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Ostwald ripening with kinetically limited bond formation

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Abstract. We present Monte Carlo simulations of the ripening of 2D islands in the case when the formation of the monomer-monomer bonds is kinetically limited. The results obtained indicate that such limitations may modify the early stage of the kinetics. Asymptotically, the ripening is described by the Lifshitz-Slyozov law.

PACS. 05.10.Ln Monte Carlo methods – 05.50.+q Lattice theory and statistics (Ising, Potts, etc.) – 05.70.Fh Phase transitions: general studies

1 Introduction

Ostwald ripening is a very general phenomenon occuring in liquids, solids, and on solid surfaces. Basically, it takes place in the late stages of first-order phase transitions, when larger droplets, grains, crystallites, or islands, grow at the expense of smaller ones *via* evaporation, diffusion, and condensation. The physical driving force for this process is a decrease in interface energy with increasing the average size, $l(t)$, characterizing phase separation. Phenomenologically, the ripening is usually described by employing a power law,

$$l(t) \simeq \mathcal{A} + \mathcal{B}\, t^{x}, \qquad (1)$$

where $\mathcal{A}$ is the constant introduced to take into account that in the beginning the growth is far from the asymptotic regime, $\mathcal{B}$ the constant corresponding to the asymptotic growth, and x the growth exponent.

The applicability of equation (1) was first analytically demonstrated four decades ago by Lifshitz and Slyozov (LS) [1]. Using the Kelvin equation describing the relationship between the solubility of a particle and its radius, they found that $x = 1/3$ in the limit of widely spaced 3D droplets of the dense phase. Since then, the first-order phase transitions with conserved fields (*i.e.*, with the conserved number of particles or spins of different orientations) have attracted considerable attention [2]. The approaches used to analyze the kinetics of such phase transitions at *finite* particle density can be divided into four groups. (i) There are many treatments [3] extending the LS approach. The approximations employed in such treatments are however open for discussions. (ii) The kinetics of first-order phase transitions have been analyzed on the basis of the phenomenological equations. For example, Bray [4] has applied the renormalization-group technique to the phenomenological equation of the Cahn-Hilliard (CH) type. The 2D CH model has been studied numerically in detail [5]. (iii) Extensive Monte Carlo (MC) simulations of the 2D lattice-gas and spin-exchange dynamics have been executed in references [6–8] (see also references in [8]). (iv) There are also attempts to combine analytical and Monte Carlo calculations [9]. The results obtained in all these treatments are supporting $x = 1/3$.

Traditionally, the Ostwald ripening is assumed to occur in the *diffusion-limited* regime (in particular, all the studies quoted above treat this case). Physically, this means that the monomers belonging to the dilute phase form bonds with particles forming islands of the dense phase as soon as they reach the island boundaries (for definiteness, we discuss the coexistence of the 2D lattice gas and liquid). In the case of atoms or simple molecules, this limit is very reasonable. For complex particles, existing in two or more configurations, there are however situations when the formation of new bonds occurs in the *kinetically limited* regime. Practically, this means that a particle belonging to the dilute phase is primarily in such a state that its interaction with other particles is negligible. To form bonds, the particle should first be reconfigurated. In other words, it should first transit to the excited state and only then the latter state may be stabilized by the particle-particle interactions. Likely candidates for this scenario are complex biological molecules, *e.g.*, proteins. In the native state, the protein-protein interaction is usually repulsive or negligible. The free energy difference for reconfiguration of proteins is however fairly low. After reconfiguration, the protein-protein interaction may become attractive. The latter may result in protein aggregation. (An appropriate note here is that the formation

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of large mesoscopic (up to 100 μm) protein islands have recently been observed in several studies [10] of protein adsorption at the gas-liquid interface (especially on lipid monolayers).)

In this paper, we present the first MC simulations illustrating the effect of kinetic limitations in the bond formation on the Ostwald ripening.

2 Model

As an example, we explore the island growth on a 200×200 square lattice (with periodic boundary conditions). Diffusing particles are allowed to be in two states (1 and 2). For separate particles, state 1 is assumed to be ground and the rate constants of the transitions $1 \rightarrow 2$ and $2 \rightarrow 1$ are considered to be $k_{12}^{(0)}$ and $k_{21}^{(0)}$ (according to the detailed balance principle, $k_{12}^{(0)}/k_{21}^{0} = \exp(-\Delta F/k_{\mathrm{B}}T)$, where $\Delta F > 0$ is the free energy difference of states 2 and 1). The formation of bonds is allowed only between particles in state 2. Specifically, the nearest-neighbour (NN) interaction between such particles is considered to be attractive, $\epsilon_1 < 0$. The other interactions are neglected. The bonds between particles in state 2 may stabilize this state provided that ΔF is not too large. At low temperatures and appreciable coverages (inside the spinodal region), we will have in this case the dense islands formed primarily by particles in state 2 and the dilute phase consisting primarily of separate particles in state 1.

To describe the island growth in the framework of the model introduced, we need to define the normalized dimensionless probabilities of diffusion jumps and transitions between states 1 and 2. In our simulations, the parameter characterizing the ratio of the rates of particle reconfiguration and diffusion is considered to be $\mathcal{P}$ (the rates of these processes are assumed to be proportional to $\mathcal{P}$ and $(1-\mathcal{P})$, respectively). The reconfiguration rates are normalized to $k_{21}^{(0)}$. With this normalization, the probability of the transition $1 \rightarrow 2$ is equal to

$$p_{12} = \exp(-\Delta F/k_{\mathrm{B}}T) < 1, \tag{2}$$

for all the arrangements of particles in adjacent sites. For the probability of the transition $2 \rightarrow 1$, we have

$$p_{21}^{(n)} = \exp(n\epsilon_1/k_{\mathrm{B}}T), \tag{3}$$

where $n \leq 4$ is the number of the nearest neighbours in state 2.

Diffusion is assumed to occur *via* jumps to NN vacant sites. To simulate this process, one could use the Metropolis or Kawasaki dynamics. The shortcoming of these dynamics is that the jump rate of monomers in the dilute phase is predicted to be equal to that of holes in the dense phase. In real systems, however, these rates are usually not equal. In our work, we employ the "initial-state" dynamics which is widely used in simulations of diffusion of adsorbed particles [11]. Basically, this dynamics is similar to that introduced above for the transitions between states 1 and 2. Specifically, the jump probability for particles in state 1 is considered to be independent of the arrangements of particles in adjacent sites,

$$P_1 = 1. \tag{4}$$

For particles in state 2, we use

$$P_2^{(n)} = \exp(n\epsilon_1/k_{\mathrm{B}}T), \tag{5}$$

where n is the number of the nearest neighbours in state 2.

3 Algorithm of simulations

With the specification above, the MC algorithm for describing the ripening of islands is as follows: (i) A site for one of the elementary processes is chosen at random. (ii) If the site selected is vacant, the trial ends. (iii) If the site is occupied, the reconfiguration or diffusion channels are chosen with the probabilities $\mathcal{P}$ and $1 - \mathcal{P}$, respectively. In the former case, the $1 \rightarrow 2$ or $2 \rightarrow 1$ transitions are realized with the probabilities p_{12} and $p_{21}^{(n)}$ (Eqs. (2, 3)), respectively. In the latter case, a NN site is selected at random, and if this site is vacant, the A particle jumps to it with the probabilities P_1 or $P_2^{(n)}$ (Eqs. (4, 5)) depending on the particle state. If the NN site is occupied, the trial ends.

Initially (at $t = 0$), the adsorbed particles are considered to be located at random, and the average occupations of states 1 and 2 are chosen to be $1/(1 + p_{12})$ and $p_{12}/(1 + p_{12})$, respectively (these occupations corresponds to equilibrium between states 1 and 2). Time is measured in MC steps (1 MCS corresponds to $L \times L$ attempts of diffusion). The duration of runs was 10^6 MCS.

To characterize the size of islands, we have calculated the occupation-number correlation function,

$$G(r) = \langle n(0)n(r)\rangle - \langle n\rangle^2. \tag{6}$$

The average linear island size, R, was defined as the position of the first zero of $G(r)$.

For comparison, we have also simulated the conventional island-growth kinetics when all the particles are in state 2 and the transitions to state 1 are prohibited ($\mathcal{P} = 0$). In this case, the critical temperature is given by the well-known Onsager expression, $T_{\mathrm{c}} = 0.567|\epsilon_1|/k_{\mathrm{B}}$.

4 Results of simulations

The island-growth kinetics and typical lattice snapshots obtained for one-half and one-quarter monolayer at $T = 0.5T_{\mathrm{c}}$ are shown in Figures 1–4. For the one-state model, the kinetics are seen (Figs. 1 and 3) to follow the LS law at both coverages. The two-state model (with $p_{12} = 0.1$ and $\mathcal{P} = 0.5$) predicts deviations from the LS law for one-half monolayer at $t < 8 \times 10^8$ MCS (Fig. 1). For one-quarter

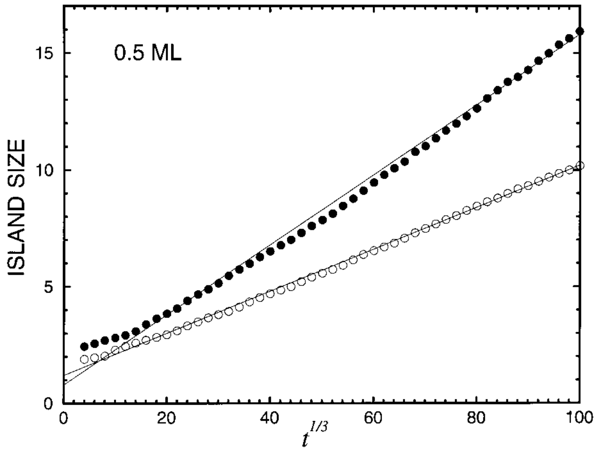

Fig. 1. Average island size as a function of $t^{1/3}$ ($t^{1/3} = 100$ corresponds to 10^6 MCS) for one-half monolayer of particles on the 200×200 lattice at $T = 0.5T_c$ ($T_c = 0.567|\epsilon_1|/k_B$). Open and filled circles correspond to the one- and two-state models, respectively. Every curve has been obtained by averaging the data for five MC runs. The error in the data is smaller then or comparable with the size to the symbols (at earlier stages, the error is actually much smaller than the size of the symbols because the number of islands is large). In fact, the scale of the error is clearly seen from the scattering of the data points.

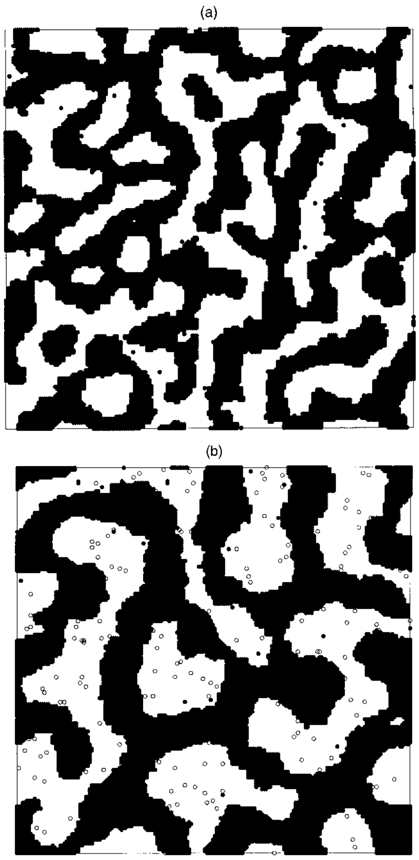

Fig. 2. One-half monolayer of particles on the 200×200 lattice at $T = 0.5T_c$ after 10^6 MCS. Panels (a) and (b) correspond to the one- and two-state models, respectively. Particles in states 1 and 2 are shown by open and filled circles.

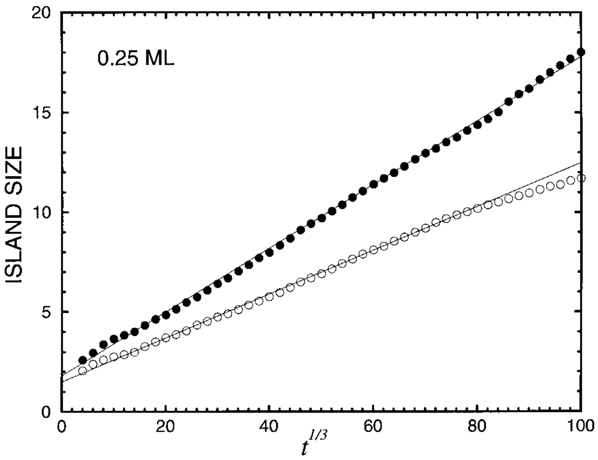

Fig. 3. As Figure 1 for one-quarter monolayer.

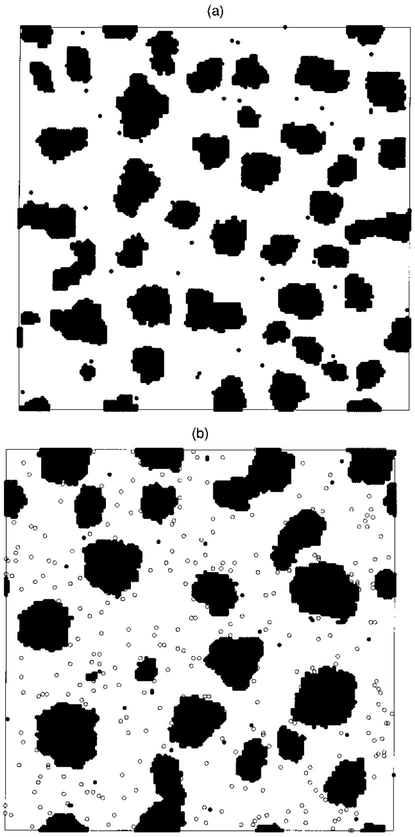

Fig. 4. As Figure 2 for one-quarter monolayer.

monolayer, the deviations are negligible. The growth rate is always higher for the two-state model. This effect seems to be connected with the fact that after evaporation a monomer may rapidly transit to state 1 and then easily migrate a rather long period before the transition back to state 2 and the formation of new bonds with other monomers located in islands.

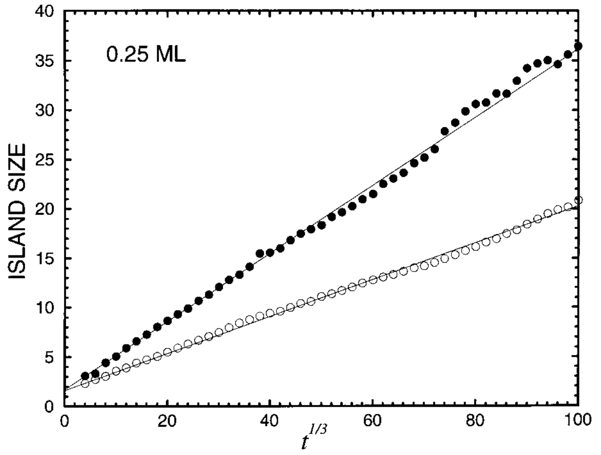

Fig. 5. As Figure 1 for one-quarter monolayer at $T = 0.75T_c$.

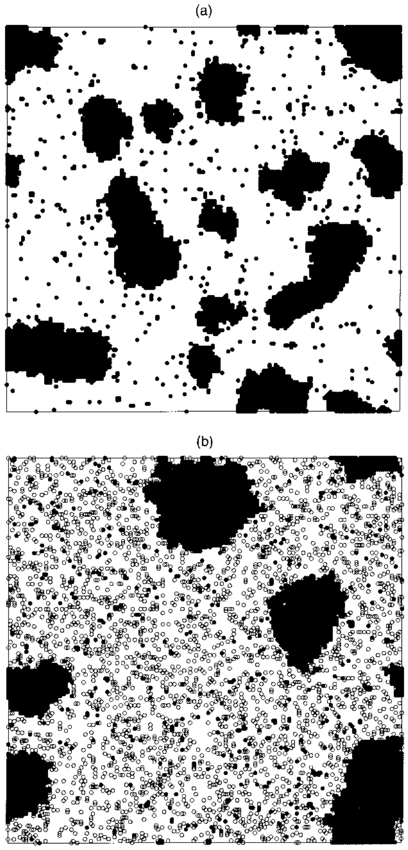

Fig. 6. As Figure 2 for one-quarter monolayer at $T = 0.75T_c$.

The kinetics calculated for other temperatures and for other values of p_{12} and $\mathcal{P}$ were found to be qualitatively similar to those presented above (see, *e.g.*, Figs. 5 and 6 for $T = 0.75T_c$).

5 Conclusion

The results obtained indicate that the kinetic limitations for the formation of the monomer-monomer bonds may modify the early stage of the kinetics of the Ostwald ripening. Asymptotically, the ripening is described by the LS law. Physically, this finding can be rationalized if one takes into account that the late stages of the ripening are very slow and accordingly on these stages the local equilibrium can easily be maintained even if the monomer-monomer bonds are not formed just after contacts between monomers. The existence of local equilibrium is known to be one of the main conditions of the applicability of the LS law. For this reason, this law is asymptotically correct.

The results of our simulations may be of interest, *e.g.*, for interpretation of the growth of islands in adsorbed protein overlayers (see the Introduction). As we have already noted, the formation of 100-μm-sized protein islands have recently been observed in several studies [10]. The kinetics of the growth of such islands have not been explored however quantitatively. For this reason, comparing our predictions with experiment is now hardly possible.

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