Van der Waals forces for mica and quartz: calculations from complete dielectric data

By D. Chan† and P. Richmond

Unilever Research Port Sunlight Laboratory, Unilever Limited,
Port Sunlight, Wirral, Merseyside L62 4XN

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By using dielectric data, based on electron energy loss spectroscopy, the Lifshitz–van der Waals force for interacting mica and quartz plates is calculated. Comparisons with experiment and earlier theoretical calculations are made. In the non-retarded region (≤10 nm) experimental values for the Hamaker constant for mica are up to 50% higher than those obtained from Lifshitz theory. The agreement between theory and experiment is much better for distances of ca. 100 nm. Various errors which may be responsible for the disagreement are discussed.

1. Introduction

The theory of van der Waals forces is now well established (Langbein 1974; Mahanty & Ninham 1976; Faragian 1975; Richmond 1975). Theoretical expressions are available for many different geometries and many applications have been made. However, many of these calculations have been made using only partial dielectric data based on a method suggested by Ninham & Faragian (1970). As a result, the calculations, particularly for condensed media interactions, may tend to be in error for separations less than about 5 nm and it is not possible to obtain an accurate value for the Hamaker constant. Fortunately, this situation is being alleviated and optical reflection and electron energy loss methods are now being used to obtain more complete dielectric data for a number of solids and liquids. Recently, such data have been published for mica and quartz (Atkins & Miscell 1972; Buehner 1975; le Calvez, Stephan & Robin 1968). Natural muscovite (KAl$_3$ (AlSi$_2$O$_{10}$) (OH)$_2$), phlogopite KMg$_6$ (AlSi$_2$O$_{10}$) (OH)$_2$, biotite (K(Mg, Fe)$_3$ (AlSi$_2$O$_{10}$) (OH)$_2$) and synthetic fluorophlogopite KMg$_6$ (AlSi$_2$O$_{10}$) (F$_2$) were all found by Buehner to have similar spectra. The van der Waals force between mica and quartz plates has been measured (Tabor & Winterton 1975; Israelachvili & Tabor 1972; Wittmann, Splittgerber & Ebert 1971) and may now be compared with calculations based on this new dielectric data. In addition, we can compare these calculations with previous calculations for mica which used only partial dielectric data (Richmond & Ninham 1972; Lodge 1975).

The paper is set out as follows. In §2 we show how, using the dielectric data, s.
function $\varepsilon(\xi)$ for computation may be obtained. This is compared with earlier approximate expressions. In §3 we present an analysis of our results for the Hamaker functions, power law exponents, etc., for mica. These are then discussed in relation to experiment. In §4 a similar albeit briefer presentation is given for quartz. We close with a short discussion.

2. DIELECTRIC FUNCTIONS

The Lifshitz–van der Waals energy of interaction per unit area for two media 1 and 3 interacting across medium 2 of width $l$ may be written as follows:

$$E(l) = k_BT \sum_{n=0}^{\infty} \int_0^l \frac{d\xi}{2\pi} \left[ \ln \left(1 - A_{123} \rho_{123} \right) + \ln \left(1 - \frac{3}{2} A_{123} \rho_{123} \right) \right],$$

(1)

where $A_{123} = \frac{\varepsilon_{13} \varepsilon_{23} - \varepsilon_{12} \varepsilon_{23}}{\varepsilon_{13} \varepsilon_{23} + \varepsilon_{12} \varepsilon_{23}}$, $A_{12} = \frac{\varepsilon_{1} \varepsilon_{2} - \varepsilon_{1} \varepsilon_{3}}{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}$, $\rho_{123} = \frac{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}$, $\rho_{12} = \frac{\varepsilon_{1} \varepsilon_{2} - \varepsilon_{1} \varepsilon_{3}}{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}$, $\rho_{23} = \frac{\varepsilon_{2} \varepsilon_{3} - \varepsilon_{1} \varepsilon_{3}}{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}$, $\rho_{13} = \frac{\varepsilon_{1} \varepsilon_{3} - \varepsilon_{1} \varepsilon_{2}}{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}$, $\rho_{1} = \frac{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}$, $\rho_{2} = \frac{\varepsilon_{1} \varepsilon_{2} - \varepsilon_{1} \varepsilon_{3}}{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}$, $\rho_{3} = \frac{\varepsilon_{2} \varepsilon_{3} - \varepsilon_{1} \varepsilon_{3}}{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}$, $\rho_{4} = \frac{\varepsilon_{1} \varepsilon_{3} - \varepsilon_{1} \varepsilon_{2}}{\varepsilon_{1} \varepsilon_{2} + \varepsilon_{1} \varepsilon_{3}}$.

where $\xi_n = 2\pi n \lambda T/H$. The underlying physical principles and derivation of this equation can be found in the references referred to at the beginning of §1.

The dielectric permittivities $\varepsilon(\xi)$ are related to the imaginary part of the complex dielectric permittivity $\varepsilon'(\omega)$ evaluated at real frequencies by a Kramers–Kronig relation:

$$\varepsilon'(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\varepsilon''(\omega')}{\omega'^2 - \omega^2} d\omega'.$$

(2)

Usually, it has been assumed that $\varepsilon'$ may be written as a sum of $\delta$ functions:

$$\varepsilon''(\omega) = \sum_{\omega} A_\omega \delta(\omega - \omega),$$

(3)

and from (2) and (3) we have:

$$\varepsilon'(\omega) = 1 + \sum_{\omega} A_\omega \frac{\ln(1 + \frac{\omega}{\omega_0})}{\omega_0}.$$

(4)

This procedure is equivalent to the assumption that $\varepsilon''$ can be decomposed into a sum of sharp absorption peaks centred at some $\omega$, with area $A_\omega$ and half width $A_\omega$ under each peak.

Typically, two terms may be retained and the frequencies identified as say, near infrared and ultraviolet absorption frequencies (\omega_1, \omega_2). Introducing

$$\varepsilon(\omega) = 1 + \sum_{\omega} A_\omega,$$

(5)

$$\varepsilon(\omega) = 1 + A_\omega,$$

(6)

We may now write

$$\varepsilon'(\omega) = 1 + \sum_{\omega} \left(1 - \frac{\omega}{\omega_0} - 1\right),$$

(7)

Clearly $\varepsilon(0)$ is the static dielectric permittivity.

Various methods have been used to obtain $\varepsilon'(\omega)$. For example, if $\omega_1 < \omega_2$ then a so-called Cauchy plot of $1/(\varepsilon(\omega) - 1)$ against $\omega^2$ should yield a straight line in the visible frequency regime where $\varepsilon(\omega)$ is taken as the square of the refractive index at the same frequency. $\varepsilon(\omega)$ is then given by the intercept on the $1/(\varepsilon - 1)$ axis; $\omega_0$ is the intercept on the $\omega^2$ axis. Reasonable values for the van der Waals energy for distances $l \gtrsim 5$ nm have been obtained by such procedures. Below this distance the van der Waals energy becomes sensitive to the details of $\varepsilon(\xi)$ in the near ultraviolet frequency range and equation (7) no longer provides a good representation for $\varepsilon(\xi)$.

For $\xi > \omega_0$, $\varepsilon(\xi) = 1 + \omega_0^2/\xi^2$ where $\omega_0 = (4\pi e^2/m)$. This is a characteristic plasma frequency for the solid, and $n$ is the electron number density in the material. Various interpolation schemes have been used but none resolve the basic uncertainty in the van der Waals energy.

As stated in the introduction a number of authors have recently obtained dielectric data for mica and quartz by using both electron energy loss spectroscopy and optical reflectance techniques. The former gives $\varepsilon'(\omega)$ directly up to 40 eV; the latter yields the refractive index, $n$, and extinction coefficient, $k$, up to about 30 eV from which $\varepsilon(\xi)$ may be derived by using Kramers–Kronig techniques. We shall be concerned here merely with how a function $\varepsilon'(\xi)$ suitable to compute van der Waals energies may be constructed from the measured dielectric data. We may start with the measured values of $\varepsilon'(\omega)$. (Note that this is immediately obtained from $n$ and $k$ since $\varepsilon' = 2\pi n k$.) One point to note first is that in order to obtain $\varepsilon'(\xi)$ from $\varepsilon'(\omega)$ using equation (2) one strictly needs $\varepsilon'(\omega)$ measured for all frequencies. In practice only measurements up to some cut off frequency, $R$, are possible. Knowledge of the error in the resulting expression for $\varepsilon'(\xi)$ is therefore necessary.

This error is

$$\Delta\varepsilon'(\xi) = \frac{2}{\pi} \int_0^\infty \frac{\varepsilon''(\omega)}{\omega^2 + \xi^2} d\omega.$$
interpolation over the range $10^8$-$10^9 \text{rad/s}$ between the Lorentzian and this plasma curve will result in a gross overestimate for $\varepsilon(\xi)$ and the resulting van der Waals energy. It has been suspected for some time that this is the case (Richmond & Ninham 1971).

The faint curve shows a plasma curve $\varepsilon(\xi) = 1 + \omega_p^2/\xi^2$ calculated by using a lower plasma frequency, $\omega_p = 2.59 \times 10^8 \text{rad/s}$, which fits to the high frequency end of the exact curve. Clearly an interpolation between the Lorentzian and the latter plasma curve provides a better representation of the true data. However all this can only be said after the true data had been obtained. If the exact data are not available and one is forced into using a Lorentzian type form, the interpolation scheme is best abandoned. Such an approach for vacuum interactions at least gives a lower bound for the van der Waals energy.

To obtain the Lifshitz–van der Waals energy given by equation (1), we can in principle use the Kramers–Kronig relation, equation (2), to evaluate $\varepsilon(\xi)$ each time it is required. In practice, for convenience and economy of computer time, we can fit $\varepsilon(\xi)$ by an appropriate function over the frequency range which contributes to the interaction energy. To this end we adopt the Lorentzian formula

$$\varepsilon(\xi) = 1 + \frac{\varepsilon_m - 1}{1 + (\xi/\omega_m)^2}.$$  \hspace{1cm} (11)

Here $\varepsilon_m$ is the near visible dielectric permittivity (cf. equations (6) and (7)) taken to be 2.45. This corresponds to the value of $\varepsilon(\xi)$ at $\xi = 0$ as given by the Kramers–Kronig relation in equation (1). The remaining constants $\omega_m$ and $g$ can be obtained from the slope and intercept of a plot of $(1/\xi)(\varepsilon_m - 1)/(\varepsilon(\xi) - 1)$ against $\xi$ where the values of $\varepsilon(\xi)$ are obtained from equation (1). We have made such a plot in the range $\xi = 0.5 \times 10^8 \text{rad/s}$ to $1.0 \times 10^9 \text{rad/s}$ and found for the constants

$$\omega_m = 2.38 \times 10^8 \text{rad/s},$$

$$g = 4.89 \times 10^8 \text{rad/s}.$$  

With these parameters, equation (11) agrees with the 'exact' values of $\varepsilon(\xi)$ to better than 2% for $\xi < 1.0 \times 10^9 \text{rad/s}$ and to better than 2% for $\xi > 1.0 \times 10^9 \text{rad/s}$.

At high frequencies, equation (11) assumes the form

$$\varepsilon(\xi) = 1 + \omega_p^2/\xi^2,$$

where the plasma frequency can be identified as $\omega_p(\varepsilon_m - 1)$. From the given parameters we obtain $\omega_p = 2.85 \times 10^8 \text{rad/s}$ which is equivalent to an energy of 18.8 eV. This is in good agreement with the experimental value found to be $18.8 \pm 0.5 \text{eV}$ (Atkins 1972). We must emphasize that this is merely an approximation to the function $\varepsilon(\xi)$. Clearly it does not reproduce the fine structure in $\varepsilon'(\omega)$ nor is it the aim of such a procedure to mimic the behaviour of $\varepsilon'(\omega)$. Obviously, it is possible to construct a function to fit $\varepsilon(\xi)$ as well as the real and imaginary parts ($\varepsilon'(\omega)$, $\varepsilon''(\omega)$) of the complex dielectric permittivity on the real frequency axis. But in view of the
accuracy of equation (11) such efforts are not worthwhile until more accurate experimental data are available.

Finally we comment on the contribution to \( \varepsilon(\omega) \) from the microwave and infrared regions of the electromagnetic spectrum. In the absence of reliable infrared data for mica a single Lorentzian type contribution to \( \varepsilon(\omega) \) was included by Richmond and Ninham (1972) and Lodge (1975). Such a term may also be included in our data. The static dielectric constant equals 5.4 and this may be included in the Lifshitz calculation by setting \( \varepsilon(0) = 5.4 \) in the zero frequency term rather than 2.45 which is obtained from the visible/ultraviolet data. It turns out that for the systems considered in this paper the result is completely insensitive to the accuracy of the measurements to the details of the infrared data although if an intervening medium is present this may not still be the case. For very large values of the separation distance, \( l \), the term for which \( \varepsilon = 0 \) in equation (1) contributes significantly to the interaction energy. The remaining terms are damped by retardation effects (Ninham and Parsegian 1970; Richmond, Ninham and Ottewill 1973).

3. VAN DER WAALS CALCULATIONS FOR MICA

By means of the procedure given in the previous section, we have computed the Lifshitz–van der Waals interaction energy and force for two mica half spaces interacting across a vacuum. The results are given in Table 1 and Figure 2 in terms of Hamaker functions \( A \). These are conventionally expressed in units of \( k_B T \) \( (T = 300 \text{ K} \text{ and } k_B T = 4.14 \times 10^{-20} \text{ J}) \). Thus we define the energy Hamaker function \( A_E \) where

\[
E(l) = -A_E(l)/12\pi l^3.
\]

Similarly one may define the force Hamaker function \( A_F \):

\[
F(l) = -\frac{dE(l)}{dl} = -A_F(l)/6\pi l^3.
\]

Higher derivatives may also be defined, thus

\[
F'(l) = \frac{d^2F(l)}{dl^2} = A_{F'}(l)/6\pi l^4,
\]

\[
F''(l) = \frac{d^3F(l)}{dl^3} = -2A_{F''}(l)/9\pi l^5.
\]

The Hamaker functions defined in this manner should all tend to the same constant value in the non-retarded limit \( l \to 0 \). We see from Figure 2 that the higher derivative functions tend to remain effectively non-retarded for higher values of \( l \) and also they then tend to deviate from the non-retarded value faster. None of the functions ever become fully retarded since at large distances, the non-retarded zero frequency term begins to dominate and the Hamaker functions tend to a new constant value

\[
A(\infty) = \frac{3}{4} k_B T^2 \int_0^\infty dx \ln \left( 1 - \frac{\varepsilon(0)-1}{\varepsilon(0)+1} e^{-x} \right) = 0.38 k_B T^2,
\]

where \( \varepsilon(0) = 5.4 \).

<table>
<thead>
<tr>
<th>( l/\mu m )</th>
<th>( \text{Hamaker function, } (k_BT) )</th>
<th>( l/\mu m )</th>
<th>( \text{Hamaker function, } (k_BT) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>21.84</td>
<td>17.8</td>
<td>12.65</td>
</tr>
<tr>
<td>0.178</td>
<td>21.84</td>
<td>21.5</td>
<td>9.14</td>
</tr>
<tr>
<td>0.210</td>
<td>21.81</td>
<td>56.2</td>
<td>6.10</td>
</tr>
<tr>
<td>0.253</td>
<td>21.74</td>
<td>100.0</td>
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<tr>
<td>1.0</td>
<td>21.55</td>
<td>177.8</td>
<td>2.39</td>
</tr>
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<td>1.78</td>
<td>21.11</td>
<td>316.0</td>
<td>1.50</td>
</tr>
<tr>
<td>5.16</td>
<td>20.23</td>
<td>562.0</td>
<td>0.97</td>
</tr>
<tr>
<td>5.62</td>
<td>18.57</td>
<td>1000</td>
<td>0.67</td>
</tr>
</tbody>
</table>

For \( \varepsilon(0) = 3.4 \), the contribution from the term for which \( \varepsilon = 0 \) to the Hamaker function is \( 0.38k_BT \); for \( \varepsilon(0) = 2.45 \), (i.e. the optical contribution only) the zero frequency term contribution is \( 0.14k_BT \). The former value represents \( > 2.4 \% \) of the total.

**Table 1. Computed values for the force Hamaker function of mica which is measured in force balance experiments (Appendix).**

**Figure 2. Theoretical Hamaker functions \( A_E, A_F, A_{F'}, \) and \( A_{F''} \) for mica and experimental points \( \bullet \), Israelachvili & Tabor (jump method); \( \bigcirc \), Tabor & Winterton (jump method); \( \square \), Israelachvili & Tabor (resonance method).**

the total value at \( l = 10 \text{ nm} \) and increases to ca. 10% at \( l = 100 \text{ nm} \). When \( l = 1000 \text{ nm} \) this term is ca. 0.5% of the total value although the total force is very small at this large separation. The power law indices (Figure 3) give a fairly direct measure of the deviations from the ideal non-retarded situation.
The energy index \( n_p(l) \) is defined fitting a power law \( \phi = C/l^{2-n} \) to the curve for the interaction energy \( E(l) \). Choosing \( C \) and \( n \) such that \( \phi \) fits locally the energy \( E(l) \) and its gradient \( F(l) \) we obtain

\[
\frac{\Delta E}{E(l)} = -\frac{n_p(l)}{E(l)}.
\]

One may also define higher order indices by fitting to higher order derivatives e.g. fitting \( \phi \) to the force rather than the energy. Thus,

\[
\frac{\Delta F}{F(l)} = -\frac{n_p'(l)}{F(l)},
\]

\[
\frac{\Delta F'}{F'(l)} = -\frac{n_p''(l)}{F'(l)}.
\]

If the interactions are non-retarded, the r.h.s. of equations (16)–(18) are equal to \( 2 \); if the interactions are retarded, they are \( 3 \). The completely retarded region is never reached because the zero frequency contribution dominates large separation. This is illustrated further by a plot of the so-called ‘B’ parameter defined in terms of the force

\[
B_p = F(l)/l^2.
\]

As before

\[
B_p' = F'(l)/l^{2.5}.
\]

If the interactions are completely retarded than \( B = B_p = constant \). Figure 4 shows that this is not the case; here we have plotted both \( B_p \) and \( B_p' \) over the region which is commonly thought to be retarded. The theoretical value \( B_p = 0.93 \times 10^{-23} J/m \) obtained earlier by Richmond & Ninham was based on a one point fit at large distances of \( \approx 10^5 \) nm. The theoretical value \( B_p' = 0.84 \times 10^{-23} J/m \) obtained by Lodge (1975) was based on an average taken over a range where the energy power low index was a maximum.

To measure van der Waals forces, Israelachvili & Tabor used the jump method for distances \( l \leq 10 \) nm and the resonance method for distances \( l \geq 10 \) nm. It may be shown that the former method measures \( F(l) \) and the latter method measures \( F'(l) \) of flat plates (see appendix). However the accuracy of current experiments is not sufficient to pick up the relatively fine differences between \( F \) and \( F' \). In figure 2 we have superimposed results for the Hamaker function obtained by Tabor and Winterton and Israelachvili and Tabor. In figure 3 we have superimposed a power law index published by Israelachvili and Tabor. In figure 5 we compare our results more directly with the observations of Israelachvili & Tabor. The curves are calculated by using equation (A 5) and represent log (jump distance) against \( K/R \). The latter parameters are defined in the appendix. The solid curve is our theoretical result, the dotted curve shows the asymptotic behaviour of our result in the non-retarded limit. The dashed curve is the line of best fit used by Israelachvili & Tabor to obtain a Hamaker constant \( A \), power law index \( n \). The marked differences between theory and experiment might be due to a number of things.

Firstly the dielectric data could be in error. In order to obtain \( e'(\omega) \) from electron energy loss measurements the data must be processed using Kramer-Kronig methods and a normalization must be effected. To do the latter a value for the free electron number density, \( \alpha \), must be assumed but a number of sum rules are used to check the answer self-consistently.

Maximizing all errors then at the very worst the values for \( e'(\omega) \) could be in error by 15% (Malsell, private communication). The positions of the primary peaks are determined much more accurately. The effect on \( e'(\omega) \) is that the oscillator strength, \( (e^2 - 1) \), in equation (11) carries an error of 15%. We have calculated numerically the resulting error in the Hamaker constant \( A \) and obtain 25% which is not sufficient to account for the observed difference of 50% in the non-retarded region. The difference is less in the retarded regime and here agreement may be obtained within experimental error between theory \( (A_p) \) and experiment (resonance method).
This is shown graphically in figure 2 where the points represent experimental points deduced from measurements by Tabor and his co-workers.

A second possibility for error which occurs in the jump method has been discussed by Israelachvili (1972a) in his Ph.D. thesis. Here the radius of curvature of the cylinders is measured by using an optical method. The radius of curvature required is that the mica cylinders have over the small region where they ultimately come into contact. Constant jumps and creep of the glue layer between the mica and the cylinder cause this region to have a local radius of curvature larger than that obtained from the optical measurement. It is not possible to estimate the difference with any certainty but 20–30% appears possible. This is a systematic error which would revise the experimental data down and agreement within experimental error might then be possible. Such a scaling factor would also bring the power law indices more into agreement. In passing we mention that White, Israelachvili & Ninham (1976) have also suggested the experiments of Israelachvili & Tabor may contain systematic errors of this nature. Clearly more experiments are necessary. It is also important to try and extend the distance range to beyond 100 nm to see if the zero frequency contribution can be observed. At present all one can say is that the agreement between theory and experiment for the $B$ parameter is fortuitous since by coincidence all theoretical values were fitted to the force at 100 nm.

4. VAN DER WAALS CALCULATIONS FOR QUARTZ

A similar analysis as the above was made for quartz (SiO$_4$ tetrahedra crystal structure) by using dielectric data obtained by Buechner (1975) from electron energy loss measurements.

TABLE 2. VAN DER WAALS FORCE PER UNIT AREA FOR QUARTZ COMPUTED USING DIELECTRIC DATA OF BUECHNER

<table>
<thead>
<tr>
<th>$l$ (nm)</th>
<th>$F(l)/(N \cdot m^{-2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>$-4.97 \times 10^4$</td>
</tr>
<tr>
<td>0.178</td>
<td>$-8.83 \times 10^4$</td>
</tr>
<tr>
<td>0.316</td>
<td>$-1.67 \times 10^5$</td>
</tr>
<tr>
<td>0.662</td>
<td>$-2.78 \times 10^5$</td>
</tr>
<tr>
<td>1.0</td>
<td>$-4.91 \times 10^5$</td>
</tr>
<tr>
<td>1.76</td>
<td>$-8.54 \times 10^5$</td>
</tr>
<tr>
<td>3.16</td>
<td>$-1.46 \times 10^6$</td>
</tr>
<tr>
<td>5.02</td>
<td>$-2.38 \times 10^6$</td>
</tr>
<tr>
<td>10.0</td>
<td>$-3.86 \times 10^6$</td>
</tr>
</tbody>
</table>

The dielectric data were analysed in the same way as for mica. We found the approximate function

$$\varepsilon(\xi) = 1 + \frac{c_{sw} - 1}{1 + \xi\omega_0 + \xi^2\omega_0^2}$$

$$\xi = \frac{\omega}{\omega_0}$$

$$\omega_0 = 2.35 \times 10^{14} \text{ rad/s}$$

$$\ln(g) = 8.99 \times 10^{14} \text{ rad/s}$$

The agreement with $\varepsilon(\xi)$ computed from experimental data was as good as that found for mica.

In table 2 we have tabulated the van der Waals force which has been calculated from equation (21).

This leads to a Hamaker constant: $A_p(0) = 22.83 k_BT$. Using dielectric data obtained independently for quarts whose structure is unspecified Wittman, Splittgerber & Eberk (1971) obtain $A_p(0) = 15.75 k_BT$. In doing their theoretical calculations they use an expression for $F(l)$ which is only valid at zero temperature. Thus they obtain an unambiguous value for the retarded parameter $B = 5.87 \times 10^{-33}$ J m.

Our results vary in the same manner as mica and as we have shown such a parameter is not meaningful for quartz. More detailed experiments taken over a broader distance range are necessary before a comparison as detailed as that for mica is possible.
5. Discussion

We conclude with a few general comments. Our results indicate that certain parameters frequently used to characterise the results are not in fact firmly based. Specifically it has been common to assume beyond about 10 nm the forces are retarded and that \( F = -B/i^4 \) where \( B \) is a constant. According to theory this is not true, \( B \) varies quite strongly with \( i \) and the forces may in fact never be retarded. Therefore any value quoted for \( B \) is meaningless unless it is stated at which value of \( i \) it was calculated. It is better merely to quote either the values obtained for the energy, force, etc., or express them in the form of a Hamaker function \( A(i) \). This has the advantage that it may be illustrated graphically on a log-log plot rather than a log-log plot. The latter are well known to reduce errors and differences between sets of data. From figure 2 \( A_p(i) \) and \( A_p(i) \) differ by ca. 13% at \( i = 20 \) nm therefore as more accurate methods become available the experimentalist should be sure that he compares his results with the appropriate van der Waals function.

One of us (D.C.) wishes to thank CSIRO (Australia) for a fellowship during the period this work was done. P.R. thanks D. L. Misell for a useful discussion and access to A. J. Atkins' Ph.D. thesis. We are also grateful to Professor D. Tabor, F.R.S., for helpful comments and suggestions.

References

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Appendix

Full details of the apparatus and experimental procedures used by Israelachvili & Tabor are given in their papers (1972). Our aim here is simply to reformulate the equations which describe the force balance and show how different Hamaker functions are measured with the two techniques.

(a) Jump method

In this method, the spring constant, \( K \), of a support is adjusted until the restoring force is balanced by the van der Waals force, \( P \), with another support. At equilibrium, the total force is

\[
F = P(i) - Kx = 0.
\]

The jump occurs where \( \delta F = P(i) \delta l - K \delta x = 0 \).

But \( \delta l = -\delta x \); therefore the jump distance, \( l_p \), is given by

\[
K = -P(i_p).
\]

Now if we use the Derjaguin method to relate the van der Waals forces for crossed cylinders (the geometry used in the experiments) to the van der Waals interaction per unit area for flat plates we obtain

\[
P(i) = 2\pi R P(i),
\]

where \( R \) is the radius of each mica cylinder. From equations (13), (A 3) and (A 4) we have

\[
P(i) = 2\pi R P(i) K / K,
\]

which is the expression we used to plot the jump method data on figure 2.

(b) The resonance method

In this method the spring constant is fixed and the piezo electric effect is used to achieve resonant vibrations of the two supports. In this case the equation of motion which determines the relative motion of the supports is

\[
M \ddot{x} + \gamma \dot{x} + K(x + \delta x e^{i\omega t}) + P(i + \delta l e^{i\omega t}) = 0,
\]

where \( \gamma \) is a viscous damping factor and \( \omega \) is the frequency of vibration in rad/s. Expanding (A 6) and noting that at equilibrium \( P(i) = Kx \) we obtain

\[
\delta x = \frac{\delta l P(i)/m}{K [m + 16\pi^2 r^2 m/w^2 + P(i)/m^2]}
\]

At resonance

\[
\omega_n^2 = \frac{K}{m},
\]

where

\[
\omega_n = \frac{K}{m}.
\]
Differentiating gives

\[ 2\omega \frac{\partial \omega}{\partial \Delta l} = \frac{P''(l)}{\Delta l} \omega^3. \]  

(A 10)

Again using the Deryaguin method (differentiate (A 4)) we obtain

\[ A_{P'}(l) = 2\pi \left( \frac{\Delta}{\Delta l} \right) \left( \frac{\omega}{\Delta l} \omega^3 \right)^{-1} \]  

(A 11)

which may be used to obtain \( A_{P'}(l) \) from the results of Israelachvili & Tabor.