Cahn-Hilliard Simulation

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Introduction

When a two-phase mixture in its homogeneous phase is quenched below the critical coexistence temperature, it becomes thermodynamically unstable and evolves towards a new equilibrium state, consisting of regions which are rich in one or the other constituents of the mixture *[1]*. In this situation, nuclei of the minority phase are formed. Then, on a slower timescale, the spatial regions of the separated material begin to grow. This process is called "coarsening". The Cahn-Hilliard model describes how the concentration of the constituents diffuse through the system. In this model the basic ingredient is a conserved concentration field, $\psi(\mathbf{r},t)$, representing the difference in concentration of the two components of the mixture. Two examples are the segregation of a binary alloy or the separation of two-component fluid like oil and water. One prediction is that the characteristic domain size obeys the Lifshitz-Slyozov (LS) relation $R(t) \sim t^{1/3}$, where $R(t)$ is a characteristic domain size and t is the time.

Numerical simulations carried out by Prof. Timothy Sullivan in the Department of Physics at Kenyon College and Prof. Peter Palffy-Muhoray at Kent State University's Liquid Crystal Institute revealed that for some compositions of the mixtures in a system, the LS relation does not hold even at late time*[2]*. Numerical simulations were carried out on a system with various concentrations of the two components for initial conditions with a random distribution using a standard deviation of 0.5. This paper is the follow up of this investigation for initial conditions with random distribution using the standard deviation of 0.001 to see how the standard deviation affects the results.

Cahn-Hilliard model & Data Analysis Procedure

The dimensionless Cahn-Hilliard(CH) equation can be expressed as :

$$\frac{\partial \psi}{\partial t} = \frac{1}{2}\nabla^2(-\psi - \nabla^2\psi + \psi^3), \qquad (1)$$

where ψ is the dimensionless local difference in concentration between the two components of the system. We denote the average value of ψ at the initial condition as $\langle\psi\rangle_o$.

The structure formation in the system during the phase separation process is analyzed in terms of the normalized time-dependent structure factor s(**k**,t):

$$s(\mathbf{k},t) = \frac{S(\mathbf{k},t)}{\langle\psi^2(\mathbf{k})\rangle - \langle\psi\rangle^2} = \frac{\langle\frac{1}{N}\sum_{i,j}\exp^{-i\mathbf{k}\cdot[\psi(i,t)-\psi(j,t)]}|F|^2\rangle}{\langle\psi^2(\mathbf{k})\rangle - \langle\psi\rangle^2} \qquad (2)$$

The pair correlation function G(**r**,t) was calculated by taking the Fourier Transform of s(**k**,t):

$$G(\mathbf{r},t) = \frac{1}{N}\sum_{r'}[\psi(\mathbf{r}+\mathbf{r}',t)\psi(\mathbf{r}',t) - \langle\psi\rangle^2] \qquad (3)$$

The first zero of the circularly averaged pair correlation function, $R_G(t)$, was taken to be the characteristic length of the pattern. Finally $R_G(t)$ was fitted to the form:

$$R_g(t) = at^b + c \qquad (4)$$

at each $\langle\psi\rangle$o, where a, b and c are the constants determined by the fits.

The classical Lifshitz-Slyozov (LS) relation predicts that $R_G(t) \sim t^{1/3}$ if the system is in the scaling regime. For different $\langle\psi\rangle_o$ the scaling regime is reached at different times. The process of phase separation is faster at the beginning and slower at later time, which the R_G function does not represent explicitly. Thus we need a quantity independent of the domain size which can represent the structure of the minority component regions in a better way. To achieve this, the concept of a "moment ratio" was investigated*[3]*. To determine whether the system was in the scaling regime, the "moment ratio" was calculated by taking the ratio of the moment of inertia of the actual blob to the moment of inertia of a circular disk with an area equal to that blob. Then η was defined as: η = Moment ratio – 1, which is a measure of the non-circularity of a blob. By observing the change of η as a function of time, we can determine the scaling regime. For our experiment, the data was defined to be in the scaling regime if it satisfied the condition: $\eta = \eta + 0.1\ \eta_o$, where η_o is the value of η at t = 200000. The fit for $R_G(t)$ was then restricted to the scaling regime and the value of b($\langle\psi\rangle_o$) was determined at each $\langle\psi\rangle$o.

Time evolution of the minority region forms extended blobs for values of $\langle\psi\rangle_o$ near the critical quench but forms circular blobs for values further from the critical quench. For $\langle\psi\rangle_o$ near the critical quench, the value of η does not reach 0 in a finite time as the blobs don't really form circular pattern, while for greater $\langle\psi\rangle$o, the value of η reaches near to 0 in finite time. To investigate the transition of these two regimes as $\langle\psi\rangle_o$ changes from 0 to 1, we calculated the value of η_o = at t $\rightarrow\infty$ (∞ = 200000 in our case) for each $\langle\psi\rangle_o$ By looking at the graph of η_o as a function of $\langle\psi\rangle_o$ we can determine the region where the transition between the two regimes occur.

For our numerical simulations, the two-dimensional CH equation was solved for various values of ψ_o from 0 to 0.5. Eq(1) was discretized using the forward-time, centered-space (FTCS) scheme. The algorithm was coded in C and C++. The grid size in space was 540 x 540 with step one in dimensionless length. Simulations on a grid size of 100 x 100 and 50 x 50 were also carried out for $\langle\psi\rangle_o$ = 0, 0.2, and 0.5 to see the effect of the domain size on the time evolution of the minority region. For reasons of stability, the time step used was Δ t = 0.001 for 0 $\leq$ t $\leq$ 100, Δ t = 0.025 for 100 $\leq$ t $\leq$ 1000, and Δ t = 0.04 for t > 1000. Periodic boundary condition were used for all the simulations.

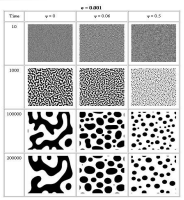

Fig. 1 Example patterns of minority region (in black) as a function of ψ_o and time for σ = 0.001.

In each case, the initial conditions were created by assigning each node a value of ψ chosen using a Gaussian distributed random number generator with mean value $\langle\psi\rangle_o$ and a standard deviation of σ. For each $\langle\psi\rangle_o$, 60 different random initial conditions were created and the 2D CH equation was solved for each condition.

Independently the sixty sets of data were analyzed. For each composition the data were collected at a time interval of 1000 for t $\leq$ 20000, at an interval of 2000 for 20000 < t $\leq$ 100000 and 5000 for t > 100000. To investigate the effect on the time evolution due to the difference in standard deviation of the random distribution at the initial condition, simulations were carried out at different σ for a given $\langle\psi\rangle_o$. For $\langle\psi\rangle_o$ = 0, 0.2, 0.5, simulations were carried out for σ= 0.001, 0.01, 0.1, 0.2, 0.5 up to a dimensionless time of 20,000. For $\langle\psi\rangle_o$ = 0, 0.025, 0.05, 0.06, 0.075, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5 (all at σ = 0.001), simulations were run for a dimensionless time of 200000 to investigate the late time evolution of the minority regions.

Numerical Results

Figs. 1 and 2 show that the time evolution of the minority region forms extended blobs for values of $\langle\psi\rangle_o$ near the critical quench but forms circular blob for values further from the critical quench. For greater values of $\langle\psi\rangle_o$ circular blobs are formed at very early time while for $\langle\psi\rangle_o$ at critical quench even at t=200,000 the blobs are not close to becoming circular. This indicates that there is a critical value of $\langle\psi\rangle_o = \langle\psi\rangle_c$ such that the time evolution of the minority constituent in the system is determined by which side of $\langle\psi\rangle_c$ lies the given $\langle\psi\rangle_o$.

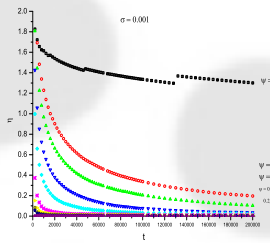

Figure 2. η *as a function of time.*

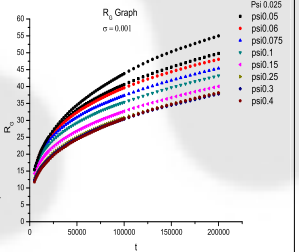

Figure 3. R_G *vs t for different ψ_o at σ = 0.001.*

Fig. 2 shows the value of η as a function of time for various $\langle\psi\rangle_o$. The measure of the non-circularity of the minority component, η, seems to follow a double exponential decay curve as a function of time. We can clearly see that the value of η for $\langle\psi\rangle_o$ at the critical quench is asymptotic to a non-zero value but for higher value of $\langle\psi\rangle_o$ the curve exponentially decays to zero. This confirms the evidence from Fig. 1 that the blobs for $\langle\psi\rangle_o$ less than $\langle\psi\rangle_o$ do not form circles in a finite time. For $\langle\psi\rangle_o$ greater than $\langle\psi\rangle_o$, the blobs do form isolated circles in finite time.

For each value of $\langle\psi\rangle_o$, the data in the scaling regime was fitted to Eqn 4 using the nonlinear Levenberg-Marquardt χ^2 minimization as implemented in the data analysis software package *Origin*. Fig 3 shows the fits to the data.

For smaller value of $\langle\psi\rangle_o$ the concentration of the minority component in the system is greater. Thus the characteristic length of the pattern, R_G is greater for smaller value of $\langle\psi\rangle_o$. Also notice that as the value for$\langle\psi\rangle_o$ gets larger the R_G graphs look similar.

Finally, the resulting fit exponent, b<(>ψ_o), was plotted against$\langle\psi\rangle_o$.

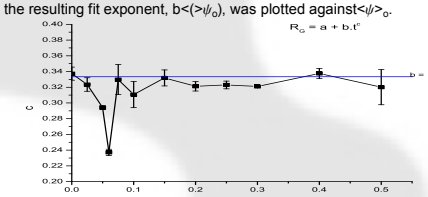

Figure 5.*b(<ψ>o) obtained from the fit of $R_G(t)$ to the form $R_G(t) = a\,t^b + c$.*

Fig. 4 shows that for 0.025 < $\langle\psi\rangle_o$ < 0.1, $R_G^{\psi}(t)$ does not follow the Lifshitz-Slyozov (LS) relation in the time interval over which the simulations were carried out. The largest deviation from LS relation is observed at $\langle\psi\rangle_o$ = 0.06, where b = (0.237 $\pm$ 0.001). This is evidence that there is a critical value of $\langle\psi\rangle_o$ above which the system quickly evolves to isolated circular blobs which grow in time. To further investigate this transition we now look at the moment ratio for each $\langle\psi\rangle_o$ as time goes to infinity (t = 200,000 in our case).

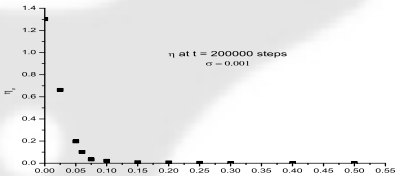

Figure 6 (η *at t = 200000 vs $\langle\psi\rangle_o$*

The rate of change of slope of the graph in Fig. 5 is maximum as $\langle\psi\rangle_o$ goes from 0.05 to 0.1. This is the region we see in Fig. 4 where $R_G(t)$ deviated most from the LS relation. This further indicates that there is a critical region of $\langle\psi\rangle_o$ which acts as a boundary for the two regimes.

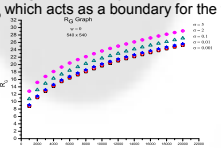

Figure 7. R_G *graph for different values of σ.*

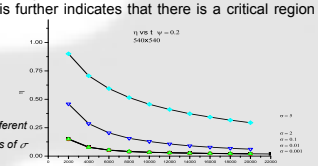

Figure 8 η *for different values of σ*

Figures 6 and 7 show the dependence of the time evolution on the standard deviation used for the random initial conditions. We can also see that for small values of σ the R_G graphs are similar. The moment ratio graph shows that the geometric structure of the blobs are similar at a given time for smaller σ. It also shows that the difference in the value of η for different σ is decreasing as the time increases. We could see that the moment ratio will eventually converge to a single asymptotic horizontal line for all σ at a given $\langle\psi\rangle_o$.

Discussion

One end of an oil molecule is hydrophilic while the other is hydrophobic. When two fluids with different chemical properties, such as oil and water, are mixed then the enthalpy of the homogeneous state is greater than the separated state. Under these conditions, infinitesimal variations in the local composition of the mixture lower its free energy and lead to phase separation. This is called spinodal decomposition which takes place at a very early stage of the separation process. In the initial decomposition, the two components separate into regions containing dominantly one type of fluid. In the late stage, surface tension is the driving force for domain coarsening.

The Lifshitz-Slyozov relation does not account for cluster correlations. For greater $\langle\psi\rangle_o$, the cluster interactions are reduced. So the LS prediction is more likely to be valid. For smaller $\langle\psi\rangle_o$, cluster interaction is stronger in the earlier stages, resulting in convoluted, noncircular domains (see Fig. 1). Thus, for different $\langle\psi\rangle_o$, the scaling regime is different. The scaling regime is the time interval where the blobs slowly grow in size rather than change shape. This is the region where the LS relation is expected to be valid. The measure of non-circularity, η, is used to determine the scaling regime during the phase separation. This is affected by the shape of the blob but not the size. Thus, the scaling regime is said to be reached if η stops changing with time.

Eqn. 1 assumes that the only force acting on the two components of the mixture is the inter-molecular force due to the difference in their local concentrations. Thus, the simulation of the CH equation requires that the size of the domain be infinitely large as compared to the blobs. For the grid size of 100x100 the periodic boundary condition influences the time evolution of the minority regions. For 540x540 grid size the boundaries had less effect. Thus the time evolution of the blobs follow the LS relation more closely. Also for the smalerl grid size, a smaller number of blobs are produced which quickly forms into a single blob making it more difficult to investigate the phase change statistically.

When σ is smaller, the blobs are concentrated into points at the initial time step. The average blob separation is large. Thus it takes some time for them to get organized into larger blobs. Whereas for larger σ the blobs at the initial time are more loosely packed and their outer layer can be easily attracted by the neighboring blobs. Thus, they quickly form larger blobs and grow faster in time as compared to the mixtures with smaller σ.

References:

[1] J.D. Gunton, M. San Miguel, and P.S. Sahni, *Phase Transitions and Critical Phenomena*, 1983, vol 8. p 267.

[2] Timothy S. Sullivan, Peter Palffy-Muhoray, "Late-time dynamical scaling in the dimensionless Cahn-Hilliard model" (unpublished).

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