

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 viscosity coefficients η_{fl} is calculated. This contribution is determined by nonlinear interaction of hydrodynamic modes with bending mode, describing the relaxation of the shape of micelles. At high frequencies η_{fl} behaves as $\omega^{-1/4}$. In the low-frequency limit η_{fl} does not depend on frequency and is of the order of $(\xi_p/\xi)\eta$ (ξ is the average distance between crosslinks of the micelles, ξ_p is the persistent length, η is the viscosity of the pure solvent). Therefore in the case $\xi_p \gg \xi$ the value of η_{fl} exceeds the bare viscosity η .

When amphiphilic molecules are brought into water they can assemble in aggregates of various shapes [1]. In the present work we focus on the particular situation where these aggregates are long cylindrical (wormlike) micelles. Lyotropic systems (dilute amphiphilic solutions) showing one-dimensional aggregation actually provide an realization of an interesting physical object – fluctuating lines. In lyotropic systems long wormlike aggregates can break and recombine reversibly. The possibility of these processes (look like as in so called living polymers [2]) differs lyotropic systems from ordinary polymers, where the molecular chains are unbreakable.

In the recent article [3] the authors investigated the structure and dynamical properties of lyotropic systems, constructed from wormlike aggregates. It turns out that static structural properties of the systems are look like of polymers. In particular the scaling laws characteristic of polymers [4] are observed. However the dynamical properties of wormlike lyotropic systems and polymers are different. This difference could be associated with the peculiarities of reptation, scission and recombination processes in lyotropic systems. Just this explanation has been proposed in [3]. Here we investigate effects related to the fact that in lyotropic systems wormlike micelles can be considered as roughly straight on distances much exceeding their thickness d . Dynamical fluctuations of micelles on these scales prove to provide a relevant contribution to the viscosity of the system.

The system of wormlike micelles can be characterized by the typical length scale ξ , which is the average distance between neighboring crosslinks of micelles. Besides a micelle like a polymer is characterized by the persistent length ξ_p [4]. We will suppose that $\xi_p \gg d$ (such situation in polymerphysics termed "semiflexible" polymers). We will consider the case $\xi \ll \xi_p$. Then on scales smaller than ξ we can consider wormlike micelles as independent almost straight cylinders. We will also believe that the system is dilute which implies that $\xi \gg d$. The main fluctuation effects are related to scales from d to ξ 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_l related to variations of the shape of a micelle can be written in the form

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

analogous to the well known Helfrich energy [5] related to membranes (which are $2d$ objects). In (1) κ is the bending module, 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 of the possibility of breaking and recombining micelles. The persistent length ξ_p determined by (1) is

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

In addition to the energy (1) one must also take into account the elastic energy, related to variations of the linear density of molecules n_l , constituting the micelle. In the approximation 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 a 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 κ and B there are the natural estimations

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

Here T is the temperature, a is the characteristic atomic size (T/a^3 is the estimation for the Young module), and d is the thickness of the micelle. Usually the thickness d exceeds largely 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 $\xi_p \gg r \gg d$ where we may neglect the thickness of the micelle and consider it as approximately straight.

To investigate dynamic fluctuational effects we need nonlinear equations describing dynamics of a wormlike micelle immersed in a liquid. These equations can be formulated using the Poisson brackets method and the dissipative function [6]. We give here only ultimate expressions which we need, omitting details. The stress tensor of a micelle per its unit length constructed according to (1), (3) is

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

Here ν_i is the unit vector along the micelle. The equation for the linear density n_l is

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

which has the meaning of the conservation law of the number of molecules of the micelle. Besides we can assert that the micelle moves with the velocity v_i of the liquid near the micelle.

To proceed further we have to 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 [7]). The Lamb's solution for the velocity has the logarithmic singularity near the cylinder

$$v \simeq m \ln |r_{\perp}| + \text{const} \quad (8)$$

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

Expressions (6), (7), (8) can be employed 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 will term it as the bending mode) has the dispersion law

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

where

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

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

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

Note that these modes are analogous to the soft surfacial modes for membranes [8,9].

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

In our case the effective action I consists of two parts - the bulk one related to the liquid and the part related to micelles. Bulk degrees of freedom can be

effectively excluded from the consideration by minimization over these variables of the effective action. After the minimization we arrive at the term attached to the micelle and describing the interaction between the micelle and the liquid. This procedure is analogous to one proposed in the work [19] for 2d micelles (see also [9]). As a result one can find the explicit expression for the effective action I_l for a 1d micelle

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

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

We believe that the micelle is approximately straight. In this case it is naturally to introduce the Z -axis in the direction of the micelle and to describe its deviations from the straight shape in terms of the displacement vector u_α (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 dynamical equation for u_α is

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

This equation alongside (7) should be implied at exploiting (12).

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

$$D_{\alpha\beta}(\omega, q) = \delta_{\alpha\beta} \frac{2T\Gamma}{\Gamma^2 \omega^2 + \kappa^2 q^8} . \quad (14)$$

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

$$G_{\alpha\beta}(\omega, q) = -\delta_{\alpha\beta} (\Gamma\omega + i\kappa q^4)^{-1} . \quad (15)$$

The higher order terms of I determines fluctuational corrections to the bare values (14), (15).

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

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

are relevant. It can be demonstrated 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 correlation functions. Here the quantity F is

$$F(\omega) = \int \frac{d\omega_1 dq}{(2\pi)^2} q^4 D_{\alpha\beta}(\nu) G_{\alpha\beta}(\omega + \omega_1) , \quad (18)$$

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

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

Let us note that the function $F(\omega)$ is analytical in the upper half-plane. The most interesting is the region of parameters where $BF \gg 1$ (i. e. where fluctuations strongly renormalize the module B). In this region

$$B_R \simeq i/F \quad (20)$$

Due to softness of the bending mode (9) the interaction of sound (and other hydrodynamic modes) with fluctuations of micelles proves to be relevant. The interaction induces anomalous contributions to such directly observable quantities as viscosity. Using the same procedure as for membranes [9] we can find the fluctuational contributions to viscosity coefficients of lyotropic systems with wormlike micelles. For this purpose we have to average the fluctuational contribution to the stress tensor over 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 micelles per unit volume. (l/V has the dimension cm^{-2}). We see that the fluctuation viscosity has the nontrivial frequency dependence. If (20) is correct

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

The region of the applicability of (22) is limited from below. The problem is that at the derivation of this expression we have believed the micelles to be approximately straight and non-interacting. It is true only if the characteristic wave vector q is larger than ξ^{-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 viscosity η_{fl} will not depend on frequency and will be of the order

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

In the case $\xi_p \gg \xi$ the ratio η_{fl}/η will be of the order of this large factor and therefore the fluctuation viscosity η_{fl} will exceed the viscosity η of the pure solvent.

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

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