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Self-assembled fluids with order-parameter-dependent mobility: The large-N limit

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Abstract. The effect of the order-parameter-dependent mobility, $\Gamma(\vec{\phi}) \propto (1 - g\frac{\vec{\phi}^2}{N})^\alpha$, on phase-ordering dynamics of self-assembled fluids is studied analytically within the large-N limit. The study is for quenching from an uncorrelated high temperature state into the Lifshitz line within the microemulsion phase. In the later stage of the ordering process, the structure factor exhibits multiscaling behavior with characteristic length scale $(t/\ln t)^{1/2(2\alpha+3)}$. The order-parameter-dependent mobility is found to slow down the rate of coarsening.

Keywords. Morphological instability; phase changes; nonequilibrium; irreversible thermodynamics.

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1. Introduction

The dynamics of self-assembled fluids such as mixtures of water, oil and surfactants have attracted considerable interest [1] as they display richer thermodynamic behavior than simple fluids [1,2]. These mixtures have a tendency to spontaneously form very complex structures. The variation of the surfactants' concentration may lead to either microemulsion phase, oil-rich or water-rich regions. Macromolecules like monopolymer blend and diblock copolymers also form such complex structures [3].

In the later stage of a coarsening process following a quench from uncorrelated high-temperature phase, it is well-established that in most systems the standard scaling exists [4]. By standard scaling, it is meant that, the structure factor $S(\vec{k},t) = L^d g(kL)$, where $g(kL)$ is the scaling function, $L(t) \sim t^{1/z}$ is the characteristic length scale in the system and z is the growth exponent.

A lot of studies have been done to find the effects of an order-parameter-dependent mobility [5–13] in phase separation. It has been argued that mobility of the form $\Gamma(\phi) = 1 - \phi^2$, where ϕ is the order parameter, is appropriate for deep quenches [5,14] and accounting for the effects of external fields such as gravity [6]. Simulational calculations have been done on phase separation kinetics [7] and block copolymers [8,9] with $\Gamma(\phi) = 1 - a_0\phi^2$. It was found that in the case of phase separation kinetics, for $a_0 = 1$, $z = 4$ instead of 3 which is the case for constant mobility, while for block copolymers $z = 5$ was obtained (note that in this case $z = 4$ for constant mobility). A different form of mobility, $\Gamma(\phi) = 1/[1 + \exp(\alpha\phi - \beta\phi^2)]$, where both α and β are positive (with $\beta > \alpha$) was used by Ahluwalia [10] in simulating the Cahn-Hilliard model of phase separation. The domain patterns in this case were found to be similar to the ones observed in viscoelastic phase separation. Recently, a Monte Carlo study has been done to study phase separation in kinetic Ising model where the coarsening is mediated by surface diffusion [15]. Here the order-parameter-dependent mobility effectively eliminates bulk diffusion leading to coarsening by surface diffusion.

For an N-vector order parameter, simulational calculations [11] with $\Gamma(\vec{\phi}) = 1 - a_0\vec{\phi}^2/N$ for $N = 2$, 3 and 4, show a cross-over from $z = 6$ to $z = 4$ for $a_0 < 1$, while for $a_0 = 1$, $z = 6$. Emmott and Bray [12,13] considered a more general expression for the mobility given by $(1 - \vec{\phi}^2)^\alpha$, where α is a positive real number. For scalar fields [12] in the Lifshitz–Slyozov limit, the growth exponent was found to be $z = 3 + \alpha$, for vector fields [13] within the large-N limit, $z = 2(1 + \alpha)$ for nonconserved order parameter while for conserved order parameter, multiscaling was found with length scales $t^{1/2(2+\alpha)}$ and $k_m^{-1} \sim (t/\ln t)^{1/2(2+\alpha)}$. It is evident that different forms of mobility are used depending on the type of problem concerned.

n this paper we are mainly interested in the dynamics of the self-assembled fluids within the large-N limit with an order-parameter-dependent mobility of the form

$$\Gamma(\vec{\phi}) = \left(1 - g\frac{\vec{\phi}^2}{N}\right)^\alpha, \tag{1}$$

where α is the positive real number and $g > 0$, following a quench from high-temperature uncorrelated phase to zero temperature. We note that $g = 1$ and $\alpha = 1$ are relevant for deep quenches as discussed before. We show that in the late stage, the structure factor $S(\vec{k}, t)$ has a multiscaling behavior with characteristic length scale

$$L \sim k_m^{-1} \sim \left(\frac{t}{\ln t}\right)^{1/2(2\alpha+3)}, \tag{2}$$

along the Lifshitz line (LL). From the above equation it is evident that order-parameter-dependent mobility slows down the coarsening process in the phase-ordering kinetics of the self-assembled fluids (i.e. $L(\alpha \neq 0) < L(\alpha = 0)$).

The paper is organized as follows: The next section introduces the model equations, §3 deals with an exact solution in the scaling limit and concluding remarks are given in §4.

2. Model equations

In order to study phase-ordering dynamics of self-assembled fluids we consider the free energy functional $\mathcal{F}$ as proposed by Gompper and Schick [2] and generalized to large-N by Marconi and Corberi [16] given by

$$\mathcal{F}\left[\vec{\phi}(\mathbf{r},t)\right] = \int \mathrm{d}\vec{r}\left[\frac{1}{2}\left(\vec{\nabla}^2\vec{\phi}(\mathbf{r},t)\right)^2 + \frac{b}{2}\left(\vec{\nabla}\vec{\phi}(\mathbf{r},t)\right)^2 + \frac{c_2}{2N}\left(\vec{\phi}(\mathbf{r},t)\right)^2 \right. \\ \left. \times\left(\vec{\nabla}\vec{\phi}(\mathbf{r},t)\right)^2 + \frac{r}{2}\left(\vec{\phi}(\mathbf{r},t)\right)^2 + \frac{g}{4N}\left(\left(\vec{\phi}(\mathbf{r},t)\right)^2\right)^2\right]. \quad (3)$$

The first term in the bracket represents a curvature energy contribution which stabilizes the system. Terms related to surface tension are the ones containing b and c_2 while r and g are the quadratic and quartic terms of the Ginzburg Landau theory [17]. The sign of b and the higher order derivatives in the gradient expansion distinguish self-assembled fluids from the simple binary fluids.

The equation of motion for zero temperature quench with order-parameter-dependent mobility becomes [4]

$$\frac{\partial\phi_l}{\partial t} = -\vec{\nabla}\Gamma(\vec{\phi})\vec{\nabla}\frac{\delta\mathcal{F}}{\delta\phi_l}, \quad (4)$$

where ϕ_l is any one component of the vector field $\vec{\phi}$ and $\Gamma(\vec{\phi})$ is the order-parameter-dependent mobility given by eq. (1). In the limit $N \to \infty$, $\vec{\phi}^2/N$ is replaced by its average in the usual way [17] and eq. (4) leads to a linear self-consistent equation whose Fourier transform is given by

$$\frac{\partial\phi_{\vec{k}}}{\partial t} = -k^2\dot{p}^\alpha(t)\left[k^4 + \dot{B}(t)k^2 + \dot{Q}(t)\right]\phi_{\vec{k}}, \quad (5)$$

where

$$\begin{aligned} \dot{p}(t) &= 1 - gS_0(t), \\ \dot{B}(t) &= b + c_2S_0(t), \\ \dot{Q}(t) &= r + gS_0(t) + c_2S_2(t), \\ S_n &= \int\frac{\mathrm{d}^dk}{(2\pi)^d}k^nS(k,t). \end{aligned} \quad (6)$$

Note that for constant mobility, $\dot{p}(t)$ is absent from eq. (5). Marconi and Corberi [16] studied eq. (5) with constant mobility, $b < 0$ (which applies to lamellar phase for b sufficiently negative) and $c_2 = 0$. We shall study the ordering dynamics of a system quenched from uncorrelated high-temperature phase into the low temperature for different choices of b_r in the late stage of the coarsening process, where

$$b_r = \lim_{t\to\infty}\dot{B}(t). \quad (7)$$

The initial state is uncorrelated and $S(\vec{k},0)$ will be chosen as $S(\vec{k},0) = \Delta =$ constant.

3. Exact solution in the scaling limit

3.1 *The case $b_r > 0$*

For self-assembled fluids, $b_r > 0$ is in the microemulsion phase, and in this region the curvature term is asymptotically irrelevant [16]. Guided by $\alpha = 0$ [16] and dimensional analysis, $\dot{B} \sim$ constant, which implies that $B(t) \to t$. In this case then, eq. (5) simplifies to

$$\frac{\partial \phi_{\vec{k}}}{\partial t} = -k^2 \dot{p}^{\alpha}(t)[k^2 - \dot{p}(t)]\phi_{\vec{k}}, \tag{8}$$

where the values $b = 1$, $r = -1$ and $c_2 = 0$ have been used without loss of generality. The above equation was solved by Emmott and Bray [13] in the study of the effect of order-parameter-dependent mobility for conserved order parameter with $O(N)$ symmetry in the large-N limit and the details can be found there. The equal time structure $S(\vec{k}, t) = \langle \phi_{\vec{k}}(t)\phi_{-\vec{k}}(t)\rangle$ is given by

$$S(k, t) \sim L^{d\psi(q)}, \tag{9}$$

with logarithmic corrections, where

$$L = \left(\frac{2(2+\alpha)t}{d \ln t}\right)^{1/2(2+\alpha)} \tag{10}$$

is the characteristic length and

$$\psi(q) = 2q^2 - q^4, \tag{11}$$

with $q = kL$. The exponent $\psi(q)$ of the 'scale volume' L^d in eq. (9) depends continuously on the scaling variable q. This type of behavior is referred to as 'multiscaling', and was first noted by Coniglio and Zanetti for $\alpha = 0$ [18].

3.2 *The effect of the order-parameter-dependent mobility along the Lifshitz line (LL)*

In this subsection we consider a quench from high-temperature phase into the Lifshitz line (i.e. $b = 0$) [16] with $c_2 = 0$, which further implies that $b_r = 0$. The LL is contained in the microemulsion phase and terminate at the tricritical point. The LL can be assessed experimentally, for example, by changing concentration of the surfactants [19] or oil/water ratio [20]. Along the LL, eq. (5) can be written as

$$\frac{\partial \phi_{\vec{k}}}{\partial t} = -k^2 \dot{p}^{\alpha}(t)[k^4 - \dot{p}(t)]\phi_{\vec{k}}, \tag{12}$$

where $\dot{p}(t) = 1 - gS_0(t) = -\dot{Q}(t)$. From (12) it is straightforward to show that the equal time structure is given by

$$S(\vec{k},t) = \Delta\ \exp[-2k^6 b(t) + 2k^2 c(t)], \tag{13}$$

where

$$b(t) = \int_0^t \dot{p}^{\alpha}(t')\ \mathrm{d}t',$$
$$c(t) = \int_0^t \dot{p}^{\alpha+1}(t')\ \mathrm{d}t'. \tag{14}$$

The relation between $b(t)$ and $c(t)$ follows from eqs (14) above and is given by

$$\dot{c}(t) = \dot{b}^{(\alpha+1)/\alpha}. \tag{15}$$

The following change of variables

$$\vec{k} = \left(\frac{c(t)}{b(t)}\right)^{1/4} \vec{x} \tag{16}$$

simplifies expression (13) for the equal time structure factor to

$$S(k,t) = \Delta \exp[2\beta(x^2 - x^6)], \tag{17}$$

where $\beta = \sqrt{\frac{c^3(t)}{b(t)}}$. The next step is to find β from the self-consistent equation

$$1 - \dot{p}(t) = g \int \frac{\mathrm{d}^d k}{(2\pi)^d} S(k,t)$$
$$= \frac{g\Delta}{(2\pi)^d} \left(\frac{c(t)}{b(t)}\right)^{d/4} \int \mathrm{d}^d x \exp[2\beta(x^2 - x^6)]. \tag{18}$$

In order to make progress we make the following ansatz (to be verified *a posteriori*): In the later stage (i.e. for large t) $\dot{p}(t) \ll 1$ (this is true for constant mobility) and $\beta \to \infty$ as $t \to \infty$. Then the second term on the left-hand side of (18) is negligible for large t, and the integral in (18) can be done by the method of steepest descent to give

$$1 = H_d \beta^{-1/2} \left(\frac{\beta}{b}\right)^{d/6} \exp[2\beta F_m], \tag{19}$$

where H_d is an uninteresting constant and $F_m = 2/3\sqrt{3}$. From the above equation it follows that

$$\beta \simeq \frac{d}{12F_m} \ln[b(t)] + \frac{3-d}{12F_m} \ln\{\ln[b(t)]\}. \tag{20}$$

Using the definition of $\beta = \sqrt{c^3/b}$ and eq. (20), $c(t)$ can be expressed in terms of $b(t)$ as follows:

$$c(t) \simeq b^{1/3} \times \left(\frac{d}{12F_m} \ln[b(t)] + \frac{3-d}{12F_m} \ln\{\ln[b(t)]\}\right)^{2/3}. \tag{21}$$

Differentiating the above equation gives to leading order in $b(t)$

$$\dot{c}(t) \simeq \frac{1}{3}\left(\frac{d\ln[b(t)]}{12F_m b(t)}\right)^{2/3}\dot{b}(t). \tag{22}$$

Using (22) in eq. (15), $\dot{c}(t)$ is eliminated in favor of $\dot{b}(t)$ leading to the differential equation

$$\dot{b}(t) \simeq \left(\frac{d\ln[b(t)]}{12\sqrt{27}F_m b(t)}\right)^{2\alpha/3}. \tag{23}$$

From the above it can be shown that to leading order in t

$$b(t) \simeq \left[\frac{(2\alpha+3)t}{3}\right]^{3/(2\alpha+3)}\left(\frac{3d\ln t}{12\sqrt{27}F_m(2\alpha+3)}\right)^{2\alpha/(2\alpha+3)}. \tag{24}$$

Substituting eq. (24) in (20) gives

$$\beta = \frac{d}{4F_m(2\alpha+3)}\ln t + \frac{1}{4F_m}\left(\frac{2\alpha+3-d}{2\alpha+3}\right)\ln[\ln t] \tag{25}$$

to leading order in t in the scaling limit. Note that eqs (24) and (25) justify our original ansatz that $\dot{p}(t) \ll 1$ and $\beta \to \infty$ for large t.

We now define the characteristic length scale $L \sim k_m^{-1}$, where k_m is the peak position of the structure factor, which gives

$$L \sim k_m^{-1} = \left(\frac{b(t)}{3c(t)}\right)^{1/4} \approx \left(\frac{t}{d\ln t}\right)^{1/2(2\alpha+3)}. \tag{26}$$

Using eqs (25) and (26) in eq. (17), it is straightforward to show that the equal time structure factor has the form

$$S(k,t) \sim L^{dF(q)/F_m}, \tag{27}$$

with logarithmic corrections, where $F(q) = \sqrt{3}(q^2 - 3q^6)$ and $q = kL$. Equation (27) shows the multiscaling behavior [18] (i.e. the power of the scale volume L^d depends continuously on the scaling variable q). The coarsening length $L(t)$ shows that coarsening is slowed down in the presence of the order-parameter-dependent mobility.

4. Concluding remarks

The effect of an order-parameter-dependent mobility in self-assembled fluids has been studied analytically within the large-N limit. Similar to studies carried in binary mixtures, order-parameter-dependent mobility is found to reduce the rate of coarsening in self-assembled fluids [i.e. $L(\alpha = 0) > L(\alpha \neq 0)$]. We believe that even in the self-assembled fluids, the multiscaling found is due to large-N approximation and that the standard scaling will be found for finite N with characteristic length scale: $L \sim t^{1/2(2\alpha+3)}$ (without $\ln t$ terms) [21]. However, the problem of showing analytically that standard scaling is reinstated for large but finite N in the presence of an order-parameter-dependent mobility is still open, even in the simple binary mixtures.

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