On the Thermodynamics of Thin Wetting Films

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Abstract – An equation based on thermodynamics and correlating the spreading coefficient of the wetting film and two empiric constants in the approximated dependence of the disjoining pressure on the film thickness was derived.

The disjoining pressure of the wetting film formed on a nucleus as well as the spreading coefficient of the film on the nucleus surface are important concepts in the thermodynamics of the heterogeneous condensation of vapor on macroscopic nuclei [1 - 3]. It was established that thin films with low concentrations of the dissolved substance of a nucleus are of critical importance for the thermodynamics of heterogeneous condensation on macroscopic nuclei, even when the nucleus substance is considerably dissolved in the liquid condensing from the vapor [1 - 3].

Macroscopic dimensions of the condensation nuclei make it possible to neglect the influence of the curvature of the nucleus surface on the disjoining pressure of the film. In turn, a low concentration of the dissolved nucleus substance inside the film allows one to ignore the influence of the dissolved substance on the disjoining pressure of the film and its thickness. Due to these circumstances, the relationship between the coefficient of the film spread on the wetted surface of the nucleus and the disjoining pressure of the film may be derived in a simple way. The aim of this paper is to find this relationship.

We consider a thin wetting film formed from the vapor on a plane solid substrate. The concentration of the dissolved substance of the substrate inside the film is assumed to be small and, hence, the effect of the dissolved substance on the disjoining pressure of the film Π and its thickness h may be ignored. In this case, the main component of the film is the liquid condensed there from the vapor.

We have [4 - 6]

$$d\sigma/d\Pi = h, \tag{1}$$

where σ is the surface tension (taking into account that the film is formed on the surface). The derivative is taken at a fixed temperature (at supposedly low concentrations of the substrate substance dissolved inside the film, we disregard the influence of the dissolved substance on the film thickness).

We, obviously, also have

$$\sigma = \sigma_1 \quad (h = 0), \tag{2}$$

$$\sigma = \sigma_2 + \sigma_3 \quad (h = \infty). \tag{3}$$

where σ_1 is the surface tension at the interface of the initial direct contact between the vapor and the solid substrate, σ_2 is the surface tension at the interface between the vapor and the liquid condensed from the vapor, and σ_3 is the surface tension at the interface between the liquid condensed from the vapor and the solid substrate. It should be mentioned that σ_1 and σ_3 are [7 - 11] thermodynamic quantities; i.e., they are determined by the work of the formation per unit area of a new surface, whereas σ_2 may be interpreted in terms of both thermodynamic and mechanical approaches; that is, it is determined by both the work of the formation of the new unit surface area and the excess tension in the vicinity of the surface.

The expression

$$s = \sigma_1 - \sigma_2 - \sigma_3 \tag{4}$$

gives the spreading coefficient s for the wetting film. Because the expression $\sigma_1 > \sigma_2 + \sigma_3$ [12] is valid for the surface tensions at the interfaces between pure substances, the spreading coefficient $s > 0$.

The spreading coefficient s in this case has nonequilibrium nature because surface tension σ_1 is related to a nonequilibrium state at the interface between the vapor and the solid substrate, which has not yet been covered by the wetting film. This state is an initial state for the heterogeneous vapor condensation on nuclei. The nonequilibrium initial state, however, does not preclude its thermodynamic interpretation in terms of the grand thermodynamic potential and the associated surface tension σ_1.

For the dependence of the disjoining pressure in film Π on its thickness h at fixed temperature, we have an approximation derived from experimental data [13]:

$$\Pi = K\exp(-h/l), \tag{5}$$

where K and l are two empirical constants, providing that the effect of the dissolved substance of the substrate on the disjoining pressure may be ignored because of supposedly low concentration of the dissolved substance in the film.

Our objective is to find a relationship between the spreading coefficient s, given by equation (4), with two

constants K and l in the disjoining pressure Π approximation (5).

Approximation (5) leads to

$$d\Pi/dh = -(K/l)\exp(-h/l), \tag{6}$$

which enables us to rewrite thermodynamic equation (1) as follows

$$d\sigma/dh = -(K/l)h\exp(-h/l). \tag{7}$$

According to (2) - (4),

$$s = -\int_0^{\infty} (d\sigma/dh)\,dh. \tag{8}$$

Although, when $h \to 0$, approximation (5) becomes rather rough (does not follow the Henry law). Nevertheless, due to factor h (which is small at $h \to 0$) on the right side, equation (7) provides sufficient accuracy for the integral in equation (8).

By calculating this integral through equation (7), we derive the final relationship as follows

$$s = Kl. \tag{9}$$

Only two constants out of the three (s, K, and l) in this relationship are independent.

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