

The effect of shear in self-assembled fluids: The large- N limit

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Received 1st September 2004

Published online 18 January 2005 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2004

Abstract. The dynamics of self-assembled fluids subjected to a uniform shear are solved for large- N component model of microemulsions. The dynamical structure factor $S(\mathbf{k}, t)$ is studied for quenches from an uncorrelated high temperature state into the Lifshitz line within the microemulsion phase. The structure factor shows multiscaling behavior with characteristic length scales $(t^7/\ln t)^{1/6}$ in the flow direction and $(t/\ln t)^{1/6}$ in directions perpendicular to the flow. The structure factor shows two parallel ridges in the shear-flow plane.

PACS. 47.20.Hw Morphological instability; phase changes – 05.70.Ln Nonequilibrium and irreversible thermodynamics – 83.50.Ax Shear flows

1 Introduction

The behavior of self assembled fluids such as: mixtures of water, oil and surfactants have attracted considerable interest [1]. These mixtures can spontaneously form very different complex structures. For example, the variation in concentration of the surfactants can lead to different phases. It is well known that the increase in the surfactant concentration reduces the surface tension, thus leading to microemulsion phase while high surface tension leads to oil-rich or water-rich regions. Similar complex structures are also formed by macromolecules such as: homopolymer blend and diblock copolymers [2].

Initially most of the studies were focused on the equilibrium properties of the self assembled fluids, but in the last two decades there has been great interest in both the theoretical and experimental studies of the complex fluids far from equilibrium [3]. Recently there has been interest also on the effect of shear in both binary and self-assembled fluids [4,5], and macromolecules [3]. In all these cases, shear introduces anisotropy in the structure factor $S(\mathbf{k}, t)$ [4,6]. This is due to the fact that, in the scaling limit, the characteristic length scale L_x in the flow direction is greater than characteristic length scales in the perpendicular directions (i.e. L_y, L_z). Shear may also induce phase transition [4,7], for example, shear-induced shift of the phase transition temperature in the microphase separation in diblock copolymers has been observed [8].

In this paper we study the effect of shear on the Ginzburg Landau model for self assembled fluids, proposed by Gompper and Schick [1], and generalized to large

number of components by Marconi and Corberi [9], where the free energy functional \mathcal{F} is given by

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

The terms, r and g (with $g > 0$) are the quadratic and quartic terms of the Ginzburg Landau theory. The terms containing b and c_2 are related to surface tension while the first term represents a curvature energy contribution which stabilizes the system. The sign of b and the higher order derivatives in the gradient expansion distinguish self assembled fluids from simple binary fluids [1,10].

The equation of motion for zero temperature quench becomes [4]

$$\frac{\partial \phi_\alpha}{\partial t} = -\Gamma \nabla^2 \frac{\delta \mathcal{F}}{\delta \phi_\alpha}, \quad (2)$$

where ϕ_α is any one component of the vector field ϕ and Γ is the mobility coefficient. We are interested in a system with a uniform shear flow which has a velocity field of the form $\mathbf{v} = \gamma y \mathbf{e}_x$, where γ is the constant shear rate and \mathbf{e}_x is a unit vector in the flow direction. In the presence of shear, the term $(\mathbf{v} \cdot \nabla) \phi_\alpha = \gamma \partial_x \phi_\alpha$ is added to the left hand side of equation (2) leading to

$$\frac{\partial \phi_\alpha}{\partial t} + \gamma y \partial_x \phi_\alpha = -\nabla^2 \frac{\delta \mathcal{F}}{\delta \phi_\alpha}. \quad (3)$$

Note that the mobility Γ has been absorbed into the time scale of the problem.

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In the limit $N \rightarrow \infty$, one can replace $(\phi)^2/N$ in (3) by its mean in the usual way [11], leading to the self-consistent equation, which after Fourier transforming becomes

$$\frac{\partial \phi_{\mathbf{k}}}{\partial t} - \gamma k_x \frac{\partial \phi_{\mathbf{k}}}{\partial k_y} = -k^2 \left[k^4 + \dot{B}(t)k^2 + \dot{Q}(t) \right] \phi_{\mathbf{k}}, \quad (4)$$

where $\dot{B}(t) = b + c_2 S_0(t)$, $\dot{Q}(t) = r + g S_0(t) + c_2 S_2(t)$ and $S_n = \int \frac{d^d k}{(2\pi)^d} k^n S(k, t)$. Equation (4) has been considered by Corberi et al. [12] with $b < 0$ (which describes the lamellar phase for b sufficiently negative) and $c_2 = 0$.

In the scaling limit, we find that the structure factor $S(\mathbf{k}, t)$ has multiscaling behavior, and four maxima, located at

$$\mathbf{k} = \pm(k_{mx}, -k_{my}, \pm k_{mz}), \quad (5)$$

with characteristic length scales:

$$L_x \sim k_{mx}^{-1} \sim \left(\frac{t^7}{\ln t} \right)^{1/6},$$

$$L_y (\sim k_{my}^{-1}) = L_z (\sim k_{mz}^{-1}) \sim \left(\frac{t}{\ln t} \right)^{1/6}, \quad (6)$$

along the Lifshitz line (LL). Thus the rotational symmetry of the zero-shear limit is completely broken. In the $k_y = 0$ plane, the structure factor $S(\mathbf{k}, t)$ has two maxima terminating two parallel ridges while in the $k_x = 0$ plane, there are four maxima.

We shall consider phase ordering dynamics of a system quenched from high temperature phase for different choices of b_r and $r = -1$, where

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

The initial state will be assumed uncorrelated and $S(\mathbf{k}, 0)$ will be chosen as $S(\mathbf{k}, 0) = \Delta = \text{const.}$

This paper is organized as follows: In the next section, an exact solution for the structure factor is obtained in the scaling limit along the Lifshitz line, followed by discussion of the results. Concluding remarks are given in Section 3.

2 Results and discussion

2.1 The case $b_r > 0$

$b_r > 0$ is in the microemulsion phase of the self assembled fluids [9]. In this region, the curvature term is asymptotically irrelevant [9]. Guided by the $\gamma = 0$ case [9] and dimensional analysis, $\dot{B}(t) \sim \text{Constant}$, implying that $B(t) \rightarrow t$. Then equation (4) simplifies to

$$\frac{\partial \phi_{\mathbf{k}}}{\partial t} - \gamma k_x \frac{\partial \phi_{\mathbf{k}}}{\partial k_y} = -k^2 \left[k^2 + \dot{Q}(t) \right] \phi_{\mathbf{k}}, \quad (8)$$

where the value $b_r = 1$ has been used without loss of generality. The above equation is similar to the one solved

by Rapapa and Bray [13] for simple binary fluids and the details can be found there. The equal time structure factor $S(\mathbf{k}, t) = \langle \phi_{\mathbf{k}}(t) \phi_{-\mathbf{k}}(t) \rangle$ is given by [13]

$$S(k, t) = \text{const.} \times (\ln V_s)^{3/2} V_s^{F(\mathbf{q})/F_m}, \quad (9)$$

where the ‘scale volume’ $V_s = L_x L_y L_z \sim \gamma t^{7/4} / (\ln t)^{3/4}$, with characteristic length scales

$$L_x \sim \gamma (t^5 / \ln t)^{1/4}, \quad L_y = L_z \sim (t / \ln t)^{1/4}, \quad (10)$$

scaled momentum

$$\mathbf{q} = (k_x L_x, k_y L_y, k_z L_z) = (u, v, w), \quad (11)$$

$F_m = 0.3833$ and

$$F(\mathbf{q}) = -\frac{1}{5u} \left[(u+v)^5 - v^5 \right] + \frac{8}{15} u^2$$

$$+ \frac{4}{3} uv + v^2 + w^2 - w^4$$

$$- \frac{2}{3} w^2 (u^2 + 3uv + 3v^2). \quad (12)$$

Equation (9) does not have a form consistent with conventional scaling, $S(\mathbf{k}, t) = V_s g(\mathbf{q})$, but exhibits multiscaling behavior (i.e., the power of the ‘scale volume’ depends continuously on the scaling variables) [14]. Interestingly, the exponent 5/4 has also been found for lamellar phase under shear flow [12].

2.2 The effect of Shear along the Lifshitz Line (LL)

Here we consider a quench along the Lifshitz Line (i.e. $b = 0$) [9] with $c_2 = 0$. Note that for $c_2 = 0$, $b_r = b$. The LL is contained in the microemulsion phase of the self assembled fluids and terminate at the tricritical point. The Lifshitz line can be assessed experimentally, for example, by changing the oil/water ratio [15] or concentration of the surfactants [16]. Equation (4) then simplifies to

$$\frac{\partial \phi_{\mathbf{k}}}{\partial t} - \gamma k_x \frac{\partial \phi_{\mathbf{k}}}{\partial k_y} = -k^2 \left[k^4 - \dot{p}(t) \right] \phi_{\mathbf{k}}, \quad (13)$$

where $\dot{p}(t) = -\dot{Q}(t) = 1 - g S_0(t)$.

We first consider the above equation in the absence of shear. This case was first done by Corberi and Marconi [9]. It follows from (13) that for $\gamma = 0$, the equal time structure factor $S(\mathbf{k}, t)$ becomes

$$S(k, t) = \Delta \exp \left[-2k^6 t + 2k^2 p(t) \right]. \quad (14)$$

The next step is to find $p(t)$ from the self consistent equation

$$1 - \dot{p}(t) = g \int \frac{d^d k}{(2\pi)^d} S(k, t)$$

$$= \frac{g\Delta}{(2\pi)^d} \left(\frac{p}{t} \right)^{d/4} \int d^d x \exp \left[2\sqrt{\frac{p^3}{t}} (x^2 - x^6) \right], \quad (15)$$

where the substitution $k = (p/t)^{1/4}x$ has been used. Naive power counting in (14) suggest that characteristic length scale $L \sim t^{1/6}$ and $p(t) \sim t^{-1/3}$ (i.e. $\dot{p}(t) \sim t^{-2/3}$). In fact we will find that the above still holds but modified with logarithmic terms. In the limit $t \rightarrow \infty$, $\dot{p}(t)$ can be dropped in (15) since it vanishes (like $t^{-2/3}$) leading to following result, after integrating (15) with method of steepest descent

$$1 = Ct^{\frac{1-d}{4}}p^{\frac{d-3}{4}} \exp \left[4 \times \sqrt{\frac{p^3}{27t}} \right] \quad (16)$$

where C is a constant. It follows from (16) that to leading order in t at late times

$$p(t) \sim \left(\frac{d}{24} \sqrt{27t \ln t} \right)^{2/3}, \quad (17)$$

which justifies the assumption that $\dot{p}(t) \sim t^{-2/3}$. We can now define characteristic length scale $k_m^{-1} \sim (t/p)^{1/4}$ where k_m is the position of the peak of $S(k, t)$. Then characteristic length scale $L \sim k_m^{-1} = (24t/d \ln t)^{1/6}$. It is now straight forward to show that the structure factor has multiscaling form [9]

$$S(k, t) = \text{const.} \times (\ln L)^{1/2} L^{ds(q)}, \quad (18)$$

where $q = kL$ and $s(q) = (3q^2 - q^6)/2$.

We now consider equation (13) with a shear term which we solve via change of variables:

$$(k_x, k_y, k_z, t) \rightarrow (k_x, \sigma, k_z, \tau), \quad (19)$$

where $\tau = t$ and $\sigma = k_y + \gamma k_x t$. Then the left hand side of equation (13) becomes $\partial \phi_{\mathbf{k}} / \partial \tau$ and as a result (13) can be integrated directly to give (after transforming back to original variables) $\phi_{\mathbf{k}}(t) = \phi_{\mathbf{k}'}(0) \exp[f(\mathbf{k}, t)]$ where $\mathbf{k}' = (k_x, k_y + \gamma k_x t, k_z)$ and

$$\begin{aligned} f(\mathbf{k}, t) = & - (k_x^2 + k_z^2)^3 t - \frac{[(k_y + \gamma K_x t)^7 - k_y^7]}{7\gamma k_x} \\ & - \frac{(k_x^2 + k_z^2)^2}{\gamma k_x} \times [(k_y + \gamma k_x t)^3 - k_y^3] \\ & - \frac{3(k_x^2 + k_z^2)}{5\gamma k_x} \times [(k_y + \gamma k_x t)^5 - k_y^5] \\ & + [(k_y + \gamma k_x t)^2 + k_x^2 + k_z^2] p(t) \\ & - 2\gamma k_x (k_y + \gamma k_x t) c(t) + \gamma^2 k_x^2 e(t), \quad (20) \end{aligned}$$

with $c(t) = \int_0^t t' \dot{p}(t') dt'$ and $e(t) = \int_0^t t'^2 \dot{p}(t') dt'$. Guided by $\gamma = 0$ we make the following ansatz, $p(t) \sim (t^{1/2} \ln t)^{2/3}$ as $t \rightarrow \infty$, which will be justified *a posteriori*. Then to leading logarithmic accuracy $c(t) \rightarrow \frac{1}{4} t p(t)$ and $e(t) \rightarrow \frac{1}{7} t^2 p(t)$. Making the following change of variables:

$$\gamma k_x = \left(\frac{p}{t^5} \right)^{1/4} u, \quad k_y = \left(\frac{p}{t} \right)^{1/4} v, \quad k_z = \left(\frac{p}{t} \right)^{1/4} w, \quad (21)$$

substituting these results in (20), the structure factor $S(\mathbf{k}, t)$ follows

$$S(\mathbf{k}, t) = \Delta \exp \left[2 \sqrt{\frac{p^3}{t}} F(u, v, w) \right], \quad (22)$$

where

$$\begin{aligned} F(u, v, w) = & (v + u)^2 + w^2 + \frac{u^2}{7} - \frac{u}{2} [v + u] \\ & - \frac{3}{5} \frac{w^2}{u} [(v + u)^5 - v^5] - w^6 \\ & - \frac{w^4}{u} [(v + u)^3 - v^3] - \frac{[(v + u)^7 - v^7]}{7u}. \quad (23) \end{aligned}$$

Note that contributions to F which vanish at fixed (u, v, w) as $t \rightarrow \infty$ have been dropped. $p(t)$ can be found self consistently from

$$1 - \dot{p}(t) = g \int \frac{d^d k}{(2\pi)^d} S(\mathbf{k}, t), \quad (24)$$

with $S(\mathbf{k}, t)$ given by (22). In the limit $t \rightarrow \infty$, $\dot{p}(t)$ above vanishes and can be dropped leading to

$$\begin{aligned} 1 = & g \int \frac{d^3 k}{(2\pi)^3} S(\mathbf{k}, t) \\ = & \frac{g \Delta p^{3/4}}{(2\pi)^3 \gamma t^{7/4}} \int du dv dw \exp \left[2 \sqrt{\frac{p^3}{t}} F(u, v, w) \right]. \quad (25) \end{aligned}$$

The maximum of F , $F_m = 0.5617$ occurs at four points in uvw space, namely,

$$(u, v, w) = \pm(1.6413, -0.5957, \pm 0.4717). \quad (26)$$

These points corresponds to points in momentum space via (21). Using the method of steepest descent to evaluate the integral in (25) leads to

$$1 = \frac{\text{const.} \Delta}{\gamma t p^{3/2}} \exp \left[2 \sqrt{\frac{p^3}{t}} F_m \right]. \quad (27)$$

Then it follows that to leading logarithmic accuracy

$$p(t) = \left(\frac{t^{1/2} \ln t}{2F_m} \right)^{2/3}, \quad (28)$$

which justifies our original ansatz. We now define characteristic length scales

$$L_x = \gamma \left(\frac{t^5}{p} \right)^{1/4} \sim \gamma \left(\frac{t^7}{\ln t} \right)^{1/6} \quad (29)$$

and

$$L_y = L_z = \left(\frac{t}{p} \right)^{1/4} \sim \left(\frac{t}{\ln t} \right)^{1/6}. \quad (30)$$

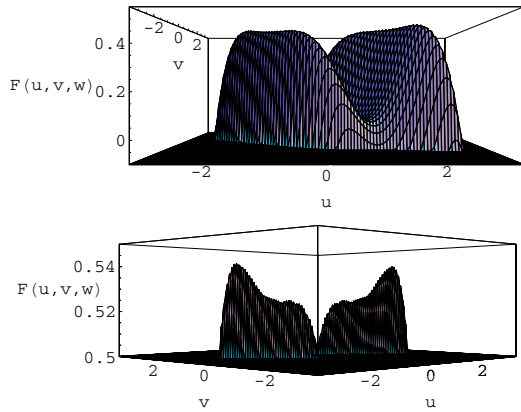


Fig. 1. Projections of $F(u, v, w)$ on the plane $w = 0$. The top figure shows the two parallel ridges while the bottom figure shows the peaks on the ridges. Values for $F < -0.1$ and $F < 0.5$ are not shown on the top and bottom figures respectively.

Using equations (28, 29, 30) in (22) leads to the structure factor

$$S(\mathbf{k}, t) = \text{const.} \times (\ln V_s)^{3/2} V_s^{F(\mathbf{q})/F_m}, \quad (31)$$

where the scaled momentum $\mathbf{q} = (k_x L_x, k_y L_y, k_z L_z)$ and ‘scale volume’ $V_s = L_x L_y L_z$. Equation (31) shows that $S(\mathbf{k}, t)$ has multiscaling form. As has been explicitly shown in zero shear in simple fluids [17], we expect the $\ln t$ terms (which appear in the characteristic length scales) to be absent for finite N . The global picture of the structure factor $S(\mathbf{k}, t)$ is determined by $F(u, v, w)$ via the relation $\ln S(\mathbf{k}, t) = [F/F_m] \ln V_s$ (plus \mathbf{k} -independent terms), so $F(u, v, w)$ is essentially $\ln S(\mathbf{k}, t) / \ln t$.

Figure 1 shows $F(u, v, w)$ in the (u, v) plane which has two parallel ridges terminated by two global peaks located at $\pm(1.9588, -0.7598)$ with ‘height’ 0.5400. The ridge-like structure has also been observed in experiments for binary fluids [18] and polymer solutions [19]. These two dominating peaks have been found in the steady state of the microemulsion where one-loop self-consistent approximation has been used [20]. Note that the relations $\ln S \propto F \ln t$, $k_x = u/L_x$ etc imply that the ridges in S become higher, narrower and move closer together with increasing time t . The angle between the ridges and shear direction (k_y direction in this case) is given by $\tan(\theta) \propto 1/\gamma t$. The relation between θ and time t shows that the ridges tend to align close to shear direction with increasing time. The angle θ is known to be the good measure of experiment and theory in the binary fluids [18].

In the (u, w) plane, $F(u, v, w)$ is shown in Figure 2, and has our peaks located at $\pm(0.9908, \pm 0.4128)$ with ‘height’ 0.5344. The structure factor pattern in the (k_x, k_z) plane will decrease faster in the flow direction (i.e. k_x direction) with increasing time t , resulting in an elliptical shape with major axis along the k_z direction. The peaks become sharper with increasing time. The elliptical shape has been observed in segregating mixtures [18].

Finally in the (k_y, k_z) plane $S(\mathbf{k}, t)$ has a full circular symmetry as shown in Figure 3.

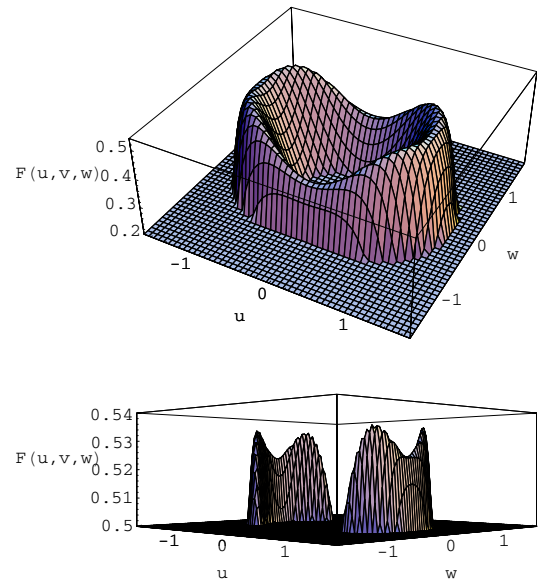


Fig. 2. Projections of $F(u, v, w)$ on the plane $v = 0$. The bottom figure shows clearly the four peaks. Values for $F < 0.2$ and $F < 0.5$ are not shown on the top and bottom figures respectively.

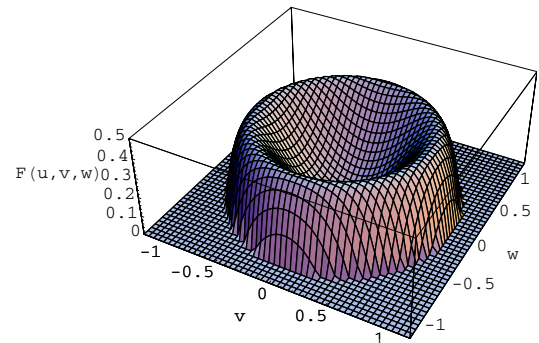


Fig. 3. Projections of $F(u, v, w)$ on the plane $u = 0$. Values for $F < 0$ are not shown.

3 Conclusion

We have calculated the structure factor $S(\mathbf{k}, t)$ for self-assembled fluids in the scaling limit. Although the problem was simplified by looking only in the microemulsion phase along the Lifshitz line, the basic features of the structure factor resembles those found in ‘self-consistent one loop approximation’ for the microemulsion [20]. Similar to binary mixtures, shear introduces anisotropy in the structure factor $S(\mathbf{k}, t)$ of self assembled fluids. This is due to different growth rates in the flow direction and directions perpendicular to the flow. We believe the multiscaling found here to be the result of the large- N theory approximation and that for any finite N , standard scaling will be found with the same characteristic length scales but without $\ln t$ terms, $L_x \sim t^{7/6}$ and $L_y = L_z \sim t^{1/6}$. However, the problem of showing analytically, that the conventional scaling is reinstated for large but finite N in the presence of a uniform shear remains to be solved, even in the simple binary fluids.

We thank National University of Lesotho - NUL through RRC Research Grant (NR, NM), Swedish International Development Agency - SIDA (NR) and The Abdus Salam International Centre for Theoretical Physics - ICTP (NR) for financial support. We also thank the American Physical Society - APS for free online access to APS Journals through Department of Physics and Electronics - NUL (NR, NM). We thank Ramollo for useful discussions.

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