INTERMOLECULAR FORCES

A. D. Buckingham

University Chemical Laboratory, Cambridge, England

ABSTRACT

The general nature of molecular interactions is discussed; a molecule is defined as an atom or group of atoms whose binding energy is much larger than the thermal energy *kT*. The interaction energy is broken down into electrostatic, induction, dispersion, resonance and overlap energies. The theory of the long-range interaction energy is developed using quantum mechanical perturbation methods, and the electrostatic, induction and dispersion energies written in terms of the free-molecule electric moments and polarizabilities. The theory of short-range overlap forces is briefly considered. Various manifestations of intermolecular forces are discussed, including equilibrium properties of fluids, the structure of crystals and large molecules, spectroscopic properties, molecular beam scattering, chemical effects and forces between macroscopic bodies.

FIRSTLY, I want to say how very happy I am to be back in Australia and in the city and University in which I grew up. I am grateful to the Organizers of the Congress for their kind invitation.

Molecules attract one another when they are far apart—since liquids and solids exist—and repel one another when very close—since densities are finite. This important truth is illustrated in *Figure 1* and is well known; it is the kind of generalization that can be revealed with pleasure to kind aunts and others. The details and origin of curves of the type shown in the figure form the subject of this lecture. It is an important topic, for the study of intermolecular forces impinges on many branches of science. In its purer, more mathematical, forms it has important roles in physics and chemistry, and its applications are significant in molecular biology, crystallography, polymer science, surface and colloid chemistry, etc.

In a lecture entitled 'Intermolecular Forces' one should, I think, explain the meaning of the terms 'molecule' and 'force'. This follows the example set by Longuet-Higgins in the Spiers Memorial Lecture introducing the Discussion of the Faraday Society on this topic in Bristol in 1965[1]. A molecule is a group of atoms (or a single atom) with a binding energy that is large in comparison to the thermal energy *kT*. It can, therefore, interact with its environment without losing its identity—it is not normally dissociated by collisions with neighbouring molecules. Thus H_2 and O_2 are molecules, and so too is the formic acid dimer $(HCOOH)_2$. However, we do not normally consider an interacting pair of argon atoms Ar_2 as a molecule, although the general shape of the potential energy curve is qualitatively the same for Ar_2 as it is for H_2 and O_2 and of the form illustrated in *Figure 1*. The difference is in the depth of the well which is only approximately $\frac{1}{2}kT$ at room temperature for Ar_2 and hundreds of times larger for H_2 and O_2. Thus what we can usefully call a molecule depends on the temperature. At very low temperatures molecules tend to associate with their neighbours, and at a few degrees Kelvin the molecule $(H_2)_2$, i.e. H_4, has an identity and spectrum, as demonstrated by Watanabe and Welsh in Toronto[2].

And what is a force? For two interacting atoms the force is simply $-\partial u/\partial \boldsymbol{r}$, where u is the potential energy and $\boldsymbol{r}$ the internuclear vector. For molecules one must also consider the vibration and rotation of the nuclei. The interaction energy is normally small compared with electronic and vibrational energies, so there is no difficulty in assigning the molecules to particular internal states. For most purposes the energy is averaged over the nuclear vibrational motion. However, in the study of environmental influences on vibrational spectra, and in some other similar instances, the dependence of the energy of interaction on the nuclear positions is needed. The interaction energy may be large compared with the difference between rotational energy levels; the rotational (and translational) motion of the pair of molecules may therefore be very different from those of the free molecules. The basic problem is the evaluation of the energy as a function of the relative position and orientation of the molecules. When this has been solved, the dynamics of the interaction can be determined by considering the translational and rotational motion; in some cases this is a formidable task, but often the occupied states have energy separations that are small compared with kT, and a classical treatment suffices.

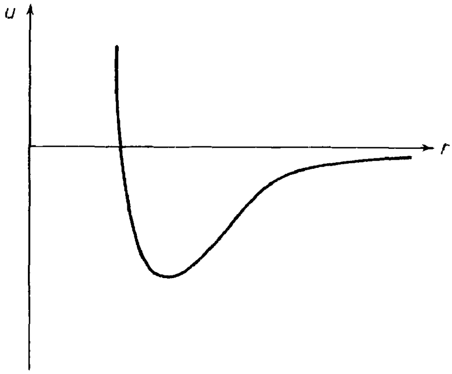

Figure 1. Variation of interaction energy u with separation $\boldsymbol{r}$

When the two interacting molecules are in the presence of others, such as those of a solvent or a surface, it is necessary to average over all configurations of the molecules of the medium, while holding the interacting pair fixed. This averaging introduces a temperature-dependent intermolecular force which is now given by $-(\partial A/\partial \boldsymbol{r})_{T,V}$ where A is the Helmholtz free energy of the system for fixed positions of the two molecules.

Let us now enquire into some of the details and origins of the interactions represented in *Figure 1.*

TYPES OF MOLECULAR INTERACTION

It is convenient to break down the interaction energy u into various components. Each component can be classified according to its *range* which may be *long* or *short* depending on whether it varies with the separation r as r^{-n} (where n is some positive integer) or as $\exp(-ar)$ (where a is a positive constant). Each contribution is either *attractive* (u negative, or more correctly $\partial u/\partial r$ positive) or *repulsive* ($\partial u/\partial r$ negative), and *additive* or *non-additive* according to whether or not it satisfies the equation

$$u_{123} = u_{12} + u_{23} + u_{31} \tag{1}$$

for the interaction energy of the trio of molecules 123.

Table 1 shows the most important contributions to molecular interaction energies and their properties. There is now general agreement that the significant forces between atoms and molecules have an electric origin. It is true that other sources exist, such as *magnetic* interaction, but these can normally be neglected. Even when the cooperative nature of ferromagnetism is invoked the purely magnetic forces are weak. When the molecules are far apart and the separation is large compared with the dimensions of the molecules, the interaction energy is determined by the permanent electric moments, and their interactions comprise the *electrostatic* energy. The permanent moments produce a field that distorts the electronic structures of neighbouring molecules and introduces an additional interaction, the *induction* energy. Since the distortions of molecules in their ground states always lower the total energy, the induction energy is associated with an attractive intermolecular force. Both the electrostatic and induction energies are determined by the properties of the free molecules; also the *dispersion* energy of Fritz London[3] may be approximately related to the polarizabilities describing the distortion of the free molecules by external electric fields and to their ionization potentials. Hence a detailed knowledge of molecular charge distributions and polarizabilities is essential for an understanding of intermolecular forces. *Resonance* energy is present when one or both of the molecules is in a degenerate state and the degeneracy is lifted by the interaction. Thus a hydrogen atom in the $2p$ excited state interacts with an H atom in the $1s$ ground state with an energy that varies as r^{-3}; the excitation energy is shared by the two atoms. The resonance energy may be considered to arise from photon exchange by a dipolar mechanism. The energy varies as r^{-3} even though neither free atom possesses a permanent dipole moment. If the excited

Table 1. The classification of molecular interaction energies. They are of *long* range if they vary as r^{-n} and of *short* range if they depend exponentially on r. They are *additive* or *non-additive* according to whether or not they satisfy equation 1.

Electrostatic	Long (±)	Additive
Induction	Long (−)	Non-additive
Dispersion	Long (−)	~ Additive
Resonance	Long (±)	Non-additive
Overlap	Short (±)	Non-additive
Magnetic	Long (±)	Weak

H atom were in a 3*d* state then the resonance energy would vary as r^{-5} and be related to the exchange of a photon through a transition quadrupole. Resonance forces are treated in the well-known book by Hirschfelder, Curtiss and Bird[4].

When the electron clouds of the interacting molecules overlap significantly it is necessary to allow for the exchange of electrons. The resulting *overlap* energy varies exponentially with *r* and may be attractive or repulsive, although at very short distances repulsion invariably occurs. This overlap energy may be appreciated from the molecular orbital viewpoint; when there are more electrons in the bonding than the anti-bonding orbitals energy is required to dissociate the molecule. However, it is important to bear in mind the dependence of the energy of the molecular orbitals on *r*. The total electron density is not just a superposition of contributions from the atomic orbitals; thus in the case of two helium atoms the antisymmetry of the wavefunction with respect to electron exchange reduces the electron density between the two nuclei, leading to a repulsive force. The effects of electron correlation, associated with the breakdown of the orbital approximation, are generally to reduce the magnitude of both the long range and the overlap forces.

THE THEORY OF LONG RANGE INTERACTIONS

When a pair of molecules, 1 and 2, are far apart, electron exchange can be neglected and the interaction Hamiltonian treated as a perturbation to the Hamiltonian $\mathscr{H}^{(0)}_1 + \mathscr{H}^{(0)}_2$ of the free molecules[5,6]. The eigenvalues and eigenfunctions of the unperturbed system are $W_{i_1} + W_{j_2}$ and $\Psi_{i_1}\Psi_{j_2}$, and the perturbation is

$$\begin{aligned}\mathscr{H}'_{12} &= \sum_{i,j}\frac{e_i^{(1)}e_j^{(2)}}{r_{1_i2_j}} = q^{(1)}\phi_1 - \mu_\alpha^{(1)}F_{1\alpha} - \tfrac{1}{3}\Theta_{\alpha\beta}^{(1)}F'_{1\alpha\beta} - \dots \\ &= q^{(1)}q^{(2)}(r^{-1}) + (q^{(1)}\mu_\alpha^{(2)} - q^{(2)}\mu_\alpha^{(1)})\nabla_\alpha(r^{-1}) \\ &\quad - \mu_\alpha^{(1)}\mu_\beta^{(2)}\nabla_\alpha\nabla_\beta(r^{-1}) - \tfrac{1}{3}(\mu_\alpha^{(1)}\Theta_{\beta\gamma}^{(2)} - \mu_\alpha^{(2)}\Theta_{\beta\gamma}^{(1)})\nabla_\alpha\nabla_\beta\nabla_\gamma(r^{-1}) \\ &\quad + \tfrac{1}{9}\Theta_{\alpha\beta}^{(1)}\Theta_{\gamma\delta}^{(2)}\nabla_\alpha\nabla_\beta\nabla_\gamma\nabla_\delta(r^{-1}) + \dots \end{aligned} \tag{2}$$

where $r_{1_i2_j}$ is the distance from the particle of charge $e_i^{(1)}$ in molecule 1 to the charge $e_j^{(2)}$ in 2; $q^{(1)} = \sum_i e_i^{(1)}$, $\boldsymbol{\mu}^{(1)} = \sum_i e_i^{(1)}\boldsymbol{r}_i$ and $\boldsymbol{\Theta}^{(1)} = \frac{1}{2}\sum_i e_i^{(1)}(3\boldsymbol{r}_i\boldsymbol{r}_i - r_i^2\mathbf{1})$ are the instantaneous charge, dipole and quadrupole moment of molecule 1; ϕ_1, $\boldsymbol{F}_1 = -\nabla\phi_1$ and $\boldsymbol{F}'_1 = \nabla\boldsymbol{F}_1 = -\nabla\nabla\phi_1$ are the potential, field and field gradient at some arbitrary centre in molecule 1. The Hamiltonian is independent of the choice of molecular centres, but the potential and its gradients due to the charges of the other molecule must be taken at the same point from which the electric moments of the molecule are calculated (i.e. the origin of the vectors $\boldsymbol{r}_i$). Movement of the origin affects all but the first non-vanishing term in equation 2 although it leaves $\mathscr{H}'_{12}$ unchanged. The term in 2 in $q\mu$ varies as r^{-2} and, like the first in $q^{(1)}q^{(2)}$, is non-zero only for ions; the terms in $\mu^{(1)}\mu^{(2)}$, $\mu\Theta$ and $\Theta^{(1)}\Theta^{(2)}$ vary as r^{-3}, r^{-4} and r^{-5}.

The wavefunction of the interacting pair when the free molecules are in the stationary states Ψ_{n_1} and Ψ_{n_2} is obtained by perturbation theory and is

$$\Psi_{n_1n_2}(12) = \Psi_{n_1}\Psi_{n_2} + \sum_{i_1,j_2}' \frac{\langle i_1j_2|\mathscr{H}'_{12}|n_1n_2\rangle}{W^{(0)}_{n_1} - W^{(0)}_{i_1} + W^{(0)}_{n_2} - W^{(0)}_{j_2}} \Psi_{i_1}\Psi_{j_2} + \dots \tag{3}$$

and the corresponding energy is

$$\begin{aligned} W_{n_1n_2} = W_{n_1} + W_{n_2} + \langle n_1n_2|\mathscr{H}'_{12}|n_1n_2\rangle \\ + \sum_{i_1,j_2}' \frac{\langle i_1j_2|\mathscr{H}'_{12}|n_1n_2\rangle^2}{W^{(0)}_{n_1} - W^{(0)}_{i_1} + W^{(0)}_{n_2} - W^{(0)}_{j_2}} + \dots \end{aligned} \tag{4}$$

where Σ' is a summation over all unperturbed states except $\Psi_{n_1}\Psi_{n_2}$. The first order energy $\langle n_1n_2|\mathscr{H}'_{12}|n_1n_2\rangle$ is the *electrostatic* energy $u_{\text{electrostatic}}$ and is the interaction energy of the permanent electric moments (charge, dipole, quadrupole, etc.) of 1 and 2. It vanishes if either 1 or 2 is an inert gas atom.

The second order perturbed energy in equation 4 includes both the *induction* energy and the *dispersion* energy. The sets of excited unperturbed states $\Psi_{i_1}\Psi_{n_2}$ and $\Psi_{n_1}\Psi_{j_2}$ in which one of the molecules is in its original state produce the induction energy $u_{\text{induction}}$ and the remaining excited states yield $u_{\text{dispersion}}$. Thus

$$\begin{aligned} u_{\text{induction}} &= -\sum_{i_1 \neq n_1} \frac{\langle n_1n_2|\mathscr{H}'_{12}|i_1n_2\rangle^2}{W^{(0)}_{i_1} - W^{(0)}_{n_1}} - \sum_{j_2 \neq n_2} \frac{\langle n_1n_2|\mathscr{H}'_{12}|n_1j_2\rangle^2}{W^{(0)}_{j_2} - W^{(0)}_{n_2}} \\ &= u^{(n_1)}_{\text{induction}} + u^{(n_2)}_{\text{induction}} \end{aligned} \tag{5}$$

It represents the energy arising from the distortion of each molecule by the permanent charge distribution of the other.

$$u_{\text{dispersion}} = -\sum_{\substack{i_1 \neq n_1 \\ j_2 \neq n_2}} \frac{\langle n_1n_2|\mathscr{H}'_{12}|i_1j_2\rangle^2}{W^{(0)}_{i_1} - W^{(0)}_{n_1} + W^{(0)}_{j_2} - W^{(0)}_{n_2}} \tag{6}$$

and arises from the interaction of the fluctuating charge distributions in the two molecules. If Ψ_{n_1} and Ψ_{n_2} are the ground electronic states of 1 and 2 then both $u_{\text{induction}}$ and $u_{\text{dispersion}}$ are negative and produce attractive long range forces. Neither of these energies is strictly additive, although the non-additivity of $u_{\text{dispersion}}$ is normally small since it comes from the third order perturbed energy in equation 4. The non-additivity of $u_{\text{induction}}$ can easily be appreciated by considering an argon atom midway between two protons; if just one proton were present its field would distort the atom and induce a dipole which would interact with the field and lower the energy by $-\frac{1}{2}\alpha F^2$, where α is the polarizability of the atom. However, with both protons present there is no field at the atom and the dipole contribution to $u_{\text{induction}}$ is zero.

Equations 5 and 6 can be simplified and rendered practical by introducing the molecular polarizabilities; these describe the interaction of a molecule with an external electric field $\boldsymbol{F}$, $\boldsymbol{F}'$, etc. The energy of the state Ψ_n is written as a power series in $\boldsymbol{F}$, $\boldsymbol{F}'$, etc.:

$$W_n = W_n^{(0)} - \boldsymbol{\mu}_0^{(n)} \cdot \boldsymbol{F} - \tfrac{1}{2}\boldsymbol{\alpha}^{(n)} : \boldsymbol{F}^2 - \tfrac{1}{6}\boldsymbol{\beta}^{(n)} \vdots\, \boldsymbol{F}^3 - \tfrac{1}{3}\boldsymbol{\Theta}_0^{(n)} : \boldsymbol{F}' - \tfrac{1}{3}\boldsymbol{A}^{(n)} \vdots\, \boldsymbol{F}\boldsymbol{F}' - \tfrac{1}{6}\boldsymbol{C}^{(n)} \vdots\, \boldsymbol{F}'^2 - \ldots \tag{7}$$

The total molecular dipole and quadrupole moments are:

$$\boldsymbol{\mu}^{(n)} = -\frac{\partial W_n}{\partial \boldsymbol{F}} = \boldsymbol{\mu}_0^{(n)} + \boldsymbol{\alpha}^{(n)} \cdot \boldsymbol{F} + \tfrac{1}{2}\boldsymbol{\beta}^{(n)} : \boldsymbol{F}^2 + \tfrac{1}{3}\boldsymbol{A}^{(n)} : \boldsymbol{F}' + \ldots \tag{8}$$

$$\boldsymbol{\Theta}^{(n)} = -3\frac{\partial W_n}{\partial \boldsymbol{F}'} = \boldsymbol{\Theta}_0^{(n)} + \boldsymbol{A}^{(n)} \cdot \boldsymbol{F} + \boldsymbol{C}^{(n)} : \boldsymbol{F}' + \ldots \tag{9}$$

where $\boldsymbol{\mu}_0^{(n)} = \langle n | \boldsymbol{\mu} | n \rangle$ and $\boldsymbol{\Theta}_0^{(n)} = \langle n | \boldsymbol{\Theta} | n \rangle$ are the permanent dipole and quadrupole moments and

$$\boldsymbol{\alpha}^{(n)} = 2 \sum_{i \neq n} \frac{\langle n | \boldsymbol{\mu} | i \rangle \langle i | \boldsymbol{\mu} | n \rangle}{W_i^{(0)} - W_n^{(0)}} \tag{10}$$

$$\boldsymbol{A}^{(n)} = 2 \sum_{i \neq n} \frac{\langle n | \boldsymbol{\mu} | i \rangle \langle i | \boldsymbol{\Theta} | n \rangle}{W_i^{(0)} - W_n^{(0)}} \tag{11}$$

$$\boldsymbol{C}^{(n)} = \tfrac{2}{3} \sum_{i \neq n} \frac{\langle n | \Theta | i \rangle \langle i | \Theta | n \rangle}{W_i^{(0)} - W_n^{(0)}} \tag{12}$$

are polarizabilities describing the distortion of the molecule by $\boldsymbol{F}$ and $\boldsymbol{F}'$. The higher polarizability $\boldsymbol{A}$ is a third rank tensor giving both the dipole induced by $\boldsymbol{F}'$ and the quadrupole induced by $\boldsymbol{F}$; it vanishes if the molecule has a centre of inversion, but is otherwise non-zero. The higher polarizabilities depend on the choice of origin[7]. The number of independent constants needed to determine $\boldsymbol{\mu}_0$, $\boldsymbol{\Theta}_0$, $\boldsymbol{\alpha}$, $\boldsymbol{A}$, $\boldsymbol{C}$, etc. is governed by the symmetry of the molecule. *Table 2* gives the number for some important symmetry types; a more extensive list is available[7].

The above equations for the induction and dispersion energies can be reduced to

$$u_{\text{induction}}^{(n_1)} = -\tfrac{1}{2}\boldsymbol{\alpha}^{(n_1)} : \boldsymbol{F}^2 - \tfrac{1}{3}\boldsymbol{A}^{(n_1)} \vdots\, \boldsymbol{F}\boldsymbol{F}' - \tfrac{1}{6}\boldsymbol{C}^{(n_1)} \vdots\, \boldsymbol{F}'^2 - \ldots \tag{13}$$

and a similar equation for $u_{\text{induction}}^{(n_2)}$, and[7]

$$\begin{aligned} u_{\text{dispersion}} = -\frac{U^{(n_1)}U^{(n_2)}}{4(U^{(n_1)} + U^{(n_2)})} \Big[& \alpha_{\alpha\gamma}^{(n_1)}\alpha_{\beta\delta}^{(n_2)} \nabla_\alpha \nabla_\beta (r^{-1}) \nabla_\gamma \nabla_\delta (r^{-1}) \\ & + \tfrac{2}{3}(\alpha_{\alpha\gamma}^{(n_1)} A_{\beta,\delta\varepsilon}^{(n_2)} - \alpha_{\alpha\gamma}^{(n_2)} A_{\beta,\delta\varepsilon}^{(n_1)}) \nabla_\alpha \nabla_\beta (r^{-1}) \nabla_\gamma \nabla_\delta \nabla_\varepsilon (r^{-1}) \\ & + (\tfrac{1}{3}\alpha_{\alpha\delta}^{(n_1)} C_{\beta\gamma,\varepsilon\phi}^{(n_2)} + \tfrac{1}{3}\alpha_{\alpha\delta}^{(n_2)} C_{\beta\gamma,\varepsilon\phi}^{(n_1)} - \tfrac{2}{9}A_{\alpha,\varepsilon\phi}^{(n_1)} A_{\delta,\beta\gamma}^{(n_2)}) \nabla_\alpha \nabla_\beta \nabla_\gamma (r^{-1}) \\ & \times \nabla_\delta \nabla_\varepsilon \nabla_\phi (r^{-1}) - \tfrac{2}{9} A_{\alpha,\gamma\delta}^{(n_1)} A_{\beta,\varepsilon\phi}^{(n_2)} \nabla_\alpha \nabla_\beta (r^{-1}) \nabla_\gamma \nabla_\delta \nabla_\varepsilon \nabla_\phi (r^{-1}) + \ldots \end{aligned} \tag{14}$$

where the approximation of using a constant excitation energy U (Unsöld[8]) has been used; since a similar approximation is applied to the equations for the polarizabilities, some cancellation of errors occurs. The leading term in equation 14 is a generalization of London's well-known approximate formula for calculating the longest range dispersion energy. This varies as r^{-6}, and the higher terms in 14 are proportional to r^{-7}, r^{-8}, etc.

If one averages over all molecular rotations, and if the angular dependent energy is much smaller than kT, the polarizabilities must be replaced by their isotropic parts, yielding

$$u^{(n_1)}_{\text{induction}} = -\tfrac{1}{2}\alpha^{(n_1)}F^2 - \tfrac{1}{6}C^{(n_1)}F'^2 - \dots \tag{15}$$

and for two like atoms

$$u_{\text{dispersion}} = -(3U\alpha^2/4r^6)\,[1 + (10C/\alpha r^2) + \dots] \tag{16}$$

where the scalar F'^2 is $\boldsymbol{F}':\boldsymbol{F}'$. The ratio of the r^{-8} to the r^{-6} term in the dispersion energy is therefore equal to $10C/\alpha r^2$ in this approximation. For the H atom $\alpha = 9a^3/2$ and $C = 15a^5/2$, where a is the Bohr radius, and the above ratio is $(50/3)(a/r)^2$; the accurate value[9, 10] is $19{\cdot}14\ (a/r)^2$.

If one or both of the interacting molecules is in an excited state, the long-range energy may be very different from its value for the ground state. If the molecules are identical, resonance may occur through the exchange of excitation energy.

Table 2. The number of parameters required to specify the dipole moment, the quadrupole moment, the polarizability, and higher polarizabilities for various symmetries.

	sphere	O_h	T_d	$C_{\infty v}$	C_{3v}
μ	0	0	0	1	1
Θ	0	0	0	1	1
α	1	1	1	2	2
β	0	0	1	2	3
A	0	0	1	2	3
C	1	2	2	3	4

Equations 6 and 14 for the dispersion energy contain terms varying as r^{-7}. These could be eliminated for a particular relative orientation by appropriately choosing the molecular centres; the point at which the r^{-7} contribution vanishes could be considered as the 'centre of action' of the dispersion energy[11]. However, it turns out that this point moves as the molecule

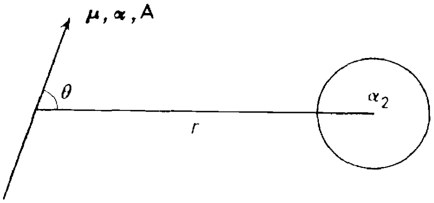

Figure 2. A spherical atom in position r,θ relative to a linear molecule.

rotates, so in reality there is no true centre of action. Of course when considering the dynamics of the interaction of two gaseous molecules the natural choice of origin is the molecular centre of mass, and relative to this point there is in general an important angle-dependent interaction energy varying as r^{-7}. As can be seen from *Table 2* it is present[7] even in the collision of an argon atom with the tetrahedral CH_4.

A special case of interest is the interaction of a spherical atom with a dipolar molecule (see *Figure 2*). In this case there is no electrostatic energy and

$$\begin{aligned} u &= u_{\text{induction}} + u_{\text{dispersion}} + u_{\text{overlap}} \\ &= -\tfrac{1}{2}(\alpha_2\mu^2 r^{-6})(3\cos^2\theta + 1) - (6\alpha_2\mu\Theta r^{-7})\cos^3\theta + \ldots \\ &\quad - Dr^{-6}\Big[1 + \frac{\alpha_{\|} - \alpha_{\perp}}{3\alpha}(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}) + (2A_{\|}/\alpha r)\cos^3\theta \\ &\qquad + (4A_{\perp}/\alpha r)(3\cos\theta - 2\cos^3\theta) + \ldots\Big] + u_{\text{overlap}} \end{aligned} \tag{17}$$

The dipole–quadrupole induction energy proportional to $\mu\,\Theta\,r^{-7}\cos^3\theta$ was first added to the well-known dipole term by Anderson[12] to explain the pressure broadening of the microwave spectrum of ammonia by inert gas atoms. The additional terms in equation 17 in $A_{\|}r^{-7}\cos^3\theta$ and $A_{\perp}r^{-7}(3\cos\theta - 2\cos^3\theta)$ are likely also to be important in these and other collisional experiments. They are probably the principal cause of inelastic scattering of atoms by alkali halide molecules[13].

SHORT RANGE INTERACTIONS

The effects of electron exchange must be included in the theory when the molecular charge clouds overlap. The above approach used for describing long-range interactions is not applicable, for the wavefunction 3 is not antisymmetric with respect to the exchange of electrons between molecules 1 and 2.

Various attempts have been made to develop perturbation theories of exchange interactions and the relative merits of some of these for evaluating the interaction of hydrogen atoms assessed by comparison with accurate numerical computations[14]. However, there would seem to be much to be said for calculating interaction energies at short range by direct variational methods. This view is apparently shared by Margenau and Kestner[15] whose recent book on the subject of this lecture contains a detailed account of various theories of short-range forces. We can expect rapid progress in this field in the near future.

The Hellmann–Feynman theorem, relating the force on the nuclei to the distribution of charge, provides some insight into the origin of short-range forces—thus the attraction between two H atoms in the $^1\Sigma_g^+$ state arises from the increase in electron density between the nuclei. Salem[16] showed that the repulsion between two He atoms can be attributed to the reduction in the electron density in the region between the nuclei.

The interaction energy of two He atoms has been calculated by Phillipson and others using a variational method[17]. He used wavefunctions containing from 10 to 64 electron configurations, so chosen that they went properly into the ^1S ground state of Be as $r \rightarrow 0$ and into a product of two ^1S helium functions as $r \to \infty$. The latest scattering data of Amdur[18] are in reasonable agreement with the computed curve.

The interaction of two H_2 molecules has been investigated by Magnasco and Musso[19] using valence bond wavefunctions. Like the He_2 problem, the potential surfaces for $He—H_2$ and $(H_2)_2$ should be accurately calculable and they should now be investigated. It may be useful to express[20] the surfaces in terms of a sum of spherical harmonics times a function of r, thereby reducing the many-dimensional surface to a number of simple one-dimensional functions.

It should be possible to apply similar variational methods to the study of the hydrogen bond, e.g. to $(HF)_2$. If this potential energy surface were accurately calculated, a hydrogen bond would at last be fully exposed. The impressive calculation of the NH_3 + HCl surface by Clementi[21] has already greatly increased our knowledge of the hydrogen bond. This is one intermolecular force that probably should not be divided into components, although no doubt electrostatic and overlap interactions account for most of the energy. It is not easy to study experimentally the energy of an H-bond as a function of the various internuclear distances involved, so there has been much discussion about the nature of the surface. Another short range force of great interest is the Mulliken force contributing to the binding of charge-transfer complexes; here the attractive force arises partly from a distortion which may be represented by a transfer of an electron from donor to acceptor[22].

The *a priori* calculation of overlap energies does not normally lead to the evaluation of the weak long range forces. However, the perturbation methods discussed in the previous section are suitable for this purpose. There are now accurate semi-empirical methods for calculating the r^{-6}, r^{-8}, etc. terms in the dispersion energy of atoms[23].

MANIFESTATIONS OF INTERMOLECULAR FORCES

We now turn to a brief discussion of the relationship between molecular interactions and observables.

(a) Equilibrium properties of imperfect gases

If a bulk observable Q is expanded as a power series in the number density ρ

$$Q = A_Q + B_Q\rho + C_Q\rho^2 + \dots \tag{18}$$

then A_Q is the limit of Q at zero density and is the ideal gas contribution to Q. The appropriate second coefficient B_Q represents the mean contribution of interacting pairs of molecules[24].

$$A_Q = Nq_1 \tag{19}$$

$$B_Q = N \int (\tfrac{1}{2}q_{12} - q_1) \exp(-u/kT)\, \mathrm{d}v_2 \tag{20}$$

where N is the number of molecules, q_1 the mean contribution of an isolated molecule to Q and q_{12} the contribution of the interacting pair 1, 2 in a particular configuration whose probability of occurrence is proportional to $\exp(-u/kT)$.

Measurements of the second virial coefficient in the equation of state have been used for many years to yield useful empirical intermolecular energies.

More recently, other equilibrium properties, such as the dielectric polarization, have given new information about intermolecular forces, and particularly about their angle dependence[24]. Improved experimental methods for measuring the second dielectric virial coefficient have been developed by Cole and his group[25]; an expansion method would seem to offer outstanding possibilities for measuring this and other second coefficients, since it could lead to the elimination of the ideal gas contribution to the observable.

(b) Non-equilibrium properties of fluids

The early theoretical work of Enskog, Chapman and Cowling and the important book by Hirschfelder, Curtiss and Bird[4] provide expressions relating the transport coefficients of gases to the intermolecular potential. Unfortunately the relevant theory is much more difficult than that for equilibrium properties, for the dynamics of the collision must be considered, but useful information about intermolecular forces between atoms and simple molecules may be obtained from these sources. The subject has been briefly reviewed by Mason and Monchick[26]. Non-equilibrium properties and spectral line shapes are now generally interpreted in terms of autocorrelation functions in the system at equilibrium; this development is surprisingly recent and is based on the fluctuation–dissipation theorem[27].

(c) The structure of crystals and of large molecules

The structure of crystals and the tertiary structure of macromolecules reflect the inter- and intra-molecular forces. Attempts are being made to calculate the structures of minimum energy U for model potentials[28, 29]. This is an area where our knowledge of actual intermolecular forces should lead to considerable progress in the near future; the general methods are similar to those that have been used for some time to interpret and predict the conformations of single molecules. Actually, of course, it is the free energy A that must be minimized to obtain the stable structure, but at the absolute zero U and A are equal. With biological macromolecules, it is their structure at room temperature and in a complex environment that is relevant, posing a formidable theoretical problem.

Other properties of crystals, including their sublimation energy, compressibility, heat capacity and lattice vibrations, reflect the intermolecular potentials. The non-additivity of the interactions contributes to crystal properties; indeed the fact that the inert gases (except helium) yield face-centred cubic, rather than hexagonal close-packed, lattices is probably due to non-additivity[30].

(d) Spectroscopic properties

Perturbations arising from molecular interactions affect spectra in a variety of ways. Changes in the energy levels lead to shifts in absorption and emission maxima, distortion of the molecules leads to changes in intensities (including the appearance of forbidden lines), and simultaneous transitions may occur in interacting molecules, yielding completely new spectral lines, and there may be changes in line width and shape, reflecting the lifetimes of the relevant states. Broadly speaking, the various forms of spectroscopy permit different aspects of the interaction to be studied; for example, perturbation of rotational states is caused by angle-dependent interactions and vibrational spectra reflect the dependence of the interaction on the nuclear coordinates.

Optical, microwave, Raman and resonance spectroscopy are all relevant and so too are some of the non-linear effects, such as second harmonic generation, caused by intense laser light[31]. The transient dipole moments arising from interacting pairs of dissimilar inert gas atoms lead to broad 'translational' absorption bands first found by Kiss and Welsh[32–34], and yield important information about the interaction of these simple atoms. There is evidence for both a short-range overlap dipole and an r^{-7} dispersion contribution[35]. Microwave multiple resonance techniques provide a new tool that is both beautiful and powerful[36, 37]. Oka's work yields direct information about the transitions caused by collisions and has exposed the role of the angle-dependent r^{-7} dispersion energy in causing $\Delta K = 3, 6, 9, \ldots$ transitions in NH_3–inert gas collisions[36]. This interaction is also important in determining the infra-red line shape of gaseous CH_4–inert gas mixtures[38]. The structure in the infra-red spectrum of HCl–inert gas mixtures at low densities has been successfully related to bound pairs by Bratoz and Martin[39] and others. Lattice vibrations in molecular crystals are being followed in the far-infra-red and excitons in molecular crystals form the subject of a recent book by Craig and Walmsley[40].

This whole field looks rich and ripe for picking.

(e) Molecular beam scattering

This is probably the most powerful method for probing intermolecular forces. The collisions may be elastic, inelastic or reactive and all three are highly relevant to our subject. The field has been well reviewed recently[41–43], so I shall mention only 'rainbow' scattering because of its beauty and usefulness for determining the well-depth. At the point of balance between the attractive and repulsive forces the rate of change of the scattered intensity with angle is zero, yielding a maximum in the intensity and the rainbow. By varying the beam velocity the collision diameter can also be determined.

This is a field that is bound to progress rapidly, especially as detection techniques improve.

(f) Chemical effects

The molecular environment may affect a chemical reaction, as illustrated in surface chemistry, catalysis and by solvent effects. This wide subject is being pursued in many laboratories, including some in our host country. To some it justifies the study of intermolecular forces.

(g) Forces between macroscopic bodies

This is a field in which Dutch and Soviet scientists have excelled, and particularly Derjaguin[44]. The forces are the retarded dispersion forces of Casimir and Polder[45] and have been related to macroscopic dielectric properties in the theory of Lifshitz[46]. With more slowly fluctuating dipole–dipole forces, as between droplets of water, retardation is negligible as it occurs at distances of hundreds of microns and at these separations the force is infinitesimal; this r^{-6} energy is therefore dominant at large separations and it may be expressed in terms of the static dielectric constant of the material[7]. Overbeek and others have studied the interaction of colloidal particles[47] and the distinguished Australian scientist Bowden (whose recent death is a tragedy) has carried out some highly ingenious measurements of the forces between mica sheets[48].

REFERENCES

[1] H. C. Longuet-Higgins, *Disc. Faraday Soc.* **40**, 7 (1965).
[2] A. Watanabe and H. L. Welsh, *Canad. J. Phys.* **43**, 818 (1965); **45**, 2859 (1967).
[3] F. London, *Z. Phys. Chem. B*, **11**, 222 (1930); *Trans. Faraday Soc.* **33**, 8 (1937).
[4] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids.* Wiley: New York (1954). See also J. O. Hirschfelder and W. J. Meath, *Advanc. Chem. Phys.* **12**, 3 (1967).
[5] H. Margenau, *Rev. Mod. Phys.* **11**, 1 (1939).
[6] H. C. Longuet-Higgins, *Proc. Roy. Soc. A*, **235**, 537 (1956).
[7] A. D. Buckingham, *Advanc. Chem. Phys.* **12**, 107 (1967).
[8] A. Unsöld, *Z. Phys.* **43**, 563 (1927).
[9] L. Pauling and J. Y. Beach, *Phys. Rev.* **47**, 686 (1935).
[10] J. O. Hirschfelder and P. O. Löwdin, *Molec. Phys.* **2**, 229 (1959); **9**, 491 (1965).
[11] R. M. Herman, *J. Chem. Phys.* **44**, 1346 (1966).
[12] P. W. Anderson, *Phys. Rev.* **80**, 511 (1950).
[13] A. D. Buckingham, *J. Chem. Phys.* **48**, 3827 (1968).
[14] P. R. Certain, J. O. Hirschfelder, W. Kołos and L. Wolniewicz, *J. Chem. Phys.* **49**, 24 (1968).
[15] H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces*, Pergamon: Oxford (1969).
[16] L. Salem, *Proc. Roy. Soc. A*, **264**, 379 (1961).
[17] P. E. Phillipson, *Phys. Rev.* **125**, 1981 (1962);
G. H. Matsumoto, C. F. Bender and E. R. Davidson, *J. Chem. Phys.* **46**, 402 (1967).
[18] J. E. Jordan and I. Amdur, *J. Chem. Phys.* **46**, 165 (1967). See also I. Amdur and J. E. Jordan, *Advanc. Chem. Phys.* **10**, 29 (1966).
[19] V. Magnasco and G. F. Musso, *J. Chem. Phys.* **46**, 4015 (1967).
[20] J. A. Pople, *Proc. Roy. Soc. A*, **221**, 498 (1954).
[21] E. Clementi, *J. Chem. Phys.* **46**, 3851 (1967).
[22] J. N. Murrell, *Quart. Rev. (Chem. Soc. London)*, **15**, 191 (1961).
[23] A. Dalgarno and W. D. Davison, *Advanc. Atom. Molec. Phys.* **2**, 1 (1966);
A. Dalgarno, *Advanc. Chem. Phys.* **12**, 143 (1967).
[24] A. D. Buckingham and J. A. Pople, *Disc. Faraday Soc.* **22**, 17 (1956).
[25] R. H. Orcutt and R. H. Cole, *J. Chem. Phys.* **46**, 697 (1967).
[26] E. A. Mason and L. Monchick, *Advanc. Chem. Phys.* **12**, 329 (1967).
[27] R. Kubo, *Rep. Progr. Phys.* **29**, 255 (1966).
[28] D. E. Williams, *J. Chem. Phys.* **47**, 4680 (1967).
[29] H. A. Scheraga, S. J. Leach, R. A. Scott and G. Némethy, *Disc. Faraday Soc.* **40**, 268 (1965).
[30] L. Jansen and E. Lombardi, *Disc. Faraday Soc.* **40**, 78 (1965).
[31] A. D. Buckingham and B. J. Orr, *Quart. Rev. (Chem. Soc. London)*, **21**, 195 (1967).
[32] Z. J. Kiss and H. L. Welsh, *Phys. Rev. Letters*, **2**, 166 (1959).
[33] D. R. Bosomworth and H. P. Gush, *Canad. J. Phys.* **43**, 751 (1965).
[34] P. Marteau, R. Granier, H. Vu and B. Vodar, *C.R. Acad. Sci., Paris*, **265B**, 685 (1967).
[35] H. B. Levine, *Phys. Rev. Letters*, **21**; 1512 (1968).
[36] T. Oka, *J. Chem. Phys.* **49**, 3135 (1968).
[37] A. M. Ronn and E. B. Wilson, *J. Chem. Phys.* **46**, 3262 (1967).
[38] C. G. Gray, *J. Chem. Phys.* **50**, 549 (1969).
[39] S. Bratož and M. L. Martin, *J. Chem. Phys.* **42**, 1051 (1965).
[40] D. P. Craig and S. H. Walmsley, *Excitons in Molecular Crystals*, Benjamin: New York (1968).
[41] *Molecular Beams*, Ed. J. Ross, *Advanc. Chem. Phys. No. 10* (1966).
[42] *Disc. Faraday Soc.* **44** (1967).
[43] R. B. Bernstein and J. T. Muckerman, *Advanc. Chem. Phys.* **12**, 389 (1967).
[44] B. V. Derjaguin, I. I. Abrikosova and E. M. Lifshitz, *Quart. Rev. (Chem. Soc. London)*, **10**, 295 (1956).
[45] H. B. G. Casimir and D. Polder, *Phys. Rev.* **73**, 360 (1948).
[46] E. M. Lifshitz, *Soviet Phys. J.E.T.P.* **2**, 73 (1956).
[47] See *Molecular Forces* (Proceedings of a Study Week arranged by the Pontifical Academy of Sciences, Rome 1966), North-Holland: Amsterdam (1967).
[48] F. P. Bowden in ref. 47, p 247.