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Master-equation approach to stochastic models of crystal growth

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A master-equation approach is formulated to obtain kinetic equations for stochastic models of the crystal-vapor interface. The properties of two Ising-type models are studied in stable and metastable states. General transition probabilities for the adsorption and evaporation of atoms at the interface are introduced, which may account for different types of dynamic behavior. Marked dependence of the interface kinetics upon the details of the transition probabilities is found, in contrast to the case of homogeneous systems.

I. INTRODUCTION

The theory of crystal growth is usually based on two kinds of mathematical approaches, i.e., a macroscopic approach using phenomenological thermodynamics[1-5] and a microscopic approach using stochastic models[6-11] on a molecular length scale. For the investigation of the surface property of a growing crystal, stochastic models appear to be very appropriate.

In these models, the equations of motion are replaced by kinetic equations where the "dynamics" enter through appropriately chosen transition probabilities.[12,13]

These transition probabilities can, in principle, be constructed according to the details of chemical kinetics of adsorption, evaporation, desolvation, etc. (within the frame of a detailed balance condition), thus accounting for different types of dynamic behavior.

However, presently available analytical treatments use a transition probability where the adsorption of atoms does not depend upon the surface structure of the crystal, which enters into the desorption probability only. But for the kinetics of systems with an interface, one cannot expect that different transition probabilities lead just to a renormalization of the respective time scale, as in the case of homogeneous systems[12] near the thermal equilibrium.

On the other hand, the different models proposed so far[1,6-11] exhibit quite similar static properties and finally they correspond to a great extent to the well-known Ising models for binary mixtures.[12-15]

It, therefore, seems desirable to use a more general approach than the ones at present available, which allows for a unified treatment of a variety of models representing different physical situations.

In Sec. II a master-equation approach is formulated following the methods developed for Ising models and is applied to two different models. The kinetics of one model is investigated in Sec. III and the influence of a variation of the transition probability upon the kinetics is studied. Section IV gives some concluding remarks.

II. MASTER EQUATION

Stochastic models of crystal growth are defined on the basis of a three-dimensional lattice structure which may be successively filled with molecules during the growth process. The "filled" part of the lattice then represents the "crystal"; the "empty" part represents the "vapor." The state of a lattice site j is defined by the site variable C_j, where $C_j = 1$ indicates a molecule, $C_j = 0$ is an empty lattice point. The interaction between molecules is, for simplicity, restricted to nearest neighbors (six in a simple cubic (sc) lattice). For symmetry reasons, we have changed to Ising variables[12-14] $S_j = 2C_j - 1 = \pm 1$. Then the Hamiltonian of the models is defined as

$$\mathcal{H} = -J \sum_{\langle ik \rangle} S_i S_k - \Delta\mu \sum_i S_i + V(\{S\}), \tag{1}$$

where J is the interaction parameter, $\Delta\mu$ is the chemical potential difference between the crystal and the vapor phase, and $V(\{S\}) = \{0, \infty\}$ is an additional potential accounting for certain restrictions for the arrangement of molecules in the lattice, as discussed below. The first sum goes over all pairs of neighboring sites, and the second over all lattice sites. The master equations can now be formulated according to the methods developed for homogeneous Ising models[12-14]

$$\frac{d}{dt}\langle S_j \rangle = -2\langle S_j W(S_j \to -S_j)\rangle, \tag{2}$$

where $W(S_j \to -S_j)$ is the conditional probability that the site variable S_j changes its sign. This may depend on all lattice sites, but for short-range interactions, it is reasonable to assume W depending on the environment of the considered site only.

In order to have a steady-state solution[12] of Eq. (2), the principle of detailed balance is applied to the probabilities $W(S_j \rightarrow -S_j)$ giving

$$\frac{W(S_j \rightarrow -S_j)}{W(-S_j \rightarrow S_j)} = \exp\left(\frac{\mathcal{H}(S_j) - \mathcal{H}(-S_j)}{k_B T} \right) , \tag{3}$$

where $\mathcal{H}(S_j)$ is the energy of the respective state of the system and $\mathcal{H}(-S_j)$ is the energy of the same state but with reversed S_j.

A general form for the transition probability is now

$$W(S_j \rightarrow -S_j) = u(\{S_j\})(1/2\tau)[1 - S_j \tanh(E_j)], \tag{4a}$$

$$E_j = \frac{1}{k_B T} \left(J \sum_{i(\mathrm{NN})} S_i(j) + \Delta\mu \right), \tag{4b}$$

where $u(\{S_j\})$ can be an arbitrary function of all variables except S_j and τ is some characteristic time constant. The two models to be considered are described by the following definitions:

(a) Simple Ising model [9,10,12–14]:

$$V(\{S\}) \equiv 0 \quad \text{in Eq. (1)}, \tag{5}$$

$$u(\{S_j\}) \equiv 1 \quad \text{in Eq. (4a)}. \tag{6}$$

If the interface crystal vapor is assumed to be extended normal to the "z" direction, then the boundary conditions are: $\lim \langle S_j \rangle = \mp 1$. $z \rightarrow \pm\infty$. (This model is discussed with respect to static properties only.)

(b) Ising type model, where no overhanging molecular structures are allowed (solid-above-solid restriction, also no molecular defects can exist in the solid part[6,7,11]):

$$V(\{S\}) = \infty \tag{7a}$$

for all configurations $\{S\}$, where in the $+z$ direction a $(S_j = -1)$ site is followed by a $(S_j = +1)$ site,

$$V(\{S\}) = 0 \quad \text{otherwise}. \tag{7b}$$

In order to take this restriction properly into account in some decoupling approximation[15,16] of Eq. (2) also, we set

$$u(\{S_j\}) = \tfrac{1}{4}[2 + S^i_{j-1} - S^i_{j+1} - S^i_j(S^i_{j-1} + S^i_{j+1})], \tag{8}$$

where j is now the index of a plane normal to the z direction, while i represents a site within such a plane. (Note that because of the $\{1, 0\}$ property of u and the $\{0, \infty\}$ property of V, the detailed balance condition is not violated.)

Starting now from a configuration in accordance with the Hamiltonian [Eq. (1)], Eq. (8) ensures that the transition probability Eq. (4a) vanishes, if an attempt is made to reach an unallowed state. (This model is discussed with respect to both static and kinetic properties in detail.)

Equation (2) with Eq. (4) is now decoupled in mean-field approximation (MFA) giving a coupled set of nonlinear differential equations. While for a model (a) [Eqs. (5) and (6)] the procedure is exactly the same as for the homogeneous Ising model,[12–14] the transition probability for model (b) [Eqs. (7) and (8)] is split up into two parts for adsorption and desorption, turning Eq. (2) into

$$\frac{d}{dt} \langle S^i_j \rangle = -[\langle (S^i_j - S^i_{j+1}) W^i_{j-} \rangle + \langle (S^i_j - S^i_{j-1}) W^i_{j+} \rangle], \tag{9}$$

with

$$W^i_{j\pm} = \tfrac{1}{2}(1 \mp S^i_j)(1/2\tau)(1 \pm \tanh E^i_j). \tag{10}$$

From the Hamiltonian equations (1) and (7), it is clear that

$$S^i_j \geqslant S^i_{j+1} \quad \text{for all } j, i, \tag{11a}$$

$$S^i_{j-1} = -S^i_{j+1} \quad \text{for } W(S^i_j \rightarrow -S^i_j) \neq 0. \tag{11b}$$

Therefore, without losing the generality of Eq. (9), one can reduce Eq. (10) to the simple form

$$W^i_{j\pm} = \frac{1}{2\tau} \left\{ 1 \pm \tanh\left[\frac{1}{k_B T} \left(J \sum_i S^i_j + \Delta\mu \right) \right] \right\}, \tag{12}$$

where the sum goes only over the four nearest neighbors of S^i_j within the plane j.

This elimination of redundant information does not change the properties of Eq. (9) but is convenient in order to avoid ambiguity in the MFA decoupling of this nonergodic model.

Now, replacing in the usual way,[12,13] the local field acting on S^i_j by its expectation value, one finally has the set of differential equations

$$\frac{d}{dt} \langle S_j \rangle = -[(\langle S_j \rangle - \langle S_{j+1} \rangle) \overline{W}_{j-} + (\langle S_j \rangle - \langle S_{j-1} \rangle) \overline{W}_{j+}], \tag{13a}$$

$$\overline{W}_{j\pm} = (1/2\tau)(1 \pm \tanh \overline{E}_j), \tag{13b}$$

$$\overline{E}_j = (1/k_B T)(4J\langle S_j \rangle + \Delta\mu). \tag{13c}$$

In order to integrate this system numerically, a total number of 200 equations instead of the infinite set was considered, corresponding to 200 lattice planes parallel to the crystal-vapor interface. The boundary conditions were $\langle S_j \rangle = \pm 1$, respectively.

The result for the steady-state solution $\Delta\mu = 0$ in Eq. (4b) corresponds, for the solid-above-solid (SAS) model (b), to the one found by Temkin[6] and Leamy *et al.*[7] The simple Ising model (a) corresponds, to an extent, to the model recently studied by v. Leeuwen *et al.*[8] and to the Ising model with particle conservation used in a Monte Carlo simulation by Leamy *et al.*[9]

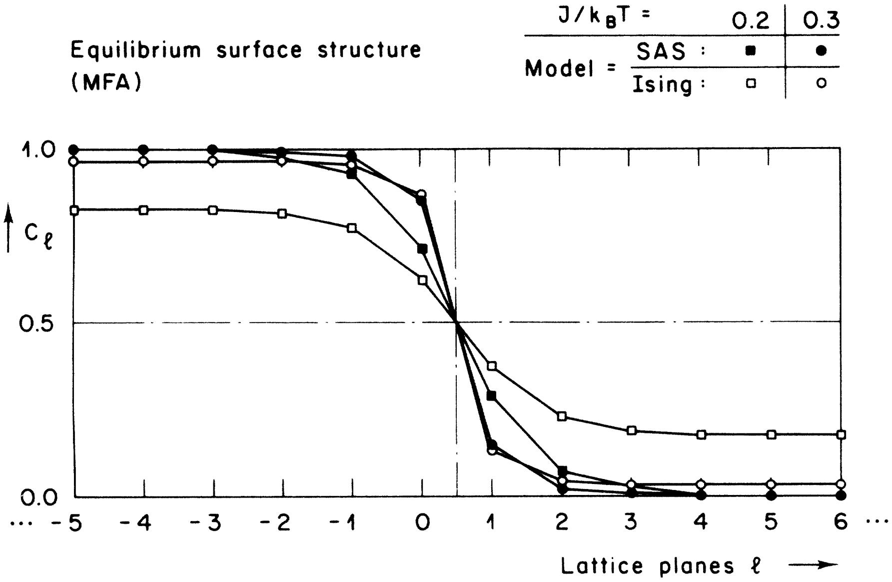

FIG. 1. Equilibrium surface structure of two models [simple Ising model (a) and solid-above-solid model (b)] at two temperatures.

In Fig. 1, the steady-state solutions of both models at two temperatures are exhibited. The simple Ising model (a), clearly goes to the equilibrium state of the homogeneous model in the limit $z \rightarrow \pm\infty$, the SAS model (b) converges rapidly towards $\langle S_j \rangle \rightarrow \pm 1$ a few planes away from the interface.

In addition to these stable solutions, there also exist steady-state solutions which are unstable under small perturbations, corresponding to a saddle point[6] of the free energy. These are characterized by a lattice plane with $\langle S_j \rangle = 0$. Applying now a small chemical potential difference $\Delta\mu = 0$ to model (b), the saddle-point solution decays to a metastable solution after some relaxation time τ', as plotted in Fig. 2. Here the interface position Y is defined as

$$Y = \lim_{n\rightarrow\infty}\left(\frac{1}{\langle S_{-n} - S_{+n}\rangle}\sum_{j=-n}^{+n}\langle S_j \rangle\right) \tag{14}$$

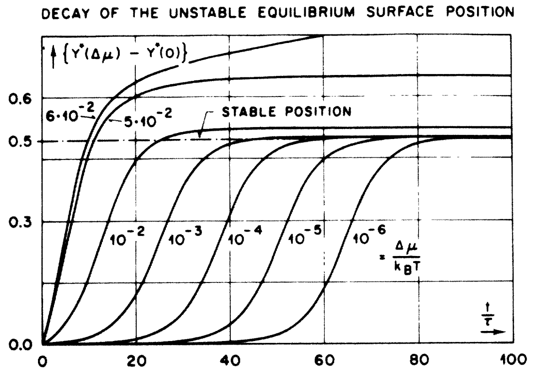

FIG. 2. Changeover of the saddle-point solution for the interface position to the metastable solution at constant temperature.

and the relaxation time τ' as

$$\tau'(\Delta\mu) = \frac{1}{Y^*(\Delta\mu,\infty) - Y^*(\Delta\mu,0)} \times \int_0^\infty [Y^*(\Delta\mu,\infty) - Y^*(\Delta\mu,t)]\,dt, \tag{15}$$

where the asterisk denotes the saddle-point solution.

Plotting τ' vs $\Delta\mu$, one obtains a dependence

$$\tau' \sim -\ln(\Delta\mu/k_B T) \tag{16}$$

as $\Delta\mu \rightarrow 0$. This logarithmic behavior means that even for small $\Delta\mu$, the system would switch over to the "stable" state after a very short time. Therefore, the saddle-point solution cannot be important in practice.

A small chemical potential difference acting on the stable solution of Eq. (9) leads only to a displacement of the interface position, as shown in Fig. 3. For very small $\Delta\mu$, the displacement may be obtained from the original stable solution in the following way, using a Taylor expansion in the perturbation $h \equiv \Delta\mu/k_B T$,

$$Y(h) = Y(0) + Y'(h=0)h + O(h^3) + \cdots . \tag{17}$$

Setting $d\langle S_j \rangle/dt = 0$ one obtains, from Eqs. (13) together with Eqs. (14) and (17),

$$Y(h) - Y(0) = h \times \frac{1}{2}\sum_{j=-\infty}^{+\infty}[(\langle S_{j-1}\rangle - \langle S_{j+1}\rangle) \times \bar{W}_{j-}(0)\bar{W}_{j+}(0)], \tag{18}$$

under the assumption that the shape of the interface remains essentially unchanged.

For larger $\Delta\mu/k_B T$ a weak singularity appears (Fig. 3) for the displacement and finally a spinodal

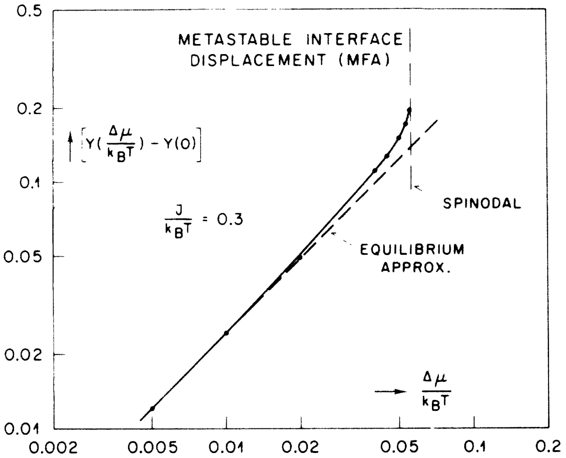

FIG. 3. Deviation of the average position $Y(\Delta\mu)$ of the interface from the equilibrium position versus the chemical potential difference in the metastable region.

limit of the metastable region, where crystal growth starts. The temperature dependence of this spinodal is found to be in agreement with the mean-field spinodal of the two-dimensional ($d = 2$) homogeneous Ising model

$$\frac{\Delta\mu^*}{k_BT} = \operatorname{arc\,tanh}\left(1 - \frac{k_BT}{2dJ}\right)^{1/2} - 2d\left(\frac{J}{k_BT}\right)\left(1 - \frac{k_BT}{2dJ}\right)^{1/2}, \tag{19}$$

in a simple square lattice, for both model types considered up to $k_BT/J \lesssim 3.3$. (In the limit $T \to 0$, the attachment of a molecule to a flat surface corresponds to a spin-flip in the completely ordered two-dimensional Ising model. This spinodal potential difference is just $\frac{2}{3}$ of the three-dimensional solution in the limit $T \to 0$.)

The existence of a spinodal line is a well-known feature of the MFA and other approximations,[14] although its physical reality is rather doubtful, since these approximations do not fully allow for the possibility of nucleation.

III. KINETICS OF SAS MODEL

In order to investigate the kinetic properties of the SAS model (b), a few additional quantities were evaluated in MFA, the definitions of which follow the suggestions of Temkin[6] and Leamy *et al.*[7]

The growth velocity is defined as

$$V = \frac{dY}{dt}; \tag{20}$$

the interface roughness

$$R = \sum_{j=-\infty}^{+\infty} 4C_j(1 - C_j) \tag{21}$$

corresponds to the energy of the open bonds within the interface, and the surface extent

$$S = \sum_{j=-\infty}^{+\infty} (C_j - C_{j+1}C_j^4) \tag{22}$$

corresponds to the number of interface atoms per unit area.

A chemical potential difference $|\Delta\mu|$ larger than the spinodal $|\Delta\mu^*|$ causes the interface position to move with periodically varying velocity. Plots of the interface velocity V and roughness R are given in Fig. 4(a) versus the reduced time t/τ and in Fig. 4(b) versus the interface position Y (relative to the stationary initial position). While the existence of a spinodal line is due to the approxi-

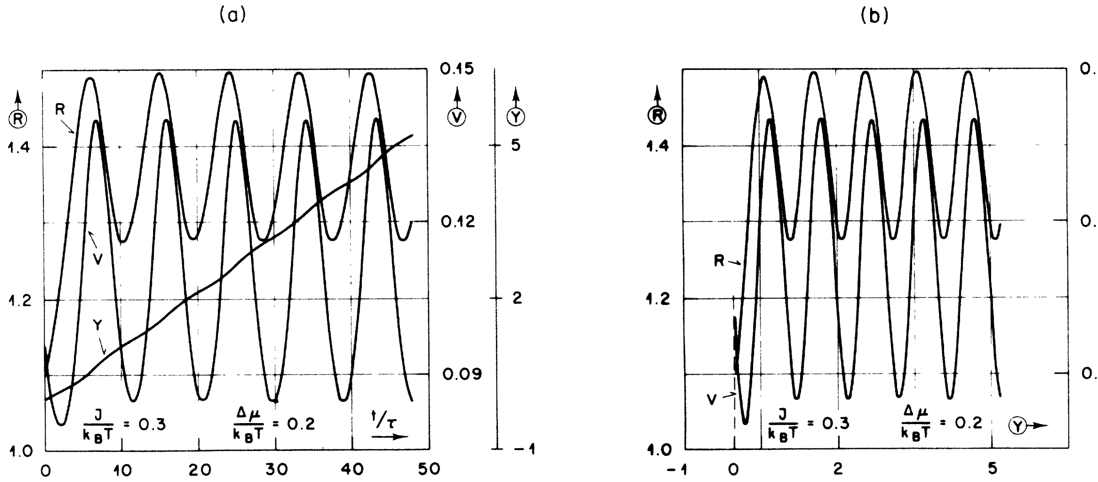

FIG. 4. (a) Surface roughness R, velocity V and position Y as a function of time. (b) Surface roughness R and velocity V as a function of the interface position Y.

mation used, the periodic fluctuation essentially comes from the nonlinearity of the set of Eqs. (9) and (13), although in reality it might be too small to be detected, e.g., by computer experiments. Furthermore, the amplitude of the fluctuation decreases as the average velocity increases.

This periodicity again appears in the plot of a limit cycle (a typical feature of a nonequilibrium process[17]) in Fig. 5, where the roughness R is plotted versus the velocity V. The transient phase from the initial state (I.S.) depends, of course, on the initial conditions; the form of the limit cycle depends on all parameters entering the kinetic equations except the initial conditions.

In the following, the dependence of the kinetics upon different transition probabilities is now studied. As already mentioned above, Eq. (4) together with Eq. (8) is not the only possible way of defining a transition probability for the SAS model (b). In order to introduce a variable form for the transition probabilities,[12] we multiply Eq. (4a) by a factor

$$g(E_j) = 1 - \sinh^2(E_j)\left(\frac{\tanh(E_j/\zeta)}{\tanh(E_j)} - 1\right), \quad 0 < \zeta \leq 1, \tag{23}$$

with a free additional parameter ζ. Since $g(E_j)$ does not depend upon S_j, the detailed balance condition Eq. (3) is not affected. For $\zeta = 1$, Eq. (4a) remains in its original form. In that case, the decay probability of an energetically unfavorable state increases with increasing energy abundance over the final state, corresponding in some way to a transition over a potential barrier. For $\zeta \to 0$, instead Eq. (4a) combined with Eq. (12) then reduces to the transition probability originally chosen by Metropolis *et al.*[18] implying that the conditional decay probability be the same for all energetically unfavorable states.

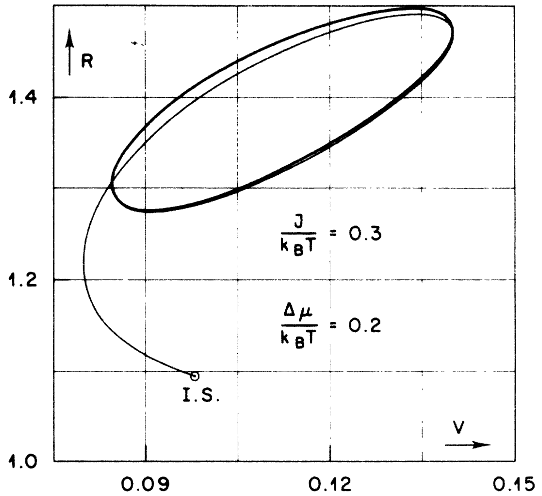

FIG. 5. Formation of a limit cycle during the movement of the interface through the lattice.

The variation of ζ between 0 and 1 thus causes a variation of the form of the probability function Eqs. (4) and (23). This now allows one to study the influence of the particular choice of the transition probability upon the kinetic properties of the system. As could be expected from earlier calculations in homogeneous systems,[12] a change of the time-averaged growth velocity $\overline{V}$ occurs as plotted in Fig. 6. (The vertical tangent to the $\overline{V}(\Delta\mu)$ curves at the spinodal is again a consequence of the MFA.[14])

The interface variables $\overline{R}$ and $\overline{S}$ are plotted in Fig. 7, as functions of the chemical potential difference and with ζ as parameter. The dependence of both quantities upon ζ is obvious, especially the change of these quantities being contrary to the change of the velocity $\overline{V}$ at some constant $\Delta\mu/k_BT$: Increase of ζ from 0 to 1 leads to an increase of the velocity $\overline{V}$, but to a decrease of $\overline{R}$ and $\overline{S}$, while in general $\overline{R}$ and $\overline{S}$ increase with increasing $\overline{V}$. This effect can be seen even more clearly in Fig. 8, where $\overline{R}$ is plotted vs $\overline{V}$ for $\zeta = 0, 1$. Points on different curves corresponding to the same $\Delta\mu/k_BT$ are connected by arrows. A very important result is, that no simple transform exists from the points on the $\overline{R}(\overline{V})$ curve with $\zeta = 1$ to the curve with $\zeta = 0$. One would only have a simple transform if either $\overline{R}$ remained constant or if a simultaneous change of $\overline{R}$ and $\overline{V}$ occurred in such a way that the new point came to lie on the same curve $\overline{R}(\overline{V})$. Since this is not the case there is no unique interrelation between the average surface roughness $\overline{R}$ and the velocity $\overline{V}$ independent of the chosen transition probability.

However, it appears that at least for this special class of transition probabilities, a power law

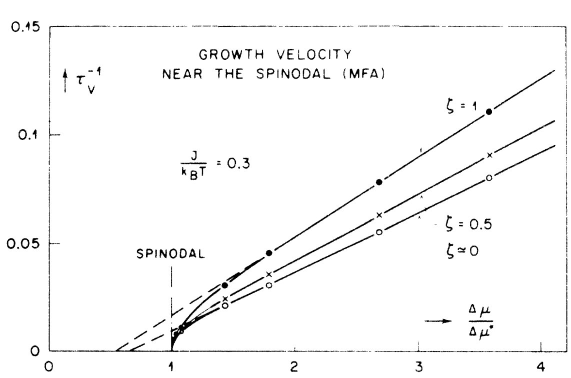

FIG. 6. Growth velocity $v \equiv \tau_v^{-1}$ near the spinodal versus chemical potential difference. Parameter of the curves is the transition probability parameter ζ.

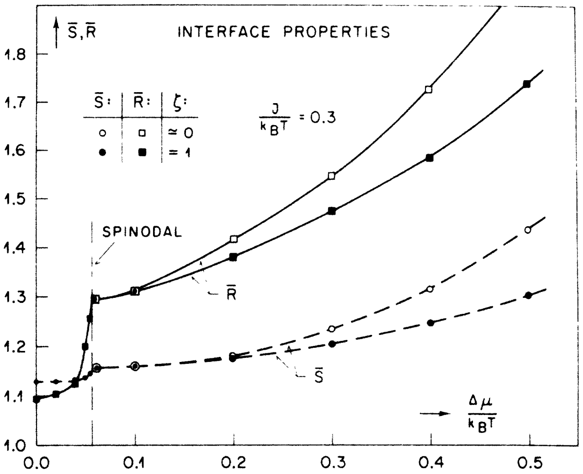

FIG. 7. Interface roughness $\bar{R}$ and interface extent $\bar{S}$ vs chemical potential difference $\Delta\mu/k_BT$. In the kinetic region $\Delta\mu > \Delta\mu^*$, $\bar{R}$, and $\bar{S}$ increase if ζ is changed from 1 to 0.

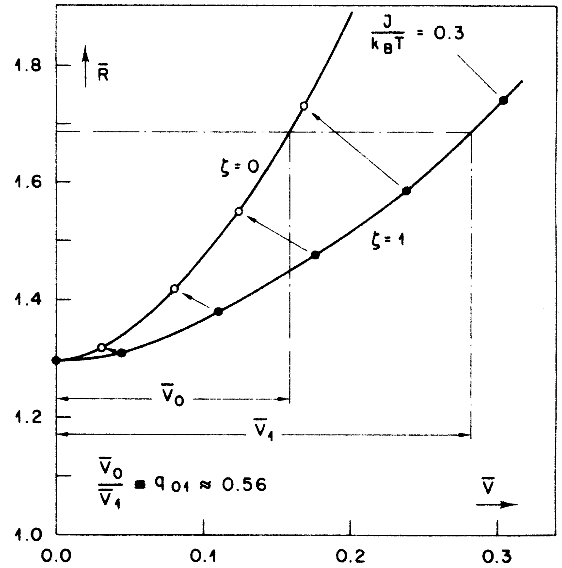

FIG. 8. Average interface roughness $\bar{R}$ vs velocity $\bar{V}$ for two values of ζ. The points connected by arrows correspond to the same chemical potential difference.

$$\bar{R}(\bar{V}) - \bar{R}(0) \sim \bar{V}^2 \tag{24}$$

gives a reasonable representation for the interrelation of $\bar{R}$ and $\bar{V}$.

IV. CONCLUSION

A master-equation approach was formulated to study the metastable and kinetic properties of a crystal-vapor interface model. The conditional probabilities for evaporation and adsorption, governing the resulting set of equations were both assumed to depend on the local energy changes. This leads to a highly symmetric form of the kinetic equations.

Since these transition probabilities are only defined as a ratio, a normalizing multiplier may be introduced to construct probabilities according to the assumed chemical kinetics. Taking advantage of this arbitrariness, a particular variable multiplier was used, in order to investigate the influence of different molecular attachment mechanisms upon the kinetics of crystal growth. It was found that surface roughness $\bar{R}$ and growth velocity $\bar{V}$ depend rather strongly on the particular choice of the probabilities in a nontrivial way, so that the changes cannot be compensated by simply adjusting the time scale appropriately.

Therefore, it is finally concluded that the microscopic process of attachment of molecules at the crystal surface plays an important role for the interrelation of surface parameters such as roughness and growth velocity.

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