The Forces between Simple Molecules

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Despite intensive investigation over a period of many decades, the quantitative determination of the forces between molecules has proved one of the most intractable problems in physical chemistry. These forces are important in determining both the equilibrium properties of matter and the course of collision processes and thus play a central role in many areas of chemistry. Chemists are frequently concerned with complex systems such as those involving polyatomic molecules, biological macromolecules and surfaces. However at the present time it is not possible to make quantitative estimates of the forces in such complicated systems. Indeed it is only in the past three years that sufficient progress has been made to enable us to define, with reasonable accuracy, the forces between the molecules of the inert gases. This review will be principally concerned with these recent advances.

1 Intermolecular Potential Energies

It is usual to describe the interaction between a pair of spherically symmetrical molecules in terms of the potential energy of the system, $U(r)$. This is the so-called intermolecular pair potential energy function, which is related to the force between the molecules $F(r)$ by

$$U(r) = \int_r^\infty F(r)\,\mathrm{d}r$$

It represents the potential energy of interaction as a function of internuclear separation r and in this case is independent of the line of approach. The concept of a potential energy function rests on the Born–Oppenheimer approximation[1,2] which is based on the fact that the electron velocities are very large compared with those of the nuclei. Consequently $U(r)$ is independent of the velocity of approach and can in principle be obtained by solving the time-independent Schrödinger equation for each value of r by use of the electrostatic Hamiltonian in the clamped-nuclei approximation. Calculations show that even for H_2, with

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[1] M. Born and J. R. Oppenheimer, *Ann. Phys.*, 1927, **84**, 457.

[2] J. O. Hirschfelder and W. J. Meath, *Adv. Chem. Phys.*, 1967, **12**, 3.

the lightest nuclei, the Born–Oppenheimer approximation is excellent,[3] and for interactions involving heavier nuclei it should be even more accurate. Only in a limited number of situations (such as when nuclear velocities are large as in hot-atom collisions) does the coupling of electronic and nuclear motions become significant.

The general form of $U(r)$ is illustrated in Figure 1. Its shape is determined by the combination of attractive energies which prevail at large separations and the repulsive energies which occur at small separations. This curve may be characterized in terms of several parameters: σ, the separation for which the energy is zero $[U(\sigma) = 0]$; r_{m}, the separation for which the energy is a minimum $[(\mathrm{d}U(r)/\mathrm{d}r)_{r=r_{\mathrm{m}}} = 0]$; and ϵ, the depth of the potential well $[U(r_{\mathrm{m}}) = -\epsilon]$. There have been many attempts to describe $U(r)$ in terms of an analytic function, the most famous and widely used of which is the Lennard-Jones (12—6) potential:[4]

$$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

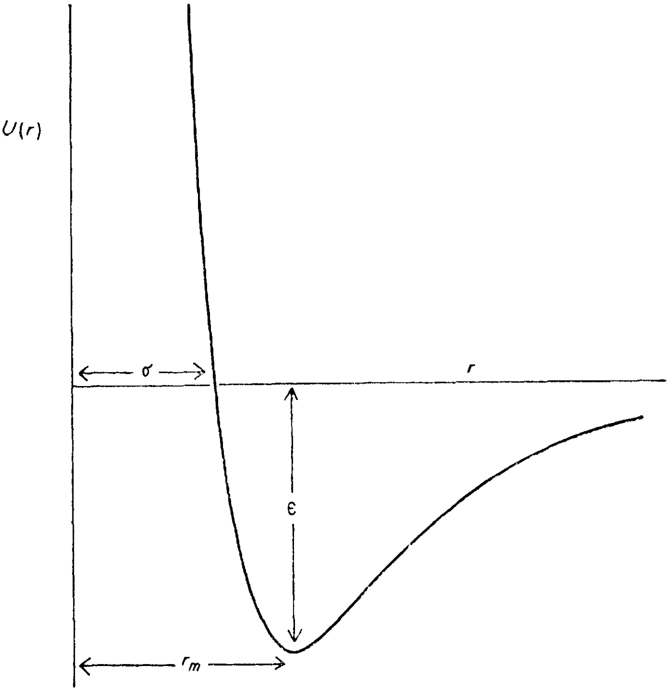

Figure 1 *Intermolecular potential energy as a function of separation*

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[3] W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, 1965, **43**, 2429; L. Wolniewicz, *ibid.*, 1966, **45**, 515.

[4] J. E. Lennard-Jones, *Proc. Roy. Soc.*, 1924, **106**, *A*, 463.

From 1930 to 1960 the study of intermolecular energies and their relation to the bulk properties of matter was developed largely by the application of this simple potential energy function. It was almost invariably assumed that the intermolecular energy of a number of molecules was the sum of the energies of all pairs of molecules in the system:

$$U = \tfrac{1}{2} \sum_{\substack{i=1 \\ i \neq j}}^{N} \sum_{j=1}^{N} U(r_{ij})$$

These assumptions appeared to give a satisfactory basis for the interpretation of most of the experimental data then available for simple substances in both the gaseous and solid states.[5] It was suggested that the equation of state of argon at liquid densities calculated in a Monte Carlo calculation by Wood and Parker[6] using a 12—6 potential function and assuming pair-wise additivity might be even more accurate than the experimental data at high pressures. However our present knowledge about both the potential function of argon and the limitations of pairwise additivity suggest that, unfortunately, the good agreement with the data at moderate pressures was fortuitous.

Although the 12—6 potential is still extensively used in model calculations,[7] it is now known to be a poor representation of inert-gas interactions. It is not capable of satisfactorily describing properties at the extremes of high and low temperature[8] and leads to estimates of long-range attractive energies which are a factor of two greater than the best theoretical calculations.[9] Early efforts to determine more satisfactory potential functions led to varied and mutually inconsistent results. This can be illustrated by a comparison of recent estimates of ϵ and r_m for the argon *intermolecular* energy function with the corresponding values for the *intramolecular* energy function of the iodine molecule I_2. Analysis of the vibration–rotation fine structure of the electronic spectrum of iodine has led to very accurate values for ϵ and r_m (which correspond to the dissociation energy D_e and the equilibrium separation r_e in spectroscopic notation).[10] In the case of argon our knowledge of these parameters was obtained largely from the analysis of bulk properties which are only indirectly related to the intermolecular forces. Table 1 compares the range of values proposed for the ϵ and r_m of argon

Table 1 *Comparison of the potential parameters for* I_2 *and* Ar_2

	I—I (ref. 10)	Ar - - - Ar (ref. 9)
r_m (nm)	0.2666 ± 0.0002	0.374—0.393
ϵ (J)	$2.4699 \pm 0.0002 \times 10^{-19}$	1.63—2.21×10^{-21}

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[5] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, 'Molecular Theory of Gases and Liquids,' Wiley, New York, 1954.

[6] W. W. Wood and F. R. Parker, *J. Chem. Phys.*, 1957, **27**, 720.

[7] For example, J. V. L. Singer and K. Singer, *Mol. Phys.*, 1972, **24**, 357.

[8] B. E. F. Fender and G. D. Halsey, *J. Chem. Phys.*, 1962, 36, 1881.

[9] Data summarized in E. B. Smith, *Ann. Reports*, 1966, **63**, 13.

[10] G. Herzberg, 'Spectra of Diatomic Molecules,' Van Nostrand, New York, 1950, p. 540.

over the past ten years with the corresponding data for I_2. Despite the fact that the maximum energy of interaction for I_2 is roughly 100 times greater than for Ar_2 it is known with much greater *absolute* accuracy.

However, in the past three years or so some important advances have been made, and we are now in a position to define the intermolecular potential energy functions of the inert gases with considerable accuracy. As often is the case, this progress cannot be ascribed to any single factor. A major contribution was undoubtedly the intensive investigations of Barker and his colleagues[11—13] using very flexible mathematical functions to represent the intermolecular energy. They also considered a wider range of experimental data, and by making some judicious assumptions were able to reconcile most of this data with their potential functions. New experimental measurements, first of low-temperature gas imperfections[14,15] and later of gas viscosities,[16] showed that many of the earlier data were in error. The new data removed some of the inconsistencies that had hindered progress in the field of intermolecular forces for many years.

Before these recent developments may be discussed, it is necessary to consider in more detail the origins of molecular interactions and their relation to the bulk properties of matter.

2 The Origins of Intermolecular Energies

It is convenient to classify, somewhat arbitrarily, the interaction energy of a pair of molecules into three regions of intermolecular separation: short ($r < \sigma$), intermediate ($\sigma < r < 2\sigma$) and long ($r > 2\sigma$) range.

A. Short-range Energies.—The Pauli exclusion principle requires that the wavefunction of the system in this region be antisymmetric with respect to the exchange of electrons between the two molecules. For closed-shell systems this causes the internuclear charge density to be reduced, so decreasing the screening of the nuclei by the electrons and resulting in a net repulsion. The resulting energies, which may be calculated by first-order perturbation theory, are referred to as *first-order exchange energies*. They may be represented over a wide range of separations by

$$U^{(1)}(\text{exch}) = A\exp(-Br)$$

where A and B are constants.

B. Long-range Energies.—For separations at which the overlap of the molecular wavefunctions can be neglected, the exchange energies are negligible and the

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[11] J. A. Barker and A. Pompe, *Austral. J. Chem.*, 1968, **21**, 1683.

[12] M. V. Bobetic and J. A. Barker, *Phys. Rev.* (*B*), 1970, **2**, 4169.

[13] J. A. Barker, R. A. Fisher, and R. O. Watts, *Mol. Phys.*, 1971, **21**, 657.

[14] M. A. Byrne, M. R. Jones, and L. A. K. Staveley, *Trans. Faraday Soc.*, 1968, **64**, 1747.

[15] R. D. Weir, I. Wynn Jones, J. S. Rowlinson, and G. Saville, *Trans. Faraday Soc.*, 1967, **63**, 1320.

[16] For a compilation of recent data see G. C. Maitland and E. B. Smith, *J. Chem. Eng. Data*, 1972, **17**, 150.

wavefunction need not be made antisymmetric with respect to the exchange of electrons. The dominating energies in this region are attractive in nature.

The first-order perturbation energies, $U^{(1)}(r)$, correspond to the interaction of the permanent moments of the molecules, and are commonly referred to as *electrostatic* or *orientation* contributions. For neutral polar molecules the leading term corresponds to a dipole–dipole interaction with the energy proportional to r^{-3}. Boltzmann averaging over all orientations and expansion in powers of $(kT)^{-1}$ gives for the leading term

$$U^{(1)}(dd) = \frac{-\,2\mu_a{}^2\mu_b{}^2}{3kTr^6}$$

where μ_a, μ_b are the molecular dipole moments. Similar equations are obtained for the interaction of higher-order multipoles.[17]

Second-order perturbation theory gives rise to two kinds of terms. The first correspond to transitions in which the state of only one of the interacting molecules changes. They are *induction energies* which arise from the polarization of one molecule by the other. Dipole-induced dipole interactions lead to another attractive energy term varying as r^{-6}:

$$U^{(2)}(dd_i) = \frac{-\,\mu_a{}^2\alpha_b}{r^6}$$

where α is the dipole-polarizability.

Except for small, highly polar molecules, these two types of energy are often small compared with the third kind of attractive term—the *second-order dispersion energy.* This exists for non-polar as well as polar molecules and hence explains the long-range interactions between inert gas molecules. London[18] first showed that this contribution to the energy could be expressed in the form

$$U^{(2)}(\text{disp}) = C_6r^{-6} + C_8r^{-8} + C_{10}r^{-10} + \ldots\ldots$$

The accurate perturbation expression for the coefficient of the leading term is[19]

$$C_6 = -\frac{3}{2}\frac{e^4h^4}{m^2}\sum_{i,j\neq 0}\frac{f_{1i}f_{2j}}{(E_{10}-E_{1i})\,(E_{20}-E_{2j})\,(E_{10}+E_{20}-E_{1i}-E_{2j})}$$

where E_{ki} is the energy of the ith electronic state of the kth atom; f_{ki} is the corresponding dipole oscillator strength of the transition from the ground state, 0, to the ith electronic state; e is the charge on the electron and m its mass. This energy corresponds to transitions in which the states of both molecules change. Unlike the electrostatic and induction energies, dispersion energies cannot be understood classically. They may be thought of as arising from the coupling between instantaneous dipoles occurring in the interacting molecules.

At very large separations ($r > 100\sigma$) so-called *retardation effects*[20] arise because

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[17] Reference 5, p.28.

[18] F. London, *Z. phys. Chem. (Leipzig)*, 1930, **B11**, 222.

[19] H. Margenau, *Rev. Mod. Phys.*, 1939, **11**, 1.

[20] H. B. G. Casimir and D. Polder, *Phys. Rev.*, 1948, 73, 360.

of the finite time taken for electromagnetic radiation to be propagated between the interacting molecules. This causes the leading term of the dispersion energy to vary as r^{-7} at very long range. Such effects are not, however, relevant to the situations covered in this review.

C. Intermediate-range Energies.—A significant contribution to the energy at these separations comes from *second-order exchange energies*. These are insignificant compared with the other energies at both very short and long ranges but in the intermediate region they are far from negligible and prevent the simple addition of the short- and long-range terms.[21] However, their evaluation in a second-order calculation using a fully antisymmetrized wavefunction has proved to be extremely difficult.

D. Theoretical Approaches.—The following account of attempts to calculate intermolecular energies theoretically is necessarily brief. For a more detailed survey the reader is referred to the recent reviews of Buckingham and Utting[22] and of Certain and Bruch.[23]

At large separations it is usually more accurate to use experimental multipole moments and polarizabilities to calculate the electrostatic and induction contributions. Consequently quantum calculations have concentrated on the accurate evaluation of dispersion energies and, in particular, the coefficient C_6. The various approaches differ in the procedures used to estimate f_{ki} and E_{ki} in the perturbation expression for C_6 given above. Direct *ab initio* calculations have been successful only for helium.[24,25] However, long-range energies have the great advantage of being expressible in terms of the properties of the separated molecules. A large number of semi-empirical methods have been devised in recent years[26—31] which use experimental information, such as refractive indices, polarizabilities, and photoionization cross-sections, to estimate f_{ki} and E_{ki} in conjunction with oscillator strength sum rules, $S(j)$:

$$S(j) = \sum_i f_i (E_i - E_0)^j$$

It is now possible to determine not only C_6 but also accurate error bounds on the resulting values;[29—31] for the inert gases these have been reduced to *ca.* ± 3%.

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[21] H. Marganau, *Phys. Rev.*, 1939, **56**, 1000.

[22] A. D. Buckingham and B. D. Utting, *Ann. Rev. Phys. Chem.*, 1970, **21**, 287.

[23] P. R. Certain and L. W. Bruch, 'Intermolecular Forces' MTP International Review of Science, Physical Chemistry Section, Theoretical Chemistry Volume, Medical and Technical Publishing Co., Oxford, 1972.

[24] W. D. Davison, *Proc. Phys. Soc.*, 1966, **87**, 133.

[25] Y. M. Chan and A. Dalgarno, *Proc. Phys. Soc.*, 1965, **86**, 777.

[26] A. Dalgarno and A. E. Kingston, *Proc. Phys. Soc.*, 1961, **78**, 607.

[27] J. A. Barker and P. J. Leonard, *Phys. Letters*, 1964, **13**, 127.

[28] R. J. Bell, *Proc. Phys. Soc.*, 1965, **86**, 17.

[29] R. G. Gordon, *J. Chem. Phys.*, 1968, **48**, 3929.

[30] P. W. Langhoff and M. Karplus, *J. Chem. Phys.*, 1970, **53**, 233.

[31] G. Starkschall and R. G. Gordon, *J. Chem. Phys.*, 1971, **54**, 663.

These calculations represent the best theoretical estimates of long-range energies and are not restricted to light molecules. Where adequate experimental data is available, they have superseded earlier calculations based on variational theory[32—34] and on the harmonic oscillator model.[35] The results of these simpler methods are compared with recent sum rule values for the inert gases in Table 2.

In contrast, short-range energies cannot be treated in terms of the properties of the separated molecules and semi-empirical methods have been of little value. The most successful calculations have used variational procedures, the 64 configuration computation of Phillipson[36] for helium probably being the most accurate. For heavier molecules such configuration interaction calculations become lengthy and complicated. Molecular Hartree–Fock calculations for Ne_2 and Ar_2 give an upper limit to the correct energies owing to incomplete account being taken of electron correlation.[37] On the other hand, calculations using a statistical model of the atom[38,39] should improve in accuracy as the number of electrons involved increases.

There have been relatively few calculations for intermediate separations because of difficulties connected with antisymmetrization of the wavefunction.[23] Again helium has been the most widely studied system. Several schemes have been proposed for the treatment of exchange effects in this region, notably those of Sinanoglu[40] and Murrell *et al.*[41] Recent multiconfiguration SCF calculations for He_2[42,43] suggest that significant progress is being made towards the calculation of the complete potential function for this simple molecule. The bivariational procedures developed by Boys and co-workers[44] should also prove useful in the future. However, prospects for the accurate calculation of $U(r)$ at all separations for larger molecules remain bleak and we must continue to rely heavily on experimental methods of studying intermolecular energies.

3 Traditional Sources of Information

Much of our information about intermolecular forces has come from the analysis of the bulk properties of matter. Unfortunately this information is often deeply buried and can only be extracted by rather indirect methods. The traditional approach has been to assume a functional form for $U(r)$ and to fix the values of its disposable parameters by obtaining the best overall fit to the experimental

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[32] Values quoted in K. S. Pitzer, *Adv. Chem. Phys.*, 1959, **2**, 59.
[33] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, 1931, **37**, 682.
[34] J. G. Kirkwood, *Z. Physik.*, 1932, **33**, 57; A. Müller, *Proc. Roy. Soc.*, 1936, **A154**, 624.
[35] P. R. Fontana, *Phys. Rev.*, 1961, **123**, 1865.
[36] P. E. Phillipson, *Phys. Rev.*, 1962, **125**, 1981.
[37] T. L. Gilbert and A. C. Wahl, *J. Chem. Phys.*, 1967, **47**, 3425.
[38] A. A. Abrahamson, *Phys. Rev.*, 1963, **130**, 693.
[39] R. G. Gordon and Y. S. Kim, *J. Chem. Phys.*, 1972, **56**, 3122.
[40] N. R. Kestner and O. Sinanoglu, *J. Chem. Phys.*, 1966, **45**, 194.
[41] J. N. Murrell and G. Shaw, *Mol. Phys.*, 1967, **12**, 475; *ibid*, 1968, **15**, 325
[42] P. Bertocini and A. C. Wahl, *Phys. Rev. Letters*, 1970, **25**, 991.
[43] H. F. Schaefer, D. R. McLaughlin, F. E. Harris, and B. J. Alder, *Phys. Rev. Letters*, 1970, **25**, 988.
[44] S.F. Boys and F. Bernadi, *Mol. Phys.*, 1970, **19**, 553.

Table 2 *Dipole–dipole interaction coefficients,* $-C_6$, ($\times 10^{79}$ J m^6)

Approximate calculations and experimental

	London (1930)	Slater–Kirkwood (1931)	Kirkwood–Müller (1936)	Fontana (Harmonic Oscillator) (1961)	Molecular Beams (1965)	Low Temp. viscosity (1969)
Ref.	32	33	34	35	56	50
He	1.30	1.66	1.63	1.26		
Ne	4.14	7.75	11.5	4.70		
Ar	50.3	64.1	129	55.9	58 ± 10	61
Kr	103	120	282	107	111 ± 19	133
Xe	235	248	699	236		299

Sum rule calculations

	Dalgarno and Kingston (1961)	Barker and Leonard (1964)	Bell (1965)	Gordon (1968)	Langhoff and Karplus (1970)	Starkschall and Gordon (1971)
Ref.	26	27	28	29	30	31
He	1.40	1.43	1.38	1.40 ± 0.024	1.42 ± 0.11	1.3989 ± 0.0004
Ne	6.04	6.15	5.92	6.28 ± 0.69	6.78 ± 1.81	6.27 ± 0.83
Ar	65.6	63.8	62.2	65.5 ± 6.0	69.3 ± 12.8	64.9 ± 1.9
Kr	125	125.2	123.4	137 ± 18		127 ± 1
Xe	257	264.8	260	301 ± 49		288 ± 13

data. One of the most important sources of information is the imperfection of gases. The equation of state of a gas may be written:

$$\frac{p\bar{V}}{RT} = 1 + \frac{B(T)}{\bar{V}} + \frac{C(T)}{\bar{V}^2} + \ldots\ldots.$$

where $\bar{V}$ is the volume per mole, $B(T)$ is the second virial coefficient, $C(T)$ the third virial coefficient, and p, T, and R are the pressure, temperature and gas constant respectively. The classical second virial coefficient which depends only on pair interactions, is related to the intermolecular potential energy function $U(r)$ by the relation

$$B(T) = -\ 2\pi N \int_0^\infty [\exp(-\ U(r)/kT) - 1]r^2 \mathrm{d}r$$

At very low temperatures, where classical mechanics is no longer valid, quantum mechanical expressions must be used to calculate $B(T)$. However, at moderately low temperatures small 'quantum corrections' may be used to correct the classical equation.[45]

$B(T)$ may also be expressed in the form

$$B(T) = \frac{2\pi N\alpha}{3T} \int_0^\epsilon \Delta\exp(-\Phi/T)\mathrm{d}\Phi + \frac{2\pi N\alpha}{3T} \int_\epsilon^\infty r^3\exp(-\Phi/T)\mathrm{d}\Phi$$

where Δ is $r_L{}^3 - r_R{}^3$, r_L and r_R being the co-ordinates of the inner and outer walls of the potential well at an energy Φ. Φ is defined by $\Phi = U(r)/k + \epsilon$ and $\alpha = \exp(\epsilon/T)$. The first term corresponds to the contribution of the potential well to the virial coefficient at temperature T and the second term arises from the repulsive forces. This equation shows that $B(T)$ does not uniquely determine $U(r)$ except in the repulsive region $[(U(r) > 0)]$[45,46] so that a knowledge of second virial coefficients as a function of temperature is not sufficient information with which to evaluate intermolecular potential energy functions. At very high temperatures $B(T)$ was analysed directly (by a so-called *data inversion* technique) to give $U(r)$ for helium.[47] At low temperatures $B(T)$ may provide information about the width of the potential energy bowl as a function of its depth.[46]

The transport properties of dilute gases also depend on the pair potential and have been widely used (particularly the viscosity) in its determination. The low-pressure transport properties result from bimolecular collisions and are related to $U(r)$ by 'collision integrals'[48] which may be regarded as corrections to a hard-sphere collision cross-section resulting from the continuous nature of intermolecular forces. The very low temperature viscosities, unlike virial coefficients, are not determined by the lower part of the bowl, but by the behaviour of

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[45] Reference 5, p. 392.

[46] J. B. Keller and B. Zumino, *J. Chem. Phys.*, 1959, **30**, 1351; H. L. Frisch and E. Helfand, *J. Chem. Phys.*, 1960, **32**, 269.

[47] D. A. Jonah and J. S. Rowlinson, *Trans. Faraday Soc.*, 1966, **62**, 1067.

[48] Reference 5, p. 523.

the potential energy function at large separations. To this extent they are complementary to the gas imperfection data and have been used to estimate the dispersion force coefficient C_6[49—51] (see Table 2). At high temperatures gas viscosities reflect the repulsive energy function and methods have been devised to obtain $U(r)$ directly from such data.[52]

A wide range of properties can be readily measured in the solid state and they have been used extensively in the determination of potential energy functions. Traditionally the lattice energy and the nearest neighbour distances have been most important in these studies but the specific heat, bulk modulus and elastic constants may be used to provide more sensitive tests of potential functions. The major difficulty with solid-state data is that an assumption about the degree to which the total energy is pair-wise additive must be made[4] before they can be interpreted using intermolecular pair potentials. It is now widely accepted that there are important contributions from many-body interactions and that the total potential energy of a system containing N molecules is of the form

$$U_{\text{total}} = \sum_{i<j} U_2(r_{ij}) + \sum_{i<j<k} U_3(r_{ij}, r_{ik}, r_{kj}) + \ldots\ldots\ldots$$

$$U_{\text{total}} = U_{\text{pair}} + \triangle U$$

It will be seen later that there is still great uncertainty about both the precise form of the many-body potentials and the relative magnitudes of the various contributions to $\triangle U$.

The elastic scattering of high-energy molecular beams (5—5000 eV) has provided important information on the repulsive energies of the inert gases.[53, 54] The beams are generated by accelerating the atoms as ions and subsequently neutralizing them by resonant charge exchange with neutral atoms. The incomplete total cross-section, $Q'(v)$, is measured as a function of the beam energy. This is the fraction of beam particles which is scattered at an angle greater than some small angle θ_0:

$$Q'(v) = 2\pi \int_{\theta_0}^{\pi} I(\theta,v) \sin\theta \mathrm{d}\theta$$

where $I(\theta,v)$ is the differential cross-section, which is related to the intensity scattered at angle θ, and v is the relative collisional velocity. The repulsive energies of the colliding atoms may be obtained from the variation of the total cross-section with energy by a simple analysis.[53] Measurements of the total cross-section [($Q(v)$ when $\theta_0 = 0$)] at thermal energies have been used to confirm that the long-range energy varies as r^{-6} and to obtain estimates of C_6 which are in

[49] R. J. Munn, *J. Chem. Phys.*, 1965, **42,** 3032.
[50] A. G. Clarke and E. B. Smith, *J. Chem. Phys.*, 1969, **51,** 4156.
[51] J. S. Rowlinson, *Discuss. Faraday Soc.*, 1965, **40,** 19.
[52] J. H. Dymond, *J. Chem. Phys.*, 1968, **49,** 3673.
[53] I. Amdur and J. E. Jordan, *Adv. Chem. Phys.*, 1966, **10,** 29.
[54] A. B. Kamnev and V. B. Leonas, *High Temp.*, 1965, **3,** 744.

good agreement with the theoretical values (see Table 2).[55,56] Under high resolution, the total and differential cross-sections at thermal energies possess oscillatory fine structure, which arises because of interference phenomena.[57] Glory undulations in $Q(v)$ and rainbow maxima in $I(\theta,v)$ both contain much information about $U(r)$.[58] For instance the energy dependence of the rainbow maximum has been used to determine ϵ and σ for inert-gas alkali-metal interactions,[59] but until recently it was necessary to interpret the results using an assumed potential model. Buck[60] has proposed a method for directly inverting differential cross-sections to give the potential energy curve numerically. However since the method requires extremely detailed $I(\theta,v)$ data, it has so far been applied to only a few systems (Na–Hg, K–Hg).[61,62] The more recent developments in molecular beam studies for the inert gases will be discussed later.

4 Potential Energy Functions for the Inert Gases

Following the discovery that the 12—6 potential function was unsatisfactory, numerous simple functions were proposed in its place. Most work has concentrated on argon for which there exists the largest body of experimental data. The literature of the 1950s and 60s introduced many proposed pair potentials for argon[9,63] which at first appeared to be successful, only to be rejected as experimental data for more properties became available or as the old results were modified. The parameters ϵ/k and σ for some of these functions are given in Table 3.

The construction of suitable potential energy functions for the inert gases has to some extent been aided by the fact that interaction energies at the extremes of small and large separations are known with some accuracy. The precision with which C_6 coefficients can be determined theoretically and experimentally has been illustrated in Table 2. Some progress has also been made towards the more accurate evaluation of the higher coefficients C_8 and C_{10}.[64—66] Repulsive energies determined by theoretical calculations, molecular beam measurements and the inversion of high-temperature gas properties are in good agreement with one another, as illustrated in Figures 2 and 3 for helium and argon. However, the determination of the potential functions at intermediate separations has proved to be extremely difficult and it is only in the past three years that significant

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[55] H. Pauly and J. P. Toennies, *Adv. Atomic and Mol. Phys.*, 1965, **1**, 302.

[56] E. W. Rothe and R. H. Neynaber, *J. Chem. Phys.*, 1965, **43**, 4177.

[57] R. B. Bernstein and J. T. Muckerman, *Adv. Chem. Phys.*, 1967, **12**, 409.

[58] E. A. Mason, R. J. Munn, and F. J. Smith, *Endeavour*, 1971, **30**, 91.

[59] P. Barwig, U. Buck, E. Hundhausen, and H. Pauly, *Z. Physik.*, 1966, **196**, 343.

[60] U. Buck, *J. Chem. Phys.*, 1971, **54**, 1923.

[61] U. Buck and H. Pauly, *J. Chem. Phys.*, 1971, **54**, 1929.

[62] U. Buck, M. Kick, and H. Pauly, Abstracts of VIIth ICPEAC, p. 543, North-Holland, Amsterdam, 1971.

[63] D. D. Fitts, *Ann. Rev. Phys. Chem.*, 1966, **17**, 59.

[64] G. Starkschall and R. G. Gordon, *J. Chem. Phys.*, 1972, **56**, 2102.

[65] G. Starkschall and R. G. Gordon, *J. Chem. Phys.*, 1972, **56**, 2801.

[66] (*a*) D. A. McQuarrie, J. Terebey, and S. J. Shire, *J. Chem. Phys.*, 1969, **51**, 4863; (*b*) W. D. Davison, *J. Phys.* (*B*), 1968, **1**, 139.

Table 3 *Recent estimates of ϵ and σ for argon*

Potential	*Ref.*	*Year*	ϵ/k (K)	σ (nm)
12—6	5	1954	119.8	0.3405
Guggenheim–McGlashan	*a*	1960	137.5	0.3812
Kihara	*b*	1964	142.9	0.3363
exp – 6	*c*	1964	152	0.3644
Munn–Smith	*d*	1965	153	0.331
Dymond–Rigby–Smith	*e*	1965	147	0.328
18—6	*f*	1966	160.3	0.3277
Barker–Pompe	11	1968	147.7	0.3341
Dymond–Alder	80	1969	138.2	0.3280
11—6—8	81	1970	153	0.3290
Barker–Bobetic	12	1970	140.2	0.3367
Barker–Fisher–Watts (BFW)	13	1971	142.1	0.3361
Maitland–Smith (BBMS)	87	1971	142.5	0.3355
Parson–Siska–Lee (MSV)	84	1972	140.7	0.3345

(*a*) E. A. Guggenheim and M. L. McGlashan, *Proc. Roy. Soc.*, 1960, **A255**, 456; (*b*) J. A, Barker, W. Fock, and F. J. Smith, *Physics Fluids*, 1964, **7**, 897; (*c*) A. E. Sherwood and J. M. Prausnitz, *J. Chem. Phys.*, 1964, **41**, 429; (*d*) R. J. Munn and F. J. Smith, *J. Chem. Phys.*, 1965, **43**, 3998; (*e*) J. H. Dymond, M. Rigby, and E. B. Smith, *J. Chem. Phys.*, 1965, **42**. 2801; (*f*) J. H. Dymond, M. Rigby and E. B. Smith, *Physics Fluids*, 1966, **9**, 1222.

progress has been made towards the satisfactory solution of the problem. It can be seen from Table 3 that recent estimates of the parameters for argon appear to be converging around $\sigma \simeq 0.335$ nm, $\epsilon/k \simeq 140$ K. The origin of these latest studies may be traced back to the work of Barker and Pompe[11] (1968) which was based on four principles:

(*a*) the use of highly flexible multiparameter potential energy functions of the form

$$U(r)/\epsilon = \sum_{i=0}^{n} A_i(r^* - 1)^i \exp[\alpha(1 - r^*)] - \sum_{j=0}^{2} C_{2j+6}/(\delta + r^{*2j+6})$$

where $r^* = r/r_m$ and $n = 3$;

(*b*) the use of accurate theoretical calculations of dispersion energies and molecular beam determinations of repulsive energies to fix the coefficients C_{2j+6} and A_i;

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[67] G. H. Matsumoto, C. F. Bender, and E. R. Davidson, *J. Chem. Phys.*, 1967, **46**, 402.

[68] (*a*) J. E. Jordan and I. Amdur, *J. Chem. Phys.*, 1967, **46**, 165; (*b*) I. Amdur, J. E. Jordan, and S. O. Colgate, *J. Chem. Phys.*, 1961, **34**, 1525; (*c*) I. Amdur and A. L. Harkness, *J. Chem. Phys.*, 1954, **22**, 664.

[69] G. C. Maitland and E. B. Smith, *J. Chem. Phys.*, 1970, **52**, 3848.

[70] N. C. Blais and J. B. Mann, *J. Chem. Phys.*, 1960, **32**, 1459.

[71] H. W. Berry, *Phys. Rev.*, 1949, **75**, 913; 1955, **99**, 553.

[72] (*a*) I. Amdur, J. E. Jordan, and R. B. Bertrand, 'Atomic and Collision Processes,' North-Holland Publishing Co., Amsterdam, 1964; (*b*) I. Amdur and E. A. Mason, *J. Chem. Phys.*, 1954, **22**, 670.

[73] S. O. Colgate, J. E. Jordan, I. Amdur, and E. A. Mason, *J. Chem. Phys.*, 1969, **51**, 968.

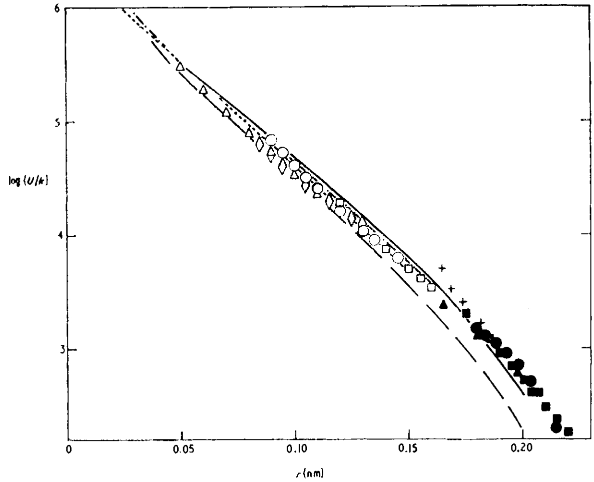

Figure 2 *The repulsive pair potential energy of helium. The units of U/k are* K
Theoretical: ———————— Phillipson (ref. 36), — — — — — — — —. Matsumoto *et al.* (ref. 67), — • — • — • — • — • — • — Abrahamson (ref. 38), — — — — — Gordon and Kim (ref. 39).
Molecular beams: △ Amdur and Jordan (ref. 68*a*), ◇ Kamnev and Leonas (ref. 54), ○ Amdur *et al.* (ref. 68*b*), □ Amdur and Harkness (ref. 68*c*).
Bulk Properties: Second virial coefficients: ● Jonah and Rowlinson (ref. 47), Viscosities: ■ Maitland and Smith (ref. 69), Thermal conductivities: + Dymond (ref. 52), ▲ Blais and Mann (ref. 70)

(*c*) the acceptance of the non-additivity of energies for dense systems and the assumption that the contribution of many-body forces ΔU may be accurately represented by the Axilrod–Teller triple-dipole term[74] alone:

$$\Delta U_{\mathrm{TD}} = \frac{\nu(1 + 3\cos\theta_{12}\cos\theta_{23}\cos\theta_{13})}{(r_{12}r_{23}r_{13})^3}$$

where θ_{12}, θ_{23}, θ_{13} are the angles of the triangle with sides r_{12}, r_{23}, and r_{13}; (the coefficient ν can be evaluated[29,75] to within a few per cent by the sum rule techniques already discussed for C_6. An approximate value is $\frac{3}{4}\alpha C_6$);
(*d*) the neglect of all transport data in the determination of the potential parameters for argon. In particular, it was suspected that despite the good agreement between the data of several workers, the high-temperature viscosities were in error. Consequently, the remaining potential parameters were fixed using virial coefficient and solid-state data only.

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[74] B. M. Axilrod and E. Teller, *J. Chem. Phys.*, 1943, **11**, 299.
[75] T. K. Tang, *Phys. Rev.*, 1969, **177**, 108.

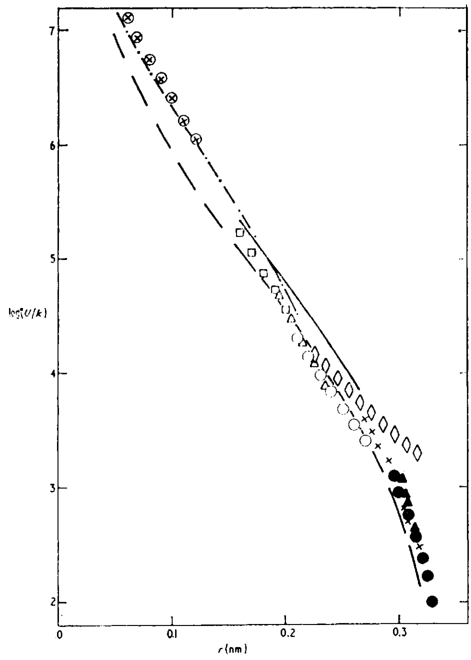

Figure 3 *The repulsive pair potential energy of argon. The units of U/k are* K
Theoretical: ———————— Gilbert and Wahl (ref. 37), —·—·—· Abrahamson (ref. 38), – – – – – – – – Gordon and Kim (ref. 39).
Molecular beams: ⊗ Berry (ref. 71), □ Amdur *et al.* (ref, 72*a*), ○ Amdur and Mason (ref. 72*b*), △ Colgate *et al.* (ref. 73), ◇ Kamnev and Leonas (ref. 54).
Bulk Properties: Second virial coefficients: ▲Maitland and Smith (ref. 114), Viscosities: ●Gough *et al.* (ref. 117), Thermal conductivities: × Dymond (ref. 52)

Errors in the earlier viscosity data of up to 8% were subsequently confirmed by a number of workers using different techniques.[76–78] These new results were in better, though not perfect, agreement with those calculated using the Barker–Pompe potential. They extended the range of existing data up to 2200 K and are one of several sets of measurements of equilibrium[14,15] and transport properties at both high and low temperatures that have played a significant role in the

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[76] F. A. Guevara, B. B. McInteer, and W. E. Wageman, *Phys. Fluids*, 1969, **12**, 2493.

[77] R. DiPippo and J. Kestin, Proc. 4th Symposium on Thermophysical Properties, College Park, A.S.M.E. 1968; A. S. Kalelkar and J. Kestin, *J. Chem. Phys.*, 1970, **52**, 4248; J. Kestin, W. Wakeham, and K. Watanabe, *J. Chem. Phys.*, 1970, **53**, 3773.

[78] R. A. Dawe and E. B. Smith, *J. Chem. Phys.*, 1970, **52**, 693.

recent progress which has been made in the study of pair potentials. These are important because it is only at these extremes of temperature that bulk properties become very sensitive to the precise nature of the potential energy function.[79]

Despite the success of the Barker–Pompe function in interpreting a wide range of argon data, its validity was still in dispute and a number of other potentials were proposed which were based on gas equilibrium and transport data alone. The first and most promising of these was due to Dymond and Alder[80] (1969) who suggested a numerically tabulated potential which has a wider bowl and a steeper outside wall than the Barker–Pompe potential. This study has also given valuable insight into the dependence of bulk properties on the different regions of $U(r)$. In contrast to this multivariational approach and to the large number of complex analytical functions suggested in recent years, Klein and Hanley[81] (1970) have shown that all the argon second virial and viscosity data may be reconciled, using the relatively simple 11—6—8 function which, as suggested by theory, introduces a second attractive energy term varying as r^{-8}:

$$U(r)/\epsilon = 2.4\,(r_\mathrm{m}/r)^{11} - 0.4\,(r_\mathrm{m}/r)^{6} - 3.0\,(r_\mathrm{m}/r)^{8}$$

Using r_m and ϵ values determined from the argon data, this potential is somewhat narrower and deeper than that of Barker and Pompe.

Meanwhile Barker and co-workers continued to refine their potential by the inclusion of extra parameters to improve its flexibility and the use of additional experimental data. Bobetic and Barker[12] (1970) studied the specific heat, thermal expansion, bulk modulus, elastic constants, and phonon dispersion curves of crystalline argon, at the same time showing that the Dymond–Alder potential is inconsistent with the low-temperature specific heats. Barker, Fisher, and Watts[13] (BFW) (1971) have made further refinements by calculating thermodynamic properties of liquid argon using Monte Carlo and molecular dynamics techniques.

During the past two years several independent studies have confirmed that the final BFW potential is essentially correct and that the other recently proposed potentials have serious deficiencies. These have made use of two new and important pieces of experimental information: the vibrational fine structure of the argon dimer u.v. absorption spectrum[82] and the fine structure details of the differential scattering cross-section for argon obtained in high-resolution low-energy molecular beam experiments.[83,84] The spectroscopic data have been analysed in three ways. Bruch and McGee[85] and Chen and Present[86] have solved the Schrödinger radial wave equation for several proposed potential functions and

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[79] H. J. M. Hanley and G. E. Childs, *Science*, 1968, **159**, 1114.
[80] J. H. Dymond and B. J. Alder, *J. Chem. Phys.*, 1969, **51**, 309.
[81] M. Klein and H. J. M. Hanley, *J. Chem. Phys.*, 1970, **53**, 4722.
[82] Y. Tanaka and K. Yoshino, *J. Chem. Phys.*, 1970, **53**, 2012.
[83] M. Cavallini, G. Gallinaro, L. Meneghetti, G. Scoles, and U. Valbusa, *Chem. Phys. Letters*, 1970, **7**, 303.
[84] J. M. Parson, P. E. Siska, and Y. T. Lee, *J. Chem. Phys.*, 1972, **56**, 1511.
[85] L. W. Bruch and I. G. McGee, *J. Chem. Phys.*, 1970, **53**, 4711.
[86] C. T. Chen and R. D. Present, *J. Chem. Phys.*, 1971, **54**, 3645.

compared the eigenvalues obtained with the observed vibrational levels. A more detailed analysis of the data was made by Maitland and Smith[87] who performed a Rydberg–Klein–Rees analysis to give the width of the potential well as a function of its depth. These results which are illustrated in Figure 4 showed clearly that the Dymond–Alder potential has too low a curvature at its minimum and too wide a bowl at higher energies. The 11—6—8 potential is too narrow for much of its depth and has the wrong long-range behaviour. This work, incidentally, also provided a direct demonstration of the inadequacy of the 12—6 potential for argon, a fact which had been deduced from indirect evidence many years earlier. The RKR analysis was used in conjunction with second virial coefficient

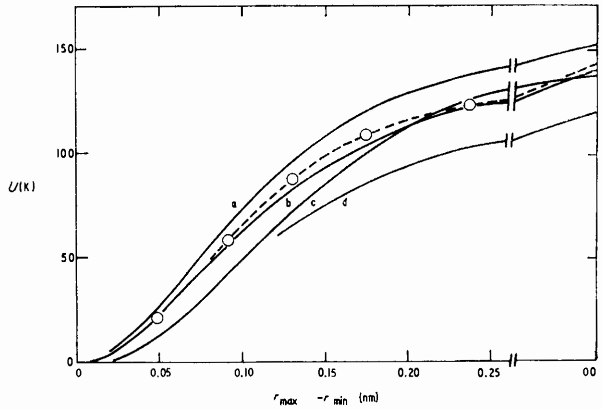

Figure 4 *The width,* $r_{\max} - r_{\min}$, *of the argon intermolecular potential curve as a function of energy, U, measured from the minimum of the potential well*
○Spectroscopic (RKR) calculations (ref. 87);
Potential energy functions: (*a*) 11—6—8 (ref. 81); (*b*) Barker–Bobetic (ref. 12); (*c*) Dymond–Alder (ref. 80); – – – – BBMS (ref. 87)

and gas transport data to give a potential function (BBMS) which was proposed simultaneously with the most sophisticated Barker potential (BFW), with which it was found, encouragingly, to be almost identical. The well-depths, ϵ/k, for these two potentials (142.5 K and 142.1 K respectively) are in excellent agreement with the values determined by Leroy[88] (142.2 K) and Present[89] (140.0 K) from an analysis of the same spectroscopic data, using the known long-range behaviour of the vibrational levels and the potential energy respectively.

The recent advent of supersonic nozzle beams has enabled scattering measurements to be made in the intermediate energy region between the very high energy beams obtained by ion acceleration and thermal energy beams obtained using

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[87] G. C. Maitland and E. B. Smith, *Mol. Phys.*, 1971, **22**, 861.
[88] R. J. Leroy, *J. Chem. Phys.*, 1972, **57**, 573.
[89] R. D. Present, *J. Chem. Phys.*, to be published.

effusion oven sources. The higher intensities and narrower velocity distributions involved have also greatly improved the resolution of the scattering experiments. These techniques have been used recently by two groups of workers to obtain high-resolution measurements of differential cross-sectons for the inert gases. Cavallini *et al.*[83,90] have reported values for He, Ar, and Kr and related the rainbow structure to $r_i(\mathrm{d}U/\mathrm{d}r)_{r=r_i}$ (where r_i is the separation at the inflection point of the potential) without assuming a potential function. Lee and his co-workers[84,91,92] have observed symmetry oscillations at high angle, arising from the indistinguishability of the like scattering atoms, in addition to the usual quantum and rainbow interference effects. Their results for He, Ne, Ar, and Kr have been interpreted in terms of various multi-parameter potential functions. The function for argon[84] is very similar to the BFW and BBMS potentials, having a well-depth of 140.7 K. The BFW potential itself has been shown to reproduce the oscillations in the scattering intensities almost perfectly.[13]

Both the shape and the parameters of the argon pair potential, therefore, now appear to be defined to within narrow limits, as illustrated in Figure 5. On the scale of this Figure, the potential function of Lee and co-workers,[84] the BFW and the BBMS potential functions are almost identical. The small differences between them are shown in a deviation plot from the BFW function. However, despite the similarity between these independent estimates, there is still not perfect agreement with all the experimental data. For example, significant discrepancies occur for second virial coefficients below 90 K,[87] the low-temperature bulk modulus and the elastic constants of crystalline argon.[12,13] It remains to be seen whether such discrepancies are due to deficiences in the experimental data or in the theoretical analysis.

Considerable progress has also been made in the study of intermolecular forces for the other inert gases. A similar approach to that used for argon has been applied to krypton,[93] although a smaller number of experimental properties have been studied. The only other gas for which extensive pair potential studies have been made is helium. Here careful account must be taken of quantum cons tributions to the bulk properties, which are far from negligible at normal temperatures. On the other hand, there are considerably more theoretical estimates of $U(r)$ available and a judicious mixing of these with experimental data has enabled Beck[94] and Bruch and McGee[95] to devise multi-parameter functions which are reasonably successful. However, there remain large discrepancies with some data such as high-temperature viscosities and these studies have not yet reached the same level of sophistication as those for argon.

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[90] (*a*) M. Cavallini, L. Meneghetti, G. Scoles, and M. Yealland, *Phys. Rev. Letters*, 1970, **24**, 1469; (*b*) M. Cavallini, M. G. Dondi, G. Scoles, and U. Valbusa, Symposium on Molecular Beams, Cannes, 1971.

[91] P. E. Siska, J. M. Parson, T. P. Schafer, and Y. T. Lee, *J. Chem. Phys.*, 1971, **55**, 5762.

[92] T. P. Schafer, P. E. Siska, and Y. T. Lee, Abstracts of VIIth ICPEAC, 1971, North-Holland Publishing Co., Amsterdam, Holland, p.546.

[93] M. V. Bobetic, J. A. Barker, and M. Klein, *Phys. Rev.* 1972, **B5**, 3185.

[94] D. E. Beck, *Mol. Phys.*, 1968, **14**, 311.

[95] L. W. Bruch and I. G. McGee, *J. Chem. Phys.*, 1970, **52**, 5884.

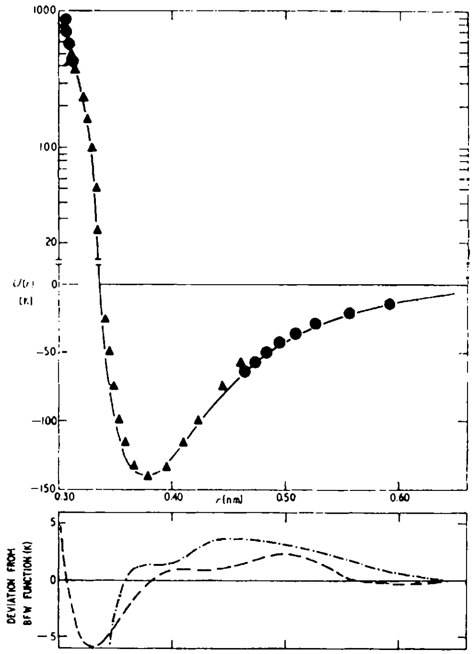

Figure 5 *The intermolecular pair potential energy function of argon*
———— Multiparameter potentials (refs. 13, 84, 87).
▲ Inversion of gas viscosities (ref. 117).
● Inversion of second virial coefficients (ref. 114);
Deviations from the BFW function (ref. 13): – – – – – – – – BBMS (ref. 87), –•–•–•–•– Parson *et al.* (ref. 84)

An increasing amount of attention has been paid to neon and xenon, from the point of view of both experimental data[91,96] and their potential energy functions.[97,98] Now that the situation for argon appears to be largely resolved it is reasonable to suppose that the potential energy functions of all the inert gases will be accurately determined within a relatively short period of time.

Despite the rapid progress of the past few years, there are still important gaps in our knowledge of intermolecular forces even for these simple systems. For instance, the precise nature of non-additive contributions to the energy remains a matter of some controversy. The assumption of Barker and co-workers that the triple-dipole term dominates these many-body interactions and is an adequate approximation to the total non-additive energy appears to be justified

[96] Y. Tanaka and K. Yoshino, *J. Chem. Phys.*, 1972, **57**, 2964.

[97] J. A. Barker, *Chem. Phys. Letters*, 1972, **14**, 243.

[98] D. W. Gough, G. C. Maitland, and E. B. Smith, *Mol. Phys.*, in the press.

by the ability of potential functions consistent with two-body properties to reproduce accurately many-body properties when used in conjunction with the Axilrod–Teller formula. However, recent estimates of other non-additive effects do not confirm this point of view. Although non-additive exchange energies appear to be relatively small,[99,100] the contributions to the dispersion energy from higher-order multipole three-body interactions and higher n-body terms may be far from negligible.[101–104] It may well be that the success of the triple-dipole term in representing the total non-additive energy is somewhat fortuitous, being due to a large degree of self-cancelling by the other terms. Recent calculations of Chen and Present[105] support this argument.

Another outstanding problem is the determination of the forces between unlike molecules and their relation to those between like molecules. The determination of the so-called mixing-rules for the parameters ϵ_{12} and σ_{12} has proved particularly difficult. These rules have usually been based on formulae for the intermolecular energies at large separations and the parameters obtained either by using some characteristic experimental properties, such as those at the critical[106] or Boyle temperatures,[14] or by using an inadequate pair potential function to fit the data.[107] It is now widely agreed that the traditional mixing rules

$$\epsilon_{12} = (\epsilon_{11}\,\epsilon_{22})^{\frac{1}{2}} \quad \sigma_{12} = (\sigma_{11} + \sigma_{22})$$

are inadequate for most purposes, but despite the investigation of many alternative schemes, none has proved to be entirely satisfactory. There has been increased activity in recent years in the study of equilibrium[14,108,109] and transport properties[110] of mixed gases and of their scattering cross-sections[111] in an attempt to solve this problem. It is undoubtedly true that one of the reasons for the slow progress in studies of both non-additive and mixture interactions has been uncertainties about the exact form of the pair potential function for the pure components. The improvements of our knowledge of the latter should aid considerably future studies in these areas.

5 Data Inversion Techniques

Recently a number of so-called data inversion techniques have been proposed.

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[99] R. D. Present, *J. Chem. Phys.*, 1967, **47**, 1793.

[100] C. E. Swenberg, *Phys. Letters*, 1967, **24**, *A*, 163.

[101] R. J. Bell, *J. Phys.* (*B*), 1970, **3**, 751.

[102] M. B. Doran and I. J. Zucker, *J. Phys.* (*C*), 1971, **4**, 307.

[103] C. H. J. Johnson and T. H. Spurling, *Austral. J. Chem.*, 1971, **24**, 2205.

[104] J. A. Barker, C. H. J. Johnson, and T. H. Spurling, *Austral. J. Chem.*, 1972, **25**, 1811.

[105] C. T. Chen and R. D. Present, *J. Chem. Phys.*, 1972, **57**, 757.

[106] G. H. Hudson and J. C. McCoubrey, *Trans. Faraday Soc.*, 1960, **56**, 761.

[107] R. J. Good and C. J. Hope, *J. Chem. Phys.*, 1971, **55**, 111.

[108] D. R. Douslin, R. H. Harrison, and R. T. Moore, *J. Phys. Chem.*, 1967, **71**, 3477.

[109] N. K. Kalfoglou and J. G. Miller, *J. Phys. Chem.*, 1967, **71**, 1256.

[110] J. Kestin, S. T. Ro, and W. A. Wakeham, *J. Chem. Phys.*, 1972, **56**, 4086, and references therein.

[111] J. M. Parson, T. P. Schafer, F. P. Tully, P. E. Siska, Y. C. Wong, and Y. T. Lee, *J. Chem. Phys.*, 1970, **53**, 2123, 3755.

They provide methods whereby the precise information about $U(r)$ contained in experimental measurements is determined directly without assuming a form for the potential energy function. They eliminate the need for the unsatisfactory trial-and-error methods that have been traditionally employed. Methods of data inversion for spectroscopic and molecular beam data have been discussed earlier. In a similar way, X-ray[112] and neutron scattering[113] data may also be used to give $U(r)$ directly. However, the results for dense gaseous argon have only produced density-dependent *effective* pair potentials owing largely to the problem of accounting for non-pairwise additive energy contributions.

Of even greater interest is the development of such techniques for bulk properties, which are readily available for a wide variety of substances. The first efforts in this direction were those of Jonah and Rowlinson[47] who inverted the high-temperature second virial coefficients of helium by use of an inverse Laplace transform method to obtain a portion of the repulsive potential curve at high energies. Semi-empirical methods have recently been proposed to extend the inversion of second virial coefficients to lower temperature data.[114,115] These give information about the energies of the heavier inert gases in the low-energy repulsive region. They also provide information about the shape of the potential energy well. Simple methods for the inversion of high energy transport data have been described by Dymond[52] and Donth.[116] More sophisticated developments of Dymond's technique, using iterative procedures, have enabled both the repulsive energies and a large part of the potential well to be characterized for argon using viscosity data.[117] Apart from reasonably accurate transport data, the technique requires only an estimate of the depth of the potential energy well. In the case of argon this was established by recourse to spectroscopic data. The results of the application of these inversion methods to the data for argon are illustrated in Figure 5.

It is probable that these techniques may find even wider application for molecules, more complex than the inert gases, for which only the most common bulk properties have been measured.

6 Concluding Remarks

The pair potential energy functions of the inert gases, and of argon in particular, may now be defined with some accuracy. This position has been reached after many years of investigation and has been made possible by a combination of several factors:

(1) the increased accuracy with which theoretical calculations can now be made, particularly for long-range forces;

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[112] P. G. Mikolaj and C. J. Pings, *J. Chem. Phys.*, 1967, **46**, 1401.

[113] (*a*) C. D. Andriesse and E. Legrand, *Physica*, 1972, **57**, 191; (*b*) L. A. De Graff and B. Mozer, *J. Chem. Phys.*, 1971, **55**, 4967.

[114] G. C. Maitland and E. B. Smith, *Mol. Phys.*, 1972, **24**, 1185.

[115] E. Donth, *Physica*, 1970, **49**, 383.

[116] E. Donth, *Physica*, 1968, **38**, 357.

[117] D. W. Gough, G. C. Maitland, and E. B. Smith, *Mol. Phys.*, 1972, **24**, 151.

(2) the determination of bulk properties with greater accuracy and over wider temperature ranges than were previously available, particularly where this has revealed large errors in the existing well-established data;

(3) the measurement of new experimental data which are more directly related to $U(r)$ than these bulk properties, in particular the determination of high resolution scattering cross-sections and the spectroscopic detection of the vibrational and rotational energy levels associated with inert gas dimers;

(4) the use of increasingly sophisticated methods to analyse all the available data.

There will no doubt be developments in each of these areas in the future, leading to the gradual refinement of the potential energy functions. The recent work should, however, also provide a stimulus for increased activity in areas of more general chemical interest than the dilute inert gases. These include the study of dense gases and liquids (for real rather than model systems), mixtures, and the interactions between polyatomic molecules, and polar molecules.