EFFECT OF CONVECTION AND VISCOELASTICITY ON SPINODAL DECOMPOSITION IN FLUIDS

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Current analytical work on the effect of convection and viscoelasticity on the early and late stages of spinodal decomposition is briefly described. In the early stages, the effect of viscoelastic stresses was analysed using a simple Maxwell model for the stress, which was incorporated in the Langevin equation for the momentum field. The viscoelastic stresses are found to enhance the rate of decomposition. In the late stages, the pattern formed depends on the relative composition of the two species. Droplet spinodal decomposition occurs when the concentration of one of the species is small. Convective transport does not have a significant effect on the growth of a single droplet, but it does result in an attractive interaction between non - Brownian droplets which could lead to coalescence. The effect of convective transport for the growth of random interfaces in a near symmetric quench was analysed using an 'area distribution function', which gives the distribution of surface area of the interface in curvature space. It was found that the curvature of the interface decreases proportional to t in the late stages of spinodal decomposition, and the surface area also decreases proportional to t.

1 Introduction

The classical theories for spinodal decomposition, such as the Cahn - Hilliard theory for the early stages and the Lifshitz - Slyozov theory for droplet growth, were developed for metal alloys and for the magnetisation transition in solids. It might be expected that the decomposition is faster in liquids, due to the higher diffusion rates. However, there is experimental evidence to indicate that the decomposition process is qualitatively different due to convective effects and due to viscoelastic processes. For example,

1. It has been known for some time now from the experiments[1] and theoretical studies[2] that convection has an effect on the early stage growth of fluctuations in spinodal decomposition. However, some recent experiments by Wiltzius and Bates[3] indicate that the spinodal decomposition in viscoelastic fluids could be very different from that in simple fluids. In addition to the early, transition and late stage growth, there is an intermediate stage where the scaling laws are different from those predicted by current theories of spinodal decomposition. Viscoelastic effects have not been included in the current models for the spinodal decomposition of fluids.

- 2. In the late stages, the type of spinodal decomposition depends on the relative composition of the two species. For nearly symmetric mixtures, the coarsening takes place due to the motion of random interfaces. The characteristic length scale for these interfaces increases proportional to $t^{1/2}$ in solids undergoing a magnetisation transition[4, 5]. The scaling behaviour for fluids is very different, and it is found[6] that the characteristic length increases proportional to t. A qualitative explanation for this increase was provided on the basis of a capillary instability mechanism by Siggia[12], but a quantitative description of this growth process is still lacking.
- The experiments of Tanaka[8] on the droplet growth in late stage decomposition show that there is an attractive interaction between non - Brownian droplets, which could lead to the spontaneous approach and coalescence of these droplets in the late stages of spinodal decomposition.

In the present article, some analytical work on the early and late stages of spinodal decomposition related to the above issues is presented. For the early stage spinodal decomposition in viscoelastic fluids, Langevin equations which incorporate viscoelasticity are formulated, and these are solved using diagrammatic techniques to determine the effect of viscoelasticity on the rate of decomposition. The motion of random interfaces in the late stage is analysed using an 'area distribution function', which gives the fraction of area of the interface having a specified curvature. This is determined using conservation equations for the rate of change of curvature in the system, and predictions are made for the change in the average curvature as a function of time. The effect of convection on the late stage droplet growth and droplet interactions is also analysed.

2. Effect of viscoelasticity on early stage spinodal decomposition

In the early stage spinodal decomposition in simple fluids[2], the dynamics of the system is described using a coupled set of Langevin equations for the concentration and velocity fields in the fluids, which are similar to the model H equations[9] for a fluid with conserved order parameter in critical phenomena. These equations were modified[10] in order to include viscoelastic effects. The constitutive equation for the microscopic stress tensor was the simple Maxwell model with an additional noise source to satisfy the fluctuation dissipation theorem

$$(\tau \partial_t + 1)\sigma_{ij} = \mu(\partial_i v_j + \partial_j v_i) + \theta_{ij} \tag{1}$$

In the above equation, indicial notation has been used to represent vectors and tensors, $\partial_t \equiv (\partial/\partial t)$ and $\partial_i \equiv \partial/\partial x_i$, σ_{ij} is the stress tensor, v_i is the velocity field, μ is the viscosity of the fluid, τ is the relaxation time in the Maxwell model. Higher order derivatives in the corotational Maxwell model were neglected, since they represent higher order non - linear corrections to the stress field. The noise correlation θ_{ij} is chosen to satisfy the fluctuation dissipation theorem, and for this it is necessary to define a free energy for the system which includes both inertial and elastic effects. The appropriate free energy is the usual Ginzburg - Landau free energy with additional contributions due to the kinetic energy and elastic strain energy of the fluid

$$F = \int d\mathbf{x} \left[\frac{K}{2} (\partial_i \psi)^2 \right) - \frac{r}{2} \psi^2 + \frac{u}{4} \psi^4 + \frac{\rho}{2} v_i^2 + \frac{1}{4G} \sigma_{ij} \sigma_{ji} \right]$$
(2)

where $G = (\eta/\tau)$ is the shear modulus. Using the above definition of the free energy, the constitutive equation for the stress tensor can be recast in the form

$$\partial_t \sigma_{ij} = -G\tau^{-1} (\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl}) \frac{\delta F}{\delta\sigma_{lm}} + G(\partial_i v_j + \partial_j v_i) + \tau^{-1}\theta_{ij}$$
(3)

from which it is evident that the noise correlation is of the form

$$^{-2}\langle\theta_{ij}\theta_{lm}\rangle = 2TG\tau^{-1}\delta(\mathbf{x} - \mathbf{x}')\delta(t - t')(\delta_{il}\delta_{jm} + \delta_{im}\delta_{jl})$$
(4)

The equations for the concentration and the transverse component of the momentum are

$$\partial_t \psi(\mathbf{x}, t) = \lambda \partial_i^2 \frac{\delta F}{\delta \psi(\mathbf{x}, t)} - v_i(\mathbf{x}, t) \partial_i \psi(\mathbf{x}, t) + \zeta(\mathbf{x}, t)$$
(5)

$$\left[\partial_j \sigma_{ij}(\mathbf{x}, t) + \partial_i \psi \frac{\delta F}{\delta \psi}\right]_{\perp} = 0 \tag{6}$$

where inertial effects have been neglected in the momentum equation, and $[\ldots]_{\perp}$ represents the transverse component of the vector. The random noise $\zeta(\mathbf{x},t)$ is white and Gaussian with zero mean and the following second moment to satisfy the fluctuation dissipation theorem

 $\langle \zeta(\mathbf{x}, t)\zeta(\mathbf{x}', t')\rangle = 2T\Lambda \partial_i^2 \delta(\mathbf{x} - \mathbf{x}')\delta(t - t')$ (7)

It can be shown[10] that the above equations satisfy the necessary fluctuation dissipation relations, and that they reduce to the equations for a Newtonian fluid in the limit $\tau = 0$.

The momentum and stress equations can be combined to obtain an equation for the velocity

$$v_i(\mathbf{x},t) = (\tau \partial_t + 1) \int d\mathbf{x}' J_{ij}(\mathbf{x} - \mathbf{x}') \left[\partial_j \psi(\mathbf{x}',t) \frac{\delta F}{\delta \psi(\mathbf{x}',t)} \right]$$
(8)

where $J_{ij}(\mathbf{x} - \mathbf{x}')$ is the Oseen tensor

$$J_{ij}(\mathbf{x} - \mathbf{x}') = \frac{1}{8\pi\mu} \left[\frac{\delta_{ij}}{|\mathbf{x} - \mathbf{x}'|} + \frac{(x_i - x_i')(x_j - x_j')}{|\mathbf{x} - \mathbf{x}'|^3} \right]$$
(9)

This is inserted into the concentration equation, and solved using a diagrammatic perturbation expansion in order to determine the effect of the non linearities on the transport coefficient λ and the noise correlation.

The results of the analysis indicate that there is a significant increase in the rate of spinodal decomposition due to the elasticity of the fluid, and this increase is due to the presence of an additional contribution to the convective force in (8) (due to the term proportional to the relaxation time τ) which generates an increase in the fluid velocity. This additional fluid velocity increases the rate of separation of the two phases, and thereby hastens the decomposition process.

3. Coarsening of Random Interfaces

In the late stages of spinodal decomposition, the kind of structure formed depends on the relative concentrations of the two phases[11]. When there is a bicontinuous structure consisting of the two phases separated by a random interface. The growth of this interface in a fluid is determined by a balance between viscous stresses and the normal forces generated by surface tension, since fluid inertia is negligible. Using simple dimensional arguments, Siggia[12] obtained the scaling relation $l \propto t$, where l is the characteristic length scale and t is the time. This scaling law has been observed in experiments of near symmetric quenches[6]. A more quantitative description of this process can be obtained as follows.

The shape of an interface is determined by the 'principal curvatures' K_1 and K_2 , which are the extrema of the curvatures at any point of the interface, or by the magnitude $K = (K_1^2 + K_2^2)^{1/2}$ and the angle $\tan(\theta) = (K_2/K_1)$. The 'area distribution function' $A(K, \theta, t)$ of the interface is defined so that $A(K, \theta, t)KdKd\theta$ is the fraction of the interface having a curvature in the interval dK about K and $d\theta$ about θ at time t. The area distribution function changes due to a change in the curvature due to the normal motion of the interface, and a change in the surface area due to the tangential motion of material points along the interface. The conservation equation for the area distribution function is

$$\frac{dA}{dt} = -\frac{dK}{dt}\frac{\partial A}{\partial K} - \frac{d\theta}{dt}\frac{\partial A}{\partial \theta} + \frac{\partial_c A}{\partial t}$$
(10)

where $(\partial_c A/\partial t)$ is the rate of change of surface area due to the tangential motion of the interface. The conservation equation is further simplified by averaging over the coordinate θ if one is only interested in the variation of the curvature K

$$\frac{dA(K,t)}{dt} = -\frac{dK}{dt}\frac{\partial A(K,t)}{\partial K} + \frac{\partial_c A(K,t)}{\partial t}$$
(11)

To solve the above equations it is necessary to formulate constitutive relations for (dK/dt) and $(\partial_c A/\partial t)$. If one assumes that the only fluid properties affecting the motion of the interface are the viscosity μ and surface tension γ , and the only relevant length scale at a point on the interface is the inverse of the curvature, the constitutive relations have the form

$$\frac{dK}{dt} = -\frac{a_1\gamma K^2}{\mu} \quad \frac{1}{A}\frac{\partial_c A}{\partial t} = -\frac{a_2\gamma K}{\mu} \tag{12}$$

The conservation equation and the constitutive relations can be solved using a similarity variable $\eta = (a_1 \gamma K t / \mu)$ for the case where the area distribution function is a constant at t = 0.

$$A = A_0 (1 - \eta)^a \quad \text{for} \quad \eta \le 1$$

$$A = 0 \quad \text{for} \quad \eta \ge 1$$
(13)

where $a = (a_2/a_1)$. Therefore, the specific shape of the distribution function depends on the parameters a_2 and a_1 in the constitutive relations, but the rate of change of mean curvature and the area of the interface are both proportional to t^{-1} .

ature in the inbution function 4. Droplet interaction

The spinodal decomposition in a highly asymmetric mixture takes place due to the growth of droplets of the minority phase in a matrix of the majority phase. The earlier theories of droplet growth in fluids have identified two mechanisms^[8]

- 1. the diffusion mechanism, which involves the growth of droplets with radius larger than a critical value and the shrinking of droplets with radius smaller than this value due to diffusion of the dispersed phase through the matrix,
- 2. the coagulation mechanism, where droplets of different sizes undergoing Brownian motion collide and coalesce to give a larger droplet.

However, some recent experimental work by Tanaka[8] has shown that there is spontaneous coalescence even between non - Brownian droplets, and it was suggested that the coalescence may be due to the effect of the concentration gradients at the interface on the momentum equation. To study this effect, the interaction between a pair of droplets was examined in the limit where their separation is large compared to the droplet radius, and Brownian effects are negligible[13].

The model H momentum equation for the fluid in the absence of Brownian motion and fluid inertia is

$$\mu \partial_j^2 v_i + \left[\partial_i \psi \frac{\delta F}{\delta \psi} \right]_\perp = 0 \tag{14}$$

The second term on the left side of the above equation, which is reciprocal to the convective term in the concentration equation, has two contributions one due to the square gradient of the concentration field and the other due to the dependence of the free energy on the concentration. The latter does not contribute to the transverse component of the momentum field, and the equation (14) can be solved using the Landau - Ginzburg form of the free energy to obtain

$$v_i(\mathbf{x}) = \int d\mathbf{x}' J_{ij}(\mathbf{x} - \mathbf{x}') \left[-K \partial_i \psi(\mathbf{x}') \partial_j^2 \psi(\mathbf{x}') \right]$$
(15)

In the late stages of spinodal decomposition, the dominant contribution to the fluid velocity is from the interfacial region where the concentration gradients are sharp. In this region, the gradient of the concentration can be approximated as $\partial_i \psi = n_i \partial_z \psi$, where n_i is the unit normal to the interface and z is the coordinate normal to the interface. It turns out that the induced velocity is zero if the interface is at equilibrium, but it could be non - zero if the interface

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is moving due to the flux of solute across the interface. If the outward normal velocity of the droplet interface is $u(\mathbf{x}_s)$ at the point \mathbf{x}_s on the surface, the velocity induced in the fluid due to this motion is

$$v_i = -\int d\mathbf{x}_s J_{ij}(\mathbf{x} - \mathbf{x}_s) n_j(\mathbf{x}_s) \left(\frac{K(\Delta \psi)^2 u(\mathbf{x}_s)^2}{2D^2}\right)$$
(16)

where $\Delta \psi$ is the difference in the equilibrium concentration of the droplet and matrix, and D is the coefficient of diffusion.

The fluid velocity at any point is determined by carrying out the integral in (16) over the surface of the droplet. For a uniformly growing droplet with $u(\mathbf{x}_s)$ independent of \mathbf{x}_s , it can be shown that the fluid velocity is identically zero. However, if there is an interaction between two droplets, the flux at the interface of a droplet is not uniform, and the flux at points on the surface of the droplet facing towards the second droplet is smaller than at points facing away from the second droplet. In this case, it can be shown using a dipole approximation for the concentration field that there is a spontaneous motion of the equal sized droplets towards each other, and the velocity along the line of centers is

$$V = \frac{2Kc_s^2 RL_i}{3\mu L^3} \tag{17}$$

where L_i is the vector in the direction of the line joining the centers of the droplets, and c_s is the difference in concentration between the matrix and the surface of the droplet which drives the flux. The above analysis indicates that there is a spontaneous attractive motion of droplets towards each other provided there is a departure of the interface from its equilibrium profile, and there is a variation in the concentration at the surface of the interacting droplets. This provides an explanation for the spontaneous coalescence of non - Brownian droplets in the spinodal decomposition of a binary fluid.

5. Conclusions

Three analytical studies on the early and late stage spinodal decomposition were discussed in the present article. The salient results of these studies are

1. Viscoelastic effects were included in the dynamical equations for the early stage spinodal decomposition. The model H equations for a binary fluid have been modified to include viscoelastic effects, and the constitutive relation used for the stress tensor is the simple Maxwell equation. The resulting set of Langevin equations satisfy the fluctuation dissipation theorem, and reduce to the model H equations when the relaxation time in the Maxwell model is set equal to zero. The results of the analysis indicate that viscoelasticity tends to increase the rate of spinodal decomposition.

- 2. The coarsening of a random interface in a symmetric fluid mixture in the late stages was described using a 'curvature distribution function', which gives the probability that a differential surface area of the interface has a certain curvature. A conservation equation was written for the curvature distribution function, and this was solved using constitutive models for the rate of change of curvature and surface area. This model gives the scaling for the mean curvature as a function of time which is in agreement with experimental results.
- 3. The interaction between droplets in the late stage of spinodal decomposition was studied. It was found that a variation in the flux at the interface due to the droplet interaction could cause an attraction between the non Brownian droplets, thereby increasing the rate of coalescence in the late stages. This provides an explanation for earlier experimental observations which found that non Brownian droplets tend to attract and spontaneously coalesce in the late stages of spinodal decomposition.

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