Anomalous metastability in a temperature-driven transition

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Abstract – The Langer theory of metastability provides a description of the lifetime and properties of the metastable phase of the Ising model field-driven transition, describing the magnetic-field–driven transition in ferromagnets and the chemical-potential–driven transition of fluids. An immediate further step is to apply it to the study of a transition driven by the temperature, as the one exhibited by the two-dimensional Potts model. For this model, a study based on the analytical continuation of the free energy (Meunier J. L. and Morel A., Eur. Phys. J. B, 13 (2000) 341) predicts the anomalous vanishing of the metastable temperature range in the large-system-size limit, an issue that has been controversial since the eighties. By a GPU algorithm we compare the Monte Carlo dynamics with the theory. For temperatures close to the transition we obtain agreement and characterize the dependence on the system size, which is essentially different with respect to the Ising case. For smaller temperatures, we observe the onset of stationary states with non-Boltzmann statistics, not predicted by the theory.

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Metastability is ubiquitous in Nature and in technology \cite{1}. It is an important concept in many fields of physics \cite{2–4} and, in particular, in the context of the glass transition problem \cite{1,5,6}. It is also present in many biological systems, such as proteins \cite{7} or nucleic acids \cite{8} but, despite the relevance of the subject, there is no general theoretical framework allowing for the computation of the properties of the Metastable Phase (MP), e.g. its lifetime, provided the details of the microscopic interaction \cite{9}. On the other hand, understanding how finite-size effects can influence this peculiar regime is becoming more and more relevant with the increasing development of miniaturization processes and of nano- and bio-sciences \cite{10–12}.

Beyond the mean-field approximation, metastable states correspond to local free-energy saddle points in phase space, irrelevant with respect to the stable state, and standard methods of statistical physics are not able to capture their properties \cite{9}. The main theoretical tools to tackle them are based on restricted ensembles \cite{13–16}, which exclude inhomogeneous configurations from the partition function. Of particular relevance is the study by Langer \cite{17,18}, based on Fisher’s droplet theory \cite{19}, which describes the condensation of the Ising/Lattice Gas Model (ILGM) as an ensemble of non-interacting condensed droplets. Within Fisher’s theory, MPs cannot be obtained as a continuation of the stable phase properties beyond the condensation point \cite{9}. Langer showed, however, that they can indeed be described by the analytical continuation of the free energy $f$ in the unstable phase, $\tilde{f}$, its real part $\text{Re} \tilde{f}$ resulting in the free energy of the MP, that in Fisher theory is realized restricting the ensemble of clusters to those smaller than the critical cluster. Moreover, $\text{Im} \tilde{f}$ is proportional to the nucleation rate, $I$, for a wide class of model dynamics \cite{20}. Such an approach allows for the computation of $I(h,T)$ as a function of the under-critical temperature $T$ and of the field $h > 0$, corresponding to the MP with negative magnetization \cite{17,18,20–22}. The Langer description of the ILGM has been compared with dynamical methods \cite{2}, in which the MP is characterized by the stationarity of observables under a Markov-Chain Monte Carlo local dynamical update \cite{23–26}. In this way, a general agreement between theory and dynamics is found in 2D, 3D. Finite-size effects
are also well understood in the ILGM \cite{24}, and absent when the system linear size $L$ is much larger than the length scales involved in the nucleation process. While the relationship between $\text{Im } f$ and $I$ has been proved for several systems, its general applicability is not known \cite{2}.

The analytical continuation of $f$ à la Langer has been computed for the order-disorder, $T$-driven transition of the $q$-color Potts model in 2D \cite{27}. This study predicts an anomalous vanishing of the metastable temperature interval for increasing size. In the present work we employ a Graphics Processing Unit (GPU) algorithm for testing the analytical predictions in a dynamical setup, and to determine the range of validity of the theory. The Potts model \cite{28} has had for a long time a strong role in the modelization of disordered and soft matter \cite{29,30}, and absent also well understood in the ILGM \cite{24}, and absent from pseudo-critical approaches, which find critical

existence of a metastable temperature interval results as attempts \cite{37–39}, indicating the existence of a metastable interval for large sizes, and those based on stability conditions of the MP \cite{27}, or on dynamics \cite{40,41}. Secondly, the metastable dynamics at $\delta \beta > 0$ has also been studied in \cite{41}, where an anomalous finite-size behavior shrinks to zero in the large-$N$ limit \cite{27}. In other words, no metastability is found to exist for $N \rightarrow \infty$.

In agreement with the results of \cite{27}, a shrinking of the metastable interval for large $N$ is also found in \cite{40} by means of Monte Carlo dynamics in the MP at small $\delta \beta > 0$. The metastable dynamics at $\delta \beta > 0$ has also been studied in \cite{41}, where an anomalous finite-size behavior has been pointed out.

There are several questions to be clarified. First, the apparent disagreement between the results of pseudo-critical attempts \cite{37–39}, indicating the existence of a metastable interval for large sizes, and those based on stability conditions of the MP \cite{27}, or on dynamics \cite{40,41}. Secondly, to what extent the results of ref. \cite{27} coincide with those of a dynamic sampling for $\delta \beta > 0$ \cite{27,40,41}. Finally, the microscopic origin of the shrinking of the metastable interval for large sizes, which is absent in the ILGM paradigm.

In this letter we perform a comparison (the first one, to our knowledge) between the results from the DT and the dynamical averages under a local Monte Carlo updating rule. We report evidence that the dynamical metastable temperature interval shrinks with the system size also for large sizes, in agreement with the DT, approximately

\begin{equation}
\phi(z) = \int_0^\infty \frac{dz}{\sqrt{2}} e^{-z} \left(e^{-z^{3/2}} - 1 - z^{3/2}\right).
\end{equation}
as $\sim N^{-1/3}$. A devoted GPU parallel algorithm has been developed for the efficient simulation of large sizes ($L \sim 1024$), and a method has been devised, based on the stationarity of the Monte Carlo sequence of configurations, allowing for an accurate comparison with the DT of ref. [27].

Let us describe our method. The $q$-Potts model [28] is defined on a configuration of $q = 12$, for which $\delta\beta$ requires to be of the order of its fluctuations in $P$ "stationary ensemble" to be compared with the restricted Markov chains which generate $\tau$-processes for moderate values of $q$, since $\delta\beta > \delta\beta^*$, the agreement between theory and numerics is good. We attribute the progressive discrepancy for large $|\epsilon|$'s to a statistical underestimation for low probabilities and to a different finite-size effect, presumably a consequence of the continuum description of eq. (1). On the other hand, for $\delta\beta > \delta\beta^*$ the difference between theory and numerics becomes essential: while the theory predicts the absence of metastability (no convex $P_{\delta\beta,N}$), we nevertheless still observe stationary states with convex EPD. Moreover, as illustrated in the inset, the EPD curves for different values of $\delta\beta > \delta\beta^*$ are not derivable one from the other by re-weighting (as they do for $\delta\beta < \delta\beta^*$, see eq. (2)). This is an evidence that these stationary states do not obey Maxwell-Boltzmann statistics. An interesting question is whether the lifetime of these non-equilibrium stationary states at $\delta\beta > \delta\beta^*$ remains finite in the large-$N$ limit. This point will be discussed below.

At the pseudo-spinodal point $\delta\beta^*(N)$, the slope of the theoretical EPD vanishes at $\epsilon^*(N)$. We have estimated this point by extrapolating in $\delta\beta$ our data for $(\partial \ln P_{\epsilon^*})_{\delta\beta,N}$ down to zero, obtaining values of $\delta\beta^*(N)$ in reasonable agreement with those of the DT, the better the larger the size (see fig. 3). The data approximately exhibit the size dependence $\delta\beta^*(N) = C + DN^{-1/3}$, with a small $C$. The $\delta\beta^* \sim N^{-1/3}$ scaling is compatible with the DT, as we find $\delta\beta^* < 0$ in the saddle-point approximation [27,43]. The numerical results for $\delta\beta < \delta\beta^*$ are, hence, compatible with the DT picture, which predicts the absence of equilibrium metastability for large $N$. 

![Fig. 1](image-url)
A direct comparison with the theory is possible also for the lifetime $\tau(\delta \beta, N)$. We assume that the lifetime of the MP is the time needed to create a fluctuation with energy lower than the limit of stability $\epsilon_m(\delta \beta, N)$, i.e., $\tau/\tau_i \sim P_{\delta \beta, N}(\epsilon_m(\delta \beta, N))^{-1}$. $\tau$ is to be measured in units of the self-correlation time $\tau_i$, since the probability of a critical configuration is inversely proportional to the average number of uncorrelated configurations before leaving the plateau. By using $P_{\delta \beta, N}(\epsilon_m)$ from the solution of eq. (2) (and neglecting the $\delta \beta$-dependence of $\tau_i$) we have estimated the $\beta$-dependence of $\tau$, which agrees with our numerical results in the DT validity region $\delta \beta < \delta \beta^*(N)$. The comparison is illustrated in fig. 2, in which we also report the expression for $\tau$, that we have obtained in the saddle-point approximation to eq. (2) for $\delta \beta \searrow 0$ [43]:

$$\ln \tau(\delta \beta, N) \sim p \ln \frac{2w_{\delta \beta} + 4w_{\delta \beta}^3}{27} \frac{1}{\delta \beta^2} + K_N,$$  

with $p = 7$, and $K_N$ being a decreasing function of the system size, not dependent on $\delta \beta$. Our numerical data for $\tau$ systematically decrease with $N$ at fixed temperatures, in agreement with the DT. Interestingly, assuming $\tau \sim I^{-1}$ with $I$ given by the Langer relation $I \sim \text{Im} \phi(z \nearrow 0)$, leads alternatively to the same law, eq. (3), with $p = 5$ (see fig. 2), although this simpler approach does not provide information about $K_N$.

From our data for $\tau$ we estimate the dynamical temperature $\delta \beta_I(N,t)$ at which the average lifetime is $t$. Remarkably, also our results for $\delta \beta_I$ present a clear scaling:

$$\delta \beta_I(N,t) = C_I N^{-1/3} + D_I t$$

with non-zero $D_I$ (see fig. 3). We define in this way a temperature endpoint of the stationary phase, defined by the temperature at which $\tau$ becomes small. By choosing $t_{\text{min}} = 6 \cdot 10^3$ Monte Carlo steps, we obtain a threshold, $\delta \beta_{\nu}(N,t_{\text{min}})$, below which stationary states are no longer observable in practice. Equation (4) suggests that in the large-$N$ limit there may be a non-zero temperature interval $[\beta_c, \beta_c + D_{\text{min}}]$ in which the non-Boltzmann stationary states indeed survive with a non-zero lifetime.

Our findings are summarized in fig. 3. For $\delta \beta < \delta \beta^*(N)$ the local dynamics leads to Boltzmann DT-describable metastable states. On the other hand, for sufficiently low $\delta \beta > \delta \beta^*$, we expect stationary states with non-Boltzmann statistics. Finally, for $\delta \beta \geq \delta \beta_{\nu}(N,t_{\text{min}})$, no stationary states, just off-equilibrium relaxation towards the ordered phase is observed.

The shrinking of the metastable interval may not be in contradiction with the results of the aforementioned pseudo-critical studies: the limit $\beta_c$, where $\tau_i$ is supposed to diverge, cannot be reached in a dynamical scheme, in which metastability is supposed to end at a smaller $\beta$ when $\tau_i$ becomes of the order of $\tau$. The hypothesis $\tau(\delta \beta^*, N) \sim \tau_i(\delta \beta^*, N)$ is indeed compatible with the decrease of $\delta \beta^*(N)$ since, as $N$ increases, $\tau$ decreases and $\tau_i$ anomalously increases [43]. This dynamical role of $\delta \beta^*$ seems to be compatible with our data, as we anticipate in fig. 2 and will discuss further elsewhere.

An important point concerns the microscopic origin of the observed different behaviors, which remains unknown. In [41] it is conjectured that the canonical spinodal point is associated to the evaporation-condensation transition [44,45], a finite-size effect occurring at coexistence in the micro-canonical ensemble, and that has been observed for the Potts model in 2D (the micro-canonical endpoint of the stable energy branch is again at a value $\delta \beta \sim N^{-1/3}$) [41,46–48] and 3D [49]. The authors of [41] also conjecture the existence of a length scale $\ell$ (suggested to be the typical distance between critical droplets, $R_0$)
such that the condition $N \sim \ell^2$ would trigger a crossover between different dynamical regimes (see also [49]). In any case, in the so-called deterministic region, $N \gg R_0^2$, finite-size effects should disappear, as happens in the ILGM [24]. The decrease of $\tau$ with $N$ for arbitrarily large $N$ is essentially different with respect to the ILGM paradigm, and implies a size-dependent nucleation rate. While the bulk term in $\ln \Xi_0$ of the ILGM is size independent, in the Potts model case it may come from an entropy-maximizing constraint, such that clusters of a given color are confined to avoid the breaking of the symmetry between colors. In larger systems, clusters would be less confined since they contribute less to the magnetization [40].

The DT cannot validate this idea since it is obtained from an infinite-volume free energy, eq. (1), not allowing for a microscopic formulation in terms of droplets. We are investigating an alternative scheme by estimating the form of the size-dependent droplet free-energy $\ln \Xi_{a,N}$ [43]. The dependence of the results on the lattice geometry, algorithm dynamics and $q$ value are also being examined.

Summing up, we have provided a picture of the metastable dynamics of the 2D Potts model. The MPs present a strong finite-size scaling, well described by the DT. Such an anomalous finite-size scaling, whose microscopic origin is not known, is different from the ILGM case, and might be found in other first-order transitions.

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