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Calculation of van der Waals interactions in free liquid films from Lifshitz theory

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With 2 figures

The general equation of *Dzyaloshinskii, Lifshitz* and *Pitaevskii* (1) enables us to calculate the van der Waals force per unit area (the disjoining pressure Π) between two identical semi-infinite media (of substance 1) devided by a plane parallel film (of substance 2) with thickness h. The use of the general equation is possible when the dependence of the dielectric susceptibility ε on the imaginary frequency $i\xi$ ($0 < \xi < \infty$) for the substances (1) and (2) is known. *Ninham* and *Parsegian* (2) calculate $\varepsilon(i\xi)$ for $0 < \xi < 10^{16}$ rad/s from a resonance formula and for $10^{17} < \xi < \infty$ – from a plasma formula. The application of the above procedure to the general equation does not give the precision sought for, in the case of free films ($\varepsilon_1 = 1$), because it needs interpolation in $\varepsilon(i\xi)$ in the region $10^{16} < \xi < 10^{17}$ (3). For small and great values of h the limiting expressions $\Pi = -K/h^3$ and $\Pi = -B/h^4$ respectively, where K and B are characteristic constants for the interacting media, are often employed (141). Our purpose is – using some known approximations and the empirical dependence (5)

$$\bar{\Delta} = [\varepsilon_2(i\xi) - 1]/[\varepsilon_2(i\xi) + 1] = a.e^{-b\xi} \qquad [1]$$

(a and b are empirical constants) – to derive a relatively simple expression for the disjoining pressure in free films, valid for arbitrary thickness. In fig. 1 eq. [1] is tested for H_2O and C_6H_6 (the values of ε are calculated from spectral data and the resonance and plasma formulae). It is clear that in a wide frequency range this dependence is followed with enough accuracy. Moreover, the interpolation is no more arbitrary: with only one analytical expression for $\bar{\Delta}(\xi)$ almost all frequency regions (except the very low frequencies $\xi < \xi_m$) are described – those for which relatively reliable experimental or theoretical data exist and the region $10^{16} < \xi < 10^{17}$ rad/s, where such data are not available.

The dependence of Π on h can be written in the form of the Hamaker law (6):

a) $\Pi(h,T) = -A(h,T)/6\pi h^3$

b) $A(h,T) \approx \dfrac{3}{4} kT \left[\bar{\Delta}_0^2 + 2 \sum_{n=1}^{\infty} \bar{\Delta}^2 \left(1 + r_n + \dfrac{r_n^2}{2}\right) . e^{-r_n} \right], \qquad [2]$

where $\bar{\Delta}_0 = \bar{\Delta}(\xi = 0)$, $\xi_n = 2\pi k T n/h$, $r_n = 2h\varepsilon_2^{\frac{1}{2}} \xi_n/c$, $A(h,T)$ is the so-called Hamaker function, $2\pi\hbar$, *k*,

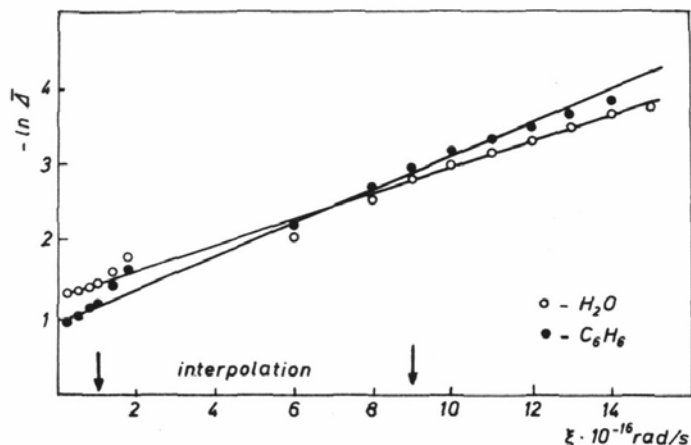Fig. 1. Test of the empirical equation [1] for H_2O and C_6H_6.

T and c are respectively *Planck*'s and *Boltzmann*'s constants, absolute temperature and velocity of light in vacuo.

If in the region $\xi > \xi_m$, where [1] holds, we replace the summation on n by integration on ξ and in the expression for r we replace $\varepsilon_2^{\frac{1}{2}}$ by its mean value $\overline{\varepsilon_2^{\frac{1}{2}}}$ in the integration interval, from [2] we obtain:
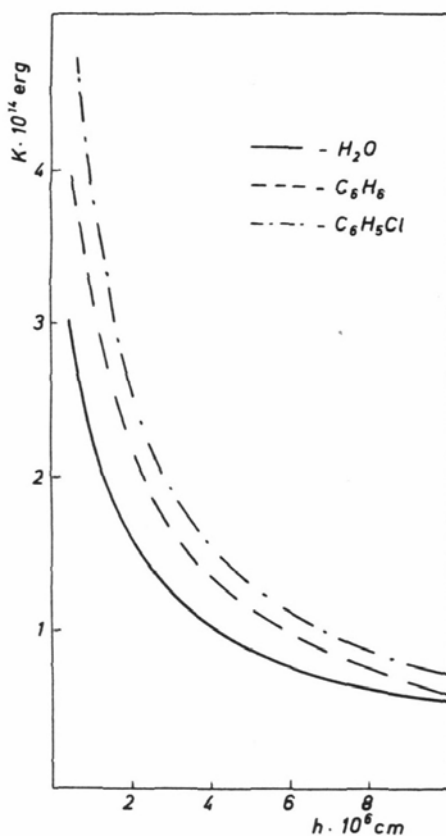

Fig. 2. "Van der Waals–Hamaker functions" $K(b) = A(b)/6\pi$ at 20 °C for free films of H_2O, C_6H_6 and C_6H_5Cl calculated from eq. [3].

$$A(b,T) = A_{m-1} + \frac{3\hbar}{4\pi} a^2 \frac{e^{-(2b+C)\xi_m}}{2b+C}$$
$$\cdot \left[1 + C\xi_m + \frac{C^2\xi_m^2}{2} \right.$$
$$\left. + \frac{C(1+C\xi_m)}{2b+C} + \frac{C^2}{(2b+C)^2} \right]; \quad [3]$$

where $C = 2\hbar\overline{\varepsilon_2^{\frac{1}{2}}}/c$ and A_{m-1} is given by [2b] with upper summation limit $n = m - 1$. The above method was applied to calculate $K(b,T) = A(b,T)/6\pi$ for free films of H_2O, C_6H_6 and C_6H_5Cl, which have been experimentally investigated. The functions $K(b)$ at 20 °C so obtained are plotted in fig. 2.

It is experimentally found that the isotherms $\Pi(b)$ have the form $\Pi = -K/b^3$ ($K = (2 \pm 1).10^{-14}$erg) for H_2O (171) and $\Pi = -B/b^4$ for C_6H_6 ($B = 1,9.10^{-19}$erg. cm) and C_6H_5Cl ($B = 4,9.10^{-19}$ erg.cm) (181) in the thickness range 300–600 Å. Our calculations showed that the above limiting expressions do not appear in a pure form for $50 < b < 1000$ Å. In order to compare our results with the experiment and with the limiting values $B = 0,56.10^{-19}$ erg.cm for C_6H_6 and $B = 0,6.10^{-19}$ erg.cm for C_6H_5Cl obtained by *Churaev* (4), the functions $\Pi(b)$ calculated by us were plotted in coordinates Π vs.b^{-3} for H_2O and Π vs.b^{-4} for C_6H_6 and C_6H_5Cl. In the range $300 < b < 600$ Å these functions were approximated by straight lines whose slopes were $1,4.10^{-14}$ erg for H_2O, $0,5.10^{-19}$ erg.cm for C_6H_6 and $0,6.10^{-19}$ erg.cm for C_6H_5Cl. These values agree well with the theoretical calculation of B of *Churaev* and with the experimental results for H_2O. However in the case of C_6H_6 and C_6H_5Cl the discrepancy between theory (both *Churaev*'s and ours) and experiment is considerable. This is probably due to the fact that the experimental values for H_2O films are determined by measuring the equilibrium thicknesses, while for C_6H_6 and C_6H_5Cl films the dynamic method, having a lower precision, has been used.

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