

Dynamics and roughness of reaction fronts in heterogeneous solid-state chemical reactions

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A mesoscopic model to describe the reaction fronts in solid-state reactions is proposed. The model predicts the existence of the linear regime ($\sigma \sim t$, σ is the average thickness of the reaction layer, t is the time) and the parabolic regime ($\sigma \sim \sqrt{t}$). The roughness of the reaction front is also considered. [S1063-651X(98)04805-3]

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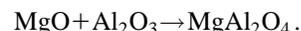
I. INTRODUCTION

In heterogeneous solid-state reactions the reaction products separate spatially the initial materials. For a continuation of the reaction process the reacting species have to diffuse across the reaction product. Therefore, these interface reactions are controlled by both the elementary reaction rates between two neighboring atoms (or molecules) of the reacting species and the diffusion constants for the motion through the reaction product. At the initial stage of the interface reactions the film of reaction products between the bulks of reacting species is thin. Therefore, the transport of reacting species through the dead zone of reaction products is sufficiently fast and the rates of the chemical processes at the interfaces control the reaction velocities and therefore the growth of the product phase [1]. Usually the interfacial reactions are not time dependent [2–5], which results in a linear reaction rate law in the regime controlled by interfacial reactions. On the other hand, the diffusion processes become relevant with increasing thickness of the reaction product layer. The diffusion determines the reaction rate for a sufficiently large size of the product layer. Consequently, the thickness of this layer follows a parabolic rate law in the long time regime of heterogeneous solid-state reactions [6].

Two general principles acting at the reaction front of a solid-state reaction have to be considered: (i) the minimization of the interfacial energy, which is the energy of the atomic arrangement along the interface; (ii) the minimization of the activation energy for the interface movement, for example, the movement of the interfacial dislocations. Both demands cannot be fulfilled simultaneously (see [7]). At the initial stage of the reaction, where the interfacial processes determine the reaction rate, the activation energy for the interface motion is minimized by the reaction front assuming an appropriate structure, even if the latter does not involve a minimum of the interfacial energy. This corresponds to the well-known fact that the interface is not in the chemical equilibrium during the reaction controlled regime [6]. With the further advancing of the reaction front, the diffusion controlled regime may become appropriate, so that the reaction front due to a decrease of the reaction velocity at the interfaces may rearrange to adapt a structure according to the minimum of interfacial energy. This behavior corresponds to the interface being in chemical equilibrium during the diffusion-controlled regime. Besides the above minimal principles, the fluctuations of the diffusing reagent species may

influence the morphology of the reaction front. From the general point of view one expects that the fluctuations favor an increase of the roughness of the initially smooth interfaces.

There exists a versatile spectrum of underlying processes and chemical reaction mechanisms, e.g., the detachment of atoms (ions, molecules) from the front of the reactants [8], the diffusion of the reactant particles through the product layer [9], the real chemical reaction at the interfaces between reacting species and reaction product, the relaxation of the final molecules in the corresponding lattice of the reaction products [9], the nucleation rate of possible interfacial growth ledges [10], and motion of possible dislocation misfits [7]. For a more detailed discussion we analyze the reaction processes of a spinel formation; see Fig. 1. Such a reaction can be described by an overall reaction equation, e.g.,



There exists a large class of spinel reactions containing various metal atoms [11–13]. A general property of all these reactions is the relatively high mobility of the cations and the extremely low mobility of the (oxygen) anions. In other words, the anions form an immobile sublattice, which is approximately stable during the reaction processes. The initial reactants and the reaction products have, of course, different lattice constants. This misfit is equalized by various lattice dislocations. Only some few materials show a very low misfit, e.g., the interfaces $\text{TiMg}_2\text{O}_4/\text{MgO}$ and $\text{MgFe}_2\text{O}_4/\text{MgO}$, respectively [14]. Distribution, mobility, and possible transformations of these dislocations determine also the evolution of the interfaces. However, it can be assumed that the contributions of these dislocations to the roughness of the interface are sufficiently small for the short time regime (increas-

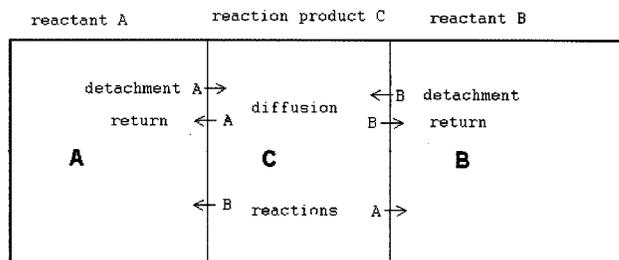
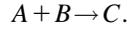


FIG. 1. Reaction fronts and processes at the interfaces for the chemical reaction process $A + B \rightarrow C$.

ing roughness). On the other hand, the interfaces become smooth at very long times (corresponding to a large thickness of the reaction product zone) and only the dislocations remain effective. Thus, the final interface structure is mainly determined by the equilibrium distribution of the dislocations.

The formation and evolution of misfits is a result of the anion sublattice deformation during the spinel reaction. All other elementary steps are mainly determined by properties of the cations and the corresponding cation sublattice. We consider the reaction of the general type



The solid-state reaction is separated into the following characteristic steps, see also Fig. 1.

(1) Processes at the interface A/C : (i) detachment of A particles from the A surface with the rate α_A ; (ii) integration of returning A particles into phase A with the rate $q_A n_A(A/C)$ [$n_A(A/C)$ is the concentration of A particles in the reaction product zone at the interface A/C]. (iii) Reaction of B particles with particles of the phase A with the rate $\gamma_B n_B(A/C)$. (iv) Relaxation of the rough interface A/C into an energetically favorable configuration.

(2) Processes in the reaction product zone: diffusion of A and B particles with diffusion coefficients D_A and D_B , respectively.

(3) Processes at the interface C/B : (i) detachment of B particles from the B surface with the rate α_B ; (ii) integration of returning B particles into phase B with the rate $q_B n_B(C/B)$ [$n_B(C/B)$ is the concentration of B particles in the reaction product zone at the interface C/B]; (iii) reaction of A particles with particles of the phase B with the rate $\gamma_A n_A(C/B)$; (iv) relaxation of the rough interface C/B into an energetically favorable configuration.

The aim of the present paper is to give a theoretical description of these processes on a mesoscopic level. Section II introduces the model. The time evolution of the thickness of the reaction product layer is considered in the first part of Sec. III. The roughness and other characteristic quantities of the interface structure are considered in the second part of Sec. III. Section IV contains the conclusion.

II. THE MODEL

As mentioned above, we consider the chemical reaction $A + B \rightarrow C$. The materials A and B occupy the regions $-\infty < z < z_A(\rho, t)$ and $z_B(\rho, t) < z < \infty$, respectively. The range between the two interfaces $z_A(\rho, t) < z < z_B(\rho, t)$ is filled with the reaction product C . The reagents A and B diffuse through the "neutral" region C with the diffusion coefficients D_A and D_B , respectively. The concentrations n_A and n_B of diffusing reagents within the C layer are assumed to be very small as compared to their concentrations N_A and N_B in the bulk A and B materials. For not too large thickness of the C layer, this allows us to consider the chemical reaction only on the interfaces, neglecting the reaction processes in the bulk of the C layer.

In analogy with the interface growth models [15] we assume that in the continuous limit the interface evolution is sufficiently described by the following linear equation:

$$N_{A(B)} \frac{\partial}{\partial t} z_{A(B)}(\rho, t) = -L_{A(B)}(\nabla) z_{A(B)}(\rho, t) + j_{A(B)}(t) + \eta_{A(B)}(\rho, t), \quad (1)$$

where the first ("dynamical") term in Eq. (1) describes smoothening of the interface roughness, the second term corresponds to an averaged escape of $A(B)$ reagents from the interfaces to the C layer caused by both adsorption-desorption and reaction processes, and the last ("stochastic") part describes fluctuations in these processes, which lead to the interface roughness. It is assumed that the stochastic term $\eta_{A(B)}(\rho, t)$ corresponds to the Gaussian process of zero average value ($\langle \eta_{A(B)}(\rho, t) \rangle = 0$) and the correlation function

$$\langle \eta_I(\rho, t) \eta_J(\rho', t') \rangle = \Delta_{IJ} \Delta_I(t) \Delta(\rho - \rho') \Delta(t - t'), \quad (2)$$

where $I, J = \{A, B\}$, and the functions $\Delta_{A(B)}(t)$ as well as the operator $L_{A(B)}(\nabla)$ and the current $j_{A(B)}$ in Eq. (1) will be specified below.

First, we consider the dynamics of an averaged interfaces motion. The averaged positions of the interfaces are determined as $z_{A(B)}(t) = \langle z_{A(B)}(\rho, t) \rangle$ and obey the dynamical equation, which stems from Eq. (1) after the averaging over the random noise:

$$N_{A(B)} \frac{d}{dt} z_{A(B)}(t) = j_{A(B)}(t). \quad (3)$$

The rates $j_{A(B)}(t)$ at the two boundaries are given by the following expression:

$$j_{A(B)}(t) = \mp q_{A(B)} [n_{A(B)}^0 - n_{A(B)}(z_{A(B)}(t), t)] \mp \gamma_{B(A)} n_{B(A)} \times [z_{A(B)}(t), t]. \quad (4)$$

Here $n_{A(B)}(z, t)$ is the averaged concentration of the $A(B)$ reagents in the layer C . The first term in Eq. (4) describes the escape of the reagent $A(B)$ from the bulk $A(B)$ material to the layer C and the return process, i.e., $q_{A(B)} n_{A(B)}^0 = \alpha_{A(B)}$ and $q_{A(B)} n_{A(B)} [z_{A(B)}(t), t]$, respectively; $n_{A(B)}^0 = \alpha_{A(B)} / q_{A(B)}$ corresponds to the equilibrium (or saturation) concentration of the $A(B)$ "vapor" on the "solid-gas" interfaces $A(B)/C$. The second term in Eq. (4) describes erasing of the $A(B)$ surface due to the chemical reaction with the diffusing reagent $B(A)$.

As mentioned above, we assume that $n_{A(B)}^0$ (and therefore the ratio $\alpha_{A(B)} / q_{A(B)}$) are very small as compared to the concentrations N_A and N_B in the bulk A and B materials

$$n_{A(B)}^0 \ll N_{A(B)}, \quad (5)$$

that is why we consider the reactions only on the interfaces. Propagation of the reagents A and B through the reaction product region C is described by the diffusion equations

$$\frac{\partial}{\partial t} [n_{A(B)}(z, t)] = D_{A(B)} \frac{\partial^2}{\partial z^2} n_{A(B)}(z, t), \quad (6)$$

with the following boundary conditions on the moving interfaces:

$$D_{A(B)} \frac{\partial}{\partial z} n_{A(B)}(z, t) \Big|_{z=z_{A(B)}(t)} = \mp q_{A(B)} [n_{A(B)}^0 - n_{A(B)} \times (z_{A(B)}(t), t)]; \quad (7)$$

$$D_{A(B)} \frac{\partial}{\partial z} n_{A(B)}(z, t) \Big|_{z=z_{B(A)}(t)} = \mp \gamma_{A(B)} n_{A(B)}(z_{B(A)}(t), t). \quad (8)$$

These conditions describe the dependence of the diffusing reagent density on the evaporation-desorption processes on the ‘‘own’’ and on the chemical reaction on the ‘‘foreign’’ interfaces.

The system of equations (3), (4), and (6)–(8) determines completely the dynamics of the averaged interface motion.

III. INVESTIGATION OF THE MODEL

A. Dynamics of the interfaces motion

The system of dynamical equations is still too complicated for a straightforward solution. To proceed, we will get rid of the above condition (5). As will be shown below, this condition results in relatively small shifts of the interfaces during the typical diffusion time $t_D = (z_B - z_A)^2 / D$. It allows one to consider the density distribution of the reagents in the layer C as the stationary solution to the diffusion equations (6) with the boundary conditions (7), (8), which contain the time variable t only as a parameter.

These solutions are easily obtained in the following form:

$$n_{A(B)}(z, t) = \mp \frac{q_{A(B)} n_{A(B)}^0 [z - z_{B(A)} \mp D_{A(B)} / \gamma_{A(B)}]}{D_{A(B)} (1 + q_{A(B)} / \gamma_{A(B)}) + q_{A(B)} \sigma(t)}, \quad (9)$$

where

$$\sigma(t) = z_B(t) - z_A(t) \quad (10)$$

is the averaged distance between the interfaces. With use of Eqs. (3) and (6) we obtain the equation for the interfaces motion:

$$\frac{d}{dt} z_{A(B)}(t) = \mp \frac{N}{N_{A(B)}} \frac{d\sigma(t)}{dt}, \quad (11)$$

and therefore

$$\frac{d\sigma(t)}{dt} = \frac{1}{N} \sum_{I=A,B} \frac{D_I q_I n_I^0}{D_I (1 + q_I / \gamma_I) + q_I \sigma(t)}, \quad (12)$$

where $N = N_A N_B / (N_A + N_B)$. The solution to Eq. (12) with the initial condition $\sigma(0) = 0$ obeys the following transcendental equation:

$$\begin{aligned} \frac{1}{2} \sigma^2 + (\xi_A \mu_A + \xi_B \mu_B) \sigma - \xi_A \xi_B (\mu_A - \mu_B)^2 \\ \times \ln \left(1 + \frac{\sigma}{\xi_A \mu_B + \xi_B \mu_A} \right) \\ = \frac{D_A n_A^0 + D_B n_B^0}{N} t, \end{aligned} \quad (13)$$

where some shortened notations have been introduced:

$$\xi_{A(B)} = \frac{D_{A(B)} n_{A(B)}^0}{D_A n_A^0 + D_B n_B^0}, \quad (14)$$

$$\mu_{A(B)} = D_{A(B)} \left(\frac{1}{q_{A(B)}} + \frac{1}{\gamma_{A(B)}} \right). \quad (15)$$

As follows from Eq. (13), $\sigma(t)$ grows linearly at small t :

$$\sigma(t) \approx \left[\frac{q_A n_A^0 \gamma_A}{q_A + \gamma_A} + \frac{q_B n_B^0 \gamma_B}{q_B + \gamma_B} \right] \frac{t}{N} \quad (16)$$

while at large t this growth slows down:

$$\sigma(t) \approx \left[2 \frac{D_A n_A^0 + D_B n_B^0}{N} t \right]^{1/2}. \quad (17)$$

Thus, the short time behavior is mainly determined by the velocity of the chemical reactions at the interfaces (defined by the reaction coefficient $\gamma_{A(B)}$) while the diffusion effects are unimportant (reaction controlled regime). On the other hand, the long time behavior is determined by the diffusion effects, whereas the reaction constants have no noticeable influence (diffusion controlled regime). The crossover time t_c is determined by comparison of Eqs. (16) and (17):

$$t_c \sim 2N (D_A n_A^0 + D_B n_B^0) \left[\frac{q_A n_A^0}{1 + q_A / \gamma_A} + \frac{q_B n_B^0}{1 + q_B / \gamma_B} \right]^{-2}. \quad (18)$$

For comparable parameters for A and B reagents, we would obtain a simplified estimate for t_c :

$$t_c \sim D \left(\frac{1}{q} + \frac{1}{\gamma} \right) \frac{N}{n^0}. \quad (19)$$

The obtained results determine completely the dynamic evolution of the interfaces. In conclusion of this section we will demonstrate the validity of the quasistationary approximation used in solving the dynamical equations (3), (4), and (6)–(8). The criterion for the validity of this approximation is

$$t_D \frac{d\sigma(t)}{dt} \ll \sigma(t), \quad (20)$$

where $t_D = \min\{\sigma^2(t)/D_A, \sigma^2(t)/D_B\}$ is the characteristic time of the relevant reagent transport from one of the interfaces to the other one. With use of Eqs. (16), (17), and (18), the inequality (20) reduces to

$$\frac{D_A n_A^0 + D_B n_B^0}{\max\{D_A, D_B\} N} \min \left\{ \frac{t}{t_c}, 1 \right\} \ll 1, \quad (21)$$

whose validity is guaranteed by the inequality (5).

B. Roughness of the interfaces

The above analysis of the dynamical growth of the interface separation length was based on a quite simple macro-

scopic description, which is not too sensitive with respect to the microscopic details. On the contrary, the interface roughness growth is caused by microscopic fluctuations of adsorption-desorption and reaction processes, and its description, in general, depends on the concrete microscopic model. Within the framework of the effective phenomenological description Eq. (1), the choice of the model corresponds to the choice of the operator $L_{A(B)}(\nabla)$ and the functions $\Delta_{A(B)}(t)$ in Eq. (2).

The interface roughness may be characterized by its mean-square value

$$R_{A(B)}(t) = \langle h_{A(B)}^2(\rho, t) \rangle, \quad (22)$$

where

$$h_{A(B)}(\rho, t) = z_{A(B)}(\rho, t) - z_{A(B)}(t). \quad (23)$$

The quantity $h_{A(B)}(\rho, t)$ obeys the equation

$$N_{A(B)} \frac{\partial}{\partial t} h_{A(B)}(\rho, t) = -L_{A(B)}(\nabla) h_{A(B)}(\rho, t) + \eta_{A(B)}(\rho, t). \quad (24)$$

Using the Fourier representation

$$h_{A(B)}(\rho, t) = \int d^2k / (2\pi)^2 h_{A(B)}(k, t) \exp(ik\rho) \quad (25)$$

[and similarly for $\eta_{A(B)}(\rho, t)$], we obtain from Eq. (23)

$$h_{A(B)}(k, t) = \frac{1}{N_{A(B)}} \int_0^t dt' \exp[-L_{A(B)}(ik) \times (t-t') / N_{A(B)}] \eta_{A(B)}(k, t'). \quad (26)$$

Finally, we get a general expression for the roughness parameter $R_{A(B)}(t)$ Eq. (22):

$$R_{A(B)}(t) = \frac{1}{N_{A(B)}^2} \int_0^t dt' \int d^2k / (2\pi)^2 \exp[-2L_{A(B)}(ik) \times (t-t') / N_{A(B)}] \Delta_{A(B)}(t'). \quad (27)$$

The operator $L_{A(B)}(\nabla)$ describes the smoothening of the interface due to the change of the cation positions along the interface and due to the reorientation of the anion sublattice in the case of a nonvanishing lattice misfit. In principle, this operator corresponds to the linear response to an available disturbance of a smooth interface. Such a representation is always possible at a mesoscopical level under the consideration that only small local interface gradients are observable. This condition is almost fulfilled for real experimental situations. Generally, $L_{A(B)}(ik)$ depends on the orientation with respect to the underlying lattice. We restrict our investigation to the isotropic case, but a generalization to the anisotropic case is always possible. Furthermore, the influence of dislocations on $L_{A(B)}(\nabla)$ is neglected. But it should be remarked that for vanishing chemical reactions and particle exchange [$\eta_{A(B)}(k, t) = 0$] the number of particles is conserved, i.e., $\int h_{A(B)}(\rho, t) d^2\rho = 0$. Thus, one obtains immediately $\lim_{k \rightarrow 0} L_{A(B)}(ik) = 0$. For a further discussion we restrict our investigations to the isotropic power-law function $L_{A(B)}(ik)$

$$L_{A(B)}(ik) = f_s k^s \quad (s > 0). \quad (28)$$

Thus, we may rescale the variable

$$k \rightarrow k [2f_s(t-t') / N_{A(B)}]^{-1/s} \quad (29)$$

and obtain a simplified expression for $R_{A(B)}(t)$:

$$R_{A(B)}(t) = \frac{\Gamma(2/s)}{2\pi s (2f_s)^{2/s} N_{A(B)}^{(2-2/s)}} \int_0^t dt' \frac{\Delta_{A(B)}(t')}{(t-t')^{2/s}}. \quad (30)$$

Now we should specify the correlation function $\Delta_{A(B)}(t)$ of the stochastic noise variable $\eta_{A(B)}(\rho, t)$. As mentioned above this noise stems from the fluctuations of adsorption-desorption and reaction processes. The average rates of these three processes on the interface $A(B)$ are given by $q_{A(B)} n_{A(B)} [z_{A(B)}(t), t]$, $q_{A(B)} n_{A(B)}^0$, and $\gamma_{B(A)} n_{B(A)} [z_{A(B)}(t), t]$, respectively; see Eq. (4). We assume that these processes possess the Poisson statistics, which originates from the discrete nature of the reagents (shot noise). Below we consider the two noise models:

(1) The model where there is no correlation between the above three processes. In this model, the correlation function $\Delta_{A(B)}(t)$ is given by

$$\Delta_{A(B)}(t) = q_{A(B)} [n_{A(B)}(z_{A(B)}(t), t) + n_{A(B)}^0] + \gamma_{B(A)} n_{B(A)}(z_{A(B)}(t), t). \quad (31)$$

(2) The model where the adsorption and desorption are well correlated so that they do not contribute to the interface roughness. In this model, the correlation function $\Delta_{A(B)}(t)$ is determined only by fluctuations of the reaction process:

$$\Delta_{A(B)}(t) = \gamma_{B(A)} n_{B(A)}(z_{A(B)}(t), t). \quad (32)$$

1. Model 1

Consider the time dependence of $\Delta_{A(B)}(t)$ in more detail. At short times ($t \ll t_c$) we find

$$\Delta_{A(B)}(t) \approx q_{A(B)} n_{A(B)}^0 \frac{1 + 2q_{A(B)}/\gamma_{A(B)}}{1 + q_{A(B)}/\gamma_{A(B)}} + \frac{q_{B(A)} n_{B(A)}^0}{1 + q_{B(A)}/\gamma_{B(A)}}. \quad (33)$$

At long times ($t_c \ll t$)

$$\Delta_{A(B)}(t) \approx 2q_{A(B)} n_{A(B)}^0. \quad (34)$$

Thus, in the model 1 there is no essential time dependence of $\Delta_{A(B)}(t)$ in both time limits.

In further analysis we set $s=4$ in Eq. (28), as it has been accepted for the MBE growth process (for explanation see, for example, [16]). In this case, the time integral in Eq. (30) may be written in an approximate form:

$$\int_0^t dt' \frac{\Delta_{A(B)}(t')}{(t-t')^{1/2}} \approx 2\Delta_{A(B)}(t) \sqrt{t}, \quad (35)$$

where the left-hand side approaches the exact value of the integral in both time limits. We arrive at the following expression for the roughness dispersion (for $s=4$):

$$R_{A(B)}(t) = \frac{\Gamma(1/2)}{4\pi(2f_4)^{1/2}N_{A(B)}^{(3/2)}} \Delta_{A(B)}(t) \sqrt{t}. \quad (36)$$

In this model the roughness dispersion grows like \sqrt{t} .

Note briefly that for the model with $s=2$ in Eq. (28) the above expression (36) would be replaced by

$$R_{A(B)}(t) = \frac{\Gamma(1/2)}{4\pi f_2 N_{A(B)}} \Delta_{A(B)}(t) \ln(t/\tau), \quad (37)$$

where the microscopic cutoff time τ has been introduced to eliminate the singularity of the integral kernel $1/(t-t')$ at $t=t'$. Note that this cutoff is a natural quantity that descends from the limited number of k vectors of the first Brillouin zone.

2. Model 2

According to Eqs. (32) and (9), time dependence of the correlation function $\Delta_{A(B)}(t)$,

$$\Delta_{A(B)}(t) = \frac{D_{B(A)}q_{B(A)}n_{B(A)}^0}{D_{B(A)}(1+q_{B(A)}/\gamma_{B(A)})+q_{B(A)}\sigma(t)}, \quad (38)$$

is governed by the function $\sigma(t)$. At short times ($t \ll t_c$) we find

$$\Delta_{A(B)}(t) \approx \frac{q_{B(A)}n_{B(A)}^0}{1+q_{B(A)}/\gamma_{B(A)}}, \quad (39)$$

while at long times ($t_c \ll t$)

$$\Delta_{A(B)}(t) \approx \frac{D_{B(A)}n_{B(A)}^0}{[2(D_A n_A^0 + D_B n_B^0)/N]^{1/2}} \frac{1}{\sqrt{t}}. \quad (40)$$

There is a remarkable difference in the long-time behavior of the noise correlation function for the two models, Eqs. (34) and (40), respectively. The long time decay Eq. (40) results in the finite asymptotic value of the roughness dispersion. For $s=4$ we find that the time integral in Eq. (30) is given by Eq. (35) at $t < t_c$, while at long times $t_c < t$, its value is

$$\int_0^t dt' \frac{\Delta_{A(B)}(t')}{(t-t')^{1/2}} \approx \frac{\pi D_{B(A)}n_{B(A)}^0}{[2(D_A n_A^0 + D_B n_B^0)/N]^{1/2}}. \quad (41)$$

Thus, for the second model, the initial growth ($\sim \sqrt{t}$) of the interface roughness Eq. (36) saturates at longer times ($t_c < t$) by the value

$$R_{A(B)}(t) = \frac{\Gamma(1/2)}{8\pi(2f_4)^{1/2}N_{A(B)}^{(3/2)}} \frac{\pi D_{B(A)}n_{B(A)}^0}{[2(D_A n_A^0 + D_B n_B^0)/N]^{1/2}}. \quad (42)$$

Note that for the model 2 with the dynamic exponent $s=2$ instead of $s=4$, we would have a similar saturation of the initial roughness growth Eq. (37) by the value

$$R_{A(B)}(t) \sim \frac{1}{4\pi f_2 N_{A(B)}} \Delta_{A(B)}(t_c) \ln(t_c/\tau). \quad (43)$$

In the light of a large amount of work that has been done on kinetic roughening showing the importance of nonlinear and nonequilibrium terms (for references see [16]–[18]) a relevant question is how the nonlinearities modify the results obtained above. In the case of a growth model with conservation, a nonlinear term associated with the lateral growth can be added on the right-hand side of Eq. (1) in the form $\lambda \nabla^2 [\nabla z_{A(B)}(\rho, t)]^2$. It is easy to see that such a nonlinear term does not change the results obtained in Sec. III A on the time dependence of the average thickness of the reaction product layer. On the other hand, the nonlinear term will change the results on the roughness obtained in Sec. III B. In analogy to growth models with conservation [16], we expect that the nonlinear term will decrease the roughness. The main purpose of this article is the description of the time dependence of the average thickness of the reaction product layer, where a lot of experimental results are available. So far, there are no clear experimental evidences whether the nonlinear terms are important for the growth of reaction fronts. A detailed theoretical study of the effects of nonlinearities on the growth of the reaction front is left to a future work.

C. Transversal fluctuations

The roughness shows also a short time regime and a long time regime. But it should be remarked that $R_{A(B)}(t)$ is a global quantity. Especially the long time behavior is mainly determined by large scales. Note that one obtains the same roughness for interface fluctuations of the same order of magnitude independent from the characteristic length scale of the fluctuations, i.e., fluctuations on a microscopical or mesoscopical length scale leads to the same roughness $R_{A(B)}$ as fluctuations on a large macroscopical scale. Therefore a discussion of the corresponding differential coefficients is helpful. We obtain as a generalization of Eq. (27):

$$\langle (\nabla^m h_{A(B)})^2 \rangle = \frac{1}{N_{A(B)}^2} \int_0^t dt' \int k^{2m} d^2k / (2\pi)^2 \exp[-2L_{A(B)}(ik)(t-t')/N_{A(B)}] \Delta_{A(B)}(t') \quad (44)$$

or

$$\langle (\nabla^m h_{A(B)})^2 \rangle = \frac{\Gamma((2m+2)/s)}{2\pi s (2f_s)^{(2m+2)/s} N_{A(B)}^{(2-(2m+2)/s)}} \int_0^t dt' \frac{\Delta_{A(B)}(t')}{(t-t')^{(2m+2)/s}}.$$

The long time behavior of the first two differential coefficients of sufficiently realistic MBE case ($s=4$) becomes now for model 1

$$\langle(\nabla h_{A(B)})^2\rangle \approx \frac{\Delta_{A(B)}(t)}{16\pi f_4 N_{A(B)}} \ln(t/\tau) \quad \text{and} \quad \langle(\Delta h_{A(B)})^2\rangle \approx \frac{\Gamma(3/2)\Delta_{A(B)}(t')}{4\pi(2f_4)^{3/2}N_{A(B)}^{1/2}} \frac{1}{\sqrt{\tau}},$$

whereas model 2 is characterized by the mean square interface gradient

$$\langle(\nabla h_{A(B)})^2\rangle \approx \frac{1}{16\pi f_4 N_{A(B)}} \frac{D_{B(A)} n_{B(A)}^0}{[2(D_A n_A^0 + D_B n_B^0)/N]^{1/2}} \frac{1}{\sqrt{t}} \ln(t/\tau)$$

and the mean square curvature

$$\langle(\Delta h_{A(B)})^2\rangle \approx \frac{\Gamma(3/2)}{8\pi(2f_4)^{3/2}N_{A(B)}^{1/2}} \frac{D_{B(A)} n_{B(A)}^0}{[2(D_A n_A^0 + D_B n_B^0)/N]^{1/2}} \frac{1}{\sqrt{t\tau}}.$$

It is remarkable that both the gradient fluctuations and the curvature fluctuations of model 2 decrease for $t \rightarrow \infty$. Thus the microscopical (and mesoscopical) roughness vanishes and only the roughness at large scales remains effective. On the other hand, model 1 retains a certain roughness because $\langle(\Delta h_{A(B)})^2\rangle$ converges to a finite limit and $\langle(\nabla h_{A(B)})^2\rangle$ converges. However, that is not a surprising result because although the influence of the chemical reactions on the interface decreases with increasing time (and therefore an increasing thickness of the product layer) but the detachment of the atoms of type $A(B)$ from the interface $A/C(C/B)$ and the returning of these atoms is always active. The last effect is suppressed in model 2. The returning atoms have a sufficiently long time to find a energetically favorable place at the interface. Such a correlation between the detachment and the returning of particles leads to the fact that only chemical reactions at the interface remain effective; i.e., the interface shows an increasing smoothing at mesoscopical scales. If the interface becomes sufficiently smooth, the influence of dislocations becomes relevant. Such a regime can be explained by a usual equilibrium dynamics of the dislocations at the analyzed interface.

IV. CONCLUSION

To conclude, we proposed a mesoscopic model, which describes the dynamics and the roughness of the reaction

fronts in heterogeneous solid state chemical reactions. The long time regime and the short time regime of the growing interface can be described by a few mesoscopic parameters. The relation between these parameters and microscopical quantities can be obtained by standard techniques of solid state quantum mechanics. The crossover between the two time regimes corresponds to a change from reaction controlled processes at short times to diffusion controlled processes at long times. The characteristic crossover time is defined by Eq. (18). The averaged thickness of the reaction product layer increases monotonously and behaves like $\sim t$ at short times and $\sim \sqrt{t}$ at long times. This crossover behavior is well known from various experiments [1,4,6,7]. Furthermore, the influence of the regimes to the roughness of interfaces was also observed at least qualitatively [7,8,11].

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