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Absence of a trapping effect on the kinetic critical radius in nucleation and growth processes

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Abstract

In a recent paper by Erdélyi et al. [Acta Mater. 58 (2010) 5639–5645] it is claimed by way of kinetic Monte Carlo simulations that the actual critical nucleus size can deviate from the thermodynamical prediction by orders of magnitude due to effects of the difference between the diffusivities in the matrix and the nucleus. Here these issues are critically re-examined both by simulations and theoretical considerations. The growth probability curves for nuclei of different sizes are obtained for different diffusion asymmetries, which show no effect of diffusion asymmetries on the critical size. The time evolution of the simulated nucleus sizes does show an effect, however: while the mean time until a nucleus has either evaporated or grown is comparable, fluctuations on small timescales are much larger for faster diffusion in the nucleus. Finally it is argued that a dynamical trapping effect is actually in conflict with the principle of detailed balance.

Keywords: Monte Carlo techniques; Homogeneous nucleation of phase transformations; phase transformation kinetics

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1. Introduction

Classical nucleation theory explains the nucleation of grains from supersaturated solutions in terms of thermodynamics alone: the free energy of a system containing a nucleus is modelled by the gain in free energy due to the transformation of the volume within the nucleus, and the loss due to the interfacial energy. For small nuclei, the latter term dominates, therefore the equilibrium concentration of nuclei with a size of n particles falls with n in this regime. At the critical size n_c, however, the interfacial energy loss when enlarging the nucleus by a given volume falls behind the constant gain in voluminal energy, therefore the equilibrium concentration of nuclei with $n \to \infty$ formally diverges. The picture of nucleation is therefore that small nuclei form due to spontaneous fluctuations, and most of them will evaporate again. A few will reach the critical size, however, and these will tend to grow and therefore consume the matrix supersaturation, as this lowers the free energy of the system. The actual microscopic transition rates only enter the nucleation rate; the critical size n_c, which is the nucleus size where the probability of growing equals the probability of evaporating, only depends on thermodynamics in this model.

Erdélyi, Balogh and Beke [1] challenge this picture. They differentiate the thermodynamically defined critical size n_c, defined as the size where the nucleus free energy reaches its maximum, from the kinetically defined critical size n^*, which is defined by equal probability for growth and evaporation [2]. They performed kinetic Monte Carlo simulations with atom-vacancy exchanges, and by choosing interaction potentials so as to get different diffusivities in A- and B-rich domains (still within values that are not unrealistic in alloy physics), but without changing the thermodynamics of the system and therefore n_c, they obtained differences in n^* of an order of magnitude. They explain this observation by a trapping effect, in that the atoms cannot be ejected from the nucleus sufficiently fast before new ones arrive, even if this raises the free energy of the system.

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Essentially, the microscopic transition rates beat thermodynamics. This interpretation seems to be at odds with the principle of detailed balance and therefore allow the breaking of fundamental thermodynamic laws, which provided the motivation for critically re-examining the issue, both by simulations and theoretical considerations, as reported here.

2. Model

The interaction energies used by Erdélyi et al. [1] correspond to a Hamiltonian of the system of

$$H(\sigma) = -V/4\sum_{\vec{x}}\sum_{\Delta\vec{x}}\sigma(\vec{x})\sigma(\vec{x}+\Delta\vec{x}) + M/2\sum_{\vec{x}}\sum_{\Delta\vec{x}}\Big(\sigma^2(\vec{x})\sigma(\vec{x}+\Delta\vec{x})+\sigma(\vec{x})\sigma^2(\vec{x}+\Delta\vec{x})\Big), \quad (1)$$

where $\sigma(\vec{x})$ is equal to 1, 0, or -1 if site $\vec{x}$ is occupied by an A-atom, a vacancy, or a B-atom, respectively, and $\Delta\vec{x}$ enumerates the Z nearest-neighbour vectors. Note that for fixed composition of the system and small vacancy concentrations the energy of the system is only given by the first term, therefore the thermodynamics are completely specified by V.

Above Hamiltonian has already been used for Monte Carlo studies of nucleation and growth (e.g., [3–6]). For modelling the microscopic dynamics, additional assumptions are needed. In Ref. [5] the parameter M is used to control only the preferred environment of a vacancy with a constant migration energy for every kind of atom, whereas in the model of Erdélyi and coworkers (which coincides with the choice of Refs. [3, 4]) the saddle point in the energy landscape is when all the jumping atom's bonds are broken, and the migration energy is therefore set equal to the energy necessary to extract the atom from the crystal. While this broken-bond model indeed has a certain stylistic appeal, it could be argued which of the two models captures the physical situation more accurately, as the vacancy formation energy depends more on valence electronic structure, while the migration energy follows mainly from the core repulsion that the jumping atom experiences while passing through the window [6, 7].

If the binding energy of an AA-pair is larger than a BB-pair's, as quantified by a negative parameter M, it is energetically more favourable for the vacancy to be in a B-rich domain. In Erdélyi and coworkers' model, the effect of $M < 0$ on the respective diffusivities is therefore twofold: it both raises the vacancy concentration in the B-domain and the exchange frequency of a vacancy-B-pair. These two effects are independent of each other, as the Monte Carlo model used, e.g., in Ref. [5] gives only the former, and it is easy to construct a model giving only the latter. The connection between vacancy formation and migration energy has been recognized previously as a constraint of the present model [8].

In Ref. [1] the diffusion asymmetry m' (which is the ratio of diffusivities in pure A and B-matrices, given in orders of magnitude) is related to the asymmetry of the pair potentials M by

$$m' = -2\log_{10}(e)ZM/kT, \quad (2)$$

where Z is the coordination number (the misprint concerning the role of $\log_{10}(e)$ has been corrected here). This formula has initially been derived for an ideal solid solution with diffusion by direct atom exchange [9] and therefore misses both the effects due to the ordering energy V and the different vacancy concentrations [8] (even though the authors seem to be aware of the latter issue as evidenced by the pertinent discussion in Appendix A of Ref. [1]). The ratio of the vacancy concentrations between pure A and B-matrices is $\exp(-ZM/kT)$, which in a first approximation enhances the diffusion asymmetry compared to the value of Eq. (2). Also note that even in the case of no diffusion asymmetry ($M = 0$), but still with positive enthalpy of mixing ($V > 0$), the impurity diffusion constant is larger than the self diffusion constant for both elements due to the fact that an impurity atom is less tightly bound to the crystal than a host atom. It therefore follows that $m_A = -m_B \neq 0$ (see also the pertaining results obtained by Athénes et al. [3]), contrary to Erdélyi and coworkers' implicit assumption that $m_A = m_B$.

For a rigorous treatment of the diffusion asymmetries m_A and m_B one would need to solve the five frequency models [10] for both the cases of B-impurities in A and A-impurities in B and compare to the respective self diffusion constants. This is possible for the present model [8], but not the aim of this publication.

3. Simulations

3.1. System

In the following a report of an attempt to reproduce the results of Erdélyi and coworkers' Monte Carlo simulations as closely as possible, with the same simulation method and analysis unless where noted, is given. They present a case for both an fcc- and a bcc-system, but do not state for which system the simulations were actually performed. However, as the maximum number of neighbours in the legend of Fig. 3 is 8, it seems safe to assume that they used a bcc-system. This assumption also fits better with the quoted solubility (which is about 12.5% at the given V/kT for a bcc-lattice, but only about 1.5% for a fcc-lattice, as obtained by grand-canonical simulations).

Residence-time Monte Carlo simulations were performed on a bcc-lattice in the canonical ensemble with one vacancy. The simulation box consisted of 64^3 cubic bcc-cells with periodic boundary conditions. Note that the resulting vacancy concentration of 1.9×10^{-6} is within the range quoted by Erdélyi et al. [1], who report no influence of the actual vacancy concentration on the outcome. This was checked by performing additional simulations with 128^3 cells. The interaction parameter was chosen as $V/kT = 0.3626$, in accordance with Ref. [1]. The initial state was generated by defining a sphere of given radius, then going over each site of the system and randomly setting it to A with a probability of 85% if it was within the sphere or 15% if it was without (otherwise it was set to B), as it was done by Erdélyi et al. [1]. In view of the fact that the quantitative relation between the asymmetry in the pair potentials M and the asymmetry in the diffusivities m' is anything but trivial, I will follow established practice [3–6] and directly quote the used M

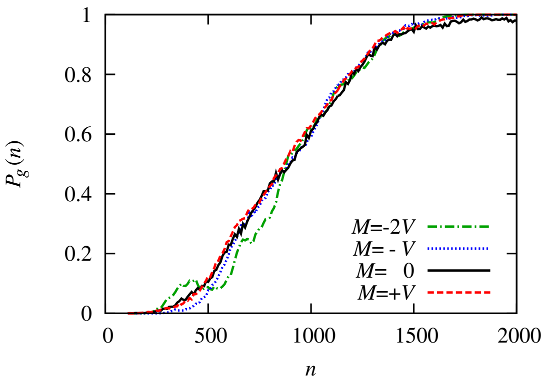

Fig. 1: Growth probabilities for various choices of M. Note that the graph for $M = -2V$ corresponds to less simulation runs and has therefore a higher noise level.

in units of V. Note that by taking Eq. (2) at face value, Erdélyi and coworkers' $m' = 4$ corresponds to $M \approx -1.56V$. Time is measured in units of MC-steps, where one MC-step equals N vacancy jumps, with $N = 2^{19}$ the number of atoms in the system. The cluster size was determined by a connectivity analysis as in Ref. [1] for the bcc-case.

3.2. Results

At a minority concentration of 15%, the nucleation rate is vanishingly small. At $M = 0$, only a few times during 5000 MC-steps a cluster reaches a size of 300 atoms, but dissolves again immediately. The evolution of the size of a given cluster can therefore be followed by placing the cluster into the simulation box and monitoring the size of the largest cluster. Once this maximum size has dropped consistently below 300 atoms, the initial cluster is considered to have dissolved. The criterion for successful growth is set at 2500 atoms, as clusters above this size are growing more or less monotonically.

If an initial cluster of 900 atoms grows during the simulation run to a size of 2500 atoms (after which the simulation is stopped), the matrix supersaturation drops by about 15%. Such a change is in general not negligible, but as in the present case only the behaviour of the cluster in a small range around the critical size is of interest (which is on the order of 900 atoms), it should be acceptable for the present purposes. This is corroborated by the fact that no significant deviations are seen in the simulations with the eight-fold simulation volume.

For a given M, a number of simulation runs were performed with different initial cluster sizes. Every 10 MC-steps, the size of the largest cluster was determined. The growth probability $P_g(n)$ is determined by the number of instances that the cluster size was equal to n among the simulation runs that resulted in a growing cluster divided by the total number of instances that the cluster size was equal to n. With such an evaluation it is possible to obtain rather smooth growth probability curves from around 200 simulation runs per choice of M.

Fig. 1 presents the obtained growth probability curves for a few choices of M. The reason for the failure to present simulations over the whole range of M as probed in Ref. [1] lies in the fact that the simulations become increasingly more CPU-intensive for large diffusion asymmetries: while for $M = 0$ the timescale for a critical cluster to become definitely sub- or supercritical is on the order of 10^4 MC-steps, for $M = 2V$ it is at about 10^6 MC-steps, and for $M = -2V$ at about 2×10^6 MC-steps. Therefore, for $M = -2V$ only 35 simulation runs have been performed, which is the reason for the non-smooth appearance of the pertinent graph in Fig. 1. For $M = -3V$, which corresponds to the highest asymmetry reported in Ref. [1], an initial cluster of 900 atoms had not fluctuated by more than 200 atoms after 5×10^6 MC-steps, at which point the simulation was aborted, with stretches of 100 MC-steps without any size evolution at all.

The kinetically defined critical size n^* is given where $P_g(n^*) = 0.5$. Observing that the position of the intercept is essentially given by how many simulation runs lead to a growing cluster, which follows a binomial distribution, the statistical uncertainty is about 5% in the vertical dimension, and therefore about 50 atoms in the horizontal dimension (120 atoms in the case of $M = -2V$). In the light of this, no significant influence of M on the critical size, which is at about 900 atoms, can be seen, in contrast to the results reported in Ref. [1].

These long timescales at high diffusion asymmetries are to be expected: High asymmetries imply that most of the vacancy jumps are self-diffusion events, therefore the fraction of vacancy jumps that lead to an evolution of the nucleation state of the sample vanishes. From this point of view it seems impossible to observe an evolution of the cluster size in simulations with diffusion asymmetries as large as those claimed in Ref. [1]. Also observe that the diffuse interfaces reported by Erdélyi et al. for higher diffusivities in the precipitates (which they identify as the equilibrium shape) diametrically opposes the findings of Roussel and Bellon [4], who found (non-equilibrium) diffuse interfaces in the case of higher diffusivities in the matrix.

Samples of the temporal evolution of the nucleus sizes for the highest simulated diffusion asymmetries are given in Fig. 2, and here clearly an effect is to be seen: while the fluctuations on timescales of 10^4 MC-steps are comparable, those on timescales of 10 MC-steps show a much higher magnitude in the case of positive M, that is faster diffusion in the nucleus. This is not hard to understand: Due to the high effective temperature the shape of the nucleus is rather diffuse, that is, it is only weakly interconnected. For positive M, these connections are rapidly shuffled around, because most of the atomic exchanges happen within the nucleus. Parts of the nucleus are therefore repeatedly detached and reattached. The random walk of the size of the nucleus is therefore highly correlated: if it has dropped due to the detachment of a cluster, it is likely that it will rise again when this cluster is reattached. Over longer timescales, these fluctuations therefore average out for the most part, so that a system with positive M will show much larger short-timescale fluctuations than a system with negative M, if both have comparable timescales of growth and dissolution.

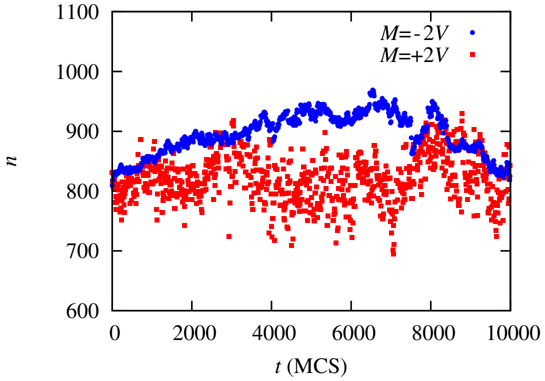

Fig. 2: Detail of the time evolution of the nucleus size for two choices of M.

4. Implications of detailed balance

Finally, I want to discuss here the implications of the principle of detailed balance and demonstrate explicitly why a dynamical trapping effect of solutes at the nuclei as claimed by Erdélyi and coworkers is impossible. Consider two microscopic states i and j with the conditioned transition frequency $\nu_{i\to j}$, which is defined so that $\nu_{i\to j}\mathrm{d}t$ is equal to the probability that the system transitions from i to j within the infinitesimal time $\mathrm{d}t$ *under the condition* that the system is in state i, and let $\nu_{j\to i}$ be defined analogously. For now, consider only neighbouring pairs of states, i.e., where $\nu_{i\to j} \neq 0$, for the case at hand this would be states that are connected by a single vacancy jump. To derive the relation between the two conditioned transition frequencies we use the principle of detailed balance, which states that there are no net fluxes between any pair of states in equilibrium, that means back and forth transition rates are equal $p_i\nu_{i\to j} = p_j\nu_{j\to i}$, where p_i and p_j are the equilibrium probabilities for the system to be in state i or j, respectively [11, 12]. As $p_i/p_j = \exp((E_j - E_i)/kT)$, it follows from above condition that $\nu_{i\to j}/\nu_{j\to i} = \exp((E_i - E_j)/kT)$. Note that this is a strict relation of microscopic quantities and holds irrespective of whether the system is in equilibrium or not as seen from the thermodynamic point of view.

Consider now the particular path of the system through configuration space which is given by the system staying for a time t_0 in state 0, crossing over into state 1 within the infinitesimal time $\mathrm{d}t$, and then staying in state 1 for t_1. Let the probability for this path be $P_\rightarrow$. Define the probability of the inverse process, which consists in staying in state 1 for t_1, then crossing over to 0 and staying for t_0, as $P_\leftarrow$. It follows that

$$\frac{P_\rightarrow}{P_\leftarrow} = \frac{\nu_{0\to 1}}{\nu_{1\to 0}} = \exp\Big((E_0 - E_1)/kT\Big), \tag{3}$$

as the other quantities cancel. For a two-jump path $0 \to 1 \to 2$ it again follows that

$$\frac{P_\rightarrow}{P_\leftarrow} = \frac{\nu_{0\to 1}\nu_{1\to 2}}{\nu_{2\to 1}\nu_{1\to 0}} = \exp\Big((E_0 - E_2)/kT\Big), \tag{4}$$

and obviously also for paths composed of n jumps.

Eq. (4) was derived for any given choice of residence times t_i. By integrating over all choices it immediately follows that it also holds for the quotient of the probabilities when only the sequence of states, but not the respective residence times, are specified. With a similar argument one can also sum over all sequences of states connecting the initial and the final state, so that the following statement follows from the microscopic principle of detailed balance: Let i and j be arbitrary states of the system (not necessarily neighbouring), with the respective energies E_i and E_j. Then the probability that a system that is initially in state i evolves to j within time t is equal to the probability for the reverse evolution multiplied by $\exp((E_i - E_j)/kT)$, irrespective of whether these states are near thermodynamic equilibrium or not.

Detailed balance is a generally accepted principle and follows from microscopical time reversal symmetry [13]. Note that it is a stronger requirement than thermodynamics, as a circular net flow $A \to B \to C \to A$ would violate time reversal symmetry, but not thermodynamics. The model as given by Erdélyi et al. fulfills detailed balance, along with every model conventionally used in kinetic Monte Carlo studies. From the viewpoint of solid state physics, detailed balance follows also from classical transition state theory [14].

5. Discussion

Erdélyi and coworkers interpret their results by a trapping effect for positive m': They postulate that an A-atom that has impinged on the nucleus cannot be ejected again sufficiently fast before new ones arrive, because the jump frequency in the matrix is much higher due to the microscopic transition rates given by the kinetic parameters, even if this increases the free energy of the nucleus. Specifically, they suppose that the trapped atom is held in its state of higher energy by a bias between incoming and exiting attempt frequencies.

Their error is that they equate the impinging rate with the jump rate in the matrix and the ejection rate with the jump rate in the nucleus, or, in other words, any jump that an A-atom on the surface of the nucleus can make, including the jump back into the matrix, happens with the same rate. This is physically not realistic, and also in conflict with their model. The rigorous derivation in the above section shows that, even while the paths that lead from a state where the atom is dissolved in the matrix to a state where it is attached can be arbitrarily complex when a vacancy is involved, the ratio between attaching and detaching frequency is given only by the difference in energy. Figuratively speaking, in the geography of solid state physics there are no one-way streets, atoms choose their way only due to the inclination (i.e., energetic differences). Therefore no such trapping as understood by Erdélyi et al. [1] can occur.

The assumption of such a trapping effect would have a very drastic consequence for the long-time limit of the system under consideration: The configuration of minimum free energy for a system in the miscibility gap is reached when it has decomposed into an A-rich and a B-rich domain, separated by an interface (in a simulation this can be realized as two slabs within the simulation box with periodic boundary conditions). Thermodynamics dictate that the concentration of B-atoms in the A-domain is

$\exp(-E_B/k_BT)$ for small concentrations, where E_B is the energy that it costs to immerse a B-atom in the A-rich matrix. If dynamical effects would lead to an impinging rate higher than the ejection rate by a trapping effect, the B-concentration in the A-rich domain would drop further, until this bias between the two rates had been compensated by a depletion of the B-atoms in the A-matrix that can impinge. The system would therefore evolve to a steady state that is different from the thermodynamical ground-state, i.e. the state of minimum free energy. Therefore such a trapping effect would as a consequence violate the second law of thermodynamics.

The argumentation above shall by no means imply that microscopic dynamics have no influence on precipitate nucleation apart from a trivial scaling in time. In fact, it is well possible that the greatly enhanced mobility of small (subcritical) nuclei as observed by Soisson and Fu [6] results in the formation of stable precipitates due to random coagulations (without having to directly cross the free energy barrier of the critical nucleus), or that the supersaturation of the precipitates reported by Roussel and Bellon [4] gives a higher kinetical critical size. More generally, for nucleation processes that happen far from equilibrium, such as when a solid solution is quenched rapidly deep into the miscibility gap, the availability of specific transition paths can likely affect the nucleation kinetics. This is not the case reported here, however: the very small supersaturation (a minority concentration of 15% compared to a solubility of about 12.5%), the large critical nucleus size, and the very wide range of sizes within which a nucleus has comparable possibilities for growing or dissolving are all indications for the applicability of equilibrium concepts. Therefore it seems unlikely that dynamical effects could amount to changes of the kinetical critical size of one order of magnitude as observed by Erdélyi and coworkers for the present choice of parameters. This is supported by the simulations reported here. The differing results of Erdélyi and coworkers remain inexplicable.

6. Conclusion

In conclusion, I have shown here that the model given by Erdélyi et al. [1] respects the principle of detailed balance, and that a violation of this principle as manifested in the results of Erdélyi et al. implies a violation of the second law of thermodynamics. Even though the dynamical fluctuations displayed by the size evolution of near-critical nuclei depend on the microscopic transition rates, an effect on the kinetically defined critical nucleus size cannot be reproduced by simulations in the probed range of parameter space.

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