

Dispersion forces at planar interfaces in anisotropic ceramics

K.M. Knowles*

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, U.K.

Calculations are presented for the magnitude of the dispersion forces at rutile – vacuum – rutile, rutile – silica – rutile and rutile – water – rutile planar interfaces for the non-retarded limit. The calculations for rutile – vacuum – rutile and rutile – silica – rutile predict values of the Hamaker constant close to those determined through full spectral calculations using experimentally-determined interband transition strengths. However, subtle differences between these two approaches emerge when predicting trends in the Hamaker constant as a function of the orientation of the anisotropic rutile grains.

Key words: Anisotropy, Hamaker constant, optical properties, planar interfaces, rutile, thin films.

Introduction

The magnitudes of the dispersion forces arising from the van der Waals interaction between bulk materials are important in a number of processes relevant to ceramics at the nanometre level [1]. Thus, for example, dispersion forces help to determine both the behaviour of colloidal suspensions and the equilibrium thickness of remnant silica-rich amorphous intergranular thin films at interphase boundaries in engineering ceramics. Dispersion forces have their origin in induced-dipole/induced-dipole interactions arising from electrodynamic fluctuations at an atomic level [1-3]. When describing dispersion forces for a particular geometry of materials it is often useful to quote their magnitude in terms of a Hamaker constant, A . One geometry of particular interest to engineering ceramics because of its wide applicability to many practical situations is that of two parallel planar surfaces between which there is an intervening medium. While analytical formulae of differing degrees of complexity and approximations are readily available in the literature to calculate A for the case of a thin isotropic medium between two isotropic media [1-6], there are relatively few discussions of the effect of anisotropy arising from the dielectric properties of these different media.

In their analysis of interphase boundaries between hexagonal boron nitride, a highly anisotropic material in terms of its optical and dielectric properties, and 3C SiC, Knowles and Turan demonstrated that in the non-retarded limit A will be sensitive to the orientation of the interphase boundary relative to the crystal axes of hexagonal boron nitride [7]. French *et al.* [8] have

determined values of A for boundaries with either vacuum or silica glass between rutile single crystals through full spectral calculations using experimentally-determined interband transition strengths and have reported a slight dependence of A in the non-retarded limit on the orientation of the rutile single crystals relative to the boundary orientation. It is noteworthy in the work of French *et al.* that, for the particular boundaries they considered, there is a large discrepancy between the Hamaker constants they determined through the full spectral method and those they determined by calculation through the Tabor-Winterton approximation using a common characteristic absorption frequency ν_e of $3 \times 10^{15} \text{ s}^{-1}$ for both rutile and silica glass. French *et al.* rationalised this discrepancy in terms of the relatively high refractive indices exhibited by rutile causing the Tabor-Winterton approximation to become invalid. However, they did not undertake any calculations to demonstrate this conclusively.

In this paper, the mathematical analysis of Knowles and Turan [7], which uses the approach of Parsegian and Weiss [9] to analyse the van der Waals interaction between two semi-infinite anisotropic media either side of a slab of anisotropic material in the non-retarded limit, is extended to theoretical calculations of Hamaker constants between crystals of rutile with an intervening thin film of either vacuum, silica glass or water. These revised calculations produce improved predictions of the Hamaker constants much closer to those determined through the full spectral method, while also highlighting differences between predicted trends in A as a function of the orientation of the rutile single crystals determined from this analysis and the trends determined from the full spectral calculations of French *et al.* using the experimentally determined interband transition strengths.

*Corresponding author:
Tel : +44-1223-334312
Fax: +44-1223-334567
E-mail: kmk10@cam.ac.uk

Analytical approximations of Hamaker constants for isotropic media

For the case of a thin planar slab of material '3' of thickness L between two materials '1' and '2' in the form of semi-infinite plates, the interaction energy per unit area, $G(L)$, takes the form

$$G(L) = -\frac{A_{132}}{12\pi L^2} \quad (1)$$

where A_{132} is the Hamaker constant [1-6]. For accurate predictions of Hamaker constants from Lifshitz theory for such a geometry, the behaviour of the dielectric permittivity as a function of frequency needs to be known for each material in detail. However, as others have noted (e.g., [1-6]), the overwhelming contribution to the Hamaker constant in ceramics and other insulating materials comes from high frequencies in the visible and ultra-violet associated with transitions across the band gap. A lesser contribution comes from the static dielectric constants of the materials '1' and '2' and the intervening material '3'.

The most simple analytical description of the dielectric permittivity for ceramics and other insulating materials is that it can be represented in terms of a static dielectric constant together with a single high frequency absorption peak of zero bandwidth [1-6]. If the frequencies at which the absorption peaks arise in the three materials are the same, and if the contribution of the static dielectric constant is ignored, the approximation for the Hamaker constant in the non-retarded limit (when $L \rightarrow 0$) takes the form

$$A_{132} = \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2} (n_2^2 + n_3^2)^{1/2} ((n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2})} \quad (2)$$

where ν_e is the common characteristic absorption frequency for all three materials, h is Planck's constant and n_1 , n_2 and n_3 are the refractive indices of the three materials, extrapolated to zero energy, or equivalently, zero frequency [1]. This is generally known in the literature as the Tabor-Winterton approximation [e.g., 1, 8]. Tabor and Winterton were the first to derive a special form of equation (2) for the situation where materials '1' and '2' are the same and where material '3' is air or vacuum [10].

A modified form of equation (2) which takes the static dielectric constants ϵ_1 , ϵ_2 and ϵ_3 of the three phases into account is

$$A_{132} = \frac{3}{4} k_B T \frac{(\epsilon_1 - \epsilon_3)(\epsilon_2 - \epsilon_3)}{(\epsilon_1 + \epsilon_3)(\epsilon_2 + \epsilon_3)} + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2} (n_2^2 + n_3^2)^{1/2} ((n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2})} \quad (3)$$

where k_B is Boltzmann's constant and T is temperature [3]. It is usual in calculations using either equation (2) or equation (3) for the common characteristic absorption frequency ν_e to be taken to have a value of $3 \times 10^{15} \text{ s}^{-1}$ (see, for example, [1, 3]). Horn and Israelachvili [11] have derived a slightly more complex form of equation (3) for the situation where materials '1' and '2' have the same absorption frequency but '3' has a different value of absorption frequency, and Prieve and Russel [5] have derived a form of A_{132} for the most general situation where the three materials have different absorption frequencies ν_1 , ν_2 and ν_3 .

Analytical approximations of Hamaker constants for anisotropic media

For materials with a relatively large birefringence, such as hexagonal boron nitride, calomel, HgCl, and rutile, TiO_2 , for which values of $n_o = 2.6158$ and $n_e = 2.9029$ at the wavelength of sodium light have been reported in a geological sample as long ago as 1883 [12], it is not immediately apparent how the analytical approximations for A in equations (2) and (3) valid for isotropic media in the non-retarded limit should be modified to take anisotropy into account without looking at the underlying physics, nor is it immediately apparent how to deal with cases where the anisotropic materials have markedly different characteristic absorption frequencies. Fortunately, however, it is possible to extend the work of Knowles and Turan [7] and Parsegian and Weiss [9] relatively straightforwardly to the systems rutile – vacuum – rutile, rutile – silica glass – rutile and rutile – water – rutile of interest here to take account of anisotropy, and then combine the results from this extension with formulae given by Prieve and Russel [5] to give predictions of Hamaker constants for anisotropic materials with different characteristic absorption frequencies. Although these predictions are simplified approximations, because of the description of the dielectric permittivities of rutile, silica and water in terms of a static dielectric constant and a single high frequency absorption peak of zero bandwidth, this analytical approach is computationally much simpler than the full spectral method and also has the added attraction of being transparent in the way in which it deals with dielectric anisotropy.

For this, the general equations stated by Knowles and Turan for the geometry shown in Fig. 1 can be used. For anisotropic media 1-3, the dielectric tensors will be of the form

$$\epsilon^{(r)} = \begin{pmatrix} \epsilon_{11}^{(r)} & \epsilon_{12}^{(r)} & \epsilon_{31}^{(r)} \\ \epsilon_{12}^{(r)} & \epsilon_{22}^{(r)} & \epsilon_{23}^{(r)} \\ \epsilon_{31}^{(r)} & \epsilon_{23}^{(r)} & \epsilon_{33}^{(r)} \end{pmatrix}, \quad r=1, 2, 3 \quad (4)$$

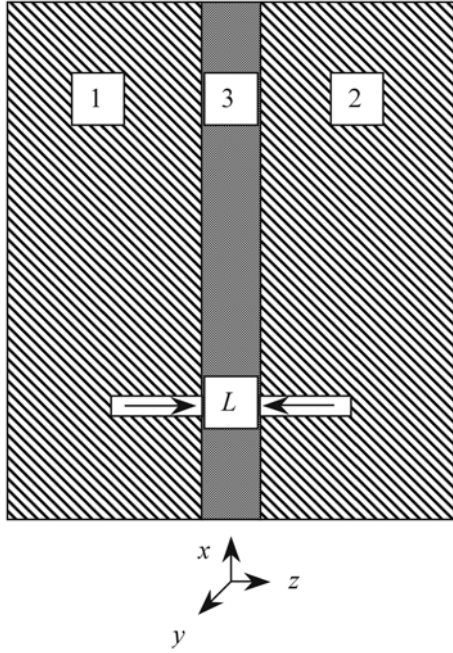


Fig. 1. A planar slab of an anisotropic medium '3' of width L sandwiched between two semi-infinite anisotropic media '1' and '2', together with a reference orthonormal axis system.

where the superscripts r specify the medium under consideration. It is implicit in the analysis that the coefficients of these dielectric tensors are frequency dependent.

In the non-retarded limit, Knowles and Turan have used the approach of Parsegian and Weiss [9] to show that in its most general form $G(L)$ is given by the expression

$$G(L) = \frac{k_B T}{4\pi} \sum_{n=0}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} du dv \ln \left[1 - \left(\frac{a-1}{a+1} \right) \left(\frac{b-1}{b+1} \right) e^{-2\beta_3 L} \right] \quad (5)$$

where the prime on the summation indicates that the $n = 0$ term is to be multiplied by 1/2 and where the sum is to be taken over imaginary frequencies $i\xi_n$ where $\xi_n = 4\pi^2 n k_B T / h$. Terms within the integral are defined through the expressions

$$a = \frac{\epsilon_{33}^{(1)} \beta_1}{\epsilon_{33}^{(3)} \beta_3} \quad (6)$$

$$b = \frac{\epsilon_{33}^{(2)} \beta_2}{\epsilon_{33}^{(3)} \beta_3} \quad (7)$$

where

$$\beta_r^2 = \epsilon_{11}^{(r)} u^2 + 2\epsilon_{12}^{(r)} uv + \epsilon_{22}^{(r)} v^2 - \frac{(u\epsilon_{31}^{(r)} + v\epsilon_{23}^{(r)})^2}{\epsilon_{33}^{(r)}}, \quad r=1, 2, 3 \quad (8)$$

For the situations in which we are interested here, medium 3 can be taken to be isotropic, so that $\epsilon^{(3)} =$

$\epsilon_3 \mathbf{I}$, where $\mathbf{I}$ is the unit 3×3 matrix. Defining $u = \rho \cos \phi$ and $v = \rho \sin \phi$, it is apparent from equation (8) that $\beta_3 = \rho$. Expanding the logarithm term within equation (5) in terms of an infinite power series and performing the integration over ρ in equation (5), it follows that the expression for $G(L)$ becomes

$$G(L) = -\frac{k_B T}{16\pi^2 L^2} \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{1}{m^3} \int_0^{2\pi} \left(\frac{a-1}{a+1} \right)^m \left(\frac{b-1}{b+1} \right)^m d\phi \quad (9)$$

and so using equation (1) the general expression for the Hamaker constant A_{132} with this simplification becomes

$$A_{132} = \frac{3k_B T}{4\pi} \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \frac{1}{m^3} \int_0^{2\pi} \left(\frac{a-1}{a+1} \right)^m \left(\frac{b-1}{b+1} \right)^m d\phi \quad (10)$$

The first two very reasonable approximations to this analytically correct expression for A_{132} are that the term in $m = 1$ is the dominant term within the summation over m and is the only term which needs to be retained, and that secondly the summation over n can be replaced by an integral from 0 to ∞ [3, 6]. These approximations lead to the simplified expression

$$A_{132} = \frac{3k_B T}{4\pi} \left\{ \frac{1}{2} \int_0^{2\pi} \Delta^2(0, \phi) d\phi + \frac{h}{2\pi k_B T} \int_0^{\infty} dv \int_0^{2\pi} \Delta_n^2(v, \phi) d\phi \right\} \quad (11)$$

where the frequency-dependent term

$$\Delta_n^2(v, \phi) = \left(\frac{a-1}{a+1} \right) \left(\frac{b-1}{b+1} \right) \quad (12)$$

and where the first term in the curly brackets in equation (11) is this term evaluated at zero frequency.

If in Fig. 1 we assign media '1' and '2' to be semi-infinite single crystals of rutile, the 'c' directions of both crystals will in general make angles of θ_1 and θ_2 respectively with the normal to the interface planes between '1' and '3' and '3' and '2'. Here, we will restrict ourselves to cases where these two 'c' directions and the normal are coplanar. Under these circumstances, we can assign the 'y' axis in Fig. 1 to be parallel to a rutile ordinary ray direction in both crystals, so that the particular forms of the dielectric tensor in media '1' and '2' are

$$\epsilon^{(r)} = \begin{pmatrix} \epsilon_{r0} + (\epsilon_{re} - \epsilon_{r0}) \sin^2 \theta & 0 & (\epsilon_{r0} - \epsilon_{re}) \sin \theta \cos \theta \\ 0 & \epsilon_{r0} & 0 \\ (\epsilon_{r0} - \epsilon_{re}) \sin \theta \cos \theta & 0 & \epsilon_{re} + (\epsilon_{r0} - \epsilon_{re}) \sin^2 \theta \end{pmatrix}, \quad r = 1, 2 \quad (13)$$

For this geometry,

$$\Delta_n^2(v, \phi) = \frac{(K_1 - \epsilon_3)(K_2 - \epsilon_3)}{(K_1 + \epsilon_3)(K_2 + \epsilon_3)} \quad (14)$$

where

$$K_r^2 = \epsilon_{re}\epsilon_{ro} + \epsilon_{ro}(\epsilon_{ro} - \epsilon_{ro})\sin^2\theta_r\sin^2\phi, \quad r = 1, 2 \quad (15)$$

Using the approximations to evaluating the integrals in equation (11) discussed by Knowles and Turan [7], we find that to a very good approximation the integral over ϕ in the zero frequency term is

$$\int_0^{2\pi} \Delta_n^2(0, \phi) d\phi = 2\pi \frac{(\epsilon_{1eff}(0) - \epsilon_3(0))(\epsilon_{2eff}(0) - \epsilon_3(0))}{(\epsilon_{1eff}(0) + \epsilon_3(0))(\epsilon_{2eff}(0) + \epsilon_3(0))} \quad (16)$$

and the integral over ϕ in the frequency-dependent term is

$$\int_0^{2\pi} \Delta_n^2(v, \phi) d\phi = 2\pi \frac{(\epsilon_{1eff}(iv) - \epsilon_3(iv))(\epsilon_{2eff}(iv) - \epsilon_3(iv))}{(\epsilon_{1eff}(iv) + \epsilon_3(iv))(\epsilon_{2eff}(iv) + \epsilon_3(iv))} \quad (17)$$

where

$$\epsilon_{re}(0) = (\epsilon_{ro}(0))^{1/2} \left\{ \epsilon_{re}(0) + (\epsilon_{ro}(0) - \epsilon_{re}(0)) \frac{\sin^2\theta_r}{2} \right\}^{1/2} \quad r = 1, 2 \quad (18)$$

and

$$\epsilon_{re}(iv) \approx \frac{1}{2}\epsilon_{ro}(iv) + \frac{1}{2}\epsilon_{re}(iv) + (\epsilon_{ro}(iv) - \epsilon_{re}(iv)) \frac{\sin^2\theta_r}{4} \quad r = 1, 2 \quad (19)$$

Thus, from both equations (18) and (19) it is apparent that the effective dielectric constants of both '1' and '2' have contributions from both ϵ_{ro} and ϵ_{re} for all θ_r .

The expressions for $\epsilon_{re}(iv)$ gives an expression for the refractive index extrapolated to zero frequency:

$$n_{re}^2 \approx \frac{1}{2}n_{ro}^2 + \frac{1}{2}n_{re}^2 + (n_{ro}^2 - n_{re}^2) \frac{\sin^2\theta_r}{4} \quad r = 1, 2 \quad (20)$$

so that $\epsilon_{re}(iv)$ is of the form

$$\epsilon_{re}(iv) = 1 + \frac{C_{UVr}}{1 + (v^2/v_{UVr}^2)} \quad r = 1, 2 \quad (21)$$

where it is assumed for simplicity here that, even though media '1' and '2' are both anisotropic, they can both be modelled as having a single ultra-violet (UV) absorption peak at a frequency v_{UVr} of zero width for their ordinary and extraordinary rays.

With these algebraic manipulations, we find

$$A_{132} \approx \frac{3}{4}k_B T \left(\frac{\epsilon_{1eff}(0) - \epsilon_3(0)}{\epsilon_{1eff}(0) + \epsilon_3(0)} \right) \left(\frac{\epsilon_{2eff}(0) - \epsilon_3(0)}{\epsilon_{2eff}(0) + \epsilon_3(0)} \right) + \frac{3h}{4\pi} \int_0^\infty R_{13}R_{23}dv \quad (22)$$

where

$$R_{i3} = \frac{C_i - C_3 + v^2 \left(\frac{C_i}{v_3^2} - \frac{C_3}{v_i^2} \right)}{2 + C_i + C_3 + v^2 \left(\frac{2 + C_i}{v_3^2} + \frac{2 + C_3}{v_i^2} \right) + \frac{2v^4}{v_i^2 v_3^2}} \quad i = 1, 2 \quad (23)$$

and where the subscript UV has been dropped for C_i and v_i , $i = 1, 2, 3$. The integral over dv is non-trivial, but can be evaluated using the method of partial fractions (see, for example, [5]). The result for A_{132} is then the same as the general result for A_{132} quoted by Prieve and Russel [5] with the effective static dielectric constants and refractive indices extrapolated to zero frequency in equations (18) and (20) replacing the values for isotropic materials. Equation (22) reduces to the simple isotropic case of equation (3) if $\epsilon_{10} = \epsilon_{1e}$, $\epsilon_{20} = \epsilon_{2e}$ and $v_1 = v_2 = v_3$.

We are now in a position to examine predictions of Hamaker constants in the non-retarded limit for crystals of rutile with an intervening thin film of either vacuum, silica glass or water using this more general form of the Tabor-Winterton approximation. To determine the positions of the absorption peaks of rutile and silica, it is convenient to plot the variation of the relevant refractive indices as a function of either wavelength or frequency in the visible part of the spectrum in the form of a Cauchy plot [4-6], in which, for example, $(n^2 - 1)$ is plotted against $(n^2 - 1)v^2$, where n is the relevant refractive index and v the wavelength [4-6]. This arises from a consideration of equation (21) since in the visible

$$\epsilon(v) = 1 + \frac{C_{UV}}{1 - (v^2/v_{UV}^2)} = n^2(v) \quad (24)$$

where v_{UV} is the characteristic absorption frequency in the ultra-violet. After some algebraic manipulation we find

$$(n^2(v) - 1) = C_{UV} + (n^2(v) - 1)(v^2/v_{UV}^2) \equiv C_{UV} + (n^2(v) - 1)(\lambda_{UV}^2/\lambda^2) \quad (25)$$

where λ_{UV} is the characteristic wavelength of absorption. The refractive index predicted at zero frequency (infinite wavelength) from this analysis, n_{vis0} , is then the required refractive index for the modified Tabor-Winterton approximation in equation (22).

Cauchy plots for rutile and amorphous silica are shown in Figs. 2 and 3 respectively using data from [13] and [14]. Values of v_{UV} , C_{UV} and n_{vis0} derived from these plots are shown in Table 1. Not surprisingly, the values for amorphous silica show good agreement with those derived from a Cauchy plot by Hough and White [4]. The data for rutile agree reasonably well

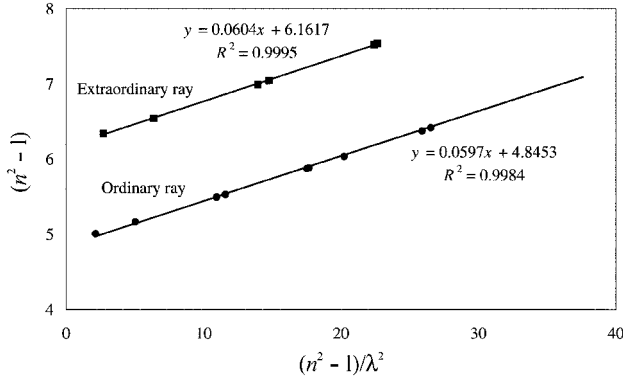


Fig. 2. Cauchy plots for the ordinary and extraordinary ray directions of rutile in which n is the relevant refractive index and λ is the wavelength in micrometres. The source data for the refractive indices of the ordinary ray and the extraordinary ray as a function of wavelength are from [13].

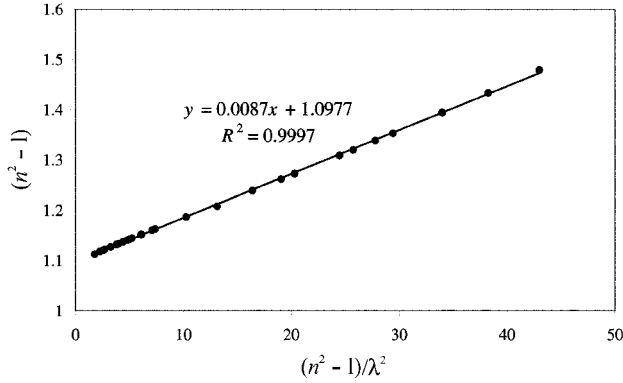


Fig. 3. Cauchy plot for vitreous silica. The source data for the refractive index as a function of wavelength are from [14].

with data obtained from Cauchy plots by Buscall [15] and Larson *et al.* [16] using other source data. The data in Table 1 show that, to a very good approximation indeed, the ordinary ray and the extraordinary ray in rutile can be considered to have a common UV absorption peak of zero width at a frequency of $1.20 \times 10^{15} \text{ s}^{-1}$. This frequency is markedly lower than the absorption frequency for amorphous silica of $3.211 \times 10^{15} \text{ s}^{-1}$ which by comparison is very close to the widely used value of $3 \times 10^{15} \text{ s}^{-1}$. That the absorption peaks for the ordinary and extraordinary rays for rutile are at relatively low frequencies is consistent with the comment by DeVore [13] that rutile has its absorption band close to the visible region.

It follows from the data in Table 1 and a consideration of the form of n_{eff} in equation (20) that when

Table 1. Values of ν_{UV} , C_{UV} and $n_{\text{vis}0}$ for rutile and vitreous silica

	ν_{UV} $\times 10^{15} \text{ s}^{-1}$	C_{UV}	$n_{\text{vis}0}$
Rutile ordinary ray	1.227	4.845	2.418
Rutile extraordinary ray	1.182	6.108	2.666
Vitreous silica	3.211	1.098	1.448

interfaces ‘1’-‘3’ and ‘2’-‘3’ are both parallel to (001) rutile, n_{eff} is 2.545, whereas when these interfaces are parallel to (100) rutile, n_{eff} is 2.482 because of the dominant contribution to n_{eff} of the component of the dielectric tensor parallel to the z-axis in Fig. 1 and the lesser contributions of the components along the the x- and y-axes. This is in contrast to the trends in the $n_{\text{vis}0}$ used by French *et al.* [8] in their Tabor-Winterton calculations using equation (3) with a ν_e of $3 \times 10^{15} \text{ s}^{-1}$.

Examples of calculated non-retarded Hamaker constants at 300 K for rutile – vacuum – rutile and rutile – silica – rutile geometries in Fig. 1 are shown in Figs. 4 and 5 respectively. The static dielectric constants used for rutile in the ordinary and extraordinary ray directions are those quoted by Parker [17] and the static dielectric constant for silica is the one quoted for fused silica by Hough and White [4]. In these two figures the Hamaker constants are plotted as a function of the angle θ that the ‘c’ axes in both rutile grains are each taken to make with the z-axis in Fig. 1. Thus when $\theta = 0^\circ$, the geometry describes the arrangement (001) rutile – medium – (001) rutile and when $\theta = 90^\circ$ the arrangement (hk0) rutile – medium – (hk0) rutile is described within which the two [001] rutile directions lying in the boundary planes at $z = 0$ and $z = L$ are parallel. In Fig. 4 the temperature-dependent term which contains the static dielectric constants in equation (22) contributes a value between 2.990 zJ (for $\theta = 90^\circ$) and 3.005 zJ (for $\theta = 0^\circ$) at 300 K, emphasising the overwhelming importance of the term in equation (22) dependent on the various UV oscillator strengths.

Using averaged values of ν_{UV} and C_{UV} from his analysis of Cauchy plots for rutile Buscall [15] reports a Hamaker constant of 155.9 zJ for rutile – vacuum – rutile at 298 K. Bergström [6] quotes a Hamaker constant of 143 zJ at 298 K for rutile – vacuum – rutile using equation (3) and the value of the characteristic absorption frequency for ‘average’ rutile quoted by Buscall [15]. Both these single-valued estimates are significantly closer to the data in Fig. 4 and the Hamaker constants of 170-180 zJ obtained by French *et al.* [8] through the full spectral method using interband transition strengths than the values of ~ 400 zJ quoted by Israelachvili [3] and French *et al.* [8] using the Tabor-Winterton approximation with ν_e of $3 \times 10^{15} \text{ s}^{-1}$.

The other significant feature of Fig. 4 is that the slight dependence of the Hamaker constant on the crystal orientation of rutile has a trend opposite to that determined through the full spectral method by French *et al.* [8]. Thus, for example, they determine Hamaker constants of 181.5 zJ for (100) rutile – vacuum – (100) rutile, 177.2 kJ for (110) rutile – vacuum – (110) rutile and 173.5 zJ for (001) rutile – vacuum – (001) rutile. This feature is repeated for the rutile – silica – rutile Hamaker constants shown in Fig. 5 – although the values of 43.5-48.2 zJ agree very well with the spread of values of 39.7-44.9 zJ obtained by French *et al.*

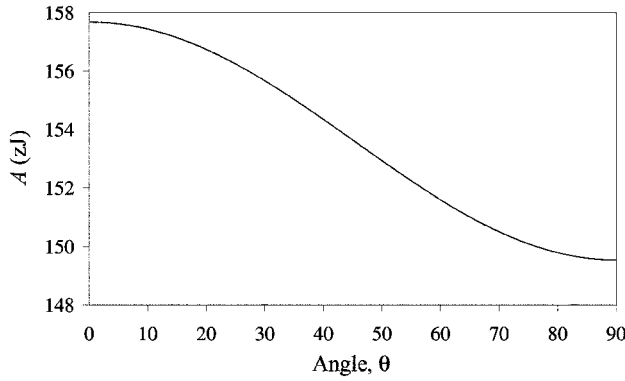


Fig. 4. Plot of Hamaker constant, A , at 300 K as a function of orientation for rutile – vacuum – rutile. The angle θ plotted on the horizontal axis is the angle between the ‘ c ’ axis in each rutile grain and the co-planar z -axis in the geometry of Fig. 1.

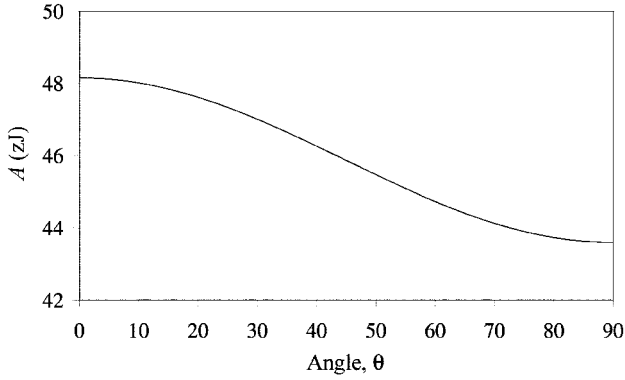


Fig. 5. Plot of Hamaker constant, A , at 300 K as a function of orientation for rutile – silica – rutile. The angle θ plotted on the horizontal axis is the angle between the ‘ c ’ axis in each rutile grain and the co-planar z -axis in the geometry of Fig. 1.

through the full spectral method, the trend as a function of θ in Fig. 5 is opposite to that determined through the full spectral method. A similar graph for Hamaker constants for rutile – water – rutile at 300 K is shown in Fig. 6. Here, the values of C_{UV} and ω_{UV} ($= 2\pi\nu_{UV}$) for water and its static dielectric constant of 79.69 quoted by Prieve and Russel [5] were used in the calculations. The range of the values of A of 60–66 zJ agree very well with other calculated values in the range 53–77 zJ [6, 15, 16] using averaged dielectric permittivity data and also with an experimental measurement of A in the non-retarded limit of 60 ± 20 zJ at the isoelectronic point [16].

Although the dependencies of the calculated Hamaker constants on crystal orientation determined through the approach here and the full spectral approach of French *et al.* [8] are slight, and certainly much less than the range of absolute values of the Hamaker constants for rutile – vacuum – rutile, rutile – silica – rutile and rutile – water – rutile, more significant differences in predictions between these two methods will arise in other situations, such as where medium ‘3’ has a n_{vis0} intermediate between the extraordinary and ordinary

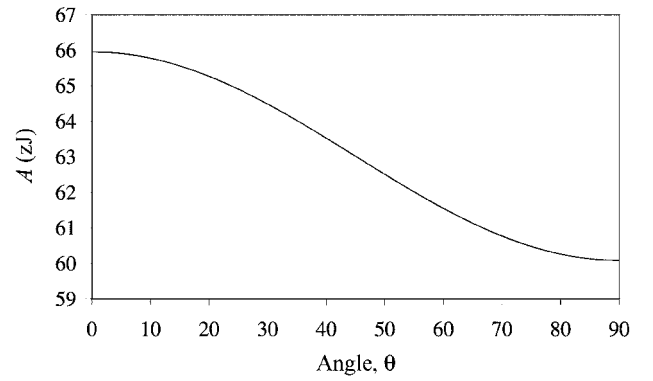


Fig. 6. Plot of Hamaker constant, A , at 300 K as a function of orientation for rutile – water – rutile. The angle θ plotted on the horizontal axis is the angle between the ‘ c ’ axis in each rutile grain and the co-planar z -axis in the geometry of Fig. 1. Water is modelled as a material with a single zero-bandwidth absorption peak together with a static dielectric constant using the material parameters quoted by Prieve and Russel [5].

refractive indices of media ‘1’ and ‘2’ extrapolated to zero frequency, for example. Under such circumstances Parsegian and Weiss [9] have considered a different geometrical situation to the one considered here. Although the magnitudes of the anisotropic effects in the situation considered by Parsegian and Weiss were small, they depend critically on the relative orientations between grains ‘1’ and ‘2’ around the z -axis. These examples highlight the need for further work in this area clarifying in detail the way anisotropy is treated in the analytical approach, through full spectral calculations and experimentally when extracting Hamaker constants from surface force apparatus and atomic force microscopy experiments.

Conclusions

The effect of crystal anisotropy, although very small for most anisotropic materials, needs to be taken into account when predicting Hamaker constants for situations where materials with very high birefringence such as rutile and hexagonal boron nitride are involved. While these effects of anisotropy are modest even for rutile grain boundaries containing thin films of intervening fluid, and are likely to be less significant than differences in the magnitudes of the Hamaker constants determined using different computational approaches, such effects need to be analysed and modelled to ensure that the reasons for differences which arise in predictions using the various approaches are fully understood and appreciated.

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