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Time lag in nucleation: Monte Carlo simulations

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Abstract. Numerical simulations show that the time lag between the quench and the establishment of a steady-state regime of nucleation depends on the quench rate. For the fast quenches the time lag is found to be exponentially, rather than linearly, dependent on the radius of the critical nucleus. It is shown qualitatively that the time lag for slow quenches is smaller than that for the fast quenches. All these results are obtained in the framework of Glauber dynamics. For Kawasaki dynamics it is much harder to detect the beginning of the steady-state regime, and the results are less convincing.

1. Introduction

The classical theory of nucleation (Zettlemoyer 1969) describes the relaxation of a metastable state by the distribution function $W(r, t)$ of nuclei of the stable phase of size r at time t. This function satisfies the continuity equation:

$$\frac{\partial W(r, t)}{\partial t} = -\frac{\partial J(r, t)}{\partial r} \tag{1}$$

where the nucleation rate $J(r, t)$ in turn depends on the nuclei provided. One usually assumes that the equation

$$J(r, t) = -F(r)\, W(r, t) - D(r)\frac{\partial W(r, t)}{\partial r} \tag{2}$$

describes the systematic growth (decay) and the diffusive growth of the nuclei respectively. By taking one or another form of the functions $F(r)$ and $D(r)$, one can easily find the steady-state solution of equation (1). In fact, the small nuclei tend to shrink because of their high surface to volume ratio. Eventually some nuclei will grow to the so-called critical size r_c beyond which they are stable and the system will then develop into one containing two phases. Hence, the 'steady-state' solution will no longer exist. One 'achieves', however, a steady-state regime by the theoretical assumption that all nuclei of a critical size, when they appear, decompose and return to the system. The smallest size ξ of a nucleus has to be defined, along with the maximum size r_c. Indeed, the statistical mechanical description of metastable states requires some additional constraints, such as a coarse graining procedure (Gunton *et al* 1983), i.e. the introduction of this minimal length ξ.

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The time-independent steady-state solution of equation (1), $W_{ss}(r)$, for some given functions $F(r)$ and $D(r)$, can be easily found from equation (2) with the constant nucleation rate (flux) J_{ss}. The latter defines the number of new phase nuclei, say, liquid droplets in the vapour environment, formed per second per cubic centimetre.

Another quantity which can be observed in laboratory experiments is the so-called integrated flux $N(t)$, i.e. the number of critical nuclei appearing during the observation time t:

$$N(t) = \int_0^t J(r_c, \tau)\, d\tau \qquad N_{ss} = J_{ss} t. \tag{3}$$

The second formula in equation (3) indicates that in the steady-state regime the integrated flux increases linearly with time.

We are interested, however, in the transient processes which can be characterised by the time until the steady state is established. This time is usually called the time lag θ (Kelton *et al* (1983).

There are two possible definitions of this time lag, θ_J and θ_N, associated with the time dependence of the flux $J(r, t)$ (or the distribution function $W(r, t)$) and the integrated flux $N(t)$, respectively. In the simplest case, where $J(r, t) = J_{ss}[1 - \exp(-t/\theta_J)]$ and we define θ_N by $N \simeq J_{ss}(t - \theta_N)$, it is clear from equation (3) that $\theta_J = \theta_N$. If, on the other hand, $J(r, t) = J_{ss}[1 - A \exp(-t/\theta_0)]$, it follows from equation (3) that $N = J_{ss}(t - A\theta_0)$. Therefore, in this case the characteristic time for the flux $J(r, t)$, derived from $-t/\theta_0 + \ln A = -1$, will be $\theta_J = \theta_0(1 + \ln A)$. On the other hand, in this case the characteristic time defined by the integrated flux $\theta_N = A\theta_0$. Hence the difference between the two definitions of the time lags is now very important. Indeed, the form of A depends on the initial conditions, i.e. on the ratio r_c/ξ. If, for example, $A \sim \exp(\gamma(r_c^2/\xi^2))$, $\gamma \leqslant 1$ as we found previously (Rabin and Gitterman 1984), then the time lags, θ_N, defined by the integrated flux will be (exponentially) larger than that defined by the flux, θ_J (or by the distribution function, θ_w). One concludes, therefore, that even if θ_J and θ_W are quite small, the time lag θ_N which contains the time integral of the small differences between $J(r, t)$ and J_{ss} may be large. It is this time θ_N which we use as the time lag. Such a definition seems to be natural, because in laboratory experiments only θ_N can be directly or indirectly observed. The main aim of the present analysis is to find θ_N from numerical simulations.

Recently we formulated a new approach to transient phenomena in nucleation theory (Rabin and Gitterman 1984). It was shown, in part, that one has to distinguish between 'fast' and 'slow' quenches. The metastable state is a state of incomplete equilibrium, i.e. only small nuclei of size less than some characteristic radius λ come to equilibrium immediately after a quench. The magnitude of λ is determined by the rate of the quench. If a quench is performed slowly enough, so that even the nuclei of large size manage to come to equilibrium straight after a quench, then λ is very close to r_c. It is precisely this case that is usually considered in the time-dependent nucleation theory (Kelton *et al* 1983). All dynamic events are occurring now in the range of nuclei sizes close to r_c and the integrals involved are calculated by the method of the steepest descent. The final result is that $\theta \sim r_c^2/K$ where K is the typical diffusion coefficient in liquids, $K \simeq 10^{-5}\ \mathrm{cm^2\ s^{-1}}$.

The situation is quite different for a 'fast' quench where only small nuclei of a new phase are in equilibrium immediately after a quench (λ close to ξ). It takes a long time $(\theta_N)_{fast}$ to establish the steady-state regime. According to our previous papers

(Rabin and Gitterman 1984, Gitterman *et al* 1984, Edrei and Gitterman 1986a) one finds that $(\theta_N)_{\text{fast}} \sim \exp(\gamma(r_c^2/D_0))$ where γ is the numerical coefficient of order unity. Here D_0 has the dimensions of length squared and can be expressed in terms of the surface tension σ, $D_0 = 4\pi\sigma\beta$, where $\beta = (kT)^{-1}$. For calculations, one can assume that $D_0 \simeq \xi^2$.

At the end of our previous theoretical analysis (Rabin and Gitterman 1984, Gitterman *et al* 1984), we found two new results which need experimental verification.

(1) For fast quenches in the three-dimensional case the time lag θ_N depends exponentially on r_c^2 and not linearly as it is usually assumed (Kelton *et al* 1983).

(2) A decline in the quench rate results in a decrease of θ_N, and its exponential dependence on r_c^2 changes gradually into a linear one.

We now describe the Monte Carlo simulations which clearly show the dependence of the time lag on the rate of quench. To the best of our knowledge this is the first systematic analysis of this kind, although one can see, for example from figure 1 in Kelton *et al* (1983), that the time lag depends on the minimal size of the nuclei present immediately after a quench.

In our calculations we analyse the dynamics of the Ising systems with nearest-neighbour interaction in two different models: those of Glauber and Kawasaki. The Kawasaki dynamics (KD) describe a system with conserved order parameter like binary alloys AB, while the Glauber dynamics (GD) are related to systems with non-conserved order parameter, such as ferromagnets or liquid-gas systems. In the GD one starts from a state with all spins oriented in one direction and then one quenches the system into a metastable state by applying a field h antiparallel to the spins. Analogously, in the KD the initial state is given by a random distribution of B atoms in an 'host' lattice of A atoms and a quench is achieved by changing the temperature. The probability of a change of configuration on site i is given by $P_i = \exp(-\beta\Delta u_i)[1+\exp(-\beta\Delta u_i)]^{-1}$, where Δu_i is the change in the energy of the system which results from one flip in the GD or from an exchange of the occupation of two nearest sites in the KD. One Monte Carlo step per site is defined as going over all sites in a system and checking each one to determine whether to change configuration or not. After any specified number of steps the computer program lists the existing nuclei (clusters) and their respective sizes. In the KD we call 'nuclei' of size n the group of B atoms located on n nearest sites independent of its shape. Nuclei in the GD are a set of neighbouring spins parallel to the external field. Consideration of the distribution of nuclei on different steps gives an idea of the evolution of the system.

We are interested in the transient process before the steady-state regime is started. One has to find, therefore, some criterion describing the beginning of the steady-state regime. Then, the required number of steps will be proportional to the time lag. The next stage will be a comparison of the time lags for fast quenches, when one goes straight away to a given metastable state, with those of slow quenches when a final state can be reached by a set of changes of the temperature or the magnetic field, waiting some time at each value.

According to our theoretical approach described above, the steady state is defined by the linear increase of the number of critical nuclei. Therefore, for each quench one has to estimate first the appropriate critical radius and then analyse the distributions of nuclei on different Monte Carlo steps to find when the number of critical nuclei starts to increase linearly with the number of steps. We have indeed proceeded in this way in the GD. It is quite clear that the KD is much slower than the GD, so that it is more difficult to discern when the steady-state regime has started. As a criterion in

the KD we consider a number of steps after which the numbers of small nuclei remain constant with time. We now turn to a more detailed discussion of our simulations.

2. The Glauber dynamics

We have worked with the three-dimensional simple cubic lattice consisting of $168 \times 168 \times 168$ sites with periodic boundary conditions in the x and y directions (these numbers came from the computer program kindly given to us by Dr D Stauffer). Most of the runs were done at $T = 0.59 T_c$ and with the magnetic field h (in units $kT_c/2$) varying between 0.41-0.52. For larger h the decay of a metastable state is too rapid, and for smaller h nothing could be seen due to computing time limitations. For each h the size of a critical nucleus r_c is given by the following formula (Burkner and Stauffer 1983): $r_c \sim (2\Gamma/3h)$, where Γ is related to the bulk surface tension γ, $\Gamma = (36\pi)^{1/2}(kT_c)^{-1}\gamma$. The data for γ were taken from the Monte Carlo simulation done by Burkner and Stauffer (1983).

It should be noted that the above formula for r_c holds, strictly speaking, only for $h \to 0$ and $T \to T_c$. Therefore, we use it only as a rough guide for an estimate of the critical radius which is improved afterwards during numerical simulations.

The results of numerical simulations for external field $h = 0.45$ are shown in table 1. Preliminary estimates show that the number of sites in the critical nucleus is about 100. One can see from table 1 that the first nucleus larger than r_c appears at step 150, the second one at 165, the third at 170, etc. (At step 220 the nuclei are so large that coagulation begins.) We therefore conclude that for this special h, i.e. for given r_c, the time lag $(\theta_N)_{\text{fast}}$ is equal to 150 steps. Furthermore, one can see from the table that the latter result is not too sensitive to the precise value of r_c.

In order to find reliable average results one needs to perform many runs. We have performed 46 different runs for external fields h varying between 0.41 and 0.50. For every field one can find a typical time lag $(\theta_N)_{\text{fast}}$. Figure 1 shows $\ln(\theta_N)_{\text{fast}}$ against r_c^2, found by averaging all runs. One can see that $\ln(\theta_N)_{\text{fast}}$ is (approximately) proportional to r_c^2, in accordance with our theoretical predictions.

The agreement between the theory and simulations should be considered qualitative rather than quantitative because of the small accessible range of fields h, inaccuracy in an estimate of r_c, statistical uncertainty of numerical simulations, etc. However, figure 1 seems to indicate that the dependence obtained cannot be described by the usual formula, $\theta_N \sim r_c^2$ (Kelton *et al* 1983) and it is, in fact, much closer to an exponential dependence.

We also examined slow quenches within the framework of the GD. One has to decide, first of all, the meaning of a 'slow' quench. In fact, we have only an upper limit for 'slowness', namely, the time lag of the slow quench has to be certainly smaller than that of the fast quench, $(\theta_N)_{\text{fast}}$. There are, however, still many 'slow' quenches. If, for example, for $h = 0.45$ the time lag for a fast quench is equal to 150 steps, it is obvious that a 'slow' quench means that it is performed during a time shorter than 150 steps. However, it could also be 20, 40 or 60 steps, which can be performed in a different number of field jumps. One needs to do much more detailed calculations in order to check the dependence of the time lag on different choices. For general orientation we have chosen the first intermediate field h_i, i.e. one performs the fast quench from the fully oriented state to the intermediate state, and then several jumps until one reaches the final field h_f. We used two sets of states: $h_i = 0.41$; $h_f = 0.45$ and

Table 1. Appearance of large nuclei (containing at least 50 sites) at different Monte Carlo steps for the Glauber dynamics for an external field $h = 0.45$ with the critical nucleus containing approximately 100–124 sites. The second column gives the size of the largest nucleus, while the third–sixth columns show the second, third, ..., largest nucleus, respectively.

Steps	First	Second	Third	Fourth	Fifth	Sixth
130						
135	60					
140	52					
145	79					
150	167					
155	254	71				
160	578	107				
165	1 229	163	57			
170	2 367	329	122			
175	4 374	642	169			
180	7 760	1 321	218	51		
185	13 133	2 407	413	66		
190	20 864	4 531	773	258		
195	31 646	7 984	1 119	959	84	
200	44 395	13 484	2 286	2 176	110	
205	60 779	21 223	4 150	3 876	136	
210	80 910	31 413	6 964	5 853	245	
215	106 514	44 767	11 319	8 652	455	
220	137 435	61 860	17 295	11 975	1 020	80
225	257 144	25 496	16 566	2 218	341	
230	324 719	35 288	22 412	4 240	813	484
235	397 292	48 577	29 370	7 230	3 915	1635
240	476 572	63 858	37 895	11 822	10 281	2644
245	661 818	52 604	20 579			
250	782 365	66 693	35 029	281	86	72

$h_i = 0.40$; $h_f = 0.44$. Then we performed a set of different slow quenches covering $\Delta h = 0.04$ with different 'slowness' by changing the number of stages. Upon reaching the final state we checked how many additional steps one has to perform before the steady-state regime appears. Unfortunately, the scatter in our data is too large to provide reliable quantitative conclusions. However, one finds that, after a final state is reached, the requisite number of steps before the appearance of the critical nucleus is of the order of 50 and 120 for $h_f = 0.45$ and $h_f = 0.44$, respectively. These numbers are much lower than the corresponding step numbers 150 and 200 for $(\theta_N)_{\text{fast}}$. These results are in qualitative agreement with our theory (Edrei and Gitterman 1986a).

3. The Kawasaki dynamics

All dynamic events in the KD are much slower compared with those in the GD. We started with the three-dimensional system, but then we turned to a two-dimensional lattice, which is more convenient for our purposes. We considered a two-dimensional 500×500 square lattice with nearest-neighbour interactions J. Initially, atoms B are randomly distributed in the lattice, which corresponds to a very high temperature.

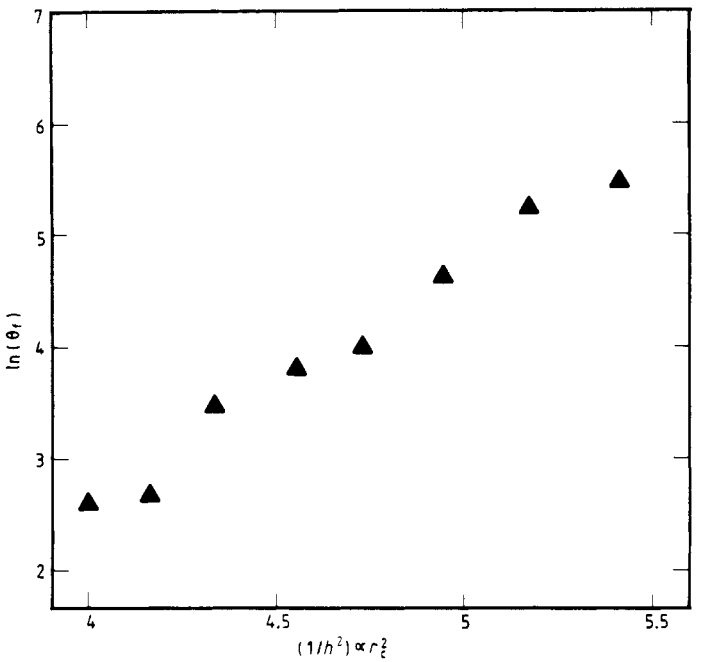

Figure 1. Time lag for fast quenches plotted logarithmically against squared critical radius for the temperature $T/T_c = 0.59$ for the Glauber dynamics in the three-dimensional $168 \times 168 \times 168$ simple cubic Ising lattice.

Then the system is quenched to $T = 0.59T_c$ where $T_c = 2.269J/k$. The fraction of B atoms was taken from 5% to 30%. For each concentration c, one calculates the appropriate r_c which is proportional to $(\ln S)^{-1}$ where the super-saturation $S = c/c_e$ and the equilibrium concentration c_e corresponding to $T = 0.59T_c$ is equal to 3.05×10^{-3} (Rao *et al* 1976).

We have met with difficulties in detecting the onset of the steady-state regime. In contrast to the GD nothing conclusive can be obtained by considering the appearance of one, two, three, ..., nuclei of the critical size. However, it is possible to suggest another criterion for the appearance of the steady-state regime: the steady state is reached when the number of small nuclei remains constant with time (Stauffer *et al* 1982). Our simulations show that for a system of 12% B atoms a distribution of single atoms hardly changes with time after 600 steps. We use the latter requirement as the criterion for the establishment of the steady-state regime ($\theta_N \approx 600$ steps) because there is a large body of data for single atoms. Some reservations regarding the criterion chosen have to be made. Detailed analysis (Binder and Muller-Krumbhaar 1974, Binder and Stauffer 1976) shows that after this 'time lag' the cluster concentrations stay nearly constant and then decrease slightly once again, showing that the 'truly' stationary steady state is not reached.

We have performed 80 runs for different concentrations of B atoms. These data form the basis for figure 2 which gives a nearly linear plot of $(\ln \theta_N)_{\text{fast}}$ against r_c which was predicted theoretically for the two-dimensional case (Edrei and Gitterman 1986b). One can conclude from figure 2 that the time lag for the fast quench is described by (approximately) exponential rather than by linear dependence on r_c. Hence, in general, the results obtained for the KD are similar to those obtained by the GD.

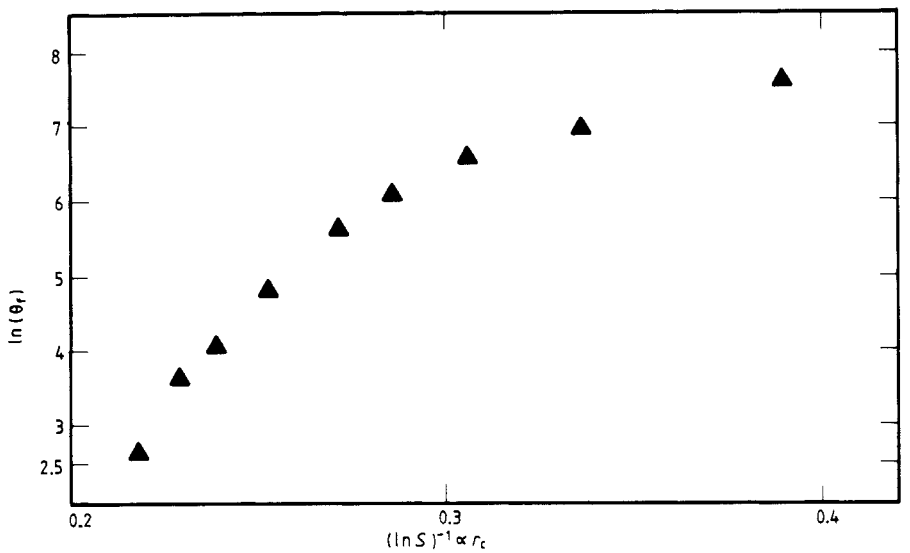

Figure 2. Logarithmic plot of the time lag for fast quenches as a function of critical radius for the temperature $T/T_c = 0.59$ for the Kawasaki dynamics in the two-dimensional 500×500 square Ising lattice.

4. Conclusion

The following results have been obtained.

(1) Numerical simulations confirm our theoretical predictions that the time lag for the fast quenches (based on the integrated flux) depends exponentially rather than linearly on the squared radius of the critical nucleus.

(2) Numerical simulations for the Glauber kinetics qualitatively support the dependence of the time lag on the rate of quench. Additional simulations for different slow quenches are needed.

(3) The Kawasaki dynamics seems to be less appropriate for the numerical simulations of the transient processes compared with the Glauber dynamics.

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