# ISING MODEL SIMULATIONS AS A TESTBED FOR NUCLEATION THEORY

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ABSTRACT. In this short review article, we discuss the use of the Ising lattice model as a testbed for improving the theory of both homogeneous and heterogeneous nucleation. First, we briefly review classical nucleation theory (CNT), and two typical simple systems on which simulations are performed — hard spheres, and the Ising lattice model. Then we review some results obtained by this approach, and point to possible new directions for research and improvement.

KEYWORDS: nucleation, Ising model, classical nucleation theory.

## 1. NUCLEATION

As a process naturally occuring on the scale of individual atoms to thousands of atoms, the nucleation has always been a window to the nanoscale world. It was studied well before the current advances in nanoscience and nanotechnology in various phase transitions including condensation, cavitation, solidification, crystallization and precipitation. It has also been studied in various fields of physics and technology, ranging from atmospheric physics concerned with condensation of water vapor to studies of radiation damage in materials important for reactor technology applications [1], and even in fields seemingly detached from the nanoscale, such as the technology of building materials [2].

In most of these situations, some general properties are the same. Discontinuous phase transitions usually proceed in three steps. First, some small clusters of the new phase — "embryos" — appear due to stochastic fluctuations. If they reach a certain critical size, the embryos become growable and stable "nuclei". This stage of the transition is called nucleation. In the second stage, the particles grow. Finally, in closed systems, the growth is limited by the supply of the untransformed, remaining phase.

The formation of nuclei is associated with an energy barrier, which limits the process, and allows metastable phases to persist over long periods of time. The barrier may be lowered if the cluster forms on the site of an existing impurity or on the boundary of some other material, leading to heterogeneous nucleation. The barrier may also be lowered if the nucleus is of some intermittent phase, different in structure or composition from the stable phase [3, p. 93].

Nucleation is naturally also important in nanotechnology and in the science of nanostructures. One entire approach to the formation of nanostructures — the self-assembly (or "bottom-up" approach) can often be considered as a case of controlled nucleation, and crucial nanotechnologies such as thin layer construction are in a sense a case of heterogeneous nucleation. In technology, the aim is usually to control the distribution of the sizes, the placement or the shape of the nanoparticles, for example by changing the external parameters of the system, by using surfactants, or by patterning the substrate.

Nucleation was first described in classical nucleation theory, dating back to Volmer, Weber and Farkas [4, 5] and Becker and Döring [6]. Despite its age, the theory is still widely used to describe the nucleation stage of phase transition in many contexts.

## 2. CLASSICAL NUCLEATION THEORY

### 2.1. NUCLEATION BARRIER

In the simplest case, we start with a single component system, such as the liquid phase condensing from a gas, or precipitation from a liquid solution. In classical nucleation theory, the capillarity approximation is frequently used - the values of the parameters used in the model are taken to be the same as in macroscopic objects.

Initially, the system is in some $\alpha$-phase, which is metastable with regard to the $\beta$-phase. In order to change to the $\beta$-phase, first some small cluster of $\beta$-phase must be formed.

The energy balance for the formation of a small cluster consisting of $N$ particles (atoms, ions, etc.) is thermodynamically given as

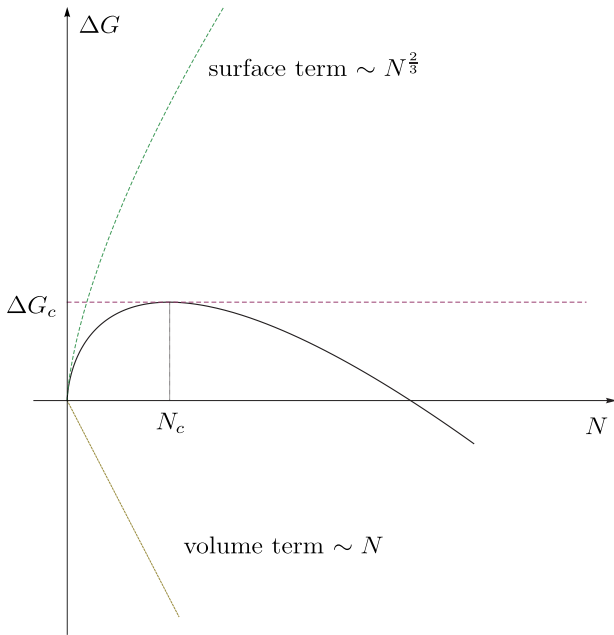$$\Delta G_N = N(\mu^\beta - \mu^\alpha) + \Delta G_{\text{interface}}, \qquad (1)$$

Figure 1. Free energy $\Delta G(N)$ as a function of cluster size $N$ in the nucleation regime

where $\mu^\beta$ (resp. $\mu^\alpha$) are chemical potentials in the $\beta$-phase (resp. $\alpha$-phase) and $\Delta G_{\text{interface}}$ is the energy of the newly formed interface.

The first term is always negative and represents the driving force of the process. The surface term is positive and competes with the first (volume) term.

For small radii, the surface-to-volume ratio is large, and the surface term dominates — in effect creating a barrier for nucleation. The nature of the dependence becomes clear if we rewrite (1) to be

$$\Delta G_N = N(\mu^\beta - \mu^\alpha) + \eta N^{\frac{2}{3}}\sigma, \tag{2}$$

where $\eta$ is a shape-factor surface/$N^{\frac{2}{3}}$ (constant for a given shape), and $\sigma$ denotes the interfacial energy per unit area (see Fig 1).

For small radii, the surface-to-volume ratio is large, and the surface term dominates, forming a barrier for nucleation of height $\Delta G_c$. A cluster of the corresponding size is known as the critical nucleus $N_c$, with critical radius $r_c$, etc. While clusters smaller than $N_c$ tend to go down the energy slope and shrink, clusters larger than $N_c$ grow further and form stable particles of the new phase.

In our simple case, the classical theory with isotropic interfacial energy leads to a cluster which takes a spherical form, and critical parameters may easily be found:

$$N_c = \left(\frac{2\sigma\eta}{3\Delta\mu}\right)^3 \tag{3}$$

and

$$\Delta G_c = \frac{4(\sigma\eta)^3}{27\Delta\mu^2}. \tag{4}$$

The picture described above can be adapted to more complicated systems and scenarios by accounting for other contributions to the nucleus energy. The

contributions of strain (early studies Nabarro [7]), incoherency of the interfaces, anisotropy of the surface energy and the effects of vacancies are often important.

## 2.2. Nucleation rate

Classical nucleation theory then proceeds to determine the nucleation rate — defined as the rate at which stable nuclei are formed within a unit volume in unit time. This is also often the quantity connecting theory with experiment.

Here, we use the cluster dynamics approach, which allows us to derive both the classical theory and its flavors and some recent models, and it naturally shows the links between them.

In the non-nucleation regime, the new phase $\beta$ is not stable, $\Delta G_N$ is always positive, no stable nuclei form, and the nucleation rate is zero. The equilibrium distribution of clusters, minimizing the free energy of the systems, is

$$X_N = \exp\left(-\frac{\Delta G_N}{\text{k}T}\right), \tag{5}$$

where $X_N$ is the fraction of clusters of size $N$ to all clusters and $\Delta G_N$ is the free energy of clusters of size $N$.

In the nucleation regime, the system is out of equilibrium and clusters larger than $N_c$ grow to stable sizes.

The growth can be described as a flux of clusters in size-space. If the coalescence rate is small (which is most often true at least in the early stage of nucleation), it can be assumed that the growth is governed by single particle processes - the addition or loss of one particle (a so-called step-by-step process). Using more simplifying assumptions, such as steady supply of monomers and removal of large clusters, the classical theory then derives a cluster flux in a "steady-state" where $J(N)(t) = J$.

$$J(N)(t) = J = \left(\frac{\Delta G_c}{3\pi N_c^2 kT}\right)^{\frac{1}{2}}\beta_c\mathcal{F}e^{(-\Delta G_c+\Delta G_1)/kT}. \tag{6}$$

.

The first dimensionless term is called the Zeldovich factor and its magnitude is typically $10^{-1}$ [8, p. 466], the frequency term $\beta_c$ expresses the number of monomers within jump distance from the embryo mutiplied by jump requency, and $\Delta G_c$ is the free energy of critical clusters.

## 3. Improvements to nucleation theory

In the development of nucleation theory, there is obviously a huge space for extensions and improvements of classical theory.

The first big class results from lifting some of the simplifying assumptions, e.g., not assuming the steady state we can examine the time lag to nucleation [9]

or we can study the theory of nucleation in closed systems [10]. Another big class consists of attempts to improve the core of the theory, for example by including some seemingly neglected entropy contributions, or by imposing some formal requirements on consistency (e.g., note that in the above derivation the "formation energy" of a size 1 "cluster" is nonzero, which seems unnatural).

Until recently, such modifications were typically very hard to test. Individual nuclei are usually too small to be directly observed, particularly "in vivo", when the nucleation process is happening. The quantity accessible to experiment is often only the total nucleation rate partially obscured by subsequent growth processes. Due to the exponential dependence of the nucleation rate on parameters including temperature and the energy barrier, it is often very hard to distinguish experimentally whether some proposal is really an improvement to the theory, or if it just happens to push the predicted nucleation rate in the "correct" direction, compensating for often large errors of experimental data or parameter control. The difficulty with experimental tests is also related to the fact that predictions for a relatively small space of experimental data (e.g., the dependence of the nucleation rate on a single parameter such as temperature) are based on a much bigger space of model parameters and assumptions (e.g., chemical potentials, surface energies taken from macroscopic systems, assumptions such as the insignificance of the time scale with which the system is tempered in relation to the nucleation time scale, etc.)

This is a situation where computer simulations can be of enormous use, allowing precise control over the big parameter space, and allowing individual aspects of the theory to be tested.

## 4. Modern statistical sampling methods

The difficulty with computer simulations of nucleation lies in the rarity of nucleation events. For example, in the case described bellow of nucleation in the lattice Ising model, the typical time until one nucleation event occurs is $10^5$ simulation steps. Straightforward simulation may wander endlessly in the initial phase, then the nucleation event proceeds very fast in a few steps, and then the systems remains in the final phase. To obtain a meaningful statistical sample, or any sample at all, it is therefore necessary to employ algorithms which enhance the probability of rare events and lead to a detailed exploration of the phase space close to the transition point. A detailed description or a comparison of these methods is beyond the scope of this paper — for a comprehensive review including practical comparisons, see Van Erp [11].

From several typically used methods to study nucleation an example can be Forward Flux Sampling (FFS) [12, 13].

## 5. Testbed systems and results

Even in a simulation, when modeling real systems using molecular dynamics, nucleation theory gets tested along with various other simulation properties (e.g., a description of interatomic forces). For a systematic improvement of nucleation theory itself, the ideal case is a system with as few as possible arbitrary parameters of both the system and the simulation. Two such model systems are particularly important. The system of hard spheres, often used as a reference model of a liquid, is also used for studies of nucleation. The second system is the lattice Ising model, one of the simplest statistical systems exhibiting phase transitions.

### 5.1. Hard spheres

In 2001, Auer and Frenkel [14] used a model of hard spheres to predict absolute crystal nucleation rates without any adjustable parameters and most of the assumptions of CNT. In their comparison of the results with CNT, their conclusion was that the CNT predictions for the height of the nucleation barrier $\Delta G$ are not accurate (30–50 % too low), but the data from the simulation can be fitted to the functional form given by CNT (6) except for very small clusters. Auer and Frenkel also studied the nucleation pathway — the sequence of structures of small clusters. This topic was later also studied by O'Malley and Snook [15] and others.

Prestipino et al. [16] used the hard sphere model to systematically test the assumptions of CNT, giving particular attention to the definition of clusters and related problems with cluster shape and interfacial energy, leading to corrections to the first part of the theory (determining the nucleation barrier, capillarity approximation).

Heterogeneous nucleation of hard spheres on walls was examined by Auer and Frenkel [17]. Drastic lowering of the nucleation barrier was observed, as would be expected from classical heterogeneous nucleation theory. An interesting observation was that the nucleation barrier was dominated by line tension. Xu et al. [18] also studied heterogeneous nucleation of hard spheres on patterned substrates (consisting of patterns of the same spheres in fixed positions). They noted that the time required for crystallization can be greatly reduced on a suitable substrate and the crystallizing phase can to a large extent be influenced by the substrate. Even if in some of the studies no explicit comparison with classical theory was made, or the results are mostly qualitative, there seemed to be at least qualitative agreement, and not surprisingly, a problem of CNT with correct interface energies.

Sandomirski et al. [19] used hard and soft sphere models to study heterogeneous crystallization on flat and curved interfaces.

## 5.2. Ising model

Detailed comparisons of classical nucleation theory with simulations of nucleation in the 2D and 3D lattice Ising model were made by Ryu and Cai [20, 21]. A particularly interesting aspect of this study was the independent testing of the "nucleation barrier" part and the "nucleation rate" part of CNT. The two parts in fact rest on different sets of assumptions, and their validity is relatively independent. In the case of the 2D lattice Ising model, Ryu and Cai demonstrated good agreement of CNT with simulation with no adjustable parameters. The CNT model in this case included two important improvements to classic theory - the Langer field theory correction [22] to nucleus energy, and corrected temperature dependent interfacial energy, taking into account anisotropy of the surface energy in the Ising model and changes in the shape of the equilibrium nucleus with temperature. The results of these studies establish the Ising model as an extremely useful reference point for testing various fundamental improvements to nucleation theory, and also for testing changes and additions to CNT that are necessary in different scenarios.

Brendel et al. [23] studied the nucleation times in the two-dimensional Ising model, using cluster energies and transition rates directly obtained from simulation. With the input of these parameters, the nucleation times predicted by CNT were in reasonable agreement with the simulation.

Page and Sear [24] studied the influence of pores and surface patterning on the heterogeneous nucleation rate and energy barriers, finding a significant change in the nucleation rate caused by the presence o the pores, and satisfactory agreement with CNT if different nucleation rates are assigned to nucleation in and out of pores. Building on this work, Hedges and Whitelam [25] asked how to pattern the surface in order to maximally speed up nucleation, and as the answer studied nucleation in the presence of pores with various dimensions. An interesting and potentially practically useful result is that the maximum nucleation rate is achieved if one dimension of the pore has the critical length.

Kuipers and Barkema [26] focused on memory effects (non-Markovian dynamics) in the Ising model with local spin-exchange dynamics, which introduces diffusion-like properties to the model. In such circumstances, events of particle attachment and detachment from the cluster are often strongly correlated, and the moves in cluster size space are no longer Markovian. Accounting for this by introducing new events, such as "particle leaving to infinity", "particle leaving to return", Kuipers and Barkema demonstrated an influence of memory effect on dynamics. Effectively, the outcome was increased fluctuations around the critical size, leading to a smaller time spent on the "energy plateau" of the nucleation barrier, and hence an increased nucleation rate. An analytical description of the situation remains an open topic.

Allen et al. [27] focused on another important scenario, ie. nucleation in the presence of shear, in the 2D Ising system. They observed a peak in the nucleation rate in the intermediate nucleation rates, and suppression of nucleation in high shear rates. It seems to remain an open question whether concepts from CNT, especially cluster size as a reaction coordinate, are suitable simplification.

Recently, Schmitz et al. [28] carefully examined the definitions of the clusters used in most of the studies, showing that the most commonly used "geometrical" definition is unsuitable for defining clusters at higher temperatures. On the other hand, at low temperatures the cluster energy and the shape are grossly anisotropical. A big part of the previous results need to be reconsidered in light of more physical definitions of clusters.

## 6. Conclusions and prospects for future research

The results described above clearly show that agreement of CNT with simulation in simple cases is a great starting point for understanding nucleation in more complex scenarios.

From a comparison with earlier studies of CNT and hard spheres, we can propose several directions in which a comparison of the theory with numerical simulations in the Ising model can be made, and the required additions to the theory can be tested. One big relatively sparsely explored topic is the field of non-stationary systems and conditions. We can vary not only the external driving force, but also the temperature may be varied, as is often the case in experimental scenarios. In the case of surface nucleation, the surface energy may also be non-stationary. Other interesting cases may be generated by lifting the condition of spatial homogeneity. For example, we can introduce a temperature gradient, or we can orm a more complicated and more realistic surface, which may exhibit heterogeneous surface energy, roughness, or curvature.

Another promising direction is to reconsider discrepancies between CNT, simulations and other models in light of more correct definitions of clusters [28], possibly leading to a model that is consistent across a broad range of temperatures and cluster sizes.

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