Modulation of the nucleation rate pre-exponential 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 pre-exponential 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 $T \to 0$, but become detectable and eventually dominate at higher temperatures.

In a general case, the nucleation-controlled lifetime of a metastable state can be written as

$$\tau = A \exp \left( \frac{W^*_c}{T} \right)$$

with $W^*_c$ being the minimal work (free energy change) to form a critical nucleus and the temperature $T$ measured in units of Boltzmann constant. The exponential term was anticipated already in the earliest estimations of the nucleation rate $I \sim 1/\tau$, which further found an enormous amount of applications in systems ranging from vapors to glass-forming or quantum liquids. The structure of the pre-exponential, $A$, however, is not known in a general case. The difficulty of its derivation, whether in an analytical, numerical or experimental study, stems from the dominant contribution of the exponential in eq. (1), with minor uncertainties in $W^*_c$ (say, due to inaccuracies in the measured interfacial tension) implying large, orders of magnitude, discrepancies in the values of $A$.

With this, much attention is devoted to models which can exhibit nucleation and which are close to exact solvability. Here one can obtain an accurate expression for $W^*_c$, subsequently focusing on the pre-factor issue.

One of the best known example is the two-dimensional nearest neighbor Ising model, where metastability is achieved by orienting initially all spins one way (down) while non-zero magnetic field $h$ prescribes an opposite (upward) orientation. Allowing spin flips of non-conserved or conserved type adds the required dynamics to the problem. In a closely related lattice gas model the role of $h$ is played by supersaturation.

The pre-exponential in such systems attracts much attention both for the high- and low-temperature regions. For $h \to 0$ the nucleus is macroscopic and its shape, as well as the value of $W^*_c$, can be obtained from the Wulff droplet construction. Monte Carlo simulations are possible for $W^*_c \lesssim 10 - 15 T$ which, for small $h$, restricts such studies to the aforementioned high-temperature region; transfer-matrix approaches also are available here. For larger fields a straightforward Wulff construction may be inadequate, but for $T \to 0$ analytical treatment becomes possible due to dominant contribution of low-energy configurations. Technique of absorbing Markov chains also can be used for simulations in the low-temperature region.

Neves and Schonmann evaluated $W^*_c$, the zero-temperature limit of $W^*_c$, obtaining the exponential part of the metastable lifetime. Their result is insensitive to specifics of the dynamics. Novotny further showed that for discrete-time dynamics and a relatively large field, the pre-exponential remains finite in the limit $T \to 0$, approaching a piece-wise constant function of $h$, pointing towards a discontinuity at an integer value of the inverse field. Similar features will be observed at weaker fields as well. Integer values of inverse field, 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 $T > 0$.

The present Letter aims to evaluate the pre-exponential 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 $W^*_c$, will provide predictive expressions for $\tau(T, h)$ at $T > 0$. We will show that in contrast to intuitive expectation of discontinuities spreading out in a standard, $tanh$-like fashion, they are replaced by sharp peaks which persist, with finite heights and self-similar shapes, up to $T = 0$.

A lattice gas model with continuous time dynamics will be considered. Specifically, the probability of creation of a particle on an empty site 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. Alternatively, the annihilation probabilities are proportional to $dt \exp(-\Delta E/T)$, with $\Delta E$ being the energy change due to broken bonds and field (“supersaturation”) which increases the energy by $2h$ when a particle is removed. This model, with various generalizations, is popular, e.g. in Monte Carlo simulations of the dynamic interface in crystallization problems - see, e.g. and references therein. It is expected that qualitatively the model also remains similar to the discrete-time Glauber type dynamics of Refs. (and the generalized Becker-Döring approach employed below bears certain parallels with the technique of absorbing Markovs chains), although the dynamics-sensitive pre-
exponentials will not be identical even at $T = 0$.

For a long time of the order of $\tau$ the rare particles will form isolated clusters of various sizes and shapes \((\text{classes})\), 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 numbers of particles, \(s(i)\), the number of bonds \(b(i)\) and the statistical weight \(w_i \leq S\). One can define the (quasi) equilibrium distribution
\[
f_i^{eq} = w_i z^{2s(i) - b(i) \delta s(i)}
\]
with $z = e^{-\varphi/T}$ and $\delta = z^{-2h}$ describing the temperature and field dependencies, respectively. $\varphi$ is the bond energy, subsequently taken as 1 for simplicity of notations. In the \(s, b\) space the function $f_i^{eq}$ has a saddle point (for non-special fields - a single one \([\text{13}]\)) 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 \([\text{19}]\) for smaller $s$.

Once equilibrium properties are specified, one can introduce kinetic fluxes as a multidimensional version of the classical approach \([\text{1}]\), since in a low-temperature Ising system growth or decay of a cluster predominantly proceeds via random gain or loss of a single particle \([\text{20}]\). 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
\[
I_{ik} = \beta_{ik} f_i^{eq} (v_i - v_k), \ i < k
\]
with $v_i = f_i / f_i^{eq}$ and $v_0 = 1$. The Master Equation for the kinetic distributions $f_i$ takes the form
\[
\frac{df_i}{dt} = \sum_{k=0}^{i-1} I_{ki} - \sum_{k=1}^{k_{\max}+1} I_{ik}
\]
which automatically satisfies detailed balance.

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

Due to an exponentially long lifetime, one can neglect the depletion of empty sites (for which, otherwise, an integral conservation law \([\text{21}]\) should be employed instead of $v_0 \equiv 1$). With this, eqs. (3), (4) can be solved in the steady-state approximation; transient effects \([\text{22}]\) also can be neglected here.

Introducing $b_{ik} = \beta_{ik} f_i^{eq} + \beta_{ki} f_k^{eq}$ \((0 \leq i, k \leq k_{\max} + 1)\) and
\[
M_{ik} = b_{ik} - \delta_{ik} \sum_{l=0}^{k_{\max}+1} b_{il}, \ 1 \leq i, k \leq k_{\max}
\]
one can show that the steady-state distributions \((v_1, v_2, \ldots)\) 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
\[
I = (\hat{M}^{-1})_{11} + 1
\]

For a single nucleation path, which leads to a tridiagonal structure of the matrix $\hat{M}$, one recovers the classical result by Farkas \([\text{1}]\) $I^{-1} = b_{01} + b_{12} + \ldots$. Otherwise, the actual evaluation of $I$ via eq. (3) is limited by one’s ability to obtain all classes and transition rates $\beta_{ik}$ for a sufficiently large $s_{\max}$, and the ability to inverse analytically a large matrix $\hat{M}$. At present, we were able to proceed up to $s_{\max} = 9$ (1818 classes representing a total of 13702 cluster configurations) which allows us to consider fields $h > 1/6$ with the critical number $s_* \leq 7$. A full exact expression for $\tau$ can be surveyed by a human eye only for more modest values of $s_{\max}$, which implies a relatively small critical cluster (larger fields).

For example, for $s_{\max} = 4$ kinetics is determined by 9 distinct classes with a total of 28 shapes (see, e.g. Fig. 2 in Ref.\([\text{4}]\)). Transition rates are easy to obtain (say, there are two ways a 3-particle "minus" shaped cluster can turn into 4-particle "T" shaped one, four ways it can turn into an "L" shaped one, etc.). The result which follows from eq. (3), is expressed as a rational function of $\tau$ and $\delta$
\[
\tau_4 = P(\delta, z) / Q(\delta, z)
\]
with the subscript indicating the value of $s_{\max}$, and polynomials $P$ and $Q$ given by
\[
P(\delta, z) = 384 + 210000 \delta^2 z^9 + 16 \delta (48 + 185 z) + 45^2 z (1576 + 2655 z) + 86^2 z^2 (3081 + 3230 z) + 2500 \delta^2 z^7 (21 + 250 z + 36 z^2) + 2505^2 z^6 (695 + 2650 z + 1036 z^2) + 54^2 z^3 (65740 + 57797 z + 15360 z^2) + 56^2 z^2 (28574 + 28155 z + 19680 z^2) + 56^2 z (43375 + 70546 z + 50000 z^2)
\]
\[
Q(\delta, z) = 84^2 z^4 (384 + 80 (24 + 85 \delta) z + 2505^2 (25 + 64 \delta) z^3 + 1250 \delta (259 + 625 \delta) z^4 + 20 \delta (615 + 1753 \delta) z^5 + 3750 \delta^2 (3 + 7 \delta) z^6)
\]
Eq. (7) is expected to be accurate in strong fields, $h \gtrsim 1/2$, 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 \([\text{23}]\)). More consistently, this result should be treated asymptotically for $z \to 0$ and $\delta \to \infty$ with certain combinations of powers of $z$ and $\delta$ remaining finite, depending on the interval of field.

In order to isolate the pre-exponential, eq. (3) should be multiplied by $\exp(-W_\star / T) = z^{W_{\star}}$. 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, $W_0$, 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 piece-wise linear structure, and $\exp(-W_*/T)$ is reduced to a product of integer powers of $z$ and $\delta$: 1 for $h \geq 1$, $z^\delta$ for $1/2 \leq h < 1$, $z^4\delta^3$ for $1/4 \leq h < 1/2$, etc. The resulting $A(h)$ is shown by a dashed line in Fig. 1, where numerical results, given as filled circles, were obtained for a much larger $s_{\text{max}}$ and can be treated as "exact" in the present context. The case $T = 0$ would correspond to a piece-wise constant structure of $A$, similar to Ref. [1] but with different constants and an additional "excluded singularity" at $h = 1/2$: $A = 1$ 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 more elaborate expressions). This limit, however, becomes apparent only at a very low temperature, $z = 10^{-7}$.

For a larger cut-off, 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: $b_k(k) \geq b_{\text{max},s(k)} - r$, where $b_{\text{max},s}$ 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 $s_{\text{max}} = 9$) 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 [2], 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 the pre-exponential, although one needs to include $r \geq 1$ for correct evaluation of their heights.

For the case $r = 1$ and $z \ll 1$ the pre-exponential $A(h)$ 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

$$y = \delta z^{1/n}$$

with $n = 1, 2, \ldots$ 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

$$\tau_9 = \frac{1}{z^{5/2}} \frac{T_1(y)}{8y^2 T(y)} - \frac{1}{z^2} \frac{T_2(y)}{16y^3 T^2(y)} + \frac{1}{z^{3/2}} \frac{T_3(y)}{672y^4 T^3(y)} + \ldots$$

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

$$T_1(y) = 8 + 63y^2$$
$$T_2(y) = 4 + 29y^2 + 79y^4 + 126y^6$$
$$T_3(y) = -208 - 1432y^2 + 3461y^4 + 49855y^6 + 89649y^8 + 87318y^{10}$$
$$T_3(y) = 89152 - 297840y^2 - 13174644y^4 - 62801445y^6 + 146767614y^8 + 1284356493y^{10} + 957680010y^{12} + 55660422y^{14}$$

The approximation works accurately in the vicinity of $h = 1/4$, describing the rather complex near- and off-peak behavior - see Fig. 3. The coefficient of $z^{-5/2}$ in eq. (10) 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 $T \to 0$, 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 $z \to 0$.

An important question is the sensitivity of the results to variations in $r$ and $s_{\text{max}}$. A smaller $r = 0$ can reproduce the coefficient of $z^{-5/2}$ in eq. (10) in the limits $y \to \infty$ or $y \to 0$ (i.e. on both sides of the peak for $T \to 0$), but will not give the proper peak height for $y = 1$, or scaling for finite $y$, or the correct higher-order terms. 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 data, indicating the limits of 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 $h \gg 1/4$. An similar expansion in $z$ for $r = 1$ and $s_{\text{max}} = 8$ also was performed, leading to a 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 $0.4167 - 2.92z^{1/2} + \ldots$ and $0.4190 - 2.83z^{1/2} + \ldots$ in the 8- and 9-particle approximations. On the other hand, unlike the 9-particle case, $s_{\text{max}} = 8$ does not yield a proper $T \to 0$ limit for weaker fields $h < 1/4$ since the boundary here is too close to the critical size $s_9 = 7$.

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") also will be observed in systems other than nearest-neighbor Ising models with non-conserved 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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