Neutron Scattering and Monte Carlo Determination of the Variation of the Critical Nucleus Size with Quench Depth[†]

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Received: September 15, 2005; In Final Form: November 3, 2005

We have used a combination of neutron scattering experiments and Monte Carlo simulations to study the initial stages of first-order phase transitions. We focus on quenches wherein the nascent phase is formed by homogeneous nucleation, and we approach the spinodal, i.e., the quench depth at which the original phase becomes unstable. In this regime, we show how critical nuclei sizes are determined from neutron scattering structure factors. Prevailing thought is that the size of the critical nucleus should increase with increasing quench depth and diverge at the spinodal. To the contrary, our experiments and simulations indicate that the critical nucleus size decreases monotonically as quench depth is increased and is finite at the spinodal.

The kinetics of first-order phase transitions such as boiling, crystallization, magnetization, and liquid−liquid phase separation are hindered due to the presence of nucleation barriers. This hindrance arises from the free energy penalty to form interfaces during the initial nucleation of the stable phase after a quench. Once these nuclei reach a critical size, the favorable bulk free energy balances the surface free energy, and the phase transition can then proceed spontaneously.[1,2] An understanding of the dependence of critical nucleus size on quench depth is thus of considerable fundamental importance. It is generally agreed that the free energy barrier to nucleation should decrease and become comparable to the characteristic energy of thermal fluctuations at the spinodal where nucleation and growth is no longer the dominant mechanism for the phase transition.[3] Until recently,[4−8] however, it was also believed that in the vicinity of the spinodal the size of the critical nucleus should increase with increasing quench depth, and diverge at the spinodal.[3] The divergence is the result of a linearization of mean field theory. Here we use a combination of neutron scattering on polymer blends and Monte Carlo simulations of the Ising model to show that the critical nucleus size does not diverge at the spinodal but, in fact, decreases with increasing quench depth.

It is straightforward to determine the size of the critical nucleus in computer simulations because the atomic coordinates of nucleating trajectories are known. As a result, information regarding the growth and decay of clusters is available directly in position space. Similar data are generally unavailable for many experimental systems − important exceptions are the data found in refs 9 and 10. An important goal of this work is to demonstrate that time-resolved structure factors obtained from

metastable systems during nucleation provide a robust measure of the critical nucleus size. Our approach is valid for shallow quenches and deep quenches in the vicinity of the spinodal.

The Ising model and other related lattice models have proven invaluable for understanding phase transitions in a variety of systems.[11,12] Here, we consider the application of the Ising model to the kinetics of first-order phase transitions.[13−16] Its connection to binary fluid mixtures follows from an approximate coarse graining of atomic coordinates. We imagine superimposing a cubic grid with cells of edge length l onto a binary mixture and assigning each cell, s_i, a value of $+1$ if it contains a majority of one component and with a value of -1 if it contains a majority of the other component. The net energy of the model is

$$E(s_1, s_2, ..., s_i, ...) = -J \sum_{\langle ij \rangle} s_i s_j + h \sum_i s_i \qquad (1)$$

where the sums run over all the cells in the lattice and the brackets denote a restriction to nearest neighbor cells. The coupling constant J (>0) sets the energy of interaction between the two components, and h (>0) is proportional to their chemical potential difference. This model is therefore a caricature of any two-component system that can mix and demix where $s_i = +1$ and $s_i = -1$ represent the two phases. In its magnetic context, the s_i values refer to domains of up and down spins, J describes the energy of interactions between those domains, and h is related to an external magnetic field. We use the thermal energy, $k_B T$, as our basic energy unit where k_B is Boltzmann's constant and T is temperature, kept constant at 0.6 times the critical temperature T_c. The critical temperature, T_c, is the temperature at which the Ising model undergoes an order−disorder phase transition, and its value is known from numerical calculations.[11] In other words, the value of J in these simulations is always 1/0.6 times J_c, the critical point coupling, or $J = 0.369 k_B T$. To study nucleation, an initial configuration with all spins up is quenched to a nonzero positive value of the field, h, and is subsequently propagated using single spin flip Metropolis Monte Carlo dynamics.[17] Despite the fact that a phase rich in down spins is thermodynamically stable following the quench, the system will remain for a relatively long time in a metastable

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Figure 1. (a) Free energy or reversible work, ΔG, to create a nucleus of size N spins in the three-dimensional Ising model at a quench depth (i.e., Ising field) of $h/J = 0.30$ where J is 1/0.6 times the critical coupling, J_c. Statistical uncertainties are roughly the thickness of the graphed line. The critical nucleus size, R_c, is defined to be $N_c^{1/3}$, where N_c is the value of N at the maximum value of ΔG. (b) Scaling of R_c with inverse quench depth at fixed J on a log–log scale to emphasize power law scaling. The dashed line is $R_c \approx 1/h^3$, indicating that R_c and h obey the scaling predicted by classical nucleation theory.

configuration rich in up spins, at least at moderate quench depths, until a large enough nucleus of down spins forms with sufficient bulk free energy to overcome the penalty of creating an interface.

This picture is borne out by Figure 1a, which shows the free energy for creating a nucleus of size N in the three-dimensional Ising model at $h/J = 0.30$. In our simulations, a nucleus is defined as a cluster of nearest neighbor down spins. The free energy curve in Figure 1a was calculated using umbrella sampling with hard walls on a cubic lattice with 64 spins on a side.[11] More simulation details can be found in ref 15, where the methods of transition path sampling[18] are used to establish that cluster size is indeed a reasonable reaction coordinate for the nucleation process. Namely, cluster size provides a good measure of the phase toward which a molecular configuration is biased. Figure 1b shows the scaling of the critical nucleus length scale, R_c, with quench depth at constant J. The critical length scale decreases with increasing quench depth and follows the inverse cube scaling predicted from classical nucleation theory for the entire range of quench depths studied.[1,2] Here, we define R_c to be the cube root of the critical cluster size, N_c, determined from the maximum of free energy curves. That is, $R_c \approx N_c^{1/3}$, where N_c is the value of N at the maximum of plots such as Figure 1a. As we are concerned primarily with scaling behavior, we ignore constants of proportionality such as those that have to do with the shape of clusters.

Since experimental measurements of growth and decay of clusters are generally not available, we use a recently developed experimental framework based on scattering measurements that gives a signature of the critical nucleus length scale. Structure factors, $S(q)$ where q is the scattering vector, were measured

on a series of blends of two model polyolefins, polymethylbutylene (PMB) and polyethylbutylene (PEB), undergoing liquid–liquid phase separation, as described in detail in refs 4–6. The homogeneous blends were quenched into the metastable regime by a pressure quench, and the initial stages of liquid–liquid phase separation were studied by recording the time-resolved structure factor using small-angle neutron scattering (SANS). In Figure 2a we show $S(q)$ for various times, obtained from one of the PMB/PEB blends (designated B5) containing 20 vol % deuterium-labeled PMB (molecular weight = 150 kg/mol) and 80 vol % PEB (molecular weight = 200 kg/mol) at 59 °C and 1.52 kbar. The radius of gyration, R_g, of the chains was 15.4 ± 1 nm. The high molecular weight of the polymers ensured that our blend was composed of highly interpenetrating, entangled chains.

To make a direct comparison between theory and experiment, we computed the Ising model structure factor along nucleating trajectories.[16,19,20] In Figure 2b we show $S(q)$ at selected time intervals for a quench depth of $h/J = 0.20$. The structure factors obtained from the PMB/PEB blends undergoing nucleation and those obtained during nucleation of the Ising model are qualitatively similar (Figure 2). They show the presence of two regimes of scattering vectors, a low q regime where the intensity increases with time and a high-q regime where the intensity is independent of time. We define the critical scattering vector q_c to be the point of division between the low-q and high-q regimes. The systematic numerical method used for extracting q_c from the raw data is described in ref 5 (method 2 only). It was argued that during nucleation the structure factor is expected to be time-independent at q values greater than $q_c \approx 1/R_c$ due to the absence of growing structures with length scales smaller than R_c. In other words, q_c was believed to be a signature of the critical nucleus length scale.[4,5] The Ising model simulations allow us to evaluate this interpretation.

In Figure 2c, we show probability distributions of cluster sizes in the Ising model as a function of time during the initial stages of nucleation at conditions for which the structure factors of Figure 2b were calculated. At $t = 0$, a metastable equilibrium of smaller clusters is present without any larger clusters. As time progresses, this initial distribution of small clusters remains essentially unchanged as a very small number of larger clusters gradually appear. This suggests that a system during the initial stages of nucleation can be pictured as containing a large, but rare, density fluctuation growing amidst a background of much smaller clusters. This picture is consistent with the observation of time-independent high-q tails described in the previous paragraph.

Using the probability distributions in Figure 2c, we can make a quantitative calculation of the Ising structure factors using a simple sphere model. During the initial stages of nucleation, the density of nucleated regions is low and clusters are uncorrelated in space. Therefore, we imagine that the major contribution to the scattering profile comes from the sum of scattering due to uncorrelated clusters of varying size N, distributed according to $P(N,t)$ as in Figure 2c. The red dashed lines in Figure 2b are the results of scattering profiles calculated using this simple model, assuming that the clusters are spherical. The agreement between the model and the simulations is very good, especially at small scattering vectors.[21] The discrepancy at higher q results from the granularity of the lattice. That is, at small length scales, the measured Ising structure factors begin to probe distances on the order of several lattice spacings whereas the simple model assumes smooth spherical structures down to the smallest possible length scales.
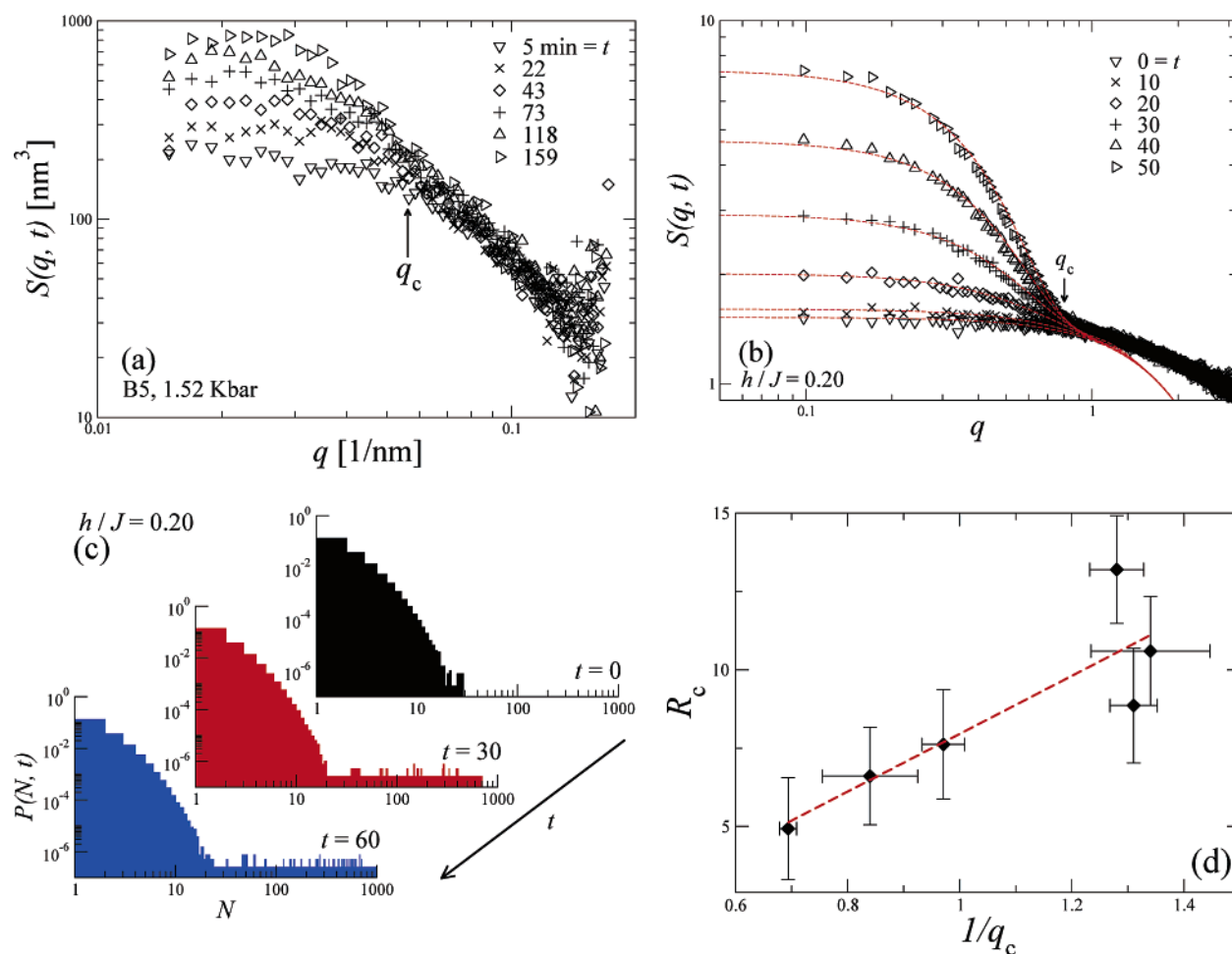
Figure 2. Time-dependent structure factor $S(q,t)$ for nucleation in (a) the PMB/PEB polymer blend and (b) the Ising model. The different curves are for different times t along the nucleating trajectory as indicated. The arrows indicate the location of q_c, the critical scattering vector where all of the $S(q)$ curves merge. For the Ising model, units of space and time refer to lattice spacings, l, and Monte Carlo sweeps, respectively, and the zero of time corresponds to the time when the system has established a metastable equilibrium in the quenched state. One Monte Carlo sweep corresponds to L^3 attempts to flip a randomly chosen Ising spin where L is the edge length of the cubic system in units of lattice spacings. The dashed lines in part b are calculated with a simple sphere model.[21] (c) Probability of finding a cluster of size N in the Ising model at different time slices along the reactive trajectory corresponding to the regime of times at which the structure factors in part b were measured. (d) Scaling of the critical nucleus size, R_c, with the inverse critical scattering vector, q_c, determined from the Ising model. The dashed line is a linear regression fit to the data. The error bars in R_c were taken to be the $k_B T$ variation of the nucleus size around its value at the maximum of ΔG (Figure 1a), and those in q_c were based on extractions of the merge vector from 10 independent sets of data.

In Figure 2d, we plot $1/q_c$ extracted from structure factors of the Ising model versus R_c determined independently from the maximum of the nucleation-free energy curves (i.e., Figure 1a). This comparison is justified because, as was shown in ref 15, cluster size is a good reaction coordinate for describing the dynamics of nucleation in the Ising model. The approximate linear relationship between $1/q_c$ and R_c implies that these two quantities scale in a similar manner, especially as the spinodal is approached. Therefore, the critical scattering vector, q_c, is indeed a signature of the critical nucleus. The error at larger wave vectors may be due to the larger size of the critical nucleus ($\sim$1000−2000 cells for the three rightmost points), giving rise to greater fluctuations in linear size when determining q_c from time-dependent structure factors.

We turn now to the scaling of R_c with quench depth. Classical nucleation theory predicts that the size of the critical nucleus decreases monotonically with quench depth.[1] More recent theories, beginning with the pioneering work of Cahn and Hilliard,[3] predict that the interface between the nuclei and the surroundings becomes diffuse near the spinodal. This prediction

leads to a nonmonotonic dependence of the critical nucleus size on quench depth with the predicted critical nucleus size increasing with increasing quench depth near the spinodal and ultimately diverging at the spinodal. This imagined result has been embraced in a number of contexts, including liquid−liquid phase separation,[3,22] liquid−gas transitions,[23] cavitation in expanded liquids,[24] solid-to-liquid transition,[25] and crystallization near a metastable critical point.[26] In particular, according to this view, the critical nucleus size in polymer blends undergoing liquid−liquid phase separation is expected to increase sharply with increasing quench depth in the vicinity of the spinodal.[22,27] To probe for evidence of such a divergence in our polymer blend system, we examine the scaling of the critical nucleus length scale with quench depth. A convenient measure of quench depth is the Flory−Huggins interaction parameter, χ, which is a measure of the interactions between monomers on the PMB and PEB chains. The temperature and pressure dependence of χ is given in ref 4. In addition, the values of χ at the binodal, χ_b, the lower limit of metastability, and thermodynamic spinodal, χ_s, the upper limit of metastability, have been established. In
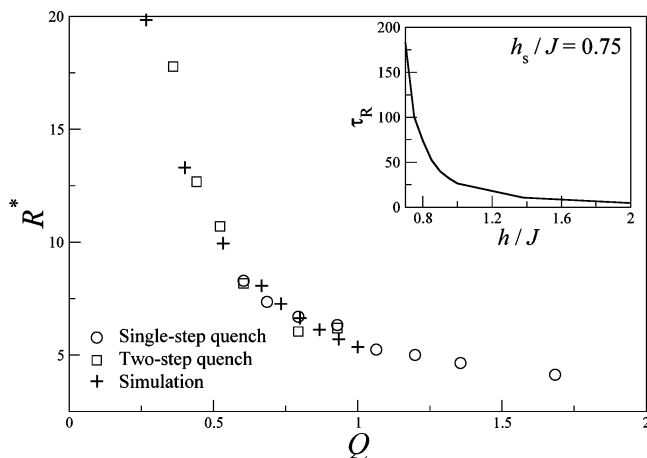
Figure 3. Size of the scaled critical nucleus R^* as a function of normalized quench depth determined from phase-separating polymer blends (squares and circles) and the Ising model (pluses). The inset shows the $1/e$ time decay constant, τ_R, of the nonequilibrium relaxation function, $\mu(t)$, eq 3, as a function of the field. The value of the spinodal field, h_s, in the Ising model is taken to be the value of h when τ_R is about 100 sweeps (see text).

particular, χ_s is the quench depth at which the static structure factor of the metastable blend diverges. We define the normalized quench depth, Q, as

$$Q = \frac{\chi - \chi_b}{\chi_s - \chi_b} \qquad (2)$$

The metastable region of the phase diagram is bounded by $Q = 0$ and $Q = 1$. For values of $Q < 0.60$ (Figure 2a), direct quenches did not result in any observable change in the structure factor on experimental time scales. To expand the Q range over which nucleation could be observed, blend B5 was first quenched from the single-phase regime to $Q = 1.06$ and held there for 100 min; this was followed by a decrease in pressure to obtain a lower final Q. Q values between 0.93 and 0.36 were accessed by these two-step quenches. The methodology for obtaining q_c from the two-step quenches was quite similar to that used for the one-step quenches.[28] The squares and circles in Figure 3 show the dependence of the experimentally determined critical nucleus size on Q, obtained from two-step and one-step quenches, respectively. The ordinate in Figure 3, R^*, is the size of the critical nucleus normalized by the radius of gyration of the chains, R_g, which, as mentioned above, was 15.4 ± 1 nm for the chains studied here. That is, $R^* = 2\pi/(q_c R_g)$. At quench depths where both one- and two-step quenches were conducted ($0.60 \leq Q \leq 0.93$), the values of R^* obtained from the two types of experiments are in quantitative agreement (Figure 3). The two-step quenches, however, substantially widen the Q window over which nucleation in our polymer blends can be studied. The experiments clearly show that R^* is a monotonically decreasing function of quench depth over the entire accessible experimental window.

To compare the scaling of critical nucleus length scales with experiment, we determine a kinetic spinodal in the Ising model. That is, we find the field h_s that characterizes the boundary between long-lasting and short-lived metastable states, which we do as follows.[29] We compute the nonequilibrium relaxation function

$$\mu(t) = \frac{\langle m(t) \rangle - \langle m(\infty) \rangle}{\langle m(0) \rangle - \langle m(\infty) \rangle} \qquad (3)$$

at different values of the field, h. Here, $m(t)$ is the magnetization, or sum over all spins, of the Ising model at time t, and the angled brackets denote a nonequilibrium average of $m(t)$ given that the system starts in a metastable state where the spins point against the field. We define the decay time of the relaxation function, τ_R, as the time where $\mu(\tau_R) = 1/e$. We then determine the field at the spinodal, h_s, as the field where this $1/e$ decay time is approximately 100 sweeps. The inset of Figure 3 shows τ_R at different values of the field, which gives $h_s/J = 0.75$ for h_s so defined.[30] The location of phase coexistence (i.e., the binodal) for the Ising model occurs at zero field. We thus define the theoretical quench depth, Q, as

$$Q = \frac{h - h_b}{h_s - h_b} = \frac{h}{h_s} \qquad (4)$$

The pluses in Figure 3 show the dependence of the normalized critical nucleus size determined from the Ising model, R^*, on quench depth, Q. For the Ising model simulations, we define $R^* = 1.5\,R_c$; the normalization constant was determined by scaling the size of R_c for the Ising model such that the data agreed with experiments. This numerical factor, or parametrization, is due to coarse graining a polymer blend to an Ising magnet. With this factor, the dependence of the normalized critical nucleus size of quench depth obtained from the simulations is in good agreement with the experimental data. At higher field values where $Q > 1$, the large majority of the Ising spins align with the field after one sweep or less, and the concept of a critical nucleus becomes ill-defined. That is, on the time and length scales that we are probing here, the critical nucleus may only be 1−2 cells and appear at times less than one full sweep at quench depths greater than $Q = 1$. No evidence of a diverging length scale at $Q = 1$ is seen in either simulation or experiment. In fact, the value of R^* at $Q = 1$ is about 5 for the polymer blend system. We cannot estimate the free energy barrier for nucleation in the experimental system because we have not yet determined the composition of the critical nuclei. However, the simulation results show that the free energy barrier for forming critical nuclei with $R^* \approx 5$ near the spinodal is of order $k_B T$.

To summarize, our neutron scattering from polymer blends and computer simulations of Ising magnets show that time-resolved structure factors of metastable systems can be used to measure the critical nucleus size over a broad range of quench depths. Contrary to prevailing thought, our results indicate that the critical nucleus size decreases monotonically with increasing quench depth. The striking similarity in the behavior of polymer blends and Ising magnets and the fact that many physical systems map onto the Ising model (e.g., binary liquid mixtures, simple fluids near the liquid−gas transition, ferromagnets, superconductors, superfluids, etc.) suggest that our description of the nucleation of new phases may be applicable to diverse materials of practical importance.

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(30) Different values of h_s change the rescaling factor used to determine R^* from R_c for the Ising model as well as change the proximity of the simulation points to $Q = 1$ but do not change the agreement with the experimental scaling.

(31) Disclaimer: Certain commercial equipment, instruments, or materials (or suppliers or software) are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.