Limitations of a Fokker-Planck description of nucleation

J. Kuipers*
Institute for Theoretical Physics, Utrecht University, Utrecht, The Netherlands

G. T. Barkema
Institute for Theoretical Physics, Utrecht University, Utrecht, The Netherlands
and Instituut-Lorentz for Theoretical Physics, Leiden University, Leiden, The Netherlands

(Received 28 May 2009; revised manuscript received 11 April 2010; published 20 July 2010)

In most nucleation theories, the dynamics of nucleation is characterized by the evolution in time of the mass of droplets, and this time evolution is described as a combination of drift and diffusion. This assumes that the mass fluctations are described by a Markovian, i.e., memoryless, stochastic process. This paper presents a method to assess in how far this assumption of Markovianity is valid. The method is employed in nucleation studies in a two-dimensional Ising model at temperature $T=0.88T_c$, both with spin flip dynamics and with local spin exchange dynamics. In the first case, it shows that the evolution of droplet masses might be effectively described by a Markov process on large time scales. In the latter case, however, the dynamics are far from Markovian. We argue that this is due to the presence of a locally conserved quantity.

DOI: 10.1103/PhysRevE.82.011128 PACS number(s): 64.60.De, 64.60.qe, 05.10.−a, 05.45.Tp

I. INTRODUCTION

Nucleation is a thermally activated process, in which stable nuclei randomly emerge in a metastable environment. A prototypic example is the formation of ice crystals in supercooled water. Nucleation has been studied extensively; a long list of books and review articles on it can be found in a recent book of Kashchiev [1]. A theoretical description of the process was first given by Becker and Döring [2] in the first half of the previous century, which is known as *classical nucleation theory* (CNT). In CNT, the central concept is the distribution of droplet masses, which evolves via a Fokker-Planck equation. The central goal of this paper is to investigate the limitations of this description.

The organization of this paper is as follows. In Sec. II CNT is reviewed. Next, Sec. III presents a method to analyze time series and test whether they could have been produced by a Fokker-Planck equation. This method is based on earlier work, in which time series on the strength of the geomagnetic dipole were investigated [3,4]. This method is employed in Sec. IV to analyze simulation data of nucleation in the Ising model [5], either with spin flip dynamics or with local spin exchange dynamics. The results, together with their implications for nucleation theory, are discussed in Sec. V.

Earlier work on the limitations of CNT in the Ising model is in Refs. [6,7] and the references therein. These references focus on spin flip dynamics, where CNT works rather well. This paper confirms that result. Furthermore, in this paper it is shown that nucleation with local spin exchange dynamics cannot be described within CNT. This is also consistent with our theoretical description of local spin exchange dynamics of Ref. [8].

II. CLASSICAL NUCLEATION THEORY

CNT describes the formation of droplets in a metastable environment. It assumes that the state of a droplet is fully characterized by its mass. In equilibrium, the number of droplets of mass m satisfies

$$n^{(\mathrm{eq})}(m) = \mathcal{N} e^{-\beta F_m}, \tag{1}$$

with $\beta=1/k_BT$ the inverse temperature and F_m the free energy of a droplet with mass m. $\mathcal{N}$ is just a normalization factor. Most of the physics is in the free energy landscape F_m. The classical assumption is that this free energy is the sum of two terms, namely a (negative) bulk term equal to the chemical potential difference per unit mass μ times the droplet mass, and a (positive) surface term equal to the surface area times the average surface tension σ,

$$F_m = -\mu m + \Omega_d \sigma m^{(d-1)/d}, \tag{2}$$

where d is the dimension of the system and Ω_d is a geometrical factor. The free energy function increases for small droplet masses, but decreases for large masses. It achieves its maximum value at the so-called critical droplet mass. Therefore nucleation is an activated process. Once a droplet grows beyond this critical mass, the system is likely to nucleate.

In CNT, a state of the system is described by the distribution $n(m,t)$ of nuclei that have mass m at time t. The variations in the mass of a nucleus are described as a *Markovian* stochastic process in which single units attach and detach from a nucleus. A stochastic process is Markovian if it is memoryless, i.e., the numbers of nuclei $n(m,t+dt)$ only depend on $n(m,t)$ and not on the numbers for $t'<t$. The distribution then evolves via the Fokker-Planck equation [10].

$$\frac{\partial n(m,t)}{\partial t} = \frac{\partial}{\partial m}\left[R(m)\left(\beta \frac{\partial F}{\partial m} + \frac{\partial}{\partial m} \right) n(m,t) \right], \tag{3}$$

with $R(m)$ the rate at which nuclei of mass m grow to nuclei of mass $m+1$. The boundary conditions for this equation are given by $n(1,t)=n^{(\mathrm{eq})}(1)$ and $n(\infty,t)=0$.

*jkuipers@phys.uu.nl

While the dynamics in the full phase space, i.e., the values of all spins, is Markovian by construction, the effective dynamics in the reduced phase space, i.e., in this case the distribution of masses of the nuclei, need not be Markovian anymore. In fact, this Markov assumption in the reduced phase space is debatable, especially if a locally conserved quantity is present, which is the case in, e.g., nucleation in binary mixtures of fluids. The conservation law leads to strong correlations in time between attachment and detachment events: after a particle detaches from the nucleus, it remains in its neighborhood for a relatively long time and is therefore likely to reattach. This clearly contradicts the Markov assumption on short time scales. It is possible though, that the dynamics are effectively Markovian on longer times scales. If so, our method is able to extract that time scale.

III. FITTING FOKKER-PLANCK EQUATIONS

A Markovian stochastic process of which the probability $n(m,t+dt)$ for small dt only depends on $n(m+dm,t)$ for small dm, is described by a Fokker-Planck Eq [10]. Such an equation is generally of the form

$$\frac{\partial n(m,t)}{\partial t} = -\frac{\partial}{\partial m}[v(m)n(m,t)] + \frac{1}{2}\frac{\partial^2}{\partial m^2}[D(m)n(m,t)]. \quad (4)$$

The function $v(m)$ is called the *drift velocity* and $D(m)$ is called the *diffusion coefficient*. Equation (3) is an example of such an equation.

To find the Fokker-Planck equation that best describes the dynamics of a variable $m(t)$, the variable m in binned into a number of bins of size Δm and a time interval τ is chosen. From a long time series, the number N_{ij} of transitions from bin j to bin i after time τ is counted. This results in a transition matrix T, of which element T_{ij} gives the probability that a state belonging to bin j evolves to a state of bin i after a time τ:

$$T_{ij} = \frac{N_{ij}}{\sum_{i'} N_{i'j}}. \quad (5)$$

The denominator is the total number of times that a state belonging to bin j is observed. The error in the number of transitions N_{ij} is roughly the square root of the number and therefore the error in the matrix element T_{ij} is approximately

$$\sigma_{ij} \approx \frac{\sqrt{N_{ij}}}{\sum_{i'} N_{i'j}}. \quad (6)$$

To find the Fokker-Planck equation that best describes the time series, one should discretize Eq. (4) into bins of size Δm as well. This is done as follows

$$\frac{n_i(t+\Delta t) - n_i(t)}{\Delta t} = -\frac{v_{i+1}n_{i+1} - v_{i-1}n_{i-1}}{2\Delta m} + \frac{D_{i+1}n_{i+1} - 2D_i n_i + D_{i-1}n_{i-1}}{2\Delta m^2}, \quad (7)$$

which can be rewritten as

$$n_i(t+\Delta t) = \sum_j (\delta_{ij} + \Delta t M_{ij}) n_j(t). \quad (8)$$

The matrix M_{ij} is tridiagonal with zero column sums. Its nonzero entries are

$$M_{i-1,i} = \frac{v_i}{2\Delta m} + \frac{D_i}{2\Delta m^2}, \quad (9a)$$

$$M_{i,i} = -\frac{D_i}{\Delta m^2} \quad (9b)$$

$$M_{i+1,i} = -\frac{v_i}{2\Delta m} + \frac{D_i}{2\Delta m^2}. \quad (9c)$$

Subsequently, the following expressions for the drift velocity and the diffusion coefficient can be obtained:

$$v_i = (M_{i+1,i} - M_{i-1,i})\Delta m, \quad (10a)$$

$$D_i = (M_{i+1,i} + M_{i-1,i})\Delta m^2. \quad (10b)$$

In terms of the matrix M, the solution to the Fokker-Planck equation can be written as

$$n(t+\tau) = \exp(\tau M) n(t), \quad (11)$$

with the exponential of a matrix defined by the power series

$$\exp(M) = \sum_{i=0}^{\infty} \frac{1}{i!} M^i. \quad (12)$$

The Fokker-Planck equation that best describes the sampled transition matrix T, is now determined by minimizing the function

$$\sum_{i,j} \left(\frac{T_{ij} - \exp(\tau M)_{ij}}{\sigma_{ij}} \right)^2 \quad (13)$$

with respect to M. Equation (10) then yields the drift velocity and diffusion coefficient as function of the variable m.

IV. DATA ANALYSIS

The main application of the method of the previous section is, given a time series, to extract the drift velocity and diffusion coefficient of a Markov process, that is described by a Fokker-Planck equation. It can also be used, however, to test whether a time series is described by such a Markov process or not. For a Markov process, the transition matrix after a time interval of 2τ, for example, is equal to the square of the transition matrix after a time interval of τ. More generally, since for Markov processes Eq. (11) holds, the method returns the same matrix M, regardless of which value for τ is chosen, and finds therefore the same drift velocity and diffusion coefficient if a Fokker-Planck description is possible. If the process is, on the other hand, not Markovian, the method returns different matrices M for different values of τ. The matrices M may also converge to a constant matrix for $\tau > \tau_0$; if so, the dynamics are effectively Markovian on times larger than τ_0.

This idea is used to verify how well the growth and shrinkage of spin clusters in the Ising model are described by a Fokker-Planck equation. An Ising model on a 64×64 square lattice with periodic boundary conditions has been used for the simulations. The simulations are performed in the absence of an external field. The Hamiltonian is given by [5]

$$H = -J\sum_{\langle i,j\rangle} s_i s_j, \tag{14}$$

with the summation over all pairs of neighboring sites. The coupling constant is chosen as $\beta J=0.5$, where β is the inverse temperature. The simulations are performed in equilibrium; for each size in the range 1–250 spins, random configurations are generated and simulated in time. This process is repeated for days to collect statistics.

The simulations are performed with two different dynamics: spin flip and local spin exchange, often referred to as Glauber and Kawasaki dynamics, respectively. The moves are accepted with Metropolis acceptance probabilities [9]. In the case of spin flip dynamics, a system with periodic boundary conditions is used to minimize finite-size effects. Time is expressed in the number of attempted spin flips per site. In the case of local spin exchange dynamics, strictly enforced periodic boundary conditions cause the magnetization to be globally conserved, which, in the relatively small systems used in computer simulations, causes severe finite-size effects in the free energy as a function of cluster size, since cluster growth induces depletion of particles in the remainder of the system. In a large system, particles from far away would flow into this depleted volume, but that is impossible in the small systems of the simulations. Therefore, the boundary conditions are opened by performing spin flip moves in two strips of the system (one in each principal direction). These strips are moving, always located as far away from the cluster as possible to minimize side effects. The strips mimick an infinite reservoir containing a given fraction of minority spins at a fixed temperature. Time is now expressed as the number of attempted local spin exchanges per site.

The variable that is used to characterize a configuration is the mass m of the largest cluster in the system. One bins this variable into bins of size $\Delta m=5$ and transition matrices are sampled for different time intervals $\tau=2^i$, with i ranging from -12, i.e., one single attempted move, to 2, i.e., 4 attempted moves per site. This results in 15 different values for τ. The sampled transition matrices of spin flip dynamics are in Fig. 1 (top) and the matrices of local spin exchange dynamics are in Fig. 2 (top). A color scale is used to display values and the legend is underneath the matrices.

As a first qualitative check for the Markovianity, each transition matrix is raised to the power $4/\tau$ (note that this power is always integral) and compared to the transition matrix for $\tau=4$. For a Markov process, all these matrices are identical, but Figs. 1 and 2 (center) clearly show that this is not the case for the simulations of the Ising model. The transition matrices for small τ raised to the power $4/\tau$, show much more diffusion than is observed for the corresponding matrix with time interval $\tau=4$.

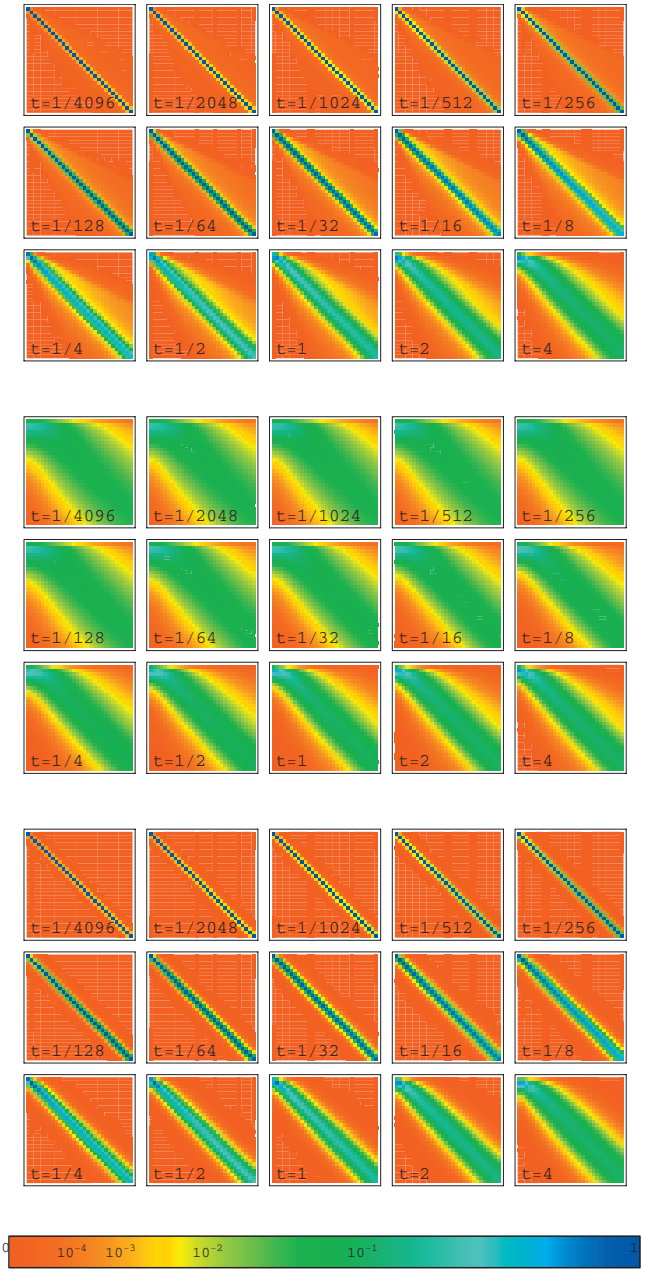

FIG. 1. (Color) Transition matrices for the Ising model with spin flip dynamics. The top block of 15 matrices displays the observed transition matrices, the middle block displays the observed matrices to the power $4/\tau$ and the bottom block displays the fitted matrices $\exp(\tau M)$. Underneath the matrices is the color legend.

For a quantitative analysis, the method of the previous section is employed to extract the drift velocities and diffusion coefficients, as a function of cluster mass m, of the transition matrices for various values of the time interval τ. Therefore it is assumed that the dynamics are described by a Fokker-Planck equation. Note that this assumption was not required for the first qualitative check for Markovianity. The fitted matrices $\exp(\tau M)$ are displayed in Figs. 1 and 2 (bottom) for comparison with the observed transition matrices. Around the diagonal, which covers the vast majority of the transitions, the fits are really good. Further away from the

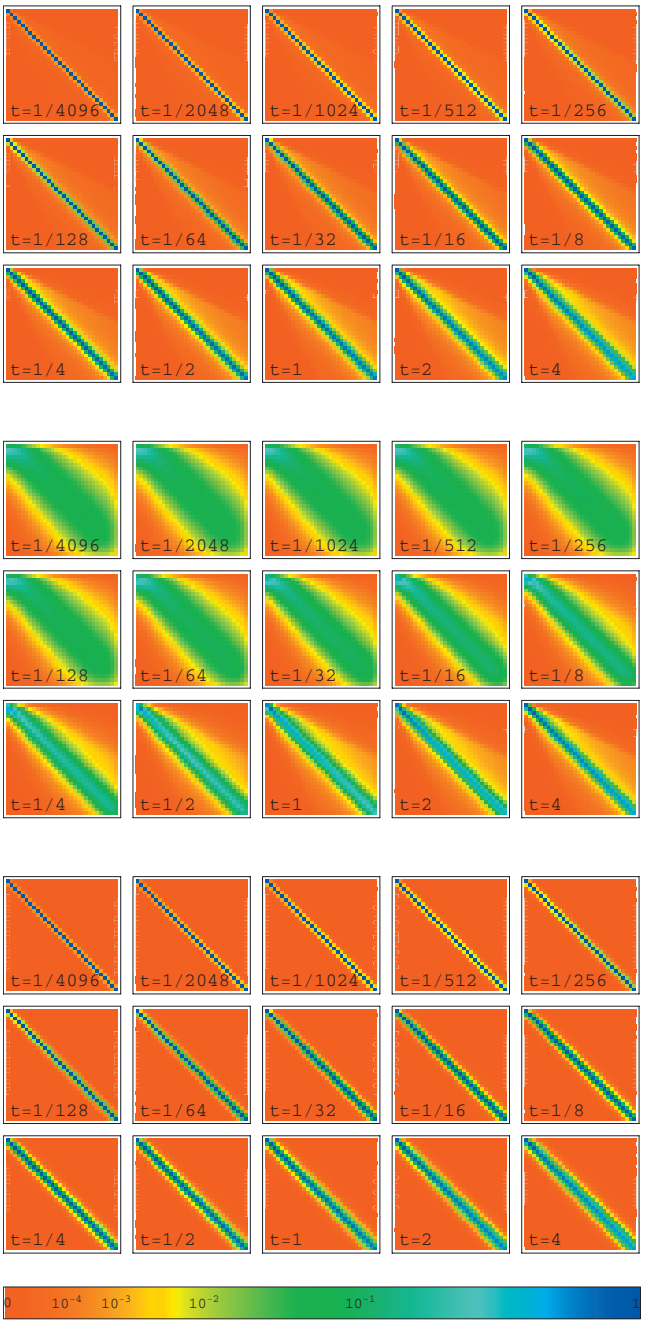

FIG. 2. (Color) Transition matrices for the Ising model with local spin exchange dynamics. The top block of 15 matrices displays the observed transition matrices, the middle block displays the observed matrices to the power $4/\tau$ and the bottom block displays the fitted matrices $\exp(\tau M)$. Underneath the matrices is the color legend.

diagonal, however, the fitted matrix has fewer transitions than observed. The explanation for this is, that for the fitted matrix it is assumed that the mass of a droplet changes with unit steps, while in the full simulations it occassionally changes with larger steps due to the splitting and merging of clusters.

These fitted tridiagonal matrices M are used to obtain the drift velocities and diffusion coefficients via Eq. (10). The drift velocities are almost constant (small and negative).

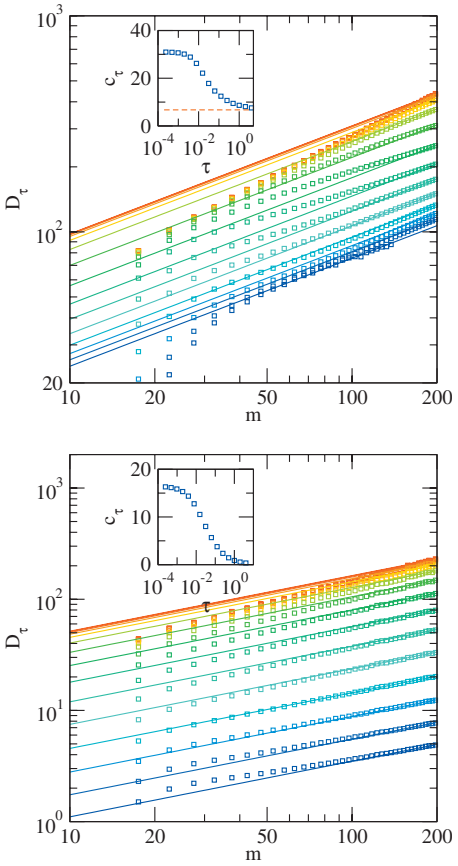

FIG. 3. (Color) The diffusion coefficient as function of cluster mass for the Ising model with spin flip dynamics (top) and local spin exchange dynamics (bottom). The different colors indicate τ increasing with factors of two. Red corresponds to $\tau=1/4096$, while blue corresponds to $\tau=4$. The solid lines are fitted functions $D_\tau(m)=c_\tau\sqrt{m}$. The insets show the fit constants as function of τ as blue squares. The red dashed line in the top inset is the diffusion coefficient per unit interface length, as measured in Ref. [11].

Since they do not show much interesting behavior, they are not displayed. The diffusion coefficients as function of cluster mass are displayed in Fig. 3. Since the diffusion coefficients are expected to scale with the size of the surface, i.e., the square root of the mass in the case at hand, the figures are double-logarithmic plots, and lines with a slope of one half are fitted to the data.

V. DISCUSSION

Looking at the resulting fitted diffusion coefficients (average square deviation in droplet mass per unit of time) for both spin flip and local spin exchange dynamics, the data are well fitted by lines proportional to $\sqrt{m}$, as long as the cluster masses are not too small. For small cluster masses, however, the fits are rather poor. A reason for this is that small clusters deviate strongly from a spherical shape, and the size of the interface between the cluster and its surroundings as a function of mass is thus not well fitted by $\sqrt{m}$.

Next, the diffusion coefficients as function of τ are considered. For both spin flip and spin exchange dynamics, the

diffusion coefficient is constant for very small values of the time interval, i.e., for values of τ corresponding to a few moves. This makes sense, since at those time scales the moves are spatially separated and thus independent of each other, and therefore the process behaves Markovian. At larger time intervals, however, the observed diffusion coefficients depend on the value of τ. This shows that the dynamics are not correctly described by a Markov process at large time scales.

For spin flip dynamics, this deviation from Markovianity is mostly explained by spin flips in the interior of the cluster. These flips lead to a relatively large diffusion coefficient for small τ, however, they do not contribute to the variations in cluster size for large τ. At times larger than one spin flip per site, the diffusion due to these flips is negligible. Indeed, as the inset of the top panel of Fig. 3 shows, the diffusion coefficient seems to be converging to a positive constant for time scales beyond $\tau \approx 10$ attempted spin flips per site. The figure also displays the expected constant, i.e., the diffusion constant per interface length as measured in Ref. [11]. Note that the data converge to a constant, even if plotted with a logarithmic horizontal scale. At time scales at which the matrix M has converged to a constant, spin flip dynamics is effectively described by a Markov process. The spin flip moves in the interior also explain why the fits in Fig. 3 (top panel) are bad for small τ: the number of such moves scales namely with m instead of $\sqrt{m}$.

Local spin exchange dynamics, on the other hand, show different behavior. The inset of the bottom panel of Fig. 3 shows that the diffusion coefficient is decreasing to zero, with increasing τ. This indicates that these dynamics are not described by a Markov process at all. In a recent paper [8], we suggested that the cluster growth shows *anomalous diffusion*, as a consequence of the observation that spins detaching from the cluster stay in the neighborhood for a long time and are likely to reattach. In fact, the theory of Brownian motion states that in two dimensions every spin that detaches from the droplet, is eventually returning to it [12]. In this case, this results in quasi-one-dimensional behavior and variance in cluster size scaling as

$$\langle [m(t) - \langle m(t) \rangle]^2 \rangle \sim \sqrt{t} \tag{15}$$

for several orders of magnitude in time after $t=1$ spin exchange per site. This explains the diffusion coefficient decreasing to zero with increasing τ. This behavior lasts until the detached particles are so far away from the cluster, that the higher dimensionality of the system becomes apparent. Since Fokker-Planck processes always yield

$$\langle [m(t) - \langle m(t) \rangle]^2 \rangle \sim t, \tag{16}$$

a description of anomalous diffusion, and therefore of local spin exchange dynamics, by a Fokker-Planck equation is impossible.

VI. SUMMARY AND CONCLUSIONS

In summary, we have shown that time series of the mass of the largest droplet, in simulations of the Ising model with spin flip or with spin exchange dynamics, cannot be described by a Fokker-Planck equation. On large time scales, however, spin flip dynamics might be effectively described as such, while local spin exchange dynamics are not.

This reveals a limitation of a Markovian description of nucleation. In fact, a description of nucleation in terms of a Fokker-Planck equation for $n(m,t)$, the number of droplets of mass m, cannot be correct. For a better description, one should resort to another description of the state space, or include non-Markovian effects in the dynamics.

ACKNOWLEDGMENT

We thank Henk van Beijeren for useful discussion.

[1] D. Kashchiev, *Nucleation: Basic Theory with Applications* (Butterworth-Heinemann, Oxford, 2000).
[2] R. Becker and W. Döring, Ann. Phys. **24**, 719 (1935).
[3] K. Brendel, J. Kuipers, G. T. Barkema, and P. Hoyng, Phys. Earth Planet. Inter. **162**, 249 (2007).
[4] J. Kuipers, P. Hoyng, J. Wicht, and G. T. Barkema, Phys. Earth Planet. Inter. **173**, 228 (2009).
[5] M. E. J. Newman and G. T. Barkema, *Monte Carlo methods in statistical physics* (Oxford University Press, Oxford, 1999).
[6] V. A. Shneidman, K. A. Jackson, and K. M. Beatty, Phys. Rev. B **59**, 3579 (1999).
[7] V. A. Shneidman, K. A. Jackson, and K. M. Beatty, J. Chem. Phys. **111**, 6932 (1999).
[8] J. Kuipers and G. T. Barkema, Phys. Rev. E **79**, 062101 (2009).
[9] N. Metropolis *et al.*, J. Chem. Phys. **21**, 1087 (1953).
[10] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (Elsevier, Amsterdam, 1981).
[11] K. Brendel, G. T. Barkema, and H. van Beijeren, Phys. Rev. E **71**, 031601 (2005).
[12] Z. Schuss, *Theory and Applications of Stochastic Differential Equations* (Wiley, New York, 1980).