\}, \tag{6}$$

and

$$W_{des} = \min\left\{1, \frac{1}{C_I} \exp\left(-\frac{\Delta E}{k_B T}\right)\right\}, \tag{7}$$

where ΔE is the difference between final-state energy and initial-state energy. $\Delta E = k\varepsilon_0$ in Eq. 6, and $\Delta E = -k\varepsilon_0$ in Eq. 7.

A Monte Carlo Step (MCS) is achieved when M k-uples have been tested to change its occupancy state. In our MC simulations, the equilibrium state can be well reproduced after discarding the first 10^6 MCS. Then, averages are taken over 10^6 MCS successive configurations.

The adsorption isotherm (surface coverage as a function of the concentration) is obtained as:

$$\theta_k(C_I) = \frac{k\langle N_k\rangle}{M}, \tag{8}$$

where the brackets mean the time average over the MC simulation runs.