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# Complex Shear Viscosity of Dilute Microemulsions

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Properties of membranes made of amphiphilic molecules are of current interests in connection with statistical mechanics of fluctuating surfaces, biophysics of membranes and also high-energy physics [1]. Such membranes are typically realized in microemulsion system being homogeneous mixtures of oil, water and surfactants. Since the surface tension of the membranes is zero or practically zero, the system can contain large internal interfacial areas separating oil and water. Instead of the surface tension, the deformation of the surface is governed mainly by the elastic bending energy [2]. Since the associated bending rigidity is known to be the order of  $k_B T$ , membranes fluctuate due to thermal excitations and hence one should consider this problem from the point of view of statistical mechanics.

We have calculated the oscillation frequencies and the relaxation times of a spherically closed fluid membrane [3] whose equilibrium shape is determined by the minimization of the following shape energy;

$$H = \frac{1}{2} \kappa \oint dA (c_1 + c_2 - c_0)^2 + \Sigma \oint dA + \Delta P \int dV. \quad (1)$$

In the above,  $dA$  and  $dV$  are surface and volume elements, respectively,  $\kappa$  the bending rigidity,  $c_1$  and  $c_2$  are two principal curvatures,  $c_0$  the spontaneous curvature,  $\Sigma$  the surface tension and  $\Delta P$  the (osmotic) pressure difference  $\Delta P \equiv P - P'$

measured between outside and inside. (Here and below we use the prime in order to distinguish the quantities of the inside fluid from the corresponding quantities of the outside fluid.)

We construct the boundary condition that must be satisfied at the interface between two viscous fluids in motion. In the presence of both surface tension and bending rigidity, the equality of the forces on the surface of each fluid can be written as

$$(P - P')\mathbf{n}_\alpha - (\sigma_{\alpha\beta} - \sigma'_{\alpha\beta})\mathbf{n}_\beta + [-2\Sigma c + \kappa(2c + c_0)(2c^2 - 2k - c_0c) + 2\kappa\nabla_{LB}^2 c]\mathbf{n}_\alpha = 0, \quad (2)$$

where  $\mathbf{n}_\alpha$  are components of the normal vector,  $\sigma_{\alpha\beta}$  the viscous stress tensor,  $\nabla_{LB}^2$  the Laplace-Beltrami operator on the surface,  $c$  and  $k$  are mean curvature and Gaussian curvature, respectively. We assume that the fluctuating deviations from the spherical shape can be represented by

$$r = r_0 + l(\theta, \varphi, t). \quad (3)$$

Expanding  $l(\theta, \varphi, t)$  in terms of the spherical harmonics  $Y_{nm}(\theta, \varphi)$ , we obtain the sequence of the relaxation time as [3]

$$\frac{1}{\tau_{nm}} = \frac{1}{\eta r_0^3} \frac{(n-1)n(n+1)(n+2)(2n+1)(E+1)}{[(2n^2 + 4n + 3)E + 2n(n+2)][2(n^2 - 1)E + 2n^2 + 1]} \times \left[ \Sigma r_0^2 + \kappa \left\{ n(n+1) - 2c_0 r_0 + \frac{1}{2} c_0^2 r_0^2 \right\} \right], \quad (4)$$

where  $\eta$  is the fluid viscosity outside of the vesicle and  $E \equiv \eta'/\eta$ .

We further investigate the influence of thermal shape fluctuations on the complex shear viscosity of microemulsions which is expected to exhibit a relaxation process. This relaxation time can be possibly attributed to the relaxation of stress in the surface of droplets governed by the bending rigidity. As for the viscoelastic model, we investigate the case where the emulsion system is Newtonian at

infinitely long time scale and still viscous at infinitely short time scale. In other words, we shall employ the so called Maxwell model where the complex shear viscosity  $\eta^*$  is given by

$$\eta^* = \eta_\infty + \sum_{n,m} \frac{G_{nm}\tau_{nm}}{1 + i\omega\tau_{nm}}. \quad (5)$$

In the above,  $\eta_\infty$  is the viscosity for  $\omega \rightarrow \infty$ ,  $\tau_{nm}$  the relaxation time and  $G_{nm}$  the relaxation strength. The complex shear viscosity of microemulsion system is calculated by assuming that (1) emulsion droplets are monodisperse; (2) the volume fraction  $\phi$  is small enough so that the linear viscoelasticity can be considered to be the sum of the single droplet effects.

Here we consider a pure straining motion which has in polar coordinates the  $Y_{20}$ -symmetry. Then the relaxation strength  $G_{nm}$  turns out to be

$$G_{nm} = \frac{2\phi}{5r_0^3} \left[ \frac{\eta_\infty - \eta}{\phi(\eta' - \eta)} \right]^2 \left\{ \frac{1}{2}(n-1)(n+2) [\Sigma r_0^2 + \kappa \left\{ n(n+1) - 2c_0r_0 + \frac{1}{2}c_0^2r_0^2 \right\}] \delta_{n2}\delta_{m0} + \frac{1}{2}k_B T \sum_{k=|n-2| \geq 2}^{n+2} F_k^2 C_{km}^2 C_{k0}^2 \right\} \quad (6)$$

where

$$F_k = \sqrt{\frac{5(2k+1)}{4\pi(2n+1)}}, \quad (7)$$

and  $C_{km} = \langle k \ 2 \ m \ 0 \mid k \ 2 \ n \ m \rangle$  are Clebsch-Gordan coefficients.

Here we consider the case of vanishing surface tension and spontaneous curvature, i.e.,  $\Sigma = 0$  and  $c_0 = 0$  but  $\kappa \neq 0$ . In the figure, real and imaginary part of the rescaled relative viscosity

$$\bar{\eta} \equiv \frac{\eta^* - \eta_\infty}{\eta} \left[ \frac{\phi(\eta' - \eta)}{\eta_\infty - \eta} \right]^2 \frac{5}{\phi}, \quad (8)$$

are plotted for  $k_B T / \kappa = 0$  and 10, respectively. For simplicity we took  $E = 1$  and other parameters are  $r_0 = 100\text{\AA}$  and  $\eta = 1.0 \times 10^{-3}\text{Pas}$ .

The relaxation process of the complex viscosity has been observed in the experiment by Mellema, Blom and Beekwilder [4] who although attributed it to

the stress relaxation due to the surface tension. However in the system of the microemulsion or fluid membranes, the surface tension of these membranes is practically zero. From this point of view, we can not agree with their interpretation and consider that the observed relaxation should be explained from the point of view of the bending rigidity.

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