The effect of adsorbed layers on van der Waals forces in thin liquid films

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With 3 figures and 2 tables

Introduction

References (1–6) developed the theory of van der Waals forces acting in an interlayer found between flat surfaces coated with adsorbed layers.

As in a simpler case, i.e., in the absence of adsorbed layers, both the microscopic and macroscopic theories yield similar expressions for \( \Pi_M \), differing only in the calculation method applied and in the numerical value of constants \( C, D \), and \( E \). The first theoretical works (1–3) developed a microscopic approach yielding the following expressions:

\[
C = (\sqrt{A_{33}} - \sqrt{A_{22}})^2
\]

\[
D = 2(\sqrt{A_{33}} - \sqrt{A_{22}})(\sqrt{A_{22}} - \sqrt{A_{11}})
\]

\[
E = (\sqrt{A_{22}} - \sqrt{A_{11}})^2
\]

where \( A_{ii} \) are Hamaker constants describing the interaction of similar bodies “i” in vacuum. The calculations were done on the basis of the known Hamaker equation (7) describing by means of the constants of pairwise interaction in vacuum the interaction of bodies “i” and “k” through medium “l”:

\[
A_{ik} = A_{ik} - A_{il} - A_{kl}\]

It was also assumed that \( A_{ik} \sim \sqrt{A_{il}A_{kk}} \).

Ninham and Parsegian (4) calculated \( \Pi_M(h) \) by using a variant of the macroscopic theory of dispersion forces (8, 9), which was developed by van Kampen et al. (10). In the first approximation, while neglecting the expansion terms of higher orders, they derived for constants \( C, D \), and \( E \) formulas wherein the Hamaker constants \( A \) were essentially substituted by their corresponding macroscopic expressions:

\[
C = A_{232} = \frac{3}{4\pi} \int_A^\infty d\xi \int_0^\infty d\zeta \]

\[
D = -2A_{123} = \frac{3}{2\pi} \int_0^\infty A_{21} A_{32} d\xi
\]
\[ E = A_{121} = \frac{3\hbar}{4\pi} \int A_{21}^2 d\xi. \]  \[ \text{(4)} \]

Here \( \hbar \) is the Planck constant; \( A_{ik} = (\varepsilon_i - \varepsilon_k) / (\varepsilon_i + \varepsilon_k) \), wherein \( \varepsilon = \varepsilon(i\xi) \) are the dielectric susceptibilities on an imaginary axis of frequencies \( \omega = i\xi \) \( (8, 9) \).

A new approach \( (5, 6) \) has recently been applied to solving the same problem. It involved an image charge method for calculating an energy change in the fluctuation electromagnetic field, which results from the effect of the interface of media with different dielectric susceptibilities. This approach yielding for the simplest case of a flat slit a solution coinciding with that obtained earlier \( (8, 9) \), proved to be especially convenient when calculating the interaction in multilayer systems.

For a system which is represented in fig. 1a the Langbein method \( (6) \) yields:

\[ C = \frac{3\hbar}{4\pi} \int A_{32}^2 d\xi \]

\[ D = \frac{6\hbar}{\pi} \int \frac{\varepsilon_2\varepsilon_3}{(\varepsilon_2 + \varepsilon_3)^2} A_{32} A_{21} d\xi \]

\[ E = \frac{12\hbar}{\pi} \int \frac{\varepsilon_2^2\varepsilon_3^2}{(\varepsilon_2 + \varepsilon_3)^4} A_{21}^2 d\xi. \]  \[ \text{(5)} \]

These expressions were obtained in the first order of reflection \( (6) \). Taking into account the second order of reflection results in certain additions to coefficients \( C \) and \( D \), and the new term \( F/(2\hbar + \delta)^3 \) in eq. \[1\].

The solution obtained by Israelachvili \( (5) \) when retaining square terms \( A \) for \( C \), \( D \), and \( E \), gives expressions coinciding with those obtained earlier \( (4) \) (cf. eq. \[4\]).

Comparing eqs. \[4\] and \[5\] one easily notices these assume identical form at \( \varepsilon_2 = \varepsilon_3 \), that is, when the properties of adsorbed layers 2 not much differ from those of a liquid interlayer 3. At \( \varepsilon_2 \neq \varepsilon_3 \) the Langbein method \( (6) \) yields, in comparison with the earlier obtained solutions, some new information on the effect of adsorbed layers on the disjoining pressure acting in a 'at slit.

Results and discussion

It has been of interest to compare the calculation results for a number of specific cases, in order to assess eventual discrepancies in the evaluation of dispersion forces by using different methods. The following cases have been analyzed:

1. An interlayer of water 3 between solid surfaces 1 coated with adsorbed layers 2 (fig. 1a);
2. A free film of water 3 with adsorbed layers 2 (fig. 1b);
3. A wetting film of water 3 on a solid surface 1 complete with an adsorbed layer 2 near to the solid surface (fig. 1c), or at the liquid-gas interface (fig. 1d).

In the case of water the dependence \( \varepsilon_2(i\xi) \) was used, as derived by the Ninham and Parsegian method \( (4) \) in ref. \( (11) \). The Hamaker constant was found to be \( A_{33} = 5.1 \cdot 10^{-15} \) erg. Calculations were done for the solid dielectric (quartz) and metal (gold) surface. The dependence \( \varepsilon_1(i\xi) \) for quartz was calculated earlier using real absorption spectra; \( A_{11} = 7.9 \cdot 10^{-13} \) erg \( (12) \). For gold \( \varepsilon_1(i\xi) \) were derived in ref. \( (13) \); \( A_{11} = 4.1 \cdot 10^{-12} \) erg.

Two types of adsorbed layers were considered, viz., a) surfactant layers, and b) boundary layers of water exhibiting a structure modified as compared with that of bulk water. In the first case, there were used spectral characteristics of hydrocarbon (tetradecane), which had been calculated earlier \( (12) \); \( A_{21} = 4.8 \cdot 10^{-13} \) erg. In the second case, it was assumed that characteristic infrared frequency of a boundary phase was shifted into the low-frequency region of spectrum \( (14) \). This assumption corresponds \[ as also in the case of decreasing water temperature \( (15) \] to a strengthening of the intermolecular H-bond. Simultaneously, an increase in the coefficient of absorption within the same spectral range was taken into account \( (15, 16) \). The degree of structural modifications, i.e. the shifting of frequency and the increase in absorption by 10%, is here chosen arbitrarily \( 1 \). In the further course, therefore, only the qualitative consequences of the change in the spectral characteristics of boundary phases will be considered.

Since the values of the statical dielectric susceptibilities of boundary layers are markedly reduced \( (17) \), one may disregard the contribution of rotational relaxation. Unfortunately, any data on a change in the ultraviolet spectrum for the boundary layers of water so far are unavailable. Therefore, in contrast to the earlier calcu-