Relaxation of surface tension after a large initial perturbation

KRÜSS GmbH – Germany, www.kruss.de

Krassimir Danov, www.lcpe.uni-sofia.bg

1. Introduction

KRÜSS GmbH – Germany is the world's leading supplier of measuring instruments for surface and interfacial tension, contact angles, foam analysis, interfacial rheology, etc. KRÜSS GmbH – Germany not only provide high quality product solutions – their offers are a combination of technology and scientific consulting. The adequate mathematical modeling of precise measured data makes the apparatuses attractive for many applications in the chemical and pharmaceutical industries, medicine, biotechnology, ecology, food and beverages production, etc. The problem for one component solution, which is described below, is the starting point for the intensive future developments. The fast and stable algorithms can be extended for: a) multi component systems; b) mixed barrier-diffusion control; c) ionic surfactants in the presence of salt; d) protein and polymer solutions, etc.

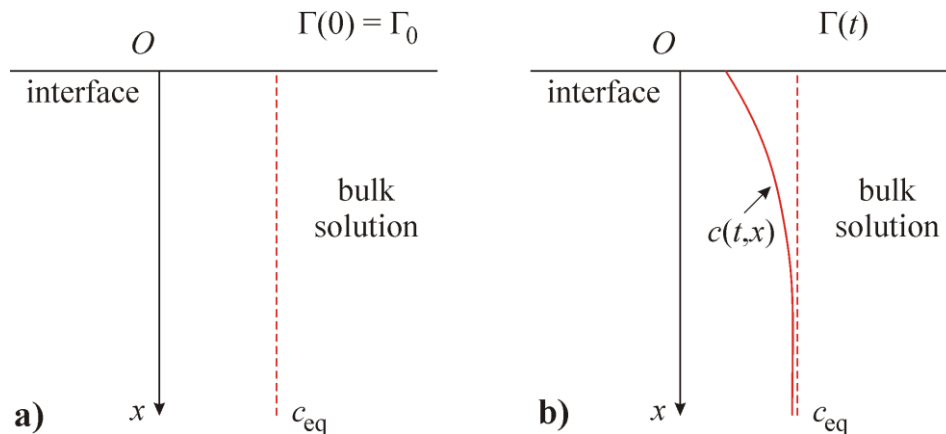## 2. Mathematical formulation of the problem

Fig. 1. Sketch of the diffusion problem: a) initial conditions; b) concentration profile at a given moment of time.

The diffusion process of a simple one component solution is described by the following linear partial differential equation:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{for} \quad t > 0 \quad \text{and} \quad x > 0 \tag{1}$$

where x is the spatial coordinate, t is time, D is the diffusion coefficient, and $c(t,x)$ is the bulk concentration of surfactant (see Fig. 1). The input concentration in the solution is c_{eq} so that the initial condition and the boundary condition at large distances from the interface for Eq. (1) read:

$$c(0,x) = c_{eq} \quad \text{for} \quad x > 0 \quad \text{and} \quad \lim_{x \to \infty} c(t,x) = c_{eq} \quad \text{for} \quad t \geq 0 \tag{2}$$

Table 1. Typical adsorption isotherms and surface equations of state

	Adsorption isotherm	Equation of state
Frumkin	$Kc_s = \dfrac{\theta}{1-\theta} \exp(-\beta\theta)$	$\dfrac{\sigma_0 - \sigma}{E_B \Gamma_\infty} = -\ln(1-\theta) - \dfrac{\beta}{2}\theta^2$
Van der Waals	$Kc_s = \dfrac{\theta}{1-\theta} \exp(\dfrac{\theta}{1-\theta} - \beta\theta)$	$\dfrac{\sigma_0 - \sigma}{E_B \Gamma_\infty} = \dfrac{\theta}{1-\theta} - \dfrac{\beta}{2}\theta^2$
Helfand, Frisch, Lebowitz	$Kc_s = \dfrac{\theta}{1-\theta} \exp[\dfrac{3\theta - 2\theta^2}{(1-\theta)^2} - \beta\theta]$	$\dfrac{\sigma_0 - \sigma}{E_B \Gamma_\infty} = \dfrac{\theta}{(1-\theta)^2} - \dfrac{\beta}{2}\theta^2$

The main difference from the classical diffusion problems arises because of the adsorption, $\Gamma(t)$, at the interface, $x = 0$. The change of the adsorption is compensated by the diffusion flux from the bulk:

$$\frac{d\Gamma}{dt} = D\frac{\partial c}{\partial x} \quad \text{for} \quad t > 0 \quad \text{and} \quad x = 0 \tag{3}$$

Eq. (3) plays a role of the boundary condition for the diffusion problem. At initial time, $t = 0$, the interface contains a given amount of surfactants, Γ_0, so that:

$$\Gamma(0) = \Gamma_0 \tag{4}$$

To close the problem (1)–(4) one needs a relationship between the subsurface concentration, $c_s(t)$, defined as

$$\lim_{x \to 0} c(t,x) = c_s(t) \quad \text{for} \quad t \geq 0 \tag{5}$$

and the adsorption, $\Gamma(t)$. This relationship is called "the adsorption isotherm". Different surfactants obey different adsorption isotherms. Usually three typical adsorption isotherms are used (see Table 1), where K is the adsorption constant, β is the interaction parameter, Γ_∞ is the maximum possible adsorption, and θ is the surface coverage, given by the expression

$$\theta(t) \equiv \frac{\Gamma(t)}{\Gamma_\infty} \quad \text{and} \quad 0 \leq \theta(t) < 1 \tag{6}$$

Note that the adsorption isotherms are nonlinear equations so that the problem has not an analytical solution.

Mathematical problem: Solve the diffusion equation (1) with initial and boundary conditions (2)–(6) for a given adsorption isotherm (see Table 1) to obtain the change of adsorption with time, that is $\Gamma(t)$.

3. Application of the mathematical model for the characterization of surfactants

Available apparatuses measure indirectly the relaxation of adsorption. The most sensitive to the change of adsorption is the surface tension, $\sigma(t)$. Fig. 2 shows the measured relaxation of surface tension at air-solution interface for 0.1 mM SDS. One sees that all 6 different runs have excellent reproducibility.
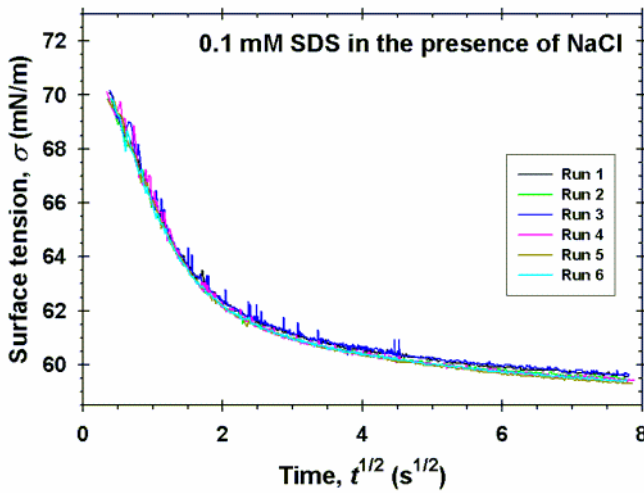

Fig. 2. Relaxation of surface tension $\sigma(t)$ at air-solution interface. The solution contains 0.1 mM SDS (sodium dodecyl sulfate) and 100 mM NaCl. The initial adsorption is zero and the temperature is 25 $^{\circ}$C.

The surface tension is related to the adsorption by the so called "2D equation of state". Different adsorption isotherms have different equations of state (see Table 1), where σ_0 is the surface tension without added surfactants and E_B is the Boltzmann energy.

Practical problem: Characterize the surfactant SDS from measured relaxation of surface tension (Fig. 2). That is, fit the experimental data using the van der Waals model (Table 1) to obtain the parameters K and Γ_{∞}.

Note that the addition of 100 mM NaCl is used to suppress the electrostatic interactions. NaCl is not a surface active substance and the concentration of NaCl is not included in the calculations. The values of the known parameters are:

$$c_{eq} = 0.1\,\text{mol/m}^3, \quad \Gamma_0 = 0\,\text{mol/m}^2, \quad D = 5.5 \times 10^{-10}\,\text{m}^2/\text{s}, \quad \beta = 1.62$$

(7)

$$\sigma_0 = 72.2\,\text{mN/m} = 0.0722\,\text{N/m}, \quad E_B = 2479\,\text{N} \cdot \text{m/mol}$$

For convenience the surface tension measurements are presented in mN/m – for calculations one needs to use N/m, so that for example 70 mN/m (experimental data) corresponds to 0.07 N/m (for numerical calculations).

4. Ward-Torday integral equation

The numerical solution of the partial differential equation is time consumable. For that reason in the literature the following equivalent approach is used. The integral Laplace transform with respect to time of the function $f(t,x)$ is defined as follows:

$$F(s,x) = L[f] = \int_0^\infty f(t,x)\exp(-st)\,\text{d}t$$

(8)

where s is the parameter of the Laplace transform and $F(s,x)$ is the Laplace image. We introduce the Laplace images:

$$C(s,x) \equiv L[c(t,x) - c_{eq}], \quad C_s(s) \equiv L[c_s(t) - c_{eq}]$$

(9)

The solution of the diffusion problem (1) with the initial and boundary conditions (2) reads:

$$C(s,x) = C_s(s)\exp(-x\sqrt{\frac{s}{D}})$$

(10)

The Laplace transform of the boundary condition (3) with initial condition (4) gives:

$$sL[\Gamma - \Gamma_0] = D\frac{\text{d}C}{\text{d}x} \quad \text{at} \quad x = 0$$

(11)

From Eqs. (10) and (11) one derives

$$L[\Gamma - \Gamma_0] = -C_s\sqrt{\frac{D}{s}} \quad \Rightarrow \quad L[\Gamma - \Gamma_0] = -\sqrt{\frac{D}{s}}L[c_s(t) - c_{eq}]$$

(12)

Finally, applying the convolution theorem for Eq. (12) the Ward and Torday integral equation is obtained:

$$\Gamma(t) = \Gamma_0 - (\frac{D}{\pi})^{1/2}\int_0^t \frac{c_s(\tau) - c_{eq}}{(t-\tau)^{1/2}}\,\text{d}\tau$$

(13)

Eq. (13) is the Volterra type equation, in which the kernel has a weak Abel type singularity.

Mathematical problem: Solve the integral equation (13) for a given adsorption isotherm (see Table 1) to obtain the change of adsorption with time, that is $\Gamma(t)$.