Philosophical Magazine

Ordering dynamics in the presence of multiple phases

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Online publication date: 04 December 2010

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The dynamics of the 2D Potts ferromagnet, when quenched below the transition temperature, is investigated in the case of a discontinuous phase transition. This is useful for understanding the non-equilibrium dynamics of systems with many competing equivalent low-temperature phases, which appears not to have been explored much. After briefly reviewing some recent findings, we focus on the numerical study of quenches just below the transition temperature on square lattices. We show that, up to a certain time, metastable states can be observed, for which energy stays constant above the equilibrium energy and the self-correlation function displays a fast decay.

Keywords: phase transition; lattice dynamics; metastability; non-equilibrium phenomena

1. Introduction

The way in which thermodynamical systems attain equilibrium when driven through a phase transition has been the subject of much work [1–4]. In fact, while equilibrium generally requires an infinite time to be reached, different dynamical regimes can be observed, which often present peculiar properties (different kinds of dynamic scaling, critical slowing-down, spatial self-affinity, etc.) depending on the thermal history and the system. The dynamics of different phase transitions have been widely investigated, e.g. from a disordered to an ordered phase, or between two ordered phases. Among the model systems, the Ising model displays both instances: in zero magnetic field it undergoes a continuous phase transition from the high-temperature paramagnetic phase to the low-temperature ferromagnetic phase; the transition is discontinuous when at constant low temperature, and the external magnetic field is reversed. Both problems have been widely investigated. In the first case, one of the main results is contained in the Allen-Cahn law for the ordered phase domain growth at low temperature, which predicts a power law decay of the energy $\simeq t^{-1/k}$, with $k = 2, 3$ [1,2]. In terms of the second case, the metastability associated with the field-driven first-order phase transition has been studied with nucleation theory and its generalizations [3,4], which describe effectively the nucleation time and other features of the metastable states [4–7].

In contrast, not many results seem to be available for the ordering dynamics of systems possessing many equivalent ordered phases [1]. On one hand, the coarsening at low

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temperature presents peculiar properties not well described by the Allen-Cahn theory. This is predicted on a general bases by the Lifshitz criterion [8], according to which, a system possessing many equivalent ordered phases may equilibrate towards non-homogeneous phases when quenched below its critical point, if their number is larger than the real space dimensionality. Thus, equilibrium phases at low temperature may not be uniquely defined and systems may display complex behavior. On the other hand, unlike the Ising case, there exists little theoretical study of the metastability near the temperature-driven transition of the 2D q-Potts model (which is the first order for $q > 4$). A recent study [9] predicts in particular that, for this model, metastability is a finite size effect. The study is based on a droplet expansion and, to our knowledge, has not yet been related to the underlying dynamics [10] (metastability in the Potts model has been investigated with different aims in [11], and for the field-driven transition in [12]).

The aim of the present paper is to summarize some recent findings on the dynamics of the $d = 2$ Potts model [13] and to present some new results concerning metastability in the undercooled states just below the transition. Investigation of temperature-driven metastability in this model seems particularly important for several reasons: the model is interesting in itself, being an effective model for systems with many possible broken symmetries, and mimics the dynamics of a large variety of real systems, such as gas adsorption [13], froth [14], grain growth [15], and biological cell [16,17]. On the other hand, as mentioned before, the existence (or not) of metastable states associated with the temperature-driven first-order transition of the Potts model, is an old problem, first proposed by Binder [10], and which still remains open.

The next section briefly recalls the Potts model and presents a brief review of some recent findings on its dynamics on the square lattice in different temperature regions below the transition temperature. After introducing some elementary notions about metastable states in thermodynamical systems and a brief discussion on some recent findings concerning the metastable states of the Potts model, Section 3 points out the presence of metastable states for the model on square lattice simulations in terms of energy and the self-correlation function. Section 4 presents a short summary and perspectives.

2. Potts model dynamics below the transition temperature

The Potts model is described by a Hamiltonian of the kind [13]:

$$\mathcal{H}\{\eta\} = \sum_{\langle ij \rangle} (1 - \delta_{\eta_i, \eta_j}), \tag{1}$$

where η_i is the state of site i that can assume one out of q different values, usually identified by an integer: $\eta_i \in [1, q]$. When $q = 2$, Equation (1) reduces to the Ising Hamiltonian (within multiplicative and additive constants). Here, the case of nearest neighbor interactions on a square lattice will be considered. It presents a discontinuous equilibrium temperature-driven phase transition at T_q for $q > 4$ [13].

The non-equilibrium dynamics of the Potts model presents several peculiar features. For example, the determination of the domain growth exponents in the Allen-Cahn law at low temperature remained problematic for a long time [14,18], whereas it was just an artifact of the residual energy [19,20] (see below). From a general point of view, a recent

survey on the different dynamical regimes displayed by the Potts model has been done by Ferrero and Cannas [21]. These regimes are observed in numerical realizations of the system when they are cooled below the transition temperature T_q, and depend on the final temperature T that, according to the dynamical features, can be grouped into roughly three different ranges [21], delimited by the temperatures $0 < T_g < T^* < T_c < T_q$.

- For $T^* \lesssim T < T_c$ relaxation is dominated by simple coarsening, which follows the quench according to the Allen-Cahn law [1] for the growth of the domain size, with energy per site decaying as: $e(t) \simeq t^{-1/2}$.
- For $T_g \lesssim T \lesssim T^*$ the simple coarsening is interrupted at long time-scales and the system is trapped with finite probability in some configurations of high symmetry, with characteristic lengths that grow with the system size [21]. These states can be identified with those predicted by Lifshitz, from which the system escapes by activated dynamics.
- For $T \lesssim T_g$ the system gets stuck in some kind of frozen or glassy states with well-defined lifetime, which diverges with $T \to 0$ as $e^{c/T}$ [21]. An interesting aspect [20,22,23] is that during relaxation the system obeys a generalized Allen-Cahn law which includes an additive constant e_0:

$$e(t) \simeq e_0 + a \cdot t^{-1/2}.$$

The value of the constant corresponds to the average energy of the glassy states at zero temperature [23]. The existence of freezing at zero temperature and the role of activated process at low temperature was first pointed out by Vinals and Grant. Domains are pinned by some local finite energy barrier [24,25] which cannot be overcome if $T \simeq 0$. For low finite temperature these states present a lifetime independent of the system size [21], which is determined by the predominance of the activation time with respect to the equilibration time [24].

In addition to the above temperature ranges it is seen that, in the range just below the transition T_q, some metastable states with energy and structure similar to the disordered phase can be observed [21,26]. Investigation of the nature of these states is the subject of the next section.

3. Metastable states

3.1. *Theoretical premises*

The existence of metastable states just below a discontinuous transition is predicted by phenomenological theories like the Van der Waals equation for liquid–gas transitions [3] and are a general feature of theories with mean-field or long-range interactions [4]. As in the Van der Waals equation, metastable branches appear as a continuation of the stable branch beyond the transition point, and have to be replaced by the coexistence curve, e.g. via the Maxwell construction. Along these branches the metastable state is thermodynamically stable as long as the second free energy derivative is positive and the escape from the local minimum takes places via thermal activation. The theory of Ginzburg and Landau takes into account localized fluctuations, but these cannot be very large, therefore excluding interesting regions from its range of validity, like the one around the critical temperature. At the end of the metastable branch, is the spinodal point.

There, the second derivative of the free energy changes sign, making the whole system unstable. The decay to the stable phase is global and quick.

Beyond the mean field, statistical mechanics of short-interacting systems cannot account properly for metastability, since the partition function in ensemble theory is dominated by the global minimum of the free energy functional in phase space.

At equilibrium, metastable states in short-range systems with translational invariance are thermodynamically forbidden by stability requirements [27], although they can be obtained by setting specific constraints to the accessible phase space, or taking suitable limits in some perturbative approaches [4]. The constraint is related to a time-scale, up to which the metastable phase does not explore the whole available phase space. In this context, in the droplet theory for the condensation of the field-driven Ising transition [5], the fluctuations neglected in mean-field approaches give rise, locally, to droplets of the stable phase. An ensemble of non-interacting droplets of the stable phase is considered, its growth being favoured by the bulk free energy, which is lower in the presence of an external field, and hindered by the surface tension. The model has been extensively tested in two and three dimensions [7].

Meunier and Morel [9] considered an adaptation of the droplet approach to the 2D Potts model. According to their findings, for the T-driven Potts model transition, unlike in the Ising case, the growth of the droplet just below T_q is favored by the tendency to lower the total energy of the system (the interface perimeter between droplets), in favor of the system entropy (which increases where many small droplets are present). In this case, the ensemble of droplets is also different with respect to the Ising case in that droplets have an intrinsic entropy, and can assume different shapes. The theory by Meunier and Morel leads to a temperature range in which metastability is present in finite-size systems, a range which, however, shrinks to zero in the thermodynamic limit. This behavior, related in some way to the anomalous growth of fluctuations with the system size near the critical point, has, to our knowledge, not yet been confirmed by dynamic calculations. Investigation of metastable states from a pure dynamical point of view seems, therefore, to deserve interest.

3.2. *Some numerical results*

Numerical simulations of the Potts model with more than four states in 2D, constitutes a very stimulating and effective way of investigating the nature of metastable states in systems with many low-temperature stable phases.

A way of identifying metastable states just below the transition temperature is to look at the time behavior of the energy per site, $e(t)$. As a test system we have considered the Potts model on square lattices with $q = 12, 50$. Simulations have been performed by preparing the system in the high-temperature disordered phase and then quenching it by Metropolis dynamics below the transition temperature T_q.

For the $q = 12$ system, for which $= T_q = 1/\beta_q = 0.668$, we have taken the quench inverse temperature at $\beta = \beta_q \cdot + j \cdot 0.005$, with $j = 1, \ldots, 10$. The resulting time behavior for lattices of size $L = 250$ is shown in Figure 1. Each line is obtained by averaging over 50 different realizations of initial conditions and thermal noise, and the errors are the resulting standard deviations. It is seen that for temperature close to T_q, $e(t)$ stays stationary (a signature of metastability [4]) until large times, at an excess energy with respect to the
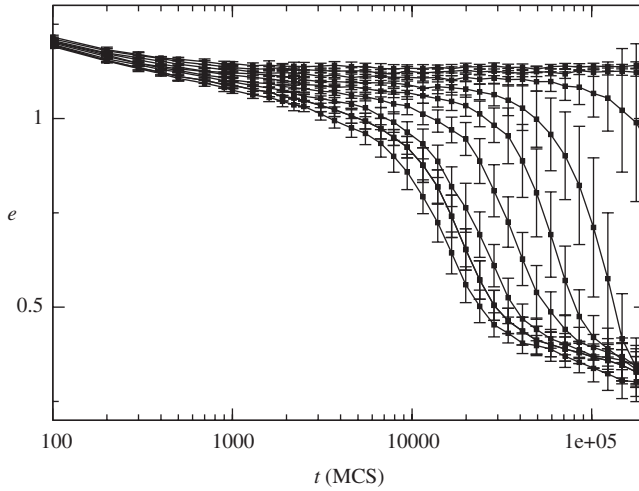
Figure 1. Time behavior of the energy per site, after the quench of the model with $q = 12$ at different quenching temperatures below T_q (see text). The quenching temperature increases from bottom to top.

equilibrium state. The existence of these metastable states is in agreement with [9], who however predict their disappearance in the thermodynamic limit.

From the point of view of the local dynamics, if the system is in a metastable state just below the transition temperature, it is expected to be indistinguishable from one in equilibrium. This property is reflected in the time behavior of the self-correlation function. In the equilibrium disordered phase ($T > T_q$), this function displays a fast (exponential) relaxation. The same behavior is therefore expected for the metastable states below T_q, but will no longer be true after the decay towards the stable state has begun. The correlation function computed waiting different times t_w after the quench time and should therefore signal this decay through the onset of a slower decay (ageing). The self-correlation function can be computed as

$$c(t, t_w) = \frac{1}{q-1} \left(\frac{q}{N} \sum \delta_{\eta_i(t+t_w), \eta_i(t_w)} - 1 \right), \tag{2}$$

where t_w is the time elapsed after the quench before starting the computation, and the sum is over all the lattice sites (to reduce statistical fluctuations, averages over different realizations of initial conditions and thermal noise can be taken).

As mentioned before, it is expected that for t_w short enough the relaxation is fast. Figure 2 shows $c(t, t_w)$ for different t_w for a system with $q = 50$, $L = 100$ and $T = 0.470$, being $T_q = 0.479$. Curves are obtained by averaging over 10 realizations (except one indicated in the legend). It is seen that after a very short transient time, $c(t, t_w)$ becomes translationally invariant for long periods of time, also showing no dependence on the size in the investigated range.

Figure 3 shows $c(t, t_w)$ vs. time t for $q = 50$, $t_w = 1000$ and different temperatures. Ageing becomes larger when the temperature is decreased, showing that the system is already relaxing towards the ordering phase.
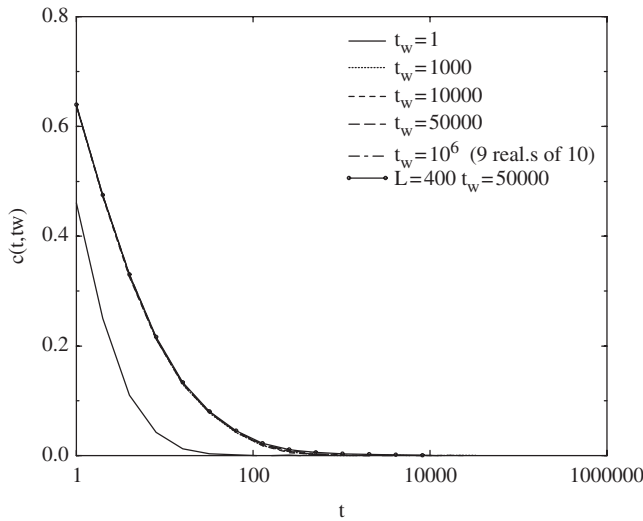
Figure 2. Time behavior of the self-correlation function for different waiting times for a system with $q = 50$. The lattice is $L = 100$ in size and the quench is at the temperature $T = 0.470$ ($T_q = 0.479$).
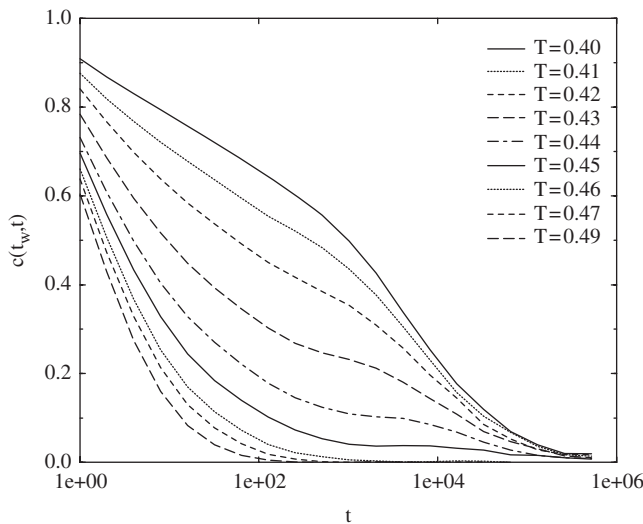

Figure 3. Time behavior of the self-correlation function for $t_w = 1000$ after quenching at different temperatures below $T_q = 0.479$. At low temperatures ageing appears.

These results show the existence of well defined metastable states on square lattices of finite size. The question of their existence in the thermodynamic limit is, however, open. Meunier and Morel [9] have recently faced the problem by investigating the energy probability distribution at the transition temperature, concluding that metastability is observable only in systems of finite size, the anomalous growth of energy fluctuations near the critical point being the origin of this fact. However, their analysis does not focus on the

microscopic mechanisms behind this shrinking of the metastability interval for increasing system size. It would be very interesting to have a description of this phenomenon in terms of microscopic clusters, and to compare the nucleation mechanism in this case with the predictions of classical nucleation theory for the field-driven Ising case.

According to nucleation theory the finite lifetime is usually determined by the time needed by the system for nucleating a drop of the stable phase bigger than the critical size. At the same time, as mentioned above, the metastable state displays short relaxation times similar to the high-temperature phase. The latter usually increase when the temperature decreases, and may happen to become equal to the nucleation time at a certain temperature T_s. This temperature corresponds to a pseudo-spinodal point [28] and sets a limit on the observability of undercooled metastable states. The first point is thus to establish if $T_s < T_q$ even for infinite systems, or if the two temperatures merge. Another point concerns the growing dynamics following the nucleation. In the Ising model the metastable state nucleates a critical droplet that afterward grows very fast because of its favorable free energy, with respect to the unstable phase. In the temperature-driven Potts model, however, each phase is equivalent to the others and competes with them for growth.

4. Conclusions

We have discussed some aspects of the off-equilibrium dynamics of the $q > 4$ Potts model quenched below the transition temperature. We believe that this can be relevant for understanding the non-equilibrium and the ordering dynamics of systems below a first-order phase transition temperature, in the presence of many competing equivalent ground states. After recalling some recent findings we have focused on some characterizations of the undercooled metastable states, which are observable after a quench below the transition temperature. These states display a finite lifetime (which depends on the temperature) and are detectable through the existence of a plateau in the energy (well above the equilibrium energy) and the fast relaxation time. Since their existence in the thermodynamic limit has been questioned by recent work, more extensive numerical simulations will be necessary to support this statement. More work in this field is also highly desirable for understanding the detailed mechanism, through which a system starts to order after the quench in the presence of many degenerate states, which is not yet well established.

References

[1] A. Bray, Adv. Phys. 43 (1994) p.357.
[2] P. Hohenberg and B. Halperin, Rev. Mod. Phys. 49 (1977) p.435.
[3] J. Gunton, M.S. Miguel and P.S. Sahni, *Phase Transitions and Critical Phenomena*, Vol. 8, Academic Press, New York, 1983.

[4] K. Binder, Rep. Prog. Phys. 50 (1987) p.783.
[5] J.S. Langer, Ann. Phys. 41 (1967) p.108.
[6] P.A. Rikvold, H. Tomita, S. Miyashita et al. Phys. Rev. E 49 (1994) p.5080.
[7] M.A. Novotny, G. Brown and P.A. Rikvold, J. Appl. Phys. 91 (2002) p.6908.
[8] I. Lifshitz, Zh. Eksp. Teor. Fiz. 42 (1962) p.1354.
[9] J.L. Meunier and A. Morel, Eur. Phys. J. B 13 (2000) p.341.
[10] K. Binder, J. Stat. Phys. 24 (1981) p.69.
[11] B.A. Berg, U.M. Heller, H. Meyer-Ortmanns et al., Phys. Rev. D 69 (2004) p.034501.
[12] S.B. Rutkevich, Internat. J. Mod. Phys. C 13 (2002) p.495.
[13] I. Wu, Rev. Mod. Phys 54 (1982) p.235.
[14] G.S. Grest, M.P. Anderson and D.J. Srolovitz, Phys. Rev. B 38 (1988) p.4752.
[15] G.L. Thomas, R.M.C. de Almeida and F. Graner, Phys. Rev. E 74 (2006) p.021407.
[16] M.P. Anderson, G.S. Grest and D.J. Srolovitz, Phil. Mag. B 59 (1989) p.293.
[17] F. Graner and J.A. Glazier, Phys. Rev. Lett. 69 (1992) p.2013.
[18] B. Derrida, P.M.C. de Oliveira and D. Stauffer, Physica A 224 (1996) p.604.
[19] M.J. de Oliveira and A. Petri, Phil. Mag. B 82 (2002) p.617.
[20] M. Ibáñez de Berganza, E.E. Ferrero, S.A. Cannas et al., Eur. Phys. J. Special Topics 143 (2007) p.286.
[21] E. Ferrero and S. Cannas, Phys. Rev. E 76 (2007) p.031108.
[22] M. Ibáñez de Berganza, V. Loreto and A. Petri, Phil. Mag. B 87 (2007) p.779.
[23] M.J. de Oliveira, A. Petri and T. Tomé, Europhys. Lett. 65 (2004) p.20.
[24] J. Vinals and M. Grant, Phys. Rev. B 36 (1987) p.7036.
[25] M.J. de Oliveira, A. Petri and T. Tomé, Physica A 342 (2004) p.97.
[26] M. Ibáñez de Berganza, V. Loreto and A. Petri, *Dynamics Metastability in the 2D Potts Ferromagnet*, submitted to Phys. Rev. E.
[27] R.B. Griffiths, J. Math. Phys. 5 (1964) p.1215.
[28] P.G. Debenedetti, *Metastable Liquids: Concepts and Principles*, Princeton University Press, Princeton, 1996.