

## Linear viscoelasticity in lipid bilayers of vesicles

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In two preceding articles the complex shear viscosity of a dispersion of vesicles has been determined and from an observed macroscopic relaxation time that pertains to deformation of vesicles a value of the static shear modulus has been calculated with the use of the Oldroyd model. In the present paper this model has been extended by incorporating in the shear behavior of the lipid bilayer a linear viscoelastic behavior with one relaxation time in order to be able to relate the macroscopic relaxation time to a dynamic shear modulus instead of a static shear modulus. The latter is believed not to exist. With the extended Oldroyd model the experimental results can be interpreted. This leads to a value of the dynamic shear modulus.

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### I. INTRODUCTION

Vesicles are liquid spheres enclosed by a lipid bilayer. The linear viscoelastic behavior of a colloidal dispersion of vesicles has been determined in two previous papers [1,2]. The complex viscosity  $\eta^*$  has been measured as a function of angular frequency  $\omega$ . For fresh egg-yolk bilayer vesicles two sets of relaxation processes can be seen in the frequency range between 70 Hz and 235 kHz. With increasing age of the bilayers a third relaxation process becomes visible at high frequencies. The longest relaxation time is of entropic nature and is also seen in colloidal hard-sphere dispersions. The shorter second and third relaxation times have been analyzed with a theoretical model developed by Oldroyd [3,4]. The second relaxation time occurs as a consequence of the deformation of the vesicles and was related to the influence of the static surface shear modulus of the bilayer. The shortest relaxation time occurs also as a consequence of the deformation of the vesicles, but is dominated by a static surface dilatational modulus. From these measurements bounds of the static surface shear modulus, static surface dilatational modulus, static surface shear viscosity, and the curvature modulus have been determined.

In biophysical and chemical literature it is believed that the static shear modulus of a lipid bilayer does not exist, see literature in [1]. This is substantiated in the following reasoning. At temperatures above the transition temperature  $T_c$  the lipid bilayer is in a liquid-crystalline state and a lipid molecule can move freely through the membrane at time scales longer than its self-diffusion time over a distance in the order of the size of a molecule. Therefore at sufficient long time scales no energy can be stored in the displacement of lipid molecules with respect to each other and then a static shear modulus does not exist. However, at sufficient short time scales a dynamic shear modulus can exist and if relevant the measured relaxation time should be related to this quantity. In the Oldroyd model no relaxation processes are incorporated in the constitutive equation of the vesicle

membrane. Consequently the Oldroyd model has to be adapted to the case where a dynamic shear modulus is present. We have extended the constitutive equation of the vesicle membrane with a frequency dependent part that describes one relaxation process pertaining to shear behavior and we have derived analytical results. We will show that the mentioned relaxation time in our viscoelastic experiment can be related to the dynamic shear modulus and that its numerical value is accidentally equal to the value of the static shear modulus deduced with the original Oldroyd model. We will also show that the extended model has one more macroscopic relaxation time compared to the known Oldroyd model.

In Sec. II we will outline the procedure that is followed to derive the new model and some analytical results will be given. In Sec. III an analysis of the measurements with the new model will be carried out.

### II. THEORY

The first attempt to describe the viscoelastic behavior of a suspension of deformable droplets has been made by Oldroyd [3,4]. The main advantage of this model is that it is rather simple and can easily be derived analytically. The interface between the droplet and the solvent is infinitesimally thin and is characterized by an interfacial tension  $\gamma$ , a surface shear modulus  $\mu$ , a surface shear viscosity  $\zeta$ , a surface dilatational modulus  $\kappa$ , and a surface dilatational viscosity  $\sigma$ . These mechanical parameters are all constants, thus being static or stationary quantities.

There is no need to describe again the Oldroyd model in detail or to give a thorough derivation of the extended model. We refer to [3–5] for a detailed analysis of the original model. We have followed the procedure outlined in [5] and will only present a brief reminder here.

A monodisperse dispersion of vesicles of radius  $a$  and volume fraction  $c$  is modeled in the following. One vesicle with internal viscosity  $\eta_i$  surrounded by a solvent with viscosity  $\eta$  is considered. At radius  $b$  there is an imagi-

nary interface between the solvent and a liquid with the macroscopic dynamic viscosity  $\eta^*$  of the dispersion. This model is a cell model and the space inside the imaginary interface will be referred to as the cell. The volume of the artificial cell is chosen to be the total dispersion volume divided by the number of vesicles. The fluid outside the cell is assumed to follow the macroscopic flow exactly. For convenience this is a three-dimensional harmonic oscillating elongational flow with small amplitude, thus modeling linear viscoelastic behavior.

The solution of the flow field according to the Stokes equations in spherical coordinates  $(r, \theta, \phi)$  with the same symmetry as the macroscopic flow is well known [6]. The  $\phi$  component of the fluid velocity is not present here, because the deformation of a vesicle is symmetric with respect to  $\phi$ . Therefore two velocity components remain, as well inside as outside the vesicle, and they are known except for a number of undetermined constants. At the cell interface and the vesicle interface the velocity components are continuous and so we obtain two equations at each interface as a result of these boundary conditions. The two components of the stress tensor that are relevant are  $T_{rr}$  and  $T_{r\theta}$ . They are not continuous across the vesicle interface, for the surface stress has to be taken into account. These boundary conditions result in another two equations. The system of six equations that remains contains six undetermined constants and therefore can be solved. The macroscopic dynamic viscosity can be related to one of the constants that has to be determined [5].

The Oldroyd model is a single droplet model not taking into account direct or indirect interactions between droplets. Thus it only is valid to first order in  $c$ .

In the original Oldroyd model the complex shear modulus of the vesicle surface is given by

$$\mu^* = \mu + i\omega\zeta. \quad (1)$$

We have extended the complex shear modulus with a viscoelastic term with one relaxation time  $\tau_s$ :

$$\mu^* = \mu + \frac{G\tau_s^2\omega^2}{1 + \omega^2\tau_s^2} + i\omega \left( \zeta + \frac{G\tau_s}{1 + \omega^2\tau_s^2} \right). \quad (2)$$

The parameter  $G$  will be called the dynamic shear modulus. As mentioned earlier the static shear modulus  $\mu$  is believed not to exist. We will not yet omit the static shear modulus because we want to point out the difference between the original model and the extended one. At time scales much longer than  $\tau_s$  the effective shear modulus is  $\mu$  and the effective shear viscosity is  $\zeta + G\tau_s$ , and at short time scales they are  $\mu + G$  and  $\zeta$ , respectively.

The new complex shear modulus is incorporated in the two-dimensional surface stress tensor and this results in an altered boundary condition for the  $T_{r\theta}$  components of the macroscopic stress tensor across the vesicle interface. Thus with just one of the six equations altered the extended Oldroyd model has been calculated analytically. This result has been verified with REDUCE 3.4.

The macroscopic viscosity now becomes

$$\eta^* = \eta \left( \frac{A_1 + i\omega A_2 - \omega^2 A_3 - i\omega^3 A_4}{B_1 + i\omega B_2 - \omega^2 B_3 - i\omega^3 B_4} \right) \quad (3)$$

with  $A_i$  and  $B_i$  functions of  $a$ ,  $\eta$ ,  $\eta_i$ ,  $\kappa$ ,  $\mu$ ,  $\sigma$ ,  $\zeta$ ,  $G$ ,  $\tau_s$ , and  $c$ . The complete solution is given in the Appendix. This equation is rewritten as

$$\eta^* = \eta_0 \frac{(1 + i\omega\lambda_1)(1 + i\omega\lambda_2)(1 + i\omega\lambda_3)}{(1 + i\omega\tau_1)(1 + i\omega\tau_2)(1 + i\omega\tau_3)}. \quad (4)$$

We see that the extended Oldroyd model contains three relaxation times  $\tau_i$  and three retardation times  $\lambda_i$ . This means that by incorporating the relaxation process in the vesicle membrane an extra macroscopic relaxation time occurs, for the original model contains two relaxation times. The low frequency limit of the complex viscosity is the well-known Einstein expression  $\eta_0 = \eta(1 + \frac{5}{2}c)$ . The analytical equations of the relaxation times are rather complex and would take a few page's space. Therefore we only will consider the case that the relaxation times are far apart. Then they can be approximated by

$$\tau_1 = \frac{B_2}{B_1}, \quad (5a)$$

$$\tau_2 = \frac{B_3}{B_2}, \quad (5b)$$

$$\tau_3 = \frac{B_4}{B_3}, \quad (5c)$$

with  $\tau_1 \gg \tau_2 \gg \tau_3$ . The concentration dependence of the functions  $B_i$  will be omitted. They cannot be determined uniquely, because Eq. (3) only is valid to first order in  $c$ . The functions  $B_i$  can be rewritten as

$$B_1 = C_1, \quad (6a)$$

$$B_2 = C_2 + C_1\tau_s + D_1G\tau_s, \quad (6b)$$

$$B_3 = C_3 + C_2\tau_s + D_2G\tau_s, \quad (6c)$$

$$B_4 = C_3\tau_s. \quad (6d)$$

The functions  $C_i$  are the coefficients of the second order polynomial in  $\omega$  in the denominator of the expression of the macroscopic complex viscosity in the original Oldroyd model [5]. The functions  $D_i$  are new and are

$$D_1 = 64(\gamma + \kappa), \quad (7a)$$

$$D_2 = 8(12a\eta + 13a\eta_i + 8\sigma). \quad (7b)$$

We see that when  $\tau_s = 0$  the relaxation times of the Oldroyd model are recovered directly. When  $G$  is small enough, depending on the values of  $C_i$ , the relaxation times of the Oldroyd model also can be recovered and the other relaxation time equals  $\tau_s$ . In the discussion we return to this with an example.

The approximate expressions of the relaxation times can be simplified when *a priori* assumptions are made about the values of  $G$ ,  $\mu$ ,  $\kappa$ , and  $\gamma$ . The motive of this work was the nonexistence of the static shear modulus

and from now on we will set  $\mu$  equal to 0. The literature value of  $\kappa$  is in the order of  $0.1 \text{ N m}^{-1}$  while the value of  $\gamma$  is much smaller than  $10^{-3} \text{ N m}^{-1}$ , see, e.g., [1]. The value of  $\gamma$  is so small that we only have to consider the cases  $\kappa \gg G \gg \gamma$  and  $G \gg \kappa \gg \gamma$ . For both cases a simplified expression for each relaxation time is obtained and from the measurements we will show which one is relevant here. In both cases another assumption is necessary to obtain manageable expressions. These are  $\kappa\tau_s \gg a\eta; a\eta_i; \zeta; \sigma$  in the first case and  $G\tau_s \gg a\eta; a\eta_i; \zeta; \sigma$  in the second one. We will show below that these approximations are justified in the case considered.

When  $\kappa \gg G \gg \gamma$  the approximate relaxation times become

$$\tau_1 = \frac{1}{24\gamma} (\mathcal{A}_I + 16\zeta) + \frac{2G\tau_s}{3\gamma}, \quad (8a)$$

$$\tau_2 = \frac{1}{16G} \left( \frac{\mathcal{A}_I + 16 \left( \zeta + \frac{G\sigma}{\kappa} \right)}{\frac{1+16\zeta}{16G\tau_s} + 1} \right), \quad (8b)$$

$$\tau_3 = \frac{1}{2\kappa} \left( \frac{\mathcal{A}_{III} + 2\sigma\mathcal{A}_I + 4\zeta\mathcal{A}_{II} + 32\sigma\zeta}{\mathcal{A}_I + 16 \left( \zeta + \frac{G\zeta}{\kappa} \right)} \right), \quad (8c)$$

and when  $G \gg \kappa \gg \gamma$  they become

$$\tau_1 = \frac{2G\tau_s}{3\gamma}, \quad (9a)$$

$$\tau_2 = \frac{1}{8\kappa} \left[ \mathcal{A}_{II} + 8 \left( \sigma + \frac{\kappa\zeta}{G} \right) \right], \quad (9b)$$

$$\tau_3 = \frac{1}{4G} \left( \frac{\mathcal{A}_{III} + 2\sigma\mathcal{A}_I + 4\zeta\mathcal{A}_{II} + 32\sigma\zeta}{\mathcal{A}_{II} + 8 \left( \sigma + \frac{\kappa\zeta}{G} \right)} \right). \quad (9c)$$

We have used the following abbreviations:

$$\mathcal{A}_I = 32a\eta + 23a\eta_i, \quad (10a)$$

$$\mathcal{A}_{II} = 12a\eta + 13a\eta_i, \quad (10b)$$

$$\mathcal{A}_{III} = 48a^2\eta^2 + 89a^2\eta\eta_i + 38a^2\eta_i^2. \quad (10c)$$

### III. REANALYSIS OF MEASUREMENTS

The Oldroyd model only is valid in dilute dispersions because the hydrodynamic and direct interactions between the vesicles have been neglected and its solution is correct in first order of the vesicle concentration. The experiments have been carried out with concentrated dispersions of vesicles above the lipid transition temperature and it is obvious that vesicle interactions should be taken into account. The direct interactions between the vesicles

are such that only hard sphere behavior can be expected. This leads to the already mentioned longest relaxation time. The hydrodynamic interactions are taken into account in an average way. The viscosity outside a vesicle is strongly influenced by the presence of other vesicles. Therefore  $\eta$  will be replaced by  $\eta_{\text{eff}}$ , which is an effective value that accounts for the viscosity felt by the vesicle (see [1,2]).

In the original Oldroyd model the relaxation time that is dominated by the shear modulus is given by

$$\tau = \frac{\mathcal{A}_I}{16\mu} + \frac{\zeta}{\mu}. \quad (11)$$

This is valid when  $\kappa \gg \mu \gg \gamma$  so that it is far apart from the other present relaxation time. In the viscoelastic experiment the complex viscosity was measured as a function of angular frequency; the vesicle concentration and vesicle radii have been varied. The measured second relaxation time as a function of  $\mathcal{A}_I$  is given in Fig. 1. From this figure and Eq. (11) the following values were calculated:

$$\mu = (2.1 \pm 0.2) \times 10^{-3} \text{ N m}^{-1}, \quad (12a)$$

$$\zeta \leq 1.3 \times 10^{-10} \text{ N s m}^{-1}. \quad (12b)$$

Equation (11) is valid, because  $\mu$  satisfies the approximation  $\kappa \gg \mu \gg \gamma$ . As a further check on the model the same experiment was done with a highly concentrated vesicle system that was slightly aged and was diluted during the experiment. This result is displayed in Fig. 2.

We will now use the extended Oldroyd model and show that the experimental results can again be interpreted. In the previous section Eqs. (8) and (9) are the approximations of the three relaxation times when  $\kappa \gg G \gg \gamma$  and  $G \gg \kappa \gg \gamma$ , respectively. The longest relaxation times Eqs. (8a) and (9a) are dominated by  $\gamma$  and are too long and their strength too weak to be a possible candidate for the measured relaxation time. So in both approximations two possible relaxation times remain: Eqs. (8b), (8c), (9b), and (9c).

We have four different equations that have to be evaluated in order to determine which one is the correct one to

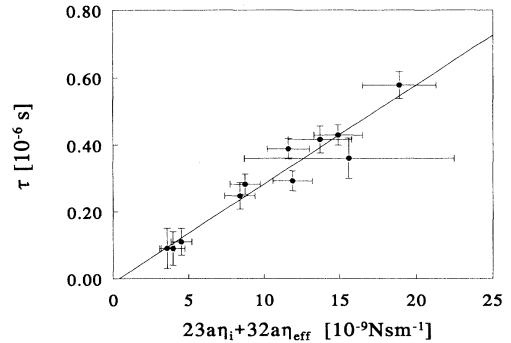


FIG. 1. The measured second relaxation time as a function of  $\mathcal{A}_I = 32a\eta_{\text{eff}} + 23a\eta_i$  for a freshly made vesicle dispersion. The best fit of the extended Oldroyd model is shown.

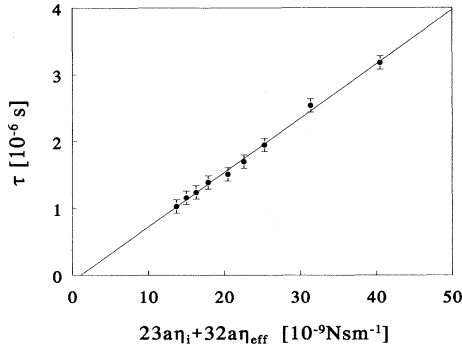


FIG. 2. The measured second relaxation time as a function of  $\mathcal{A}_I = 32a\eta_{\text{eff}} + 23a\eta_i$  for a dilution series of a slightly aged vesicle dispersion. The best fit of the extended Oldroyd model is shown.

describe the measured relaxation time. All four equations can be fitted well to the measured data. When we use Eq. (8c) or (9b) we obtain a value of  $\kappa$  of order  $10^{-3} \text{ N m}^{-1}$  and using Eq. (9c) we obtain  $G = (1.0 \pm 0.1) \times 10^{-3} \text{ N m}^{-1}$ , which means that  $\kappa$  would even be smaller than  $10^{-3} \text{ N m}^{-1}$ . These values are not realistic, for we expect a value of  $\kappa$  of order  $10^{-1} \text{ N m}^{-1}$  or longer. When the relaxation strength is calculated, in both cases we see that the relaxation processes that are dominated by the dilatational modulus are not as strong as the ones dominated by the dynamic shear modulus. With all this information we can state that the relaxation time  $\tau_2$  in Eq. (8b) is the one that should be used to describe the measured relaxation time.

In Figs. 1 and 2 the results of the best fits for this relaxation time are shown. We find that for  $\tau_s \geq 2 \times 10^{-6} \text{ s}$  Fig. 1 can be fitted well and for  $\tau_s \geq 10^{-5} \text{ s}$  Fig. 2 can be fitted well also. For a freshly made vesicle dispersion we have

$$G = (2.0 \pm 0.2) \times 10^{-3} \text{ N m}^{-1}, \quad (13a)$$

$$\zeta + \frac{G\sigma}{\kappa} \leq 4 \times 10^{-11} \text{ N sm}^{-1}, \quad (13b)$$

$$\tau_s \geq 2 \times 10^{-6} \text{ s}. \quad (13c)$$

From Eq. (13b) we obtain

$$\zeta \leq 4 \times 10^{-11} \text{ N sm}^{-1}, \quad (14a)$$

$$\frac{\sigma}{\kappa} \leq 2 \times 10^{-8} \text{ s}, \quad (14b)$$

and since  $\kappa \geq 10^{-1} \text{ N m}^{-1}$  we have

$$\sigma \leq 2 \times 10^{-9} \text{ N sm}^{-1}. \quad (15)$$

So with the extended model not only a maximum value of  $\zeta$  is obtained, but also a maximum value of  $\sigma$ . The effective viscosity at angular frequencies far below  $\tau_s^{-1}$  is now given by

$$\zeta_{\text{eff}} = \zeta + G\tau_s \geq 4 \times 10^{-9} \text{ N sm}^{-1}. \quad (16)$$

Its lowest value is of the same order as the maximum values found in literature [1]. Therefore we can expect that the relaxation time  $\tau_s$  will not be larger than  $10^{-5} \text{ s}$  by orders of magnitude, for then our effective viscosity will be far too large. It is easily verified that the assumption  $\kappa\tau_s \gg a\eta_{\text{eff}}; a\eta_i; \zeta; \sigma$  is valid.

The relaxation time in Eq. (8c) is the same as the relaxation time that was dominated by the dilatational modulus in the original Oldroyd model. Therefore the interpretation of the measured third relaxation time is not affected by the extension of the model.

#### IV. DISCUSSION

We have incorporated one relaxation time in the complex shear modulus of the lipid bilayer. An extension to a series of relaxation times is straightforward, but is analytically less transparent. Each incorporated relaxation time brings about another macroscopic relaxation time. Therefore we would obtain a macroscopic series of relaxation times. Approximations according to Eqs. (5) are not allowed because the relaxation times are not all far apart anymore.

At first sight the replacement of a static shear modulus  $\mu$  by a dynamic shear modulus  $G$  may look logical and trivial. The value of  $\mu$  according to the Oldroyd model and the value of  $G$  according to the extended model are nearly equal. But when the relaxation times are plotted as a function of  $G$  with  $\tau_s$  as the parameter it becomes clear that only in a certain range of  $G$  the inversely linear relation between  $\tau_2$  and  $G$  in Eq. (8b) exists. In Fig. 3 these relaxation times are shown. The parameter values are of the experimentally necessary order of magnitude, except for  $\gamma$  for which no accurate literature values is

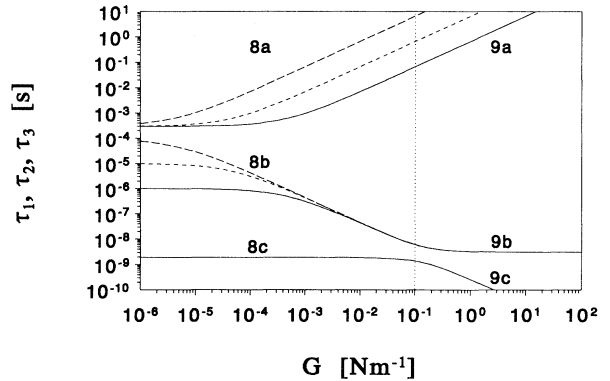


FIG. 3. The three relaxation times predicted by the extended Oldroyd model as a function of  $G$  with  $\tau_s = 10^{-6} \text{ s}$  (—),  $\tau_s = 10^{-5} \text{ s}$  (- - -), and  $\tau_s = 10^{-4} \text{ s}$  (- · -). The corresponding approximate equations are given and the vertical dotted line marks their validity limit. The lines for the shortest relaxation time coincide. The other parameter values are  $\eta_i = \eta_{\text{eff}} = 1 \times 10^{-3} \text{ Pa s}$ ,  $a = 1 \times 10^{-7} \text{ m}$ ,  $\kappa = 0.1 \text{ N m}^{-1}$ ,  $\zeta = 1 \times 10^{-10} \text{ N sm}^{-1}$ ,  $\mu = \sigma = 0$ , and  $\gamma = 1 \times 10^{-6} \text{ N m}^{-1}$ .

known. For convenience  $\sigma$  has been omitted. The reader is reminded that Eqs. (8) and (9) are not valid when the times are close to each other.

For the original Oldroyd model approximate relations for the relaxation times according to Eqs. (5) have been presented earlier [5]. It was shown that each relaxation time could be written as a product of a two-dimensional viscosity divided by a two-dimensional modulus times a function of dimensionless parameters. In the extended model this can also be done. When we rewrite Eq. (8b) the dependence on  $\tau_s$  can be illustrated in another way:

$$\tau_2 = \tau_s \left( \frac{1 + \frac{23}{32} \frac{\eta_i}{\eta_{\text{eff}}} + \frac{1}{2} \left( \frac{\zeta}{a\eta_{\text{eff}}} + \frac{G\sigma}{\kappa a\eta_{\text{eff}}} \right)}{1 + \frac{23}{32} \frac{\eta_i}{\eta_{\text{eff}}} + \frac{1}{2} \frac{\zeta}{a\eta_{\text{eff}}} + \frac{1}{2} \frac{G\tau_s}{a\eta_{\text{eff}}}} \right). \quad (17)$$

When the dimensionless quantities in numerator and denominator are small with respect to 1 we have  $\tau_2 \approx \tau_s$ . Thus in the extended model the intrinsic relaxation time  $\tau_s$  can almost explicitly appear macroscopically with only weak influence of a geometrical parameter and involved viscosities and elasticities. It is not always realized that this is possible.

The shortest relaxation time Eq. (8c) is independent of  $G$  and  $\tau_s$ , but when  $G \gg \kappa$  it goes over in Eq. (9c); an inversely linear relation in  $G$  results. For this relaxation time a transition when  $G \approx \kappa$  is visible in Fig. 3. The longest relaxation times are given by Eqs. (8a) and (9a). For low  $G$  it is constant, at higher values it is linearly increasing with  $G$ . The transition occurs when  $G\tau_s$  is of the same order as the maximum of  $a\eta_{\text{eff}}$ ,  $a\eta_i$ , and  $\zeta$ . As observed it follows from Eq. (17) (=8b), that at low values of  $G$  the middle relaxation time equals  $\tau_s$ . We see that there is a range for the middle relaxation time where it is inversely linear in  $G$  at moderate values of  $G$  and at sufficiently high values of  $\tau_s$ . In this inversely linear range our experimental results could be fitted well. The transition at low  $G$  occurs when  $G\tau_s$  is of the same order as the maximum of  $a\eta_{\text{eff}}$ ,  $a\eta_i$ , and  $\zeta$ , while the transition at high values of  $G$  occurs when  $G \approx \kappa$ . When  $G$  is very small the values of the longest and the shortest relaxation times correspond to the values of the two relaxation times in the original Oldroyd model.

This study sheds also another light on the interpretation of the viscoelastic behavior of aging vesicles. It was noticed [2] that during the aging process the measured second relaxation time increased and after a certain time it became constant. The conclusion was that fully aged vesicles have a constant minimum value of  $\mu$ . In the ex-

tended model this conclusion cannot be drawn. We do not know what happens to the relaxation time  $\tau_s$ , but suppose that it almost remains constant, then it is possible that the value of  $G$  becomes arbitrarily small and the measured relaxation time equals  $\tau_s$ . So there may be no minimum value of  $G$ .

## V. CONCLUSIONS

We have shown that the interpretation of the measured second relaxation time in the viscoelastic behavior of a dispersion of vesicles can be related to a dynamic shear modulus. This interpretation is consistent with the conviction that a static shear modulus cannot be present at temperatures above the transition temperature of the lipid bilayer.

## APPENDIX

The complete analytical solution of the extended Oldroyd model will be given in this appendix. We rewrite Eq. (3) in the more convenient form

$$\frac{\eta^* - \eta}{\eta} = \frac{5}{2} c \left( \frac{H_1 + i\omega H_2 - \omega^2 H_3 - i\omega^3 H_4}{B_1 + i\omega B_2 - \omega^2 B_3 - i\omega^3 B_4} \right) \quad (A1)$$

with  $B_i$  and  $H_i$  functions of  $a$ ,  $\eta$ ,  $\eta_i$ ,  $\kappa$ ,  $\mu$ ,  $\sigma$ ,  $\zeta$ ,  $G$ , and  $\tau_s$ . The functions  $B_i$  are equal to the functions  $B_i$  in Eq. (3) when the terms that depend on concentration are omitted. The macroscopic complex viscosity in the original Oldroyd model is given by

$$\frac{\eta^* - \eta}{\eta} = \frac{5}{2} c \left( \frac{E_1 + i\omega E_2 - \omega^2 E_3}{C_1 + i\omega C_2 - \omega^2 C_3} \right). \quad (A2)$$

The functions  $B_i$  and  $H_i$  are

$$\begin{aligned} B_1 &= C_1, \\ B_2 &= C_2 + C_1\tau_s + D_1G\tau_s, \\ B_3 &= C_3 + C_2\tau_s + D_2G\tau_s, \\ B_4 &= C_3\tau_s, \\ H_1 &= E_1, \\ H_2 &= E_2 + E_1\tau_s + F_1G\tau_s, \\ H_3 &= E_3 + E_2\tau_s + F_2G\tau_s, \\ H_4 &= E_3\tau_s. \end{aligned}$$

The functions  $C_i$ ,  $D_i$ ,  $E_i$ , and  $F_i$  are

$$\begin{aligned} C_1 &= 64\gamma\mu + 96\gamma\kappa + 64\kappa\mu, \\ C_2 &= 104a\eta_i\mu + 92a\eta_i\kappa + 80a\eta_i\gamma + 64\gamma\zeta + 96\gamma\sigma + 64\kappa\zeta + 64\mu\sigma + 96a\eta\mu + 128a\eta\kappa + 80a\eta\gamma, \\ C_3 &= 76a^2\eta_i^2 + 104a\eta_i\zeta + 92a\eta_i\sigma + 64\sigma\zeta + 96a^2\eta^2 + 178a^2\eta\eta_i + 96a\eta\zeta + 128a\eta\sigma, \\ D_1 &= 64\gamma + 64\kappa, \\ D_2 &= 104a\eta_i + 64\sigma + 96a\eta, \\ E_1 &= C_1, \\ E_2 &= C_2 - 32a\eta\mu - 192a\eta\kappa - 48a\eta\gamma, \\ E_3 &= C_3 - 160a^2\eta^2 - 190a^2\eta\eta_i - 32a\eta\zeta - 192a\eta\sigma, \\ F_1 &= D_1, \\ F_2 &= D_2 - 32a\eta. \end{aligned}$$

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