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ON THE HYDRODYNAMICS OF A SOLVENT-SATURATED LIPID BILAYER.
II. STABILITY CRITERIA

by

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Abstract

The semiphenomenological model introduced in Part I is used to investigate the role of steric forces on the dynamics of black lipid films. We perform a linear stability analysis of hydrodynamic fluctuations for lipid films submitted to an applyed electric field. By neglecting dissipation, we concentrate our analysis on the competitive effects of electrostatic, van der Waals and steric forces. In the long wavelenght limit we show that the stability of the film against bending deformations is governed by the total film tension. Similarly, for periodic thickness fluctuations the stability is determined by the film elasticity. In both cases we met a stabilizing positive contribution of steric forces produced by the overlap of lipid chains at the center of the film. The stability diagram shows a region, for sufficiently small thickness, where only bending modes are unstable.

Key-words: Black lipid films, stability analysis; Film thickness and shape fluctuations; Dynamics of lipid films, steric repulsion.

I. Introduction

In Part I [1] of this series we have developed a semiphenomenological theory of steric repulsion in solvent-saturated black lipid films (LF). This approach enable us to calculate the macroscopic stress resulting from the anisotropic interactions of ordered hydrocarbon segments inside the film. The results of Ref. (1) are used here to study the dynamic stability of black lipid films against thermally induced hydrodynamic fluctuations.

The relevance of this study is primarilly related to the formation and stabilization of solvent saturated black lipid films[2,3]. In particular films submitted to an applied electric field[3]. Second, but a less strictelly application, consernes the mechanical deformation and rupture of lipid membranes in biological systems[4]. Finally, the present results apply also to study the frequency of propagating modes of stable lipid films as detected by ligth scattering mesurements [5,6].

Previous attempts to treat dynamics and stability of lipid films were restricted to coloured films [7,8,9] and biological viscoelastic membranes [10,11]. The former models we already critically reviewed in Part I [1]; the latter models aimed high in trying to describe actual membranes with their detailed morphology beign unknown up to date. Thus to our opinion these models had to fall short; they introduced only additional adjustable parameters into the problem without gainning further insight. Also none of models above is suited to treat coloured and black LF on the same framework. They generate then, an artificial distinction which is not justified according to observed experimental fact of a continuos transition from coloured to black films [2].

In Ref. (12) we sketched a semi-phenomenological model which unifies colored and black lipid films also from a theoretical point of view. This model is being detailed in the present series of papers. Recently Gallez [13], following the lines of Ref. (12), have proposed an alternative purely phenomenological model to treat steric repulsion. Unfortunately the microscopic origin of the repulsive forces cannot be traced in this last theory. Finally, a static analysis for thickness fluctuations of lipid films was performed by Hladky and Gruen [14], but using also a pure phenomenological model without any wevelength dependence of fluctuating forces.

In this paper we consider a solvent saturated lipid film submitted to an electric potential difference with negligible surface charge [7]. Following the lines of our previous studies on coloured films [7,8,9], we start from the simplest situation by neglecting any dissipative effect [7]. We are mainelly interested here in the competition between the destabilizing forces of van der Waals and electric origin and the stabilizing effect of the steric repulsion. Our purpose is to derive stability criteria for both squeezing (SQ) and bending (BE) deformation modes [12]. Besides the simplifications, this approach can be used, as a first attempt, to describe the linear dynamics of stable black lipid films.

In Section II we describe the model adopted by us and the decomposition of forces acting in the film system. Section III is devoted to discuss the film at mechanical equilibrium, take as the reference state in the following dynamic studies. Especial attention is payed to evaluate the film elasticity and the film tension; the later being calculated in detail in Appendix. In Section IV we performe a linear dynamic analysis of fluctuations. We neglect any viscous effect and restrict the analysis to the slow regime; i.e. instantaneous restored "chemical" equilibrium by diffusion and molecular reorientation. Based on this dynamic study, in Section V we derive the stability criteria in the long wavelenght limit. We draw stability diagrams as a function of the applied potential difference and the film thickness. Finally, Section VI is devoted to the concluding remarks.

II. Film Forces

In this Section we briefly describe the formal film model which is employed in the following. We argue how this model imposes a natural division of the forces involved and we discuss these forces in detail.

Here we are interessed in the long time and large scale dynamics of a lipid film well above its gel-liquid transition temperature. Thus our formal model assumes the hydrocarbon segments of both lipid chains and organic solvent to be distributed such as to form a dielectric fluid film with its bulk phase displaying uniform mass density ρ_2 and uniform dielectric constant ε_2. The film (bulk) does not exhibit any free electric charge, yet, it displays an order parameter density profile $\eta(\vec{r})$ reflecting the orientational order of the hydrocarbon segments. The film is sandwiched between two electrolytes each with uniform mass density ρ_1 and uniform dielectric constant ε_1. The electrolytes give rise to a charge distribution $\tau(\vec{r})$. Here they are also supposed to be biased on different electric potentials causing thus an electric field across the film. The film boundaries are thought to be made up of the hydrophilic lipid head groups. In our present treatment we assume the heads to be dissociated only very weakly such as to justify the assignment of a vanishing surface charge. In the film boundaries, the chemical composition changes fast in a transition zone whose width is small compared to h . Thus the zone is modeled as a singular two dimensional surface phase with intrinsic physico-chemical variables[8] which in the present paper reduce to the surface tension σ_s only.

This model leads immediately to distinguishing three types of forces: i) Isotropic forces due to short range interactions in a quasi uniform environnement; these forces are *globally* accounted for by the *isotropic* pressure: ii) Forces arising due to interactions which couple to densities varying on a scale shorter than the one set by the spacial extension of the interface; these forces arise in the interfacial region and are thought to be taken care of by the parameters describing the surface phase. iii) Forces caused by interactions coupling to densities varying on the scale of the interfacial width or on a larger scale; they with be modelled explicity and include forces of the van der Waals type and of electrostatic origin. They also comprise the part of the anisotropic forces of orientational origin which arises from the ("slowly" varying) pseudo order density coinciding with the real order density in some region around the film center (cf. Part I). The forces of type iii) are treated *explicity* in the equations describing the bulk properties of the film or external phases, respectively.

The bulk force acting in a volume element of the system reads then,

$$\vec{F} = \vec{\nabla} p + \rho \, \vec{\nabla} W - \vec{\nabla}.(\vec{\vec{T}} + \vec{\vec{\Pi}}) \qquad (1)$$

The potential $W(\vec{r})$ accounts for isotropic interactions of van der Waals-London type; it is determined self-consistent by the fluid density $\rho(\vec{r})$

$$W(\vec{r}) = \int w(\vec{r}-\vec{r}\,') \, \rho \, (\vec{r}\,') dr \qquad (2)$$

where $w(\vec{r})$ is the long-range part of the two body potential acting between molecules, i.e. $w(\vec{r})=-\frac{\lambda}{r6}$ for large r.
The electrostatic forces due to free charges or external applied fields are given by the Maxwell stress tensor

$$\overset{\rightarrow}{\vec{T}} = \frac{\varepsilon}{4\pi} \vec{E}\vec{E} - \frac{1}{8\pi} E^2 \overset{\rightarrow}{\vec{I}} \tag{3}$$

where $\overset{\rightarrow}{\vec{I}}$ is the unity tensor, ε is the dielectric constant and $\vec{E}=-\vec{\nabla}\psi$ is the electric field. The electric potential ψ is determined by the Poisson equation

$$\vec{\nabla}.(\varepsilon\vec{\nabla}\psi) = 4\pi\tau \tag{4}$$

The charge density τ vanishes in the film. In the external aqueous solution τ is given by the equilibrium Boltzmann distribution for free ions, i.e.

$$\tau(\vec{r}) = n_0 e \exp[-e\psi(\vec{r})/KT] - n_0 e \exp[e\psi(\vec{r})/KT] \tag{5}$$

where n_0 is a given number density, e is the ionic charge, K is the Boltzmann's constant, and T the absolute temperature. Equation (4) is supplemented by the electrical bondarie conditions at the film surfaces, where we neglect dipole moments and take into account that surface is uncharged.
Finally, the stress tensor $\overset{\rightarrow}{\vec{\Pi}}$ describing the anysotropic short ranged interactions; was derived in Part I as

$$\overset{\rightarrow}{\vec{\Pi}} = A\,\{\vec{\nabla}\eta\,\vec{\nabla}\eta - \frac{1}{2}(\vec{\nabla}\eta)^2\,\overset{\rightarrow}{\vec{I}}\} \tag{6}$$

η is the order parameter density associated with the orientational order of hydrocarbons segments of both lipids and solvent molecules. The constant A mesures the relative strenght of the spacial correlation of the order parameter (see Part I). The order parameter η is determined through the condition of thermodynamic equilibrium. For small variations $\hat{n}=(n-n_b) << 1 (0 \leq \eta \leq 1)$, we have

$$(\nabla^2 - \beta^2)\,\hat{\eta} = 0 \qquad (7)$$

where η_b is the value of η in the reference bulk phase and $\beta^2 = \frac{\partial \mu_o(\eta)}{\partial \eta}\Big|_{\eta_b} / A(\eta_b)$, $\mu_o(\eta)$ being the homogeneous part of the chemical potential (see part I). The order parameter η is identically zero in the external phases. Inside the film its maximum, η_s, is reached at the film surfaces. Besides the jump of the mass density ρ at the film surfaces, the inhomogeneities of the bulk phases are associated with the variations of charge densities and electric potential, and also with the variation of the order parameter η inside the film. Eqs. (6) and (7) are valid in the region near the center of the film, and for small deviation of its bulk value, η_b. Indeed for our purposes only the overlap region in the center of the film matters. Any deviation further away from the center is formally incorporated in the properties of the surface layers and results in a contribution to the surface tension

III. Mechanical Equilibrium

We consider a flat lipid film in mechanical equilibrium with the film forming phase and surrounded by two aqueous solutions (cf. Fig. 3, Part I). In mechanical equilibrium the total force (Eq. (1)) vanishes at any point and in any direction. Thus following along the lines of Section II of part I one demonstrates that the (normal) stress difference between the external and the film phase is

$$p_1 - p_{N_2} = (\rho_1 - \rho_2)\, W^s \tag{8}$$

Here p_1 is the isotropic pressure prevailing in the bulk of the electrolyte, p_{N_2} is the total normal stress in the film. W^s represents the value of the van der Waals potential at the film surfaces. From Eq. (2) it holds

$$(\rho_1 - \rho_2)\, W^s = - \frac{H}{6\pi h^3} \tag{9}$$

with $H = \pi^2 (\lambda_{11} (\rho_1)^2 + \lambda_{22} (\rho_2)^2 - 2\lambda_{12}\, \rho_1 \rho_2)$ being the Hamaker constant.

We now use the fact that the electric and steric forces defined in Section 2 derive from a potential, i.e.,

$$\vec{\nabla} \cdot (\vec{\vec{T}} + \vec{\Pi}) = \nabla \phi \tag{10}$$

with

$$\phi = \frac{\varepsilon-1}{8\pi}(\vec{E})^2 + \frac{1}{2}A\,\beta^2\,(\vec{\eta})^2 . \qquad (11)$$

Then the mechanical equilibrium in the x-direction (film phase) asks for

$$p_{N_2}-p_2 = -[T_{zz}(\vec{r}_2) + \Pi_{zz}(\vec{r}_2) - \phi(\vec{r}_2)] . \qquad (12)$$

Here $\vec{r}_2$ is a point in the film phase, and p_2 represents the isotropic pressure in the bulk of the film forming phase. In deriving Eq. (11) we used that the electric field $\vec{E}$ and the order parameter $\vec{\eta}$ vanish in the meniscus. From Eqs. (3), (4) with $\tau=0$, (6), (7) and (11) we get

$$T_{zz}(\vec{r}_2) + \Pi_{zz}(\vec{r}_2) - \phi(\vec{r}_2) = \frac{\varepsilon_2}{8\pi}(E_2)^2 - \frac{A_0\beta^2}{2}(\eta_s)^2/\cosh^2(\beta h/2) \qquad (13)$$

where E_2 is the constant electric field inside the film.
The disjoining pressure is then obtained from Eqs. (8), (9), (12) and (13);

$$\Pi_D = p_1-p_2 = -\frac{H}{6\pi h^3} - \frac{\varepsilon_2(\varepsilon_2)^2}{8\pi} + \frac{A\,\beta^2}{2}(\eta_s)^2/\cosh^2(\beta h/2) \qquad (14)$$

As in the soap films (see ref. 15) the disjoing pressure accumulates pressure jumps both across the external phase/film interface (Eq. (8)) and across the film/meniscus transition zone (Eq. (12)). The physical origin of the jump in the film phase is however quite different in the lipid film. There are two contributions (Eq. (13)), one due to the variations of the applied field E_2 which varies from zero at meniscus to $E_2(h)$ at the film. The other comes from the increasing order of hidrocarbon chains going from the meniscus to the film phase. This contribution is discussed in detail in Ref. (16). In the case of a lipid film submitted to an external electric field, both the van der Waals and the electric terms are negative and these forces tend to compress the film. If we consider only these two contributions the pressure at the meniscus has to be larger than the pressure in the external phase to equilibrize the film. The only positive term comes from the ordering of hidrocarbon segments at the center of the film. This disjoing action comes from the reduction of configurational entropie of hidrocarbon chains, due to the superposition of the two lipid layers.

In the case of an external applied field and negligible surface charges, and for sufficiently concentrated solutions ($2\varepsilon_2/\varepsilon_1\kappa_1 h \ll 1$, where $1/\kappa = (\varepsilon_1 KT/8\pi n_0)^{1/2}$ is the Debye screening length) the electric field inside the film reads.

$$E_2 = \Delta/h \qquad (15)$$

where Δ is the total potential drop between the external phases. For this condition, Eq. (14) simplifies to

$$\Pi_D = -\frac{\varepsilon_2 \Delta^2}{8\pi h^2} - \frac{H}{6\pi h^3} + \frac{A\ \beta^2 (n^s)^2}{2} \Big/ \cosh^2(\beta h/2) \qquad (16)$$

This expression is useful for interpreting electro-compression experiments on solvent saturated lipid films as performed by Andrews et al.[3]. As argued by Fettiplace at al.[17], for this experimental set up the total disjoing pressure Π_D is nearly equal to zero. This mean, the compressive action of electric and van der Waals forces is compensated by the steric repulsion given by the last term in (16). In fact this expression, with $\Pi_D=0$, was used in part I to fit the experimental results (cf. discussion in section III of part I).

As will be discussed in the following sections the stability of the film against small shape fluctuations is mainly related to the film tension and to the variation of disjoining pressure with film thickness, i.e. the film elasticity. With the reference state being in mechanical equilibrium, the film tension is obtained from the Bakker integral[18]

$$\gamma_F = \int_{-\infty}^{+\infty} (p_N - p_T)\, dz \tag{17}$$

where p_N and p_T are the normal and transversal components of the total stress. The explicit form of γ_F is derived in the Appendix, it reads

$$\gamma_F = 2\gamma_s - \frac{A}{4\pi h^2} - \frac{\varepsilon_2 \Delta^2}{4\pi h} + (n^s)^2 \beta [1 + \frac{\beta h}{2} / \cosh^2(\frac{\beta h}{2}) - \tanh(\frac{\beta h}{2})] \tag{18}$$

The film elasticity is defined by

$$\varepsilon_F = -(\frac{\partial}{\partial h} \Pi_D)\, h^2 \tag{19}$$

The explicit form is obtained directly as the first derivative of Eq. (16). We get

$$\varepsilon_F = -\frac{H}{2\pi h^2} - \frac{\varepsilon_2 \Delta^2}{4\pi h} + \frac{A\,(\eta^s)^2}{2}\,\beta^2 h^2\,\frac{\tanh(\beta h/2)}{\cosh^2(\beta h/2)} \tag{20}$$

The physical significance of the various contributions to the film tension and to the film elasticity is presented in section V together with the discution of the film stability.

IV. Linear Dynamics

In the following we perform a linear stability analysis of the dynamic fluctuations of the film system. Starting from the reference state of a plane film with parallel surfaces, we study shape disturbations on the hydrodynamic scale. Yet, we restrict ourselves to the analysis of sufficiently slow perturbations such that "chemical" equilibrium is maintained during the motion. This means that diffusion and molecular reorientation are sufficiently fast such that Equations (5) and (7) are still valid for the perturbed state. For the surface layer this approach corresponds to neglecting any viscous or elastic effects due to the transport of mass and charge (see slow regime in Ref. (19)), or due to the molecular reorientation. Further we neglect any intrinsic viscous effects in the bulk phase and in the surface layers. For the case of vanishing surface charges, discussed here, this amounts to considering only transversal motion of the surfaces as discussed in Ref. (7).

The assumptions above impose restrictions on the time and length scales the model can deal with. Yet, these limitations have no impact on the study of low frequency modes, on the determination of marginal states, and on the stability diagram been the major gool of this paper (Section V). The generalization of these investigations which especially also includes dissipative effects follows along the lines of Ref. (8) and is subject of separate study.

In the perturbed state the velocity field is obtained from the dynamical equation,

$$\rho \frac{d\bar{v}}{dt} = - \bar{F} \tag{21}$$

and from the imcompressibility condition

$$\bar{\nabla}.\bar{v} = 0 \tag{22}$$

The bulk force $\bar{F}$ defined in Eq. (1) is explicity evaluated from equations (1) to (7). This set of equations is supplemented by the following boundary conditions: i) continuity of velocities at the film surfaces,

$$\Delta_s[\bar{v}] = 0 \ , \tag{23}$$

ii) surface balance of the normal stress

$$\Delta_s[p - T_{zz} - \pi_{zz}] = \sigma_s(\frac{1}{R_1} + \frac{1}{R_2}) \tag{24}$$

where σ_s is the surface tension and R_1, R_2 are the principal radii of curvatures of the surface. iii) continuity of electric potential and electric displacement at the film surfaces. iv) the conditions of constant surface potential and of constant density η^s, arising from the slow regime assumptions. v) The condition of vanishing perturbations in the external phases far from the film surfaces.

The perturbed quantities are decomposed, then into normal modes characterised by a complex frequency ω ($e^{\omega t}$ is the time factor) and a wave vector $\vec{k}$ parallel to the unperturbed surfaces. In solving the linearized equations we decompose the velocity field into symmetric and antisymmetric components, giving rise to two modes of the film, a <u>bending mode</u> (BE)[*] with the two surfaces of the film moving in phase and a <u>squeezing mode</u> (SQ) in which the two surfaces move out of phase. In linear order, the two motions decouple, due to the symmetry of the reference state[7]. The condition for non trivial solutions yields the following dispersion relation for the BE - modes

$$
\begin{aligned}
&\omega^2\left[\frac{\rho_2}{k}\tanh\left(\frac{kh}{2}\right)+\frac{\rho_1}{k}\right] = -\{k^2\sigma_s + H(a+b)\\
&+\frac{\varepsilon_2(E_2^0)^2}{4\pi}\left[(k^*-g)\left(\frac{\varepsilon_2}{\varepsilon_1}-1-\frac{\varepsilon_2(g-k^*)-\varepsilon_1 g}{\varepsilon_1 g+\varepsilon_2 k\tanh(kh/2)}\right)\right.\\
&\left.+k\left(\frac{\varepsilon_2(g-k^*)-\varepsilon_1 g}{\varepsilon_1 g\coth(kh/2)+\varepsilon_2 k}\right)\right]\\
&-A(\eta^s)^2\beta^2\tanh\left(\frac{\beta h}{2}\right)\left[p\tanh\left(\frac{\beta h}{2}\right)\coth\left(\frac{ph}{2}\right)-\beta\right]\}
\end{aligned}
\qquad (25)
$$

For the SQ - modes we obtain

$$
\begin{aligned}
&\omega^2\left[\frac{\rho_2}{k}\coth\left(\frac{kh}{2}\right)+\frac{\rho_1}{k}\right] = -\{k^2\sigma_s - A(b-a)\\
&+\frac{\varepsilon_2(E_2^0)^2}{4\pi}\left[(k^*-g)\left(\frac{\varepsilon_2}{\varepsilon_1}-1-\frac{\varepsilon_2(g-k^*)-\varepsilon_1 g}{\varepsilon_1 g+\varepsilon_2 k\coth(kh/2)}\right)\right.\\
&\left.+k\left(\frac{\varepsilon_2(g-k^*)-\varepsilon_1 g}{\varepsilon_1 g\tanh\left(\frac{kh}{2}\right)+\varepsilon_2 k}\right)\right]\\
&+A(\eta^s)^2\beta^2\tanh\left(\frac{\beta h}{2}\right)\left[p\tanh\left(\frac{\beta h}{2}\right)\tanh\left(\frac{ph}{2}\right)-\beta\right]\}
\end{aligned}
\qquad (26)
$$

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[*] We have used the word "stretching" in our previous articles. By now we are convinced that "bending" describes better the picture of this mode.

In these equations we have used

$$a = \frac{1}{2\pi h^4} \quad , \quad b = \frac{1}{2\pi}\left(\frac{k}{2h}\right)^2 K_2(kh) \tag{27}$$

where $K_2(x)$ is a modified Bessel function of second order. Further

$$k^* = \kappa \frac{1+\chi_o^{\,2}}{1-\chi_o^{\,2}}$$

$$g = (\kappa^2+k^2)^{1/2} + \frac{4\,\kappa^2\chi_o^{\,2}}{[\kappa + (\kappa^2+k^2)^{1/2}](1-\chi_o^{\,2})^2 + 2\kappa\chi_o^{\,2}(1-\chi_o^{\,2})}$$

$$\chi_o = \tanh\{\frac{en_o}{4KT}(E_2^0 h - \Delta)\}$$

$$p = [\beta^2 + k^2]^{1/2} \tag{28}$$

The dispersion relations (25) and (26) show how the various interactions generate very specific k-dependences in ω. In particular we draw attention to terms related to the variations of the interfacial order parameter η. They are new compared to our previous work[7,8,9]. For $h\to\infty$, corresponding to two infinitely distant interfaces; $kh >> 1$, $ph >> 1$ and $\tanh(\frac{kh}{2})$, $\coth(\frac{kh}{2})$, $\tanh(\frac{ph}{2})$, $\coth(\frac{ph}{2}) \to 1$; and the van der Waals contributions $H(b-a)$ and $H(b+a)$ vanish. In this limit Eqs. (29) and (30) become identical to each other, and represent the dispersion relation of a single non-interacting interface. The long wavelenght limit $(kh) \to 0$ is discussed in detail in the next section. The intermediate domain $k \approx 1/h$, needs a complex numerical study of the k-dependency and is beyond the scope of this paper.

V. Stability of Long Wavelenghts

In previous studies[7,9] of coulored lipid films the instability of the SQ-mode was emphasied for wave-lenghts large in comparison with the film thickness. The purpose of this section is to show that the SQ-modes of black LF are stabilized in the long wavelenght limit, due to the overlap of the lipid interfaces. Further, we discuss the complete stability diagram demonstrating the possibility of an exclusive instability of the BE-modes. We restrict ourselves to the long wavelenght limit, a detailed analysis in the whole domain of wavelenghts will be the subject of a forthcoming paper.

In studing the domain of stability the wavelenght of fluctuations ($2\pi/k$) has to be compared with the characteristic lengths of the system; i.e. the film thickness h, the Debye screaning length $1/\kappa$ and the length $1/\beta$ mesuring the interaction range between oriented hydrocarbon bonds. The film thickness is typically of order 50-100 Å for black lipid films. For concentrated solution $n_0 > 0.01M$, thus $1/\kappa < 100$ Å, i.e., $\kappa h \gtrsim 1$. Since the ratio $\varepsilon_2/\varepsilon_1$ between the dielectric constants in the film phase and in the water is much less than unity, it is also true that $2\varepsilon_2/\varepsilon_1 \kappa h \ll 1$. This fact implies that $en_0(\Delta - E_2^0 h)/4kT$ goes to zero, allowing us to neglect terms proportional to χ_0^2 in Eq. (28). Finally, the fitting in part I confirms the assumption of small overlap between adjacent lipid layers i.e., $h \gg 1/\beta$. The long wave lenght limit corresponds then to take

$$1/k \gg h,\ 1/\kappa,\ 1/\beta \tag{29}$$

In this limit, the dispersion relations (24) and (25) reduce to

$$\omega^2 = - \frac{k^3}{2\rho_1} \gamma_F \qquad \text{(BE)} \qquad (30)$$

and

$$\omega^2 = - \frac{k^2}{h\rho_2} \varepsilon_F \qquad \text{(SQ)} \qquad (31)$$

where γ_F and ε_F are given by Eqs. (18) and (20) respectively.

Depending on the sign of the L.H.S. of Eqs. (30) and (31) the roots ω are two pure imaginary numbers or two real roots with opposite sign. The first situation corresponds to propagating modes whithout damping (marginal stability). In the second case the positive root leads to a growth of perturbations, corresponding to an unstable situation. Physical arguments and experience suggest that dissipation, neglected here, renders the propagating modes assymptotically stable. Thus we adopt the following stability critenia; negative r.h.s. of Eqs. (30) or (31), respectively, correspond to stable solutions, positive r.h.s. implies unstable mode, zero values corresponds to the transition between stable and unstable regimes.

Equations (30) and (31) show that in the longwave-length limit the stability of BE and SQ modes depend on the sign of the film tension and of the film elasticity respectively. Indeed, the film tension represents the mechanical resistence to bending the film, and film elasticity is related to the restoring forces opposing thickness changes. If the film tension is negative the film has the tendency to be bent and consequentially the planar configura tion is unstable. Similarly, negative film elasticity describes the tendency of the film to shrink.

For $\beta h >> 1$ the film tension reads

$$\gamma_F = 2\gamma_s - \frac{H}{4\pi h^2} - \frac{\varepsilon_2\Delta^2}{4\pi h} + 2\ (\eta^s)^2\ \beta(\beta h)\exp(-\beta h) \qquad (32)$$

where γ_s is the interfacial tension of a single non-interacting interface, which is positive. The van der Waals interactions produces a decrease of the free energy $(-H/4\pi h^2)$ as the film surfaces approach each other. The increase of the negative strored energy $(-E_2\Delta^2/4\pi h)$ corresponds to an increase of electric capacitance as the film becomes thinner. Finally the last term in (33) corresponds to an increase of free energy due to the increase of order in the center of the film as the two lipid layers are superposed. The various contributions to $\gamma_F - 2\gamma_s$, as a function of h are shown in Fig. 1. The resulting curves for $\Delta=0$, and $\Delta=100$ mV are also shown. In Fig. 1 we have take $A=3.48\mathrm{x}10^{-14}$erg and $\varepsilon_2=2.1$ [3]. For the constants $2A(n^s)^2\beta$ and β, we chose the values obtained in Part I, by fitting the experiments by Andrews et al. [3] on lipid films saturated with hexame. This figure shows that the BE modes can be stabilized in the whole domain of h even for small values of γ_s ($\gamma_s > 0.003$ dyn/cm for $\Delta=0$, and $\gamma_s>0.03$ for $\Delta=100$mV). For increasing applied potential, however, the BE mode becomes unstable. The critical value of Δ above which the BE mode becomes unstable is plotted in Fig. 2. For realistic values of γ_s of order $\frac{1}{2}\frac{\mathrm{dyn}}{\mathrm{cm}}$ this potential is of order of 190mV.

The film elasticity reads $(\beta h>>1)$

$$\varepsilon_F = - \frac{H}{2\pi h} - \frac{\varepsilon_2 \Delta^2}{4\pi h^2} + 2A\beta (n^s)^2 (\beta h)^2 \; e^{-\beta h/2} \qquad (33)$$

The response to the changes of film thickness has the negative contributions due to the van der Waals attraction and to the electric compression. The repulsive (positive) contribution comes from the overlap of the lipid chains at the center of the film, and increases exponentially as h decreases. This various contributions are plotted in Fig. 3. The resulting curve shows that the film is unstable againsts SQ deformation for sufficiently large h for which repulsive forces vanishe, in accordance with previous studies[9]. The new result, however, is that for small h($h \leq 61.7$ for $\Delta=0$, $h<59.2$ for $\Delta=100$mV) the SQ modes are stable due to the action of the repulsive forces. More, interesting, is that for certain values of h($40<h<60$) the SQ mode is stable and the BE mode is unstable. This means that in a certain domain of h the film will become unstable not due to the changes of thickness but through a bending deformation. This bending of lipid membranes is already observed in experiments which heated erytrocites, as described by Cockley et al.[4]. It is also interesting to note that such kind of phenomena occurs, although less understanding, in many biological process like phagocytosis. The complete stubility diagram for the SQ and ST modes is presented in Fig. 4. It can be see that above a critical value of Δ, after which the BE mode becomes unstable, there is a region where only ST perturbations are unstable.

VI. Conclusions

In studying the formation of solvent-saturated lipid films a central question arises concerning the mechanism responsible for the stabilization of black films as experimentally observed [2]. The steric repulsion model introduced in Part I [1] gives a simple picture of this mechanism. Our theory is based on the microscopic orientational order of hydrocarbon segments inside the film, and predicts an increase of order in the center of the film as the film thickness decreases, resulting in a macroscopic disjoining action. This positive contribution to the total disjoining pressure was explicitally calculated in Part I.

In the present paper we have investigate the role of steric forces on the stability of the film against shape and thickness thermal induced fluctuations. For that we have introduced a film model which consist of a dielectric fluid phase surrounded by two electrolytic aqueous solutions biased at different electric potentials. The linear dynamic analysis was performed by accounting for the fluctuations of van der Waals, electric and steric forces. We have then obtained dispersion relations for both SQ and BE-modes, and finally used this result to derive a stability criteria for the film system.

While neglecting dissipative effects this paper represents a first, important, step to understand the black lipid film dynamics. Yet, the dispersion relations of section IV can be used, as a first attempt, to describe dynamic fluctuations in stabilized films as detected by light scattering experimentals [5,6]. The most important result of this paper is, however, the stability criteria derived in section V for long-wavelenghts. In this limit we have shown that SQ-modes are stabilized by the positive contribution of steric repulsion to the film elasticity. This result contrast with our previous fiding [7,8,9] where SQ -instability was always met, drived by van der Waals and electrostatic attractions. Further, we obtain also a positive contribution of steric forces to the total film tension, acting to prevent bending instability.

The parameters used to draw the figures in section V correspond to realistic values take from the experiments performed by Andrews et al. [3] in solvent-saturated lipid films. We show that for small values of the single surface tension ($\gamma_s \geq 0.05$) the bending modes are stable even for more or less strong applied potentials ($\Delta \lesssim 200$mV). Further, the stability diagram (Fig. 5) shows that both SQ- and BE-modes are stable for sufficiently small thickness, predicting the formation of stable films as experimentally observed [3]. The unstable domain is separated into three different regions; i) only SQ-modes are unstable, ii) both SQ and BE-modes are unstable, iii) only BE-modes are unstable. Although there are no available systematic experimental studies on the unstable regimes of lipid films, our results are in a qualitativelly agreement with some observed facts. For example, the thickness fluctuations preceding the shrink of solvent-saturated lipid films submitted to an applied field as reported by Andrews et al. [3] can be ascribed to the SQ-instability as predicted by our theory. Also, bending deformation of lipid membranes was observed in heated erythrocytes [4]. Following the authors the observed instability is caused by electric constraints, and occurs when the cytoskeletal proteins are thermally impaired. Although less strict, this example shows that our theory could have an impact even on biological systems.

In conclusion, the extension of the present theory is under investigation. Especial attention will be payed to the interpretation of light scattering experiments. Also, further experimental developments will be suitable to check the stability diagram as draw in Fig. 4 or to suggest new theoretical developments.

Acknowledgements

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Appendix:

The subject of this appendix is the explicit calculation of the film tension (18). We start to divide the domain of integration as follows

$$\gamma_F = \int_{-\infty}^{-h/2-\delta} (P_N-P_T)\,dz + \int_{-h/2-\delta}^{-h/2+\delta} (P_N-P_T)\,dz + \int_{-h/2+\delta}^{+h/2-\delta} (P_N-P_T)\,dz + \int_{+h/2-\delta}^{+h/2+\delta} (P_N-P_T)\,dz + \int_{+h/2+\delta}^{\infty} (P_N-P_T)\,dz \qquad \text{(A-1)}$$

where $\delta << h$ is a small distance from the mathematical film surfaces. Now, we calculate separate each contribution;

A) Surface Layers: For symmetric films we have

$$\sigma_F = \int_{-h/2-\delta}^{-h/2+\delta} (P_N-P_T)\,dz = \int_{+h/2-\delta}^{+h/2+\delta} (P_N-P_T)\,dz \qquad \text{(A-2)}$$

σ_F has to be decomposed into two contributions

$$\sigma_F = \sigma_S + 1/2\,\sigma_W \qquad \text{(A-3)}$$

where σ_S is the single surface tension accounting for the variations, through the surface layer, of the tangencial component of the stress as compared to a constant reference normal stress. The second contribution σ_W arrives from the variations of the normal stress as compared to the same reference pressure. This last contribution is due to the change of the van der Waals interactions as the two surfaces are approached (see discution in Ref. (20)). We note that the choice of a reference pressure makes these decomposition not unique. However we take here σ_S independent of h and equal to the surface tension of non-interacting surfaces ($h \to \infty$), fixing then an unique value for σ_w.

B) External phases. The anysotropy comes only from the electrical interactions in the diffuse layers, then we have

$$\sigma_{E1} = \int_{-\infty}^{-h/2} (P_N - P_T)\, dz = \int_{+h/2}^{+\infty} (P_N - P_T)\, dz =$$

$$= -\int_{-\infty}^{-h/2} \frac{\varepsilon}{4\pi} (E_z)^2\, d\,z = -\frac{\varepsilon_1}{8\pi\kappa} (E_1^0)^2 [1 - \chi_0{}^2] \qquad \text{(A-4)}$$

In deriving (A-4) we have used the solutions of Eqs. (4) and (5). $E_1^0 = \frac{\varepsilon_2}{\varepsilon_1} E_2^0$ is the electric field in phase 1 taken at the film surfaces and $\chi_0 = \tanh\{\frac{en_0}{4KT}(E_2^0 h - \Delta)\}$.

C) Film phase: Inside the film the stress anysotropy comes both from the constant electric field and from the short-ranged orientational interactions.

$$\int_{-h/2+\delta}^{+h/2-\delta} (P_N - P_T) = \int_{-h/2}^{+h/2} [-A(\frac{d}{dz}\eta^0)^2 - \frac{\varepsilon}{4\pi}(E_z^0)^2]\, d\,z$$

$$= \sigma_R + \sigma_{E2} \qquad \text{(A-5)}$$

where

$$\sigma_R = - [\eta^S]^2\, \beta\, [\tanh(\frac{\beta h}{2}) - \frac{\beta h}{2}/\cosh^2(\frac{\beta h}{2})] \qquad \text{(A-6)}$$

and

$$\sigma_{E2} = - \frac{\varepsilon_2}{4\pi} h(E_2^o)^2 \tag{A-7}$$

The total film tension becomes

$$\gamma_F = 2\sigma_S + \sigma_w + 2\sigma_{E1} + \sigma_{E2} + \sigma_R \tag{A-8}$$

In order to get the contribution σ_w we have to know the single surface tension γ_S when h→∞. For zero surface charge both σ_{E1} and σ_{E2} vanishes, since $E_2^o \to 0$ as h→∞. Further the short-ranged interactions for a single interface gives

$$\sigma_{RS} = - \frac{A}{2} [\eta_S^o]^2 \beta \tag{A-9}$$

Finally the contribution σ_w is defined such that it goes to zero when h→∞ and σ_s remains constant. Therefore the single surface tension reads:

$$\gamma_S = \sigma_S + \sigma_{RS} \tag{A-10}$$

On the other hand the thermodynamic definition of the film tension is [18,20]

$$\gamma_F = 2\gamma_S + \Pi_D h + \int_h^\infty \Pi_D(h)\, dh \tag{A-11}$$

where Π_D is the disjoining pressure of Eq. (16). For integrating (A-11) we assume:

i) the value of the order parameter at the film surfaces, η^s, is a constant independent of h.

ii) the external aqueous solution is sufficiently concentrated such that $2\varepsilon_2/\varepsilon_1\kappa h \ll 1$ and $\frac{ne}{4kT}(\Delta - E_2^0 h) \ll 1$. Thus Eqs. (A-11) and (16) yield

$$\begin{aligned}\gamma_F &= 2\gamma_S + 2\sigma_{E1} + \sigma_{E2} + \sigma_R - 2\sigma_{RS} - \frac{A}{4\pi h^2} \\ &= 2\sigma_S + 2\sigma_{E1} + \sigma_{E2} + \sigma_R - \frac{A}{4\pi h^2} \qquad \text{(A-12)}\end{aligned}$$

Comparing Eqs. (A-8) and (A-12) shows that

$$\sigma_W = -\frac{H}{4\pi h^2} \qquad \text{(A-13)}$$

Finally, by substituting Eqs. (A-4), (A-6) and (A-7) into (A-12) we get the expression (18) in Section III.

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Figure Captions

Fig. 1:

The various contributions to $\gamma_F-2\gamma_S$ (----): $\gamma_\omega=-H/4\pi h^2$, $\gamma_E=-E_2\Delta^2/4\pi h$ (Δ=100mV) and $\gamma_R=2(\eta^s)^2\beta\,(\beta h)\exp(-\beta h)$; and the resulting curves (——) for $\Delta=0$ (γ_1) and for Δ=100mV (γ_2).

Fig. 2:

Stable domain for BE-modes, i.e. positive γ_F, as a function of the single surface tension γ_S and the applied potential Δ.

Fig. 3:

The various contributions to the film elasticity ε_F (----): $\varepsilon_\omega=-H/2\pi h^2$, $\varepsilon_E=-E_2\Delta^2/4\pi h$ (Δ=100mV) and $\varepsilon_R=2(\eta^s)\beta(\beta h)^2\exp(-\beta h)$; and the resulting curves (——) for $\Delta=0$ (ε_1) and Δ=100mV (ε_2).

Fig. 4:

Stability diagram for the film system; (——) separates stable from unstable domains. The unstable region is separated (----) into three domains; i) only SQ-modes are unstable, ii) both SQ and BE-modes are unstable, iii) only BE-modes are unstable.

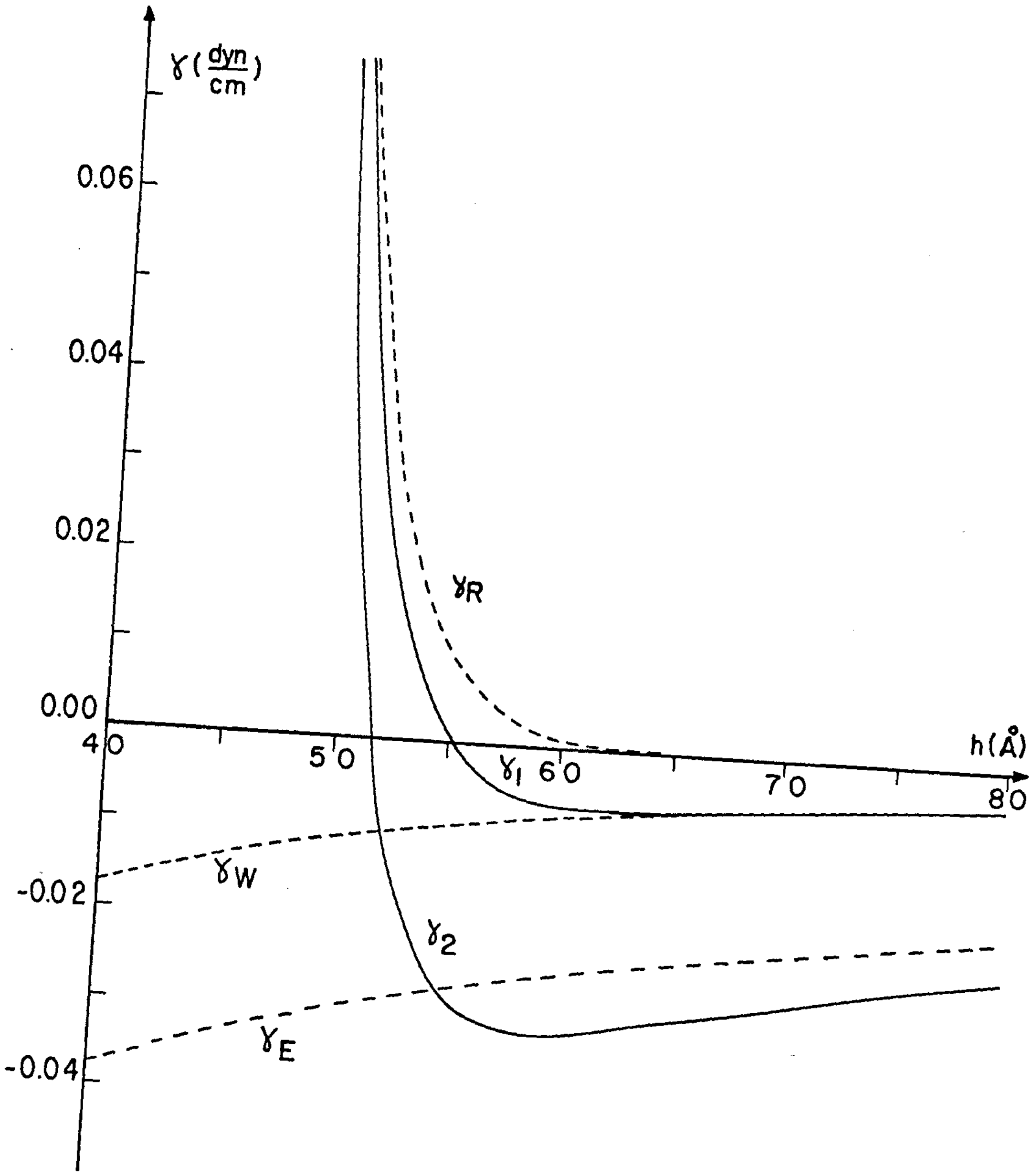

Fig. 1

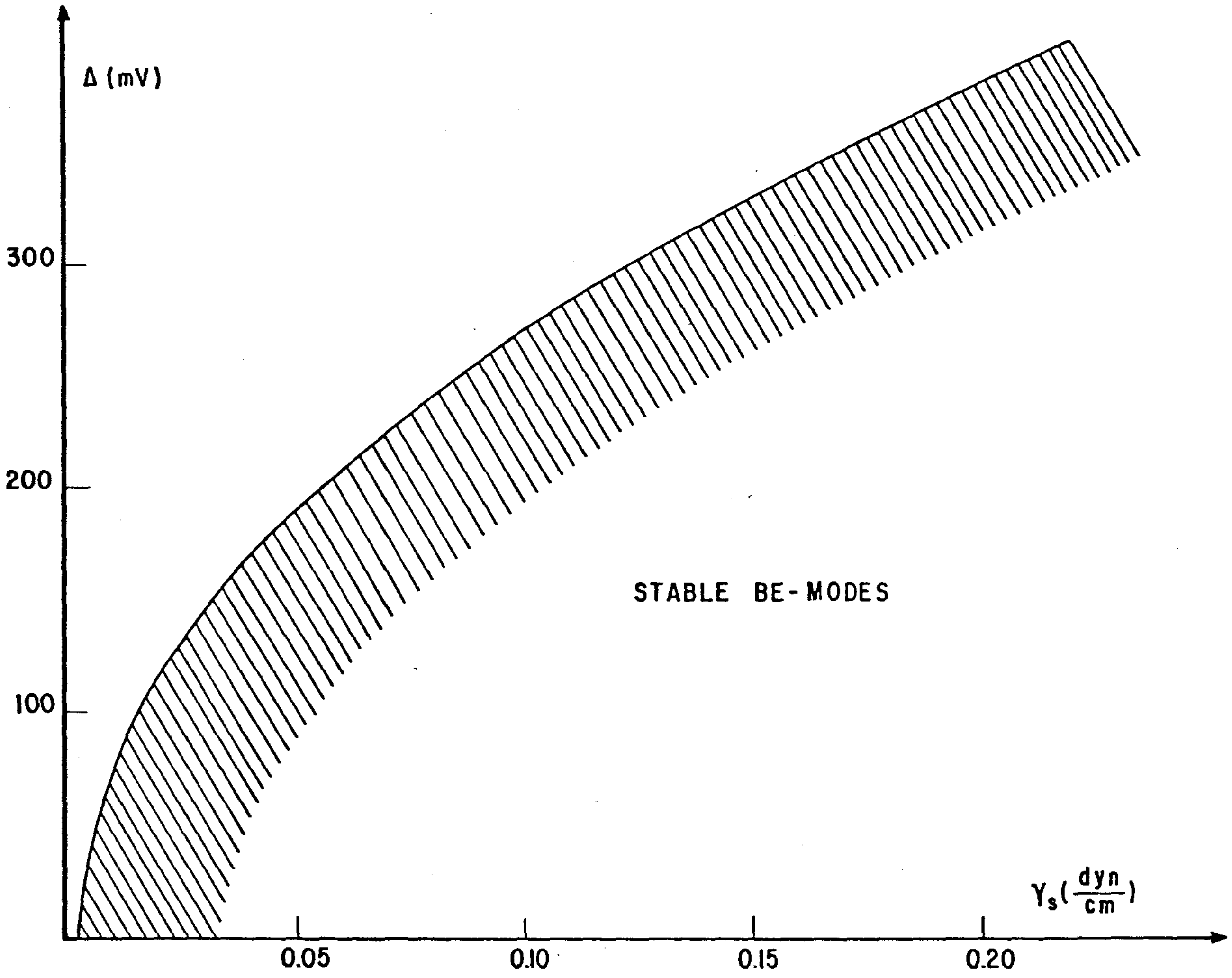
Δ (mV)
300
200
100
STABLE BE-MODES
$\gamma_s(\frac{dyn}{cm})$
0.05
0.10
0.15
0.20

Fig. 2

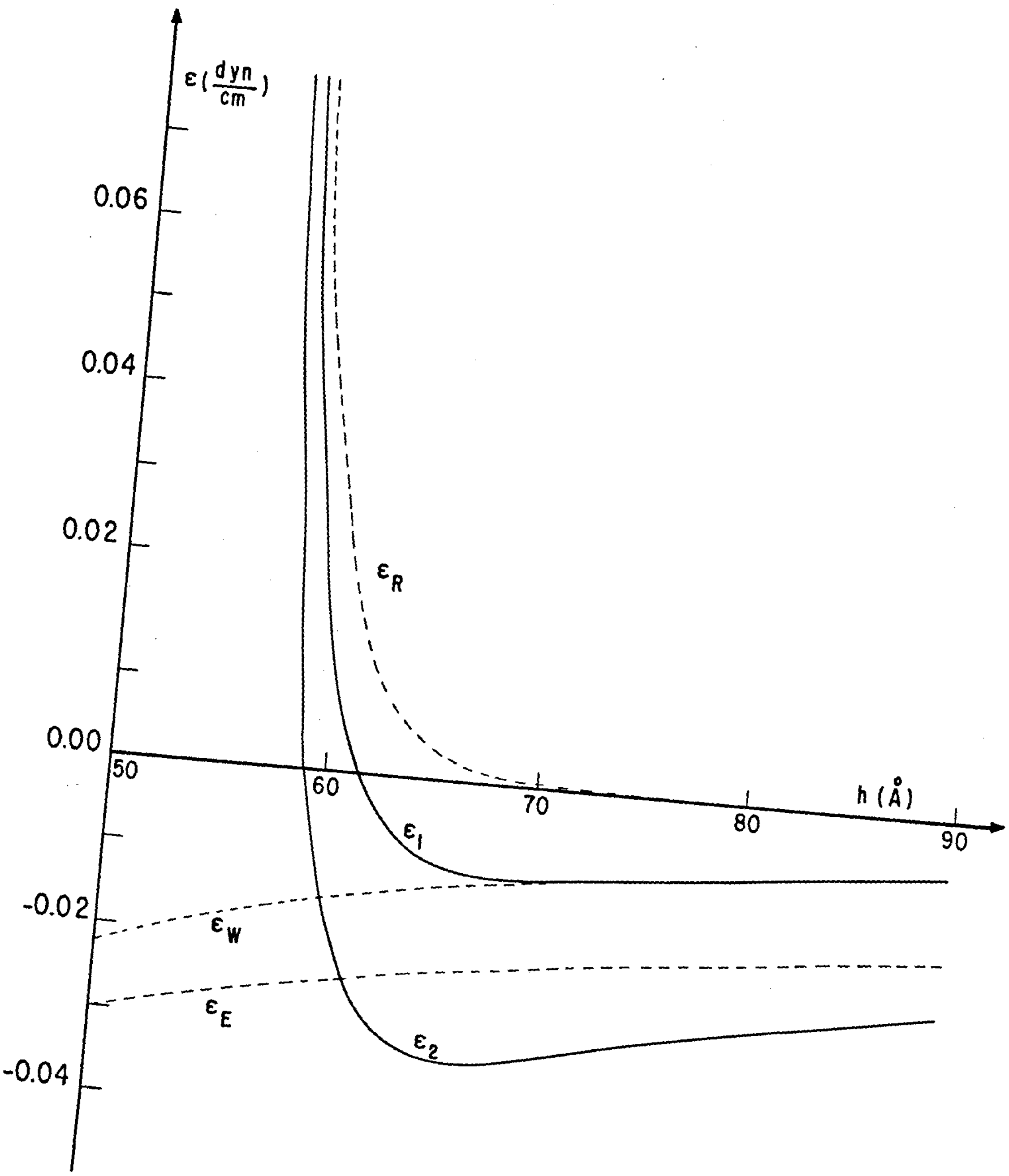

Fig. 3

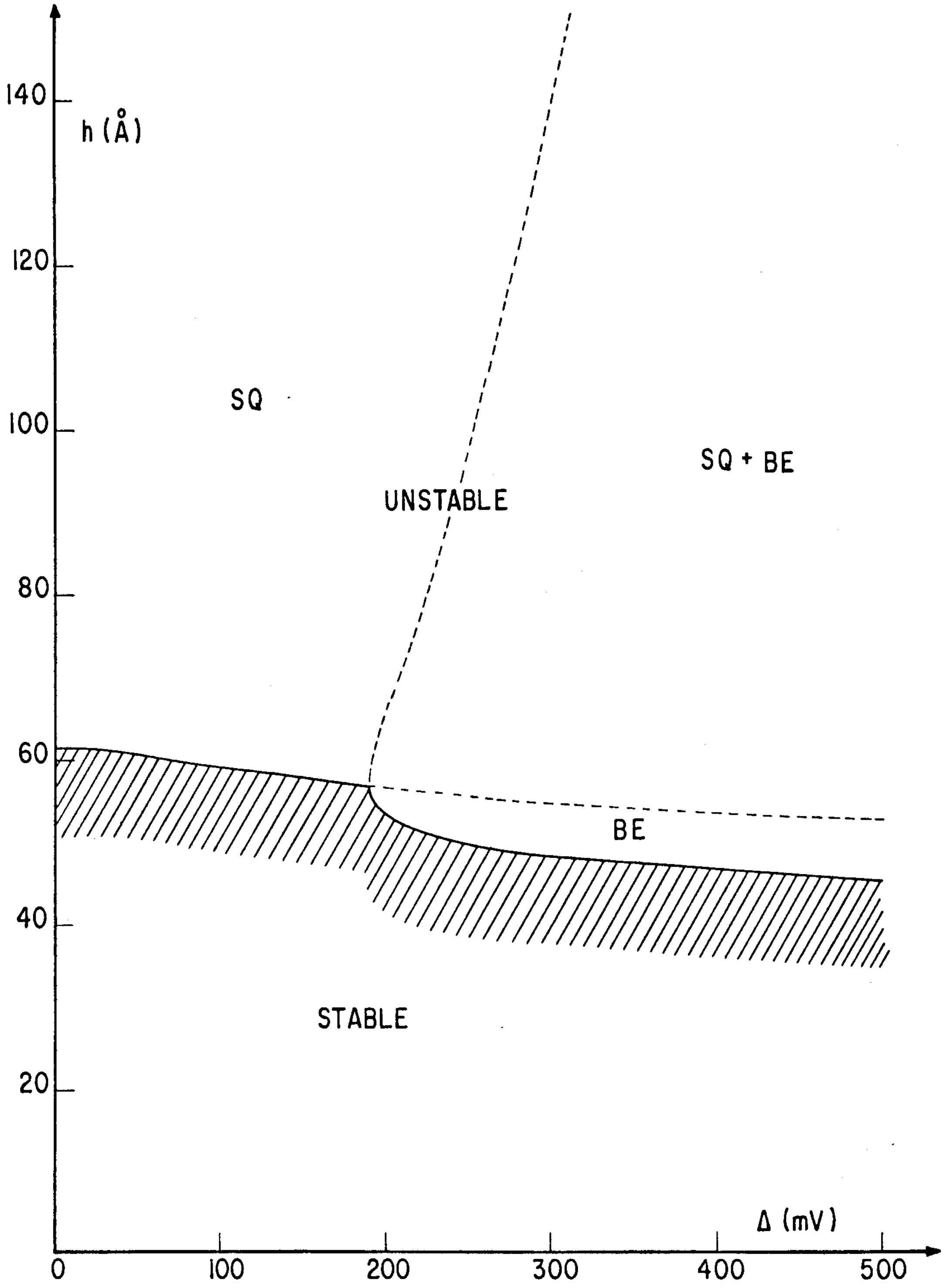
h (Å)
140
120
100
80
60
40
20
SQ
UNSTABLE
SQ + BE
BE
STABLE
Δ (mV)
0
100
200
300
400
500

Fig. 4