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Elastic moduli for strongly curved monolayers. Position of the neutral surface

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Abstract. — The existing approaches to interface mechanics describe almost flat interfaces and use two elastic moduli corresponding to extension and bending deformations. Recently these theories have been applied to systems with a strong curvature and hereby the finite thicknesses of interfaces come into play. We show that for such systems the elastic moduli considerably depend on the choice of the dividing surface. For an arbitrary dividing surface one has to take into account the coupling between the extension and bending deformations and therefore to use a third elastic modulus corresponding to mixed deformation. We give the expressions relating the set of elastic moduli defined for one dividing surface to the corresponding set for another arbitrary dividing surface. The dividing surface with vanishing modulus of mixed deformation is defined as the neutral surface. We find the position of the neutral surface in terms of elastic moduli for any arbitrary dividing surface.

Introduction.

The investigation of interfaces with low surface tension and large curvature became one of the recent topics [1] in physical chemistry. At least two of such systems have an important impact on widespread areas such as, e.g., oil-recovery and even biology. We can first name the microemulsion of surfactant/water phases. One example we like to mention are the investigation [2] of the ternary phases of Aerosol-OT/W/O microemulsion which shows highly curved interfaces with curvature radii even less than 2 nm. Other examples are lipid/water mesophases. Although these nonbilayer phases seem to have little direct significance in membranes, a better understanding might give information on the local processes that take place during membrane fusion. Recently several laboratories [3-5] investigated the inverted hexagonal \( \text{H}_{11} \) phase of DOPE/DOPC/water mixtures. Typical observed interfacial radii are again around 10 nm and even less.

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Elastic moduli of interfaces have been investigated [6-13] both experimentally and theoretically. Most of these studies deal with lipid monolayer and bilayer. Until nowadays for the mechanics of interfaces only two elastic moduli have been so far considered: the area extension elastic modulus [6, 7] \((E_{AA})\) and the bending elastic modulus [8-11] \((E_{12})\). The notions of these moduli are defined for planar interfaces and the measurements were performed on interfaces or bilayer membranes with small or zero curvature. The experimental data obtained by the micro-pipette techniques for the area extension modulus for planar lipid bilayers cover, for different compositions, a wide range of values, starting from 50 up to 1 700 mN/m [6, 7]. Due to the experimental difficulties only a few data are available on the bending moduli, for different compositions varying [9-11] from \(0.5-2 \times 10^{-19} \text{ J}\)

Usually the theoretical description of the membrane elasticity is made in the framework of a specified microscopic model of interfacial structure [12-14]. In the case of a lipid monolayer such models specify the different parts occupied by polar heads and hydrophobic chains of molecules and the associated distribution of microscopic tensions in the direction normal to the plane of monolayer. In these theories, the neutral surface defined as that of constant area during the bending deformation plays a crucial role. The elastic properties of the interface are then described in terms of this neutral surface. The position of the neutral surface with respect to the different structural parts of interface was \textit{a priori} unknown. Both, the elastic moduli and the position of the neutral surface are defined through a hypothetical distribution of microscopic tensions. At the same time the information on the microscopic structure of interfaces is poor and therefore the models on distributions of microscopic tensions are always of a speculative character.

Recently, a new general theory based on the traditional notation of Gibbs [15] has been developed [16]. This approach uses the description of interface in terms of Gibbs dividing surface and does not require a specific model of the internal structure of the system. It was shown within this approach that the interface elastic properties are described in the general case by six independent elastic moduli. In addition to the two possible deformations like the area extension and bending, a third one, the change of Gaussian curvature, has to be considered. In addition to the three moduli of pure deformations cited above, one has also to take into account three moduli of mixed deformations. It follows from the general analysis that the values of elastic moduli depend on the dividing surface chosen. However, the character of such a dependence has not yet been analysed.

In this work we will analyse the elastic moduli of an interface formed by a dense monolayer of surface-active substance in the general case without requiring a microscopic model for the stress distribution. Without loosing generality we will demonstrate this in the simplified case of a cylindrical monolayer. This geometry has two advantages. First, these results have a simple form and at the same time allow us to understand the main properties of the system. Secondly, such results can be applied to the analysis of experiments devoted to the investigation of hexagonal lipid mesophases [3-5]. The dependence of the elastic moduli of the monolayer on the position of the dividing surface will be pointed out and a clear definition of the neutral surface will be given. The position of the neutral surface will be calculated in terms of elastic moduli of an arbitrary dividing surface. The importance of the choice of the dividing surface for the treatment of experimental results will be discussed.

**Main definitions.**

\textbf{GIBBS DIVIDING SURFACE.} — Let us consider a monolayer of surface-active substance. The monolayer has a cylindrical shape (Fig. 1) separating the internal water phase from the external hydrophobic phase. To describe the system we have to choose the Gibbs dividing surface [15]. \textit{A priori} we can see only one dividing surface having the specified properties.
Such a dividing surface is situated in the region of polar heads of molecules and forms the physical boundary between water and the monolayer. In exact terms, this is a dividing surface with Gibbs excess of water [15] equal zero. This dividing surface will be referred to as the internal surface of the monolayer and designated as $\Sigma_i$. All the other dividing surfaces are parallel to $\Sigma_i$. We will analyse the properties of the monolayer in terms of an arbitrary dividing surface $\Sigma$, characterized by the coordinate $z$, measured from internal surface $\Sigma_i$ (Fig. 1).

**SPONTANEOUS STATE.** Let us consider an element of monolayer corresponding to the element of dividing surface with area $A$ and curvature $J$ During the deformations the number of molecules forming the monolayer element remains constant. The area $A$ and the curvature $J$ are independent geometrical characteristics. The change of free energy corresponding to the deformation of the monolayer element is equal to [15, 16]

$$dF = \gamma dA + C_1 A dJ$$  (1)

The force factors of the monolayer are assumed to be uniformly distributed. The first term in (1) corresponds to the area extension (or compression), with $\gamma$, the surface tension. The second term corresponds to the bending, where $C_1$ stands for the bending moment of monolayer. The force factors $\gamma$ and $C_1$ depend both on the position of the dividing surface, and on the monolayer deformation [16]: $\gamma = \gamma(A, J)$; $C_1 = C_1(A, J)$. In the spontaneous state both force factors are equal zero, $\gamma = 0$, $C_1 = 0$ [16]. The element of the dividing surface $\Sigma$ in the spontaneous state is characterized by the spontaneous geometrical characteristics: spontaneous area $A_s$ and curvature $J_s$. The first order change of free energy of deformation (1) with respect to the spontaneous state is equal zero. The spontaneous state is the physical unstressed state of the monolayer. In the spontaneous state the force factors $\gamma$ and $C_1$ are equal zero for all dividing surfaces simultaneously. The spontaneous geometrical characteristics for different dividing surfaces are related by simple expressions. The equations

$$A_s = A_u(1 + zJ_u)$$

$$J_s = \frac{J_u}{(1 + zJ_u)}$$  (2)
relate the spontaneous area $A_s$ and the spontaneous curvature $J_s$ of internal surface $\Sigma$, with the spontaneous geometrical characteristics $A_s$ and $J_s$ of any other dividing surface $\Sigma$.

**ELASTIC MODULI** — The elastic moduli are defined as the second derivative of the monolayer free energy with respect to the deformation at the spontaneous state $A$ general deformation containing area extension $(A - A_s)$ and bending $(J - J_s)$ leads to the following change in free energy

$$\Delta F = \frac{1}{2} E_{AA} A_s \left( \frac{A_s - A}{A_s} \right)^2 + \frac{1}{2} E_{JJ} A_s (J_s - J)^2 + E_{AJ} A_s (A_s - A) (J_s - J).$$

In this expression $E_{AA}$ denotes the elastic modulus of area extension, $E_{JJ}$ the elastic modulus of bending, and $E_{AJ}$ the elastic modulus of mixed deformation [16]. The mathematical definitions of elastic moduli have the following form

$$E_{AA} = A_s \left( \frac{\delta^2 F}{\delta A^2} \right)_{A_s}, \quad E_{JJ} = \frac{1}{A_s} \left( \frac{\delta^2 F}{\delta J^2} \right)_{J_s}, \quad E_{AJ} = \left( \frac{\delta^2 F}{\delta A \delta J} \right).$$

The definitions of elastic moduli (4) together with (1) and (3) yield the surface tension $\gamma$ and the bending moment $C_1$ after the deformation with respect to the spontaneous state:

$$\gamma = E_{AA} \left( \frac{A - A_s}{A_s} \right) + E_{AJ}(J - J_s)$$

$$C_1 = E_{AJ} \left( \frac{A - A_s}{A_s} \right) + E_{JJ}(J - J_s)$$

Obviously for an arbitrary dividing surface both force factors are functions of both kinds of deformations

**The dependence of elastic moduli on the position of dividing surface.**

Let us determine the relationship between two sets of elastic moduli corresponding to the two different dividing surfaces: one set is related to the surface $\Sigma$ with e.g. the coordinate $z$ and the other set is related to the surface $\Sigma_\xi$ having the coordinate $z + \xi$ (Fig. 1).

For the determination of this relationship we will use the definition of elastic moduli (4). We also have to know the relations between the deformations of two dividing surfaces under consideration. However, this depends on the boundary conditions of deformation. Let us assume that the volume between the dividing surface $\Sigma$ and $\Sigma_\xi$ remains constant during the deformation. A different possibility, assuming a fixed distance between both, is outlined in the Appendix.

Simple geometrical consideration for cylindrical symmetry and constant volume yields the relation between the area extension $dA$ and the bending $dJ$ of the dividing surface $\Sigma$ to the corresponding deformations $dA_\xi$, $dJ_\xi$ of the dividing surface $\Sigma_\xi$ by the following expressions

$$dA = \frac{(1 + J_s \xi + \frac{1}{2} J_s^2 \xi^2)}{(1 + J_s \xi)} dA_\xi - A_s \xi (1 + J_s \xi) \left( 1 + \frac{1}{2} J_s \xi \right) dJ_\xi$$

$$dJ = A_s \left( \frac{1}{2} J_s \xi \left( 1 + \frac{1}{2} J_s \xi \right) \right) dA_\xi - \frac{1}{A_s} \left( 1 + J_s \xi \right) \frac{J_s^2 \xi \left( 1 + \frac{1}{2} J_s \xi \right)}{(1 + J_s \xi)} dA_\xi$$
The free energy (3) is independent of the position of the dividing surface. A comparison of the expressions obtained by differentiating (4) with respect to the deformation defined in the dividing surface $\Sigma_\xi$ with those defined in $\Sigma$ leads to the desired relationship between the elastic moduli $E^\xi_{AA}, E^\xi_{Ji}, E^\xi_{AJ}$ of the dividing surface $\Sigma_\xi$ and the elastic moduli $E_{AA}, E_{Ji}, E_{AJ}$ of the dividing surface $\Sigma$.

$$
E^\xi_{AA} = \frac{1}{(1 + J_s \xi)} \left\{ \left( 1 + J_s \xi + \frac{1}{2} J_s^2 \xi^2 \right)^2 E_{AA} + J_s^2 \xi^2 \left( 1 + \frac{1}{2} J_s \xi \right)^2 E_{JJ} - 2 J_s \xi \left( 1 + \frac{1}{2} J_s \xi \right) \left( 1 + J_s \xi + \frac{1}{2} J_s^2 \xi^2 \right) E_{AJ} \right\}
$$

$$
E^\xi_{Ji} = \left( 1 + J_s \xi \right) \left\{ \left( 1 + J_s \xi + \frac{1}{2} J_s^2 \xi^2 \right)^2 E_{JJ} + \xi^2 \left( 1 + \frac{1}{2} J_s \xi \right)^2 E_{AA} - 2 \xi \left( 1 + \frac{1}{2} J_s \xi \right) \left( 1 + J_s \xi + \frac{1}{2} J_s^2 \xi^2 \right) E_{AJ} \right\}
$$

$$
E^\xi_{AJ} = \left\{ \left( 1 + J_s \xi + \frac{1}{2} J_s^2 \xi^2 \right)^2 + J_s^2 \xi^2 \left( 1 + \frac{1}{2} J_s \xi \right)^2 \right\} E_{AJ} - \xi \left( 1 + \frac{1}{2} J_s \xi \right) \left( 1 + J_s \xi + \frac{1}{2} J_s^2 \xi^2 \right) \left( E_{AA} + J_s^2 E_{JJ} \right).
$$

The spontaneous curvature $J_s$ of such a monolayer might have any value. Let us discuss some limiting cases. If the spontaneous curvature of monolayer is e.g. equal zero, the expressions for the elastic moduli reduces to the simple form

$$
E^\xi_{AA} = E_{AA}
$$

$$
E^\xi_{Ji} = E_{JJ} + \xi^2 E_{AA} - 2 \xi E_{AJ}
$$

$$
E^\xi_{AJ} = E_{AJ} - \xi E_{AA}.
$$

It follows from expressions (12)-(14) that, in the case of a monolayer with zero spontaneous curvature, the modulus of area extension $E_{AA}$ has the same value for all dividing surfaces. On the contrary the bending modulus $E_{JJ}$ and the modulus of mixed deformation $E_{AJ}$ depend on the position of the dividing surface. In the case of a monolayer with large spontaneous curvature, all three elastic moduli considerably depend on the position of the dividing surface. In the accompanying paper [17] we illustrate the dependence of all monolayer elastic moduli on the coordinate of the dividing surface for the case of DOPE and DOPE/DOPC inverted hexagonal phase. One can see that the area extension modulus $E_{AA}$ varies only slightly, e.g. $E_{AA}$ for the internal dividing surface is about 1.5 times smaller than the corresponding modulus of the outer dividing surface. The elastic modulus of mixed deformation changes even sign during the transition from the internal to outer dividing surface of the monolayer. The value of the bending modulus $E_{JJ}$ depends dramatically on the position of the dividing surface. The value of the bending modulus of the internal dividing surface is about four times smaller than the corresponding modulus of the outer dividing surface of the monolayer.

Neutral surface.

The elastic moduli can be expressed for any dividing surface, however, there is one distinguished surface, furthermore called the neutral surface, with zero elastic modulus of mixed deformation $E_{AJ} = 0$ The advantages of describing the monolayer in terms of the neutral surface are obvious because, for the neutral surface, the deformations of area
extension and of bending work independently. Namely, the expression for free energy include only two terms corresponding to the pure area extension and pure bending:

$$\Delta F = \frac{1}{2} E_{AA}^N A_s^N \left( \frac{A_s^N - A_s^N}{A_s^N} \right)^2 + \frac{1}{2} E_{JJ}^N A_s^N (J_s^N - J_s^N)^2.$$  (16)

The surface tension of the neutral surface caused by deformation is determined only by area extension

$$\gamma^N = E_{AA}^N \left( \frac{A_s^N - A_s^N}{A_s^N} \right).$$  (17)

The bending moment of the neutral surface is related only to bending

$$C_1^N = E_{JJ}^N (J_s^N - J_s^N).$$  (18)

The position of the neutral surface is a priori unknown. Setting equation (11) equal zero gives the following equation to determine the distance $\xi^N$ between the arbitrary dividing surface $\Sigma$ and the neutral surface $\Sigma^N$

$$\frac{E_{AJ}}{E_{AA} + J_s^N E_{JJ}} \times \left( \xi^N \left( 1 + \frac{1}{2} J_s^N \right) \left( 1 + \frac{1}{2} J_s^N + \frac{1}{2} J_s^2 \right)^2 + \frac{1}{2} J_s^N \left( 1 + \frac{1}{2} J_s^N \right)^2 \right).$$  (19)

Equation (19) in the case of the monolayer with large spontaneous curvature does not allow any analytical solution, but can be easily solved numerically. However, for a monolayer with zero spontaneous curvature equation (19) gives the simple form of a quotient of two moduli

$$\xi^N = \frac{E_{AJ}}{E_{AA}}.$$  (20)

If the spontaneous curvature is not zero but the distance between the dividing surface $\Sigma$ and the neutral surface is small, $J_s^N \xi^N \ll 1$, an approximate solution of equation (19) has the form

$$\xi^N = \frac{\frac{E_{AJ}}{E_{AA} + J_s^N E_{JJ}}}{1 - \frac{1}{2} J_s^N \left( \frac{E_{AJ}}{E_{AA} + J_s^N E_{JJ}} \right)}.$$  (21)

Conclusion.

The results obtained show that a set of elastic moduli depends on the position of the dividing surface. Especially strong dependence takes place for the bending modulus, which is widely discussed in the literature and often applied to analyse the experimental data. The example with data obtained for highly curved monolayer shows that the bending modulus for internal dividing surface is four times smaller than the same modulus for outer dividing surface. This means that the dependence of the elastic modulus on the position of the dividing surface has to be taken into account for the analysis of experiments made with strongly curved monolayers.
The expressions derived in the present work relate the elastic moduli of different dividing surfaces. This gives the possibility to determine the elastic moduli for every dividing surface if the characteristics for one dividing surface are known from the experiment. This results are especially important for the determination of the position of neutral surface as defined to have zero modulus of mixed deformation. The equations derived allow us to determine the position of the neutral surface through the known values of elastic modulus of certain dividing surface.

The approach developed has a general character and does not use any specified model of monolayer structure and distribution of microscopic tension inside the system. This allows us to apply the results obtained to the analysis of a wide spectrum of interfaces formed by dense monolayers of surface-active substances. Obviously the approach developed in this work can also be applied to the analysis of mechanical properties of lipid bilayers.

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Appendix.

In the main part of this work we analysed the dependence of elastic moduli on the position of the dividing surface for the case of constant volume between two arbitrary dividing surfaces. This requirement causes a change of distance between two dividing surfaces during the deformation. Such consideration is appropriate for dense monolayers of surface-active substances, when no material exchanges with some reservoir. The volume density of such monolayers is constant and the molecules from outer hydrophobic medium do not penetrate into monolayers during the deformation.

One can also analyse a different boundary condition named as diluted monolayer. In this case the molecules from the hydrophobic outer phase can penetrate during the deformation into the monolayer and change the effective volume per molecule of surface-active substance.

Let us consider the interface between water and oil formed by a diluted monolayer of molecules of surface-active substance. Assume that the effective volume per molecule in the monolayer changes during the deformation, but the distance between two arbitrary dividing surfaces remains constant. The expressions relating the deformation $dA$, $dJ$ of the dividing surface with the coordinate $z$ to the deformation $dA_\xi$, $dJ_\xi$ of the dividing surface with the coordinate $z + \xi$, have the following form

$$dA_\xi = (1 + J_\xi) dA + \xi A dJ$$

$$dJ_\xi = \frac{dJ}{(1 + J_\xi)^2}$$

A similar calculation as in the main part gives us again an expression relating the elastic moduli of the dividing surfaces considered

$$E_{AA}^\xi = \frac{E_{AA}}{(1 + J_\xi)^2}$$

$$E_{IJ}^\xi = (1 + J_\xi) \{ (1 + J_\xi)^2 E_{IJ} + \xi^2 E_{AA} - 2 \xi (1 + J_\xi) E_{AJ} \}$$

$$E_{AJ}^\xi = - \xi E_{AA} + (1 + J_\xi) E_{AJ}.$$
The main difference between these results and those obtained for a dense monolayer is the opposite dependence of area extension modulus on the position of the dividing surface. The modulus $E_{AA}$ for the dilute monolayer decreases from the internal to the external dividing surface. For the case of a dense monolayer, $E_{AA}$ increases with the coordinate $z$. This difference is due to a different mechanism of deformation. In the case of dilute monolayer the distance between dividing surfaces remains constant. Therefore the deformation of pure area extension with respect to one dividing surface leads to the deformation of pure area extension with respect to another dividing surface. Only the values of deformations are different. The higher the dividing surface, the greater the area extension. The corresponding area extension modulus is smaller. For the case of a dense monolayer there is no such simple relation between the extensions of different dividing surfaces. The pure area extension of one dividing surface corresponds to the area extension and bending of another one. The bending effects lead to another dependence of $E_{AA}$ on the coordinate of the dividing surface $z$.

The expression for the coordinate of the neutral surface $(E_{AA} = 0)$ has in the case of dilute monolayer the following form

$$\xi^N = \frac{E_{AA}^i E_{AA}^e}{1 - J_0 E_{AA}^i E_{AA}^e}.$$  \hfill (A6)

References