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THIN FILMS INCLUDING LAYERS: TERMINOLOGY IN RELATION TO THEIR PREPARATION AND CHARACTERIZATION

(IUPAC Recommendations 1994)

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Thin films including layers: terminology in relation to their preparation and characterization

Abstract. This document deals with the terminology in relation to the preparation and characterization of liquid and solid thin films and layers. It is not comprehensive, in that no consideration is given to certain types of layers such as ferromagnetic, ferroelectric, He or liquid metal films. Topics covered include: general terminology and characterization methods applicable to *both* solid and liquid films; terminology and characterization methods applicable *specifically* to either liquid or solid films, layers and multilayers. Comprehensive indexes of terms and methodologies (preparation and characterization) are given.

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The explosive growth of technologies based on thin films and layers of condensed matter (solid or liquid) has stimulated considerable research in physics, chemistry and biology. The terminology used to describe the characteristics of the thin films are often specific to these disciplines. As a result, confusing terminology (thin, ultrathin, ultra-ultrathin, thin-thin, thick-thin, etc.) has emerged in the scientific literature.

The present document deals with terminology related to the preparation and characterization of solid and liquid thin films and layers which are at least one atom or molecule thick. It expands previous IUPAC recommendations to these systems and should be used in conjunction with the "Manual of Symbols and Terminology for Physico-Chemical Quantities and Units; Appendix II, Definitions, Terminology and Symbols in Colloid and Surface Chemistry" [1], "Reporting Experimental Pressure-Area Data with Film Balances"[2], "Quantities, Units and Symbols in Physical Chemistry"[3] and "Symbols, Units, Nomenclature and Fundamental Constants in Physics"[4].

The discussion of the properties of liquid thin films and layers involves, mainly, concepts of classical physics and surface thermodynamics. The discussion of solid thin film and layer properties (e.g. charge and heat transfer, catalysis, etc.) involves also quantum mechanical concepts.

The list of films and layers considered in this document is not comprehensive. For example, the terminologies applicable to solid layers of ferromagnetic, ferroelectric, helium and liquid metal films are not considered.

General terminology applicable to solid films and layers and liquid films is presented in section II. Methods used to characterize features common to certain solid and liquid films are listed in Table III.1. Terminology specific to liquid film preparation and characterization is dealt with in section IV. There, definitions of physical quantities are presented in a format consistent with that of reference [3] (also recommended by IUPAC-IDCNS, IUPAC-Interdivisional Committee for Nomenclature and Symbols), whereas methods of characterization are presented briefly in a (six column) table format. The terminology related to the preparation and characterization of floating or deposited, organized or amorphous, organic or inorganic solid films or layers is presented in Section V in a format similar to that used in Section IV. The tables in these sections can be read as "check lists" and should be useful to referees of scientific articles. By juxtaposing in the same document terminology, "caveats" and recommendations, the efficiency of the present document should be enhanced. When needed, concepts and quantities specific to liquid interfaces are described or defined in footnotes and annexes. In the concluding Section VI several types of indexes are given. The symbols, abbreviations, acronyms and terms are indexed in Sections VI.1.- VI.3. An index of the terms related to film preparation methods is given in Section VI.4. The list of terms in Section VI.3 does not include those related to film characterization methodologies. Their alphabetical list is given in Section VI.5. The tables and figures are listed in Sections VI.6.and VI.7. Helpful suggestions and comments on the document, have been received from several colleagues. This is acknowledged in Section VII.

[1] Definitions, Terminology and Symbols in Colloid and Surface Chemistry, *Pure Appl. Chem.*, **31**, 579-638 (1972).

[2] Reporting Experimental Pressure Data with Film Balances, *Pure Appl. Chem.* **57**, 621-632 (1985).

[3] *Quantities, Units and Symbols in Physical Chemistry*, Blackwell Scientific Publications, Oxford, 56 (1988); 2nd Edition (1993).

[4] Symbols, Units, Nomenclature and Fundamental Constants in Physics, Document IUPAP-25, *Physica A*, **146**,1-68 (1987).

II. GENERAL TERMINOLOGY APPLICABLE TO LIQUID AND SOLID FILMS

II.1. The term **film** is a generic one referring to *condensed* matter restricted in one dimension.

II.2. The term **layer** designates any conceptual region of space restricted in one dimension, within or at the surface of a condensed phase or a film. In the previous IUPAC recommendations (reference [1], pages 583-584), this term is used to describe an interface (e.g. interfacial layer) and interfacial processes and systems (e.g. adsorption and adsorption layers). The usage of the term "film" for an adsorption layer is confusing and discouraged. The term **double-layer** applies to layers approximated by two "distinct" sublayers (see "electrical double-layer" in *II.A. Annex of Section II*).

II.3. The terms **substrate** and **subphase** refer to a condensed phase that physically supports a film or layer. The term substrate should be used with care in the light of the existing *double meaning* of the term substrate in film science and technology, on the one hand, and in biochemistry, on the other. The term subphase applies, mainly, to a liquid phase underlying an adsorption layer or a floating spread monolayer (see ref. [2]).

II.4. The recommended abbreviation for film systems consists of three capital letters and two slashes (/): the middle letter representing the restricted phase or film, the two other letters corresponding to the adjacent bulk phases ([1], p. 613). For example, V/L/S applies to a liquid film bounded by a vapour V and a solid S bulk phase; W/O/W designates the oil film, O, bounded by aqueous, W, phases. For solid films the boundaries are often represented by hyphens (e.g. Al-SiO-Al abbreviates the S / S/ S system : bulk Al / solid film SiO / bulk Al).

II.5. A film bounded by two different bulk phases is referred to as an **asymmetric film** (first example above and $\alpha/\gamma/\beta$ in Fig. II.1) and as a **symmetric film** when the bulk phases (α and β) are identical.

II.6. A film is referred to as **open film** (as in Fig. II.1) when mass transfer can occur between the film and the coexisting bulk phases, for *all* the components. The terms **transition zone** (Fig. II.1) and **Plateau border** (defined in [1]) refer to the regions of space located at the periphery of certain open liquid films which ensure the continuity (no interface) between the film and the parent bulk phase (e.g. γ in Fig. II.1). The term **partly open film** applies to the film shown in Fig. II.2 when mass transfer can occur only for *certain* components. The term **closed film** applies to the films with *fixed mass*.

II.7. The terms **nanoscopic film** , **microscopic film** and **macroscopic film** should apply specifically to films which have *lateral* dimensions in the range of several $0.1\text{nm}^{[5]}$ - 100 nm, 0.1-100 μm and above 100 μm , respectively.

II.8. The term **planar film** refers to the film whose boundaries are represented by ideal parallel planes (e.g. α/γ and γ/β in figures II.1 and II.2). The **planar film thickness** is defined as the distance between these planes. The terms **nanometer thick film**, **micrometer thick film**, **millimeter thick film**, etc. must refer specifically to film thicknesses in the ranges 0.1-100 nm, 0.1- 100 μm , 0.1-100 mm, respectively.

II.9. The boundary separating a film from an adjacent solid bulk phase (e.g. S/L/S, V/S/S, V/L/S, L/S/S, Al/SiO/Al) is a surface defined by the position and geometric shape of the solid bulk phase, provided no mass

[5] Contemporary lithographic fabrication methods make it possible to produce such small structures.

transfer occurs across the boundary. The interfacial region of a liquid film in chemical equilibrium with an adjacent, liquid bulk phase (e.g. V/L/L and L/L/L) is inhomogeneous and is similar to any liquid interfacial layer. A solid/liquid film interface, sharp at equilibrium, becomes inhomogeneous in the direction normal to the film interface when interdiffusion occurs.

II.10. The film continuity in the x and y directions (figures II.1 and II.2) is a significant issue. Films are referred to as **discontinuous film** (consisting of discrete islands of material, on the substrate, without physical connection), **network film** (partially connected islands) or **continuous film**.

II.11. Films are classified qualitatively as either **thin film** or **thick film**. **Thin** applies only to films whose thickness is of the order of a characteristic scale or smaller. Since a film may "look" operationally thin or thick, according to the procedure applied, it is also recommended that the measurement procedure employed be specified (e.g. ellipsometrically thin film, X-ray thick film, optically thin film, etc.). It is recommended that the physical specification of the film thickness be used, whenever possible (e.g., thick compared to the electron mean free path, thin compared to the optical wavelength, etc.).

II.12. The term **monolayer** refers to a single, closely packed layer of atoms or molecules. The term **floating monolayer** is used for certain spread monolayers or films which are in the condensed - often solid - state (see reference [2], page 627). The term *Langmuir monolayer* has been, recently, coined for spread monolayers. This usage is not recommended by IUPAC (see ref. 2).

II.13. The term **multilayer** refers to a system of adjacent layers or monolayers. The term **bilayer** applies to the particular case of a multilayer two monolayers thick. Monolayers and multilayers may be alternatively named "films" provided boundaries can be defined for them as for the films in Fig. II.3.

II.14. The term **superlattice** refers to a **periodic multilayer** which is synthetic and where a unit cell, consisting of successive layers that are chemically different from their adjacent neighbours, is repeated. The term **quantum well multilayer** applies to the superlattices with artificially created electronic band structures.

II.15.

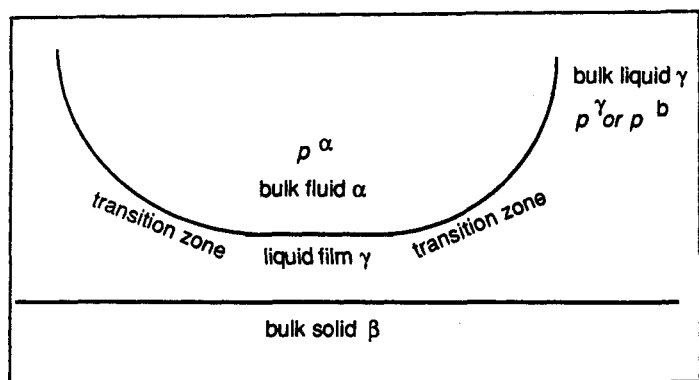


Fig. II.1. Film γ bounded by bulk phase β (solid), bulk phase α (fluid) and the transition zone; open film; asymmetric film; p^α and $p^\gamma(p^b)$ are the pressures inside bulk phases α and γ , respectively

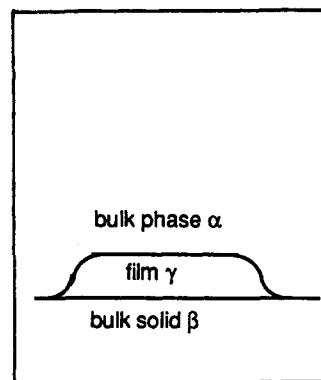
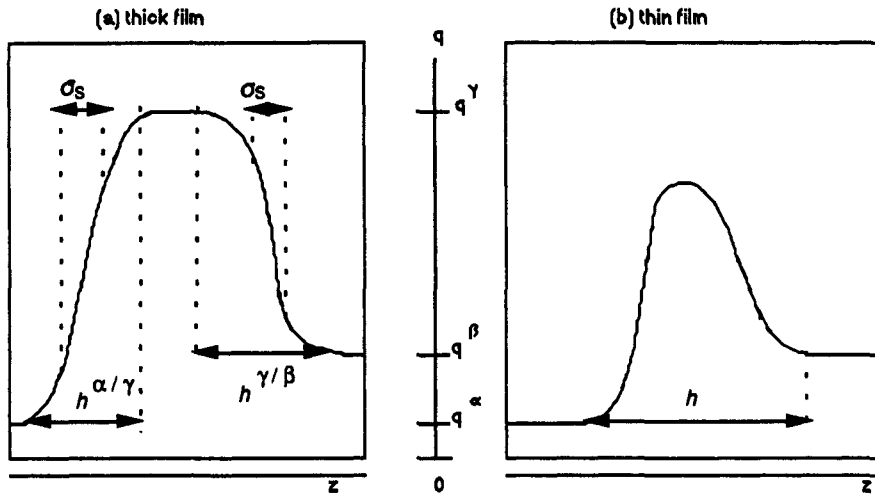


Fig. II.2. Film γ at the α/γ interface; either closed film or partly open film



II.16.

Fig. II.3. Films of γ continuous with bulk phase γ and bordered by bulk phases α and β . Asymmetric films; open films; planar films

II.17. Profile in direction z (of restriction), of a quantity $q(z)$ (where q may designate concentration or specific mass, energy, enthalpy, etc.); q^α , q^β and q^γ are specific to phases α , β , and γ , respectively; (a) thick film with distinct inhomogeneous interfacial layers α/γ and γ/β of, so-called, interfacial layer width, σ_s , and interfacial layer effective thickness, $h^{\alpha/\gamma}$ ($h^{\gamma/\beta}$), (defined in II.A. Annex); (b) inhomogeneous thin film with overlapped interfacial layers; the film effective thickness, h , is defined in Table IV.3.1.1.

II.A. ANNEX TO SECTION II. MOLECULAR INTERACTIONS AND CHARACTERISTIC LENGTHS AT INTERFACES

II.A.1. The **interfacial layer** is defined as the inhomogeneous space region intermediate between two bulk phases in contact, and where properties are significantly different from, but related to, the properties of the bulk phases [6]. Examples of such properties are: composition, molecular density, orientation or conformation, charge density, pressure tensor, electron density, etc. The interfacial properties vary in the direction normal to the surface. For example, the simple profile of the quantity $q(z)$ across the interfacial layer α/γ in Fig. II.3a could be that of the molecular density profile in the case of a one component L/V interface. Complex profiles of interfacial properties occur in the case of multicomponent systems with coexisting bulk phases [7] where attractive/repulsive molecular interactions (see below) involve adsorption or depletion of one or several components.

II.A.2. The term **interfacial layer effective thickness** is defined as the separation between the "effective limits" of simple or of complex interfacial profiles, and depends on both the type of the profile and on the chosen profile limits (in fig. II.3a $h^{\alpha/\gamma}$ is the effective thickness of the interfacial layer α/γ defined by the simple profile of the quantity $q(z)$ between phase α and film core γ).

II.A.3. Examples of the main attractive/repulsive interactions leading to complex profiles of interfacial properties are listed below.

II.A.4. The **unretarded dispersion** (van der Waals) energy and the **retarded dispersion** (van der

[6] ref. [1] page 583.

[7] ref. [1] page 584.

Waals) **energy**. This energy is referred to as **unretarded** when the attractive interaction between two molecules^[8], arising from fluctuation of their electronic activity and related properties (e.g. optical polarization), decays as r^{-6} , where r , the intermolecular separation, is much larger than the molecular dimension. The term **retarded** applies to the intermolecular dispersion energy effective in the case of large r when the attractive energy decays as r^{-7} , since the finite speed of electromagnetic radiation cannot be ignored. The transition "unretarded/retarded" occurs at an intermolecular separation defined by $r \approx \lambda_c$ ^[9], where λ_c is the specific wave length of the electromagnetic radiation. The terms retarded and unretarded dispersion energy are applied also in other systems where intermolecular dispersion forces are involved, for example, when two macroscopic (semi-infinite) bodies interact at separations, h , much smaller than their size. Then, the unretarded dispersion energy varies as h^{-2} and the retarded as h^{-3} .

II.A.5. The Coulombic interaction of interfacial charges (e.g. ions) and the magnetic or electrostatic interaction of interfacial molecules lead to particularly complex interfacial structures. Complex interfacial profiles that can be approximated by two distinct sub-layers with different physical properties (e.g. structure and/or nature and/or composition), are referred to as **interfacial double-layers**. Examples of such approximated complex profiles are: the **electrical double-layer** consisting of a **surface charge layer** (i.e. a two dimensional, 2D, distribution of one type of ions) and a **diffuse charge layer** (counter-ions distributed over the space region next to the surface) ^[10]; the approximated profile of the orientation angle of anisotropic liquid molecules within a "double-layer" consisting of a distribution of so-called **anchored molecules** which are perturbed (strongly bound and orientated) by the surface, and the adjacent, so-called, **transition layer**, i.e. the region where the surface perturbation is damped.

II.A.6. The term **characteristic length** or **scale** refers, in general, to the parameter which characterizes a density profile (of a given physical quantity). The *static* (equilibrium) or *dynamic* character of a characteristic length must be specified. The terms **out of plane** and **in plane** refer to characteristic lengths normal or parallel to the interface, respectively. Since interfacial layer "thickness" and characteristic length correspond to various concepts, the current usage where an out of plane characteristic length is referred to as the interfacial layer thickness, is confusing and should be abandoned. Some typical out of plane, static scales are listed and defined below. The list is not comprehensive.

II.A.7. The so-called **interfacial layer width**, σ_s (Fig. II.3a), is the characteristic length defined by the variance of the Gaussian function fitted to the *gradient* of the electron density profile established by X-ray specular reflectivity studies of the liquid interface.

II.A.8. The **pair correlation length**, ξ , approximates to the characteristic length associated with certain number density profiles of diffuse layers. ξ is defined as the separation between two interacting entities (molecules, macromolecular segments, ions, spins), either in bulk or interfacial regions, beyond which an appropriate function, referred to as **pair correlation function**^[11], either decays (e.g. to 1/e of an "initial" value)

^[8] ref.[1] page 616.

^[9] λ_c corresponds to the wavelength in the absorption spectrum of interacting species (mainly in UV and near X-ray wavelengths) that gives the main contribution to the dispersion interaction.

^[10] Interphases in Systems of Conducting Phases, *Pure Appl. Chem.*, **58**, 437-454 (1986).

^[11] The pair correlation function defines the degree of interdependence between microscopic properties of two distinct regions within a system (e.g. molecular or ionic density correlation functions in the case of liquids or electrolyte solutions, respectively).

or vanishes. For example, (κ^{-1}) [12] or (L_D) [13], the **Debye screening length**, characterizes charge density correlation functions ($\propto e^{-z/\kappa}$ or $\propto e^{-z/L_D}$). The scale κ^{-1} applies to the case of electrolyte solutions or gas plasmas and to the profile of space charge density in diffuse charge layers of electrical double-layers. The scale L_D applies to the diffuse space charge region of semiconductor interfacial layers. A characteristic length must be confused neither with the effective thickness of the interfacial layer defined above, nor with the *range* (effective distance) of the intermolecular (pair) potential. This range is defined by the distance over which this potential and the corresponding correlation function both vanish.

II.A.9. The **coherence length**, ζ , refers to the distance over which order is maintained. As an example, there can be long-range atomic or molecular order, i.e. coherence. Coherence lengths are significantly larger than molecular size. Normally, coherence length is estimated from electron, neutron or X-ray scattering and scales the size of ordered domains in materials where long range ordering occurs (as in liquid crystals, for example). The term coherence length is also used for the *scale* characterizing the profile of molecular axis orientation in the distorted, so-called, transition layers formed at a solid/liquid-crystal boundary when an appropriate external field is applied (e.g. when the orientation of anchored surface molecules of a nematic liquid crystal is unaffected by an external field - magnetic or electric - whereas the bulk molecules reorient freely). This scale is referred to as **electric coherence length**, ζ_E , or **magnetic coherence length**, ζ_M , depending on the nature of the applied field.

II.A.10. The **dispersion (van der Waals) interaction characteristic length** may be designated by the symbol l_m defined as follows: l_m is equal to the separation between the interacting species (e.g. molecules, bodies, etc.) where, specifically, *the character of dispersion energy changes from unretarded to retarded*. It is suggested that l_m be identified with λ_c which is of the order of 10 nm (see [6]).

III. METHODS OF CHARACTERIZATION APPLICABLE TO ORGANIC OR INORGANIC, LIQUID OR SOLID FILMS OR LAYERS

A certain number of characterization methods are *common* to a variety of films irrespective of their physical state and chemical nature. In the present context, *common* signifies that a *given technique and associated technology* permits *one* to *derive information* on a feature specific to more than a single type of films or layer. Examples of such common features and related methods of characterization appear in Table III.1. These common features, referred to as *derived information* in Table III.1 (first column) are: average thickness, thickness uniformity, texture, crystalline structure, lattice parameters, molecular/atomic organization, chemical composition, surface roughness, functionality (first column in Table III.1). Techniques and associated methodologies used to study these features appear in the second and third columns of Table III.1.

Further specific details regarding each type of film are to be found in Tables IV.7.1, V.1.1.2.1, V.1.2.2.1 and V.3.4.1, below.

[12] [ref.3] page 53, note 21.

[13] Terminology in Semiconductor Electrochemistry and Photoelectric Energy Conversion, A. J. Bard, R. Memming, B. Miller, IUPAC Document, Commission I.3, page 19.

TABLE III.1. Characterization methods applicable to liquid and solid layers and films**III.1.**

<i>Derived Information</i>	<i>Technique</i>	<i>Methodology</i>
Mass surface concentration (mass / film unit surface area)	acoustic	acoustic waves (bulk or surface waves)
Equivalent thickness / (*)	optical	surface plasmon extinction
	electrical	conductance; capacitance
Thickness (including optical)	optical (visible range)	ellipsometry, interferometry
	neutron and X- ray beams	specular reflection; interferometry
Thickness uniformity / (**) Surface roughness, capillary ripples	optical (visible range), neutron and X-ray beams	interferometry, differential interferometry and radiation scattering (visible range)
Elasticity, viscosity, viscoelasticity	mechanical, dynamic	rheometry, acoustic waves, direct stress
Texture and architecture	optical (visible range)	microscopic birefringence, fluorescence and Brewster angle microscopies
	electron beam	scanning electron microscopy, scanning tunneling microscopy
Phase identification / transition, film stability	calorimetry, thermal analysis	quantity of heat, specific heat, heat capacity
	electrical	in plane and out of plane conductance; capacitance; dielectric loss
Composition / composition profile	analytical	radiochemical
	electron and X-ray beams	ESCA (****), XPS(°)
	neutron beam	specular reflection ; H/D contrast
Molecular organization: tilt, crystal structure, lattice parameters, coherence length / (***)	neutron beam, X-radiation	specular reflection and diffraction; H/D contrast (neutron only).
	optical	vibrational (IR and Raman) and electronic(UV and visible) spectroscopies; dichroic absorption, evanescent waves
	magnetic + radio frequency	nuclear magnetic resonance
Chemical functionality	chemical	heterogeneous reactions
Charge transfer	photochemical /optical	fluorescence and flash spectroscopy , electronic and vibrational spectroscopies
	electrical	conductance (electronic)
Charge transport	electrical (dc, hf) (°°)	galvanomagnetic measurements

(*) See Table IV.3.1.1.1 .

(**) See Section IV.4.

(***) See II A. Annex .

III.2. (****) ESCA: electron spectroscopy for chemical analysis.**III.3.** (°)XPS: X - ray photoelectron spectroscopy.**III.4.** (°°) dc: direct current; hf: high frequency.

IV. LIQUID THIN FILMS

IV.1. CLASSIFICATION

In general, the widely accepted categories of liquid films are :

IV.1.1. **foam films**, V/LV, separating two vapour phases as in bubbles;

IV.1.2. **emulsion films**, L/L/L, separating two droplets or drops;

IV.1.3. **suspension films**, S/L/S, a new term recommended for liquid films separating two solid surfaces (by analogy with emulsion films);

IV.1.4. **wetting films**, V/L/S and V/L/L, recommended exclusively for the asymmetric films separating a liquid or a solid from a vapour.

IV.2. FILM FORMATION

The description of thin, liquid and planar film formation covers all the stages whereby a film of given thickness, h , and surface area, A , is obtained from a vapour or a liquid. The time evolution of a liquid film area and/or thickness, depends on the film dynamics involved in the process of film formation (e.g. spreading, drainage, etc.).

IV.2.1. The term **adsorption wetting film** designates the layer formed by the adsorption of a vapour onto the surface of a condensed phase referred to as substrate (defined in section II). In this case, the term "**adsorption wetting layer**" is more appropriate since it is consistent with the definition of the term "layer" in section II. The wetting layer in equilibrium with a vapour and formed by the *evaporation* of a thick liquid layer deposited on the substrate must also be referred to as adsorbed. The symmetric liquid film S/L/S formed by *capillary condensation* of adsorbed vapours in porous solids should also be referred to as adsorbed.

IV.2.2. **Liquid spreading**, often called **film spreading**, refers to the process of **wetting film formation** from a liquid (e.g. γ) drop deposited at the substrate interface (e.g. α/β) and leads to V/L/S and V/L/L films. **Film expansion** (not to be confused with film spreading) refers to the process where a film area increases at constant film mass. This term applies specifically to semi-closed or closed planar wetting films (see asymmetric film in Fig. II.2.). Liquid spreading and film expansion are characterized by the quantity called **work of liquid spreading** which is defined by the net change in interfacial tensions in the system involved in spreading and is expressed by $w_{spr} = (\sigma^{\alpha\beta} - \sigma^{\alpha\gamma} - \sigma^{\beta\gamma})$ (see [1]p. 597).

IV.2.3. **Drainage** of a horizontal or vertical liquid layer either supported by a frame or a substrate, or intercalated between two bulk phases, applies to the process of thin film formation by outflow of liquid (e.g. γ in fig. II.3a&b) from the core of the layer (see also following section IV.6.2.) For example, drainage is involved in V/L/V, S/L/S, L/L/L, V/L/S and V/L/L film formation.

IV.3. MAIN QUANTITIES IN THE CONTEXT OF PLANAR FILMS

IV.3.0.1. Quantities particular to planar and thin liquid films which require special consideration, are: **thickness** (and **volume**), **composition** (2D concentration), **film tension**, **film disjoining pressure** and **film energy of interaction**. Mechanical and/or thermodynamic definitions of these quantities for planar

symmetric films, are given in Table IV.3.1.1, Table IV.3.1.2, Fig. IV.3.1 and Fig. IV.3.2. Remarks concerning asymmetric thin films may be found in table footnotes or in figure captions. The terminology concerning liquid interfacial layers, that is relevant to liquid films, is defined in footnotes or annexes.

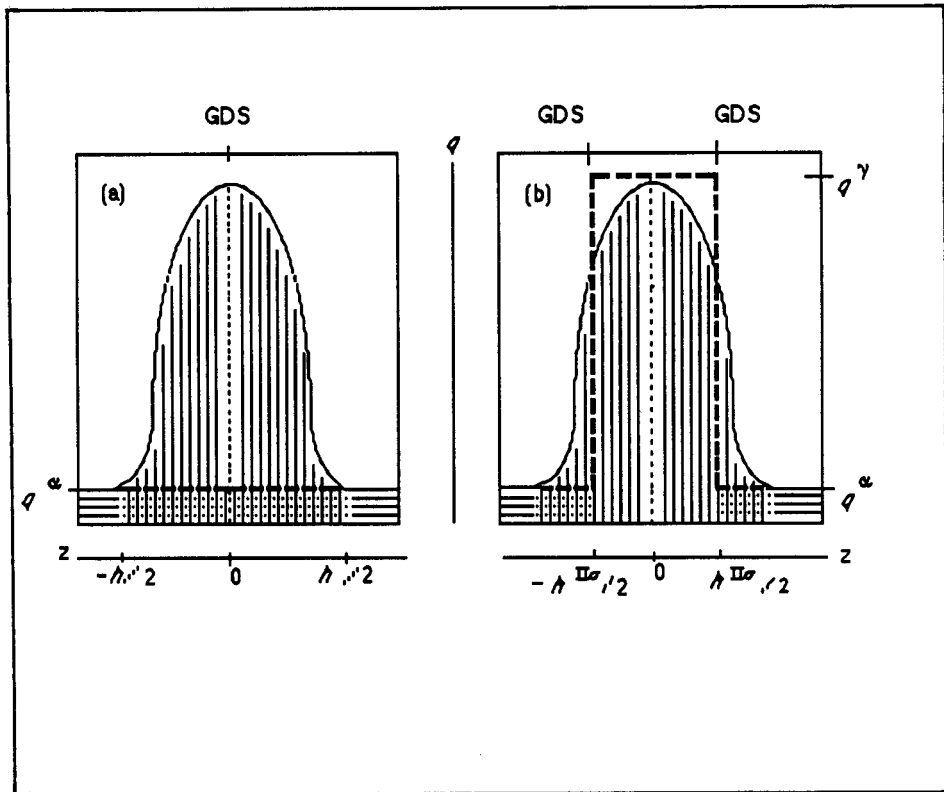


Fig. IV.3.1. Illustration of thermodynamic definitions of film properties using conventions $I\sigma$ and $II\sigma$ for a thin film of liquid γ ; symmetric film with respect to a mid plane at $z=0$ (thin dashed line) and bordered by two bulk phases α

IV.3.0.3. Continuous curve: distribution of the quantity q (e.g. concentration, density) in the direction z of film restriction. Horizontal full lines: bulk phase α where $q = q^\alpha$; vertical full lines: inhomogeneous region. h : is the (inhomogeneous) film effective thickness (see Fig. (a) above and definition in Table IV.3.1.1.) or the separation between the S/L interfaces of S/L/S film. When $q(z)$ designates the 3D (three-dimensional) concentration $c_i(z)$, of a substance in the film, the film surface concentration of component i , Γ_i^S (defined in Table IV.3.1.1.) of the substance corresponds to the area filled by the vertical full lines.

IV.3.0.4. (a) Single Gibbs dividing surface convention, GDS located at $z=0$. In the case of the asymmetric wetting films S/L/V and S/L/L, the single GDS is located at the S/L interface (β/γ in Fig. II.1). The horizontally dotted lines and thick dashed line illustrate a reference system consisting of two bulk phases α homogeneous up

to the single GDS. In this thermodynamic convention, the film thickness, $h^{\text{I}\sigma}$, and volume $V^{\text{I}\sigma}$, are equal to zero; a film excess quantity is associated with the single GDS (e.g. the film excess concentration of component i , $\Gamma_i^{\text{I}\sigma}$, defined in Table IV.3.1.1) and are illustrated by the vertical full lines *above* the thick and dashed horizontal line in Fig. IV.3.1.1a. The film surface area and film Gibbs dividing surface area are identical and noted A^{f} .

IV.3.0.5. (b) Two Gibbs dividing surfaces convention, GDSs, separated by a distance noted h^{f} or $h^{\text{II}\sigma}$ and referred to as the **film thermodynamic thickness** (defined in Table IV.3.1.1. and shown in Fig. IV.3.1.1b). The horizontal dotted lines and thick dashed line illustrate the reference system consisting of: i) two bulk phases α homogeneous up to the two GDSs and ii) a homogeneous region of phase γ ($q = q^{\gamma}$) which is $h^{\text{II}\sigma}$ thick (Fig. IV.3.1b). In this two GDSs convention, the **film thermodynamic volume** is $V^{\text{II}\sigma} = A^{\text{f}}h^{\text{II}\sigma}$ (Table IV.3.1.1) and the film surface excess quantities (e.g. the film surface excess concentration of component i , $\Gamma_i^{\text{II}\sigma}$ (Table IV.3.1.1), is associated with one of the *two* GDSs which exhibit a film surface total area equal to $2A^{\text{f}}$.

IV.3.0.6. The term **thermodynamic definition** applies when the film property (e.g. the 2D concentration) is defined as an *excess quantity relative to a chosen reference system* that is defined by using the **Gibbs dividing surface, GDS, convention**, as in the case of interfaces [14]. For thick (either asymmetric or symmetric) liquid films *two* GDSs are required (e.g. the asymmetric thick film shown in Fig. II.3a). For symmetric thin liquid films some authors prefer the use of a *single* GDS (Fig. IV.3.1a), whilst others prefer to retain two GDSs (Fig. IV.3.1b). Some authors designate the excess quantities of thin films by a subscript **0** and a subscript **f**, when the **film single GDS convention** or the **film two GDSs convention**, respectively, is used. Since these conventions lead to essentially different excess quantities, namely, a **film excess quantity** and a **film surface excess quantity** (see Table IV.3.1.1), a clear statement should be made in every case regarding which convention is being adopted. In order to be consistent with the symbols recommended in [1] for surface excess quantities designated by a superscript σ (upright), it is recommended (see Fig. IV.3.1 and legend of Table IV.3.1.1) to designate the excess quantities of a thin film represented by the **film single GDS convention**, by the **I σ superscript**, and the excess quantities of thin films represented by the **film two GDSs convention**, by the **II σ superscript**.

[14] For a single interface, with regard to the 2D concentration of species i , one may define either the *total* number of moles of i per unit area (of xy plane), Γ_i^{f} , associated with the total effective volume, or thickness, of the interfacial region (Guggenheim convention, [1] p.584), or the *excess* amount of moles of i per unit area (of xy plane), Γ_i^{σ} , with respect to the stoichiometry corresponding to a reference system of homogeneous adjacent bulk phases α, β, γ (Gibbs convention). This convention defines the volumes of these bulk phases by locating the Gibbs dividing surface, GDS. Γ_i^{σ} is referred to as either **surface excess concentration** or **Gibbs surface concentration** of component i . In the case of S/L interfaces, the solid phase surface is the chosen GDS. In the case of multicomponent liquids, the location of the GDS is chosen, by convention, as the plane where the surface excess of a reference component (e.g. the most abundant component present viz. the "solvent" designated by the subscript 0) becomes zero. The corresponding **relative Gibbs surface concentration** of component i is designated by the symbol $\Gamma_{i,0}^{\sigma}$.

IV.3.1. Film thickness, composition, tension and disjoining pressure

TABLE IV.3.1.1. Planar symmetric thin liquid films: Thickness and 2D-concentration

<u>Name/Notes</u>	<u>Symbol</u>	<u>Definition</u>	<u>S.I. Unit</u>
film effective thickness / [*]	h	"thickness" of the inhomogeneous film region (Figs. IV.2.1a and IV.2.2a)	m, nm
film or layer surface concentration of i (amount /unit film area / [**][**])	Γ_i^s	$\Gamma_i^s = 2 \int_0^x c_i(z) dz$ $x = h/2$ $c_i(z) = q(z)$ in Fig. IV.2.1	mol m ⁻²
film equivalent thickness / [***][**][***]	h_e	$h_e = \Gamma_i^s / c_i^\gamma$ $c_i^\gamma = q^\gamma$ in Fig. IV.1	m, nm
film excess concentration for component i / [**][§]	$\Gamma_i^{I\sigma}$	$\Gamma_i^{I\sigma} = 2 \int_u^\infty [c_i(z) \cdot c_i^\alpha] dz$ $I\sigma$ convention Fig. IV.1a	mol m ⁻²
film surface excess concentration of i / [**][§]	$\Gamma_i^{II\sigma}$	$\Gamma_i^{II\sigma} = \int_0^x [c_i(z) \cdot c_i^\gamma] dz + \int_x^\infty [c_i(z) \cdot c_i^\alpha] dz$ $x = (1/2)h$ $II\sigma$ convention Fig. IV.1b	
relative film surface excess concentration of i / [§§]	$\Gamma_{i,0}^{II\sigma}$	the choice of the two GDSs satisfies the condition : $\Gamma_{i,0}^{II\sigma} \equiv 0$ for the reference component 0	
thermodynamic film thickness $h^{II\sigma}$	$h^{II\sigma}$	distance between two GDSs $II\sigma$ convention Fig. IV.1b	
relative thermodynamic film thickness / [§§§]	$h_0^{II\sigma}$	$h_0^{II\sigma} = \Gamma_0^{I\sigma} (c_0^\gamma - c_0^\alpha)^{-1}$ when $\Gamma_0^{II\sigma} \equiv 0$	m, nm
film volume / [§§§§]	$V, V_e, V^{II\sigma}$	film volume = film thickness x film area	nm ³ , m ³

IV.3.1.1.

IV.3.1.2. [*] h : film effective thickness (Fig. IV.3.1a); applies also to asymmetric films (figures II.1 and II.3).

IV.3.1.3. [**] $c_i(z)$, c_i^α , c_i^γ are concentration of component i (density for single component systems) in the film inhomogeneous region and bulk phases α and γ , respectively; Γ_i^s : film surface concentration of i .

IV.3.1.4. [***] The term "film equivalent thickness" h_e designates the thickness of a layer in a bulk phase (e.g. γ) of uniform composition and/or density (e.g. $q^\gamma = c_i^\gamma$), which (layer) has an area A^f and matches a selected film property (e.g. moles/unit area of the layer Γ_i^s). The value of h_e approximates that of h .

IV.3.1.5. [§] The film excess concentration of component i , $\Gamma_i^{I\sigma}$, is associated with the unit area of the single GDS of the film (Fig. IV.3.1a). The (thermodynamic) film surface excess concentration of i , $\Gamma_i^{II\sigma}$, is the excess concentration associated with the unit area of each one of the two GDSs of the film. (Fig. IV.3.1b). $\Gamma_i^{I\sigma}$ ($\Gamma_i^{II\sigma}$) multiplied by the film area, A^f (film surface area $2A^f$), is equal to $n_i^{I\sigma}$ ($n_i^{II\sigma}$) the film (film surface) excess amount of component i present in the actual film $\alpha/\gamma\alpha$ in Fig. IV.3.1a (Fig. IV.3.1b), over the amount present in the homogeneous reference system defined in the Fig. IV.3.1a (Fig. IV.3.1b) exhibiting the same volume as the real system. The unit of the excess amount is mol. This "film" thickness and volume are zero (caption (a) of Fig. IV. 3.1).

IV.3.1.6. [§§] The subscript 0 of $\Gamma_{i,0}^{II\sigma}$ and $h_0^{II\sigma}$ implies that the film surface excess concentration of component 0 is zero, by analogy with interfacial terminology (footnote 14); $\Gamma_{i,0}^{II\sigma}$ relative film surface excess concentration of component i . [§§§] The film volume definitions: V^f , V_e , $V^{II\sigma}$, correspond to film thickness definitions: h , h_e , $h^{II\sigma}$.

Table IV.3.1.2. Planar symmetric thin films. Film tension and disjoining pressure

a. Operational and mechanical definitions. [*]

Name/Note	Symbol	Definition	S I Unit	Remarks
Film Tension (operational definition) / [**]	Σ^f or γ^f	$\Sigma^f = \left[\frac{\text{amount of reversible work done by the surroundings}}{\text{film area increase}} \right]_{\text{specified conditions}}$		$\Sigma^f > 0$ corresponds to a contractile force (see [*] and [**])
Film Tension (mechanical definition) / [***]	Σ^f	$\Sigma^f = 2 \int_0^\infty [p^\alpha - p_T(z)] dz$ $\Sigma^f = 2 \sigma^\alpha \gamma^\infty \cos \theta \Pi \sigma$	Nm^{-1} or Jm^{-2}	quantity associated with the single GDS (Fig. IV.3.1a and Fig. IV.3.1.1a).
Film Surface Tension (mechanical definition) / [****]	σ^f	$\sigma^f = \int_0^x [p^\gamma - p_T(z)] dz + \int_x^\infty [p^\alpha - p_T(z)] dz$ $x=(1/2) h \Pi \sigma$ $\sigma^f = \sigma^\alpha \gamma^\infty \cos \theta \Pi \sigma$		adequate to the two GDS convention (see Fig. IV.3.1b and Fig. IV.3.1.1b); it is assigned to each GDS (see Fig. IV.3.1.1b)..
Disjoining pressure (operational definitions) / [♦]	$\Pi_D(h)$	$\Pi_D(h) = p_N - p^b = p^\alpha - p^\gamma$ (specified conditions)	Nm^{-2}	$p_N = p^\alpha \neq p^b = p^\gamma$ (Fig. II.1 and Fig. IV.3.1.1)

IV.3.1.7.

IV.3.1.8. [*] Mechanical definitions of liquid interfacial tension $\sigma^{\alpha\gamma}$ (see IV.3.1.A Annex below), of liquid film tension Σ^f and liquid film surface tension σ^f are needed to express conditions of mechanical equilibrium of the inhomogeneous interfacial layers and thin films.

IV.3.1.9. [**] The film tension Σ^f or γ^f of a liquid film bounded by fluid phases is defined as the reversible work, done by the surroundings *on the system*, per unit of film area extension. Conditions to be specified are: state for all the bulk phases and their interfacial layers, temperature T and either volume V or pressure p of the system (e.g. fixed T, V, p , etc). The film tension of asymmetric or symmetric thick films (non-overlapping interfacial layers) is designated by a superscript ∞ and is defined in terms of bulk interfacial tensions (also designated by superscript ∞), viz., $\Sigma^{f\infty} = \sigma^\alpha \gamma^\infty + \sigma^\beta \gamma^\infty$ in the case of a thick asymmetric film (Fig. II.3a) or $\Sigma^{f\infty} = 2\sigma^\alpha \gamma^\infty$ in the case of a thick symmetric film (Fig. IV.3.1a).

IV.3.1.10. [***] Definitions of $p_T(z)$ and $p^\alpha = p_N$ are given in Table IV.3.1.2 Annex (below). Film single GDS convention: the GDS is the thin film surface of tension; film two GDSs convention: the GDSs are surfaces of tension associated with the thin film surface tension; $\theta^I \sigma$ and $\theta^{II} \sigma$: contact angles defined in Fig. IV.3.2. and its legend.

IV.3.1.11. [♦] The disjoining pressure, $\Pi_D(h)$, of an *open*, planar liquid thin film bounded by fluid bulk phases is defined, operationally, by the pressure shift or excess ($p^\alpha - p^\gamma$) equal to the difference between the pressure normal to the film p_N (equal to p^α), and the pressure p^γ (or p^b) of the parent bulk phase (Fig. II.1 and Fig. IV.3.2). This excess pressure is associated with the film thickness under given conditions (e.g. temperature, composition, state of bulk phases, film area, etc.) which must be specified. Currently, the adsorption wetting layer disjoining pressure is defined by the expression: $\Pi_D(h) = - (RT/V_m) \ln [p(h)/p_{sat}]$, where V_m is the partial molar volume for the adsorbate in bulk liquid and $p(h)$ and p_{sat} are the vapour pressures at equilibrium with the layer and with the bulk liquid, respectively. $\Pi_D(h) > 0$ implies a film swelling pressure.

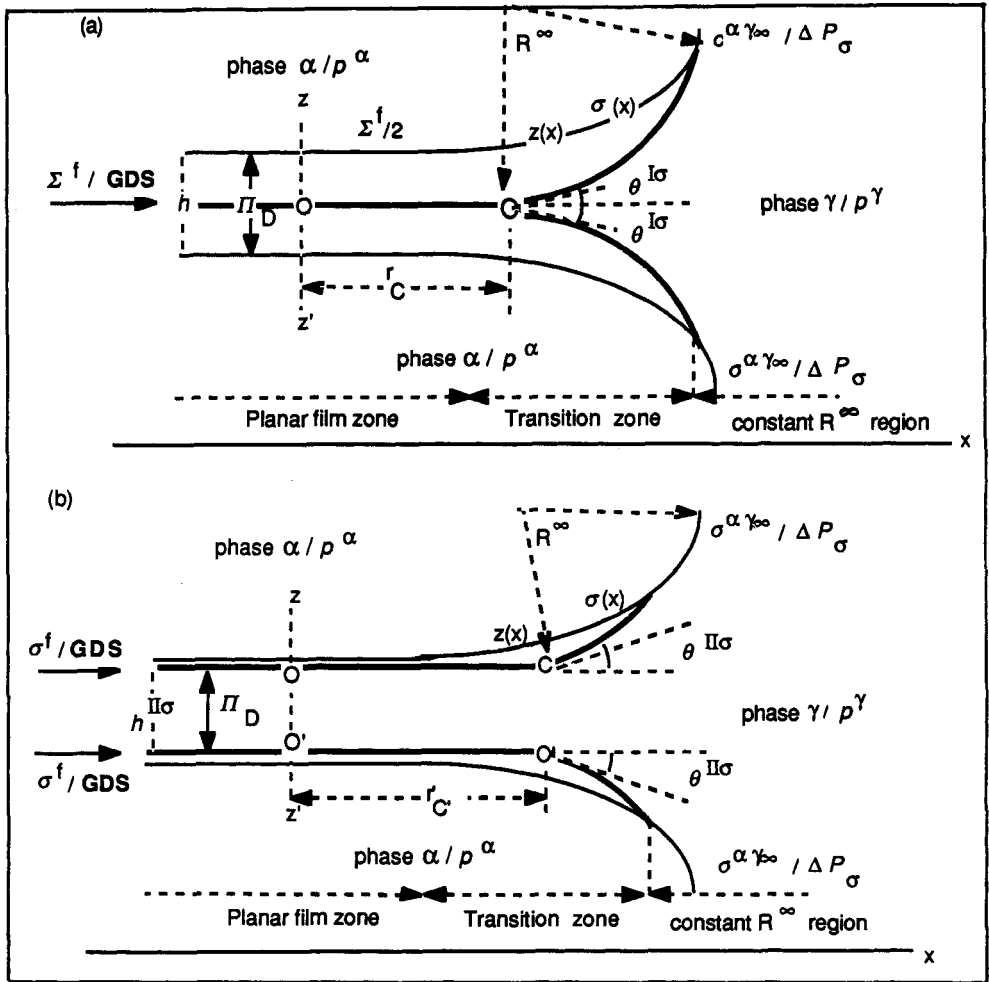


Fig. IV.3.2. Individual thin liquid film and thin liquid film periphery; planar, symmetric open film.

IV.3.1.13 *Thin, full* : liquid interface between the phase α , on the one hand, and the thin film, the transition zone and the bulk phase γ , on the other hand. $z=0$: film mid-plane; h : film effective thickness ; R^∞ : interfacial radius of curvature and interfacial tension $\sigma^{\alpha\gamma\infty}$ of the α/γ interface associated with Laplace pressure ΔP_σ . The superscript ∞ refers to a region far away from the planar film zone ; zOz' , $zOO'z'$: axis of circular film; $z(x)$, $\sigma(x)$ profile of the interface and interfacial tension in the *transition zone*; r_C , $r'C'$: contact line radius for reference systems.

IV.3.1.14 (a) film single GDS convention. *Thick full* : extrapolated, constant curvature GDSs (plane or curved) which define the reference system volume (homogeneous phases α , α and γ , in Fig. IV.3.1a), the *single* (reference) contact line C (in the film, xy , plane) and *two* (reference) contact angles $\theta^{I\sigma}$, as shown. Σ^f/GDS : film tension associated with the single GDS. [15]

IV.3.1.15 (b) film two GDSs convention. *Thick full* : extrapolated, constant curvature GDSs which define the reference system volume (homogeneous phases α , α and γ in Fig. IV.3.1b), *two* (reference) contact lines C , C' and contact angles $\theta^{II\sigma}$, $\theta'^{II\sigma}$; $h^{II\sigma}$, σ^f/GDS , $\sigma^{f'}/GDS$: film thermodynamic thickness (Table IV.3.1.1.) and film surface tensions (Tables IV. 3.1.2a and IV.3.1.2b) associated with the film (two) GDSs; II_D : disjoining pressure (Table IV.3.1.2) effective on the film (two)GDSs.

[15]For the wetting films $\alpha/\gamma/\beta$ (figure II.1), the single GDS and thermodynamic contact line C are located at the γ/β interface. Hence, only one reference contact angle can be defined.

TABLE IV.3.1.2. Planar symmetric thin films. Film tension and disjoining pressure

b. Thermodynamic Definitions

Name / Notes	Symbol	Definition	Remarks
Film tension / [*]	Σ^f, γ^f	$\Sigma^f = (\partial A / \partial A^f)$ fixed T, V, n_i	quantities associated with the whole system
Disjoining pressure / [*]	Π_D	$\Pi_D = -(\partial A / \partial h) (1/A^f)$	
Film excess Helmholtz energy / [**]	$A^{I\sigma}$	$A^{I\sigma} = 2 A^f \int_0^\infty [a(z) - a^\alpha] dz$	convention I σ : quantities associated with the surface area A^f (single GDS, Fig. IV.3.1a, Fig. IV.3.1.1a)
Film tension / [***]	Σ^f	$\Sigma^f = (\partial A^{I\sigma} / \partial A^f)$; fixed $T, n_i^{I\sigma}$ (closed films)	
Film grand potential / [♦]	$\Omega^{I\sigma}$	$\Omega^{I\sigma} = \Sigma^f A^f = A^{I\sigma} - \sum_i n_i^{I\sigma} \mu_i$	
Film tension / [♦]	Σ^f	$\Sigma^f = (\partial \Omega^{I\sigma} / \partial A^f)$; fixed T, μ_i (open films)	
Film surface excess Helmholtz energy / [♦♦]	$A^{II\sigma}$ $2\tilde{A}$	$A^{II\sigma} = 2A^f \int_0^x [a(z) - a^\gamma] dz + 2A^f \int_x^\infty [a(z) - a^\alpha] dz$ $x = (1/2) h^{II\sigma}$ (closed films)	convention II σ : quantities associated with the surface area $2A^f$ (two GDSs, Fig. IV.3.1b, Fig. IV.3.1.1b)
Film tension / [♦♦][♦♦♦]	Σ^f	$\Sigma^f = (\partial A^{II\sigma} / \partial A^f) = 2\sigma^f + \Pi_D h^{II\sigma}$; fixed $T, V, n_i^{II\sigma}$	
Film surface tension / [♦♦]	σ^f	$2\sigma^f = (\partial A^{II\sigma} / \partial A^f)$; fixed $T, h^{II\sigma}, n_i^{II\sigma}$	
Film disjoining pressure / [♦♦]	Π_D	$\Pi_D = \partial A^{II\sigma} / \partial h^{II\sigma} (1/A^f)$; fixed $T, A^f, n_i^{II\sigma}$	
Film grand potential / [♦][♦♦]	$\Omega^{II\sigma}$	$\Omega^{II\sigma} = 2\sigma^f A^f + \Pi_D V^{II\sigma} = A_i^{II\sigma} - n_i^{II\sigma} \mu_i$ (open films)	
Film tension / [♦][♦♦]	Σ^f	$\Sigma^f = (\partial \Omega^{II\sigma} / \partial A^f) = 2\sigma^f + \Pi_D h^{II\sigma}$ fixed T, μ_i	

IV.3.1.16.

IV.3.1.17. [*] A : system Helmholtz energy, V : system volume and n_i : system component amounts of (Ref. [1], p. 616); $\partial A^f > 0$ refers to film (area) dilation; Σ^f : film tension; Π_D : disjoining pressure. [**] film single GDS convention. $a(z)$, a^α and a^γ : Helmholtz energy density in the film inhomogeneous region and bulk phases α and γ , respectively (e.g. $a(z) = q(z)$ in Fig. IV.3.1.1b). $A^{I\sigma}$: film excess Helmholtz energy; $\Omega^{I\sigma}$ film grand potential; other film excess quantities can be associated with the GDS (e.g. film excess Gibbs energy, $G^{I\sigma} = A^{I\sigma}$, film excess amount of component i , $n_i^{I\sigma}$).

IV.3.1.18. [***] $n_i^{I\sigma} = \Gamma_i^{I\sigma} A^f$ defines $n_i^{I\sigma}$: the film excess amount of component i ; $\Gamma_i^{I\sigma}$ is defined in Table IV.3.1.1.

IV.3.1.19. [♦] μ_i : chemical potential of component i in the system.; $n_i^{II\sigma}$: see [***]. [♦♦] film two GDSs convention. $n_i^{II\sigma} = 2 \Gamma_i^{II\sigma} A^f$ defines $n_i^{II\sigma}$: the film surface excess amount of component i ; $h^{II\sigma}$: film thermodynamic thickness; $\Gamma_i^{II\sigma}$: film surface excess concentration of component i (see Table IV.3.1.1); Σ^f : film tension; σ^f : film surface tension; Π_D : film disjoining pressure. [♦♦♦] film two GDSs convention; $V^{II\sigma}$: film thermodynamic volume (see [§§§] in Table IV.3.1.1); $\Omega^{II\sigma}$: film grand potential; Σ^f : film tension; σ^f : film surface tension.

IV.3.1.A. Annex of Table IV.3.1.2. Mechanical and thermodynamic definitions of interfacial tension

IV.3.1.A.1. *Mechanical definition.* The *interfacial tension* is the excess tangential tension related to the anisotropic distribution of pressure tensor (stress) components associated with the inhomogeneous interfacial layer structure (see Fig. IV.3.1A.1): the tangential component $p_T(z)$, tangent to the surface, and the component p_N normal to the surface. The interfacial tension is a surface force since it is exerted at the boundary of bulk phases. For example, the interfacial tension $\sigma^{\alpha\gamma}$ of the liquid interface α/γ is defined by

$$\text{IV.3.1.A.2.} \quad \sigma^{\alpha\gamma} = \int_{-\infty}^{\infty} [p_N - p_T(z)] dz.$$

IV.3.1.A.3. The interfacial tension is associated with the *interfacial surface of tension*, a geometrical surface whose location is defined by the distribution of the tangential component ([¹], page 596).

IV.3.1.A.4. For planar interfaces, p_N is uniform over the interfacial layer and is defined by the hydrostatic pressure in the adjacent bulk phases; namely, $p_N = p^b = p^\alpha = p^\gamma$.

IV.3.1.A.5. For curved interfaces, the Laplace pressure, ΔP_σ , dependent on the curvature of the surface of tension and the interfacial tension, $\sigma^{\alpha\gamma}$, compensates the difference between the bulk hydrostatic pressures p^α and p^γ .

IV.3.1.A.6.

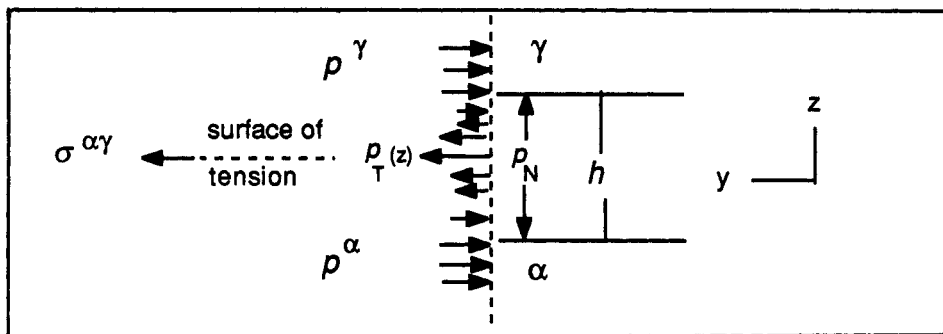


Fig. IV.3.1.A.1. Mechanical definition of interfacial tension $\sigma^{\alpha\gamma}$

IV.3.1.A.7. h : interfacial layer effective thickness; $p^\alpha = p^\gamma$: hydrostatic pressures of the bulk phases α and γ , respectively; horizontal arrows: distribution of the (anisotropic) pressure tensor components: $p_T(z)$, pressure tensor: tangential component; p_N : pressure tensor normal component ($= p^\alpha = p^\gamma$); dashed horizontal: surface of tension parallel to the xy plane and associated with $\sigma^{\alpha\gamma}$.

IV.3.1.A.8. *Thermodynamic definitions.* The *interfacial tension* is the intensive factor in the differential expression for the reversible work required to increase the interfacial area (conjugated extensive variable of the interfacial tension) under specified conditions ([¹] p. 597).

IV.3.1.A.9. For closed interfacial layers, the interfacial tension is defined by $\sigma = (\partial A^\sigma / \partial A_s)$ at fixed T and n_j^σ , where the reversible surface work is expressed by the change in the surface excess Helmholtz energy, A^σ , associated with the GDS, and dA_s is the variation of GDS area. Definitions of σ based on various excess surface quantities are given in [¹] (section 1.2.4.).

IV.3.1.A.10. For open interfacial layers, the interfacial tension is defined by $\sigma = (\partial \Omega^\sigma / \partial A_s)$ at fixed T and μ_j^σ where the reversible surface work is expressed by the change in the surface grand potential associated with the Gibbs dividing surface $\Omega^\sigma = \sigma A_s$.

IV.3. 2. Film Interaction energy, surface forces and disjoining pressure

Film interaction energy

IV.3.2.1. The amount of *reversible work*, $W(h)$, required to form a planar thin film of effective thickness h from a bulk phase or a thick film ($h = \infty$) under specified conditions (temperature, volume or pressure, composition or chemical potentials, etc.) defines the *change in potential energy* of the system (including the film). The potential energy of a system including a *thick*, planar film with non overlapping interfacial profiles (Fig. II.3a) defines the *zero* level of the potential energy of the thin and planar film (Fig. II.3b). Hence, the work $W(h)$ is the mechanical definition of the **planar film interaction energy**. This quantity is ascribed to the coupling of interactions associated with the overlapped interfacial structures (See II.A. Annex). In the case of deformed films (bent, curved, etc.) the thin film interaction energy includes the various work contributions due to film deformation.

IV.3.2.2. 'Interaction' thermodynamic functions, related to $W(h)$ and film thickness dependent, are given in Table IV.3.2.1 for planar, symmetric liquid films, either open or closed. For example, the term **film Interaction Helmholtz energy**, $\Delta A(h)$, applies when the reversible process of film formation occurs isothermally in a closed system under appropriate volume and film area, A' , conditions. $\Delta A(h)$ divided by A' should be represented by the symbol $\Delta a'(h)$. It is referred to as the **film interaction specific Helmholtz energy**.

IV.3.2.3. The **grand potential change**, $\Delta \Omega(h)$, (Table IV.3.2.1 below) is associated with the formation of a thin film of thickness h from an infinitely thick one and may be referred to as the **film formation grand potential**. This quantity is a function of various changes in film properties including the change $\Delta \Gamma_i^{\Pi \sigma}$ in the film surface excess concentration (Table IV.3.1 below). This change may occur in multicomponent open films.

Surface forces and disjoining pressure

IV.3.2.4. The planar film quantity derived from the variation, with thickness, of the film interaction Helmholtz energy is referred to as either the **disjoining pressure**, Π_D , (see Tables IV.3.1.2a, IV.3.1.2b and IV.3.2.1) or the **surface force**. The term *disjoining pressure* is more appropriate. It is preferred and recommended.

IV.3.2.5. A disjoining pressure may be either positive or negative. It is equivalent to a, so called, 'repulsive' effect (between the film interfaces), in the first case, and to a, so called, 'attractive' effect in the latter.

IV.3.2.6. The order of magnitude of a film effective thickness where surface structure overlapping becomes significant is determined by the characteristic length (see II.A. Annex) of the interfacial structure which *actually* overlaps. For example, in the case of a thin film with overlapping interfacial electrical double layers, only the diffuse layers actually overlap and the effective film thickness is of the order of the diffuse layer characteristic length ($h \approx 2\kappa^{-1}$).

Definitions of the main disjoining pressure components and corresponding characteristic lengths are listed in Table IV.3.2.2. The list is not comprehensive.

Table IV.3.2.1. Planar symmetric films. Film energy of Interaction

Name / Note	Symbol	Definition	S.I. Unit	Remarks
Film interaction potential energy / [*]	$W(h)$	$W(h) = A^f (\Sigma^f - 2\sigma^{\alpha\gamma^\infty})$	J	definitions based on observed mechanical quantities : $\Sigma^f, \sigma^{\alpha\gamma^\infty}, \Pi_D$
Film interaction Helmholtz energy / [**]	$\Delta A(h)$	$\Delta A(h) = A^f \int_{\infty}^h \Pi_D dh = W(h)$ fixed T, n_j, V, A^f (closed system)		
Film excess interaction Helmholtz energy / [***]	$\Delta A^{I\sigma}$	$\Delta A^{I\sigma}(h) = 2\sigma^{\alpha\gamma^\infty} (\cos\theta^{I\sigma} - 1) A^f$ fixed $T, n_j^{II\sigma}, A^f$ (film closed interfaces)		thermodynamic definition : $I\sigma$ convention (Fig. IV.3.1a, Fig. IV.3.1.1a)
Film surface excess Helmholtz energy / [♦]	$\Delta A^{II\sigma}$	$\Delta A^{II\sigma} = -A^f \int_{\infty}^x \Pi_D dh$ $x = h^{II\sigma}$ $\Delta A^{II\sigma} = 2\sigma^{\alpha\gamma^\infty} (\cos\theta^{II\sigma} - 1) A^f$		
Film interaction Gibbs energy / [♦]	$\Delta G^{II\sigma}$	$\Delta G^{II\sigma} = \Delta A^{II\sigma} + \Pi_D V^{II\sigma}$ $\Delta G^{II\sigma} = A^f \int_0^{\Pi_D} h d\Pi_D$		
Film interaction specific Gibbs energy / [♦]	$\Delta g^{II\sigma}$	$\Delta g^{II\sigma} = \Delta G^{II\sigma} / A^f$ $\Delta g^{II\sigma} = 2\sigma^{\alpha\gamma^\infty} (\cos\theta^{II\sigma} - 1) + \Pi_D h^{II\sigma}$	$J m^{-2}$	
Film formation grand potential / [♦♦]	$\Delta\Omega$	$\Delta\Omega = W(h) - \Delta(A^f \Sigma^f)$ fixed T, μ_i, A^f (open interfaces)	J	Ω : grand potential of the system
Film formation surface excess concentration/ [♦♦♦]	$\Delta\Gamma_i^{II\sigma}$	$\Delta\Gamma_i^{II\sigma} = \Gamma_i^{II\sigma} - \Gamma_i^{\alpha\gamma^\infty} = -\sigma^{\alpha\gamma^\infty} (d \cos\theta^{II\sigma} / d\mu_i)$ fixed $T, A^f, h^{II\sigma}, \mu_{\neq i}$ (open interfaces)	$mol m^{-2}$	$\Delta\Gamma_i^{II\sigma}$: shift in film surface excess concentration

IV.3.2.7.

IV.3.2.8. [*] $W(h)$: reversible work supplied to the system on film formation; h : film effective thickness (Table IV.3.1.1 & Fig. IV.3.1); Σ^f : film tension; $\sigma^{\alpha\gamma^\infty}$: α/γ interfacial tension (Fig. IV.3.2)

IV.3.2.9. [**] $\Delta A(h)$: system Helmholtz energy change on isothermal film formation ($\Delta A(h) = W(h)$) ; definition consistent with that of film disjoining pressure, Π_D , in Table IV.3.1.2b, line 2.

IV.3.2.10. [***] $W(h)$ when film single GDS convention (see Fig. IV.3.2a) is used for defining Σ^f .

IV.3.2.11. [♦] $\Delta A^{II\sigma}$ and $\Delta G^{II\sigma}$: surface excess Helmholtz energy and film interaction Gibbs energy on isothermal thin film formation defined by the film two GDSs convention (Fig. IV.3.2b); definition consistent with that of Π_D in Table IV.3.1.2b; $\Delta g^{II\sigma}$: film surface interaction Gibbs energy defined per unit surface area of the film.

IV.3.2.12. [♦♦] $\Delta\Omega(h)$: system grand potential change on formation of open surface thin films of film effective thickness h . $\Omega(h)$ has two forms corresponding, respectively, to the application of convention $I\sigma$ or $II\sigma$ for defining Σ^f (see notes [♦] and [♦♦♦] of Table IV.3.1.2.

IV.3.2.13. [♦♦♦] $\Gamma_i^{II\sigma}, \Gamma_i^{\alpha\gamma^\infty}$: thin film surface excess concentration of component i and thick film surface excess concentration of component i (definition of $\Gamma_i^{II\sigma}$ in Table IV.3.1.1.); $\theta^{II\sigma}, \sigma^{\alpha\gamma^\infty}$ (defined in Fig. IV.3.2b).

TABLE IV.3.2.2. Thin liquid films. Theoretical disjoining pressure components. Interfacial structures and characteristic lengths.

Component Name / Note	Symbol	Definition	Overlapped structure / (Characteristic length)	Remarks
Long-range dispersion (van der Waals) component / [*] Hamaker constant	Π_m $A_{\alpha\gamma\beta}$	$A_{\alpha\gamma\beta} > 0$ attractive Π_m $\Pi_m = -\frac{A_{\alpha\gamma\beta}}{6\pi h^3}$ $A_{\alpha\gamma\beta} < 0$ repulsive Π_m	homogeneous and continuum film	
Short-range solvation (structural) component / [**]	Π_s	$\Pi_s(h)$:oscillatory(monotonous) decay with h (simulated and observed)	periodic, exponential distribution of density / (correlation length ξ)	generally repulsive $\Pi_s > 0$
Long-range adsorption (excess) component / [***]	Π_a	$\Pi_a(h) = \Pi_D(h) - \Pi_D(h, c^\infty)$	diffuse adsorption layer (Boltzmann distribution) /	repulsive or attractive
Long-range electrostatic (ionic) component / [♦]	Π_e	$\Pi_e(h)$:excess pressure maintaining the ionic diffuse layers overlapped	Boltzmann distribution of counter and co-ions / (Debye screening length κ^{-1})	repulsive or attractive
Short- or long-range steric component / [♦♦]	Π_{st}	$\Pi_{st}(h)$:excess pressure maintaining the interpenetration of molecular segments	sub-surface distribution of molecular segments	mainly repulsive
Long-range elastic (distortion) component / [♦♦♦]	Π_{el}	$\Pi_{el}(h)$:excess pressure maintaining the thin film inhomogeneous molecular orientation	interfacial layers with dissimilar molecular orientations / (coherence length ζ)	repulsive

IV.3.2.14.

IV.3.2.15. [*] Definitions applicable to S/L/S and L/L/L planar films; a) asymmetric film $\alpha\gamma\beta$ (Fig. II.3b) of a non polar liquid γ ; Π_m : dispersion component of disjoining pressure; $A_{\alpha\gamma\beta}$: Hamaker constant; (non-retarded dispersion interaction) $A_{\alpha\gamma\beta}(h)$: Hamaker parameter is a function of h in the range of retarded dispersion interaction (see also Section II Annex);

IV.3.2.16. [**] $\Pi_s(h)$: disjoining pressure solvation component: (short-range, decaying and oscillatory function of h observed with liquid films bounded by *molecularly* smooth surfaces (e.g. S/L/S); examples: i) non polar liquid films bounded by non polar solids; ii) water thin films bounded and orientated by *hydrophilic* solids; iii) nematic liquid crystalline thin films *anchored* (fixed orientation) at their boundaries; ξ : (molecular size) positional correlation length (see Section II.A Annex) characterizing the "exponential" decay of the oscillation ($\sim \exp[-h/\xi]$);

IV.3.2.17. [***] $\Pi_a(h)$: disjoining pressure adsorption component: *excess* disjoining pressure of an actual thin film with overlapped diffuse layers, $\Pi_D(h)$, over that of a homogeneous film of bulk solution (concentration c^∞) of thickness h , $\Pi_D(h, c^\infty)$; the pressure $\Pi_a(h)$ maintains the film in the "overlapped state"; $\Pi_a(h) < 0$ (negative excess pressure, attractive effect) corresponds to film *depletion* (exclusion of constituents).

IV.3.2.18. [♦] $\Pi_e(h)$: disjoining pressure electrostatic(ionic) component: deriving from ionic interaction energy between overlapping double layers; $\Pi_e(h)$ decay is "exponential" at low film surface charge and potential, the characteristic length being the Debye screening length, $\kappa^{-1} = (\epsilon RT / 2F^2 I)^{1/2}$, where ϵ, R, T, F, I are bulk permittivity, gas constant, temperature, Faraday constant and ionic strength (Section II.A. Annex).

IV.3.2.19. [♦♦] $\Pi_{st}(h)$: disjoining pressure steric component arises in thin films from the interpenetration of segments of overlapped interfacial layers of (long chain) molecules or macromolecules; the range of $\Pi_{st}(h)$ (short or long) depends on the average molecular or macromolecular conformation (e.g. radius of gyration of macromolecules, etc.).

IV.3.2.20. [♦♦♦] $\Pi_{el}(h)$: disjoining pressure elastic component; applicable to planar films of liquid crystals anchored (strongly fixed and orientated) at the film boundaries (see Section II.A .Annex).

IV.4. PERIPHERY OF INDIVIDUAL FILMS. PHYSICAL QUANTITIES AND GEOMETRICAL PARAMETERS.

IV.4.1. The periphery region of a liquid film is often referred to as the **film meniscus** on account of the curved shape of its interfaces (Fig.IV.3.2). The terminology related to the circular meniscus of the simplest model for the liquid films, viz. the open, planar, symmetric, individual liquid film, in the absence of external forces (e.g. gravity), is dealt with below. An example of such a film is the individual foam film, V/L/V, separating two small contacting bubbles (phases α) within a liquid (phase γ) (Fig.IV.3.2). The case of deformed thin films, i.e. curved (bent), dilated (stretched) or twisted films, is not dealt with.

IV.4.2. The term **transition zone** refers *specifically* to the *inhomogeneous* region of a film periphery. In this region, local properties (composition, interfacial tension, $\sigma(x)$, disjoining pressure, $\Pi_D(x)$, etc), which are different from those of both the film and the three coexisting bulk phases (α , α and γ in Fig.IV.3.2.), may vary in both the normal, z , and in the film plane (x and/or y) directions. In the case of individual films, the transition zone covers completely the film periphery [16]. Quantities and parameters which are specific to, and characterize, the transition zone of the film periphery, may be defined (see below and Table IV.3.2.1). The specific quantities of the film periphery are relative to its unit of length.

IV.4.3. The term **film line tension**, κ , refers to the reversible work per unit change of length of the film periphery under specified conditions (e.g. chemical and temperature equilibrium, external force effects, etc.). The line tension is equivalent to a *force* tangential to the film. The **contractile line tension** is taken as *positive* when it opposes the dilation of the film contact line.

IV.4.4. The line tension is an excess quantity which derives from the inhomogeneous transition zone of the meniscus. It is the one dimensional, 1D, analogue of the 2D interfacial tension (see IV.3.1.A. Annex of Table IV. 3.1.2.) or thin film tension (Section IV.3.1.). The definition of the excess quantities which characterize the film meniscus and follow from those used to define the excess quantities characterizing films and interfaces. The system comprising the coexisting bulk phases, the interfaces, the thin film and its periphery, are compared to a reference (ideal) system consisting of homogeneous bulk phases, particular GDSs (thick lines in Fig.IV.3.2) and contact line(s) (Fig. IV.3.2a and Fig IV.3.2b). A particular GDS is the **extrapolated surface of tension** associated with the film tension Σ^f (or σ^f) or with the (bulk) interfacial tensions $\sigma^{\alpha\gamma}$ (see Fig.IV.3.2a and Fig IV.3.2b, Table IV.3.1.2a and IV.3.1.A. Annex of Table IV.3.1.2). The intersecting extrapolated surfaces of tension define the **reference contact lines** (e.g.C in Fig.IV.3.2a). The quantities **contact line length**, L^c , of a reference contact line and the associated **film contact line excess quantity** (e.g. the line tension κ), characterize the film periphery region.

IV.4.5. Since a thin film may be defined either in terms of the film single GDS convention, $I\sigma$, or the film two GDS convention, $II\sigma$, (Section IV.3.1), two corresponding reference systems (see (a) and (b) in Fig.IV.3.2) may be used for defining the film periphery and the associated excess quantities. This is illustrated below in the particular case of an individual, planar, symmetrical and circular thin film.

[16] The term **Plateau border** applies in the case of liquid films supported by bulk surfaces, frames or other films (as in foams). For them, the region intermediate between the film proper and the film support includes some bulk liquid (ref. [1]page 613).

IV.4.6. If the film single GDS convention is used, then, *one* equilibrium reference contact line (C in Fig.IV.3.2a) is obtained at the intersection of the *extrapolated* single GDS of the film with the two extrapolated GDSs of the meniscus interfaces(as in Fig.IV.3.2a). The film line tension, $\kappa^{I\sigma}$, defined by the condition of thermodynamic (thermal, chemical and mechanical) equilibrium of the film with its surroundings, is effective *in* the plane of the single surface of tension of the film (e.g. along CO in Fig.IV.3.2a). The condition of mechanical equilibrium for the reference system (film, interfacial surfaces of tension and film line of tension) defines the **reference contact angle** (Fig.IV.3.2a).

IV.4.7. The film two GDSs convention leads to two equilibrium reference contact lines (C,C' in Fig.IV.3.2b), since, each reference (extrapolated interfacial) surface of tension intersects separately with one of the *two* extrapolated surfaces of tension of the film. In this case, the condition of thermodynamic equilibrium between the film and the surroundings, defines two types of line tension: a line tension $\kappa^{II\sigma}$, associated with each of the two surfaces of tension (GDSs) of the film (e.g. along CO and C'O' in Fig.IV.3.2b), and a transversal tension τ associated with, and effective on, each contact line in the direction *normal* to each surface of tension of the film (e.g. along CC' in Fig.IV.3.2b). As in the case of the $I\sigma$ convention, the reference contact angles are defined by the condition of mechanical equilibrium for the reference system (surfaces of tension of the film and of the interfaces, and the film line of tension).

IV.4.8. Of particular interest for the characterization of the periphery of individual, open, symmetric, planar, circular liquid films in the absence of external forces are the parameters defined below and the quantities defined in Table IV.3.2.1.

IV.4.9. $-h(x)$, the profile of the liquid effective thickness in the transition zone (viz., $z(x)$ the profile of the meniscus surface, Fig.IV.3.2.);

IV.4.10. $-R^*$, interfacial curvature radius of the surface of tension in the meniscus region (*away* of the film and the transition region) where the interfacial tension becomes equal to $\sigma^{\alpha\beta}$ (see Fig.IV.3.2) and the Laplace or capillary pressure is $\Delta P_G \propto \sigma^{\alpha\beta}/R^*$; R^* is also the radius of curvature of the *extrapolated* GDSs that define the reference systems for the liquid films (see example in figures IV.3.2.a and b).;

IV.4.11. $-r_C$, circular film reference contact line radius (C and C' defined in Fig. IV.3.2.a and Fig IV.3.2b) ; a film contact line lies in the corresponding surface of tension of the film;

IV.4.12. $-\theta_C$, film reference contact angle defined (within the phase γ), exclusively, *at a reference contact line*, by the *extrapolated* surfaces of tension of the film and interfaces (as shown in Fig. IV.3.2a and Fig IV.3.2b).

IV.4.13. The geometrical parameters relative to the reference system considered above and the analogous *apparent* parameters (e.g. obtained by optical methods) are essentially different. The mechanical equilibrium of the thin film periphery cannot be described rigorously in terms of the apparent parameters.

Film periphery effect. Definitions of circular film properties

IV.4.14. The definitions of the disjoining pressure and of the film formation energy given in sections IV.3.1 and IV.3.2. do not apply to small circular films. A small circular film is the 2D analog of a small spherical 3D droplet where Laplace pressure contributes significantly to the average properties of the droplet material.

IV.4.15. Definitions correct for circular films are obtained by combining those for the planar (rectilinear) films (Tables IV.3.1.2a, IV.3.1.2b and IV.3.2.1) with the definitions for the periphery quantities (Table IV.4.1). The examples below, given in the case of the convention $I\sigma$ (single Gibbs dividing surface), demonstrate the film size effect on the definitions of *circular* film properties.

Interaction energy $W = \Delta(\Sigma^I A^I + \kappa L^I) = \Delta[A^I(\Sigma^I + 2\kappa/r_c)]$ (Caveat : r_c may vary on film formation)

Disjoining pressure $\Pi_D = -(\partial A/\partial h)(A^I)^{-1}$ (fixed T, V, n_j, r_c) (Caveat : r_c needs to be fixed on film thinning)

**TABLE IV.4.1. Individual, open, planar, symmetric thin liquid films
Geometric parameters and physical quantities of film periphery**

Name/Note	Symbol	Definition	S.I. Unit	Remarks
film periphery line tension (thermodynamic definition) [*]	κ	$\kappa = \left[\frac{\text{reversible work of the surroundings}}{\text{unit of film periphery linear dilation}} \right]$ (specified conditions)	N	specified conditions: fixed T, V, A and μ_j
length of (reference) contact line of tension [**]	L^{IC} L^{IIC}	contact lines defined in Fig.IV.2.2a and IV.2.2b	m	
film line tension [***a]	κ^{IC}	[***] <u>Thermodynamic Definitions</u> $\kappa^{IC} = (\partial \Omega^{IC} / \partial L^{IC})_{T, \mu_j}$	N	convention $I\sigma$ (Fig. IV.3.2a)
film (surface) line tension [***b]	κ^{IIC}	$\kappa^{IIC} = \frac{1}{2}(\partial \Omega^{IIC} / \partial L^{IIC})_{T, \mu_j, h^{II\sigma}}$	N	convention $II\sigma$ (Fig. IV.3.2b)
film (contour) transversal tension	τ^{IIC}	$\tau^{IIC} = \frac{1}{L^{IIC}} (\partial \Omega^{IIC} / \partial h^{IIC})_{T, \mu_j, L^{IIC}}$	N/m	
film line tension [♦a]	κ^{IC}	[♦] <u>Mechanical Definitions</u> $\kappa^{IC} = (2\sigma^{\alpha\beta\infty} \cos \theta^{IC} - \Sigma^I) r_c$	N	convention $I\sigma$ (Fig. IV.3.2a)
film (surface) line tension [♦b]	κ^{IIC}	$\kappa^{IIC} = (\sigma^{\alpha\beta\infty} \cos \theta^{IIC} - \sigma^I) r_c$	N	convention $II\sigma$ (Fig. IV.3.2b)
film (contour) transversal tension	τ^{IIC}	$\tau^{IIC} = \sigma^{\alpha\beta\infty} \sin \theta^{IIC}$	N/m	

IV.4.16.

IV.4.17. [*] V and A : system volume and area (system: bulk phases, thin film and interfaces). κ : film line tension: intensive factor in the differential expression for the reversible work required to dilate the film periphery; [**] superscripts IC and IIC: recommended for symbols of single (two) reference contact line(s) and associated quantities by analogy with superscripts $I\sigma$ and $II\sigma$ applicable in the case of thin films (see section IV.3).

IV.4.18. [***] Thermodynamic definitions. [***a] Conventions $I\sigma$ and IC. $\Omega^{IC} = \kappa^{IC} L^{IC}$: single contact line grand potential of a thin film. The contact line and the associated film line tension lie in the surface of tension (fig. IV.3.2a); [***b] conventions $II\sigma$ and IIC. $\Omega^{IIC} = (2\kappa^{IIC} + \tau^{IIC}) L^{IIC}$: contact line grand potential defined for the film thermodynamic thickness $h^{II\sigma}$ (figures IV.3.1b and IV.3.2b and Table IV.3.1.1.). The film surface contact lines and film surface line tensions κ^{IIC} lie in the two surfaces of tension defined for the film (fig. IV.3.2b); the film transversal tension τ^{IIC} associated with the two reference contact lines is normal to the film surfaces of tension (direction CC' in fig.IV.3.2b).

IV.4.19. [♦] Mechanical definitions. (♦a) Convention $I\sigma$ and IC: the film line tension is defined by the condition of mechanical equilibrium of the reference contact line, subject to the effect of surface tensions associated with the reference surfaces which intersect at the single contact line; $\theta^{IC} = \theta^{I\sigma}$, $\sigma^{\alpha\beta\infty}$ and r_c : reference contact angle; surface tension and contact line radius of curvature defined in fig. IV.3.2a ; (♦b) Convention $II\sigma$ and IIC: the film surface line tensions and film transversal tensions associated with the reference contact lines are defined by individual conditions of mechanical equilibrium applicable to each one of the two contact lines defined for the thin film; $\theta^{IIC} = \theta^{II\sigma}$, $\sigma^{\alpha\beta\infty}$, r_c : reference contact angle, surface tension, contact line radius of curvature (fig. IV.3.2b).

IV.5. COMPRESSION ISOTHERM OF PLANAR FILMS AND STABILITY OF EQUILIBRIUM STATE

IV.5.1. The term **film compression isotherm** refers to the curve representing the isothermal variation of any (film) property with film thickness h . Calculated (simulated) and experimental compression isotherms, Π_D - h and W - h , are available for the disjoining pressure, Π_D , or the film interaction energy, W , defined in Tables IV.3.1.2 and IV.3.2.1, respectively.

IV.5.2. Experimental, equilibrium film compression isotherms represent the reversible isothermal variation of planar film thickness, h , when an excess pressure is applied to compensate the difference between two bulk pressures, $\Delta P = p^l - p^a = \Pi_D$ (defined in Table IV.3.1.2). For example, ΔP may be compensated either by a hydrostatic pressure, equal to $(p^l - p^a)$, by the Laplace pressure ΔP_c , defined by the film meniscus surface curvature and tension (Fig. IV.3.2) or, for the S/L/S films, by pressing on the solids, S.

IV.5.3. In the case of force-film thickness compression isotherms observed with S/L/S films bordered by convex interfaces, the reported experimental isotherms are often curves representing the variation of an *effective* film interaction Helmholtz energy with an *effective* film thickness. This energy definition is $W_{\text{eff}}(h_{\text{min}}) = [F/g(R)]$, where F is the force applied when the gap between the apexes of the convex boundaries is equal to h_{min} , and $g(R)$ is a geometrical factor that depends on the main radii of curvature R of the film curved boundaries. A geometrical factor used, currently, for films bounded by the surfaces of two crossed cylinders is $g=2\pi R$. It is referred to as **Derjaguin's approximation**. It is recommended that the term *effective* or *equivalent* be used when referring to $W_{\text{eff}}(h_{\text{min}})=[F/g(R)]$, since $W_{\text{eff}}(h_{\text{min}})$ is the interaction energy of an equivalent planar film h_{min} thick.

IV.5.4. The equilibrium of a planar, rectilinear or relatively large circular thin film is referred to as **film stable equilibrium** (in a given range of film thickness) when the gradient of the isotherm, $(\partial\Pi_D/\partial h)$ is negative at fixed T, μ_i , and A^l . It is referred to as **film unstable equilibrium** when this gradient is positive. The equilibrium stability condition is $(\partial\Pi_D/\partial h) < 0$ at fixed T, μ_i, A^l (and r_c for the planar, circular liquid films). The terms **film stabilizing component** and **film destabilizing component** apply to the disjoining pressure contributions which are *positive* or *negative*, respectively. The equilibrium stability of certain thin films (e.g. wetting thin films) is subject to the additional condition that $\Pi_D > 0$.

IV.5.5. The term **DLVO Isotherm** (Derjaguin-Landau-Vervey-Overbeek) refers to the theoretical isotherm applicable to liquid thin films with overlapped ionic double layers where there are only two contributions to Π_D :

IV.5.6. Π_m (destabilizing dispersion component) and Π_e (stabilizing electrostatic component). This combination may result in a variety of Π_D - h theoretical curves having two minima (Fig. IV.5.1.): a shallow minimum referred to as **secondary minimum** and a deeper one referred to as **primary minimum**.

IV.5.7. The term **black film** is generic. It applies to films which are characterized by a very small reflectance of visible light and, hence, look black. The term **common black film, CBF**, refers to a stable black film characterized by an equilibrium thickness h in the range of the left-hand branch of the secondary minimum (Fig. IV.5.1). A stable, black film of thickness h in the range of the left-hand branch of the primary minimum is referred to as **Newton black film, NBF**. In the case of surfactant black films, C_{b1} (C_{N1}) designate the bulk concentrations of the surfactant solution, above (at) which CBF (NBF) occur. A discontinuous change (Fig. IV.5.1.) of black film

thickness (CBF-NBF), is referred to as a **film thickness transition** (between two states of equilibrium). For example, such a transition may be initiated by the nucleation of Newton black spots in a CBF, which grow and lead to uniform and stable NBFs. The symbol $C_{el,cr}$ designates the **critical electrolyte concentration** for which a CBF-NBF transition occurs in films with overlapping ionic diffuse layers.

IV.5.8.

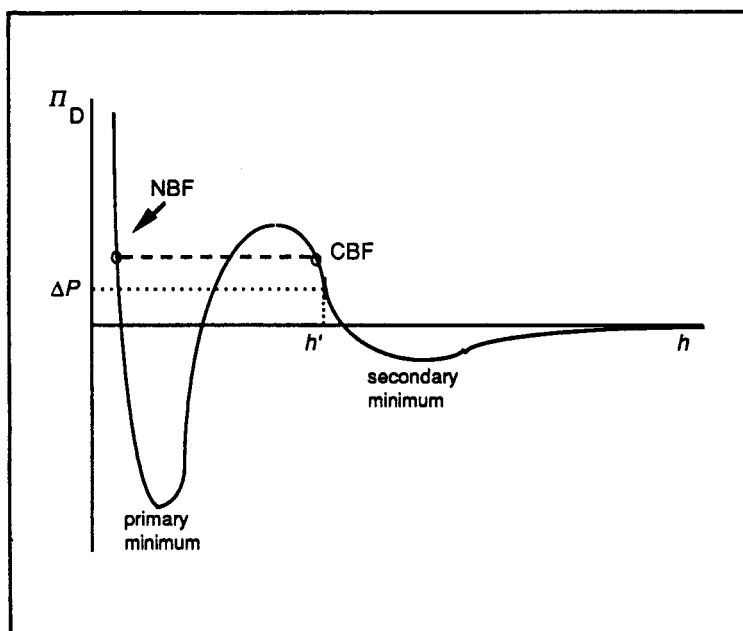


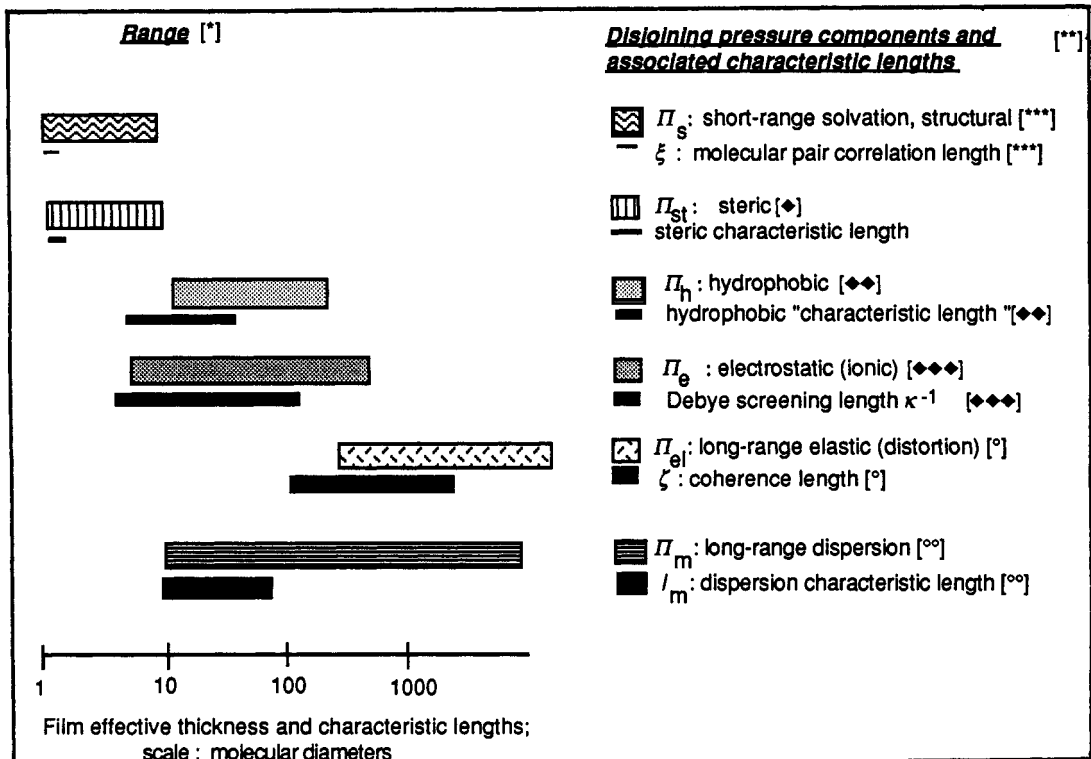
Fig. IV.5.1. Compression isotherm of a L/L film with overlapped ionic double layers.

Full line: DLVO isotherm; dashed: film thickness transition; CBF(common black film) ; NBF(Newton black film); $\Delta P (= \Pi_D)$: pressure needed to compensate the disjoining pressure and maintain the film equilibrium thickness $h = h'$.

IV.5.9. The term **solvation isotherm** (**hydration isotherm** in the case of aqueous films) refers to the oscillatory decay function $\Pi_D - h$ specific to the liquid thin films which characterizes the discrete behaviour of thin liquid films several molecular diameters thick which are bounded by molecularly smooth solid surfaces (e.g. cleaved mica). The isotherm is a combination of an oscillatory, repulsive, short-range solvation component, Π_s , and of an attractive long-range component, Π_m , involving also the interaction between the adjacent solids.

IV.5.10. The following Table IV.5.1 summarizes the range of liquid film effective thickness (wetting films included) corresponding to significant values of certain disjoining pressure components (see also Table IV.3.2.2). Corresponding characteristic lengths are also shown in Table IV.5.1. This term refers to the scale which characterizes a *disjoining pressure isotherm* and is, often, related to the characteristic length specific to the overlapped interfacial layers of the thin film (e.g. case of the disjoining pressure components of films stabilized by adsorbed macromolecules or ionized surfactants; see II.A. Annex of Section II). The characteristic length of the dispersion component has not been defined yet. A proposal for such a definition and a symbol, l_m , can be found in the caption [°] of Table IV.5.1 below. The list of the components in this table is not comprehensive.

TABLE IV.5.1. Range of effective film thickness and characteristic length specific to disjoining pressure components



IV.5.11.

IV.5.12. [*] Range of film effective thickness and characteristic length corresponding to significant values of various components under various conditions; unit of scale = one molecular diameter.

IV.5.13. [**] Disjoining pressure components (defined in Table IV.3.2.2) and characteristic lengths of interfacial structures (defined in II A. Annex of Section II).

IV.5.14. [***] $\Pi_s(h)$: disjoining pressure *solvation* component; ξ : molecular pair correlation length; films several molecular diameters thick, with discrete compression behaviour (steps); see [**] in Table IV.3.2.2.

IV.5.15. [♦] $\Pi_{st}(h)$: disjoining pressure *steric* component; films several molecular diameters thick (molecules or macromolecules); unit of scale: one molecular or macromolecular effective diameter depending on molecular conformation and/or orientation in the film (e.g. $2R_G$) where R_G is the macromolecular radius of gyration (relevant to a gaussian radial distribution of macromolecular segments). The steric component and its characteristic length are scaled using molecular diameters for molecular or macromolecular stabilized films.

IV.5.16. [♦♦] $\Pi_h(h)$: disjoining pressure *hydrophobic* component; this range and the disjoining pressure hydrophobic component: characteristic length are defined operationally.

IV.5.17. [♦♦♦] $\Pi_e(h)$: disjoining pressure *electrostatic* (ionic) component; κ^{-1} : Debye screening length; scale unit: d is the diameter of a water molecule; the range shown corresponds to supporting electrolyte concentrations: 10^{-4} - 10^{-1} M.

IV.5.18. [°] $\Pi_{el}(h)$: disjoining pressure *elastic* component; standard theories predict infinite coherence lengths, ζ , at certain transition temperatures, for certain liquid crystals (e.g. nematic).

IV.5.19. [°°] $\Pi_m(h)$: disjoining pressure *dispersion* component; suggested disjoining pressure dispersion component: characteristic length, $l_m \cong \lambda_c$, where λ_c is the specific wavelength in the absorption spectrum of interacting species which gives the maximum contribution to the dispersion interaction (see end of II A. Annex of Section II) and footnote [9] in page 9.

IV.6. FILM DYNAMICS

IV.6.1. Film drainage

On film drainage, (see IV.6.2), the outflow of liquid from the film core may be driven by the gravitational force, a normal (squeezing) stress or the disjoining or capillary pressures. The forces opposing liquid outflow may be due to both film core and interfacial viscous stresses (see IV.6.2. below) and are dependent on the system rheology.

IV.6.1.1. The film interface where liquid flow may occur (e.g. V/LV or L/L/L films) is referred to as **mobile interface**. In the case of a zero surface flow rate (e.g. for S/L and certain liquid interfaces with adsorbed layers) the surface is called **immobile surface**.

IV.6.1.2. The **Marangoni effect** designates the hydrodynamic motion of the fluid next to its surface where an interfacial tension gradient has been established. This term appears in reports on drainage of films with mobile surfaces, since, when the outflow of liquid core causes a surface tension gradient a surface flow occurs and opposes the gradient.

IV.6.1.3. The **thinning rate** of draining planar films is defined as the rate of decrease in film average thickness $(-dh/dt)$. The symbol $v_{Re} = -(dh/dt)_{Re}$, where Re stands for "Reynolds", designates the so-called **Reynolds rate of thinning**. In the case of circular, non-deformable planar films bounded by "immobile" surfaces where the film core liquid outflow is laminar, the expression of v_{Re} is: $v_{Re} = [2 h^3(t) / 3 \eta r^2] \Delta P$ where η is the liquid film core viscosity, r the film radius and ΔP an external stress normal to the film.

IV.6.1.4. The term **dimple** designates the region of a draining liquid film, with a one or two deformable interfaces, which exhibits particular interfacial shapes (e.g. bell-shape), instead of the interfacial curvature of the equilibrium film. For example, a circular dimple is characterized by its radius r and the two thickness parameters h_{max} and h_{min} , shown in Fig. IV.6.2.1. below.

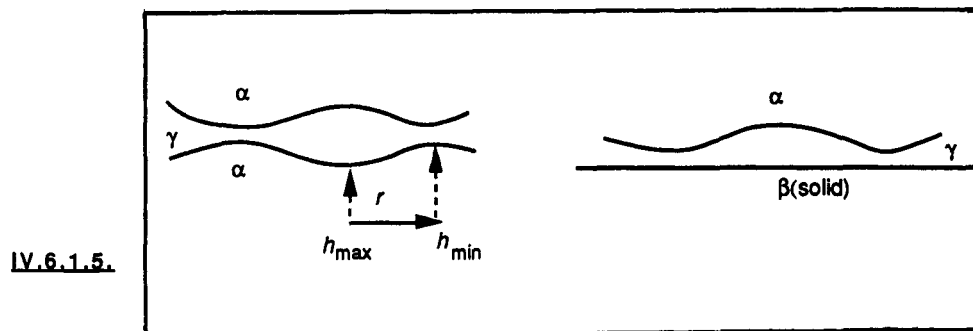


Fig. IV.6.1.1. Dimples of draining, horizontal, circular liquid films
left: film with deformable interfaces; right: film with a single deformable interface.

IV.6.2. Film stability and related parameters

IV.6.2.1. **Film stability** is a generic term which refers to the response of the drained film to mechanical and thermal perturbations.

IV.6.2.2. Associated with **film rupturing** is a **probability of rupturing** defined as the percentage of films that have ruptured within a given time interval. This probability plotted against the film mean thickness displays a maximum at a thickness referred to as **critical film thickness**.

IV.6.2.3. Film rupturing may be **spontaneous** or **forced**. Forced rupturing applies when films are subject to an external force (e.g. electric fields, radioactive α -radiation, etc.) ; spontaneous rupturing applies when thermally excited ripples (on the film interfaces) are coupled coherently . Two types of coupling of interfacial film ripples are defined in figures IV.6.2.1a & V.6.2.1b. They are referred to as **squeezing mode** and **bending mode**, respectively^[17]. For example, the probability of rupturing is significant mainly in the squeezing mode. In this mode, the **critical thickness** h_c and **critical wavelength** λ_c are defined by the *mean* thickness and thickness fluctuation wavelength for which the film rupturing probability is maximum.

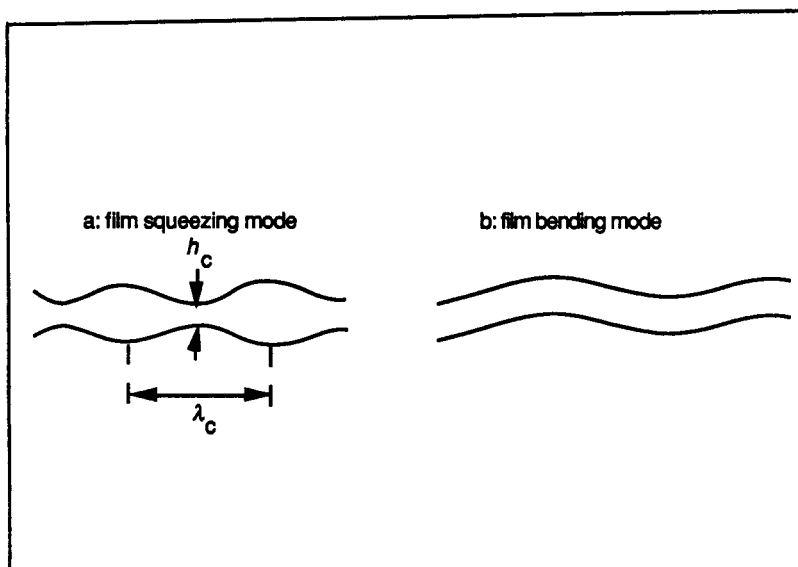


Fig. IV.6.2. 1. Modes of film deformation due to coupling of interfacial ripples.

IV.6.2.5. Film rupturing stability is characterized by a parameter referred to as **film life time**, τ . It is defined as the total time interval necessary to drain and rupture the film. In the case of film thickness transition, τ includes also the time for black film spot nucleation and growth (see section IV.5).

IV.6.2.6. Parameters characterizing the response of planar, non-rupturing liquid films to mechanical perturbations are defined below . The types of deformation considered are those referred to as film **dilatational** deformation, film **shearing** deformation and film **compression** (no bending nor twisting).

IV.6.2.7. The film **elasticity modulus** is defined by analogy to the Young modulus for bulk phases reference ([⁴] page 29) and is currently noted Y_{\perp}^f or E_{\perp}^f . It is defined as the ratio of *excess pressure* (stress normal to the film) to the *relative variation in film thickness* (linear compression): Y_{\perp}^f or $E_{\perp}^f = -(\partial P / \partial \ln h)$ [N/m^2] at constant surface area and shape of the film at equilibrium.

IV.6.2.8. The **dilatational elasticity modulus** or **Gibbs elasticity modulus** of a thin film, noted E^f , is defined as the ratio of change in film tension, Σ^f , to the corresponding change in film area A^f : $E^f = (\partial \Sigma^f / \partial \ln A^f)$ [N/m] at constant curvature and shape of the film (e.g. increasing the area of a planar and circular large area film). This definition is operational. It is relevant for the Gibbs convention ($I\sigma$ or $II\sigma$) applied to define Σ^f .

[¹⁷] The two modes in Fig. IV.6.2.1 are referred to as symmetric and anti-symmetric Lamb waves, in acoustics.

IV.6.2.9. The film **shear modulus** or film **shear rigidity modulus**, G^f , applies in the case of deformations involving a film shape change at constant surface area and curvature. For example, when a square film becomes a rectangle, the deformation is referred to **pure shear deformation** and as **simple shear deformation** when the deformed film does not remain rectangular. When necessary, the use of the complete term, viz., *shear rigidity modulus*, is recommended, since, *rigidity* is often applied also in the case of bending and twisting film deformations.

IV.6.2.10. The surface and bulk viscosities associated with the dilational and shear deformations of the film are referred to as **film dilational viscosity** and **film shear viscosity**.

IV.6.2.11. Under dynamic conditions, the planar film tension may be time and rate of deformation dependent. Then, the instantaneous and local film tension is referred to as the **dynamic film tension**.

IV.6.2.12. The term **Gibbs-Marangoni effect** refers to the film stabilizing effect due to inflow of liquid into the film core, provided the liquid inflow is induced by film surface tension gradients (occurring, for example, in the case of very high rates of dilational deformation of films).

IV.7. CHARACTERIZATION OF LIQUID FILMS

Thickness, area, film tension, line tension, disjoining pressure, capillary pressure (Section IV.3.) and their combinations (e.g. disjoining pressure/ thickness or circular film radius/contact angle isotherms) are important mechanical characteristics of liquid films. Information on the molecular structure and other properties of the liquid films may be obtained by using spectroscopic, electric, etc. approaches. Methods used to characterize the liquid films at mechanical equilibrium, mainly, are listed in the following Table IV.7.1. The list is not comprehensive.

The methods listed in Table IV 7.1 below are for liquid films. In this table, the characterization methods are listed in the first and second column, such that the methodologies (second column) associated with a given technique (first column) appear in a distinct column. For example, both the (usual) two-beam reflected interferometry and the topographical method are optical methods for assessing liquid thickness. Sampled area scale (fourth column) refers to the order of magnitude of the area or length which is sampled, i.e. effectively investigated by the technique and methodology under consideration (e.g. 100 sq. μm in the case of Newton rings seen in a microscope; 1sq. mm in the case of the "topographic" method). Primary information (third column) refers to the raw information (usually experimental data) needed to obtain further information (viz. by interpreting the data) which is then referred to as derived information (fifth column). An example of primary information is the observed interferometric pattern (e.g. Newton rings) and the calculated optical thickness (path length). The equivalent film thickness is the information derived by using the bulk refraction index of the solution from which the film is prepared. Under the heading Caveats (sixth column) are listed factors and basic "traps" limiting the validity of the derived information (column five) and hence of the data interpretation and of final conclusions (based on the interpretation). For example the assessment of the film material refraction index might be needed for deriving the real film thickness from the corresponding primary information.

TABLE IV.7.1. Characterization of liquid films (Part I)[*]**IV.7.1.**

Techniques	Methodology	Primary (raw) information	Sampled area scale	Derived information	Caveats
optical	interference microscopy (visible light); differential interferometry (topographical method)	Interferometric patterns: Newton rings for Plateau border, fringes etc; optical thickness; film geometry (static and dynamic)	100 μm^2 - 1 mm ²	film thickness and thickness inhomogeneity; profile of transition zone; contact angle film /bulk ; Plateau border surface curvature & capillary pressure; film tension, film line tension, permeability, diffusion coefficients	separate assessment of film local refractive index (es) is required
	polarized light interference microscopy	interferometric patterns; optical thickness, birefringence	1 mm ²	film equivalent thickness, film texture, domain orientation	global information
	vibrational spectroscopy : FT- IR, and Raman; UV, visible.	absorption spectra, light scattering	1 - 100 mm ²	vibrating bond identification; film equilibrium and dynamic composition, order parameter, tilt (average); order/disorder transition	no access to molecular angle distribution
	light diffraction : time averaged scattering	mean scattered intensity vs. direction (scattering angle) of diffracted wave ;	mm ²	mean-square amplitude of film surface ripples; disjoining pressure components: dispersion & electrostatic	surface and film contamination sensitive
	light diffraction : dynamic light scattering	time fluctuations of scattered light intensity	mm ²	time evolution of film deformation (squeezing, bending) modes; film dynamic surface tension and viscosity; disjoining pressure components	surface and film contamination sensitive
	ellipsometry and Brewster angle microscopy	ellipticity [**]; optical thickness	100 μm^2 - 1 mm ²	thickness or/and refractive index[**]	refractive index might be needed
neutron beam	specular reflection at various wavelengths λ and incidence angle θ	reflectivity vs wavelength λ , incidence angle θ and κ [***], interference pattern	1-100 mm ²	neutron refractive index profile, film structure, thickness, interfacial capillary ripples	averaged small scale inhomogeneities

[*] The quantities concerned by the methods of characterization in this table have been defined in sections IV.1-IV.6.

IV.7.2. [**] **Ellipticity** (of the reflected radiation) is the ratio of amplitudes for electric fields polarized parallel and normal to the incidence plane; thickness *and* refractive index are obtained by the ellipsometry referred to as spectroscopic.

IV.7.3. [***] $\kappa = 4\pi \sin\theta / \lambda$ is referred to as **momentum transfer**.

TABLE IV.7.1. Characterization of liquid films (Part II)[*]**IV.7.4.**

Techniques	Methodology	Primary (raw) Information	Sampled area scale	Derived Information	Caveats
mechanical	mechanical stress normal to film : dynamic or static conditions	normal to film: capillary or hydrostatic pressures or normal stress	100 μm^2	disjoining pressure: isotherms, characteristic lengths[**], Hamaker constant; film stabilisation, rheology, Gibbs / Helmholtz energy of interaction; elastic modulus	evaporation; mechanical artefacts (vibrations); contamination sensitive; thermodynamic conditions (T, P, etc.) ambiguous
	film tensiometry (of macroscopic, planar, stretched films);	film area and tensile force; capillary pressure of curved films	0.1 mm^2 - 100 mm^2	interaction Helmholtz energy; film contact angles, rheological parameters (shear, dilational)	as above
electrical	dc, ac experiments	film conductance (in plane)	50 mm^2	equivalent thickness of aqueous layers in complex films; ion transport numbers in the film	thickness calculation involves bulk composition and conductivity
	dielectric experiments	capacitance, permittivity (dielectric constant)	100 mm^2	equivalent film thickness	information dependent on the permittivity assigned to the film
radiotracer	radiochemical analysis	film radioactivity (emission/unit film area)	100 mm^2	film surface area and average surface composition (concentration of radiolabeled molecules/unit film area)	accuracy of film composition is dependent on the calibration method ; device geometry dependent

[*] The quantities concerned by the methods of characterization in this table have been defined in sections IV.1-IV.6.

[**] Characteristic lengths are defined in II.A. Annex to section II. See also Table IV.3.2.2 and Table IV.5.1.

V. SOLID LAYERS AND FILMS

V.1 ORGANIZED ORGANIC LAYERS

The strongly growing interest in organic monolayer assemblies is due to the fact that chemists are becoming increasingly aware of the importance of constructing organized aggregates of molecules. These have potential interest in any field which require materials with basically new properties depending on the exact location of each molecular component.

V.1.1. The generic term **organizate** refers to organized molecular assemblies where each molecule has its individual purposely planned place. **Supramolecular machines** or **supramolecular devices** are assemblies of basic, molecular functional units, each contributing to the achievement of a specific complex function. "Supramolecular machine" may apply even to a very simple arrangement. For example, a dye molecule and an electron acceptor molecule, fixed at some separation, are basic functional units designed to form a photoinduced electron transfer unit which acts as a machine consisting of fixed parts (dye and acceptor) and moving parts (photon, electron). The term **supramolecular engineering** refers to the engineering of supramolecular machines and organizates, as well as of organized monolayers and monolayer assemblies.

V.1.2. A monolayer, either floating (see definition of floating monolayer in section II), deposited on a solid substrate (see section V.1.2.1a) or adsorbed from solution (see section V.1.2.1b), exhibiting structural order at the molecular scale, is referred to as an **organized monolayer** or **designed monolayer** when the organization of the molecules within the monolayer is *purposely planned at the molecular level*. The term **designed (organized) monolayer assembly** applies to multilayers of monolayers superimposed in a purposely planned sequence.

V.1.1. Floating monolayers

V.1.1.1. The term **mixed monolayers** refers to multicomponent organic floating monolayers. The term **compound monolayer** applies to the mixed floating monolayer in which different components *interlock*, i.e. gradually aggregate to form a planned 2D compound. The terms **2D self-assembling** or **2D self-organization**^[18] designate a process leading to a compound floating monolayer.

V.1.1.2. A mixed floating monolayer is qualified as a **homogeneous mixed monolayer** when the monolayer composition is uniform in two dimensions. It is referred to as a **heterogeneous mixed monolayer** when 2D-demixing ^[19] occurs, i.e. domains of homogeneous but different composition coexist. The term **two-dimensional (2D) crystallite** applies in the case of monocrystalline 2D domains.

V.1.1.1. Preparation methods

V.1.1.1.1. The basic fabrication (i.e. spreading and compressing) and characterization procedures applicable to one component and mixed (two or more components) monolayers floating on the surface of a liquid, referred to

[18] Self-organization of molecules should be seen as a key feature of supramolecular architecture. The fabrication of increasingly complex self-organizing layers is a challenge in future developments. The use of the term "2D self-organization" focuses on that point.

[19] For example in the mixed monolayer consisting of a dye with a long hydrocarbon chain and arachidic acid, under certain conditions, two 2D mixed crystals may coexist: dye rich and arachidic rich 2D-crystals.

as a **subphase**, are described in [2]. In this section we focus on particular aspects concerning the preparation of mixed and compound floating monolayers.

V.1.1.1.2. Homogeneous mixed monolayers may also include non-amphiphilic components incorporated from the subphase, the gas or the spreading solution. For example, the substance referred to as a **molecular lubricant** is a molecule which is temporarily incorporated into the monolayer to assist molecular organization and/or 2D homogenization of the monolayer. Because the molecular lubricant is essentially an "impurity", it needs to be eliminated from the final, organized monolayer.

V.1.1.1.3. Components originally present in the spreading solution or in the subphase may contribute to compound monolayer formation. The new term **co-amphiphilic compound** is recommended for the compound consisting of an amphiphilic and a non-amphiphilic component, the non-amphiphilic component being necessary to the specific functionality of the monolayer. This non-amphiphilic component is often a solute of the subphase. Compound formation between monolayer and subphase species are critically dependent on the micro-environmental conditions and functional group positioning (e.g. hidden or exposed to the subphase). Therefore, it is strongly recommended that information be provided about the actual composition of the subphase, the structure of the monolayer (at least after deposition on the solid plate) and the nature of the monolayer functionality (e.g. protonation or complex-equilibria or enzymatic reactions).

V.1.1.2. Characterization of floating monolayers

The methods listed in Table V 1.1.2.1. below apply to organized monolayers at gas-liquid interfaces. In this table, the characterization methods are listed in the first and second column, such that the methodologies (second column) associated with a given technique (first column), appear in a distinct column. For example, both the film balance and the surface tensiometry, used to establish $\Pi-A$ isotherms, involve the measurement of a mechanical force by techniques referred to as mechanical; in the methodology referred to as static the monolayer surface pressure, Π , is permitted to relax at each value of surface area, A , in contrast to the continuously compressed monolayers for which the $\Pi-A$ isotherm is continuously recorded. Sampled area scale (fourth column) refers to the order of magnitude of the area or length which is sampled, i.e. effectively investigated by the technique and methodology under consideration (e.g. subphase surface area, $\approx 10^{-2}$ sq m, in the case of Langmuir troughs, beam or slit area in the case of optical or spectroscopic methods). Primary information (third column) refers to the raw information (usually experimental data) needed to obtain (viz. by interpreting the data) further information which is then referred to as derived information (fifth column). For example, partial molar areas and 2D Helmholtz energies of monolayer constituents are pieces of derived information (from the raw compression isotherms). Under the heading Caveats (sixth column) are listed factors and basic "traps" limiting the validity of the derived information (column five) and hence of the data interpretation and of final conclusions (based on the interpretation).

TABLE V.1.1.2.1. Characterization of floating organized organic monolayers**V.1.1.2.1.**

Technique	Methodology	Primary (raw) Information	Sampled area scale	Derived Information	Caveats
mechanical	film (monolayer) balance, surface tensiometry; (static or continuous compression procedure)	monolayer area, A , molecular area, a , surface pressure, Π , isotherms Π - A and Π - a , isothermal compressibility, κ_T	10^{-2} m ² (subphase surface area)	2D/2D and 2D/3D (collapse) phase transitions, 2D phase diagrams and miscibility, partial molecular area, Helmholtz energy, etc.	smaller scale monolayer heterogeneities ignored; monolayers continuously compressed may be out of equilibrium
electrical	surface potentiometry:	voltage step ΔV across the monolayer, ΔV - a isotherms	10-100 mm ²	molecular dipole moment, degree of apparent molecular orientational order, monolayer heterogeneity	smaller scale heterogeneities ignored; (see above)
optical	polarized light reflectivity spectroscopy	absorption/reflectio n spectrum, ratio of in-plane to out-of-plane refractive index	mm ²	molecular orientation and tilt	smaller scale heterogeneities ignored
	polarized fluorescence spectroscopy	excitation/emission spectrum, degree of polarization, life time of excited state	1-100mm ²	molecular orientation, intermolecular energy transfer, quenching mechanisms	rigorous interpretation requires additional structural studies
	ellipsometry with Brewster angle microscopy	ellipticity [*], map of deviation from Brewster extinction, phase transition (non-uniform monolayers)	mm ²	thickness and/or refractive index [*]; optical anisotropy, optical thickness distribution, domain size and shape	limited to optical size or larger homogeneous patches, refractive index might be needed
	fluorescence microscopy	distribution map of fluorescent molecules	mm ²	phase transitions, molecular segregation, domain size and shape	dye miscibility; unobservable submicroscopic inhomogeneities
	vibrational spectroscopy: IR and Raman	reflection spectrum, light scattering	1-100 mm ²	molecular orientation, order-disorder transition	no access to molecular angle distribution
	generation of non-linear (second and third order) radiation	amplitudes of second and third harmonic radiation	0.01-1mm ²	second and third order molecular hyper-polarisability, molecular orientation and orientational ordering	smaller scale heterogeneities ignored
X-ray, neutron beam	specular reflection (diffraction and diffuse scattering)	reflectivity vs angle θ , wave length λ or momentum transfer [**]; interference pattern	1-100 mm ²	monolayer thickness and roughness, 2D lattice constant and homogeneity, molecular tilt, 2Dcoherence length, composition and 2D density profiles; H ₂ O profiles (neutron only)	smaller scale heterogeneities ignored

V.1.1.2.2. [*] Ellipticity (of reflected radiation) is the ratio of amplitudes for electric fields polarized parallel and normal to the incidence plane; thickness and refractive index may be obtained by spectroscopic ellipsometry.

[**] Momentum transfer is defined as $\kappa = 4\pi \sin\theta / \lambda$; λ = radiation wavelength; θ = angle of incidence.

V.1.2. Organized layers (films) on solid substrates

An organized layer (film), either *deposited* or *adsorbed* (including the *chemisorbed*) on a solid substrate, may be a monolayer or a multilayer which exhibits a certain degree of order. The terms defined below are general and refer to any solid-supported monolayers or multilayers, independently of their specific formation method (see section below), chemical nature and applicability.

V.1.2.1. **Homolayer** refers to the multilayer consisting of chemically identical monolayers. **Heterolayer** applies to the deposited multilayer consisting of a periodic or non-periodic^[20] stack of chemically different monolayers.

V.1.2.2. The periodic multilayer consisting of two alternating monolayers (e.g. A and B) is referred to as **alternate multilayer**. **Centrosymmetric multilayer** applies to an alternate multilayer in which the molecular assembly has a center of symmetry, as in the sequence -A-B-B-A-. Otherwise, they are referred to as **non-centrosymmetric multilayers**.

V.1.2.3. The multilayers consisting of alternating pairs of identical monolayers (as in -AA-BB-) are referred to as **paired multilayers**.

V.1.2.4. The term **two-dimensional (2D) molecular pattern** designates a specific lateral molecular arrangement, in floating or substrate-supported mixed monolayers, designed to act as a template for further deposition. These templates may serve as matrices to induce **epitaxial growth** of 3D crystals (i.e. growth of crystals whose lattice has an organizational relationship with the lattice of the matrix) from an adjacent liquid phase components.

V.1.2.5. **Molecular epitaxy** applies to the process of rearrangement in a depositing monolayer, induced by the lattice of the distinct 2D template (solid substrate) in contact with a monolayer. For instance, molecular epitaxy can occur in a floating monolayer on temporary transfer of this monolayer onto a solid substrate surface (see following section V.1.2.) which acts as a matrix. The induced, specific 2D molecular arrangement or pattern may be preserved in the monolayer after its separation from the template.

V.1.2.6. **Molecular recognition** ^[21] refers to the process of specific adsorption of a type of molecule on a particular molecular pattern (in a monolayer) specific to the adsorbing species. When the pattern is created in some way by the adsorbing molecule, it is referred to as a **molecular replica** or **molecular print**. For example, a molecular replica can be "printed" on a floating mixed monolayer consisting of an assembly of flexible molecules surrounding a weakly bound adsorbate (dye for instance), which organizes the assembly, i.e. creates the pattern, around it. This pattern may be "fixed" by deposition of the layer onto a solid substrate, for example (see following section V.1.2.), and the adsorbed molecule removed. Subsequently, only the "printed in" dye molecule is "recognized" by the fixed pattern, i.e. can be re-adsorbed on the imprinted layer.

[20]. The supramolecular machines (see above) consist, often, of non-periodic multilayers (e.g. the pile of monolayers ABCD, where A, B, C and D designate different monolayers).

[21] This term must not be confused with the similar one used in enzymology to designate the property of natural macromolecules to associate with small molecules when the geometry of their "interfaces" is complementary and permits a significant number of weak interactions to be established.

V.1.2.1 Preparation methods of organized layers

V.1.2.1a. Vertical and horizontal deposition procedures

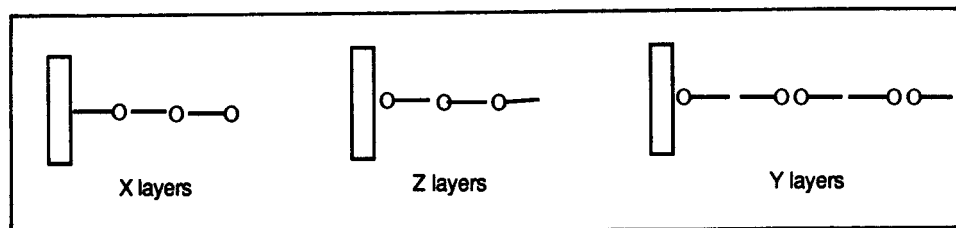
V.1.2.1a.1. The term **Langmuir-Blodgett deposition method**, (LB), applies to the method where a floating monolayer (see V.1.1.) in a well defined thermodynamic state (monolayer surface pressure, composition and temperature, subphase pH, etc.) is transferred from the air water interface onto the surface of a slide referred to as the **multilayer substrate**.

V.1.2.1a.2. The **Langmuir sequence** is the *discontinuous* procedure for monolayer preparation and deposition which operates in the single compartment film balance (see ref. 2) often referred to as the **Langmuir trough**. The Langmuir sequence consists in four successive steps: floating monolayer spreading, solvent evaporation, monolayer compression and monolayer deposition.

V.1.2.1a.3. A **continuous trough** is a device which permits monolayer preparation and deposition by a *continuous* procedure. It consists of a multicompartment film trough in which a distinct compartment is dedicated to each one of the four steps of the above mentioned sequence, the trough compartments being connected *in series* to operate *simultaneously*.

V.1.2.1a.4. The term **vertical lifting LB technique** (VLLB) refers to the technique where the substrate is vertical and is alternately dipped into (**down stroke**) and pulled out (**up stroke**) from the subphase of the floating monolayer. The **speed of film transfer** under the given thermodynamic conditions is defined by the vertical lifting velocity [m/sec] of the (often) rectangular solid substrate. The **maximum speed of film transfer** refers to the vertical lifting velocity above which subphase liquid is dragged along and the substrate emerges apparently wet [22]. The **monolayer transfer ratio** characterizes the floating monolayer deposition process. It is defined by the ratio between the change (decrease) in the area of the *floating* monolayer ΔA (molecules are removed from this monolayer) and the change (increase) of the *deposited* monolayer area $\Delta A'$ (on the solid substrate).

V.1.2.1a.5. The term **Y monolayer deposition** applies when monolayer deposition occurs on down and up strokes. **X monolayer deposition** applies when the floating monolayer deposition occurs only on the downstrokes; **Z monolayer deposition** applies when it occurs only on the upstrokes. The type of deposition depends on the deposited molecules and deposition conditions. Only if the vectorial orientation of the deposited layer is proved to be that corresponding to the X, Y, Z type defined in Fig. V.1.2.1.1 below, can they be called **X multilayers**, **Y multilayers** or **Z multilayers** respectively.



V.1.2.1a.6.

Fig. V.1.2.1.1. Vectorial orientation of deposited monolayers in X, Y and Z multilayers (O—): deposited monolayer of amphiphilic molecules

[22] Visual inspection under grazing illumination during floating monolayer transfer permits observing whether the pulled out substrate is dry or wet.

V.1.2.1a.7. The preparation of **designed heterolayers** involves the deposition of a designed sequence of chemically different floating monolayers (e.g. ABCD,ABA).

V.1.2.1a.8. **Monolayer horizontal lifting** refers to the monolayer deposition procedure where the substrate is in a horizontal position during either or both of the up and down-stroke steps. For example, in the case of alternate layer deposition, the operational sequence may consist of the following steps: horizontal down-stroke, removal of remaining floating layer, spreading, evaporation and compression of an appropriate new type of floating layer and vertical up-stroke lifting (deposition of the second type of monolayer).

Since the quality of the deposited layers (e.g. degree of organization) depends critically on the properties of the substrate (chemical nature, roughness, cleanliness, etc) and on the conditions of the floating monolayer deposition (speed of transfer, surface pressure, etc.), information on these factors must be included in the reports. A transfer ratio equal to one(1) is considered as satisfactory. Speeds of transfer less than the maximum speed are recommended (see definition of maximum speed above and footnote [20]).

V.1.2.1b. Controlled layer adsorption from solution and stepwise film growing

V.1.2.1b.1. **Controlled layer adsorption** from solution (including chemisorption) applies to the procedure specific to the preparation of chemisorbed organized multilayers. In this procedure, chemical reactions are carried out between the multilayer "end groups" (in contact with a solution) and molecules adsorbed on the multilayer interface. This results in designed, complex multilayer assemblies where the successive monolayers are chemically bound.

V.1.2.2. Methods of characterization

Essential characteristics of solid, organized organic layers are: thickness, structure, organization (molecular and supramolecular) and functionality (e.g. molecular recognition, energy or electron intermolecular transfer, 2D electrical conductivity, etc.).

The main methods of characterization applicable to these layers deposited on solid substrates are listed in Table V.1.2.2.1, below. The technique (first column) associated with a given methodology (second column) appears in a separate column (e.g. fluorescence microscopy is a methodology involving optical techniques). Sampled area scale (fourth column) refers to the order of magnitude of the area or length which is sampled, i.e. effectively investigated by the standard technique and methodology under consideration (e.g. mm² in the case of microscopy). Primary information (third column) refers to the type of information (usually sets of raw experimental data) from which further information on a system (e.g. state, structure, behaviour, composition, physical quantities), referred to as derived information (fifth column), can be obtained (e.g. the distribution map of fluorescent molecules refers to the image provided by the microscope, from which information on the 2D inhomogeneity of a layer is derived). Under the heading Caveats (sixth column) are listed factors and basic "traps" limiting the validity of the derived information (column five) concerning the system (e.g. in the case of fluorescence microscopy and domains smaller than microscope resolution, the layer appears homogeneous).

TABLE V.1.2.2.1.Characterization of organized organic layers (Part I)**V.1.2.2.1.**

Technique	Methodology	Primary (raw) information	Sampled area scale	Derived information	Caveats
optical	fluorescence microscopy	distribution map of fluorescent molecules	mm ²	2D homogeneity, molecular segregation, domain size and shape	limited to microscopic or larger domains; dye solubility in layers
	ellipsometry and Brewster angle microscopy	ellipticity [*]; map of deviation from Brewster extinction, uniformity defects	mm ²	layer thickness and /or refractive index[*]; optical anisotropy and thickness distribution	limited to optical size or larger domains
	polarized light microscopy	birefringence; crystalline domains visualisation	mm ²	layer texture and crystalline structure	limited to microscopic or larger domains
	Nomarski interference microscopy	map of thickness distribution; film discontinuity	mm ²	film quality, uniformity, defects, collapse	destructive method sign of surface gradients ambiguous;
	IR spectroscopy, IR linear dichroism (FTIR-ATR [**] included)	absorption spectra ; dichroic ratio of polarized absorption intensities	100mm ²	vibrating bond identification; bond transition moment, order parameter and orientation (in and out of layer plane); charge transport mechanism; charge transfer ratio	no access to the molecular angular distribution
	UV, visible spectroscopy; UV, visible linear dichroism	electronic absorption spectra; dichroic ratio of polarized absorption intensities	100mm ²	electronic transition identification; oscillator strength; orientation of molecular axes	no access to the angular distribution of molecular axes
	polarized light Raman spectroscopy	Raman spectra at various exciting light wavelengths	mm ²	molecular polarisability and tilt; film order	film damaging
	absorption / emission spectroscopy	fluorescence spectra excited state life time action spectra	100mm ²	energy transfer efficiency; donor / acceptor separation; quenching mechanism	average values
microwave + magnetic	anisotropic, electron spin resonance ESR	microwave absorption spectrum vs. magnetic field and film relative orientation	100mm ²	access to paramagnetic group angular distribution and surface concentration	limited to paramagnetic layers; probe may affect layer organization

V.1.2.2.2 [*] Ellipticity (of the reflected radiation) is the ratio of amplitudes for electric fields polarized parallel and normal to the incidence plane; thickness *and* refractive index are obtained by the ellipsometry referred to as spectroscopic.

V.1.2.2.3 [**] ATR: attenuated total reflectance.

TABLE V.1.2.2.1.Characterization of organized, organic layers (Part II)**V.1.2.2.4.**

Technique	Methodology	Primary (raw) Information	Sampled area scale	Derived Information	Caveats
X-ray beams	fluorescence spectroscopy	spectrum	1-100 mm ²	composition, chemical interactions	information averaged on large areas;
X-ray and neutron beams	specular reflection (diffraction and diffuse scattering) at various wavelengths λ and/or incidence angles θ	reflectivity, θ and θ_c (limit angle of total reflection), reflectivity vs. κ (*), interference pattern	1-100 mm ²	profiles of electron density (X-ray) or (neutron) refractive index; layer thickness, homogeneity and roughness, molecular tilt, crystalline lattice constant, coherence length	information averaged on large areas; limited to crystallized material
electron beam	electron diffraction	diffraction pattern or energy spectra	1-100 mm ²	crystalline lattice structure and parameters; molecular tilt and packing, positional and orientational long range order	film damaging; film evaporation (vacuum)
	scanning electron microscopy	map of secondary electron emission	5-10 nm	layer roughness, morphology and homogeneity	film damaging and charging effects; image interpretation
	Auger spectroscopy and microscopy	energy spectrum of secondary electrons; distinct map for each film element	10 ⁻² - 10 ⁴ μ m ²	film chemical composition; nature of film defects	film damaging and evaporation; contaminant sensitive
secondary photo-electron emission	secondary electron spectroscopies XPS, UPS, ESCA, EXAFS[**]	secondary electron kinetic energy spectrum vs. irradiation wave length;	1-100 mm ²	ionization energy, electron binding energy, composition near film interface	contaminant sensitive; average information; film evaporation
electrical	dc current / voltage and high frequency experiments;	anisotropic (in and out of plane) conductance;	1-100 μ m ²	anisotropic conductivity; defect and grain boundary effects; supramolecular architecture	film thickness is required; contamination sensitive; test of functionality
	dielectric experiments	capacitance; losses; dc leakage current	mm ²	thickness, water content, pinhole overall area[***]	permittivity values needed, as appropriate
electro-chemical	electrolytic metal deposition on the substrate free surface	metal deposits (decoration) at film pinholes [***]		layer continuity and quality; pinholes [***]	decoration technique

V.1.2.2.5. (*) $\kappa = 4\pi \sin\theta/\lambda$ is referred to as momentum transfer.

V.1.2.2.6. [**] UPS(UV photoelectron spectroscopy), XPS(X-ray photoelectron spectroscopy), ESCA(electron spectroscopy for chemical analysis), EXAFS(extended X-ray absorption fine structure).

V.1.2.2.7. [***] Pinhole: local discontinuity in the deposited layer, i.e. free substrate surface (typically 50 nm large in LB films).

TABLE V.1.2.2.1.Characterization of organized, organic layers (Part III)**V.1.2.2.8**

Technique	Methodology	Primary (raw) Information	Sampled area scale	Derived Information	Caveats
mechanical	acoustic	frequency shift	100 mm ²	film mass surface concentration (mass / film unit area)	average information; wave damping
micro-mechanical	atomic force microscopy	surface profilometry; force between surfaces	≤5 nm ²	molecular scale surface roughness, surface interactions; interfacial elastic modulus	questionable image interpretation; highly sensitive to probe quality
radiotracer	radioactivity emitted by radioactive or radiolabeled components	intensity of radioactive emission/unit area of the film	1000 mm ²	average surface composition and concentration	information averaged over a large film area
chemical	reactivity: catalysis, polymerization, charge transfer	reaction rate, reaction efficiency, turnover, reaction mechanism, group accessibility	1000 mm ²	molecular orientation and conformation, film permeability	highly indirect and global information; functionality test
thermal	photothermal (PT) spectroscopy	PT signal (pyroelectrical detection of evolved heat) vs. absorbed energy of radiation.	mm ²	film electrical polarization; characteristics of thermal depolarization	global functionality test

V.2. AMORPHOUS AND LOW CRYSTALLINITY ORGANIC LAYERS

V.2.0. Thin layers of amorphous or low crystallinity organic materials with high optical clarity are technologically important in many areas. They are used as optical structures, photoresists, electrophotographic layers, piezoelectric and pyroelectric elements or simply as free-standing films. The latter are used as substrates or as barrier or sealant materials.

V.2.1 Preparation methods

Amorphous organic layers or films can be prepared by various deposition methods on various substrates (glass, metals or plastics). Many organic amorphous film materials consist of macromolecules which have viscoelastic properties used to facilitate thin layer formation.

V.2.1.1. The terms **cast film** and **extruded film** refer to films formed directly from the melt phase or solution. **Cast films** are those that are spread into a layer using a metal cylinder as a temporary supporting mechanical platform to aid the film formation process during cooling of the melt, before the film is transferred to a final support; **extruded films** emanate as a melt from a tooled die and are deposited directly onto the substrate. Micrometer to millimeter (20-500 μm) thick films can thus be prepared.

V.2.1.2. The terms **dip-coating method** and **spin-coating method** (or "spin-casting" in section V.3.3.5) refer, mainly, to methods of nanometer to many micrometer (1-100 μm) thick film formation

from solution. In the first method the substrate is dipped into a solution of the film-former in a volatile solvent and then removed for drying. The residue remaining after evaporation of the solvent constitutes the film. In spin-coating, a rapidly spinning solid substrate is coated with a wetting film of a solution containing the film material in a volatile solvent of appropriate viscosity. The solvent evaporates during the spinning cycle leaving the organic film on the substrate.

V.2.1.3. The **spreading method** applies to the method of film formation by solvent evaporation from a uniformly thick layer of solution spread (smeared) onto a substrate using either a **doctor blade** or a **wire-bound bar**. A **doctor blade** is a barrier device with a preset gap which meters the solution layer thickness. A **wire-bound bar** is a similar device which employs a thin wire wrapped helically around a metal bar to produce a series of fine gaps to aid the spreading of the film.

V.2.1.4. The term **lamination method** refers to the procedure whereby pre-formed films may be transferred to one substrate from another.

V.2.1.5. The **plasma polymerization method** or the **electropolymerization method** are processes used to form nanometer to micrometer thick films (e.g. used in PC Board industry). **Plasma polymerization** refers to processes in which ionized gas atmospheres of a monomer are allowed to condense, with electrical neutralization, onto a substrate to form a thin macromolecular deposit; **electropolymerization** refers to a similar deposition process initiated by electrochemical processes at electrode surfaces. Radicals or ions produced at the electrode are formed and initiate polymerization directly on the electrode material surface. Multilayer amorphous organic films can be built by either of the above processes or by combinations of processes.

V.2.2. Characterization of amorphous organic layers

Amorphous organic solid films may be characterized by many of the methods appropriate for liquid films, organized organic layers or inorganic solid layers.

Methods of characterization applicable to the amorphous organic layers are listed in Table V.2.2.1, below. The "Technique" (first column) associated with a given "Methodology" (second column) appears in a separate column (e.g. ellipsometry is a methodology involving optical techniques). "Sampled area scale" (fourth column) refers to the order of magnitude of the area or length which is sampled, i.e. effectively investigated by the standard technique and methodology under consideration (e.g. $100\mu\text{m}^2$ - 1mm^2 in the case of ellipsometry). "Primary information" (third column) refers to the type of information (usually sets of raw experimental data) from which further information on a system (e.g. state, structure, behaviour, composition, physical quantities) referred to as Derived information (fifth column) can be obtained (e.g. the film thickness and/or refractive index). Under the heading "Caveats" (sixth column) are listed factors and basic "traps" limiting the validity of the derived information (column five) concerning the system (e.g. in the case of classical ellipsometry, the actual refractive index of the film material must be known to determine the film thickness, in contrast to the new spectroscopic ellipsometry which permits simultaneous measurement of both film thickness and refractive index; see footnote [*] in the following Table V.2.2.1).

TABLE V.2.2.1.Characterization of amorphous organic layers**V.2.2.1.**

Technique	Methodology	Primary Information	Sampled area scale	Derived Information	Caveats
optical	ellipsometry	ellipticity [*]	mm ²	layer thickness and/or refractive index[*]	only optical size homogeneities
	IR spectroscopy, linear dichroism (FTIR-ATR and RAS included)	absorption spectra ; dichroic ratio of polarized absorption intensities	100mm ²	vibrating bond identification; bond transition moment and orientation; transport mechanism; charge transfer ratio	no access to the bond angular distribution
	UV, visible spectroscopies	spectrum	100mm ²	composition	average information
	polarized light Raman spectroscopy	Raman spectra at various exciting light wavelengths	mm ²	molecular polarisability ; film order	film damaging
	absorption / emission spectroscopy	emission spectra vs time; excited state life time	100mm ²	film thickness and uniformity; quenching mechanism; probe mobility (diffusion); domain structure	average values
photo-electron emission	XPS (photo-electron spectroscopy) [**]	energy spectrum of emitted electrons	1-100mm ²	surface composition and geometry	contamination, average values
thermal	thermal analysis (DSC, TGA [***])	calorimetric	mm ²	phase transitions; thermal stability	average values
micro-mechanical	AFM (atomic force microscopy)	surface profilometry; force between surfaces	<5 nm ²	surface roughness at molecular scale , surface interactions; interfacial elastic modulus	image interpretation difficult; highly sensitive to probe quality
mechanical	impact tensile dilatometry	strength at impact, strength at break tension	cm ²	hardness, strength modulus, surface tension	destructive (some methods)
electrical	dc current / voltage and hf experiments	anisotropic (in and out of plane) conductance	1-100 μm ² to bulk	average conductivity anisotropy; surface conductance; pinhole overall area[****]	film thickness is required; contamination sensitive
	dielectric measurements	capacitance; dielectric loss	mm ²	thickness;polarisability microstructure; relaxation processes; phase transitions	permittivity values needed, as appropriate
	photo-conductivity	conductivity; carrier concentrations; transport properties	100 mm ²	carrier mobility; photoresponse spectrum; trap depths	impurity sensitive
chemical	chromatography	composition	100 mm ²	composition	limited to soluble organic layers

V.2.2.2. [*] Ellipticity (of the reflected radiation) is the ratio of amplitudes for electric fields polarized parallel and normal to the incidence plane; thickness and refractive index can be obtained by *spectroscopic* ellipsometry.

V.2.2.3. [**] XPS: X - ray photoelectron spectroscopy.

V.2.2.4. [***] DSC: differential scanning calorimetry; TGA: thermal gravimetric analysis.

V.2.2.5. [****] Pinhole: local discontinuity in the deposited layer, i.e. free substrate surface.

V.3. INORGANIC DEPOSITED LAYERS

V.3.1. Introduction

To fully describe these film materials reference should be made to their crystalline, preparative and/or material properties, e.g. amorphous silicon films, microcrystalline sputtered films. The description of the films as discontinuous, network, continuous or superlattice (defined in Section II, above) should also be included, when appropriate. The present project considers only continuous films.

V.3.2. Characteristics by layer crystallinity

V.3.2.1. Introduction

Generally speaking, the categories of thin films that are widely accepted are :

1. single crystalline film
2. polycrystalline film
 - 2a macrocrystalline film
 - 2b microcrystalline film
3. amorphous film

When the geometric scale of the film (thickness is an example) becomes comparable to a physical scale (e.g. the mean free path, the wavelength of electromagnetic radiation, etc.) the physics of the film may become complicated and, eventually, geometric scale dependent. Hence, the distinction between geometric and physical scales (see Table V.3.2.1.1) is essential for thin solid films. Relative values of various solid film scales and solid film geometric scales, for various inorganic materials, are illustrated in Fig. V.3.2.1.1. The geometric scales and the physical scales or characteristic lengths are defined in Table V.3.2.1.1. This list is not exhaustive.

TABLE V.3.2.1.1. Definition of important scales for solid thin films

<u>Name</u>	<u>Symbol</u>	<u>Definition</u>
<u>V.3.2.1.1.</u>		
a) geometric scales		
film geometric (effective) thickness	d (h)	see definition of h in Table IV.3.1.1.
grain size	d_g	average dimension of the single crystal element in polycrystalline film
quantum wall thickness	$d_{qw} = Na_0$	repeat scale defined as the number, N , of lattice constants, a_0 , in a specific epitaxial layer in a multilayer film
<u>V.3.2.1.2.</u>		
b) physical scales or characteristic lengths		
electromagnetic wavelength (scale)	λ	repeat distance for electromagnetic waves
phonon wavelength (scale)	λ_{ph}	repeat distance for quantized lattice vibrations
charge carrier mean free path	λ_{mfp}	average distance between collisions by free carriers
Debye screening length (in a solid)	L_D	distance over which an electric field is screened to e^{-1} of its surface value (see similar definition of Debye screening length, κ^{-1} , in Section II Annex)

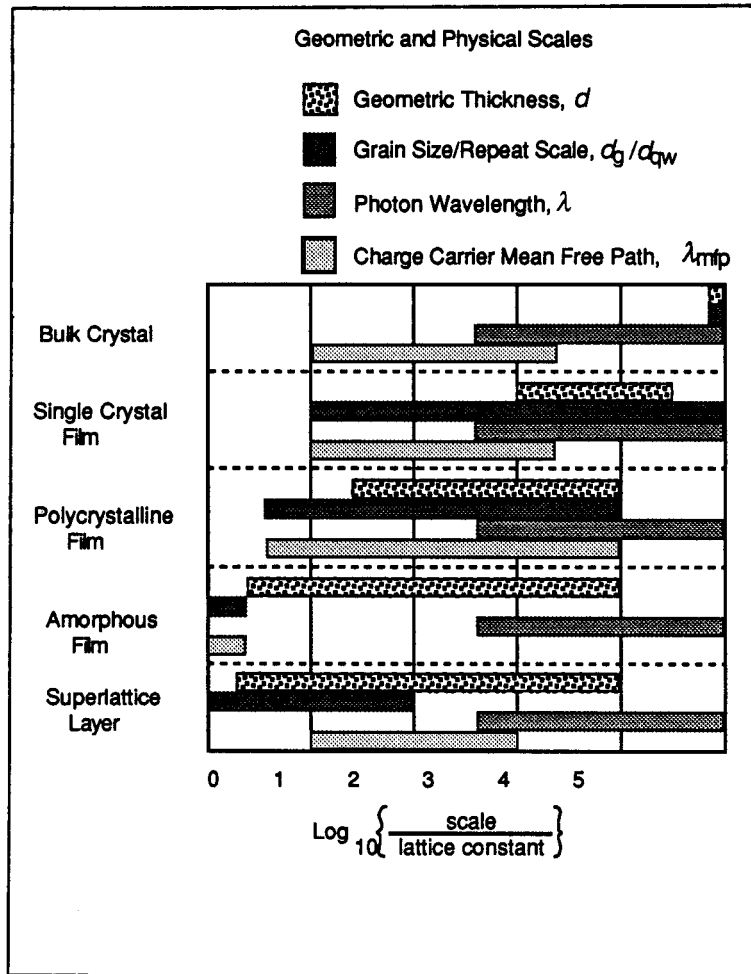


Fig. V.3.2.1.1. Relative values of various physical characteristic lengths or geometric scales in bulk crystals and certain types of inorganic solid films

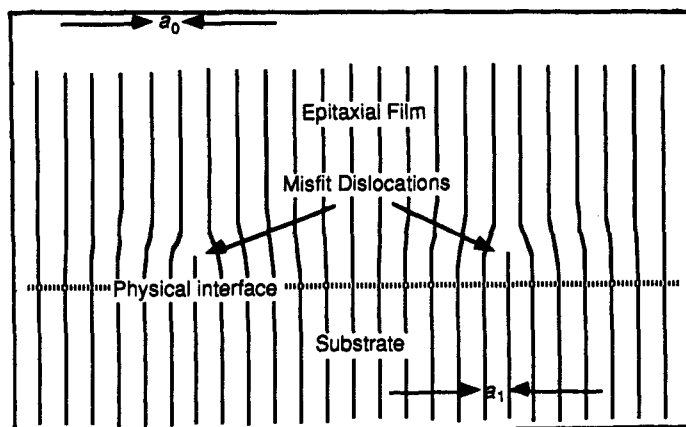
V.3.2.1.3.

V.3.2.2. Single crystalline films, including epitaxial films

V.3.2.2.1. A single crystalline film is a single crystal restricted in one dimension (z direction, see Section II).

V.3.2.2.2. **Epitaxy** is defined as the crystalline overgrowth of a material referred to as the **epitaxial film**, on a crystalline substrate where the crystal axes have a definite relationship to the crystal axes of the substrate. The epitaxial film is a typical example of a single crystalline film. **Homoeptaxy** refers to the ordered (single crystalline) overgrowth of a film on a single crystal substrate of the same material, e.g. **homoeptaxial** film of Si on Si. **Heteroepitaxy** refers to the overgrowth of a single crystalline film on a single crystal substrate of a different material, e.g. **heteroepitaxial** film of $\text{Ga}_{1-x}\text{Al}_x\text{As}$ on GaAs. In some instances, the lattice constants, a_i , may not be equal (see Fig. V.3.2.2.1).

V.3.2.2.3. The **lattice mismatch** is the relative difference between substrate and film material lattice constants: $(a_i - a_j)/a_j$. The term **misfit dislocation** applies to a localized dislocation (see Fig. V.3.2.2.1) which accommodates a misfit in the lattice constants of the two materials and makes possible the existence of the normal periodicity at some distance from the surface.

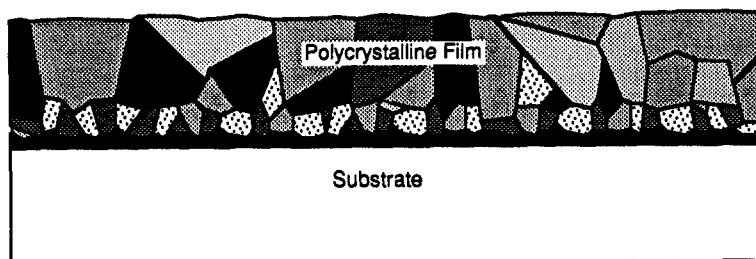


V.3.2.2.4.

Fig. V.3.2.2.1. Schematic illustration of an epitaxial film (lattice constant, a_0) on a substrate (lattice constant, a_1) depicting the misfit dislocations

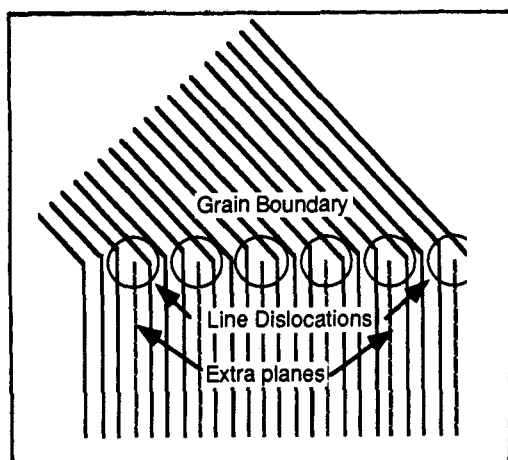
V.3.2.3. Polycrystalline films

V.3.2.3.1. The term **polycrystalline film** refers to films which are composed of individual adjoining single crystals. (Fig. V.3.2.3.1). The term **line dislocation** (Fig. V.3.2.3.2) refers to the termination of a partial plane of atoms or molecules (dashed lines in Fig. V.3.2.3.2) inserted into the crystal. The array of line dislocations is referred to as the **grain boundary** for the crystallite.



V.3.2.3.2.

Fig. V.3.2.3.1. Illustration of the cross sectional structure of a polycrystalline film



V.3.2.3.3.

Fig. V.3.2.3.2. Depiction of a grain boundary showing the additional planes of atoms or molecules that produce line dislocations (indicated by circles)

V.3.2.3.4. The lateral dimension, d_g , of the individual grains (Fig. V.3.2.3.1), depends on the film preparation conditions. A macrocrystalline film is significantly larger than the film effective thickness while it is considerably

smaller in microcrystalline films. For historical reasons, the term "thin film", often designates *arbitrarily*, insulator, semiconductor and metal films 1 μm or thinner.

V.3.2.4. Amorphous vs. microcrystalline films

V.3.2.4.1. A film is, usually, referred to as an **amorphous film** when second nearest neighbor order is not exhibited. (This does not exclude nearest neighbor order). Examples of inorganic amorphous films are: silica, hydrogenated sputtered silicon, etc.

V.3.2.4.2. A solid film having sufficient long range order so that X-ray or electron diffraction measurements give a *significant number* of diffraction maxima should be referred to as a **microcrystalline film**. Typically this occurs when the effective crystallite dimensions d_c are equal to or larger than 2-5 nm ($5 - 20a_0$).

V.3.3. Methods of preparation

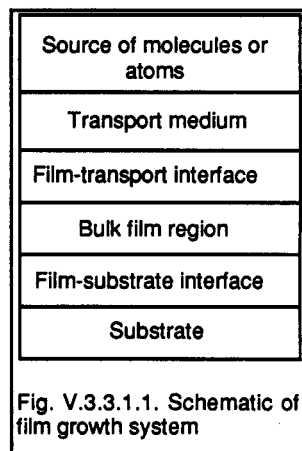
V.3.3.1. Introduction

The creation of a film of solid involves virtually every known method of material processing. The methods described below have the common feature that they involve deposition of material, to form the film, rather than depletion of material [23]. This list is not exhaustive.

IUPAC does not recommend the proliferation of abbreviations and acronyms. Hence upon describing the method of preparation it is strongly recommended that the use of acronyms should be restricted to those used in this chapter and they must be defined once in any paper to assist the reader.

V.3.3.1.1. The term **deposition** refers to the methods where atoms or molecules accrete to a film growing on the surface of a **substrate** which is a *condensed* phase distinct from the phase which acts as the **film material source**. The overall system is illustrated schematically in Fig. V.3.3.1.1. The means for the preparation of the film are as varied as the materials themselves. They may be grouped together in the general classes treated below.

V.3.3.1.2. The term **annealing** refers to a post deposition process specifically carried out to relieve mechanical stress and stabilize the film properties. Annealing is often accompanied by grain growth.



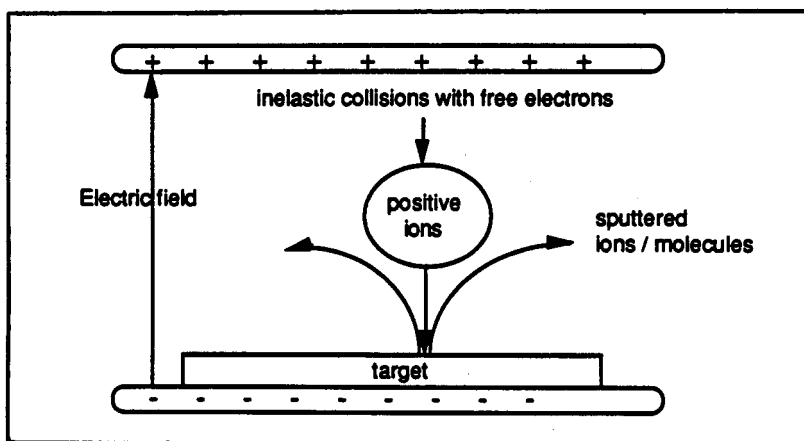
When reporting on solid films, a description of the preparative conditions as complete as possible is needed to assess the film quality and the effect of film substrate on film properties. Specification of the predeposition vacuum conditions is one of the prime pieces of information to be reported since the residual impurity level in many classes of solid films is strongly influenced by these conditions. Whenever possible, direct analytical methods should be employed and information on the final chemical composition of a film should be included in the description of the method of its preparation.

V.3.3.2. Sputtering and ion assisted deposition

V.3.3.2.1. **Sputtering** is a general process. In the case of solid film preparation, sputtering refers to

[23] Micron thick membranes of silicon can be fabricated using etching methods from a bulk single crystal.

technologies where the source of material called a **sputtering target** is impacted by ions accelerated from a gaseous plasma. As a result, these ions eject, viz. sputter atoms/molecules, aggregates or clusters, from the source surface. This is distinct from physical vapour deposition and chemical vapour deposition. Plasma refers to the partially ionized gas formed by the electrical discharge at reduced pressures when a suitable electric field is established between anode on which the substrate is usually placed, and cathode, the sputtering target (Fig. V.3.3.2.1)[²⁴]. The plasma is maintained by the secondary electrons emitted by the sputtering target which is surrounded by a positive ion rich plasma region called **negative glow plasma**.



V.3.3.2.2.

Fig. V.3.3.2.1. Depiction of the sputtering process

The efficiency of the sputtering process is highly dependent on the operational conditions of the plasma and geometry of the excitation chamber which must be described. In reporting on the operational conditions of the plasma and associated sputtering process, it is recommended that as many parameters as possible *be specified*, e.g. applied potential and magnetic fields (where appropriate), gas composition, chemical characteristics of the source and substrate, operational pressure, type and geometry of the discharge or excitation chamber and presence of insulator surfaces in the sputtering system, and specify the associated matching networks, if any.

Classification of the various sputtering and ion assisted methods is generally based on the excitation used for plasma or ion generation[²⁵].

V.3.3.2.3. **dc-sputtering** refers to the method where a dc-field is applied across a simple two electrode (substrate/target) configuration (diode). It may be employed whenever charging of the target surface is not a problem (e.g. metals).

V.3.3.2.4. **RF-sputtering** refers to the method where an intense high frequency electric field is established across the electrodes. It is appropriate for sputtering insulating materials (e.g. ZnO).

[²⁴]. For further details see sections 10.1.5 and 10.1.6. In *IUPAC Compendium of Analytical Nomenclature, Definitive Rules 1987* prepared by H. Freiser and H. Nancolas, Blackwell Scientific Publications, Oxford(1987).

[²⁵] Nomenclature relative to plasma or ion generation procedures used in analytical chemistry is recommended in sections 10.1.2.1, 10.1.5, 10.1.8 and 17.2.38 of *IUPAC Compendium of Analytical Nomenclature, Definitive Rules 1987* prepared by H. Freiser and H. Nancolas, Blackwell Scientific Publications, Oxford(1987).

V.3.3.2.5. Magnetron sputtering is a magnetic field assisted, low pressure sputtering method in which the efficiency of the gas ionization (plasma formation) is greatly increased by spiraling the electron path. As a result of the reduced background pressure, film contamination by gas components can be substantially reduced.

V.3.3.2.6. Reactive sputtering refers to a method whereby the plasma can produce active species which by reacting with *either* the target *or the sputtered* material *produces appropriate compound films*. Careful control of the gas composition is required for optimum film properties.

V.3.3.2.7. Ion beam sputtering also called **ion milling** refers to a plasma free, extremely low pressure sputtering procedure whereby a beam of ions formed in an independent ion gun is used to sputter the target. This procedure leads to high purity deposited films. The term **reactive ion milling** refers to a variant of reactive sputtering which can be used to deposit compound materials or etch surfaces.

V.3.3.3. Physical vapour deposition (PVD)

V.3.3.3.1. Physical vapour deposition method, PVD, refers to the method where thermal energy is used to transform the source material into vapor which is then deposited by adsorption and solidification onto the substrate at another site of the system. The specific step in PVD is the incorporation of the adsorbate (atoms and/or molecules) into the film structure.

V.3.3.3.2. The kinetics of material deposition onto the substrate depend on the vapour pressure and the **sticking coefficient** or **sticking probability** which is the probability that an incident vapour atom or molecule condenses on the substrate. The main critical parameters in PVD are: the vacuum conditions (pressure, vacuum system, type and material construction, residual gas composition, presence of ionized and accelerated atoms or clusters in the vapour, etc.); the temperature of the source, substrate and walls of the chamber; the purity of the source material. It is recommended that publication of articles describing the properties of films should either include information on the factors mentioned above to the greatest extent practical, or should be traceable to such descriptions.

V.3.3.3.3. The three basic techniques defined below are commonly employed for metals and semi-conductors evaporation or sublimation:

- molecular beam oven** refers to the heated enclosure with a small exit aperture;
- **open source** refers to the film material source consisting in an electrically heated spiral wire;
- electron beam heated cold hearth technique** refers to the technique where an electron beam bombards the source to heat it.

Variants of the above basic methods involve intense laser and electron or ion beams (for ion beams see also section V.3.3.2.) for local heating and material emission by the source.

V.3.3.3.4. Flash evaporation method refers to an obsolete method where a small particle of material is dropped onto a very hot surface causing it to melt and evaporate, or sublimate extremely quickly.

V.3.3.3.5. Molecular beam epitaxy method (MBE) refers to the PVD method which is collision free in the transport step and permits extremely fine control of film composition and impurity down to single atomic layer thickness. This process involves no chemical reaction other than compound formation on the substrate. An important example of MBE application is the preparation of complex, i.e. multicomponent and periodic multilayer

(*quantum well*) semiconducting materials [26].

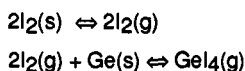
V.3.3.3.6. The term **cold wall system** refers to the ultra-high vacuum systems used in conventional MBE, operating at residual pressures on the 10^{-7} - 10^{-9} Pa range in chambers which are normally at or near room temperature. In addition, MBE is generally characterized by : single crystal substrates ; in situ monitoring of the oriented overgrowths, with electron diffraction and various types of spectroscopies; extreme attention to detail and cleanliness.

V.3.3.3.7. **Hot wall epitaxy method** refers to a specialized PVD method which involves a reactor referred to as **hot wall system**. It employs a temperature gradient $T_{\text{substrate}} \leq T_{\text{source}} \leq T_{\text{transport zone}}$ which limits the material deposition to the substrate and allows the temperatures to be adjusted so that near equilibrium conditions can be maintained.

V.3.3.3.8. The **cluster deposition system** refers to a variant of the conventional PVD system. Cluster deposition proceeds under conditions where atoms/molecule clusters referred to as **hyper-thermal clusters**, are formed and accelerated onto the substrate. Good quality polycrystalline films are rapidly formed by this process. The method is appropriate also to the deposition of metallic layers.

V.3.3.4. Chemical vapour deposition (CVD)

V.3.3.4.1. The term **chemical vapour deposition method (CVD)** applies to the deposition methods which involve in the set of processes leading to the formation of the film, at least one intermediate *chemical* reaction. It is generally distinguished from PVD-MBE where compound formation takes place on the substrate (see Section V.3.3.3), by the intermediate reaction being other than compound formation. This reaction may take place in the gas phase or between adsorbates at/with an appropriate substrate. An example is given below.



The same class of physical and chemical parameters recommended for reporting on PVD (Section V.3.3.3.) should also be reported for CVD whenever possible. In addition, specific information that should be reported is listed in the following sections.

V.3.3.4.2. The terms **high pressure chemical vapour deposition, HPCVD**, and **low pressure chemical vapour deposition, LPCVD**, refer to the two general strategies in CVD.

In HPCVD, gases or combinations of gases and vapors are at or above atmospheric pressure. Gas flow and mass transport (diffusion and/or convection) limit the uniformity of the film properties (thickness, composition, etc.). Hence, when possible and appropriate, information should be given on: the methods used to obtain the flow and temperature patterns inside the system, the location of the film studied relative to flow patterns and the temperature profiles in the system. In LPCVD the pressure is significantly lower than atmospheric pressure. The rates of interfacial reaction and of the removal of reaction products are controlling factors, as a rule. Gas flow and mass transport are generally more readily controlled. Details on the temperature profiles and mass flow control at

[26]. A wide range of semiconducting compounds and alloys in the II-VI, III-V and IV-VI families are routinely prepared using MBE. Molecular beam ovens supply the various constituents (e.g. Al, Ga, In, P, As, Sb, for II-V compounds) as well as a variety of dopant atoms (Zn, Si).

these low pressures are important and should be reported. Since these systems operate below atmospheric pressure, information on the ultimate pressure both before and after the deposition should also be reported.

V.3.3.4.3. Plasma enhanced chemical vapour deposition method, PECVD, refers to the variant of CVD wherein an electric field is applied to produce ion and active species by electrical breakdown of the reactor gases. By this technique various reactions may be promoted, molecular beams of chemically reactive species developed, geometric reaction zones limited and background purity improved.

V.3.3.4.4. Organo-metallic chemical vapour deposition method, MOCVD, refers to the variant of CVD procedure where the active species in a metallo-organic compound usually is carried by an inert gas. The species involved [e.g. $\text{As}(\text{CH}_3)_5$] are less hazardous than the gaseous hydrides (e.g. AsH_3) used in ordinary CVD. The reporting recommendations are the same as for other CVD methods.

V.3.3.4.5. Chemical molecular beam epitaxy method, CMBE, refers to the LPCVD method where the sources for the film growth are chemical compounds supplied through fine nozzles that react on the substrate surface. The basic system is identical in most respects to an ultra-high vacuum MBE system which allows a combination of the relatively cleaner and simpler approach of CVD and better controlled environment of an MBE system. For example the composition and structure of the film can be directly monitored during the CVD growth process.

V.3.3.5. Liquid phase film growth

V.3.3.5.1. The methods referred to as **liquid phase film growth** consist of various physical chemical reactions between a liquid and the solid substrate. These reactions fall into three broad categories: **electrically mediated** (including **electrochemical**) deposition methods, **heterogeneous precipitation** methods (including **epitaxy**) and **spin casting** methods. In the liquid phase film growth process, the deposition of film material is, mainly, controlled by the transfer properties of the liquid.

Electrochemical deposition is a widely used method for growing metal films onto surfaces. The following terms refer to the three types of processes occurring at the (deposition) surface.

V.3.3.5.2. -i) **Electrolytic deposition method** refers to the method where an adsorbed metallic ion is reduced (neutralized) on the cathode. The specific reduction potentials, electrolytes present, deposition geometry and additives that control the character and quality of the deposited films are critical. Chemical purity and electrode cleaning procedures are important. Because of the industrial significance of electrolytic deposition, publication of these details is often omitted for commercial reasons. Nevertheless, reporting this information is essential when the electrochemically deposited film properties are the subject of a scientific publication.

V.3.3.5.3. -ii) **electroless deposition method** refers to the variant of electrolytic deposition where the film growth consists of the heterogeneous precipitation of the metal. This metal then acts as a catalyst for further deposition of metal present as ions in the interfacial region of the working electrode. For example, interfacial, solvated Ni^{2+} ions are reduced by the hydrogen produced locally (at the *metal* surface) by the decomposition of an anion, e.g. sulphoxylate ion (also called hyposulfite), decomposition catalysed by the presence of the metallic Ni film. The following information on the deposition conditions must be reported : temperature and pH, metal ion concentration, complete information on the chemical composition of the deposition medium (concentration of reducible anions, etc.).

V.3.3.5.4. -iii) **anodic oxidation method** refers to the growth of oxide layers *on* metal anodes (e.g. Al, Ta, etc.) in the presence of aqueous solutions. The growth rate generally depends on the current density. The layer thickness depends on the applied potential, temperature and chemical composition of the aqueous solution. Information on these parameters should be included in publications on these materials.

V.3.3.5.5. **Liquid phase epitaxy method** refers to a heterogeneous precipitation method (from saturated solution) in which the temperature is reduced sufficiently slowly to allow the solute to precipitate epitaxially onto the substrate surface. An example is the film growth of III-V compounds (see Section V.3.3.3.), where the metallic constituent acts as the solvent for the group V species. Essential for successful epitaxial film growth are extreme material purity and strict temperature control, hence information on these parameters should be reported.

V.3.3.5.6 **Spin-casting method** (spin-coating in section V.2.1) refers to the method of deposition whereby a centrifugal technique is used to thin down a thick wetting liquid film supported by a rotating solid substrate. The wetting film consists of a solution of a non-volatile solute in a volatile solvent. Simultaneous controlled evaporation of the solvent results in a smooth, uniform solid film of solute. The solute may be inorganic, organic or organo-metallic.

V.3.4. Characterization of solid Inorganic films

The characterization of solid inorganic films involves virtually every known type of measurement made on solids^[27]. It would be pointless to attempt to cover all these methods in this project. However, specific to films is their geometry (see film definition in section II) and the possible thickness dependence of film properties (see the definition of a *thin film* in section II).

Thickness and *structural* characteristics are generally agreed to be the two most important pieces of information about a thin solid film. *Thickness* assessment relies on physical, optical and electrical measurements for all classes of films. *Structural* studies most commonly employ diffraction or are derived from diffraction methods (e.g. specular reflection studies). Aside from these diffraction measurements, optical and electron micrographic studies are the other major physical means for establishing the structure of thin films. In a limited number of situations, electrical measurements can also supply valuable insight into the structure of semiconductor films. In the case of crystalline films mainly, a number of characteristics other than thickness and structure are needed since these characteristics may permit comparing the properties of bulk and film material.

In any description of the properties of semiconductor or metal films, it is necessary and recommended to include the specific methods of solid film preparation since they are essential for film characterization. The more commonly employed methods of characterization applicable to the inorganic solid films are listed in Table V.3.4.1, below. The methods are listed in the first and second columns, such that the Technique (first column) associated with a given Methodology (second column), appears in a separate column (e.g. in the electrical experiments the relationship current/voltage is the methodology associated with a particular electrical technique). Sampled area scale (fourth column) refers to the order of magnitude of the film area which is sampled, i.e. effectively characterized by the standard technique and methodology under consideration (e.g. 1-100 μm^2 in the first line of the table V.5.3.4.1 below). Primary information (third column) refers to the information (usually experimental data) from which further

[27] A Survey of Experimental Techniques in Surface Chemical Physics, *Pure. Appl. Chem.* **62**, 2297-2322 (1990).

information referred to as Derived information (fifth column) can be obtained (e.g. the film material resistivity is derived from the measured ratio current/voltage, i.e. the film resistance). Under the heading Caveats information (sixth column) are listed factors and basic "traps" limiting the validity of the above derived information (e.g. the resistivity is affected by the film morphology).

TABLE V.3.4.1. Characterization of inorganic solid film(Part I)

V.3.4.1.

Technique	Methodology	Primary Information	Sampled area scale	Derived Information	Caveats Information
electrical	current - voltage relationship	resistance	1 - 100 μm^2	resistivity / carrier concentration and mobility	preparation dependent, geometry sensitive
	current - voltage versus temperature	resistance versus temperature, thickness	1 μm^2 - 100 mm^2	energy levels of impurities	preparation dependent, geometry sensitive
	Hall effect	Hall voltage	> 1 μm^2	temperature dependence of scattering	strongly preparation dependent
	generation / recombination of minority carriers	free carrier bulk and surface lifetime	1 μm^2 - 100 mm^2	density, energy and cross section of recombination centers	as above and geometry sensitive
	carrier trapping	carrier lifetime	1 μm^2 - 100 mm^2	density, energy and cross section of traps	preparation dependent, geometry sensitive
	scanning - tunneling microscopy	local current - voltage plot, image	4 10^{-2} - 10^4 nm^2	morphology and / or chemical composition of the outermost layer	requires ultra-clean surfaces in high vacuum
photo-electron emission	photoelectron spectroscopies (UPS, XPS, Auger, ESCA, EXAFS) [*]	energy distribution (spectrum) of emitted photo electrons	1- 100 mm^2	surface atomic composition, atomic bond orientation & length, surface geometries, energy gaps	contamination sensitive, high vacuum needed, average information
electron beam	scanning electron microscopy	local secondary electron emission, imaging	10^{-4} - 10^4 μm^2	surface morphology, lattice spacing, surface charging effects	surface limited, lateral dimension limited to 10 nm
	transmission electron microscopy	electron current, image	10^{-6} - 100 μm^2	film morphology	acceleration voltage is film thickness dependent
	electron diffraction	diffraction pattern	1- 100 mm^2	atomic arrangement in outermost layers, structure-lattice constant	
	Auger electron spectroscopy	spectrum of secondary electrons	10^{-2} - 10^4 μm^2	surface chemical composition	contamination sensitive, radiation damage

[*] UPS (UV photoelectron spectroscopy), XPS(X-ray photoelectron spectroscopy), ESCA(electron spectroscopy for chemical analysis), EXAFS(extended X-ray absorption fine structure) .

TABLE V.3.4.1. Characterization of Inorganic solid films (Part II)**V.3.4.2.**

Technique	Methodology	Primary Information	Sampled area scale	Derived Information	Caveats Information
X-ray beams	fluorescence spectroscopy	spectrum	1-100 mm ²	composition, chemical interactions	average information on large film areas
neutron and X-ray beams	specular reflection (diffraction and diffuse scattering)	reflectivity vs. θ and $\kappa = 4\pi \sin\theta / \lambda$ [♦], interference pattern	100 - 4000 mm ² and 1-100 mm ²	film composition, thickness, roughness, structure- lattice constant, coherence length [♦♦]	average primary information (as above)
heavy ion beam	Rutherford backscattering (surface analysis)	ion currents	10-100 μm^2	single crystallinity, impurity distribution	preparation dependent, geometry sensitive
	ion probe and milling (surface) microanalysis	mass spectroscopy of secondary or sputter ions	10 μm^2	spatial distribution	surface cleanliness
optical	ordinary and polarized light microscopy	image, bi-refringence	10 ⁻² -10 ⁴ μm^2	physical morphology, chemical composition, crystalline axes	surface limited, Rayleigh crit. on lateral dimension
	IR and Raman spectroscopies	absorption, dielectric constant, light scattering, polarizability	1-100 mm ²	carrier concentration and band gap, phonon spectrum, impurity states	preparation dependent
	visible, UV, soft X-ray spectroscopies	absorption, dielectric constant	1-100 mm ²	band structure	preparation dependent
	ellipsometry	ellipticity ratio[*]	1-10 mm ²	film thickness and/or refractive index[*], map of optical thickness	assessed refractive index might be required for measuring film thickness
thermal / electrical / mechanical	heat flow experiments	heat flow rate, thermal conductivity	10-100 μm^2	scattering processes	preparation dependent, geometry sensitive
	thermo-electrical experiments	thermoelectric potential, power,	10-100 μm^2	type of carriers, scattering processes	
	thermo-mechanical experiments	thermal expansion, pyroelectricity	1-100 μm^2	piezoelectric tensor, thermal expansion tensor	built-in stress may mask intrinsic properties

V.3.4.3. (♦) $\kappa = 4\pi \sin\theta / \lambda$ is referred to as **momentum transfer**; θ , λ are the beam angle of incidence and w : length.

[♦♦] The coherence length is defined in Section II Annex.

V.3.4.4. [*] Ellipticity (of the reflected radiation) is the ratio of amplitudes for electric fields polarized parallel and normal to the incidence plane; thickness and refractive index are obtained by the "new" ellipsometry referred to as spectroscopic.

TABLE V.3.4.1. Characterization of Inorganic solid films(Part III)**V.3.4.5.**

Technique	Methodology	Primary Information	Sampled area scale	Derived Information	Caveats Information
mechanical / electrical	stress/strain relationship	resonant response	1 - 100 μm^2	elastic tensor, yield	preparation dependent, geometry sensitive
	electro-mechanical	piezoelectric behaviour	1 - 100 μm^2	piezoelectric tensor	built-in stress may mask intrinsic properties
	microscopy / tribology	force , wear and erosion	10- 100 μm^2	friction coefficient, electrons	surface chemically sensitive, built-in stress may mask intrinsic properties
micro-mechanical	atomic force microscopy	force of probe tip displacement	$4 \cdot 10^{-2}$ - 10^4 nm^2	image, morphology of the outermost atomic layer	
chemical	reactivity : heterogeneous catalysis (film functionality)	film quality impact on catalysis	100 mm^2	mechanism of catalysis	preparation and contamination sensitive

VI. INDEXES

The *upright, bold and underlined* numbers appearing in the *left margin* of a page are *paragraph* numbers. Figures, tables as well as figure or table captions are classed and numbered as paragraphs.

VI.1. INDEX OF SYMBOLS

The symbols representing physical quantities are in italics as recommended in reference [3]. The upright, bold and underlined number following the name of the physical quantity corresponding to a symbol, is the paragraph number where the symbol is defined. For example, the symbols a_0 , a_1 , lattice constants, are defined in paragraph **V.3.2.2.4**, (a figure). When the symbol is defined in a table or figure and also in a (figure or table) caption, the corresponding paragraph number is indicated. For example, $A_{\alpha\gamma\beta}$, the Hamaker parameter, is defined in two paragraphs : **V.2.3.14**, (a table); **V.3.2.15**, (the table caption).

VI.1.1. Latin symbols

$a(z)$, a^α , a^γ : local Helmholtz energy density **V.3.1.16** ; **V.3.1.17**

a_0 , a_1 : lattice constants **V.3.2.2.4**,

$A_{\alpha\gamma\beta}(h)$: Hamaker constant (retarded) **V.3.2.14** ; **V.3.2.15**,

$A_{\alpha\gamma\beta}$: Hamaker constant (non-retarded) **V.3.2.14** ; **V.3.2.15**,

A^f : film surface area **V.3.4** ; **V.3.15**,

A_s : surface area of an interface **V.3.1.A.10**,

- A : Helmholtz energy of the system IV.3.1.16. ; IV.3.1.17
 $A^{I\sigma}$: film excess Helmholtz energy IV.3.1.16. ; IV.3.1.17
 $A^{II\sigma}$: film surface excess Helmholtz energy IV.3.1.16. ; IV.3.1.19
 $\Delta A(h)$: liquid film interaction Helmholtz energy IV.3.2.2. ; IV.3.2.7. ; IV.3.2.9.(operational definition)
 $\Delta A^{I\sigma}(h)$: liquid film interaction Helmholtz energy IV.3.2.7. (convention $I\sigma$)
 $\Delta A^{II\sigma}(h)$: liquid film surface interaction Helmholtz energy IV.3.2.7. ; IV.3.2.11. (convention $II\sigma$)
- c_{bl} , c_N : surfactant bulk concentrations IV.5.7.
 $c_{el\ cr}$: critical electrolyte concentration IV.5.7.
 $c_j(z)$, c_j^a , c_j^γ : three dimensional concentration of component i IV.3.1.1. ; IV.3.1.3.
- d : film geometric (effective) thickness: V.3.2.1.3.
 d_g : grain size of polycrystalline film: V.3.2.1.3.
 d_{qw} : quantum wall thickness : V.3.2.1.3.
 DLVO : (isotherm) IV.5.5. ; V.5.8.
- E^f : film dilational (Gibbs) elasticity modulus IV.6.2.8.
 E_\perp^f : film (Young) elasticity modulus IV.6.2.7.
- F : Faraday constant IV.3.2.18.
 F : force IV.5.3.
- $\Delta G^{II\sigma}(h)$: liquid film interaction excess Gibbs energy IV.3.2.7. ; IV.3.2.11.
 $\Delta g^{II\sigma}$: liquid film specific interaction excess Gibbs energy IV.3.2.7. ; IV.3.2.11.
- h : film effective thickness IV.3.0.2. ; IV.3.1.1. ; IV.3.1.2 ; IV.3.1.12. Fig. IV.3.2a
 h_θ : film equivalent thickness IV.3.1.1. Table IV.3.1.1 ; IV.3.1.4.
 $h^{II\sigma}$: film thermodynamic thickness IV.3.0.2. ; IV.3.0.5. ; IV.3.1.1
 $h_0^{II\sigma}$: relative thermodynamic film thickness IV.3.1.1. ; IV.3.1.6
- I : ionic strength in bulk solution IV.3.2.18.
- $I\sigma$ superscript (single Gibbs dividing surface convention) IV.3.0.2.
 IC superscript : reference contact line corresponding to convention $I\sigma$ IV.4.17.
 $II\sigma$ superscript : (two Gibbs dividing surfaces convention) IV.3.0.2.
 IIC (superscript) : reference contact line corresponding to convention $II\sigma$ IV.4.17.
- L_D : Debye screening length (in a solid) : II.A.8. ; V.3.2.1.2.
 L^{IC} , L^{IIC} : lengths of reference contact lines IC and IIC IV.4.16. ; IV.4.17.
 l_m : dispersion component characteristic length II.A.10. ; IV.5.19.
- n_j : amount of component i in the system IV.3.1.16. ; IV.3.1.17
 $n_j^{I\sigma}$: film excess amount of component i IV.3.1.5. ; IV.3.1.16. ; IV.3.1.18
 $n_j^{II\sigma}$: film surface excess amount of component i IV.3.1.5. ; IV.3.1.16. ; IV.3.1.19.
- ΔP_σ : Laplace pressure IV.3.1.12. ; IV.3.1.A.5.

p_N : pressure tensor (stress) normal component [IV.3.1.7.](#) ; [IV.3.1.10.](#); [IV.3.1.11.](#) ; [IV.3.1.A.1.](#)

$p_T(z)$: pressure tensor (stress) tangential component [IV.3.1.7.](#) ; [IV.3.1.10.](#); [IV.3.1.11.](#) ;

[IV.3.1.A.1.](#)

$p^b(p^\alpha, p^\gamma)$: isotropic pressure in a bulk, b, phase (α or γ) [IV.3.1.7.](#) ; [IV.3.1.10.](#); [IV.3.1.11.](#) ;
[IV.3.1.12.](#) ; [IV.3.1.A.4.](#)

R : gas constant [IV.3.1.11.](#)

R^∞ : meniscus radius of curvature [IV.3.1.12.](#)

R_g : macromolecular radius of gyration [IV.5.15.](#)

r_c, r'_c : contact line radii of curvature [IV.3.1.12.](#)

T : temperature [IV.3.1.11.](#) ; [IV.3.1.18.](#)

V : volume of the system [IV.3.1.17.](#)

V_e : equivalent film volume [IV.3.1.1.](#) ; [IV.3.1.6.](#)

V^f : film effective volume [IV.3.1.1.](#) ; [IV.3.1.6.](#)

$V^{II\sigma}$: film thermodynamic volume [IV.3.0.5.](#) ; [IV.3.1.1.T.](#) ; [IV.3.1.6.](#)

$W(h)$: film interaction potential energy [IV.3.2.7.](#) ; [IV.3.2.8.](#) ; [IV.3.2.10.](#)

Y^f_\perp : film elasticity (Young) modulus [IV.6.2.7.](#)

VI.1.2. Greek symbols.

ε : bulk permittivity [IV.3.2.18.](#)

$\Gamma_i^{I\sigma}$: film excess concentration of component i [IV.3.0.2.](#) ; [IV.3.0.4.](#) ; [IV.3.1.1.](#) ; [IV.3.1.5.](#)

$\Gamma_i^{II\sigma}$: film surface excess concentration of component i [IV.3.0.2.](#) ; [IV.3.0.5.](#) ; [IV.3.1.1.](#) ; [IV.3.1.5.](#)

$\Delta\Gamma_i^{II\sigma}$: film formation surface excess concentration [IV.3.2.7.](#)

$\Gamma_{i,0}^{II\sigma}$: relative film surface excess concentration of component i [IV.3.1.1.](#) ; [IV.3.1.6.](#) ;

Γ_i^s : film surface concentration of component i [IV.3.1.1.](#) ; [IV.3.1.3.](#)

$\gamma^{f\infty}$: (thick) liquid film tension [IV.3.1.7.](#) ; [IV.3.1.9.](#)

γ^f : (thin) liquid film tension [IV.3.1.7.](#) ; [IV.3.1.9.](#) ; [IV.3.1.16.](#) (general definition)

κ^{-1} : Debye screening length [II.A.8.](#) ; [IV.3.2.14.](#) ; [IV.3.2.18.](#) ; [IV.5.11.](#) ; [IV.5.17.](#)

κ : film (periphery) line tension [IV.4.16.](#) ; [IV.4.17.](#)

κ : momentum transfer [V.1.2.2.4.](#) ; [V.1.2.2.5.](#)

κ^{IC} : film line tension [IV.4.16.](#) ; [IV.4.18.](#)

κ^{IIC} : film surface line tension [IV.4.16.](#) ; [IV.4.18.](#)

λ : electromagnetic wavelength [V.3.2.1.2.](#)

λ_c : specific wavelength in absorption spectrum [II.A.4.](#) ; footnote [9]; [II.A.10.](#)

λ_{ph} : phonon wavelength: [V.3.2.1.2.](#)

λ_{mfp} : charge carrier mean free path : [V.3.2.1.2.](#)

μ_i : chemical potential of component i in the system [IV.3.1.16.](#)

$\Pi_a(h)$: disjoining pressure adsorption component [IV.3.2.14.](#) ; [IV.3.2.17.](#)

$\Pi_D(h)$: disjoining pressure [IV.3.1.7.](#) ; [IV.3.1.11.](#) ; [IV.3.1.12.](#) ; [IV.3.1.16.](#)

$\Pi_e(h)$: disjoining pressure electrostatic(ionic) component [IV.3.1.14.](#) ; [IV.3.1.18.](#) ; [IV.5.11.](#) ; [IV.5.17.](#)

$\Pi_{el}(h)$: disjoining pressure elastic component [IV.3.2.14.](#) ; [IV.3.2.20.](#) ; [IV.5.11.](#) ; [IV.5.18.](#)

$\Pi_h(h)$: disjoining pressure hydrophobic component [IV.5.11.](#) ; [IV.5.16.](#)

$\Pi_m(h)$: disjoining pressure dispersion component [IV.3.2.14.](#) ; [IV.3.2.15.](#) ; [IV.5.11.](#) ; [IV.5.19.](#)

$\Pi_s(h)$: disjoining pressure solvation component [IV.3.2.14.](#) ; [IV.3.2.16.](#) ; [IV.5.11.](#) ; [IV.5.14.](#)

$\Pi_{st}(h)$: disjoining pressure steric component [IV.3.2.14.](#) ; [IV.3.2.19.](#) ; [IV.5.11.](#) ; [IV.5.15.](#)

$\theta I\sigma$ (θIC), $\theta II\sigma$ (θIIC) : reference contact angles for conventions $I\sigma(IC)$ and $II\sigma(IIC)$ [IV.3.1.12.](#) ; [IV.3.1.14.](#) ; [IV.3.1.15](#)

Σ^f : (thin) liquid film tension [IV.3.1.7.](#) ; [IV.3.1.9.](#) ; [IV.3.1.12.](#) ; [IV.3.1.16.](#) ; [IV.3.1.19.](#) (general definition, convention $I\sigma$ and convention $II\sigma$)

$\Sigma^{f\infty}$: (thick) liquid film tension [IV.3.1.19.](#)

σ^f : thin liquid film surface tension [IV.3.1.7.](#) ; [IV.3.1.8.](#) ; [IV.3.1.12.](#) ; [IV.3.1.15.](#) ; [IV.3.1.16.](#) ; [IV.3.1.19.](#)

$\sigma, \sigma^{\alpha\gamma}$: interfacial tension between liquid α and γ [IV.3.1.A.2.](#) ; [IV.3.1.A.6.](#) ; [IV.3.1.12.](#)

σ_s : interfacial layer width [II.17.](#) ; [II.A.7.](#)

τ^{IC} : film (contour) transversal tension [IV.4.16.](#) ; [IV.4.18.](#) ; [IV.4.19.](#)

Ω^{IC} : grand potential of film line (convention IC) [IV.4.16.](#) ; [IV.4.18.](#)

Ω^{IIC} : grand potential of film line (convention IIC) [IV.4.19.](#)

Ω^σ : interfacial grand potential [IV.3.1.A.10.](#)

$\Omega^{I\sigma}$: film grand potential (convention $I\sigma$) [IV.4.16.](#) ; [IV.4.17.](#)

$\Omega^{II\sigma}$: film grand potential (convention $II\sigma$) [IV.4.16.](#) ; [IV.4.19.](#)

$\Delta\Omega(h)$: change of grand potential of the system on thin liquid film formation [IV.3.2.7.](#) ; [IV.3.2.12.](#)

ξ : molecular pair correlation length [II.A.8.](#) ; [IV.5.11.](#) ; [IV.5.14](#)

ζ : coherence length [II.A.9.](#) ; [IV.5.11.](#) ; [IV.5.18](#)

ζ_e : electric coherence length [II.A.9.](#)

ζ_m : magnetic coherence length [II.A.9.](#)

VI. 2. INDEX OF ABBREVIATIONS AND ACRONYMS

The underlined number following the explanation of an abbreviation or acronym is the paragraph number where they appear.

1D : one dimensional

2D : two dimensional

3D : three dimensional

AFM: atomic force microscopy [V.2.2.1.](#)

Al / SiO / Al : recommended abbreviation for the film system Al / solid film / Al [II.10](#)

ATR: attenuated total reflectance V.1.2.2.1 ; V.2.2.1.

ac: alternative current IV.7.4.

CBF : common black film IV.5.7.

CMBE : chemical molecular beam epitaxy V.3.3.4.5.

CVD : chemical vapour deposition IV.3.3.4.1.

DLVO : Derjaguin- Landau- Vervey-Overbeek IV.5.5.

DSC: differential scanning calorimetry V.2.2.1.

dc: direct current III.1 ; IV.7.4.

ESCA: electron spectroscopy for chemical analysis III.1 ; III.2 ; V.1.2.2.4 ; V.1.2.2.6 ; V.3.4.1.

ESR: electron spin resonance V.1.2.2.1.

EXAFS: extended X- ray absorption fine structure V.1.2.2.4 ; V.1.2.2.6 ; V.3.4.1.

FTIR: Fourier transform infrared IV.7.1 ; V.1.2.2.1 ; V.2.2.1.

GDS : Gibbs dividing surface IV.3.6.

HPCVD : high pressure chemical vapour deposition V.3.3.4.2.

hf: high frequency III.1

IR Infrared III.1 ; V.1.1.2.1 ; V.2.2.1 ; V.3.4.2.

L: liquid II.10.

L/L/L : emulsion film system liquid / liquid film / liquid IV.1.2 ; IV.2.2

LB : Langmuir-Blodgett V.1.2.1a.1.

LPCVD : low pressure chemical vapour deposition V.3.3.4.2.

MBE : molecular beam epitaxy V.3.3.3.5.

MOCVD : metallo-organic chemical vapour deposition V.3.3.4.4.

NBF : Newton black film IV.5.7.

O : oil II.10.

PECVD: plasma enhanced chemical vapour deposition : V.3.3.4.3.

PT: photothermal V.1.2.2.8.

PVD : physical vapour deposition V.3.3.3.1.

S: solid II.10

S/L/S : suspension film system solid / liquid film / solid IV.1.3.

S/S/S/ : solid / solid film / solid II.10.

UPS: ultraviolet photoelectron spectroscopy V.1.2.2.4 ; V.1.2.2.6 ; V.3.4.1.

UV: ultraviolet III.1 ; IV.7.4 ; V.1.2.2.1 ; V.2.2.81

V: vapour II.10.

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