TEMPERATURE-DEPENDENT
VAN DER WAALS FORCES

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ABSTRACT   Biological systems can experience a strong van der Waals interaction involving electromagnetic fluctuations at the low frequency limit. In lipid-water mixtures the free energy of this interaction is proportional to temperature, primarily involves an entropy change, and has qualitative features of a "hydrophobic bond." Protein-protein attraction in dilute solution is due as much to low frequency proton fluctuation (Kirkwood-Shumaker forces) and permanent dipole forces as to high frequency (infrared and UV) van der Waals intreactions. These conclusions are described in terms of numerical calculations via the Lifshitz theory of van der Waals forces.

INTRODUCTION

In earlier papers (1–3)[1] we have applied the theory of van der Waals forces as given by Lifshitz (4) to a detailed study of these forces in systems of biological interest. In particular, references 1 and 3 were devoted to the attractive forces between water media interacting across a thin lipid film. Van der Waals forces in lipid-water systems are qualitatively different from those which exist for condensed media interactions across a vacuum. The important new feature is that the main contributions to temperature-independent forces do not come simply from electromagnetic fluctuations at UV frequencies as has been assumed in the past. The infrared spectrum is equally significant.

In this paper we extend our earlier analysis to temperature-dependent forces. We will show that there is a large long-range contribution to the van der Waals force[2] from molecular interactions of the permanent dipolar molecules in liquid water. This interaction occurs at essentially zero frequency and increases almost linearly with temperature. As discussed by Lifshitz (5), for interactions involving

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[1] Also Ninham, B. W., and V. A. Parsegian. 1970. Manuscript submitted.
[2] We call any forces deriving from electromagnetic fluctuations "van der Waals" interactions. That component of the interaction which is explicitly temperature independent will be called a "dispersion force," and the remainder a "molecular force."

most materials this additional contribution to the force is usually quite negligible at room temperature and at small film thicknesses where the effects of retardation can be ignored. Indeed in their books, Landau and Lifshitz (6) and Abrikosov, Gorkov, and Dzyaloshinskii (7) assert that temperature-dependent terms are *always* negligible for film thicknesses $l \ll 0$ ([hc]/[kT]). ([hc]/[kT] $\approx 10^5$ A at room temperature.) The inequality is a necessary condition for the neglect of molecular forces, but is not sufficient.

At least for the special case of lipid-water systems, and probably for some cases of protein or nucleic acid aggregates in water, the peculiar properties of water dictate that temperature-dependent intermolecular correlations are always very important. On the basis of our analysis we shall show that Kirkwood-Shumaker fluctuation forces (8) can easily be estimated via Lifshitz theory. We suggest further that the molecular forces examined here may give a quantitative expression for so-called "hydrophobic bonding" (9).

THE TEMPERATURE-DEPENDENT LIFSHITZ FORMULA

The most general expression for the van der Waals force due to interactions of media 1 across a planar slab of medium 2 and thickness l has been given by Dzyalo-shinskii, Lifshitz, and Pitaevskii (4). By integration with respect to l of their result one has for the free energy of interaction per cm²

$$G(l, T) = \frac{kT}{8\pi l^2} \sum_{n=0}^{\infty} {}'I(\xi_n, l),$$ (1)

where

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

$$\left. + \ln\left[1 - \Delta^2 \exp\left(\frac{-2p\xi_n l \sqrt{\epsilon_2}}{c}\right)\right]\right\}$$ (2)

$$\Delta = \frac{s\epsilon_2 - p\epsilon_1}{s\epsilon_2 + p\epsilon_1}; \quad \bar{\Delta} = \frac{s - p}{s + p}$$

$$s = \sqrt{(\epsilon_1/\epsilon_2) - 1 + p^2}; \quad \xi_n = (2\pi n kT)/\hbar.$$ (3)

Here $2\pi\hbar$ is Planck's constant, k is Boltzmann's constant, T absolute temperature, and c the velocity of light. The dielectric susceptibilities ϵ_1, ϵ_2 are to be evaluated on the imaginary frequency axis

$$\epsilon_1 = \epsilon_1(i\xi_n), \qquad \epsilon_2 = \epsilon_2(i\xi_n),$$ (4)

and the prime on the summation symbol in equation 1 indicates that the term in

$n = 0$ is to be taken with a factor $\frac{1}{2}$. In the limit of low temperatures, the sum in equation 1 can be replaced by an integral through the transformation

$$d\xi = \frac{2\pi kT}{\hbar} \, dn, \qquad (5)$$

which yields the dispersion force contribution to the free energy

$$\tilde{G}(l) = \frac{\hbar}{16\pi^2 l^2} \int_0^\infty d\xi \, I(\xi, l). \qquad (6)$$

This approximate expression was analyzed in detail in reference 3 for both large and small distances of separation l. We found there that for hydrocarbon-water interactions this limiting form gave strong spectral contributions from the infrared region besides the expected contribution from UV fluctuations. However, contributions to the integral from the microwave region due to orientation correlation of polar molecules are neglected in this approximation. To take account of these correlations it is necessary to return to the general expression equation 1.

At room temperature, $T \approx 293°K$, the frequencies ξ_n at which terms in the sum in equation 1 are to be evaluated are

$$\xi_n = 2.41 \times 10^{14} n \text{ rad/sec}, \, n = 0, 1, 2, \cdots . \qquad (7)$$

The term in $n = 0$ uses zero frequency dielectric susceptibilities corresponding to infrared and higher frequencies. Thus, the effects of molecular correlations will show up primarily in the term $n = 0$. We therefore consider this term separately to examine its distinctive properties. To conform with the usual notation we write the free energy in terms of an effective Hamaker coefficient $A(l)$ such that

$$G = -\frac{A(l)}{12\pi l^2}, \qquad (8)$$

where

$$A = A_{n=0} + A_{n>0} . \qquad (9)$$

From equations 1 and 8 we obtain

$$A_{n=0} = \frac{3}{4} kT \, I(0, l)$$

$$= \frac{3}{4} kT \int_0^\infty q dq \ln [1 - \Delta_0^2 e^{-q}]$$

$$= \frac{3}{4} kT \sum_{j=1}^\infty \frac{\Delta_0^{2j}}{j^3} . \qquad (10)$$

where

$$\Delta_0 = \left[\frac{\epsilon_2(0) - \epsilon_1(0)}{\epsilon_2(0) + \epsilon_1(0)}\right] \qquad (11)$$

and

$$A_{n>0} = \frac{3}{2} kT \sum_{n=1}^{\infty} I(\xi_n, l). \qquad (12)$$

For purposes of comparison, we shall also define

$$\tilde{A} = \frac{3\hbar}{4\pi} \int_0^{\infty} d\xi\, I(\xi, l), \qquad (13)$$

where $\tilde{A}$ corresponds with the low temperature integral approximation.

Several remarkable features of the zero frequency $n = 0$ contribution will now be presented, and a comparison made with the van der Waals dispersion interaction considered previously.

TEMPERATURE-DEPENDENT VAN DER WAALS INTERACTION

Our first observation is that the zero frequency term equation 10 in lipid-water systems is of comparable magnitude with infrared and UV contributions. Thus, for $kT = 4.04 \times 10^{-14}$ erg, we have

$$A_{n=0} = 3.03 \times 10^{-14} \sum_{j=1}^{\infty} \left[\frac{\epsilon_w(0) - \epsilon_{hc}(0)}{\epsilon_w(0) + \epsilon_{hc}(0)}\right]^{2j} \Big/ j^3, \qquad (14)$$

where subscripts w and hc denote water and hydrocarbon respectively. Taking $\epsilon_{hc}(0) \approx 2$, $\epsilon_w(0) \approx 80$, equation 14 gives

$$A_{n=0} \approx 3.2 \times 10^{-14} \text{ erg.}$$

In Table I we summarize numerical estimates of the Hamaker coefficient defined by equations 8, 9, and 13. These calculations are for water acting across a hydrocarbon flim of 50 A thickness. Experimental dielectric data for water and hydrocarbon are fitted to the form

$$\epsilon(i\xi) = 1 + \frac{C_{mw}}{1 + \xi/\omega_{mw}} + \frac{C_{ir}}{1 + (\xi/\omega_{ir})^2} + \frac{C_{uv}}{1 + (\xi/\omega_{uv})^2} \qquad (15)$$

as in references 1–3.

Not only is the contribution $A_{n=0}$ similar in magnitude to the high frequency terms, but it is an infinite wavelength contribution. *This circumstance assures that*

TABLE I

ESTIMATES OF HAMAKER COEFFICIENTS $A_{n=0}$, $A_{n>0}$, $\bar{A}$ FROM EQUATIONS 8–13

Data for water susceptibility $\epsilon_w(i\xi)$:

$C_{mw} = 75.2$, $C_{ir} = 3.42$, $C_{uv} = 0.78$.

$\omega_{mv} = 1.06 \times 10^{11}$, $\bar{\omega}_{ir} = 5.66 \times 10^{14}$, $\bar{\omega}_{uv} = 1.906 \times 10^{16}$ rad/sec.

Data for hydrocarbon susceptibility $\epsilon_{hc}(i\xi)$:

$C_{mw} = 0$, $C_{ir} = 0$, $C_{uv} = (n_{ho}^2 - 1)$, $\bar{\omega}_{uv}$ as below.

$l = 50$ A, $T = 20°C$.

$\bar{\omega}_{uv}^{hc}$	n_{hc}^2	$A_{total} \times 10^{14}$	$A_{n=0} \times 10^{14}$ (equation 10)	$A_{n>0} \times 10^{14}$ (equation 12)	$\bar{A} \times 10^{14}$ (equation 13)
		erg	erg	erg	erg
1.54×10^{16} rad/sec	1.9	5.8	3.2	2.6	3.4
Decane ionization po-	2.0	5.5	3.2	2.3	3.
tential	2.143	5.7	3.2	2.5	3.2
	2.208	6.1	3.2	2.9	3.5
1.76×10^{16} rad/sec	1.9	5.8	3.2	2.6	3.3
Ethane ionization po-	2.	5.8	3.2	2.6	3.3
tential	2.143	6.5	3.2	3.3	4.
	2.208	7.1	3.2	4.	4.6

in lipid-water systems the van der Waals energy will have a short-distance or non-retarded form even at very large distances. This previously neglected feature may be important in the study of lyophobic colloid flocculation. The low frequency van der Waals force in this case shows up strongly because the dielectric properties of water and hydrocarbon are fairly close in the visible to UV region but are vastly different at $\xi = 0$.

INTERMOLECULAR FORCES IN PROTEIN SOLUTION; KIRKWOOD-SHUMAKER FORCES

It has been suggested (8) that proton fluctuations in the microwave region can correlate to produce an effective attractive force between protein molecules. In fact, any induced orientation or distortion of a molecule can cause local electromagnetic fluctuations and contribute to an attractive force between like molecules. Now the magnitude of these forces can easily be estimated by the Lifshitz formalism, for the capacity for these electromagnetic fluctuations will increase the effective dielectric constant $\epsilon_p(0)$ of a protein solution. To calculate the microwave frequency forces we proceed as follows.

Through the full frequency range the dielectric susceptibility of a dilute protein solution may be written as (4)

$$\epsilon_p(i\xi) = \epsilon_w(i\xi) + N \frac{\partial \epsilon_p(i\xi)}{\partial N}, \qquad (16)$$

where subscripts p and w denote protein solution and water respectively, while N is the number density of protein molecules. If we imagine an interaction of protein molecules acting between two solutions separated by a gap l containing pure water, the free energy of interaction follows from equations 1–3. Treating medium 1 as protein solution and medium 2 as water, and using equation 16 we have

$$G(l, T) = \frac{kT}{8\pi l^2} \sum_{n=0}^{\infty} {}' \int_0^{\infty} q\,dq \ln \left[1 - \left(\frac{N}{2} \frac{\partial \epsilon_p}{\partial N} \Big/ \epsilon_w \right)^2 e^{-q} \right]. \qquad (17)$$

To obtain this expression we have made the change of variable $([2\rho\xi_n l \sqrt{\epsilon_w}]/c) = q$ in equation 2 and ignored retardation effects. Since $N(\partial\epsilon_p/\partial N) \ll \epsilon_w$, equation 17 reduces to the approximate form

$$G(l, T) = -\frac{kTN^2}{32\pi l^2} \sum_{n=0}^{\infty} {}' \left[\frac{\partial\epsilon_p(i\xi_n)}{\partial N} \Big/ \epsilon_w(i\xi_n) \right]^2. \qquad (18)$$

This is precisely what one would have obtained by a pairwise summation of individual protein-protein free energies of interaction of the form

$$g(r) = -\frac{3kT}{8\pi^2 r^6} \sum_{n=0}^{\infty} {}' \left[\frac{\partial\epsilon_p(i\xi_n)}{\partial N} \Big/ \epsilon_w(i\xi_n) \right]^2. \qquad (19)$$

As in our previous analysis we decompose this free energy of interaction into two terms and write

$$g(r) \approx \frac{3}{16\pi^2 r^6} \left\{ kT \left[\frac{\partial\epsilon_p(0)}{\partial N} \Big/ \epsilon_w(0) \right]^2 \right.$$
$$\left. + \frac{4\hbar}{\pi} \int_{2\pi kT/\hbar}^{\infty} \left[\frac{\partial\epsilon_p(i\xi)}{\partial N} \Big/ \epsilon_w(i\xi) \right]^2 d\xi \right\}. \qquad (20)$$

The first term concerns relaxation in the microwave region, while the second accounts for fluctuations at infrared and UV frequencies. The error in replacing the second term by an integral is not serious for our present first estimate. It is tantamount to ignoring the absorption of protein solution in the near infrared.

We can now compare the magnitude of these two terms using available data for the dielectric increment $(\partial\epsilon_p(0)/\partial\rho)$ at zero frequency, where ρ is weight density of protein in solution, and index of refraction change $(\partial n/\partial\rho)$ at optical frequencies. For example for hemoglobin we have (10)

$$\frac{\partial\epsilon_p(0)}{\partial\rho} \sim 0.3 \quad \text{liter/g}, \qquad (21)$$

and for most proteins in the visible range

$$\frac{\partial \epsilon_p(i\xi)}{\partial \rho} = 2n_w \frac{\partial n_p}{\partial \rho}; \qquad \frac{\partial n_p}{\partial \rho} = 1.8 \times 10^{-4} \text{ liter/g.} \qquad (22)$$

These data are for hemoglobin. In order of magnitude the first term in the curly bracket of equation 20 is $kT(3/80)^2 \approx 5.6 \times 10^{-19}$ apart from the common scaling factor $(\rho/N)^2$. The second can be evaluated if we assume that the principal UV absorption of protein is at $\lambda \lesssim 200$ mμ, or $\xi \gtrsim 10^{16}$ rad/sec. Thus,

$$\frac{4\hbar}{\pi} \int_{2\pi kT/\hbar}^{\infty} \left[\frac{\partial \epsilon_p(i\xi)}{\partial \rho} \Big/ \epsilon_w(i\xi) \right]^2 \approx \frac{4\hbar}{\pi} \int_0^{10^{16}} d\xi \frac{4(1.8)^2 \times 10^{-8}}{n_w^2} \approx 5 \times 10^{-19}, \quad (23)$$

so that for the data of equations 21 and 22 microwave contributions to the protein-protein interaction are of the same order of magnitude as high frequency van der Waals forces in the short-distance regime. To the extent that the dielectric increment is due to proton fluctuations, the microwave contribution is due to Kirkwood-Shumaker forces (8). For highly polar protein molecules the dielectric increment could easily increase by a factor of 10 to make the microwave contribution dominate the interaction by several orders of magnitude. The important observation, however, is that the magnitude and selectivity of van der Waals forces acting between macromolecules should be accessible through macroscopic measurements which are model independent. The necessary modifications of the above argument required to take account of interaction between dissimilar macromolecules, of macromolecular adsorption, and effects of solutes are obvious.

LOW DENSITY LIMIT

In the limit of very low density, the contribution to the energy due to the $n = 0$ term reduces exactly to the old Keesom force (11) acting between permanent dipolar molecules. To see this, consider two clouds of water molecules interacting across a vacuum, a planar gap of width $l \gg N^{-1/3}$ where N is the number density of water molecules. For water vapor (12), we take

$$\epsilon_w(0) = 1 + \frac{4\pi\mu^2 N}{3kT}, \qquad (24)$$

where μ is the dipole moment of an individual molecule. From equations 1, 8, and 10, we then have

$$G_{n=0} = -\frac{kT}{16\pi l^2} \left(\frac{\epsilon_w(0) - 1}{\epsilon_w(0) + 1} \right)^2$$

$$= -\frac{\pi}{36l^2} \frac{\mu^4 N^2}{kT}. \qquad (25)$$

The entropy associated with this free energy is

$$S = -\left(\frac{\partial G}{\partial T}\right)_p = G/T. \qquad (26)$$

Hence the enthalpy H, (or equivalently energy here) is

$$H = 2G. \qquad (27)$$

This is precisely what one obtains by carrying out a pairwise addition of the Keesom intermolecular interaction energies

$$V_K(r) = -\frac{2\mu^4}{3kTr^6}, \qquad (28)$$

acting between two permanent dipoles in this configuration. For interactions across a dilute intermediate substance consisting of nonpolar molecules, the free energy corresponding to equation 25 includes also the Debye force due to dipole-induced dipole interactions. We note in passing that the temperature dependence of the intermolecular force as predicted by pairwise summation is completely wrong for condensed media interaction, and totally misleading.

ENTROPIC CONTRIBUTIONS TO THE VAN DER WAALS FORCE

The term in $n = 0$ for condensed lipid-water systems is primarily an entropy contribution to the free energy. From equation 10 the zero frequency free energy change in bringing two hydrocarbon bodies separated by water from infinite separation to a distance l is to leading order

$$G_{n=0} \approx -\frac{kT}{16\pi l^2}\left(\frac{\epsilon_w(0) - \epsilon_{hc}(0)}{\epsilon_w(0) + \epsilon_{hc}(0)}\right)^2. \qquad (29)$$

Here the ϵ refer to static susceptibilities. Since

$$G_{n=0} = H_{n=0} - TS_{n=0}, \qquad (30)$$

the entropy change corresponding to this free energy change is

$$-TS_{n=0} = T\frac{\partial G_{n=0}}{\partial T}$$

$$= -\frac{kT}{16\pi l^2}\Delta_0^2\left[1 - \frac{2T}{\Delta_0}\frac{\partial \Delta_0}{\partial T}\right]$$

$$= G_{n=0}\left[1 - \frac{2T}{\Delta_0}\frac{\partial \Delta_0}{\partial T}\right], \qquad (31)$$

where

$$\Delta_0 = (\epsilon_w(0) - \epsilon_{hc}(0))/(\epsilon_w(0) + \epsilon_{hc}(0)).$$

Similarly the enthalpy change is

$$H_{n=0} = -T^2 \frac{\partial (G/T)}{\partial T} = -G_{n=0} \frac{2T}{\Delta_0} \frac{\partial \Delta_0}{\partial T}. \qquad (32)$$

Now at 20°C,

$$\epsilon_w(0) \approx 80, \qquad \epsilon_{hc}(0) \approx 2, \qquad \Delta_0 \approx 0.95, \qquad (33)$$

and (13)

$$\frac{\partial \epsilon_{hc}(0)}{\partial T} \approx -0.016, \qquad \frac{\partial \epsilon_w(0)}{\partial T} \approx -0.37, \qquad (34)$$

whence

$$\frac{\partial \Delta_0}{\partial T} \approx -1.8 \times 10^{-4}. \qquad (35)$$

Then from equation 31 we have

$$-TS_{n=0} \approx G_{n=0}[1 - 0.11] \approx 0.9G. \qquad (36)$$

This equation implies that the entropy *increases* upon approach of the lipid bodies, and that the free energy change is almost all due to an entropy change for the $n = 0$ contribution. The enthalpy contribution in this case is relatively small,

$$H_{n=0} \approx 11 \% G, \qquad (37)$$

but is of the same sign as the free energy change.

CONCLUDING COMMENTS

The analysis of lipid-water interactions presented here and in the preceding paper (3) prove most emphatically the impropriety of the usual assumptions (14–17) that van der Waals forces are primarily due to electromagnetic fluctuations at UV frequencies. The peculiar dielectric properties of water insure that at ordinary temperatures fluctuations at all frequency regions from zero through the microwave, the infrared and the mid-UV are of comparable importance in contributing to the van der Waals force. There is a strong temperature dependence which has been neglected entirely in previous studies.

These conclusions are unambiguous since one needs rely on dielectric data in a range where they are readily available. It is remarkable that mid-to-high UV frequency electric properties, difficult to obtain experimentally, are unimportant because of similarities in the dielectric properties of hydrocarbon and water in that range (see reference 3).

We have dealt here especially with the strong fluctuations in the limit of zero frequency due to dielectric dispersion in the microwave region. With dielectric constants $\epsilon_w(0)$ and $\epsilon_{hc}(0)$ at $\omega = 0$, this contribution to free energy of attraction between two like semi-infinite media separated by a planar gap l is approximately (equations 8 and 10)

$$G_{n=0} = -\frac{kT}{16\pi l^2} \sum_{j=1}^{\infty} \left(\frac{\epsilon_w - \epsilon_{hc}}{\epsilon_w + \epsilon_{hc}}\right)^{2j} \bigg/ j^3$$

$$\approx -\frac{kT}{16\pi^2 l^2} \left(\frac{\epsilon_w - \epsilon_{hc}}{\epsilon_w + \epsilon_{hc}}\right)^2. \tag{38}$$

This free energy is primarily due to entropy rather than energy or enthalpy changes with spacing l, strongly reminiscent of "hydrophobic" interactions described in polar-nonpolar mixtures (9).

In addition, the free energy stemming from the zero frequency van der Waals interaction maintains the inverse square dependence on l at all distances while contributions from the UV and then infrared frequencies are systematically damped out by retardation effects (3). Thus, the van der Waals force in lipid-water systems has a nearly "short-distance" form at all distances.

To keep our notation consistent with other presentations we have expressed the free energies in terms of Hamaker functions A such that (equation 8)

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

Our estimates for A(50 A) ("A_{total}" entries in Table I) range from 5.5 to 7.1 $\times$ 10^{-14} erg of which 3.2 $\times$ 10^{-14}, or about one-half, is a zero frequency contribution.

We expect that the same features of van der Waals forces as studied here will appear in modified form in protein-protein interactions such as for example viral assembly and possibly muscle structure. The entropy-driven long-range interaction requires only that the static frequency dielectric constant of the interacting particles differ markedly from that of the suspending medium. This interaction will dominate at large distances and when the indices of refraction of particles and medium are of similar magnitude.

More important than its ability to predict energies quantitatively, the Lifshitz theory of van der Waals forces should continue to reveal a rich diversity of unexpected qualitative features peculiarly pertinent to biological systems.

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