Precursors of a phase transition in a simple model system

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Abstract
Most theoretical and numerical studies of phase transitions are concerned with the thermodynamics and with critical phenomena such as correlation lengths and critical slowing down as the temperature T is lowered towards the critical temperature T_c of the phase transition. However, an understanding of the microscopic properties of the system is required in order to find simple precursors of the phase transition which indicate that it is imminent. Our studies show that the ferromagnetic 3-spin Potts models is a simple system in which these properties can readily be studied, and we have shown elsewhere that changes in the environments of the states with time and temperature are responsible for its relaxation properties. Our new calculations indicate that the most reliable precursor of the phase transition is a dramatic increase in the tendency of the spins at most sites after changing to return to their original values (which corresponds to the disapperance of diffusion of molecules in liquids as they freeze) as the temperature is lowered towards T_c. The relevance of these results to the behavior of other complex systems is discussed.

1. Introduction

Phase transitions in physical systems are typical of many types of transition that occur in complex systems. Other transitions that are potentially of a similar nature include the formation and disintegration of a strongly bound community or of an economic conglomerate. While such transitions often appear to occur quite suddenly when the appropriate conditions actually occur, there are usually some indications before they happen, which we call precursors. In the theory of phase transitions, these precursors are usually examined in terms of the thermodynamic properties of the system as the critical temperature T_c of the phase transition is approached. The reason for this is that these properties are very general and occur in a large range of systems, without any consideration of the microscopic properties. However, it is also interesting to look for precursors in the microscopic properties of specific systems (or types of system), in order to be able to predict from them whether a phase transition is imminent. An understanding of these can lead to some ideas about when to expect such transitions, and also how to prevent or encourage them, both in similar physical systems and in more general complex systems.

As a well-known example of a phase transition, which will guide us in the analysis of our model system, we consider first the transition between a liquid and a

solid. One obvious apparent difference between these two states of matter is that the atoms or molecules in a solid make transitions much more slowly than in a liquid. A second difference is in the nature of the transitions. In a crystal the atoms mostly make transitions either by jumping into interstitial positions, which requires a high activation energy, or by moving across the grain boundary between one crystallite to another, which is also a rare process. Similar processes can also be defined for non-crystalline solids or glasses [Granato, 1992 ; Granato and Khonik, 2004]. In a liquid near the freezing temperature, on the other hand, molecules are much more mobile, and are continuously leaving and joining different sub-critical clusters. Thus, one possible precursor of a phase transition ia a dramatic slowing down in the rate at which transitions occur, and another is a change in the predominant type of transition that occurs. In addition, the molecules in a liquid are free to diffuse over large distances, while in a solid there is very little or no diffusion. This implies that in the solid there is a strong correlation between the positions of the atoms at different times, which is not present in the liquid, so that a third possible precursor of the phase transition is a change in this correlation. As we discuss at the end of this paper, analogous processes can occur in other complex systems.

In this paper, we examine the approach to a phase transition in a very simple model system, namely the q-state ferromagnetic Potts model on a square lattice [Baxter, 1973]. In this system, there is associated with each site of the lattice a spin that can take any one of q distinct values, while there is an attractive interaction between spins having the same value which encourages the formation of blocks or clusters of identical spins as the temperature is lowered towards the critical temperature of the phase transition. This transition is second order for $q \leq 4$ and first order for $q > 4$ [Baxter, 1973]. We have recently shown [Halpern, 2006] that the dependence on time and temperature of the relaxation properties of this system can readily be understood in terms of the changes in the environments of the sites, and that the system's behavior has some similarities to that of supercooled liquids. In that paper we only considered temperatures T above the critical temperature $T_c(\infty)$ of the infinite system, and were not particularly interested in the phase transition. By contrast, in this paper we examine the system's properties as the temperature passes through the critical temperature of the phase transition. For finite systems, with sides of length L, it is well known [Priman, 1990] that the phase transition temperature $T_c(L)$ may differ from that of the infinite system, so that we do not know in advance the exact critical temperature for the finite systems examined in our simulations. However, this is not of crucial importance for examining the precursors of an impending phase transition. In section 2 we describe briefly the system, as well as our motivation for studying it, and present the results of our calculations. These results and their significance are discussed in section 3, at the end of which we consider their relevance to other complex systems. Our conclusions are summarized in section 4.

2. The Potts model

The Hamiltonian for the ordered ferromagnetic q-spin Potts model with interactions only between the spins at adjacent sites can be written as [Wu, 1982]

$$H = -J\, \Sigma_i \Sigma_{j(i)} \delta(\sigma_i, \sigma_j) \qquad (1)$$

where $J > 0$, the first sum is over all the sites i in the system and the second one over all the sites $j(i)$ that are nearest neighbors of the site i, the spins σ_i can take any integer value between 1 and q, and $\delta(a,b) = 1$ if $a=b$ and 0 if $a \neq b$. Hence, the local energy associated with a spin having z adjacent sites with the same spin is just $-zJ$. The probability w of a change in the spin at a site which involves an increase of energy ΔE at temperature T was taken to have the standard form

$$w = \begin{cases} w_0\,, & \Delta E<0 \\ w_0 \exp(-\Delta E/k_B T), & \Delta E>0 \end{cases} \qquad (2)$$

Before describing the properties of this system, we will discuss briefly the reason why we were interested in it, since this affects the way that we analyze its results. The Potts model can be regarded as a schematic model for a plastic crystal, in which the molecules are often treated as thin rods with their centres fixed on the sites of a lattice [Bermejo et al, 2000]. If the possible positions of these rods are restricted to a finite number q of orientations, then each orientation can be represented by a different value of the spin in the q-spin Potts model, and the Hamiltonian of equation (1) favors all the rods being parallel. These plastic crystals have properties very similar to those of supercooled fluids [Benkhof, 1998], with random molecular orientations corresponding to the liquid state and a state with the orientations of the molecules frozen corresponds to the glassy (or crystalline) state. Hence, the behavior of the Potts model can be expected to shed some light on the properties of supercooled liquids, as we have shown elsewhere [Halpern, 2006].

For our simulations we considered a square lattice of 200 x 200 sites, which was large enough to give reproducible results for different runs, and we chose $w_0 = 0.5$. In order to save CPU time, we only performed extensive calculations for the case of 3 spins, $q = 3$, for which $T_c(\infty) = 1.005J/k_B$ where k_B is the Boltzmann constant [Baxter, 1973]. The simulation techniques used were the same as in our previous paper [Halpern, 2006], apart from starting the anneals from an initial state of all identical spins instead of one with random spins. Once a seady state was reached, a set of five successive simulation runs was performed on the system, with each run proceeding until the spin had changed at least once at 99% of the sites. In order to study the temperature dependence of the structure of the system and the nature of the transitions in it, we examined the fraction of sites cl_4 within clusters of identical spins, i.e. with $z = 4$, and the fraction of sites ch_4 at which the first change of spin occurs from within such a cluster. The reason for considering the first change of spin at a site rather than all the changes of spin is that the latter will be swamped by the sites at which the spin can change freely, even if their number is small. The other property that we study is the normalized fraction of sites at which the spin is unchanged, or correlation function, at the end of one run, fr_1, and at the end of five runs, fr_5. Since for two completely random systems the probability that the spins at any given site are equal is $1/q$, this correlation function is related to the actual fraction s of sites at which the spin is unchanged by

$$fr = (s-1/q)/(1-1/q) = \tfrac{1}{2}(3s-1), \qquad (3)$$

which is zero if there is no correlation between the initial and final states of the system and unity if these states are identical.

In order to provide an indication of what our system looks like at various temperatures, the results that we show first, in figure 1, are maps of the system, where the three different colors correspond to the three different values of the spin. The color

green tends to dominate the figures because the initial state from which the systems were obtained by annealing (or thermalizing) was one with green at all the sites.

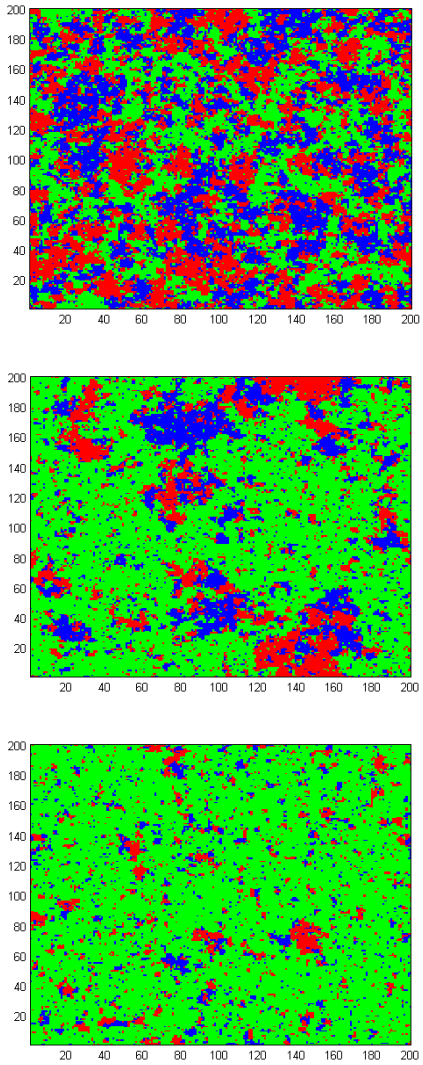

Figure 1 : Distribution of states for $T_c(\infty)/T$ = 0.95 (top), 1.00, and 1.01(bottom)

From these maps, we can see clearly how the system consists of small clusters at high temperatures, and tends towards a single phase as the temperature is lowered. The big difference between the figures for $T_c(\infty)/T$ = 1.0 and for $T_c(\infty)/T$ = 1.01 suggests that the latter is close to the phase transition temperature. However, even for $T_c(\infty)/T$ = 1.05 we find that there are small pockets of spins that differ from the majority. The presence of

these pockets is associated with the fact that for our system there is always a finite probability of a spin changing within a cluster, and any such change increases the probability that an adjacent spin changes.

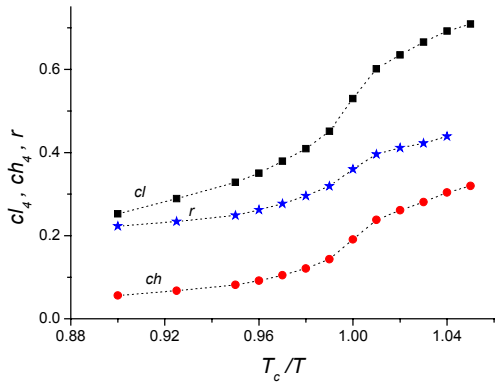

Figure 2 : The fraction of sites in clusters cl_4 (black squares), the fraction of sites from which the first change of spin is made from within a cluster ch_4 (red circles), and their ratio $r = ch_4/ cl_4$ (blue stars), as functions of the reduced inverse temperature $T_c(\infty)/T$.

We now turn to the possible precursors of a phase transition listed above. Our previous results [Halpern, 2006], together with our subsequent extensions of them, do not show any dramatic slowing down in the rates at which spins change as the temperature is lowered towards and beyond T_c. Accordingly we now turn to the second possible precursor, and examine whether ther is a change in the predominant type of transition. For our system, this corresponds to a change from the transitions of spins taking place on sites at the edge of clusters at temperatures well above T_c to transitions from sites within clusters below T_c. In figure 2, we show the fraction of sites within clusters cl_4 and the fraction of sites ch_4 at which the first change of spin occurs from within such a cluster, as functions of the reduced inverse temperature $T_c(\infty)/T$, and also their ratio $r = ch_4/cl_4$. For an ideal single phase system, all these three quantities would be unity. The difference between ch_4 and cl_4 is just the fraction of sites initially inside clusters that have changed their environments before the spins on them first change. As the temperature is lowered, so that $T_c(\infty)/T$ increases, cl_4 increases, as is to be expected from the thermodynamics of the system [Halpern, 2006]. There is also amore rapid increase in ch_4, so that the ratio r of the number of sites at which the first transition occurs within clusters to the total fraction of sites within clusters increases. A detailed discussion of the source of these increases is beyond the scope of this paper. However, we do not find any dramatic increase in these quantities for values of $T_c(\infty)/T$ up to 1.05, which according to figure 1 should certainly include the phase transition temperature. This result is associated with the small pockets of different spins which are present in our systems at all temperatures, and which reduce considerably the fraction of sites cl_4 inside clusters. The changes of spin at sites on the edges of these pockets require less energy than at sites inside clusters, and so the presence of these pockets

also reduces appreciably the fraction of sites ch_4 at which the first change of spin occurs from inside a cluster. Incidentally, we see from figure 2 that the rate of change with temperature of all these quanities does have a maximu (an inflexion point in the curves) close to T_c, but its position is not easy to measure accurately.

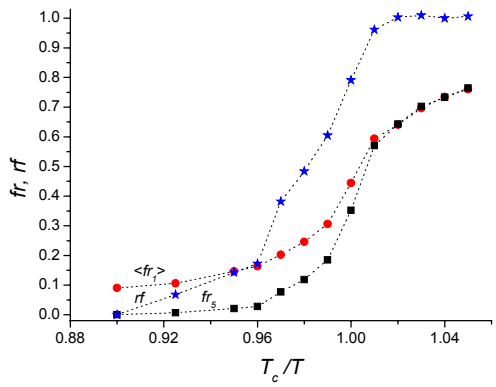

Figure 3: The average correlation function (the reduced fraction of sites at which the spin has not changed) after a single run $<fr_1>$ (red circles),and after five successive runs fr_5 (black squares), and their ratio $rf = fr_5/<fr_1>$ (blue stars), as functions of the reduced inverse temperature $T_c(\infty)/T$.

Finally, we consider the changes in the average values of the correlation function fr_n between the original values of the spins and their values after n successive runs, where in each run the spins at 99% of the sites have changed at least once. In figure 3, we show, as functions of the reduced inverse temperature $T_c(\infty)/T$, the mean value $<fr_1>$ of the correlation function fr_1 for five successive runs and its value fr_5 after these five successive runs. The increase in both these quantities as the temperature is lowered is associated with the increase in cl_4, since it can be shown that the return of a spin to its original value is more probable for sites inside clusters than for sites outside them. One expects that after five runs the correlation function will be less than after a single run unless most of the system (apart from the pockets of different spins) is in a frozen state, in which case they will tend to be equal. Thus the increase in these correlations and their tendency to equalize could be a precursor of the phase transition. As we see from figure 3, the ratio $rf = fr_5/<fr_1>$ increases rapidly with decreasing T, and is close to unity for $T_c(\infty)/T \geq 1.02$, i.e. below the critical temperature for the finite system in accordance with the conclusions about its value that we deduced from figure 1.

3. Discussion

In the results presented in the last section, we found that for the Potts model there are three significant properties of the system that change as the temperature is

reduced towards that of the phase transition. Firstly, the size of the clusters of sites having the same spin increases, as shown in figure 1, and there is a corresponding increase in the fraction of sites cl_4 inside such clusters, as shown in figure 2. Secondly, the fraction of the sites initially inside a cluster at which the first transition occurs before any of the spins on adjacent sites have changed, the ratio r in figure 2, also increases. Finally, as shown in figure 3, the corrrelation function (the reduced fraction fr of sites at which a spin returns to its original value rather than to a random value) increases as the temperature is lowered, and becomes independent of the total number of changes of spin ($rf= fr_5/<fr_1> \approx 1$) at temperatures below the critical temperature. Of these three precursors, only the last one shows a dramatic increase as T approaches T_c and so provides a clear indication of the actual phase transition temperature.

In order to interpret and appreciate the significance of these precursors, we return to the analogies of the glass transition in supercooled liquids and of the freezing of a liquid and melting of a solid. A change in the spin at a site in our model corresponds to the motion of an atom or of a molecule, and a cluster of sites with identical spins corresponds to a droplet of liquid or to a solid-like region, depending on how long its size and shape remain unchanged. In that case, for the freezing transition the first of our three precursors corresponds to an increase in the fraction of molecules in droplets and in the size of the droplets, which is rather obvious and does not provide a sensitive test of the location of the critical temperature. The second of our precursors corresponds to an increasing fraction of molecules starting to diffuse via interstitial sites within a droplet, as proposed by Granato [Granato, 1992 ; Granato and Khonik, 2004] rather than freely between droplets. However, this does not show any dramatic change as the temperature was lowered, a result that corresponds to some recent experimental resdults on transitions in supercooled liquids as the glass temperature is approached [Huang and Richert, 2006]. By contrast, our third precursor corresponds to molecules that have left their original position (or orientation, as represented by the spin in our model) tending to return to it rather than diffusing freely away. This property is measured by the average value of the correlation function after different time intervals, and their ratio (corresponding to fr) is not affected by the presence of small pockets of unfrozen regions (provided that the first time interval is long enough for the molecules in these regions to diffuse away). Thus, just as for the Potts model, a rapid increase in this ratio is a clear precursor of the transition from a liquid to a frozen state, with the ratio reaching unity when the system freezes.

We now turn to the implications of our results for other complex systems, and consider as a typical example a closely coordinated community of individuals. For such a community, the energy J in our model corresponds to the attractiveness (or reduction in unpleasantness) of belonging to the community, and the temperature T (which entered our transition probabilities in the ratio $exp[-\Delta E/k_BT]$) to the stimulus to leave it. Just as our system is only in a frozen state for $T < T_c$, where $T_c(\infty) = 1.005J/k_B$, so for a community even if it is very difficult to leave (low T) the community, it will not be stable ($T > T_c$) and will eventually disintegrate if there are insufficient attractive forces to bind it together (very low J). Similarly, in order for a group of individuals to unite to form a stable community (or political party) it is essential that the advantages of belonging to that community outweigh those of being completely free. While these statements are fairly obvious (although not always remembered by dictators) our model shows that the existence of small pockets of dissenters does not necessarily lead to the

dissolution of the community. In fact, it follows from our results for *fr* that such a community can be stable even if most of the members leave it temporarily, provided that most of those that leave return to it rapidly. Our model can easily be extended to allow for different values of *J* and *T* at different sites or in different regions, and an examination of the stability of a "frozen" state (*fr = 1)* under these conditions can shed light on the stability of a community in which the attractiveness of belonging and the temptation to leave is not uniform among all its members.

4. Conclusions

Our results show that the clearest precursor of the phase transition in the 3-state ferromagnetic Potts model is provided by the correlation function between the spins, which increases rapidly as the critical temperature is approached and becomes independent of the number of transitions made by the spins below the critical temperature. This result suggests that in other complex systems the corrrelation function between the state of the system at different times can also be used as a reliable test of whether the system is approaching a dramatic change in its properties.

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