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Abstract

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DISJOINING PRESSURE OF A GAS FILM

As was shown in (1−3), between two identical bodies separated by a gap of small thickness H, an attraction always arises (i.e., a negative disjoining pressure), caused by the interaction of the fluctuating electromagnetic fields of both bodies. If the gap between the bodies is filled with a liquid with a dielectric constant different from unity, then the force of attraction decreases (since the electric-field strength in the gap decreases), but the sign of the disjoining pressure remains the same (1−3). We note that the latter assertion is based on the very essential assumption that the liquid film is homogeneous and that its properties are indistinguishable from those of the bulk phase.

During the last two or three years, a stability effect of thin films of concentrated solutions (4,5) has been discovered that is completely incomprehensible from the standpoint of the theory (1−3). Since the films may be inhomogeneous (with respect to composition) across their thickness, the theory (2,3) may turn out to be inapplicable to them. It is therefore of interest to determine the features introduced by a violation of the film’ s homogeneity. The simplest example of such a film is a film of an ideal gas, whose particles are attracted by molecular forces to the surface of the interacting bodies.

Let us consider a certain volume of gas V, inside which two plates are placed, separated by a plane-parallel gap of thickness H. It is obvious that V can be divided into three parts: the volume of gas $V^\alpha = AH$ enclosed between the plates; the volume of gas $V^e = 2AL$, situated in the immediate vicinity of each plate but outside them; and the remaining volume of gas V^g ($V = V^\alpha + V^e + V^g$). The gas in V^α and in V^e is within the range of action of the molecular attractive forces of the plates, whereas the gas in V^g is outside the range of action of these forces. If we denote by F^α the free energy of the gas in the gap, by F^e the free energy of the gas in V^e, and, finally, by F^g the free energy of all the remaining gas, then the change in the disjoining pressure $\Delta\Pi$ caused by the inhomogeneity of the gas film will be

$$\Delta\Pi = -\frac{1}{A}\left(\frac{\partial F}{\partial H}\right)_{T,V,A,N}, \tag{1}$$

where $F = F^\alpha + F^e + F^g$, T is the temperature, and $N = N^\alpha + N^e + N^g = \text{const}$ is the total number of particles in the system. Treating the molecular forces of attraction to the surfaces of the plates as an external field, one may at once write the expression for the free energy (^{6})

$$F^\alpha = -N^\alpha kT \ln \frac{e}{N^\alpha} \int_{V^\alpha} e^{-u^\alpha/kT}\, dV + N^\alpha f(T); \tag{2^1}$$

$$F^e = -N^e kT \ln \frac{e}{N^e} \int_{V^e} e^{-u^e/kT}\, dV + N^e f(T); \tag{2^2}$$

$$F^g = -N^g kT \ln \frac{eV^g}{N^g} + N^g f(T), \tag{2^3}$$

where u^α and u^e are the potential energies of gas molecules in the gap and near the plates, respectively. If we denote by

$$n^g = \frac{N^g}{V^g} = \frac{N - N^\alpha - N^e}{V - V^\alpha - V^e}$$

the number of particles per unit volume of the bulk gas, then the total number of particles in V^α and V^e will be

$$N^\alpha = n^g \int_{V^\alpha} e^{-u^\alpha/kT}\, dV, \qquad N^e = n^e \int_{V^e} e^{-u^e/kT}\, dV.$$

Substituting this value into (2), we obtain

$$F = \sum_{i=1}^{3} F^i = -NkT \ln \frac{e}{n^g} + Nf(T). \tag{3}$$

Finally, substituting F into (1), we find that

$$\Delta\Pi = kT \left[1 + \frac{N^\alpha + N^e}{N^g}\right] \left\{ \frac{d}{dH} \left(\frac{N^\alpha + N^e}{A} \right) - n^g \right\}. \tag{4}$$

Let us assume, for simplicity, that the surfaces of both plates are perfectly homogeneous. Then u^α, u^e will depend only on the coordinate z (normal to the surface of the bodies), and

$$N^\alpha = An^g \int_0^H e^{-u^\alpha/kT}\, dz, \qquad N^e = 2An^g \int_0^\Delta e^{-u^e/kT}\, dz.$$

Suppose, moreover, that $N^g \gg N^\alpha + N^e$. Then (4) takes the form

$$\Delta\Pi = n^g kT \frac{d}{dH} \int_0^H \left(e^{-u^\alpha/kT} - 1\right) dz. \tag{5}$$

(Here we have taken into account that, because of the smallness of $V^\alpha + V^e$ in comparison with V^g, the quantity $dn^g/dH \simeq 0$, and that L does not depend on H.)

In order to proceed further, it is necessary to specify the form of the function u^α. Let us suppose that the interaction energy of a molecule with each of the plates is determined only by its distance from that plate and does not depend on the distance to the other plate, i.e.,

$$u^\alpha(z) = u^e(z) + u^e(H - z). \tag{6}$$

Then

$$\Delta\Pi = n^g kT \left[e^{-2u^e(h)/kT} - 1\right] + 2\int_0^h \left(-\frac{\partial u^e(H-z)}{\partial H}\right) n^g e^{-u^\alpha(z)/kT}\, dz, \tag{7}$$

where $h = H/2$. Since $p^g = n^{gkT}$, $p^\alpha(z) = p^g e^{-u^\alpha(z)/kT}$, the first term on the right-hand side is simply the difference between the pressure at the center of the film (where the force $f = -\partial u^\alpha/\partial z$ acting on the gas molecules is equal to zero) and the pressure in the bulk gas. This "osmotic" (i.e., due to a change in concentration) component of the disjoining pressure is always positive, since $u^\alpha(h) < 0$ (the gas is drawn into the gap!). Conversely, the second term in (6) is always negative, since $\partial u^e/\partial z > 0$ (the interaction energy of a molecule and a plate, as the distance between them increases, tends to zero, i.e., increases).

Let us now make more detailed assumptions about the form of the function $u^e(z)$. Suppose that at distances $z < r_0$, where $2r_0 = d$ is the diameter of the molecule, $u^e \to \infty$, which reflects the fact that the particle cannot approach the wall to a distance smaller than its radius. On the other hand, for $z > \Delta$, where $\Delta \simeq d$, $u^e \simeq -\alpha/z^3$, $\alpha > 0$ [7]. In the interval $\delta = \Delta - r_0$, the form of the function $u^e(z)$ is determined by short-range forces and depends substantially both on the properties of the gas molecules and on the properties of the body itself. Therefore we shall not specify here the form of u^e, but replace it by some average (for this interval) value $u_0^e (< 0)$. Then, assuming that $\Delta \ll h$, and taking-

assuming that, owing to the very sharp decrease of u^e with increasing z in the interval $\Delta \ll z \ll h$, the quantity $-u^e \ll kT$ and $e^{-u^e/kT} \simeq 1$, while in the interval $r_0 \leq z \ll \Delta$ the quantity $u^e(z) \simeq u_0^e \gg u^e(H - z)$ and $u^x \simeq u_0^e$, we obtain, instead of (7),

$$\Delta\Pi \simeq \frac{16n^g\alpha}{H^3} - 6n^g\alpha\left\{e^{-u_0^e/kT}\int_{r_0}^{\Delta}\frac{dz}{(H-z)^4} + \int_{\Delta}^{h}\frac{dz}{(H-z)^4}\right\} =$$

$$= \frac{2n^g\alpha}{H^3}\left\{1 - 3\delta\,\frac{e^{-u_0^e/kT}}{H}\right\}. \tag{8}$$

The quantity $\Gamma_0 = n^g\delta e^{-u_0^e/kT}$ is the number of particles adsorbed in a monolayer per unit surface of the first plate in the absence of the second plate. Therefore (8) can be written as

$$\Delta\Pi \simeq \frac{2n^g\alpha}{H^3}\left\{1 - \frac{3}{H}\left(\frac{\Gamma_0}{n^g}\right)\right\}. \tag{9}$$

It follows from this that for $H > H_0 = 3(\Gamma_0/n^g) = \delta e^{-u_0^e/kT}$ the quantity $\Delta\Pi > 0$, i.e., the "osmotic" effect predominates. Conversely, for $H < H_0$ the "force" effect of attraction outweighs it, and $\Delta\Pi < 0$. Since in most cases $-u_0^e \simeq (1 \div 5)\,kT$, H_0 may be of the order of one hundred angstroms.

Let us note that the dependence $\Delta\Pi = f(H)$ obtained for a gas film is qualitatively very similar to the dependence $\Pi = f(H)$ in the case of films of concentrated solutions, determined experimentally ([4],[5]). It must be emphasized, however, that in the case of a gas film the entire effect considered is only a small correction (of order n^g/n, where n^g is the gas density and n is the density of the interacting bodies*) to the main effect, whereas in films of concentrated solutions the emergence of a positive disjoining pressure at large H and a negative one at small H is the main effect.

At the same time, the change in the disjoining pressure caused by the inhomogeneity of the gas film is always of the same order as the effect caused by the change in the dielectric permittivity of the gap between the two bodies. Indeed, according to ([3]), for a homogeneous film

$$\Pi = \frac{\hbar}{8\pi^2H^3}\int_0^\infty\left[\frac{\varepsilon(i\xi) - \varepsilon^g(i\xi)}{\varepsilon(i\xi) + \varepsilon^{(g)}(i\xi)}\right]^2 d\xi, \tag{10}$$

where $\varepsilon, \varepsilon^g$ are the dielectric permittivities of the plates and of the gap, considered as functions of the imaginary frequency ξ. Since for a gas $\varepsilon^g - 1 = \varepsilon^* \ll 1$, the total disjoining pressure is

$$\Pi = \Pi_0 + \Delta\Pi_\varepsilon,$$

where the disjoining pressure at $\varepsilon^g = 1$ is

$$\Pi_0 = \frac{\hbar}{8\pi^2 H^3}\int_0^\infty \left(\frac{\varepsilon-1}{\varepsilon+1}\right)^2 d\xi$$

and $\Delta\Pi_\varepsilon$ is the change in the disjoining pressure caused by the deviation of the dielectric permittivity of the gas from unity,

$$\Delta\Pi_\varepsilon = -\frac{\hbar}{4\pi^2 H^3}\int_0^\infty \varepsilon^*_\xi \frac{\varepsilon-1}{(\varepsilon+1)^3}\, d\xi \simeq -\frac{\hbar}{4\pi^2 H^3}\left(\frac{n^g}{n}\right)\int_0^\infty \varepsilon^2 \frac{\varepsilon-1}{(\varepsilon+1)^3}\, d\xi, \quad (11)$$

since, in order of magnitude, $\varepsilon^*/\varepsilon \sim n^g/n$. Since the integral in (11) is of the same order as the integral in the expression for Π_0, we immediately obtain that $\Delta\Pi_\varepsilon/\Pi_0 \simeq n^g/n$, as was required to be proved.

However, a case is possible in which the positive disjoining pressure of the gas film will be of the same order as the molecular attraction of the plates Π_0, or will even exceed it. This concerns two thin films of thickness a, separated by a layer of air $H \gg a$. As is known, the van der Waals attraction of such films, under the assumption of additivity, is equal to[9]

$$\Pi_0 = -2\pi n^2 \beta_{11}\frac{a^2}{H^5}, \quad (12)$$

where β_{11} is the constant of attraction of the film molecules to one another. Taking

$$u^a(z) = -\frac{\pi n \beta_{11}}{6}\left\{\left[\frac{1}{z^3} - \frac{1}{(z+a)^3}\right] + \left[\frac{1}{(H-z)^3} - \frac{1}{(H-z+a)^3}\right]\right\} \quad (13)$$

and carrying out calculations analogous to those made in deriving formula (9), we obtain, for $H \gg a$,

$$\Delta\Pi \simeq \pi\beta_{12} n n^g \frac{a}{H^4}, \quad (14)$$

whence

$$\frac{\Delta\Pi}{\Pi_0} = \frac{1}{2}\left(\frac{n^g}{n}\right)\left(\frac{\beta_{12}}{\beta_{11}}\right)\left(\frac{H}{a}\right). \quad (15)$$

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* Since $A = 2n\alpha$ is the van der Waals attraction constant of two condensed bodies ([8]), then, according to (9)

Thus, for $H > H_0$, where $H_0 = 2a\left(\frac{\beta_{11}}{\beta_{12}}\right)\left(\frac{n}{n^g}\right)$, the positive disjoining pressure of the gas film becomes greater than the molecular attraction of the plates to one another; moreover, the total disjoining pressure $\Pi = \Pi_0 + \Delta\Pi$ reaches a maximum

$$\Pi_m = \frac{1}{5} n n^g \beta_{12} \frac{a}{H_m^4} \quad \text{for} \quad H_m = \frac{5}{2} H_0. \tag{16}$$

However, since at atmospheric pressure $n/n^g \simeq 10^3$, and the film thickness is always greater than $(50 \div 100)$ Å, H_m is sufficiently large and, correspondingly, Π_m is very small. Only if $\beta_{12} \simeq 10^3 \beta_{11}$ can the effect be significant, since $H_0 \simeq a$. Therefore the possibility of explaining in this way, for example, the noncoalescence of soap bubbles enclosed one inside another for a long time—a phenomenon observed by Dewar—remains open to question.

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Note: Figure translations are in progress. See original paper for figures.