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Branching of nucleation paths in a metastable lattice gas with Metropolis dynamics

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Abstract. A cold, supersaturated gas on a square lattice with nearest-neighbour interaction is considered. The problem is equivalent to a metastable Ising ferromagnet with Metropolis dynamics in external magnetic field. Using the electric analogy established earlier for this problem by Shneidman (2003 *J. Stat. Phys.* **112** 293), the inverse of the nucleation rate is expressed as an equivalent resistance of a complex electric network. Explicit expressions for the equivalent resistance of the network can be obtained from an analysis of series-parallel connections, and the nucleation rate can be evaluated with accuracy which is sufficient not only for the exponential part, but also for the prefactor. At low temperatures and non-special values of the supersaturation S the path of the lowest energy dominates. On the other hand, for $1/2S = 1, 2, \dots$, (with $S \geq 1$ corresponding to instability) paths with temporal excursions towards higher energies also contribute, leading to the renormalization of peaks in the prefactor of the inverse rate even in the limit of zero temperature. Results can be used to construct a Becker-Döring type picture which views nucleation as a random walk in a one-dimensional space of the cluster sizes. However, the 'size' cannot be characterized by any integer n , the number of particles in a cluster, but only by an n which is close to a perfect square. Other clusters are to be combined into physical 'droplets', which presumably will play the role of nuclei in the Becker-Döring description.

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1. Introduction

Origins of the conventional theory of nucleation can be traced to the works of Kelvin, who introduced the concept of a critical nucleus and of Gibbs, who calculated the work to form a nucleus with n monomers $W(n)$, and suggested to associate its maximum W_* with the stability of the metastable phase. However, the modern state of this theory (at least in the part usually referred to as ‘classical’) goes directly to two formulas obtained by Einstein during the first decade of the 20th century.

The first formula connected the diffusion coefficient with mobility for Brownian motion of particles. The second formula expressed the probability of a fluctuation w through the associated change in entropy Δs via

$$w \propto \exp\{\Delta s\} \quad (1)$$

(Boltzmann constant will be taken as 1).

Equation (1) was used by Volmer and Weber [1] to estimate the exponential part of the nucleation rate

$$I \propto \exp\{-W_*/T\}. \quad (2)$$

Subsequently, Farkas [2] and later Becker and Döring [3] suggested treating nucleation as a random walk in the n -space. This random walk is characterized by an analogue of a size-dependent diffusion coefficient $\beta(n)$ which at least in the context of nucleation from a dilute vapour follows from a simple kinetic model. Later Zeldovich [4] invoked the other Einstein’s formula, the one connecting the mobility and the diffusion coefficient, which in the nucleation context is given by

$$v(n) = -(\beta/T) dW/dn. \quad (3)$$

Here $v(n)$ is the deterministic (neglecting fluctuations) growth rate, and the advantage of using equation (3) is that it allows one to obtain the diffusion coefficient β once the macroscopic kinetics $v(n)$ and the thermodynamics $W(n)$ are specified. In particular, in this manner, the problem of

cavitation could be treated [4], where, unlike the case vapour condensation, a microscopic model for β is less obvious.

Despite the success of the classical theory of nucleation in application to various experimental systems, several fundamental issues remain unresolved. One is related to the uncertainty in selecting the prefactor in equation (1), with a similar difficulty in equation (2). Next, what is the appropriate way to calculate W_* for a *finite* nucleus, which typically contains several tens of molecules and has properties rather different from those of a bulk phase? On the level of kinetics, one of the key questions is justification of the one-dimensional random walk picture in view of the variety of possible states of a nucleus, and the multiplicity of the possible transition paths between various states of nuclei with different sizes.

With this, there is a strong interest in models which exhibit nucleation and which, at the same time, are close to exact solvability. Typically, those are lattice-type models, similar to the Ising ferromagnet, with a certain spin-flip dynamics of non-conserved type, and at sufficiently low temperatures.

In the present work the simplest of such models, namely a two-dimensional lattice gas on a square lattice will be considered. The model is equivalent to a two-dimensional nearest-neighbour Ising model in magnetic field H (analogue of the supersaturation S , see the more precise definition in the next section). The spin flips are driven by Metropolis dynamics. The temperature T is assumed to be much lower than the critical temperature, T_c . This model was originally studied in the mathematical literature where the nucleation barrier was obtained exactly at $T = 0$ [5] for arbitrary H , and the pre-exponential was evaluated at large [6] and small H [7], respectively. Integer values of $2/H$ were excluded from the aforementioned treatments. Later it was shown [8, 9] that for $T \geq 0$ and arbitrary moderate-to-large H (including integer $2/H$) the problem can be treated analytically using symbolic computations. A special ‘lattice gas’ spin flip dynamics [8] as well as the more standard Glauber and Metropolis dynamics [9] were considered. In particular, it was discovered that the preexponential of the inverse rate I^{-1} has sharp peaks at integer $2/H$. The problem was also studied numerically using the method of Monte Carlo with absorbing Markov chains ([10] and earlier references therein) in a similar domain of fields, and good correspondence between the results at not-too-high temperatures was observed [9]. For strong fields non-Glauber dynamics was also considered recently [11, 12].

Although numerical and symbolic computational approaches can produce accurate expressions for the nucleation rate, they consider a finite (even if large) amount of cluster configurations and thus are necessarily restricted to a small nucleus. This is in contrast with the classical theory where the nucleus is large (equivalently, H is small), and an analytical approach which would be capable of bridging the two limits would be extremely instructive.

In [13] an electric analogy of the corresponding nucleation problem was established which allowed to treat analytically the domain of small H and finite, albeit small T for several Glauber-type dynamics, including the ‘lattice gas’ and the Metropolis one. A lowest-energy nucleation path was identified which is expected to provide the leading contribution at small T . In particular, the limit $T = 0$ was re-examined and the pre-exponential of the inverse nucleation rate turned out to be smaller than the one suggested earlier [7]. Peaks at integer $2/H$ also appear in the approach of [13]. Nevertheless, in the domain of H and $T > 0$ where numerical and symbolic computational data are also available, the analytical values were slightly higher, indicating the potential contribution of the higher-energy paths, and at the peak values a minor difference persisted up to $T = 0$.

The present study intends to generalize the analytical treatment by including higher energy paths which leads to a more elaborate branching of the electric network. This is a rather challenging problem which can be of independent interest due to the extraordinary status of the two-dimensional Ising model in our understanding of the phase transitions. However, since the Ising model provides a non-trivial example of a system where the nucleation rate can be calculated from ‘first principles’ (after the dynamics is specified), the results also can shed light on the general status of the classical theory of nucleation.

2. The lattice gas

2.1. Analogy with the Ising model and equilibrium properties

Consider a standard Ising ferromagnet with interaction energies between the nearest-neighbour spins given by $\pm J$ and the interaction with external field given by $\pm JH$. If the flip of a given spin changes the total energy by ΔE , then in Metropolis dynamics the rate of such a flip is $\min\{1, \exp(-\Delta E/T)\}$.

Let the system be prepared in a metastable state, with all spins originally pointing down and a small upward external field. At low temperature, the original state will persist for an exponentially long time, except for the formation of a dilute gas of up spins, and possibly a few larger clusters. The gas, however is supersaturated and will eventually condense into a ‘liquid’ of up spins. The analogy with the lattice gas can be made more precise (see e.g., [14] or [13]) with the following convention. The ‘down’ spins are considered as background, while the ‘up’ spins are treated as molecules of the lattice gas. If two molecules are nearest neighbours, they interact with energy $-\phi = -4J$. There is no interaction between non-nearest-neighbour molecules, or between a molecule and the background. Adding a molecule to the system increases the total free energy by μ , the chemical potential, in addition to the possible changes in the energy associated with interactions. For $\mu_0 = -2\phi$ the gas is in equilibrium with the liquid phase (which corresponds to $H = 0$ in the Ising case). Otherwise, for $\mu > -2\phi$ the gas is supersaturated, and the dimensionless supersaturation, defined as $S = (\mu - \mu_0)/2\phi$ is equivalent to $H/4$.

Clusters of various shapes will be combined in classes k , and within a given class all shapes are equivalent with respect to rotation or reflection. Only compact clusters, where each particle is connected by at least one bond, will be considered. The following characteristics of a class will be used: $n(k)$, the number of particles in a cluster, P_k , the perimeter (with lattice constant taken as 1), and w_k a geometric factor associated with the symmetry of a cluster, with $w_k = 1$ for a perfect square and $w_k = 8$ for a non-symmetric cluster. The label k is assumed to increase monotonically with n , but otherwise there is no restriction on the numbering of classes, and there can be several k with the same $n(k)$.

The (quasi)equilibrium number of clusters in a given class is given by

$$f_k^e = w_k \exp \left\{ -\frac{\phi}{T} (P_k - 2Sn(k)) \right\}. \quad (4)$$

In a supersaturated system with $S > 0$ the function f_k^e passes through a minimum, corresponding to the critical cluster. In a rather profound mathematical study Neves and Schonmann [5] calculated the work to form such a cluster at $T \rightarrow 0$:

$$W_*^0 = 2\phi \{m_* - S(m_*^2 - m_* + 1)\} \quad (5)$$

with

$$m_* = \left[\frac{1}{2S} \right] + 1, \quad (6)$$

where $[x]$ is the largest integer not to exceed x . An elementary derivation of the above expressions is also available [13] (note, however, the difference of notations for $[x]$ as well as for m_* which differ by 1 in the present version).

2.2. Kinetics

It is convenient to introduce the following notations

$$z = e^{-\phi/T}, \quad \delta = e^{2S\phi/T} \quad (7)$$

for the two small and large parameters of the problem, respectively. Of main interest will be the transition rates $\beta_{i,k}$ between a cluster of class i and one from class k , with $n(k) = n(i) + 1$. The treatment will be restricted to $S \leq 1/2$ (or $z\delta \leq 1$) where these rates are analytic in the Metropolis dynamics.

Neglecting clusters with ‘holes’ (four bonds are added when a particle is introduced) and ‘depressions’ (three bonds added), one has the following transition rates:

$$\beta_{i,k} = C_{i,k}, \quad (8)$$

where $C_{i,k}$ is the number of appropriate corners (two bonds added), and

$$\beta_{i,k} = \mathcal{F}_{i,k} z \delta, \quad (9)$$

where $\mathcal{F}_{i,k}$ is the number of appropriate ‘flats’.

Once the rates are known, one can define the fluxes between classes

$$j_{i,k} = \beta_{i,k} f_i^e (V_i - V_k) \quad (10)$$

with $V_i = f_i/f_i^e$, the ratio of kinetic and equilibrium distributions. The total fluxes in and out of the class k are given, respectively, by

$$I_k^+ = \sum_i j_{i,k}, \quad I_k^- = \sum_i j_{k,i}. \quad (11)$$

The kinetic equation can then be written in a generalized Becker–Döring form

$$\frac{df_k}{dt} = I_k^+ - I_k^-. \quad (12)$$

Currently, of main interest is the steady state with

$$I_k^+ = I_k^- = I, \quad (13)$$

which is the nucleation rate. Once I is evaluated, the preexponential A is obtained from

$$I^{-1} = A \exp\{W_*^0/T\} \quad (14)$$

as was defined in [8]. To a certain extent, separation of an observable quantity I into a product (14) is a convention since there is no unique way of defining a ‘true’ nucleation barrier. The zero- T value W_*^0 of [5] is used for convenience as it leads to finite (non-exponential) A at small T .

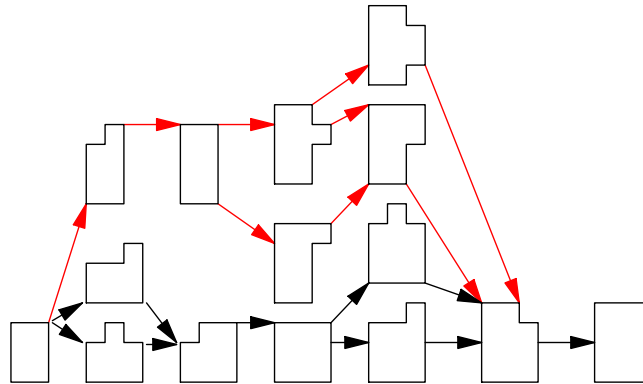


Figure 1. Nucleation paths linking the $m \times (m - 1)$ and the $m \times (m + 1)$ rectangles with $m = 3$. The black arrows indicate the path of the lowest energy [13]. Red arrows indicate the paths which at some point involve excited configurations, and only paths which return to the lowest energy path are shown. In the electric analogy, arrows correspond to ‘resistances’. Some of the resistances are negligible for $z \ll 1$ and/or $\delta \gg 1$, and the equivalent resistance of the above circuit is given by equation (18).

2.3. The electric analogy

In the electric analogy [13] classes are treated as ‘junctions’, a flux $j_{i,k}$ is an ‘electric current’ between the corresponding junctions, while V_i is the ‘voltage’. With

$$R_{i,k} = (\beta_{i,k} f_i)^{-1} \quad (15)$$

defined as a resistance which links the two junctions, equation (10) is ‘Ohm’s law’. Furthermore, in steady state equation (13) is equivalent to the ‘junction rule’ and I^{-1} equals the equivalent resistance of the corresponding electric network for which a system of Kirchoff’s equations is to be solved.

3. Analysis of the nucleation path

The goal of the study is to identify finite stretches of the electric network which can be replaced by single equivalent resistances. If that can be done throughout the network, the latter will be reduced to an infinite linear chain, in analogy with the one-dimensional random walk in the Becker–Döring nucleation picture [13].

3.1. The general result

Branching of paths appears already if only clusters with the lowest energies are considered since such clusters can have distinct shapes—see figure 1. Adding higher energy paths makes the situation more complex. Nevertheless, one notes that only selected paths eventually return to the lowest energy path, and thus expected to contribute at $T \rightarrow 0$. The important point is that the lowest energy and the higher (‘h’) energy paths which connect an $m \times (m - 1)$ and $m \times (m + 1)$ rectangles and can be considered independently for $m \geq 3$. This allows one to

calculate the corresponding resistances separately, each one as a combination of series and parallel connections. Furthermore, many resistances, such as those connecting the 10- and the 11-spin clusters in figure 1, will have a negligible contribution which simplifies intermediate results. The actual technique is rather similar to the one used in [13] for the lowest energy path (R) and can be directly generalized for the path with the higher-energy configurations (R^h). One has

$$R_{m \times (m-1), m \times (m+1)} = \frac{3(z\delta^m + 1)}{(8m - 4)\delta^{m^2+1}z^{2m+1}} \quad (16)$$

and

$$R_{m \times (m-1), m \times (m+1)}^h = \frac{3}{\delta^{m^2+1}z^{2m+1}} \left(\frac{z\delta^m}{8m - 12} + \frac{\delta}{8m + 4} \right). \quad (17)$$

After that, one considers a parallel connection:

$$R_{m \times (m-1), m \times (m+1)}^{eq} = \left(\frac{1}{R_m} + \frac{1}{R_m^h} \right)^{-1}. \quad (18)$$

For $m = 2$ the general pattern is not followed since transitions between the higher and the lower energy paths are possible. This leads to a more complex expression

$$R_{2,6}^{eq} = \frac{96z^3\delta^4 + 149z^2\delta^3 + 45z\delta^2 + 30}{8\delta^5z^5(144\delta^2z^2 + 101\delta z + 15)}. \quad (19)$$

Finally, there is no branching on the path between an empty site and a two-particle cluster, so that

$$R_{0,2}^{eq} = \frac{1}{\delta z^2} + \frac{1}{4\delta^2 z^3} \quad (20)$$

(here the reader is reminded that only $S \leq 1/2$ is considered, otherwise a minimum of competing terms would have to be selected in Metropolis dynamics).

The total resistance of the network can be written as

$$R^{eq} = R_{0,2}^{eq} + R_{2,6}^{eq} + \sum_{m=3}^{\infty} R_{m \times (m-1), m \times (m+1)}^{eq}. \quad (21)$$

The first two terms are written separately to indicate violation of the general pattern of equations (16)–(18).

Now the pre-exponential can also be given as a sum of individual contributions,

$$A = \sum_{m=1}^{\infty} a_m \quad (22)$$

with

$$a_m = z^{W^0/\phi} R_{m \times (m-1), m \times (m+1)}^{eq} \quad (23)$$

and is illustrated in figure 2. At higher supersaturations, $1/2S \lesssim 6$, and compared to the lowest energy approximation of [13], the results substantially improve agreement with data obtained numerically [10] or using symbolic computations [9] (the latter paper also compares those two types of data with each other). The correction due to higher energy paths is the strongest at S close to $1/2$ where it allows to explain the interesting effect of the pre-exponential going below its zero-temperature limit.

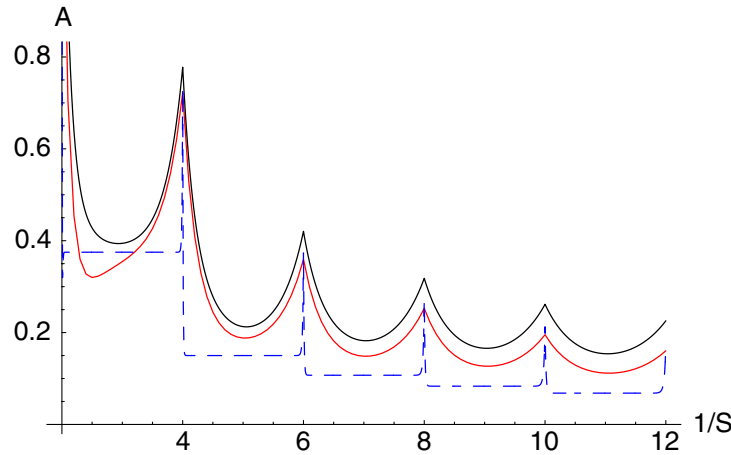


Figure 2. The preexponential of the inverse nucleation rate. Lower solid line, equation (22) which includes higher energy paths at $T = 0.1\phi$. Upper solid line, the lowest energy path only [13]. The dashed line is the zero-temperature limit of the more accurate description. Note that at peak values (integer $1/2S$) the difference between the two approximations persists all the way to $T = 0$.

3.2. The limit $T \rightarrow 0$

Consider first non-special values of S , away from the peaks in figure 2. Here only a single term with $m = m_*$ contributes to the sum in equation (22). In addition, compared to the lowest energy path, the path with excited configurations will have an asymptotically large resistance and, since it is in parallel, can be neglected. One thus has ($S < 1/2$):

$$A^0 = a_{m_*}^0 = \frac{3}{8m_* - 4}, \quad \frac{1}{2S} \neq 1, 2, 3, \dots \quad (24)$$

in agreement with [13].

A more interesting situation happens at integer values of $1/2S$. In that case, in the sum of equation (22) another term, the one with $m = m_* - 1$ will have a contribution comparable to the leading term. In addition, the higher-energy paths also must be included when calculating a_{m_*} . One thus has

$$a_{m_*-1}^0 = \frac{3}{2(2m_* - 3)}, \quad a_{m_*}^0 = \frac{3(2m_* - 1)}{2(12m_*^2 - 12m_* + 1)}, \quad \frac{1}{2S} \equiv m_* - 1 = 2, 3, \dots \quad (25)$$

and

$$A_{peak}^0 = a_{m_*-1}^0 + a_{m_*}^0. \quad (26)$$

One can check that asymptotically, for $S \rightarrow 0$, contribution of higher energy paths reduces the peak values by 1/9 of their original value.

Equation (26) is also valid for $S = 1/2$ ($m_* = 2$) but the terms a_1^0 and a_2^0 do not follow the pattern of equation (25). Here one obtains $A_{peak}^0 = 289/208$ in agreement with the results obtained in [9] using symbolic computations.

4. Discussion

From a technical point, the main result of the present study is an analytic ‘first principle’ evaluation of the nucleation rate in a two-dimensional lattice gas at low temperatures. The result is expected to be valid at any finite supersaturation, not to exceed $1/2$. The accuracy is sufficient to determine not only the leading exponential part of the rate [5] but also the rather delicate preexponential, and exceeds the accuracy of previous analytical approximations [13]. The latter is achieved due to inclusion of higher-energy nucleation paths. Remarkably, at special values of the supersaturation, contributions of those paths are important up to $T = 0$.

Besides the technical aspect, the study can shed new light on the general nucleation picture. Note that although the problem could be reduced to a linear chain, which is equivalent to a one-dimensional random walk, the standard Becker–Döring picture does not emerge. Indeed, there is no random walk between clusters of $n - 1$, n , $n + 1$ particles, etc, as in the conventional approach. Instead, one needs to construct a ‘droplet’ with a ‘size’ $m \sim \sqrt{n}$ which combines many clusters between the $m \times (m - 1)$ and $m \times (m + 1)$ rectangles, as in figure 1. The nucleation barrier for such droplets will be smaller than W_*^0 , but the transition rates between droplets with neighbouring m will be exponentially slow since an extra nucleation of a kink on a flat surface is required. In a sense, the nucleation picture becomes closer to the one discussed by Zeldovich who, in the cavitation context, wrote a Fokker–Planck equation in the space of size r , which is an analogue of m in the present case. The actual realization of the construction of the ‘best’ physical droplet, however, will likely require consideration of the transient kinetics, as well as the study of deterministic growth and decay of individual clusters, and extends beyond the scope of the present paper.

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