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## Intermolecular Forces

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## Intermolecular forces\*

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The nature of molecular interactions is examined. Intermolecular forces are divided into long-range and short-range components; the former operate at distances where the effects of electron exchange are negligible and decrease as an inverse power of the separation. The long-range interactions may be subdivided into electrostatic, induction and dispersion contributions, where the electrostatic component is the interaction of the permanent charge distributions and the others originate in the fluctuations in the distributions. Typical magnitudes of the various contributions are given. The forces between macroscopic bodies are briefly considered, as are the effects of a medium. Some of the manifestations of molecular interactions are discussed.

## INTRODUCTION

Molecules attract one another when they are far apart – since liquids and solids exist – and repel one another when close – since densities are finite and have the magnitude found under normal conditions. This well-known truth is illustrated in figure 1 which shows a typical

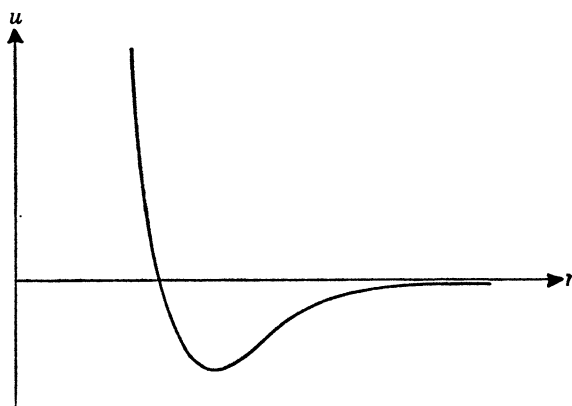


FIGURE 1. The interaction energy  $u$  as a function of the separation  $r$  of two atoms.

interaction energy  $u$  of a pair of spherical molecules as a function of their separation  $r$ . It is the generalization of this simple one-dimensional function  $u(r)$  to include relative orientations, internal coordinates, and the presence of additional molecules making up the medium, that is central to this discussion. It is normal, and indeed necessary if potential energy functions are to be used as in figure 1, to invoke the Born–Oppenheimer separation of the nuclear and electronic motion and to represent the interaction energy as a function of the positions of the nuclei (Hirschfelder & Meath 1967).

A molecule may be defined as a group of atoms (or a single atom) whose binding energy is sufficiently large to permit it to interact with its environment without losing its identity

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(Longuet-Higgins 1965). Thus the hydrogen molecule  $H_2$  may conveniently be called a molecule, but  $Ar_2$  is better considered as a bound pair of argon atoms. The potential curves for both  $H_2$  and  $Ar_2$  are of the form shown in figure 1, but in  $Ar_2$  the well-depth is only about one-half the thermal energy  $kT$  at room temperature, so  $Ar_2$  is readily dissociated on collision. Two molecules of  $H_2$  may associate to form  $H_4$  which, at about 20 K, has a beautiful infrared spectrum (Watanabe & Welsh 1965, 1967); however, two of the bonds in  $H_4$  are very like those in  $H_2$  and it is convenient to look upon  $H_4$  as  $(H_2)_2$ , that is, as a bound complex of two  $H_2$  molecules. If a molecule is tightly bound, then its thermally-populated vibrational and rotational states have similar structure and properties; however, with a shallow, anharmonic potential well, as in  $Ar_2$  or  $ArHCl$  (Novick, Davies, Harris & Klemperer 1973), the structure and properties vary substantially from state to state. In a non-rigid molecule, such as ammonia, an amide or a polypeptide, there may be only a small change in energy with large changes in certain internal coordinates; great interest may be attached to changes in the conformation of such a molecule with alteration of the environment. Changes in interaction energy with small changes in internal coordinates can conveniently be studied through observations of environmental effects on vibrational spectra (Buckingham 1960).

While the interaction energy  $u(r)$  in figure 1 is appropriate to two isolated monatomic molecules, it is more convenient to consider the temperature-dependent Helmholtz free-energy  $A(r)$  when other molecules are present;  $A(r)$  is a 'potential of average force' obtained by performing an average (at a fixed temperature and volume) over all configurations of the molecules other than the pair under consideration at a separation  $r$ . The free-energy  $A(r)$  is often accessible through macroscopic theoretical techniques. It is, of course, a combination of an energy  $u(r)$  and an entropy term  $-TS(r)$ , and at absolute zero  $A(r) = u(r)$ . The effective force is  $-(\partial A(r)/\partial r)_{T,V}$  and a significant part of it may arise from the entropy change with  $r$  (as in a stretched piece of rubber).

#### THE ORIGIN AND MAGNITUDE OF INTERMOLECULAR FORCES

It is often convenient to divide intermolecular forces into long-range forces and short-range forces. Long-range forces act when the molecules are sufficiently far apart that their electron clouds overlap insignificantly; then the interaction energy varies as a power series in  $1/r$ . Short-range forces result from the overlap; they originate in the coulomb and exchange interactions (Margenau & Kestner 1970) and increase exponentially with decreasing  $r$ .

Long-range forces can be subdivided into a number of distinct types as shown in table 1 (Buckingham 1967). The *electrostatic* energy is the interaction of the permanent charge distribution of the molecules. If the interaction is treated as a perturbation to the non-interacting and non-overlapping molecules, the electrostatic energy is the first-order perturbed energy; it may be positive (giving a repulsive force, as between charges of the same sign) or negative (giving an attractive force) and is additive (i.e., the electrostatic energy of three molecules 1, 2, 3, is the sum of the three pairs 12, 23, 31). The *induction* energy is due to the distortion of the charge distribution of one molecule by the permanent charge distribution of its neighbours. At large separations it is equal to  $-\frac{1}{2}\sum_i \alpha_i F_i^2$  where  $\alpha_i F_i$  is the induced dipole of molecule  $i$ ,  $F_i$  being the electric field at it resulting from the permanent charge distribution of its neighbours (Buckingham 1967). Since the polarizability  $\alpha_i$  is positive for molecules in their ground electronic states, the induction energy is negative; this remains true at shorter range when

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TABLE 1. A CLASSIFICATION OF INTERMOLECULAR FORCES

range	type	attractive (-) or repulsive (+)	additive or non-additive
long	electrostatic	+	additive
	induction	-	non-additive
	dispersion	-	~ additive
	resonance	+	non-additive
	magnetic	+	(weak)
short	overlap	+	non-additive

induced quadrupole and higher moments are significant since the distortion of each molecule must be such as to lower the total energy. The *dispersion* energy results from a correlation in the fluctuations of the electron positions and is therefore negative. At large separations it can be represented as  $-Cr^{-6}$  but there are shorter-range terms including an angle-dependent term in  $r^{-7}$  if either molecule lacks a centre of symmetry (Buckingham 1967). Rigorous formulae exist relating the dispersion energy to the polarizabilities of the free molecules at imaginary frequencies (McLachlan 1963, Dalgarno 1967), but these polarizabilities are not normally available. Semi-empirical techniques may be used to obtain accurate values of  $C$  for simple molecules (Dalgarno 1967; Langhoff & Karplus 1970; Starkschall & Gordon 1971). London (1937) deduced a very useful approximate formula for  $C$  involving the ionization energies  $I$  and polarizabilities  $\alpha$  of each molecule:

$$u_{\text{dispersion}} = -Cr^{-6} = -\frac{3}{2} \frac{I_1 I_2}{I_1 + I_2} \frac{\alpha_1 \alpha_2}{r^6} (4\pi\epsilon_0)^{-2},$$

where  $\epsilon_0$  is the permittivity of free space ( $4\pi\epsilon_0 = 1.11265 \times 10^{-10} \text{ C V}^{-1} \text{ m}^{-1} = 1 \text{ e.s.u.}$ ). *Resonance* energy exists only when one of a pair of identical molecules is excited, so that the excitation may be supposed to be shared by the pair. Thus a hydrogen atom in the ground 1s state has an  $r^{-3}$  dipolar interaction with a 2p H atom and an  $r^{-4}$  quadrupolar interaction with a 3d H atom. The *magnetic* interactions are very weak – in paramagnetic dipolar molecules the magnetostatic energy is of the order of  $10^{-4}$  times the electrostatic and one can normally safely assume that intermolecular forces arise from the coulombic interaction of electric charges.

Short-range forces are present when the molecules are close enough for their electron clouds to overlap. The electrons are exchanged between the molecules and it is not possible to write the electronic wavefunction as a product of the wavefunctions of the two molecules. In the orbital approximation the interaction energy can be related to coulomb and exchange integrals (Margenau & Kestner 1970). Unlike the long-range energy, it is not possible to represent short-range interactions in terms of properties, such as the charge distribution and polarizabilities, of the non-interacting molecules. The short-range energy is evaluated by performing a quantum-chemical calculation on the interacting system for various intermolecular separations, and this laborious and rather inaccurate procedure must be applied to each system – there are no reliable general formulae for short-range interaction energies. Unfortunately calculated values of the intermolecular potential are not normally either upper or lower bounds to the true value, since although the computed total energy is an upper bound for any separation  $r$ , the difference  $u(r)$  is not bounded because of uncertainties in the energy of the non-interacting molecules. These energies determine the size and shape of a molecule. Since they increase very rapidly as  $r$  decreases from its equilibrium value, the structure and properties of interacting

molecules may not be sensitive to the precise form of the repulsive potential, so empirical representations can be useful.

It can be useful to know the approximate magnitude of the various contributions to the intermolecular potential. The relative importance of each varies from system to system. Thus electrostatic and induction energies are zero in the inert gases, in which the dispersion force is the sole source of attraction between these atoms, whereas in hydrogen-bonded systems the electrostatic energy is predominant.

The energy of interaction of singly-charged positive and negative ions at a separation  $r$  is  $-e^2/(4\pi\epsilon_0 r)$  which is  $-46 \times 10^{-20} \text{ J}$  ( $= -280 \text{ kJ mol}^{-1}$ ) for  $r = 5 \times 10^{-10} \text{ m}$ . This could be substantially reduced by the presence of a polar medium (Schwarzenbach 1936; Pressman, Grossberg, Pence & Pauling 1946). The energy of two colinear dipoles  $\mu$  ( $\mu = \sum_i e_i z_i$ ) of magnitude 1D ( $1\text{D} = 3.336 \times 10^{-30} \text{ C m}$ ) separated by  $r = 5 \times 10^{-10} \text{ m}$  is  $-2\mu^2/(4\pi\epsilon_0 r^3)$  is  $-0.16 \times 10^{-20} \text{ J}$  ( $= -0.98 \text{ kJ mol}^{-1}$ ), and that of two perpendicular linear quadrupoles  $\Theta$  (e.g. as in  $+ - - +$ ) of magnitude  $3.336 \times 10^{-40} \text{ C m}^2$  ( $\Theta = \frac{1}{2} \sum_i e_i (3z_i^2 - r_i^2)$ ) is  $-3\Theta^2/(4\pi\epsilon_0 r^5)$  is  $-0.010 \times 10^{-20} \text{ J}$  ( $= -0.058 \text{ kJ mol}^{-1}$ ); these electrostatic interactions could also be substantially reduced by the presence of a medium. The dispersion energy between a pair of  $-\text{CH}_2-$  groups separated by  $5 \times 10^{-10} \text{ m}$  is approximately  $-0.060 \times 10^{-20} \text{ J}$  ( $= -0.36 \text{ kJ mol}^{-1}$ ) (Salem 1962). For two long parallel linear chains, each containing  $n$   $\text{CH}_2$  groups, at a separation  $d$ , the total dispersion energy varies as  $nd^{-5}$  and for  $d = 5 \times 10^{-10} \text{ m}$  is equal to  $-0.3n \times 10^{-20} \text{ J} = -1.7n \text{ kJ mol}^{-1}$  (Salem 1962). These forces provide a simple explanation of differences in the cohesive energy of *cis*-unsaturated fatty acids as compared to *trans*-unsaturated or saturated fatty acids (Deuel 1951; Gurd 1960; Salem 1962).

The heat of sublimation of crystalline carbon dioxide at 0 K is  $27 \text{ kJ mol}^{-1}$  (Pople 1954) and of this approximately 45% is due to the electrostatic quadrupole-quadrupole interactions ( $\Theta = 14 \times 10^{-40} \text{ C m}^2$  for  $\text{CO}_2$  (Buckingham & Disch 1963)) and 55% to the dispersion forces.

#### FORCES BETWEEN MACROSCOPIC BODIES

The interaction of two macroscopic bodies can sometimes be obtained by summing the dispersion energy between all pairs of molecules or unit cells in the two bodies. There is no electrostatic or induction contribution when the material is uncharged and isotropic. If the separation of the units is large compared to the reduced wavelength  $\lambda$  associated with the strong electronic transitions, the dispersion interaction is retarded and therefore weakened; it varies as  $r^{-7}$  rather than  $r^{-6}$  (Casimir & Polder 1948). If the dispersion energy between the units is

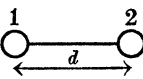
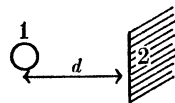
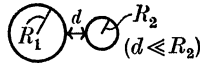
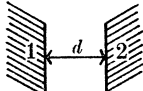
$$\begin{aligned} u(r) &= -Cr^{-6} & \text{for } r \ll \lambda, \\ u(r) &= -Kr^{-7} & \text{for } r \gg \lambda, \end{aligned}$$

the interaction of macroscopic bodies may be written in terms of  $n_1 n_2 C$  or  $n_1 n_2 K$  where  $n_1$  and  $n_2$  are the number of units per unit volume of bodies 1 and 2. Some representative energies are shown in table 2 (see de Boer 1936; Israelachvili & Tabor 1973).

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TABLE 2. DISPERSION ENERGIES FOR MACROSCOPIC BODIES

system		non-retarded	retarded
atom-atom		$u = -Cd^{-6}$	$u = -Kd^{-7}$
atom-flat		$u = -\frac{1}{6}\pi n_2 Cd^{-3}$	$u = -\frac{1}{10}\pi n_2 Kd^{-4}$
sphere-sphere		$u = -\frac{1}{6}\pi^2 n_1 n_2 \left( \frac{R_1 R_2}{R_1 + R_2} \right) Cd^{-1}$	$u = -\frac{1}{30}\pi^2 n_1 n_2 \left( \frac{R_1 R_2}{R_1 + R_2} \right) Kd^{-2}$
flat-flat		$\frac{u}{\text{area}} = -\frac{1}{12}\pi n_1 n_2 Cd^{-2}$	$\frac{u}{\text{area}} = -\frac{1}{30}\pi n_1 n_2 Kd^{-3}$

## THE EFFECT OF A MEDIUM

A medium of relative permittivity, or dielectric constant,  $\epsilon_r$  reduces the electrostatic energy of interaction of two molecules immersed in it by  $\epsilon_r$ . The effects of the medium on dispersion energy have been examined (McLachlan 1965, Kestner & Sinanoğlu 1963, Israelachvili & Tabor 1973); it is convenient to introduce an 'effective' or 'excess' polarizability  $\alpha^*$  which may be used to give the effective intermolecular energy. The dispersion force between any two similar spherical systems is always attractive, regardless of the nature of the medium, so that two bubbles or two colloidal particles attract one another.

The presence of polarizable matter between interacting molecules may *increase* their mutual potential energy. For example, if a sphere of polarizability  $\alpha$  is at the point midway between a pair of charges  $+q$  and  $-q$  at a separation  $r$  the interaction energy is  $u(r) = -q^2(4\pi\epsilon_0 r)^{-1} \times [1 + 32\alpha(4\pi\epsilon_0 r^3)^{-1}]$ . However, the sphere would not change the potential energy of two charges of the same sign, for which  $u(r) = q^2(4\pi\epsilon_0 r)^{-1}$ . If spheres of polarizability  $\alpha$  are at a fixed distance  $d$  beyond each of the charges  $q$  and  $-q$ , the magnitude of the force between the charges is *reduced*, and takes the value

$$-q^2(4\pi\epsilon_0 r^2)^{-1} [1 - 4\alpha d^{-2} r^{-1} (1 + 2dr^{-1}) (1 + dr^{-1})^{-5} (4\pi\epsilon_0)^{-1}].$$

If the two charges have the same sign, the force of repulsion is *enhanced* to

$$q^2(4\pi\epsilon_0 r^2)^{-1} [1 + 4\alpha d^{-2} r^{-1} (1 + 2dr^{-1} + 2d^2 r^{-2}) (1 + dr^{-1})^{-5} (4\pi\epsilon_0)^{-1}].$$

## MANIFESTATIONS OF INTERMOLECULAR FORCES

The forces between molecules influence the properties of matter in the bulk and at a microscopic level. In this final section, various manifestations of intermolecular forces are mentioned and their importance for revealing the magnitude and nature of the force is briefly discussed.

(i) *Equilibrium properties of imperfect gases*

Early studies, beginning with van der Waals, concentrated on the pressure-volume-temperature relationships of gases. This is still an important source of information about molecular

interactions and simple relations exist between any bulk equilibrium property and the average contributions of interacting pairs, or larger clusters, of molecules (Buckingham & Pople 1956).

(ii) *Non-equilibrium properties of fluids*

While equilibrium properties are determined by the partition function, non-equilibrium properties, such as viscosity, thermal conductivity and dielectric loss, depend on the dynamics of the molecular collisions. Hence except for simple systems it is a difficult task to obtain information about the molecular interactions from observations of transport properties.

(iii) *Structure and properties of crystals and conformations of molecules*

The structure of a crystal and its properties such as compressibility, heat of sublimation, and lattice vibrations, reflect the intermolecular potential. Similarly, the conformations of molecules, and the tertiary and quaternary structure of macromolecules, is determined by the interactions of non-bonded atoms. Slow progress is being made in relating these properties to the potentials (Kitaigorodski 1973; Hopfinger 1973).

(iv) *Spectroscopic properties*

Molecular interactions affect the frequency, intensity and line shape of spectra. Topics of current interest include the spectra of complexes (Welsh 1972) and double-resonance spectroscopy, which probes the effects of interactions on molecules in particular quantum states (Oka 1973).

(v) *Molecular beam scattering*

This important technique can provide reliable information about the intermolecular potentials of simple molecules (see *Molecular beam scattering*, *Faraday Discuss. Chem. Soc.*, 1973, 55).

(vi) *Forces between macroscopic bodies*

This topic was touched on in the previous section. It has recently been reviewed by Israelachvili & Tabor (1973).

(vii) *Chemical effects*

The environment of a molecule may affect chemical reactivity, as in surface chemistry or through solvent effects. Progress in these broad areas will be assisted by the advancement of knowledge of intermolecular forces.

REFERENCES (Buckingham)

- Buckingham, A. D. 1960 *Trans. Faraday Soc.* **56**, 753.  
 Buckingham, A. D. 1967 *Adv. Chem. Phys.* **12**, 107.  
 Buckingham, A. D. & Disch, R. L. 1963 *Proc. R. Soc. Lond. A* **273**, 275.  
 Buckingham, A. D. & Pople, J. A. 1956 *Discuss. Faraday Soc.* **22**, 17.  
 Casimir, H. B. G. & Polder, D. 1948 *Phys. Rev.* **73**, 360.  
 Dalgarno, A. 1967 *Adv. Chem. Phys.* **12**, 143.  
 de Boer, J. H. 1936 *Trans. Faraday Soc.* **32**, 10.  
 Deuel, H. 1951 *The lipids*, p. 52. New York: Interscience.  
 Gurd, F. R. N. 1960 In *Lipide chemistry* (ed. D. J. Hanahan), p. 222. New York: Wiley.  
 Hirschfelder, J. O. & Meath, W. J. 1967 *Adv. Chem. Phys.* **12**, 3.  
 Hopfinger, A. J. 1973 *Conformational properties of macromolecules*. New York: Academic Press.  
 Israelachvili, J. N. & Tabor, D. 1973 *Prog. Surface Membrane Sci.* **7**, 1.  
 Kestner, N. R. & Sinanoğlu, O. 1963 *J. Chem. Phys.* **38**, 1730.  
 Kitaigorodsky, A. I. 1973 *Molecular crystals and molecules*. New York: Academic Press.

- Langhoff, P. W. & Karplus, M. 1970 *J. Chem. Phys.* **53**, 233.  
 London, F. 1937 *Trans. Faraday Soc.* **33**, 8.  
 Longuet-Higgins, H. C. 1965 *Discuss. Faraday Soc.* **40**, 7.  
 McLachlan, A. D. 1963 *Proc. R. Soc. Lond. A* **271**, 387.  
 McLachlan, A. D. 1965 *Discuss. Faraday Soc.* **40**, 239.  
 Margenau, H. & Kestner, N. R. 1970 *Theory of intermolecular forces*, 2nd ed., chap. 2. Oxford: Pergamon Press.  
 Novick, S. E., Davies, P., Harris, S. J. & Klemperer, W. 1973 *J. Chem. Phys.* **59**, 2273.  
 Oka, T. 1973 *Adv. At. & Mol. Phys.* **9**, 127.  
 Pople, J. A. 1954 *Proc. R. Soc. Lond. A* **221**, 508.  
 Pressman, D., Grossberg, A. L., Pence, L. H. & Pauling, L. 1946 *J. Am. Chem. Soc.* **68**, 250.  
 Salem, L. 1962 *Can. J. Biochem. Physiol.* **40**, 1287.  
 Schwarzenbach, G. 1936 *Z. Phys. Chem. A*, **176**, 133.  
 Starkschall, G. & Gordon, R. G. 1971 *J. Chem. Phys.* **54**, 663.  
 Watanabe, A. & Welsh, H. L. 1965 *Can. J. Phys.* **43**, 818.  
 Watanabe, A. & Welsh, H. L. 1967 *Can. J. Phys.* **45**, 2859.  
 Welsh, H. L. 1972 In *M.T.P. review of physical chemistry*, series 1, vol. 3 (ed. D. A. Ramsay), chap. 2. London: Butterworths.

### Discussion

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I would like to enlarge on two points made by Dr Buckingham. First, dispersion (electrodynamic) forces do not necessarily lead to attraction between either atoms or macroscopic bodies. It is certainly true that if two interacting bodies having identical macroscopic dielectric susceptibilities,  $\epsilon_1$ , are separated by a medium of different dielectric susceptibility,  $\epsilon_2$ , the energy of interaction is negative, and attraction occurs. However, if the interacting bodies have different dielectric susceptibilities,  $\epsilon_1$ ,  $\epsilon_3$ , such that  $\epsilon_1 > \epsilon_2 > \epsilon_3$  it is easy to show that the energy of interaction is positive and a repulsive component is generated at electromagnetic frequencies where the inequality holds. If the frequency range over which this happens is sufficiently broad to make the major contribution to the interaction energy, overall repulsion will occur. It is an intriguing and seldom appreciated fact that since the relative frequency contributions to the electrodynamic interaction between bodies depend upon the distance of separation, it is possible for attraction to change to repulsion as distance decreases. A potential energy minimum might therefore arise at a critical distance due to electrodynamic forces alone.

Related to these points, and pertinent to the theme of this meeting, is the fact that electrodynamic forces naturally display specificity, as was first emphasized by Jehle (1969). If  $G_{AA}$ ,  $G_{BB}$ ,  $G_{AB}$  represent electrodynamic interaction energies of bodies A with A, B with B and A with B, it can be shown that  $G_{AA} + G_{BB} < 2G_{AB}$ . In other words, 'like prefers like' – a feature which may be partly responsible for certain biological interaction specificities. A statement of this argument in the context of cell–cell adhesion has appeared recently (Parsegian & Gingell 1973).

My second point concerns the calculation of electrodynamic forces by the Lifshitz method. It has been known for several years (Ninham & Parsegian 1970) how to utilize spectroscopic data in order to construct the necessary dielectric functions. Frequencies of maximum absorption from the infrared to the ultraviolet together with refractive index measurements are sufficient and these can be conveniently obtained from reflexion spectroscopy. The way in which such data can be used to calculate forces between biological materials is explained in detail by Gingell & Parsegian (1972).

Finally, I would like to add that X-ray measurements on the spacing of lipid lamellae in



sugar solutions as a function of sugar concentration provides striking confirmation of the existence and importance of electrodynamic forces in biological media. (Rand, Le Neveau, Gingell & Parsegian, in preparation.)

*References*

Gingell, D. & Parsegian, V. A. 1972 *J. theor. Biol.* **36**, 41–52.

Jehle, H. 1969 *Ann. N.Y. Acad. Sci.* **158**, 240.

Ninham, B. & Parsegian, V. A. 1970 *Biophys. J.* **10**, 646–663.

Parsegian, V. A. & Gingell, D. 1973 In *Recent advances in adhesion* (ed. L. H. Lee), pp. 153–192. London: Gordon & Breach.