

# Viscosity of self-assembled fluids

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We consider a Hamiltonian for a complex fluid. The linear excess bulk viscosity due to a spatially varying order parameter is investigated. We calculate the dependence of the excess viscosity  $\Delta\eta$ , on the fundamental parameters  $d$  and  $\xi$ , everywhere within the disordered phase ( $d$  being the domain size of water or oil and  $\xi$  being the correlation length between domains). It is found that there is a crossover region in the isotropic disordered phase of this model. More specifically, in the structured region of the isotropic disordered phase  $\Delta\eta$  grows as  $\xi^3$  in the vicinity of disordered-lamellar transition. This is quite distinct from the behavior of the excess viscosity in the unstructured region where  $\Delta\eta$  grows as  $\xi$  in the vicinity of the order-disorder transition.

## I. INTRODUCTION

Self-assembled fluids (mixtures of oil, water, and surfactant) have been a recent topic of considerable interest by theorists and experimentalists. A number of quite successful models have been proposed to explain the rich variety of novel phenomena that occur in these systems. One of the earliest models was introduced by Widom.<sup>1</sup> He proposed an extended Ising Hamiltonian in which there are competing interactions between the nearest neighbors and the next nearest neighbors on the lattice. This, in turn, causes spatial frustration which is an essential ingredient in modeling complex fluids. One can also study a continuous version of the Widom Hamiltonian.<sup>2</sup> In fact, one can construct an effective Landau–Ginzburg–Wilson (LGW) Hamiltonian from a lattice model Hamiltonian by introducing an order parameter field  $\varphi$ . Retaining terms up to quadratic order in  $\varphi$ , the following Hamiltonian is obtained:

$$H = \int d^3\mathbf{x} \frac{1}{2} \{ [\nabla^2\varphi(\mathbf{x})]^2 + b[\nabla\varphi(\mathbf{x})]^2 + c\varphi(\mathbf{x})^2 \}. \quad (1)$$

Hamiltonian (1) is precisely the phenomenological Hamiltonian proposed by Teubner and Strey.<sup>3</sup> For the present paper  $b$  and  $c$  should be thought of as purely phenomenological coefficients such that Hamiltonian (1) is dimensionless. It can be shown that one can relate the parameters  $b$  and  $c$  to the lattice model parameters.<sup>2</sup> Teubner and Strey found that Hamiltonian (1) describes the structural properties of a class of self-assembled fluids called microemulsion quite well.

Microemulsion is a thermodynamically stable phase of oil, water, and surfactant. Many experiments have been performed yielding phase diagrams and structure factors to aid in the understanding of this system.<sup>4</sup> In fact, one of the successes of Hamiltonian (1) is that it predicts a Fourier transform of a structure factor to have the form

$$S(\mathbf{q}) = \frac{1}{q^4 + bq^2 + c}. \quad (2)$$

This is the structure factor first introduced by Teubner and Strey to fit the scattering data in the isotropic microemulsion phase.<sup>3</sup> Thus, if  $c - (b^2/4) > 0$ , and  $c > 0$  Teubner and Strey found the real-space correlation function to be of the form

$$g(\mathbf{r}) = \frac{\xi d}{16\pi^2} \frac{\exp(-|\mathbf{r}|/\xi)}{|\mathbf{r}|} \sin \frac{2\pi|\mathbf{r}|}{d}. \quad (3)$$

Here  $\xi$  and  $d$  are the two fundamental length scales of the theory;  $d$  being the domain size of water or oil and  $\xi$  being the correlation between domains. The length scales  $d$  and  $\xi$  can be related to the parameters  $b$  and  $c$  by

$$\frac{1}{\xi} = \left( (\sqrt{c}/2) + \frac{b}{4} \right)^{1/2} \quad (4)$$

$$\frac{2\pi}{d} = \left( (\sqrt{c}/2) - \frac{b}{4} \right)^{1/2}. \quad (5)$$

When  $c - (b^2/4) < 0$ ,  $c > 0$ , and  $b > 0$ , the real-space correlation function assumes the usual Ornstein–Zernike form

$$g(\mathbf{r}) \cong \frac{\exp(-|\mathbf{r}|/\xi^-)}{|\mathbf{r}|}, \quad (6)$$

where  $\xi^-$  is distinct from  $\xi$ .

One can also get a sense of topology of the phase diagram for these self-assembled systems. The phase diagram arising from Hamiltonian (1) is given in Fig. 1. Special attention should be given to the dashed curve in Fig. 1. This is the curve described by  $c - (b^2/4) = 0$ , and is known as the disorder curve.<sup>2,5</sup> The disorder curve is not a phase boundary but it separates two distinct regions of paramagnetic phase. To its left the correlation function takes the form given by Eq. (3) while to the right Eq. (6) applies. The two regions are known, respectively, as structured and

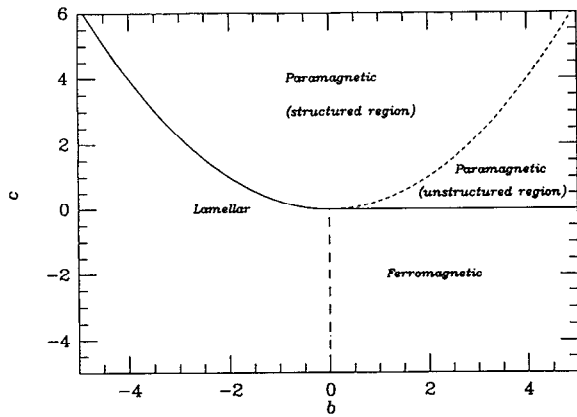


FIG. 1. Phase diagram of Hamiltonian (1) in the parameter space of  $b$  and  $c$ . It should be noted that without the inclusion of higher-order nonlinearities of the order parameter field, Hamiltonian (1) will only describe the paramagnetic phase. Here we have included the mean-field phase diagram which has been derived in a previous paper (Ref. 2). Special attention should be brought to the dashed line in the paramagnetic phase which is known as the disorder line. The phase transitions between isotropic-disordered phase and the ordered phases are predicted to be second order within mean-field theory.

unstructured. The structured region is associated with bicontinuous microemulsion. It should also be pointed out that all phase transitions between the isotropic disordered phase to any other phase predicted within mean-field theory are second order. This is not the case in real systems and, in fact, the transition from the paramagnetic to the lamellar phase is weakly first order. The modification of the order of the transitions can be understood by studying the fluctuation effects beyond the mean-field level.<sup>6,2</sup>

In the present paper we will consider the excess bulk viscosity due to the fluctuations in the order parameter. We will conduct this study using a dynamical mean-field theory in the structured and unstructured region of the isotropic disordered phase. In the past there have been attempts to measure the viscosity of microemulsion, but no fit to any theory which encompasses the viscosity across this disorder boundary is known.<sup>7</sup> To derive the equations for the excess viscosity we will follow closely an approach first introduced by Fredrickson and Larson<sup>8</sup> and later generalized by Onuki.<sup>9</sup>

## II. DYNAMICAL EQUATIONS

We consider the set of stochastic hydrodynamic equations that describe the evolution of the order parameter:<sup>10</sup>

$$\frac{\partial \varphi}{\partial t} = -\nabla \cdot (\varphi \mathbf{v}) + \Gamma \nabla^2 \frac{\delta H}{\delta \varphi} + \theta, \quad (7)$$

$$\frac{\partial \mathbf{v}}{\partial t} = -\frac{1}{\beta} \varphi \nabla \frac{\partial H}{\delta \varphi} + \eta \nabla^2 \mathbf{v} + \xi. \quad (8)$$

Here,  $\mathbf{v}$  is the transverse velocity field and  $\theta$  and  $\xi$  are Gaussian noise terms related to the Onsager kinetic coefficient  $\Gamma$ , and the viscosity  $\eta$ , through Einstein relations. One will recognize Eq. (7) as the Langevin equation for the conserved order parameter with a convection term.

Since we are interested in the disordered phase where  $\langle \varphi \rangle = 0$ , we will use a linearized version of Eq. (7). If the velocity field is divergenceless, Eq. (7) becomes

$$\frac{\partial \varphi}{\partial t} = -\mathbf{u} \cdot \nabla \varphi + \Gamma \nabla^2 \frac{\delta H}{\delta \varphi} + \theta, \quad (9)$$

where  $\mathbf{u} = \langle \mathbf{v} \rangle$ .

From Eq. (9) it is straightforward to write the equation for the Fourier transform of the structure factor  $\langle |\varphi(\mathbf{q}, t)|^2 \rangle \equiv S(\mathbf{q}, t)$ . Here the averages are taken with respect to the Gaussian random noise  $\theta$ . In the presence of shear flow  $\mathbf{u} = \dot{\gamma} y \hat{\mathbf{x}}$  this equation becomes

$$\left( \frac{\partial}{\partial t} + 2\Gamma \mathbf{q}^2 K_{\mathbf{q}} - 2q_x \dot{\gamma} \frac{\partial}{\partial q_y} \right) S(\mathbf{q}, t) = 2\Gamma \mathbf{q}^2, \quad (10)$$

where

$$K_{\mathbf{q}} = \mathbf{q}^4 + b\mathbf{q}^2 + c. \quad (11)$$

The approximation leading to Eq. (9) is not necessary and a more general study can be performed.<sup>11</sup> It should also be pointed out that the aforementioned analysis can be easily modified to introduce higher-order nonlinearities into Hamiltonian (1). However, such nonlinear interactions will not affect the results presented later.

## III. THE STRESS TENSOR

In order to proceed, we derive an expression for the pressure tensor. This can be done in a variety of ways.<sup>12,8,9</sup> The pressure tensor  $P_{ij}$  is defined by

$$\frac{\partial v_j}{\partial t} \equiv -\partial_i P_{ij} + \zeta. \quad (12)$$

Comparing Eq. (8) to Eq. (12) we obtain

$$P_{ij} = \delta_{ij} \tilde{p} + \frac{1}{\beta} \left( \left( \frac{b}{2} (\partial \varphi)^2 - \frac{1}{2} (\partial_k \partial \varphi)^2 - \partial \varphi \partial_k \partial_k \partial \varphi \right) \delta_{ij} - b(\varphi \partial_i \partial_j \varphi) + \partial_k \partial_i \varphi \partial_k \partial_j \varphi + \varphi \partial_i \partial_k \partial_k \partial_j \varphi - \eta(\partial_i \mu_j + \partial_j \mu_i) \right), \quad (13)$$

where repeated index summation convention is used. It is also easy to verify that the term in the Hamiltonian (1) that contains no derivatives will contribute only to the pressure  $\tilde{p}$ . The gradient terms in Eq. (13) can be thought of as additional contributions to the bulk pressure  $\tilde{p}$  due to a spatially varying order parameter.

Specifically, for shear flow  $\mathbf{u} = \dot{\gamma} y \hat{\mathbf{x}}$ , the average shear stress can be written as

$$\sigma_{xy} \equiv -\langle P_{xy} \rangle = \eta \dot{\gamma} + \frac{b}{\beta} \langle \varphi \partial_x \partial_y \varphi \rangle - \frac{1}{\beta} \langle \varphi \partial_x \nabla^2 \partial_y \varphi \rangle - \frac{1}{\beta} \langle \partial_x \partial_i \varphi \partial_j \partial_i \varphi \rangle. \quad (14)$$

Equation (14) can be conveniently expressed in terms of the structure factor  $S(\mathbf{q}, t)$  as

$$\sigma_{xy}(t) = \eta \dot{\gamma} - \frac{b}{\beta} \int_{\mathbf{q}} S(\mathbf{q}, t) q_x q_y - \frac{2}{\beta} \int_{\mathbf{q}} S(\mathbf{q}, t) q_x q_y \mathbf{q}^2, \quad (15)$$

where

$$\int_{\mathbf{q}} \equiv \frac{1}{(2\pi)^3} \int d\mathbf{q}.$$

#### IV. THE STRUCTURE FACTOR UNDER OSCILLATORY SHEAR

In this section we investigate the structure factor under oscillatory shear. We will be interested in small shear rate so that the system can be treated within linear response theory. Therefore, topics like shear thinning will not be discussed in this paper.

The shear rate for oscillatory shear is given by

$$\dot{\gamma}(t) = \dot{\gamma}_0 \cos(\omega t). \quad (16)$$

If the shear rate is small we can solve Eq. (10) in the vicinity of the equilibrium structure factor

$$\Delta(\mathbf{q}, t) = S(\mathbf{q}, t) - S_\infty(\mathbf{q}), \quad (17)$$

where  $S_\infty(\mathbf{q})$  is the equilibrium structure factor. Assuming that  $\Delta$  is of order  $\dot{\gamma}_0$ , substituting Eq. (16) into Eq. (10) and collecting terms to  $O(\Delta^2)$ , we obtain

$$\left( \frac{\partial}{\partial t} - 2\Gamma \mathbf{q}^2 K_{\mathbf{q}} \right) \Delta = 2q_x \dot{\gamma}_0 \frac{\partial S_\infty}{\partial q_y} \cos(\omega t). \quad (18)$$

Equation (18) can be easily solved to yield a particular solution

$$\Delta(\mathbf{q}, t) = \text{Re} \left( \frac{2q_x \dot{\gamma}_0 (\partial S_\infty / \partial q_y) \exp(i\omega t)}{i\omega + 2\Gamma \mathbf{q}^2 K_{\mathbf{q}}} \right), \quad (19)$$

where  $\text{Re}(\dots)$  denotes the real part of the expression.

The shear stress can also be written in terms of the stress relaxation function  $G^*(\omega)$ :<sup>13</sup>

$$\sigma_{xy}(t) = \text{Re} \left( \frac{G^*(\omega) \dot{\gamma}_0 \exp(i\omega t)}{i\omega} \right). \quad (20)$$

Combining Eqs. (15), (17), and (19) and comparing the result to Eq. (20), we can derive an expression for the stress relaxation function. After angular integrals have been performed the expression is

$$\frac{G^*(\omega)}{i\omega} = \eta + \frac{1}{\beta 30\pi^2} \int dq \frac{16q^6 [q^4 + bq^2 + (b^2/4)]}{K_{\mathbf{q}}^2 (i\omega + 2\Gamma \mathbf{q}^2 K_{\mathbf{q}})}. \quad (21)$$

The total bulk viscosity is related to the imaginary part of the stress relaxation function by<sup>13</sup>

$$\lim_{\omega \rightarrow 0} \frac{\text{Im}[G^*(\omega)]}{\omega} = \eta_t. \quad (22)$$

Taking the imaginary part of Eq. (20), we obtain the following expression for the excess viscosity  $\Delta\eta$ :

$$\eta_t - \eta = \Delta\eta = \frac{4}{15\pi^2 \beta \Gamma} \int_0^\infty \frac{q^4 [q^4 + bq^2 + (b^2/4)]}{K_{\mathbf{q}}^3} dq. \quad (23)$$

The aforementioned integral can be done analytically and the excess viscosity can be computed in terms of the parameters of Hamiltonian (1):

$$\Delta\eta = \left[ \frac{b}{4} + \frac{\sqrt{c}}{2} + \frac{1}{4} \left( -\frac{b}{4} + \frac{\sqrt{c}}{2} \right) \right] / 120\pi\beta\Gamma \sqrt{c} \left( \frac{b}{4} + \frac{\sqrt{c}}{2} \right)^{3/2}. \quad (24)$$

At this point nothing has been said about the proximity to the disorder curve. In fact, Eq. (24) is valid in all regions of the isotropic phase and is analytic across the disorder curve.

We first consider the excess viscosity in the structured region of disordered phase (microemulsion). It has already been discussed that in this region there are two dominant length scales given by Eqs. (4) and (5). The excess viscosity can now be expressed in terms of

$$\Delta\eta = \frac{1}{120\pi\beta\Gamma} \xi^3 f\left(\frac{\xi}{d}\right), \quad (25)$$

where

$$f(x) = \frac{1 + \pi^2 x^2}{1 + 4\pi^2 x^2}. \quad (26)$$

The most salient feature of this expression is that the excess viscosity can be written in terms of experimentally accessible parameters  $d$  and  $\xi$ . The other point of great interest is that the excess viscosity is predicted to diverge as a third power of correlation length in the vicinity of disordered-lamellar transition. Since in reality this phase transition is first order, we do not expect to see such a sharp divergence in viscosity. Nevertheless, since the phase transition is only weakly first order there should be a large region of a cross-over behavior were a sharp rise in the viscosity should be observed.

We now turn our attention to the paramagnetic-unstructured region of the phase diagram. Here the correlation function takes the usual Ornstein-Zernike form given by Eq. (6). To see how this comes about we analytically continue Eq. (3) into the region  $b > 0$ , and  $c - (b^2/4) < 0$ . We obtain:

$$g(\mathbf{r}) = \frac{1}{2\pi(b^2 - 4c)^{1/2}} \left( \frac{\exp(-|\mathbf{r}|/\xi^-)}{2|\mathbf{r}|} - \frac{\exp(-|\mathbf{r}|/\xi^+)}{2|\mathbf{r}|} \right), \quad (27)$$

where

$$\frac{1}{\xi^-} = \left( (\sqrt{c}/2) + \frac{b}{4} \right)^{1/2} - \left( \frac{b}{4} - (\sqrt{c}/2) \right)^{1/2}, \quad (28)$$

$$\frac{1}{\xi^+} = \left( (\sqrt{c}/2) + \frac{b}{4} \right)^{1/2} + \left( \frac{b}{4} - (\sqrt{c}/2) \right)^{1/2}. \quad (29)$$

It is easy to see that  $0 < 1/\xi^- < 1/\xi^+$ , and the second term in Eq. (27) decays much faster giving the single length scale behavior. In the vicinity of the transition from unstructured paramagnetic to a ferromagnetic phase ( $c=0$ ) the excess viscosity behaves as

$$\Delta\xi \approx \xi^-. \quad (30)$$

We observe that there exists a distinct change in the behavior of the viscosity as one moves from one side of the disorder curve to the other. For low surfactant concentration the excess viscosity is proportional to the cube of the correlation length inside the structured paramagnetic phase (microemulsion), while in the unstructured paramagnetic phase the excess viscosity increases linearly with the correlation length.

We now present a simple physical argument to explain the behavior of viscosity in the unstructured paramagnetic phase. Unfortunately, no such simple argument has been found so far to understand the behavior in the structured phase where there are two dominant length scales.

Consider an object of characteristic size  $\xi$  diffusing through a liquid of viscosity  $\eta$  the diffusion constant is given by<sup>14</sup>

$$D\beta \approx \frac{1}{\xi\eta}. \quad (31)$$

This is a well-known Einstein–Stokes relation. If the mean free path is of the order  $\xi$ , then the mean free time is of the order

$$\tau \approx \frac{\xi^2}{D}. \quad (32)$$

Combining Eqs. (32) and (31) we obtain

$$\tau \approx \eta\xi^3\beta. \quad (33)$$

On the other hand, each mode  $q$ , in the case of the conserved order parameter, relaxes with a characteristic time given by a dynamical scaling hypothesis,<sup>15</sup>

$$\tau_q \approx \xi^z f(q\xi), \quad (34)$$

with the dynamical exponent  $z=4$ . On physical grounds the mode,  $q$  for the length scale that we are interested in is on the order of the inverse length of the correlated region  $1/\xi$ . Using this fact, and substituting Eq. (34) back into Eq. (33), we have an expression for the scaling of the viscosity in the vicinity of a critical point:

$$\eta \approx \xi. \quad (35)$$

This is the same result as the one given by Eq. (30).

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