

## Ostwald ripening of faceted two-dimensional islands

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We study Ostwald ripening of two-dimensional adatom and advacancy islands on a crystal surface by means of kinetic Monte Carlo simulations. At large bond energies, the islands are square shaped, which qualitatively changes the coarsening kinetics. The Gibbs-Thomson chemical potential is violated: the coarsening proceeds through a sequence of “magic” sizes corresponding to square or rectangular islands. The coarsening becomes attachment limited, the asymptotic law is reached only after a very long transient time. The unusual coarsening kinetics obtained in the Monte Carlo simulations is well described by the Becker-Döring equations of nucleation kinetics. These equations can be applied to a wide range of coarsening problems.

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### I. INTRODUCTION

Domains of a guest phase inside a matrix tend to coarsen, thus reducing their specific interface energy. The prominent mechanism of coarsening was proposed by Ostwald<sup>1</sup> more than a hundred years ago: larger domains grow at the expense of smaller ones by exchanging atoms. The net atom flux is directed to larger domains since they possess smaller interface energy per atom. The seminal theory of Ostwald ripening was proposed by Lifshitz and Slyozov<sup>2</sup> and by Wagner.<sup>3</sup> They showed that, at late times, the system is characterized by a single characteristic scale, namely, the average domain size  $R(t)$ . The time evolution of the system consists in changing the scale: the domain distribution, shape of the diffraction peaks, etc., remain unchanged when scaled by  $R(t)$ . The average domain size follows, in turn, universal laws:  $R(t) \propto t^{1/3}$  if the atom diffusion is the rate limiting process,<sup>2</sup> and  $R(t) \propto t^{1/2}$  if the attachment-detachment at the domain interface is the limiting one.<sup>3</sup>

The kinetic scaling is essentially based on the Gibbs-Thomson formula  $\mu = \gamma/R$  for the excess chemical potential of a gas that is in equilibrium at the curved surface of a liquid droplet (the constant  $\gamma$  is proportional to the surface tension). The aim of the present work is to study the Ostwald ripening kinetics at low temperatures (or large bond energies) when the crystalline droplets are faceted. The energy of a small crystalline droplet is minimum at “magic” sizes when all facets are completed. The coarsening proceeds as a sequence of jumps from one magic size to the next. We perform kinetic Monte Carlo simulations of Ostwald ripening kinetics for faceted two-dimensional (2D) islands and find a very long transient behavior of the system, so that the universal asymptotic laws are still not reached. We develop a mean-field theory for Ostwald ripening, based on the Becker-Döring<sup>4</sup> equations. We show that these equations, being the basic equations of nucleation theory,<sup>5,6</sup> can be used to describe the coarsening kinetics in a wide range of sizes, starting from monomers up to the long-time asymptotics that

are not available in Monte Carlo simulations. Both the Lifshitz-Slyozov-Wagner regime and the coarsening through a sequence of magic sizes are well described. This approach requires only the knowledge of the cluster energy dependence on the number of atoms in the cluster and can be applied to a wide range of coarsening problems in other systems as well.

The original analytical theories of nucleation<sup>5,6</sup> and Ostwald ripening<sup>2,3</sup> are based on distinct assumptions and describe different kinetic processes: nucleation theory predicts the rate of formation of stable embryos, while Ostwald ripening theory follows the coarsening of large clusters. Langer and Schwartz<sup>7</sup> proposed a mean-field approach to study the nonlinear dynamical equations of motion for a phase separating system with both nucleation and growth of droplets. The unified theory of nucleation and coarsening was further developed by Sagui and Grant<sup>8</sup> by taking into account the correlation effects in a Thomas-Fermi approximation. We show in the present paper that the ordinary differential equations by Becker and Döring are well suited to describe both nucleation and coarsening kinetics. One can proceed, by solving a system of ordinary differential equations, from monomers to clusters containing millions of atoms. Although this approach cannot be extended to arbitrarily large clusters, it can be used to test theories that intend to describe both nucleation and coarsening processes. We restrict ourselves to small concentrations and take into account the screening effects<sup>9</sup> to avoid divergence of solutions of the two-dimensional diffusion equation. A more accurate description of screening that takes into account spatial correlations<sup>10</sup> only slightly changes the screening length in the case of small concentrations.

From the experimental studies of 2D coarsening, we mention the ones that report time exponents  $n$  in the coarsening law  $R(t) \propto t^n$ . These include low-energy electron diffraction from a chemisorbed monolayer of oxygen on W(110),<sup>11,12</sup> helium atom beam diffraction from 0.5 monolayer (ML) of Cu on Cu(100),<sup>13</sup> optical microscopy of a thin layer of suc-

cinonitrile within the liquid-solid coexistence region,<sup>14,15</sup> a binary mixture of amphiphilic molecules,<sup>16</sup> and low-energy electron microscopy of Si on Si(001).<sup>17,18</sup> In these works,<sup>11–16</sup> time exponents somewhat smaller than 1/3 were found and explained by the Lifshitz-Slyozov law with finite-size corrections. The time exponent 1/2 obtained for Si on Si(001) (Refs. 17 and 18) was treated as the case of kinetics limited by the attachment and detachment of adatoms to steps.<sup>3</sup> Our recent x-ray diffraction study of coarsening of 2D GaAs islands on GaAs(001),<sup>19</sup> which showed an apparent time exponent close to 1, was the experimental inspiration for the present work.

Two-dimensional islands of magic sizes were observed on several surfaces, such as Pt(111),<sup>20</sup> Si(111)<sup>21</sup> and Ag(111)<sup>22</sup> (see also a review<sup>23</sup>). Calculations with realistic model potentials show that magic sizes are inherent to metal fcc (001) surfaces.<sup>24</sup> It was shown theoretically that the presence of magic island sizes disrupts the scaling law of submonolayer molecular beam epitaxy growth.<sup>25</sup> Magic sizes of three-dimensional Pb nanocrystals on Si(111) lead to a breakdown of the classical Ostwald ripening laws.<sup>26</sup> The magic thicknesses of three-dimensional islands arise from a competition between quantum confinement, charge spilling, and interface-induced Friedel oscillation.<sup>27</sup> The magic sizes of two-dimensional islands are due to lateral electron confinement.<sup>22</sup> In our kinetic Monte Carlo study, the energies of 2D islands are obtained simply by bond counting, and the magic sizes are those of squared or rectangular islands. However, we formulate the Becker-Döring equations in such a way that they are applicable to any (possibly nonregular) discrete dependence of the island energy on the number of atoms in it. The proposed approach allows us to describe the Ostwald ripening kinetics once the island energetics is established.

Faceted islands are commonly observed on metal surfaces. The adatom and vacancy islands on the (111) surfaces of Cu, Ag, and Au are equilateral hexagons, while these are squares on the (100) surfaces (see Ref. 28 for a review). Studies of these islands are performed mostly by scanning tunneling microscopy, which is well suited to provide a detailed microscopic view of the individual processes. However, the data are not sufficient to obtain the time evolution of average quantities, such as the mean island size, during Ostwald ripening. In our kinetic Monte Carlo simulations, the equilibrium island shape evolves from rounded to square as the bond energy is increased. We do not analyze the individual events, such as sintering,<sup>29</sup> but concentrate on the average quantities (mean island size and size distribution) in the process of Ostwald ripening.

Monte Carlo simulations of Ostwald ripening were performed using the 2D Ising model.<sup>30–32</sup> Spin conservation was achieved by flipping pairs of neighboring opposite spins (Kawasaki spin-exchange dynamics). The simulations were limited to rather small values of the coupling constant, so that the domains are rounded and faceting is absent. Time exponents were found to be smaller than 1/3, which was explained by finite-size corrections to the Lifshitz-Slyozov law. Further discussion of theoretical and simulation studies can be found in several reviews.<sup>33–35</sup> Despite kinetic Monte Carlo simulations being routinely used to model epitaxial

growth,<sup>36–41</sup> we are aware of only one such study of coarsening of 2D islands on a crystal surface.<sup>42</sup> This latter simulation was limited to small bond energies and rounded islands, similar to the simulations in the Ising model.

Faceting effects were found in the kinetics of nonconserved systems. Here, the velocity of a domain wall  $v$  is proportional to its curvature  $K$ ,  $v = \alpha K$ , which gives rise to kinetic scaling with a universal law  $R(t) \propto t^{1/2}$  for the domain coarsening.<sup>43–46</sup> In the seminal Allen-Cahn theory,<sup>44</sup> the coefficient  $\alpha$  does not depend on temperature. However, kinetic Monte Carlo simulations of the nonconserved Ising model (the Glauber single-spin-flip dynamics) show that, at low temperatures, the anisotropy of surface tension gives rise to square-shaped domains (in accordance with the Wulff construction) and results in smaller  $\alpha$ .<sup>47</sup> In the opposite case of high temperatures, thermal roughening reduces  $\alpha$ .<sup>48</sup> Both effects do not alter the coarsening law. In somewhat more complicated models, allowing soft domain walls<sup>49</sup> or both ferromagnetic and antiferromagnetic orderings,<sup>50</sup> the time exponent decreases with decreasing temperature and reaches a universal value of 1/4 at  $T=0$ . In the latter model, the domain walls consist of curved parts and straight stacking faults (facets) with zero curvature, which move by creation and propagation of kinks.

A physical difference between the coarsening kinetics of 2D epitaxial islands and that of Ising spins becomes evident when we compare adatoms and advacancies with up and down spins. The first two objects possess qualitatively different kinetics (motion of an advacancy is a result of the collective motion of atoms), while up and down spins are equivalent. This distinction manifests itself in the transition probabilities, as discussed below. The fundamental laws of Ostwald ripening are expected to be independent of the transition probability distribution, so that a kinetic Monte Carlo simulation of the coarsening of epitaxial islands allows one to test this prediction. Here, we perform kinetic Monte Carlo simulations of Ostwald ripening of 2D adatom islands (surface coverage 0.1 ML) and 2D advacancy islands (surface coverage 0.9 ML) in a wide range of bond energies (or temperatures). Our particular aim is to perform simulations in the case of large bond energies (low temperatures) when the islands are faceted, which was not studied previously.

In our simulations, no step edge barrier is imposed. The atoms can freely detach from an island and attach, after diffusion on the upper or lower levels, to the same or another island. The microscopic probability of an atom movement is given by the number of bonds in its initial state before the movement. The resulting net flux of atoms from smaller to larger islands decreases the total energy of surface steps (island borders). The simulation model is similar to the one used in our preceding work,<sup>51</sup> but with a fundamental difference that leads to a different coarsening mechanism. In Ref. 51, the escape of an atom from a vacancy island to a higher level was prohibited by an infinite step edge barrier, which resulted in Brownian motion and coalescence of whole islands due to atom detachment and reattachment within an island. Such coarsening by dynamic coalescence is much less effective than Ostwald ripening considered in the present paper, and becomes essential only when the detachment of atoms from islands is prohibited.

## II. MONTE CARLO SIMULATIONS

### A. Simulation method

We employ the well-established generic model developed for kinetic Monte Carlo simulations of molecular beam epitaxy.<sup>36–42</sup> Atoms occupy a simple cubic lattice and interact with a pair energy that depends only on the number of bonds. An alternative approach to simulate surface kinetics is a detailed Monte Carlo simulation of a particular surface with energetic parameters taken from *ab initio* calculations, as was done for GaAs(001) or InAs(001).<sup>52–56</sup> Such simulations are very time consuming, and hence, are limited to small time and spatial scales. They can hardly be applied to study the coarsening process. Some characteristic features of compound semiconductors can, however, be included in the generic model as a compromise.<sup>57–59</sup>

We use an algorithm<sup>60</sup> that advances simulated time depending on the probability of the chosen event. This algorithm is commonly used in epitaxial growth simulations. We note that the Ostwald ripening simulations of the 2D Ising model<sup>30–32</sup> have employed the Metropolis accept-reject algorithm. This algorithm becomes inefficient at low temperatures, since most of the attempts are rejected and computer time is wasted. That is why previous simulations<sup>30–32</sup> were performed at relatively high temperatures  $T > 0.5T_c$ , where  $T_c$  is the Ising phase transition temperature. Of course, both algorithms give the same results and differ only in the computation time.

The choice of the probability  $w(\mathbf{x} \rightarrow \mathbf{y})$  for the transition from the state  $\mathbf{x}$  to the state  $\mathbf{y}$  introduces the physics of the system into the simulations. The choice is made differently for the epitaxial growth and the Ising model simulations. It is worthwhile to compare these probabilities briefly. A sufficient condition that the system evolves to thermodynamic equilibrium is the detailed balance condition,  $w(\mathbf{x} \rightarrow \mathbf{y})/w(\mathbf{y} \rightarrow \mathbf{x}) = \exp(-\Delta E/k_B T)$ . Here,  $\Delta E = E(\mathbf{y}) - E(\mathbf{x})$  is the energy difference between the states  $\mathbf{x}$  and  $\mathbf{y}$ ,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature. The simulations of the Ising model use a probability that depends on  $\Delta E$  (either the Metropolis or the Glauber probability). These probabilities favor transitions which reduce the energy of the system,  $\Delta E < 0$ . On the other hand, for an atom jump on the crystal surface, the transition probability does not depend on the final state  $\mathbf{y}$  but only on the height of the energy barrier that needs to be overcome.<sup>61</sup> The probability is  $w(\mathbf{x} \rightarrow \mathbf{y}) \propto \exp[E(\mathbf{x})/k_B T]$ , where  $E(\mathbf{x}) < 0$  is the energy of the initial state with respect to the barrier. Such a probability obviously satisfies the detailed balance condition. The system evolves into a lower-energy state since it escapes higher-energy initial states with larger probabilities.

In the present study, no step edge barrier is imposed. An atom detaching from a step edge can go to the lower or the upper terrace with equal probabilities. In particular, atom exchange between adatoms is achieved predominantly by adatoms diffusing on the top level rather than by the diffusion of vacancies, despite the fact that the latter process is not forbidden. Similar simulations, but with an infinite step edge barrier, were performed in our preceding work.<sup>51</sup> The infinite step edge barrier leads to Brownian mo-

tion of the islands and their dynamic coalescence, which is a much slower process than Ostwald ripening and leads to much less effective coarsening. It becomes essential only if the exchange of atoms between islands is prohibited, e.g., by a step edge barrier. In the present simulations, the dynamic coalescence process is not forbidden, but its contribution is negligible.

An atom that has  $n$  neighbors in the initial state with equal bond energies  $E_b$  to these neighbors possesses an energy  $E(\mathbf{x}) = -(nE_b + E_D)$ , where the activation energy of surface diffusion  $E_D$  is the barrier height. It determines the time scale  $\tau$  of the problem,  $\tau^{-1} = \nu \exp(-E_D/k_B T)$ , where  $\nu \approx 10^{13} \text{ s}^{-1}$  is the vibrational frequency of atoms in a crystal. In the epitaxial growth simulations, the time scale  $\tau$  is to be compared with the deposition flux, which determines an appropriate choice of  $E_D$ . We do not consider deposition, and the choice of  $E_D$  is arbitrary. Note that the works on the Ising model kinetics measure time simply in the flip attempts (sweeps) per lattice site. We take the same values of  $E_D$  as in the preceding work,<sup>51</sup> with the aim to compare time scales of Ostwald ripening (in absence of the step edge barrier) with that of dynamic coalescence (infinite step edge barrier). Namely, we choose  $E_D = 0.2, 0.1, \text{ and } 0 \text{ eV}$  for  $E_b = 0.2, 0.3, \text{ and } 0.4 \text{ eV}$ , respectively.

The ratio of the interaction energy between neighboring atoms to the temperature  $E_b/k_B T$  is the only essential parameter for the coarsening problem. We fix the temperature at 400 K and vary the bond energy  $E_b$  from 0.2 to 0.4 eV. In terms of our model, the Ising phase transition takes place at  $E_b/k_B T = 2 \ln(1 + \sqrt{2})$ . Our choice of bond energies corresponds to  $T/T_c$  varying from 0.15 to 0.3, temperatures much lower than the ones used in previous kinetic Monte Carlo studies of Ostwald ripening.<sup>30–32,42</sup> Here,  $T_c$  is the Ising phase transition temperature.

We perform kinetic Monte Carlo simulations on a  $1000 \times 1000$  square grid with periodic boundary conditions. Each simulation is repeated 25 times to obtain sufficient statistics for the island size distribution. In the initial state, either 0.1 or 0.9 ML is randomly deposited. Adatom islands form in the first case and advacancy islands in the second.

### B. Simulation results

Snapshots of the simulated system at the end of a simulation are presented in Fig. 1(a). As the bond energy  $E_b$  is increased (from left to right), the island shape continuously transforms from more circular to almost square. Since faceting transitions are absent in 2D systems, we refer to the almost square islands as faceted in order to stress the qualitative shape difference at small and large bond energies. Apart from the change in shape, the equilibrium density of adatoms between islands exponentially decreases as the bond energy increases.

Figures 1(b) and 1(c) show time variations of average island diameters  $2R(t)$  in logarithmic and linear scales, respectively. The sizes of all islands in the simulated system are obtained by using an algorithm<sup>62</sup> that allows one to count all topologically connected clusters in the system. The radii of individual islands are calculated as  $r_n = \sqrt{n/\pi}$ , where  $n$  is

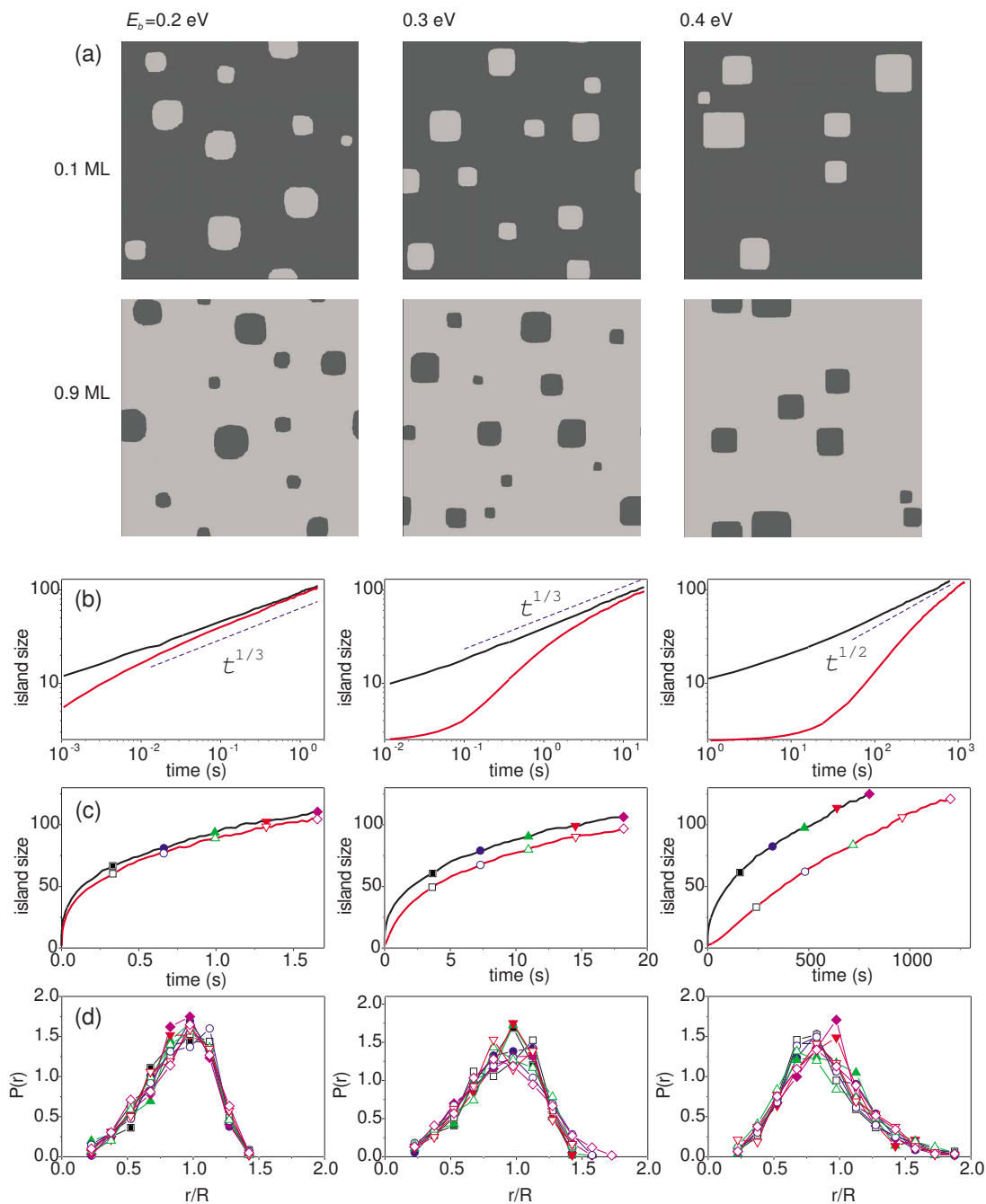


FIG. 1. (Color online) Results of kinetic Monte Carlo simulations: (a) snapshots of the  $1000 \times 1000$  simulation cells at the end of the simulations, (b) and (c) time dependence of the average island size in logarithmic and linear scales, and (d) the island size distributions. The gray levels in the snapshots vary from black to white as the surface height increases. Different columns show results for different bond energies  $E_b$ , with the temperature fixed at  $T=400$  K. The size distributions are obtained at the time moments marked in (c) by the corresponding symbols.

the number of atoms in a cluster. At small bond energies (left column in Fig. 1), the process of Ostwald ripening follows the Lifshitz-Slyozov law  $R(t) \propto t^{1/3}$ . As the bond energy increases, the coarsening law for advacancy islands deviates from that for adatom islands and from the expected  $t^{1/3}$  law. At large bond energies (right column in Fig. 1), the coarsening behavior of advacancy islands is qualitatively different and close to a linear dependence, in a wide range of island sizes. The coarsening of adatom islands also notably deviates

from the Lifshitz-Slyozov law. The attachment-limited asymptotic  $t^{1/2}$  can be inferred from the figure, but it is not really reached.

Figure 1(d) shows the island size distributions at different times. The uniformly spaced time instances are marked on the curves in Fig. 1(c) by the same symbols as used for the corresponding size distributions. The distributions are scaled by the average size  $R(t)$ : instead of the probability  $p(r)$ , we plot the scaled probability  $P(r) = Rp(r)$  versus  $r/R$ . The

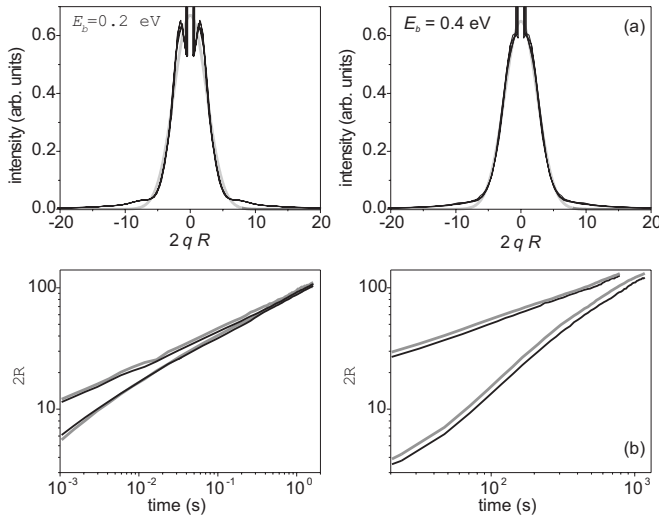


FIG. 2. (a) Diffraction peaks obtained from the Monte Carlo simulation results (the gray curves are Gaussian fits). (b) Time dependence of the average island sizes obtained from the numbers of atoms in the clusters (black curves) and from the widths of the diffraction peaks (gray curves).

scaled distributions do not change in time even at large bond energies, where the average island sizes do not show a power law behavior. However, the island size distribution does change with increasing bond energy, Fig. 1(d). The distribution develops a tail extended to  $2R$ , while at smaller bond energies it is limited to  $1.5R$ .

We also use the Monte Carlo simulations to verify the average island size determination in diffraction studies. In a diffraction experiment, one has access to the peak profile only and obtains the average size from its width. Using the island distribution obtained in the simulation and calculating the peak profiles, we can compare the average sizes obtained from the real-space and reciprocal-space distributions. The diffraction peaks (structure factors) obtained from the simulations are presented in Fig. 2(a). We consider the anti-Bragg condition (adjacent atomic layers contribute to the scattering function with a phase shift of  $\pi$ ) and obtain two-dimensional intensity distributions  $I(q_x, q_y)$  from Fourier transformation of  $\exp[i\pi h(x, y)]$ . Here, an integer function  $h(x, y)$  is the surface height. Then, we take into account that in a diffraction experiment, the scattered intensity is usually collected by a wide open detector that integrates over one of the components of the scattering vector  $\mathbf{q}$ .<sup>19</sup> Hence, we integrate the distributions  $I(q_x, q_y)$  over one of the components of the scattering vector, either  $q_x$  or  $q_y$ . The resulting diffraction peaks  $I(q)$  are presented in Fig. 2(a). The peaks corresponding to different time moments [the same time moments as in Fig. 1(d)] coincide once the wave vectors  $q$  are scaled by the average island size. Kinetic scaling is thus confirmed. The shapes of the peaks depend on the bond energy  $E_b$ , thus showing that the island size distribution and the correlations between the islands change.

The quantity most commonly measured in a diffraction experiment is the full width at half maximum of a peak obtained by an appropriate fit. Considering islands of linear size  $2R$ , one obtains a structure factor  $\sin^2(qR)/\sin^2(qa)$ ,

which can be approximated by  $\exp(-q^2R^2/\pi)$ .<sup>63</sup> Here,  $a$  is the lattice spacing. We obtain the average size  $2R$  by fitting the peaks to this Gaussian function, despite the peaks being not Gaussian, especially for small bond energies. Figure 2(b) compares these sizes with the ones obtained from the real-space island size analysis described above. The values are in good agreement, thus confirming that the average quantities can be obtained from the diffraction peak widths even if the profiles deviate notably from Gaussian.

### III. COARSENING EQUATIONS

#### A. Becker-Döring equations for the three-dimensional problem

The process of Ostwald ripening can be described by two alternative approaches, either in terms of a continuous function  $f(r)$  representing the number density of clusters of radius  $r$ , or in terms of discrete numbers  $c_n$  representing the densities of clusters containing  $n$  atoms ( $n$ mers). The first approach was employed by Lifshitz and Slyozov<sup>2</sup> and by Wagner.<sup>3</sup> The equations for discrete quantities  $c_n$  were first formulated by Becker and Döring<sup>4</sup> and ever since formed the basis of nucleation theory.<sup>5,6</sup> Closely related equations, the rate equations, were used in the description of crystal growth.<sup>64-66</sup> They contain an additional deposition term, while the detachment process is not essential and the corresponding terms in the equations are frequently omitted. Similar discrete equations for the Ostwald ripening process were introduced under the names of microscopic continuity equations,<sup>67,68</sup> population balance equations,<sup>69-71</sup> or rate equation approach.<sup>72</sup> Mathematical aspects of the relationship between the discrete and continuous equations were also considered.<sup>73,74</sup> The aim of the present section is to link the discrete and continuous approaches and obtain equations that can be used for a numerical study of the Ostwald ripening process.

The number of atoms  $n$  in a cluster increases or decreases by 1 when an atom is attached to the cluster or detached from it. Let  $J_n$  be the net rate of transformation of  $n$ mers into  $(n+1)$ mers. The number  $c_n$  of  $n$ mers increases due to the transformation of  $(n-1)$ mers into  $n$ mers, and decreases because of the transformation of  $n$ mers into  $(n+1)$ mers:

$$dc_n/dt = J_{n-1} - J_n. \quad (1)$$

This equation is valid for  $n \geq 2$ . The equation describing the number of monomers  $c_1$  is obtained by requiring that the total number of atoms in the system

$$N = \sum_{n=1}^{\infty} nc_n \quad (2)$$

does not change in time. The condition  $dN/dt=0$  gives, after substitution of Eq. (1) and rearrangement of the terms,

$$\frac{dc_1}{dt} = -2J_1 - \sum_{n=2}^{\infty} J_n. \quad (3)$$

This equation takes into account that each transformation of an  $n$ mers into an  $(n+1)$ mers decreases the number of mono-

mers by 1, except in the case  $n=1$ , where two monomers form a dimer.

The net rate  $J_n$  is a result of two processes. First, an  $n$ mer catches a monomer. The rate of this process is proportional to the densities of the  $n$ mers and the monomers, and can be written as  $a_n c_1 c_n$ , where  $a_n$  is a time-independent coefficient that remains to be determined. The second process is a spontaneous detachment of a monomer from an  $(n+1)$ mer. It is proportional to the density of  $(n+1)$ mers solely and can be written as  $b_n c_{n+1}$ , where  $b_n$  is another time-independent coefficient to be specified. Hence, we obtain

$$J_n = a_n c_1 c_n - b_{n+1} c_{n+1}. \quad (4)$$

Equations (1), (3), and (4) are the Becker-Döring equations.

If the time limiting process is the adatom diffusion between clusters, the attachment and detachment coefficients  $a_n$  and  $b_n$  for the three-dimensional (3D) problem are calculated, for large  $n$ , as follows. The cluster of  $n$  atoms is considered as a sphere of radius  $r_n$ , so that  $n=4\pi r_n^3/3$ . To calculate the attachment coefficient, we solve the steady-state diffusion equation  $\nabla^2 c(r)=0$  with two boundary conditions: the concentration of the monomers far away from the cluster is equal to their mean concentration,  $c(r)|_{r=\infty}=c_1$ , while the concentration of the monomers at the cluster surface is zero,  $c(r)|_{r=r_n}=0$ , since the monomers are attached to the cluster as soon as they reach it. The solution is  $c(r)=(1-r_n/r)c_1$ . The total atom flux at the cluster surface

$$j_n = 4\pi r_n^2 D \nabla c(r)|_{r=r_n}, \quad (5)$$

where  $D$  is the diffusion coefficient of the monomers, is equal to  $4\pi D r_n c_1$ , and hence, the attachment coefficient is

$$a_n = 4\pi D r_n. \quad (6)$$

The detachment coefficient is calculated assuming that the concentration of the monomers at the cluster surface is equal to the equilibrium monomer concentration  $c_{\text{neq}}$ , while there is an ideal sink for monomers at infinity,  $c(r)|_{r=\infty}=0$ . The solution of the steady-state diffusion equation with these boundary conditions is  $c(r)=c_{\text{neq}}r_n/r$ , and the corresponding detachment flux of the monomers is  $b_{n+1}=4\pi D r_n c_{\text{neq}}$ . Here, we take into account that this flux refers to the detachment from the  $(n+1)$ mers. The ratio of the detachment and attachment coefficients is then

$$b_{n+1}/a_n = c_{\text{neq}}. \quad (7)$$

The equilibrium density of monomers at the surface of a cluster is given by the Gibbs-Thomson formula

$$c_{\text{neq}} = c_{\infty\text{eq}} \exp(\gamma/r_n) \approx c_{\infty\text{eq}}(1 + \gamma/r_n), \quad (8)$$

where  $\gamma$  is a constant proportional to the surface tension. The explicit expression for  $\gamma$  is given in the next section. A correction to Eq. (8) for small clusters consisting of very few atoms, while important for the nucleation theory, is not essential for the Ostwald ripening problem. Then, Eqs. (1)–(8) form a complete set that describes the process of Ostwald ripening.

When the clusters are large enough,  $n$  can be treated as a continuous variable. Let us verify that the continuous equa-

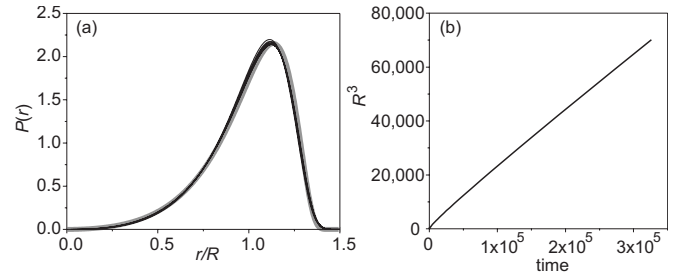


FIG. 3. (a) The cluster size distribution obtained by numerical solution of the Becker-Döring equations at different times (thin black lines; the lines closer to the gray line correspond to later times) and the analytical solution by Lifshitz and Slyozov (thick gray line). (b) The time dependency of  $R^3$ . A linear asymptotic is evident from the plot.

tions derived from the set of equations above are the Lifshitz-Slyozov equations. The cluster size distribution function  $f(r,t)$  is defined so that  $f(r,t)dr$  is the number of clusters per unit volume in an interval from  $r$  to  $r+dr$ . Then,  $f(r,t)dr=c_n(t)dn$  and, keeping in mind that  $n=4\pi r^3/3$ , we obtain  $f(r,t)=4\pi r^2 c_n(t)$ . The mass conservation law (2) can be rewritten, by separating monomers and larger clusters, as

$$c_1(t) + \frac{4\pi}{3} \int_0^\infty r^3 f(r,t) dr = N = \text{const}. \quad (9)$$

The finite-difference equation (1) transforms into the continuity equation

$$\partial f / \partial t + \partial J / \partial r = 0. \quad (10)$$

To calculate the flux in the cluster size space  $J(r,t)$ , one can neglect the difference between  $c_n$  and  $c_{n+1}$  in Eq. (4). Then, substituting Eqs. (7) and (8), one obtains

$$J(r,t) = \frac{D}{r} \left( c_1 - c_{\infty\text{eq}} - \frac{\gamma c_{\infty\text{eq}}}{r} \right) f. \quad (11)$$

Equations (9)–(11) coincide with the Lifshitz-Slyozov equations.<sup>2</sup>

As an example, we compare in Fig. 3 numerical solutions of the ordinary differential equations (1)–(8) with the analytical result.<sup>2</sup> To solve the Becker-Döring system, we employ a second-order Rosenbrock method, which is essentially based on a Pade approximation of the transition operator (see, e.g., Ref. 75). A version of this method<sup>76</sup> that fits well to stiff systems of differential-algebraic equations was used. Practically, we solve a set of up to  $10^6$  ordinary differential equations on a personal computer. The solutions in Fig. 3 are obtained by taking  $\gamma=5$  and, as the initial condition at  $t=0$ , only monomers with the initial supersaturation  $c_1/c_{\infty\text{eq}}=10^5$ . The figure shows that the numerical solutions asymptotically converge to the analytical formula, which validates our approach.

## B. Attachment and detachment coefficients

Equation (7) can be derived in a more general form that will be useful for the considerations below. In equilibrium,

all fluxes  $J_n$  are identically equal to zero. Then, denoting by  $C_n$  the equilibrium concentrations of the  $n$ mers, we have, from Eq. (4),

$$b_{n+1}/a_n = C_1 C_n / C_{n+1}. \quad (12)$$

The equilibrium concentrations calculated in the framework of equilibrium thermodynamics are<sup>77</sup>

$$C_n = C_1^n \exp[-(E_n - nE_1)/k_B T], \quad (13)$$

where  $E_n$  is the energy of an  $n$ mer and  $E_1$  is the energy of a monomer. This relation can be treated as the mass action law for the equilibrium between  $n$ mers and monomers,  $C_n \rightleftharpoons nC_1$ . Substitution into Eq. (12) gives

$$b_{n+1}/a_n = c_{\infty \text{eq}} \exp[(E_{n+1} - E_n)/k_B T], \quad (14)$$

where  $c_{\infty \text{eq}} = \exp(-E_1/k_B T)$  is the concentration of monomers that are in equilibrium with an infinite cluster. For spherical clusters, Eq. (14) reduces to the Gibbs-Thomson formula. The energy of a spherical cluster is  $E_n = 4\pi r^2 \sigma$ , where  $\sigma$  is the surface tension, with the radius  $r$  defined by  $nv = 4\pi r^3/3$ , where  $v = a^3$  is the volume per atom. The radius increase due to the attachment of an atom to an  $n$ mer is given by  $v = 4\pi r^2 \Delta r$ . The change of the energy due to the attachment of a single atom is  $E_{n+1} - E_n = 8\pi \sigma r \Delta r = 2v\sigma/r$ . Thus, we arrive at Eq. (8) with  $\gamma = 2v\sigma/k_B T$ . A similar calculation for the 2D case gives  $\gamma = s\sigma/k_B T$ , where  $s$  is the area per atom.

Equation (14) is more general than the Gibbs-Thomson formula and can be used in situations when the latter is not applicable. Figure 4(a) presents the island size distribution obtained in our kinetic Monte Carlo simulations at an early stage of coarsening for the largest bond energy we have studied,  $E_b = 0.4$  eV. The distribution is not smooth but consists of peaks at magic island sizes corresponding to a product of two close integers, like  $30 = 6 \times 5$ . Accordingly, the inset in the figure shows that the islands are mainly rectangles with an aspect ratio close to 1. The origin of such a distribution is evident: when an island consisting, for example, of 30 atoms grows by one atom, its energy increases by  $2E_b$ , while further growth to 36 atoms does not change its energy at all. Thus, we solve the Becker-Döring equations with the energy of a 2D island of  $n$  atoms calculated as follows. First, we find the largest square that still contains fewer atoms than  $n$ . Then we add, as long as the number of atoms does not exceed  $n$ , rows of atoms to the side of the square. The last row may be incomplete. The number of broken bonds for such an island is calculated. Figure 4(b) presents a numerical solution of the Becker-Döring equations with the island energies  $E_n$  thus calculated and the attachment-detachment coefficient ratio given by Eq. (14). The approximation for  $a_n$  appropriate for the 2D case is given below in Sec. III C. The size distribution closely reproduces the one obtained in the Monte Carlo simulations: squared or rectangular (with aspect ratio close to 1) islands are discrete barriers to be overcome, while the filling of an atomic row does not change the island energy and proceeds relatively fast. This example shows that Eq. (14) can be used when the island energy  $E_n$  is known but is not described simply by the surface tension, so that the Gibbs-Thomson formula is not applicable.

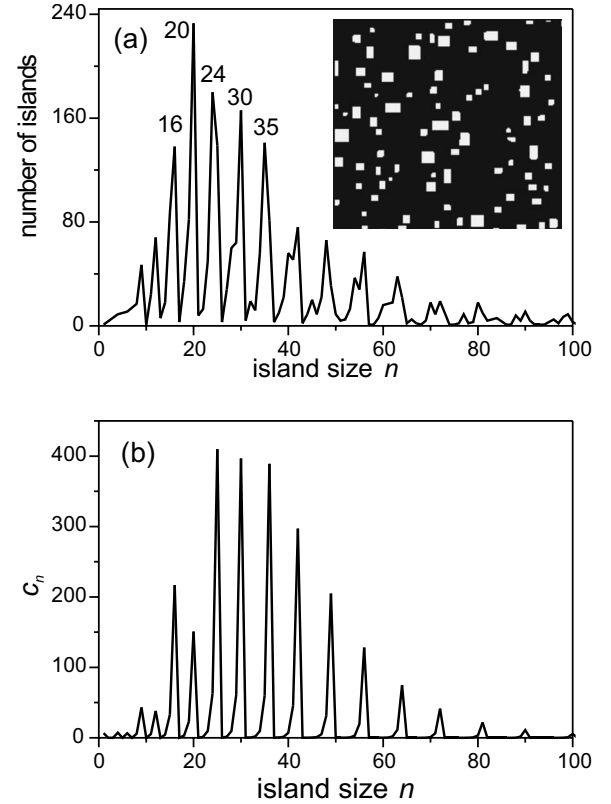


FIG. 4. Island size distribution of faceted islands obtained (a) in the kinetic Monte Carlo simulations and (b) by numerical solution of the Becker-Döring equations. The strong preference of magic island sizes is obvious.

### C. Coarsening equations in two dimensions

The Becker-Döring equations (1)–(4) and Eq. (14) for the ratio of the coefficients  $b_{n+1}/a_n$  do not depend on the dimensionality of the system and can be applied to both 2D and 3D problems. (It may be worthy to note that the radius  $r_n$  entering the Gibbs-Thomson law is expressed differently through  $n$  in the 2D and 3D cases.) The only formula that has to be reconsidered is expression (6) for the attachment coefficients  $a_n$ , since it is based on the solution of the 3D diffusion equation. The solution of the 2D diffusion equation behaves as  $c(r) \propto \ln r$ , and the boundary condition  $c(r)|_{r=\infty} = c_1$  cannot be imposed. A simple approximation is to place this condition at a finite distance  $l$ , given by an average distance between the islands.<sup>68,78–81</sup> Then, in the case of diffusion-limited kinetics, the attachment coefficient  $a_n$  does not depend on  $n$  and is proportional to  $(\ln l)^{-1}$ . Proceeding to the continuous distribution function, one arrives at Eq. (11), with the conservation law (9) rewritten for the 2D case. The coarsening equations are solved analytically in this case.<sup>79,80,82</sup>

A self-consistent description of two-dimensional diffusion can be obtained by taking into account its screening by the island distribution.<sup>9</sup> A solution of the 2D screened diffusion equation, satisfying the boundary conditions  $c(r)|_{r=\infty} = c_1$  and  $c(r)|_{r=r_n} = 0$ , is  $c(r) = c_1 [1 - K_0(r/\xi)/K_0(r_n/\xi)]$ , where  $K_0(x)$  is the zeroth modified Bessel function and  $\xi$  is the

screening length that remains to be defined. Then, one obtains the attachment coefficient

$$a_n = DK(r_n/\xi), \quad (15)$$

where

$$\mathcal{K}(x) = 2\pi x K_1(x)/K_0(x) \quad (16)$$

and  $K_1(x)$  is the first modified Bessel function. The self-consistency condition for the screening length  $\xi$  is<sup>9</sup>

$$\xi^{-1} = \int_0^\infty \mathcal{K}(r/\xi) f(r,t) dr. \quad (17)$$

Expressions very similar to Eqs. (15) and (16) are used in studies of crystal growth from the gas phase,<sup>6,65,66</sup> with one essential difference: for the latter problem, the length  $\xi$  is the mean diffusion length of an adatom on the surface before its reevaporation. It is a well-defined time-independent constant, so that no self-consistency condition is involved.

In the case of attachment-limited kinetics, the boundary condition for the concentration field  $c(r)$  at the island surface is the absence of the flux,  $\nabla c|_{r=r_n} = 0$ , which gives a constant solution,  $c(r) = c_1$ . Then, the attachment coefficient is

$$a_n = 2\pi K r_n, \quad (18)$$

where  $K$  is the attachment coefficient. The result is independent of screening in this case. The same expression is obtained in the approximation of a constant screening distance equal to the mean distance between islands.<sup>68,78–81</sup>

#### D. Coarsening equations for advacancy islands

In our Monte Carlo simulations, a step edge barrier is absent and an atom detaching from a vacancy island ascends to the higher terrace. The vacancy island size increases by one vacancy at the same time. The coarsening proceeds by exchange of adatoms between vacancy islands and can be described by equations similar to the Becker-Döring equations. Let us denote by  $g(t)$  the concentration of adatoms, while  $c_n$  are the concentrations of 2D islands of  $n$  vacancies. Then, the continuity equation (1) for the density of clusters  $c_n(t)$  remains unchanged. The fluxes  $J_n$  in these equations describe two processes. The first process is the spontaneous emission of an adatom. Its rate is proportional to the density of  $n$ mers. The second process is the absorption of an adatom by the vacancy type  $(n+1)$ mer, which gives rise to an  $n$ mer. Its rate is proportional to the density  $g$  of adatoms and the density of  $(n+1)$ mers, so that

$$J_n = b_n c_n - a_{n+1} g c_{n+1}. \quad (19)$$

The annihilation of an atom and a single vacancy is described by the flux  $J_0 = -a_1 g c_1$ . Then, the set of equations (1) is valid for  $n \geq 1$ . The creation of an adatom-vacancy pair from a flat surface is prohibited in our model.

Since the growth of a vacancy cluster by one vacancy is accompanied with the emission of an adatom, the conserved total amount of atoms in the system is given by

$$N = \sum_{n=1}^{\infty} n J_n - g, \quad (20)$$

which replaces Eq. (2). By differentiating this equation with respect to time and rearranging the terms, the condition  $dN/dt = 0$  leads to an equation for the time variation of the adatom density:

$$\frac{dg}{dt} = \sum_{n=0}^{\infty} J_n. \quad (21)$$

The mass action law now has to be written for an equilibrium between an advacancy island and adatoms that annihilate,  $C_n + ng \rightleftharpoons 0$ . Hence, instead of Eq. (13), we have

$$C_n g^n = \exp[-(E_n + nE_1)/k_B T]. \quad (22)$$

The requirement of zero fluxes at equilibrium gives rise to the detailed balance condition

$$b_n/a_{n+1} = c_{\infty \text{eq}} \exp[-(E_{n+1} - E_n)/k_B T] \quad (23)$$

that differs from Eq. (14) by the sign in the exponent. For circular islands, the same calculation as above leads to the Gibbs-Thomson formula (8) with negative  $\gamma$ , which corresponds to a negative curvature of the vacancy island surface.

#### E. Solutions of the coarsening equations

Figure 5 presents the results of the numerical solution of the Becker-Döring equations for adatom and advacancy islands. With the aim to quantitatively compare the solutions with the results of kinetic Monte Carlo simulations in the whole time interval, we use the same initial conditions. The initial random adatom distribution with the coverage 0.1 ML contains not only monomers, but also dimers, trimers, etc., the densities of which quickly decrease with increasing cluster sizes. By simple statistical analysis of the initial distribution in kinetic Monte Carlo simulations, we find that at  $t = 0$ ,  $c_n \approx c_1 \times 10^{(n-1)/2}$ . This distribution was used as the initial condition for the Becker-Döring equations. The initial conditions are essential only at the initial stages of coarsening. The results of the calculations do not depend on the initial monomer concentration  $c_1$ , as long as the initial supersaturation  $c_1(t=0)/c_{\infty \text{eq}}$  is much larger than unity. The time scale of the solutions is adjusted to these of the Monte Carlo simulations.

The case of small bond energies (left column in Fig. 5) is well described by the 2D diffusion-limited kinetics with screening (15) and the ratio of the detachment and attachment coefficients given by the Gibbs-Thomson formula (8). The calculations in the left column of Fig. 5 are made with  $\gamma = 3.7$ . The solutions of the Becker-Döring equations (black lines) are in good agreement with the results of the kinetic Monte Carlo simulations (gray lines), repeated from Fig. 1. The coarsening laws for adatom and advacancy islands almost coincide and quickly reach the Lifshitz-Slyozov  $t^{1/3}$  asymptotic. The island size distributions, Fig. 5(c), also almost coincide for adatom and advacancy islands, obey kinetic scaling, and agree well with the ones obtained in the kinetic Monte Carlo simulations, cf. Fig. 1(d).



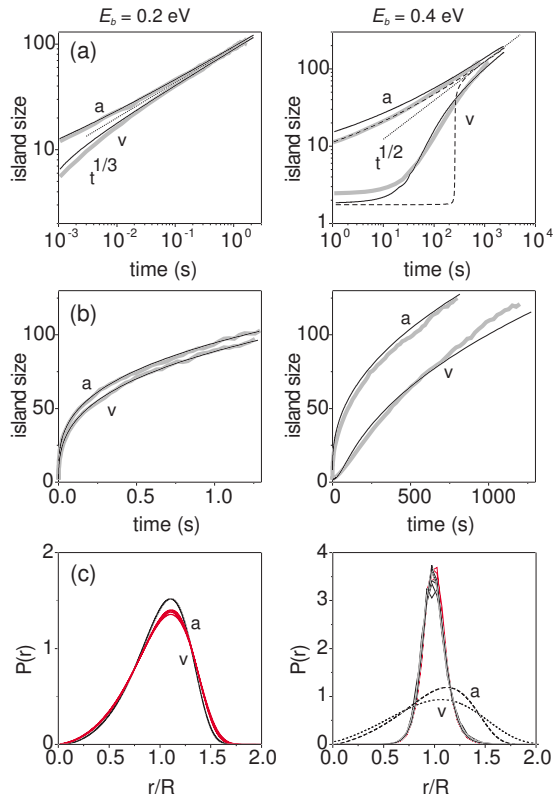


FIG. 5. (Color online) Results of numerical solutions of the Becker-Döring equations: time evolution of the average island sizes in (a) logarithmic and (b) linear scales and (c) the island size distributions. The left column presents calculations for a bond energy  $E_b=0.2$  eV with diffusion-limited kinetics, while the right column shows the results for a bond energy  $E_b=0.4$  eV with attachment-limited kinetics. The solutions of the Becker-Döring equations are shown in (a) and (b) by black lines, and the results of the kinetic Monte Carlo simulations by gray lines. Symbols “a” and “v” on the plots denote the results for adatom and advacancy islands, respectively. Full lines in the right column show the calculations for the discrete island energies with “magic” sizes, while the broken lines are calculations for the continuous Gibbs-Thomson chemical potential.

For large bond energies (right column in Fig. 5), the calculations are performed with attachment-limited kinetics, Eq. (18), since the kinetic Monte Carlo simulations point to the Wagner  $t^{1/2}$  asymptotic. We compare the discrete distribution of island energies that takes into account the magic island sizes as described in Sec. III B (full black lines), with the continuous distribution given by the Gibbs-Thomson formula (broken lines). The relationship between the discrete and continuous models is established by calculating the energy of a square island and a circular one with the same number of atoms:  $E_b/k_B T = \sqrt{\pi} \gamma / 2$ . The calculations are performed for  $\gamma=9$ . The effect of magic sizes is slightly different for adatom and advacancy islands. For adatom islands, the detachment coefficients  $b_n$  given by Eq. (14) are exceptionally large for  $n=m+1$ , where  $m$  is a magic number. Thus, a monomer that has attached to a magic island detaches again with a high probability. For advacancy islands, the detachment coefficients  $b_m$  for magic islands are exceptionally

small, so that the detachment of an atom from a vacancy island (this atom becomes an adatom on the higher level) proceeds at a small rate. Both processes make each magic size a trap for further island growth, giving rise to the discrete island size distribution peaked at the magic sizes shown in Fig. 4. The island size distributions presented in Fig. 5(c) for this case are obtained by averaging over finite ranges of the sizes, just as for the kinetic Monte Carlo simulations.

The time dependence of the average island sizes obtained for coarsening through the sequence of magic islands (full black lines in right column of Fig. 5) are in good agreement with the results of kinetic Monte Carlo simulations (gray lines). For vacancy islands, the continuous island size distribution with the Gibbs-Thomson formula gives rise to a notably different coarsening behavior (broken lines), with a very fast increase of the island sizes in the intermediate range. The island size distributions obtained in the discrete (with magic sizes) and continuous models are also notably different, see Fig. 5(c). The distribution obtained in the discrete model is symmetric with respect to the maximum, similar to the one obtained in the Monte Carlo simulations, but notably narrower, cf. Fig. 1(d). It is worthy to note that the distribution scaled by the average island size does not change in time and is the same for the adatom and advacancy islands, despite the time evolutions of the average island sizes not coinciding and not following a power law. In other words, the solution of the Becker-Döring equation obeys kinetic scaling in the sense that the island size distribution is a function of  $r/R(t)$  that does not depend on time. However,  $R(t)$  is not described by a power law. The continuous model gives a much broader and asymmetric island size distribution, shown by broken lines in Fig. 5(c). The broken-bond counting scheme described in Sec. III B adequately represents the energies  $E_n$  of small islands and quantitatively describes the island size distribution at the initial stage of coarsening, see Fig. 4. However, for larger islands, it oversimplifies the island energy distribution and gives rise to a narrower distribution than found in the simulations. A better model for the island energies  $E_n$  is needed to describe this distribution correctly.

To summarize this section, we show that the Ostwald ripening kinetics can be described as an initial value problem for the ordinary differential equations (1)–(8) that can be solved by standard numerical methods. This approach can be applied to various coarsening problems by replacing the Gibbs-Thomson formula (8) with Eqs. (14) and (23) that admit any dependence of the island energy  $E_n$  on the number of atoms  $n$  in it. The alternative approach, a numerical implementation of the integrodifferential equations (9)–(11),<sup>83,84</sup> seems much more difficult.

#### IV. CONCLUSIONS

Our kinetic Monte Carlo simulations show that the Ostwald ripening of 2D islands qualitatively changes with increasing bond energy (or decreasing temperature). The islands become faceted and the coarsening proceeds through a sequence of magic sizes. The Gibbs-Thomson chemical potential is not applicable, and the detachment of monomers

from islands is governed by the discrete energies of the islands. The coarsening is diffusion limited at small bond energies and becomes attachment limited at large bond energies. In this latter case, Wagner's asymptotic law is reached only after a very long transient regime.

We show that the Becker-Döring equations of nucleation kinetics are well suited to study the process of Ostwald ripening. Two- and three-dimensional coarsening processes with diverse limiting mechanisms can be simulated by solving a system of ordinary differential equations. Concentrations of clusters of all sizes, from monomers to those consisting of millions of atoms, can be traced simultaneously. The calculations are not necessarily based on the Gibbs-

Thomson formula, but adopt any continuous or singular dependence of the cluster energy on the number of atoms in it. This approach can be applied to a wide range of coarsening problems for two- and three-dimensional islands on a surface.

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