Evidence for sharper than expected transition between metastable and unstable states

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Abstract

In mean-field theory, i.e. infinite-range interactions, the transition between metastable and unstable states of a thermodynamic system is sharp. The metastable and the unstable states are separated by a spinodal curve. For systems with short-range interaction the transition between metastable and unstable states has been thought of as gradual. We show evidence, that one can define a sharp border between the two regions. We have analysed the lifetimes of states by considering the relaxation trajectories following a quench. The average lifetimes, as a function of the quench depth into the two-phase region, shows a very sharp drop defining a limit of stability for metastable states. Using the limit of stability we define a line similar to a spinodal in the two-phase region.

1 Introduction

Metastability has traditionally been studied by looking for droplets [1, 2]. In this framework density fluctuations are produced from the initially homogeneous matrix following a sudden quench from a stable equilibrium state to a state underneath the coexistence curve. After a time-lag a quasi-equilibrium is established and a size distribution for the fluctuations (droplets) develops, yielding droplets up to a critical size [3, 4, 5].

Behind this approach to metastability is a geometric interpretation, fostered by experimental observations of droplets [6]. The experimentally observed droplets are, however, in size much larger than the critical droplets so that the evidence for nucleation is indirect [7]. Also in computer simulations one can follow the development of the droplet [8]. Close to the coexistence curve the droplet picture seems to hold to a good degree [9], while deeper into the two-phase region considerable doubt has been raised as to the validity of the nucleation theory [10].

To take the point of view of density fluctuations [11] is by no means the only possible. Here we want to follow a different point of view. What we want to consider are the fluctuations of a macroscopically available observable and the ensemble of these fluctuations [13]. To be specific and to link to the simulation results that we present below, consider a non-conserved order parameter. We start out from a given equilibrium state and suddenly bring the system into a non-equilibrium state underneath the coexistence curve. The order parameter will follow this change. Again, after some time–lag the order parameter will fluctuate around some quasi-equilibrium value and suddenly change to the stable equilibrium state. We now consider the ensemble of such trajectories of the order-parameter. We avoid to take an average of the order-parameter in the non-equilibrium situation so as not wash out any of the abrupt changes that take place while the system seeks its way out of the quasi-equilibrium state into the stable equilibrium state. For each of the trajectories we define a lifetime and consider the distribution of the lifetimes and also consider the average lifetime! We show below that the average lifetime dramatically decreases at particular values depending on the imposed parameters giving rise to a possible dynamic definition of a spinodal.

So far the existence of a spinodal in the sense of a line of second order phase transition inside the two-phase region has been denied for systems with short range interactions. Only for systems with infinite range interaction (mean field theory) this concept has been thought to make sense [2]. The concept is based on the existence of a free energy and is purely static. Here we side step this and look at metastability in a dynamical way and find a clear distinction between metastable and unstable states.

2 Methodology

The trajectories discussed above can be obtained naturally using the Ising model together with the Monte Carlo Method [14, 15, 16]. The Monte Carlo method defines the transition probabilities between states starting from an initial state.

The Hamiltonian of the Ising model for a simple cubic lattice L^3 is defined by the

$$\mathcal{H}_{\text{Ising}}(s) = -J \sum_{<ij>} s_i s_j \quad + h \sum_i s_i, \qquad s_i = \pm 1 \tag{1}$$

where $\langle ij \rangle$ are nearest-neighbour pairs of lattice sites. The exchange coupling J is restricted in our case to be positive (ferromagnetic). s_i is called a spin and the sum over all lattice sites is the magnetization M (we define m to be the magnetization per spin). h is a dimensionless magnetic field.

The dynamics of the system is specified by the transition probabilities of a Markov chain that establishes a path through the available phase space. Here we use a Monte Carlo algorithm [14, 15, 16] to generate Markov Chains. We used the Metropolis transition probabilities

$$P(s_i \to s_i') = \min\{1, \exp(-\Delta\mathcal{H})\} \quad . \tag{2}$$

Time t in this context is measured in Monte Carlo steps per spin. One Monte Carlo step (MCS) per lattice site, i.e. one sweep through the entire lattice, comprises one time unit. Neither magnetization nor energy are preserved in the model which makes possible to compute both quantities as a function of temperature, applied field and time.

Typically we started the simulation runs with a magnetization of -1, i.e. in equilibrium and a predefined starting point for the random numbers for the Monte Carlo process. We then turn on the temperature and the applied field. This brings us instantly below the coexistence curve into the two-phase region. Due to the transitions induced by the Metropolis transition probabilities the magnetization (and the energy as well) develops in time and yields a trajectory of magnetization (energy) values

$$m(0), m(1), ..., m(n) \quad . \tag{3}$$

The magnetization was traced to a specific number of Monte Carlo steps. After the prescribed number of steps were reached, the system was brought back to the magnetization -1 and a new quench performed with a new and different starting point for the random numbers. The statistics was gathered over these trajectories and quenches with each trajectory kept on file.

3 Relaxation paths and their statistics

Let us for the moment fix the temperature ($T = 0.59$) and analyse the distribution of lifetimes. Figure 1 shows a typical relaxation path. After fluctuating around some value the magnetization drops sharply. At this point we say that the lifetime of the quasi-stable state has been reached. After the sharp drop the magnetization reached quickly its value in equilibrium on the other side of the phase diagram.

For every quench depth, i.e., applied magnetic field, we can compile a statistics on the lifetimes. This is shown in Figure 2. Plotted there is the probability for the occurrence of a specific lifetime as a function of the quench depth. Note first that the distribution of lifetimes gets narrower as we quench deeper into the two-phase region. Closer to the coexistence curve, i.e. for shallow quenched, the average lifetime increases but the width of the distribution broadens. This is of particular interest for experiments. There we also should expect a huge variety of lifetimes after a quench making it difficult to interpret the data. Even a quench close to the coexistence curve can lead to a very short lifetime and thus to an interpretation that the state may have been unstable. In passing we note that the distribution is not Poissonian.

We can plot the average lifetime, at fixed temperature and plot this as a function of the quench depth. This is shown in Figure 3. While the average lifetime of the states close to the coexistence curve must be very large, we expect the lifetime to drop as we quench deeper into the two-phase region. The plot shows that the average lifetime decreases rapidly at some "critical quench depth". The inset in Figure 3 shows that the average lifetime decreases exponentially fast close to that field and then saturates. This saturation depends on the precise nature of the Monte Carlo move but must always be present since it always takes a minimum number of steps to proceed from one state to another.

Clearly, the location of the "limit of stability"-line depends on the kind of Monte Carlo moves that we implement. But, the line will always be present for all local move algorithms. For all natural systems we expect this result to carry over. Indeed for a pure CO_2-system a similar result has been seen [17]. There the stability line for states in the two-region was also much closer to the coexistence curve then expected.

4 Finite-Size Effects

Figure 4 shows the finite-size effects for the average lifetime. We have performed simulations with the linear system sizes of $L = 32$, $L = 42$ and $L = 96$ for the temperature $T/T_c = 0.58$. First we note that the *pseudo spinodal* shifts towards the coexistence with increasing system size. A simple extrapolation gives a 30% shift with respect to the $L = 32$ result. We further note the decrease in the average lifetime for those quench depths that extend beyond the *pseudo spinodal* point. Similar finite-size effects have also been seen by Novotny et. al. [18, 19].

The inset in Figure 4 shows the extrapolation of the value of the limit of stability to the infinite system size.

In Figure 5 we have compiled the results of our findings in a phase diagram. The new limit of stability is far away from the mean field spinodal curve.

5 Conclusions

Relaxation paths and their statistics yield a fresh outlook on metastability. Here the emphasis is on the dynamics of the single events and not on the average behaviour of the system. Our point of view is that averaging in the non-equilibrium situation can wash away or hide the phenomenon. Here we have shown that the statistics of the relaxation paths can lead to a sharp distinction between meta- and unstable states.

A surprising finding is that the distribution of the lifetime broadens significantly. Opposite to the intuition we found that close to coexistence curve the distribution is broad and very flat. Close to the limit of stability the distribution is very narrow and sharply peaked.

Clearly further work needs to be done, cementing the evidence for the sharp border, in the sense defined above. As pointed out above, simulations using different transition probabilities would be helpful to investigate the dependence of this dynamic phenomenon on the imposed dynamics, at least for those systems that do not have an intrinsic dynamics.

It would also be of interest to perform molecular dynamics simulations of systems using realistic interaction potential. There the question would also be how far the metastable region really extends and compare this to experimental evidence for nucleation or spinodal decomposition in the light of the relaxation trajectories.

It is also unclear at the moment how to extend the definition to systems with a conserved order parameter.

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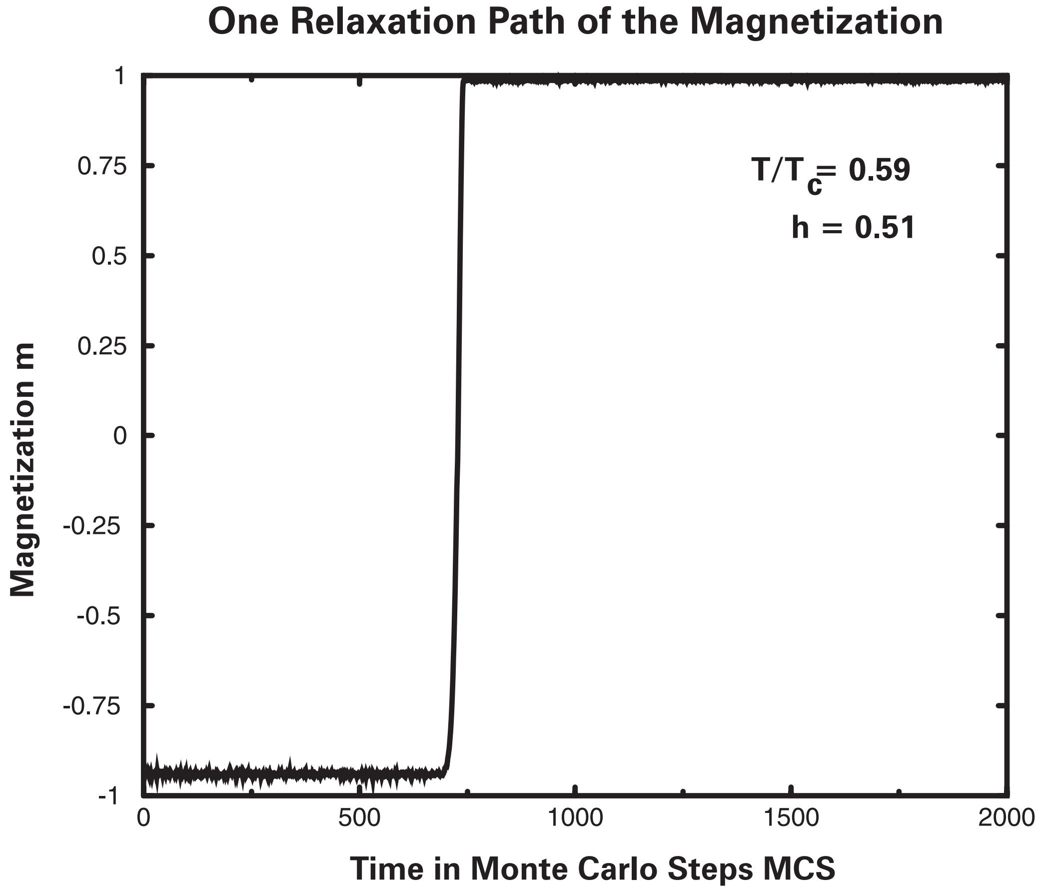

Figure 1: The figure shows one example of relaxation path. Here we display the magnetization as a function of time following the instant change in the applied magnetic field h opposite to the magnetization. The system suddenly leaves the quasi-stable state for the stable equilibrium state corresponding to the temperature and applied field.

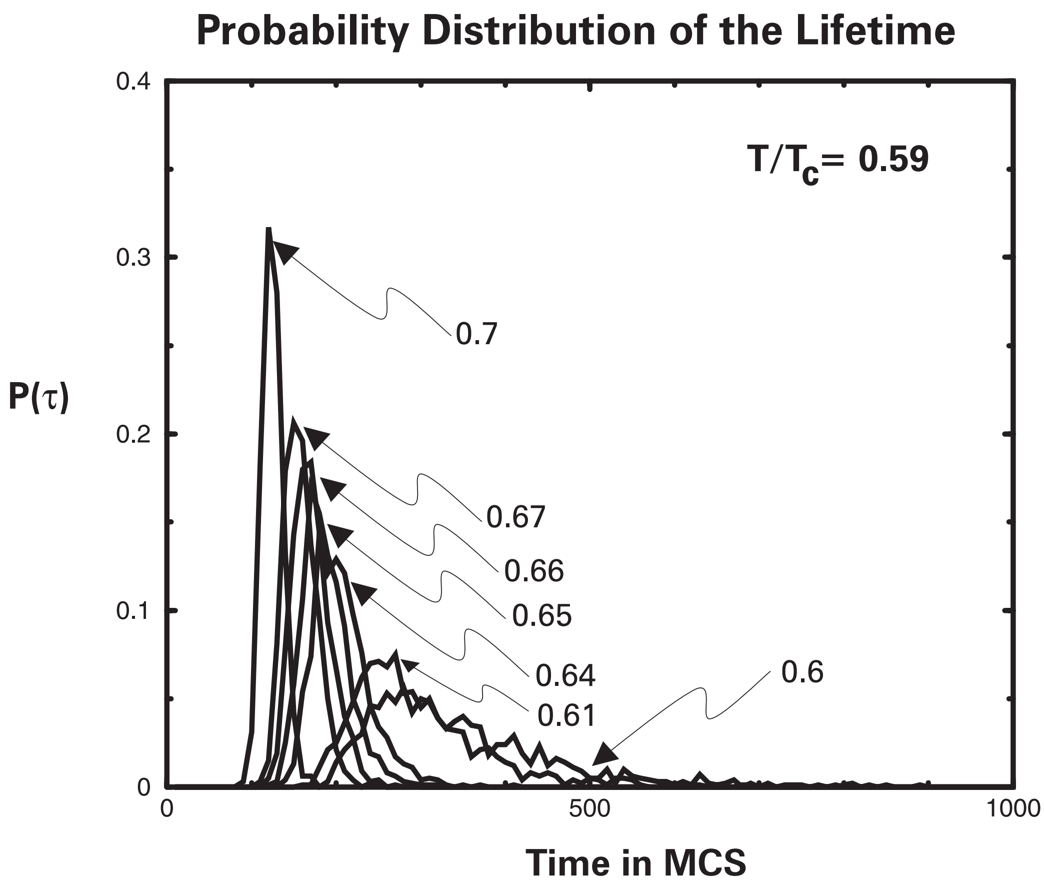

Figure 2: The figure shows the distribution of lifetimes for various applied fields, i.e. quench-depths. Note that the distribution widens and flattens out as we get closer to the coexistence curve (h=0). The distribution sharpens as the lifetime gets smaller, i.e. we quench deeper into the two-phase region!

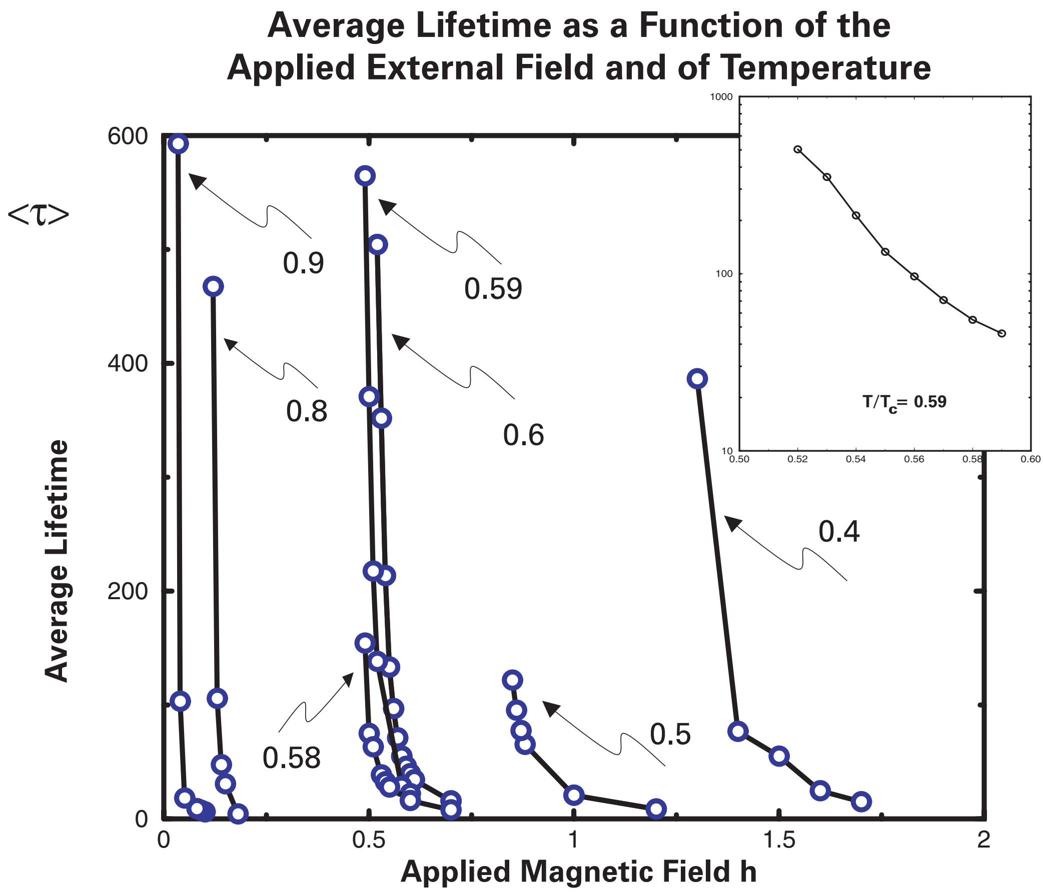

Figure 3: The average lifetime drops sharply as a function of the applied field, i.e. quench-depth. Shown are the results for various temperatures. The inset shows that the drop is exponential making it possible to define a reasonably sharp boundary between an an observable lifetime (metastable state) and those that are inherently unstable.

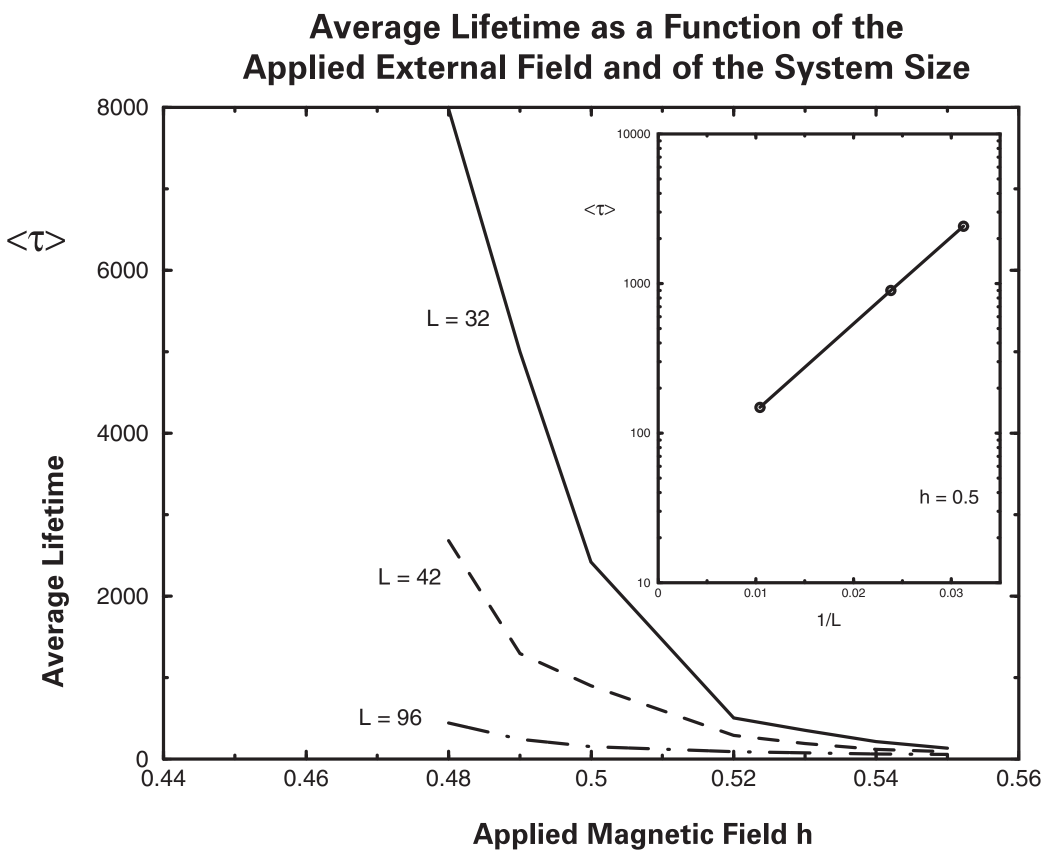

Figure 4: Finite-size effect for the average lifetime. Shown are the results for the linear system sizes $L = 32$, $L = 42$ and $L = 96$ at the temperature $T/T_c = 0.58$. The finite-size effect shows that the pseudo-spinodal will shift closer to the coexistence curve.

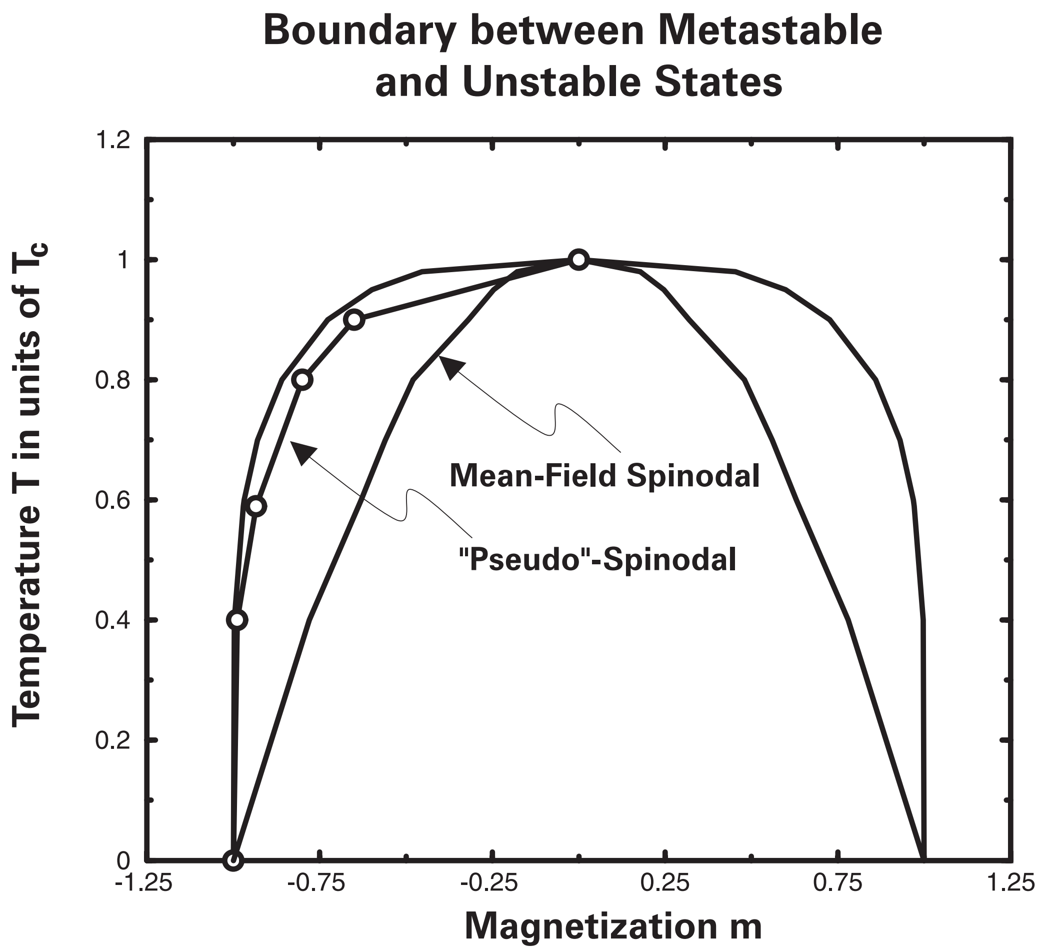

Figure 5: The figure shows the resulting phase diagram. The phase diagram includes the well-known coexistence curve and the mean spinodal curve. The transition line between metastable and unstable states (pseudo spinodal) is marked by the open circles. Note that the metastable region is extremely small.