

# Effect of thin surface films on the van der Waals interaction of macroscopic objects and on the properties of liquid films

Yu. S. Barash

*P. N. Lebedev Physics Institute, Academy of Sciences of the USSR*

(Submitted 30 January 1987)

*Pis'ma Zh. Eksp. Teor. Fiz.* **45**, No. 6, 294–296 (25 March 1987)

Under certain conditions thin surface films are found to have a strong effect on the van der Waals interaction of macroscopic objects and on the properties of the wetting liquid films. The theoretical results found in this study permit a direct experimental study.

In the case of thin films, the functional dependence of the van der Waals interaction on the distance is linked, to a greater extent than is usually the case, with their particular properties and, in particular, with the collective effects occurring in them. A summation of pairwise van der Waals interaction of atoms that form two thin films separated a distance  $l$  from each other shows that the interaction energy of the thin films is proportional to  $l^{-4}$  if the retardation is disregarded. At the same time, as Tan and Anderson<sup>1</sup> have noted, analysis of a simple model for electron gas shows that the van der Waals attraction energy of two thin metallic films under similar conditions decreases with the distance much slower, specifically as  $l^{-5/2}$ . Of importance here is the particular nature of the dispersion  $\omega(k)$  for the long-wave plasma waves in 2D metals (the situation is similar for 1D metals<sup>1,2</sup>).

In the present experiments we analyzed the van der Waals interaction in a system shown schematically in Fig. 1. We describe below two special cases which are amenable to a direct experimental study. A full account of the study will be published elsewhere.<sup>3</sup>

Working from the results of the general theory of van der Waals forces, we can show that the behavior of the van der Waals interaction in objects with a thin film depend essentially on the difference between the dielectric constant  $\epsilon_2(i\tilde{\omega})$  of a given film and the dielectric constants,  $\epsilon_1(i\tilde{\omega})$  and  $\epsilon_3(i\tilde{\omega})$ , of the media adjacent to it in the characteristic range of the imaginary frequencies. An important function here is performed by the dimensionless parameter

$$\frac{a}{l} \gamma(i\tilde{\omega}) = \frac{a}{l} \frac{[\epsilon_2(i\tilde{\omega}) - \epsilon_1(i\tilde{\omega})][\epsilon_2(i\tilde{\omega}) - \epsilon_3(i\tilde{\omega})]}{\epsilon_2(i\tilde{\omega})[\epsilon_1(i\tilde{\omega}) + \epsilon_3(i\tilde{\omega})]}, \quad (1)$$

where  $l$  is the distance between the film and another object, and  $a$  is the thickness of a thin film ( $a \ll l$ ). If the condition  $\epsilon_2(i\tilde{\omega}) \sim \epsilon_1(i\tilde{\omega})$  or  $\epsilon_2(i\tilde{\omega}) \sim \epsilon_3(i\tilde{\omega})$  is satisfied, we will have  $a|\gamma(i\tilde{\omega})|/l \ll 1$ . Only the first terms of the perturbation theory in powers of the parameter  $a/l$  will then be the important terms in the description of the interaction. On the other hand, each one of the cases  $\epsilon_2(i\tilde{\omega}) \gg \epsilon_{1,3}(i\tilde{\omega})$ ,  $\epsilon_2(i\tilde{\omega}) \ll \epsilon_{1,3}(i\tilde{\omega})$  has a range of distances where  $a|\gamma(i\tilde{\omega})|/l \gtrsim 1$  and where the analysis cannot be restricted

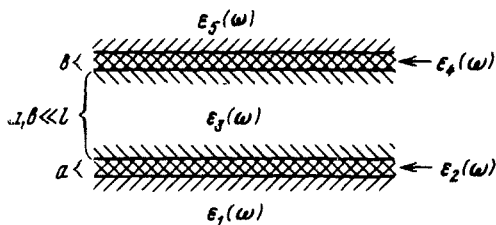


FIG. 1.

to taking account of a finite number of perturbation-theory terms in power of  $a/l$ .

The inequality  $a|\gamma(i\tilde{\omega})|/l \gtrsim 1$  usually holds for thin metallic films surrounded by dielectric media. This circumstance should be taken into account, for example, in the determination of the van der Waals interaction of two identical macroscopic dielectric solids which have thin metallic films at the surface ( $a = b \ll l$ ) and which are separated by an empty planar gap ( $\epsilon_3 = 1$ ). For  $T \ll \hbar\tilde{\omega} \ll \hbar c/l$  the behavior of the dielectric constants in the important region on the upper imaginary frequency axis can be described by the simple expressions  $\epsilon_{1,5}(i\omega) = 1 + \Omega_1^2/(\omega^2 + \omega_1^2)$  and  $\epsilon_{2,4}(i\omega) = 1 + \Omega_p^2/\omega^2$ . Here  $\tilde{\omega} \sim (a/l)^{1/2}\omega_1\Omega_p/(2\omega_1^2 + \Omega_1^2)^{1/2}$ . For the interaction energy of the solids corresponding to a unit contract area we thus find

$$E_S = -\frac{\hbar}{64\sqrt{2}\pi l^2} \frac{\Omega_1^4}{(2\omega_1^2 + \Omega_1^2)^{3/2}} \left[ 1 + 3 \left( \pi \frac{a}{l} \right)^{1/2} \frac{\Omega_p \omega_1^3 (\omega_1^2 + 2\Omega_1^2)}{\Omega_1^4 (2\omega_1^2 + \Omega_1^2)} \right]. \quad (2)$$

An important point is that the ratio of the second term to the first term here need not be small at all. If, for example, we tentatively set  $l = 10a$  and  $\Omega_1 \cong 1.5\omega_1$ , this ratio will be roughly  $\Omega_p/2\Omega_1$ . The effect of thin metallic films on the van der Waals interaction of insulators thus differs qualitatively and quantitatively from the effect produced by insulating layers of the same thickness. This effect becomes more pronounced with increasing ratio of the plasma frequency of the metal to the frequency which characterizes the spectrum of the insulating objects. The corresponding increment in the energy can easily amount to 100% of the interaction between the insulating objects if there are no metallic films on their surfaces.

The presence of a thin metallic film on the insulating substrate leads to the following increment in the chemical potential of particles in a liquid insulating film of thickness  $l$  at a given surface:

$$\Delta_2\mu(l) = -\frac{m}{\rho} \frac{15\hbar\Omega_p a^{1/2}}{128\sqrt{2}\pi l^{7/2}} \frac{\omega_3\omega_1^3(\omega_3^2 + \Omega_3^2)\Omega_3^2}{(2\omega_3^2 + \Omega_3^2)(2\omega_1^2\omega_3^2 + \omega_1^2\Omega_3^2 + \omega_3^2\Omega_1^2)^{3/2}}. \quad (3)$$

Here  $\rho$  is the mass density, and  $m$  is the mass of an individual molecule (or atom) in a simple, one-component liquid; the dielectric constant of vapor is assumed to be unity ( $\epsilon_4 = \epsilon_5 = 1$ ) and the dielectric constants of the substrate and film are given by  $\epsilon_{1,3}(i\omega) = 1 + \Omega_{1,3}^2/(\omega^2 + \omega_{1,3}^2)$ . In the absence of the surface layer of a metal we have  $\Delta_2\mu(l) = m\hbar\tilde{\omega}/\rho 8\pi^2 l^3$ . The expression for  $\tilde{\omega}$  in terms of the dielectric constants

$\epsilon_1(i\omega)$  and  $\epsilon_3(i\omega)$  is given in Ref. 4. It follows from a comparison of the values  $|\Delta_2\mu(l)|$  and  $|\Delta_1\mu(l)|$  that they may be of the same order of magnitude, even if the dielectric constants  $\epsilon_1(i\omega_0)$  and  $\epsilon_3(i\omega_0)$  differ appreciably. If  $\epsilon_1(i\omega_0) < \epsilon_3(i\omega_0)$ , the sign of  $\Delta_2\mu(l)$  will be different from that of  $\Delta_1\mu(l)$ , and the thin metallic film at the insulating surface will, due to the van der Waals forces, stabilize the liquid polymolecular insulating film, which would otherwise be unstable. The thin metallic film on the vertical insulating wall may lead to a marked change in the profile of the insulating liquid which wets this wall [consistent with the relation  $\Delta_1\mu(l) + \Delta_2\mu(l) + mgh = 0$ , where  $h$  is the height above the bulk liquid].

Thin films also have an inordinately strong effect on the van der Waals interaction, which occurs under the condition  $\epsilon_2(i\tilde{\omega}) \gg$  (or  $\ll$ )  $\epsilon_{1,3}(i\tilde{\omega})$ , in several other cases.<sup>3</sup> This involves not only thin metallic films which adjoin insulating media but also thin insulating films surrounded by metallic media. The temperature-induced contribution to the van der Waals interaction is modified markedly for thin layers of polar (or nonpolar) dielectric materials which are adjacent to nonpolar (polar, respectively) media. Barash<sup>3</sup> studied the interaction of insulating films with metallic films and the interaction of atoms with thin films.

I wish to thank V. L. Ginzburg and L. P. Pitaevskiĭ for a discussion of this study and for useful comments.

<sup>1</sup>S. L. Tan and P. W. Anderson, Chem. Phys. Lett. **97**, 23 (1983).

<sup>2</sup>D. B. Chang, R. L. Cooper, J. E. Drummond, and A. C. Young, Phys. Lett. **A37**, 311 (1971).

<sup>3</sup>Yu. S. Barash, in Problems of Theoretical Physics and Astrophysics (L. V. Keldysh and V. Ya. Fainberg, editors), Nauka, Moscow, No. 4, p. 77.

<sup>4</sup>I. E. Dzyaloshinskiĭ, E. M. Lifshitz, and L. P. Pitaevskiĭ, Usp. Fiz. Nauk **73**, 381 (1961) [Sov. Phys. Usp. **4**, 153 (1961)].

Translated by S. J. Amoretty