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Interfacial Lifshitz–van der Waals and Polar Interactions in Macroscopic Systems

CAREL J. VAN OSS*

Departments of Microbiology and Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14214

MANOJ K. CHAUDHURY

Dow Corning Corporation, Midland, Michigan 48686

ROBERT J. GOOD

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

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I. Introduction

The concept of a general attractive interaction between neutral atoms was first proposed by van der Waals in 1873, to account for certain properties of nonideal gases and liquids.[1] Three different but nevertheless related phenomena were subsequently shown to contribute to these "van der Waals" interactions: (1) randomly orienting dipole–dipole (or orientation) interactions, described by Keesom;[2-5] (2) randomly orienting dipole–induced dipole (or induction) interactions, described by Debye;[6,7] (3) fluctuating dipole–induced dipole (or dispersion) interactions, described by London.[8] Of these three, Keesom and Debye interactions are found with molecules that have permanent dipole movements. The London interaction is universal and is present in atom–atom interactions as well. All three interaction energies between atoms or small molecules decay very steeply with distance (d), as d^{-6}. For various reasons, only van der Waals–London (dispersion) interactions have been held to be of preponderant importance between macroscopic bodies in condensed systems.[9,10] Hamaker developed the theory of van der Waals–London interactions between macroscopic bodies in 1937 and showed that the additivity of these interactions renders them considerably more long-range; i.e., the dispersion energy between two semiinfinite parallel flat slabs decays with distance as d^{-2}[11] for relatively short distances ($d < 100$ Å) and, due to retardation, as d^{-3} at greater distances.[9,12]

The realization of the existence of these relatively long-range attractive forces made possible the first

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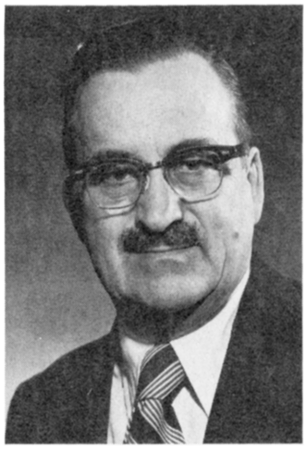
Carel J. van Oss studied in The Netherlands and France (Ph.D. 1955, Sorbonne, Paris; Physical Biochemistry). After postdoctoral studies in The Netherlands (van't Hoff Laboratory of Physical and Colloid Chemistry, University of Utrecht) and in France (Electrochemistry Laboratory, Sorbonne, Paris) he was Director of the Laboratory of Physical Biochemistry in the National Veterinary College of Alfort (Paris) (1958–1963). In 1963 Dr. van Oss became Assistant Director of the Department of Microbiology at Montefiore Hospital and Medical Center, New York, NY. From 1965 to 1968 he was Director of the Serum, Plasma, and Immunochemistry Departments of the Milwaukee Blood Center and Adjunct Associate Professor of Biology at Marquette University, Milwaukee, WI. In 1968 Dr. van Oss joined the Department of Microbiology, SUNY at Buffalo. He currently is Professor of Microbiology and Adjunct Professor of Chemical Engineering at the State University of New York at Buffalo. He is Head of the Laboratory of Immunochemistry of the Department of Microbiology and a member of the Ernest Witebsky Center for Immunology at SUNY at Buffalo. He has held visiting positions at the Central Laboratory of the Netherlands Red Cross Blood Transfusion Service at Amsterdam, and at the University of Bristol. Dr. van Oss is Editor-in-Chief of the journals *Preparative Biochemistry*, *Immunological Investigations*, and *Separation and Purification Methods* and serves on the editorial boards of various other journals. He is the author of 235 papers and numerous abstracts and coauthor or coeditor of five books; he holds eight patents. His current research involves studies of polar and apolar interactions in macroscopic systems, cell separation methods, the nature of the interaction between antigens and antibodies, and physicochemical and immunochemical cell surface characterization.



Robert J. Good received his B.A. in Chemistry from Amherst College in 1942, his M.S. from the University of California, and his Ph.D. from the University of Michigan. He has been employed by Monsanto, Dow, American Cyanamid, and General Dynamics. He taught from 1956 to 1959 at the University of Cincinnati, and since 1964 he has been Professor of Materials Science at the State University of New York at Buffalo. He has held visiting positions at the NIH, at the University of Bristol, at Imperial College, London, and at the City University, London; he was Visiting Scholar at the Kendall Corp., Lexington, MA, in 1987. In 1957, with one of his first students (Louis A. Girifalco) and with Dr. Gerhard Kraus, he proposed the "geometric mean" relation for the energy of adhesion between two phases across an interface and the energies of cohesion of the separate phase. His recent interests include hydrogen bonding across interfaces, contact angles of liquids on solids, surface thermodynamics, microemulsions, the role of viscoelasticity and elongational viscosity in practical adhesion, and the theory of passivity. He received the Kendall Award of the ACS in 1976 and the Schoellkopf Award of the Western New York Section of the ACS in 1979. He is the author or coauthor of 120 papers and one patent and is coeditor of three books.

Manoj K. Chaudhury graduated with a Ph.D. in Chemical Engineering from the State University of New York at Buffalo in 1984. He carried out his doctoral research under Professor R. J. Good on topics related to contact angle and wettability. Currently he is employed at Dow Corning Corp., Silicone Research Division. His research interests are in surface chemistry and adhesion. Dr. Chaudhury is the recipient of the V. K. LaMer Award in Surface Chemistry and the H. Doan Industrial Scientist Award.

theories of the stability of hydrophobic colloids, as a balance between van der Waals attraction and electrical double-layer repulsion, by Hamaker[13] and de Boer.[14] These theories were further elaborated by Derjaguin[15,18] and Derjaguin and Landau[19] and, independently, by Verwey and Overbeek.[20,21] The general theory of colloidal stability, based on these considerations, has become known as the DLVO theory, by combining the initials of these four authors.[15–21]

Hamaker already indicated in 1937 that it was possible for the van der Waals–London interaction between two *different* materials immersed in a liquid to be repulsive.[11] This was reaffirmed by Derjaguin in 1954,[22] and Visser subsequently established the precise conditions necessary for the occurrence of repulsive van der Waals–London forces.[23,24] Fowkes was the first to indicate a few possible examples of such repulsions,[25] and van Oss et al. demonstrated the existence of many such systems, leading to phase separations[26] as well as to particle exclusion.[27]

It had, however, long been surmised that physical forces other than van der Waals attraction and electrostatic repulsions could also play a role in colloidal interactions. An important force among these is often alluded to as "hydrophobic interaction",[28] an effect that has resisted quantitative experimental determination as well as precise theoretical definition until relatively recently;[29,30] see also section IIIC. Closely linked to hydrophobic interaction, which is generally so called when attractive, is "hydration pressure",[31] which is its repulsive counterpart.[32,33] It now transpires that these interactions, which are of polar (but not electrostatic) origin, either in the attractive (hydrophobic interaction) or in the repulsive mode (hydration pressure) represent energies that may be up to two decimal orders of magnitude higher than those commonly encountered among the components of traditional DLVO energy balances.[29,30,32,33] These polar interactions are largely based on electron acceptor–electron donor (Lewis acid–base) interactions between polar moieties in polar media (such as water)[30,32–35] and are at the origin of virtually all the anomalies that have beset the interpretation of interfacial interactions in polar media for many years.[36–38]

Another category of physical interactions that are neither van der Waals nor electrostatic interactions comprises osmotic interactions of the type described by Derjaguin as excess osmotic pressure.[39] Such osmotic interactions can give rise to a (relatively weak) repulsion, e.g., between solid particles immersed in a liquid that have an adsorbed (or covalently bound) layer of polymer molecules that are soluble in the liquid. This repulsive osmotic interaction is to an important extent responsible for the "steric stabilization"[40] of particles immersed in apolar liquids. In polar liquids (such as water), however, the osmotic interaction energy represents only a small proportion of the total energy of the steric stabilization repulsion; the major repulsive component in these cases is of polar origin.[33] Structural forces, however, may also play a role in steric stabilization; these forces are not treated here.

II. Theory

A. Lifshitz–van der Waals (LW) Interactions in the Condensed State

1. Lifshitz Approach

The Lifshitz theory of condensed media interaction[41] has its origin in Maxwell's equations, where the electric and magnetic fields are subjected to fast temporal fluctuations. In order to accommodate the temporal fluctuations of the fields, Lifshitz utilized the fluctuation theory developed by Rytov.[42] The integration of the Fourier transform of the normal component of Maxwell's stress tensor over all the allowed frequencies resulted in an expression for the van der Waals pressure of two semiinfinite parallel slabs separated by a finite distance in a vacuum or in another dielectric phase. The van der Waals pressure according to Lifshitz's theory can be expressed in terms of the continuum properties, i.e., dielectric susceptibilities of the interacting phases under consideration. Later, Dzyaloshinskii, Lifshitz, and Pitaevskii[43] gave an alternate derivation of Lifshitz's formula by adopting a more sophisticated approach of quantum electrodynamics. Recently, Parsegian[44,45] has offered an excellent heuristic derivation of Lifshitz's formula for the free energy of interaction of two phases through a third dielectric by summing the individual oscillator free energies over an allowed set of frequencies, where the latter was derived from the solution of Fourier transformed Maxwell equations.

An excellent historical review will be found in Mahanty and Ninham[46] and in Nir.[47]

According to Lifshitz's theory,[42,43] the approximate expression for the free energy of interaction, $\Delta F_{132}(l)$,[128] between two semiinfinite parallel slabs of phases 1 and 2 separated by a film of phase 3 of thickness l is

$$\Delta F_{132}(l) = \frac{kT}{\pi c^3}\int_{P=1}^{\infty} \sum_{n=0}^{\infty}{}' \epsilon_3{}^{3/2}\omega^2{}_n \int_l^{\infty} P^2\left[\frac{\exp(2P\omega_n l\epsilon_3{}^{1/2}e)}{\Delta_1\Delta_2} - 1\right]^{-1} \mathrm{d}P\,\mathrm{d}l \quad (1)$$

where k is Boltzmann's constant, T is the absolute temperature, c is the velocity of light in vacuo, ϵ_i are the permittivities, and P is an integration parameter. Δ_1, Δ_2, and ω_n are given as follows:

$$\Delta_1 = \frac{\epsilon_1(i\omega_n) - \epsilon_3(i\omega_n)}{\epsilon_1(i\omega_n) + \epsilon_3(i\omega_n)} \quad (2)$$

$$\Delta_2 = \frac{\epsilon_2(i\omega_n) - \epsilon_3(i\omega_n)}{\epsilon_2(i\omega_n) + \epsilon_3(i\omega_n)} \quad (3)$$

$$\omega_n = \frac{4\pi^2 nkT}{h} \quad (4)$$

where h is Planck's constant, ω_n is the frequency, n is the quantum number of the relevant oscillation, and $\epsilon(i\omega_n)$ is the dielectric susceptibility along the complex frequency axis $i\omega_n$ ($i = \sqrt{-1}$). The prime in the summation of eq 1 indicates that the zero frequency term is to be multiplied by one-half.

When the integration is performed in eq 1, it is found that

$$\Delta F_{132}(l) = -\frac{kT}{8\pi l^2}\sum_{n=0}^{\infty}{}' \sum_{j=1}^{\infty}(\Delta_1\Delta_2)^j\left(\frac{X_0}{j^2} + \frac{1}{j^3}\right)\exp(-jX_0) \quad (5)$$

where

$$X_0 = (2\omega_n l\epsilon_3{}^{1/2})/c \quad (6)$$

and $j = 1, 2, 3, \ldots$ When the separation distance, l, is very small, i.e., when $l \to 0$, X_0 also tends to zero. One then obtains an expression for the nonretarded van der Waals energy as

$$\Delta F_{132}(l) = -\frac{kT}{8\pi l^2}\sum_{n=0}^{\infty}{}' \sum_{j=1}^{\infty}\frac{(\Delta_1\Delta_2)^j}{j^3} \quad (7)$$

If the materials interacting with each other are of similar kinds and the phase 3 is vacuum, eq 7 in view of equations 2 and 3 reduces to

$$\Delta F_{11}(l) = \frac{kT}{8\pi l^2}\sum_{n=0}^{\infty}{}' \sum_{j=1}^{\infty}\left[\frac{\epsilon_1(i\omega_n) - 1}{\epsilon_1(i\omega_n) + 1}\right]^{2j} / j^3 \quad (8)$$

The free energy of interaction, when expressed in conventional form, involving Hamaker's constant A[11,23] appears as

$$\Delta F_{11}(l) = -\frac{A_{11}}{12\pi l^2} \quad (9)$$

where A_{11} is the familiar Hamaker constant of interaction of material 1 through vacuum. From eq 8 and 9 it is found that

$$A_{11} = \frac{3kT}{2}\sum_{n=0}^{\infty}{}' \sum_{j=1}^{\infty}\left[\frac{\epsilon_1(i\omega_n) - 1}{\epsilon_1(i\omega_n) + 1}\right]^{2j} / j^3 \quad (10)$$

In the low-temperature limit, the sum over n in eq 10 can be replaced by an integral (8). Equation 10 can then be expressed as

$$A_{11}(l) = \frac{3h}{4\pi}\int_0^\infty d\omega \sum_{j=1}^{\infty}\left[\frac{\epsilon_1(i\omega_n) - 1}{\epsilon_1(i\omega_n) + 1}\right]^{2j} / j^3 \quad (10a)$$

If the dielectric permeability of a material is known along the imaginary frequency axis, $i\omega_n$, the Hamaker constant of the material and hence the free energy of interaction at small separation distances can be calculated from eq 9 and 10.

The dielectric permeability of the material along the imaginary frequency axis $i\omega_n$ can be expressed in terms of the Kramers–Kronig relation[41] as

$$\epsilon(i\omega_n) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\omega\epsilon''(\omega)\, d\omega}{\omega^2 + \omega_n^2} \quad (11)$$

where $\epsilon''(\omega)$ is the loss component of the frequency-dependent dielectric function $\epsilon(\omega) = [\epsilon'(\omega) - i\epsilon''(\omega)]$. For dielectrics Ninham and Parsegian[48] have considered the major contribution to $\epsilon(i\omega_n)$ arising from microwave, infrared, and ultraviolet relaxations and obtained a simplified expression for $\epsilon(\omega_n)$ as

$$\epsilon(i\omega_n) = 1 + \frac{\epsilon_\infty - \epsilon_0}{1 + \omega_n/\omega_{\mathrm{MW}}} + \frac{\epsilon_0 - n_0^2}{1 + (\omega_n/\omega_{\mathrm{IR}})^2} + \frac{n_0^2 - 1}{1 + (\omega_n/\omega_{\mathrm{UV}})^2} \quad (12)$$

where ϵ_∞ is the static dielectric constant, ϵ_0 is the dielectric constant when the microwave relaxation ends and the infrared relaxation begins, n_0 is the refractive index in the visible range, and ω_{MW}, ω_{IR}, and ω_{UV} are the characteristic microwave, infrared, and ultraviolet absorption frequencies.

For general situations, the microwave component to $\epsilon(i\omega_n)$ is better expressed as

$$\frac{\epsilon_\infty - \epsilon_0}{1 + (\omega_n/\omega_{\mathrm{MW}})^{(1-\alpha)}}$$

where α is a Cole–Cole parameter.[60]

Israelachvili[49] assumed that the major part of the dispersion interaction originates from electronic excitation in the ultraviolet frequency range. In this case, eq 12 simplifies to

$$\epsilon(i\omega_n) = 1 + \frac{n_0^2 - 1}{1 + (\omega_n/\omega_{\mathrm{UV}})^2} \quad (13)$$

With the above simplifications and considering only the first terms of the j summation, Israelachvili obtained by integrating eq 10a the following expression:

$$A_{11} = \frac{3}{16\sqrt{2}}\frac{(n_0^2 - 1)^2}{(n_0^2 + 1)^{1.5}}\hbar\omega_{\mathrm{UV}} \quad (14)$$

Assuming a characteristic value of ω (2.63×10^{16} rad/s), Israelachvili calculated the Hamaker constants of different liquids from the data of their refractive indices. Then he calculated the surface tensions of these liquids by combining eq 1 and 9 to obtain

$$\gamma_1 = A_{11}/(24\pi l_0^2) \quad (15)$$

where l_0 is the separation distance between the two semiinfinite slabs when they are in van der Waals contact. Israelachvili ignored the Born repulsion[37] in his treatment; see ref 52. We will discuss this approximation in section IIIA4.

TABLE I. Dielectric Dispersion Data of Some Materials in the Microwave Region

material	ϵ_∞	ϵ_0	α (Cole–Cole)	ω_{MW} rad/s	ref
ethanol	25.07	4.2	0	6.97×10^9	a
methanol	33.64	5.7	0	1.88×10^{10}	a
glycerol	42.5	4.16	0.3	8×10^8	b
water	80.1	5.2	0	1.06×10^{11}	a

[a] *Tables of Dielectric Dispersion Data of Pure Liquids and Dilute Solutions*; National Bureau of Standards: Washington, DC, Circular, p 589. [b] Reference 60.

2. *Interfacial LW Interactions*

Surface tension (or surface free energy per unit area) of a liquid or solid is defined as half of the free energy change due to cohesion of the material in vacuo;[50] i.e.

$$\gamma_i = -\tfrac{1}{2}\Delta F_{ii} \quad (16)$$

where γ_i is the surface tension of the ith species and ΔF_{ii} is the free energy of cohesion of species i in vacuo.

Since the free energy of cohesion is contributed to by a number of more or less independent forces, Fowkes[38] proposed that the surface tension can also be broken down into its separate components; i.e.

$$\gamma_i = \textstyle\sum_j \gamma_i^j \quad (17)$$

where j stands for dispersion, polar, induction, H-bonding, and metallic interactions and γ_i^j stands for the component of the surface tension arising from the jth type of interaction.

Out of all the many components of the surface tensions of different materials, only the Lifshitz–van der Waals component (we will refer to them by the symbol LW) can be estimated at present with a certain degree of confidence; see section IIIA2.

For all exclusively Lifshitz–van der Waals interactions, i.e., interactions between two completely apolar compounds 1 and 2, the Good–Girifalco–Fowkes combining rule[36] is applicable:

$$\gamma_{12}^{\mathrm{LW}} = (\sqrt{\gamma_1^{\mathrm{LW}}} - \sqrt{\gamma_2^{\mathrm{LW}}})^2 \quad (18)$$

which may also be written as

$$\gamma_{12}^{\mathrm{LW}} = \gamma_1^{\mathrm{LW}} + \gamma_2^{\mathrm{LW}} - 2\sqrt{\gamma_1^{\mathrm{LW}}\gamma_2^{\mathrm{LW}}} \quad (18a)$$

The interaction energy between materials 1 and 2 in vacuo then is according to the Dupré equation

$$\Delta F_{12}^{\mathrm{LW}} = \gamma_{12}^{\mathrm{LW}} - \gamma_1^{\mathrm{LW}} - \gamma_2^{\mathrm{LW}} \quad (19)$$

and the interaction energy between molecules or particles of material 1 immersed in a liquid 2 is

$$\Delta F_{121}^{\mathrm{LW}} = -2\gamma_{12}^{\mathrm{LW}} \quad (16a)$$

while the cohesive energy of material i is

$$\Delta F_{ii}^{\mathrm{LW}} = -2\gamma_i^{\mathrm{LW}} \quad (16b)$$

Finally, the interaction energy between materials 1 and 2 immersed in a liquid 3 is

$$\Delta F_{132}^{\mathrm{LW}} = \gamma_{12}^{\mathrm{LW}} - \gamma_{13}^{\mathrm{LW}} - \gamma_{23}^{\mathrm{LW}} \quad (20)$$

TABLE II. Spectroscopic Constants of Several Materials

material	n_0^2	$\omega_{IR} \times 10^{-14}$ rad/s	$\omega_{UV} \times 10^{-16}$ rad/s	ref
helium	1.048		3.73	*a*
hydrogen	1.228		2.33	*a*
nitrogen	1.4		2.36	*a*
argon	1.53		2.39	*a*
hexane	1.864	5.54	1.873	*b*
PTFE	1.846	2.27	1.793	*b*
heptane	1.899	5.54	1.87	*b*
octane	1.925	5.54	1.863	*b*
water	1.755	5.66	1.793	*b*
methanol	1.7349	3.52	1.87	*a, c, d*
ethanol	1.831	2.588	1.924	*a, c, d*
decane	1.965	5.54	1.873	*b*
dodecane	1.991	5.54	1.877	*b*
hexadecane	2.026	5.54	1.848	*b*
benzene	2.179	2.165	1.348	*a, c, d*
chlorine	2.1		1.93	*c*
carbon disulfide	2.49	3.33	1.05	*a, c, d*
glycerol	2.136	3.28	1.895	*e*
PMNA	2.189	5.54	1.915	*b*

[a] Weast, R. C., Ed., *Handbook of Chemistry and Physics*, 56th ed.; Chemical Rubber Co.: Cleveland, 1972. [b] Reference 93. [c] Pouchert, C. S., Ed. *The Aldrich Library of Infrared Spectra*; Aldrich *Chemical Co.*: Milwaukee, 1975. [d] *American Institute of Physics Handbook*, 3rd ed.; McGraw-Hill: New York. [e] *Tables of Dielectric Dispersion Data of Pure Liquids and Dilute Solutions*; National Bureau of Standards: Washington, DC, Circular, p 589.

3. *Attractive and Repulsive LW Interactions*

In combination with eq 18a, eq 20 can also be expressed as

$$\Delta F_{132}{}^{LW} = (\sqrt{\gamma_1{}^{LW}} - \sqrt{\gamma_3{}^{LW}})(\sqrt{\gamma_3{}^{LW}} - \sqrt{\gamma_2{}^{LW}}) \quad (21)$$

from which it is clear that $\Delta F_{132}{}^{LW} < 0$ only when

$$\gamma_3{}^{LW} > \gamma_1{}^{LW} \text{ and } \gamma_3{}^{LW} > \gamma_2{}^{LW} \quad (22a)$$

or when

$$\gamma_3{}^{LW} < \gamma_1{}^{LW} \text{ and } \gamma_3{}^{LW} < \gamma_2{}^{LW} \quad (22b)$$

Similarly, $\Delta F_{132}{}^{LW} > 0$ when

$$\gamma_1{}^{LW} > \gamma_3{}^{LW} > \gamma_2{}^{LW} \quad (23a)$$

and when

$$\gamma_1{}^{LW} < \gamma_3{}^{LW} < \gamma_2{}^{LW} \quad (23b)$$

The conditions obeying eq 23a and 23b result in *repulsive* Lifshitz–van der Waals forces.[26,27] It is clear that these conditions are by no means rare or exceptional. Hamaker already indicated the possibility of such repulsive (dispersion) forces in 1937,[11] which was reiterated by Derjaguin in 1954.[22] The precise conditions under which a repulsion could be expected to occur were first given by Visser in 1972.[23,24] All of these considerations[11,22–24] initially involved only van der Waals–London or Hamaker constant combing rules. It can, however, be shown that the surface thermodynamic approach (eq 20–23) is essentially the same as the Hamaker constant approach[51,52] (see also section IIA4), as long as eq 18 and 18a are valid. That is to say, this validity remains strictly limited to Lifshitz–van der Waals interactions; see section IIA1.

It should be emphasized that there is nothing inherently self-contradictory in repulsive van der Waals forces. The LW interaction between two molecules or particles (identical or different) in vacuo is always attractive. Also the LW interaction between two identical molecules or particles S immersed in a liquid L is always attractive, although it can become zero when $\gamma_S{}^{LW} = \gamma_L{}^{LW}$; see eq 18 and 16a. But when two *different* materials 1 and 2 interact, immersed in liquid 3, and when $\gamma_1{}^{LW} \neq \gamma_2{}^{LW}$ and the conditions in eq 23a and 23b prevail, a net repulsion occurs. To quote Israelachvili:[53] "Repulsion is not confined to van der Waals attractive fields but has a close analogy, e.g., to Archimedes' principle as applied to gravitational fields. For example, even though a gravitational attraction occurs between the earth and both cork and iron in air, the net interaction is very different in water. Cork floats on water (i.e., there is a net repulsion) whereas iron sinks (i.e., in there is a net attraction)". In terms of the oscillator model, this amounts to a condition such as, given in eq 23, in a situation where one material with a positive excess polarizability interacts with another, in a net negative polarizability state. Consequently, when an instantaneous dipole of one material induces a dipole in another, the dipoles orient in the same spatial direction, which then leads to a repulsion.

4. *Young's Equation*

For LW interactions the free energies of interaction between two identical or different materials, in vacuo or immersed in a liquid, can be directly obtained from the surface tensions of the materials (and/or liquids) in question (eq 16 and 18–20). Therefore all that is needed for obtaining these ΔF values is the prior establishment of the surface tension values of each of the interacting materials.

The total surface tensions of liquids are easily determined by a variety of methods[54] or can in many cases be found in published tables.[55] Once the total surface tension of a liquid (L) is known, the γ^{LW} component of the surface tension of two (partly) polar liquids can be found by contact angle (θ) measurement on a completely apolar surface (S), such as Teflon or polyethylene, by a variant of Young's equation[56] developed by Good et al.[36,37] and by Fowkes:[38]

$$\gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_S{}^{LW}\gamma_L{}^{LW}} \quad (24)$$

The γ^{LW} component of the surface tension of solids can also be determined by contact angle measurement with strictly apolar liquids for which $\gamma_L = \gamma_L{}^{LW}$ using eq 24 in the form

$$1 + \cos\theta = 2\sqrt{\gamma_S{}^{LW}/\gamma_L} \quad (24a)$$

While the notion of surface tension of liquids is fully accepted, the concept of a surface tension of solids on occasion elicits an intuitive resistance among some scientists. An effective way to assuage such concerns is to point out that one may simply identify the surface tension of any material (solid or liquid) as minus one-half its free energy of cohesion (viz., eq 16, which is valid for polar as well as for apolar materials).

5. *Decay with Distance of LW Interactions*

In accord with Hamaker's treatment[11] for semiinfinite parallel flat slabs the free energy of LW interaction decays as the square of the distance (d) at fairly close range (i.e., in the nonretarded regime):

$$\Delta F_d^{\mathrm{LW}} = -A/12\pi d^2 \tag{25}$$

where A is the Hamaker constant. This constant was originally linked solely to van der Waals–London or dispersion interactions[11] but as shown in section IIA1, it actually applies to all three electrodynamic interactions in condensed systems, i.e., to the sum of the dispersion, orientation, and induction interactions:

$$A = A_{\mathrm{dispersion}} + A_{\mathrm{orientation}} + A_{\mathrm{induction}} + \text{coupling terms} \tag{26}$$

However, in polar condensed media, especially in the presence of electrolytes, $A_{\mathrm{dispersion}}$ usually is the only significant term. It should be noted that while Dzyaloshinskii et al. criticized Hamaker's reasoning,[43] the validity of eq 25 remains unchanged. It must be stressed that for any single material i (see eq 16b) or combinations of materials (eq 16a, 19, and 20), the relation between ΔF^{LW} and the γ_i^{LW} and $\gamma_{ij}^{\mathrm{LW}}$ values applies solely to $d = d_0$. In the "molecular hard sphere" approximation,[49] the Born repulsion (which is the r^{-12} term in the Lennard-Jones potential) is replaced by a vertical rise in the potential, to infinity, when $d < d_0$ in eq 25. If d_0 is the equilibrium distance, then for semiinfinite parallel flat slabs

$$\Delta F_d^{\mathrm{LW}} = \Delta F_{d0}^{\mathrm{LW}}(d_0/d)^2 \tag{27}$$

Similarly, for two spheres of radius R

$$\Delta F_d^{\mathrm{LW}} = \frac{-AR}{12d} = \Delta F_{d_0}^{\mathrm{LW}}\frac{Rd_0}{12d} \tag{28}$$

and for a sphere of radius R and a flat slab as well as for two crossed cylinders of radius R

$$\Delta F_d^{\mathrm{LW}} = \frac{-Ar}{6d} = \Delta F_{d_0}^{\mathrm{LW}}\frac{Rd_0}{6d} \tag{29}$$

Equations 28 and 29 are valid only for $R \gg d$;[24] d is measured from the edge of the sphere or cylinder. A number of decay vs distance equations for more elaborate geometries are given by Nir.[47]

The *forces* in these systems may be expressed as follows.[24] For two semiinfinite parallel flat slabs, for $d > d_0$

$$F^{\mathrm{LW}} = A/6\pi d^3 \tag{30}$$

where F^{LW} is the LW component of the force per unit area, or *pressure*. For a sphere of radius R and a flat plate as well as for two crossed cylinders

$$F^{\mathrm{LW}} = AR/6d^2 \tag{31}$$

and for two spheres of radius R

$$F^{\mathrm{LW}} = AR/12d^2 \tag{32}$$

where F^{LW} is the LW component of the *force* of interaction.

It should be noted that the best empirical value for d_0 (eq 27) is 1.58 ± 0.08 Å; see section IIIA2. The Born repulsion is not taken into account in eq 25 and 27–32; for a treatment that includes it, see ref 52.

B. Polar or Electron Acceptor–Electron Donor Interactions

1. Surface Thermodynamics of (Lewis) Acid–Base (AB) Interactions

In many nonmetallic condensed materials, liquid or solid, in addition to apolar Lifshitz–van der Waals interactions, polar interactions of the hydrogen-bonding type often occur. In order to embrace all possible interactions of this class, all electron acceptor–electron donor interactions, or Lewis acid–base (AB) interactions (which include the special case of hydrogen donor–hydrogen acceptor interaction), will be considered. In this context, these AB interactions will be alluded to as *polar* interactions, a designation that is not here extended to *electrostatic* interactions (treated in section IIC).

Unlike apolar Lifshitz–van der Waals interactions, electron acceptor–electron donor, or polar, interactions are essentially asymmetrical and can only be satisfactorily treated by taking that asymmetry into account. The electron acceptor and electron donor parameters of the polar component (γ_i^{AB}) of the surface tension of compound i are thus expressed as, respectively, γ_i^+ and γ_i^-.[30,32–35,129]

The polar component of the free energy of interaction between materials 1 and 2 can then be expressed as

$$\Delta F_{12}^{\mathrm{AB}} = -2(\sqrt{\gamma_1^+\gamma_2^-} + \sqrt{\gamma_1^-\gamma_2^+}) \tag{33}$$

to take into account the electron acceptor interaction of material 1 with the electron donor of material 2, as well as the electron donor interaction of material 1 with the electron acceptor of material 2.[57] The negative sign is dictated by the usual surface thermodynamic convention ($\Delta F_{12}^{\mathrm{AB}}$ always represents an attraction and thus must be negative), while the factor 2 is necessitated by the concern to maintain values of a comparable order of magnitude for γ_i^+ and γ_i^-, and γ_i^{AB}.

The polar component of the free energy of cohesion of any compound i then is

$$\Delta F_{ii}^{\mathrm{AB}} = -4\sqrt{\gamma_i^+\gamma_i^-} \tag{34}$$

so that

$$\gamma_i^{\mathrm{AB}} = 2\sqrt{\gamma_i^+\gamma_i^-} \tag{35}$$

(see eq 16, which is valid irrespective of polarity or apolarity). The polar component of the free energy of interaction between materials 1 and 2 can also be expressed by means of the Dupré equation (see eq 19):

$$\Delta F_{12}^{\mathrm{AB}} = \gamma_{12}^{\mathrm{AB}} - \gamma_1^{\mathrm{AB}} - \gamma_2^{\mathrm{AB}} \tag{36}$$

Combining eq 33, 35, and 36, one can now formulate an expression for the polar component of the interfacial tension between materials 1 and 2:

$$\gamma_{12}^{\mathrm{AB}} = 2(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}) \tag{37}$$

which can also be written as

$$\gamma_{12}^{\mathrm{AB}} = 2(\sqrt{\gamma_1^+} - \sqrt{\gamma_2^+})(\sqrt{\gamma_1^-} - \sqrt{\gamma_2^-}) \tag{37a}$$

It should be noted that an equation of the type of eq 37 was proposed by Small as early as 1953[58] (see eq 18 of ref 58).

When eq 37a is compared with eq 18, it becomes clear that while $\gamma_{12}^{\mathrm{LW}}$ cannot be less than zero, $\gamma_{12}^{\mathrm{AB}}$ can readily be negative,[30,32-35] i.e., when

$$\gamma_1^+ > \gamma_2^+ \text{ and } \gamma_1^- < \gamma_2^- \tag{38a}$$

or when

$$\gamma_1^+ < \gamma_2^+ \text{ and } \gamma_1^- > \gamma_2^- \tag{38b}$$

2. The Young–Duprê Equation

Expressing the Young–Duprê equation[47] as

$$(1 + \cos\theta)\gamma_L = -\Delta F_{SL}^{tot} \tag{39}$$

and taking into account that[30,32-35]

$$\Delta F^{tot} = \Delta F^{LW} + \Delta F^{AB} \tag{40}$$

we obtain

$$(1 + \cos\theta)\gamma_L = -\Delta F_{SL}^{LW} - \Delta F_{SL}^{AB} \tag{39a}$$

which, upon combination with eq 18a, 19, 33, and 35 becomes

$$(1 + \cos\theta)\gamma_L = 2\left(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+}\right) \tag{41}$$

Thus, by contact angle (θ) measurement with three different liquids (of which two must be polar) with known γ_L^{LW}, γ_L^+, and γ_L^- values, using eq 41 three times, the γ_S^{LW}, γ_S^+, and γ_S^- of any solid can be determined.[30,32-35] Similarly, by contact angle measurement of a liquid on various solids (of which two must be polar) the γ_L^{LW}, γ_L^+, and γ_L^- can be determined. It is always necessary to determine (or to know) the value of γ_L (see eq 41). Knowledge of γ_L is also useful in connection with the rule of additivity of surface tension components:

$$\gamma = \gamma^{LW} + \gamma^{AB} \tag{42}$$

which, in conjunction with eq 35, furnishes another equation that (in addition to Young's equation) may be taken into account in the interpretation of contact angle data. It may also be stressed that using a totally apolar (LW) solid such as Teflon (see section IIA4) by means of a contact angle determination and using eq 41, γ_L^{LW} can be found. Then, as γ_L is known, γ_L^{AB}, may be obtained by means of eq 42.

3. Positive and Negative Interfacial Tensions

(a) Positive Interfacial Tensions and Interfacial Attractions. Positive interfacial tensions γ_{13} between a polar liquid 3 (e.g., water) and a substance 1 give rise to a negative value of ΔF_{131}^{tot} since

$$\Delta F_{131}^{tot} \equiv -2\gamma_{13} \tag{16c}$$

which will result in a net attraction between molecules or particles 1 immersed in liquid 3. Similarly, a negative value for the free energy of interaction between substance 1 and substance 2 immersed in a polar liquid 3

$$\Delta F_{132}^{tot} \equiv \gamma_{12} - \gamma_{13} - \gamma_{23} \tag{20a}$$

will result in a net attraction between substances 1 and 2, immersed in liquid 3.

The values of ΔF_{131}^{tot} and/or of ΔF_{132}^{tot}, when negative, quantitatively define the *hydrophobic interaction energy*[29,30] of attraction between two similar, or two dissimilar, molecules or particles in a polar liquid medium.

Most strictly apolar substances have γ^{LW} values that are fairly close to that of water ($\gamma_{water}^{LW} = 21.8$ mJ/m²),[10] so that in all such cases $\gamma_{13}^{LW} < 1$ mJ/m²; see eq 18. For such apolar substances immersed in water the main contribution to the negative values of ΔF_{131}^{tot} and ΔF_{132}^{tot} thus originates in the relatively large, positive value of γ_{13}^{AB}, and in such cases, the last three terms of eq 37 are zero, so that $\gamma_{13}^{AB} = 2\sqrt{(\gamma_3^+\gamma_3^-)} = 51$ mJ/m²;[60] see eq 37. The ΔF_{131}^{tot} and ΔF_{132}^{tot} values thus will always be very close to −102 mJ/m² (see eq 16c and 20a) for strictly apolar substances immersed in water.

Even in the case of moderately polar substances immersed in water, the value of γ_{13} is usually positive, and therefore the values of ΔF_{131}^{tot} and ΔF_{132}^{tot}, leading to a modest degree of mutual attraction. Thus the adsorption of proteins onto low-energy surfaces[29,30] and the interaction between protein molecules[30,59,61] via "hydrophobic interactions" can be quantitatively accounted for. However, it would appear from the foregoing that interactions of this class would be more cogently described as *interfacial attractions*[29,30] than with the malappropriate and hazy designation of "hydrophobic interactions" or "hydrophobic bonds". Earlier considerations on hydrophobic interactions in macroscopic systems may be found in ref 28 and 62.

(b) Negative Interfacial Tensions and Interfacial Repulsion. As is clear from eq 37a, 38a, and 38b, the polar component of the interfacial tension (γ_{12}^{AB}) between compounds 1 and 2 can become negative under circumstances that occur quite commonly. Clearly, if γ_{12}^{AB} becomes sufficiently negative, the positive value of γ_{12}^{LW} may not suffice to counterbalance that negative value, so that the total interfacial tension (see eq 18, 37, and 42) then also becomes negative:[32-35]

$$\gamma_{12} = \left(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_2^{LW}}\right)^2 + 2\left(\sqrt{\gamma_1^+\gamma_1^-} + \sqrt{\gamma_2^+\gamma_2^-} - \sqrt{\gamma_1^+\gamma_2^-} - \sqrt{\gamma_1^-\gamma_2^+}\right) \tag{43}$$

It is also clear from eq 43 that while pronounced polar *cohesion* of compound 1 or 2 causes a high γ_{12} value, a strong polar *adhesive* interaction between compounds 1 and 2 will give rise to a much decreased γ_{12}.

A closer inspection of eq 43 is helpful in elucidating why the value of the interfacial tension between apolar or moderately polar compounds on the one hand, and very polar materials on the other, can range from very high to very low values. This range was strikingly demonstrated by Girifalco and Good in 1957 in tables displaying the interfacial tensions between a large number of organic liquids and water.[37] Most of these organic liquids had γ_1 values between 20 and 29 mJ/m², and so the interfacial tensions with water ($\gamma_2 = 72.8$ mJ/m²) should have been in the range of $\gamma_{12} = 10$–17 mJ/m² if eq 18 held for determining γ_{12}^{tot}. In reality, the measured γ_{12}^{tot} values for such liquids ranged from 1.7 to 51 mJ/m². (The measurements of the interfacial tensions were done by various authors, usually by drop weight or hanging-drop methods.) To reconcile these large deviations between the measured values obtained for γ_{12} and the γ_{12} values expected from eq 18, Girifalco and Good inserted an *interaction parameter* Φ into eq 18a:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\Phi\sqrt{\gamma_1\gamma_2} \tag{18b}$$

where Φ ranged from 0.53 to 1.17.[37] The parameter Φ was calculated from the assumption of pairwise additivity of intermolecular forces, which is not strictly valid in the condensed state, particularly for Keesom and Debye interactions. (This treatment has been reviewed in ref 65.) The inexact expression for Φ, as it has been continually used, has caused some confusion in this field of research. However, while the introduction of the phenomenological factor Φ did not directly elucidate the physical causes underlying the considerable deviations from the values expected via eq 18, it has been an important incentive for the development of solutions for the problem.[25,38]

Splitting off the polar interactions from the LW interactions in the following manner

$$\gamma_{12} = (\sqrt{\gamma_1^{\mathrm{LW}}} - \sqrt{\gamma_2^{\mathrm{LW}}})^2 + (\sqrt{\gamma_1^{\mathrm{AB}}} - \sqrt{\gamma_2^{\mathrm{AB}}})^2 \qquad (18c)$$

does not furnish the right answer either, except when material 1 is very hydrated[29] or for totally apolar materials 1 (where in all cases material 2 is water). The reasons for this become clearer when eq 43 is expressed as

$$\gamma_{12} = (\sqrt{\gamma_1^{\mathrm{LW}}} - \sqrt{\gamma_2^{\mathrm{LW}}})^2 + \gamma_1^{\mathrm{AB}} + \gamma_2^{\mathrm{AB}} - 2(\sqrt{\gamma_1^{+}\gamma_2^{-}} + \sqrt{\gamma_1^{-}\gamma_2^{+}}) \qquad (43a)$$

On the other hand, when 1 is a particularly asymmetrical material, such as an oxide, a sulfide, an alcohol, a ketone, an ether, etc.,[34,35] the value of $\sqrt{(\gamma_1^{-}\gamma_2^{+})}$ tends to be considerable, while γ_1^{AB} and $\sqrt{(\gamma_1^{+}\gamma_2^{-})}$ are close to zero. As a first approximation, eq 28a then becomes

$$\gamma_{12} = (\sqrt{\gamma_1^{\mathrm{LW}}} - \sqrt{\gamma_2^{\mathrm{LW}}})^2 + \gamma_2^{\mathrm{AB}} - 2\sqrt{\gamma_1^{-}\gamma_2^{+}} \qquad (43b)$$

where $\gamma_2^{\mathrm{AB}} = 51$ mJ/m^2 and $-2\sqrt{(\gamma_1^{-}\gamma_2^{+})}$ may vary widely from ≈ -6 to ≈ -49 mJ/m^2 according to the electron donicity of material 1. The experimental values found for the γ_{12} with water, of a variety of organic liquids,[37] will then be seen to become entirely plausible.

Fowkes has pointed out that polar interactions do not follow the combining rule that is valid for apolar interactions;[10] in other words, eq 18c is, in general, wrong. We have indicated some of the limiting conditions under which eq 18c might be used as a first approximation only.[29] A number of authors have used eq 18c,[63,63a–k] and this would leave the interpretation of their results open to some modification. Andrade et al.[63l] and, more recently, Dalal[63m] have contemplated using the geometric mean (eq 18c), as well as the harmonic mean, as combining rules for the polar surface tension components. Ström et al.[63n] recently introduced a characteristic multiplication constant, or "hydrophilicity number", for the polar surface tension component of photooxidized polystyrene surfaces relative to water. The difficulty with the use of geometric mean or harmonic mean combining rules or multiplication factors for the polar surface tension components is that *none* of these treatments (see also the Φ interaction parameter,[37] mentioned above) can account for the (very common) occurrence of a zero polar surface tension component among otherwise quite polar liquids and solids (which are, in such cases, monopolar). To take these phenomena into account, it is indispensable to treat the electron acceptor–electron donor and the electron donor–electron acceptor interactions between two different materials *as separate terms*. If one of these two interactions becomes zero on account of the monopolarity of one of its components, its polarity will still be reflected in the other term, e.g., for interactions between a monopolar solid and a bipolar liquid, or for interactions between a bipolar solid and a monopolar liquid.

Zisman has earlier indicated a certain degree of correlation between γ_{S} and the values of γ_{L} found by an extrapolation of $\cos\theta$ to $\cos\theta = 1$ when measured with a number of liquids L.[64] In view of eq 18 and 24, this holds true only for completely apolar liquids, and the Zisman method can only yield $\gamma_{\mathrm{S}}^{\mathrm{LW}}$, for which (in principle) the measurement of with only one apolar liquid would suffice. Actually, Zisman determined γ_{c}, the critical surface tension of wetting, by this approach, and he refused to identify γ_{c} as equal to γ_{S}, as he was aware of the potential difficulties in his method. In any event, it has been pointed out that it would have been more appropriate to correlate the $\cos\theta$ values with $\sqrt{\gamma_{\mathrm{L}}^{\mathrm{LW}}}$, rather than with $\gamma_{\mathrm{L}}^{\mathrm{LW}}$;[65] see eq 18. Finally, some mention should be made of "equations of state"[66,67] that purport to obtain γ_{S} from contact angle measurements with only one liquid for all possible materials. This claim is based on the premises that the surface tension may not be divided into components[68] and that γ_{12} cannot be negative (note that the computer program in ref 66 explicitly excludes negative values of γ_{12}). Thus the results obtained with such equations of state, while fairly reasonable in certain instances, can be quite aberrant in others.[69]

It should also be pointed out that, contrary to the claims of ref 66, the measurement of γ_{S} alone does not allow the determination of γ_{12}, ΔF_{12}, ΔF_{121}, or ΔF_{132} (where S is substance 1). To determine these entities, knowledge of the $\gamma_{\mathrm{L}}^{\mathrm{LW}}$, $\gamma_{\mathrm{S}}^{\mathrm{LW}}$, γ_{L}^{+}, γ_{L}^{-}, and γ_{S}^{-} values is essential; see sections IIB1 and IIB2.

Moreover, there are many cases in which the total interfacial tension γ_{12} between water and various polar solids, or liquids, actually has a negative value,[33,35] i.e., when $|\gamma_{12}^{\mathrm{AB}}| > \gamma_{12}^{\mathrm{LW}}$ and $\gamma_{12}^{\mathrm{AB}} < 0$. In most of these cases, a negative γ_{12} persists for only a relatively short time, because these are systems in which, at equilibrium, there is complete miscibility. In the case of immiscible liquids, a negative γ_{12} imparted to the system by means of a surfactant with a strongly asymmetrical polarity can be the driving force for the formation of a stable microemulsion[33] in which the ultimate γ_{12} value is only of the order of $+10^{-5}$ to $+10^{-3}$ mJ/m^2, i.e., only barely on the positive side of zero. That low equilibrium value, however, was reached from a starting point of, e.g., $\gamma_{12} \approx -16$ mJ/m^2.[33]

In some cases, however, a negative interfacial tension may persist for a long time, or even indefinitely. Negative interfacial tensions between water and polymers that are slowly soluble on account of their high molecular weight, such as dextran,[34] may persist for an appreciable time before solubilization ensues. And negative interfacial tensions between water and polymers that are insoluble in water such as zein (a protein from corn) or agarose (a neutral polysaccharide from seaweed) persist indefinitely.[34] The implications and various manifestations of permanent negative interfacial tensions are discussed in section IIIA3.

4. Monopolar Surfaces

As already mentioned in the preceding section, there are many polar surfaces with a markedly asymmetrical polarity, i.e., usually with a very strong electron donor (γ^-) (Lewis base) and a negligible or even nonexistent electron acceptor (γ^+) (Lewis acid) capacity.[33] Such surfaces are best described as monopolar.[33-35] The interfacial tension between such a monopole (substance 1) and a polar liquid, 2, such as water, then is described by eq 38b; it will be negative when $2\surd(\gamma_2^-\gamma_1^+) > (51 \text{ mJ/m}^2 + \gamma_{12}^{LW})$. For many polymers and bipolymers $\gamma_1^{LW} = 40 \text{ mJ/m}^2$, while for water $\gamma_2^{LW} = 21.8 \text{ mJ/m}^2$,[10] so that typically $\gamma_{12}^{LW} \approx 2.7 \text{ mJ/m}^2$.[2]

We need, at this point, to assume a pair of reference values for γ_W^+ and γ_W^- of water. We can obtain for any substance i, and without any assumptions, the ratios of the values of γ_i^+ to γ_W^+ and of γ_i^- to γ_W^-: $\delta_i^+ \equiv \surd(\gamma_i^+/\gamma_W^+)$ and $\delta_i^- \equiv \surd(\gamma_i^-/\gamma_W^-)$. Using these ratios, one can readily obtain the correct values of γ_1^{AB}, γ_{12}^{AB}, ΔF_{12}^{AB}, ΔF_{121}^{AB}, and ΔF_{132}^{AB}.[33-35] These values are identical with the ones that may be obtained with the help of postulated values for γ_W^+ (or γ_W^-) for water. The advantage of assuming arbitrary (but plausible) values for γ_W^+ (or γ_W^-) lies in the possibility they provide for expressing γ_i^+ or γ_i^- of other substances in SI units, thus affording an estimate of the order of magnitude of these entities. We will, for convenience, assume the reference values for water, $\gamma_W^+ = \gamma_W^- = 25.5 \text{ mJ/m}^2$. Then the relation $2\surd(\gamma_W^+\gamma_W^-) = 51$ yields the reference value of γ_W^-. Thus, the interfacial tension between water and a γ^- monopolar surface will be negative when for such a monopole $\gamma^- \geq 28 \text{ mJ/m}^2$.[33]

In accordance with eq 16a, when $\gamma_{12} < 0$, $\Delta F_{121} > 0$. Thus, γ^- monopolar substances with $\gamma^- \geq 28 \text{ mJ/m}^2$ (see above) when dissolved or suspended in water will repel each other. Apart from solubility, or microemulsion formation, that repulsion can lead to stability of aqueous suspensions[33] or to aqueous phase separation.[26,30] Among γ^- monopolar substances with a $\gamma^- > 28 \text{ mJ/m}^2$ are dimethyl sulfoxide[35] (DMSO) and (Lewis) basic polymers such as agarose,[34] gelatin,[33] dextran,[70] poly(ethylene glycol),[70] ribosomal RNA,[71] cellulose acetate,[71] and poly(vinyl alcohol);[33] some of these are internally self-associated, while others such as poly(ethylene glycol) are not. At close range, the repulsive energy ΔF_{121} between two layers of poly(ethylene glycol) immersed in water is of the order of $+50 \text{ mJ/m}^2$.[26] That energy of repulsion is considerably higher than both the osmotic repulsion energy and the energy of electrostatic repulsion found in most instances (see section IIC1), and it is an order of magnitude higher than that of the Lifshitz–van der Waals attraction between two poly(ethylene glycol) layers in water.

Monopolar repulsion appears to represent a quantitatively preponderant repulsive factor in the energy balances of systems where strong monopoles occur in polar media. See section IID.

5. Decay with Distance of AB Interactions

The decay with distance (d) of hydration pressure at $d > \lambda$ (where λ is the correlation length pertaining to water molecules[72]) is given by

$$P(d) = P(d_0)\exp(-d/\lambda) \qquad (44)$$

See Parsegian et al.,[73] Rand and Parsegian,[74] and the basic work of Marcelja and Radic.[75] By integration, one obtains

$$\Delta F^{AB}(d) = \Delta F^{AB}(d_0)\exp[(d_0 - d)/\lambda] \qquad (45)$$

for the parallel flat plate conformation.[33] For pure water, the value for λ is close to 2 Å.[72-74] At high ionic strengths, however, λ is more closely linked to the dimension of the hydrated ions, so that its value may then be as high as 12 Å.[76] More recently reported experimentally obtained values for λ of water have been as high as 130 Å.[123,124] The observed forces often are oscillatory at short distances.[123]

C. Electrostatic Interactions

1. The Electrokinetic Potential

In polar systems, and especially in aqueous media, very few macromolecules or particles (or indeed any inorganic or organic surfaces) are entirely devoid of electrical surface charge. Polymers or particles with the same sign of charge will, when immersed in a polar liquid such as water, repel each other. In many such systems the resulting energy of intermolecular or interparticulate repulsion may well be too strong, in comparison with the apolar and polar interaction energies (discussed in sections IIA and IIb), to be neglected in the context of the total energy balance (section IID). Thus, in all cases where the outcome of the total energy balance of a polar system is necessary for the prediction of particle stability, polymer solubility, polymer compatibility, particle adhesion, or polymer adsorption, the electrostatic interaction energy (EL) component must be ascertained. Thus for the sake of completeness, electrostatic interactions are also briefly discussed here, even though they are not of the same nature as either Lifshitz–van der Waals or electron donor–electron acceptor interactions.

The electrokinetic potential, or ζ-potential, of macromolecules, particles, or larger surfaces is the potential measured at the slipping plane by electrokinetic methods such as electrophoresis, electroosmosis, streaming potential, etc.; see section IIIB. The ζ-potential of a surface is rarely directly related to its γ^{AB}. Contact angle measurements usually are not affected by the ζ-potential of the solid surface. One exception may be the measurement of the contact angle on an amphoteric surface with drops of buffered water. Here the pH of the water can influence the γ^{AB} of the surface, because it affects the degree of dissociation of charged as well as of electron-donating or electron-accepting groups.[77] Conversely, electrokinetic migration appears to be at least qualitatively linked to electron donor or electron acceptor properties.[78-80]

The connection between electrokinetic phenomena, the electrical double layer, and the ζ-potential has been discussed in depth in the colloid and surface science and in the electrochemical literature for the past 4 decades, especially by Overbeek and his collaborators;[9,81,82] see also Hunter's recent treatise on the subject.[83]

2. Free Energy and Decay with Distance of Electrostatic Interactions

Traditionally, the energy of electrostatic interaction is not linked directly to the (measured) electrokinetic (ζ) potential at the slipping plane, but to the ψ_0 potential at the exact interface between the charged surface and the polar liquid. For relatively low ζ-potentials the two are connected as[9]

$$\psi_0 = \zeta(1 + z/a)e^{\kappa z} \qquad (46)$$

where z is the distance from the charged particles' surface to the slipping plane (usually $z \approx 5$ Å), a is the Stokes radius of the particles, and κ is the inverse Debye length

$$\kappa = [(4\pi e^2 \sum v_i^2 n_i)/(\epsilon kT)]^{1/2} \tag{47}$$

where e is the charge of the electron ($e = 4.8 \times 10^{-10}$ esu, or 1.6×10^{-19} C), $\sum v_i n_i$ (2×) is the ionic strength, with v_i the valence of each ionic species and n_i the number of ions of each species per cm^3 of bulk liquid, ϵ is the dielectric constant of the liquid medium, k is Boltzmann's constant ($k = 1.38 \times 10^{-16}$ erg/K, or 1.38×10^{-23} J/K), and T is the absolute temperature in kelvin.

An important problem connected to the extrapolation from ζ to ψ_0 for the expression of ΔF^{EL} (see below) is that (in aqueous systems in particular) inside the slipping plane, the value of the dielectric constant is much less than the value of 80, of the bulk liquid, due to the orientation of the water molecules close to the polar surface.[84] A pronounced orientation of this type was recently demonstrated experimentally in the first molecular layer of hydration of serum albumin.[85] From the slipping plane on outward, however, that orientation has largely decayed (see section IIB2), so that it is actually much safer to consider the surface of a particle, *at the slipping plane*, as the relevant surface and thus to use the actually measured ζ-potential, instead of ψ_0, in the equations that follow. Recently, Zukoski and Saville[86] showed that when instead of measuring the ζ-potential by electrokinetic methods, a particle potential is measured by conductivity determinations, a higher potential than the ζ-potential is found, which includes potentials originating from within the Stern layer, in other words, from well within the slipping plane. However, for electrostatic macromolecule–macromolecule, particle–particle, or macromolecule–flat surface or particle–flat surface interactions, the operative boundary of the particle or surface is best taken to begin at the slipping plane and not inside of it; see also ref 84 and 85.

For not too large values of ζ (i.e., below ≈25–50 mV), the electrostatic interaction energy between two plane parallel flat plates, at distance l, may be expressed as[9,21]

$$\Delta F^{\mathrm{EL}} = (1/\kappa)(64nkT)\gamma_0^2 \exp(-\kappa l) \tag{48}$$

where n is the number of counterions in the bulk liquid per cm^3 and

$$\gamma_0 = \frac{\exp(ve\psi_0/2kT) - 1}{\exp(ve\psi_0/2kT) + 1} \tag{49}$$

where v is the valency of the ions in the electrolyte. For the goodness of fit of eq 48, see ref 87, p 52.

Under the same conditions, the interaction energy between two spheres of radius R[9,21,87] is

$$\Delta F^{\mathrm{EL}} = (1/2)\epsilon R \psi_0^2 \ln [1 + \exp(-\kappa l)] \tag{50}$$

while for a sphere of radius R and a flat plane

$$\Delta F^{\mathrm{EL}} = \epsilon R \psi_0^2 \ln [1 + \exp(-\kappa l)] \tag{51}$$

See, e.g., Visser.[24] Here d is measured from the outer edge of the sphere. For dissimilar double-layer interactions, see ref 87, p 68. All of these approximations were derived for a constant surface potential model. For a constant surface charge model, see ref 87, pp 70 ff.

Due to the strong dependence of κ on the ionic strength (eq 47), the ζ-potential (eq 46) and the repulsion energies derived from it (eq 48, 50, and 51) are much decreased at higher ionic strengths.

D. Energy Balance

For similar materials 1 immersed in a liquid 3 the interaction energies (at $d = d_0$) can be found for LW interactions with eq 16a, for AB interactions with eq 16, together with eq 35 and 37, and for EL interactions (for parallel flat surfaces) with eq 48. For each of these three interactions, the rate of decay with distance is known (e.g., for parallel flat surfaces): for LW interactions, eq 27; for AB interactions, eq 44; for EL interactions, the rate of decay has been incorporated in eq 48.

Thus, once the $\Delta F_{131}(d_0)$ value for each of these is known, separate energy vs distance balances can be constructed. From these the *total* energy balance curve can be obtained by summation. The best value for d_0 for LW interactions may be taken as 1.58 Å (see section IIIA4). For EL interactions d_0 is best taken to begin at the slipping plane; see section IIC. For ΔF_{132}, interactions between two dissimilar materials 1 and immersed in a liquid 3, see eq 52 for the LW and AB components and ref 87 for the EL components.

Osmotic (OS) interactions, which may be of some importance in the stabilization by polymer molecules (soluble in an apolar liquid) adhering to particles suspended in that apolar liquid,[88] can be estimated from the local concentration and the molecular weight of the adhering polymer. The rate of decay of OS interactions has not been studied in depth. It would depend to a considerable extent on whether the polymer molecules adhere to the particle by adsorption (i.e., in the presence of a sizeable concentration of free polymer in solution) or by covalent attachment and also on the molecular size of the polymer molecules. OS interaction energies tend to be quantitatively much smaller than AB energies, but their rate of decay with distance is much more gradual.

Steric interactions[40] of a structural nature (involving entropic or steric hindrance, or other such effects) are not treated here.

In energy balances, for similar materials 1 immersed in a polar liquid 3 $\Delta F_{131}{}^{\mathrm{LW}}$ is always negative (or zero), $\Delta F_{131}{}^{\mathrm{EL}}$ is always positive (or zero), and $\Delta F_{131}{}^{\mathrm{AB}}$ can be positive, zero, or negative. High salt concentrations have little influence on $\Delta F_{131}{}^{\mathrm{LW}}$, they strongly attenuate $\Delta F_{131}{}^{\mathrm{EL}}$, and they have little influence on $\Delta F_{131}{}^{\mathrm{AB}}$ except at very high salt concentrations, in which case the rate of decay may be decreased because of an increase in the liquid's correlation length λ. For water, λ typically is of the order of 2 Å; but at high salt concentrations in water λ may reach κ12 Å.[89] In practice, in polar (aqueous) media, $\Delta F_{131}{}^{\mathrm{AB}}$ usually is quantitatively the preponderant factor, typically surpassing $\Delta F_{131}{}^{\mathrm{LW}}$ by factors of 10–100×; $\Delta F_{131}{}^{\mathrm{AB}}$ usually is also larger than $\Delta F_{131}{}^{\mathrm{EL}}$ by several fold, for $\zeta \leqslant 15$ mV, and is much larger than $\Delta F_{131}{}^{\mathrm{OS}}$.

A very important aspect of $\Delta F_{131}{}^{\mathrm{AB}}$, which as yet does not appear to be widely recognized, is the fact that it can readily assume a strongly positive value (in the case of strongly monopolar surfaces[33]). In hydrophobic interactions, on the other hand, the strongly negative value of $\Delta F_{131}{}^{AB}$ is the main driving force for the attraction; see the discussion in section IIIC).

III. Experimental Approaches and Verification

A. Contact Angle Determination of LW and AB Interactions

1. Young's Equation and Its Utilization

For any flat solid S, using three liquids L_1, L_2, and L_3, $\gamma_S{}^{LW}$, $\gamma_S{}^+$, and $\gamma_S{}^-$ can be found by contact angle (θ) determination, provided $\gamma_{L_i}{}^{LW}$, $\gamma_{L_i}{}^+$, and $\gamma_{L_i}{}^-$ are known for all three liquids, using eq 41.[30,33-35] At least two of the three liquids must be polar. It usually is most expedient to determine $\gamma_S{}^{LW}$ first, with the help of a high-energy apolar (or virtually apolar) liquid such as α-bromonaphthalene and diiodomethane. The other two liquids must be polar and have high energy and high values of γ^+ and γ^-. Water and glycerol fit these criteria well.[30,33-35] Conversely, for any liquid $\gamma_L{}^{LW}$, $\gamma_L{}^+$, and $\gamma_L{}^-$ can be determined by contact angle determinations on three solids S_1, S_2, and S_3, of which two should be polar[34] and for which the components $\gamma_S{}^{LW}$, $\gamma_S{}^+$, and $\gamma_S{}^-$ are known. Advancing contact angles may be measured not only by the conventional methodology[90] but also, e.g., by "wicking",[91] in the case of particles or powders. Receding contact angles may also be measured and treated in the same way. If hysteresis is caused by patchwise heterogeneity of a solid, the advancing angle gives a measure of γ_S properties of the lower energy component, and the receding angle gives a measure of the properties of the higher energy component.[90]

2. Interfacial Tensions between Liquids

The interfacial tension between two liquids is measured by a variety of approaches, such as hanging drop, spinning drop, and drop weight methods.[54] By making use of eq 43, one can obtain $\gamma_L{}^{LW}$, $\gamma_L{}^+$, and $\gamma_L{}^-$ once the interfacial tensions γ_{12} between this liquid and three other completely characterized liquids (that are immiscible with the first liquid) have been determined. The interfacial tension between miscible liquids can be obtained from contact angle measurements of one liquid deposited on a gel encasing the other liquid.[35,92] Interfacial tension data between water and a large number of organic liquids have been published by Girifalco and Good.[37]

3. Interfacial Interactions between Different or Similar Materials Immersed in Liquids

From the Dupré equation (20), which is valid for AB as well as for LW interactions, and eq 43 for γ_{ij}, the total interfacial interaction between materials 1 and 2 immersed in liquid 3 is expressed as[30,33-35]

$$\Delta F_{132}{}^{tot} = \gamma_{12}{}^{LW} - \gamma_{13}{}^{LW} - \gamma_{23}{}^{LW} + 2[\sqrt{\gamma_3{}^+}(\sqrt{\gamma_1{}^-} + \sqrt{\gamma_2{}^-} - \sqrt{\gamma_3{}^-}) + \sqrt{\gamma_3{}^-}(\sqrt{\gamma_1{}^+} + \sqrt{\gamma_2{}^+} - \sqrt{\gamma_3{}^+}) - \sqrt{\gamma_1{}^+\gamma_2{}^-} - \sqrt{\gamma_1{}^-\gamma_2{}^+}] \quad (52)$$

while the interaction between similar materials 1 immersed in liquid 3, $\Delta F_{131}{}^{tot}$, is expressed by eq 16c, in which γ_{13} is found according to eq 43. With the appropriate number of determinations of $\Delta F_{132}{}^{tot}$ or $\Delta F_{131}{}^{tot}$ the values of $\gamma_i{}^{LW}$, $\gamma_i{}^+$, and $\gamma_i{}^-$ can be found for $i = 1$ or $i = 2$, provided these properties are known for the other interacting material and/or liquid; see sections IIIC and IIID.

4. Relation between the LW Surface Tension and the LW Constant A

A particularly simple relation between $\gamma_i{}^{LW}$ and A_{ii} can be shown to exist if l_0 is constant for all materials i: A_{ii}/γ_i = constant. Assuming the minimum van der Waals separation distance to be an average atom-to-atom separation distance of the molecules in close-packed planes, Israelachvili calculated the values of the surface tensions of various liquids.[49] The calculated values of the surface tensions very closely matched the dispersion components of the surface tensions of these liquids. The average value of l_0 for these liquids was found to be nearly 2 Å, and on the basis of this, the empirical proportionality factor between the Hamaker constant and the Lifshitz–van der Waals (LW) component of the surface tension (γ^{LW}) then would amount to

$$A_{ii}/\gamma_i{}^{LW} = \text{constant} = 3.01 \times 10^{-14}\ \text{cm}^2 \quad (53a)$$

Fowkes,[25] on the other hand, obtained an empirical proportionality factor between A_{ii} and $\gamma_i{}^{LW}$ of the organic liquids as

$$A_{ii}/\gamma_i = \text{constant} = 1.51 \times 10^{-14}\ \text{cm}^2 \quad (53b)$$

Fowkes' calculation of the Hamaker constant, however, was based on the pairwise additivity approach to Hamaker,[11] which is not strictly valid for condensed media interactions.

Hough and White[93] in a recent review paper have correlated the Hamaker constants and surface tensions of a number of different alkanes. In this calculation, a value of the parameter $<_0$ emerged as being nearly 1.6 Å for the alkanes under consideration. Van Oss and Good[52] have utilized a similar distance parameter in the case of solids interacting through liquid. Israelachvili has more recently used a similar distance parameter ($l_0 \approx 1.65$ Å) and obtained improved estimates of the Hamaker constants for different materials.[94]

We have extended the computation of Hamaker constants for a wide variety of materials by using the Lifshitz formula. The materials considered here are low-temperature liquids, H-bonding liquids, organic liquids, polymers, and a liquid metal (mercury). Only those materials were considered for which the values of γ^{LW} were known and for which the necessary spectroscopic data also were available. Having the estimates of the Hamaker constants and the values of γ^{LW} of these materials, we determined the values of l_0. From this an attempt was made to determine an empirical proportionality factor between the parameters A_{ii} and $\gamma_i{}^{LW}$.

It is assumed here that the equilibrium separation between two semiinfinite parallel slabs is determined by the balance between the Born repulsion and the van der Waals attraction. The subject was explicitly discussed by Good and Girifalco[36,37] and also by van Oss and Good.[52] According to van Oss and Good,[52] the relation between the Hamaker constant and the London–Lifshitz component of the surface tension is better expressed according to eq 54 than eq 16.

$$A_{ii} = \gamma_i^{\mathrm{LW}}/32\pi l_{\mathrm{eq}}^2 \qquad (54)$$

The Hamaker constants of the several solids and liquids were determined by using eq 10 and 12 at room temperature and by using eq 14 at low temperatures. For most of the dielectric substances, the necessary parameters of eq 12 were determined by the methodology described by Ninham and Parsegian[48] and Hough and White.[93] For low-temperature liquids, the data of the refractive indices as a function of frequency were not available and therefore the values of n_0 and ω_{UV} could not be determined from Cauchy plots, which was used for other dielectric substances. In the case of low-temperature liquids, the values of ω_{UV} were estimated from the first ionization potential, and the values of n_0 were determined from the square root of static dielectric constants. For the liquid metal, mercury, A_{ii} was estimated from refractive index data, $\epsilon(i\omega_n)$, obtained by ellipsometry.

The calculated Hamaker constants and experimentally determined London–Lifshitz components of the surface tensions of a number of different materials are listed in Table III. From the knowledge of Hamaker constants and LW components of the surface tensions of these materials, the separation distance (l_{eq}) was calculated by employing eq 54 (column A) and l_0, using eq 15 (column B). It is worthy of note from Table III that in the majority of the cases the values of the equilibrium separation distances lie between 1.3 and 1.5 Å (column A). The average separation distance l_{eq} is found to be 1.36 Å with a standard deviation of 0.07 Å; or using eq 15 (column B), $l_0 = 1.58 \pm 0.08$ Å. If we employ the equilibrium separation distance for all the materials, an empirical proportionality factor between the Hamaker constant and the LW component of the surface tension, using eq 15, emerges as $(1.88 \pm 0.19) \times 10^{-14}$ cm^2.

The employment of this proportionality factor will make the determination of the Hamaker constant from surface tension measurements uncertain by about ±8%. This range of uncertainty is not unsatisfactory, considering the fact that the present Lifshitz theory calculations, owing to the lack of detailed spectroscopic data, yield values of Hamaker constants that are uncertain by a similar magnitude.[93] As in some cases it may be more convenient to use eq 15 for arriving at the Hamaker constant (e.g., in conjunction with decay with the distance computation; see eq 11a and 27), l_0 values derived from eq 15 are also given; see column B of Table III.

The small variability of the empirical proportionality factor, $(1.88 \pm 0.19) \times 10^{-14}$ cm^2, makes it a useful experimental constant, linking A_{ii} and γ_i^{LW} for all condensed materials i.

TABLE III. Listing of Hamaker Constants and γ^{LW} Values for Various Liquids, Showing the Minimum Equilibrium Distance l_{eq} according to Eq 54 (Column A) and l_0 from eq 15 (Column B)

material	temp, °C	Hamaker constant (×10^{20}), J	γ^{LW}, mJ/m^2	l_{eq},$^{\mathrm{A}\,a,d}$ Å	l_0,$^{\mathrm{B}\,a,d}$ Å
helium	−271.5	0.0535	0.353	1.26	1.45
hydrogen	−255	0.511	2.31	1.48	1.71
nitrogen	−183	1.42	6.6	1.46	1.69
argon	−188	2.33	13.2	1.32	1.52
hexane	25	3.91	18.4	1.45	1.68
poly(tetrafluoroethylene)	25	3.8	19	1.41	1.63
heptane	25	4.03	20.14	1.4	1.62
octane	25	4.11	21.8	1.37	1.58
water	25	4.62	21.8	1.45	1.67
methanol	25	3.94	18.5[b]	1.46	1.68
ethanol	25	4.39	20.1[b]	1.47	1.70
decane	25	4.25	23.9	1.33	1.54
dodecane	25	4.35	25.4	1.3	1.50
tetradecane	25	4.38	26.6	1.28	1.48
chloroform	25	5.34	27.14	1.39	1.61
hexadecane	25	4.43	27.7	1.26	1.45
benzene	25	4.66	28.9	1.26	1.45
chlorine	50	5.4	29.2	1.35	1.56
carbon disulfide	25	5.07	32.3	1.26	1.45
glycerol	25	6.7	34	1.4	1.62
polystyrene	25	6.58	8	1.31	1.51
poly(methyl methacrylate)	25	7.11	40	1.33	1.54
mercury	25	33[c]	200	1.28	1.48

[a] Column A, using eq 54; column B, using eq 15. [b] Taken from ref 34. [c] For more recent calculations on A and γ^{LW} of mercury, see: Chaudhury, M. K. *J. Colloid Interface Sci.* **1987**, *119*, 174. See also: Chaudhury, M. K. Ph.D. Thesis (ref 60). [d] Average l_{eq} = 1.36 ± 0.07 Å; l_0 = 1.58 + 0.08 Å.

5. *Implications of AB Interactions*

In view of the quantitative preponderance of AB interactions in polar (e.g., aqueous) media (which has been established on the basis of contact angle and interfacial tension measurements as outlined in sections IIB and IID), it would seem unlikely that such strong interactions could have remained unobserved until recently. Many of the manifestations of AB interactions have indeed been observed, but they were not usually recognized as electron acceptor–electron donor interactions.

(a) Attractive Interactions. For instance, the importance of hydrophobic interactions in macroscopic systems has long been acknowledged,[28] but their first quantitative measurement, by Pashley et al.,[95] could only be done after the fairly recent development of a force balance, capable of operating in liquid media, by Israelachvili and his colleagues.[96,97] The observed attraction energy[95] between two hexadecyl surfaces in water agrees well with the (strongly negative) $\Delta F_{121}^{\mathrm{tot}}$ value derived from the known surface tensions and the observed[95] contact angle data; see section IIIC.

The observed energy of adsorption of proteins onto low-energy surfaces (also largely due to hydrophobic interactions) conforms well with the calculated $\Delta F_{132}^{\mathrm{LW}} + \Delta F_{132}^{\mathrm{AB}}$ values derived from contact angle data.[29,30] Most other recent protein adsorption studies, however, focus mainly on the quantitative influence of the electrostatic surface charge of adsorbants and proteins and only briefly treat the influence of hydrophobic interactions in qualitative terms; see, e.g., Norde's recent review.[98]

The ready adsorption of DNA onto cellulose ester membranes and the failure of RNA to adsorb onto that material (properties that are of importance in modern molecular genetics methodology) were shown to be due to a negative $\Delta F_{132}^{\mathrm{AB}}$ for DNA and a positive $\Delta F_{132}^{\mathrm{AB}}$ for RNA, vis-<<avua-vis cellulose nitrate (and cellulose acetate).[71] Protein adsorption onto cellulose ester membranes was also studied.[71] Serum protein–protein

interactions and their role in protein solubility and in protein precipitation under various circumstances also appeared mainly governed by the sign and the value of $\Delta F_{131}{}^{\mathrm{AB}}$.[59,60]

(b) Repulsive Interactions. The hydration repulsion observed by Parsegian and his colleagues[31,99] is a result of the hydration orientation at the interface of monopolar (usually solely electron donor) surfaces[33] and water,[85] although it should be noted that electrostatically charged surfaces also will give rise to hydration orientation. But the ζ-potentials of such surfaces can be negligibly low or even zero. It is by the orientation of water molecules of hydration at monopolar surfaces that the repulsion between two monopolar surfaces of the same sign of polarity can make itself felt at finite (albeit usually at relatively short) distances; see section IIB4 and the exponential equations (44) and (45).

The repulsion between monopolar macromolecules of the same sign of polarity when dissolved in polar organic solvents[100] or in water[70] appears to be the underlying cause of the phase separation of polymer solutions in the great majority of cases. Phase separation is observed to occur when $\Delta F_{132}{}^{\mathrm{tot}} > 0$, while mixing takes place when $\Delta F_{132}{}^{\mathrm{tot}} < 0$.[100] In aqueous systems, the phase separation most frequently utilized is that between poly(ethylene glycol) and dextran.[101] Both polymers have strong (electron donor) monopolar properties.[30,70] A strong repulsion was recently reported between surfaces coated with poly(ethylene glycol) immersed in water;[102] see also section IIIC. Phase separation by monopolar repulsion by dextran is also the most plausible mechanism for red cell agglomeration at medium-high ($\approx$5%) dextran concentrations.[103,125] Hydration orientation (or in nonpolar solvents, solvation orientation) appears to be the vehicle by which the repulsion between (Lewis) basic polymers is propagated ("hydration pressure") (Parsegian et al.). This type of phase separation is equivalent to simple coacervation in the sense of Bungenberg de Jong:[126,127] the interaction between a (Lewis) basic polymer with a (Lewis) acid polymer.

The pronounced stability of neutral (uncharged) phospholipid vesicles in water is also most plausibly explained by monopolar (electron donor) repulsion.[104] One can break that stability by adding Ca^{2+} (with electron-acceptor properties), which ultimately gives rise to vesicle fusion.[105] The presence of poly(ethylene glycol) facilitates vesicle fusion but cannot alone cause fusion in the absence of divalent cations.[105,106] This is readily understandable when it is realized that the strongly (electron donor) monopolar poly(ethylene glycol) can cause a closer approach of the vesicles, by a phase separation effect between the poly(ethylene glycol) solution and the vesicles,[93,105] but cannot alone overcome the hydration pressure that still keeps the membranes some 10–20 Å apart.[106] The addition of divalent cations (e.g., Ca^{2+}), which are strong electron acceptors,[107] is needed to counterbalance the (electron donor) monopolarity of the vesicles' surface, which then causes a strong enough decrease in the hydration orientation, and thus in the hydration pressure, to allow a sufficiently close approach between vesicle membranes to achieve fusion.[105]

B. Electrokinetic Measurements and EL Interactions

There is a vast literature both on electrokinetic measurement methodology[108] and fundamentals[20,21,81–83,87] and on the connection between electrokinetic potentials and particle or polymer stability or flocculation.[20,21,87] It suffices to say that the correlation is excellent[87,98] within the strict framework of EL interactions.

In biological systems, the (usually negative) ζ-potentials tend to be rather low. With the exception of red blood cells, with a ζ-potential of ≈ -18 mV,[104] and serum albumin, also with a ζ-potential of ≈ -18 mV,[110] the other blood cells and serum proteins have ζ-potentials of ≈ -10 to -12 mV (leukocytes[109]) and -2 to -16 mV[110] (serium proteins). Especially in the case of leukocytes, their ζ-potential does not alone suffice to ensure their stability in suspension in water. That stability is for an important part supplemented by the monopolarity of the polysaccharides that form their glycocalix.[111]

C. Direct Measurement of Interfacial Interaction Forces

1. Attractive Forces between Apolar Surfaces Immersed in Water

With the force balance developed by Israelachvili et al.,[96,97,112] where the force between crossed glass cylinders (coated with molecularly smooth sheets of mica) is accurately measured as a function of distance to within a few angstroms,[112] Pashley et al. measured the attraction between two hexadecyl surfaces (obtained by coating monolayers of positively charged quaternary ammonium bases with hexadecylalkyl groups onto the negatively charged mica) vs distance in water.[95,113–115] At contact, an attractive energy $\Delta F_{131}{}^{\mathrm{tot}} \approx -60\ \mathrm{mJ/m^2}$ was found.[95] Given the surface tensions of hexadecane ($\gamma = \gamma^{\mathrm{LW}} = 27.5\ \mathrm{mJ/m^2}$) and of water $\gamma^{\mathrm{LW}} = 21.8$ and $\gamma^{\mathrm{AB}} = 51\ \mathrm{mJ/m^2}$), according to eq 43 and 16, ideally a value should have been found for $\Delta F_{131}{}^{\mathrm{tot}} = -102.7\ \mathrm{mJ/m^2}$. However, from contact angle measurements on the hexadecyl layers with water ($\theta = 95°$[95]), with eq 41, the expected value for $\Delta F_{131}{}^{\mathrm{tot}}$ would be $-67\ \mathrm{mJ/m^2}$. Given the likelihood, in view of the above contact angle, that the coverage of the mica with protruding hexadecyl groups was not completely perfect, so that some residual $\Delta F_{131}{}^{\mathrm{EL}}$ effects may also have played a slight (repulsive) role, the agreement between the observed $-60\ \mathrm{mJ/m^2}$ and the calculated $-67\ \mathrm{mJ/m^2}$ would seem quite satisfactory. More recently, Claesson et al. did similar measurements (with octadecyl moieties) with comparable results.[116] It is striking that by far the dominant contribution to the total "hydrophobic" attraction energy in all these cases originates from the γ^{AB} of water.

2. Interactions between Weakly Polar Surfaces Immersed in Water

Using the same methodology, Marra measured the attraction between layers of phospholipids deposited on crossed mica cylinders in water.[117] The measured long-range attraction force appeared lower than the one corresponding to the accepted Hamaker constant (A_{131}) for phospholipids immersed in water, of about 5.3×10^{-21} J. However, it should be noted that this would be based on an A_{11} value of $\approx 7.1 \times 10^{-20}$ J for phospholipids, while for *hydrated* phospholipids a value of

$A_{11} \approx 5.4 \times 10^{-20}$ J is more realistic and yields a value for A_{131} 1.3×10^{-21} J, as was observed.[117]

Luckham et al. measured the interaction between mixed bilayers of cerebroside sulfate and cholesterol (two constituents of the myelin sheath) adsorbed onto mica cylinders.[118] They found a strong repulsion at all distances. However, that repulsion became an *attraction* when myelin basic protein (another constituent of the myelin sheath) was incorporated into that bilayer.[118] Part of the loss of repulsion is no doubt due to the neutralization of the negative ΔF^{EL} of the sulfate groups by the basic protein. However, both cerebroside sulfate and myelin basic protein (van Oss, unpublished observations) are (electron donor) monopolar. As such, either substance separately would still be expected to give rise to a net repulsion between layers. It should, however, be kept in mind that upon the mutual neutralization of their electrostatic charges, the *combination* between cerebroside sulfate and meylin basic protein also causes a sharp decrease in the γ^- of each (much in the way that Ca^{2+} facilitates membrane fusion; see section IIIA5b). The complex then becomes mostly apolar, and a "hydrophobic" attraction ensues.

3. Repulsion Forces between Strongly Polar Surfaces Immersed in Water

Cain et al., using an apparatus built along the same principle as Israelachvili's[96,112-114] but of a somewhat different construction (using, e.g., silicone rubber rather than mica cylinders[119]), found a strong repulsion between layers of poly(vinyl alcohol) (PVA). We observed earlier that PVA is strongly monopolar, with γ_i^- values up to 57 mJ/m^2.[33] As shown above (section IIB3) a repulsion between two such layers immersed in water should indeed occur once their γ_i^- value exceeds 28 mJ/m^2.

Recently, Claesson and Golander observed a strong repulsion between poly(oxyethylene) layers adsorbed on to mica,[120] using an Israelachvili device.[95,112-114] Poly(oxyethylene) (or poly(ethylene glycol)) also is strongly monopolar, with $\gamma^- \approx 64$ mJ/m^2 [33,70] and thus should cause a strong mutual repulsion. Klein and Luckham also observed a repulsion between poly(ethylene oxide) layers physically adsorbed onto the mica surfaces.[121]

Finally, repulsive forces between phospholipid bilayers can be estimated by an osmotic stress technique developed by LeNeveu et al.[31] and Cowley et al.[122] In this method the distance between phospholipid lamellae (determined by X-ray diffraction) is measured as a function of the force exerted on the lamellae by the outside osmotic pressure of concentrated dextran solutions, usually separated from the lamellae by a semipermeable membrane. The membrane may be dispensed with if the molecular size of the dextran molecules is large enough for the macromolecules to be unable to penetrate into the interlamellar interstices.[31,122]

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(128) The authors, in their other publications, comply with IUPAC (1971) and use the SI symbols, for example, G for Gibbs free energy and A for Helmholtz free energy. At the request of the referees who examined this paper, we have employed F for free energy, as they feel that we are mainly dealing with Helmholtz free energy. We should, however, note that, in surface phenomenon, the physical volume change is invariably small, so that there is no operational value in debating whether the thermodynamic function such as the free energy of adhesion is Gibbs or Helmholtz free energy. (In this paper the term A is reserved for the Hamaker constant.)

(129) In other publications of the authors, γ_i^+ and γ_i^- have appeared with circles around the superscript plus and minus. The symbols, while different in appearance, have identical meanings.