

## Modulation of the Nucleation Rate Preexponential in a Low-Temperature Ising System

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A metastable lattice gas with nearest-neighbor interactions and continuous-time dynamics is studied using a generalized Becker-Döring approach in the multidimensional space of cluster configurations. The preexponential of the metastable-state lifetime (inverse of nucleation rate) is found to exhibit distinct peaks at integer values of the inverse supersaturation. Peaks are unobservable (infinitely narrow) in the strict limit  $T \rightarrow 0$ , but become detectable and eventually dominate at higher temperatures.

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Nucleation phenomena are observed in an enormous variety of physical systems, including vapors [1], and glass-forming [2] and quantum [3] liquids, to name just a few. Already in the early treatment [4], Volmer and Weber indicated an Arrhenius structure of the exponential part of the nucleation rate  $I$ , with the barrier  $W_*$  given by the minimal work to form a critical nucleus. There remained, however, a fundamental issue of the preexponential, which was considered in subsequent classical [4] and postclassical [5] nucleation developments. Although in most metastable systems the exponential term dominates, the nucleation picture is not complete without a reasonable estimation of the prefactor, and misunderstandings here can have far-reaching consequences [6]. In practice, such estimations are often hindered by minor uncertainties in  $W_*$ , which can imply large (orders of magnitude) discrepancies in the values of the preexponential.

With this, much attention is devoted to models where exact values of  $W_*$  can be obtained, and thus reliable conclusions about the prefactor can be made. One of the best known examples is the two-dimensional Ising model, where metastability is achieved by orienting initially all spins one way (down) while nonzero magnetic field  $h$  prescribes an opposite (upward) orientation. Allowing spin flips of nonconserved [7] or conserved [8] types adds the required dynamics to the problem. In a closely related lattice gas model the role of  $h$  is played by supersaturation.

The preexponential in such systems attracts much attention both for the high- [5,9–12] and low-temperature [13–15] regions. For  $h \rightarrow 0$  the nucleus is macroscopic and its shape, as well as the value of  $W_*$ , can be obtained from the Wulff droplet construction [16]. Monte Carlo simulations are possible for  $W_* \lesssim 10$ –15 T (temperature is measured in units of Boltzmann constant) which, for small  $h$ , restricts such studies to the aforementioned high-temperature region; transfer-matrix approaches are also available here [17]. For larger fields a straightforward Wulff construction may be inadequate [18], but for  $T \rightarrow 0$  analytical treatment becomes possible due to the dominant contribution of low-energy configurations. The technique of absorbing Markov chains [13–15] can also be used for simulations in the low-temperature region.

Neves and Schonmann [19] evaluated  $W_*^0$ , the zero-temperature limit of  $W_*$ , obtaining the exponential part of the metastable lifetime  $\tau = 1/I$ . Their result is insensitive to the specifics of the dynamics. Novotny [13] further showed that, for discrete-time Glauber dynamics and a relatively large field, the preexponential of  $\tau$  remains finite in the limit  $T \rightarrow 0$ , approaching a piecewise constant function of  $h$  and pointing towards a discontinuity at an integer value of  $1/2h$ . Similar features will be observed at weaker fields as well [15]. Integer values of  $1/2h$ , however, were excluded from the aforementioned rigorous mathematical treatments, leaving open questions with regard to this intriguing effect, especially in the physically more realistic case of  $T > 0$ .

This Letter aims to evaluate the preexponential at higher temperatures and in a finite domain of fields, spanning several integer values of  $1/h$ . This will clarify the nature of the discontinuities and, together with the available  $W_*^0$ , will provide predictive expressions for  $\tau(T, h)$  at  $T > 0$ . We will show that, in contrast to an intuitive expectation of discontinuities spreading out in a standard tanh-like fashion, they are replaced by sharp peaks which persist up to  $T = 0$ , having finite heights and self-similar shapes as functions of reduced deviations of the field from “magic” values with integer  $1/2h$ .

A lattice gas on a square lattice with standard nearest-neighbor interactions described by the bond energy  $\varphi$  will be considered. Supersaturation (“field”) provides an additional decrease in energy by  $2h$  when a new particle is created. The probability of the latter event in an infinitesimal time interval  $dt$  is taken as  $\beta dt$ , regardless of the surrounding; without restrictions, the time scale  $\beta^{-1}$  can be taken as 1. The annihilation probabilities are sensitive to the surroundings, and are determined by detailed balance. With various generalizations, this model is popular, e.g., in Monte Carlo simulations of the dynamic interface in crystallization problems—see [20] and references therein. The dynamics is different from Glauber’s, and preexponentials will not be identical, but qualitative similarities are still expected since both dynamics are nonconserved (and the generalized Becker-Döring approach employed below bears certain parallels with the technique of absorbing Markov chains [13,14]).

For a long time of the order of  $1/I$ , the rare particles will form isolated clusters of various sizes and shapes (*classes*), which will be distinguished by a running index,  $i$ . An empty site corresponds to  $i = 0$ . Cluster shapes will be considered identical (and thus belonging to the same class) if they can be made such by rotation or reflection. The key characteristics of each class are the number of particles,  $s(i)$ , the number of bonds,  $b(i)$ , and the statistical weight,  $w_i \leq 8$ . One can define the (quasi)equilibrium distribution

$$f_i^{\text{eq}} = w_i z^{2s(i)-b(i)} \delta^{s(i)} \quad (1)$$

with  $z = e^{-\varphi/T}$  and  $\delta = z^{-2h}$  describing the temperature and field dependencies, respectively. Subsequently,  $\varphi$  will be taken as 1 for simplicity of notations. In the  $s, b$  space the function  $f_i^{\text{eq}}$  has a saddle point (for nonspecial fields, a single one [15]) and the corresponding value of  $s$  determines the critical cluster number,  $s_*$ . In a general case computer assistance is required in order to characterize all classes. Consistency of such predictions can be checked, e.g., against standard tables [21] for smaller  $s$ .

Once equilibrium properties are specified, one can introduce kinetic fluxes as a multidimensional version of the classical approach [4] since, in a low-temperature Ising system, growth or decay of a cluster predominantly proceeds via random gain or loss of a single particle [22]. If  $\beta_{ik} dt$  is the probability to transform a cluster from class  $i$  to class  $k > i$  by adding a particle [with  $\beta_{ik} = 0$  if  $s(k) \neq s(i) + 1$ ], the corresponding flux is given by

$$I_{ik} = \beta_{ik} f_i^{\text{eq}} (v_i - v_k), \quad i < k \quad (2)$$

with  $v_i \equiv f_i/f_i^{\text{eq}}$  and  $v_0 = 1$ . The master equation for the kinetic distributions  $f_i$  takes the form

$$\frac{df_i}{dt} = \sum_{k=0}^{i-1} I_{ki} - \sum_{k=i+1}^{k_{\text{max}}+1} I_{ik} \quad (3)$$

which automatically satisfies detailed balance.

For closing conditions, absorbing states are placed at all classes  $k$  with  $s(k) = s_{\text{max}} + 1$ . Equivalently, all those absorbing states can be combined in a single absorbing class  $k_{\text{max}} + 1$ .

Because of an exponentially long lifetime, one can neglect the depletion of empty sites (for which, otherwise, an

integral conservation law [23] should be employed instead of  $v_0 \equiv 1$ ). With this, Eqs. (2) and (3) can be solved in the steady-state approximation; transient effects [24] can also be neglected here.

By introducing  $b_{ik} = \beta_{ik} f_i^{\text{eq}} + \beta_{ki} f_k^{\text{eq}}$  ( $0 \leq i, k \leq k_{\text{max}} + 1$ ) and

$$M_{ik} = b_{ik} - \delta_{ik} \sum_{l=0}^{k_{\text{max}}+1} b_{il}, \quad 1 \leq i, k \leq k_{\text{max}}, \quad (4)$$

one can show that the steady-state distributions ( $v_1, v_2, \dots$ ) correspond to the first column of the matrix  $-\hat{M}^{-1}$  (since only class 1, with single-particle clusters, is connected to empty sites). The total flux  $I$  coincides with  $I_{01}$ , where branching of paths does not yet occur. This gives

$$I = (\hat{M}^{-1})_{11} + 1. \quad (5)$$

For a single nucleation path, which leads to a tridiagonal structure of the matrix  $\hat{M}$ , one recovers the classical result by Farkas [4]  $I^{-1} = b_{01}^{-1} + b_{12}^{-1} + \dots$ . Otherwise, the actual evaluation of  $I$  via Eq. (5) is limited by one's ability to obtain all classes and transition rates  $\beta_{ik}$  for a sufficiently large  $s_{\text{max}}$ , and the ability to inverse analytically a large matrix  $\hat{M}$ . At present, we are able to proceed up to  $s_{\text{max}} = 9$  (1818 classes representing a total of 13 702 cluster configurations) which allows us to consider fields  $h > 1/6$  with the critical number  $s_* \leq 7$ . A full exact expression for the lifetime  $\tau = 1/I$  can be surveyed by a human eye only for more modest values of  $s_{\text{max}}$ , which implies a relatively small critical cluster (larger fields). For example, for  $s_{\text{max}} = 4$ , kinetics is determined by nine distinct classes with a total of 28 shapes (see, e.g. Fig. 2 in Ref. [12]). Transition rates are easy to obtain (say, two ways a 3-particle "minus" shaped cluster can turn into a 4-particle "T" shaped one and four ways it can turn into an "L" shaped one, etc.). The result which follows from Eq. (5) is expressed as a rational function of  $z$  and  $\delta$ ,

$$\tau_4 = P(\delta, z)/Q(\delta, z) \quad (6)$$

with the subscript indicating the value of  $s_{\text{max}}$ , and polynomials  $P$  and  $Q$  given by

$$\begin{aligned} P(\delta, z) = & 384 + 210000\delta^9 z^9 + 16\delta(48 + 185z) + 4\delta^2 z(1576 + 2655z) + 8\delta^3 z^2(3081 + 3230z) \\ & + 2500\delta^8 z^7(21 + 250z + 36z^2) + 250\delta^7 z^6(695 + 2650z + 1036z^2) \\ & + \delta^4 z^3(65740 + 57797z + 15360z^2) + 5\delta^5 z^4(28574 + 28155z + 19680z^2) \\ & + 5\delta^6 z^5(43375 + 70546z + 50000z^2), \\ Q(\delta, z) = & 8\delta^4 z^4[384 + 80(24 + 85\delta)z + 250\delta^2(25 + 64\delta)z^3 + 125\delta^3(259 + 625\delta)z^4 \\ & + 20\delta(615 + 1753\delta)z^2 + 3750\delta^4(3 + 7\delta)z^5]. \end{aligned} \quad (7)$$

Equation (6) is expected to be accurate in strong fields,  $h \geq 1/2$ , with rather relaxed restrictions on temperature since all cluster configurations at  $s \leq 4$  are taken into account (although, for higher  $T$ , eventual destruction of the steady state due to neglected cluster interactions should be kept in mind [25]). More consistently, this result should

be treated asymptotically for  $z \rightarrow 0$  and  $\delta \rightarrow \infty$  with certain combinations of powers of  $z$  and  $\delta$  remaining finite, depending on the interval of the field.

In order to isolate the preexponential, Eq. (6) should be multiplied by  $\exp(-W_*/T) = z^{W_*}$ . In principle, an

“observable” is  $\tau$  itself, rather than  $A$  or  $W_*$  taken separately. To avoid ambiguity, the value of  $W_*$  will be associated with its zero-temperature limit  $W_*^0$  [19], with all temperature-dependent corrections being in the pre-exponential; for  $h > 1$  the barrier will be taken as zero. The function  $W_*^0(h)$  has a piecewise linear structure, and  $\exp(-W_*/T)$  is reduced to a product of integer powers of  $z$  and  $\delta$ : 1 for  $h \geq 1$ ,  $z^2\delta$  for  $1/2 \leq h < 1$ ,  $z^4\delta^3$  for  $1/4 \leq h < 1/2$ , etc. Resulting  $A(h)$  are shown by dashed lines in Fig. 1 where numerical results, given as filled circles, were obtained for a much larger  $s_{\max}$  and can be treated as “exact” in the present context. The case  $T = 0$ , for nonspecial  $h$ , would correspond to a piecewise constant structure of  $A$ , similar to the one for Glauber dynamics [13,15] but with different constants:  $A = 1$  for  $h > 1$ ,  $A = 1/4$  for  $1 > h > 1/4$  ( $h \neq 1/2$ ),  $A = 1/16$  for  $1/4 > h > 1/6$ , etc. (These numbers can be deduced from the lowest energy path—see below—serving as a checkpoint for more elaborate expressions). This limit, however, becomes apparent only at a very low temperature,  $z = 10^{-7}$ . At  $h = 1, 1/2$ , etc., the limit is singular, though finite, reflecting the peaks.

For a larger cutoff, simplifications of analytics can be achieved due to the dominant contribution of low-energy configurations. Among all classes  $k$  of clusters with the same  $s(k)$ , one can select only those which have a sufficiently large number of bonds:  $b_s(k) \geq b_{\max,s(k)} - r$ , where  $b_{\max,s}$  is the number of bonds in the most compact cluster for a given  $s$ . An integer parameter  $r$  indicates how close a cluster should be to the most compact configuration in order to be included in the kinetics. For sufficiently large  $r$  ( $r = 4$  for  $s_{\max} = 9$ ) all configurations are recovered. Alternatively,  $r = 0$  corresponds to the lowest energy path description, which is the closest to the kinetic part of the conventional one-dimensional random walk approach to nucleation [4], although with microscopic rather than phenomenological coefficients. In addition, branching of paths is added starting from  $s = 7$ . Already in the  $r = 0$  approximation, peaks at integer  $1/2h$  will appear in

$$T(y) = 8 + 63y^2,$$

$$T_1(y) = 4 + 29y^2 + 79y^4 + 126y^6,$$

$$T_2(y) = -208 - 1432y^2 + 3461y^4 + 49855y^6 + 89649y^8 + 87318y^{10}, \quad (10)$$

$$T_3(y) = 89152 - 297840y^2 - 13174644y^4 - 62801445y^6 + 146767614y^8 + 1284356493y^{10} + 957680010y^{12} + 556604622y^{14}.$$

The approximation works accurately in the vicinity of  $h = 1/4$ , describing the rather complex near- and off-peak behavior—see Fig. 2. The coefficient of  $z^{-5/2}$  in Eq. (9), multiplied, respectively, by  $y^3$  at  $h > 1/4$  or by  $y^7$  at  $h < 1/4$ , determines the scaling structure of the peak in the limit  $T \rightarrow 0$ , if the difference  $h - 1/4$  scales together with temperature. The structure of the neighboring peak at  $h = 1/2$  ( $n = 1$ ) follows the 4-particle approximation, Eq. (6), with  $\delta = y/z$  and  $z \rightarrow 0$ .

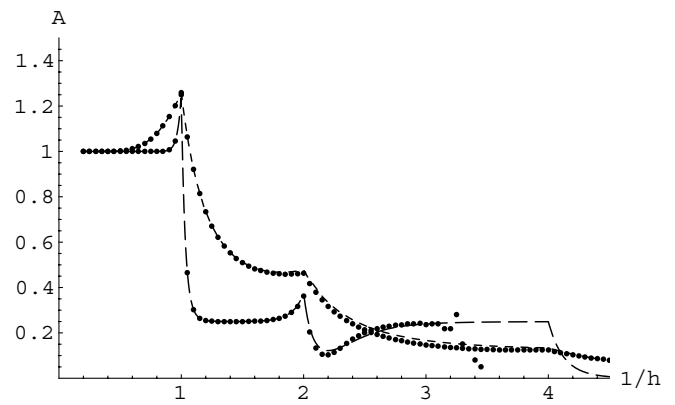


FIG. 1. The preexponential of the metastable-state lifetime. Lines: the 4-particle approximation, Eq. (6), at a higher temperature,  $z = 10^{-1}$  (short dashed line) and at a low temperature,  $z = 10^{-7}$  (long dashed line). Points: numerical results for  $s_{\max} = 9$  and  $r = 2$ .

the preexponential, although one needs to include  $r \geq 1$  for correct evaluation of their heights.

For the case  $r = 1$  and  $z \ll 1$  the preexponential  $A(h)$  can be described analytically in restricted domains of fields, the most interesting being those near the peaks [general expressions for  $A(h)$  are also available, but are useless due to their size].

Introducing a *finite* combination

$$y = \delta z^{1/n} \quad (8)$$

with  $n = 1, 2, \dots$  determining a corresponding peak, one can perform analytical expansions of  $1/I$  in fractional powers of  $z$ . Symbolic computations with MATHEMATICA were used here.

For  $n = 2$ , one obtains

$$\tau_9 = \frac{1}{z^{5/2}} \frac{T_1(y)}{8y^7 T(y)} - \frac{1}{z^2} \frac{T_2(y)}{16y^8 T^2(y)} + \frac{1}{z^{3/2}} \frac{T_3(y)}{672y^9 T^3(y)} + \dots \quad (9)$$

with the coefficients in this  $s_{\max} = 9$  approximation given by

An important question is sensitivity of the results to variations in  $r$  and  $s_{\max}$ . A smaller  $r = 0$  will give identical values of the leading term in the preexponential in the limits  $y \rightarrow \infty$  or  $y \rightarrow 0$  (i.e., on both sides of the peak for  $T \rightarrow 0$ ), slightly overestimating the height of the peak at  $y = 1$ . Cases with larger  $r \geq 2$  presently could be studied only numerically and are shown by symbols in Fig. 2. At small  $h$ , scatter appears in the data, indicating the limits of

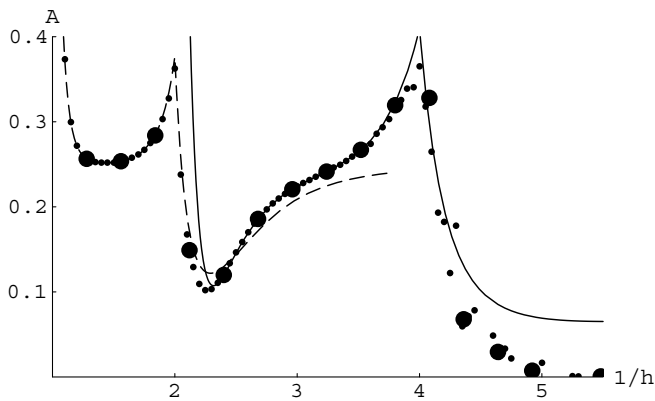


FIG. 2. “Fine structure” of the two peaks near  $h = 1/2$  and  $h = 1/4$  for  $z = 10^{-5}$ . Solid line: the 9-particle approximation for  $r = 1$ , Eq. (9). Dashed line: the full 4-particle approximation, Eq. (6). Symbols: numerical data for  $s_{\max} = 9$  and  $r = 2$  (small circles) and  $r = 4$  (large circles).

numerical accuracy for very small  $z$ . There is no detectable difference with the analytical approximations in the regions of their validity for fields up to  $h \geq 1/4$ . A similar expansion in  $z$  for  $r = 1$  and  $s_{\max} = 8$  also was performed, leading to a rather different structure of the  $y$ -dependent polynomials. The first coefficients in the  $z$  expansion are nevertheless numerically close for stronger fields  $h \geq 1/4$  in the vicinity of the peak. So are the heights of the peak given, respectively, by  $0.4167 - 2.92z^{1/2} + \dots$  and  $0.4190 - 2.83z^{1/2} + \dots$  in the 8- and 9-particle approximations. On the other hand, unlike the 9-particle case,  $s_{\max} = 8$  does not yield a proper  $T \rightarrow 0$  limit for weaker fields  $h < 1/4$  since the boundary here is too close to the critical size  $s_* = 7$ .

In summary, for a moderate field (supersaturation) the metastable-state lifetime of a supersaturated lattice gas has been evaluated for  $T \ll T_c$ . The main result is the pre-exponential which, for the first time, was evaluated analytically beyond the zero-temperature limit, and which exhibits distinct peaks as a function of field. One can anticipate that similar peaks (which appear due to competition of several “critical sizes”) will also be observed in systems other than nearest-neighbor Ising models with nonconserved dynamics, whenever the nucleation barrier has a well-defined zero-temperature limit and the critical nucleus contains a reasonably small number of particles.

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