

# Modeling arrested cluster growth in quenched nanoparticle solutions

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We have carried out numerical simulations on a model of phase separation in a binary mixture in the presence of a third, surface-active component. Based on this model we study phase separation in a quenched solution of gold nanoparticles with dodecane thiol ligands in a mixed solvent of butanone and toluene. In our model gold nanoparticles–butanone correspond to the generic binary mixture, while toluene is modeled as a surface-active third component. Our results show that the surface-active component acts as an inhibitor for the phase separation process but its effect decreases with the increase in quench temperature. Simulation results are consistent with two major findings in recent experiments: (a) growth of gold nanoparticle clusters gets arrested at late times and (b) the saturation value of the cluster size is smaller at lower temperatures of quench. © 2008 American Institute of Physics. [DOI: [10.1063/1.2953323](https://doi.org/10.1063/1.2953323)]

## I. INTRODUCTION

Recent advances in synthetic chemistry have given rise to a wide variety of nanoparticles (NPs) with a high degree of both chemical and physical uniformities.<sup>1–4</sup> These NPs are surface ligated with a variety of organic compounds and the ligands cause colloids of the NPs to be stable against irreversible aggregation. Often these colloids act as solutions with the NPs displaying temperature and solvent dependent solubility. Also in many cases the precipitating solid is a two- or three-dimensional superlattice of the NPs.<sup>5,6</sup> A detailed understanding of the interactions between NPs is needed to control the self-assembly of NPs into two-dimensional superlattices, wetting layers, and films on surfaces, aggregation to a variety of ramified aggregates, gels, and three-dimensional superlattices. Only recently however, experimental studies have been directed to explore and understand NP solution and interfacial behavior and how these solutions can be used to create self-assembled structures and ordered networks of NP compounds.

Recent light scattering experiments<sup>7</sup> suggest a complex phase behavior and arrest of growth in quenched gold NP solutions. Arrested cluster growth has drawn recent attention in various colloidal and protein solutions.<sup>8–15</sup> Experimental studies find the formation of stable cluster phases in both depletion colloids and in salted protein solutions. If the colloids or proteins contain residual unscreened charges, then one can understand the formation of equilibrium clusters resulting from the competition of short-range attractions and long-range repulsions.<sup>12</sup> However, recent experiments which sufficiently screen Coulomb repulsions still observe the formation of a long-lived cluster phase.<sup>9</sup> A possibility is that the nucleation and growth of clusters can be self-limiting, leading to a cluster fluid phase.<sup>13,14</sup> This is closely related to the proposed mechanism of a cluster phase by Lu *et al.*,<sup>9</sup> where

the time scale of rearrangement of particles on the surface is different from the diffusive time scales of clusters moving away from each other. Gold NPs with dodecane thiol ligands are stable at room temperatures in toluene or *t*-butyl-toluene. If a small amount of such a solution is added to a larger amount of a different solvent such as butanone, gold NPs start forming clusters in solutions. One expects such a behavior as butanone is a much poorer solvent for the dodecane ligands when compared to toluene. It was found in recent experiments<sup>7</sup> that the size of the gold NP clusters quickly increased with time and saturated at a finite value after a temperature quench from the one- to the two-phase regime. In addition, the saturation value of the cluster size was smaller for deeper quenches, i.e., for lower temperature quenches (see Fig. 1 for a quick survey of relevant, experimental results).

In this paper, we focus on theoretical modeling of two important aspects of the light scattering experiments: cluster size as a function of quench depth and the arrested cluster growth after a temperature quench. We view the experimental system as having three components: the ligated NPs, the butanone, and the toluene. The NPs and the butanone mix poorly and the toluene mixes well with both and hence can act as a liaison between each, much, like a surfactant. Thus to model the kinetics of phase separation we revisit a model<sup>16</sup> originally proposed to study liquid-liquid phase separation in the presence of surfactants. In the model considered here the surfactants stay at the interface between two liquids. Arrested cluster growth is found as the interfacial tension is lowered by the presence of surfactants. However, the model does not consider the intermolecular structure of the surfactants and, thus, is somewhat ill suited to deal with surfactants.<sup>17</sup> For the mixed solvent case under study, however, such a model might be quite useful. When a small amount of NP solution in toluene is mixed with a larger amount of a poor solvent such as butanone and the whole system is quenched to a lower temperature, it is expected that

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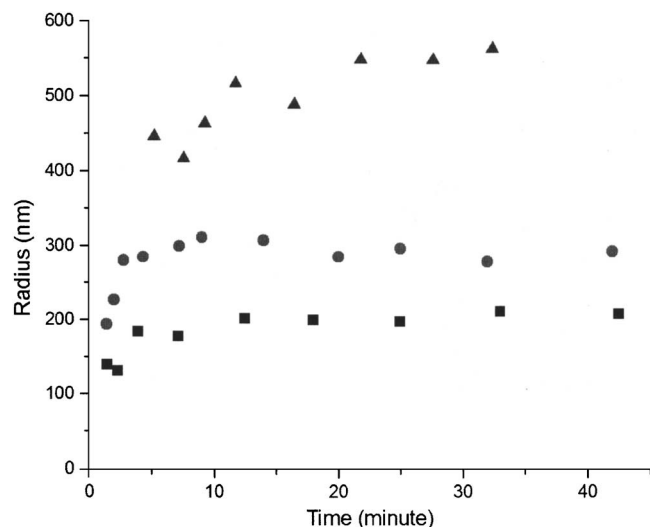


FIG. 1. Average radius of clusters computed from dynamic light scattering experiments (Ref. 7) plotted against time after quench for various quench temperatures. Gold NPs ligated with dodecanethiol samples (gold concentration: 0.0332 mg/ml, solvent mixture: 40 ml *t*-butyl toluene+960 ml 2-butanone) were quenched from 65 °C (single phase) to 25 °C (square), 35 °C (circle), and 45 °C (triangle), respectively.

the toluene, being a good solvent for the ligated NPs, would wet the ligand layer and stay at the interface. Since one can ignore intermolecular structure of toluene in a coarse-grained model, the previously mentioned model<sup>16</sup> should work quite well for this physical system. However, one must add a thermal noise term in the model to study cluster growth for various temperatures of quench. Effects of such a thermal noise term is critical for the present study but has not been considered in any previous work.

The rest of the paper is organized as follows. In Sec. II, we discuss the model and the numerical procedure. In Sec. III, we present our simulation results and, finally, in Sec. IV, we conclude with a brief summary and discussion of our results.

## II. MODEL AND NUMERICAL PROCEDURE

We consider a coarse-grained model with two scalar fields representing the order parameter of a binary mixture and the concentration of a surface-active third component. In this phenomenological approach the concentration field  $\phi(\vec{r}, t)$  is chosen to be the local concentration difference between the two components of the binary mixture, and  $\rho(\vec{r}, t)$  describes the concentration of the surface-active third component. Following Laradji *et al.*,<sup>16</sup> we write the system's free-energy functional (in units of  $k_B T$ ) as

$$F[\varphi(\vec{r}, t), \rho(\vec{r}, t)] = \int d\vec{r} [-r\varphi^2 + u\varphi^4 + K(\vec{\nabla}\varphi)^2 - s\rho(\vec{\nabla}\varphi)^2 + g\rho^2\varphi^2 + a\rho^2], \quad (1)$$

where  $r$ ,  $u$ ,  $K$ ,  $s$ ,  $g$ , and  $a$  are positive constants below the critical temperature. The first three terms in the model correspond to a Landau–Ginzburg form for the order parameter

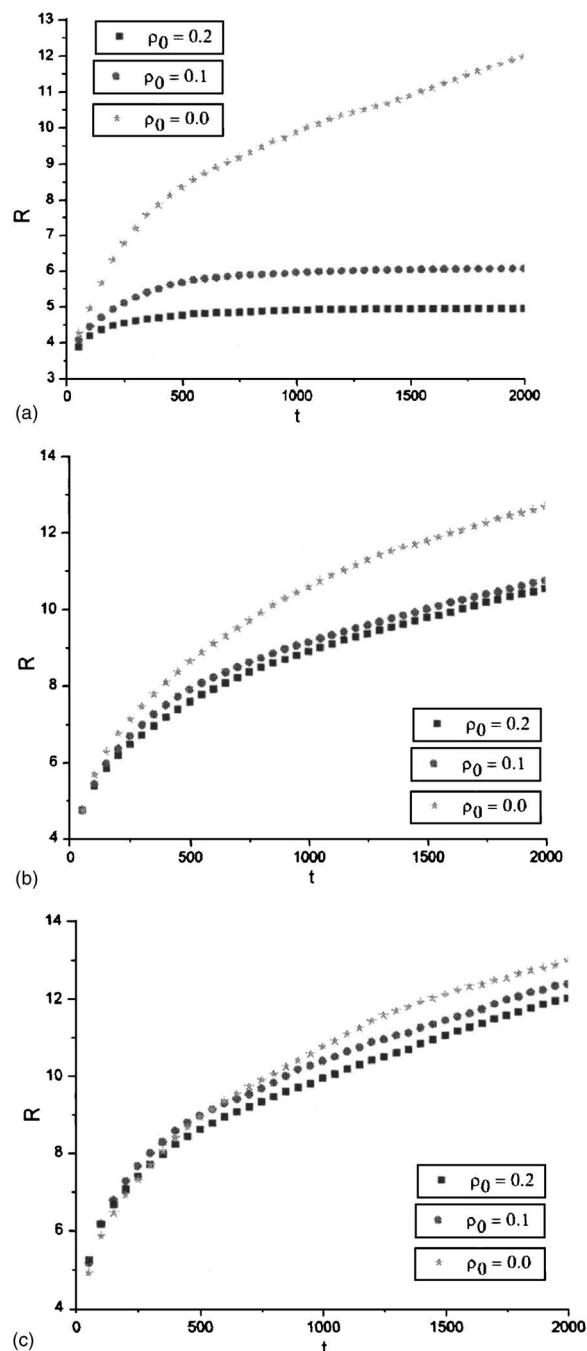


FIG. 2. (a) Kinetics of the phase separation process for a quench to  $\varepsilon=0.0$  for different concentrations of the surface-active component  $\rho_0$ . Domain growth gets completely arrested for nonzero values of  $\rho_0$ ; the larger the concentration of the surface active component, the smaller the saturation domain size. (b) Same as in (a) except for  $\varepsilon=0.1$ . At this higher temperature of quench, domain growth is slower in the presence of the surface-active component but depends weakly on its concentration. (c) Same as in (b) but for an even higher temperature of quench,  $\varepsilon=0.2$ . Here, domain growth is weakly perturbed by the presence of the surface-active component and no saturation in domain size seems to take place within the simulation time.

of the binary mixture, while the fourth term preferentially forces a concentration of  $\rho(\vec{r}, t)$  at the interface between different values of  $\varphi(\vec{r}, t)$ . The last two terms in the free-energy functional provide a minimum coupling between the two concentration fields.

The dynamical evolution after a quench from a high temperature disordered state to a final temperature below the

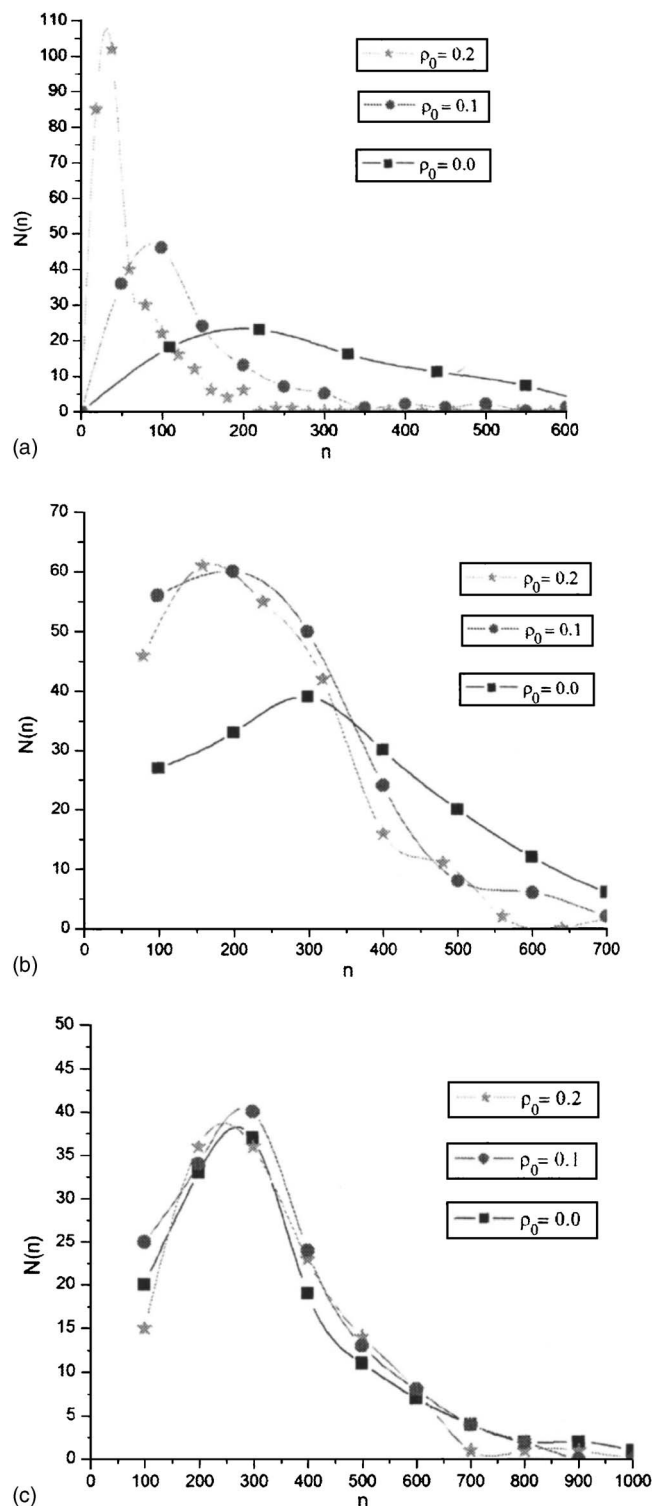


FIG. 3. (a) Cluster size distribution at the final simulation time corresponding to a quench depth  $\varepsilon=0.0$ . Note that the peak of the cluster size distribution shifts to smaller values of cluster size as the concentration of the surface-active component  $\rho_0$  is increased. This is consistent with the kinetics of domain growth observed in Fig. 2(a). The solid lines are guide to the eye. (b) Same as in (a) except for a quench temperature  $\varepsilon=0.1$ . The effect of the concentration of surface-active component  $\rho_0$  on the cluster size distribution is much weaker here than in Fig. 2(a) and gets totally washed out at a higher temperature of quench,  $\varepsilon=0.2$  [Fig. 1(c)]. The solid lines are guide to the eye. (c) Same as in (a) except for an even higher quench temperature  $\varepsilon=0.2$ . The effect of the concentration of surface-active component  $\rho_0$  on the cluster size distribution gets totally washed out at this high temperature of quench. The solid lines are guide to the eye.

critical temperature is modeled by the Cahn–Hilliard—type equation.<sup>18</sup> The equations of motions for the two scalar fields are given by

$$\frac{\partial \varphi}{\partial t} = M_1 \nabla^2 \frac{\delta F}{\delta \phi} + \xi_1,$$

$$\frac{\partial \rho}{\partial t} = M_2 \nabla^2 \frac{\delta F}{\delta \rho} + \xi_2,$$

respectively. The thermal noise for either variable satisfies

$$\langle \xi(\vec{r}, t) \xi(\vec{r}', t') \rangle = -2Mk_B T \nabla^2 \delta(\vec{r} - \vec{r}') \delta(t - t').$$

In our simulations, we consider the following values for the parameters:  $r = \frac{1}{2}$ ;  $u = \frac{1}{4}$ ;  $K = \frac{1}{2}$ ;  $s = \frac{1}{4}$ ;  $g = \frac{5}{2}$ ; and  $a = \frac{1}{4}$ . After a suitable rescaling of time and space,<sup>19</sup> the dynamical equations can be written in a simple dimensionless form as

$$\frac{\partial \phi}{\partial t} = \nabla^2 \left\{ -\phi + \phi^3 - \nabla^2 \phi + \frac{\rho}{2} \nabla^2 \phi + 5\rho^2 \phi + \frac{1}{2} \rho^2 \right\} + \xi_1,$$

$$\frac{\partial \rho}{\partial t} = \nabla^2 \left\{ -\frac{1}{4} (\nabla^2 \phi)^2 + 5\rho \phi^2 + \frac{1}{2} \rho \right\} + \xi_2.$$

The rescaled noise terms now have the following correlations:

$$\langle \xi(\vec{r}, t) \xi(\vec{r}', t') \rangle = -\varepsilon \nabla^2 \delta(\vec{r} - \vec{r}') \delta(t - t'),$$

where  $\varepsilon$  is a parameter corresponding to the strength of the noise term.

We numerically integrate the above equations in a two-dimensional systems of size  $L \times L$ , with  $L=256$ . We consider two possible values for the average concentration of the surface-active component  $\rho_0$ :  $\rho_0=0.1$  and  $\rho_0=0.2$ ; while the average concentration of the binary mixture is  $\phi_0 = \langle \phi \rangle = 0.25$  which corresponds to an *off-critical* system with 62.5:37.5 ratio. We probe the effect of temperature in the growth process by considering three values of  $\varepsilon$ :  $\varepsilon=0.0$ ,  $\varepsilon=0.1$ , and  $\varepsilon=0.2$ . As  $\varepsilon$  is increased, the quench temperature is increased. For these choices of  $\varepsilon$ , the system remains in the two-phase region.<sup>20</sup> As a measure of domain size at some time  $t$  after the quench, we compute the location of the first zero<sup>21</sup> of the (spherically averaged) equal-time correlation function  $g(\vec{r}, t) = \langle \phi(\vec{r}', t) \phi(\vec{r} + \vec{r}', t) \rangle - \langle \phi \rangle^2$ .

### III. RESULTS

In our numerical simulations we consider the butanone-gold NP mixture as the binary mixture, with toluene as the surface-active third component. In Figs. 2(a)–2(c) we show the kinetics of domain growth for various temperatures of quench. For a very deep quench, corresponding to  $\varepsilon=0.0$ , we find that domain growth gets arrested as the concentration of the surface-active component  $\rho_0$  increases from zero [Fig. 2(a)]. The saturation domain size is smaller as  $\rho_0$  is increased. At a higher temperature of quench  $\varepsilon=0.1$ , domain growth is slower in the presence of the surface-active component but depends weakly on its concentration [Fig. 2(b)]. At even higher temperature of quench,  $\varepsilon=0.2$ , domain



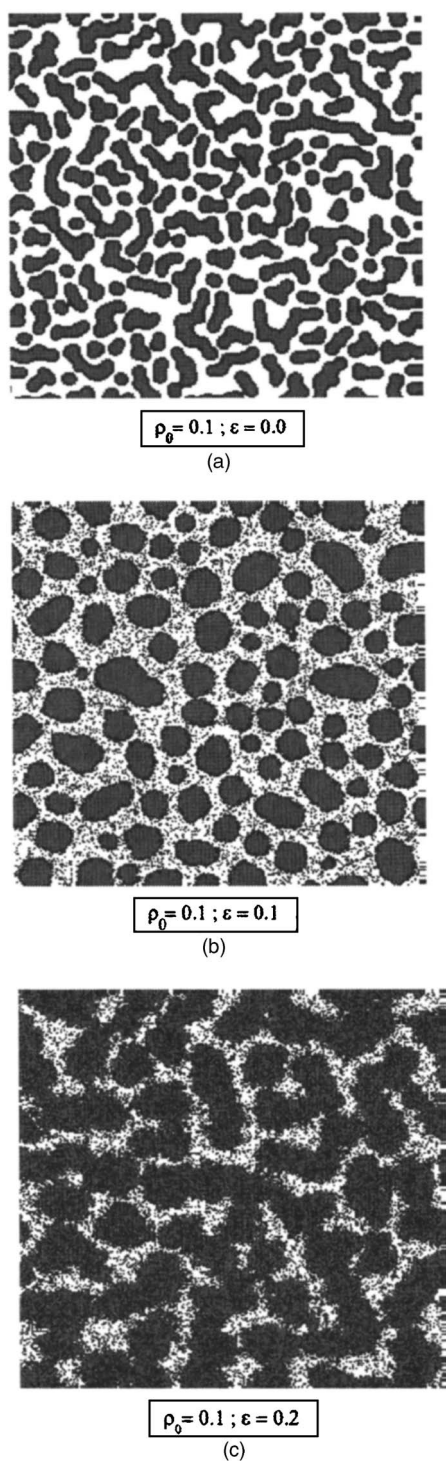


FIG. 4. (a) Snapshot at the final simulation time for temperature of quench  $\varepsilon=0.0$ , and the concentration of the surface-active component  $\rho_0=0.1$ . In this figure, gray and white are the two phases of the binary mixture and black shows the concentration of the surface-active component. The surface-active component is predominantly at the interface between the two components of the binary mixture and domain growth gets arrested [see Fig. 2(a)]. (b) Snapshot of the whole system for a higher temperature of quench  $\varepsilon=0.1$ . Now, some of the surface-active component remains at the interface between the two components of the binary mixture but part of it is dispersed throughout both the bulk phases due to entropic reasons. (c) Snapshot of the whole system for an even higher temperature of quench  $\varepsilon=0.2$ . Now the surface-active component is almost uniformly dispersed through the system and loses its effectiveness to reduce the interfacial tension between the two bulk phases. As a result domain growth continues and no saturation in domain size is observed in Fig. 2(c).

growth is weakly perturbed by the presence of the surface-active component and no saturation in domain size seems to take place within the simulation time.

In Figs. 3(a)–3(c) we show the cluster size distributions corresponding to three different temperatures of quench mentioned earlier. Here  $N(n)$  is the number of clusters of size  $n$  at the final simulation time. For deeper quenches (such as  $\varepsilon=0.0$ ), the peak of the cluster size distribution shifts to smaller values of cluster size as the concentration of the surface-active component is increased. This is consistent with the kinetics of domain growth observed in Fig. 2(a). The effect of the concentration of surface-active component on the cluster size distribution is weaker in Fig. 3(b) and gets totally washed out at a higher temperature of quench,  $\varepsilon=0.2$  [Fig. 3(c)]. To understand the reason for the diminishing effect of the surface-active component on slowing down the domain growth kinetics as the temperature of quench is increased, we show several snapshots of the system next for  $\rho_0=0.1$ . Results are similar for  $\rho_0=0.2$ . In Fig. 4(a) a snapshot at the final simulation time is shown for temperature of quench  $\varepsilon=0.0$  and the concentration of the surface-active component  $\rho_0=0.1$ . In this figure, gray and white are the two phases of the binary mixture, and black shows the concentration of the surface-active component. Note that at this low temperature quench, the surface-active component stays predominantly at the interface between the two components of the binary mixture.

Next, we look at the snapshot for a higher temperature of quench  $\varepsilon=0.1$  in Fig. 4(b). Now, some of the surface-active component remains at the interface between the two components of the binary mixture but part of it is dispersed throughout both the bulk phases. As the confinement of the surface-active phase to the interface is unfavorable for entropic reasons, the concentration of this third phase gets more dispersed as the temperature of quench is increased.

The entropic contribution is even more prominent when the temperature of quench is increased to an even higher temperature  $\varepsilon=0.2$ . This is shown in the snapshot in Fig. 4(c). Now the surface-active component is almost uniformly dispersed through the system and loses its effectiveness to reduce the interfacial tension between the two bulk phases. As a result domain growth continues and no saturation in domain size is observed.

#### IV. SUMMARY AND CONCLUSIONS

We have carried out detailed numerical simulations on a model of phase separation in a binary mixture in the presence of a third surface-active component. Our goal is to model phase separation in a quenched solution of gold NPs with dodecane thiol ligands. In particular, we would like to investigate the experimental situation where a small amount of gold NP solutions in a relatively good solvent such as toluene or *t*-butyl-toluene is added to a larger amount of a poor solvent such as butanone. In our model then NP-butanone corresponds to the generic binary mixture, while toluene is modeled as a surface-active third component.

Recent experimental studies of such a ternary system show a complex phase behavior and kinetics of growth after

a rapid quench from a high temperature to a lower temperature. In our simple model, however, we focus on two major aspects of the experimental results: (a) growth of gold NP clusters gets arrested at late times and (b) the saturation value of the cluster size is smaller at lower temperatures of quench.

Simulation results from this simplified model qualitatively agree with experimental findings. We find that at low temperatures, the surface-active component (toluene) stays predominantly at the interface between the two components of the binary mixture and effectively inhibits domain growth. However, as the quench temperature is increased, the confinement of the surface-active phase to the interface of the binary mixture becomes more and more unfavorable for entropic reasons. Thus the saturation domain size increases with increasing temperature of quench.

The model free-energy functional used in this study was proposed by Laradji *et al.*<sup>16</sup> to model the phase separation in binary mixtures in the presence of surfactants. In the work of Laradji *et al.*, no thermal noise is used, and it was argued that thermal noise is not to change the dynamics significantly. However, as we show in our work, thermal noise changes the dynamics of the system substantially. In the absence of thermal noise, the surface-active component accumulates at the interface and cluster growth gets arrested. This is a zero temperature scenario valid for a very deep quench in experimental situations. But, when the system is quenched at a higher temperature (this can only be modeled by adding a thermal noise to the simulation), the entropic penalty for being confined to the interface results into a large free-energy cost. Thus, the surface-active component starts leaving the interface as the quench temperature is increased. This is the mechanism for observing larger saturation cluster sizes in experiments (Fig. 1) at higher quench temperatures. These phenomena cannot be explained if no thermal noise is included in the simulation. Thus the inclusion of thermal noise in the model is essential for explaining experimental observations.

Although our numerical simulations are carried out in two dimensions, we believe that the main conclusions of the

simulations will be applicable in three dimensions as well if one incorporates thermal noise in the simulations. The model considered in this paper treats the third component or toluene just as a surface-active component. This is definitely an oversimplification. Future studies should consider different degrees of interaction between NP and the two solvents (butanone and toluene) explicitly. Such a study is underway.

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