

NOTE

Hamaker Constants of Systems Involving Water Obtained from a Dielectric Function That Fulfills the f Sum Rule

Hamaker constants of systems involving liquid water are evaluated, within the full Lifshitz theory, by means of a recently proposed model of the dielectric function of this substance [Dingfelder *et al.*, *Radiat. Phys. Chem.* 53, 1 (1998)], which has been extended in the present work by including terms corresponding to infrared excitations and microwave relaxation. An important feature of the complete model is that, besides a good fit to experimental data, it satisfies the physical constraint provided by the f sum rule. For symmetrical systems interacting across water, calculated Hamaker constants are generally in good agreement with results obtained using the Ninham–Parsegian representation with the Roth and Lenhoff parameters for water. © 2000 Academic Press

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The forces between surfaces in close proximity appear at the basis of many important phenomena in a number of fields such as physics, chemistry, materials science, and biology. One type of interaction that is always present is the van der Waals force, which arises from electrodynamic interactions between permanent or induced dipoles within the intervening media. The van der Waals free energy per unit area corresponding to two halfspaces of materials 1 and 3 interacting over medium 2 is conventionally written as (1)

$$E_{123} = -\frac{A_{123}}{12\pi L^2}, \quad [1]$$

where L is the separation distance and A_{123} is the so-called Hamaker constant (2); for other geometrical configurations, the functional form of Eq. [1] is different (1). Within the framework of the full Lifshitz theory (3, 4), the (nonretarded) Hamaker constant is given by

$$A_{123} = -\frac{3k_B T}{2} \sum_{n=0}^{\infty} \int_0^{\infty} x \ln[1 - y_{12} y_{32} e^{-x}] dx \quad [2]$$

or, in a form that is more convenient for numerical calculation,

$$A_{123} = \frac{3k_B T}{2} \sum_{n=0}^{\infty} \sum_{s=1}^{\infty} \frac{(y_{12} y_{32})^s}{s^3}, \quad [3]$$

where T is the absolute temperature and k_B is Boltzmann's constant; the prime in the sum over n denotes the convention of dividing the $n = 0$ term by 2. The y_{ab} values are defined by

$$y_{ab} \equiv \frac{\varepsilon_a(iE_n) - \varepsilon_b(iE_n)}{\varepsilon_a(iE_n) + \varepsilon_b(iE_n)}, \quad (a, b = 1, 2, 3; a \neq b), \quad [4]$$

where the dielectric functions with imaginary argument, $\varepsilon(iE)$, of media a and b are evaluated at the discrete set of energies $E_n \equiv n2\pi k_B T$ ($n = 0, 1, 2, \dots$); at room temperature $E_1 \approx 0.16$ eV. Typically about a thousand terms are necessary to attain convergence in the sum over n in Eq. (3). Thus, E_n samples about 20 terms in the IR and visible and several hundred terms in the UV and soft X-ray energy region. Detailed knowledge of $\varepsilon(iE)$ in the latter regions is therefore essential to obtain accurate values of the Hamaker constant.

Although the real-valued function of imaginary argument $\varepsilon(iE)$ has no direct physical meaning, it can be easily related to the complex dielectric function, $\varepsilon(E) = \varepsilon'(E) + i\varepsilon''(E)$, through the Kramers–Kronig relation (see, e.g., Ref. (5))¹:

$$\varepsilon(iE) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{x \varepsilon''(x)}{x^2 + E^2} dx. \quad [5]$$

Then, a proper description of the complex dielectric function (in particular, of its imaginary part $\varepsilon''(E)$) is necessary in order to obtain reliable values of $\varepsilon(iE)$ and, in turn, of the Hamaker constant.

The calculation of $\varepsilon(iE)$ by means of the Kramers–Kronig relation requires knowledge of the absorption spectrum $\varepsilon''(E)$ over the entire energy range $0 \leq E < \infty$. When $\varepsilon''(E)$ is not known for all energies, the standard procedure is to use a mathematically convenient functional form for $\varepsilon(iE)$. The most widely used representation of $\varepsilon(iE)$ is that of Ninham and Parsegian (6),

$$\varepsilon(iE) = 1 + \frac{B}{1 + \tau E} + \sum_j \frac{f_j}{E_j^2 + g_j E + E^2}, \quad [6]$$

with the parameters B , τ , f_j , E_j , and g_j obtained by fitting the corresponding real and imaginary parts of the complex dielectric function to experimental data. In his comprehensive work on Hamaker constants of inorganic materials, Bergström (7) adopts this representation and gives values of f_j and E_j (B and g_j were set to zero in most cases) for 31 such materials including diamond. For liquid water (denoted in what follows by the subindex “w”), Bergström uses the parameters recommended by Roth and Lenhoff (8), which yield A_{1w1} constants substantially lower than those calculated using Parsegian's original set of parameters (9).

The aim of this note is the calculation of the Hamaker constant of systems involving water, a substance that is present in many situations of interest. Values previously reported in the literature were normally obtained by resorting to the Ninham and Parsegian representation of $\varepsilon(iE)$ (Eq. [6]) with different parameter sets (9, 5, 8). Our purpose here is, instead, to evaluate the Hamaker constant starting from Eq. [5] with an $\varepsilon''(E)$ function for liquid water which is based on the model recently proposed by Dingfelder *et al.* (10). A relevant property of the present model is that it satisfies the f sum rule, a constraint that any realistic dielectric function has to fulfill (11).

¹ The cgs system of units is used throughout this work.

Dingfelder *et al.* (10) express the absorption spectrum $\varepsilon''(E)$ of liquid water as

$$\varepsilon''(E) = E_p^2 \left[\sum_k D^*(E, E_k) + \sum_j \int_{E_j - \Delta_j}^{E_j + \Delta_j} D(E, E') \times \Theta(E - E') G(E', E_j) dE' \right], \quad [7]$$

where the nominal (free-electron) plasma energy of the medium is given by $E_p = \hbar(4\pi\mathcal{N}Ze^2/m)^{1/2}$; \hbar is the reduced Planck constant, and e and m are the electron charge and mass, respectively. \mathcal{N} is the number of molecules per unit volume and Z is the number of electrons per molecule. Ionizations are described by Drude functions

$$D(E, E_j) = \frac{f_j \gamma_j E}{(E^2 - E_j^2)^2 + \gamma_j^2 E^2} \quad [8]$$

multiplied by the step function $\Theta(E - E')$ and smeared out by a Gaussian

$$G(E, E_j) = \exp\left(-\frac{(E - E_j)^2}{2\Delta_j^2}\right), \quad [9]$$

while discrete excitations are modeled as derivative Drude functions

$$D^*(E, E_k) = \frac{2f_k \gamma_k^3 E^3}{[(E^2 - E_k^2)^2 + \gamma_k^2 E^2]^2}. \quad [10]$$

The parameters f_j , E_j , γ_j , Δ_j , f_k , E_k , and γ_k are listed in Ref. (10); they were obtained primarily by fitting Eq. [7] to the experimental data of Heller *et al.* (12).

The model of Dingfelder *et al.* was designed for the calculation of cross sections corresponding to the inelastic interactions of swift charged particles (electrons, protons, etc.) in liquid water. Contributions to the absorption spectrum $\varepsilon''(E)$ below a few electron volts were ignored due to their vanishing effect on the energy loss of the particle. Even though this energy range has a limited impact on the evaluation of accurate Hamaker constants, we have completed their model by including in $\varepsilon''(E)$ additional terms $f_j/(E_j^2 + g_j E + E^2)$ describing IR excitations and a microwave relaxation $B/(1 + \tau E)$, as in the Ninham–Parsegian representation, with parameters from Ref. (9). The microwave relaxation term was set to zero above a cutoff energy of 5 eV (see discussion below). This introduces small discontinuities in ε' and ε'' which, however, have a negligible effect on the $\varepsilon(iE)$ function evaluated through Eq. [5]. This function is also very insensitive to the actual value of the selected cutoff energy.

The dielectric (or optical) properties of any substance have to comply with certain restrictions that arise from causality and the dynamical laws of motion. In this respect, an important feature of the present model lies in the fact that the complex dielectric function is constrained to fulfill the well-known f sum rule (11),

$$\int_0^\infty E \varepsilon''(E) dE = \frac{\pi}{2} E_p^2, \quad [11]$$

or alternative forms in terms of the energy-loss function $\text{Im}(-1/\varepsilon) = \varepsilon''/(\varepsilon'^2 + \varepsilon''^2)$ or the extinction coefficient κ (11). Besides, the model completed with IR and microwave terms also satisfies the inertial sum rule and the static-limit sum rule (11). The use of such constraints makes it possible to assess the quality of the experimental optical or dielectric data employed in the fitting procedure. Moreover, the risk of unrealistic features of the fitted function in some energy interval is lowered. We note in passing that the Ninham and Parsegian representation, Eq. [6], cannot fulfill the f sum rule given in Eq. [11] due to the unphysical asymptotic behavior at high energies of the microwave relaxation term $B/(1 + \tau E)$; this is the reason for setting the microwave relaxation contribution to zero above a given cutoff energy.

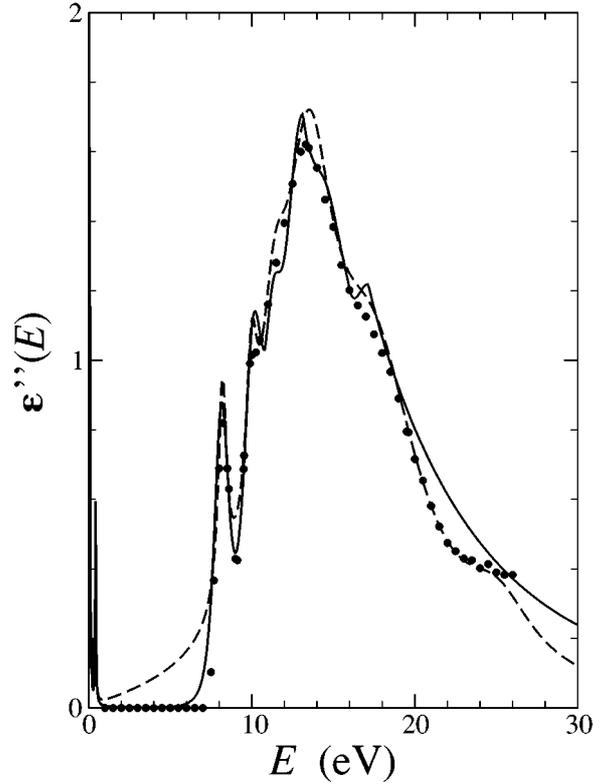


FIG. 1. Imaginary part of the complex dielectric function, $\varepsilon''(E)$, of liquid water as a function of E . Continuous curve: present model, Eq. [7] plus contributions from IR excitations and microwave relaxation; dashed curve: Ninham and Parsegian's representation, Eq. [6], with parameters from Ref. (8). Symbols, experimental data of Heller *et al.* (12).

Figure 1 shows the imaginary part of the dielectric function of liquid water calculated from the model presented in this work (continuous curve) and from the Ninham–Parsegian representation with parameters given by Roth and Lenhoff (8) (dashed curve). The experimental values by Heller *et al.* (12) are also displayed (symbols). We recall that the parameters in the dielectric functions of Dingfelder *et al.* and also Roth and Lenhoff were obtained by numerical fit to these measured data (12). In the interval from about 1 to 8 eV, the Dingfelder *et al.* $\varepsilon''(E)$ curve, Eq. [7], is close to the experimental values (liquid water is transparent in the visible and near UV), due to the sophisticated modelization of discrete excitations by means of derivative Drude functions. On the other hand, the good agreement of the Roth and Lenhoff $\varepsilon''(E)$ with the experimental data above 18 eV is not conclusive. In fact, recent measurements of dielectric properties of liquid water using inelastic X-ray scattering spectroscopy (13, 14) reveal limitations of the data from Heller *et al.* above about 15 eV. The new experiments indicate that, in the soft X-ray region, $\varepsilon''(E)$ is somewhat larger than hitherto assumed. It may then be advantageous to use a model that fulfills, among others, the f sum rule and thus diminishes the risk of introducing systematic errors in $\varepsilon''(E)$ or $\varepsilon(iE)$. Hamaker constants evaluated from such a model are expected to be, as a consequence, more reliable.

The dielectric function described above has been employed to calculate the Hamaker constant of systems involving liquid water. Room temperature ($T = 298$ K) was assumed and 2000 terms were included in the sum over n in Eq. [3]. We refrain from comparing our results with experimental values since uncertainties in measured Hamaker constants are rather large for such systems (15). Instead, our data are compared with calculations, also carried out within the full Lifshitz theory, by other authors.

For the water/vacuum/water case, we obtain $A_{\text{wvw}} = 55.0$ zJ ($1 \text{ zJ} = 10^{-21} \text{ J}$), whereas values of 50.0 and 38.9 zJ are obtained by using the Ninham–Parsegian

representation with parameters from Refs. (8) and (9), respectively. Our result is in good agreement with the Roth and Lenhoff value, while Parsegian's A_{ww} is considerably lower. On the other hand, Hough and White quoted 37.0 zJ (5), but they used a single oscillator in the UV with frequency and oscillator strength determined from a Cauchy plot.

Calculated values $A_{1\text{w}1}$ for symmetrical systems interacting across water are presented in Table 1. We have selected substances (monoatomic and polyatomic, semiconductors and insulators) that cover a wide range of Hamaker constants, between a few zJ and nearly 140 zJ. For materials other than water, we have used the Ninham–Parsegian representation with parameters taken from Refs. (16) or (7). For comparison purposes, we also quote Hamaker constants from Refs. (5, 16, 15, 7). Our values are in good agreement with those reported by Bergström (7), who employed the Roth and Lenhoff $\varepsilon(iE)$ function for liquid water. In most cases, differences are of the order of 10% or smaller. As pointed out by Ackler *et al.* (15), the Hamaker constant of the mica/water/mica system evaluated by several authors show a poor agreement, with differences up to a factor of 7; discrepancies are also large for $\text{SiO}_2/\text{water}/\text{SiO}_2$. On the other hand, good accordance is obtained for the $\text{TiO}_2/\text{water}/\text{TiO}_2$ system. The largest differences between present results and values given by Bergström occur for the alkali halides studied here, whose Hamaker constants are less than 8 zJ. The Senden and Drummond data (16) are systematically larger than ours. Notice, however, that these authors used Parsegian's original parameter set for water.

Within the Lifshitz formalism, these discrepancies have their origin in the adopted dielectric functions of imaginary argument. In Fig. 2 we have plotted the $\varepsilon(iE)$ function of liquid water as evaluated from different models. Notice the logarithmic energy scale. The Dingfelder *et al.* original $\varepsilon(iE)$ (dotted curve) departs, below about 2 eV, from the model completed with IR excitation and microwave relaxation terms (continuous curve), which tends to the correct static dielectric constant $\varepsilon(i0) = \varepsilon'(0) = 80$. The $\varepsilon(iE)$ functions given by Eq. [6] with parameters from Refs. (8) and (9) are also displayed (dashed and dot-dashed curves, respectively). The present dielectric function of imaginary argument is in much better agreement with Roth and Lenhoff's parameters for the Ninham–Parsegian representation than to Parsegian's original parameter set, which underestimates $\varepsilon(iE)$.

In conclusion, in this note we have studied the convenience of using accurate dielectric properties to evaluate Hamaker constants. In particular, the full Lifshitz formalism has been applied to the case of systems involving liquid water, for

TABLE 1

Hamaker Constant $A_{1\text{w}1}$ (in zJ; 1 zJ = 10^{-21} J) for Symmetrical Systems (1 = 3) Interacting across Water, Calculated at $T = 298$ K

1	$A_{1\text{w}1}$ (zJ)			
	Present results	Ref. (5)	Ref. (16)	Ref. (15) Ref. (7)
Si (amorphous) (16)	88.4		97.5	
SiO_2 (silica) (16, 7)	4.3	8.5	7.7	1.6 4.6
Si_3N_4 (amorphous) (16, 7)	45.7		60.7	45 48.5
Muscovite mica (16, 7)	11.8		20.1	2.9 13.4
C (diamond) (7)	130.2			138
CaCO_3 (5, 7)	13.1	22.3		14.4
TiO_2 (7)	54.2		60	53.5
MgO (7)	20.2			22.1
Al_2O_3 (7)	33.0		27.5	36.7
CaF_2 (7)	3.9	10.4		4.9
LiF (7)	2.7			3.6
NaCl (7)	5.9			5.2
KBr (7)	7.1			5.5
CdS (7)	35.8			34.0

Note. The parameters for Eq. (6) were taken from the Refs. quoted in column 1.

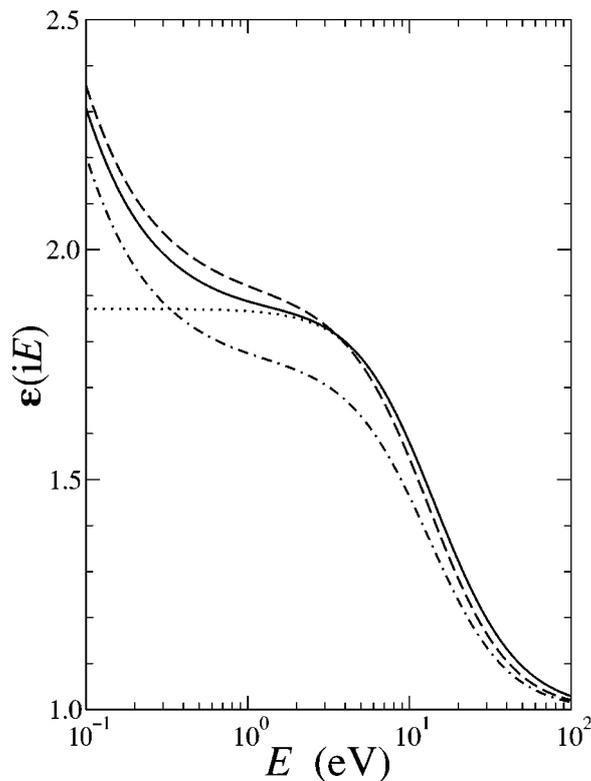


FIG. 2. Dielectric function of imaginary argument, $\varepsilon(iE)$, of liquid water as a function of E . The continuous and dotted curves indicate functions obtained from the Dingfelder *et al.* model (10) with and without the contribution of the IR excitations and microwave relaxation terms, respectively. The dashed and dot-dashed curves correspond to the Ninham–Parsegian representation with parameters from Refs. (8) and (9), respectively.

which we have taken a dielectric function model that fits reasonably well the available experimental data and, at the same time, fulfills important physical constraints in the form of sum rules. For symmetrical systems with an aqueous interlayer, there is good agreement with other recent calculations of Hamaker constants but, due to the consistency of the present method, our results should be, in principle, more reliable. Finally, it may be pointed out that Eq. [6] with $g_j = 0$ is equivalent to an oversimplified model of $\varepsilon''(E)$ expressed as a sum of Dirac delta functions (except for the microwave relaxation term) (5). Therefore, the use of sum-rule-constrained dielectric functions for other materials would yield improved values of the Hamaker constant.

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