

# Fluctuation viscosity of a solution of wormlike micelles

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Dynamic fluctuation phenomena in a solution of wormlike micelles are investigated. The anomalous fluctuation contribution to the viscosity coefficients  $\eta_{fl}$  is calculated. This contribution is determined by the nonlinear interaction of hydrodynamic modes with the bending mode, which describes the relaxation of the shape of micelles. At high frequencies  $\eta_{fl}$  behaves as  $\omega^{-1/4}$ . In the low-frequency limit  $\eta_{fl}$  does not depend on the frequency and is on the order of  $(\xi_p/\xi)\eta$  ( $\xi$  is the average distance between crosslinks of the micelles,  $\xi_p$  is the persistent length, and  $\eta$  is the viscosity of the pure solvent). In the case  $\xi_p \gg \xi$  the value of  $\eta_{fl}$  therefore exceeds the bare viscosity  $\eta$ .

When amphiphilic molecules are immersed in water, they can assemble in aggregates of various shapes.<sup>1</sup> In the present work we focus on the particular case in which these aggregates are long, cylindrical (wormlike) micelles. Lyotropic systems (dilute amphiphilic solutions), which shows one-dimensional aggregation, actually provide a realization of an interesting physical object—fluctuating lines. In lyotropic systems long wormlike aggregates can break and recombine reversibly. The possibility that these processes can occur (which look like those in the so-called living polymers<sup>2</sup>) distinguishes lyotropic systems from ordinary polymers in which the molecular chains are unbreakable.

In a recent article<sup>3</sup> the authors investigated the structure and dynamic properties of lyotropic systems which are constructed from wormlike aggregates. It turns out that static structural properties of the systems look like those of polymers. In particular, the scaling laws characteristic of polymers<sup>4</sup> have been observed. However, the dynamic properties of wormlike lyotropic systems and of polymers are different. This difference could be associated with the peculiarities of creep, scission, and recombination processes in lyotropic systems. This explanation has been proposed in Ref. 3. Here we investigate the effects related to the fact that in lyotropic systems wormlike micelles can be considered as roughly straight at distances much greater than their thickness  $d$ . Dynamic fluctuations of micelles on these scales provide a relevant contribution of the viscosity of the system.

The system of wormlike micelles can be characterized by the typical length scale  $\xi$ , which is the average distance between neighboring crosslinks of micelles. A micelle,

like a polymer, is characterized by the persistent length<sup>4</sup>  $\xi_p$ . We assume that  $\xi_p \gg d$  (in polymer physics these are called "semiflexible" polymers). We will consider the case  $\xi \ll \xi_p$ . On the scales smaller than  $\xi$  we can then assume wormlike micelles to be independent, almost straight cylinders. We can also assume that the system is dilute, which implies that  $\xi \gg d$ . The main fluctuation effects are linked with scales ranging from  $d$  to  $\xi$ , where wormlike micelles can be considered as 1D objects, i.e., lines.

The static properties of the micelles can be formulated in terms of the energy of these lines. The energy  $E_b$ , which is related to the variations of the shape of a micelle, can be written in the form

$$E_b = \frac{1}{2} \int dl \kappa \frac{1}{R^2}. \quad (1)$$

This energy is analogous to the well-known Helfrich energy<sup>5</sup> related to membranes (which are 2D objects). In (1)  $\kappa$  is the bending modulus,  $dl$  designates the integration along the micelle, and  $R$  is its curvature radius. Note that in (1) there is no term related to the surface tension, since it is equal to zero because micelles can break and recombine. The persistent length  $\xi_p$  determined by (1) is

$$\xi_p \approx \frac{\kappa}{T}. \quad (2)$$

In addition to the energy (1) one must also take into account the elastic energy, which is related to variations of the linear density of molecules  $n_l$  constituting the micelle. In the approximation which we need such a contribution is

$$E_n = \frac{1}{2} \int dl B \zeta^2. \quad (3)$$

Here

$$\zeta = \frac{n_l - n_0}{n_0}, \quad (4)$$

where  $n_l - n_0$  is the deviation of the linear density of molecules from its equilibrium value  $n_0$ , and the coefficient  $B$  has the meaning of the inverse compressibility of the micelle.

For coefficients  $\kappa$  and  $B$  the natural estimates are

$$\kappa \sim \frac{T}{a^3} d^4, \quad B \sim \frac{T}{a^3} d^2. \quad (5)$$

Here  $T$  is the temperature,  $a$  is the characteristic atomic size ( $T/a^3$  is the estimate of Young's modulus), and  $d$  is the thickness of the micelle. Usually the thickness  $d$  greatly exceeds the atomic size  $a$ , and consequently  $\xi_p \sim d^4/a^3 \gg d$ . The inequality shows that there exists the region of scales  $\xi_p \gg r \gg d$  in which we can ignore the thickness of the micelle and consider it to be approximately straight.

To investigate dynamic fluctuational effects, we need nonlinear equations which describe the dynamics of a wormlike micelle immersed in a liquid. These equations can

be formulated by using the Poisson-brackets method and the dissipative function.<sup>6</sup> We give here only the final expressions which we need, omitting the details. The stress tensor of a micelle per unit length constructed according to (1) and (3) is

$$T_{(\omega)}^{ik} = -\frac{\kappa}{2}(\nu_m \nabla_m \nu_j)^2 \nu_i \nu_k + \kappa \nu_j \nabla_j \nu_n \nu_m \nabla_m \nu_n \nu_i \nu_k + \kappa \nu_k (\delta_{ij} - \nu_i \nu_j) \nu_n \nabla_n (\nu_m \nabla_m \nu_j) + B \zeta \nu_i \nu_k. \quad (6)$$

Here  $\nu_i$  is the unit vector along the micelle. The equation for the linear density  $n_l$  is

$$\frac{\partial n_l}{\partial t} = -\nu_i \nabla_i n_l - n_l \nu_i \nu_k \nabla_k \nabla_k \nu_i. \quad (7)$$

This equation has the meaning of the conservation law of the number of molecules of the micelle. We can assume that the micelle moves at a velocity  $v_i$  of the liquid near the micelle.

To proceed further, we must solve the bulk hydrodynamic equations and express bulk velocities in terms of the velocity of the micelle. For a straight cylinder this problem has been solved by Lamb in 1911 (see, e.g., the monograph in Ref. 7). Lamb's solution for the velocity has a logarithmic singularity near the cylinder

$$\mathbf{v} \simeq m \ln |\mathbf{r}_\perp| + \text{const}. \quad (8)$$

Here  $\mathbf{v}$  is the velocity of the liquid near a micelle,  $m$  determines the value of the derivatives of the velocity near the micelle, and  $r_{\perp i} = (\delta_{ij} - \nu_i \nu_j) r_j$ . This solution correctly describes the velocity near any micelle on the scales smaller than the curvature radius of a micelle  $R$  or of the value  $q^{-1}$ , where  $q$  is the wave vector of the hydrodynamic motion. We consider the case in which the shape of the micelle differs only slightly from the straight line, so the cutoff factor is  $q^{-1}$ .

Expressions (6)–(8) can be used to study the eigenmodes of a wormlike micelle. There are two soft modes where the motion of the solvent is localized near the micelle. One of these modes (actually it is not one but two degenerate modes) is related to the relaxation of the shape of a micelle. This mode (we call it the bending mode) is governed by the dispersion law

$$\omega = -\frac{i\kappa q^4}{\Gamma}, \quad (9)$$

where

$$\Gamma = \frac{8\pi\eta}{|\ln(qd)|}. \quad (10)$$

We assume here that  $|\ln(qd)| \gg 1$ . The other characteristic mode is related to the variations of the density  $n_l$  of a micelle. The dispersion law for this mode (which may be called elastic) in the linear approximation is

$$\omega = -\frac{i2B}{\Gamma} q^2. \quad (11)$$

Note that these modes are analogous to the soft surface modes for membranes.<sup>8,9</sup>

Because of the softness of the bending mode (9), the dynamic effects which are related to the bending fluctuations of micelles are relevant. To examine these effects, we will use a diagram technique of the type first developed by Wyld<sup>10</sup> for the hydrodynamic turbulence and extended to a wide class of physical systems by Martin, Siggia, and Rose.<sup>11</sup> A textbook description of the diagram technique can be found in the book by Ma.<sup>12</sup> Note that this diagram technique is a classical limit of the Keldysh diagram technique,<sup>13</sup> which is applicable to any physical system. As was demonstrated by de Dominicis<sup>14</sup> and Janssen<sup>15</sup> (see also Refs. 16 and 17), Wyld's diagram technique is generated by a conventional quantum field theory starting from an effective action  $I$ . The corresponding methods of investigation can be found in the monograph by Popov<sup>18</sup> (see also Ref. 6).

In our case the effective action  $I$  consists of two parts—the bulk part, which is related to the liquid, and the part which is related to the micelles. Bulk degrees of freedom can be effectively excluded from the consideration by minimization of the effective action over these variables. After the minimization we obtain the term which is associated with the micelle and which describes the interaction between the micelle and the liquid. This procedure is analogous to the one proposed in Ref. 19 for 2D micelles (see also Ref. 9). As a result, we find the explicit expression for the effective action  $I_l$  for a 1D micelle

$$I_l = \int dt dl \left( -\nabla_k p_i T_{ik}^{(\omega)} + \Gamma \left( p_i v_i - \frac{1}{2} v_i v_k p_i p_k \right) \right). \quad (12)$$

Here  $p_i$  is the auxiliary field which is conjugated to the velocity of the liquid. This expression is valid within logarithmic accuracy.

We believe that the micelle is approximately straight. In this case it is natural to introduce the  $Z$  axis in the direction of the micelle and to describe its deviation from the straight line in terms of the displacement vector  $u_\alpha$  (where the Greek index runs over  $x$  and  $y$ ). The fact that the micelle moves with the velocity  $v_i$  of the liquid near the micelle means that the dynamic equation for  $u_\alpha$  is

$$\frac{\partial u_\alpha}{\partial t} = v_\alpha - v_z \nabla_z u_\alpha. \quad (13)$$

This equation, along with (7), should suggest the use of (12).

The quadratic part of the effective action (12) determines the bare correlation function and the response function. In the Fourier representation the correlation function  $D_{\alpha\beta} = \langle u_\alpha u_\beta \rangle$  is

$$D_{\alpha\beta}(\omega, q) = \delta_{\alpha\beta} \frac{2T\Gamma}{\Gamma^2 \omega^2 + \chi^2 q^2}. \quad (14)$$

The response function  $\langle u_\alpha p_\beta \rangle = G_{\alpha\beta}$ , which corresponds to  $D_{\alpha\beta}$ , has the form

$$G_{\alpha\beta}(\omega, q) = -\delta_{\alpha\beta} (\Gamma \omega + i\chi q^2)^{-1}. \quad (15)$$

The higher-order terms of  $I$  determine the fluctuational corrections to the bare values, (14) and (15).

An analysis shows that on the scales  $d \ll r \ll \xi_p$  only the higher-order terms contained in the combination

$$I_\zeta = \int dt dz B(\nabla_z p_z + \nabla_z u_\alpha \nabla_z p_\alpha) (\partial/\partial t)^{-1} \left( \nabla_z v_z + \frac{1}{2} \partial/\partial t (\nabla_z u_\alpha)^2 \right) \quad (16)$$

are relevant. It can be shown that the interaction terms in (16) lead to the redefinition of the coefficient  $B$ ,

$$B \rightarrow B_R = \frac{B}{1 - iBF}, \quad (17)$$

in the correlation functions. Here the quantity  $F$  is

$$F(\omega) = \int \frac{d\omega_1 dq}{(2\pi)^2} q^A D_{\alpha\beta}(v) G_{\alpha\beta}(\omega + \omega_1). \quad (18)$$

From (14), (15), and (18) it follows that

$$F = \frac{iT}{\kappa^{5/4}} \left( \frac{1}{2\Gamma} \right)^{3/4} \left( \frac{i}{\omega} \right)^{3/4}. \quad (19)$$

We note that the function  $F(\omega)$  is analytical in the upper half-plane. The most interesting region of parameters is the one in which  $BF \gg 1$  (i.e., where the fluctuations strongly renormalize the modulus  $B$ ). In this region we have

$$B_R \approx i/F. \quad (20)$$

Because of the softness of the bending mode (9), the interaction of sound (and of other hydrodynamic modes) with the fluctuations of the micelles proves to be relevant. The interaction induces anomalous contributions to such directly observable quantities as viscosity. Using the same procedure as for the membranes,<sup>9</sup> we can find the fluctuational contributions to the viscosity coefficients of lyotropic systems with wormlike micelles. For this purpose we must average the fluctuational contribution to the stress tensor over the micelles. As a result, we find

$$\eta_{fl} = -\frac{1}{15} \frac{l}{V} \frac{\text{Im} B_R}{\omega}, \quad (21)$$

where  $l/V$  is the average length of the micelles per unit volume ( $l/V$  has the dimension  $\text{cm}^{-2}$ ). We see that the fluctuation viscosity has the nontrivial frequency dependence. If (20) is correct,

$$\eta_{fl} \sim \frac{1}{V} \frac{\kappa^{5/4} \Gamma^{3/4}}{T} \omega^{-1/4}. \quad (22)$$

The region of the applicability of (22) is bounded below. The problem is that in the derivation of this expression we have assumed the micelles to be approximately

straight and noninteracting. This assumption is true only if the characteristic wave vector  $q$  is larger than  $\xi^{-1}$ . Using the dispersion law (9), we find the limiting condition for (22):  $\omega \gg \kappa \xi^{-4} / \Gamma$ . For smaller frequencies the fluctuational contribution to the viscosity  $\eta_{fl}$  does not depend on the frequency. It is of the order

$$\frac{\eta_{fl}}{\eta} \sim l / V \kappa \xi / T. \quad (23)$$

In the case  $\xi_p \gg \xi$  the ratio  $\eta_{fl} / \eta$  is on the order of this large factor and therefore the fluctuation viscosity  $\eta_{fl}$  exceeds the viscosity  $\eta$  of the pure solvent.

The theoretical results obtained by us are in qualitative agreement with the experimental data [?] for dilute solutions of wormlike micelles. A quantitative comparison with experiment is now difficult. We believe that there are two predictions of the theory which can be verified experimentally. First, it follows from (23) that the low-frequency value of  $\eta_{fl}$  should be proportional to  $\sqrt{c}$ , where  $c$  is the concentration of the amphiphilic molecules. Secondly, in the high-frequency region,  $\omega \gg \kappa \xi^{-4} / \Gamma$  [and if expression (20) holds] the sound absorption should be proportional to  $\omega^{7/4}$  (instead of the conventional law  $\omega^2$ ).

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