Comparisons of Hamaker Constants for Ceramic Systems with Intervening Vacuum or Water: From Force Laws and Physical Properties

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Van der Waals dispersive forces produce attractive interactions between bodies, playing an important role in many material systems influencing colloidal and emulsion stability, wetting behavior, and intergranular forces in glass–ceramic systems. It is of technological importance to accurately quantify these interactions, conveniently represented by the Hamaker constant, *A*. To set the current level of accuracy for determining *A*, they were calculated from Lifshitz theory using full spectral data for muscovite mica, Al_2O_3, SiO_2, Si_3N_4, and rutile TiO_2, separated by vacuum or water. These were compared to Hamaker constants calculated from physical properties using the Tabor–Winterton approximation, a single oscillator model, a multiple oscillator model, and *A*'s calculated using force vs separation data from surface force apparatus and atomic force microscope studies. For materials with refractive indices between 1.4 and 1.8 separated by vacuum, all methods produce similar values, but for indices larger than 1.8 separated by vacuum, and any of these materials separated by water, results span a broader range. The present level of accuracy for the determination of Hamaker constants, here taken to be represented by the level of agreement between various methods, ranges from about 10% for the case of SiO_2/vacuum/SiO_2 and TiO_2/water/TiO_2 to a factor of approximately 7 for mica/water/mica. © 1996 Academic Press, Inc.

Key Words: Hamaker constant; dispersion forces; interparticle forces.

INTRODUCTION

The van der Waals interactions between bodies of material, arising from the interaction of oscillating dipoles in the interatomic bonds of each body, manifest themselves in various aspects of behavior ranging from the determination of surface energies, and consequently wetting behavior, to the stability of colloidal suspensions and emulsions (1). Van der Waals forces are expected to attract ceramic particles which are separated by a liquid glass until this attraction is balanced by repulsive forces, as found in liquid phase sintered Si_3N_4 (2–4) and thick film resistor materials (5). It is obviously of interest to be able to quantify these interactions in order to understand how to manipulate relevant material properties. The Hamaker constant is a convenient quantity with which to represent these interactions. For the vast number of systems composed of particles suspended in aqueous media, there have been only a few attempts to experimentally quantify these interactions, perhaps largely due to experimental difficulty in obtaining accurate data. At present, there are several techniques in use for the quantification of these phenomena.

In this work, the Hamaker constant is viewed as a system-specific physical constant whose value for a given system and geometry must be independent of the method of measurement. Therefore, the value of the Hamaker constant measured by any accurate technique will agree well with that from any other accurate measurement technique. To date there has been no comparison of the results of all the techniques currently in use for any system to determine how well the values may agree. The purpose of this work is to provide the first comparison of Hamaker constants determined by the six different techniques in use for several material systems and attempt to ascertain how accurately this physical constant may be determined. In this work the concept of the accuracy of a Hamaker constant will be *defined* by the level of agreement between the values obtained from the techniques compared. Better agreement will be taken to be an indication of better accuracy. Bear in mind that no technique has been proven to be accurate to any degree. A review of the techniques used will provide not only a discussion of how the measurements are done, but also of the assumptions and potential measurement errors which may influence the values obtained.

EXPERIMENTAL AND ANALYTICAL METHODS

The Hamaker constant for a system (Fig. 1) composed of two macroscopic bodies separated by vacuum, or a molten

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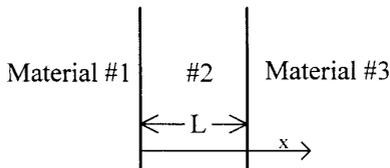
FIG. 1. Configuration of materials for a A_{123} Hamaker constant where the intervening film is of material #2 and the two adjacent grains are of material #1 and #3. For the simpler case of a A_{121} or A_{1v1}, the two grains are considered to be of the same material #1 and the intervening film is of material #2 or of vacuum (v).

material, is the force law scaling constant representing the attractive or repulsive van der Waals interactions between the bodies (6). The van der Waals interaction energy results from the electromagnetic interaction between oscillating dipoles in a material's electronic structure (1). Knowing the nature of the dipole–dipole interaction, one may integrate over all dipole pairs in the two particles involved to obtain an expression for the interaction energy as a function of interparticle separation, as originally done by Hamaker (6), to obtain

$$E(h) = \frac{-nA}{h^m}, \qquad [1]$$

where n and m are constants dependent on the particle geometry in the limit of small surface separations; A is the Hamaker constant, dependent on the electronic structure of the materials involved through the density and strength of oscillating dipoles present as the interatomic bonds; and h is the separation. The force acting between two particles, also referred to as the London dispersion force, is given by

$$F(h) = \frac{-qA}{h^{m+1}}, \qquad [2]$$

where q is another constant, also dependent on geometry.

Given data on the electronic structure and dielectric properties of materials, the Hamaker constant can be calculated by methods of varying complexity (and corresponding accuracy). The model of primary interest here is that developed by Lifshitz (7) and Dzyaloshinskii et al. (8) for the nonretarded case wherein the interparticle separations are small enough that the interactions between dipoles is considered to be instantaneous. Only the case of two like materials separated by a second is considered here. (The interested reader is referred to French et al. (9) for a thorough discussion of this theory.) It can be shown (10) that the Hamaker constant can be given by

$$A = \frac{-3\hbar L^2}{\pi} \int_0^\infty \rho \, d\rho \int_0^\infty \ln G(\xi) \, d\xi, \qquad [3]$$

where L is the distance between particle surfaces, ρ is the wave vector normal to the interface, G is a function of the material's optical properties (described below), and ξ is the imaginary frequency of the oscillating dipole. For particles of material 1 separated by material 2, $G(\xi)$ is given by

$$G_{121}^{NR}(\xi) = 1 - \Delta_{12}^2 e^{-2a\rho}, \qquad [4]$$

where a is the particle separation for planar surfaces and Δ_{12} is given by

$$\Delta_{12} = \frac{\epsilon_{2,1}(\xi) - \epsilon_{2,2}(\xi)}{\epsilon_{2,1}(\xi) - \epsilon_{2,2}(\xi)}. \qquad [5]$$

Here $\epsilon_2(\xi)$ are the London dispersion spectra obtained using the London dispersion transform (1, 10)

$$\epsilon_2(\xi) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon_2(\omega)}{\omega^2 + \xi^2} \, d\omega, \qquad [6]$$

where ω is the real frequency.

One may use the interband optical properties of a material to determine either the complex dielectric constant $\hat{\epsilon}(\hat{\omega})$, where $\hat{\omega} = \omega + i$, or interband transition strength, $\hat{J}_{cv}(\hat{\omega})$, through the Kramers Kronig (KK) relations, giving

$$\hat{J}_{cv}(\omega) = \frac{\hbar^2 \omega^2}{8\pi^2} i[\epsilon_1(\omega) + i\epsilon_2(\omega)]^* \qquad [7]$$

which is then used for the above London dispersion transform.

Sample Preparation

In the present work, VUV spectra were measured for muscovite mica (11) and polycrystalline rutile TiO_2. The spectra of Al_2O_3 (12), SiO_2 (13), and Si_3N_4 (4) were taken previously and will be presented below. The mica (14) sample used was prepared by cleaving a portion from a crystal which was placed on the sample pedestal of the spectrometer and loaded into the vacuum chamber within a few minutes of cleaving. The same sample was used for spectroscopic ellipsometry (discussed below). The crystal used was approximately 100 μm thick. The polycrystalline TiO_2 rutile sample was prepared for this study from a hot pressed pellet ($\cong 90\%$–95% dense) 0.5 inches in diameter. It was ground on both sides to obtain flat, parallel surfaces and polished to 1/4 μm diamond finish.

Optical Spectroscopy

Normal incidence optical reflectivity spectra (Fig. 2) were measured for the samples using both vacuum ultraviolet and optical spectroscopy from 2700 to 28 nm (0.46 to 44 eV)

with a resolution of 0.2 and 0.6 nm. The spectrophotometers were a VUV instrument (15) using a laser plasma light source (16) and a Perkin–Elmer Lambda 9 NIR/VIS/UV instrument. Once the reflectivity is measured, its value in the visible is compared to that calculated from the index of refraction determined using spectroscopic ellipsometry (17) on the same sample. The long wavelength indices of refraction, determined by this more direct ellipsometric measurement, (17) are 1.56 for mica and 2.6 for TiO_2. Inconsistencies in the measured value of the optical reflectivity may arise from a light collection error in the spectrophotometer and can be corrected by a simple multiplicative constant to bring the measured reflectance into agreement with that expected from the index of refraction in the visible.

Once the reflectivity of the sample is determined over a wide energy range, encompassing the interband transitions of the valence electrons, the KK transform (18) can be used to calculate the reflected phase ϕ of the light from the reflectance amplitude r, since they are conjugate variables. We have

$$\phi(\omega) = -\frac{2\omega}{\pi} P \int_0^\infty \frac{\ln r(\omega')}{\omega'^2 - \omega^2} d\omega', \qquad [8]$$

where $\hat{R} = R + i\phi$ is the definition of the complex reflectance, and $r = \sqrt{R}$, and ω is the frequency. The KK transform arises from the KK dispersion relations which are direct results of the physical principle of causality. Since the KK dispersion relation is formally correct only when the values of one variable of a conjugate pair are known at all frequencies from $\omega = 0$ to ∞, we approximate the infinite frequency range by adding analytical extensions, or wings, to the reflectance data to extrapolate these down to 0 eV on the low-energy (low-frequency) side and typically up to 1000 eV on the high-energy (high-frequency) side. We use a fast Fourier transform (FFT) based program (19) running under GRAMS/386 (20) to perform the KK transform integrals to speed the analysis and increase its accuracy.

Once the real and imaginary parts of one of the optical properties are determined, calculation of any other optical properties such as the dielectric constant and the interband transition strength (12) $[J_{cv} = (\hbar^2\omega^2/8\pi^2)i(\epsilon_1(\omega) + i\epsilon_2(\omega))^*]$ (Fig. 3) is straightforward using simple algebraic expressions (21).

Full Spectral Hamaker Constants

To calculate the Hamaker constant (22) using the full spectral method (9) it is necessary to perform another Kramers Kronig-based integral transform so as to produce the London dispersion spectrum of the interband transitions for the two grains and the intervening material. Following Lifshitz (7), Dzyaloshinskii *et al.* (8), Ninham and Parsegian (23), and Hough and White (10), we proceed to use the

TABLE 1

Full Spectral Hamaker Constants for Ceramics with Vacuum, Water, and SiO$_2$ A_{121} (zJ)

Mat. 2: Mat. 1	Vacuum $n = 1.0$	SiO$_2$ $n = 1.5$	Water $n = 1.3$
Muscovite mica $n = 1.56$	69.6	0.27	2.9
Al$_2$O$_3$ $n = 1.75$	145	19	27.5
SiO$_2$ $n = 1.5$	66	—	1.6
Si$_3$N$_4$ $n = 2$	174	33	45
TiO$_2$ rutile $n = 2.6$	181	45	60

Note. The index of refraction n is also given.

London dispersion transform (Eq. [3]) to calculate the London dispersion spectrum $\epsilon_2(\xi)$, a physical property of the material. After the London dispersion spectra $\epsilon_2(\xi)$ are calculated, they are accumulated in a spectral database (24) from which any combinations of them can be used to calculate the Hamaker constants of interest. Values of the Hamaker constants for any configuration can be determined using Eq. [3] by evaluating the integrals of the functions G (Eq. [4]) which are simple differences of the London dispersion spectra (Eq. [5]). Hamaker constants for the current cases of muscovite mica, Al$_2$O$_3$, SiO$_2$, Si$_3$N$_4$, and TiO$_2$ separated by vacuum, water, or SiO$_2$ are tabulated in Table 1.

RESULTS

Muscovite Mica

The VUV reflectivity of the muscovite mica sample is shown in Fig. 2. There are noticeable features at energies of 10, 12, 16, and 20 eV. Earlier measurements of the VUV reflectivity from 6 to 13 eV show similar features at energies of 9.9 and 11.8 eV (25) which agree with features seen in the present spectrum. From the interband transition strengths for mica (2), calculated from the reflectivity, a bulk energy loss function can be calculated (Fig. 2) which can be compared with other experimental energy loss spectra. Measured EELS spectra of mica from 0 to approximately 50 eV (26) show features at about 7, 13, 16, 21, 23, and 28 eV, in agreement with those observed using VUV spectroscopy. From the reflectivity, the interband transition strengths and London dispersion spectra for mica have been calculated and are shown in Figs. 3a and 4a, respectively.

Polycrystalline TiO$_2$ Rutile

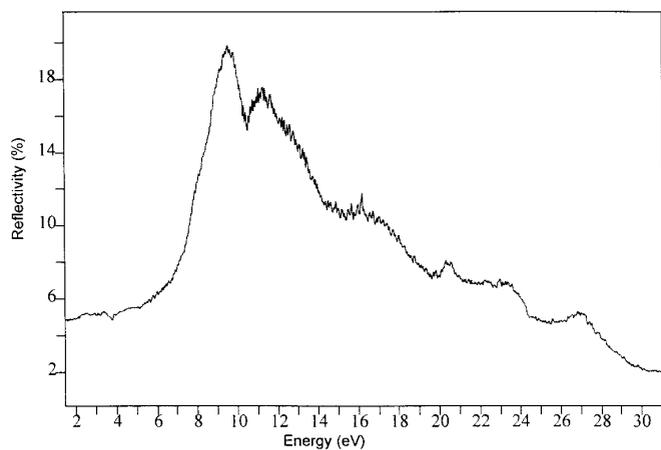Previously presented data on VUV reflectivity for TiO$_2$ rutile suffered from uncertainties due to a small sample

FIG. 2. VUV reflectance of muscovite mica and bulk energy loss function.

FIG. 3. Interband transitions of (a) mica, (b) Al$_2$O$_3$, (c) SiO$_2$, (d) Si$_3$N$_4$, (e) TiO$_2$, and (f) water.

which may have introduced errors from poor light collection (9). The larger sample used in this study eliminated sample size effects. The VUV reflectivity and London dispersion spectra for this polycrystalline TiO$_2$ rutile are shown in Figs. 2e and 3e, respectively. Features in the reflectivity at 3.5, 8, 13, and 21 eV correspond to those seen in spectra from single crystals (9).

Water

The interband transition strengths for water as a function of frequency were calculated from tabulated data (27) on the index of refraction, n, and extinction coefficient, k, over the regions 600–250 nm (28) and 400–220 nm (29) (absorption spectroscopy) and 300–105 nm (30) and 163–48.5 nm (31) (reflectance spectroscopy). The interband transition strengths and London dispersion spectrum for water are shown in Figs. 3f and 4f, respectively.

Other Systems

The interband transition strengths and London dispersion spectra for Al$_2$O$_3$, SiO$_2$, and Si$_3$N$_4$ have been determined
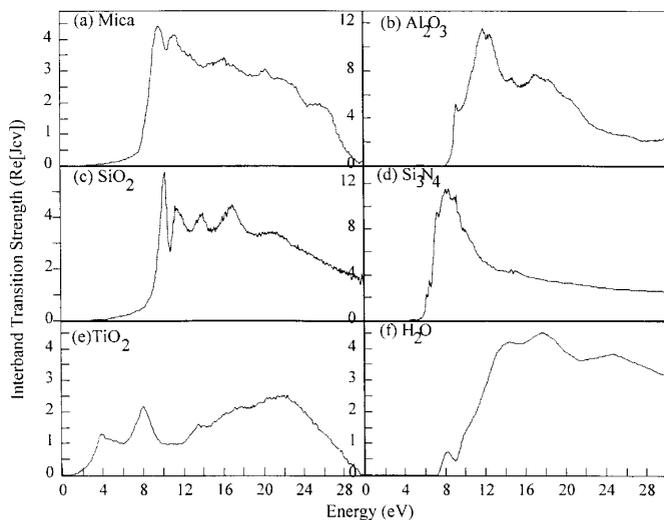
previously (12, 13, 4). The results are presented in Figs. 3b–3d and 4b–4d, respectively.

METHODS FOR DETERMINING HAMAKER CONSTANTS

Measured Force Laws

The determination of the attractive interaction between macroscopic bodies has been of interest for some time. The first attempts at measuring it began in the 1950s using SiO$_2$ plates or an SiO$_2$ sphere and plate suspended from elaborate springs or delicate balance beams. Flat plate experiments were performed with separations between 500–2000 nm
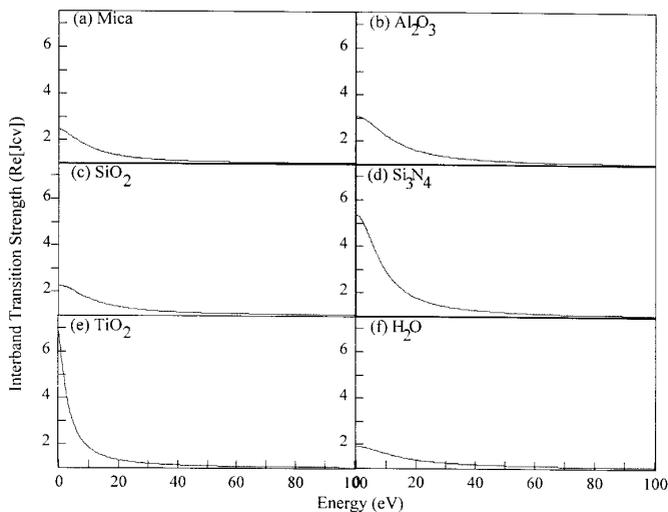

FIG. 4. London dispersion spectra of (a) mica, (b) Al$_2$O$_3$, (c) SiO$_2$, (d) Si$_3$N$_4$, (e) TiO$_2$, and (f) water.

(32) and 500–950 nm (33). Measurements between a sphere and plate were made for separations of 100–700 nm (34, 35) and 94–500 nm (33). The intersurface separations used in these experiments are beyond the range over which nonretarded van der Waals interactions dominate, usually of order 10 nm (6). These experiments were apparently constrained to larger separations due to the difficulty of obtaining molecularly smooth surfaces to achieve intersurface distances small enough to observe nonretarded van der Waals interactions (1–10 nm), as well as difficulties in mechanically controlling the separation at such close spacings. The values obtained are therefore for retarded interactions or in a transition regime between the two. The measurement of nonretarded Hamaker constants required substantial improvements in sample smoothness and control of separations, obtained only with more sophisticated devices.

Surface force apparatus. The first intersurface force measurement at separations of order 1–10 nm was conducted by Tabor and Winterton (36) using crossed cylindrical surfaces of cleaved mica, separated by air, using a piezoelectric crystal to precisely control the separation. The molecularly smooth surface of cleaved mica and the precision of piezoelectric translation eliminated the previous impediments to extremely close surface approach. The cylindrical shape of the mica was obtained by gluing thin mica crystals to glass cylinders. One surface was fixed, while the other was suspended from a cantilever spring, the stiffness of which could be varied. On approach, when the gradient in the attractive intersurface force exceeded the stiffness of the spring the surfaces would jump together. As the spring stiffness was varied, the separation at which the instability occurred was measured by optical interferometry. The critical separation vs spring stiffness was then used to calculate the intersurface force as a function of separation. By fitting their data to a form of Eq. [2] appropriate to the geometry, they arrived at a nonretarded Hamaker constant for mica/air/mica of 100 zJ (zJ, zepto J = 10^{-21} J).

The above mechanism was adapted to measure the surface forces between crossed mica cylinders in aqueous solutions by Israelachvili and Adams (37) and will hereafter be referred to as the surface force apparatus (SFA). The forces between mica surfaces were measured from 1 to 100 nm in aqueous KNO_3 solutions (10^{-4}–10^{-1} M) at pH 6. The forces were measured by suddenly reversing the voltage of the piezoelectric crystal supporting one of the mica surfaces, thereby moving it by a known amount, and measuring the actual distance between the surfaces interferometrically. Knowing the difference between these distances and the stiffness of the cantilever spring, the force (attractive or repulsive) between the surfaces could be calculated. As these measurements were conducted in aqueous electrolyte solutions, surface charge effects influenced the surface forces. By fitting their force vs separation data with DLVO (38) theory, using reasonable values for the surface potential, they arrived at a mica/water/mica Hamaker constant of 22 zJ.

The forces between the surfaces of sapphire crystals in aqueous 10^{-3} M NaCl solutions from pH 6.7–11 were measured by Horn *et al.* (39) using the surface force apparatus. Thin sapphire crystals (surface normal [0001]) were glued to cylinders of mica (as used for studies of forces between mica surfaces) and measurements were performed as described above. The measurements were made over separations of 8–40 nm. DLVO theory, using theoretical values for the surface potential, was used to fit the measured force vs separation data giving a Hamaker constant for the Al_2O_3/water/Al_2O_3 system of 67 zJ. Ducker *et al.* (40) performed similar SFA measurements between sapphire surfaces in NaBr solutions for concentrations of 10^{-3}, 10^{-2}, and 10^{-1} M for pH 3 and 6.7. They used the Hamaker constant calculated by Horn *et al.* (39) for Al_2O_3/water/Al_2O_3 to calculate DLVO forces. The observation of interest in this study was the presence of long range, i.e., >15 nm, attractive forces at pH 3 that decayed exponentially with separation. This and similar observations will be discussed later.

Atomic Force Microscopy

The atomic force microscope (AFM) is a relatively new device that has recently been used by numerous investigators to measure force vs separation between various materials separated by vacuum or liquids (41–44). Ducker *et al.* glued a SiO_2 colloid particle to the tip of an AFM and measured the interaction in aqueous solutions between the particle and a 30-nm film of SiO_2 on a silicon wafer (41). Since their study was primarily concerned with measuring DLVO forces, they did not report a measured value for the Hamaker constant, but rather used a value reported elsewhere (45) to fit their data. Larson *et al.* glued a TiO_2 colloid particle to the tip of an AFM and measured the force between it and a single crystal of TiO_2 in aqueous solutions (42). The interesting aspect of this study is that the isoelectric point of the TiO_2 particles was determined from electrophoretic mobilities to be at pH 5.6. Force vs separation measurements conducted at this pH, wherein appreciable electrostatic repulsion is not present, showed only attractive interactions up to about 10 nm where the tip jumped into contact with the surface. A Hamaker constant of 60 ± 20 zJ was found to fit the experimental data. Biggs and Mulvaney also glued a SiO_2 colloid to an AFM tip, but then coated it with 0.6 μm of gold and measured the interactions between the ''gold'' particle and a gold surface (43) in water. For this system a Hamaker constant of 250 zJ was determined.

Ducker and Clarke (46) studied the interaction between a film of Si_3N_4 on a silicon wafer and a Si_3N_4 AFM tip separated by aqueous solutions at pH 6 for separations from 7 to 30 nm. The nitride film and tip were amorphous and deposited by low-pressure CVD, and are not necessarily of

TABLE 2
Vacuum Hamaker Constants for Ceramics — A_{1v1} (Vacuum) (zJ)

Method Tech.: Material	Force measurement		Physical property measurement			
	Surface force apparatus	Atomic force microscope	Tabor winterton approx.	Single oscillator approx.	Simple spectral method	Full spectral method
Mica	135 (36)	—	100 (1)	84 (48)	100 (10)	69.6
	100 (33)		84.8			
Al_2O_3	—	—	140 (1)	113 (48)	150 (49)	145.1 (9)
			137 (9)			
SiO_2	50–60	—	63 (1)	64 (48)	65 (10)	66 (9)
	(55)		56 (9)		65 (49)	
Si_3N_4	—	—	218	147 (48)	180 (49)	174
TiO_2	—	—	430 (1)	199 (48)	—	173.1 (9)
Rutile			401 (9)			

the same composition. The tip was square pyramidal with a rounded end of radius of order 100 nm. A monotonic attractive interaction was found over these separations. Their data can be fit to a cubic equation

$$F(h) \approx \frac{10^{-34} N/m^3}{h^3} , \qquad [9]$$

where h is the separation. The h^{-3} behavior is appropriate to the interaction between to planar surfaces, rather than that for a sphere/plane interaction which seems more similar to the actual geometry. The pressure, $P(h)$, between planar surfaces is given by $P(h) = A/6\pi h^3 = F(h)/a$, where $F(h)$ is the force and a the area of the surface. Assuming the AFM tip is flat rather than rounded, and has a contact diameter from 500 to 1000 nm, this expression gives values for the Si_3N_4/water/Si_3N_4 Hamaker constant ranging from approximately 80 to 20 zJ. These estimates are completely dependent on assumptions about the AFM tip geometry. These studies clearly indicate that this instrument provides a new means of quantitatively measuring Hamaker constants for a diverse set of material systems.

The values of A from these measured force law approaches (SFA and AFM) are tabulated in Table 2 for A_{1v1} and Table 3 for A_{1w1}.

Physical Property-Based Calculations

Tabor–Winterton Approach

In the theory for calculating the Hamaker constant developed by Lifshitz and others described earlier, the dielectric properties of the materials involved must be known for all frequencies. This technique also involves some rather cumbersome calculations. Hence, in the absence of appropriate spectral data, a simplified approach is very appealing. From the Lifshitz theory, Tabor and Winterton (36) derived a simplified means of calculating the Hamaker constant. First they ignored the contribution from vibrations in the infrared and estimated the absorption in the UV by using the optical dielectric constant. Then, assuming the absorption occurs within a narrow frequency range, i.e., a single oscillator, they arrived at the Tabor–Winterton approximation (TWA), which for like bodies is given by (47)

$$A_{121}^{TWA} = \frac{3\pi\hbar\nu_e}{8\sqrt{2}} \frac{(n_{vis0,1}^2 - n_{vis0,2}^2)^2}{(n_{vis0,1}^2 + n_{vis0,2}^2)^{3/2}} , \qquad [10]$$

where $\hbar$ is Planck's constant and ν_e is the plasma frequency of about 3×10^{15} Hz. Recalling that $n = \epsilon^2$, it is apparent that the TWA enables one to calculate a Hamaker constant

TABLE 3
Aqueous Hamaker Constants for Ceramics — A_{1w1} (Aqueous) (zJ)

Method Tech.: Material	Force measurement		Physical property measurement			
	Surface force apparatus	Atomic force microscope	Tabor winterton approx.	Single oscillator approx.	Simple spectral method	Full spectral method
Mica	22 (37)	—	14	7.7 (48)	19.8 (47)	2.9
Al_2O_3	67 (39)	—	42	21 (48)	52 (49)	27.5
SiO_2	—	—	3.2	2.0 (48)	8.4 (49)	1.6
		≈80–20				
Si_3N_4	—	(46)	100	45 (48)	70 (49)	46
TiO_2 rutile	—	60 ± 20 (42)	260	94 (48)	64 (56)	60

given only physical properties such as the refractive index or dielectric constant of the materials of interest.

Single Oscillator

The single oscillator model (48) is another approximation technique analogous to the TWA. In the derivation of the TWA, the electronic structure of a material was modeled as a single oscillator. The oscillator frequency was assumed to be constant and possess the same value for *all* materials. However, the energy of such an oscillator is expected to vary with the bandgap of a material, being larger for materials with higher bandgaps. In addition, the index of refraction of a material will decrease with increasing bandgap. Thus, materials with large indices of refraction will have lower oscillator frequencies or energies. This will lead to erroneously large Hamaker constants in the TWA for large index materials. The single oscillator model allows the oscillator frequency to vary with bandgap. The Hamaker constant is given for this model as

$$A_{121} = \frac{312(n_1^2 - n_2^2)^2 zJ}{[(n_1^2 - 1)^{1/2} + (n_2^2 - n_1^2)^{1/2}](n_1^2 + n_2^2)^{3/2}}. \quad [11]$$

Simple Spectral Method

Again beginning with the Lifshitz theory, Hough and White (10) arrived at a method of determining Hamaker constants that does not require full spectral data but rather looks at a material as a set of oscillators. We will refer to this approach as the simple spectral method (SSM). Essentially these oscillators correspond to absorptions in the material at certain frequencies of given strengths which can be determined from physical properties such as absorption spectra, refractive index, or dielectric constant. In this case a model London dispersion spectra can be synthesized from the relation

$$\epsilon(i\xi) = 1 + \sum_{i=1}^{N} \frac{C_i}{1 + (\xi/\omega_i)^2}, \quad [12]$$

where $C_i = (2/\pi)(f_i/\omega_i)$ and f_i is the strength of the oscillator at frequency ω_i. After various simplifying assumptions and approximations in the calculation of the integrals in Eqs. [3]–[5], Hough and White (10) arrive at the expression

$$A_{121}^{SSM} = \frac{3kT}{2} \sum_{n=0}^{\infty} {}' \sum_{s=1}^{\infty} \frac{(\Delta_{12})^{2s}}{s^3}, \quad [13]$$

where Δ_{ij} are the same as in Eq. [5], but ξ is replaced with $\xi_n = n(2\pi kT/\hbar)$. The C_i can be calculated from the refractive index in the visible from a Cauchy plot (see Hough and White (10)) which gives, say for a UV oscillator,

$$n^2(\omega) - 1 = (n^2(\omega) - 1)\frac{\omega^2}{\omega_{UV}^2} + C_{UV}. \quad [14]$$

Hence, with relatively little data one can calculate approximations to Hamaker constants using a little more information on the material's electronic structure than the TWA, but still substantially less than required for the full spectral method.

Bergström *et al.* (49) used this technique to estimate Hamaker constants for several ceramic materials separated by vacuum (air), water, *n*-dodecane, and SiO_2 at 2000 K. They calculated their C_i oscillator parameters from optical data obtained using spectroscopic ellipsometry in the energy range 1.5–4.4 eV, or from optical data in the literature, and the Cauchy plot for the UV terms. The IR terms were calculated from the relation $C_{IR} = \epsilon(0) - C_{UV} - 1$. For the ceramic materials Bergström *et al.* used one IR and one UV term. For water they used one microwave, five IR, and one UV term based on published data. These parameters were used to calculate the Hamaker constant with Eqs. [11] and [12]. This method is essentially that of Hough and White; however, they have used measured optical properties to obtain their oscillator parameters. It is a substantial improvement over the TWA, but again misses a lot of information considered in the full spectral method. The values obtained for *A* with these approximations based on physical properties are tabulated in Table 2 for A_{1v1} and Table 3 for A_{1w1}.

DISCUSSION

Vacuum Interlayer

From the results in Table 2 it is apparent that there is reasonable agreement for A_{1v1} for materials with relatively low refractive index (note: $n_{Si_3N_4} \approx 2$, $n_{TiO_2} \approx 2.6$) between values from force measurements and those determined from physical properties approximations. This suggests that when a second material is not interfering with the electromagnetic exchange between the two bodies, modeling the dielectric properties as simple oscillators seems to adequately predict the magnitude of the interaction. We should not expect this to be the case for covalently bonded materials or those with partially filled *d* orbitals, however, because the detailed distribution of interatomic bond frequencies (or transition energies) appears to play a more important role in the development of the dispersion force.

Aqueous Interlayer

The data in Table 3 show that the values of A_{1w1} (w, water) for any one material cover a wider range than those for A_{1v1}. The values from physical measurements and the TWA and SSMs differ by about 50%, and both are greater than the FS values by about a factor of two or three, with the exception of TiO_2. For TiO_2, the AFM, SSM, and FS

values are all in very good agreement. Among the theoretical methods, the values from the TWA and SSM are larger than the FS results by a factor of about two at best, and several times larger for the case of the TiO_2 TWA value. This indicates that intervening materials can have a dramatic effect on the dispersion interaction depending on how the interference in the electromagnetic exchange between adjacent bodies is modeled. Additionally, all of the theoretical methods give values lower than those obtained from measured force laws for all materials but TiO_2 (excluding TWA).

The accuracy of the measured Hamaker constants is, of course, predicated on the notion that *all* forces acting between surfaces in aqueous (or other) media are understood. It has long been understood that a number of forces act between two like surfaces immersed in aqueous solutions. The van der Waals interaction provides a primary attraction which is countered by repulsions by electrostatic interactions due to surface charges or steric interactions between adsorbed surfactant molecules. For the case of pure water or electrolyte solutions considered in the studies referenced here, electrostatic (or DLVO) forces are the only repulsions considered to be present. For solutions of high electrolyte concentration, the electrostatic double layer is collapsed, restricting the influence of DLVO repulsion to very small separations. This extends the range over which van der Waals attractive force may be measured. When longer range DLVO forces are present, they superimpose upon the van der Waals interaction over much of its effective range and must be explicitly taken into account. This requires accurate data on the surface potential or surface charge density (the determinant parameters in DLVO theory), which are frequently not known experimentally. Theoretical values for the surface potential or surface charge density, as used for the study of intersurface forces between sapphire crystals (39), are clearly limited by the accuracy of the assumptions or approximations used in their calculation. Consequently, possible errors in the estimate of DLVO forces will be passed on to determination of the Hamaker constant. When calculating such forces, data are generally fitted by varying the parameters involved in the balance of forces between surfaces, with one or more assumed to have some value, and the values for the others that fit best are accepted. This approach assumes *all* forces are known.

Several researchers studying intersurface forces have reported the observation of what are frequently termed ''additional'' forces. These are forces with generally exponentially decaying functions and do not fit in with van der Waals or DLVO forces. An additional repulsive force was reported between mica surfaces in KNO_3 solutions at small separations which had an exponential dependence on separation (37). These researchers also reported hysteresis between the forces measured for first approach vs subsequent approaches at high electrolyte concentrations. They discussed the possibility of ordered water layers at the surfaces which may undergo rearrangement on first approach. A study of intersurface forces at very small separations noted the observation of forces attributed to structure in the liquid medium, concluding it may not be trivial to sort them out from the overall force vs separation curves (50, 51).

Pashley *et al.* measured forces between uncharged, hydrophobic surfaces created by coating mica surfaces with a monolayer of surfactant (52). They reported the observation of long-range attractive forces, acting up to 8 nm, supposedly due to a surface-induced water structure with an exponential dependence on separation. The magnitude of this interaction was observed to be larger than that due to van der Waals forces by one to two orders of magnitude and apparently dependent on the degree of hydrophobicity of the surfaces. Their conclusion was that there does not appear to be any universal hydrophobic force, but rather one that depends on the individual nature of the surfaces involved. Israelachvili *et al.* reported observations of forces between mica and hydrocarbon-coated mica in hydrocarbon liquids (53). The hydrophobic attraction was expected to be due to an entropic preference of the anisotropic liquid molecules for the bulk liquid over the supposedly ordered region near the surfaces. The Hamaker constant between the hydrocarbon-coated surfaces in a hydrocarbon liquid was expected to be very small, which would facilitate observation of the additional attractive forces. For both surfaces, an attractive force much greater than that expected for just van der Waals forces was observed over 1 to 3 nm. The researchers did not believe this attraction was due to long-range ordering of the liquid molecules. The depth of the attractive minimum was also observed to depend on the time the surfaces were in close proximity, indicating a relatively slow molecular ordering mechanism may be responsible. The researchers conclude that such entropic attractions may result whenever a surface induces ordering in the liquid.

Additional long-range attractive forces have also been measured between sapphire crystals in aqueous NaBr solutions (40). These were referred to as hydrophobic forces and were observed at separations >15 nm, with an exponentially decaying distance dependence. The authors also reported an exponential repulsive force for small separations. A brief review (54) of these ''additional'' forces pointed out the extreme difficulty in sorting out what forces are actually present and separating them from each other. These variables are expected to depend on separation and electrolyte concentration to varying degrees. It appears that the behavior of such additional forces and their origins are not well understood at present. This introduces considerable uncertainty in the accuracy of Hamaker constants determined from experimental measurements with intervening liquids. It is suggested that performing such intersurface force measurements at varying temperatures may provide information on these additional forces. Since some of these additional forces are

postulated to be structural (i.e., liquid structure) or entropic in nature they should exhibit some temperature dependence.

General Comments

As mentioned above, the TWA performs rather poorly when the materials have a high refractive index or when an intervening film is present. This may be due in large part to the assumption that the behavior of a material is approximated by a single Lorentz oscillator with a constant frequency. If it is to be modeled as a single oscillator, then one should expect the frequency to have some relation to the bandgap of the material. As the bandgap decreases so should the energy and frequency of the oscillator. Since the bandgap tends to decrease as the index of refraction increases, it seems reasonable that the constant oscillator frequency in the TWA will lead to erroneously high values of the Hamaker constant for materials with large refractive indices. With an intervening material, the individual nature of the dielectric properties of each material involved is certain to produce an interaction far more complicated than this simple model.

Analysis and Assumptions Used

Hamaker constants calculated from the FS technique are also subject to possible inaccuracies. The spectral data may contain errors; however, calculations using repeated spectra give values within ± 4 zJ for 1v1 and ± 2 zJ for a system with interlayers, which may be a measure of such errors. Additional inaccuracy may result from the extensions or wings used to extrapolate the spectral data to 0 eV and to high energy (9). These wings may neglect some transitions in the IR or those involving core electrons, but these contributions are expected to be small. For a more detailed discussion of such complications, the interested reader is encouraged to see French *et al.* (9).

CONCLUSIONS

The intention of the present work is to establish some sense of how accurately the Hamaker constant of a given material system may be determined based on a comparison of values obtained using the currently available methods. Bear in mind that no single technique has been proven to be accurate to any degree. The notion of accuracy will be defined based on the level of agreement for Hamaker constants calculated with the available techniques for a given material system, better agreement implying better accuracy. The level of agreement between the methods is system specific. The best agreement is in the SiO_2/vacuum/SiO_2 system wherein all values lie between 50–60 zJ (SFA) and 66 zJ (FS). The total spread is about 10–20% of the upper value. The poorest agreement is in the mica/water/mica system in which values range from 2.9 zJ (FS) to 22 zJ (SFA). The

spread in values for this system is greater than a factor of seven.

The TWA produces values that tend to be comparable to those from other techniques for materials with refractive indices below 1.8 separated by vacuum. This model generally produces values larger than those produced by the other techniques by a factor of two or three for materials of index larger than 1.8 separated by vacuum, and so should not be used with such systems. Inspecting the range of values for the 1v1 systems, excluding the TWA results for large index materials, we see 70–135 zJ for mica, 113–150 zJ for Al_2O_3, 50–66 zJ for SiO_2, 147–174 zJ for Si_3N_4, and 173–199 zJ for TiO_2. The spread for all these systems is less than a factor of two. Therefore, the current level of accuracy to which a 1v1 Hamaker constant may be determined is considered to be within a factor between 1.5 and 2.

In the aqueous systems, the TWA again appears to give results for higher index materials that are larger than those produced by the other techniques, and so will not be used with these materials. As mentioned under Discussion, the addition of an intervening material to the space separating the bodies complicates the interaction between them, resulting in a broader range of Hamaker constants calculated from physical properties. For the case of water as the intervening material, values from force vs separation data are subject to the uncertainties introduced by other forces which are present, again a source of inaccuracy. For the aqueous systems the ranges of values are 2.9–22 zJ for mica, 21–67 zJ for Al_2O_3, 1.6–8.4 zJ for SiO_2, about 30–80 zJ for Si_3N_4, and 60–94 zJ for TiO_2. Excluding SiO_2 and mica, the spread of values is within a factor of about three. The SiO_2 and mica values are within a factor of about seven. Since there is no clear reason why mica and SiO_2 should produce poorer agreement than other systems, the accuracy with which 1w1 Hamaker constants may be determined is limited to within a factor of approximately seven.

Further work is needed to clarify the discrepancies between values calculated using physical properties, particularly for aqueous systems. Likewise, a better understanding of the complexities of measured force vs separation data is required for these data to be meaningfully compared to the other techniques. It is suggested that the AFM, or a modification thereof such as the colloid probe, with appropriate details such as tip geometry and electrostatic forces considered, may be the instrument with enough versatility to measure force laws for a wide range of materials systems. Hopefully, future inquiries regarding the values of Hamaker constants will proceed with greater sensitivity to the complex subtleties influencing this physical parameter and a greater confidence in the ability to accurately quantify it will emerge.

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