surfactant science series

volume 57

FOAMS

Theory, Measurements, and Applications

edited by

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Saad A. Khan

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Theory, Measurements, and Applications

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MARCEL DEKKER, INC. NEW YORK • BASEL

Library of Congress Cataloging-in-Publication Data

Foams: theory, measurements, and applications / edited by Robert K.
Prud'homme, Saad A. Khan.
p. cm. – (Surfactant science series; v. 57)
Includes index.
ISBN 0-8247-9395-1
1. Foam. I. Prud'homme, Robert K. II. Khan, Saad A. III. Series.
QD549.F64 1995
541.3'4514–dc20 95-37908
CIP

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the address below.

This book is printed on acid-free paper.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5

Preface

Foams, the classic work by Bikerman [1], in 1973 defined the state of the art in foams and foaming as of the early 1970s. Since there have been significant advances in the application and understanding of foams and foaming in the last twenty-five years, we embarked on this book project to attempt to consolidate advances in the field and to make them accessible to a wider audience. Applications involving foams in modern industrial processes have grown dramatically. Foams are used in enhanced oil recovery and drilling operations in the oil industry. Benefaction of ores by foam flotation in mineral processing is used to process over 10^9 tons/year of ores. Foams are used increasingly in polymer foam insulation and construction materials. The personal care industry has found that foams provide useful texture and rheology control. Foams find increasing use in industry, such as textile and paper processing, where they act as vehicles for additives and yet minimize drying energy requirements. Antifoaming or foam breaking is an important issue in biotechnology where fermentation processes must employ antifoams to prevent foam accumulation. Clearly, an understanding of foams and foaming is of wide-ranging technological importance.

In the last twenty years the theory and fundamental understanding of foam and foaming have dramatically expanded. The understanding of interfaces and thin film physics has burgeoned. In Chapters 1 and 3 we deal with new understandings of the physics of films and interfaces. Chapter 1 provides an introduction in foam physics that can lead the reader to volume 29 of this series, *Thin Liquid Films*. The theory of structural foam models has also been developed in this period. These theories make the connection between foam microstructure and foam physical properties. These topics are covered in Chapter 2 and Chapter 3. The area of nonaqueous foams and silicone antifoams is one that has not been previously reviewed. These topics are presented in Chapters 7 and 14, respectively. Another area, defoaming, is covered in volume 45 of this series, *Defoaming: Theory and Industrial Applications.*

The structure of the book is roughly divided into three parts. The first part, that is, Chapters 1–3, explains the fundamentals of foam physics. Chapters 4–6 present measurement techniques for characterizing foams and foam properties. These include rheological measurements in Chapter 4, techniques for structure determination in Chapter 5, and measurement techniques of foam stability in Chapter 6. The third section focuses on applications and chemistry. This includes chapters on foams in the textile industry, Chapter 9; foams in personal care products, Chapter 10; foams in enhanced oil recovery, Chapter 11; foams in firefighting, Chapter 12; and foams in mineral flotation, Chapter 13. Specific issues involving the chemistry of foams are treated in Chapter 8, which covers additives for foams; Chapter 7, which covers foaming nonaqueous systems; and Chapter 14 on silicone antifoams. Attempts have been made to keep the chapters self-contained. This has necessitated the reintroduction of common background information in some chapters.

We hope this book provides both an introduction to foams for neophytes and sufficient in-depth coverage for seasoned veterans in the foam community. We have tried to incorporate material relevant to practitioners in various industries about the use of foams in those industries, as well as provide unified coverage of the important generic aspects of foaming and foams. For the academic community it provides some introduction into what is known of the physics and physical processes of foams and foaming, as well as an introduction to applications of foams.

We want to thank Dr. Martin Schick, the editor of this series, for his encouragement and patience in this process. We want to thank the coauthors of this book for their contributions (and, again, patience) and hope that this book endures for the next twenty years until it is time to resummarize advances in the field.

Robert K. Prud'homme
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Thin Liquid Film Physics

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I. INTRODUCTION

This review is devoted to a fast-developing field: thin liquid films and their importance for the stability of dispersions. Our attention is focused on foam films, since the present book is devoted to foams. Nevertheless, we will often refer to general dispersions (foams, emulsions, and suspensions) for the following two reasons:

1. The thermodynamic and hydrodynamic equations describing the properties of foam and emulsion thin films are very similar; hence a general macroscopic viewpoint is possible. In addition, from a microscopic viewpoint the various kinds of surface forces (electrostatic, van der Waals, steric, hydration, etc.) are operative in foams as well as in emulsions and suspensions.
2. From a practical viewpoint, in the process of foam application the foam is very often in contact with oil and/or solid phases (detergency, tertiary oil recovery, fire fighting, froth flotation, cosmetics, etc.).

For these reasons we have tried to present the physics of liquid films in relation to general dispersions (where possible) and then to deduce the properties of the foam films as a special case. The text is illustrated with many experimental examples, most of them with foam films.

The article is structured as follows. First we consider briefly the thermodynamic properties of a single fluid interface. Then we proceed with the case of two interfaces interacting across a liquid phase (i.e., with a thin liquid film). Special attention is paid to the surface forces, which in fact determine the properties of the liquid films in both equilibrium and dynamic conditions. A great development was achieved in the field of surface forces during the last decade:

in addition to the classical DLVO forces (electrostatic and van der Waals) the importance of many new forces of different physical origin, called "non-DLVO forces," were recognized.

If the forces acting in the thin film are known, one can predict the equilibrium properties of the film (equilibrium thickness, contact angle, surface tension) as well as the dynamic properties (drainage time, stability, etc.). Accordingly, in the subsequent sections we give a review of the thermodynamic and hydrodynamic theories of thin liquid films

II. THERMODYNAMIC PROPERTIES OF FLUID INTERFACES

A. A Foam as a Multiphase System

The macroscopic properties of a fluid dispersion (foam or emulsion) depend on the properties of the individual particles and on the interaction between them. In general a fluid dispersion can have different particle size, composition, and hence different surface tension. In the thermodynamic approach of Gibbs (1906), extended later by Boruvka and Neuman (1977), a foam (or emulsion) is to be treated as a multiphase system, which represents a set of bulk, surface, and linear phases.

For example, the continuous medium (α) in Fig. 1 as well as the three bubbles (or droplets) depicted there, can be treated as bulk phases, the interfaces α/β, α/γ, α/δ, and γ/δ as surface phases and the three-phase contact line $\alpha/\gamma/\delta$ as a linear phase. The logical scheme of the Gibbs approach is as follows.

The total amounts of all extensive parameters (internal energy U, entropy S, number of molecules N_i of the i-th component, etc.) and their densities in all phases far away from the phase boundaries are regarded in principle as being known.

An idealized system is constructed mentally in which all the phases (bulk, interface, or linear) are considered as being homogeneous, the interfacial regions are replaced by sharp boundaries (geometrical surfaces or lines), and the re-

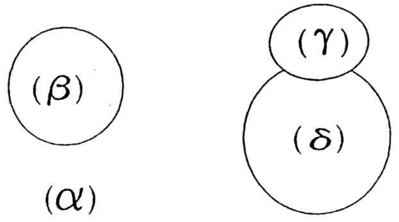


FIG. 1 Fluid particles (bubbles, droplets), β, γ, δ, dispersed in a fluid medium, α.

sulting excesses of the extensive parameters in the idealized system with respect to the real one are ascribed to these boundaries. A detailed description of this procedure can be found in the following references: Ono and Kondo (1960), Boruvka and Neuman (1977), Rowlinson and Widom (1982), Ivanov and Kralchevsky (1988).

At the next step the Gibbs fundamental equations of the various phases in the idealized system are formulated. For example, if the internal energy does not depend on the configurations of the phases or on the distance between them, one assumes that the relationship $U^V = U^V(S^V, V, N_i^V)$ holds for a bulk phase (superscript V) where V is volume; for a surface phase of area A analogous dependence, $U^s = U^s(S^s, A, N_i^s)$, for the surface internal energy is assumed. For a linear phase of length L one likewise has $U^L = U^L(S^L, L, N_i^L)$. Then it follows that for a k-component system

$$dU^V = T^V\,dS^V - P\,dV + \sum_{i=1}^{k} \mu_i^V\,dN_i^V \tag{1}$$

$$dU^s = T^s\,dS^s + \sigma\,dA + \sum_{i=1}^{k} \mu_i^s\,dN_i^s \tag{2}$$

$$dU^L = T^L\,dS^L + \kappa dL + \sum_{i=1}^{k} \mu_i^L\,dN_i^L \tag{3}$$

where P is the pressure in the (homogeneous) bulk phase, σ is the surface tension of the interface, and κ is the line tension of the linear phase. The symbols T and μ_i (with the respective superscripts) are defined through the corresponding derivatives of the internal energy and have the meaning of temperature and chemical potentials in the phases under consideration. Note that both the temperatures, T^V, T^s, and T^L, and the chemical potentials μ_i^V, μ_i^s, and μ_i^L, could in principle take different values in the different phases.

In Eqs. (1) and (2) it is supposed that the pressure tensor and the surface tension tensor are isotropic: the bulk phases and the interfaces are treated as three- and two-dimensional fluids, respectively. However, if the work of shear strain is not negligible (solid-like behavior of some phases), generalized counterparts of Eqs. (1) and (2) must be used; see, for example, Shuttleworth (1950), Benson and Yun (1967), Evans and Skalak (1979), Podstrigach and Povstenko (1985), Landau and Lifshitz (1965).

For homogeneous *fluid* phases Eqs. (1–3) can be integrated at constant values of the intensive parameters (Gibbs 1906): T^V, P, μ_i^V, T^s, σ, μ_i^S, T^L, κ, and μ_i^L:

$$U^V = T^V S^V - PV + \sum_{i=1}^{k} \mu_i^V N_i^V \tag{4}$$

$$U^s = T^s S^s + \sigma A + \sum_{i=1}^{k} \mu_i^s N_i^s \tag{5}$$

$$U^L = T^L S^L + \kappa L + \sum_{i=1}^{k} \mu_i^L N_i^L \tag{6}$$

By differentiating Eqs. (4–6) and using Eqs. (1–3) one derives the Gibbs-Duhem equations of the respective phases (bulk, surface, linear):

$$dP = \frac{S^V}{V} dT^V + \sum_{i=1}^{k} \frac{N_i^V}{V} d\,\mu_i^V \tag{7}$$

$$d\sigma = -\frac{S^s}{A} dT^s - \sum_{i=1}^{k} \frac{N_i^s}{A} d\,\mu_i^s \tag{8}$$

$$d\kappa = -\frac{S^L}{L} dT^L - \sum_{i=1}^{k} \frac{N_i^L}{A} d\,\mu_i^L \tag{9}$$

The Gibbs-Duhem equations relating the intensive parameters of each phase play an important role in the description of the phase behavior under variable temperature and composition.

The final step of the Gibbs (1906) thermodynamic approach is to impose conditions for thermodynamic equilibrium. The system is in complete thermodynamic equilibrium when there are no macroscopic convective fluxes (mechanical equilibrium), there are no diffusion fluxes (chemical equilibrium), and there is no heat transfer (thermal equilibrium). The conditions for equilibrium can be derived by requiring the appropriate thermodynamic potential of the system to have a minimum value; see, for example, Kirkwood and Oppenheim (1961).

For example, if the phase boundaries do not prevent the heat transfer and if the production of heat accompanying the thermodynamic process is slow enough one can use the condition for thermal equilibrium (Kirkwood and Oppenheim, 1961):

$$T^V = T^s = T^L = T = \text{const} \tag{10}$$

When there are no barriers preventing the exchange of component i between the phases and when the process under consideration is slow compared with the diffusion, the condition for chemical (diffusion) equilibrium likewise holds:

$$\mu_i^V = \mu_i^s = \mu_i^L, \qquad i = 1, 2 \ldots, n \tag{11}$$

The conditions for mechanical equilibrium are multiform due to the variety in the geometric configurations of the capillary systems. For example, the condition for mechanical equilibrium of each point of the dividing surface between two fluid phases α and β, is the known Laplace equation

$$2H\sigma = P_\alpha - P_\beta \tag{12}$$

where $P_\alpha - P_\beta$ is the pressure drop across the interface, and H is the mean curvature of the surface:

$$H = \frac{1}{2}(c_1 + c_2) \tag{13}$$

where c_1 and c_2 are the two principal curvatures. For a spherical interface of radius r, $H = -1/r$, and Eq. (12) reduces to

$$\frac{2\sigma}{r} = P_\beta - P_\alpha \tag{14}$$

For interfaces with rotational or translational symmetry Eq. (12) represents a second-order nonlinear ordinary differential equation determining the equilibrium interfacial shape; see, for example, Princen (1969). More complicated is the case of nonsymmetrical interfaces, when Eq. (12) is a nonlinear partial differential equation: see McConell (1957) and Finn (1986). However, the latter equation can be considerably simplified in the case of capillary waves (small surface corrugations): see Landau and Lifshitz (1984). Another example is the equilibrium force balance at each point of a three-phase contact line, the Neumann-Young equation (see Torza and Mason, 1971):

$$\sigma_{12} + \sigma_{13} + \sigma_{21} + \sigma_k = 0 \tag{15}$$

Here σ_{ik} is the surface tension of the boundary between phases i and k (see Fig. 2), considered as a vector, which is tangential to the interface and perpendicular

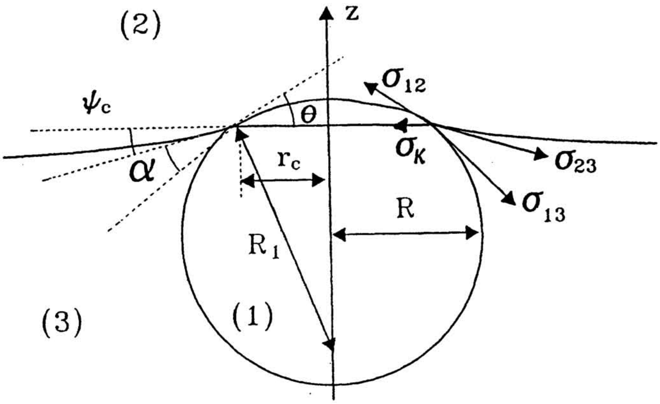


FIG. 2 Sketch of a fluid particle (1) attached to the boundary between two phases, (2) and (3).

to the contact line. The force σ_k is directed toward the center of curvature of the contact line (Veselovsky and Perzov, 1936) and its magnitude is determined by the line tension κ and the radius of curvature of the contact line r_c: $|\sigma_\kappa| = |\kappa|/r_c$. The line tension effect can be significant for small bubbles ($r_c \to 0$). In reality the equilibrium line tension, κ, as a rule turns out to be very small. However, the dynamic values of κ in some processes with advancing contact line can be larger and can give substantial contribution in Eq. (15): for review see Ivanov et al. (1992a). Such a process can be detachment of two fluid particles in foams or emulsions: see Dimitrov et al. (1992b).

A mechanical equilibrium equation, independent from Eq. (15), can be obtained from the balance of the forces, exerted on a fluid particle attached to an interface (Fig. 2):

$$F_b - F_m = 2\,\pi\,\mathrm{r}_c\,\sigma_{23}\sin\psi_c \tag{16}$$

where ψ_c is the slope of the outer meniscus at the contact line, F_m is the weight of the particle, and F_b is the buoyancy (Archimedes) force. When the buoyancy prevails ($F_b > F_m$) $\psi_c > 0$ and vice versa. F_b can be calculated from the equation (Princen, 1969; Ivanov et al., 1986):

$$F_b = g[\rho_2 V_u + \rho_3 V_l - (\rho_1 - \rho_2)V_c] \tag{17}$$

where V_u and V_l are the upper and the lower parts (with respect to the plane of the contact line) of the particle volume; V_c is the volume of the cylinder having for a base the contact circumference and with height equal to the (algebraic) value of the elevation of the contact line over the flat liquid surface away from the particle.

In summary, the Laplace equation (12) represents a differential equation for the interfacial shape and Eqs. (15–17) provide the necessary boundary conditions.

Since the mechanical equilibrium is established much more quickly than the diffusion or thermal equilibrium, for some processes one can use Eqs. (12), (15), and (16) even when Eq. (10) or (11) is not satisfied.

Applications of the thermodynamic approach of Gibbs are considered below.

B. Surface Equation of State

Because of the large total area of the surface between the continuous medium and the bubbles (or droplets), the interfacial properties, especially surface tension and surface elasticity, affect significantly the stability of a foam. Usually stability is achieved by addition of surfactants, which adsorb at the surface. The analysis of the effect of surfactants on the surface properties is based on the Gibbs-Duhem equation (8), which for isothermal processes reads

$$d\sigma = -\sum_{i=1}^{k} \Gamma_i \, d\mu_i^s \qquad (T = \text{const}) \tag{18}$$

Here $\Gamma_i = N_i^S/A$ is adsorption.

To be more specific let us use the following notation: component 1—solvent in the continuous phase; component 2—the gas in the bubble; component 3—the surfactant, which is supposed to be soluble only in the continuous phase. One can introduce an equimolecular Gibbs dividing surface for which $\Gamma_1 = 0$ (see, e.g., Ono and Kondo, 1960). In addition, by using Eqs. (7) and (14) one can derive

$$d\mu_2 = V_2 \, dP_2 = \frac{2V_2}{r} d\sigma \qquad (r = \text{const}) \tag{19}$$

where P_2 is the pressure inside the bubble and V_2 is the volume per molecule of component 2. For component 3 (the surfactant) one has

$$d\mu_3 = kT \, \mathrm{d} \ln c_3 \tag{20}$$

where c_3 is the surfactant concentration in the bulk of the continuous phase. Then Eq. (18) acquires the form

$$\left(1 + \frac{2}{r} \Gamma_2 V_2\right) d\sigma = -\Gamma_3 kT \, \mathrm{d} \ln c_3 \tag{21}$$

Γ_2 has a negative value due to the displacement of component 2 by the surfactant molecules from some interfacial layer of thickness δ: $\Gamma_2 = -\delta/V_2$. Then

$$\frac{2}{r} |\Gamma_2 V_2| = \frac{2\delta}{r} \tag{22}$$

When the bubble radius is much larger than the thickness of the interfacial zone, $2\delta << r$, Eq. (21) reduces to

$$\left(\frac{d\sigma}{d \ln c_3}\right)_T = -\Gamma_3 kT \tag{23}$$

which is usually called the Gibbs adsorption equation. Combined with the Langmuir adsorption isotherm

$$\Gamma_3(c_3) = \Gamma_\infty \frac{bc_3}{bc_3 + 1} \tag{24}$$

Eq. (23) yields the equation of Szyszkowski

$$\pi \equiv \sigma - \sigma_0 = \Gamma_\infty kT \ln (bc_3 + 1) \tag{25}$$

Here b is a parameter, dependent on temperature, σ_0 is the interfacial tension in the absence of surfactant, π is the surface pressure, and Γ_∞ is the value of Γ_3 for $c_3 \to \infty$. The elimination of c_3 between Eqs. (24) and (25) yields the two-dimensional equation of state:

$$\pi = -\Gamma_\infty kT \ln\left(1 - \frac{\Gamma_3}{\Gamma_\infty}\right) \tag{26}$$

Eqs. (24–26) are found to be appropriate for many nonionic surfactants (Lange, 1965; Joos and Rillaerts, 1981; Miller and Lunkenheimer, 1983, 1986) as well as for ionic surfactants (Lucassen-Reynders, 1966).

Another surface equation of state often used to interprete the data for surface pressure (Shchukin et al., 1982) is the Volmer isotherm:

$$\pi(A_3 - A_\infty) = kT \tag{27}$$

where

$$A_3 = 1/\Gamma_3\,, \qquad A_\infty = 1/\Gamma_\infty \tag{28}$$

It can be proven that from the physical viewpoint Eqs. (26) and (27) correspond, respectively, to localized and nonlocalized adsorption of molecules with hard-core repulsion between them only. When the attractive and long-range repulsive intermolecular forces are also taken into account, one can generalize Eq. (27) to read (Hill, 1962):

$$\left(\pi + \frac{a}{A_3^2}\right)(A_3 - A_\infty) = kT \tag{29}$$

The latter equation is obviously a two-dimensional van der Waals equation of state. The parameter a is positive for attractive and negative for repulsive forces between the adsorbed surfactant molecules. For $A_\infty/A_3 << 1$ Eq. (29) can be transformed to read

$$\frac{\pi A_3}{kT} = 1 + \left(1 - \frac{a}{A_\infty kT}\right)\frac{A_\infty}{A_3} + \mathrm{O}\left(\frac{A_\infty^2}{A_3^2}\right) \tag{30}$$

Hence, for $A_\infty/A_3 << 1$ the plot of $\pi A_3/(kT)$ vs. A_∞/A_3 is to be a straight line of intercept 1. However, in some cases an intercept close to 1/2 can be found: see Fig. 3. This can be attributed to the formation of doublets of adsorbed molecules due to their dipole moments oriented laterally to the interface (Gurkov et al., 1995).

If the interfacial equation of state, say Eqs. (26), (27), or (29), is known, one can calculate the Gibbs elasticity of the adsorbed layer

$$G = A_3\left(\frac{\partial \sigma}{\partial A_3}\right)_T \tag{31}$$

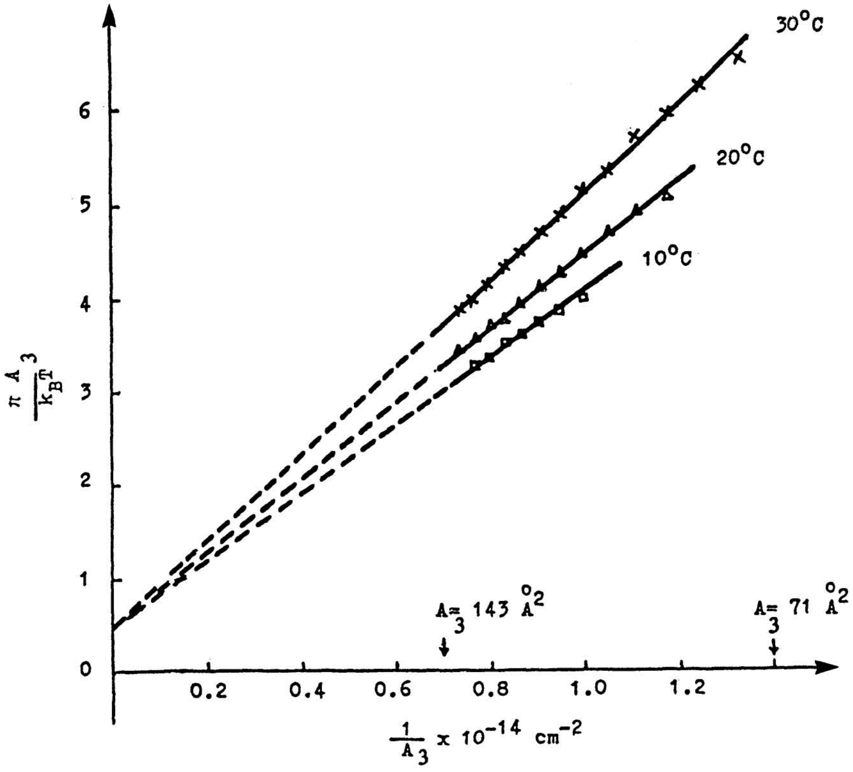


FIG. 3 Data of Yue et al. (1976) for 1,2-distearoyl-lecithin at oil/water interface plotted in accordance with Eq. (30).

As discussed in Sec. VII. G is one of the two main factors that determine the stability of foams. (The other is the repulsive disjoining pressure: see Sec. III.C.

C. Effect of the Interfacial Bending Moment

1. Bending Moment

In the case of very small bubbles or droplets, the interfacial properties are dependent on the curvature of the interface. As proven by Kondo (1956) (see also Ono and Kondo, 1960), the curvature dependence contributes an additional term to Eq. (2), which takes the form

$$dU^s = TdS^s + \sum_{i=1}^{k} \mu_i dN_i^s + \gamma\, dA + A\left[\frac{\partial \gamma}{\partial r}\right] dr \tag{32}$$

Here γ is the thermodynamic interfacial tension [for interfaces of high curvature γ is different from the mechanical interfacial tension σ: see Eq. (35)], r is the radius of the spherical dividing surface; $[\partial\gamma/\partial r]$ is a formal derivate corresponding to change in the choice of the dividing surface at fixed physical state. Correspondingly, the Laplace equation (14) takes the form (Ono and Kondo, 1960)

$$\frac{2\gamma}{r} + \left[\frac{\partial\gamma}{\partial r}\right] = P_\beta - P_\alpha \tag{33}$$

As demonstrated by Ivanov and Kralchevsky (1988) the quantity

$$B = r^2\left[\frac{\partial\gamma}{\partial r}\right] \tag{34}$$

has the meaning of an interfacial bending moment: see also Murphy (1966). In particular, B leads to a difference between the thermodynamic and mechanical interfacial tensions, γ and σ (see Gurkov and Kralchevsky, 1990):

$$\sigma = \gamma + \frac{B}{2r} \tag{35}$$

One can define the dividing surface in such a way that γ is always equal to σ:

$$B|_{r = r_s} = r_s^2\left[\frac{\partial\gamma}{\partial r}\right]_{r = r_s} = 0 \tag{36}$$

This special dividing surface is called the *surface of tension* (see Ono and Kondo, 1960) and its radius is denoted r_s. γ and γ_s (with $\gamma_s = \gamma|_{r = rs}$) are connected by the relation (Kondo, 1956; Rusanov, 1967):

$$\gamma = \gamma_s\frac{r}{r_s}\left(\frac{2}{3} + \frac{1}{3}\frac{r_s^3}{r^3}\right) \tag{37}$$

Equation (37) represents explicitly the formal dependence of γ on the choice of r at a given physical state. Equation (37) can be easily derived by integrating Eq. (33) with respect to r at constant $P_\alpha - P_\beta$. By substituting from Eq. (37) into Eq. (34) one derives the respective dependence for the interfacial bending moment (Ivanov and Kralchevsky, 1988):

$$B = 2\gamma r\frac{r^3 - r_s^3}{2r^3 + r_s^3} \tag{38}$$

2. Tolman Length

To have the radius of the dividing surface, r, uniquely defined one has to introduce an additional equation. Let this equation be

$$\frac{\partial \gamma_\nu}{\partial r_\nu} = \left[\frac{\partial \gamma}{\partial r}\right]_{r = r_V} \tag{39}$$

where r_V is the radius of a special dividing surface, called the *equimolecular dividing surface* (see Ono and Kondo, 1960), and $\gamma_v = \gamma|_{r=rv}$. The partial derivative $\partial\gamma_v/\partial r_v$ represents the physical dependence of γ_v on r_v with the remaining parameters of state fixed. The distance $\delta = r_v - r_s$ is the so-called Tolman length. Tolman (1948) has derived the following equation

$$\gamma_\nu = \gamma_o\left(1 - \frac{2\delta_o}{r_\nu} + \ldots\right), \quad \frac{\delta_o}{r_\nu} < 1 \tag{40}$$

representing the curvature dependence of γ_v: see also Ono and Kondo (1960). Here the subscript *o* denotes the value of the respective parameter for flat interface: $1/r_v \rightarrow 0$. The physical meaning of Eq. (40) can be illustrated by means of some geometric considerations; see Sharp et al. (1991) for details. Besides, Tolman length is also related to the bending moment: by setting $r = r_v$ in Eq. (38) and by expanding in series for $\delta_o/r_v << 1$ one obtains (Buff, 1955)

$$B_\nu = B/_{r = r_V} = 2\,\gamma_o\delta_o + \ldots, \quad \frac{\delta_o}{r_\nu} << 1 \tag{41}$$

The next term in the expansions (40) and (41) can be derived only when the dependence $\delta = \delta(r_v)$ is known.

The choice of the dividing surface (surface of tension, equimolecular surface, etc.) despite being a matter of a formal definition, can have important implications in the case of small fluid particles. First, when the interfacial tension is low, the surface of tension with $B \equiv 0$ can be localized far away from the real interface, which is why the choice of the equimolecular surface is advisable: see Miller (1985), Gurkov and Kralchevsky (1990), Eriksson and Ljunggren (1992). Second, when one is interpreting light-scattering data for the second virial coefficient for microemulsions the choice of the dividing surface can be a point of crucial importance: see Eq. (4.14) in the work by Denkov et al. (1991).

III. INTERACTIONS BETWEEN COLLOIDAL PARTICLES

One can identify two kinds of forces between colloidal particles: (1) hydrodynamic forces are the drag due to viscosity and the stochastic force due to Brownian motion; they are considered in Sec. VI below; (2) surface forces are determined by the molecular properties and concentrations: they are the subject of the present section.

A. Derjaguin Formula for Short-Range Forces

When the surface forces are operative at a distance, which is much smaller than the radii of the interacting particles, one can use an approximated formula derived by Derjaguin (1934):

$$U(h_o) = \frac{2\pi R_1 R_2}{R_1 + R_2} \int_{h_o}^{\infty} f(h)\, dh \tag{42}$$

Here U is the energy of interaction between two spherical particles of radii R_1 and R_2 (see Fig. 4). h_o is the shortest distance between the surfaces of the two approaching particles and h is the running distance between their surfaces; $f(h)$ is the energy of interaction due to the surface forces per unit area of an infinite plane-parallel film of thickness h. Hence, the essence of the Derjaguin approximation is the assumption that the interaction between two parcels from the particle surfaces separated at a distance h is approximately the same as between two similar parcels in a plane-parallel film. It has been established experimentally that Eq. (42) provides a good approximation in the range of its validity: see Israelachvili (1992). A more general form of Eq. (42), which is applicable also for nonspherical particles, can be found in the work by Derjaguin et al. (1987).

By differentiating Eq. (42) one obtains the total force of interparticle interaction:

$$F(h_o) = -\frac{\partial U}{\partial h_o} = \frac{2\pi R_1 R_2}{R_1 + R_2} f(h_o) \tag{43}$$

From the definition of $f(h)$ it follows that the quantity

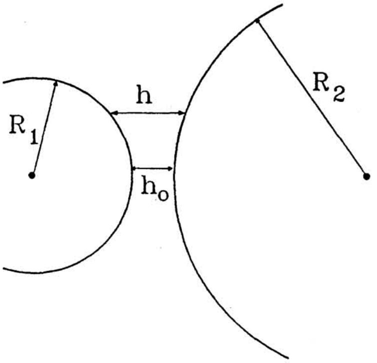


FIG. 4 Two spherical particles at surface-to-surface separation h_o.

$$\Pi = -\frac{\partial f}{\partial h} \tag{44}$$

represents the surface force, exerted per unit area of the surface of a plane-parallel film. Positive Π corresponds to repulsion between the two film surfaces (i.e., it prevents the film thinning). That is why Π was called *disjoining pressure* by Derjaguin and Kussakov (1939). If the function $\Pi(h)$ is known, one can calculate

$$f(h_o) = \int_{h_o}^{\infty} \Pi(h)dh \tag{45}$$

and then Eq. (43) yields the total interaction force between the two particles.

In summary, the main features of the Derjaguin approximation are the following: (1) it is applicable to any type of force law (attractive, repulsive, oscillatory) if the range of the forces is much smaller than the particles radii; (2) it reduces the problem for interactions between particles to the simpler problem for interactions in plane-parallel films. That is why we emphasize below the properties of planar thin films.

B. Van der Waals Forces

The van der Waals forces between molecules i and j obey the law

$$U_{ij}(r) = -\frac{\alpha_{ij}}{r^6} \tag{46}$$

where U_{ij} is the potential energy of interaction, r is the distance between the two molecules, and α_{ij} is a constant characterizing the interaction. In fact, the van der Waals forces represent averaged dipole–dipole interaction, which is a superposition of three main terms (London, 1937): (1) orientation interaction: interaction between two permanent dipoles (Keesom, 1913); (2) induction interaction: interaction between one permanent dipole and one induced dipole (Debye, 1920); (3) dispersion interaction: interaction between two induced dipoles (London, 1930).

The orientation interaction can yield from 0% (nonpolar molecules) up to 50% and more (molecules of permanent dipole moment, like H_2O) of the value of α_{ij}; the contribution of the induction interaction in α_{ij} is usually lower than 5–10%; the contribution of the dispersion interaction might be between 24% (water) and 100% (nonpolar hydrocarbons); for numerical data see Israelachvili (1992). It should be noted also that the asymptotic behavior of the dispersion interaction at large intermolecular separations does not obey Eq. (46); instead $U_{ij} \propto 1/r^7$ due to the electromagnetic retardation effect (Casimir and Polder, 1948). Different corrections of Eq. (46) accounting for the retardation effect as well as a comprehensive review of van der Waals interactions can be found in the chapter by Nir and Vassilieff (1988).

The van der Waals interaction between two macroscopic bodies can be found by integration of Eq. (46) over all couples of interacting molecules, followed by subtraction of the interaction energy at infinite separation between the bodies. The result depends on the geometry of the system. For a plane-parallel film from component 3 located between two semiinfinite phases composed of components 1 and 2, the van der Waals interaction energy per unit area and the disjoining pressure, stemming from Eq. (46), are (Hamaker, 1937):

$$f_{vw}(h) = -\frac{A_H}{12\pi h^2} \tag{47}$$

$$\Pi_{vw}(h) = -\frac{\partial f_{vw}}{\partial h} = -\frac{A_H}{6\pi h^3} \tag{48}$$

where, as usual, h is the thickness of the film and A_H is the compound Hamaker constant:

$$A_H = A_{33} + A_{12} - A_{13} - A_{23} \tag{49}$$

with

$$A_{ij} = \pi^2 \rho_i \rho_j \alpha_{ij}\,, \qquad i,j = 1,2,3 \tag{50}$$

being the Hamaker constants of components i and j; ρ_i and ρ_j are the molecular densities of components i and j. The derivation of Eqs. (47–50) can be found in the work by Derjaguin (1989). If A_{ii} and A_{jj} are known, one can calculate A_{ij} by using the Hamaker assumption

$$A_{ij} = (A_{ii} A_{jj})^{1/2} \tag{51}$$

In fact, Eq. (51) is applicable only to the dispersion contribution in the van der Waals interaction: see Israelachvili (1992).

When components 1 and 2 are identical, A_H is positive. Therefore, identical bodies, in any medium, will always attract each other. Besides, two dense bodies (even if nonidentical) will attract each other when placed in a medium 3 with low density (gas, vacuum).

When the phase in the middle (component 3) has intermediate Hamaker constant between the bodies 1 and 2, A_H can be negative and the van der Waals disjoining pressure can be repulsive (positive). For instance, such is the case of an aqueous film between mercury and gas: see Usui et al. (1986).

Another geometrical configuration, which is important for disperse systems, is the case of two spheres of radii R_1 and R_2 interacting across a medium (component 3). Hamaker (1937) has derived the following expression for the van der Waals interaction energy between the two spheres:

$$U(h_o) = -\frac{A_H}{12}\left(\frac{y}{x^2 + xy + x} + \frac{y}{x^2 + xy + x + y} + 2\ln\frac{x^2 + xy + x}{x^2 + xy + x + y}\right) \quad (52)$$

where

$$x = h_o/2R_1\,, \qquad y = R_2/R_1 \le 1 \quad (53)$$

and h_o is the same as in Fig. 4. For $x << 1$, Eq. (52) reduces to

$$U(h_o) \approx -\frac{A_H}{12}\frac{y}{(1 + y)x} = -\frac{2\pi R_1 R_2}{R_1 + R_2}\frac{A_H}{12\pi h_o} \quad (54)$$

It is worthwhile noting that the logarithmic term in Eq. (52) can be neglected only if $x << 1$. For example, even if $x = 5 \times 10^{-3}$, the contribution of the logarithmic term amounts to about 10% of the result ($y = 1$); consequently, with larger values of x this term must be retained.

Another geometrical configuration, which corresponds to two colliding bubbles or deformable emulsion droplets, is sketched in Fig. 5. In this case the interaction energy is given by the expression (Danov et al., 1993a):

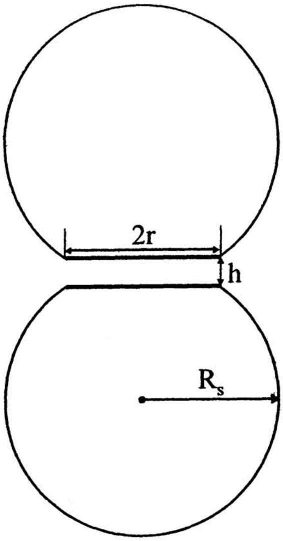


FIG. 5 Thin film of thickness *h* formed between two colliding fluid particles.

$$U(h,r) = -\frac{A_H}{12}\left[\frac{3}{4} + \frac{R_s}{h} + 2\ln\left(\frac{h}{R_s}\right) + \frac{r^2}{h^2} - \frac{2r^2}{R_s h}\right] \tag{55}$$

where h and r are the thickness and the radius of the flat film formed between the two deformed drops, respectively. R_s is the radius of the spherical part of the drop surface (see Fig. 5).

C. Electrostatic Interaction

1. Plane-Parallel Film

Here we consider the electrostatic interaction between two identical charged plane-parallel surfaces across an electrolyte solution. For the sake of simplicity we consider a symmetrical electrolyte; the charge of a counterion (i.e., ion with charge opposite to that of the surface) is Ze, whereas the charge of a coion is $-Ze$ ($Z = \pm 1, \pm 2, \ldots$) with e being the charge of the electron. If the separation between the two planes is infinitely large, the number concentration of both counterions and coions would be equal to its bulk value, n_o, in the middle of the film. However, at finite separation, h, between the interfaces the electric double layers present at each of them will overlap and the counterion and coion concentrations in the middle of the film, n_{10} and n_{20}, will be no more equal. Since the solution inside the film is supposed to be in electrochemical (Donnan) equilibrium with the bulk electrolyte solution of concentration n_o, one can write (Moelwyn-Hughes, 1961):

$$n_{10}n_{20} = n_o^2 \tag{56}$$

or, alternatively,

$$n_{10} = n_o/\sqrt{m}\,, \qquad n_{20} = n_0\sqrt{m} \tag{57}$$

where by definition

$$m = n_{20}/n_{10} \tag{58}$$

As pointed out by Langmuir (1938), the electrostatic disjoining pressure, Π_{el}, can be identified with the excess osmotic pressure in the middle of the film:

$$\Pi_{el} = kT(n_{10} + n_{20} - 2n_o) = n_o kT(m^{1/4} - m^{-1/4})^2 \tag{59}$$

Eq. (59) demonstrates that for two identically charged surfaces Π_{el} is always positive (i.e., corresponds to repulsion between the surfaces). In general, one has $0 < m \leq 1$, because the coions are repelled from the film due to the interaction with the film surfaces. To find the exact dependence of m on the film thickness, h, one must solve the Poisson-Boltzmann equation for the distribution of the electrostatic potential, φ, inside the film (see Derjaguin et al., 1987). The solution of the electrostatic problem provides the following connection between h and m:

$$h = \frac{4}{\kappa} m^{1/4}\, \mathrm{F}(\gamma_s|m), \qquad \gamma_s = \arcsin\left(\frac{y_s - 1}{y_s - m}\right)^{1/2} \tag{60}$$

where

$$y_s = \exp\left[-\frac{Ze\psi_s}{kT} + \frac{1}{2}\ln m\right] \tag{61}$$

$$\kappa^2 = \frac{8\pi Z^2 e^2}{\varepsilon kT} n_o \tag{62}$$

ε is dielectric permittivity of the solvent (water), T is temperature and

$$F(\gamma|m) = \int_0^{\gamma} (1 - m \sin^2\Theta)^{-1/2}\, d\Theta \tag{63}$$

is elliptic integral of the first kind (see Abramowitz and Stegun, 1965); for details on the derivation of Eq. (60) see Kralchevsky and Paunov (1992). Here ψ_s is the potential difference between the film surface (the latter is in fact the boundary between the diffuse and the Stern layers) and the bulk solution of electrolyte of concentration n_o. When ψ_s, which is usually called surface potential is constant, Eqs. (59–61) determine the disjoining pressure isotherm, $\Pi_{el}(h)$, in a parametric form: $\Pi_{el} = \Pi_{el}(m)$, $h = h(m)$, $0 < m \leq 1$. If the surface charge density, σ_s, is constant, instead of Eq. (61) the following equation must be used (see Kralchevsky and Paunov, 1992):

$$y_s = \frac{1}{2}\{p\sqrt{m} + m + 1 + [(p\sqrt{m} + m + 1)^2 - 4m]^{1/2}\} \tag{64}$$

where

$$p = \left(\frac{4\pi Ze\sigma_s}{\kappa\varepsilon kT}\right)^2 \tag{65}$$

There is experimental evidence (Petsev and Denkov, 1992) that the colliding particles in a latex suspension approach each other at constant surface potential, ψ_s, the latter being slightly dependent also on the electrolyte concentration. However, in principle it is possible that neither the surface potential nor the surface charge is constant. In such a case a condition for charge regulation is applied, which represents the condition for dynamic equilibrium of the counterion exchange between the Stern and diffuse parts of the electric double layer. For details see Martynov and Muller (1972), Healy et al. (1980), Chan et al. (1980), Vassilieff et al. (1983), Grimson et al. (1988). Note that for $kh \geq 1$ and $|\Phi_s| \geq 4$, where

$$\Phi_s = -\frac{Ze}{kT}\psi_s \tag{66}$$

the difference between the regimes of constant potential, constant charge, or charge regulation becomes immaterial (see Fig. 6): the usage of each of them leads to the same result for $\Pi_{el}(h)$.

When the dimensionless electrostatic potential in the middle of the film

$$\Phi_m = -\frac{Ze}{kT}\psi_m = -\frac{1}{2}\ln m \tag{67}$$

is small enough (the film thickness h is large enough), one can suppose that

$$\Phi_m \approx 2\Phi_1\left(\frac{h}{2}\right) \tag{68}$$

where Φ_1 is the dimensionless electric potential at a distance $h/2$ from the surface (of the film) when the other surface is removed at infinity. Since

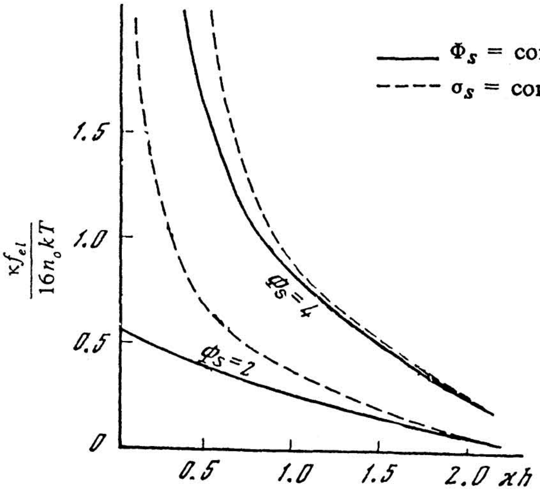


FIG. 6 Dependence of the excess electrostatic (double layer) interaction energy per unit area, f_{el}, on the film thickness, h, at different fixed values of the surface potential, Φ_s, or charge, σ_s.

$$\Phi_1(h/2) = 4\, e^{-\frac{\kappa h}{2}} \tanh\frac{\Phi_s}{2} \tag{69}$$

from Eqs. (59) and (67–69) one obtains a useful asymptotic formula

$$\Pi_{el} \approx n_o kT \Phi_m^2 \approx 64 n_o kT \tanh^2 \frac{\Phi_s}{4}\, e^{-\kappa h} \tag{70}$$

(for details see Verwey and Overbeek (1948), where Eq. (70) was first derived). It is interesting to note that when Φ_s is large enough, the hyperbolic tangent in Eq. (70) will be identically 1 and Π_{el} (as well as $f_{el} = \int_h^\infty \Pi_{el} dh$) becomes independent of the surface potential (or charge). See Fig. 6 where the curves Φ_s = const and σ_s = const come closer as Φ_s increases. Other useful expressions for Π_{el}, including the case of nonsymmetrical electrolyte not considered here, can be found in the book by Derjaguin et al. (1987).

2. Two Nonidentical Charged Surfaces

Contrary to the case of two identically charged surfaces, which always repel each other [see Eq. (59)], the electrostatic interaction between two plane-parallel surfaces of different potentials, ψ_{s1} and ψ_{s2}, can be either repulsive or attractive. This problem was first studied by Derjaguin (1954) and Devereux and de Bruyn (1963). Comprehensive review can be found in the books by Derjaguin et al. (1987) and Derjaguin (1989). Here we will restrict our considerations to the case of low surface potentials, when the Poisson-Boltzmann equation can be linearized. In spite of being not too general quantitatively, this case exhibits qualitatively all features of the electrostatic interaction between different surfaces.

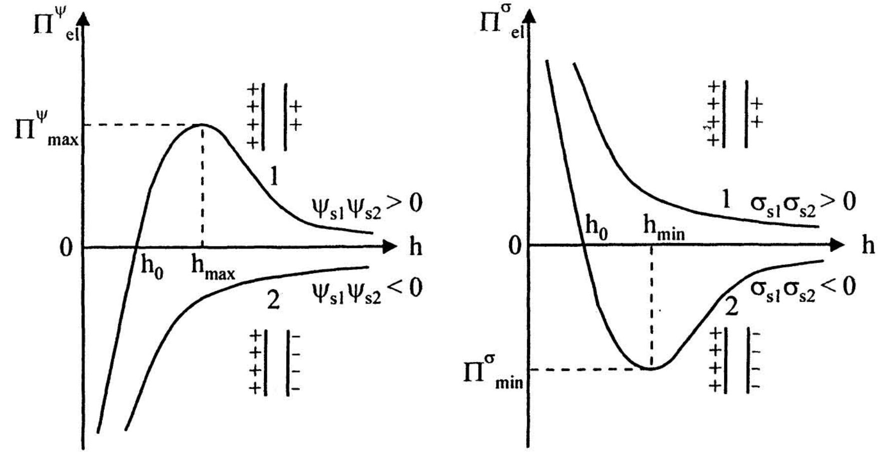
First, ψ_{s1} = const, ψ_{s2} = const. In this case the disjoining pressure at constant surface potential reads (Bell and Peterson, 1972; Derjaguin et al., 1987):

$$\Pi_{el}^{\psi} = \frac{\varepsilon\kappa^2}{8\pi} \frac{2\psi_{s1}\psi_{s2}\cosh\kappa h - (\psi_{s1}^2 + \psi_{s2}^2)}{\sinh^2 \kappa h} \tag{71}$$

When the two surface potentials have opposite signs, that is, when $\psi_{s1}\psi_{s2} < 0$, $\Pi_{el}^{(\psi)}$ is negative for all h and corresponds to electrostatic attraction (see Fig. 7a). This result could have been anticipated, since two charges of opposite sign attract each other. Much more intresting is the case, when $\psi_{s1}\psi_{s2} > 0$, but $\psi_{s1} \neq \psi_{s2}$. In the latter case the two surfaces repel each other for $h > h_o$, whereas they attract each other for $h < h_o$ (Fig. 7a); h_o is determined by the equation

$$\kappa h_o = \ln\,(\psi_{s2}/\psi_{s1})\;; \qquad \psi_{s2} > \psi_{s1} \tag{72}$$

Besides, the electrostatic repulsion has a maximum value of



(a) (b)

FIG. 7 Electrostatic disjoining pressure, Π_{el} vs. film thickness, h, for films of dissimilar surfaces at fixed surface potential (a) and fixed surface charge (b).

$$\Pi^{\psi}_{el}(\max) = \frac{\varepsilon\kappa^2}{8\pi}\psi_{s1}^2 \tag{73}$$

at

$$h_{\max} = \frac{1}{\kappa}\text{arc cosh}\,\frac{\psi_{s2}}{\psi_{s1}}, \qquad \psi_{s2} > \psi_{s1} \tag{74}$$

A similar electrostatic disjoining pressure isotherm has been used to interpret the experimental data of Usui et al. (1986) with aqueous films on mercury. It is worthwhile noting that $\Pi^{\psi}_{el}(\max)$ depends only on ψ_{s1}, that is, the maximum repulsion is determined by the potential of the surface of lower charge.

Second, σ_{s1} = const, σ_{s2} = const. When the surface charge densities are constant, the surface potentials become functions of the film thickness h:

$$\psi_{sk} = \frac{\psi_{k\infty}\cosh\kappa h + \psi_{j\infty}}{\sinh\kappa h}, \qquad j,\,k = 1,2\ ;\, j \neq k \tag{75}$$

with

$$\psi_{k\infty} = \frac{4\pi}{\varepsilon\kappa}\,\sigma_{sk} \tag{76}$$

Then instead of Eq. (71) one has (see, e.g., Derjaguin et al. [1987]):

$$\Pi^{\sigma}_{el}(h) = \frac{2\pi}{\varepsilon}\,\frac{2\sigma_{s1}\sigma_{s2}\cosh\kappa h + \sigma_{s1}^2 + \sigma_{s2}^2}{\sinh^2 \kappa h} \tag{77}$$

When $\sigma_1\sigma_2 > 0$, Eq. (77) yields $\Pi^{\sigma}_{el} > 0$ for every h (see Fig. 7b). However, when $\sigma_1\sigma_2 < 0$, Π^{σ}_{el} is repulsive for small thickness, $h < h_o$, and attractive for larger separations, $h > h_o$; h_o is determined by the equation

$$\kappa h_o = \ln\left(-\frac{\sigma_{s2}}{\sigma_{s1}}\right), \qquad |\sigma_{s2}| > |\sigma_{s1}| \tag{78}$$

The electrostatic disjoining pressure in this case has a minimum value

$$\Pi^{\sigma}_{el}(\min) = \frac{4\pi}{\varepsilon}\,\sigma_{s1}\sigma_{s2}\,, \tag{79}$$

at

$$h_{\min} = \frac{1}{\kappa}\,\mathrm{arc\,cosh}\left(-\frac{\sigma_{s2}}{\sigma_{s1}}\right) \tag{80}$$

Finally it should be noted that all curves depicted in Fig. 7 decay exponentially at $h \to \infty$. An asymptotic expression, which generalizes Eq. (70), holds (see, e.g., Verwey and Overbeek, 1948; Derjaguin et al., 1987):

$$\Pi_{el}(h) = 64 n_o k T \gamma_1 \gamma_2 e^{-\kappa h} \tag{81}$$

where

$$\gamma_k = \tanh\left(\frac{Ze\psi_{sk}}{4kT}\right), \qquad k = 1, 2$$

Equation (81) is valid for both low and high surface potentials.

3. Two Charged Spheres

When the electric double layers are thin compared with the particle radii ($\kappa^{-1} << R_1, R_2$) and the gap between the particles is small ($h_o << R_1, R_2$), one can use Eq. (81) in conjunction with the Derjaguin approximation, Eqs. (42–45). The result for the energy of electrostatic interaction between the two spheres reads

$$U_{el}(h_o) = \frac{128\pi R_1 R_2}{\kappa^2 (R_1 + R_2)}\, n_o k T \gamma_1 \gamma_2 e^{-\kappa h} \tag{82}$$

Equation (82) is valid for any surface potentials ψ_{s1} and ψ_{s2} but only for $\kappa h >> 1$. Complementary expressions, which are valid for every $h << R_1, R_2$, for small surface potentials can be derived by integrating Eqs. (71) and (77), instead of Eq. (81). In this way one can derive for $\psi_{s1} = \mathrm{const}$ and $\psi_{s2} = \mathrm{const}$ (Hogg et al., 1966)

$$U^{\psi}_{el}(h_o) = \frac{\varepsilon R_1 R_2}{4(R_1 + R_2)}[(\psi_{s1} + \psi_{s2})^2 \ln(1 + e^{-\kappa h_o}) + (\psi_{s1} - \psi_{s2})^2 \ln(1 - e^{-\kappa h_o})] \tag{83}$$

or, alternatively, for $\sigma_{s1} = \text{const}$ and $\sigma_{s2} = \text{const}$ (Usui, 1973):

$$U^{\sigma}_{el}(h_o) = -\frac{4\pi^2 R_1 R_2}{\varepsilon\kappa^2(R_1 + R_2)}[(\sigma_{s1} + \sigma_{s2})^2 \ln(1 - e^{-\kappa h_o}) + (\sigma_{s1} - \sigma_{s2})^2 \ln(1 + e^{-\kappa h_o})] \tag{84}$$

The range of validity of the different approximations involved in the derivations of Eqs. (82–84) is discussed in the book by Russel et al. (1989).

As mentioned above, Eqs. (82–84) hold for $h_o << R$. In the opposite case, when h_o is comparable to or larger than the particle radius R, one can use the equation (Derjaguin, 1989):

$$U_{el}(h_o) = \frac{\varepsilon\psi_s^2 R^2}{2R + h_o} e^{-\kappa h_o}, \tag{85}$$

stemming from the theory of Debye and Huckel (1923) for two identical particles. Eq. (85) was derived by using the superposition approximation (valid for small overlapping of the two electric double layers) and the linearized Poisson-Boltzmann equation. A simple approximate formula, representing in fact interpolation between Eqs. (85) and (83) (the latter for $R_1 = R_2 = R$), has been derived by McCartney and Levine (1969):

$$U^{\psi}_{el}(h_o) = \varepsilon R\psi_s^2 \frac{R + h_o}{2R + h_o} \ln\left(1 + \frac{Re^{-\kappa h_o}}{R + h_o}\right) \tag{86}$$

Eq. (86) has the advantage of giving a good approximation for every h_o, provided that the Poisson-Boltzmann equation can be linearized.

It is worthwhile noting that Eqs. (82–86) hold for a single couple of particles inside an infinite electrolyte solution. However, the real situation in the dispersions of charged particles is quite different. The presence of many other particles can affect the interaction between each specified pair. Such collective electrostatic effects in dispersions have been studied by Beresford-Smith et al. (1985). Perhaps, the most important effect of this kind is the contribution of the counterions (dissociated from the particles) into the Debye screening parameter, κ:

$$\kappa^2 = \kappa_o^2 + \kappa^2_{\text{counterions}}, \tag{87}$$

where κ_o^2 is determined by the concentration of the added electrolyte and the last term is due to the counterions dissociated from the surfaces of the colloidal particles. In linear approximation the theory of Beresford-Smith et al. (1985) predicts that the effective pair potential energy of interaction between charged colloidal spheres in a dispersion with low concentrations of the added electrolyte has the form of a screened Coulomb potential:

$$U_{el} = U_o \frac{e^{-\kappa r}}{r} \tag{88}$$

where r is the center-to-center distance between two spheres and

$$U_o = \frac{(Z_o e)^2}{\varepsilon} \frac{e^{2\kappa R}}{(1 + \kappa R)^2} (1 + \varphi)^2 ; \tag{89}$$

Z_o is the number of charges per particle; φ is the volume fraction of the particles. Since $h_o = r - 2R$, the exponents in Eqs. (88) and (85) are similar, with the only difference being that the κs in these two equations have different definitions, Eqs. (87) and (62), respectively. The linearized theory of Beresford-Smith et al. (1985) was applied to micellar solutions by Nikolov et al. (1989) and to latex suspensions by Petsev and Denkov (1992) and Denkov and Petsev (1992).

D. DLVO Theory

The first quantitative theory of interactions in thin liquid films and dispersions was the DLVO theory, named for its authors: Derjaguin and Landau (1941) and Verwey and Overbeek (1948). In this theory the total interaction is a superposition of van der Waals and double layer interactions. In other words, the total disjoining pressure and the total interaction energy are presented in the form:

$$\Pi = \Pi_{vw} + \Pi_{el} \tag{90}$$

$$\mathrm{U} = U_{vw} + U_{el} \tag{91}$$

A sketch of the typical behavior of U_{vw}, U_{ei}, and U as functions of the distance, h, between two identical surfaces (plane-parallel or spherical) is presented in Fig. 8. A typical curve U vs. h exhibits a maximum representing an energetical barrier against coagulation, and two minima, called primary and secondary minimum. The primary minimum appears if strong short range repulsive forces (e.g., steric forces) are present. With small particles the depth of the secondary minimum is usually small ($U_s < kT$). If the particles cannot overcome the barrier, coagulation (flocculation) does not take place and the dispersion is stable due to the electrostatic repulsion, which gives rise to the barrier. With larger colloidal particles ($R > 0.1$ μm) the secondary minimum could be deep enough ($U_s > kT$) to cause coagulation and even formation of ordered structures of particles (see Efremov, 1978).

By the addition of electrolyte or by decreasing the surface potential of the particles one can suppress the electrostatic repulsion and thus decrease the height of the barrier, $U(h_{\max})$; see the inset in Fig. 8. When $U(h_{\max}) \leq 0$ rapid coagulation

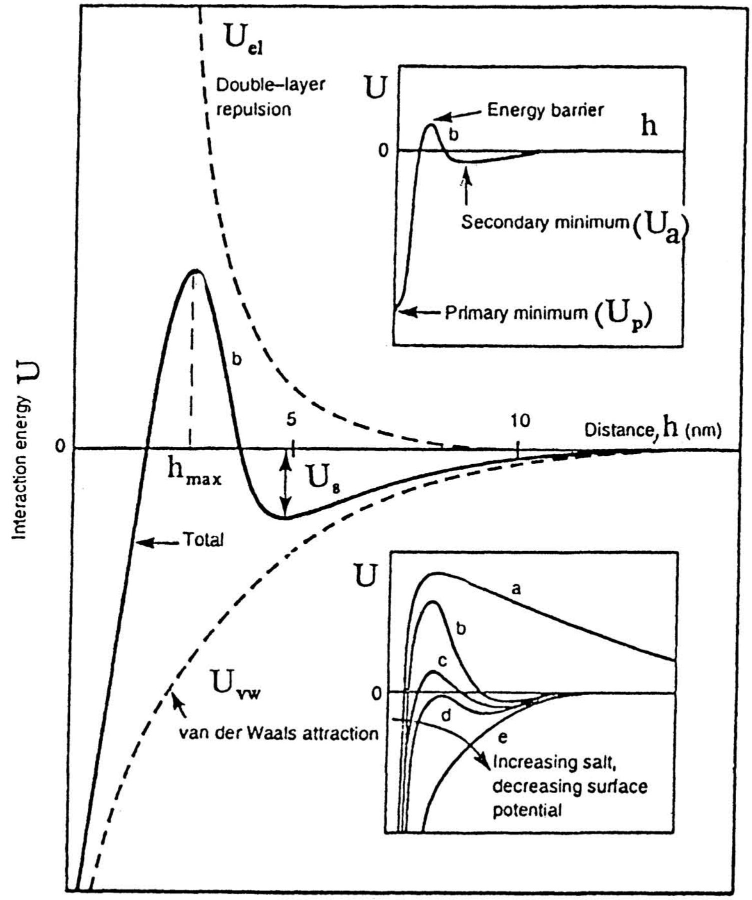


FIG. 8 A typical DLVO isotherm of interaction energy, U, vs. surface-to-surface distance h. (After Israelachvili, 1992.)

takes place in the dispersion. According to the DLVO theory the critical condition determining the onset of rapid coagulation is

$$U(h_{\max}) = 0, \qquad \left.\frac{\mathrm{d}U}{\mathrm{d}h}\right|_{h_{\max}} = 0 \tag{92}$$

By using Eq. (54) for U_{vw} and Eq. (82) for U_{el} one derives from Eqs. (90–92) the following criterion for the threshold of rapid coagulation of identical particles ($R_1 = R_2 = R$; $\gamma_1 = \gamma_2 = \gamma$):

$$\frac{\kappa^6}{n_o^2} = \left[\frac{768\pi}{A_H} kTe^{-1} \tanh^2\left(\frac{Ze\psi_s}{4kT}\right)\right]^2 \tag{93}$$

A substitution of κ^2 from Eq. (62) into Eq. (93) yields

$$n_o(\text{critical}) \propto \frac{1}{Z^6} \tanh^4\left(\frac{Ze\psi_s}{4kT}\right) \tag{94}$$

When ψ_s is high enough the hyperbolic tangent equals 1 and one obtains n_o(critical) $\sim Z^{-6}$, which is in fact the empirical rule established by Schultze (1882) and Hardy (1900).

E. Forces Due to Ionic Correlations

It is known that due to the strong interactions between the ions in a solution the positions of the ions are correlated in such a way that counterion atmosphere appears around each ion, thus screening its Coulomb potential. The theory of electrolyte solutions and ionized gases was proposed by Debye and Huckel (1923). The energy of formation of the counterion atmospheres gives a contribution to the free energy of the system called by Landau and Lifshitz (1980) ''correlation energy.'' The correlation energy also affects a contribution to the osmotic pressure of the electrolyte solution, which can be present in the form (see, e.g., Landau and Lifshitz, 1980):

$$\Pi_{osm} = kT \sum_{i=1}^{k} n_i - \frac{e^3}{3}\left(\frac{\pi}{kT}\right)^{1/2}\left(\frac{1}{\varepsilon} \sum_{i=1}^{k} Z_i^2 n_i\right)^{3/2} \tag{95}$$

The first term in the right-hand side of Eq. (95) corresponds to an ideal solution, whereas the second term takes into account the effect of electrostatic interactions between ions (the latter is accounted for thermodynamically by the activity coefficient).

The expression for Π_{el} in the DLVO theory, Eq. (59), obviously corresponds to an ideal solution, with the contribution of the ionic correlations being neglected. Hence, in a more general theory, instead of Eq. (90) one can write

$$\Pi = \Pi_{vw} + \Pi_{el} + \Pi_{cor} \tag{96}$$

where Π_{cor} is the contribution of the ionic correlations into disjoining pressure. The theory of Π_{cor} takes into account the following effects: (1) energy of formation of Debye counterion atmosphere around each ion in the film; (2) energy of deformation of the counterion atmosphere due to the image forces; (3) energy of the long-range correlations between charge density fluctuations in the two opposite electric double layers. Computer methods for calculating Π_{cor} were developed by Guldbrand et al. (1984) and Kjellander and Marčelja (1986). Analytical expressions for Π_{cor} were derived by Attard et al. (1988) and Kralchevsky and Paunov (1992). Since these expressions are very long, here we will describe briefly the most important results.

In all cases Π_{cor} is negative and corresponds to attraction, which can be comparable by magnitude with Π_{vw}. In the case of 1:1 electrolyte Π_{cor} is usually a small correction to Π_{el}: see Fig. 9 where Π_{el} and $(\Pi_{el} + \Pi_{cor})$ vs. h curves are compared. In the case of 2:2 electrolyte, however, the situation can be quite different: the attractive forces $\Pi_{cor} + \Pi_{vw}$ can prevail over Π_{el} and the total disjoining pressure, Π, can be negative: see Fig. 10 (Kralchevsky and Paunov, 1992).

The above results are obtained for two overlapping electric double layers inside the film. Such films can appear between two colliding droplets in an oil-in-water emulsion. In the opposite case of water-in-oil emulsion, the double layers are outside the film. Nevertheless, in the latter case Π_{cor} is not zero, because the ionic charge density fluctuations in the outer double layers interact through the thin dielectric (oil) film. The theory for such a film was developed by Paunov and Kralchevsky (1992). Π_{cor} turns out to be negative (attractive) and strongly dependent on the dielectric permittivity of the oil film, ε_1; for instance, when $\varepsilon_1 = 35$, Π_{cor} amounts to about 50% of Π_{vw} ($\Pi_{el} = 0$ in this case).

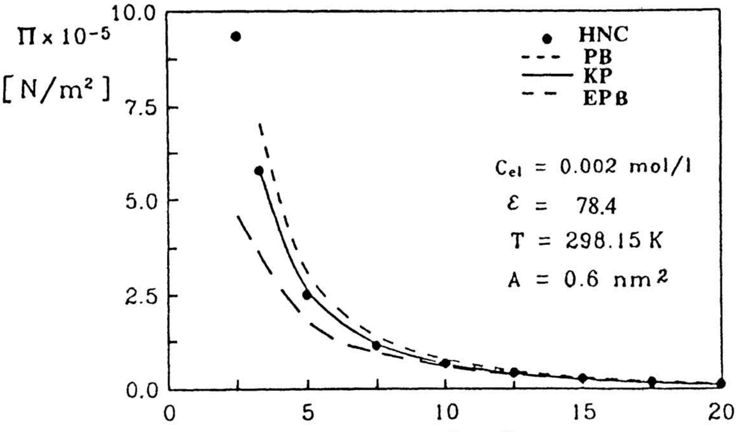


FIG. 9 Plot of $\Pi_{el} + \Pi_{cor}$ vs. film thickness h. c_{el}, electrolyte concentration; ε, dielectric permittivity; T, temperature; A, area per elementary surface charge. Short dashed curve, $\Pi_{cor} = 0$; solid curve, theory of Kralchevsky and Paunov (1992); long dashed curve and points (•), EPB theory and HNC closure from Attard et al. (1988).

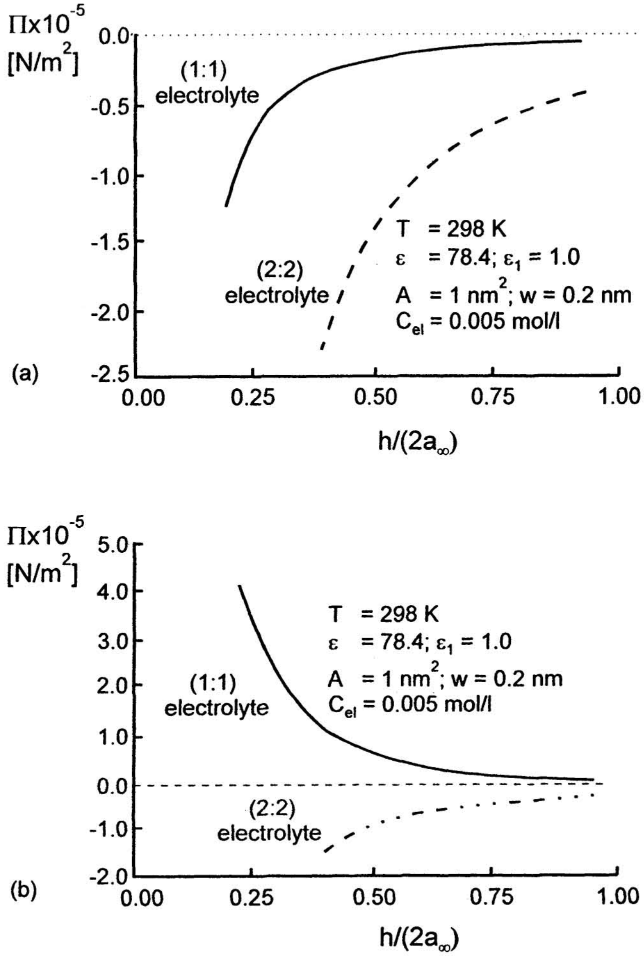


FIG. 10 Plots of (a) Π_{cor} and (b) $\Pi = \Pi_{el} + \Pi_{cor}$ vs. the film thickness for 1:1 and 2:2 electrolytes at the same electrolyte concentration, c_e. (From Kralchevsky and Paunov, 1992.)

F. Steric Interaction

The steric interactions between two surfaces appear when chain molecules, attached at some point to a surface, dangle out into the solution, where they are mobile due to Brownian motion (see Fig. 11). When two such surfaces approach each other the following effects take place. First, on approach of the surfaces

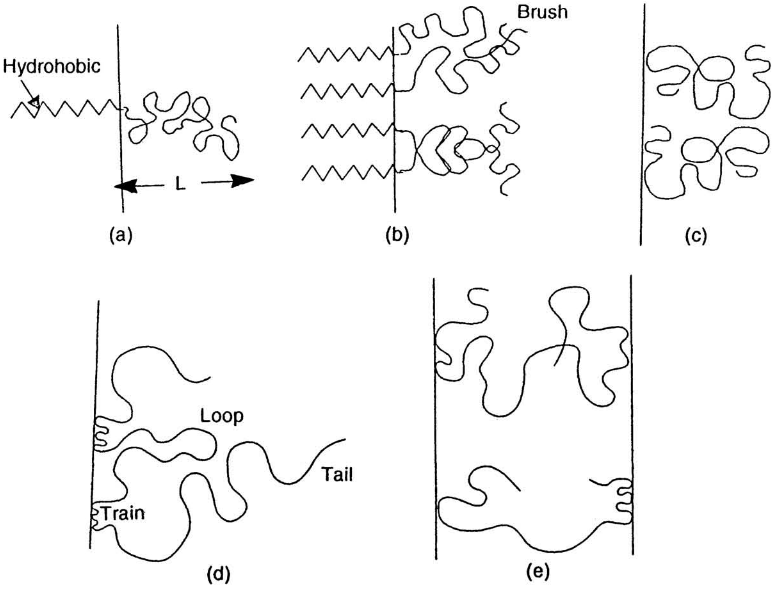


FIG. 11 Polymers adsorbed at a surface: (a) terminally anchored (grafted) polymer chain of mean end-to-end distance *L*; (b) brush of grafted chains; (c) adsorption of polymer coils; (d) tails, loops, and trains; (e) ''bridging'' of two surfaces by adsorbed polymer chains.

the entropy decreases due to the confining of these dangling chains, which results in a repulsive osmotic force known as ''steric'' or ''overlap'' repulsion. Second, in a poor solvent the segments of the chain molecules attract each other; hence the overlapping of the two approaching layers of polymer molecules will be accompanied by some intersegment attraction; the latter can prevail for a small overlap. However, at the distance of a larger overlap it becomes negligible compared with the osmotic repulsion. A third effect, known as the ''bridging attraction,'' occurs when the two opposite ends of a chain molecule can attach (adsorb) to the two opposite approaching surfaces, thus forming a ''bridge'' between them (see Fig. 11e). A short range repulsion appears between two approaching monolayers adsorbed at two fluid interfaces because of the overlapping of protruding molecules due to their fluctuation motion along the normal to the interface. This interaction, which is in principle observable with any amphiphile adsorbed molecule is called the ''protrusion force'' (Israelachvili, 1992).

Since our review is devoted to foam films, we will restrict our considerations to the first two kinds of steric effects, which provide the typical steric interaction in foam films stabilized with nonionic surfactants, or with different polymers, including proteins. The usual nonionic surfactant molecules are anchored (grafted) to the liquid interface by their hydrophobic moieties (see Fig. 11a). When the surface concentration of adsorbed molecules is high enough, the hydrophilic chains are said to form a brush (Fig. 11b). The coils of macromolecules, like proteins, can also adsorb at a liquid surface (Fig. 11c). Sometimes the configurations of the adsorbed molecules are very different from the statistical coil they form in the bulk of the solution (Fig. 11d): loops, trains, and tails can be identified. The different kinds of interface and interparticle forces in polymer-containing solutions have been recently reviewed by Tadros (1988), Patel and Tirrell (1989), Ploehn and Russel (1990), and Israelachvili (1992).

The osmotic pressure of polymer solutions at either dilute or concentrated conditions can be expressed in the form (de Gennes, 1979, §III.1):

$$\frac{P_{osm}}{nkT} = \frac{1}{N} + \frac{1}{2}nv + \frac{1}{3}n^2w + \ldots \tag{97}$$

Here N is the number of segments in the polymer chain, n is the numerical segment density, v and w account for the pair and triplet interactions between segments. In fact v and w are counterparts of the second and third virial coefficients in the theory of nonideal gases (see, e.g., Hill, 1962). v and w can be calculated if information about the polymer chain and the solvent is available (Russel et al., 1989):

$$w^{1/2} = \bar{v}m/N_A \tag{98}$$

$$v = w^{1/2}(1 - 2\chi) , \tag{99}$$

where $\bar{v}$ is the specific volume per segment in m^3/kg, m is the molecular weight per segment in kg/mol, N_A is the Avogadro number, and χ is the Flory parameter (for more details see Yamakawa, 1971).

The Flory parameter, χ, depends on both the temperature and energy of the solvent-segment interaction. Then v can be zero [cf. Eq. (99)] for some special temperature, called the theta temperature. The solvent at theta temperature is known as theta solvent or ideal solvent. The theta temperature in polymer solutions is a counterpart of the Boil temperature in nonideal gases: this is the temperature at the which the intermolecular (intersegment) attraction and repulsion are exactly counterbalanced. In a "good solvent," however, the repulsion due mainly to the excluded volume effect dominates the attraction and $v > 0$. In contrast, in a "poor solvent" the intersegment attraction prevails, so $v < 0$.

1. Thickness of the Adsorbed Layer

The steric interaction between two approaching surfaces appears when the film thickness becomes of the order of or smaller than $2L$ where L is the mean square end-to-end distance of this portion of the chain that is dissolved in the film. If the chain was entirely extended, then L would be equal to Nl with l being the length of a segment. However, due to Brownian motion $L < Nl$. For a brush of anchored chains, like those depicted in Fig. 11b, in a theta solvent L can be estimated as (see, e.g., Russel et al., 1989)

$$L \approx L_o \equiv l\sqrt{N} \tag{100}$$

In a good solvent $L > L_o$, whereas in a poor solvent $L < L_o$. In addition, L depends on the surface concentration, Γ, of the adsorbed chains, that is, L is different for an isolated molecule and for a brush (cf. Fig. 11a, b). The mean field approach, applied to polymer solutions provides the following equation for calculating L (Dolan and Edwards, 1975; Russel et al., 1989):

$$\tilde{L}^3 - \left(1 + \frac{1}{9}\tilde{\Gamma}^2\right)\tilde{L}^{-1} = \frac{1}{6}\tilde{v} \tag{101}$$

where $\tilde{L}$, Γ, and $\tilde{v}$ are the dimensionless values of L, Γ, and v defined as follows:

$$\tilde{L} = \frac{L}{l\sqrt{N}} \tag{102}$$

$$\tilde{\Gamma} = \frac{\Gamma N\sqrt{w}}{l} \tag{103}$$

$$\tilde{v} = \frac{v\Gamma N^{3/2}}{l} \tag{104}$$

In an ideal solvent ($\tilde{v} = 0$) and for isolated adsorbed molecule ($\Gamma = 0$) Eq. (101) predicts $\tilde{L} = 1$; that is, $L = L_o$ as estimated by means of Eq. (100).

The prediction of Eq. (101) is visualized in Fig. 12. One can see that $\tilde{L}$ strongly depends on $\tilde{v}$ and increases several times from the region of poor solvents ($\tilde{v} < 0$) toward the region of the good solvents ($\tilde{v} > 0$). This effect is less pronounced in the case of dense brushes (larger Γ) because of the higher osmotic pressure inside the brush, which opposes the shrinking of the polymer layer in poor solvents.

2. Interaction Between Two Overlapping Adsorption Layers

Here we will consider only the case of terminally anchored chains, like those depicted in Fig. 11a,b. Dolan and Edwards (1975) calculated the steric interaction free energy per unit area, f, as a function of the film thickness, h, in a theta solvent. Their result reads

$$f(h) = \Gamma k\mathrm{T}\left[\frac{\pi^3}{3}\frac{L_o^2}{h^2} - \ln\left(\frac{8\pi}{3}\frac{L_o^2}{h^2}\right)\right] \qquad \text{for } h < L_o\sqrt{3} \tag{105}$$

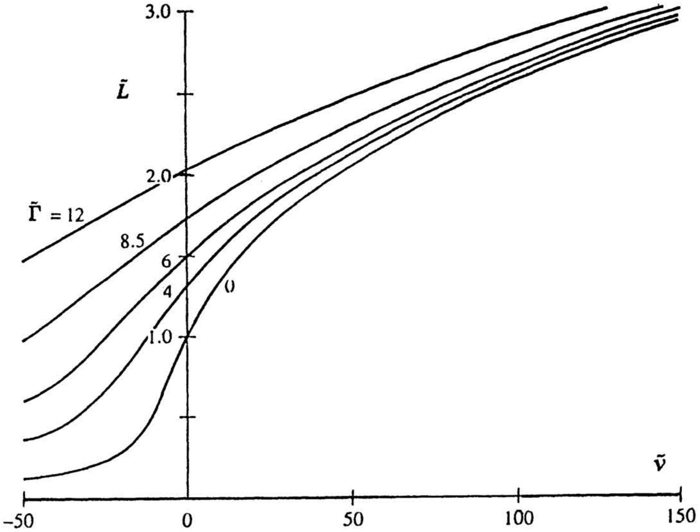


FIG. 12 Dimensionless end-to-end distance $\tilde{L}$ vs. dimensionless second virial coefficient, $\tilde{v}$, at different values of the dimensionless polymer adsorption, $\tilde{\Gamma}$. The cases $\tilde{v} > 0$, $\tilde{v} = 0$, and $\tilde{v} < 0$ correspond to a good, θ, and poor solvent, respectively. (From Russel et al., 1989.)

$$f(h) = 4\Gamma kT \exp\left(-\frac{3h^2}{2L_o^2}\right) \qquad \text{for } h > L_o\sqrt{3} \tag{106}$$

where L_o is the end-to-end distance as defined by Eq. (100). The boundary between the power-low regime ($f \sim 1/h^2$) and the exponential decay regime is at $h = L_o\sqrt{3} \approx 1.7L_o$, the latter being slightly less than $2L_o$, which is the intuitively expected onset of the steric overlapping. The first term on the right side of Eq. (105) comes from the osmotic repulsion between the brushes, which opposes the approach of the two surfaces; the second term is negative and accounts effectively for the decrease of the elastic energy of the initially extended chains when the thickness of each of the two monolayers pressed against each other decreases. We recall that Eqs. (105–106) hold for a theta solvent.

In the case of good solvent the disjoining pressure $\Pi = -df/dh$ can be calculated by means of Alexander de Gennes's theory (de Gennes, 1985, 1987) as

$$\Pi(h) = kT\Gamma^{3/2}\left[\left(\frac{2L_g}{h}\right)^{9/4} - \left(\frac{h}{2L_g}\right)^{3/4}\right] \qquad \text{for } h < 2L_g \tag{107}$$

where L_g is the thickness of a brush in a good solvent (Alexander, 1977):

$$L_g = N(\Gamma l^5)^{1/3} \tag{108}$$

The positive and the negative terms on the right side of Eq. (107) correspond to osmotic repulsion and elastic attraction. Taunton et al. (1990) measured the forces between two brush layers grafted on the surfaces of two crossed mica cylinders. Their results, shown in Fig. 13, are in a very good agreement with the theory of de Gennes. The force/radius ratio plotted in Fig. 13 in fact equals $2\pi f(h)$; note that f and Π are connected by means of Eq. (45).

A theory of steric interactions, which is applicable for both good and poor solvents, was developed by Russel et al. (1989) at the cost of some simplifications for the density profile inside the brushes. Their expression for the interaction free energy per unit area reads

$$f(h) = 2\Gamma kT\,[W(\tilde{h}, \tilde{v}, \tilde{\Gamma}) - W(\infty, \tilde{v}, \tilde{\Gamma})] \tag{109}$$

where

$$W(\tilde{h}, \tilde{v}, \Gamma) = \frac{3}{2}(\tilde{L} - \tilde{L}^{-1})^2 + \frac{3\tilde{v}}{2\tilde{L}}\left(1 - \frac{\tilde{h}}{3\tilde{L}}\right) + \frac{7\tilde{\Gamma}^2}{6\tilde{L}^2}\left(1 - \frac{3}{7}\frac{\tilde{h}}{\tilde{L}}\right) \tag{110}$$

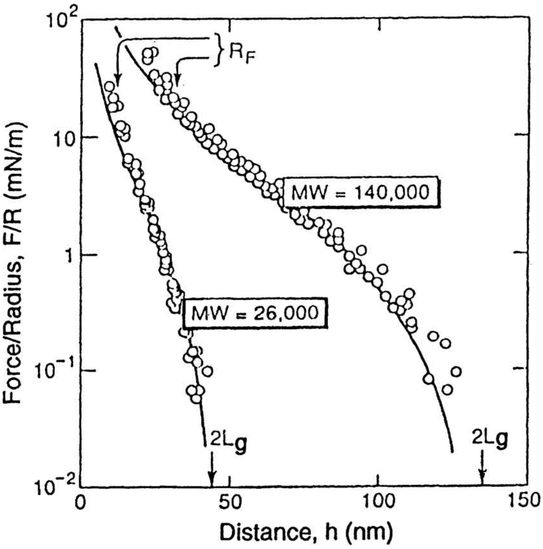


FIG. 13 Measured force (Taunton et al., 1990) between two polystyrene brush layers is a good solvent (toluene) compared with the Alexander de Gennes theory (the solid curves) for two different molecular weights (Israelachvili, 1992).

here $\tilde{L}$, Γ, and $\tilde{v}$ are defined by means of Eqs. (103–104) and $\tilde{h}$ is the dimensionless film thickness:

$$\tilde{h} = \frac{h}{l\sqrt{N}} \tag{111}$$

Γ and $\tilde{v}$ are supposed to be known from the experiment, whereas the dimensionless thickness $\tilde{L} = \tilde{L}(\tilde{h})$ is calculated as a solution of the equation

$$\tilde{L}^3 - \left[1 + \frac{7\tilde{\Gamma}}{9}\left(1 - \frac{9}{14}\frac{\tilde{h}}{\tilde{L}}\right)\right]\tilde{L}^{-1} = \frac{1}{2}\tilde{v}\left[1 - \frac{2\tilde{h}}{3\tilde{L}}\right] \tag{112}$$

The theory based on Eqs. (109–112) is found (Russel et al., 1989) to be in a good agreement with the experimental data of Hadziioannou et al. (1986) about $f(h)$ for block copolymer layers in toluene and cyclohexane. It is worthwhile noting that the theory of Russel et al. (1989) predicts an attractive minimum in a poor solvent. The condition for appearance of such a minimum reads

$$\tilde{v} = -\tilde{\Gamma}^2 \tag{113}$$

By the end of this section we will note that in the case of adsorbed molecules, like those in Fig. 11d, which are not anchored to the surface, the measured surface forces depend pronouncedly on the rate of approaching of the two surfaces (see Klein and Luckham, 1982, 1984; Luckham and Klein, 1990). This can be interpreted with the comparatively slow rate of exchange of polymer between the adsorption layer and the bulk solution. This leads to a hysteresis effect: different interaction on approach and separation between the surfaces (see Israelachvili, 1992). In addition one can observe two regimes of steric repulsion: (1) weaker repulsion at larger separations due to the overlapping of the tails (Fig. 11d), and (2) stronger repulsion at smaller separations indicating overlapping of the loops (Sonntag et al., 1982).

G. Oscillatory Structural Forces

1. Origin of the Structural Forces

Oscillatory structural forces appear in two cases: (1) thin liquid films between two solid surfaces; (2) in thin liquid films containing colloidal particles (including macromolecules and surfactant micelles). In the first case the oscillatory forces are called the ‘‘solvation forces’’ (Horn and Israelachvili, 1980); they are important for the short-range interactions between solid particles in dispersions. In the second case the structural forces affect the stability of foam and emulsion films as well as the flocculation processes in various colloids. At higher particle concentrations the structural forces stabilize the liquid films and colloids (Nikolov et al., 1989, 1990). At lower particle concentrations the structural forces degenerate into the so-called depletion forces, which are found to destabilize various dispersions (Asakura and Oosawa, 1954, 1958; de Hek and Vrij, 1981).

In all cases the oscillatory structural forces appear when spherical particles are confined between the two surfaces of a thin film. As illustrated in Fig. 14, even one "hard wall" can induce ordering among the neighboring particles. The maxima of the numerical density (the singlet distribution function), n_0, as a function of the distance from the wall, x, represent the most probable positions of the particles. This oscillatory behavior of $n(x)$ was established in a number of theoretical works with both hard sphere interparticle potential (Waisman et al., 1976; Snook and Henderson, 1978) and Lennard-Jones potential (Abraham, 1978; Snook and van Megen, 1981). The oscillatory structural force is a result of overlapping of the structured zones at two approaching surfaces (see van Megen and Snook, 1979; Snook and van Megen, 1980; Kjellander and Marčelja, 1985; Tarazona and Vicente, 1985; Rickayzen and Richmond, 1988; Evans and Parry, 1990). A simple connection between density distribution and structural force is given by the contact value theorem (Henderson, 1986; see also Evans and Parry, 1990; and Israelachvili, 1992):

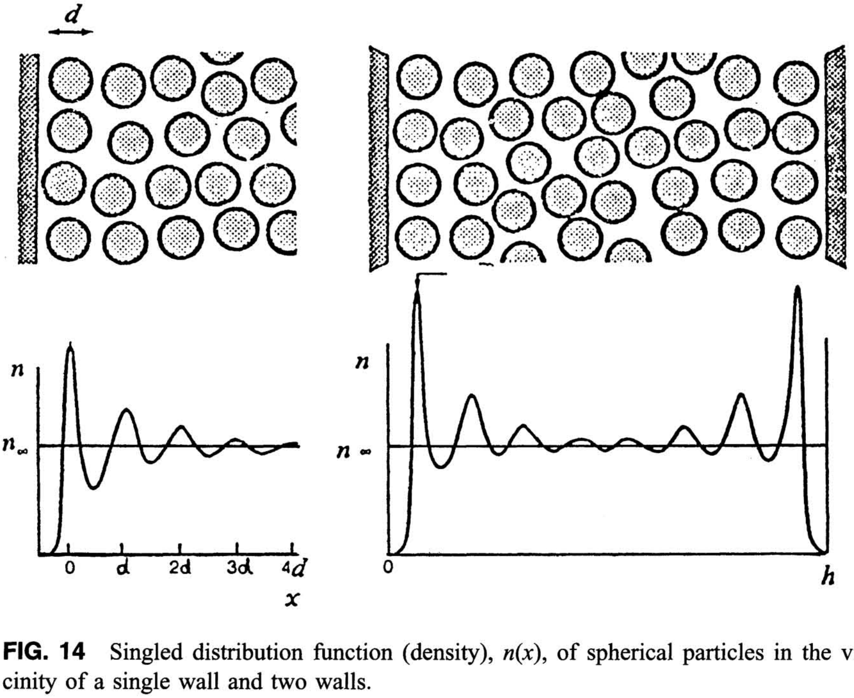


FIG. 14 Singled distribution function (density), $n(x)$, of spherical particles in the vicinity of a single wall and two walls.

$$\Pi_{os}(h) = kT\,[n_s(h) - n_s(\infty)] \tag{114}$$

where Π_{os} is the disjoining pressure component due to oscillatory structural forces, $n_s(h)$ is the numerical density of the subsurface particle layer as a function of the distance between the walls, h. Figure 15 illustrates the variation of n_s with h and the resulting disjoining pressure Π_{os}. One sees that in the limit of very small separations, as the last layer of particles is eventually squeezed out, $n_s \rightarrow 0$ and

$$\Pi_{os}(h) \rightarrow -kT\,n_s\,(\infty) \qquad \text{for } h \rightarrow 0 \tag{115}$$

In other words, at small separations Π_{os} is negative (attractive). Equation (115) holds for both solvation forces and structural forces in colloids. In the latter case Eq. (115) represents the osmotic pressure of the colloid particles and the resulting attractive force is known as the "depletion force" (for details, see below).

It is worthwhile noting that the numerical density of the subsurface layer, $n_s(h)$, depends also on the interaction between the particles and the wall, which therefore can affect the structural force. The wall can also induce structuring in the neighboring fluid only if the magnitude of the surface roughness is negligible compared with the particle diameter, d. Indeed, because of surface irregularities

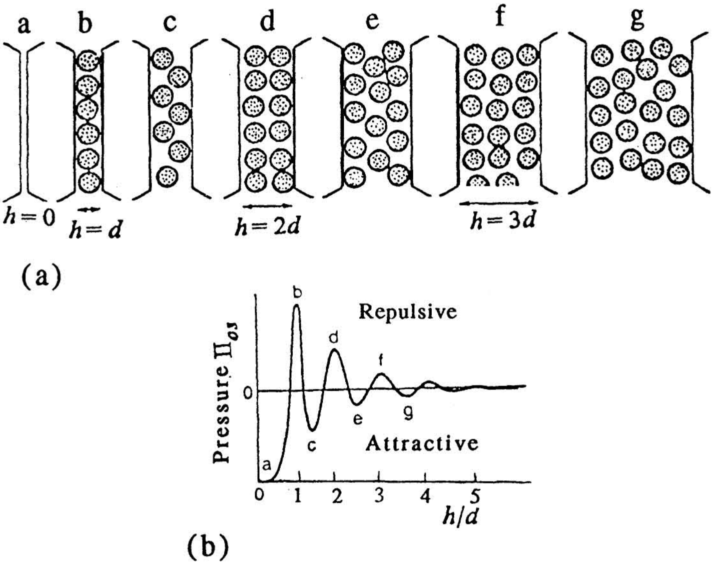


FIG. 15 Consecutive stages of thinning of a film containing spherical particles (a) and the respective oscillatory structural disjoining pressure (b). (After Israelachvili, 1992.)

the oscillations of $n(x)$ will be smoothed out and oscillatory structural force will not appear. However, if the film surfaces are fluid, the role of the surface roughness is played by the interfacial fluctuation capillary waves, whose amplitude (usually between 1 and 5 Å) is comparable with the diameter of the solvent molecules. That is why oscillatory solvation forces (due to structuring of solvent molecules) are observed only with liquid films, which are confined between smooth solid surfaces (Israelachvili, 1992). In order for structural forces to be observed in foam or emulsion films the diameter of the colloidal particles must be much larger than the amplitude of the surface corrugations, for instance $d \geq 40$ Å (see Nikolov and Wasan, 1989; Ivanov et al., 1992b).

In summary, the oscillatory structural forces are due to the overlapping of the two structured zones of spherical particles formed at two approaching smooth surfaces. The fact that each particle excludes some volume is of crucial importance: the period of the oscillations is in fact always about the particle diameter, d (Israelachvili, 1992; Ivanov et al., 1992b). In this aspect these structural forces are appropriately called the "volume exclusion forces" by Henderson (1988a,b), who derived an explicit formula for calculating the surface free energy per unit area, $f_{os}(h)$, due to the oscillatory structural forces:

$$f_{os}(h) = -\frac{6}{\pi}\eta kT\left[-\tilde{f}(h-d) + \frac{1}{2}\tilde{f}'''(h) - \tilde{f}''(h) + \tilde{f}'(h)\right] \tag{116}$$

where $\tilde{f}(h)$ is a function known analytically (see Hendereson, 1988a) and

$$\eta = \frac{\pi}{6}nd^3 \tag{117}$$

is the particle volume fraction. By substituting Eq. (116) into Derjaguin's approximation, Eq. (43), one can derive expression for the force, F, between two large spheres of radii R_1 and R_2 ($R_1, R_2 >> d$) imbedded into the hard sphere mixture. If $R_1 = R_2 = R$, one obtains $F = \pi R f_{os}(h)$. Figure 16 represents F/R vs. h/d for $nd^3 = 0.8$ calculated by Henderson (1988a) by means of Eq. (116). One sees that the structural force, F, exhibits typical decaying oscillations of period about the hard sphere diameter, d.

It should be noted that Eq. (116) is derived on the basis of the Percus-Yevick (1958) theory of a hard sphere mixture by inverting the Laplace transforms of the radial correlation function as determined by Lebowitz (1964). However, in practice the interparticle potential can be different from hard sphere potential. For example, the micelles of ionic surfactants interact via double layer repulsion (see Sec. III.C. above), whereas the micelles of the nonionic surfactants experience hydration forces, which can invert their sign depending on temperature (Kjellander, 1982; Claeson et al., 1986b). If such is the case one can obtain an estimate of the structural force by introducing an effective hard core diameter

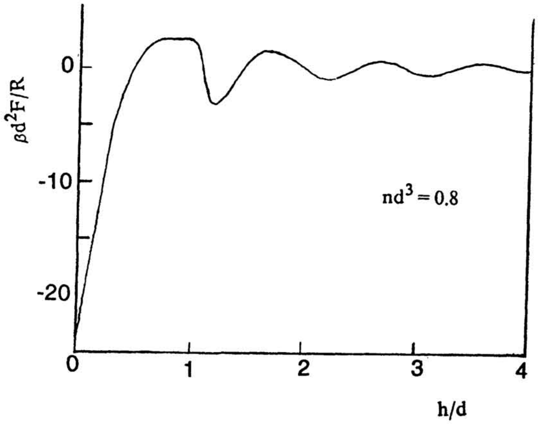


FIG. 16 Force, F, vs. surface-to-surface distance, h, between two identical spherical particles of radius R immersed in a "fluid" of smaller particles of diameter d and number density n; $1/\beta = kT$.

$$d_{eff} = \left(\frac{3}{2\pi}B_2\right)^{1/3} \tag{118}$$

where B_2 is the second virial coefficient in the virial expansion of particle osmotic pressure:

$$\frac{P_{osm}}{nkT} = 1 + B_2 n + \ldots \tag{119}$$

The value of B_2 can be determined by means of static light scattering (see, e.g. Evans, 1972).

As seen in Fig. 16 the structural force as calculated from Eq. (116) exhibits a discontinuity of the slope at $h = d$, a distance at which a hard sphere can just slip in between the solid surfaces. There are discontinuities of the higher-order derivatives at $h = md$, $m = 2, 3, \ldots$ (Henderson, 1986). Such singularities can lead to difficulties when differentiating Eq. (116) to calculate $\Pi_{osm} = \partial f_{os}/\partial h$. On the other hand, following the idea of Israelachvili (1992), one can propose a smooth function to estimate $\Pi_{os}(h)$:

$$\begin{aligned} \Pi_{os}(h) &= n(\infty)kT \cos\frac{2\pi h}{d} \exp\left(\frac{1}{2} - \frac{h}{d}\right), \qquad \text{for } h \geq \frac{d}{2} \\ &= -n(\infty)kT, \qquad \text{for } 0 \leq h \leq \frac{d}{2} \end{aligned} \tag{120}$$

where both the oscillatory period and the characteristic decay length of the envelope are equal to d, in agreement with the findings of Tarazona and Vicente (1985). In addition, Eq. (120) satisfies Eq. (115). By substituting Eq. (120) into Eq. (45) one can derive an estimate of the structural force energy:

$$\begin{aligned} f_{os}(h) &= \frac{n(\infty)kTd}{1+4\pi^2}\left(\cos\frac{2\pi h}{d} - 2\pi\sin\frac{2\pi h}{d}\right)\exp\left(\frac{1}{2}-\frac{h}{d}\right), \qquad \text{for } h \geq \frac{d}{2} \\ &= -n(\infty)kT\left(\frac{d}{1+4\pi^2}+\frac{d}{2}-h\right), \qquad \text{for } h \leq \frac{d}{2} \end{aligned} \tag{121}$$

It will be shown below that in spite of its semiempirical character, Eq. (120) can predict the number of the stepwise transitions in the thickness of stratifying foam films. We proceed with separate descriptions of solvation, depletion, and colloid volume exclusion forces.

2. Oscillatory Solvation Forces

When the role of hard spheres, like those depicted in Figs. 14 and 15, is played by the molecules of solvent, the resulting volume exclusion forces are called the ''solvation forces,'' or sometimes when the solvent is water, ''oscillatory hydration forces'' (see Israelachvili, 1992). The latter should be differentiated from the monotonic hydration forces, which have different physical origin and are considered separately in Sec. III.H., below.

The observation of oscillatory solvation forces became possible after the precise surface force balance of Israelachvili had been constructed. This balance gave the ability to measure the surface forces in thin liquid films confined between mica (or modified mica) surfaces and in this way to check the validity of DLVO theory down to thickness of about 5 Å, and even smaller. The ex-

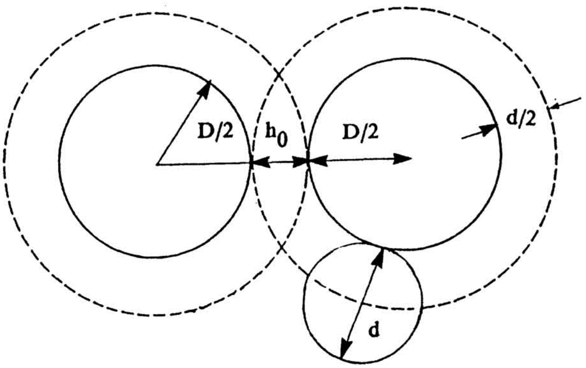


FIG. 17 Sketch of the overlap of the depletion zones around two spherical particles of diameter D separated at a surface-to-surface distance h_o; d is the diameter of the smaller particles.

perimental results with nonaqueous liquids with both spherical (CCl_4) or cylindrical (linear alkanes) shape showed that at larger separations DLVO is satisfied, whereas at separations of the order of several molecular diameters an oscillatory force is superimposed over the DLVO force law. In aqueous solutions oscillatory forces were observed at higher electrolyte concentrations with a periodicity of 0.22–0.26 nm: about the diameter of the water molecule. Since the oscillatory solvation forces can exist only between smooth solid surfaces, which is somewhat far from the scope of the present review (foam films), the reader is referred to the book by Israelachvili (1992) for more information and a comprehensive review of solvation forces.

3. Depletion Forces

Bondy (1939) observed coagulation of rubber latex in the presence of polymer molecules in the dispersion medium. This and other similar observations (for review see Vrij, 1976; de Hek and Vrij, 1981) remained unexplained until Asakura and Oosawa (1954, 1958) published a theory that attributed the observed interparticle attraction to the overlapping of the depletion layers at the surfaces of two approaching colloidal particles (see Fig. 17). The centers of the smaller particles of diameter d cannot approach the surface of a larger particle (of diameter D) at a distance shorter than $d/2$, which is the thickness of the depletion layer. When the two depletion layers overlap (see Fig. 17) some volume between the large particles becomes inaccessible for the smaller particles. This gives rise to an osmotic pressure, which tends to suck out the solvent between the bigger particles, thus forcing them against each other. The total depletion force experienced by one of the bigger particles is (Asakura and Oosawa 1954, 1958)

$$F_{dep} = -kTnS\,(h_o) \tag{122}$$

where the effective depletion area is

$$\begin{aligned} S(h_o) &= \frac{\pi}{4}(2D + d + h_o)(d - h_o), \qquad \text{for } 0 \le h_o \le d \\ S(h_o) &= 0, \qquad \text{for } d \le h_o \end{aligned} \tag{123}$$

Here h_o is the shortest distance between the surfaces of the larger particles and n is the numerical density of the smaller particles. By substituting Eq. (122) into Eq. (45) one can derive expression for the depletion interaction energy between the two larger particles, $U_{dep}(h_o)$. For $D >> d$ this expression reads (Asakura and Oosawa, 1958):

$$\frac{U_{dep}(h_o)}{kT} \approx -\frac{3}{2}\eta\frac{D}{d^3}(d - h_o)^2, \qquad 0 \le h_o \le d \tag{124}$$

where η is the small particle volume fraction as given by Eq. (117). The maximum value of U_{dep} at $h_o = 0$ is

$$\frac{U_{dep}(0)}{kT} \approx -\frac{3}{2}\eta\frac{D}{d} \tag{125}$$

For example, if $D/d = 50$ and $\eta = 0.1$, then $U_{dep}(0) = -7.5\ kT$. This depletion attraction turns out to be large enough to cause flocculation in dispersions. For example, Cowell et al. (1978), Vincent et al. (1980), and Sperry et al. (1981) examined the flocculation of polymeric latexes by water-soluble polymers, such as poly(ethylene oxide) and hydroxyethyl cellulose. De Hek and Vrij (1981) studied systematically the flocculation of sterically stabilized silica suspensions in cyclohexane by polystyrene molecules. Patel and Russel (1989a,b) investigated the phase separation and rheology of aqueous polystyrene latex suspensions in the presence of polymer (Dextran T-500); the stability of this dispersion is determined by the competition between electrostatic repulsion and depletion attraction (Aronson, 1989). An interplay of steric interaction and depletion attraction was studied theoretically by van Lent et al. (1990) for the case of polymer solution between two surfaces coated with anchored polymer layers. Joanny et al. (1979) and Russel et al. (1989) re-examined the theory of depletion interaction by taking into account the internal degrees of freedom of the polymer molecules; their analysis confirmed the earlier results of Asakura and Oosawa (1954, 1958).

In the case of plane-parallel films the depletion component of disjoining pressure is

$$\begin{aligned} \Pi_{dep}(h) &= -nkT, \qquad h < d \\ \Pi_{dep}(h) &= 0, \qquad h > d \end{aligned} \tag{126}$$

which is similar to Eq. (115). This is not surprising because in both cases we deal with excluded volume effect. In principle, it is possible to measure Π_{dep} by using the surface force balance of Israelachvili. However, this is not easy to realize experimentally, because the depletion force is often smaller than the other surface forces: see Luckham and Klein (1985). Evans and Needham (1988) succeeded in measuring the depletion energy of two interacting bilayer surfaces in a concentrated dextran solution; their results confirm the validity of Eq. (126).

In regard to the foam films, depletion interaction is present always when the film is formed from micellar surfactant solution; the micelles play the role of the particles expelled from the film. At higher micellar concentrations the volume exclusion interaction becomes more complicated: it follows the oscillatory curve depicted in Fig. 15b. In this case only the first minimum corresponds to the conventional depletion force. The physical consequences of the volume exclusion effect in foam films are considered in more details below.

4. Colloid Structural Forces: Stratifying Liquid Films

At the beginning of this century Johnnott (1906) and Perrin (1918) observed that soap films decrease their thickness by several stepwise transitions. This phenomenon, called ''stratification,'' was forgotten for a long time until Bruil and Lyklema (1971) and Friberg et al. (1974) studied systematically the role of ionic surfactant and electrolyte on the occurrence of the stepwise transitions. Keuskamp and Lyklema (1975) anticipated that some oscillatory interaction between the foam film surfaces must be responsible for the observed phenomenon. Kruglyakov (1974) and Kruglyakov and Rovin (1978) reported the existence of stratification with emulsion films. Experiments with stratifying films were carried out also by Manev et al. (1977, 1984).

The obtained experimental results call for some theoretical interpretation. Kruglyakov and Rovin (1978) and Manev et al. (1984) suggested that a possible explanation of the phenomenon can be the formation of lamellar liquid crystal structure inside the film. Such lamellar micelles are observed to form in surfactant solutions, but at concentrations much higher than those used in the experiments with stratifying films. The latter fact makes the explanation of lamellar liquid crystal problematic. Nikolov et al. (1988) and Basheva et al. (1991) observed stratification not only with micellar surfactant solutions but also with latex suspensions. The heights of the stepwise changes of the film thickness are approximately equal to the diameter of the spherical particles, contained in the foam film (Nikolov et al., 1988, 1990; Nikolov and Wasan, 1989); see Fig. 18. Hence, the experimental observations show that stratification is always observed when spherical colloidal particles are present in the film at sufficiently high concentration. Therefore, a realistic explanation can be that the stepwise transitions are due to a layer-by-layer destruction of a colloidal crystal of spherical particles formed inside the film (Nikolov et al., 1988). Similar colloidal crystals were observed in the bulk of latex suspensions by Hachisu et al. (1973), Furusawa and Tomotsu (1983), Ito et al. (1988), and many others. In other words, the oscillatory force between the two film surfaces can be attributed to the same volume exclusion effect studied theoretically by Henderson (1988a,b): the role of the hard spheres this time is played by the colloidal particles. In particular, when the particle is charged, the effective hard sphere radius includes also the thickness of the double layer around the particle (Nikolov and Wasan, 1989).

To illustrate that the colloid structural forces (the volume exclusion effects) are large enough to stabilize foam films, let us estimate the heights of the disjoining pressure maxima as predicted by Eq. (120):

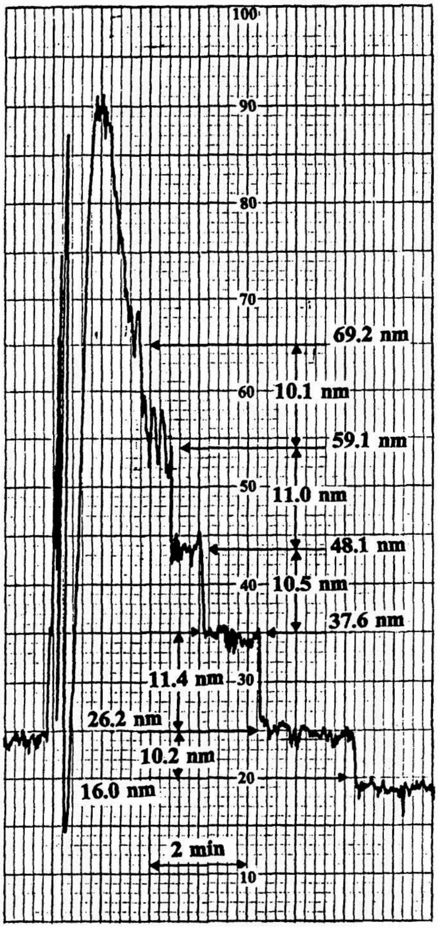


FIG. 18 Intensity of reflected light (arbitrary units) vs. time interferogram for a thinning foam film containing micelles of nonionic surfactant [$CH_3(CH_2)_{12}(O\text{-}CH_2\text{-}CH_2)_{30}OH$]. The steps are due to the stepwise thinning of the film. (From Nikolov et al. 1988, 1990.)

$$\Pi_{os}^{(1)} = n_{\infty}kTe^{-1/2}, \qquad \Pi_{os}^{(k)} = \Pi_{os}^{(1)}\, e^{-(k-1)}, \qquad k = 2,3,\ldots \tag{127}$$

Metastable films containing one or more layers of particles can be observed at film thickness h only if the equation $\Pi_{os}(h) = P_c$ is satisfied, where P_c is the outer capillary pressure forcing the film surfaces toward each other (van der Waals and double layer interactions neglected). A necessary condition for existence of solutions of this equation is

TABLE 1 Micellar Solutions of Sodium Dodecyl Sulfate (SDS)

	SDS Concentrations (mol/L)		
	0.03	0.06	0.10
n_∞	3.64×10^{-4}	8.34×10^{-4}	1.46×10^{-3}
P_c (N/m^2)	52.8	51.4	50.5
$\Pi_{os}^{(1)}$ (N/m^2)	545	1249	2186
$\Pi_{os}^{(2)}$ (N/m^2)	201	460	804
$\Pi_{os}^{(3)}$ (N/m^2)	74	169	296
$\Pi_{os}^{(4)}$ (N/m^2)	27	62	109
$\Pi_{os}^{(5)}$ (N/m^2)	10	23	40

$$\Pi_{os}^{(k)} > P_c, \qquad k = 1,2,3,\ldots \tag{128}$$

In fact, the number of maxima satisfying Eq. (128) determines the number of the observable stepwise transitions.Table 1 contains data for micellar solutions of sodium dodecyl sulfate (SDS) taken from Nikolov and Wasan (1989) and Nikolov et al. (1989). The values of $\Pi_{os}^{(k)}$ are calculated by using Eq. (127). Comparison of the data in Table 1 with Eq. (128) shows that one should expect three stepwise transitions with $C_{SDS} = 0.03$ mol/L, four transitions with 0.06 mol/L, and four to five transitions with 0.10 mol/L. This is exactly what is observed experimentally: see Nikolov et al. (1989). We are aware that such an agreement can be fortuitous because of the approximated character of Eqs. (120) and (127), and because the approximation of the osmotic repulsion between the micellar counterion atmospheres with hard core repulsion can be not entirely adequate. Table 1 nevertheless provides at least a numerical illustration of the order of magnitude of the colloid structural forces in foam films. A theoretical model of stratifying films was published by Nikolov et al. (1989). It predicted well the thickness of the metastable films; however, the existence of a colloid crystal of simple cubic packing inside the film was presupposed as a first step toward quantitative description. The mechanism of stratification was studied theoretically by Kralchevsky et al. (1990). The appearance and expansion of black spots in the stratifying films were described as a process of condensation of vacancies in the colloid crystal structure. Barker et al. (1991) investigated the diffusion of vacancies in a one-dimensional model of colloidal crystal by solving numerically the Fokker-Planck equation.Two pronounced effects with stratifying films deserve to be mentioned. First, the increase of electrolyte concentration leads to smoother and faster thinning of the foam films from ionic surfactant solutions. When the electrolyte concentration is high enough the stepwise transitions disappear. This can be explained by suppression of the oscillatory structural forces due to decrease of effective micelle volume fraction because of shrinkage of the counterion atmospheres: see Nikolov and Wasan (1989). Second, in the case of nonionic surfactant micelles the *increase* of temperature leads to a similar effect: disappearance of the stepwise character of film thinning: see Nikolov et al. (1990). This can be attributed to the change in the intermicellar interaction from repulsive to attractive with the increase of temperature (Claesson et al., 1986b). As a result the second virial coefficient and the effective particle volume fraction [cf. Eq. (118)] decrease dramatically, which causes degeneration of the oscillatory structural forces into depletion forces. In contrast, the *decrease* in temperature leads to formation of very stable thick foam films, containing several micellar layers. Such foams can find application in enhanced tertiary oil recovery (Wasan et al., 1988). The electrolyte and temperature dependence of the colloidal structural forces provide a tool for control of the stability of foams and other dispersions containing small spherical surfactant micelles or other colloidal particles. Oscillatory structural forces due to micelles and microemulsion droplets were recently directly measured by means of a surface force balance: see Richetti and Kékicheff (1992) and Parker et al. (1992).

In conclusion, the addition of small colloidal particles (macromolecules, micelles) to a liquid dispersion (foam, emulsion, suspension) leads to destabilization at small particle concentrations (due to depletion force) and to stabilization at higher concentration (due to oscillatory structural force).

H. Repulsive Hydration and Attractive Hydrophobic Forces

These surface forces are both observed in thin *aqueous* films. Their appearance is somehow connected with the unique properties of the water as solvent: high dielectric constant and formation of extensive in range H-bonding network (Stanley and Teixeira, 1980).

1. Repulsive Hydration Forces

In their experiments with films from aqueous electrolyte solutions confined between two mica surfaces Israelachvili and Pashley (1982) and Pashley (1981a,b) examined the validity of DLVO theory at small film thickness. At electrolyte concentrations below 10^{-4} mol/L (KNO_3 or KCl) they observed the typical DLVO maximum (cf. Figs. 8 and 19). However, at electrolyte concentrations higher than 10^{-3} mol/L they did not observe the expected DLVO maximum and primary minimum; instead a strong short range repulsion was detected. On an empirical basis this force, called the "hydration repulsion," appears to follow an exponential law (Israelachvili, 1992):

$$f_{\text{hydr}}(h) = f_o e^{-h/\lambda_o} \tag{129}$$

where the decay length $\lambda_o \approx 0.6$–1.1 nm for 1:1 electrolytes (Pashley, 1982)

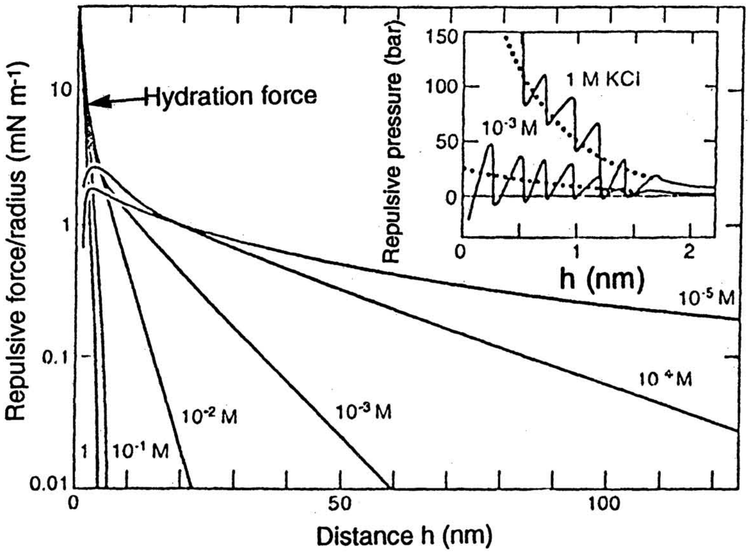


FIG. 19 Measured force between two curved mica surfaces in KCl aqueous solutions at different electrolyte concentrations. The inset shows the overlap of hydration repulsion and oscillatory structural force. (From Israelachvili, 1992.)

and f_o depends on the hydration of the surfaces but is usually below 3–30 mJ/m^2 (Israelachvili, 1992). As seen in the inset in Fig. 19, the oscillatory solvation force is superimposed on the monotonic repulsive hydration force. It appears that the oscillatory force is simply additive with the monotonic hydration and DLVO forces, suggesting that these arise from essentially different mechanisms (Israelachvili, 1992).

The physical importance of the hydration force is that it stabilizes some dispersions, preventing coagulation in the primary minimum. It is believed that the hydration force is connected with binding of strongly hydrated ions at the interface. This is probably the explanation of the experimental results of Healy et al. (1978), who found that even high electrolyte concentrations cannot cause coagulation of amphoteric latex particles due to binding of strongly hydrated Li^+ ions at the particle surfaces. If the Li^+ ions are replaced by weakly hydrated Cs^+ ions, the hydration repulsion becomes negligible compared with the van der Waals attraction, and the particles coagulate as predicted by DLVO theory. Hence, the hydration repulsion can be regulated by ion exchange. This fact can be used for controlling some technological processes related to colloidal and bubble coalescence (see Lessard and Zieminski, 1971; Frens and Overbeek, 1972; Elimelech, 1990).

For the time being there is no generally accepted theory of the repulsive hydration forces. The most simple and physically transparent model was proposed by Henderson and Lozada-Cassou, 1986, who considered two subsurface (Stern) layers of strongly oriented water molecules attached to the two approaching film surfaces. A lower dielectric constant was ascribed to these two layers, and analytical expression was derived for the hydration force from the linearized Poisson-Boltzmann equation. The results are very similar to the experimentally observed repulsion (Henderson, 1988b).

Attard and Batchelor (1988) argue that the hydration repulsion forces do not have purely electrostatic origin. Indeed, the measurements of surface forces in films from dipolar but nonassociated fluids do not give such a repulsion. These authors propose an alternative model, attributing the hydration force to the H-bond effects.

For more information on hydration force the reader is referred to the book by Israelachvili, (1992) and the literature quoted therein.

2. Attractive Hydrophobic Forces

It is a known experimental fact that if liquid helium is placed in a beaker it rapidly climbs up the walls and can leave the beaker if the latter is not properly closed (see Sabisky and Anderson, 1973). The explanation of this phenomenon is that the compound Hamaker constant of helium films on solid is negative, which leads to *repulsive* van der Waals disjoining pressure (Dzyaloshinskii et al., 1961). The latter stabilizes the liquid helium films and favors spontaneous spreading of liquid helium on substrata.

Since the compound Hamaker constant of water films on hydrocarbons (liquid or solid) is also negative, one could expect formation of stable water films on hydrocarbons and spontaneous spreading of water on hydrocarbons, if only the van der Waals interaction were operative. However, the experiments show just the opposite: the water does not spread spontaneously on hydrocarbons and the aqueous films on hydrocarbons are strongly unstable (see, e.g., Tchaliovska et al., 1990). The cause of these effects is a strong attractive *hydrophobic force*, which is found to appear in aqueous films in contact with hydrophobic surfaces. The experiments showed that the nature of the hydrophobic force is different from the van der Waals and double layer interactions (Israelachvili and Pashley, 1982; Pashley et al., 1985; Rabinovich and Derjaguin, 1988; Parker et al., 1989; Christenson et al., 1989, 1990). It turns out that the hydrophobic interactions decay exponentially with the increase of the film thickness, h. The hydrophobic free energy per unit area of the film can be described by means of the equation

$$f_{\text{hydrophobic}} = -2\gamma e^{-h/\lambda_o} \tag{130}$$

where typically $\gamma = 10$–$50\ \text{mJ/m}^2$, and $\lambda_o = 1$–2 nm in the range $0 < h < 10$ nm (Israelachvili, 1992). Larger decay length, $\lambda_o = 12$–16 nm, was reported by

Christenson et al. (1990) for the range 20 nm $< h <$ 90 nm (see Fig. 20). This amazingly long-ranged attraction entirely dominates the van der Waals forces. In particular, it can create rupture of foam films that contact small oil droplets or large hydrophobic surfaces. These effects are important for many technological and practical processes, such as enhanced tertiary oil recovery, fire fighting, and others.

There is no generally accepted explanation of hydrophobic forces. Nevertheless, many authors agree that H-bonding in water and other associated liquids is the main underlying factor (see Eriksson et al., 1989; Israelachvili, 1992). The qualitative picture of hydrophobic interaction seems to be the following. If there were no thermal motion, the water molecules would form an ice-like tetrahedral network with four nearest neighbors per molecule (instead of 12 neighbors at close packing), since this configuration is favored by the H-bond formation. However, due to the thermal motion a water molecule forms only about 3–3.5 transient H-bonds with its neighbors in the liquid (Joesten and Schaad, 1974), with the lifetime of an H-bond being about 10^{-11} s. When a water molecule is brought in contact with a non-H-bonding molecule or surface, the number of its possible favorable configurations is decreased. This effect will also reduce the number of advantageous configurations of the neighbors of the subsurface water molecules and some ordering will propagate in the depth of the liquid. Such ordering in the vicinity of the hydrophobic wall is entropically unfavorable. When two hydrophobic surfaces approach each other the entropi-

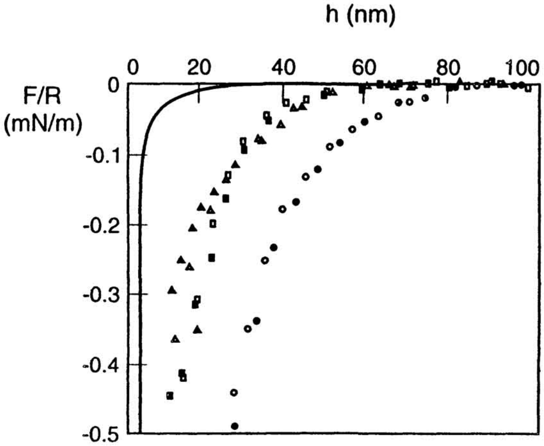


FIG. 20 Measured force of hydrophobic attraction between two hydrophobized curved mica surfaces across water; *h*, surface-to-surface separation; (●, ○), pure water; (■,□), 0.01 M $MgSO_4$; (▲,△), 0.1 M $MgSO_4$. The solid line is the expected van der Waals attraction. (From Christenson et al., 1990.)

cally unfavored water is ejected into the bulk, thereby reducing the total free energy of the system. The resulting attraction can, in principle, explain the hydrophobic forces. However, the existing theory (Eriksson et al., 1989) is still far from a quantitative explanation of the experimental data. It is worthwhile noting that an alternative theoretical approach exists (Attard, 1989; Podgornik, 1989), which attributes the hydrophobic forces to the existence of an anomalous electrostatic response in water layers adjacent to the hydrophobic surface.

A problem of practical importance is how to control the hydrophobic attraction. It was found experimentally that 1:1 and 2:2 electrolytes (Christenson et al., 1989, 1990) reduce considerably the long-range part of the hydrophobic attraction. Their results suggest that this reduction is due to ion adsorption or ion exchange at the surfaces rather than to the presence of electrolyte in the solution itself. Therefore, the practical implication (which might seem trivial) is that the hydrophobic attraction across aqueous films can be suppressed by making the surfaces more hydrophilic. Besides, some special polar solutes are found to suppress the hydrophobic interaction at molecular level in the bulk of solution: for example, urea, $(NH_2)_2CO$, dissolved in water can cause proteins to unfold. These polar solutes are believed to destroy the H-bond structuring in water; therefore they are called sometimes ''chaotropic agents'' (Israelachvili, 1992). The effect of such additives on the hydrophobic interactions between macroscopic surfaces has not yet been studied.

At the end of this section we should note that a great development has been achieved in the field of surface forces during the last 15 years. This development was undoubtedly promoted by the construction of precise surface force balances. Fig. 21 shows the newly established non-DLVO surface forces in accordance with their physical origin. A review of the fluctuation wave forces (not discussed here), which give rise to a short-range repulsion, has recently been published by Israelachvili and Wennerström, (1992).

IV. THERMODYNAMICS OF THIN LIQUID FILMS

A. Macroscopic Description of a Thin Liquid Film; Membrane and Detailed Models

1. Conditions for Equilibrium

Two different but supplementary approaches (models) are used in the macroscopic description of a thin liquid film. The first, the ''membrane approach,'' treats the film as a membrane of zero thickness and one tension, γ, acting tangentially to the membrane: see the right side of Fig. 22. In the ''detailed approach'' the film is modeled as a homogeneous liquid layer of thickness h and two surface tensions σ_1^f and σ_2^f. In the case of thin liquid film formed between two identical bubbles, one has $\sigma_1^f = \sigma_2^f = \sigma^f$, as sketched in Fig. 22. The pressure

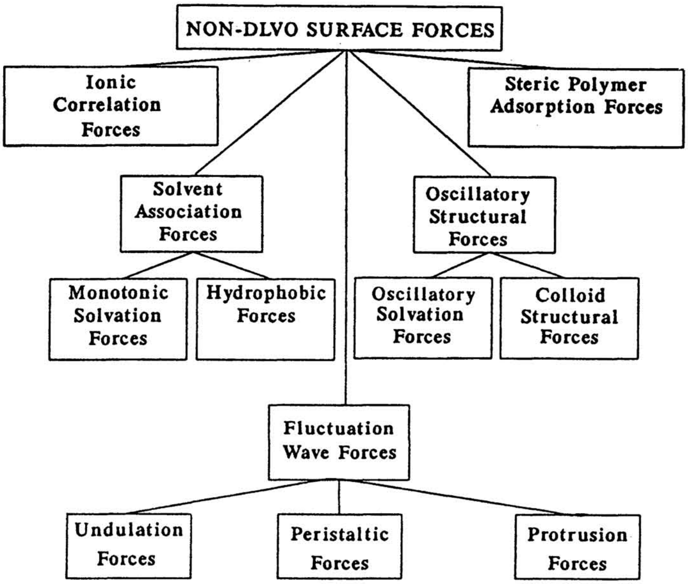


FIG. 21 Systematization of the various non-DLVO surface forces in accordance with their physical origin.

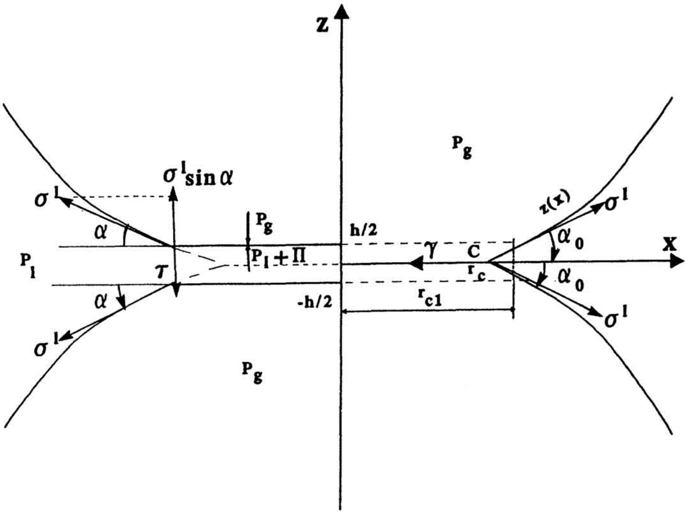


FIG. 22 The "membrane" (right) and "detailed" (left) models of a thin liquid film.

of the gas inside the bubble, P_g, is larger than the pressure, P_l, of the liquid in the Plateau border. Their difference

$$P_c = P_g - P_l \tag{131}$$

represents the capillary pressure of the liquid meniscus. By making the balance of forces acting on a plate of unit width 1 and height h placed normally to the film at $-h/2 < z < h/2$ (Fig. 22) one can derive (Rusanov, 1967)

$$\gamma = 2\sigma^f + P_c h \tag{132}$$

Eq. (132) expresses, in fact, a condition for equivalence between the membrane and detailed model with respect to the lateral force. For the normal force let us consider a parcel of unit area from the film surface in the detailed approach. Since the pressure in the gas phase, P_g, is larger than the pressure inside the liquid, P_l, the mechanical equilibrium of the film surface is ensured by the additional disjoining pressure, Π, due to the interaction between the film surfaces (Derjaguin and Kussakov, 1939):

$$P_c = P_g - P_L = \Pi \tag{133}$$

(see Fig. 22). Note that Eq. (133) is satisfied only at equilibrium conditions; at nonequilibrium conditions the viscous force can also contribute to the force balance per unit area of the film. In the case of a spherical film, the film in the membrane approach is represented as a part of spherical surface whose radius of curvature is r_o; the respective curvature radii of the film surfaces are r_1 and r_2 (see Fig. 23). Then Eqs. (132) and (133) can be generalized to read (Ivanov and Kralchevsky, 1988):

$$\gamma r_o^2 = \sigma_1 r_1^2 + \sigma_2 r_2^2 + \Pi h r_o^2, \tag{134}$$

$$\frac{2\sigma_1}{r_1} = P_\alpha - P_l - \Pi\frac{r_1^2}{r_o^2}; \qquad \frac{2\sigma_2}{r_2} = P_l - P_\beta + \Pi\frac{r_2^2}{r_o^2}, \tag{135}$$

where P_α and P_β are the pressures in the respective adjacent phases α and β (see Fig. 23), which can be two bubbles or drops of different size.

2. Basic Thermodynamic Equations

In the framework of the membrane approach the film can be treated as a single surface phase whose Gibbs-Duhem equation reads (see, e.g., Martynov and Derjaguin, 1962; Ivanov and Kralchevsky, 1988):

$$d\gamma = -s^f dT - \sum_{i=1}^{k} \Gamma_i d\mu_i \tag{136}$$

where γ is the film tension, T is temperature, s^f is excess entropy per unit area of the film, Γ_i, and μ_i is the adsorption and the chemical potential of the ith

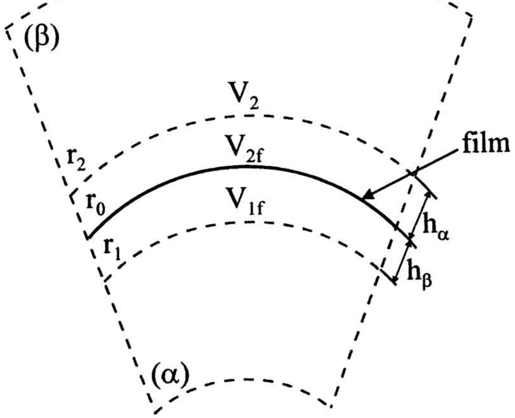


FIG. 23 Macroscopic moled of a spherical thin film. r_0, radius of the surface of film tension; r_1 and r_2, radii of the two film surfaces.

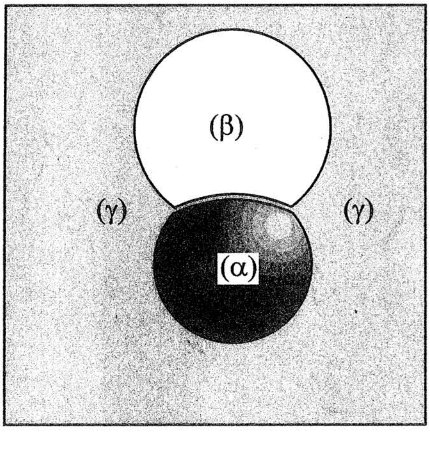


FIG. 24 Sketch of a thin film from phase γ intervening between two attached fluid particles, α and β.

component. If the film is spherical, like those depicted in Fig. 24, we suppose that the membrane of zero thickness representing the film coincides with the so-called surface of tension, hence curvature term does not appear in the right-hand side of Eq. (136). For details see, for example, Ivanov and Kralchevsky (1988). The Gibbs-Duhem equations of the three bulk fluid phases (see Fig. 24) read

$$dP_\chi = S_v^\chi dT + \sum_{i=1}^{k} n_i^\chi d\mu_i\,, \qquad \chi = \alpha,\ \beta,\ \gamma, \tag{137}$$

where S_v^χ and n_i^χ are entropy and number of molecules per unit volume, and P_χ is pressure ($\chi = \alpha,\ \beta,\ \gamma$). The capillary pressures of the two fluid particles depicted in Fig. 24 are:

$$P_{c1} = P_\alpha - P_\gamma \qquad \text{and} \qquad P_{c2} = P_\beta - \mathrm{P}_\gamma \tag{138}$$

Eq. (137) provides expressions for dP_{c1} and dP_{c2}. Let us multiply the expression for dP_{c1} by h_α and dP_{c2} by h_β and then let us subtract the resulting equations from the Gibbs-Duhem equation of the film, Eq. (136). The result can be transformed to read

$$d\gamma = -\tilde{s}dT + h_\alpha dP_{c1} + h_\beta dP_{c2} - \sum_{i=1}^{k} \tilde{\Gamma}_i d\mu_i \tag{139}$$

where

$$\tilde{s} = s^f + (s_v^\alpha - s_v^\gamma)h_\alpha + (s_v^\beta - s_v^\gamma)h_\beta \tag{140}$$

$$\tilde{\Gamma}_i = \Gamma_i + (n_i^\alpha - n_i^\gamma)h_\alpha + (n_i^\beta - n_i^\gamma)h_\beta\,, \qquad i = 1, \ldots, \mathrm{k} \tag{141}$$

The physical meaning of the above formal procedure is the following. Imagine two equidistant surfaces of radii r_1 and r_2, parallel to the surface of tension of the film (of radius r_o; see Fig. 23). The latter divides the space between them into two parts of volumes V_{1f} and V_{2f}. The layer of volume $V_{1f} + V_{2f}$ is thought to be filled with the bulk reference phase (γ). For this model liquid layer Rusanov, (1983) derived Eqs. (139–141) with

$$h_\alpha = \frac{V_{1f}}{A_o} \approx r_o - r_1\,; \qquad h_\beta = \frac{V_{2f}}{A_o} \approx r_2 - r_o \tag{142}$$

where A_o is the area of the surface of tension. $\tilde{s}$ and Γ_i (see Eqs. (140) and (141)) are the excess surface entropy and adsorption with respect to this liquid layer. A comparison between Eqs. (139) and (136) shows that there are two additional differentials in Eq. (139). They correspond to the two supplementary degrees of freedom connected with the choice of the two parameters h_α and h_β. To specify the model one needs two additional equations for the determination of h_α and h_β. For example, let these equations be

$$\tilde{\Gamma}_1 = 0, \qquad \tilde{\Gamma}_2 = 0 \tag{143}$$

Equation (143) requires h_α and h_β to be defined in such a way, that the sum $h_\alpha + h_\beta$ equals the thickness of a liquid layer from phase γ, containing the same amount of components 1 and 2 as the real film. This thickness is called the *thermodynamic thickness* of the film (Ivanov and Toshev, 1975). It can be of the order of the real film thickness if components 1 and 2 are chosen in an appropriate way.

From Eqs. (139) and (143) one obtains

$$d\gamma = -\tilde{s}\,dT + h_\alpha dP_{c1} + h_\beta dP_{c2} - \sum_{i=3}^{k} \tilde{\Gamma}_i d\mu_i \tag{144}$$

For a flat symmetrical film (e.g., when the two bubbles [or drops], α and β, depicted in Fig. 24 are identical), $P_{c1} = P_{c2} = P_c$ and from Eqs. (133) and (144) one obtains (Toshev and Ivanov, 1975)

$$d\gamma = -\tilde{s}dT + hd\Pi - \sum_{i=3}^{k} \tilde{\Gamma}_i d\mu_i \tag{145}$$

Where $h = h_\alpha + h_\beta$. A corollary of Eq. (145) is the Frumkin (1938) equation

$$\left(\frac{\partial\gamma}{\partial\Pi}\right)_{T,\mu_3,\ldots,\mu_k} = h \tag{146}$$

Equation (146) predicts a rather weak dependence of the film tension γ on the disjoining pressure, Π, in equilibrium thin films (small h). By means of Eqs. (132) and (133), Eq. (145) can be transformed to read

$$2d\sigma^f = -\tilde{s}\,dT - \Pi\,dh - \sum_{i=3}^{k} \tilde{\Gamma}_i\,d\mu_i \tag{147}$$

From Eq. (147) one can derive the following useful relations (Toshev and Ivanov, 1975):

$$2\left(\frac{\partial\sigma^f}{\partial h}\right)_{T,\mu_3,\ldots,\mu_k} = -\Pi \tag{148}$$

$$\sigma^f(h) = \sigma^l + \frac{1}{2}\int_h^\infty \Pi(h)\,dh \tag{149}$$

with σ^l being the surface tension of the bulk liquid. In particular, Eq. (149) allows calculation of the film surface tension when the disjoining pressure isotherm is known.

Note that the above thermodynamic equations are in fact corollaries from the Gibbs-Duhem equation of the membrane approach Eq. (136). There is an equivalent and complementary approach, which treats the two film surfaces as separate surface phases with their own fundamental equations (Rusanov, 1967; Kralchevsky and Ivanov, 1985a); thus for a flat symmetrical film one postulates

$$dU^f = T\,dS^f + 2\sigma^f dA + \sum_{i=1}^{k} \mu_i\, dN_i^f - \Pi A dh\,, \tag{150}$$

where A is area; U^f, S^f, and N_i^f are excess internal energy, entropy, and number of molecules ascribed to the film surfaces. Equation (150) compared with Eq. (2) contains an additional term, $\Pi A dh$, which takes into account the dependence of the film surface energy on the film thickness. Equation (150) provides an alternative thermodynamic definition of disjoining pressure:

$$\Pi = -\frac{1}{A}\left(\frac{\partial U^f}{\partial h}\right) \tag{151}$$

When the disjoining pressure isotherm is of DLVO type, see Figs. 8 and 25 (for not too large a P_c), the equilibrium condition, Eq. (133), can be satisfied in three points, depicted in Fig. 25. Point 1 corresponds to a film, which is stabilized by the double layer repulsion; sometimes such a film is called the *primary film* or *common black film*. Point 2 corresponds to unstable equilibrium and cannot be observed experimentally. Point 3 corresponds to a very thin film, which is stabilized by the short range repulsion; such a film is called the *secondary film* or *Newton black film*. Transitions from common to Newton black films are often

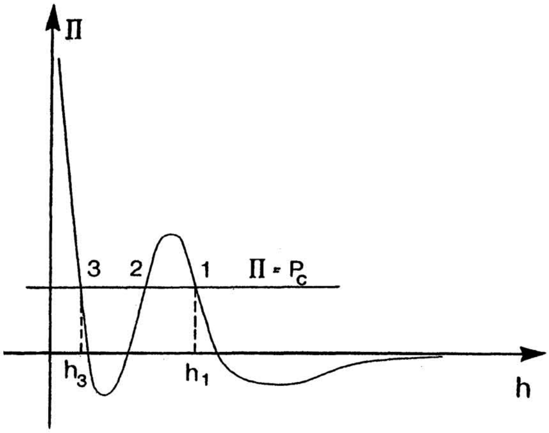


FIG. 25 Schematic disjoining pressure isotherm Π vs. h illustrates the formation of a primary film at $h = h_1$ and a secondary film at $h = h_3$.

observed with foam films: for a review of thermodynamics of flat and curved liquid films see de Feijter (1988) and Ivanov and Kralchevsky, (1988).

B. The Transition Zone Between Thin Film and Plateau Border

1. Macroscopic Description

The thin liquid films formed in foams or emulsions exist in permanent contact with the bulk liquid in the Plateau border, encircling the film. From a macroscopic viewpoint, the boundary between film and Plateau border is treated as a three-phase contact line: the line at which the two surfaces of the Plateau border (the two concave menisci sketched in Fig. 22) intersect at the plane of the film (see the right side of Fig. 22). The angle, α_o, subtended between the two meniscus surfaces represents the thin film contact angle. The force balance at each point of the contact line is given by Eq. (15) with $\sigma_{12} = \gamma$. In the case of a symmetrical flat film with circular contact line, like those depicted in Fig. 22, Eq. (15) yields

$$\gamma + \frac{\kappa}{r_c} = 2\sigma^l \cos\alpha_o \tag{152}$$

where r_c is the radius of the contact line.

There are two film surfaces and two contact lines in the detailed approach (see the left side of Fig. 22). They can be treated thermodynamically as linear phases and a one-dimensional counterpart of Eq. (150) can be postulated (Kralchevsky and Ivanov, 1985a):

$$dU^L = T\,dS^L + 2\tilde{\kappa}dL + \sum_i \mu_i dN_i^L + \tau L dh \tag{153}$$

Here U^L, S^L, and N_i^L are linear excesses, $\tilde{\kappa}$ is the line tension in the detailed approach, and

$$\tau = \frac{1}{L}\left(\frac{\partial U^L}{\partial h}\right) \tag{154}$$

is a one-dimensional counterpart of the disjoining pressure: cf. Eq. (151). The quantity τ, called the transversal tension, takes into account the interaction between the two contact lines. The force balance at each point of the contact line in general reads (Ivanov and Kralchevsky, 1988):

$$\sigma_i^f + \sigma_i^l + \sigma_i^\kappa + \tau_i = 0\,, \qquad i = 1, 2 \tag{155}$$

The quantities taking part in Eq. (155) are depicted in Fig. 26, where $|\sigma_i^\kappa| = \tilde{\kappa}_i/r_{ci}$. For the case of a flat symmetrical film (Fig. 22), the tangential and normal projection of Eq. (155) with respect to the plane of the film reads:

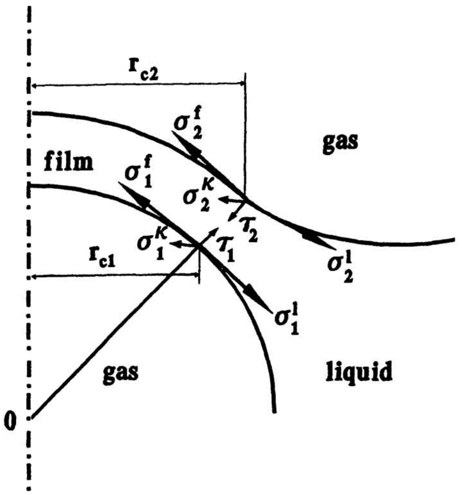


FIG. 26 The force balance in each point of the two contact lines represents the foam film periphery in the detailed macroscopic approach.

$$\sigma^f + \frac{\tilde{\kappa}}{r_{c1}} = \sigma^l \cos\alpha \tag{156}$$

$$\tau = \sigma^l \sin\alpha \tag{157}$$

Note that in general $\alpha \neq \alpha_o$ (see Fig. 22). Both α_o and α can depend on the radius of the contact line due to line tension effects. In the case of a straight contact line, from Eqs. (149) and (156) one derives (Ivanov and Toshev, 1975)

$$\cos\alpha|_{r_{c1}=\infty} = \frac{\sigma^f}{\sigma^l} = 1 + \frac{1}{2\sigma^1}\int_h^\infty \Pi(h)\,dh \tag{158}$$

Since $\cos\alpha \leq 1$, the surface tension of the film must be less than the bulk solution surface tension, $\sigma^f < \sigma^l$, and the integral term in Eq. (158) must be negative in order for a nonzero contact angle to be formed. Hence, the contact angle α and the transversal tension τ [cf. Eq. (157)] are integral effects of the long-range attractive surface forces acting in the transition zone between the film and Plateau border, where $h > h_1$ (or $h > h_3$) (see Fig. 25); see also Eq. (166). In the case of a bubble attached to a surface (Fig. 27) or in the case of two identical attached (flocculated) bubbles or drops, the integral of the pressure $P_l = P_o - \Delta\rho g z$ over the bubble surface equals the buoyancy force, F_b, which at equilibrium is counterbalanced by the disjoining pressure and transversal tension forces (Nikolov et al., 1986b):

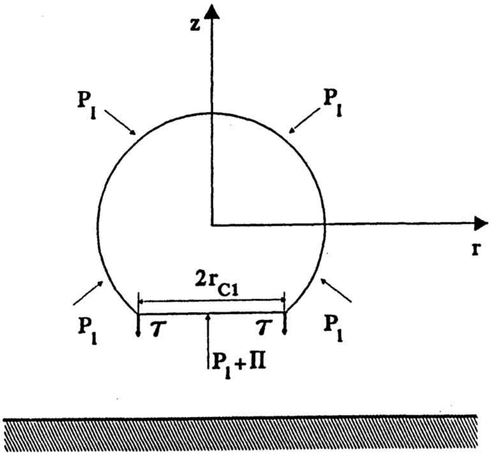


FIG. 27 Schematic presentation of the forces exerted on a fluid particle (bubble, droplet) attached to a solid substrate. Π, disjoining pressure; τ, transversal tension; P_l, pressure in the liquid phase.

$$2\pi r_{c1}\tau = F_b + \pi r_{c1}^2\,\Pi \tag{159}$$

F_b is negligible for bubbles of diameter smaller than approximately 300 μm. Then the forces due to τ and Π counterbalance each other. Hence at equilibrium the role of the repulsive disjoining pressure is to keep the film thickness uniform, whereas the role of the attractive transversal tension is to keep the bubble (droplet) attached to the surface. In other words, the bubble sticks to the surface at its contact line where the long-range attraction prevails (see Fig. 25), whereas the repulsion predominates inside the film. For zero contact angle, τ is also zero [Eq. (157)] and the particle will rebound from the surface (the other particle) if some additional external force does not keep it attached.

2. Micromechanical Description

From a microscopic viewpoint the transition between film surface and meniscus is smooth, as depicted in Fig. 28. As the film thickness increases across the transition zone, the disjoining pressure decreases and tends to zero inside the Plateau border. The surface tension varies from σ^f to σ^l in the Plateau border. By using local force balance considerations one can derive the equations governing the shape of the meniscus in the transition zone; for the case of axial symmetry depicted in Fig. 28 these equations read (Kralchevsky and Ivanov, 1985b):

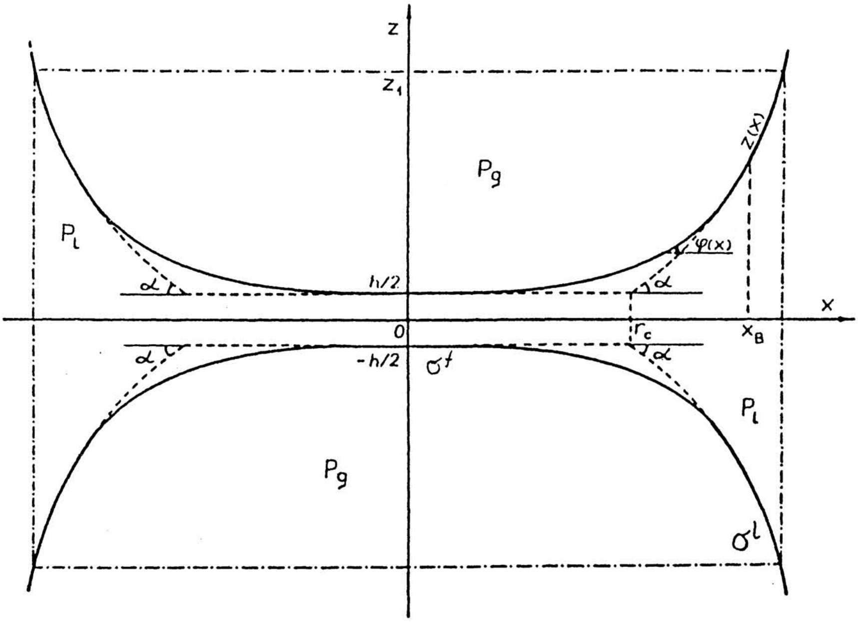


FIG. 28 Sketch of the liquid film between two attached fluid particles (bubbles, droplets). The solid and dashed lines represent the real and extrapolated interfaces, respectively.

$$\frac{d}{dx}(\sigma \sin \varphi) + \frac{1}{x}\sigma(x) \sin \varphi(x) = P_c - \Pi(x) \tag{160}$$

$$-\frac{d}{dz}(\sigma \cos \varphi) + \frac{1}{x}\sigma(x) \sin \varphi(x) = P_c \tag{161}$$

$$\tan \varphi(x) = \frac{dz}{dx} \tag{162}$$

where $\varphi(x)$ is the running slope angle. The Eqs. (160–162) allow calculation of the three unknown functions, $z(x)$, $\varphi(x)$, and $\sigma(x)$, provided that the disjoining pressure $\Pi(x)$ is known from the microscopic theory. By eliminating P_c between Eqs. (160) and (161) one can derive

$$\frac{d\sigma}{dx} = -\Pi(x)\sin \varphi(x) \tag{163}$$

This result shows that the hydrostatic equilibrium in the transition region is ensured by simultaneous variation of σ and Π. Eq. (163) represents a generalization of Eq. (148) for a film of uneven thickness and axial symmetry. Generalization of Eqs. (160–163) for the case of more complicated geometry is also available (Kralchevsky and Ivanov, 1990).

In the Plateau border $z >> h$, $\Pi \rightarrow 0$, $\sigma \rightarrow \sigma^l$ = const and both Eqs. (160) and (161) reduce to

$$\sigma \left(\frac{d}{dx} \sin \varphi + \frac{1}{x} \sin \varphi \right) = P_c \tag{164}$$

which is one of the possible forms of the usual Laplace equation, Eq. (12) (see, e.g., Princen, 1969). The macroscopic contact angle α is defined as the angle at which the extrapolated meniscus, obeying Eq. (164), meets the extrapolated film surface: see Fig. 28 and Ivanov et al. (1978). The real surface, shown with solid line in Fig. 28, differs from this extrapolated (idealized) profile, which is shown by a dashed line in Fig. 28, because of the interactions between the two film surfaces, which is taken into account in Eq. (160), but not in Eq. (164). To compensate for the difference between the real and idealized system, line and transversal tensions are ascribed to the contact line in the macroscopic approach. In particular, the line tension makes up for the differences in surface tension and running slope (Kralchevsky and Ivanov, 1985b)

$$\frac{\tilde{\kappa}}{r_c} = \int_0^{x_B} \left[\left(\frac{\sigma \sin^2 \varphi}{x \cos \varphi} \right)^{\text{real}} - \left(\frac{\sigma \sin^2 \varphi}{x \cos \varphi} \right)^{\text{idealized}} \right] dx \tag{165}$$

whereas τ compensates for the differences in surface forces (disjoining pressure):

$$\tau = \frac{1}{r_c} \int_0^{x_B} [(\Pi)^{id} - \Pi\,(x)]x\,dx \tag{166}$$

where

$$(\Pi)^{id} = P_c, \qquad \text{for } 0 < x < r_c;$$
$$(\Pi)^{id} = 0, \qquad \text{for } x > r_c.$$

The superscripts ''real'' and ''idealized'' in Eq. (165) mean that the quantities in the respective parentheses must be calculated for the real and idealized meniscus profiles; the latter coincide for $x > x_B$ (cf. Fig. 28). For more details, see de Feijter and Vrij (1972), Kralchevsky and Ivanov (1985a,b), Ivanov and Kralchevsky (1988).

In conclusion, it should be noted that the width of the transition region between a thin liquid film and Plateau border is usually very small: below 1 μm (see de Feijter and Vrij, 1972). That is why the optical measurements of the meniscus profile, for example, the interferometric techniques described below, give information about the thickness of the Plateau border in the region $x > x_B$ (Fig. 28). If the data are processed by means of Laplace equation Eq. (164), one determines the contact angle, α, as discussed above. In spite of being a purely macroscopic quantity, α characterizes the magnitude of the surface forces inside the thin liquid film, as implied by Eq. (158). This was first pointed out by Derjaguin (1940) and Princen and Mason (1965).

C. Measurements of Thin Film Contact Angles

Together with the film thickness and disjoining pressure, the contact angle is one of the characteristics of the thin liquid films that is liable to direct measurement. Measurements are possible with both microscopic and macroscopic thin films.

Prins (1969) and Clint et al. (1969) developed a method of contact angle measurement for macroscopic flat foam films formed in a glass frame in contact with a bulk liquid. They measured the jump in the force exerted on the film at the moment when the contact angle formed. Similar experimental set-up was used by Yamanaka (1975) for measurement of the velocity of motion of the three-phase contact line.

An alternative method, which can be used in both equilibrium and dynamic measurements with vertical macroscopic films, was developed by Princen (1968) and Princen and Frankel (1971). They determined the contact angle from the data for diffraction of a laser beam refracted by the Plateau border.

Systematic study of macroscopic foam films in a rectangular frame was carried out by de Feijter and Vrij (1978) with aqueous solutions of sodium dodecyl sulfate at different concentrations of NaCl. The effect of electrolyte and temperature on the magnitude of the contact angle was studied. In particular, it was found that the contact angle, unlike the surface tension, strongly depends on temperature: in these experiments variation of the temperature with 1°C resulted in a change of the contact angle of about 1°.

In the case of microscopic films, especially appropriate are the interferometric methods: light beams reflected or refracted from the liquid meniscus interfere and create fringes, which in turn give information about the shape of the liquid surfaces. The fringes are usually formed in the vicinity of the contact line, which provides a better precision for the extrapolation procedure used when determining the contact angle (see Fig. 28). One can identify several interference techniques depending on how the interference pattern is created. In the usual interferometry (UI) the fringes are due to interference of beams reflected from the upper and lower meniscus (Fig. 29a). This technique is applicable for contact angle measurements with both foam films (Schedulko et al., 1968; Haydon and Taylor, 1968; Kolarov and Zorin, 1980; Dimitrov et al., 1990) and emulsion

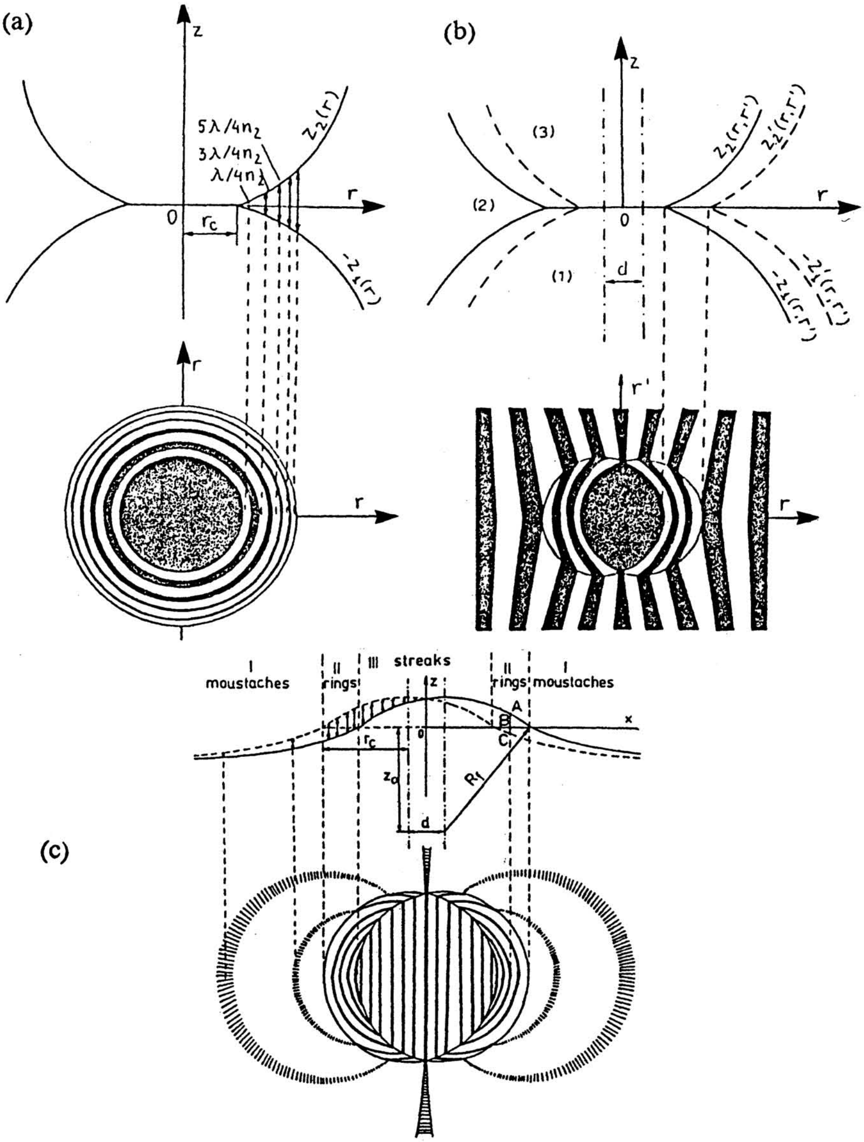


FIG. 29 Sketch of the fluid interfaces and of the observed interference fringes. (a) Usual interference in reflected light from the Plateau border; (b) differential interference in transmitted light; (c) differential interference in reflected light.

films (Kruglyakov and Rovin, 1978) The method is applicable for not too large contact angles ($\alpha < 8$–10 degrees); for larger slopes the region of fringes shrinks and measurements are not possible.

The basic principle of differential interferometry consists of an artificial splitting of the original image into two equivalent and overlapping images (see Françon, 1961; or Beyer, 1974). Thus interferometric measurements are possible with larger slope of the meniscus surfaces. The differential interferometry in transmitted light (DITL) (Fig. 29b) was used by Zorin (1977) and Zorin et al. (1983) to determine the contact angles of wetting and free liquid films. DITL is applicable when the whole system under investigation is transparent to the light. The differential interferometry in reflected light (DIRL) (Fig. 30c) allows measurement of the shape of the upper reflecting surface. This method was used by Nikolov et al. (1986a,b), Lobo et al. (1990), and Dimitrov et al. (1992b) to determine the contact angle, film, and line tension of the foam films formed at the top of small bubbles floating at the surface of ionic and nonionic surfactant solutions. An alternative method is the holographic interferometry applied by Picard et al. (1990, 1991) to study the properties of bilayer lipid membranes in

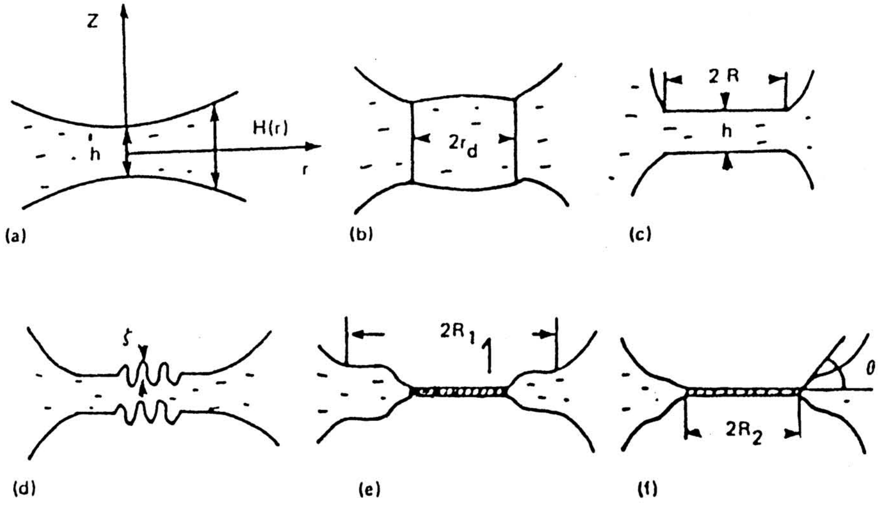


FIG. 30 Main stages of formation and evolution of a thin liquid film between two bubbles or drops. (a) Mutual approach of slightly deformed surfaces; (b) at a given separation, the curvature at $r = 0$ changes its sign and a cup-shaped formation (dimple) arises; (c) the dimple height initially increases, then decreases, and eventually an almost plane-parallel film forms; (d) thermal fluctuations or other disturbances can increase their amplitude to rupture the film or to form a thinner equilibrium state (f). (From Ivanov et al., 1975.)

solution. Film contact angles can be measured from the Newton rings of liquid lenses that form spontaneously in films from micellar surfactant solutions: see Dimitrov et al. (1990). Such a lens can exist for a long time in the film because the sucking pressure of the biconcave Plateau border is counterbalanced by the excess osmotic pressure of the surfactant micelles confined in the lens.

Finally it should be noted that contact angles can be determined by measuring several geometrical parameters characterizing the profile of the liquid meniscus and processing them by using the Laplace equation, Eq. (164) (Skinner et al., 1989; Dimitrov et al., 1992a). Modern computer techniques allow for the processing of many experimental points from the meniscus profile (Huh and Reed, 1983; Rotenberg et al., 1983) and automatic digital image analysis (Cheng et al., 1990).

V. HYDRODYNAMIC MODELING OF FOAM FILM

A. Stages of Approaching of Two Bubbles

Experimental and theoretical investigations (Ivanov et al., 1975; Ivanov and Dimitrov, 1988; Edwards et al., 1991) show that during the approach of two bubbles a specific interaction appears between their closest regions. This interaction is inherent in the presence of two surfaces and differs from the dynamics of a single surface. It is accepted that the formation and the evolution of the foam film between the bubbles phase through the following stages (Fig. 30).

1. Under the action of an outer driving force F the two bubbles approach each other. A hydrodynamic interaction between the bubbles takes place. This interaction is stronger at the front sections of the bubbles and leads to weak deformation of their surfaces. This is illustrated by the curves for the first two time intervals in Figs. 31 and 32 (Yiantsios and Davis, 1991). The dimensionless parameters in these figures are t: the time divided by $\eta a^2/4F$; h: the separation between the surfaces divided by the initial separation h_o ($h = h_o$ at $t = 0$ and $r = 0$); r: the radial coordinate divided by $\sqrt{ah_o/2}$; a: the bubble radius; η: the dynamic viscosity.
2. When a certain small separation h_i, called inversion thickness, is reached the sign of the curvature in the front section of the bubbles ($r = 0$) changes. A concave lens-shaped formation called a dimple (Frankel and Mysels, 1962) is formed. This stage is possible if the force acting on the bubbles is high enough, so it is possible to overcome the energy barrier created by the increase of surface energy during the deformation. Indeed, Danov et al. (1993a) have shown that in the case of Brownian flocculation of small bubbles at low electrolyte concentration such a dimple might not appear. In Fig. 33 (Yiantsios and Davis, 1991) two significantly different stages of approach are shown: (1) without dimple formation, when the parameter $\delta_1 = aA_H/$

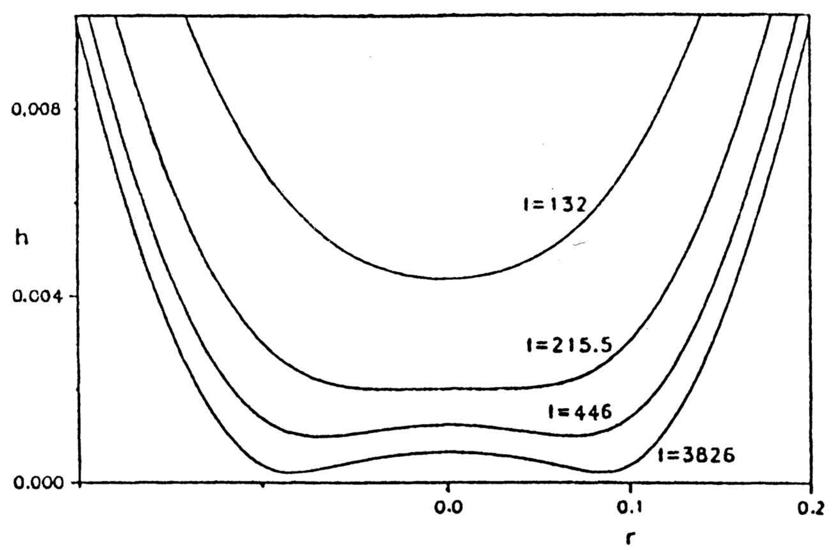


FIG. 31 The shape of the gap between the drops for characteristic times when the interfaces are nearly tangentially immobile. (From Yiantsios and Davis, 1991.)

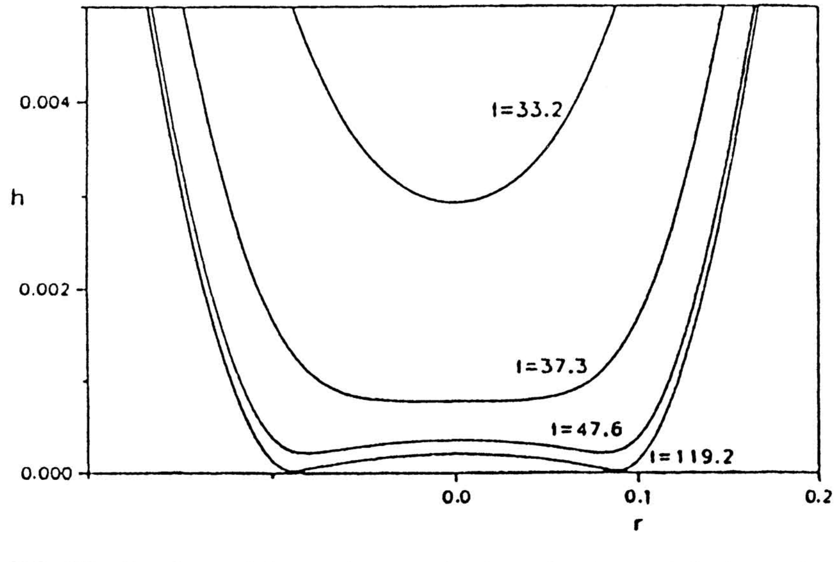


FIG. 32 The shape of the gap between the drops for characteristic times when the interfaces are nearly fully mobile. (From Yiantsios and Davis, 1991.)

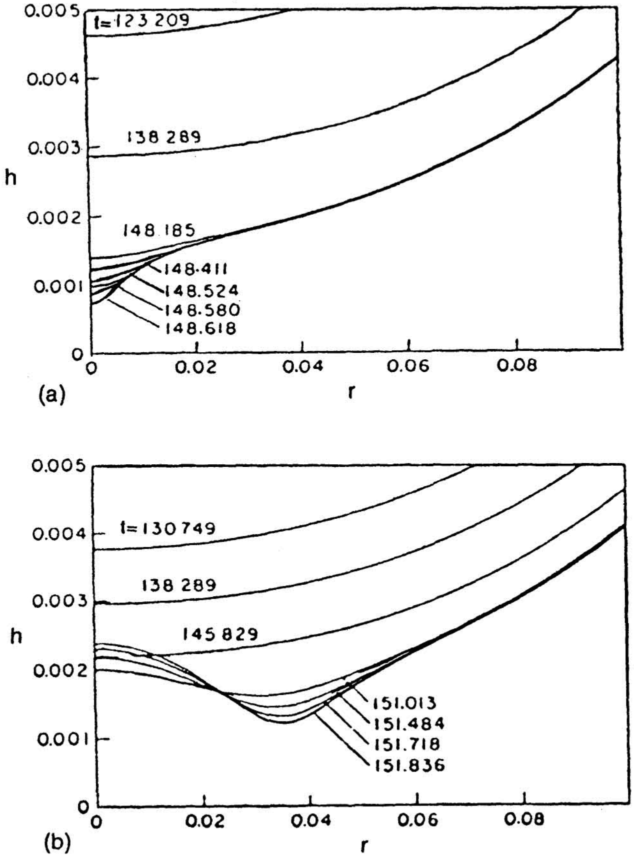


FIG. 33 Profile of the film $h = h(r)$ for different dimensionless times with gravity and molecular forces present. (a) $\delta_1 = aA_H/(12\pi h_o^2 F) = 1.3 \times 10^{-6}$; (b) $\delta_1 = 1.2 \times 10^{-6}$. (From Yiantsios and Davis, 1991.)

$(12\pi h_o{}^2F)$ is equal to 1.3×10^{-6} and (2) with dimple formation at $\delta_1 = 1.2 \times 10^{-6}$ (A_H is the Hamaker constant). One sees that at small separation the van der Waals attraction prevents the dimple formation.

3. The dimple evolves quickly. At first it grows, but as a result of the swift outflow of liquid it decreases and a virtually plane-parallel film is formed that afterwards thins at a constant radius R. In the case of films stabilized with ionic surfactants, it is possible for the electrostatic repulsion to be so strong that a primary, relatively thick equilibrium film forms, called first film or common black film. This case corresponds to point 1 in Fig. 25. Some-

times no plane-parallel film forms, but instead the dimple persists until rupture or formation of Newton black film (NBF) occurs.

4. As a result of thermodynamic fluctuations or outer disturbances of the film thinning process, the surface of the film is additionally deformed. When the derivative of the disjoining pressure $\partial\Pi/\partial h$ is positive, the amplitude of the deformation ζ spontaneously grows and the instability leads to rupture of the film or to formation of black spots with noticeably smaller thickness (Ivanov et al., 1970; Maldarelli and Jain, 1988). The appearance of unstable fluctuations is possible even in the primary equilibrium films as a result of fluctuations in the electric potential (Felderhof, 1968; Maldarelli and Jain, 1988).
5. The black spots either coalesce or grow, forming a secondary equilibrium film with a thickness h'' and radius R_g, called NBF. The thickness h'' corresponds to point 3 in Fig. 25. In the course of time the spot grows until it covers the whole film area. The typical thickness of plane-parallel films is about 200 nm (for stage c), while the characteristic thicknesses of NBF are about 5–10 nm.
6. After the whole film area is taken up by the secondary film, its radius is increased until it reaches the equilibrium film radius and an equilibrium contact angle θ is settled. An indication of that process is the movement of the Newton rings (see Sec. IV.C.) and Fig. 29.

B. Characteristic Values of the Parameters of Emulsion and Foam Films

Depending on whether or not they contain an easily ionizable group, the surfactants are classified as ionic or nonionic. In many applications, particularly in the food industry, protein isolates are widely used. In emulsion and foam systems surfactant blends are often used.

Since the surfactants and thereby the interfacial properties may widely, we have listed the ranges of these variations in Table 2. The typical values listed there will be used in the hydrodynamic numerical calculations below. The parameters include characteristical particle dimensions (Becher, 1977; Dickinson and Stainsby, 1982; Rosen, 1989; Holcomb et al., 1990; Dickinson, 1992); surface (interfacial) tension γ (Becher, 1977; Tornberg, 1978; Becher and Schick, 1987; Rosen, 1989; Mendoza-Martinez and Sherman, 1990; Gaonkar and Borwankar, 1991); the critical micelle concentration (CMC) (Rosen, 1989); the adsorption Γ at bulk concentrations close to CMC (Dickinson and Stainsby, 1982; Rosen, 1989); the Gibbs elasticity ($\partial\gamma/\partial\ln\Gamma$) of the surfactants and the surface elasticity of the protein layers (Mysels et al., 1961; van den Tempel et al., 1965; Graham and Philips, 1976; Philips, 1981; Hard and Neuman, 1981; Snik et al., 1983; Walstra, 1983); the $\partial\gamma/\partial C$ values (Lange, 1967); the surface viscosity η_s (Davies and Rideal, 1963; Lange, 1967; Carless and Hallworth, 1968; Boyd et

TABLE 2 Ranges of Variations in Interfacial Properties of Surfactants

	Foam Systems			Emulsion Systems		
	Ionic	Nonionic	Proteins	Ionic	Nonionic	Proteins
Characteristic dimensions (μm)	(5–1500) 50–500 (typ. 150)		100–1000 (typ. 200)	(0.25–500) 1–300 (typ. 2–40)		2–500 (typ. 10)
Interfacial tension (dyn/cm)	25–43 (typ. 32)	27–48 (typ. 33)	40–60 (typ. 50)	1–10 (typ. 5)		1–15 (typ. 5)
Bulk concentration (CMC)(mol/cm^3)	$5 \times 10^{-5} - 5 \times 10^{-7}$ (typ. 8×10^{-6})	$2 \times 10^{-6} - 1 \times 10^{-8}$ (typ. 5×10^{-8})	$1\text{–}100 \times 10^{-6}$ g/cm^3 (typ. 1×10^{-5})	$5 \times 10^{-5} - 5 \times 10^{-7}$ (typ. 8×10^{-6})	$2 \times 10^{-6} - 1 \times 10^{-8}$ (typ. 5×10^{-8})	$1\text{–}100 \times 10^{-6}$ g/cm^3 (typ. 1×10^{-5})
$-d\gamma/dC$ (dyn cm^2/mol)	$4\text{–}6 \times 10^8$ (typ. 5×10^8)		$5\text{–}1000 \times 10^5$ dyn cm^2/g (typ. 5×10^7)	$4\text{–}6 \times 10^8$ (typ. 5×10^8)		$5\text{–}1000 \times 10^5$ dyn cm^2/g (typ. 5×10^7)
Adsorption Γ ($\sim$CMC)(mol/cm^2)	$1\text{–}5 \times 10^{-10}$ (typ. 2×10^{-10})		$1\text{–}6 \times 10^{-7}$ g/cm^2 (typ. 3×10^{-7})	$1\text{–}5 \times 10^{-10}$ (typ. 2×10^{-10})		$1\text{–}6 \times 10^{-7}$ g/cm^2 (typ. 3×10^{-7})
Gibbs elasticity $-d\gamma/d\ln\Gamma_o$ (dyn/cm)	1–20 (typ. 7)		1–300 (typ. 20)	1–20 (typ. 5)		1–300 (typ. 20)
Surface viscosity (sp)	$1 \times 10^{-4} - 1 \times 10^{-2}$ (typ. 1×10^{-3})	$1 \times 10^{-4} - 0.5$ (typ. 1×10^{-3})	$0.1-1000$ (typ. 5)	$1 \times 10^{-4}\text{–}1 \times 10^{-2}$ (typ. 1×10^{-3})	$1 \times 10^{-4} - 0.5$ (typ. 1×10^{-3})	0.1–1000 (typ. 5)
Bulk diffusion coefficient (cm^2/s)	$3\text{–}6 \times 10^{-6}$ (typ. 5×10^{-6})	$1\text{–}5 \times 10^{-6}$ (typ. 3×10^{-6})	$8\text{–}50 \times 10^{-7}$ (typ. 1×10^{-6})	$3\text{–}6 \times 10^{-6}$ (typ. 5×10^{-6})	$1\text{–}5 \times 10^{-6}$ (typ. 3×10^{-6})	$8\text{–}50 \times 10^{-7}$ (typ. 1×10^{-6})
Surface diffusion coefficient (cm^2/s)		$1 \times 10^{-4} - 1 \times 10^{-7}$			$1 \times 10^{-4} - 1 \times 10^{-7}$	

typ., typically.

al., 1972, 1973; Poskanzer and Goodrich, 1975; Dickinson and Stainsby, 1982; Dickinson et al., 1985, 1987; Ting et al., 1984); the bulk diffusion coefficient D (Davies and Rideal, 1963; Fainerman, 1978; Maru and Wasan, 1979; Dickinson and Stainsby, 1982; Djabbarach and Wasan, 1982; Rosen, 1989); the surface diffusion coefficient D_s (Manev et al., 1976; Clark et al., 1990). In the case of emulsion systems into which the surfactant is dissolved in the continuous phase (dispersion medium), the values of the above parameters are very close to those for the analogous foam systems. The only important difference is the interfacial tension. Its much lower values for emulsions lead in turn to different characteristic dimensions: foam bubbles with radii below 100 nm are quite short-lived due to their disproportionate size (Dickinson, 1992). This determines the larger sized, thicker, and more stable foam films in comparison with the emulsion ones.

C. Basic Equations and Boundary Conditions

The laws of mass conservation and momentum balance for the bulk phases the film included, read (Batchelor, 1967; Bird et al., 1960)

$$\frac{\partial \rho}{\partial t} + \nabla\cdot(\rho \mathrm{v}) = 0 \tag{167}$$

$$\frac{\partial}{\partial t}(\rho \mathrm{v}) + \nabla\cdot(\rho \mathrm{v}\mathrm{v} - \hat{P}) = \mathrm{F} \tag{168}$$

where ρ is the density of the fluid, v is fluid velocity, $\hat{P}$ is pressure tensor, F is density of the outer body force. For a nonpolar fluid, the pressure tensor $\hat{P}$ may generally be decomposed into isotropic and deviatoric parts, as

$$\hat{P} = -p\hat{I} + \hat{\tau} \tag{169}$$

where ρ is the scalar thermodynamic pressure, $\hat{I}$ is the unit tensor in space, and $\hat{\tau}$ is the viscous stress tensor. If the density ρ is constant, the equation for conservation of the mass reduces to

$$\nabla\cdot\mathrm{v} = 0 \tag{170}$$

and the viscous stress tensor $\hat{\tau}$ for isotropic incompressible Newtonian fluids (Bird et al., 1960) may be expressed as:

$$\hat{\tau} = \eta\,(\nabla\mathrm{v} + \nabla\mathrm{v}^T) \tag{171}$$

where η is the dilatational viscosities and the superscript T denotes transposition. If η does not depend on the spatial coordinates, from Eqs. (168) and (171) one obtains the Navier-Stokes equation (Navier, 1827; Stokes, 1845)

$$\rho\left[\frac{\partial \mathrm{v}}{\partial \mathrm{t}} + \mathrm{v} \cdot \nabla \mathrm{v}\right] = - \nabla p + \eta \nabla \cdot (\nabla \mathrm{v}) \tag{172}$$

which should be solved together with Eq. (170).

If there is no chemical reaction within the system and C is the bulk concentration of surfactant, the equation for the balance of surfactants reads

$$\frac{\partial C}{\partial t} + \nabla \cdot (C\mathrm{v}) + \nabla \cdot \mathrm{j} = 0 \tag{173}$$

where the diffusion flux j could include the effects of thermal diffusion, electrical diffusion, and diffusion driven by other outer forces (Levich, 1962; Bird et al., 1960; Edwards et al., 1991). The simplest way to account for the flux is through the law of Fick

$$\mathrm{j} = C\,(\mathrm{u} - \mathrm{v}) = - D\nabla C \tag{174}$$

where u and D are, correspondingly, the velocity and the bulk diffusion coefficient of the surfactant. For surfactant mixtures the laws in Eqs. (173) and (174) could be expressed in a similar way (see Edwards et al., 1991).

The equation for the balance of the stress tensor on the film surface could be written in the form (Landau and Lifshitz, 1984; Ivanov and Dimitrov, 1988)

$$\nabla_s \cdot \hat{\sigma} = \mathrm{n} \cdot (\hat{P} + p_b \hat{I}) \tag{175}$$

where ∇_s is surface gradient operator, $\hat{\sigma}$ is the surface excess stress tensor, $\hat{P}$ is the pressure tensor in the liquid, and p_b is the scalar pressure inside the bubble. A number of Newtonian and non-Newtonian rheological models have been described in the literature (see Edwards et al., 1991; Tambe and Sharma, 1991).

In the framework of the Newtonian interfacial behavior Boussinesq (1913) and Scriven (1960) have formulated a rheological model that is a two-dimensional analogue of Eq. (171)

$$\hat{\sigma} = \gamma \hat{I}_s + (\eta_d - \eta_{sh})(\hat{I}_s : \hat{D}_s)\hat{I}_s + 2\eta_{sh}\hat{D}_s \tag{176}$$

where γ is the interfacial tension; η_d and η_{sh} are the interfacial dilatational and shear viscosities, respectively; $\hat{I}_s$ is the surface unit tensor; $\hat{D}_s$ is the surface rate of strain tensor

$$\hat{D}_s = \frac{1}{2}[(\nabla_s \mathrm{v}_s) \cdot \hat{I}_s + \hat{I}_s \cdot (\nabla_s \mathrm{v}_s)^T] \tag{177}$$

v_s is the surface velocity; n is the normal to the film surface directed toward the bubble (see Fig. 34). If the condition that η_d and η_{sh} do not depend on the surface coordinates is fulfilled, from Eqs. (175–177), after some transformations,

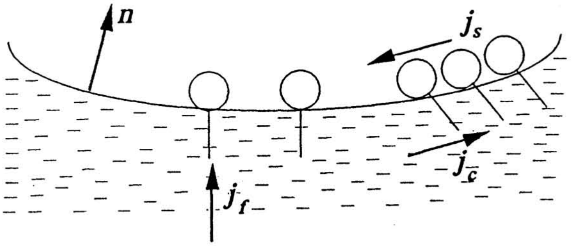


FIG. 34 The bulk flux from the film, j_f, which consists of two consequent stages: diffusion and adsorption; n, normal to the film surface directed toward the bubble.

one can obtain the equations of the interfacial stress balance resolved normally and tangentially to the surface (Aris, 1962)

$$\mathrm{n} \cdot (\hat{P} + p_b\hat{I}) \cdot \hat{I}_s = \nabla_s\gamma + (\eta_d + \eta_{sh})\, \nabla_s\, (\nabla_s \cdot \mathrm{v}_s) + \eta_{sh}\{\mathrm{n}\times\nabla_s[(\nabla_s\times\mathrm{v}_s) \cdot \mathrm{n}] - 2(\hat{b} - 2\, H\hat{I}_s) \cdot (\nabla_s\mathrm{v}_s) \cdot \mathrm{n}\} \tag{178}$$

$$\mathrm{n} \cdot (\hat{P} + p_b\hat{I}) \cdot \mathrm{n} = 2H\gamma + \eta_{sh}\, (\hat{b} - 2H\hat{I}_s) : \nabla_s\mathrm{v}_s + 2H(\eta_d + \eta_{sh})\nabla_s \cdot \mathrm{v}_s \tag{179}$$

where $\hat{b} = -\nabla_s\mathrm{n}$ is the surface curvature dyadic and $H = {}^1\!/_2\, \hat{I}_s : \hat{b}$ is the mean surface curvature.

When surfactant is present at the surface of the film with an interfacial concentration Γ, the equilibrium distribution of surfactant is disrupted as a result of the hydrodynamic interactions. As a consequence, surfactant fluxes appear (Fig. 34). The surface flux j_c is responsible for the convective transfer of surfactant and j_s - for the diffusion mass transfer (which, as with the bulk one, could include thermal diffusion, electrodiffusion, and other effects). The bulk flux from the film is j_f. Usually two limiting cases are considered: (1) for diffusion-controlled adsorption (Levich, 1962)

$$\mathrm{j}_f \cdot \mathrm{n} = -\, D\frac{\partial C}{\partial n} \tag{180}$$

and (2) for adsorption-controlled flux (Borwankar and Wasan, 1983).

$$\mathrm{j}_f \cdot \mathrm{n} = \exp\left[\frac{A}{2}\left(\frac{\Gamma}{\Gamma_\infty}\right)^2\right] \left[k_a(\Gamma_\infty - \Gamma)C_s - \Gamma\exp\left(-\, A\frac{\Gamma}{\Gamma_\infty}\right)\right] \tag{181}$$

where A is a parameter accounting for the interaction between the adsorbed surfactant molecules; Γ_∞ is the surface-excess saturation concentration; k_a is adsorption coefficient. When $A = 0$, Eq. (181) corresponds to the Langmuir adsorption model. Then the mass-balance equation of the surfactant on the surface acquires the form (Ivanov and Dimitrov, 1988)

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma \mathrm{v}_s) - \nabla_s \cdot (\mathrm{D}_s \nabla_s \Gamma) = \mathrm{j}_f \cdot \mathrm{n} \tag{182}$$

where D_s is the coefficient of interfacial diffusion.

To close the system of equations, the dependence of the interfacial tension on the concentration must be known. For that purpose Eqs. (25) or (26) can be used.

VI. RATE OF THINNING AND LIFETIME OF THIN LIQUID FILMS: LUBRICATION APPROXIMATION

A. Basic Equations and Boundary Conditions in the Lubrication Approximation

The problem for the movement of a nondeformed rigid sphere toward a plane surface was first solved by Taylor (1924). The complementary case, when a thin film is formed between two parallel plates, was considered by Reynolds (1886). The influence of surfactant on the drainage of symmetrical foam film (formed between identical bubbles), the approach of a bubble toward a solid or fluid wall, and the approach of two bubbles with differing radii and surface properties

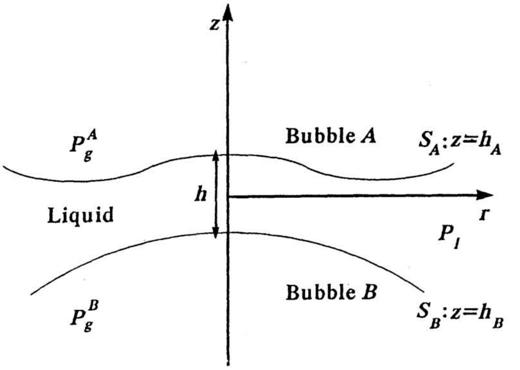


FIG. 35 Mutual approach, along the axis z of two different bubbles A and B of radii R_c^A and R_c^B and surface tension γ^A and γ^B.

has been studied by a number of authors and surveyed by Ivanov et al. (1985) and Ivanov and Dimitrov (1988).

The systems usually assumed to have rotational symmetry (Fig. 35) and the problems are considered in a cylindrical coordinate system (r,φ,z). $S_A{:}z = h_A$ and $S_B{:}z = h_B$ are the equations of the surface of the bubbles and h is the thickness of the film formed between them. At small Reynolds numbers $Re = Vh/\nu$ (where V is the velocity of thinning, ν is the kinematic viscosity, R_c is the characteristic bubble radius) and small values of the parameter h/R_c, the equations for conservation of mass (170) and motion (172) are simplified to the familiar lubrication theory equations (Reynolds, 1886)

$$\frac{1}{r}\frac{\partial}{\partial r}(r\mathrm{v}_r) + \frac{\partial \mathrm{v}_z}{\partial z} = 0 \tag{183}$$

$$\frac{\partial p}{\partial r} = \eta\frac{\partial^2 \mathrm{v}_r}{\partial z^2}, \qquad \frac{\partial p}{\partial z} = 0 \tag{184}$$

where v_r and v_z are the corresponding components of the velocity inside the film. The kinematic boundary condition for the film surfaces acquires the form:

$$\mathrm{v}_r = u_{A,B},\ \mathrm{v}_z = \frac{\partial h_{A,B}}{\partial t} + u_{A,B}\frac{\partial h_{A,B}}{\partial r} \qquad \text{at } z = \mathrm{h}_{A,B} \tag{185}$$

where u_A and u_B are the surface velocities. The general solution of Eqs. (183–185) is given by Ivanov et al. (1985) and could be written as:

$$\mathrm{v}_r = \frac{1}{2\eta}\frac{\partial p_s}{\partial r}(z - h_A)(z - h_B) + \frac{h_A - z}{h}u_B + \frac{z - h_B}{h}u_A, \qquad p = p_s(r,t) \tag{186}$$

and the equation for determining the local film thickness

$$\frac{\partial h}{\partial t} + \frac{1}{r}\frac{\partial}{\partial r}\left(rh\frac{u_A + u_B}{2}\right) = \frac{1}{r}\frac{\partial}{\partial r}\left(\frac{rh^3}{12\eta}\frac{\partial p_s}{\partial r}\right) \tag{187}$$

At small Peclet numbers ($Pe = Vh/D$), the convective terms in the equation for the diffusion Eq. (173) are negligibly small and the concentration could be expressed with an adequate precision by the relation

$$C = C^o + C_s(r,t) + C_s^1(r,t)z + c(z,r,t) \tag{188}$$

where c is the following approximation term in the solution. The interfacial concentration of surfactant and the interfacial tension are subjected to small perturbations and could be represented by the series:

$$\Gamma_{A,B} = \Gamma^o_{A,B} + \left(\frac{\partial \Gamma}{\partial C}\right)_{A,B} C_s, \qquad \gamma_{A,B} = \gamma^o_{A,B} + \left(\frac{\partial \gamma}{\partial C}\right)_{A,B} C_s \tag{189}$$

where $\Gamma^o_{A,B}$, $\gamma^o_{A,B}$ and the derivatives are equilibrium values.

By using Eqs. (173), (174), (180), (182), (188), and (189) Ivanov et al. (1985) have derived the relation between the surface velocities u_A, u_B and the surface concentration gradient

$$\Gamma^o_A u_A + \Gamma^o_B u_B = \left[D^A_s\left(\frac{\partial \Gamma}{\partial C}\right)_A + D^B_s\left(\frac{\partial \Gamma}{\partial C}\right)_B + Dh\right]\frac{\partial C}{\partial r} \tag{190}$$

In the lubrication approximation, Eq. (179) for the balance of the tangential component of interfacial tension, after accounting for the relations (186) and (189), transforms to read

$$\left(\frac{\partial \gamma}{\partial C}\right)_{A,B}\frac{\partial C}{\partial r} + \eta^{A,B}_s \frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}(r u_{A,B})\right] = \frac{h}{2}\frac{\partial p_s}{\partial r} \pm \eta\,\frac{u_A - u_B}{h} \qquad \text{at } z = h_{A,B} \tag{191}$$

where $\eta^{A,B}_s$ is the surface viscosity of S_A and S_B. The equation for the balance of the normal component of the surface tension (179) simplifies to the Laplace equation (1806)

$$p^{A,B}_g - p_s = \pm\gamma^o_{A,B}\,\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h_{A,B}}{\partial r}\right) \qquad \text{at } z = h_{A,B} \tag{192}$$

The force balance, leading to the drag force F, reads

$$F \sim 2\pi \int_0^\infty (p - p_l) r\,dr = 2\pi\gamma^{A,B}_0\left[r\,\frac{\partial(h^{A,B}_\infty - h_{A,B})}{\partial r}\right]\Bigg|_0^\infty \tag{193}$$

where $h^{A,B}_\infty$ is the equation of the unperturbed surface at r → ∞.

We are not aware of any study in which the general solution of the system of Eqs. (190–193) is presented. In particular, when the surface viscosity is low (the ratio $\eta^{A,B}_s h/(\eta R^2)$ is a small parameter) Ivanov et al. (1985) were able to simplify the problem to one equation for the film thickness

$$\frac{12\eta}{\bar{\gamma}_o}\frac{\partial h}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left\{\left(1 + \bar{b} + \frac{\bar{h}_s}{h}\right) r h^3 \frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial h}{\partial r}\right)\right]\right\} \tag{194}$$

where the mean parameters are defined as follows

$$\overline{\gamma}_o = \frac{\gamma_A^o \gamma_B^o}{(\gamma_A^o + \gamma_B^o)}; \qquad b_{A,B} = \frac{-3\eta D}{\Gamma_{A,B}^o \left(\frac{\partial \gamma}{\partial C}\right)_{A,B}}$$

$$h_s^{A,B} = \frac{-\,6\eta D_s^{A,B}}{\Gamma_{A,B}^o \left(\frac{\partial \gamma}{\partial \Gamma}\right)_{A,B}}$$

$$\overline{b} = \frac{[4\Gamma_A^o \Gamma_B^o b_A b_B + 3(\Gamma_A^o - \Gamma_B^o)(\Gamma_B^o b_B^o - \Gamma_A^o b_A)]}{(\Gamma_A^o + \Gamma_B^o)(\Gamma_A^o b_A + \Gamma_B^o b_B)} \tag{195}$$

$$\overline{h}_s = \frac{2\Gamma_A^o \Gamma_B^o (h_s^A b_B + h_s^B b_A)}{(\Gamma_A^o + \Gamma_B^o)(\Gamma_A^o b_A + \Gamma_B^o b_B)}$$

In the case of quasistationary movement the investigated problem, Eqs. (193) and (194), could be studied asymptotically (Ivanov et al., 1985; Ivanov and Dimitrov, 1988).

B. Rate of Thinning and Lifetime of Foam Film

If the quantity of surfactant in the system is large enough (Levich, 1962) and the bubbles are small, during their approach they do not deform and their surfaces are tangentially immobile. This means that they behave as hard spheres. Then from Eqs. (187) and (193) one obtains a generalized expression of the Taylor formula (1924) for the rate of thinning

$$V_{Ta} = \frac{F{\cdot}h}{6\pi\eta \overline{R}_c^2} \tag{196}$$

where $\overline{R}_c$ is the mean radius $\overline{R}_c = R_c^A R_c^B/(R_c^A + R_c^B)$. In the special case, when a solid sphere of radius R_c approaches a flat solid surface at small gap, one obtains $\overline{R}_c = R_c$. In the cases in which the convective terms could be neglected in the Navier-Stokes equations (172), the problem of the approaching of two nondeformed bubbles or drops has been solved by many authors (see, for example, Haber et al., 1973; Reed and Morrison, 1974; Morrison et al., 1978; Rushton and Davies, 1978; Hertsroni and Haber, 1978; Beshkov et al., 1978; Davies, 1978; Davies et al., 1989; Fuentes et al., 1988; Fuentes and Kim, 1989). A number of sophisticated formulae, whose precision is higher compared to that of Eq. (169), were obtained.

In the case of plane-parallel film (see stage c in Fig. 30), with tangentially immobile surfaces one obtains the well-known Reynolds equation for the velocity of thinning (Reynolds, 1886)

$$-\frac{dh}{dt} = V_{Re} = \frac{2Fh^3}{3\pi\eta R^4} \tag{197}$$

If there is also a contribution of the disjoining pressure Π, the Reynolds equation can be written in an alternative form (Scheludko, 1967):

$$V_{Re} = \frac{2\Delta P h^3}{3\eta R^2} \tag{198}$$

where $\Delta P = P_c - \Pi$ is the driving pressure and P_c is the capillary pressure.

When the film has plane-parallel mobile surfaces, one can derive from Eqs. (187), (190), (191), and (193) that the rate of thinning depends on the film surface properties:

$$\frac{V}{V_{Re}} = 1 + \bar{b} + \frac{\bar{h}_s}{h} \tag{199}$$

The influence of the surface viscosity has not been accounted for in Eq. (199). For two identical surfaces Eq. (199) was first derived by Radoev et al. (1974). Experimental data of Manev et al. (1976–7) obtained for nitrobenzene films stabilized with different concentrations of dodecanol are shown in Fig. 36. It

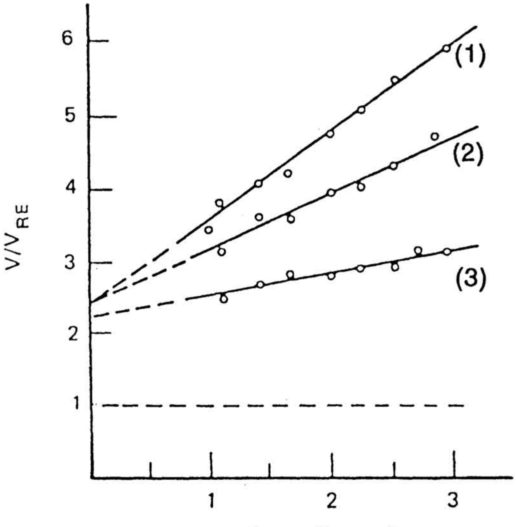


FIG. 36 V/V_{Re} vs. h^{-1} for nitrobenzene films stabilized with different concentration of dodecanol: (1), 1.1×10^{-2} M; (2), 4.4×10^{-2} M; (3), 17.8×10^{-2} M. (From Manev et al., 1976/1977.)

can be seen that the ratio V/V_{Re} depends linearly on h^{-1}, in agreement with Eq. (199).

An important practical parameter is the film lifetime τ

$$\tau = \int_{h_{cr}}^{h_i} \frac{dh}{V} \tag{200}$$

defined as the time during which the film will thin from the inversion thickness at which a planer film forms (stage b in Fig. 30) to the critical thickness of rupture h_{cr} (stage d in Fig. 30; see also Sec. VII.B.). In the case when the thinning is driven by constant force (e.g., buoyancy force) from Eqs. (197), (199), and (200) a simple analytical formula is obtained

$$\tau = \frac{3\pi\eta R^4}{2F\bar{h}_s h_{cr}} \left\{ 1 - \frac{h_{cr}}{h_i} - (1 + \bar{b}) \frac{h_{cr}}{\bar{h}_s} \ln \left[1 + \frac{\dfrac{\bar{h}_s}{h_{cr}} \left(1 - \dfrac{h_{cr}}{h_i}\right)}{\left(1 + \bar{b} + \dfrac{\bar{h}_s}{h_i}\right)} \right] \right\} \tag{201}$$

In many cases $h_i >> h_{cr}$ and Eq. (201) reduces to the equation for the lifetime of films with identical surfaces, published by Ivanov and Dimitrov (1988). It is not difficult to demonstrate that for $\bar{h}_s \rightarrow 0$ and $\bar{b} \rightarrow 0$ Eq. (201) transforms into the formula for the lifetime of a film with tangentially immobile surfaces

$$\tau = \frac{3\pi\eta R^4}{4Fh_{cr}^2} \left(1 - \frac{h_{cr}^2}{h_i^2}\right) \tag{202}$$

In the case of wetting films, the radial velocity at the solid surface is zero. The resulting equation for the rate of thinning is (Ivanov and Dimitrov, 1988)

$$\frac{V}{V_{Re}} = 4 \frac{\dfrac{3}{4} + b + \dfrac{h_s}{2h}}{3 + b + \dfrac{h_s}{2h}} \tag{203}$$

where the parameters b and h_s are defined for the liquid–gas surface. At very low surfactant concentrations $V \sim 4V_{Re}$. Thus, at low concentrations the film drains more quickly because of the high mobility of the interface. Then from Eqs. (197), (200), and (203) the lifetime at a constant force F is obtained

$$\tau = \frac{3\pi\eta R^4}{16Fh_{cr}^2}\left\{1 - \frac{h_{cr}^2}{h_i^2} + \frac{9}{h_s}\left(1 - \frac{h_{cr}}{h_i}\right) - 18\,\frac{h_{cr}^2}{h_s^2}\left(\frac{3}{4} + b\right)\ln\left[1 + \frac{\dfrac{h_s}{\mathrm{h}_{cr}}\,\dfrac{1}{2\left(\frac{3}{4} + b\right)}\left(1 - \dfrac{h_{cr}}{h_i}\right)}{\left(1 + \dfrac{h_s}{2h_i\left(\frac{3}{4} + b\right)}\right)}\right]\right\} \qquad (204)$$

We should note that at high interfacial mobility the lifetimes given by Eqs. (201) and (204) are substantially different.

C. Influence of the Surface Viscosity on the Rate of Thinning and Film Lifetime

The investigation of the influence of the interface viscosity on the rate of film thinning and the shape of the surfaces Eqs. (190–193) is a difficult task, which could be solved only numerically. The problem of a symmetrical plane-parallel foam or emulsion film is solved numerically by Zapryanov et al. (1983), Malhotra and Wasan (1987, 1988), and Edwards et al. (1991). These authors studied the hydrodynamic behavior of the systems as a function of their surface rheology. The dimensionless numbers characterizing these processes are $Bo = \eta_s/\eta R$ – Boussinesq number, giving the ratio of surface to volume friction:

$$E_s = -\left(\frac{\partial\gamma}{\partial \ln \mathrm{C}}\right)\mathrm{R}/(\eta \mathrm{D})$$

giving the contribution of the surface tension gradient term in Eq. (191), and contribution of the $N_s^D = D_s/D$: ratio of the surface to volume diffusivities. In Fig. 37 numerical results (Malhotra and Wasan, 1987) for the interfacial mobility or the dimensionless drainage velocity vs. dimensionless film thickness are presented. The curves correspond to three values of the dimensionless surface elasticity E_s. A great surface elasticity leads to "solidifying" of the interfaces, that is, the decreased surface mobility decreases the film thinning rate. On the other hand, at high Boussinesq numbers, as shown in Fig. 38, the surface viscosity effect could prevail on the effect of the surface elasticity (Mahotra and Wasan,

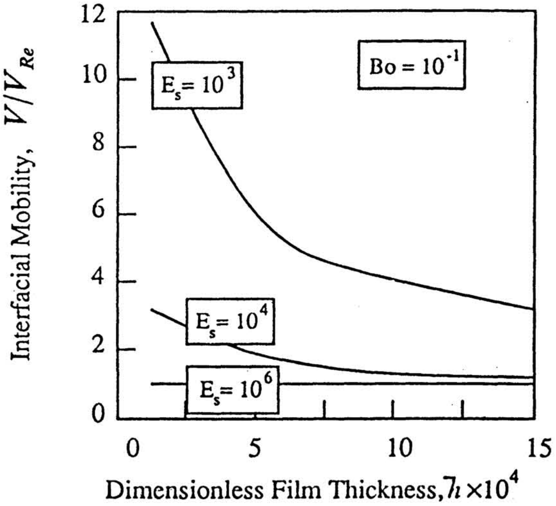


FIG. 37 Interfacial mobility, or dimensionless drainage velocity, vs. dimensionless film thickness, at three values of the dimensionless interfacial elasticity. (From Malhotra and Wasan, 1987.)

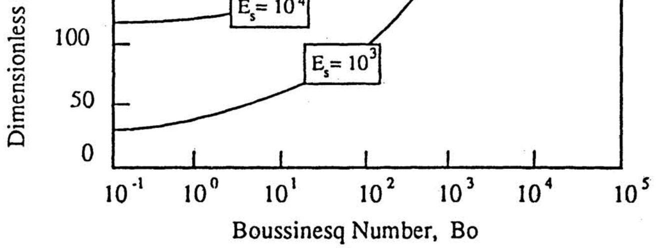


FIG. 38 Dimensionless drainage time for the film, vs. Boussenesq number at various values at the surface diffusivity number. (From Malhotra and Wasan, 1987.)

1987). It should be noted that Bo depends not only on the properties of the system but also on the geometric parameters. When the film radius R is smaller, the effect of the surface viscosity is higher, whereas E_s decreases because BoE_s is constant. The dependence of the characteristic lifetime on N_s^D and Bo is shown in Fig. 39 (Malhotra and Wasan, 1987). It is seen that the increase of the surface diffusion flux leads to a decrease of the film lifetime. The effect, in turn, could be suppressed by the increase of interfacial viscosity.

The model considered in Sec. V.C. is based on Newtonian flow behavior of the film surfaces. If the film surfaces comply with other rheological relations (e.g., when the film is stabilized with proteins), the dynamic of thinning could be different (see Tambe and Sharma, 1991).

In the results considered hitherto the influence of the Plateau border on film thinning has not been accounted for. Danov et al. (1993b) have studied the problem for the foam film drainage on the basis of Eqs. (190–193). As a first approximation one assumes that at the center a plane-parallel film exists that gradually merges with the Plateau border. An appropriate asymptotic procedure has been applied for matching the series expansions at the film–meniscus boundary. The following formula for the ratio V_{Re}/V in the case of symmetrical films with identical surfaces was obtained:

$$\frac{V_{Re}}{V} = \frac{1}{1 + b + \dfrac{h_s}{h}} + \frac{h}{h_i} + \frac{h^2}{h_i^2} + \frac{b + \dfrac{h_s}{h}}{1 + b + \dfrac{h_s}{h}} \cdot \Delta_\eta \tag{205}$$

The function Δ_η, which is parametrically presented in Fig. 40, depends only upon the dimensionless combination

$$R_\eta = \left[\frac{6\eta R^2}{\eta_s h}\left(1 + \frac{1}{b + \dfrac{h_s}{h}}\right)\right]^{1/2} \tag{206}$$

From Eqs. (205), (206), and Fig. 40 a conclusion could be drawn that smaller film thickness, lower surface viscosities, and larger film radii R lead to decreased influence of the surface viscosity on the film thinning rate. One the other hand, when $b \rightarrow 0$ and $h_s \rightarrow 0$ (corresponding to greater E_s at a fixed radius R), $\Delta_\eta \rightarrow 1$ and from Eq. (205) it follows that

$$\frac{V_{Re}}{V} = 1 + \frac{h}{h_i} + \frac{h^2}{h_i^2} = \Delta_m \tag{207}$$

This equation corresponds to tangentially immobile surfaces, but the terms h/h_i

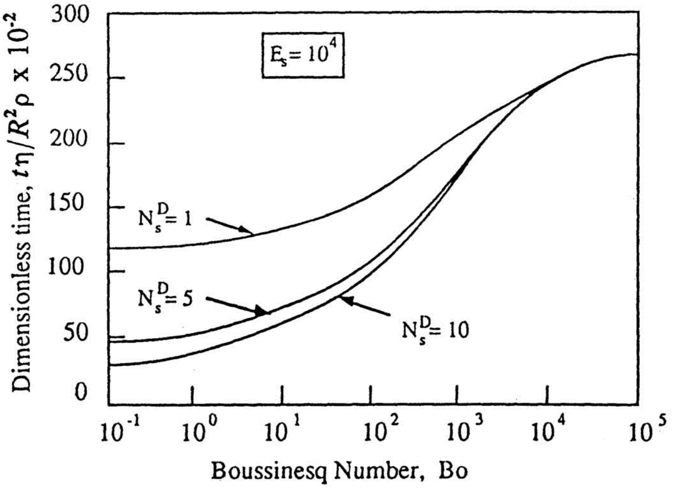


FIG. 39 Dimensionless film drainage time versus Boussinesq number at various values at the ratio of the surface to volume diffusivities. (From Malhotra and Wasan, 1987.)

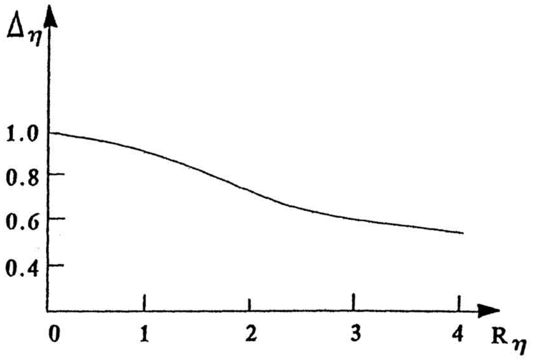


FIG. 40 Dimensionless parameter Δ_η from Eq. (205) vs. dimensionless film radius R_η from Eq. (206). (Danov et al., 1993b.)

and $(h/h_i)^2$ account for the fluid flow in the meniscus. For thin film when $h/h_i \to 0$ the velocity of thinning coincides with V_{Re}. Eq. (207) shows that when $h \approx h_i$ (Fig. 41) the velocity of thinning is about three times smaller than the Reynolds velocity. Therefore, the effect of the Plateau border during the film thinning could be negligible only at $h << h_i$.

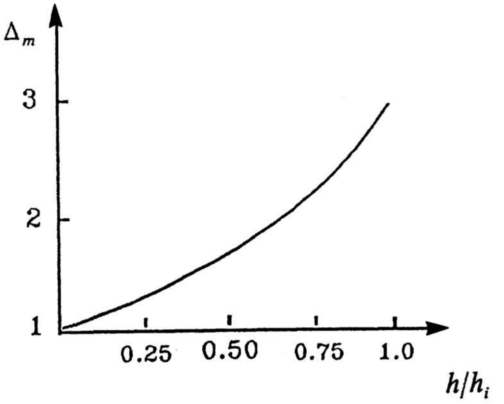


FIG. 41 Dimensionless parameter Δ_m from Eq. (207) vs. dimensionless film thickness h/h_i. (From Danov et al., 1993b.)

VII. CRITICAL AND INVERSION THICKNESS OF THIN FOAM FILM

A. Critical Film Thickness

Numerous experiments have shown (Scheludko, 1962, 1967) that even when they are plane-parallel, liquid films never thin to zero thickness but rupture or black (thinner) spots form, at a finite thickness, of the order of 5×10^{-6} cm, called critical (Scheludko, 1962). de Vries (1958, 1960) was the first to point out that local fluctuations of the film thickness (which are always present because of either mechanical perturbations or thermal fluctuations) lead to two opposite effects: positive contribution to the free energy due to the increase of the film area and negative contribution resulting from the increased negative van der Waals energy of interaction in the thinner part. The latter effect increases as the average thickness decreases so that at a given thickness, h_t, which we will call ''transitional'' (it is called ''critical'' in Scheludko, 1962, 1967), the two effects compensate each other. Below h_t the change of free energy is negative, the corrugations become unstable, and will spontaneously increase their amplitude until the film surfaces touch each other. When this happens the film will either rupture (at low surfactant concentrations) or a black spot will form, which is the nucleus of a thinner, stable, second black film. We call ''critical'' the average film thickness at which either these events occurs. Later Manev et al. (1974) were able to demonstrate experimentally the gradual transition from rupture to formation of black spots with increasing surfactant concentration. de

Vries (1958, 1960) derived an equation for the free energy change and found a very reasonable volume of the transitional thickness, $h_t \sim 10^{-5}$ cm.

Scheludko (1962) did the next important step by relating the local fluctuations of the thickness to the surface thermal capillary waves and by proposing a simpler method of calculation of the transitional thickness. He derived a simple relation between h_t and the wave length, λ:

$$h_t = \left(\frac{A_H \lambda^2}{128\pi\gamma}\right)^{1/4} \tag{208}$$

where A_H is the Hamaker constant (see Sec. III.B.). More important is that he showed that instability may occur at vanishing wave amplitudes, provided that the average film thickness is small enough; he thus opened the way to the linear stability analysis.

The latter was first applied to film rupture by Vrij (1966) and Vrij and Overbeek (1968). Vrij also realized that at the transitional thickness the rate of deeping of the corrugation is zero, so that finite time is needed for the two surfaces to touch each other, during which the average thickness of a thinning film will decrease. Also, there is not just one wave but an infinite set of them, because the ''roughness'' of the film surfaces, caused by the thermal fluctuations, can be described properly only by the superposition of an infinite number of waves with different wave lengths and amplitudes. Using the above concepts Vrij (1966) and Vrij and Overbeek (1968) developed a graphic procedure for calculating the h_{cr} of thinning films and they obtained

$$h_{cr} \sim 0.222 \left(\frac{A_H R^2}{f\gamma}\right)^{1/4} \tag{209}$$

The coefficient f varies in the narrow margin from 4.5 to 6.9 when h changes from 40 to 100 nm.

By using the stability analysis on the basis of the lubrication approximation for tangentially immobile surfaces, Ivanov et al. (1970) derived the general equation for the critical film thickness

$$\begin{gathered} h_{cr}^2 = \frac{2kT}{\Pi'(h_t)R^2} \exp \frac{\left[\dfrac{R^2\Pi'(h_t)}{4\gamma(h_t)} \displaystyle\int_{h_{cr}}^{h_t} \frac{\Pi'}{P_c - \Pi}\, dh\right]}{\displaystyle\int_{h_{cr}}^{h_t} \frac{\Pi'}{P_c - \Pi}\, dh} \\ \frac{2\Pi'(h_t)}{\gamma(h_t)} \int_{h_{cr}}^{h_t} \frac{h^3\gamma}{V(h)}\, dh = \int_{h_{cr}}^{h_t} \frac{h^3\Pi'(h)}{V(h)} dh \end{gathered} \tag{210}$$

where Π is the disjoining pressure, incorporating different interaction components (see Sec. II.). In Fig. 42 the dependence of the critical thickness of rupture

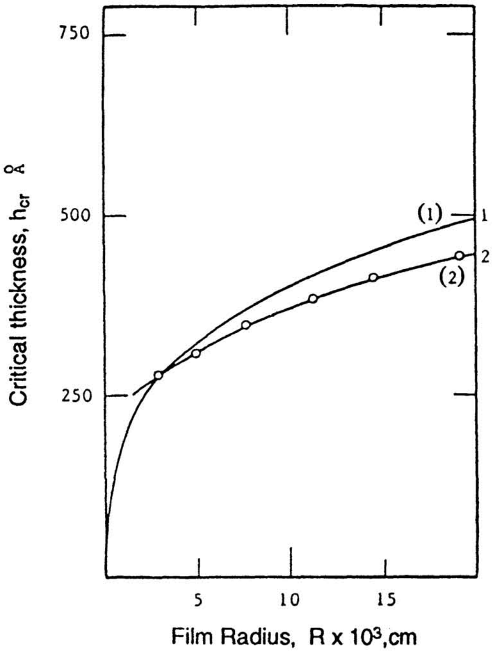


FIG. 42 Critical thickness of rupture, h_{cr}, vs. film radius, R, for free aniline films. Curve 1, theory; curve 2, experiment with 0.11 M solution of dodecanol. (From Ivanov, 1980.)

h_{cr} as a function of the film radius R is shown. Curve 1 is theoretically calculated on the basis of the Eq. (210). Curve 2 marks the experimental data for aniline films stabilized by dodecanol at a concentration of 0.11 M (Ivanov, 1980). In Fig. 43 the dependence of the critical thickness of rupture of aniline films on the concentration of dodecanol is shown (Ivanov, 1980). It is seen that when the film area increases, the critical thickness increases, while it decreases with the increase of the electrolyte concentration. For further details of the present theory one can extend a nonlinear analysis of stability, similarly to the treatment of Yiantsios and Higgins (1991) applied to wetting films.

In the case of approaching large bubbles, a dimple is formed between them and the theories cited above do not describe adequately the film rupture mechanism. As the experimental investigations of Schultze (1977) show, the most probable area of instability is the barrier ring encircling the dimple. A theory for the film rupture in such systems was developed in the work of Jain and Ivanov (1980). When small drops or bubbles collide, a plane-parallel film is formed between them and Eqs. (205) and (209) are applicable. An investigation of the influence of surfactant concentration and film radius upon the foam films

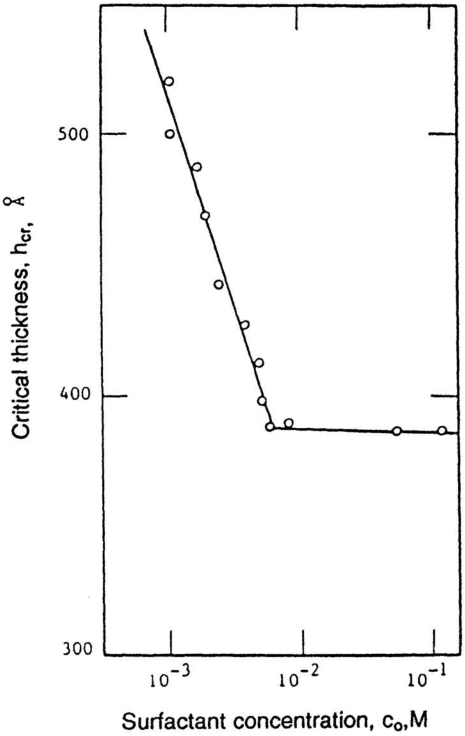


FIG. 43 Dependence of the critical thickness of rupture, h_{cr}, of aniline films on the concentration, C_o, of dodecanol. (From Ivanov, 1980.)

stability has been conducted by Ivanov et al. (1970), Ivanov and Dimitrov (1974), and for emulsion films by Traykov and Ivanov (1977); Ivanov et al. (1979) and Ivanov (1980) (see also Maldarelli and Jain, 1988). For foam films Ivanov et al. (1970) and Ivanov and Dimitrov (1974) have shown that the most probable to cause rupture are the so-called squeezing modes with wavelengths λ_n (n = 1,2 . . .) satisfying the condition $h << \lambda \leq R$. The critical wavelength in this case is on the order of 0.1 R.

The stability of thin (<100 nm) symmetrical and unsymmetrical membranes, assimilated with viscous liquids, to short- and long-wave length perturbations was investigated by Maldarelli et al. (1980). The asymmetry is due to the two different viscous phases surrounding the membrane and to the different interfacial tensions on the two faces of the membrane. An application of their results to a cell membrane shows that the growth of the instability is dominated in this case by the stretching mode, since the time scale of growth of the perturbations is four orders of magnitude less than that in the squeezing mode. For asymmetrical systems, the effect of differences between the interfacial tension on the two faces on the ratio of the amplitudes of perturbations on the two faces has been investigated by Maldarelli et al. (1980).

B. Inversion Film Thickness

As can be seen from Eq. (201), the film lifetime depends not only on h_{cr} but also on the thickness of film formation, h_i. In the limiting case $h_i >> h_{cr}$ from Eq. (201), one obtains that h_i does not influence the lifetime, but when $h_i \approx h_{cr}$ the inversion thickness becomes an important parameter. The treatment of film formation is important also for the bubble flocculation during coalescence processes (see Danov et al., 1993a). From the definition of h_i in Sec. V.A.2. and from Eq. (57) in the paper by Ivanov et al. (1985) the following equation for h_i could be derived:

$$h_i = \frac{F}{4\pi\bar{\gamma}}\left[\frac{1}{2} + \frac{1}{2}\sqrt{1 - \frac{16\pi}{3}\frac{\bar{\gamma}\bar{h}_s}{F(1 + \bar{b})}}\right] \tag{211}$$

From Eq. (211) it follows that when $\bar{h}_s << (1 + \bar{b})h_i$, the influence of the surface diffusion could be neglected; hence

$$h_i = \frac{F}{4\pi\bar{\gamma}} \tag{212}$$

For example, let F be the buoyancy force $F \sim 4/3\pi R_c^3\rho g$. In Table 2 one finds the following typical values parameters: $\bar{\gamma} = 30$ dyn/cm, $\rho = 1$ g/cm³, $R_c = 125$ μm. Then the inverse thickness is calculated to be $h_i = 210$ nm. At $R_c = 50$ μm one obtains the unrealistically small value of $h_i = 14$ nm. This means that the buoyancy force might be insufficient to explain the formation of films during the interaction of two bubbles. Danov et al. (1993a), following the scheme of Smoluchowski, have investigated the diffusion of deformable miniemulsion drops toward a given "central" drop in the presence of interaction energy U, which takes into account the van der Waals attraction and the electrostatical repulsion. The total force acting on the particles

$$F_T = kT\nabla(\ln P) + \nabla U \tag{213}$$

is a sum of the Brownian (diffusion) force and the potential force, which is due to direct interactions between the particles. In Eq. (213) P is the probability of finding another particle situated at a distance z from the central drop (more precisely, z is the distance between the centers of mass of the particles). The process of flocculation and coalescence is described by the scheme depicted in Fig. 30. After a detailed solution of the problem Danov et al. (1993a) obtained the following transcendental equation for determining h_i:

$$h_i = \frac{kT}{2\pi\gamma z_d}\left\{\int_0^{z_d}\left(\frac{z_d}{z}\right)^2 \frac{s(z)}{s(z_d)} \exp\left[\frac{U(z) - U(z_d)}{kT}\right]\frac{dz}{z_d}\right\}^{-1} \qquad (214)$$

where $s(z)$ is the hydrodynamic resistance to the mutual drop motion. In Fig. 44 the numerical solution of Eq. (214) for h_i as a function of the particle radius is shown for three different values of the Hamaker constant: $A_H = 5 \times 10^{-14}$ erg (curve 1), $A_H = 1 \times 10^{-13}$ erg (curve 2), and $A_H = 5 \times 10^{-13}$ erg (curve 3). It is seen that the van der Waals attraction promotes the film formation. At bigger droplet radii the film formation is enhanced. Curves 2 and 2' correspond to mobile and immobile interfaces. One sees that the interfacial mobility does not influence significantly the inversion thickness. When the electrostatic repulsion is taken into account (Fig. 45), the inversion thickness decreases with the decrease of the electrolyte concentration C_{el}. The points in Fig. 45 correspond to concentration at which there is still a probability for film formation. At lower electrolyte concentrations the kinetic energy of the drops is not large enough to overcome the energy barrier accompanying the drop deformation, and the particles behave like nondeformable charged spheres. In Fig. 46 the ratio of buoyancy the force F_b to the full force F_T (Danov et al., 1993a) at the moment of film formation is shown. The parameters are the same as in Fig. 44 and $\Delta\rho = 0.2$ g/cm^3. It can be seen that with the increase of the dimensions the role of

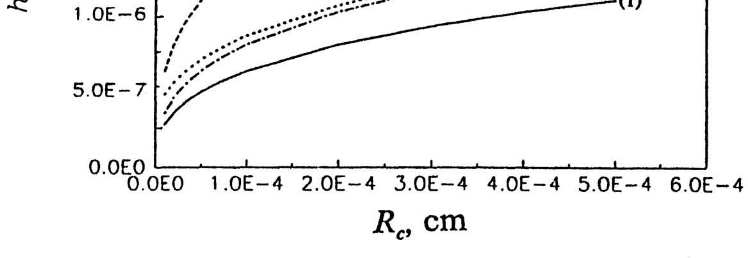


FIG. 44 Dependence of the inverse thickness h_i on the drop radius R_c: $A_H = 5 \times 10^{-14}$ erg (curve 1); $A_H = 1 \times 10^{-13}$ erg (curve 2); $A_H = 5 \times 10^{-13}$ erg (curve 3); $A_H = 1 \times 10^{-13}$ erg and tangential immobility (curve 2'). The interfacial tension is $\gamma = 1$ dyn/cm for all curves. (From Danov et al., 1993a.)

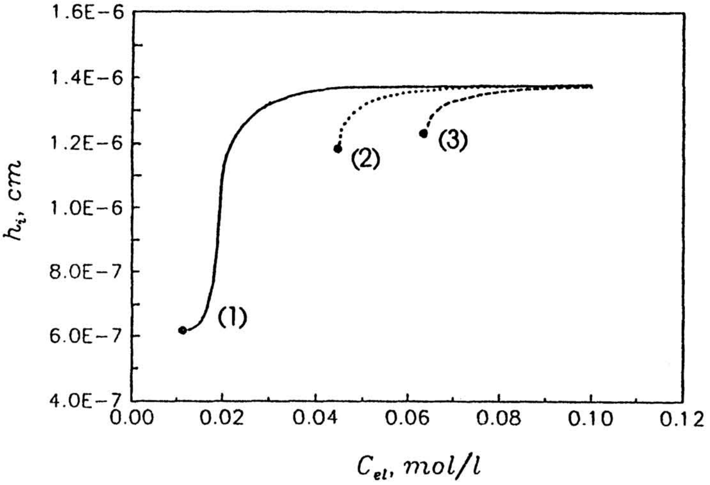


FIG. 45 Influence of the electrolyte concentration, C_{el}, on the inverse thickness h_i; $\psi_s = 50$ mV (curve 1); $\psi_s = 25$ mV (curve 2); $\psi_s = 10$ mV (curve 3). $A_H = 10^{-13}$ erg, $R_c = 5$ μm, $\gamma = 1$ dyn/cm. The full points at the ends of the curves correspond to concentrations at which the drop deformation becomes important. (From Danov et al., 1993a.)

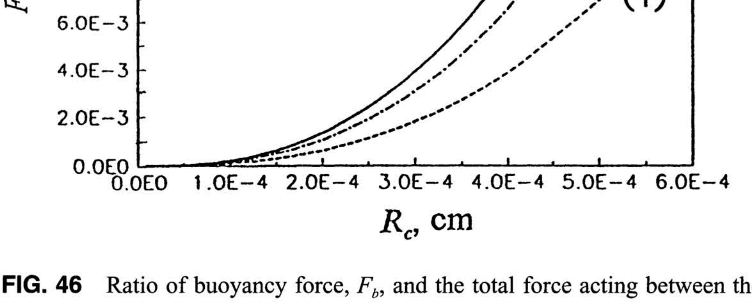


FIG. 46 Ratio of buoyancy force, F_b, and the total force acting between the drops, F_T, vs. the drop radius R_c: $A_H = 5 \times 10^{-14}$ erg (curve 1); $A_H = 1 \times 10^{-13}$ erg (curve 2); $A_H = 5 \times 10^{-13}$ erg (curve 3). (From Danov et al., 1993a.)

the Brownian force decreases, but it is predominant over the buoyancy force at small particle dimensions. For emulsion systems $\Delta\rho = 1$ g/cm^3 and the F_b/F_T ratio is five times bigger.

Another force that can be important for the emulsion and foam stability is the hydrodynamic force in a shear or nonturbulent flows (see Schowalter, 1984). An attempt at similar treatment in the case of turbulence was performed by Kumar et al. (1991, 1992).

ACKNOWLEDGMENT

The authors are indebted to Miss Mariana Paraskova for her careful work of manuscript typing and figure preparation.

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