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ON THE HYDRODYNAMICS OF A  
SOLVENT-SATURATED LIPID BILAYER.

I. MODEL OF REPULSION

by

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I. MODEL OF REPULSION

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## ABSTRACT

In two consecutive papers we study the stability of black lipid films against thermally induced hydrodynamic fluctuations. For that, in the present part we develop a semiphenomenological theory of steric repulsion in these films. The model employs the statistical mechanical formulation of the van der Waals theory of simple liquid-vapour interfaces; it is based on the picture that upon diminishing the film thickness the adjacent interfacial layers start overlapping in the film center raising the degree of orientation of the hydrocarbon segments present there. This fact causes a mutual repulsion of the two film surfaces. The general order parameter profile is found to depend on two parameters which are fixed by means of the results of an experiment which recorded the repulsive force as a function of film thickness.

Key-words: Black lipid films, steric repulsion; Lipid chains orientational order; Interfacial order parameter in lipid films.

## I. INTRODUCTION

While already a considerable amount of experimental and theoretical work on the hydrodynamics of soap films has accumulated<sup>1-3</sup>, the large scale dynamics of its topological counterpart, the lipid film (LF), has been the research community's stepchild for a long time; only scarce data on this topic exist up to date<sup>4-6</sup>. On a first glance the situation surprises somewhat since black LF<sup>7</sup> have been employed amply to simulate the so called lipid bilayer membrane (LBM), a film of biological relevance<sup>8</sup>. Yet, the experimental and theoretical research interest for the macroscopic behaviour of pure lipid films has been or still is, respectively, exhausting itself mainly in establishing their phase diagrams and studying the corresponding phase transitions<sup>9,10</sup>. We believe that the vistas are open for dynamical studies of LF. The present series of papers tries to lay the foundations for a dynamic theory of LBM on the hydrodynamic scale<sup>11</sup> (henceforth called hydrodynamics).

Black LF are formed<sup>5,6</sup> by introducing a small amount of lipid solutions onto the opening of a hydrocarbon support immersed in aqueous solution. First the film appears coloured implying a film thickness of the order of 0.1 - 1  $\mu\text{m}$ . Its bulk phase consists of a hydrocarbon solution sandwiched between two layers of surface adsorbed lipids. The surfactant layers take advantage of the amphiphilic character of the lipid molecules: their polar head groups face the aqueous phase while their hydrocarbon chains point into the hydrophobic film interior.

Under suitable conditions, the coloured film begins to drain while colour bands indicate varying thickness across the film. The bands increase in breadth and width until finally the appearance of "black spots" signals the beginning of the formation of the black film. Then the chain ends of lipids belonging to adjacent surface layers start interacting (indirectly) with each other effecting a stabilization of the LF at the quasi bimolecular thickness of the order of 60 Å.

The majority of theoretical papers on the hydrodynamics of thin films up to date <sup>3,12,13</sup>, employs the DLVO picture <sup>14</sup> and the film stability relies on the presence of overlapping diffuse layers in the film. The diffuse layers of LF extend into the disjoint aqueous bulk phases while the hydrocarbon bulk is free of charge. Thus within the framework of the theories mentioned above, LF would collapse or break up into bubbles, respectively, under the action of the van der Waals forces being the more effective the thinner the film is. This is at variance with experiment which encounters stable LF of small thickness. Thus a repulsive mechanism is called for which stabilizes black LF.

To our knowledge in the context of hydrodynamics there has been only one previous theoretical attempt to introduce a stabilizing mechanism, by means of a film elasticity <sup>15</sup>. Yet, the phenomenological theory was aimed at describing more complex films with proteins incorporated and the microscopic origin of the elasticity was not borne out. It is the purpose of part I of our

publication to formulate a (semiphenomenological) model of the repulsion in black LF based on our present microscopic understanding of LBM. This understanding arose from detailed experimental<sup>16</sup> and theoretical investigations of well defined lipid mono - and bilayers.

The bulk of theoretical work on the microscopics of lipid mono- and bilayers has been concerned with the gel to liquid crystalline transition which is of secondary interest here. In the present context we call the reader's attention to the theory of Gruen's<sup>17,18</sup> "expressis verbis" aimed at modeling the state of the lipid chains well above the thermal phase transition, in the region of biological relevance. Refs. (17,18) employ Marčelja's model<sup>19</sup> in which a single chain of a lipid molecule is embedded in a mean-field which simulates the average behaviour of the other chains. Gruen refines this model: i) he allows for a spatially varying mean field; ii) he describes in more detail the hydrocarbon-water interface as well as the influence of the headgroups; iii) he allows alkane chains (solvent) to exist in the hydrophobic core of the membrane - this fact suits well our purpose of extending our recent hydrodynamic theory of coloured films<sup>13</sup> to the regime of black LF and finally to LBM. The calculated order parameter profile along the hydrocarbon chain accommodates well the experimental data<sup>16,20</sup>. The author computed also the order parameter profile across LF which will serve as the central quantity in our theory.

The systems under consideration are very complex many body systems. The host of the microscopic studies of the statics of lipid systems supports the impression that it is hard imagining any realistic bilayer model to be accessible to an analytical treatment without excessive computer processing. This must hold true even more for the dynamics. By choosing length and time scales sufficiently coarse (hydrodynamics!) the theoretical effort may be reduced. Still modeling the dynamics remains a formidable task. On the other hand a purely phenomenological treatment with adjustable parameters bears the danger that a subsequent microscopic model may not be able to assign a strict physical meaning to the parameters involved. In the present paper we will develop an analytical semiphenomenological theory of repulsion. Its general formulation follows along the lines of the statistical mechanical formulation of the van der Waals theory of liquid-vapour interfaces<sup>21-23</sup>.

In detail, in Section II we recall two experiments and their theoretical interpretation which will help us formulating our model. We will also introduce an interpretation from the point of view of interfacial physics thus anticipating in words the formal theory put forward in Section III. Of basic interest for the latter Section is the Appendix which for our case establishes the equivalence of an order parameter theory with that of a binary liquid film. This correspondence is used in Section III to exploit the molecular theory of liquid vapour interfaces for deriving the repulsive disjoining pressure accessible to experiment. In Section IV we conclude this paper.

## II. Real and Computer Experiments; Their Hints

In this Section we want to discuss two types of real experiments<sup>16,24</sup> which will make us to propose a specific theoretical model in Section III. This model will exhibit two parameters which are being fixed by means of the quantitative results of Ref. (24).

In their experiment, Andrews, Manev, and Haydon<sup>24</sup> applied an electrical potential across different types of optically black films thus subjecting them to a large compressive force. They report that most of the films became significantly thinner presumably due to a squeezing-out process of solvent naturally present when forming the films. The authors measured the specific capacitance  $C$  of the film as a function of the applied potential  $V$  related in a simple manner to the electrically active film thickness  $\delta_e$ . Thus they could derive the magnitude of the steric repulsion<sup>25</sup> employing the following scheme: At equilibrium, the forces per unit area (pressure!) due to the London-van der Waals interaction ( $F_L$ ), the applied cross film potential ( $F_e$ ), and the steric interaction ( $F_s$ ) balance each other, i.e.,

$$F_L + F_e + F_s = 0 \quad (1)$$

with

$$F_L = -H/6\pi h^3 \quad (2a)$$

$$F_e = -CV^2/2\delta_e \quad (2b)$$



Here  $H$  is the Hamaker constant and  $h$  is the total film thickness given by  $h = (\Delta + \delta_e)$  nm with  $\Delta$  being the diameter of the polar head group of the lipid forming the film. The specific capacitance  $C$  is related to  $\delta_e$  via  $C = \epsilon_0 \epsilon / \delta_e$  where  $\epsilon$  is the dielectric constant of the hydrocarbon bulk ( $\epsilon \sim 2.1$ ).

All the quantities appearing in Eqs. (2) are accessible to experiment. The steric repulsion pressure is thus determined by

$$F_s = (H/6h^3) + (CV^2/2\delta_e). \quad (3)$$

A typical experimental result for  $F_s$  as a function of  $h$  is shown in Fig. 1<sup>24</sup>. We note the steep rise of the steric repulsion even more pronounced in some other types of film. The important conclusion of the authors of this experiment is: A very small overlap of lipid chains belonging to adjacent monolayers ("surfactant" layers) at very small segment concentration generates a repulsive force sufficient to stabilize the film.

In the foregoing experiment the integral static behaviour of LF was probed. The exact nature of the lipid conformation and dynamics was immaterial. In recent years, however, experiments emphasized the significance of phospholipid conformation for the organization of biological membranes<sup>16</sup>.

The method of deuterium nmr<sup>16</sup> contributed fundamentally to our modern view of the individual behaviour of a lipid molecule or parts of it, respectively, in the environment provided by a membrane.

In this experiment, deuterium is introduced at a specific site of the phospholipid molecule either via chemical synthesis or by means of chemical incorporation. Selected substitution of  $^1\text{H}$  by  $^2\text{H}$  does not perturb the natural arrangement of the molecule in the membrane and the small natural abundance of  $^2\text{H}$  (0.06 %) makes the  $^2\text{H}$  nmr signal to be immediately assigned to the deuterium labelled site.

The characteristic quantity measured in this experiment is the deuterium quadrupole splitting  $\Delta \nu_Q$ . The splitting is proportional to the deuterium order parameter  $S_{CD}$ , i.e.,

$$\Delta \nu_Q \sim S_{CD} = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (4)$$

where  $\theta$  denotes the instantaneous angle between the CD-bond of a selectively deuterized lipid hydrocarbon chain with the direction of the applied magnetic field, usually aligned in the direction of the bilayer normal.

Fig. 2 shows a typical order profile of a lipid bilayer (solid dots) in the fluid state above the transition temperature  $T_c$ , i.e., it depicts the order parameter  $S_{CD}$  as a function of the number of the C atom involved in the CD-bond <sup>20</sup>. Apart from a zig-zag structure at the carbon atoms 2-4, the order parameter is found to be relatively constant in a large region at the beginning of the chain (carbon atoms 2-9) and decreases subsequently towards the methyl terminal <sup>26</sup>. Also shown is the theoretical calculation (circles)

based on a mean field picture <sup>17</sup> agreeing well with experiment. In addition to these order profiles down the chain, the Figure displays also the profile across the bilayer (smooth continuous curves), i.e., as a function of the position in the bilayer. Qualitatively, though less pronounced, a similar behaviour is found: The order prevailing close to the membrane surface and continuing into an extended plateau region decays (slowly) towards the center of the membrane.

We point out that experiment and theory, respectively, of Figure 2 hold strictly only for bilayers without solvent. The theory, however, was recently extended to bilayers containing hydrocarbon solvent <sup>18</sup> and a behaviour of the order parameter qualitatively similar to that in the solvent-free film was predicted. The only major change was reported for the film center where, depending on the type of solvent and the film thickness, in most cases nearly complete disorder (order parameter identically zero) was met.

We state in words the physical picture which arose for black LF<sup>18</sup>: In a solventless LBM the lipid chains are packed closely to reduce chain-water contact. They are preferentially oriented along the normal of the plane of the bilayer in which plane the chains exert a lateral pressure. In a membrane containing a very small amount of alkane which is chemically similar to the lipid chains, the volume fraction of lipid is high throughout the membrane. Hence, the alkane chains present are subject to considerable lateral pressure

and pack with similar properties to the surrounding lipid chains. In a LF containing a substantial volume fraction of alkane the only lipid chains present in the center are those which are fully extended. In the fluid state only a small fraction of the lipid chains is fully extended. The alkane chains in the outer regions of the LF line up essentially parallel to the lipid chains, while those in the center are almost completely disordered. Thus, at the center of such a film, the alkane chains sit in an environment approaching that of bulk liquid alkane. The lateral pressure acting upon them must be smaller than for the chain segments nearer the polar interfaces and they will be subject to forces similar to those in liquid alkane. Altogether the chains (both lipid and alkane) are in an essentially liquid state with no well defined interface between opposing monolayers.

Let us analyse the problem from the point of view of interface chemical physics. A single interface represents a highly inhomogeneous transition region between two different homogeneous bulk phases. The anisotropic interactions together with the nonuniform composition in the interface give rise to a spatially varying free energy density which beyond a certain "decay length" assumes the constant values of the homogeneous bulk phases on either side. A (planar) symmetric film comprises two identical interfaces. As long as the decay length of the interfacial inhomogeneity is small compared to the film thickness the van der Waals attraction of the external phases across the film causes the film thickness to shrink (cf. discussion in Section I). From a thickness of the order of twice

the decay length on, the interfacial inhomogeneities start overlapping in the film center thus raising the value of the free energy density above its homogeneous value in the thick film. This fact manifests itself in the appearance of repulsion between the two film surfaces.

From our preceding discussion it is obvious that for constant packing density of the hydrocarbon segments, in our system the interfacial inhomogeneity in the film phase is related to the hydrocarbon order: For thick films, the order close to the film surface (head groups) "decays" into the isotropic segment orientation prevailing in bulk hydrocarbon. Upon approaching the film surfaces the order in the film center increases (cf. Fig. 3 in Ref.(11)) reducing the film entropy and thus raising the value of the free energy density as expressed by the repulsive force measured in Ref. (24).

In the next Section we model this intuitive picture.

### III. Theoretical Model

The simplest example of a fluid interface is the one-component liquid-vapour interface of simple (argon-like) fluids. Rather good progress has been achieved in understanding this type of interface on the basis of the statistical mechanics of non-uniform classical fluids, more precisely, on the basis of the density functional formalism<sup>21,23</sup>. Especially for systems exhibiting densities varying slowly on a scale set by the range of molecular interactions, the "gradient expansion approximation" has yielded many practical results<sup>23</sup>.

For complex interfaces like that in LF there is no simple statistical mechanical theory relating the molecular properties to macroscopic interfacial forces. Yet as argued in the Appendix, to a good approximation the present problem can be mapped into the problem of solving for the density profiles of a binary liquid comprised of "oriented" and "non-oriented particles". The total particle density in the map equals the hydrocarbon segment density in the real LF. Approximately this density is constant across the film<sup>18</sup>. Thus our problem is simplified even further to the case of the liquid-vapour interface of a one-component system (cf. Appendix) allowing us to employ the general ideas of the theory of simple liquid interfaces mentioned above. The spatially varying density in that theory corresponds to the concentration of the oriented particles in our map; it is numerically identical to the value of the order parameter density as measured in experiment<sup>16,26</sup> or calculated numerically<sup>17-19</sup>.

Henceforth we will therefore use the terms "order parameter density" and "concentration of oriented particles" synonymously or speak of the "density", respectively.

In the theory of nonuniform one-component fluids, the Helmholtz free energy at fixed temperature is expressed as a definite integral of a local free energy density.

$$F = \int d^3r f(\vec{r}) \quad (5)$$

with

$$f(\vec{r}) = f_0(\eta(\vec{r})) + \frac{1}{2} A(\eta(\vec{r})) \cdot (\vec{\nabla}\eta(\vec{r}))^2 \quad (6)$$

In Eq. (6) it is assumed that i) the (order parameter) density  $\eta(\vec{r})$  is sufficiently slowly varying in its spatial dependence on a scale set by the interaction range, and ii) there is no external field coupling to  $\eta(\vec{r})$ .<sup>27</sup>  $f_0(\eta(\vec{r}))$  is the local free energy density of a uniform equilibrium system displaying density  $\eta(\vec{r})$ .  $A(\eta)$  is related to the direct correlation function  $C(\vec{r}, \eta)$  of a uniform system having density  $\eta = \eta(\vec{r})$  by

$$A(\eta) = \frac{kT}{6} \int d^3r r^2 C(\vec{r}, \eta(\vec{r})) \quad (7)$$

The Ornstein-Zernike direct correlation function is derived from the interaction part of the free energy

$$c(\vec{r}-\vec{r}';\eta) = \frac{1}{kT} \frac{\delta^2 (F_{\text{ideal}} - F)}{\delta \eta(\vec{r}) \delta \eta(\vec{r}')} \quad (8)$$

where  $F_{\text{ideal}}$  is the free energy of the system in absence of interactions.

The equilibrium density  $\eta_0(\vec{r})$  arises from the minimum condition for Eq. (5) plus the condition of constant total particle number. The corresponding Euler-Lagrange equation reads

$$\mu = \mu_0(\eta(\vec{r})) - A(\eta) \cdot \vec{\nabla}^2 \eta(\vec{r}) - \frac{1}{2} \frac{\delta A(\eta)}{\delta \eta(\vec{r})} \cdot (\vec{\nabla} \eta(\vec{r}))^2. \quad (9)$$

$\mu$  is the chemical potential of the inhomogeneous system.  $\mu_0(\eta(\vec{r}))$  represents the chemical potential a homogeneous liquid of (constant) density  $\eta = \eta(\vec{r})$  would have, i.e.,

$$\mu_0(\eta(\vec{r})) = \frac{\delta f_0(\eta)}{\delta \eta(\vec{r})}. \quad (10)$$

The stress tensor derives from the condition of mechanical equilibrium and reads

$$\vec{\sigma}(\vec{r}) = -p(\vec{r}) \cdot \vec{I} + \vec{\Pi}(\vec{r}) \quad (11)$$

with

$$p(\vec{r}) = f_0(\eta(\vec{r})) - \mu \cdot \eta(\vec{r}) \quad (12a)$$



and

$$\vec{\Pi}(\vec{r}) = A(\eta) \cdot \left\{ \vec{\nabla} \eta(\vec{r}) \vec{\nabla} \eta(\vec{r}) - \frac{1}{2} (\vec{\nabla} \eta(\vec{r}))^2 \cdot \vec{I} \right\} \quad (12b)$$

with  $\vec{I}$  being the 3d-unit tensor.

In principle the quantities  $f_0(\eta(\vec{r}))$ ,  $A(\eta)$ ,  $\delta f_0 / \delta \eta(\vec{r})$  etc. can be calculated given appropriate microscopic potentials, and Eq.(9) can be solved for  $\eta(\vec{r})$  and the stress tensor Eq. (11) can be calculated.

Based on Eq. (9) we now want to derive the order parameter profile for the film system. for that we assume the film normal to be parallel to the z-axis of our Cartesian coordinate system. Further, like in the experiment, our black LF is thought to be in equilibrium with bulk alkane (cf. Fig. 3). Because of thermodynamic equilibrium, the chemical potential  $\mu$  in the film is equal to that in the homogeneous bulk phase, i.e.,

$$\mu = \mu_0(\eta_b) \quad (13)$$

where  $\eta_b$  is the constant value of the density in the homogeneous bulk phase. For film densities  $\eta$  different from  $\eta_b$  but such that  $\hat{\eta} = (\eta - \eta_b) \ll 1$ , the first term on rhs of Eq.(9) can be expanded:

$$\mu_0(\eta) = \mu_0(\eta_b) + \left. \frac{\partial \mu_0(\eta)}{\partial \eta} \right|_{\eta_b} \cdot \hat{\eta} + O(\hat{\eta}^2) \quad (14)$$

Combination of Eqs. (9), (13), and (14) while keeping only terms of order  $\hat{\eta}$  yields

$$\left( \frac{d^2}{dz^2} - \beta^2 \right) \hat{\eta} = 0 . \quad (15)$$

Here

$$\beta^2 = \frac{\partial \mu_o(\eta)}{\partial \eta} \Big|_{\eta_b} / A(\eta_b) . \quad (16)$$

The parameter  $\beta^2$  is related to the competitive mechanisms leading to an inhomogeneous profile of the order parameter: the direct correlation  $C(\vec{r})$  between different (neighbouring) points tends to increase the order, and the change in internal energy due to the variations of  $\eta$  ( $\frac{\partial \mu_o}{\partial \eta}$ , positive partial compressibility) is unfavourable for an increase of order. The length  $\beta^{-1}$  measures then an effective range of direct correlations as compared to the increase of internal energy due to the variations of  $\eta$ .

Eq. (15) represents the "asymptotic" form of Eq. (9), i.e., it holds for regions in which i)  $\eta$  is close to  $\eta_b$ , and ii)  $\frac{\partial A}{\partial \eta} \cdot \left( \frac{d \hat{\eta}}{dz} \right)^2 \ll \left| \frac{d^2}{dz^2} \hat{\eta} \right| \cdot A(\eta)$ . For symmetry reasons the latter condition is always satisfied in the center of a symmetric film independently of its thickness. So there the validity of Eq. (15) is only restricted by condition i) or, equivalently, to the treatment of films with small overlap of the interfacial inhomogenities. This limitation for its part then guarantees Eq. (15) to hold also further away from the film center.

We note that for our purpose it suffices to model well the order parameter in and close to the film center where it depends most sensitively on the film thickness <sup>17</sup>.

Finally we comment that Eq. (15) is identical to the basic equation employed ad hoc by S.Marčelja and N.Radić in their phenomenological theory on the repulsion of interfaces due to boundary water. This is not surprising because of the similarity of the two problems. Here we started out from a strict molecular formulation of the problem and arrived at Eq. (15) after a series of approximations each of which was justified individually on physics grounds.

The general solution of Eq. (15) writes

$$\eta(z) = B \cdot \cosh(\beta z) \quad (17)$$

where B is fixed by the boundary conditions either as

$$B = \hat{\eta}(0) = \eta_F - \eta_b, \quad (18a)$$

with  $\eta_F$  being the actual value of the order parameter in the film center, or as

$$B = \eta_s / \cosh(\beta h/2), \quad (18b)$$

where  $\eta_s$  is the order parameter at the film surface.  $\eta_s$  need not correspond to the real density prevailing at the film surface; it rather leads to the correct "asymptotic" solution close to the film center. As already mentioned the exact density profile or the interfacial forces close to the surface, respectively, are irrelevant for the aspect of repulsion since they contribute to the surface tension which is going to be defined in part II.

Having established the order parameter profile ( Eqs.(17), (18) ), in principle we could quantify the state of stress due to the repulsion ( Eq.(11) ) if we knew the values of the quantities  $\beta$  and  $\hat{n}(0)$  or  $\hat{n}_s$ , respectively. Lacking a microscopic theory for calculating these quantities we have to look for some other means to fix them. One could for example fit the mid film order parameter profile as a function of thickness as calculated by Gruen<sup>18</sup>. Yet, we would feel uneasy in fitting a theory to still another one. Therefore we rather regress to the macroscopic experiment discussed in Section II. For that we introduce first the notion "disjoining pressure"<sup>29</sup>.

In the film, the intermolecular forces acting on an element of volume within the film are different from those acting on an element of identical volume situated in the interior of the bulk phase and far away from a surface of discontinuity. Further, in the thin film, the two surfaces are so close to each other that no part of the thin film is out of range of the surface forces. Hence the properties of thin films are described in terms of a stress tensor ( cf. Eq.(11) ). It has, however, become customary in the literature to discuss the properties of thin films in terms of the disjoining pressure. In mechanical equilibrium, the disjoining pressure is defined as being the difference between the pressure in the external phase,  $p_1$ , and the pressure  $p_2$  in the bulk phase forming the film, i.e., in the meniscus ( cf. Fig.3 ). For equilibrium thickness, studied by Andrews et al.<sup>24</sup>, the repulsive force nearly compensates the attractive forces of electrical and van der Waals origin; the total disjoining pressure is negligibly small. Thus the pressure difference arising

exclusively in the hydrocarbon part of the film system is equal to the steric repulsion force per unit area,  $F_s$ , measured by Haydon and collaborators<sup>24</sup>.

In order to derive  $F_s$  within our theory we note that the force arising from  $\vec{\Pi}$  in Eqs. (11) and (12) when employing the solution  $\hat{h}$  of Eq. (17), derives from a potential, i.e.,

$$\vec{\nabla} \cdot \vec{\Pi}(\vec{r}) = \vec{\nabla} \phi(\vec{r}) \quad (19a)$$

with

$$\phi(\vec{r}) = 1/2 A\beta^2 (\hat{h}(\vec{r}))^2 + \text{const.} \quad (19b)$$

The pressure distribution  $p(\vec{r})$  in the film system ( film plus meniscus ) follows from the condition of mechanical equilibrium

$$\vec{\nabla} \cdot (-p(\vec{r})\vec{I} + \vec{\Pi}(\vec{r})) = 0 . \quad (20)$$

In equilibrium, integration of this equation parallel to the film surface ( Fig.3 ) leads to

$$-p(\vec{r}) + \phi(\vec{r}) = -p_2 \quad (21)$$

where  $\vec{r}$  is an arbitrary point in the film and  $p_2$  is the pressure in the isotropic bulk of the meniscus where  $\phi = 0$ .

The Laplace law ,

$$\llbracket \vec{n} \cdot (-p(\vec{r}) \vec{I} + \vec{\Pi}(\vec{r})) \cdot \vec{n} \rrbracket = 0 , \quad (22)$$

with  $\vec{n}$  being the normal to the film surface and  $\llbracket \dots \rrbracket$  indicating the jump across the surface of the quantity in between brackets, relates the surface pressure  $p(x, y, h/2)$  of the film to the pressure  $p_1$  in the external phase:

$$p_1 = p(x, y, h/2) - \Pi_{zz}(x, y, h/2) = p(\vec{r}) - \Pi_{zz}(\vec{r}) . \quad (23)$$

Combination of Eqs.(21) and (23) yields the disjoining pressure

$$p_1 - p_2 = \phi(\vec{r}) - \Pi_{zz}(\vec{r}) , \quad (24)$$

$\vec{r}$  in the film phase, or explicitly

$$F_s = p_1 - p_2 = \frac{1}{2} A \hat{\eta}_s^2 \frac{\beta^2}{\cosh^2(\beta h/2)} = \frac{1}{2} A \beta^2 \hat{\eta}^2(0) . \quad (25)$$

In order to arrive at Eq.(25), the relations (12b), (17), (18), and (19b) have been employed.

We note: the repulsive force  $F_s$  vanishes for  $\beta h \rightarrow \infty$ ; then the overlap of the adjacent interfacial layers is not sufficient as to establish in the film center an orientational order of the chain segments at least slightly superior to that in the isotropic bulk

phase. Also, the repulsive force increases with decreasing film thickness like the second power of the order parameter in the center of the film.

The parameters  $\hat{\eta}_s$  and  $\beta$  of Eq.(25) can be fixed by fitting the experimental curve  $F_s(h)$  measured by Haydon and coworkers<sup>24</sup> as discussed in Section II. The result of the fit is shown in Fig.(4) where in view of the experimental uncertainty due to both the measurement and to the inherent interpretation ( cf. Eq.(3) ), and accounting for the fact that here we are only interested in orders of magnitude, we have kept  $\hat{\eta}_s$  constant. Consistently with this assumption we have fitted best the "large"  $h$  regime of Fig.(4); there the  $h$  - dependence is mainly due to the cosh term in Eq.(25). The fit yields  $1/2 A \beta^2 \hat{\eta}_s^2 = 1.29 \cdot 10^8 \text{ N mm}^{-2}$  and  $\beta = 4.55 \text{ nm}^{-1}$ .

We note that our assumption of  $\hat{\eta}_s$  being independent of film thickness amounts to postulating  $\hat{\eta}(0) \sim \cosh^{-1}(\beta h/2)$ . From Gruen's<sup>18</sup> calculation, however, we deduce that  $\hat{\eta}(0)$  increases more slowly than  $\cosh^{-1}(\beta h/2)$  with decreasing film thickness. In view of Fig. 4, a weaker dependence of  $\hat{\eta}(0)$  on  $h$  for small thicknesses would improve the theory. Yet we are not sure whether our perturbational treatment (with the homogeneous phase as ground state) and the corresponding cut off in the perturbation expansions would still be valid.

In part II of this paper we will employ the repulsive model developed here to study the stability of black LF against hydrodynamic fluctuations.

#### IV. CONCLUSION

The principal purpose of this article was to develop a macroscopic model of the steric repulsion in black lipid films in equilibrium with bulk solution. For that we first recalled two key experiments together with their interpretations in order to familiarize the reader with the specific problem: The macroscopic experiment quantified the term "repulsion" by measuring the repulsive force as a function of film thickness; the microscopic nmr- experiment and its theoretical interpretation linked the term "repulsion" to the order prevailing along individual lipid chains or, more exactly, to the order profile across the film, i.e. to the average orientation of the hydrocarbon segments as a function of the position in the film. We then analysed the problem from the point of view of interface physics where an interface represents a non-uniform region of transition between two different homogeneous bulk phases. In this picture, the overlap of the adjacent interfaces in the black film increased the order in the film center thus causing the mutual repulsion of the two film surfaces.

For the mathematical formulation and exemplification of the theory it was of basic importance that the order parameter problem could be mapped onto the problem of deriving the density profile between two parallel plane liquid-vapour interfaces of a monomolecular system. The mapping enabled us to employ the statistical mechanical formulation of the van der Waals theory of liquid-vapour interfaces and to derive a differential equation fixing asymptotically the order parameter profile in and close to the film center. The



resulting order density profile depended i) on the ratio of the derivative of the chemical potential with respect to the order parameter density and the second moment of the two point Ornstein-Zernike correlation function, and ii) on the order at the film surface. We treated the two quantities as adjustable parameters and fixed them by means of the results of the macroscopic experiment in the large film thickness limit.

The order parameter met in this paper is supposed to coincide with the real order parameter in a more or less extended domain in the film center where there is need of a good description of the interfacial overlap; it deviates from the real order parameter in the surface region where the surface tension accounts for the molecular inhomogenities.

Consistently with the intuitive picture we found that a non-zero overlap of the interfacial layers was necessary, i.e., the order in the film center had to be raised over that in the homogeneous and isotropic bulk phase, in order to generate repulsion.

Further the theory enabled us to calculate the anisotropic state of stress due to the steric repulsion thus opening the vistas for our stability analysis in part II of this paper.

Finally, from a more general point of view we have demonstrated how a lipid film represents an excellent example for a liquid in which a measurable microscopic order links quantitatively to the macroscopically measurable disjoining pressure.

APPENDIX

Here we want to argue how on the basis of the molecular theory of interfacial phenomena by Fleming, Yang, and Gibbs<sup>20,21</sup> an equation of the form [9] arises.

For that we assume the system to be described by the classical Hamiltonian of the form

$$H_O = H_{kin}^O + H_{int}^O + \int d\theta \int d^3r V(\theta, \vec{r}) \hat{n}(\theta, \vec{r}) \quad (A.1)$$

where

$$\hat{n}(\theta, \vec{r}) = \sum_{\alpha} \delta(\vec{r} - \vec{r}_{\alpha}) \delta(\theta - \theta_{\alpha}) \quad (A.2)$$

is the microscopic density of bonds ("particles") with orientation  $\theta$ .  $U(\theta, \vec{r})$  is an angular dependent external potential. The form of  $H_{int}^O$  need not be specified. The only requirement is that the interaction potential be short ranged. The microscopic particle density  $\hat{n}(\vec{r})$  is related to  $\hat{n}(\theta, \vec{r})$  via

$$\hat{n}(\vec{r}) = \int d\theta \hat{n}(\theta, \vec{r}). \quad (A.3)$$

The grand partition function for the system is given by

$$e^W = \text{Tr}_{cl}^O \{ e^{-\beta(H_O - \mu N)} \} \quad (A.4)$$

where  $\text{Tr}_{c1}^0$  has the meaning of

$$\sum_{N=0}^{\infty} \frac{1}{N!} \prod_{\alpha=1}^N \frac{1}{h^{3N}} \int d^3 p_{\alpha} d^3 r_{\alpha} d\theta_{\alpha} \dots$$

$h$  is Planck's constant and  $\beta = 1/kT$ ,  $k$  being Boltzmann's constant.  $\mu$  is the chemical potential, and  $N$  is the total number of particles in the system.

With the dimensionless one-body potential

$$u(\theta; \vec{r}) = \beta (\mu - U(\theta; \vec{r})) \quad , \quad (\text{A.5})$$

the particle density  $n(\vec{r})$  is given as

$$\begin{aligned} n(\vec{r}) &= \langle \hat{n}(\vec{r}) \rangle_0 = \int d\theta \langle \hat{n}(\theta; \vec{r}) \rangle_0 \\ &= \int d\theta n(\theta; \vec{r}) = \int d\theta \frac{\delta W}{\delta u(\theta; \vec{r})} \quad , \quad (\text{A.6}) \end{aligned}$$

where the subscript "0" implies that the average is performed with the Hamiltonian (A.1).

The definitions up to now allow us to write the segmental order parameter  $\eta(\vec{r})$  as defined in Refs.(16-19) in the more explicit form

$$\eta(\vec{r}) = \frac{1}{2} \int d\theta (3 \cos^2 \theta - 1) n(\theta; \vec{r}) / n(\vec{r}) \quad . \quad (\text{A.7})$$

In our problem, the density  $n(\theta; \vec{r})$  displays a simple shape in each of two limits: Experiment<sup>15,20</sup> and computer modeling<sup>17,18</sup> manifested quasi perfect orientation of the chain segments close to the interface, and nearly complete disorder in the film center. Thus near the latter,  $n(\theta; \vec{r})$  is an isotropic density with equal weight for all angular orientations; close to the interface,  $n(\theta; \vec{r})$  is strongly peaked (Fig. A-1), i.e.  $n(\theta; (x, y, h/2)) \sim \delta(\theta)$ .<sup>30</sup>

Fig. A-1: Segment orientation density

$n(\theta; \vec{r})$  in the film center (a)  
and close to the interface (b).

In view of the monotonous behaviour of  $n(x, y, z)$  for  $0 \leq z \leq h/2$ <sup>16-18</sup> one is tempted to represent  $n(\theta; \vec{r})$  in Eq. (A.7) as a superposition of the densities of Fig. (A-1), i.e.,

$$n(\theta; (x, y, z)) = a_1(z) \cdot n(\theta; (x, y, h/2)) + a_2(z) \cdot n(\theta; (x, y, 0)), \quad (\text{A.8a})$$

or for the total density

$$n(\vec{r}) = a_1(z) \cdot n(x, y, h/2) + a_2(z) \cdot n(x, y, 0). \quad (\text{A.8b})$$

with  $\vec{r} = (x, y, z)$ , and  $a_i(z)$  being appropriate functions.

Representation (A.8) has two immediate consequences:

i) the  $\theta$ -integration in (A.7) can be carried out leaving us with

$$\eta(\vec{r}) = a_1(z) \cdot n(x, y, h/2) / n(\vec{r}) , \quad (\text{A.9})$$

ii) it gives rise to a model of a binary system with spatially varying number densities  $n_1(\vec{r})$  and  $n_2(\vec{r})$  of "oriented" and "unoriented particles" in the following sense: We suppose there exists a Hamiltonian H of a binary system such that

$$a_1(z) \cdot \int d\theta \frac{\delta W}{\delta u(\theta; (x, y, h/2))} = a_1(z) \langle \hat{n}(x, y, h/2) \rangle_0 =$$

$$\text{Tr}_{\text{cl}} \{ \hat{n}_1(\vec{r}) e^{-\beta(H - \mu_1 N_1 - \mu_2 N_2)} \} = \langle \hat{n}_1(\vec{r}) \rangle = n_1(\vec{r}) , \quad (\text{A.10a})$$

and

$$a_2(z) \cdot \int d\theta \frac{\delta W}{\delta u(\theta; (x, y, 0))} = a_2(z) \cdot \langle \hat{n}(x, y, 0) \rangle_0 =$$

$$\text{Tr}_{\text{cl}} \{ \hat{n}_2(\vec{r}) e^{-\beta(H - \mu_1 N_1 - \mu_2 N_2)} \} = \langle \hat{n}_2(\vec{r}) \rangle = n_2(\vec{r}) . \quad (\text{A.10b})$$

Here  $\text{Tr}_{\text{cl}} \{ \dots \} = \sum_{N=0}^{\infty} \frac{1}{N!} \prod_{\alpha=1}^N \int \frac{d^3 p_{\alpha} d^3 r_{\alpha}}{h^{3N}} \dots$ , and  $\mu_i$  and  $N_i$

are the chemical potential and total number, respectively, of species  $i$  ( $i = 1, 2$ ).

Then

$$n_1(\vec{r}) + n_2(\vec{r}) = n(\vec{r}) \quad (\text{A.11})$$

is the total particle density of the binary system which equals the segment density of the real system (Eq. (A.6)). Further, in terms of the binary system densities the order parameter  $\eta(\vec{r})$  of Eqs. (A.7), (A.9) is given by

$$\eta(\vec{r}) = n_1(\vec{r}) / n(\vec{r}), \quad (\text{A.12})$$

i.e. the order parameter is identical to the mole fraction or concentration, respectively, of species 1.

Thus we have mapped the original problem of determining the density of an order parameter depending on a spatial coordinate onto the problem of solving for the density profiles of a binary system. Henceforth we are therefore able to employ the general theory of classical nonuniform multicomponent systems<sup>21</sup>.

In this theory, the Helmholtz free energy, at fixed temperature, is expressed as the spatial integral of a local free energy density

$$F = \int d^3r f(\vec{r}) \quad (\text{A.13})$$

where for spatial inhomogeneities varying slowly on a scale set by the range of interactions,

$$f(\vec{r}) = U_1(\vec{r}) n_1(\vec{r}) + f_0(n_1(\vec{r}), n_2(\vec{r})) + \frac{1}{2} f_{ij}(n_1(\vec{r}), n_2(\vec{r})) \cdot \vec{\nabla} n_i(\vec{r}) \cdot \vec{\nabla} n_j(\vec{r}) \quad (\text{A.14})$$

Here  $i=1,2$  and a summation convention for repeated indices is implied.  $n_i(\vec{r})$  is the number density of species  $i$  at point  $\vec{r}$ .  $U_i(\vec{r})$  is an external potential as "seen" by species  $i$ .  $f_0(n_1(\vec{r}), n_2(\vec{r}))$  is the equilibrium free energy density of a spatially uniform mixture having density  $n_i$  for species  $i$ .  $f_{ij}(n_1, n_2)$  is intimately related to the molecular interaction of species  $i$  with species  $j$ . In particular

$$f_{ij}(n_1, n_2) = \frac{kT}{6} \int d^3r r^2 C_{ij}(\vec{r}; n_1, n_2) \quad (\text{A.15})$$

where  $k$  is Boltzmann's constant and  $T$  is the temperature.

$C_{ij}(\vec{r}; n_1, n_2)$  is the binary Ornstein - Zernike direct correlation function of species  $i$  with species  $j$  for a uniform binary mixture having densities  $n_i$ . Thus  $f_{ij}(n_1, n_2)$  is a direct measure of the correlation (interaction) of species  $i$  and  $j$ .

The choice of new variables  $n(\vec{r})$  and  $\eta(\vec{r})$  (Eqs. (A.11) and (A.12)) transforms Eq. (A.14) into

$$\begin{aligned} f(\vec{r}) = & U_1(\vec{r}) \cdot n(\vec{r}) + U_2(\vec{r}) \cdot n(\vec{r}) \cdot (1 - \eta(\vec{r})) + \\ & f_0(\eta(\vec{r}), n(\vec{r})) + f_{\eta\eta}(\eta(\vec{r}), n(\vec{r})) \cdot (\vec{\nabla}\eta(\vec{r}))^2 + \\ & f_{nn}(\eta(\vec{r}), n(\vec{r})) \cdot (\vec{\nabla}n(\vec{r}))^2 + \\ & f_{\eta n}(\eta(\vec{r}), n(\vec{r})) \cdot \vec{\nabla}\eta(\vec{r}) \cdot \vec{\nabla}n(\vec{r}) \end{aligned} \quad (\text{A.16})$$

with

$$f_{\eta\eta}(\eta(\vec{r}), n(\vec{r})) = \frac{1}{2} n^2(\vec{r}) [f_{11}(\eta(\vec{r}), n(\vec{r})) + f_{22}(\eta(\vec{r}), n(\vec{r})) - 2 f_{12}(\eta(\vec{r}), n(\vec{r}))] \quad (\text{A.17a})$$

$$f_{nn}(\eta(\vec{r})) = \frac{1}{2} [f_{11}(\eta(\vec{r}), n(\vec{r})) \cdot \eta^2(\vec{r}) + f_{22}(\eta(\vec{r}), n(\vec{r})) \cdot (1 - \eta(\vec{r}))^2 + 2 f_{12}(\eta(\vec{r}), n(\vec{r})) \cdot \eta(\vec{r}) \cdot (1 - \eta(\vec{r}))] \quad (\text{A.17b})$$

$$f_{\eta n}(\eta(\vec{r}), n(\vec{r})) = f_{11}(\eta(\vec{r}), n(\vec{r})) \cdot n(\vec{r}) \cdot \eta(\vec{r}) + f_{22}(\eta(\vec{r}), n(\vec{r})) \cdot n(\vec{r}) \cdot (1 - \eta(\vec{r})) + f_{12}(\eta(\vec{r}), n(\vec{r})) \cdot n(\vec{r}) \cdot (1 - 2\eta(\vec{r})) \quad (\text{A.17.c})$$

The differential equations which determine the species densities are obtained by requiring that the free energy be a minimum subject to the constraints that for fixed volume

$$\int n(\vec{r}) \eta(\vec{r}) d^3r = \int n_1(\vec{r}) d^3r = N_1, \quad (\text{A.18a})$$

and

$$\int n(\vec{r}) (1 - \eta(\vec{r})) d^3r = \int n_2(\vec{r}) d^3r = N_2, \quad (\text{A.18b})$$

where  $N_i$  is the total number of molecules of species  $i$ .



Introducing the Lagrange parameters or chemical potentials  $\mu_i$  ( $i = 1, 2$ ), respectively, leaves us then with the problem to minimize the functional

$$F - \mu_i N_i = \int \{f(\vec{r}) - \mu_1 \cdot n(\vec{r}) \cdot \eta(\vec{r}) - \mu_2 \cdot n(\vec{r}) \cdot (1 - \eta(\vec{r}))\} d^3r \quad (A.19)$$

with respect to  $n(\vec{r})$  and  $\eta(\vec{r})$ .

The common variational procedure yields the equations

$$\begin{aligned} n(\vec{r}) \cdot \{ \mu(\eta(\vec{r}), n(\vec{r})) + U(\vec{r}) - \mu \} = \\ \frac{\partial}{\partial n(\vec{r})} f_{\eta\eta}(\eta(\vec{r}), n(\vec{r})) \cdot (\vec{\nabla}\eta(\vec{r}))^2 + \\ 2 f_{\eta\eta}(\eta(\vec{r}), n(\vec{r})) \cdot \vec{\nabla}^2 \eta(\vec{r}) + \\ 2 \frac{\partial}{\partial n(\vec{r})} f_{\eta\eta}(\eta(\vec{r}), n(\vec{r})) \cdot \vec{\nabla}\eta(\vec{r}) \cdot \vec{\nabla}n(\vec{r}) \\ - \left[ \frac{\partial}{\partial \eta(\vec{r})} f_{\eta n}(\eta(\vec{r}), n(\vec{r})) - \frac{\partial}{\partial n(\vec{r})} f_{\eta n}(\eta(\vec{r}), n(\vec{r})) \right] \cdot \\ (\vec{\nabla} n(\vec{r}))^2 + f_{\eta n}(\eta(\vec{r}), n(\vec{r})) \cdot \vec{\nabla}^2 n(\vec{r}) \end{aligned} \quad (A.20a)$$

and

$$\begin{aligned} \Delta f(\eta(\vec{r}), n(\vec{r})) + \eta(\vec{r}) \cdot U(\vec{r}) + U_2(\vec{r}) = \\ \left[ \frac{\partial}{\partial \eta(\vec{r})} f_{\eta n}(\eta(\vec{r}), n(\vec{r})) - \frac{\partial}{\partial n(\vec{r})} f_{\eta n}(\eta(\vec{r}), n(\vec{r})) \right] \cdot \\ (\vec{\nabla} \eta(\vec{r}))^2 + f_{\eta n}(\eta(\vec{r}), n(\vec{r})) \cdot \vec{\nabla}^2 \eta(\vec{r}) \\ + 2 \frac{\partial}{\partial \eta(\vec{r})} f_{\eta n}(\eta(\vec{r}), n(\vec{r})) \cdot \vec{\nabla}\eta(\vec{r}) \cdot \vec{\nabla}n(\vec{r}) \\ + \frac{\partial}{\partial n(\vec{r})} f_{\eta n}(\eta(\vec{r}), n(\vec{r})) \cdot (\vec{\nabla}n(\vec{r}))^2 + 2f_{\eta n}(\eta(\vec{r}), n(\vec{r})) \cdot \vec{\nabla}^2 n(\vec{r}) \end{aligned} \quad (A.20b)$$

with  $\mu = \mu_1 - \mu_2$ ,  $\mu(\eta(\vec{r}), n(\vec{r})) = \mu_1(\eta(\vec{r}), n(\vec{r})) - \mu_2(\eta(\vec{r}), n(\vec{r}))$ ,  $U(\vec{r}) = U_1(\vec{r}) - U_2(\vec{r})$ , and  $\Delta f(\eta(\vec{r}), n(\vec{r})) = (\mu(\eta(\vec{r}), n(\vec{r})) - \mu) \cdot \eta(\vec{r}) + (\mu_2(\eta(\vec{r}), n(\vec{r})) - \mu_2)$ .

Eqs. (A.20) describe completely an inhomogeneous two component system that displays concentration and density variations across the (liquid-liquid) interface. Thus in general the system cannot be described by a single differential equation only as assumed in this paper ( Eq.(9) ) and as often practiced in literature.

Within the framework of the theory it is possible, however, to modify the external potentials such that  $n(\vec{r})$  is constant everywhere. Then Eq. (A.20a) transforms into

$$n(\vec{r}) \cdot \{ \mu(\eta(\vec{r}), n(\vec{r})) + U(\vec{r}) - \mu \} = \frac{\partial}{\partial \eta(\vec{r})} f_{\eta\eta}(\eta(\vec{r}), n(\vec{r})) \cdot (\vec{\nabla}\eta(\vec{r}))^2 + 2f_{\eta\eta}(\eta(\vec{r}), n(\vec{r})) \cdot \vec{\nabla}^2 \eta(\vec{r}), \quad (\text{A.21})$$

and Eq. (A.20b) provides the condition

$$n(\vec{r}) \cdot U(\vec{r}) + U_2(\vec{r}) = -\Delta f(\eta(\vec{r}), n(\vec{r})) + \left[ \frac{\partial}{\partial \eta(\vec{r})} f_{\eta\eta}(\eta(\vec{r}), n(\vec{r})) - \frac{\partial}{\partial \eta(\vec{r})} f_{\eta\eta}(\eta(\vec{r}), n(\vec{r})) \right] \cdot (\vec{\nabla}\eta(\vec{r}))^2 + f_{\eta\eta}(\eta(\vec{r}), n(\vec{r})) \cdot \vec{\nabla}^2 \eta(\vec{r}). \quad (\text{A.22})$$

If upon solving Eq. (21) for  $\eta(\vec{r})$  and substituting into Eq. (22) we find  $U_1(\vec{r})$  and  $U_2(\vec{r})$  to assume more or less the unmodified values of the external potentials for all  $\vec{r}$ , then we can say that  $\eta(\vec{r})$  taken to be a solution of Eq. (A.21) and  $n(\vec{r}) = \text{const.}$  is an accurate approximate solution of the system (A.20) for  $U_1 = U_2 = U_{\text{ext}}$ .

For our system and for our purpose, there exist good arguments for

Eq. (A.21) or Eq. (9), respectively, to provide a good description. Firstly, in microscopic theories constant segment concentration, i.e.,  $n(\vec{r}) = \text{const.}$  is generally assumed<sup>9,17</sup>. Secondly, in his self-consistent mean field theory, Gruen<sup>18</sup> calculates the volume weighted "amount of material" to vary at maximum by 2% from its mean across the LF. Thirdly, as reported already in Section II, the film center provides quasi the conditions of a homogeneous bulk alkane solution. So "asymptotically"  $U_1(0) = U_{\text{ext}}$ , rendering the solution  $\eta(\vec{r})$  of Eq. (A.21) an exact solution. Furthermore, Eq. (A.21) holds at all space points  $\vec{r}$  for which  $\vec{\nabla}\eta(\vec{r})$  and  $\vec{\nabla}^2\eta(\vec{r})$  are sufficiently small.

In concluding we note that Eq. (A.21) displays the general form of the corresponding equation of a one-component liquid-vapour system. This fact is used by starting out from Eq. (6) for the free energy density in the principal part of this paper.

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## References

1. A. Sheludko  
Adv. Coll. Interf. Sci. 1, 391 (1967), and references  
contained therein
2. R. Buscall and R.H. Ottewill  
Specialist Periodical Reports, Coll. Sci., D.H. Everett  
(ed.), p. 191, Chem. Soc. London, Academic Press (1975),  
and references therein
3. A. Vrij, J.G.H. Joosten and H.M. Fijnaut  
Adv. Chem. Phys. XLVIII, I. Prigogine, S.A. Rice (eds.)  
p. 329, John Wiley and Sons, 1981 and references contained  
therein
4. E.F. Grabowski and J.A. Cowen  
Biophys. J. 18, 23 (1977)
5. H.T. Tien  
"Bilayer Lipid Membranes", Marcel Dekker, New York (1974)
6. V. Vodyanoy, P. Halverson and R.M. Murphy  
J. Coll. Interf. Sci. 88, 247 (1982), and references contained  
therein
7. Because of its thickness being small compared to the wave-  
lengths of visible light, the film appears black in reflection  
due to destructive interference of the light reflected from  
the front and back film surface, respectively.
8. S.J. Singer and G.L. Nicolson  
Science 175, 720 (1972)

9. For a recent review of the theory see for example  
A. Caillé, D. Pink, F. de Vertenie and M.J. Zuckermann  
Can. J. Phys. 58, 581 (1980);  
F. Jähnig  
Biophys. J. 36, 329 (1981)
10. O. Albrecht, H. Gruler and E. Sackmann  
J. Phys. (Paris) 39, 301 (1978), and references contained  
therein
11. A sketchy account of part of the present work has been given  
in H. Wendel, P.M. Bisch and D. Gallez, Coll. Polym. Sci. 260, 425  
(1982)
12. C. Maldarelli, R.K. Jain, I.B. Jvanov, and E. Ruckenstein  
J. Coll. Interf. Sci. 78, 118 (1981), and references contained  
therein
13. H. Wendel, D. Gallez and P.M. Bisch  
J. Coll. Interf. Sci. 84, 1 (1981)  
P.M. Bisch, H. Wendel and D. Gallez  
J. Coll. Interf. Sci. 92, 105 (1983)  
D. Gallez, P.M. Bisch and H. Wendel  
J. Coll. Interf. Sci. 92, 121 (1983)
14. B.V. Derjaguin and L. Landau  
Acta Physicochimica U.R.S.S. 14, 633 (1941)  
E.J.W. Verwey and J. Th.G. Overbeek  
"Theory of the Stability of Lyophobic Colloids",  
Elsevier, Amsterdam (1948)
15. A. Steinchen, A. Gallez and A. Sanfeld  
J. Coll. Interf. Sci. 85, 5 (1982)
16. See for example J. Seelig and A. Seelig  
Quart.Rev. Biophys. 13, 19 (1980)

17. D.W.R. Gruen  
BBA 595, 161-183 (1980)
18. D.W.R. Gruen  
Biophys. J. 33, 149-166 (1981);  
D.W.R. Gruen and D.A. Haydon  
Biophys. J. 33, 167-187 (1981)
19. S. Marcelja  
BBA 367, 165-176 (1974)
20. J.N. Israelachvili, S. Marcelja and R.G. Horn  
Quart. Rev. Biophys. 13, 121 (1980)
21. A.J.M. Yang, P.D. Fleming III, and J.H. Gibbs  
J. Chem. Phys. 64, 3732 (1976)
22. P.D. Fleming III, A.J.M. Yang and J.H. Gibbs  
J. Chem. Phys. 65, 7 (1976)
23. R. Evans  
Adv. in Phys. 28, 143 (1979)
24. D.M. Andrews, E.D. Manev, and D.A. Haydon  
Spec. Disc. Faraday Soc. 1, 46 (1970)
25. Here we employ the notion "steric repulsion" in a very general sense. It covers all forces arising upon the overlap of adjacent interfaces. These forces are due to the anisotropic molecular interactions in the interface.
26. J. Seelig and A. Seelig  
Biochemistry 13, 4839-4845 (1974)

27. The external potentials generated by long range electrostatic and van der Waals forces, respectively, do not discriminate oriented and non-oriented particles. They rather act on the total density (cf. part II) and are thus omitted in Eq. (6).
28. S. Marčelja and N. Radić  
Chem. Phys. Lett. 42, 129 (1976)
29. B.V. Derjaguin and M.M. Kussakov  
Acta Physicochim. U.R.S.S. 10, 25 (1939)
30. Here we employ the definition of the angle  $\theta$  of Refs. (17)-(19) which arises from that defined in Ref. (16) by a rotation by  $90^\circ$ .

### Figure Captions

#### Fig. 1:

Steric repulsive force  $F_s$  per unit area of lipid film surface versus film thickness as measured by Andrews, Manev and Haydon<sup>24</sup> for.

#### Fig. 2:

Comparison of experimental (black dots) and theoretical (open circles connected by solid line) deuterium order parameter  $S_{CD}$  as a function of carbon atom label (upper abscissa) for one half of a lipid bilayer membrane. Also shown is the order parameter as a function of position in the lipid bilayer (lower abscissa, screen dotted stripe).

#### Fig. 3:

Schematic film set up. The film in the interior of the chamber is in equilibrium with its meniscus, i.e., with the bulk phase of the film forming material. The isotropic pressure  $p_2$  in this phase differs in general from the pressure  $p_1$  in the "gas" phase. This difference is called disjoining pressure<sup>28</sup>.

#### Fig. 4:

Comparison of the thickness dependence of experimental (dots) and theoretical (solid line) steric disjoining pressure  $F_s$ . The theoretical curve was calculated from Eq. (25) with  $\beta = 4.55 \text{ nm}^{-1}$  and



$\frac{1}{2}A\hat{\eta}_s^2 = 1.29 \times 10^8 \text{ N nm}^{-2}$ . The theoretical curve derivates from experiment for small film thickness due to the assumption of  $\hat{\eta}_s$  being constant. In reality  $\hat{\eta}_s$  should depend on the film thickness.

Fig. A-1:

Segment orientation density  $n(\theta; \vec{r})$  in the film center (a), and close to the interface (b).

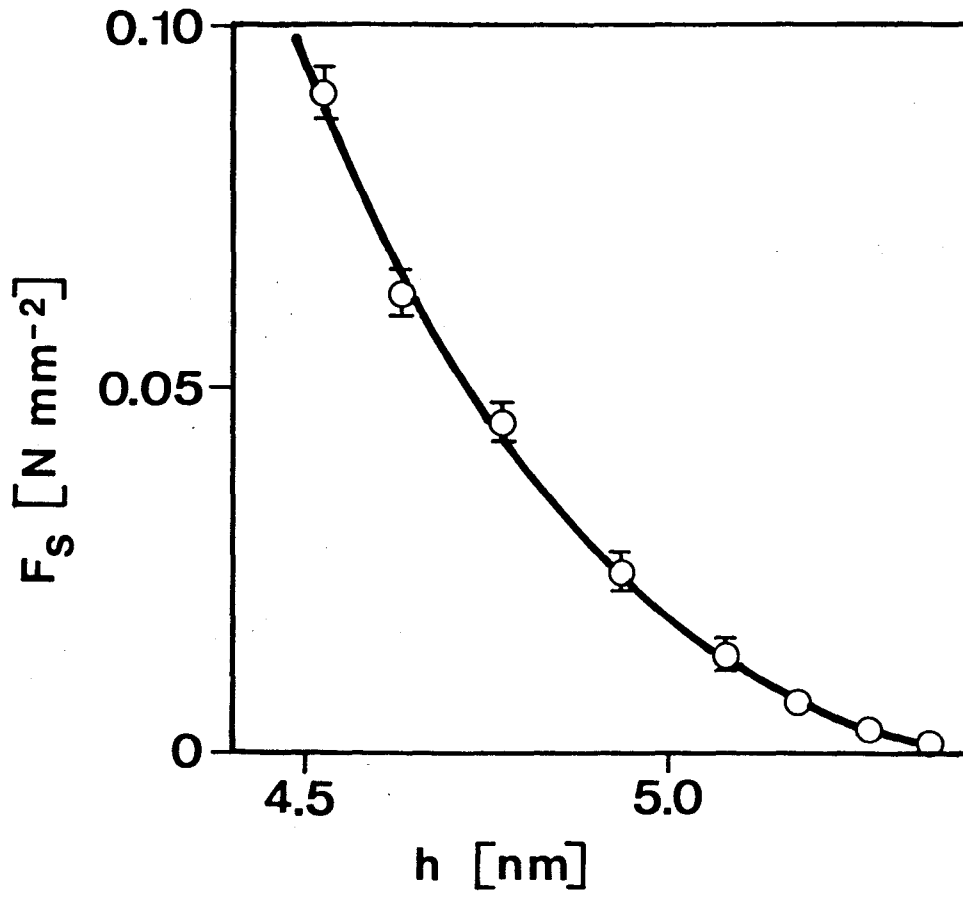


FIG. 1

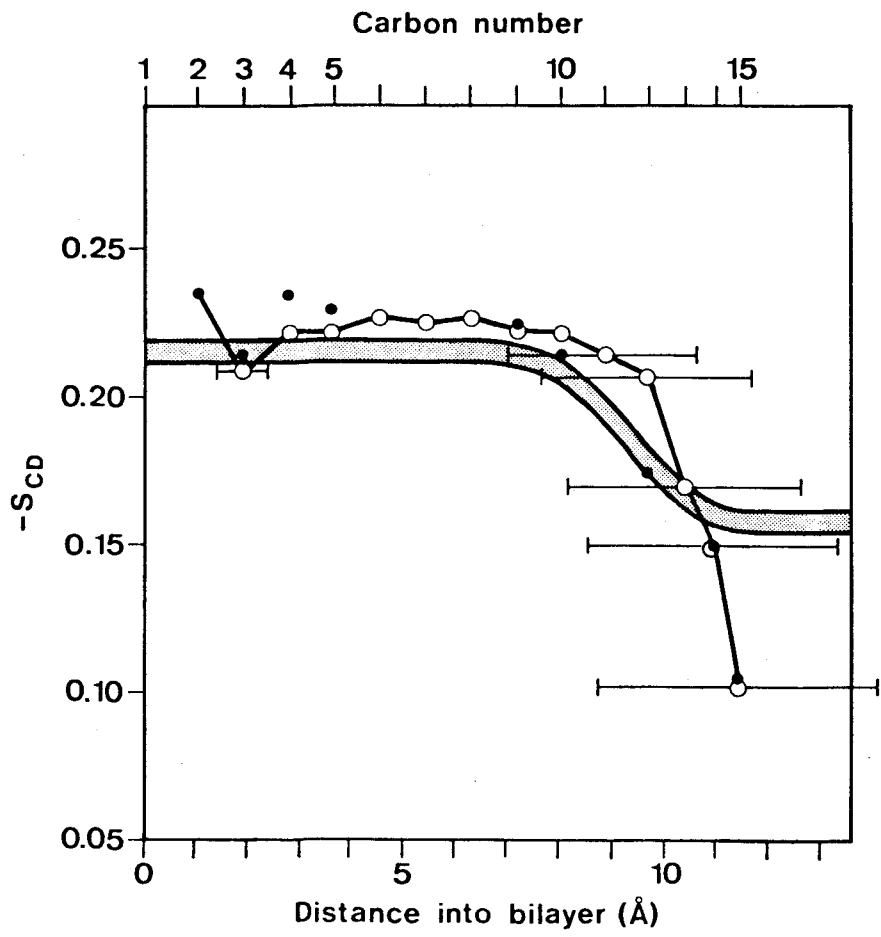


FIG. 2

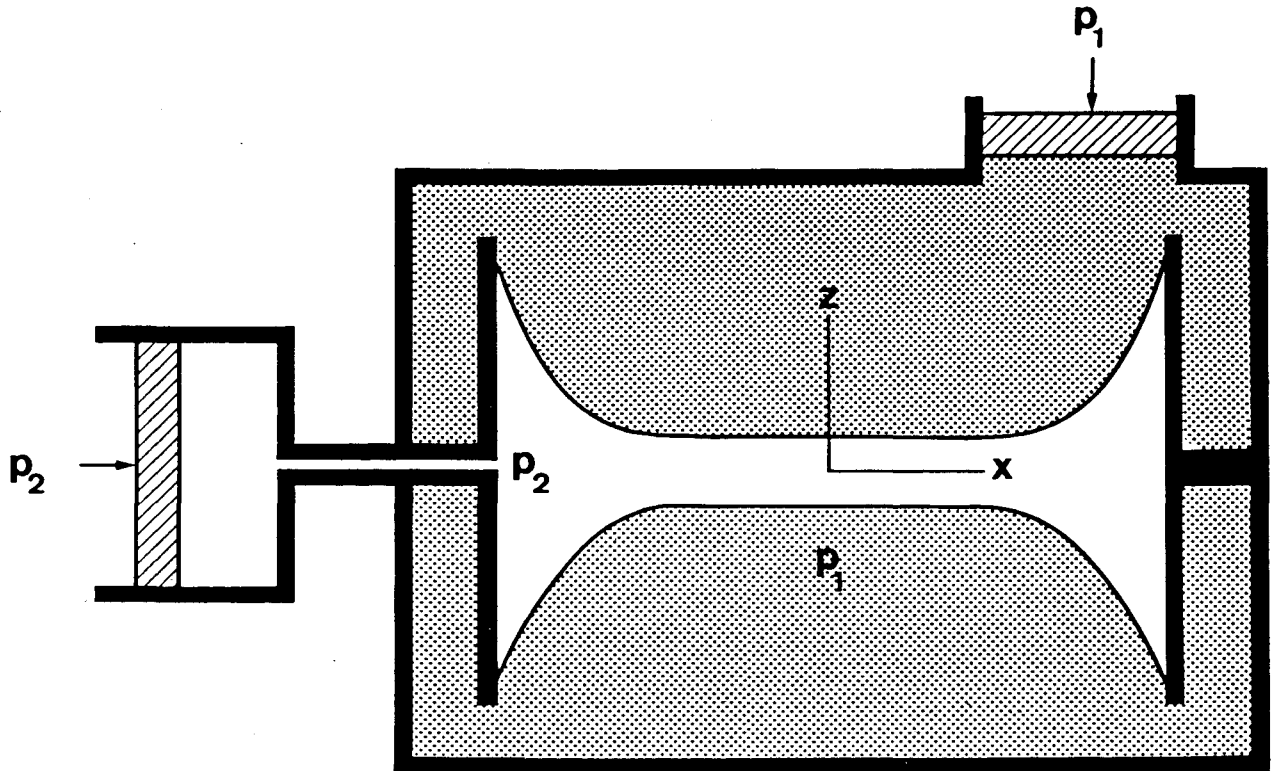


FIG. 3

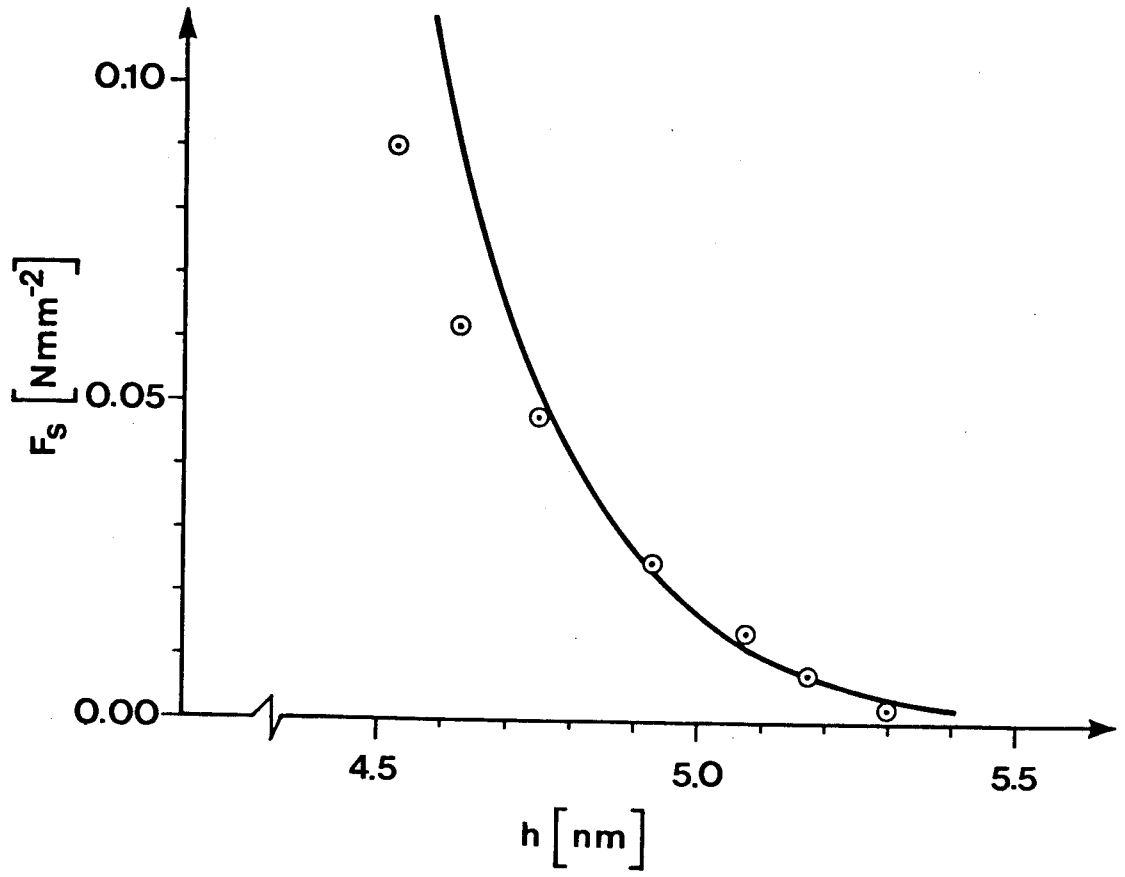


FIG. 4.

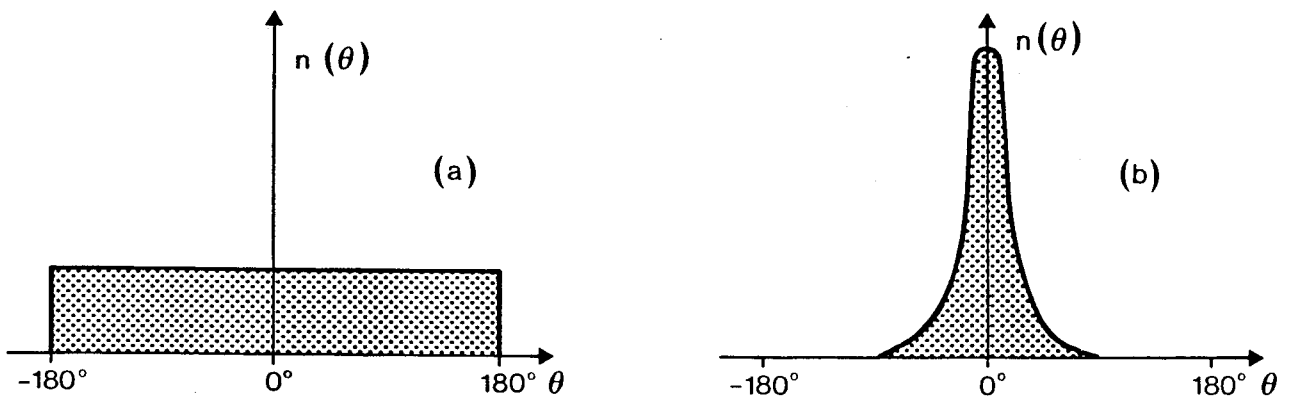


FIG. A - 1