VAN DER WAALS FORCES

SPECIAL CHARACTERISTICS IN LIPID-WATER SYSTEMS AND A GENERAL METHOD OF CALCULATION BASED ON THE LIFSHITZ THEORY

B. W. NINHAM *and* V. A. PARSEGIAN

From the Physical Sciences Laboratory, Division of Computer Research and Technology, National Institutes of Health, Bethesda, Maryland 20014. Dr. Ninham's permanent address is the Department of Applied Mathematics, University of New South Wales, Kensington, New South Wales, Australia 2033.

ABSTRACT   A practical method for examining and calculating van der Waals forces is derived from Lifshitz' theory. Rather than treat the total van der Waals energy as a sum of pairwise interactions between atoms, the Lifshitz theory treats component materials as continua in which there are electromagnetic fluctuations at all frequencies over the entire body. It is necessary in principle to use total macroscopic dielectric data from component substances to analyze the permitted fluctuations; in practice it is possible to use only partial information to perform satisfactory calculations. The biologically interesting case of lipid-water systems is considered in detail for illustration. The method gives good agreement with measured van der Waals energy of interaction across a lipid film. It appears that fluctuations at infrared frequencies and microwave frequencies are very important although these are usually ignored in preference to UV contributions. "Retardation effects" are such as to damp out high frequency fluctuation contributions; if interaction specificity is due to UV spectra, this will be revealed only at interactions across <200 angstrom (A). Dependence of van der Waals forces on material electric properties is discussed in terms of illustrative numerical calculations.

INTRODUCTION

The purpose of this and a succeeding paper (for a preliminary report, see reference 1) is to develop in some detail a general method for calculating van der Waals forces in situations of biological interest. For definiteness we shall refer in most part to the interaction of water across a thin hydrocarbon film. The energy of such a system was recently measured by Haydon and Taylor (2). We shall show that van der Waals forces in this system can be analyzed easily and accurately by the macroscopic theory of Lifshitz (3). Further, several important qualitative features of these forces, unnoticed in earlier treatments, are revealed by this analysis. The approach elaborated here allows prediction of attractive energies in other systems,

as well as pointed examination of the probable role of these forces in biological processes. In particular, we shall find that a careful analysis provides a strong hint concerning the problem of attractive specificity.

The outline of the paper is as follows:

(*a*) We define precisely what we mean by a van der Waals force and, to put our investigation into perspective, briefly summarize earlier work on the problem.

(*b*) We give a description of the formulae of Lifshitz applicable to thin films between semi-infinite media, and discuss a useful representation of dielectric susceptibility by means of which spectroscopic information may be adapted for calculation.

(*c*) Estimates of the dispersion force in lipid-water systems are obtained and compared with the measured values.

(*d*) A detailed examination is made of the high frequency spectrum of contributions to the energy in order to develop an intuitive understanding of the behavior of van der Waals forces across lipid layers, and of the experimental variables which affect forces. This is important in as much as this study throws some light on the physical origin of specificity in biological systems. It will be shown that there is as great a contribution to the energy from infrared frequencies as from the UV and the contribution from the microwave region is as great as infrared and UV combined.[1] Further, the so-called retardation effects due to the finite velocity of signal propagation emerge as a progressive damping of higher frequency contributions as film thickness is increased.

(*e*) Finally we summarize some qualitative implications concerning biological systems which can be drawn from a detailed study of van der Waals forces by Lifshitz theory.

THE VAN DER WAALS FORCE

The van der Waals force is founded on the recognition that spontaneous, transient electric polarization can arise at a center due to the motion of electrons, molecular distortion, or molecular orientation. This polarization will act on the surrounding region to perturb spontaneous fluctuations elsewhere. The interaction resulting from this perturbation is such as to lower the energy. The classes of such interaction have been extensively reviewed by Kauzmann (4) and Jehle (5).

The resulting attractive "dispersion" force for electronic fluctuations was first calculated by F. London (6) in his famous 1930 paper. He showed that the force between two isolated atoms is proportional to the inverse seventh power of distance, and the product of their polarizabilities. London's theory provided the basis for subsequent theoretical estimates (7) of dispersion forces between con-

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[1] The characteristics of the microwave-frequency fluctuations are sufficiently distinct from those of higher frequencies so that they are considered separately in the succeeding paper referred to as "two"; Parsegian, V. A., and B. W. Ninham. 1970. *Biophys. J.* **10**:664.

densed media. These estimates have been severely limited by several *ad hoc* assumptions which are:

(*a*) the assumption of pairwise additivity of individual interatomic interactions in a condensed medium;

(*b*) the approximation that contributions centered around a single dominant frequency of the electromagnetic field in the ultraviolet are important; and

(*c*) that the difficulty of dealing with an intermediate substance (e.g. hydrocarbon between aqueous regions) can be handled by the insertion of an arbitrary "dielectric constant" correction at a single frequency. In addition, detailed information about atomic polarizabilities and relaxation frequencies was required for computations. As emphasized by later workers (3) a calculation of van der Waals forces based on these assumptions (valid for dilute gases) is intrinsically unsound. This method obscures almost totally the most interesting qualitative features of van der Waals forces.

In 1955 Lifshitz (8) and later he and his coworkers (3) developed a theory based on ideas of Casimir and Polder (9) which overcomes these difficulties. His theory includes all many-body forces through a continuum picture, retains contributions from all interaction frequencies, and deals correctly with the effects of intermediate substances. More important, the information required for calculations is contained in the dielectric properties of component materials—information available in principle from independent spectroscopic measurements.

For a condensed medium, where the range of strong interaction exceeds the distance between atomic centers, Lifshitz regards the entire set of local spontaneous electric field fluctuations as an electromagnetic field which extends over the whole system. This time-varying field can be frequency analyzed; the strength of a field of a given frequency is directly dependent on the response of the material to an applied field of that frequency, i.e., its dielectric susceptibility $\epsilon(\omega)$. Boundary surfaces between unlike materials will affect these electric fields and consequently the electromagnetic energy of the system. This approach to dispersion forces examines the change in energy of a system with movement of the boundary surfaces between unlike regions.

It was thought (10) that the theory of Lifshitz could not be applied to the calculation of dispersion forces in the absence of complete spectral information. We find that such complete data are unnecessary, particularly when component substances are of similar weight density. In fact, it is possible to make several simplifying assumptions regarding spectra. All that appears necessary for the calculation of van der Waals forces in the present thin hydrocarbon film system are single average absorption frequencies in the infrared and UV for water, one average frequency in the UV for hydrocarbon, indices of refraction at visible frequencies, a limiting value for the dielectric susceptibility of water between microwave and infrared frequencies, and the simplest form for the dielectric dispersion of liquid water in the microwave region.

FORMULARY

Lifshitz Expression

The general formula for the attractive force per unit area between two semi-infinite media of substance 1 across a planar slab of substance 2 of thickness l (Fig. 1) (3) is

$$F(l) = \frac{kT}{\pi c^3} \sum_{n=0}^{\infty}{}' \epsilon_2^{3/2} \xi_n^3 \int_1^{\infty} p^2 \left\{ \left[\left(\frac{s+p}{s-p} \right)^2 \exp\left(\frac{2p\xi_n \, l\epsilon_2^{1/2}}{c} \right) - 1 \right]^{-1} \right. $$
$$\left. + \left[\left(\frac{s\epsilon_2 + p\epsilon_1}{s\epsilon_2 - p\epsilon_1} \right)^2 \exp\left(\frac{2p\xi_n \, l\epsilon_2^{1/2}}{c} \right) - 1 \right]^{-1} \right\} dp, \quad (1)$$

where k is Boltzmann's constant, T absolute temperature, c the velocity of light in vacuum, ϵ_1 and ϵ_2 the dielectric susceptibilities evaluated on the imaginary frequency axis at $\omega = i\xi_n$,

$$s = \sqrt{p^2 - 1 + \epsilon_1/\epsilon_2}, \quad (2)$$

and

$$\xi_n = \frac{2\pi kT}{\hbar} n, \quad (3)$$

with $2\pi\hbar$ Planck's constant. The sum is taken over integral n and the prime $(')$ on the sum sign indicates that the $n = 0$ term be multiplied by $\frac{1}{2}$.

By integration of the force with respect to l, the corresponding free energy of interaction per unit area (taking $G = 0$ at $l = \infty$) is

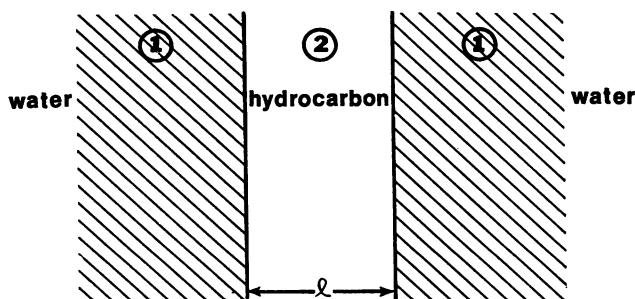$$G(l, T) = \frac{kT}{8\pi l^2} \sum_{n=0}^{\infty}{}' I(\xi_n, l), \quad (4)$$

FIGURE 1 Two semi-infinite media of substance 1 separated by a planar slab, thickness l, of substance 2. In the text we consider the case where 1 is water and 2 is hydrocarbon.

where

$$I(\xi_n, l) = \left(\frac{2\xi_n l\epsilon_2^{1/2}}{c}\right)^2 \int_1^\infty p\left\{\ln\left[1 - \bar{\Delta}^2 \exp\left(\frac{-2p\xi_n l\epsilon_2^{1/2}}{c}\right)\right]\right.$$
$$\left. + \ln\left[1 - \Delta^2 \exp\left(\frac{-2p\xi_n l\epsilon_2^{1/2}}{c}\right)\right]\right\} dp, \quad (5)$$

with

$$\bar{\Delta} = \frac{s\epsilon_2 - p\epsilon_1}{s\epsilon_2 + p\epsilon_1}, \qquad \Delta = \frac{s - p}{s + p}. \tag{6}$$

To conform with the notation of colloid chemistry, it will be convenient in the following to define a "Hamaker function," $A = A(l, T)$, such that

$$G(l, T) = -\frac{A(l, T)}{12\pi l^2}. \tag{7}$$

Comparing equation 7 with equation 4, then

$$A(l, T) = 1.5 \, kT \sum_{n=0}^\infty{}' I(\xi_n, l). \tag{8}$$

Limiting Cases. Low temperature: when $kT \ll \hbar\xi_n$, the sum in n becomes an integral in ξ and we have the integral form

$$\tilde{A}(l) = \frac{3\hbar}{4\pi} \int_0^\infty I(\xi, l) \, d\xi, \tag{9}$$

where $I(\xi; l)$ is as in equation 5 but ξ is now a continuous variable.

For $l \ll c/(2\xi_n\epsilon_2^{1/2})$, define $x = (2p\xi_n l\epsilon_2^{1/2}/c)$ and

$$I(\xi_n, 0) = \int_0^\infty x \ln\left[1 - \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1}\right)^2 e^{-x}\right] dx. \tag{10}$$

(In this case $s \approx p$ since values of $p \gg 1$ contribute to the integral in equation 5.) Sometimes $\bar{\Delta}^2 \ll 1$ and

$$I(\xi_n, 0) \approx \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1}\right)^2.$$

In the double limit $l \to 0, T \to 0$

$$\tilde{A}(0) = -\frac{3\hbar}{4\pi} \int_0^\infty \int_0^\infty x \ln\left[1 - \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1}\right)^2 e^{-x}\right] dx \, d\xi$$
$$\approx \frac{3\hbar}{4\pi} \int_0^\infty \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1}\right)^2 d\xi. \tag{11}$$

In order to use the above formulae, we need a convenient representation for the dielectric susceptibility.

The function $\epsilon(\omega)$ is a complex function $\epsilon' + i\epsilon''$ of a complex frequency $\omega = \omega_R + i\xi$. The dispersion energy depends only on the values of ϵ on the imaginary frequency axis $\epsilon = \epsilon(i\xi)$ and, from equations 4 and 5, a knowledge of $\epsilon(i\xi)$ is important only for those values of ξ for which there is a difference between the dielectric susceptibilities of the two materials at a given frequency. We seek a suitable representation for $\epsilon(i\xi)$ which will incorporate experimental data as well as satisfy general constraints which must be satisfied by any dielectric susceptibility. These constraints are that $\epsilon(i\xi)$ be a pure real quantity monotonic decreasing with ξ, and that the function $\epsilon(\omega)$ $(\omega = \omega_R + i\xi)$ have no zeros or poles in the upper half ω plane in order to satisfy the Kramers-Kronig relations (11). A suitable representation is

$$\epsilon(\omega) = 1 + \frac{C_{mw}}{1 - i\omega/\omega_{mw}} + \sum_j \frac{C_j}{1 - (\omega/\omega_j)^2 + i\gamma_j\omega}. \tag{12}$$

This representation includes simple Debye relaxation for microwave frequencies plus the classical form of Lorentz electron dispersion for infrared through mid-UV frequencies. We will describe below how the necessary constants C_{mw} and C_j (proportional to "oscillator strengths") and resonance frequencies ω_{mw}, ω_j may be determined from measurements made on the real frequency axis $\omega = \omega_R$. On the imaginary axis $(\omega = i\xi)$, we have from equation 11

$$\epsilon(i\xi) = 1 + \frac{C_{mw}}{1 + \xi/\omega_{mw}} + \sum_j \frac{C_j}{1 + (\xi/\omega_j)^2 - \gamma_j\xi}. \tag{13}$$

Now the damping term in $\gamma_j\omega$ in equation 12 is significant only when $\omega \approx \omega_j$ since bandwidths are always much less than absorption frequencies. The contribution of this term in equation 13 will be negligible $(1 + (\xi/\omega_j)^2 \gg \gamma_j\xi)$ so that we may take

$$\epsilon(i\xi) = 1 + \frac{C_{mw}}{1 + \xi/\omega_{mw}} + \sum_j \frac{C_j}{1 + (\xi/\omega_j)^2}. \tag{14}$$

Clearly then, only the oscillator strengths and absorption frequencies of component materials will determine dispersion energies.

At very high frequencies the dielectric dispersion has the limiting form (11)

$$\epsilon(\omega) = 1 - \frac{4\pi N e^2}{m\omega^2}. \tag{15}$$

Here e and m are electron charge and mass, and N is the number of electrons/cc.

On the imaginary axis equation 15 becomes

$$\epsilon(i\xi) = 1 + \frac{4\pi N e^2}{m\xi^2}. \tag{16}$$

This form holds for materials made of light elements at frequencies in and above the far-UV. It is important to emphasize that materials of light elements and similar weight density will have similar susceptibilities at these high frequencies, and consequently give a very small contribution to the force and energy integrals. This is the usual situation in systems of biological interest.

Between the low- to mid-UV region described by equation 14 and the far-UV to X-ray region described by equation 16, the simplest procedure is to construct an interpolation formula for $\epsilon(i\xi)$. Given the condition that $\epsilon(i\xi)$ be monotonic decreasing, there is little ambiguity in so doing.

However, because of the similarity of the susceptibilities of component substances in the mid-UV, the integrands or sum terms of the force and energy expressions tend to zero very rapidly in this region, and give little contribution. In practice therefore, it is usually sufficient to use the form of equation 14 for susceptibilities, and no interpolation is required. Indeed, inspection of the full expressions equations 1, 4, and 5 for the force and energy shows that the effect of the exponentials $\exp(-2p\xi l\epsilon_2^{1/2}/c)$ is to diminish contributions to the integrand severely for frequencies $\xi_* > c/(2l\sqrt{\epsilon_2})$. For example, and typically when $l \approx 50$ A, $\xi_* > (3 \times 10^{16}) \approx 10^{16.5}$, frequencies in the UV band satisfy $10^{15.8} \lesssim \xi \lesssim 10^{16.8}$ so that frequencies at and above the far-UV will be in any event unimportant. This point is illustrated in detail in the section Analysis of Integrals where we carry out an analysis of the integral of equation 9.

DATA AND CALCULATIONS

Spectroscopic Experimental Data

For water and hydrocarbons the following dielectric data are known.

Water. From audio through microwave frequencies water exhibits simple Debye relaxation from its static value of 80.4 down to 5.2 with a characteristic relaxation wavelength 1.78 cm. Thus, $C_{mw} = (80.4 - 5.2) = 75.2$, and $\omega_{mw} = 2\pi c/\lambda_{mw} = (1.06 \times 10^{11}) = 10^{11.026}$ radians/sec. (Data here (12) are for $T = 20°C$.) The infrared spectrum is dominated by three closely spaced absorption peaks (13) at $\omega_{ir} = 3.0 \times 10^{14}$, 6.89×10^{14}, and 7.08×10^{14}, after which ϵ relaxes to values observed as the square of the index of refraction n_w, where $n_w^2 = 1.78$. We shall use $C_{ir} = (5.2 - 1.78) = 3.42$ and approximate the vibration frequency by an average value $\bar{\omega}_{ir} = [\frac{1}{3}(3 + 6.89 + 7.08) \times 10^{14}] = 10^{14.75}$ radians/ sec. Insensitivity of the calculated energy to this approximation is checked below.

In the near- to mid-UV, water (14) shows a weak absorption at $\lambda = 1650$ A or

$\omega_{uv} = (1.14 \times 10^{16}) = 10^{16.058}$ and an apparently much stronger absorption at about $\lambda = 1250$ A or $\omega_{uv} = (1.507 \times 10^{16}) = 10^{16.178}$. However, the relative strength of these peaks and the presence of other absorption in the further UV are not known. Because of the slow variation of $\epsilon(i\xi)$ with ξ one may use an average frequency $\bar{\omega}_{uv}$ for the near- to mid-ultraviolet region. A common approximation is to use a frequency equivalent to the first ionization potential (4). In this case 12.62 ev $=$ $\hbar\bar{\omega}_{uv}$, or $\bar{\omega}_{uv} = (1.906 \times 10^{16}) = 10^{16.28}$ rad/sec. (Throughout paper rad used for radian.) It will be shown that use of the ionization potential value or the stronger absorption band value has little effect on the estimated energy. The value of C_{uv} for this relaxation is $(n_w^2 - 1) = (1.78 - 1) = 0.78$. We have then

$$\epsilon_{\text{water}} = \epsilon_w(i\xi) = 1 + \frac{C_{mw}}{1 + \xi/\omega_{mw}} + \frac{C_{ir}}{1 + (\xi/\bar{\omega}_{ir})^2} + \frac{C_{uv}}{1 + (\xi/\bar{\omega}_{uv})^2}, \quad (17)$$

where the constants are given above.

Hydrocarbons. There appears to be little dielectric relaxation shown by hydrocarbon liquids between audio and visible frequencies (12) where $\epsilon_{hc} = n_{hc}^2$ (n = index of refraction). By examining the reflection of laser beams from a thin lipid film, Cherry and Chapman (15) have made a precise measurement of an anisotropic index of refraction:

$n_{hc} = 1.486$ for polarization perpendicular to the plane of the film and $n_{hc} =$ 1.464 parallel to the film. These give $\epsilon_{hc} = 2.208$ and 2.143, respectively. Other possible estimates at optical frequencies are $\epsilon_{hc} = n_{hc}^2 = 1.89$ for n-hexane (12) and $\epsilon_{hc} = n_{hc}^2 = 2.0$, an average value often used as typical for hydrocarbons. Each of these numbers will be considered below.

Again we will summarize relaxation as occurring at an average frequency corresponding to the ionization potential. An appropriate value of this for a thin hydrocarbon film is not easily determined from available data. Values for decane (16), 10.19 ev or $\bar{\omega}_{uv} = 1.54 \times 10^{16}$, and for ethane (16, 14), 11.65 ev or $\bar{\omega}_{uv} =$ 1.76×10^{16}, will suffice in the present instance. Using these values we have

$$\epsilon_{hc}(i\xi) = 1 + \frac{n_{hc}^2 - 1}{1 + (\xi/\bar{\omega}_{uv})^2}$$

Theoretical Estimates

We first calculate the van der Waals energy of water acting across a lipid film (Fig. 1) 50 A thick at 20°C. Using equations 17 and 18 for $\epsilon_w(i\xi)$ and $\epsilon_{hc}(i\xi)$ with an average infrared absorption frequency for water and average UV absorption derived from ionization potentials of water and decane or ethane, we find $A(50 \text{ A})$ by equation 8 for four values of n_{hc}^2 (Table I). For these data, values of $A(l = 50 \text{ A}, T = 20°C)$ range from 5.5 to 7.1 $\times 10^{-14}$ erg. We note that A is not simply monotonic in n_{hc}.

These estimates are slightly higher than those inferred from experiments on thin lipid films (2) ($\approx$4.7 $\times$ 10^{-14} erg) but much lower than those derived from experiments on suspensions of paraffins in aqueous suspension (17) ($\approx$1.6 $\times$ 10^{-13} erg). In principle both experimental estimates should be approximately the same so that theoretical estimates here are less ambiguous than experiments but within the correct ranges.

Table II A suggests that A is relatively insensitive to the assumed $\bar{\omega}_{uv}$ as long as they are chosen in a consistent way for the two materials. Using strongest near-UV absorption peaks or ionization potentials for both materials give A estimates 6.1–7.1 $\times$ 10^{-14} for n_{hc}^2 = 2.208 that are distinct from the value obtained by using the second-strongest water peak (9 $\times$ 10^{-14}). Also, (Table II B) it makes little difference if one average $\bar{\omega}_{ir}$ is used for water or if the three main infrared peaks are equally weighted, and separately contribute to $\epsilon_w(i\xi)$.

A careful attempt to use $\epsilon(i\xi)$ that satisfy both low and high frequency behavior (equations 14 and 16) makes negligible difference to the estimated A. By straight-line interpolation between forms for near-UV and X-ray regions and using the

TABLE I

ESTIMATES OF THE HAMAKER FUNCTION A USING THE GENERAL EQUATION 7

Take ω_{ir}^w = 5.66 $\times$ 10^{14} rad/sec, C_{ir}^w = 3.4
  ω_{mw}^w = 1.06 $\times$ 10^{11} rad/sec, C_{mw}^w = 75.2. 2.
  ω_{uv}^w = 1.906 $\times$ 10^{14} rad/sec, n_w^2 = 1.78.
  l = 50 A, T = 20°C.

n_{hc}^2	A(erg), ω_{uv}^{hc} = 1.54 $\times$ 10^{16} (decane I.P.*)	A(erg), ω_{uv}^{hc} = 1.76 $\times$ 10^{16} (ethane I.P.)
	erg	erg
1.9 (n-hexane)	5.8 $\times$ 10^{-14}	5.8 $\times$ 10^{-14}
2.0 ("typical" value)	5.5	5.8
2.143 (laser expt.)	5.7	6.5
2.208 (laser expt.)	6.1	7.1

* I.P. = ionization potentials.

TABLE II A

DEPENDENCE OF A ON ω_{uv}^w

Take n_{hc}^w = 2.208, otherwise as in Table I.

ω_{uv}^{hc} $\times$ 10^{-16}	ω_{uv}^w $\times$ 10^{-16}	A $\times$ 10^{14}	Source of ω_{uv}
rad/sec	rad/sec	erg	
1.4	1.507	6.6	Strongest absorption
1.4	1.14	9.	2nd strongest H$_2$O absorption
1.76	1.906	7.1	Ionization potentials (ethane for hc)
1.54	1.906	6.1	Ionization potentials (decane for hc)

TABLE II B

EFFECT OF AVERAGING VS. EQUAL WEIGHTING OF THREE
WATER INFRARED FREQUENCIES

Data as above.

ω_{ir}^w	$A, (\omega_{uv}^{hc} = 1.54 \times 10^{16})$	$A, (\omega_{uv}^{hc} = 1.76 \times 10^{16})$
	erg	erg
3.0, 6.89, 7.88 $\times 10^{14}$ rad/sec equally weighted	5.9 $\times 10^{-14}$	7.0 $\times 10^{-14}$
$\bar{\omega}_{ir}^w = 5.66 \times 10^{14}$ rad/sec	6.1	7.1

TABLE III

$A(l)$ VS. l

Use $n_{ho}^2 = 2.208$, $\bar{\omega}_{uv}^{hc} = 1.54 \times 10^{16}$ and as in Table I.

$l(A)$	$A(l) \times 10^{14}$	$A(l)/A(0)$	$A(l)/A(0)$ old theory (18)
	erg		
0	6.36		
5	6.35	1.	1.
10	6.33	1.	0.95
50	6.09	0.96	0.84
100	5.78	0.91	0.72
500	4.74	0.75	0.28
1000	4.43	0.7	0.15
5000	3.65	0.57	0.03
10000	3.33	0.52	0.015
50000	3.16	0.5	0.003

electron density of material having 1 g/cc weight density, we find that the effect is always less than 6%. (The method of interpolation is described in detail elsewhere for the case of soap films in air [18].)

A as a Function of Thickness l. By virtue of equations 8 and 10 the value of A as $l \to 0$ converges to

$$A(l = 0, T) = 1.5kT \sum_{n=0}^{\infty}{}' \int_0^{\infty} x \ln \left[1 - \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1} \right)^2 e^{-x} \right] dx.$$

Deviations of A from this limiting form when $l > 0$ are called "retardation effects" since they are caused by the finite travel time of electromagnetic radiation across the gap l.

In Table III we have listed calculation of $A(L)$ for $l = 0$ to 50,000 A. The retardation factor of $A(l)/A(0)$ is also listed for comparison with the function used in colloid chemistry (19). Clearly the neglect of non-UV frequency fluctuations, typical of the older theory, gives vastly lower estimates at large separation distances.

The proper analysis of retardation effects is discussed in the following section and in the Appendix. At very large distances the calculation of A is dominated by the $n = 0$ term in equation 8; this term is the subject of the succeeding paper (two).

ANALYSIS OF INTEGRALS

Spectral Contributions

In order to clarify the dependence of the dispersion energy on fluctuation frequencies such that $h\omega \gtrsim kT$, we examine the integrands of the integrals which occur in equations 7 and 9. These are of the form

$$\int I(\xi, l) \, d\xi, \qquad (19)$$

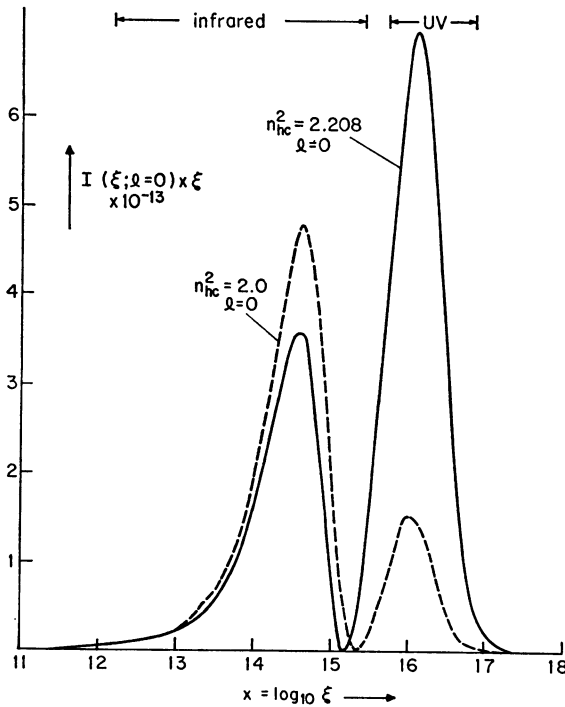where $I(\xi, l)$ defined by equations 5 and 10 measures the contribution to the energy

FIGURE 2 Spectrum of relative infrared and UV contributions to van der Waals energy in the limit $l = 0$. Use equations 17, 18, and 10 with data for water and ethane. Data for decane give sharply reduced UV peak. Note large infrared contribution, sharp decrease in UV contribution when n_{hc}^2 is reduced from 2.208 to 2.0 to bring it closer to $n_w^2 = 1.78$ for water. The factor ξ multiplying $I(\xi, l = 0)$ in the ordinate is to correct for the logarithmic scale in the abscissa.

of frequencies in the range $(\xi, \xi + d\xi)$. Changing variables to $x = \log_{10} (\xi)$, the relative contribution from the spectral range $(x, x + dx)$ is then $2.303 \, \xi I(\xi, l) \, dx$.

Fig. 2 shows plots of $I(\xi, l = 0)$ for two values of n_{hc}^2, 2.208 and 2.0 with $l = 0$. (Other data are as in Table I.) The finite frequency contribution to the total energy is cleanly divided into an infrared and an UV peak. The relative magnitude of these two peaks obviously depends on the value of n_{hc}^2. For example, with $n_{hc}^2 = 2.208$, 35 % of the integral comes from the infrared; but with $n_{hc}^2 = 2.0$, 80 % of the energy integral is due to electromagnetic fluctuations at infrared frequencies! It is remarkable that the role of the infrared spectrum of water has been ignored in previous discussions of van der Waals forces. Similarly, as already emphasized, there is an important contribution from the microwave region whose qualitative features are sufficiently unique to be considered separately (two).

For fixed l and fixed water composition, the only two parameters which can alter significantly with hydrocarbon composition are n_{hc}^2 and $\bar{\omega}_{uv}^{hc}$. The plots of $I(\xi, l)$ in Fig. 2 also show that the effect of changing n_{hc}^2 is to alter the entire spectrum of contributing frequencies. Similarly, variation in absorption frequencies $\bar{\omega}_{uv}$ will shift the position of maxima of the spectrum, and alter the height of peaks. For the present example $\epsilon_w > \epsilon_{hc}$ in the infrared, but $\epsilon_w < \epsilon_{hc}$ in the UV. Increases in ϵ_{hc} will generally increase the contribution from the UV and decrease those from the infrared.

According to Fig. 2 we see too that most of the contribution to the energy integrals occurs within the range of validity of the low frequency (i.e. $\xi < 10^{16.5}$) dielectric dispersion representation, equations 12 and 14. This is why there is little change resulting from extension of the formulae by interpolation into the plasma region, equations 15 and 16.

Retardation Effects

The case $l = 0$ considered above shows the nature of spectral contributions to the energy with variation of material properties of component substances. There is another condition imposed on the allowed correlations in electromagnetic fluctuations across a gap due to the finite velocity of light. When the travel time of a fluctuation signal across the gap is comparable to a fluctuation frequency $(2l\epsilon_2^{1/2})/c \sim 1/\xi$, the correlation in fluctuations between either side is diminished. The integrand $I(\xi, l)$ satisfies the unequality $I(\xi, l) \leqslant I(\xi, 0)$. This underlies the behavior shown in Fig. 3. Figs. 3 *a* and 3 *b* show plots of $I(\xi, l)$ for a range of values of l; $l = 0$, 50 A and 500 A, and for $n_{hc}^2 = 2.208$ and 2.0; they illustrate the progressive removal of high frequency modes with increasing l. On the same abscissa we have also plotted (Fig. 3 *c*) the ratio $I(\xi, l)/I(\xi, 0) \leqslant 1$. This rather complicated function is weakly dependent on material properties and is the multiplicative factor for damping these high frequency modes.

The frequency regime over which the integrand in ξ is damped out is about one dec-
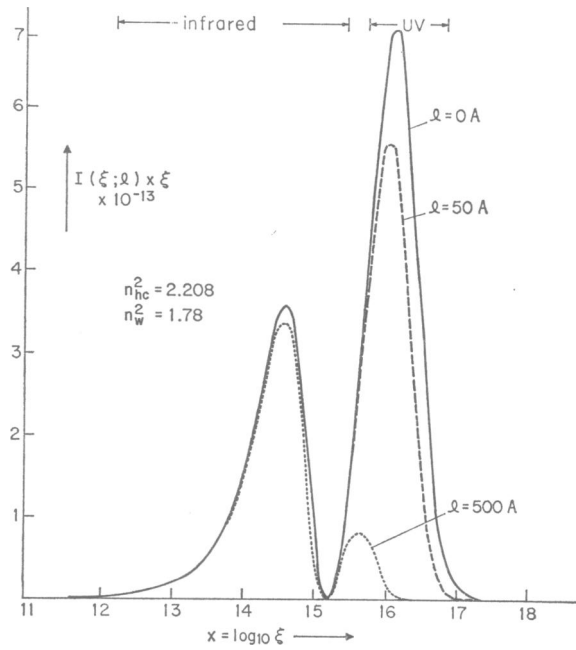
FIGURE 3 a   The influence of the finite velocity of propagation on the spectrum of infrared and UV contributions to van der Waals energies. $n^2_{hc} = 2.208$, data for ethane and water. Large UV contribution at $l = 0$ and significant decrease of A with l.
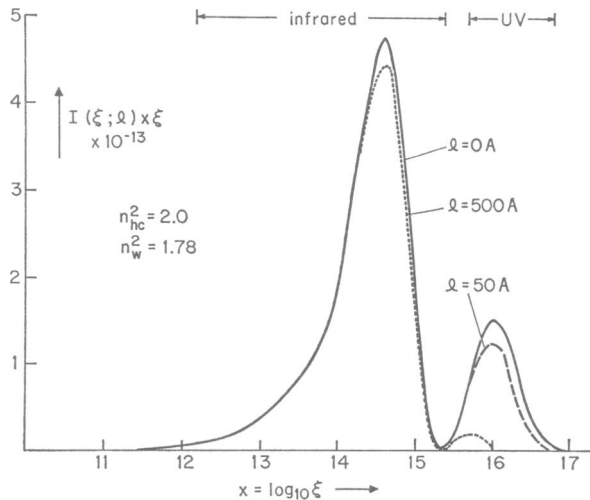

FIGURE 3 b   The influence of the finite velocity of propagation on the spectrum of infrared and UV contributions to van der Waals energies. $n^2_{hc} = 2.0$, data for ethane and water. Small UV contribution at $l = 0$ and weak dependence of A on l.
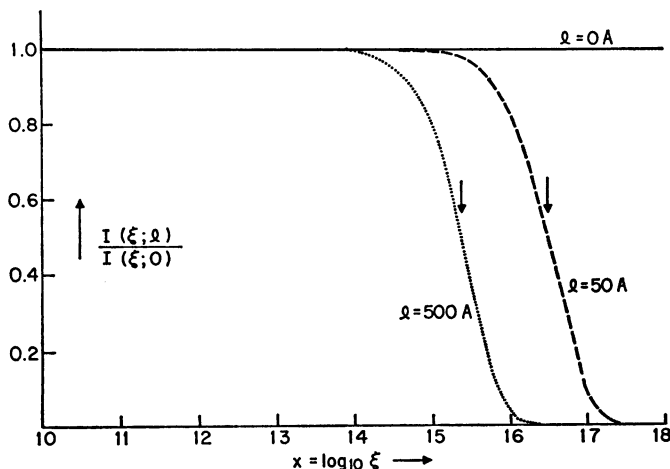
FIGURE 3 c The influence of the finite velocity of propagation on the spectrum of infrared and UV contributions to van der Waals energies. Retardation factor for damping contributions at different frequencies. Arrows ↓ indicate frequency at which $\xi = c/2l$. Note that retardation damping is effectively a shift of the curve $I(\xi; l)/I(\xi; 0)$ to the left to cut out higher frequencies. The range of damping is approximately one decade wide and centered about $\xi = c/2l$.

ade wide and roughly centered about $\xi_s = c/(2l\epsilon_{hc}^{1/2}) \sim (c/2l)$ where $\epsilon_{hc} \sim 1$. By virtue of the large infrared contribution to the energy, even at 500 A (where $\xi_s \approx 10^{15.5} <$ UV frequencies), almost half the original integral is intact when $n_{hc}^2 = 2.208$ (Fig. 3 a). For $n_{hc}^2 = 2$, (Fig. 3 b) some 78 % of the original contribution to the integral remains. It would appear then that van der Waals interactions in hydrocarbon-water systems are peculiarly long range because of the infrared and microwave spectrum of water. The effect of damping out high frequency modes by retardation is intimately connected with the magnitudes of oscillator strengths as well as absorption frequencies; both material properties and geometric factors set simultaneous conditions on the energy spectrum and must be considered together in adding up the modal energies.

CONCLUSIONS

The time is long overdue for making systematic inquiry into the nature of van der Waals forces in biological systems. The present method derived from the Lifshitz theory allows one to learn the qualitative features of these interactions as well as make satisfactory estimates of their magnitude. In addition it makes clear the dependence of van der Waals forces on both dielectric properties and dimensions of a system.

In principle it is necessary to know the dielectric dispersion of all component substances for all frequencies; in practice it is important only to know oscillator strengths and mean absorption frequencies to get a good idea of the electromagnetic

forces. We find that fitting the simple form $\epsilon(i\xi) = 1 + (C_{mw}/[1 + (\xi/\omega_{mw})]) + \Sigma(C_j/[1 + (\xi/\omega_j)^2])$ gives an adequate representation for the dielectric dispersion as it is needed here.

There is a very strong contribution to the total dispersion energy from the infrared spectrum of water. This feature, certain to hold in biological situations, is usually ignored in preference to the UV contributions and is important in calculating the long-distance behavior of the van der Waals force.

On the other hand, two phenomena militate against important contributions from the far-UV fluctuation frequencies in biological systems. First, materials of similar weight density will have similar dielectric susceptibilities at high frequencies (i.e. far- UV to X-ray region). Since the interacting surfaces are electromagnetically defined only when there are differences in dielectric susceptibility of interacting species and intervening medium, there will not be important behavior from the far-UV. This is qualitatively different from the case where bodies interact at short distance across a vacuum.

Second, the finite velocity of light, c, causes retardation damping across gaps l at and above frequencies ξ such that $1/\xi \lesssim 2l/c$ or wavelengths $\lambda \lesssim 4\pi l$. This says that at long distance, e.g. $l = 50$ mμ = 500 A, the material properties only for $\lambda < 500$ mμ = 5000 A are needed. At short distances shorter wavelengths begin to contribute.

It is clear that substances that change the index of refraction of water can change the dispersion forces. We have calculated elsewhere[2] by the present method that protein or saccharide materials on the biological cell surface can greatly increase intercell attractive forces. If the coating materials on different kinds of cells have different UV spectra, we expect specificity in attractive forces to appear for intercellular distances less than 200 A. (It would be most fortunate if the distinctive spectra were in the easily accessible 150 m$\mu \leqslant \lambda \leqslant 250$ mμ range.)

Two theoretic features of this method must be emphasized. One, it is fairly easy to generalize the force and energy formulae for geometries more complex than a single slab between two semi-infinite media, especially in the nonrelativistic ($c \rightarrow \infty$) limit. In other papers (18) we have derived formulae for triple films (e.g. soap bubbles in air), multilayers[3] (e.g. myelin figures and nerve myelin), and a large number of configurations[2] appropriate to the interaction of biological cells with each other or with a semi-infinite substratum.

Two, the representation for ϵ and numerical integration as used here are a practical and simple procedure for examining van der Waals forces quantitatively. We believe it will be useful in many connections.

It is our hope that the Lifshitz theory can be used for a useful theoretical and experimental framework in which to view electromagnetic forces in a wide variety

[2] Ninham, B. W., and V. A. Parsegian. Manuscript submitted for publication.
[3] Ninham, B. W., and V. A. Parsegian. Manuscript submitted for publication.

of biological problems. Better spectral data may alter the numerical estimates made in this paper but should not invalidate the method of calculation introduced here, or the principal qualitative features which are already apparent.

APPENDIX

Retardation Effects: Explicit Analysis

The precise nature of the damping due to retardation discussed in Analysis of Integrals can be made explicit by a careful analysis of the integral $I(\xi, l)$ which gives the spectrum of frequency contributions. We recall eq. (8) in the form

$$I(\xi; l) = -(\xi/\xi_s)^2 \int_1^\infty p \, dp \left\{ \ln \left[1 - \left(\frac{s - p}{s + p} \right)^2 e^{-(\xi/\xi_s)p} \right] \right.$$
$$\left. + \ln \left[1 - \left(\frac{s\epsilon_2 - \epsilon_1 p}{s\epsilon_2 + \epsilon_1 p} \right)^2 e^{-(\xi/\xi_s)p} \right] \right\}, \quad (A\ 1)$$

where

$$\xi_s = \left[\frac{2l\epsilon_2^{1/2}}{c} \right]^{-1}; \quad s = \sqrt{(\epsilon_1/\epsilon_2) - 1 + p^2}. \quad (A\ 2)$$

In terms of this integral, the Hamaker function and energy are given as

$$\tilde{A}(l) = \frac{3\hbar}{4\pi} \int_0^\infty I(\xi; l) \, d\xi; \quad E(l) = -\tilde{A}/(12\pi l^2). \quad (A\ 3)$$

To a good approximation the logarithms which occur in equation A 1 can be replaced by their leading terms, and we consider first

$$I_{\text{approx}} = (\xi/\xi_s)^2 \int_1^\infty p \, dp \left(\frac{s\epsilon_2 - p\epsilon_1}{s\epsilon_2 + p\epsilon_1} \right)^2 e^{-(\xi/\xi_s)p}. \quad (A\ 4)$$

For a fixed frequency ξ, the function $([s\epsilon_2 - p\epsilon_1]/[s\epsilon_2 + p\epsilon_1])$ is slowly varying as a function of p. Since the exponential is a decreasing function of p while p is increasing, the integrand of equation A 4 has a maximum at $p = p_0$ given by

$$\frac{d}{dp} (\ln p - \xi[p/\xi_s]) = 0; \quad p_0 \approx \xi_s/\xi = \frac{c}{2\xi l\sqrt{\epsilon_2}}. \quad (A\ 5)$$

This means that for a fixed value of l, and small ξ, the major contribution to the p integral comes from large values of p. On the other hand for the same given value of l, for large ξ, $p_0 \lesssim 1$ and the main contribution to the p integral comes from the region $p \approx 1$. Two cases then arise

(a)
$$\xi_s/\xi = \frac{c}{2\xi l\sqrt{\epsilon_2}} \gg 1.$$

This corresponds to the case of small distances discussed by Lifshitz (3). For these values of ξ we may put $p \approx s$ in the integrand of equation 19. The first term disappears. In the

remaining integrand the lower limit can be replaced by zero and we have

$$I(\xi; l)(<) \simeq -(\xi/\xi_s)^2 \int_0^\infty p \, dp \ln \left[1 - \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1}\right)^2 e^{-\xi_p/\xi_s}\right]$$

$$= -\int_0^\infty x \, dx \ln \left[1 - \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1}\right)^2 e^{-x}\right]$$

$$= \left(\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + \epsilon_1}\right)^2. \tag{A 6}$$

The correction terms are of the order of $(\xi_s/\xi)^2$.

At $l = 50$ A, $\xi_s \approx 3 \times 10^{16}$ which lies in the mid-UV. For $\xi > 3 \times 10^{16}$ the function $(|\epsilon_2 - \epsilon_1|/[\epsilon_2 + \epsilon_1])^2$ is already very small compared with its maximum value, so that effects of retardation are also small. On the other hand for $l = 500$ A, ξ_s lies in the near-UV and we expect these high frequency contributions to be diminished.

(b) $$\xi_s/\xi = \frac{c}{2\xi l \sqrt{\epsilon_2}} \ll 1.$$

Consider first the second integral of equation A 1

$$I(\xi; l)(>) \simeq (\xi/\xi_s)^2 \int_1^\infty p \, dp \left(\frac{s\epsilon_2 - \epsilon_1 p}{s\epsilon_2 + p\epsilon_1}\right)^2 e^{-p(\xi/\xi_s)}. \tag{A 7}$$

Writing $x = p - 1$, we have

$$I(\xi; l)(>) \simeq (\xi/\xi_s)^2 \int_0^\infty \left[\frac{s_1 - (1 + x)(\epsilon_1/\epsilon_2)}{s_1 + (1 + x)(\epsilon_1/\epsilon_2)}\right]^2 \exp\left[-(\xi/\xi_s)(1 + x)\right] dx. \tag{A 8}$$

After a further change of variable to $x\xi/\xi_s = y$, noting that the major contribution comes from the region $y = 0$, we can expand the integrand in ascending powers of y to get

$$I(\xi; l)(>) \sim (\xi/\xi_s) \exp(-\xi/\xi_s) \int_0^\infty dy$$

$$\times \exp(-y) \left(\frac{\sqrt{\epsilon_2} - \sqrt{\epsilon_1}}{\sqrt{\epsilon_2} + \sqrt{\epsilon_1}}\right)^2 (1 + 0(y[\xi_s/\xi]))$$

$$= (\xi/\xi_s) \exp(-\xi/\xi_s) \left(\frac{\sqrt{\epsilon_2} - \sqrt{\epsilon_1}}{\sqrt{\epsilon_2} + \sqrt{\epsilon_1}}\right)^2 (1 + 0(\xi_s/\xi)). \tag{A 9}$$

A similar contribution comes from the remaining integrand of equation A 1. Thus for $\xi > \xi_s$, $I(\xi; l)$ has a form essentially equivalent to equation A 6 but with exponential damping. Complete asymptotic expansions which converge rapidly for computation can easily be constructed. However, there appears to be little point in so doing—the expansions are rather complicated, and it is simpler to calculate the spectrum numerically for each case.

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