Micromechanical Description of Curved Interfaces, Thin Films, and Membranes

II. Film Surface Tensions, Disjoining Pressure and Interfacial Stress Balances

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The disjoining pressure approach for describing a thin liquid film as a liquid layer of finite and variable thickness is applied to dynamic curved films. The results, which are obtained without making any assumptions about the form of the real stress tensor, are applicable to films with both uniform and uneven thickness. The surface stress tensors of the film surfaces are expressed by integrals over the components of the bulk stress tensor. The balances of the linear and angular momenta at the film surfaces are derived from the respective balances in the bulk phases. The results show that a vectorial disjoining pressure, Π, must be included in these balances. It can be represented as a sum of static and dynamic parts each having normal and tangential components about the reference surface of the film. It is shown how the derived general equations (which serve as boundary conditions for the three-dimensional dynamic problem) simplify for some specific cases and how they are connected with the respective equations derived previously by other authors.

1. INTRODUCTION

As pointed out in some previous studies on thin films (1–3), a curved thin liquid film can be represented by means of a membrane of zero thickness with its own (film) tension γ. This model is sometimes called "the membrane model." On the other hand the film can be represented also as a homogeneous bulk phase of finite thickness h; this is the "detailed model" of the film. The most essential feature of this model is that instead of a single membrane tension (as in the membrane approach), the mechanical state of the system is characterized by two surface tensions (corresponding to the two surfaces of the film) and by an additional (disjoining) pressure inside the film. The disjoining pressure was first measured by Derjaguin and Kussakov (4) in experiments with solid plates. Thermodynamic definition of the film surface tensions was given by Rusanov (1) and a hydrostatic definition for flat films by Toshev and Ivanov (5). A comprehensive review can be found in Refs. (6–9).

In general, the film surface tensions differ from the interfacial tensions between the respective bulk phases. Moreover, when the film surfaces are not parallel, the film surface tensions and the disjoining pressure depend also on the position at the film surface (10, 11).

It is important to note that two variants of the detailed film model can be distinguished in the literature (12, 13). In the first variant, called "the body force approach," the interaction between the film surfaces is accounted for by introducing an additional "body force" term in the Navier–Stokes equation. In the second variant the interaction between the surfaces of the film is incorporated into the boundary conditions of the usual Navier–Stokes equation. This last approach, which is called "the disjoining pressure approach," is followed in the present paper.

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The purpose of this paper is to extend the disjoining pressure approach to the general case of dynamical (draining) films with curved nonparallel surfaces. As in the previous part of the present series, all macroscopic relations at the film surfaces are derived from the respective relations in the bulk phases and thus explicit expressions for the film excess parameters are obtained. Since the film surface tensions and the disjoining pressure are the most specific and important effects in this case, we have simplified the treatment by neglecting the inertial terms (low Reynolds' number) when deriving the balances of the linear and angular momenta at the film surfaces.

It is expedient to illustrate first the basic ideas with the example of a static spherical thin liquid film (for more details see Ref. (14)). In the membrane model this film is considered as a single membrane of radius r_0, which intervenes between the two bulk phases (I) and (II). For example, r_0 can be the radius of the surface of tension (see Ref. (9)). Alternatively, in the detailed model one introduces an idealized system consisting of the bulk phase (I) with pressure P^{I} (lying within $r_{\mathrm{I}} < r < \bar{r}$), bulk phase (II) with pressure P^{II} (within $\tilde{r} < r < r_{\mathrm{II}}$) and a reference phase (R) with pressure P^{R} (within $\bar{r} < r < \tilde{r}$) (Fig. 1). The film is therefore represented as a spherical layer of the phase (R) of thickness $h = \tilde{r} - \bar{r}$. The spheres of radii $\bar{r}$ and $\tilde{r}$ are called "film surfaces". (Note that $\bar{r} < r_0 < \tilde{r}$.)

The nonisotropic pressure tensor in the real interfacial region can be expressed (15, 16) as

$$\underline{\mathbf{P}} = P_{\mathrm{N}}\mathbf{e}_r\mathbf{e}_r + P_{\mathrm{T}}(\mathbf{e}_\theta\mathbf{e}_\theta + \mathbf{e}_\phi\mathbf{e}_\phi), \quad [1.1]$$

with $\mathbf{e}_r$, $\mathbf{e}_\theta$, and $\mathbf{e}_\phi$ being the unit vectors of the local basis in spherical coordinates. Then one can define the surface tensions $\tilde{\sigma}$ of the upper film surface and $\bar{\sigma}$ of the lower film surface by using the following procedure. (i) The spheres of initially arbitrary radii $r = \tilde{r}$ and $r = \bar{r}$ ($\bar{r} < \tilde{r}$) are the Gibbs dividing surfaces. They are situated on either side of the surface of tension (in the membrane model) of radius r_0, which is now called the "reference surface." (ii) An

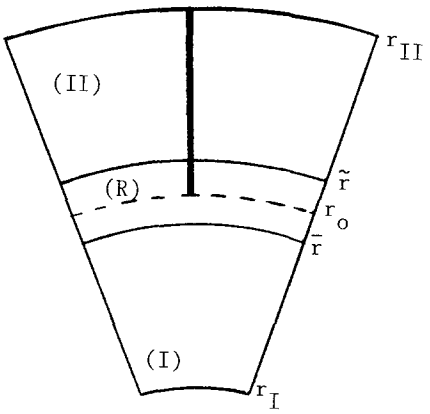

FIG. 1. Scheme of a spherical film, represented as a layer of the phase R with thickness $h = \tilde{r} - \bar{r}$. The vertical line represents the section of the imaginary strip used to define the surface tension $\tilde{\sigma}$ of the upper film surface at $r = \tilde{r}$ (see text).

imaginary sectorial strip, which has infinitesimal width but macroscopic length, $r_{\mathrm{II}} - r_0$, is located orthogonally to the upper Gibbs dividing surface (see Fig. 1); a similar strip of length $r_0 - r_{\mathrm{I}}$ is orthogonal to the lower surface. (iii) The conditions for equivalence between the real and the idealized systems with respect to the total force and force moment acting on the sectorial strips determine the radii of the film surfaces and the surface tensions; for the upper film surface these are (14)

$$\tilde{\sigma}\tilde{r} = \int_{r_0}^{r_{\mathrm{II}}} (\bar{P} - P_{\mathrm{T}})r\,dr,$$

$$\tilde{\sigma}\tilde{r}^2 = \int_{r_0}^{r_{\mathrm{II}}} (\bar{P} - P_{\mathrm{T}})r^2\,dr, \quad [1.2]$$

where

$$\bar{P} = P^{\mathrm{I}}\theta(\bar{r} - r) + P^{\mathrm{R}}[\theta(r - \bar{r}) - \theta(r - \tilde{r})] + P^{\mathrm{II}}\theta(r - \tilde{r}), \quad [1.3]$$

with

$$\theta(x) = 0 \quad \text{for} \quad x < 0,$$
$$= 1 \quad \text{for} \quad x > 0, \quad [1.4]$$

is the pressure in the idealized system. The

same procedure, applied to the lower film surface with radius $r = \tilde{r}$, yields

$$\bar{\sigma}\bar{r} = \int_{r_1}^{r_0} (\bar{P} - P_T) r dr,$$
$$\bar{\sigma}\bar{r}^2 = \int_{r_1}^{r_0} (\bar{P} - P_T) r^2 dr. \qquad [1.5]$$

The radii $\bar{r}$ and $\tilde{r}$, thus introduced, define the surfaces of tension for the two interfaces between the film and the adjacent phases (I) and (II). It should be noted that the four quantities $\bar{\sigma}$, $\tilde{\sigma}$, $\bar{r}$, and $\tilde{r}$ depend on the reference pressure P^R. That is why to different choices of P^R correspond different model systems. When the film is in contact with a bulk liquid it is convenient to use the pressure in the liquid as a reference pressure P^R (see, e.g., Ref. (11)). The dependence of the film surface tensions on the choice of P^R was discussed in Ref. (9).

Since we consider now a static system, the condition for mechanical equilibrium in the real system is $\nabla \cdot \underline{\mathbf{P}} = 0$. In view of Eq. [1.1] this condition takes the form (15, 16)

$$\frac{d(r^2 P_N)}{d(r^2)} = P_T. \qquad [1.6]$$

The integration of Eq. [1.6] yields

$$r_0^2 P_N(r_0) - r_1^2 P^I = 2 \int_{r_1}^{r_0} P_T r dr. \qquad [1.7]$$

Here we have made use of the fact that the distance $r_0 - r_1$ is large enough so that $P_N(r_1) = P^I$; similarly $P^{II}(r_{II}) = P^{II}$. Having in mind Eq. [1.3] one can eliminate $r_1^2 P^I$ between Eq. [1.7] and the first of Eqs. [1.5]. The result reads (14)

$$\frac{2\bar{\sigma}}{\bar{r}} = P^I - P^R - [P_N(r_0) - P^R] \frac{r_0^2}{\bar{r}^2}. \qquad [1.8]$$

For the upper film surface one analogously derives

$$\frac{2\tilde{\sigma}}{\tilde{r}} = P^R - P^{II} + [P_N(r_0) - P^R] \frac{r_0^2}{\tilde{r}^2}. \qquad [1.9]$$

The quantity

$$\Pi = P_N(r_0) - P^R \qquad [1.10]$$

appearing in both Eqs. [1.9] and [1.10] was termed in Ref. (14) the disjoining pressure of the spherical film. According to this definition the disjoining pressure Π is connected with the total pressure tensor $\underline{\mathbf{P}}$ and therefore Π accounts for all kinds of interactions in the film: van der Waals forces, electrostatic forces, etc. Eq. [1.10] shows that Π can be calculated from the value of P_N on the reference surface $r = r_0$; note that $P_N(r_0)$ can be expressed through integrals over the intermolecular potentials and the pair correlation functions (see, e.g., Eqs. [34.6]–[34.8] in Ref. (16)). It is worth noting that the disjoining pressure appears because the component P_N of the pressure tensor at the reference surface in the real system is different from the pressure P^R in the idealized system. Such a term does not appear in the membrane model, because then the limits of integration are always taken to be in the bulk phases, where the pressures in the real and the idealized systems are the same (see, e.g., Ref. (16)). The disjoining pressure term can be eliminated if one chooses $P^R = P_N(r_0)$ but such a choice has many inconveniences (9).

Since the disjoining pressure acts normally to the reference surface, one can write a vectorial version of Eq. [1.10]:

$$\boldsymbol{\Pi} = \mathbf{n} \cdot (\underline{\mathbf{P}} - P^R \underline{\mathbf{U}})|_{r=r_0}, \qquad [1.11]$$

where $\underline{\mathbf{U}}$ is the three-dimensional idemfactor and $\mathbf{n}$ is an outer unit normal to the reference surface.

The substitution of Eq. [1.10] in Eqs. [1.8] and [1.9] leads to

$$\frac{2\bar{\sigma}}{\bar{r}} = P^I - P^R - \Pi \frac{r_0^2}{\bar{r}^2},$$
$$\frac{2\tilde{\sigma}}{\tilde{r}} = P^R - P^{II} + \Pi \frac{r_0^2}{\tilde{r}^2}. \qquad [1.12]$$

These two equations can be interpreted as normal force balances at the two film surfaces.

Indeed, imagine a surface element of area ΔA on the reference surface $r = r_0$. The orthogonal projection of this element onto the film surface $r = \bar{r}$ (or $r = \tilde{r}$) is of area $\Delta A\bar{r}^2/r_0^2$ (or $\Delta A\tilde{r}^2/r_0^2$). The disjoining pressure, Π, as defined by Eq. [1.10], can be interpreted as an excess force per unit area acting on the reference surface. The terms $\Pi r_0^2/\bar{r}^2$ and $\Pi r_0^2/\tilde{r}^2$ in Eqs. [1.12] are the orthogonal projections of this force on the film surfaces $r = \bar{r}$ and $r = \tilde{r}$, respectively.

The first Eq. [1.12] shows that the pressure drop $P^{\mathrm{I}} - P^{\mathrm{R}}$ across the lower film surface and the interaction between the film surfaces is accounted for by two terms: the curvature term $2\bar{\sigma}/\bar{r}$ (in which the surface tension $\bar{\sigma}$, because of the interaction between the film surfaces, will be different from the surface tension of a drop of the same radius) and the disjoining pressure term $\Pi r_0^2/\bar{r}^2$. Analogous interpretation holds for the second Eq. [1.12].

In the above, we chose the surface of tension of the film, $r = r_0$, as a reference surface. However, in the general case the role of reference surface could be played by any spherical surface lying inside the film region. Hence, the disjoining pressure depends both on the choice of the reference pressure P^{R} and on the choice of the reference surface. However, once the choice of the idealized system has been made, Π has a well-defined value for any given physical state of the real system.

We will show below that a vectorial definition of the disjoining pressure, as in Eq. [1.11], is valid not only for a spherical film, but for any film of arbitrary curvature. Although mathematically the treatment of an arbitrarily curved film is much more complicated, the basic ideas are the same as outlined above for a spherical film. In the next section we will derive expressions for the excess stress tensor at the film surfaces. In Section 3 the surface momentum balances are derived. The linear momentum balances, Eqs. [3.16] and [3.17], which connect the surface and bulk stress tensors and the vectorial disjoining pressure, are general boundary conditions for the solutions of the equations of fluid motion. The angular momentum balance defines the positions of the film surfaces. In the last section the physical meaning of some results is discussed and several simplified forms of the general surface momentum balance equations are obtained.

2. SURFACE TENSIONS OF A DYNAMIC CURVED FILM

Let us consider a dynamic curved thin liquid film of variable thickness situated between two fluid phases (I) and (II). We suppose that the total stress tensor, $\underline{\mathbf{T}}(\mathbf{r})$, and the density distribution $\rho(\mathbf{r})$ are known and are continuous functions throughout the real system. For example, they can be calculated by means of the methods of statistical mechanics (see, e.g., Ref. (16)). As in the analysis of single interfaces (9) the total stress tensor $\underline{\mathbf{T}}$ is supposed to be a symmetric tensor, which can be represented as superposition of the pressure tensor $\underline{\mathbf{P}}$ and the tensor of viscous stresses $\underline{\mathbf{Q}}$:

$$\underline{\mathbf{T}} = -\underline{\mathbf{P}} + \underline{\mathbf{Q}}. \qquad [2.1]$$

Let us now introduce an idealized system in which the film is considered as a layer from the reference phase (R) enclosed between two curved dividing surfaces, which represent the surfaces of the film. In other words, the detailed model is used. The three phases (I), (II), and (R) of the idealized system preserve their bulk properties up to the dividing surfaces.

In order to give mathematical description of the system let us choose a reference surface located somewhere inside the film; for example the surface of tension of the film can serve as a reference surface. Then let (u^1, u^2) be curvilinear coordinates at the reference surface, let $\mathbf{R}(u^1, u^2)$ be its running radius vector, and let $\mathbf{n}(u^1, u^2)$ be the running normal to the reference surface. One can introduce curvilinear coordinates (u^1, u^2, λ) in the space by means of the equation (17, 19)

$$\mathbf{r}(u^1, u^2, \lambda) = \mathbf{R}(u^1, u^2) + \lambda\mathbf{n}(u^1, u^2), \qquad [2.2]$$

where $\mathbf{r}$ is the radius vector of an arbitrary point in the space and λ is the distance from this point to the reference surface. Further, let the equations of the dividing surfaces for the film be

$$\lambda = \bar{\xi}(u^1, u^2) \quad \text{and} \quad \lambda = \tilde{\xi}(u^1, u^2); \quad [2.3]$$

here and hereafter the symbols "$\bar{}$" and "$\tilde{}$" denote quantities referring respectively to the lower and the upper film surface (Fig. 2). Since there are three separate model bulk phases in the idealized system one can express the mass density profile, $\bar{\rho}$, and the stress tensor, $\underline{\bar{\mathbf{T}}}$, there as follows:

$$\bar{\rho} = \begin{cases} \rho^{\mathrm{I}} & \text{for} \quad \lambda_1 < \lambda < \bar{\xi}, \\ \rho^{\mathrm{R}} & \text{for} \quad \bar{\xi} < \lambda < \tilde{\xi}, \\ \rho^{\mathrm{II}} & \text{for} \quad \tilde{\xi} < \lambda < \lambda_2, \end{cases}$$

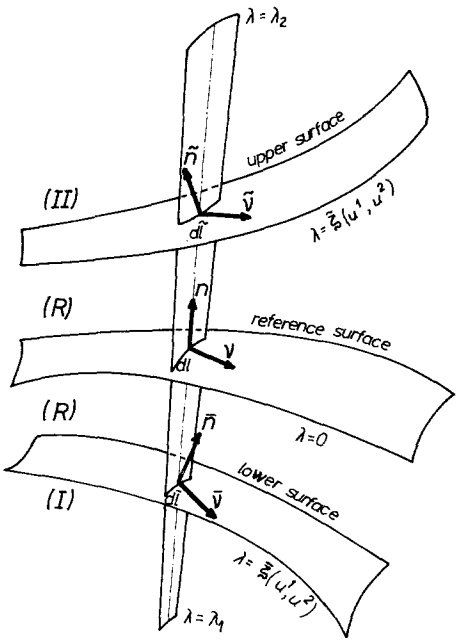

FIG. 2. A sectorial strip associated with a length element dl in the reference surface. $d\bar{l}$ and $d\tilde{l}$ are the common length elements of the sectorial strip with dividing surfaces representing the lower and the upper film surfaces. $\mathbf{n}$, $\bar{\mathbf{n}}$, $\tilde{\mathbf{n}}$ and ν, $\bar{\nu}$, $\tilde{\nu}$ are unit normals to the corresponding surfaces or line elements.

$$\underline{\bar{\mathbf{T}}} = \begin{cases} \underline{\mathbf{T}}^{\mathrm{I}} & \text{for} \quad \lambda_1 < \lambda < \bar{\xi}, \\ \underline{\mathbf{T}}^{\mathrm{R}} & \text{for} \quad \bar{\xi} < \lambda < \tilde{\xi}, \\ \underline{\mathbf{T}}^{\mathrm{II}} & \text{for} \quad \tilde{\xi} < \lambda < \lambda_2, \end{cases} \quad [2.4]$$

where the superscripts refer to the respective bulk phases. Instead of Eq. [2.1] in the idealized system one has

$$\underline{\mathbf{T}}^Y = -\underline{\mathbf{P}}^Y + \underline{\mathbf{Q}}^Y, \quad Y = \mathrm{I}, \mathrm{II}, \mathrm{R}, \quad [2.5]$$

where the pressure tensors $\underline{\mathbf{P}}^Y$ are isotropic:

$$\underline{\mathbf{P}}^Y = P^Y \underline{\mathbf{U}}, \quad Y = \mathrm{I}, \mathrm{II}, \mathrm{R}. \quad [2.6]$$

The curvilinear coordinates (u^1, u^2) on the reference surface along with Eqs. [2.2] and [2.3] generate curvilinear coordinates on the film surfaces:

$$\bar{\mathbf{R}} = \mathbf{r}(u^1, u^2, \bar{\xi}(u^1, u^2)),$$
$$\tilde{\mathbf{R}} = \mathbf{r}(u^1, u^2, \tilde{\xi}(u^1, u^2)). \quad [2.7]$$

Here $\bar{\mathbf{R}}$ and $\tilde{\mathbf{R}}$ are the running radius vectors of the two film surfaces. The respective surface basic vectors are

$$\bar{\mathbf{a}}_\alpha = \frac{\partial \bar{\mathbf{R}}}{\partial u^\alpha}, \quad \tilde{\mathbf{a}}_\alpha = \frac{\partial \tilde{\mathbf{R}}}{\partial u^\alpha}, \quad \alpha = 1, 2. \quad [2.8]$$

In order to make up for the differences between the stresses in the real and in the idealized systems one must introduce surface stress tensors $\underline{\bar{\tau}}$ and $\underline{\tilde{\tau}}$ at the surfaces of the film. If $d\tilde{l}$ is a length element on the upper dividing surface and $\tilde{\nu}$ is the unit normal to $d\tilde{l}$ ($\tilde{\nu}$ is also tangential to the upper dividing surface), $\tilde{\nu} \cdot \underline{\tilde{\tau}} d\tilde{l}$ is the force exerted on the element $d\tilde{l}$. The vector $\tilde{\nu} \cdot \underline{\tilde{\tau}}$ could have nonzero projection along the normal $\tilde{\mathbf{n}}$ to the upper film surface. This means that the matrix of $\underline{\tilde{\tau}}$ in the local basis formed by the vectors $\tilde{\mathbf{a}}_1$, $\tilde{\mathbf{a}}_2$, and $\tilde{\mathbf{n}}$ reads

$$(\underline{\tilde{\tau}}) = \begin{pmatrix} \tilde{\tau}_{11} & \tilde{\tau}_{12} & \tilde{\tau}_{13} \\ \tilde{\tau}_{21} & \tilde{\tau}_{22} & \tilde{\tau}_{23} \\ 0 & 0 & 0 \end{pmatrix} \quad [2.9]$$

with

$$\tilde{\tau}_{\alpha\beta} = \tilde{\mathbf{a}}_\alpha \cdot \underline{\tilde{\tau}} \cdot \tilde{\mathbf{a}}_\beta,$$
$$\tilde{\tau}_{\alpha 3} = \tilde{\mathbf{a}}_\alpha \cdot \underline{\tilde{\tau}} \cdot \tilde{\mathbf{n}}, \quad \alpha, \beta = 1, 2. \quad [2.10]$$

In other words, if

$$\tilde{\underline{\mathbf{U}}}_{\mathrm{II}} = \underline{\mathbf{U}} - \tilde{\mathbf{n}}\tilde{\mathbf{n}} \qquad [2.11]$$

is the idemfactor at the upper film surface, then

$$\tilde{\mathbf{n}} \cdot \tilde{\underline{\tau}} = 0, \quad \tilde{\underline{\mathbf{U}}}_{\mathrm{II}} \cdot \tilde{\underline{\tau}} = \tilde{\underline{\tau}}. \qquad [2.12]$$

Of course, analogous relationships hold for the lower film surface.

Let us consider an elementary arc dl on the reference surface and let ΔA_s be the corresponding sectorial strip normal to the reference surface (see Fig. 2). It was proven by Eliassen (17) that the vectorial surface element $d\mathbf{s}$ of a sectorial strip can be expressed as

$$d\mathbf{s} = \boldsymbol{\nu} \cdot \underline{\mathbf{L}} dl d\lambda,$$

$$\underline{\mathbf{L}} = (1 - 2\lambda H)\underline{\mathbf{U}}_{\mathrm{II}} + \lambda \underline{\mathbf{b}}, \qquad [2.13]$$

where $\underline{\mathbf{U}}_{\mathrm{II}}$, $\underline{\mathbf{b}} = -\nabla_{\mathrm{II}}\mathbf{n}$, and H are respectively the idemfactor, the curvature tensor, and the mean curvature of the reference surface. The condition for equivalence between the real and the idealized systems with respect to the force acting on the sectorial strip, applied to the lower ($\lambda_1 < \lambda < 0$) and to the upper ($0 < \lambda < \lambda_2$) parts of the system separately, provides the following equations (cf. Fig. 2):

$$d\bar{l}\bar{\boldsymbol{\nu}} \cdot \bar{\underline{\tau}} = dl\boldsymbol{\nu} \cdot \int_{\lambda_1}^{0} d\lambda \underline{\mathbf{L}} \cdot (\underline{\mathbf{T}} - \bar{\underline{\mathbf{T}}}), \qquad [2.14]$$

$$d\tilde{l}\tilde{\boldsymbol{\nu}} \cdot \tilde{\underline{\tau}} = dl\boldsymbol{\nu} \cdot \int_{0}^{\lambda_2} d\lambda \underline{\mathbf{L}} \cdot (\underline{\mathbf{T}} - \bar{\underline{\mathbf{T}}}); \qquad [2.15]$$

here $d\bar{l}$ ($d\tilde{l}$) is the common arc of the lower (upper) film surface and the sectorial strip, and $\bar{\boldsymbol{\nu}}$ ($\tilde{\boldsymbol{\nu}}$) is the normal to this arc lying in the respective film surface. Eqs. [2.14] and [2.15] are the conditions for equivalence by force between the real and the idealized systems.

The conditions for equivalence between the real and the idealized systems with respect to the force moments acting on the sectorial strip, applied to the lower and to the upper parts of the system separately, provides two more equations:

$$d\bar{l}\bar{\boldsymbol{\nu}} \cdot \bar{\underline{\tau}} \times \bar{\mathbf{R}} = dl\boldsymbol{\nu} \cdot \int_{\lambda_1}^{0} d\lambda \underline{\mathbf{L}} \cdot (\underline{\mathbf{T}} - \bar{\underline{\mathbf{T}}}) \times \mathbf{r}, \qquad [2.16]$$

$$d\tilde{l}\tilde{\boldsymbol{\nu}} \cdot \tilde{\underline{\tau}} \times \tilde{\mathbf{R}} = dl\boldsymbol{\nu} \cdot \int_{0}^{\lambda_2} d\lambda \underline{\mathbf{L}} \cdot (\underline{\mathbf{T}} - \bar{\underline{\mathbf{T}}}) \times \mathbf{r}, \qquad [2.17]$$

In order to obtain from Eqs. [2.14] and [2.15] explicit expressions for $\bar{\underline{\tau}}$ and $\tilde{\underline{\tau}}$ we need some additional mathematical formulae. We will consider first the upper film surface. By means of the known relations (17, 18)

$$\mathbf{a}_\alpha = \frac{\partial \mathbf{R}}{\partial u^\alpha}, \quad \frac{\partial \mathbf{n}}{\partial u^\alpha} = -\mathbf{a}_\beta b_\alpha^\beta \qquad [2.18]$$

one obtains from Eqs. [2.2], [2.7], and [2.8]

$$\tilde{\mathbf{a}}_\alpha = \mathbf{a}_\beta(\delta_\alpha^\beta - \tilde{\zeta} b_\alpha^\beta) + \mathbf{n}\tilde{\zeta}_{,\alpha}, \qquad [2.19]$$

where $\mathbf{a}_\beta$ ($\beta = 1, 2$) are the vectors of the covariant surface basis on the reference surface and b_α^β are the (mixed) components of the curvature tensor $\underline{\mathbf{b}}$. Then the covariant components of the metric tensor of the upper film surface are

$$\tilde{a}_{\alpha\beta} \equiv \tilde{\mathbf{a}}_\alpha \cdot \tilde{\mathbf{a}}_\beta = (1 - \tilde{\zeta}^2 K)a_{\alpha\beta} - 2\tilde{\zeta}(1 - \tilde{\zeta}H)b_{\alpha\beta} + \tilde{\zeta}_{,\alpha}\tilde{\zeta}_{,\beta}. \qquad [2.20]$$

Here we used the equation of Gauss: $b_{\alpha\gamma}b_\beta^\gamma = 2Hb_{\alpha\beta} - Ka_{\alpha\beta}$ with $a_{\alpha\beta}$ and K being the covariant metric tensor and the Gaussian curvature of the reference surface (see, e.g., Ref. (18)). The antisymmetric e-objects are defined in the following way (18):

$$e_{11} = e_{22} = 0, \quad e_{12} = -e_{21} = 1$$

$$e^{11} = e^{22} = 0, \quad e^{12} = -e^{21} = 1.$$

Then the determinants of the metric tensors $a_{\alpha\beta}$ and $\tilde{a}_{\alpha\beta}$ are

$$a = \tfrac{1}{2} e^{\alpha\gamma} e^{\beta\delta} a_{\alpha\beta} a_{\gamma\delta},$$

$$\tilde{a} = \tfrac{1}{2} e^{\alpha\gamma} e^{\beta\delta} \tilde{a}_{\alpha\beta} \tilde{a}_{\gamma\delta}. \qquad [2.21]$$

From Eqs. [2.20] and [2.21] one easily obtains

$$\frac{\tilde{a}}{a} = \chi^2(\tilde{\xi}) + \{[(1 - 2\tilde{\xi}H)^2 - \tilde{\xi}^2K]a^{\alpha\beta} + 2\tilde{\xi}(1 - \tilde{\xi}H)b^{\alpha\beta}\}\tilde{\xi}_{,\alpha}\tilde{\xi}_{,\beta}, \quad [2.22]$$

where

$$\chi(\lambda) = 1 - 2\lambda H + \lambda^2 K. \quad [2.23]$$

The standard definitions of the surface alternators are (18)

$$\epsilon_{\alpha\beta} = \sqrt{a}e_{\alpha\beta}, \quad \tilde{\epsilon}_{\alpha\beta} = \sqrt{\tilde{a}}e_{\alpha\beta},$$

$$\epsilon^{\alpha\beta} = \frac{e^{\alpha\beta}}{\sqrt{a}}, \quad \tilde{\epsilon}^{\alpha\beta} = \frac{e^{\alpha\beta}}{\sqrt{\tilde{a}}}. \quad [2.24]$$

One can show that the contravariant components of the metric tensor at the upper film surface are

$$\tilde{a}^{\alpha\beta} \equiv \tilde{\epsilon}^{\alpha\gamma}\tilde{\epsilon}^{\beta\delta}\tilde{a}_{\gamma\delta}$$

$$= \frac{a}{\tilde{a}}\{[(1 - 2\tilde{\xi}H)^2 - \tilde{\xi}^2K]a^{\alpha\beta} + 2\tilde{\xi}(1 - \tilde{\xi}H)b^{\alpha\beta} + \epsilon^{\alpha\gamma}\epsilon^{\beta\delta}\tilde{\xi}_{,\gamma}\tilde{\xi}_{,\delta}\}. \quad [2.25]$$

Then the contravariant basis at the upper film surface can be easily determined from the equation

$$\tilde{\mathbf{a}}^{\alpha} = \tilde{a}^{\alpha\beta}\tilde{\mathbf{a}}_{\beta}. \quad [2.26]$$

Since du^{α}/dl are the components of the unit tangent to the arc dl in the reference surface, one can write

$$\boldsymbol{\nu}dl = \mathbf{a}^{\alpha}\nu_{\alpha}dl = \mathbf{a}^{\alpha}\epsilon_{\alpha\beta}\frac{du^{\beta}}{dl}dl$$

$$= \mathbf{a}^{\alpha}\epsilon_{\alpha\beta}du^{\beta} \quad [2.27]$$

and similarly

$$\tilde{\boldsymbol{\nu}}d\tilde{l} = \tilde{\mathbf{a}}^{\alpha}\tilde{\epsilon}_{\alpha\beta}du^{\beta} = (\tilde{a}/a)^{1/2}\tilde{\mathbf{a}}^{\alpha}\epsilon_{\alpha\beta}du^{\beta}; \quad [2.28]$$

at the last step we used Eq. [2.24]. The substitution of Eqs. [2.27] and [2.28] in Eq. [2.15], in view of the arbitrariness of dl, leads to

$$\tilde{\mathbf{a}}^{\alpha}\cdot\underline{\tilde{\tau}} = (a/\tilde{a})^{1/2}\mathbf{a}^{\alpha}\cdot\int_0^{\lambda_2} d\lambda\underline{\mathbf{L}}\cdot(\underline{\mathbf{T}} - \underline{\bar{\mathbf{T}}}). \quad [2.29]$$

Moreover, it is known (17) that $\underline{\tilde{\mathbf{U}}}_{\mathrm{II}} = \tilde{a}_{\alpha\beta}\tilde{\mathbf{a}}^{\alpha}\tilde{\mathbf{a}}^{\beta}$. Then having in mind Eq. [2.12] one finally obtains

$$\underline{\tilde{\tau}} = \int_0^{\lambda_2} d\lambda\underline{\tilde{\mathbf{L}}}\cdot(\underline{\mathbf{T}} - \underline{\bar{\mathbf{T}}}), \quad [2.30]$$

where

$$\underline{\tilde{\mathbf{L}}} = (a/\tilde{a})^{1/2}\tilde{a}_{\alpha\beta}\tilde{\mathbf{a}}^{\alpha}\mathbf{a}^{\beta}\cdot\underline{\mathbf{L}}; \quad [2.31]$$

(cf. also Eqs. [2.13], [2.20], [2.22], and [2.26]). For the lower film surface one similarly derives

$$\underline{\bar{\tau}} = \int_{\lambda_1}^{0} d\lambda\underline{\bar{\mathbf{L}}}\cdot(\underline{\mathbf{T}} - \underline{\bar{\mathbf{T}}}), \quad [2.32]$$

where $\underline{\bar{\mathbf{L}}}$ is given by Eq. [2.30] with "$^-$" instead of "$\tilde{}$".

Equations [2.30] and [2.32] are the definitions of the tensors of the film surface stresses $\underline{\tilde{\tau}}$ and $\underline{\bar{\tau}}$. They have similar form to the definition of the film (interfacial) stress tensor $\underline{\tau}$ in the membrane model (see e.g. Eq. [3.24] in Part I). In view of Eqs. [2.1] and [2.5] $\underline{\bar{\tau}}$ and $\underline{\tilde{\tau}}$ can be represented as sums of an elastic ($\underline{\bar{\sigma}}$ or $\underline{\tilde{\sigma}}$) and a viscous ($\underline{\tau}^{(v)}$ or $\underline{\tilde{\tau}}^{(v)}$) part:

$$\underline{\bar{\tau}} = \underline{\bar{\sigma}} + \underline{\bar{\tau}}^{(v)}, \quad \underline{\tilde{\tau}} = \underline{\tilde{\sigma}} + \underline{\tilde{\tau}}^{(v)}, \quad [2.33]$$

with

$$\underline{\bar{\sigma}} = \int_{\lambda_1}^{0} d\lambda\underline{\bar{\mathbf{L}}}\cdot(\underline{\bar{\mathbf{P}}} - \underline{\mathbf{P}}),$$

$$\underline{\bar{\tau}}^{(v)} = \int_{\lambda_1}^{0} d\lambda\cdot\underline{\bar{\mathbf{L}}}(\underline{\mathbf{Q}} - \underline{\bar{\mathbf{Q}}}), \quad [2.34]$$

$$\underline{\tilde{\sigma}} = \int_0^{\lambda_2} d\lambda\underline{\mathbf{L}}\cdot(\underline{\bar{\mathbf{P}}} - \underline{\mathbf{P}}),$$

$$\underline{\tilde{\tau}}^{(v)} = \int_0^{\lambda_2} d\lambda\underline{\mathbf{L}}\cdot(\underline{\mathbf{Q}} - \underline{\bar{\mathbf{Q}}}). \quad [2.35]$$

The elastic parts, $\underline{\bar{\sigma}}$ and $\underline{\tilde{\sigma}}$, are the tensors of the film surface tensions.

In the limiting case of an equilibrium spherical film Eqs. [2.30] and [2.17] reduce to Eqs. [1.2] and Eqs. [2.32] and [2.16] reduce to Eq. [1.5]. By analogy with the case of a spherical film one can conclude that the di-

viding surfaces, introduced in the present section, are the surfaces of tension of a dynamic curved film. Indeed, they were defined from the conditions for mechanical equivalence (with respect to the forces and force moments) between the idealized and the real systems.

3. BALANCES OF THE LINEAR AND ANGULAR MOMENTA AT THE FILM SURFACES

(a) Balance of the Linear Momentum

If the inertia terms are negligible, the balance of the linear momentum in the real system reads

$$\nabla \cdot \underline{\mathbf{T}} + \rho \mathbf{f} = 0. \qquad [3.1]$$

Here ρ is the total fluid mass density and $\mathbf{f}$ is the acceleration of an external mass force (gravitational or centrifugal). The respective equations for the three model bulk phases, I, II, and R, of the idealized system read

$$\nabla \cdot \underline{\mathbf{T}}^Y + \rho^Y \mathbf{f} = 0, \quad Y = \text{I, II, R}. \qquad [3.2]$$

Our purpose now is to find some of the boundary conditions which the solutions of Eqs. [3.2] must obey at the film surfaces $\lambda = \bar{\zeta}(u^1, u^2)$ (between the phases (I) and (R)) and $\lambda = \tilde{\zeta}(u^1, u^2)$ (between the phases (R) and (II)) in the idealized system. Let A be an arbitrary parcel from the reference surface and let us consider a cylinder built on A, as shown in Fig. 3. The cylindrical surface, which is a superposition of sectorial strips like that in Fig. 2, cuts off two parcels, $\bar{A}$ and $\tilde{A}$, from the lower and the upper film surfaces. The bases $\lambda = \lambda_1$ and $\lambda = \lambda_2$ of the cylinder are thought to be far enough from the film for the condition

$$(\underline{\mathbf{T}} - \underline{\bar{\mathbf{T}}})|_{\lambda=\lambda_1} = (\underline{\mathbf{T}} - \underline{\tilde{\mathbf{T}}})|_{\lambda=\lambda_2} = 0 \qquad [3.3]$$

to hold. However, if the thickness of the film is small enough, the stress tensor in the real system $\underline{\mathbf{T}}$ at $\lambda = 0$ (at the reference surface) will be different from the reference stress tensor $\underline{\mathbf{T}}^R$, just like the normal component of the pressure tensor $P_N(r_0)$ does not coincide with the reference pressure P^R at the surface of tension $r = r_0$ (see Eq. [1.10]). Therefore, in the general case at the reference surface $\lambda = 0$ we have

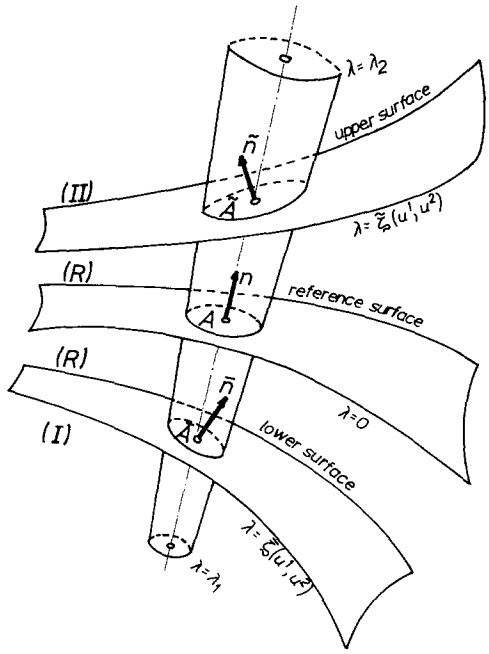

FIG. 3. A cylinder associated with the area A on the reference surface used for deriving the balances of momenta at the film surfaces (see text). $\mathbf{n}$, $\bar{\mathbf{n}}$, and $\tilde{\mathbf{n}}$ are unit normals to the respective surfaces.

$$(\underline{\mathbf{T}} - \underline{\bar{\mathbf{T}}})|_{\lambda=0} \neq 0. \qquad [3.4]$$

Let V^+ be the upper part (at $0 < \lambda < \lambda_2$) of the cylinder in Fig. 3 and let A_t^+ be the total surface of V^+. Then the integration of Eq. [3.1] yields

$$\oint_{A_t^+} d\mathbf{s} \cdot \underline{\mathbf{T}} + \int_{V^+} dV \rho \mathbf{f} = 0, \qquad [3.5]$$

where $d\mathbf{s}$ is the vectorial surface element and we have used the Gauss theorem. From Eq. [3.2] one can derive in the same way two equations of the type of Eq. [3.5] for the two parts of V^+ for the idealized system (the lower part, below $\tilde{A}$, is filled with phase (R) and the upper part, above $\tilde{A}$, is filled with phase (II)). By summing up these two equations one finds

that in the idealized system instead of Eq. [3.5] one has

$$\oint_{A_1^+} d\mathbf{s}\cdot\bar{\underline{\mathbf{T}}} + \int_{\tilde{A}} d\tilde{A}\tilde{\mathbf{n}}\cdot(\underline{\mathbf{T}}^{\mathrm{R}} - \underline{\mathbf{T}}^{\mathrm{II}}) + \int_{V^+} dV\bar{\rho}\mathbf{f} = 0. \quad [3.6]$$

Let A_1^+ be the lateral surface of the volume V^+. Then the subtraction of Eq. [3.6] from Eq. [3.5], along with Eq. [3.3], leads to

$$\int_{A_1^+} d\mathbf{s}\cdot(\underline{\mathbf{T}} - \bar{\underline{\mathbf{T}}}) - \int_A dA\mathbf{n}\cdot(\underline{\mathbf{T}} - \bar{\underline{\mathbf{T}}}) - \int_{\tilde{A}} d\tilde{A}\tilde{\mathbf{n}}\cdot(\underline{\mathbf{T}}^{\mathrm{R}} - \bar{\underline{\mathbf{T}}}^{\mathrm{II}}) + \int_{V^+} dV(\rho - \bar{\rho})\mathbf{f} = 0. \quad [3.7]$$

We will represent now, by means of known integral theorems, all terms in Eq. [3.7] as integrals over $\tilde{A}$. Let C and $\tilde{C}$ be the contours encircling A and $\tilde{A}$. Then, one finds from Eqs. [2.13] and [2.15] for the first term in Eq. [3.7]

$$\int_{A_1^+} d\mathbf{s}\cdot(\underline{\mathbf{T}} - \bar{\underline{\mathbf{T}}}) = \oint_C dl\boldsymbol{\nu}\cdot\int_0^{\lambda_2}\underline{\mathbf{L}}\cdot(\underline{\mathbf{T}} - \bar{\underline{\mathbf{T}}}) = \oint_{\tilde{C}} d\tilde{l}\tilde{\boldsymbol{\nu}}\cdot\tilde{\underline{\tau}} = \int_{\tilde{A}} d\tilde{A}\tilde{\nabla}_{\mathrm{II}}\cdot\tilde{\underline{\tau}}, \quad [3.8]$$

where $\tilde{\nabla}_{\mathrm{II}}$ and $\bar{\nabla}_{\mathrm{II}}$ are the surface gradient operators for the upper and lower film surfaces

$$\tilde{\nabla}_{\mathrm{II}} = \tilde{\mathbf{a}}^{\alpha}\frac{\partial}{\partial u^{\alpha}}, \quad \bar{\nabla}_{\mathrm{II}} = \bar{\mathbf{a}}^{\alpha}\frac{\partial}{\partial u^{\alpha}}. \quad [3.9]$$

On the other hand,

$$dA = a^{1/2}du^1du^2 = (a/\tilde{a})^{1/2}\tilde{a}^{1/2}du^1du^2 = (a/\tilde{a})^{1/2}d\tilde{A}. \quad [3.10]$$

Then the second integral in the left-hand side of Eq. [3.7] becomes

$$\int_A dA\mathbf{n}\cdot(\underline{\mathbf{T}} - \bar{\underline{\mathbf{T}}}) = -\int_{\tilde{A}} d\tilde{A}\boldsymbol{\Pi}(a/\tilde{a})^{1/2}, \quad [3.11]$$

where we have introduced the notation

$$\boldsymbol{\Pi} = \mathbf{n}\cdot(\underline{\mathbf{T}} - \underline{\mathbf{T}})|_{\lambda=0}. \quad [3.12]$$

Using the curvilinear coordinates [2.2] one can represent the volume element dV in the form (19)

$$dV = \chi d\lambda dA, \quad [3.13]$$

where the factor χ is determined by Eq. [2.23]. Then by means of Eqs. [3.10] and [3.13] one can write the last term in Eq. [3.7] as

$$\int_{V^+} dV(\rho - \bar{\rho})\mathbf{f} = \int_A dA\int_0^{\lambda_2} d\lambda\chi(\rho - \bar{\rho})\mathbf{f} = \int_{\tilde{A}} d\tilde{A}\tilde{\Gamma}\tilde{\mathbf{f}}, \quad [3.14]$$

where by definition

$$\tilde{\Gamma} = (a/\tilde{a})^{1/2}\int_0^{\lambda_2}(\rho - \bar{\rho})\chi d\lambda,$$

$$\tilde{\mathbf{f}} = \frac{1}{\tilde{\Gamma}}(a/\tilde{a})^{1/2}\int_0^{\lambda_2}(\rho - \bar{\rho})\mathbf{f}\,\chi d\lambda. \quad [3.15]$$

$\tilde{\Gamma}$ can be interpreted as mass adsorption at the upper film surface. Indeed

$$\int_{V^+} dV(\rho - \bar{\rho}) = \int_A dA\int_0^{\lambda_2} d\lambda\chi(\rho - \bar{\rho}) = \int_A dA(\tilde{a}/a)^{1/2}\tilde{\Gamma} = \int_{\tilde{A}}\tilde{\Gamma}d\tilde{A}.$$

Then $\tilde{\mathbf{f}}$ is the effective acceleration of the external mass force. (If $\mathbf{f} = \mathbf{g} = \mathrm{const}$ is the acceleration due to gravity, one obtains from Eq. [3.15] $\tilde{\mathbf{f}} = \mathbf{g}$.)

The substitution of Eqs. [3.8], [3.11], and [3.14] in Eq. [3.7], in view of the arbitrariness of $\tilde{A}$, yields the local balance of the linear momentum at the upper film surface:

$$\tilde{\nabla}_{\Pi}\cdot\tilde{\underline{\tau}} - \tilde{\mathbf{n}}\cdot(\underline{\mathbf{T}}^{R} - \bar{\underline{\mathbf{T}}}^{II})|_{\lambda=\tilde{\zeta}} + (a/\tilde{a})^{1/2}\mathbf{\Pi} + \tilde{\Gamma}\tilde{\mathbf{f}} = 0. \quad [3.16]$$

The respective balance at the lower film surface, whose derivation is quite similar, reads

$$\bar{\nabla}_{\Pi}\cdot\bar{\underline{\tau}} - \bar{\mathbf{n}}\cdot(\underline{\mathbf{T}}^{I} - \underline{\mathbf{T}}^{R})|_{\lambda=\bar{\zeta}} - (a/\bar{a})^{1/2}\mathbf{\Pi} + \bar{\Gamma}\bar{\mathbf{f}} = 0, \quad [3.17]$$

where

$$\bar{\Gamma} = (a/\bar{a})^{1/2}\int_{\lambda_1}^{0}(\rho - \bar{\rho})\chi d\lambda,$$

$$\bar{\mathbf{f}} = \frac{1}{\bar{\Gamma}}(a/\bar{a})^{1/2}\int_{\lambda_1}^{0}(\rho - \bar{\rho})\mathbf{f}\chi d\lambda.$$

The term with $\mathbf{\Pi}$ in Eqs. [3.16] and [3.17], whose appearance is a consequence of the relationship [3.4], is the only term without counterpart in the membrane model (cf. Eq. [228] in Ref. (9)). In fact, Eq. [3.12] is the most general definition of the disjoining pressure, which reveals the vectorial excess nature of this quantity. It follows from Eqs. [2.1], [2.4], and [2.5] that it consists of a hydrostatic, $\mathbf{\Pi}^{(s)}$, and of a purely viscous part $\mathbf{\Pi}^{(v)}$:

$$\mathbf{\Pi} = \mathbf{\Pi}^{(s)} + \mathbf{\Pi}^{(v)}, \quad [3.18]$$

$$\mathbf{\Pi}^{(s)} = \mathbf{n}\cdot(\underline{\mathbf{P}} - P^{R}\underline{\mathbf{U}})|_{\lambda=0},$$

$$\mathbf{\Pi}^{(v)} = \mathbf{n}\cdot(\bar{\underline{\mathbf{Q}}} - \underline{\mathbf{Q}})|_{\lambda=0}. \quad [3.19]$$

Obviously the disjoining pressure in an equilibrium system contains only the term $\mathbf{\Pi}^{(s)}$.

A geometrical interpretation of the factor $(a/\tilde{a})^{1/2}$, multiplying $\mathbf{\Pi}$ in Eq. [3.16], follows from Eq. [3.10]. Indeed, it is clear from Eq. [3.10] that $(a/\tilde{a})^{1/2}$ is the factor of extension when projecting orthogonally an element dA from the reference surface over the upper film surface. Another representation of $(a/\tilde{a})^{1/2}$, sometimes useful in applications, can be obtained by observing that (cf. Eq. [2.24])

$$\mathbf{n}\cdot\tilde{\mathbf{n}} = \mathbf{n}\cdot(\tfrac{1}{2}\tilde{\epsilon}^{\alpha\beta}\tilde{\mathbf{a}}_{\alpha}\times\tilde{\mathbf{a}}_{\beta}) = \tfrac{1}{2}(a/\tilde{a})^{1/2}\epsilon^{\alpha\beta}\mathbf{n}\cdot(\tilde{\mathbf{a}}_{\alpha}\times\tilde{\mathbf{a}}_{\beta}).$$

Along with Eq. [2.19], after some algebra one thus finds

$$(a/\tilde{a})^{1/2} = (\mathbf{n}\cdot\tilde{\mathbf{n}})/\chi(\tilde{\zeta}), \quad [3.20]$$

where χ is defined by Eq. [2.23].

(b) Balance of the Angular Momentum

The balance of the angular momentum at the film surfaces can be derived similarly to the balance of the linear momentum from the respective balances in the bulk phases of the real and of the idealized systems. Since the balance of the angular momentum in a bulk fluid phase requires that the stress tensor must be symmetric, the tensors $\underline{\mathbf{T}}$ and $\bar{\underline{\mathbf{T}}}$ must obey the identities

$$(\nabla\cdot\underline{\mathbf{T}})\times\mathbf{r} = \nabla\cdot(\underline{\mathbf{T}}\times\mathbf{r}),$$

$$(\nabla\cdot\underline{\mathbf{T}}^{Y})\times\mathbf{r} = \nabla\cdot(\underline{\mathbf{T}}^{Y}\times\mathbf{r}), \quad Y = \text{I, II, R.}$$

Then Eqs. [3.1] and [3.2] yield

$$\nabla\cdot(\underline{\mathbf{T}}\times\mathbf{r}) + \rho\mathbf{f}\times\mathbf{r} = 0 \quad [3.21]$$

$$\nabla\cdot(\underline{\mathbf{T}}^{Y}\times\mathbf{r}) + \rho^{Y}\mathbf{f}\times\mathbf{r} = 0, \quad Y = \text{I, II, R.} \quad [3.22]$$

Following the procedure used above to derive Eqs. [3.5] and [3.6], one obtains from Eqs. [3.21] and [3.22]

$$\oint_{A_t^+} d\mathbf{s}\cdot(\underline{\mathbf{T}}\times\mathbf{r}) + \int_{V^+} dV\rho\mathbf{f}\times\mathbf{r} = 0 \quad [3.23]$$

and

$$\oint_{A_t^+} d\mathbf{s}\cdot(\bar{\underline{\mathbf{T}}}\times\mathbf{r}) + \int_{\tilde{A}} d\tilde{A}\tilde{\mathbf{n}}\cdot(\underline{\mathbf{T}}^{R} - \underline{\mathbf{T}}^{II})\times\tilde{\mathbf{R}} + \int_{V^+} dV\bar{\rho}\mathbf{f}\times\mathbf{r} = 0 \quad [3.24]$$

(cf. also Eqs. [2.4] and [2.7]). The subtraction of Eq. [3.24] from Eq. [3.23], along with Eq. [3.3], leads to the integral angular momentum balance:

$$\int_{A_1^+} d\mathbf{s}\cdot(\underline{\mathbf{T}}-\bar{\underline{\mathbf{T}}})\times\mathbf{r}-\int_A dA\mathbf{n}\cdot(\underline{\mathbf{T}}-\bar{\underline{\mathbf{T}}})\times\mathbf{R}-\int_{\tilde{A}} d\tilde{A}\tilde{\mathbf{n}}\cdot(\underline{\mathbf{T}}^{\mathrm{R}}-\underline{\mathbf{T}}^{\mathrm{II}})\times\tilde{\mathbf{R}}+\int_{V^+} dV(\rho-\bar{\rho})\mathbf{f}\times\mathbf{r}=0. \quad [3.25]$$

Again we will transform all terms in Eq. [3.25] into integrals over A. By means of Eqs. [2.13], [2.17], and some known integral theorems the first term becomes

$$\int_{A_1^+} d\mathbf{s}\cdot(\underline{\mathbf{T}}-\bar{\underline{\mathbf{T}}})\times\mathbf{r}=\oint_C d\mathbf{l}\boldsymbol{\nu}\cdot\int_0^{\lambda_2}\underline{\mathbf{L}}\cdot(\underline{\mathbf{T}}-\bar{\underline{\mathbf{T}}})\times\mathbf{r}=\oint_C d\tilde{l}\tilde{\boldsymbol{\nu}}\cdot(\tilde{\underline{\tau}}\times\tilde{\mathbf{R}})=\int_{\tilde{A}} d\tilde{A}\tilde{\nabla}_{\mathrm{II}}\cdot(\tilde{\underline{\tau}}\times\tilde{\mathbf{R}}). \quad [3.26]$$

The second integral in Eq. [3.25] can be transformed by means of Eqs. [3.10] and [3.12]:

$$\int_A dA\mathbf{n}\cdot(\underline{\mathbf{T}}-\bar{\underline{\mathbf{T}}})\times\mathbf{R}=\int_{\tilde{A}} d\tilde{A}(a/\tilde{a})^{1/2}\boldsymbol{\Pi}\times\mathbf{R}. \quad [3.27]$$

By using Eqs. [2.2], [3.13], and [3.15] one obtains for the last term in Eq. [3.25]

$$\int_{V^+} dV(\rho-\bar{\rho})\mathbf{f}\times\mathbf{r}=\int_A dA\int_0^{\lambda_2} d\lambda\chi(\rho-\bar{\rho})\mathbf{f}\times(\mathbf{R}+\lambda\mathbf{n})=\int_{\tilde{A}} d\tilde{A}\tilde{\Gamma}(\tilde{\mathbf{f}}\times\mathbf{R}+\tilde{\mathbf{f}}'\times\mathbf{n}), \quad [3.28]$$

where we have denoted the first moment of the surface mass distribution by

$$\tilde{\mathbf{f}}'=\frac{1}{\tilde{\Gamma}}(a/\tilde{a})^{1/2}\int_0^{\lambda_2} d\lambda\,\lambda\chi(\rho-\bar{\rho})\mathbf{f}. \quad [3.29]$$

The substitution of Eqs. [3.26]–[3.28] in Eq. [3.25], along with Eqs. [2.2], [2.7], and the arbitrariness of $\tilde{A}$, yields

$$\tilde{\nabla}_{\mathrm{II}}\cdot(\tilde{\underline{\tau}}\times\tilde{\mathbf{R}})+\boldsymbol{\Pi}\times(\tilde{\mathbf{R}}-\tilde{\zeta}\mathbf{n})(a/\tilde{a})^{1/2}-\tilde{\mathbf{n}}\cdot[(\underline{\mathbf{T}}^{\mathrm{R}}-\underline{\mathbf{T}}^{\mathrm{II}})|_{\lambda=\tilde{\zeta}}]\times\tilde{\mathbf{R}}+\tilde{\Gamma}[\tilde{\mathbf{f}}\times(\tilde{\mathbf{R}}-\tilde{\zeta}\mathbf{n})+\tilde{\mathbf{f}}'\times\mathbf{n}]=0. \quad [3.30]$$

Eq. [2.10] allows writing the first term in Eq. [3.30] in the form

$$\tilde{\nabla}_{\mathrm{II}}\cdot(\tilde{\underline{\tau}}\times\tilde{\mathbf{R}})=(\tilde{\nabla}_{\mathrm{II}}\cdot\tilde{\underline{\tau}})\times\tilde{\mathbf{R}}-\tilde{\mathbf{n}}\tilde{\epsilon}_{\alpha\beta}\tilde{\tau}^{\alpha\beta}-\tilde{\tau}^{\alpha 3}\tilde{\mathbf{a}}_\alpha\times\tilde{\mathbf{n}}. \quad [3.31]$$

Then by means of Eq. [3.16] one obtains from Eq. [3.30]

$$\tilde{\mathbf{n}}\tilde{\epsilon}_{\alpha\beta}\tilde{\tau}^{\alpha\beta}+\tilde{\mathbf{a}}^\beta\tilde{\epsilon}_{\beta\alpha}\tilde{\tau}^{\alpha 3}+\tilde{\mathbf{F}}\times\mathbf{n}=0, \quad [3.32]$$

where

$$\tilde{\mathbf{F}}=(a/\tilde{a})^{1/2}\boldsymbol{\Pi}\tilde{\zeta}+(\tilde{\mathbf{f}}\tilde{\zeta}-\tilde{\mathbf{f}}')\tilde{\Gamma}. \quad [3.33]$$

Eq. [3.32] expresses the local balance of the angular momentum at the upper film surface. The respective balance at the lower film surface reads

$$\bar{\mathbf{n}}\bar{\epsilon}_{\alpha\beta}\bar{\tau}^{\alpha\beta}+\bar{\mathbf{a}}^\beta\bar{\epsilon}_{\beta\alpha}\bar{\tau}^{\alpha 3}+\bar{\mathbf{F}}\times\mathbf{n}=0, \quad [3.34]$$

with

$$\bar{\mathbf{F}}=-(a/\bar{a})^{1/2}\boldsymbol{\Pi}\bar{\zeta}+(\bar{\mathbf{f}}\bar{\zeta}-\bar{\mathbf{f}}')\bar{\Gamma}. \quad [3.35]$$

The projection of Eq. [3.32] along the normal $\mathbf{n}$ reads

$$(\tilde{\mathbf{n}}\cdot\mathbf{n})\tilde{\epsilon}_{\alpha\beta}\tilde{\tau}^{\alpha\beta}+(\tilde{\mathbf{a}}^\beta\cdot\mathbf{n})\tilde{\epsilon}_{\beta\alpha}\tilde{\tau}^{\alpha 3}=0,$$

which in view of Eqs. [2.19], [2.26], and [3.20] transforms into

$$\tilde{\tau}^{\alpha\beta}-\tilde{\tau}^{\beta\alpha}=\frac{1}{\chi(\tilde{\zeta})}(\tilde{a}/a)^{1/2}\times(\tilde{\tau}^{\alpha 3}\tilde{a}^{\beta\gamma}-\tilde{\tau}^{\beta 3}\tilde{a}^{\alpha\gamma})\tilde{\zeta}_{,\gamma}. \quad [3.36]$$

This result shows that unlike the bulk stress tensors the surface stress tensor $\tilde{\tau}^{\alpha\beta}$ is not in general symmetric. It will be symmetric only when either the film surfaces are parallel to the reference surface (i.e., when $\tilde{\zeta}_{,\gamma}=\bar{\zeta}_{,\gamma}=0$)

and/or when the normal stress components $\tilde{\tau}^{\alpha 3}$ ($\alpha = 1, 2$; cf. Eqs. [2.9] and [2.10]) are equal to zero. In order to obtain an equation for $\tilde{\tau}^{\alpha 3}$ let us take the projection of Eq. [3.32] along the basis vector $\tilde{\mathbf{a}}_\gamma$:

$$\tilde{\epsilon}_{\alpha\gamma}\tilde{\tau}^{\alpha 3} = \tilde{\mathbf{F}} \cdot (\mathbf{n} \times \tilde{\mathbf{a}}_\gamma). \qquad [3.37]$$

Moreover, it follows from Eq. [2.19] that

$$\mathbf{n} \times \tilde{\mathbf{a}}_\gamma = \mathbf{n} \times \mathbf{a}_\beta(\delta^\beta_\gamma - \tilde{\zeta} b^\beta_\gamma)$$
$$= \epsilon_{\beta\mu}\mathbf{a}^\mu(\delta^\beta_\gamma - \tilde{\zeta} b^\beta_\gamma).$$

Then taking also into account Eq. [2.24] one obtains from Eq. [3.37]

$$\tilde{\tau}^{\alpha 3} = -(a/\tilde{a})^{1/2}\tilde{\mathbf{F}} \cdot \mathbf{a}^\mu(\delta^\alpha_\mu + \tilde{\zeta}\epsilon^{\alpha\gamma}\epsilon_{\beta\mu}b^\beta_\gamma), \quad \alpha = 1, 2. \qquad [3.38]$$

Hence, if the quantity $\tilde{\mathbf{F}} \cdot \mathbf{a}^\mu$ (cf. Eq. [3.33]) is negligible, one can neglect also $\tilde{\tau}^{\alpha 3}$, and then according to Eq. [3.36] the tensor $\tilde{\tau}^{\alpha\beta}$ will be symmetric.

4. DISCUSSION

Equations [3.16] and [3.17] are the conditions for balance of the linear momentum at the surfaces of a thin liquid film. They must be used as boundary conditions at the surfaces of a draining film, when the velocity fields in the bulk phases I and II and in the film (phase R) obey Eqs. [3.2]. When $\Pi = 0$ (e.g., when the film is sufficiently thick), Eqs. [3.16] and [3.17] reduce to Scriven's (20) equation for the momentum balance at the interface between two bulk phases (at low Reynolds number).

In the approach used by us (called often "the disjoining pressure approach") the liquid flow in the film phase (R) is governed by the same equations (3.2) as the flow in a bulk phase and all interactions inside the film are incorporated in the boundary conditions [3.16] and [3.17]. (The alternative "body force approach" is discussed at the end of this section.) We must emphasize however, that the interactions are accounted for not only by the disjoining pressure Π. The terms $\tilde{\Gamma}\tilde{\mathbf{f}}$ and $\bar{\Gamma}\bar{\mathbf{f}}$, and more importantly, the surface stress tensors $\tilde{\underline{\tau}}$ and $\bar{\underline{\tau}}$, will also depend on the interactions inside the film. As already pointed out, this will lead to the alteration both of the viscous part $\underline{\tau}^{(v)}$ and of the elastic part $\underline{\sigma}$ (see Eqs. [2.34] and [2.35]) of the surface stress tensor. For example, in the case of an equilibrium symmetric plane-parallel film, $\underline{\sigma}$ reduces to the scalar σ^f, the film surface tension, the latter being connected with the disjoining pressure Π by the equation (21)

$$\sigma^f = \sigma^l + \tfrac{1}{2}\int_h^\infty \Pi dh, \qquad [4.1]$$

where h is the equilibrium thickness and σ^l is the interfacial tension between the bulk phases. Although much more complicated, a similar dependence between $\underline{\sigma}$ and Π exists also for an equilibrium film of uneven thickness (see below). Moreover, since $\bar{\underline{\mathbf{P}}}$ and $\underline{\mathbf{P}}$ in a draining film contain viscous parts, even the elastic part, $\underline{\sigma}$, of the surface stress tensor could depend also on the film viscous properties and the flow pattern. This dependence is analogous to the dependence of the pressure in a bulk fluid on the viscosity and the flow pattern.

By using model considerations like those in Ref. (29), from the expressions [2.34] and [2.35] for the excess surface stresses $\tilde{\underline{\tau}}^{(v)}$ and $\bar{\underline{\tau}}^{(v)}$ one can derive equations for the surface viscosity coefficients. It is obvious from Eqs. [2.34] and [2.35], that the surface viscosities of a thin film will depend on the film properties and the choice of the reference phase and the reference surface. Therefore they should be, at least in principle, different from the surface viscosities of the interfaces separating the same bulk phases.

The relative change of the tensor of the film surface tension $\underline{\sigma}$, as well as of the surface viscosities, with respect to their values for the interface between the same bulk liquids are very small; for example $(\sigma^f - \sigma^l)/\sigma^l$ for a plane-parallel film (cf. Eq. [4.1]) is usually smaller than 1%. Still, these changes may become important when the variations (or the deriva-

tives) of the respective quantities enter the equations.

Another conclusion worth noting is that the surface stress tensor $\underline{\tau}$ can have nonzero components $\tau_{\alpha 3}$ along the normal to the film surface (see Eq. [2.9]). In other words, in a dynamic system the surface tension is not bound to act only tangentially to the surface. However, this effect seems to be of lesser importance, since the quantity $\mathbf{F} \cdot \mathbf{a}^{\mu}$ is expected to be very small, which allows neglecting the normal components $\tau_{\alpha 3}$ ($\alpha = 1, 2$) (see the comments after Eq. [3.38]).

Probably the most important result of the present work is Eq. [3.12], which shows that in the general case the disjoining pressure is a vector, rather than a scalar. This means that, unlike the case of plane-parallel or spherical films, where the disjoining pressure acts always normally to the film surfaces, in the general case $\mathbf{\Pi}$ may have components tangential to the film and the reference surfaces as well. As shown below, only when the film is symmetrical with respect to a flat reference surface do the tangential components of $\mathbf{\Pi}$ in a film of uneven thickness vanish. Similarly to the surface stress tensor, the vector of the disjoining pressure can have a hydrostatic, $\mathbf{\Pi}^{(s)}$, and a viscous part, $\mathbf{\Pi}^{(v)}$ (see Eq. [3.18]). Although the hydrostatic part is analogous to the equilibrium disjoining pressure, in the sense that it accounts for the interactions in the film, it can contain in principle a viscous part as well, stemming from the viscous dependence of $\underline{\mathbf{P}}$ and P^{R}. The purely viscous disjoining pressure $\mathbf{\Pi}^{(v)}$ accounts for the difference between the bulk viscous stresses at the reference surface in the real and the idealized systems, $\underline{\mathbf{Q}}$ and $\bar{\underline{\mathbf{Q}}}$, respectively. If the velocity fields at the reference surface in both systems are the same, $\mathbf{\Pi}^{(v)}$ will be entirely determined by the difference in the viscosities, again at the reference surface.

The main results of the present study are valid also for a system containing solutes, e.g., surfactants. For example the definitions of the surface stresses, Eqs. [2.30] and [2.32], and of the disjoining pressure, Eq. [3.12], will remain the same. This does not mean, however, that the values of the disjoining pressure and the surface stresses (both elastic and viscous) will not be altered. Since the equations of motion [3.1] and [3.2] in this case are coupled with the diffusion and adsorption equations, the bulk stresses $\underline{\mathbf{T}}$ and $\bar{\underline{\mathbf{T}}}$ will be affected by the presence of the solute and this in turn will change the surface stresses and the disjoining pressure. Indeed, it is very well known that the presence of surfactants modifies the surface tension; the surface viscosities and the disjoining pressure of a film and the role of these effects on the drainage and rupture of thin films has been extensively studied (13, 22, 23). However, in all these studies, dealing only with relatively thick films with small or zero surface curvature, the disjoining pressure was treated as a scalar, having the same value as in an equilibrium film with the same thickness. Moreover, the variation of the surface tension along the film surfaces was ascribed only to the variation of the adsorption, the latter being calculated by means of an adsorption isotherm. In other words, most of the effects discussed in the present work were ignored. Without model calculations it is difficult to say how important they are and to give a recipe for applying the present theory to the solution of specific hydrodynamic problems such as movement of the three-phase contact line or capillary waves in thin films. Such calculations are now under way. Even in its present form, however, the theory gives some insight into the physical meaning and the interplay of the factors involved. Toward this aim we show below how the general equations simplify for some specific cases and how they are connected with the respective equations, derived previously by other authors and by us.

Planar Reference Surface

Since for a planar reference surface $\underline{\mathbf{b}} = 0$, $H = 0$, and $K = 0$, Eqs. [2.25], [2.26] and [3.9] yield

$$\tilde{\nabla}_{\mathrm{II}} = \nabla_{\mathrm{II}} - \frac{a}{\tilde{a}}(\nabla_{\mathrm{II}}\tilde{\zeta})(\nabla_{\mathrm{II}}\tilde{\zeta})\cdot\nabla_{\mathrm{II}} + \frac{a}{\tilde{a}}\mathbf{n}(\nabla_{\mathrm{II}}\tilde{\zeta})\cdot\nabla_{\mathrm{II}}, \quad [4.2]$$

where ∇_{II} is the surface gradient operator at the reference surface (at $\lambda = 0$); we have used the fact, that in this case (cf. Eqs. [2.22] and [2.23])

$$\frac{\tilde{a}}{a} = 1 + (\nabla_{\mathrm{II}}\tilde{\zeta})^2. \quad [4.3]$$

We will show now that if the two film surfaces are symmetric with respect to a planar reference surface the disjoining pressure acts normally to the reference surface. For a flat reference surface ($\underline{\mathbf{b}} = 0$) Eq. [3.38] along with Eq. [3.33] yields

$$\tilde{\tau}^{\alpha 3} = -(a/\tilde{a})^{1/2}[\bar{\zeta}(a/\tilde{a})^{1/2}\boldsymbol{\Pi}\cdot\mathbf{a}^{\alpha} + \tilde{\Gamma}(\tilde{\mathbf{f}}\tilde{\zeta} - \tilde{\mathbf{f}}')\cdot\mathbf{a}^{\alpha}], \quad \alpha = 1, 2. \quad [4.4]$$

According to Eq. [3.35] the analogous equation for the lower film surface reads

$$\bar{\tau}^{\alpha 3} = -(a/\bar{a})^{1/2}[-\bar{\zeta}(a/\bar{a})^{1/2}\boldsymbol{\Pi}\cdot\mathbf{a}^{\alpha} + \bar{\Gamma}(\bar{\mathbf{f}}\bar{\zeta} - \bar{\mathbf{f}}')\cdot\mathbf{a}^{\alpha}], \quad \alpha = 1, 2. \quad [4.5]$$

Since the film surfaces are supposed to be symmetric with respect to the reference surface, one must have

$$\bar{a} = \tilde{a}, \qquad \bar{\Gamma} = \tilde{\Gamma}, \qquad \bar{\mathbf{f}} = \tilde{\mathbf{f}},$$
$$\bar{\tau}^{\alpha 3} = -\tilde{\tau}^{\alpha 3}, \quad \bar{\zeta} = -\tilde{\zeta}, \quad \bar{\mathbf{f}}' = -\tilde{\mathbf{f}}'. \quad [4.6]$$

The substitution of Eq. [4.6] in Eq. [4.5] leads to

$$\tilde{\tau}^{\alpha 3} = (a/\tilde{a})^{1/2}[\tilde{\zeta}(a/\tilde{a})^{1/2}\boldsymbol{\Pi}\cdot\mathbf{a}^{\alpha} - \tilde{\Gamma}(\tilde{\mathbf{f}}\tilde{\zeta} - \tilde{\mathbf{f}}')\cdot\mathbf{a}^{\alpha}], \quad \alpha = 1, 2. \quad [4.7]$$

Equations [4.4] and [4.7] can be satisfied only when the first term in the square brackets is identically zero, i.e. when

$$\boldsymbol{\Pi}\cdot\mathbf{a}_{\alpha} = 0, \quad \alpha = 1, 2. \quad [4.8]$$

This shows that $\boldsymbol{\Pi}$ has no components tangential to the flat reference surface. This fact was already used by us (without proof) in our treatment of the transition region between a film and the axisymmetric liquid meniscus around it (11). Model calculations of the equilibrium van der Waals component of the disjoining pressure in the same system, performed by Groshev *et al.* (24) by using the Irving and Kirkwood (25) expression for the pressure tensor, showed that the tangential component of $\boldsymbol{\Pi}$ identically vanishes, which confirms Eq. [4.8]. Note, however, that Eq. [4.8] is valid also for a nonequilibrium system.

Axisymmetric System with Planar Reference Surface

To simplify the treatment we will neglect hereafter the viscous surface stresses $\underline{\tau}^{(\mathrm{v})}$, and most of the equations will be written only for the upper film surface. Then

$$\tilde{\underline{\tau}} = \tilde{\sigma}\tilde{\underline{\mathbf{U}}}_{\mathrm{II}} \quad [4.9]$$

so that

$$\tilde{\nabla}_{\mathrm{II}}\cdot\tilde{\underline{\tau}} = 2\tilde{H}\tilde{\sigma}\tilde{\mathbf{n}} + \nabla_{\mathrm{II}}\tilde{\sigma}, \quad [4.10]$$

where $\tilde{H}$ is the mean curvature of the upper film surface. By means of Eq. [4.10] the normal and the tangential projections (with respect to the upper film surface) of Eq. [3.16] can be written as

$$2\tilde{H}\tilde{\sigma} - \tilde{\mathbf{n}}\cdot[\underline{\mathbf{Q}}^{\mathrm{R}} - \underline{\mathbf{Q}}^{\mathrm{II}})|_{\lambda=\tilde{\zeta}}]\cdot\tilde{\mathbf{n}} + (P^{\mathrm{R}} - P^{\mathrm{II}})|_{\lambda=\tilde{\zeta}} + (a/\tilde{a})^{1/2}\boldsymbol{\Pi}\cdot\tilde{\mathbf{n}} = 0, \quad [4.11]$$

$$\tilde{\sigma}_{,\alpha} = -\tilde{\mathbf{a}}_{\alpha}\cdot\boldsymbol{\Pi}(a/\tilde{a})^{1/2} + \tilde{\mathbf{a}}_{\alpha}\cdot[(\underline{\mathbf{Q}}^{\mathrm{R}} - \underline{\mathbf{Q}}^{\mathrm{II}})|_{\lambda=\tilde{\zeta}}]\cdot\tilde{\mathbf{n}}, \quad \alpha = 1, 2, \quad [4.12]$$

where we have neglected the term proportional to the external (gravity) force $\tilde{\mathbf{f}}$. To utilize the symmetry of the system (see Fig. 4) it is convenient to introduce polar coordinates $u^1 = r$, $u^2 = \psi$ in the plane XY:

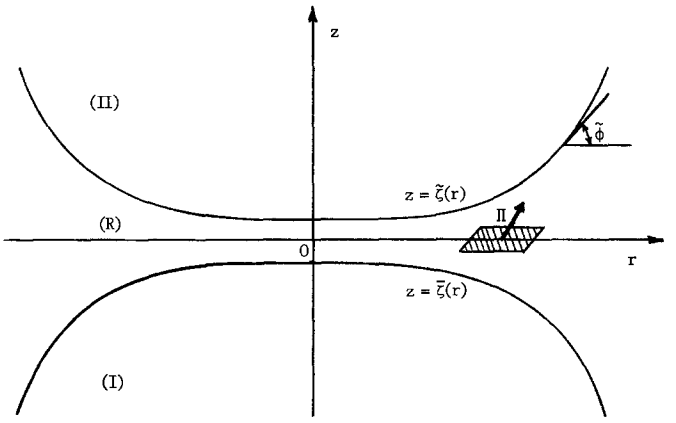

FIG. 4. Sketch of a plane thin film encircled by an axisymmetric capillary meniscus. When phases (I) and (II) are different, the disjoining pressure vector $\mathbf{\Pi}$ in general is not orthogonal to the flat reference surface $z = 0$.

$$x = r\cos\psi, \quad y = r\sin\psi.$$

Then due to the symmetry $\tilde{\zeta} = \tilde{\zeta}(r)$, $\tilde{\sigma} = \tilde{\sigma}(r)$, it follows from Eqs. [4.2] and [4.3] that

$$\tilde{\nabla}_{\mathrm{II}}\tilde{\sigma} = [\mathbf{a}_1(1+\tilde{\zeta}'^2)^{-1} + \mathbf{n}\tilde{\zeta}'(1+\tilde{\zeta}'^2)^{-1}]\frac{d\tilde{\sigma}}{dr},$$

$$\tilde{\zeta}' \equiv \frac{d\tilde{\zeta}}{dr}. \quad [4.13]$$

Similarly one derives

$$\tilde{\mathbf{n}} = -\mathbf{a}_1\tilde{\zeta}'(1+\tilde{\zeta}'^2)^{-1} + \mathbf{n}(1+\tilde{\zeta}'^2)^{-1}. \quad [4.14]$$

Moreover, due to the symmetry of the system

$$\mathbf{\Pi} = \Pi_t\mathbf{a}_1 + \Pi_n\mathbf{n}; \quad \Pi_t \equiv \mathbf{\Pi}\cdot\mathbf{a}_1,$$

$$\Pi_n \equiv \mathbf{\Pi}\cdot\mathbf{n}, \quad [4.15]$$

where Π_t and Π_n are the tangential and the normal components of $\mathbf{\Pi}$, respectively. The substitution of Eqs. [4.3], [4.10], and [4.13]–[4.15] in Eq. [3.16], along with Eqs. [2.5] and [2.6], leads to

$$\frac{d(\tilde{\sigma}\sin\tilde{\phi})}{dr} + \frac{\tilde{\sigma}\sin\tilde{\phi}}{r} = \tilde{P}_c - \Pi_n + [Q^R_{zz} - Q^{II}_{zz} - (Q^R_{rz} - Q^{II}_{rz})\tan\tilde{\phi}]|_{\lambda=\tilde{\zeta}} \quad [4.16]$$

$$-\frac{d(\tilde{\sigma}\cos\tilde{\phi})}{d\tilde{\zeta}} + \frac{\tilde{\sigma}\sin\tilde{\phi}}{r} = \tilde{P}_c + \Pi_t\cot\tilde{\phi} + [Q^R_{rr} - Q^{II}_{rr} - (Q^R_{rz} - Q^R_{rz})\cot\tilde{\phi}]|_{\lambda=\tilde{\zeta}}, \quad [4.17]$$

which are in fact the coefficients before the two perpendicular vectors $\mathbf{n}$ and $\mathbf{a}_1$ in the vectorial equation, resulting from Eq. [3.16]. Here

$$\tilde{P}_c = P^{II} - P^R, \quad \tilde{\phi} = \arctan\tilde{\zeta}' \quad [4.18]$$

and we have used also the known expression (26)

$$2\tilde{H} = \frac{d\sin\tilde{\phi}}{dr} + \frac{\sin\tilde{\phi}}{r}. \quad [4.19]$$

The "weight" $\tilde{\Gamma}\tilde{f}$ of the film surface was neglected in Eqs. [4.16] and [4.17]. However, P_c can depend on the external (gravitational or centrifugal) field due to the hydrostatic pressure. By changing to the opposite the signs before Π_n and Π_t and using barred quantities one obtains from Eqs. [4.16]–[4.19] the respective equations for the lower film surface with $\bar{P}_c = P^R - P^I$.

The elimination of P_c between Eqs. [4.16] and [4.17] yields

$$\frac{d\tilde{\sigma}}{dr} = -\Pi_n \sin\tilde{\phi} - \Pi_t \cos\tilde{\phi} + [(Q^R_{zz} - Q^{II}_{zz} - Q^R_{rr} + Q^{II}_{rr})\sin\tilde{\phi} + \frac{\cos 2\tilde{\phi}}{\cos\tilde{\phi}}(Q^R_{rz} - Q^{II}_{rz})]|_{\lambda=\tilde{\zeta}}. \quad [4.20]$$

Equation [4.20] shows that alterations in the film surface tension can be caused both by the interaction between the film surfaces (the terms with Π_n and Π_t) and by the fluid motion around and inside the film. If an equation connecting $\tilde{\sigma}$ with the surface dilation and composition is available and if the tensor $\underline{\tilde{Q}}$ is expressed according to the Stokes constitutive relations, then Eq. [4.20] can be used as a boundary condition for the equation of motion. As shown above, if the two film surfaces are symmetric with respect to the reference surface, then $\Pi_t \equiv 0$.

Axisymmetric Static Systems

For a static system $\underline{\mathbf{Q}} = 0$; if the film is thick enough $\boldsymbol{\Pi} = 0$ and the film surface tension equals the equilibrium interfacial tension between the two bulk phases $\tilde{\sigma}^l = \text{const}$. Then both Eqs. [4.16] and [4.17] reduce to a single equation, which is the known Laplace equation (cf. Eq. [4.19]):

$$\tilde{\sigma}^l\left[\frac{d\sin\tilde{\phi}}{dr} + \frac{\sin\tilde{\phi}}{r}\right] = \tilde{P}_c. \quad [4.21]$$

The approximation $\tilde{\sigma} \simeq \tilde{\sigma}^l = \text{const}$ in Eq. [4.16] for a static thin film leads to the Derjaguin's (28) equation

$$2\tilde{H}\tilde{\sigma}^l = \tilde{P}_c - \Pi_n^{(s)}, \quad [4.22]$$

($\Pi_n^{(s)} \equiv \boldsymbol{\Pi}^{(s)} \cdot \mathbf{n}$) having been derived by him from considerations for chemical equilibrium in the system (cf. also Eq. [3.18]). If one does not use this approximation, Eqs. [4.16] and [4.17] yield for a static flat film

$$\frac{d(\tilde{\sigma}\sin\tilde{\phi})}{dr} + \frac{\tilde{\sigma}\sin\tilde{\phi}}{r} = \tilde{P}_c - \Pi_n^{(s)}, \quad [4.23]$$

$$-\frac{d(\tilde{\sigma}\cos\tilde{\phi})}{d\tilde{\zeta}} + \frac{\tilde{\sigma}\sin\tilde{\phi}}{r} = \tilde{P}_c + \Pi_t^{(s)}\cot\tilde{\phi} \quad [4.24]$$

with $\Pi_t^{(s)} \equiv \boldsymbol{\Pi}^{(s)} \cdot \mathbf{a}_1$ (cf. Eqs. [3.18] and [4.15]). For a film, symmetric with respect to the flat reference surface, $\Pi_t^{(s)} = 0$. For this special case, Eqs. [4.23] and [4.24] have been previously derived respectively in Refs. (11) and (10) by using simple force balance considerations.

Equations [4.18], [4.23], and [4.24] form a full set allowing the calculation of $\tilde{\zeta}(r)$, $\tilde{\phi}(r)$, and $\tilde{\sigma}(r)$ provided that $\boldsymbol{\Pi}^{(s)}$ is known from the microscopic theory. Generally, $\boldsymbol{\Pi}^{(s)}$ is a functional of the shape $\tilde{\zeta}(r)$ of the film surfaces so that Eqs. [4.23] and [4.24] are in fact integro-differential equations. One way to solve the problem is to use an iterative procedure, starting with $\boldsymbol{\Pi}^{(s)}$ calculated for the idealized system, as zeroth approximation.

The tangential component $\Pi_t^{(s)}$ in Eq. [4.24] is not zero when the film surfaces are not symmetric with respect to a flat reference surface or when the reference surface is not flat. Then, this component can become very important: note that in Eq. [4.24] $\Pi_t^{(s)}$ is multiplied by cot $\tilde{\phi}$ and the running slope angle $\tilde{\phi}$ is usually less than 5°.

The combination of Eqs. [4.23] and [4.24] leads to a relationship, connecting $\tilde{\sigma}$ and $\boldsymbol{\Pi}^{(s)}$:

$$\frac{d\tilde{\sigma}}{dr} = -\Pi_n^{(s)}\sin\tilde{\phi} - \Pi_t^{(s)}\cos\tilde{\phi}. \quad [4.25]$$

This result, which is a special form of Eq. [4.20], shows that the hydrostatic equilibrium in the transition region around a symmetric film is ensured by simultaneous variation of $\tilde{\sigma}$ and $\boldsymbol{\Pi}^{(s)}$ (11). In other words, the assumptions $\boldsymbol{\Pi}^{(s)} \neq 0$ and $\tilde{\sigma} = \text{const}$ are incompatible. Therefore, all attempts to ascribe the interaction between the meniscus surfaces solely either to $\boldsymbol{\Pi}^{(s)}$ (with $\tilde{\sigma} = \text{const}$) or to $\tilde{\sigma}(r)$ (with

$\Pi^{(s)} = 0$) are inconsistent. The physical meaning of Eq. [4.25] is discussed in Ref. (11), where it is derived by means of transparent force balance considerations for the special case of the transition region between a plane-parallel thin film and the capillary meniscus.

On the Connection between the Disjoining Pressure and Body Force Approaches

As has already been pointed out, in the disjoining pressure approach used by us all the interactions in the film are incorporated in the boundary conditions, whereas the equations of motion, Eqs. [3.1] and [3.2], are the same as those for a bulk liquid. In the alternative "body force" approach, proposed by Felderhof (27), the interactions in the film are incorporated in the equations of motion: the electrostatic forces—in the stress tensor and the van der Walls forces—in a body force term. Since there have been controversies in the literature about the applicability of these approaches, we will establish below the connection between them. We will do this for a film without electrostatic interactions. From the formal viewpoint the difference between the two approaches consists in the choice of the idealized system, more precisely, in the definition of the pressure tensor $\underline{\bar{\mathbf{P}}}$ in the idealized system. Let us introduce a new scalar pressure P_b^Y in the model bulk phases by the relationship

$$P_b^Y = P^Y - \rho^Y W^Y, \quad Y = \text{I, II, R}, \quad [4.26]$$

where W^Y is the excess van der Waals potential in the respective bulk phases, called also the "body force potential." One assumes in this approach that the van der Waals interactions are additive, so that W^Y is defined by (12)

$$W^Y(\mathbf{r}, t) = \int_{\substack{\text{real}\\ \text{system}}} w(|\mathbf{r} - \mathbf{r}'|)\rho(\mathbf{r}', t)d\mathbf{r}' - \int_{\substack{\text{infinite}\\ \text{phase } (Y)}} w(|\mathbf{r} - \mathbf{r}'|)\rho^Y(r', t)d\mathbf{r}', \quad Y = \text{I, II, R}; \quad [4.27]$$

here the radius-vector $\mathbf{r}$ is located in the phase (Y) of the idealized system, t represents time, $\rho(\mathbf{r}, t)$ is the mass density at the source point $\mathbf{r}$, and $w(r)$ is the intermolecular potential divided by the masses (per molecule). It is clear that Eq. [4.27] defines three functions, W^{I}, W^{II}, and W^{R}, which are not bound to match at the dividing surfaces.

From Eqs. [2.5], [2.6], [3.2], and [4.26] one obtains the balance of the linear momentum in the following form (27):

$$\nabla P_b^Y = \nabla \cdot \underline{\mathbf{Q}}^Y + \rho^Y \mathbf{f} - \rho^Y \nabla W^Y, \quad Y = \text{I, II, R}. \quad [4.28]$$

One sees that because of the "body force" term $\rho^Y \nabla W^Y$ the pressure P_b^Y will not be constant throughout phases I, II, and R even when the external mass force $\mathbf{f} = 0$ and the system is in equilibrium ($\underline{\mathbf{Q}} = 0$). The subtraction of Eq. [4.28] from Eq. [3.1], along with Eq. [2.1], leads to the equation

$$\rho^Y \nabla W^Y = \nabla \cdot [(\underline{\mathbf{P}} - P_b^Y \underline{\mathbf{U}}) - (\underline{\mathbf{Q}} - \underline{\mathbf{Q}}^Y)] + (\rho - \rho^Y)\mathbf{f}, \quad Y = \text{I, II, R},$$

which reveals again the excess nature of the body force potential W^Y. The boundary conditions at the film surfaces can be obtained from Eqs. [4.11] and [4.26]. Thus, for the upper surface of a flat film one obtains

$$[-\tilde{\mathbf{n}} \cdot (\underline{\mathbf{Q}}^{\mathrm{R}} - \underline{\mathbf{Q}}^{\mathrm{II}}) \cdot \tilde{\mathbf{n}} + (P_b^{\mathrm{R}} - P_b^{\mathrm{II}}) + (\rho^{\mathrm{R}} W^{\mathrm{R}} - \rho^{\mathrm{II}} W^{\mathrm{II}})]|_{\lambda = \tilde{\xi}} + \tilde{\mathbf{n}} \cdot \mathbf{\Pi} = 0. \quad [4.29]$$

For an equilibrium film Eq. [4.29] reduces to

$$(P_b^{\mathrm{II}} - P_b^{\mathrm{R}})|_{\lambda = \tilde{\xi}} = \Pi - (\rho^{\mathrm{II}} W^{\mathrm{II}} - \rho^{\mathrm{R}} W^{\mathrm{R}})|_{\lambda = \tilde{\xi}} \quad [4.30]$$

(in this case $\Pi \equiv \tilde{\mathbf{n}} \cdot \mathbf{\Pi}$). As pointed out by Maldarelli *et al.* (12) the equation

$$\Pi = (\rho^{\mathrm{II}} W^{\mathrm{II}} - \rho^{\mathrm{R}} W^{\mathrm{R}})|_{\lambda = \tilde{\xi}} \quad [4.31]$$

in conjunction with Eq. [4.27] can serve as a model expression for the disjoining pressure Π. Then Eq. [4.29] leads to the following sim-

ple boundary condition for the pressure in the body force approach:

$$P_b^{\mathrm{R}} - P_b^{\mathrm{II}} = \tilde{\mathbf{n}} \cdot (\underline{\mathbf{Q}}^{\mathrm{R}} - \underline{\mathbf{Q}}^{\mathrm{II}}) \cdot \tilde{\mathbf{n}} \quad \text{at} \quad \lambda = \tilde{\zeta}, \quad [4.32]$$

which for an equilibrium film yields (12)

$$P_b^{\mathrm{II}} = P_b^{\mathrm{R}}. \quad [4.33]$$

In conclusion, there is no contradiction between the disjoining pressure and the body force approach. Of course, this conclusion holds for the case of van der Waals interactions in the film considered above. The case of electrically charged film surfaces requires a separate study. The disjoining pressure approach has the advantage of allowing the construction of the macroscopic theory of the curved thin films in a general form without making any model assumptions (like Eq. [4.27]) or simplifications from the very beginning.

5. CONCLUDING REMARKS

The disjoining pressure approach for describing a thin liquid film as a liquid layer of finite and variable thickness is applied to dynamic curved films. The results, which are obtained without making any assumptions about the form of the real stress tensor, are applicable to films with both parallel and nonparallel surfaces. It is demonstrated that from the condition for mechanical equivalence between the real and the idealized systems follow relationships expressing the stress tensors of the film surfaces through integrals over the components of the pressure tensor.

The balance of the linear and angular momenta at the film surfaces are derived from the respective balances in the bulk phases for low Reynolds numbers (negligible convective terms). The results show that in contrast with the case of an interface between two bulk phases an additional vectorial pressure $\mathbf{\Pi}$ must be included in these surface mechanical balances. The vectorial field $\mathbf{\Pi}$, which is defined along a reference surface inside the film, accounts for the fact that the stresses in the thin film differ from the stresses in the reference bulk phase. That is why $\mathbf{\Pi}$ is called disjoining pressure and thus the definition of Derjaguin (28) is generalized. $\mathbf{\Pi}$ can be represented as a sum of static and dynamic parts, each having normal and tangential components about the reference surface (Derjaguin's scalar disjoining pressure is in fact the normal component of the static part of $\mathbf{\Pi}$). In principle all parts and components of $\mathbf{\Pi}$ must be accounted for when describing the shape and the motion of the film surfaces or when studying the movement of a three-phase contact line. However, the problem is simpler when the surfaces of the film are symmetric with respect to a flat reference surface: the balance of the angular momentum requires that in this case the tangential component of $\mathbf{\Pi}$ must be identically zero.

The general surface balance of the linear momentum is applied for the special case of an axisymmetric film with flat reference surface and isotropic surface stress tensors. The two independent projections of this vectorial balance are in fact generalizations of the known Laplace equation and serve as boundary conditions for the three-dimensional dynamic problem. If the disjoining pressure is not zero, the film surface tensions depend in general on the position along the film, even for static films.

In the disjoining pressure approach, used in the present study, the film excess properties are accounted for only through the boundary conditions at the film surfaces. In the body force approach of Felderhof (27) an excess body force potential is included in the equations of motion in the bulk phases. It is shown that these two different approaches correspond to two different choices of the idealized system. In the case of predominating van der Waals interactions in the film the two approaches are essentially equivalent. The case when the film surfaces are electrically charged requires a particular study.

In summary, the disjoining pressure approach followed in this paper is conceptually simple and allows generalization for arbitrarily

curved films without making model simplifications.

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