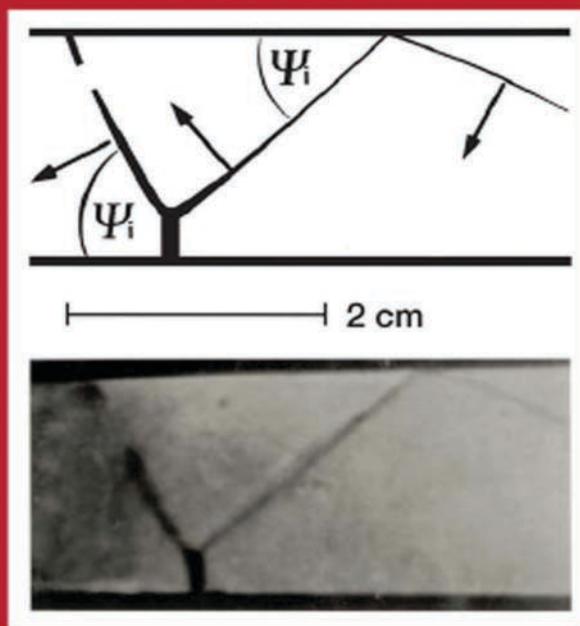


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**INTERFACIAL  
PHENOMENA  
AND CONVECTION**

ALEXANDER A. NEPOMNYASHCHY  
MANUEL G. VELARDE  
PIERRE COLINET



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*Dedicated to Professors Grigory I. Barenblatt and Robert S. Schechter and to the memory of Professors Grigory Z. Gershuni, Francisco Moran, Jose M. Saviron, and Efim M. Zhukhovitsky*



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## Preface

Interfacial phenomena (adsorption, desorption, evaporation, boiling, wetting, spreading, drop and bubble formation and migration, rippling, etc.) are essential for life and for many natural and artificial technological processes. In particular, interfacial convection is ubiquitous in nature; it appears all around us and inside us (small scale flows and microhydrodynamics when body forces and inertia, generally, have negligible influence). Its role in engineering processes (metallurgy, electrochemistry, welding, painting, drying, etc.) has been emphasized by numerous writers (see e.g. Levich and Krylov, 1969, Szekely, 1979). Recently, it has become obvious that in various processes in the (free fall) microgravity or variable effective-gravity environment of space laboratories, and the International Space Station, due to the practical absence of buoyancy, interfacial convection is the basic mechanism of fluid motion even in large scale processes (see, e.g. Ostrach, 1982; Walter, 1987; Ratke *et al.*, 1989).

At an open surface, or at the interface between two liquids, the surface or interfacial tension accounts for the jump in normal stresses proportional to the surface curvature across the interface (Laplace hypothesis), and hence affects the surface shape and its stability. Gravity competes with the Laplace (overpressure) force in accommodating equipotential levels with curvature (minimizing the corresponding free energy). This balance permits, for instance, the stable equilibrium of the (practically) spherical shape of drops and bubbles as we see them around us.

When surface tension varies with position along an interface, its change takes care of the jump in the tangential stresses. Hence its gradient acts like a shear stress applied by the interface on the adjoining bulk phases and thereby generates flow or alters an existing one (Marangoni effect). Surface tension gradient-driven (Marangoni-driven) flows are known to affect the evolution of growing fronts, and measurements of heat and other diffusion coefficients.

Gradients may be due to heat or mass transfer processes occurring along or across an interface (hence leading to thermocapillarity or solutocapillarity as forms of the Marangoni effect) or, indirectly, may originate in buoyancy-driven convection or in any other form of flow. Electric and magnetic fields can influence surface tension and hence flow at an interface. Electrocapillarity and magnetocapillarity can also, by extension, be considered as forms of the Marangoni ef-

fect. An interface, clearly, provides a nontrivial coupling mechanism between two bulk phases, surface and body forces, flow, and transport processes. From such coupling occurs a large variety of phenomena. Noticeable is that although no Marangoni effect may originally occur in a liquid-liquid system, interfacial (Marangoni-driven) convection could develop due to temperature variations resulting from positive or negative heats of solution.

Needless to say, concentration and/or temperature gradients may help in reducing or producing convection. Take the growth of crystals from a melt, which is a process where the elimination of convection in the melt is desirable because flow produces non-uniform growth conditions and, thereby, an increase in the generally uncontrollable number of dislocations and other defects in the crystal (see, e.g. Ostrach, 1982, 1983; Regel, 1987; Walter, 1987; Ratke *et al.*, 1989). The evaporative purification of a levitated melt is a process in which the opposite result is desired: convection is important here because it increases the rate of purification by replenishing the impurity concentration at the surface and because it tends to maintain a uniform composition throughout the melt. Furthermore, interfaces often contain traces of surface active substances (surfactants) that alter, significantly, the surface tension. In general, surface tension-lowering solutes adsorb preferentially in the interface (Gibbs adsorption hypothesis). The longer the characteristic time for a solute to redistribute itself between the interface and the bulk of the liquid, the more surface active the solute is. If the interface expands locally, these surfactants are swept outward with the movement, creating a gradient in their concentration. This concentration gradient implies a surface tension gradient which acts opposite to the movement. This effect was well explained by Levich (1962), particularly when dealing with drop migration in the presence of thermal gradients (see also Bakker *et al.*, 1966).

Progress in the theory, numerics, and experiments with interfacial phenomena has been made in the past decades, leading to our understanding of the conditions for interfacial instability and/or interfacial convection to occur. Some examples are the study of cellular (Benard) convection and its evolution, rippling and the generation of (nonlinear) waves and solitons, drop and bubble migration in the presence of thermal gradients, and three-dimensional surface tension gradient-driven (Marangoni-driven) flows and related spatio-temporal problems. Interfacial convection has, however, been much

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less studied than buoyancy-driven, natural convection, and other flows driven by pressure gradients and body forces. In fact, the study of liquid flow along an interface from places with low surface tension to places with a higher surface tension started long ago when the Italian scientist Marangoni studied the conditions for spreading of one liquid on another in, among other places, the largest basin of the Tuileries gardens in Paris. He stated that a liquid A spreads on a liquid B when the sum of the interfacial tension and the surface tension of A is lower than the surface tension of B. He reported on this phenomenon in an 1865 brochure, and made his research more widely available six years later (1871a,b), because of his fear that publications by the Belgian scientist, and Plateau's son-in-law, Van der Mensbrugge (1870, 1873) and the German scientist Lüdgtge (1869), the latter partially in error, would render his priority on this subject unacknowledged. Plateau, in a book published in 1873, gives proper credit to the work of Marangoni. He also describes the work of Dupre de Rennes (1869) with findings identical to those of Marangoni. Young (1805) and later Maxwell (1871, 1878) correctly stated the spreading laws that, finally, Harkins and Feldman (1922) established on sound thermodynamic ground.

James Thomson (1855, 1881), the older brother of Lord Kelvin, also established, albeit qualitatively only and not with fully correct understanding of the phenomena, though he distinguished buoyancy from surface tension effects, that when gradients in surface tension arise due to concentration differences within one fluid, flow arises as well (1855). He explained the tears found in a glass of wine or any other strong alcoholic liquor in terms of surface tension gradients, and for this reason the Marangoni effect has on occasion been referred to as the Thomson effect. Worth mentioning also is the work of Weber (1854), who described convective motions occurring at the surface of bubbles placed in alcohol solutions. Earlier, Varley (1836) had described curious motions in evaporating drops observed under a microscope.

In observing but not explaining some of the above-described phenomena, both Marangoni and Thomson were far outdated by other authors. In 1686, Heyde observed dancing camphor on olive oil. Much earlier, Plutarch and Pliny the Elder (Levich, 1962) reported the calming of the sea as a result of sailors spreading olive oil over the sea surface, a phenomenon also studied by Benjamin Franklin (1774; Tanford, 1989; see also Tomlison, 1864, 1869 and Scriven and

Sternling, 1960).

In the present book, we provide a succinct account of results concerning interfacial phenomena and convection in various systems, albeit in each case limited to the simplest possible but significant model-problem from which we have extracted universal features. In the Introduction, we give a brief description of the hydrodynamics needed to understand the remainder of the book in a relatively selfconsistent way. We recall the Navier-Stokes, Fourier, and Fick equations as well as their corresponding boundary conditions, as interfaces are treated as boundaries rather than genuine, autonomous phases. We also discuss phenomena related to chemical reaction, heat and mass transfer along or across interfaces, and features of adsorption and desorption phenomena. We delineate the role of the Marangoni effect that flow at an interface or an open surface occurs whatever there is variation of surface tension, but whether or not the initial flow disturbance is sustained and/or penetrates in the adjoining bulk phases depends on the strength of such gradient relative to viscous damping and, eventually, on the ratio of their kinematic viscosities and heat or mass diffusivities.

We then proceed with the consideration of the relatively simple but important case where convection is caused by imposed concentration or temperature gradients along the interface (Chapter 2). The following chapters are devoted to the development of linear and nonlinear theory of surface tension gradient-driven flows which appear spontaneously as a result of instability of the interface, and eventually, flow generated by growing disturbances induced by the Marangoni effect.

In Chapter 3 we concentrate on the phenomena of drop (bubble) migration and features of drop spreading due to the Marangoni effect. In particular, we show how a surface tension gradient-driven instability may either augment drag or, the opposite, may help overcoming hydrodynamic drag, hence leading to the spontaneous selfpropulsion or autonomous motion of a drop whose surface is affected by a (surface) chemical reaction or by internal heating.

In Chapter 4 we provide a succinct description of salient features of interfacial convection in the form of patterned, cellular flows. As in other cases, our study is limited to the simplest albeit significant model-problems, with particular attention paid to the consequences, hence the solutions, of an equation proposed by Knobloch, together with significant generalizations to account for the salient features

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of patterns in surface tension gradient-driven (Benard-Marangoni) convection.

In Chapter 5 we deal with oscillations and waves of different physical nature though all excited by the Marangoni effect. A detailed analysis is provided of two types of interfacial waves. One is the capillary-gravity wave which corresponds to membrane-like transverse oscillations. The other, first studied by J. Lucassen, corresponds to an elastic, longitudinal expansion-compression (sound-like) motion of a membrane that can only occur when there are tangential stresses and the Marangoni effect. The latter, as well as viscosity, indeed affect capillary-gravity waves, but as secondary factors. For the longitudinal (also called dilational) waves, the Marangoni effect and viscosity are key for their onset and evolution and hence dilational waves are strictly dissipative waves. We also provide a succinct account of recent findings about mode mixing and resonance of interfacial wave modes. Furthermore, we recall major (theoretical, numerical, and experimental) results about solitonic aspects of interfacial waves, whose observation was made three decades ago by H. Linde before the soliton concept was coined. In particular, as the simplest significant model we discuss the generalization of the Boussinesq-Korteweg-de Vries equation for waves in shallow liquid layers when the Marangoni effect is added.

In Chapter 6 discussion is provided first about the stability of flows generated by a longitudinal surface tension gradient (including a short account of the combined action of thermocapillarity and buoyancy) already introduced in Chapter 2, and subsequently, about film flows with transverse thermal gradients. In the latter case, the model-problem chosen is the Kapitza-Shkadov falling film case with the Marangoni effect added. This chapter also contains a study of flows in two-layer systems and the corresponding stability analysis.

Finally, Chapter 7 is devoted to speculative comments about a few problems and topics that we feel have great interest, both basic and application-oriented.

When writing the book we had in mind graduate students and researchers from applied mathematics, the nonlinear sciences, and various engineering branches. We have done our best to make the material reasonably self-contained and accessible to the reader. Throughout the book we offer not just a description of phenomena but as much as possible heuristic argumentation and significant portions of methodologies whose utility exists well beyond the domain of prob-

lems discussed here.

In the Bibliography we offer the reader reference to original publications as well as somewhat redundant references, thus offering alternative and diverse reading material, particularly when citing books and review articles.

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# Chapter 1

## Introduction

In this chapter we shall recall the concept of surface or interfacial tension, the Navier–Stokes, Fourier, and Fick hydrodynamic equations, and we shall discuss various heat and mass transfer phenomena occurring at an interface, deformable or not. The Marangoni effect is also discussed.

### 1.1 The interface as a physical system

#### 1.1.1 Interfacial tension

The transition layer (Fig. 1.1) between two immiscible fluids (as well as between a fluid and a solid body) has a thickness of *microscopic* size (usually few molecular diameters) and is considered as a *two-dimensional surface* from the point of view of *macroscopic* theories (thermodynamics, fluid mechanics, etc.).

In the thermodynamic approach, the interfacial region should be described as a specific two-dimensional medium which possesses its own interfacial internal energy,  $U^S$  (physically, it is the excess energy caused by the molecular interactions in the transition layer), interfacial entropy,  $S^S$  (caused by a new possibility of randomness relative to that of bulk fluids), and interfacial numbers of molecules of various species,  $n_j^S$ . Let us note that  $n_j^S$  may be either positive (*adsorption*) or negative (*desorption*). The first law of thermodynamics in reference to the interface may be written as (see, e.g. Defay, Prigogine, Bellemans and Everett, 1966; Landau and Lifshitz, 1980; Adamson, 1982)

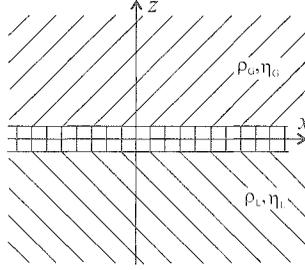


Figure 1.1: Geometry of an interface separating two liquids or a liquid (L) and ambient air, gas (G), or vapor.  $\rho_G$  ( $\rho_L$ ) and  $\eta_G$  ( $\eta_L$ ) denote density and viscosity, respectively. In the simplest case, one neglects the internal structure and when the fluctuations of the interface out of the  $z = 0$  plane can be considered small, the boundary conditions (b.c.) for each bulk phase can be expressed in terms of the fluid displacements evaluated at the geometrical level  $z = 0$ . Otherwise if one neglects the structure and transverse size of the interface but not its deformability, b.c. are taken at the moving interface surface,  $z(t)$ .

$$dU^S = TdS^S + \sum_j \mu_j dn_j^S + \sigma dA, \quad (1.1)$$

where  $T$  is temperature,  $\mu_j$  are interfacial chemical potentials,  $A$  is *area* of interface which replaces the volume characteristic for three-dimensional media. The parameter  $\sigma$  which describes the work which is necessary for changing the area of the interface is called *interfacial tension*. In the case where a liquid is in contact, equilibrium, with its own saturated vapour, this parameter is called *surface tension* of the liquid. Certainly, the interfacial internal energy may depend also on some additional thermodynamic parameters like density of electric charge, etc.

For a stable interface, the interfacial tension should be positive (otherwise, the interface would be destroyed by fluctuations). The dependence of the interfacial tension on the thermodynamic parameters (temperature, interfacial concentration of species, etc.) is similar to the equation of state for the three-dimensional medium. Generally, this dependence is not obtained from first principles and is taken from experiment. Typically, the interfacial tension decreases when the temperature is increased. This phenomenon is called *normal*

*thermocapillarity*. However, several systems are known that display an opposite kind of behavior (*anomalous thermocapillarity*).

The dependence of the interfacial tension on the interfacial concentration of species deserves a special discussion. In a thermodynamic equilibrium state where all the *intensive* variables (temperature, interfacial tension, etc.) are constant, the *extensive* variables  $U^S$ ,  $S^S$ , and  $n_j^S$  are all proportional to the area of the interface  $A$ . Thus, Eq. (1.1) may be written as

$$U^S = TS^S + \sum_j \mu_j n_j^S + \sigma A. \quad (1.2)$$

Combining Eqs. (1.1) and (1.2), one can find *the Gibbs adsorption equation*

$$-S^S dT + \sum_j n_j^S d\mu_j + A d\sigma = 0. \quad (1.3)$$

For sake of simplicity, let us consider the case of a single relevant species (e.g., the interface between a liquid and a gas soluble in the liquid) and omit the subscripts for  $n_1$  and  $\mu_1$ . For the *interfacial concentration*

$$\Gamma \equiv \frac{n^S}{A} \quad (1.4)$$

we find:

$$\Gamma = - \left( \frac{\partial \sigma}{\partial \mu} \right)_T. \quad (1.5)$$

At the same time, the following thermodynamic inequality can be established

$$\left( \frac{\partial \mu}{\partial \Gamma} \right)_T > 0. \quad (1.6)$$

Thus, the interfacial concentration

$$\Gamma = - \left( \frac{\partial \sigma}{\partial \Gamma} \right)_T \left( \frac{\partial \Gamma}{\partial \mu} \right)_T$$

is positive (positive adsorption) if and only if

$$\left( \frac{\partial \sigma}{\partial \Gamma} \right)_T < 0, \quad (1.7)$$

i.e., the interfacial tension decreases as the interfacial concentration increases. In other words, the interface tends to be enriched in the species which diminishes the surface tension.

The equilibrium interfacial concentration  $\Gamma$  depends on the *volume concentration*,  $C$ , of the species in the bulk fluid. For dilute solutions, they are proportional. For higher volume concentrations, the interfacial concentration may tend to a limit value corresponding to a *monomolecular layer* created by molecules adsorbed on the interface which are called surface-active or surfactant molecules. Typical examples of surfactants generating interfacial monolayers even for quite small volume concentrations are hydrocarbons (and other substances with molecules containing hydrocarbon chains) on the interfaces water/air or water/oil.

In some cases, the thermodynamic equilibrium between the volume and interfacial concentrations of surfactant is established during a rather long time. Therefore, the *interfacial kinetics* should be taken into account. The flux  $j$  characterized the mass exchange between the bulk solution and the interface is taken in the form

$$j = k_a C - k_d \Gamma, \quad (1.8)$$

where  $k_a$  and  $k_d$  are the adsorption and desorption rate constants. The adsorption-desorption kinetics is discussed in more detail in subsection 1.2.2.

### 1.1.2 Hydrodynamic properties of the interface

Let us discuss now the hydrodynamic phenomena caused by the presence of an interface.

First of all, the deformation of the interface changing its area changes its energy (1.1). This circumstance leads to additional force connected with the interface. Then the pressures  $p_1$  and  $p_2$  in two contacting media are not equal, and the difference (Laplace surface pressure or overpressure) is

$$p_1 - p_2 = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right), \quad (1.9)$$

where  $R_1$  and  $R_2$  are the principal radii of curvature at a given point of the interface. The pressure is higher in the medium whose surface is convex, hence it is higher inside a drop or a bubble relative to the surrounding fluid. The difference of pressures may be considered as a *normal force* per unit area

$$\mathbf{f}_n = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \mathbf{n}$$

directed along the normal  $\mathbf{n}$ .

Besides the normal force, there may be a force *tangential* to the interface if inhomogeneity of the interfacial tension exists (generated e.g. by the inhomogeneities of temperature or surfactant concentration on the interface). The tangential force per unit area is equal to

$$\mathbf{f}_t = \nabla\sigma$$

(because  $\sigma$  is defined only on the interface,  $\nabla$  denotes the surface gradient and its corresponding stress is named after Marangoni). This force produces flow or alters an existing one and hence one has a surface tension gradient-driven convection, thermocapillary convection or *Marangoni-driven convection*. Generation of motion by interfacial tension inhomogeneities has also been called the *Marangoni effect* (Block, 1956; Scriven and Sterling, 1960). Near the interface, the motion is directed towards the region with larger surface tension; because of the incompressibility of fluids, a bulk motion in the opposite direction supported by a pressure gradient will arise (Fig. 1.2).

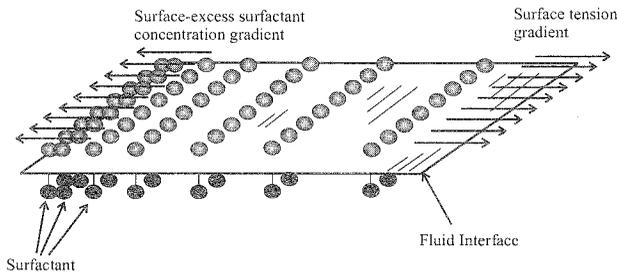


Figure 1.2: The Marangoni effect. Since surfactant adsorption at a fluid interface generally lowers the interfacial tension, an inhomogeneous distribution of surfactant within the interface results in the creation of local interfacial tension gradients. The highest tension occurs in those regions where the surfactant density is lowest; thus, the tensile restoring force acts in an opposite direction to the surfactant density gradient. The ensuing fluid motion arising from this interfacial tension gradient is named after Marangoni (reproduced by courtesy of Edwards, Brenner, and Wasan, 1991).

Thus a system with an interface between two fluids may be in a *mechanical equilibrium state* only if the surface tension is constant on the whole interface. Otherwise, convection arises, however small are the inhomogeneities of the surface tension. However, in the case

where the temperature or volume concentration gradients are *normal* to the interface, they do not produce inhomogeneity of the surface tension, and hence they do not destroy the mechanical equilibrium of the system. Thus the interfacial or surface tension (up to the sign) is to the surface what pressure is to the bulks.

It should be emphasized, however, that such a mechanical equilibrium state may be *unstable*, and one observes convection even though the external conditions may be homogeneous. As a rule, such an instability occurs only if the applied normal gradients are strong enough.

Various flows and instabilities leading to flows past a given threshold generated by interfacial tension inhomogeneities and the Marangoni effect are the subject of this book.

**Table 1.1. Surface tension of various fluids**

Liquid	$\sigma$ (mN/m)	in contact with	T(°C)
Benzene	28.9	air	20
Ethylalcohol	22.3	air	20
<i>n</i> -Hexane	18.4	air	20
Mercury	470	air	20
Water	74	air	20
Helium	0.24	vapor	-270

**Table 1.2. Order of magnitude of bulk properties of various fluids**

Liquid	$\rho$ (kg/m <sup>3</sup> ) (g/cm <sup>3</sup> )	$\eta$ (kg/m s) $\times 10^3$	$\nu$ (m <sup>2</sup> /s) $\times 10^6$ (cm <sup>2</sup> /s)	$\lambda$ (W/m K)	$\kappa$ (m <sup>2</sup> /s) $\times 10^6$ (cm <sup>2</sup> /s)	$\alpha$ (1/K) $\times 10^3$	<i>Pr</i>
Mercury and molten metals	10 <sup>4</sup> 10	1	10 <sup>-3</sup> cm <sup>2</sup> /s	10	10 <sup>-1</sup> - 10 <sup>-2</sup> cm <sup>2</sup> /s		$\geq 10^{-2}$
Helium				10 <sup>-2</sup>			
Water (room temperature)	10 <sup>3</sup>	1	1 10 <sup>-2</sup> cm <sup>2</sup> /s	10 <sup>-1</sup>	$\geq 10^{-1}$ 10 <sup>-3</sup> cm <sup>2</sup> /s	0.32	(5.85) $\leq 10$
Silicone oils	$\leq 10^3$	10	$\geq 10$ $\geq 1$ cm <sup>2</sup> /s	10 <sup>-1</sup>	$\geq 10^{-2}$ 10 <sup>-3</sup> cm <sup>2</sup> /s	1	$\geq 10^2$
Olive oil	10 <sup>3</sup>						
Glycerine		10 <sup>3</sup> - 10 <sup>7</sup>	$\geq 10$ cm <sup>2</sup> /s		10 <sup>-3</sup>		10 <sup>2</sup> -10 <sup>3</sup>
Fluorinert	$2 \times 10^3$	$\geq 10^2$	$\geq 10$	$\geq 10^{-1}$	10 <sup>-2</sup>	1	$\geq 10^2$
Ethanol	$\leq 10^3$	0.5 - 40	1.5				
Methanol	$\leq 10^3$	$\geq 10^{-1}$	$\geq 10^{-1}$	$\geq 10^{-1}$	$\geq 10^{-1}$	1	10
<i>n</i> -octane	$\leq 10^3$	$\geq 10^{-1}$	$\geq 10^{-1}$	$\geq 10^{-1}$	$\geq 10^{-1}$	1	10
Air and standard gases	1	$\geq 10^{-2}$	$\geq 10$ 10 <sup>-1</sup> cm <sup>2</sup> /s	2.2	0.02 10 <sup>-1</sup> cm <sup>2</sup> /s	3.67	(0.71) $\leq 1$

## 1.2 Mathematical formulation

In the present section we shall describe some basic mathematical models corresponding to the above-mentioned phenomena.

### 1.2.1 Heat transfer in a system with an interface

#### i. Equations and boundary conditions

Let us consider two fluids situated in regions  $L_1$  and  $L_2$  and separated by an interface. In a spatially inhomogeneous temperature field, convective motion of fluids arises for two main reasons. First, the temperature inhomogeneity produces a spatial inhomogeneity of the interfacial tension that leads to *thermocapillary forces* generating *thermocapillary convection* (Marangoni effect). Also, because of thermal expansion, the densities of fluids are spatially inhomogeneous, which may cause bulk *buoyancy forces* generating *buoyancy-driven convection* (Rayleigh, 1916).

For description of the bulk motions of both fluids we shall use the Boussinesq approximation (Oberbeck, 1879; Boussinesq, 1901, 1903; Mihaljan, 1962; Perez-Cordon and Velarde, 1975; de Boer, 1984, 1986; Joseph, 1976; Velarde and Perez-Cordon, 1976; Gershuni and Zhukhovitsky, 1976; Velarde *et al.*, 2000). This approximation is valid in the case where the density variations caused by temperature inhomogeneities are relatively small, while the characteristic temperature gradient is much larger than the adiabatic temperature gradient,  $g\beta T/c_p$ , where  $g$  is gravity acceleration,  $\beta$  is the thermal expansion coefficient,  $T$  is absolute temperature, and  $c_p$  is the specific heat at constant pressure. Within this approximation, the dependence of the density,  $\rho$ , on the pressure is ignored. Flow motions are limited to velocities much lower than the speed of sound in the liquid and hence the “incompressibility” assumed. Also, the dependence of the density on the temperature is ignored in the continuity equation, while in the equation of motion it is taken into account. The equations of motion are identical to those of an incompressible fluid with addition of a bulk *buoyancy force*,  $-\mathbf{g}\beta T$ . In the equation of heat transfer, the compressibility effects and the viscous heat generation are neglected. Also, the values of (dynamic) shear viscosity, kinematic viscosity, heat conductivity and heat diffusivity  $\eta$ ,  $\nu$ ,  $\lambda$ , and  $\kappa$  are assumed to be constant;  $\eta = \rho\nu$ .  $A$  denotes the temperature gradient.

Using the subscript  $m$  for the quantities corresponding to  $m$ -th fluid ( $m = 1, 2$ ), we can write the equations in the following form (Lamb, 1945; Moran, 1960; Chandrasekhar, 1961; Aris, 1962; Levich, 1962; Batchelor, 1967; Segel, 1972; Lin and Segel 1974; Gershuni and Zhukovitsky, 1976; Joseph, 1976; Normand et al, 1977; Segel, 1977;

Velarde and Castillo, 1982; Miller and Neogi, 1985; Rosner, 1986; Landau and Lifshitz, 1987; Acheson, 1990; Zeytounian, 1998; Guyon *et al.*, 2001):

$$\frac{\partial \mathbf{v}_m}{\partial t} + (\mathbf{v}_m \cdot \nabla) \mathbf{v}_m = -\frac{1}{\rho_m} \nabla p_m + \nu_m \nabla^2 \mathbf{v}_m + g\beta_m T_m \mathbf{e}, \quad (1.10)$$

$$\frac{\partial T_m}{\partial t} + (\mathbf{v}_m \cdot \nabla) T_m = \kappa_m \nabla^2 T_m, \quad (1.11)$$

$$\nabla \cdot \mathbf{v}_m = 0. \quad (1.12)$$

Here  $\mathbf{e}$  is a unit vector directed upward,  $p_m$  is the *hydrostatic* pressure; the total pressure is equal to  $p_m - \rho_m g z$ , where  $z$  is the vertical coordinate.

Now, we have to write down the boundary conditions on the interface between the fluids. For simplicity, we shall assume that the interface is described by the equation

$$z = h(x, y, t). \quad (1.13)$$

Taking into account both Laplace surface pressure and the thermo-capillary stresses, we can write the following boundary condition describing the balance of stresses on the interface:

$$\left[ (p_1 - \rho_1 g h) - (p_2 - \rho_2 g h) - \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \right] n_i = \quad (1.14)$$

$$(\tau'_{1,ik} - \tau'_{2,ik}) n_k + \frac{\partial \sigma}{\partial x_i},$$

where

$$\tau'_{m,ik} = \eta_m \left( \frac{\partial v_{m,i}}{\partial x_k} + \frac{\partial v_{m,k}}{\partial x_i} \right)$$

is the viscous stress tensor for the  $m$ -th fluid,  $n_i$  is the normal vector directed into the 1st fluid; because  $\sigma$  is defined only on the interface, the expression  $\frac{\partial \sigma}{\partial x_i}$  denotes a surface gradient. Introducing also orthogonal tangential vectors  $\tau^{(1)}$  and  $\tau^{(2)}$ , we can rewrite separately the balance conditions for normal and tangential stresses:

$$(p_1 - \rho_1 g h) - (p_2 - \rho_2 g h) - \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = (\tau'_{1,ik} - \tau'_{2,ik}) n_i n_k, \quad (1.15)$$

$$(\tau'_{1,ik} - \tau'_{2,ik}) \tau_i^{(l)} n_k + \frac{\partial \sigma}{\partial x_i} \tau_i^{(l)} = 0, \quad l = 1, 2. \quad (1.16)$$

Eq. (1.16) defines the Marangoni stress.

Also, at the interface the velocities of both fluids are equal:

$$\mathbf{v}_1 = \mathbf{v}_2. \quad (1.17)$$

The motion of the interface itself is governed by the following kinematic condition:

$$\frac{\partial h}{\partial t} + v_{1,x} \frac{\partial h}{\partial x} + v_{1,y} \frac{\partial h}{\partial y} = v_{1,z}. \quad (1.18)$$

Finally, the conditions for temperatures and heat fluxes should be written. The temperature field is continuous:

$$T_1 = T_2, \quad (1.19)$$

and the normal components of heat fluxes are equal:

$$\left( \lambda_1 \frac{\partial T_1}{\partial x_i} - \lambda_2 \frac{\partial T_2}{\partial x_i} \right) n_i = 0. \quad (1.20)$$

Also, some boundary conditions should be fixed on the external boundaries of domains  $D_1$  and  $D_2$ , depending on the physical nature of these boundaries.

If the energy spent by the interface deformation is taken into account, the following equation is obtained (Napolitano, 1978)

$$\left( \lambda_1 \frac{\partial T_1}{\partial x_i} - \lambda_2 \frac{\partial T_2}{\partial x_i} \right) n_i = \alpha T_1 \nabla_s \cdot \mathbf{v}_1 + \gamma \left( \frac{\partial T_1}{\partial t} + \mathbf{v}_1 \cdot \nabla T_1 \right),$$

where  $\nabla_s = \nabla - (\mathbf{n} \cdot \nabla) \mathbf{n}$ ,  $\alpha = -d\sigma/dT$ ,  $\gamma = d(\sigma + \alpha T)/dT$ . However, the correction is small under realistic conditions (Pukhnachev, 1987), and we shall neglect it.

Let us note also that the deformation and expansion of the interface may generate additional dissipation processes known as the ‘‘surface viscosity’’ (Boussinesq, 1913a-c; Scriven, 1960; Aris, 1962; Goodrich, 1981; Edwards *et al.*, 1991). Experimental data concerning this phenomenon are scarce. We shall not include the surface viscosity into our description.

## ii. One-fluid approach

In the case of a liquid/gas interface, a simplified mathematical model may be used. Because of relatively low (dynamic) shear viscosity of

the gas, we can expect that the influence of the gas motion on the motion in the liquid is negligible and hence the terminology “free surface”. Also, we can ignore the temperature field in the gas using some empirical boundary conditions for temperature. In this case, we can consider the processes that take place *only* in the liquid phase. Such a “one-fluid” approach may be justified only under some conditions (see, e.g., Golovin *et al.*, 1995), and in some cases makes it difficult to permit a comparison with experiments in the framework of such an approach (because of unmeasurable empirical coefficients used). Nevertheless, this approach may be useful for the qualitative description of the physical phenomena.

Considering the motion of just the liquid, we drop the subscripts in equations (1.10)-(1.12):

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{v} + g\beta T \mathbf{e}, \quad (1.21)$$

$$\frac{\partial T}{\partial t} + (\mathbf{v} \cdot \nabla) T = \kappa \nabla^2 T, \quad (1.22)$$

$$\nabla \cdot \mathbf{v} = 0. \quad (1.23)$$

In the boundary conditions for stresses we neglect the stresses caused by the gas ( $m=2$ ) and omit the subscript 1 corresponding to the liquid:

$$(p - \rho gh) - \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \tau'_{ik} n_i n_k, \quad (1.24)$$

$$\tau'_{ik} \tau_i^{(l)} n_k + \frac{\partial \sigma}{\partial x_i} \tau_i^{(l)} = 0, \quad l = 1, 2. \quad (1.25)$$

The condition (1.17) is cancelled, while the kinematic condition (1.18) is rewritten as

$$\frac{\partial h}{\partial t} + v_x \frac{\partial h}{\partial x} + v_y \frac{\partial h}{\partial y} = v_z. \quad (1.26)$$

Instead of exact conditions for temperatures and heat fluxes we shall use some empirical condition, say,

$$\lambda \frac{\partial T}{\partial x_i} n_i = K(T - T_g), \quad (1.27)$$

where  $K$  is a heat exchange coefficient which may depend on local curvature of the surface, local temperature etc,  $T_g$  is some characteristic temperature of the ambient gas (recall that vector  $\mathbf{n}$  is directed into the liquid).

### iii. Non-dimensional parameters or dimensionless groups

Let us rewrite the system (1.21) - (1.27) in a non-dimensional form. Let us assume that  $a$  is a characteristic spatial size of the region filled by the fluid, and  $\theta$  is a characteristic temperature difference across this region. We shall choose  $a$ ,  $a^2/\kappa$ ,  $\kappa/a$ ,  $\eta\kappa/a^2$  and  $\theta$  as units for length, time, velocity, pressure and temperature, respectively. The system of equations (1.21) - (1.27) takes the following form (expecting no confusion by the reader, we use the same letters denoting non-dimensional variables):

$$\frac{1}{P} \left[ \frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right] = -\nabla p + \nabla^2 \mathbf{v} + RT \mathbf{e}, \quad (1.28)$$

$$\frac{\partial T}{\partial t} + (\mathbf{v} \cdot \nabla) T = \nabla^2 T, \quad (1.29)$$

$$\nabla \cdot \mathbf{v} = 0, \quad (1.30)$$

where  $P = \nu/\kappa$  is the *Prandtl number* which is the ratio of the typical heat diffusion time,  $\tau_\kappa = a^2/\kappa$ , and the viscous momentum transfer time,  $\tau_\nu = a^2/\nu$ ,  $R$  is the *Rayleigh number*,  $R = \beta g a^4 A/\nu\kappa$ , which governs buoyancy-driven, natural convection. There are cases where the *Grashof number*,  $Gr = R/P$ , is used. A thorough discussion of scaling and adimensionalization can be found in the books by Palacios (1964), Lin and Segel (1974), Barenblatt (1996) and Guyon *et al.* (2001) and the reviews by Segel (1972), Ostrach (1977) and Castans (1991).

Let us assume that the dependence of the surface tension  $\sigma$  on the temperature is linear:  $\sigma = \sigma_0 - \alpha T$ . The boundary condition on the interface  $z = h$  (recall that we use the same letters denoting non-dimensional variables) are:

$$p - Gah - Ca^{-1}(1 - \delta_\alpha T) \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \tau'_{ik} n_i n_k, \quad (1.31)$$

$$\tau'_{ik} \tau_i^{(l)} n_k - M \frac{\partial T}{\partial x_i} \tau_i^{(l)} = 0, \quad l = 1, 2, \quad (1.32)$$

$$\frac{\partial h}{\partial t} + v_x \frac{\partial h}{\partial x} + v_y \frac{\partial h}{\partial y} = v_z, \quad (1.33)$$

$$\frac{\partial T}{\partial x_i} n_i = -Bi(T - \bar{T}_g), \quad (1.34)$$

where  $Ga = ga^3/\nu\kappa$  is the (*modified*) *Galileo number* (the Galileo number is, traditionally, defined as  $G = ga^3/\nu^2$  and later we shall use it like this. Then  $G$  is a ratio of length scales that recalls the role of gravity and hydrostatic pressure variations relative to viscous flow),  $Ca = \eta\kappa/\sigma_0a$  is the *capillary or crispation number* (other authors use its inverse),  $M = \alpha a^2 A/\eta\kappa$  is the *Marangoni number*,  $Bi = Ka/\lambda$  is the *Biot number*,  $\delta_\alpha = \alpha\theta/\sigma_0 = M/Ca$ , and  $\bar{T}_g = T_g/\theta$ . Let us mention here also the (static) *Bond number*  $Bo = \rho ga^2/\sigma_0 = GaCa$  and the dynamic Bond number  $Bd = \rho ga^2/\alpha = R/M$ . The physical meaning of each parameter will be discussed later. On the other hand, note that, for simplicity, here we denoted with  $R$ ,  $M$ , and  $P$  the Rayleigh, Marangoni, and Prandtl numbers, respectively. Later we shall be using  $Ra$ ,  $Ma$ , and  $Pr$  whenever we feel it might help clarity in the notation. For the Galileo number we shall be using  $Ga$  or  $G$  according to the context. The same would be the case with the capillary number,  $C$  or  $Ca$ .

#### iv. Influence of convection on the deformation of the interface

It is necessary to emphasize that the formulated boundary problem is *incorrect* from the physical point of view if both the Rayleigh number,  $R$ , and the Galileo number,  $Ga$ , are taken of the same order. The Boussinesq approximation is based on the assumption of small relative deviations of density :  $\delta_\beta = \beta\theta = R/Ga \ll 1$ . If the latter condition is violated, the consideration of non-Boussinesq corrections in the equation of motion and in the continuity equation are mandatory (Velarde *et al.*, 2000). Also, such corrections are necessary for a self-consistent description of effects caused by small but nonzero  $\delta_\beta$ . Otherwise, some spurious results may be produced by using the system (1.28) – (1.34).

Thus, when considering buoyancy-driven convection ( $R = O(1)$ ) we should assume that  $Ga \gg 1$ , to be within the Boussinesq approximation. Typically, on Earth  $Ga$  is large and  $C$  is small, while the Bond number is of order of unity. In the limit  $Ga \rightarrow \infty$ , the terms in the right-hand side of the boundary condition (1.31) may be omitted in the leading order, because they are  $O(1)$ . Also, the quantity  $p$  describing the difference of pressures on both sides of the interface may be considered as a constant, because the gradient of pressure is  $O(1)$ . Thus, as earlier noted, the shape of the interface is determined by

the balance of normal stresses which are of hydrostatic and capillary origin:

$$h + Bo^{-1}(1 - \delta_\alpha T) \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = const. \quad (1.35)$$

In the case where the motion takes place in a closed cavity, the equation (1.35) is solved with a boundary condition on a lateral boundary corresponding to a certain contact angle. The influence of the lateral boundary vanishes on distances large compared with  $Bo^{-1/2}$ . For an “infinite” layer ( $L \gg Bo^{-1/2}$ ,  $L$  is the dimensionless horizontal size of the system) one can assume  $h = 0$ . In the opposite limit (for instance, under reduced effective gravity) the second term in the left hand side of (1.35) prevails over the first term. If  $\delta_\alpha$  is small, the interface has a constant curvature.

The equation (1.35) may be considered as a zeroth approximation for the full problem in the limit of small  $\delta_\beta$ . The fields of variables (velocity, pressure, temperature) calculated in the region with the shape governed by the equation (1.35) may be used for calculations of the next order corrections to the interface shape. For instance, in the case of an infinite layer the shape of the interface  $h = O(Ga^{-1})$  in the presence of buoyancy-driven convection and with no temperature dependence of the surface tension may be calculated from the equation

$$h - Bo^{-1} \left( \frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} \right) = Ga^{-1} \left[ p - 2 \frac{\partial v_z}{\partial z} \right] \Big|_{z=0}. \quad (1.36)$$

The next step (calculation of the influence of the surface deformation on the convective motion) cannot be done within the Boussinesq approximation, because this influence is of the same order in  $\delta_\beta$  as some terms omitted in this approximation.

Let us discuss now the case of finite values of (modified) Galileo number. Within the Boussinesq approximation,  $\delta_\beta \rightarrow 0$  and thus  $R \rightarrow 0$ , so only thermocapillary convection may appear. This situation may take place in thin layers or under reduced effective gravity conditions. If the capillary number  $Ca$  is large enough, while  $\delta_\alpha$  is small, the shape of the surface is not essentially influenced by the thermocapillary motion. The zeroth order solution may be constructed for a fixed shape of the surface, then the corrections to the surface shape may be calculated, etc. However, in the case of long-wave convection on the background of a flat surface, the capillary

term in the boundary condition for normal stresses does not prevail, and the full problem should be considered.

## 1.2.2 Mass transfer in a system with an interface

### i. Mass transfer in the absence of a surface adsorption

Let us consider a binary mixture characterized by the volume concentration  $C$ . Let us assume that the interfacial kinetics is so fast that the interfacial concentration  $\Gamma$  is determined by the volume concentration  $C$  in a unique way. In this case the equations and boundary conditions governing the problem are actually identical to those formulated in the previous subsection for the case of heat transfer (1.21) – (1.27). It is sufficient to introduce the concentration  $C$  instead of the temperature  $T$ , and replace the coefficients  $\beta$  and  $\alpha$  by

$$\beta_c = -\frac{1}{\rho} \left( \frac{\partial \rho}{\partial C} \right)$$

and

$$\alpha_c = -\frac{\partial \sigma}{\partial C}$$

Besides, the coefficient  $\kappa$  (and  $\lambda$ ) should be replaced by the corresponding diffusion coefficient  $D$ . The same changes are done in the definitions of the nondimensional parameters. Thus, both models are isomorphic.

A point to be noted is that there are systems for which  $\alpha$  or  $\alpha_c$  may be negative or even vanish. Schwarz (1970) studied two-phase systems like Cyclohexanol/Water with diffusion substances Methanol, n-Propanol, n-Butanol, n-Amylol and n-Hexanol in concentrations from 2 to 8 %. These systems are characterized by  $d\sigma/dC < 0$  (the first three) and by  $d\sigma/dC > 0$  (the last two). Other cases showing positive growth in the surface tension or a minimum in the surface tension which can be considered as anomalous behavior,  $d\sigma/dC > 0$  or  $d\sigma/dT > 0$ , relative to that of pure water have been described by several authors (Vochten and Petre, 1973; Petre and Azouni, 1984; Petre *et al.*, 1993; Azouni and Petre, 1998).

In the case of a two-phase system, where the component characterized by the volume concentration  $C$  diffuses through the interface, similar substitutions should be done for each fluid. The equation are

written in the following form:

$$\frac{\partial \mathbf{v}_m}{\partial t} + (\mathbf{v}_m \cdot \nabla) \mathbf{v}_m = -\frac{1}{\rho_m} \nabla p_m + \nu_m \nabla^2 \mathbf{v}_m + g\beta_{c,m} C_m \mathbf{e}, \quad (1.37)$$

$$\frac{\partial C_m}{\partial t} + (\mathbf{v}_m \cdot \nabla) C_m = D_m \nabla^2 C_m, \quad (1.38)$$

$$\nabla \cdot \mathbf{v}_m = 0. \quad (1.39)$$

The boundary conditions (1.14), (1.17), (1.18) are not changed, the equation for normal components of fluxes is

$$\left( D_1 \frac{\partial C_1}{\partial x_i} - D_2 \frac{\partial C_2}{\partial x_i} \right) n_i = 0. \quad (1.40)$$

The essential difference between the cases of heat transfer and mass transfer is that the limit values of the concentration on the interface from both fluids are not necessarily equal but proportional:

$$C_2 = kC_1. \quad (1.41)$$

This difference may be removed by a suitable transformation of variables.

## ii. Mass transfer with surfactant adsorption-desorption

Expanding on what was said in subsection 1.1.1, let us consider now a general case where the “surface gas phase” of the surfactant is taken into account. The interfacial concentration of the surfactant should be considered as an additional variable. If there is no chemical reaction on the interface, the evolution of the interfacial concentration is governed by the following equation (Levich, 1962; Rosner, 1986; Sadhal and Johnson, 1983; Edwards *et al.*, 1991; Myers, 1999):

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma \mathbf{v}_s - D_s \nabla_s \Gamma) = j, \quad (1.42)$$

where  $\mathbf{v}$  denotes velocity along the surface,  $D_s$  is the coefficient of the surfactant surface diffusion,  $\nabla_s$  is the gradient along the surface,  $j$  is the flux of the substance from the bulk to the interface.

Because the interface unit area possesses a mass  $m\Gamma$ , where  $m$  is the mass of the surfactant molecule, the boundary condition (1.14) should be rewritten in the form

$$m \frac{d}{dt} (\Gamma v_{1,i}) = - \left[ (p_1 - \rho_1 gh) - (p_2 - \rho_2 gh) - \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \right] n_i$$

$$+(\tau'_{1,ik} - \tau'_{2,ik})n_k + \frac{\partial \sigma}{\partial x_i}, \quad (1.43)$$

where  $d/dt$  is the Lagrangian derivative with respect to time,  $\sigma$  is a function of  $\Gamma$ , which is the surface excess surfactant concentration. Usually, the mass of the surfactant layer is relatively small or processes are quasisteady, and the term in the left-hand side of (1.43) may be omitted.

The flux  $j$  characterizes the mass exchange between the bulk and the interface. If the surfactant is insoluble,  $j = 0$ . If the surfactant is soluble in the bulk liquid, the exchange is determined by its diffusion in the bulk fluid and the interfacial kinetics. From one side, the flux of the surfactant from the bulk to the surface is determined by the relation

$$j = -D\mathbf{n} \cdot \nabla C. \quad (1.44)$$

From another side, it is determined by the adsorption-desorption kinetics (1.8), recalled here:

$$j = k_a C - k_d \Gamma. \quad (1.45)$$

The adsorption-desorption kinetics may be fast or slow. For fast enough kinetics a local adsorption-desorption equilibrium could be introduced which corresponds to  $j = 0$ . That is local equilibrium of the surface excess solute with the solute in the adjacent subphase. As it follows from (1.45), the (local) equilibrium values  $C$  and  $\Gamma$  are connected by the relation

$$\Gamma = k_a k_d^{-1} C \quad (1.46)$$

which, in fact, corresponds to the ideal *Gibbs adsorption isotherm* for very dilute solutions.

Deviations from the equilibrium of the system with surfactant may be due to various reasons, namely, initial nonequilibrium conditions, desorption and adsorption of surfactant, chemical reaction at the interface, etc. If every term in the left hand side (l.h.s) of (1.45) exceeds greatly the diffusion flux  $j$ , then the mass transfer process could be treated as locally in equilibrium (then  $j$  is a small difference between two large values in the l.h.s.). In this case, at local equilibrium the relation (1.46) between  $C$  and  $\Gamma$ , as a function of space and time, is fulfilled and the adsorption and desorption processes are controlled by bulk diffusion (1.44).

For moderately dense surfactant solutions, the departure from (1.46) is governed by the *Langmuir adsorption isotherm*

$$\Gamma = \Gamma^\infty \frac{C}{a + C}, \quad (1.47)$$

and the surface tension obeys the *Szyszkowsky state equation*

$$\sigma - \sigma_0 = -RT\Gamma^\infty \ln \left( 1 + \frac{C}{a} \right), \quad (1.48)$$

that provides the surface pressure, where  $\Gamma^\infty$  corresponds to a complete coverage or the surface excess saturation or maximum realizable excess concentration, and  $a$  is constant for a given surfactant (adsorption coefficient). From (1.48) follows the relation

$$\Gamma = \left( -\frac{1}{RT} \frac{d\sigma}{dC} \right) C. \quad (1.49)$$

For small deviations from an initial equilibrium state

$$-\frac{1}{RT} \frac{d\sigma}{dC} \equiv L = \text{const.}$$

Then (1.49) takes the form of the Gibbs equation (1.46),

$$\Gamma = LC. \quad (1.50)$$

For more general adsorption-desorption kinetics one needs to apply the non-equilibrium relation (1.45) with e.g. the equilibrium Langmuir adsorption isotherm (1.47). Otherwise one could use nonlinear kinetics as

$$k_a \left( 1 - \frac{\Gamma}{\Gamma^\infty} \right) C - k_d \Gamma = j. \quad (1.51)$$

This and more general forms of nonlinear relations have been used in the literature (Bojadjev and Beshkov, 1984; Ravera *et al.*, 1993, 1994; Stebe and Barthes-Biesel, 1995; Liggieri *et al.*, 1996).

If the adsorption and desorption processes are very slow,  $k_a$  and  $k_d$  are practically zero, and again  $j$  vanishes. The mass transfer in the sublayer near the interface is kinetically frozen, so the surface excess concentration,  $\Gamma$ , is effectively unchanged.



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# Chapter 2

## Interfacial flows

As a straightforward follow-up of Chapter 1, in this second chapter we shall illustrate simple flows due to the Marangoni effect. However, we shall not consider the problem of *stability* of interfacial flows which will be the subject of subsequent chapters.

### 2.1 Flows generated by a longitudinal surface tension gradient

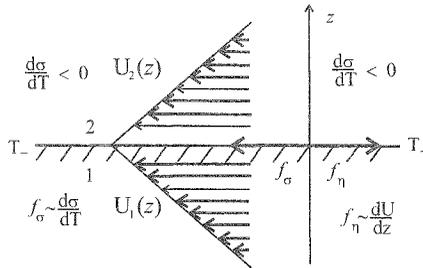


Figure 2.1: Interface between two liquids and the Marangoni effect. The actual flow fields ( $U$ ) in fluids 1 and 2, with motion from hotter to cooler regions due to the (tangential) Marangoni stress along the interface, depend on the values of the corresponding (dynamic) viscosity ( $\eta$ ).

Typical flows generated by the Marangoni effect appear in Figs. 2.1–2.3. In all cases non-uniform or unequal heating leads to inhomogeneity of the interfacial or surface tension and hence flow from points

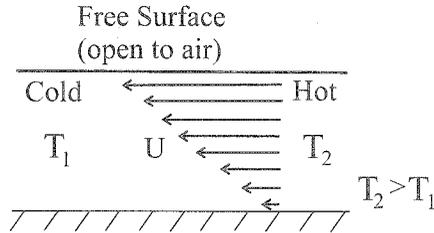


Figure 2.2: Thin liquid layer placed on a solid support and the Marangoni effect. The liquid layer is open to ambient air. Due to unequal heating ( $T_2 > T_1$ ) along the horizontal, flow ( $U$ ) driven by the Marangoni stress along the free surface brings liquid from the hotter to the cooler regions.

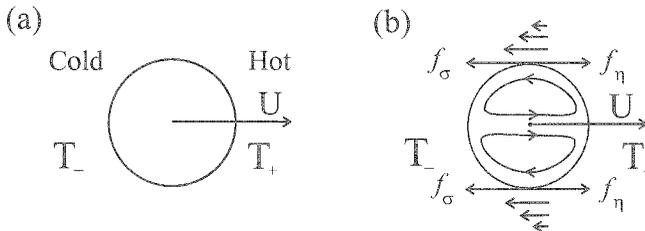


Figure 2.3: Drop or bubble subjected to unequal heating at two opposite poles and the Marangoni effect. (a) A drop or a bubble tends to move towards the hotter region as a reaction to the (outer) surface flow due to Marangoni stresses created by the unequal heating ( $T_+ > T_-$ ); (b) For a drop, flows outside and inside are schematically shown for moderate temperature differences at, say, front and rear poles.