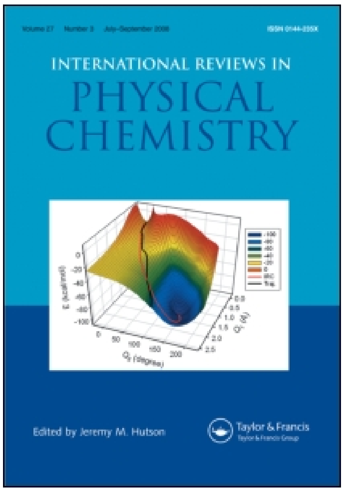

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Transport cross-sections for polyatomic gases

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Transport cross-sections for polyatomic gases

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The paper considers the current status of the study of the transport and related effective cross-sections, for dilute molecular gases, that emerge from the kinetic theory as a unifying formulation of a number of diverse phenomena. The discussion concentrates upon the effective cross-sections that occur in the description of transport and relaxation phenomena in dilute gases and gas mixtures both in the absence of magnetic or electric fields and in their presence. The relationships of these phenomena to others such as light scattering, nuclear magnetic resonance relaxation and spectroscopic phenomena through effective cross-sections is illustrated. It is argued that, in general, experimental information on the effective cross-sections is either abundant or could be made so with little technological development and an investment only in time and effort. Equally the kinetic theory of dilute polyatomic gases is now both developed and secure. Thus the stage has been set for the application of the development of new methods of evaluating the effective cross-sections from prescribed intermolecular potentials that has characterised the last decade. These particular developments are reviewed in some detail to establish a set of guidelines for their application. While the guidelines are based on a limited set of studies they indicate the most fruitful paths for further progress towards the goal of understanding the role of particular molecular collisions in determination of specific observables which is otherwise concealed by the complicated averaging processes of the kinetic theory of gases.

1. Introduction

The understanding of the relationship of the macroscopic properties of matter to the characteristics of individual molecules and of the interactions among them is the ultimate goal of statistical mechanics. For one particular state of matter the dilute gas, (where the term 'dilute' is intended to convey a restriction to states where the properties of gas depend only upon binary encounters of molecules) the relationship has now been established formally and rigorously through the kinetic theory of polyatomic gases. It has been recently summarized in a comprehensive monograph (McCourt, Beenakker, Kohler and Kuscer 1990). However, the formal establishment of the relationship has not, of itself, led to complete understanding because the complexity of the formulation is such as to obscure the physics of the fundamental processes that determine macroscopic behaviour and, at the same time, to render exact, practical calculations almost impossible even with the fastest computers available today. There remains, therefore, much to be done to uncover the underlying physics of many macroscopic observations and thereby provide the means to investigate intermolecular pair potentials for molecular systems. The intense activity in the field is illustrated in the papers contained within the proceedings of a recent NATO Advanced Research Workshop (Beenakker 1992).

The existence of the formal exact theory does however provide a unifying methodology for the approach to the problem. In particular, for those properties of the

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dilute gas that are associated with the transport of mass, linear and angular momentum and translational and internal energy, as well as a range of spectroscopic phenomena, the formal theory expresses all of the macroscopic observables in terms of *effective cross-sections.* The effective cross-sections include all the details of the dynamics of binary encounters in the gas with appropriate statistical averaging over energy and internal states. These cross-sections are therefore functionals of the intermolecular pair potential that describe a particular molecular interaction. In general, the effective cross-sections are functions only of temperature.

The investigation of these effective cross-sections is the subject of this review. We consider first the measurement of macroscopic properties, then we briefly review the kinetic theory of polyatomic gases and the relationship between the macroscopic observables and effective cross-sections as well as the relationships among different effective cross-sections. Finally, we discuss in some detail the methods of evaluating effective cross-sections from the prescribed intermolecular potentials.

The major emphasis of the review therefore echoes the remarks of J. J. M. Beenakker (Beenakker 1992) that the time for calculations of effective cross-sections has arrived. The speed and power of computers has now advanced sufficiently that, together with the culmination of a phase of development in approximate treatments of collisions of polyatomic systems, it should be possible to perform routine calculations of effective cross-sections for a given intermolecular potential. The progress in the recent past in this particular activity is therefore discussed in some detail both to elaborate what has been achieved and to formulate guidelines for performing the calculations in future. In particular, the need for systematic calculations specifically designed to improve our physical insight into the dominant microscopic processes that determine individual macroscopic observables is of paramount importance.

2. Experimental information

Modern techniques for the measurement of the transport and related properties of polyatomic gases have been comprehensively described elsewhere (Lambert 1977, Van Houten, Hermans and Beenakker 1985, Kestin and Wakeham 1988, McCourt *et al.* 1990, Wakeham, Nagashima and Sengers 1991). This review therefore makes no attempt to cover the same material again. Instead, a concise summary of the experimental information available is presented in such a way as to identify the best methods of measurement for different properties and the accuracy attainable directly in the macroscopic properties and subsequently in the derived effective cross-sections. This is intended to support the view that at present time the limiting factor in the study of the transport and related properties is their calculation *via* an established theory and their physical interpretation rather then experimentation.

2.1. *Measurements of field-free transport properties*

Measurements of the shear viscosity of gases in the absence of any external field are the most numerous and usually the most accurate among the transport properties. This situation has been achieved by the painstaking development and refinement of two types of instrument namely the oscillating disc viscometer (Kestin and Leidenfrost 1959, Vogel, Bastubbe and Rhode 1984) and the capillary viscometer (Hunter, Mattews and Smith 1989). For both instruments there exists a full working equation and, when extreme attention is paid to the details of the experimental set up, an accuracy of ±0·2% can be achieved. However, in routine measurements this level of accuracy is difficult to maintain and an accuracy of ±0·5 to ±1·0% is more realistic for the majority of gases

(Kestin and Wakeham 1988). The viscosity of a large number of simple polyatomic gases and their mixtures has been measured within the temperature range 100 K to 1500 K (Wakeham and Vesovic 1992).

The measurement of the thermal conductivity of gases turns out to be more difficult than that for the viscosity, mainly because of the presence of natural convection whenever a temperature gradient is created in a gas in the earth gravitational field. It was only with the advent of transient hot-wire instrument (Haarman 1973) that measurements with an accuracy comparable with that of the viscosity became possible. In this instrument the effects of natural convection are made negligible by performing the measurement during a short intial period smaller than the characteristic time for the onset of convection. Although a full working equation of the instrument does exist it is valid only at moderate and high pressures. Thus, the thermal conductivity in the dilute gas limit has to be obtained by extrapolation from moderate pressures (Kestin, Paul, Clifford and Wakeham 1980). For gases at supercritical temperature this introduces little error in the evaluation of the zero density value of the thermal conductivity. However, for gases at subcritical temperatures, the procedure is not reliable (Vogel, Bich and Nimz 1986, Bich and Vogel 1991) and can lead to a deterioration in accuracy. Although other methods for measuring the thermal conductivity exist (Kestin and Wakeham 1988) their accuracy is usually lower and the data obtained by them should be only considered when there are no results from transient hot-wire measurements. At the present time there are only a few sets of measurements performed by the transient hot-wire technique for polyatomic systems within the temperature range 300–500 K and their accuracy is typically ±0·5% to ±2% (Wakeham and Vesovic 1992).

No single technique has emerged as superior over a wide range of conditions for the measurements of the diffusion coefficients. Accurate measurements are possible with a two bulb instrument (Dunlop, Robjohns and Bignell 1987, Wakeham *et al.* 1991), but they are difficult to perform and time consuming, especially far removed from ambient temperature. Thus, only for a very few systems at, or near, room temperature is the diffusion coefficient known to better than ±0·5%. Even for monatomic systems, the spread of data obtained by different techniques exceeds ±3%.

Thermal diffusion is a process whereby the imposition of the temperature gradient in a gas mixture induces a partial separation of the components. Measurements of thermal diffusion coefficients are very difficult because the measured effect is very small. There exist some data (Wakeham *et al.* 1991), but the poor accuracy attained, exemplified by the inconsistencies among different authors, makes it unlikely that thermal diffusion will be useful in providing information on effective cross-sections.

The process of thermal transpiration is similar in nature to thermal diffusion, but here, the temperature gradient induces a pressure difference. Measurements of the thermal transpiration effect are also scarce. Unlike other data considered so far they suffer from the disadvantage that their interpretation is dependent on a model of the interaction of the molecules with the wall of the containing vessel. Nevertheless, they provide unique information on the translational part of the thermal conductivity and thus can be useful in evaluating, or at least checking the consistency of some effective cross-sections (Millat, Plantikow, Mathes and Nimz 1988).

Bulk viscosity is a phenomenon that, in the dilute state, only occurs in polyatomic gases. It is a measure of the efficiency of the transfer of energy between the translational and internal modes of motion of molecules. Although the measurements span several decades and a number of techniques have been employed, most notably sound absorption (Trusler 1991) and shock tube studies (Lambert 1977), the general level of accuracy is low compared with that of other transport properties. High accuracy has been only achieved when the relaxation processes involved exhibit a great difference in timescales. For instance, for rotational relaxation in H_2 or vibrational relaxation in N_2 at room temperatures. For systems where the rotational energy spacing is small or there are a number of vibrational modes the analysis of the results is fraught with difficulties and, in general, the relaxation times, and thus the bulk viscosity, can be in error as much as ±20 to ±30%.

For systems when one of the species is charged a number of additional phenomena can be studied (Mason and McDaniel 1988, Viehland 1992). In many ways the practical study of such systems has distinct advantages over the corresponding study of neutral systems because the presence of the charged particle provides an extra variable. The simplest transport process to study for ion–molecule systems is the mobility of the trace amount of ions in a dilute neutral gas. Such measurements can be performed by observing the drift velocity under the influence of an applied electrical field of ions of one species within a tube filled with neutral gas of a different species. The drift velocity is determined from the spectrum of arrival times of ions at a detector following release from a source for a particular values of the ratio of electrical field applied in the direction of the drift, E, and the number density of gas molecules, n. Studies of the arrival time spectrum over a range of values of E/n yield both the mobility of ions in the field and their diffusion coefficients. The experimental uncertainty associated with the ion mobility is generally of the order of ±1·5%.

2.2. *Measurements of field effects on transport properties*

The application of a magnetic field to a gas not at equilibrium leads to small but measurable effects on the transport properties known as Sentfleben–Beenakker effects (SBE). If the molecule possesses the dipole the presence of the electric field will produce a similar effect. The effects arise because a gradient of any macroscopic variable, such as temperature or velocity, causes a small preferential alignment of the molecules *via* collisions and thereby a partial polarization of the angular momentum vector of the molecules (spin-polarization). The application of the magnetic field causes precession of this vector at a frequency proportional to the applied field B. If the precession frequency is very high compared with the frequency of the collisions that are producing the polarization, which is proportional to the number density of molecules at the pressure P, then the polarization is entirely lost. The consequent change of the non-equlibrium distribution function reveals itself as a change in the corresponding transport property. As might be expected the effect depends on the relative orientation of the magnetic field and the applied macroscopic gradient producing a number of different observables. In general, the field can produce effects on transport properties parallel to the field or the applied gradient (longitudinal) or effects perpendicular to both (transverse). In all cases the magnitude of the effect depends upon (B/P), but while the longitudinal effect exhibits a saturation behaviour for large values of (B/P) the transverse effect goes through a maximum and is zero at large (B/P) values.

The overall effect on transport properties induced by the Sentfleben–Beenakker effect is small, of the order of ±1–2% or less. Thus the experimental measurements have to rely upon 'null methods' for the accurate determination of SBE. A number of such methods has been developed (van Houten *et al.* 1985, McCourt *et al.* 1990, Hermans 1992) and they all have some common characteristics. All the measurements are performed at very low pressures of the order of few Pascals and with fields of up to

2 Teslas. At such low pressures Knusden effects can become important and have to be taken into account. Most of the viscomagnetic SBE have been measured using a capillary viscometer apparatus while for thermomagnetic SBE parallel plate and sometimes a hot wire method have been applied. Data for numerous polyatomic systems and their mixtures exist (van Houten *et al.* 1985, McCourt *et al.* 1990, Hermans 1992) mainly between 77 K and room temperature. The accuracy of the effective cross-sections obtained from these data is not simply related to the accuracy of the direct measurements as it is for some field free transport properties. Hence, although some experiments are accurate to within few per cent, the best available effective cross-sections have an uncertainty of ±5–10% (Hermans 1992).

There is a further series of phenomena which arise directly from the non-equilibrium polarization of the velocity and angular momementum (McCourt *et al.* 1990). Their measurement can provide additional information on some of the effective cross-sections that play a part in the SBE. We shall briefly discuss one such a phenomena, namely flow birefringence. The optical properties of the system depend on the molecular polarizability which in turn is determined by the molecular orientation relative to an electric field. In non-equilibrium polyatomic gases the alignment of molecules due to collisions modifies the polarizability thus rendering the optical properties of the system anisotropic (Waldmann 1958). Flow birefringence can be detected by measuring the phase difference between two polarized light beams using a Couette flow apparatus (McCourt *et al.* 1990). Such studies have been carried for a number of gases as a function of temperature (van Houten and Beenakker 1985, van Houten *et al.* 1985) and the accuracy of the measured flow birefringence coefficient, which measures the magnitude of the effect, is estimated at ±5–10%.

2.3. *Spectroscopic and optical phenomena*

There are a number of phenomena describing the relaxation of the gas towards equilibrium following a disturbance caused by internal fluctuations (McCourt *et al.* 1990, McCaffery 1992). They can be broadly divided into phenomena describing the collisional broadening and shifting of the spectrum of scattered light, such as the broadening of the depolarized Rayleigh line and phenomena caused by the interaction of radiation with collisional processes, such as the nuclear magnetic relaxation. In general, the effective cross-sections involved in the descriptions of these processes are not directly related to those governing transport phenomena. Thus, they are, strictly speaking, outside the scope of this review and the reader is referred to van Houten *et al.* (1985), McCourt *et al.* (1990) and McCaffery (1992). However, we shall briefly review the broadening of the Depolarized Rayleigh line (DPR) for which a wealth of experimental information exists and which has provided valuable insight into the effective cross-sections governing the viscomagnetic effects.

The width of the depolarized component of Rayleigh scattering is related to the angular momentum fluctuations in a polyatomic gas. When the molecules undergo collisions the fluctuations are affected in a way which results in the broadening of DPR line (Knaap and Lallemand 1975, McCourt *et al.* 1990). Measurements of the scattered light spectrum have been performed (Keijser, Van den Hout and Knaap 1972, Keijser, Van den Hout, De Groot and Knaap 1974) and the analysis of the Fourier transform of the spectrum then yielded the effective cross-section. The working equations are based on single relaxation times using a Lorentzian lineshape and corrections have to be made if only a few rotational states are accessible. However, if the number of the rotational states is large the departure from the Lorentzian behaviour is small, since the effective relaxation time dominates the process. Thus the accuracy depends to the certain extent on the complexity of the molecule. In general an uncertainty of ± 5–10% is to be expected.

3. Theoretical formulation

The kinetic theory of dilute monatomic gases and gas mixtures was developed at the turn of the century and the resulting relationships between the transport properties of the gas and the intermolecular potential are well researched (Hirschfelder, Curtiss and Bird 1954, Chapman and Cowling 1970, Ferziger and Kaper 1972, Maitland, Rigby, Smith and Wakeham 1981). At present, the calculations of transport properties can be performed on a routine basis for any spherical pair potential with great ease. The situation for polyatomic molecules is very different for a number of reasons.

First, a polyatomic molecule possesses a number of internal energy states. Thus, there is a possibility that a collision between two molecules results in the transfer of energy between the translational and internal modes of motion so that both elastic and inelastic contributions have to be included in the analysis. Furthermore, the existence of the internal modes of motion gives rise to a series of new phenomena. For example, following a change of thermodynamic state equilibrium between translational and rotational or vibrational energy is not established immediately which gives rise to a new macroscopic observable, namely the bulk viscosity (section 2.1).

Another aspect of the existence of the internal states is the rotational angular momentum vector whose near equilibrium distribution has to be taken into account (Kagan and Maksimov 1962). Thus, the non-equilibrium distribution function of a polyatomic gas is a function not only of time, position and molecular velocity but also of the rotational angular momentum (McCourt *et al.* 1990). Furthermore, the non-equilibrium polarization in the angular momentum is coupled to the velocity polarization (McCourth *et al.* 1990). Polarization of the angular momentum in temperature or velocity fields gives rise to other phenomena which do not exist in monatomic gases, in particular to the transport property field effects (section 2.2).

Second, in contrast to the monatomic case the intermolecular potential is no longer only a function of the separation but also depends upon the relative orientation of two molecules during the collision.

All of these effects have to be taken into account when formulating the kinetic theory of dilute polyatomic gases. This has been done using both classical and quantum mechanical formalisms (Waldmann 1957, Snider 1960, Curtiss 1981, Curtiss and Tonsager 1985, McCourt *et al.* 1990). For the purposes of this review the exact form of theory is not important, but it is useful to record that the solution has many parallels with the development of the monatomic kinetic theory (McCourt *et al.* 1990). Thus, for near equilibrium phenomena the Boltzmann-like equation for the single-molecule distribution function is linearized and, because the solution cannot be obtained in closed form, a perturbation expansion around the equilibrium solution is used. The resulting linear equation is solved by expanding the unknown solution in terms of a set of orthonormal basis function. The basis functions depend generally upon the products of different powers of the reduced molecular velocity $\mathbf{W}$ and the molecular rotational angular momentum, $\mathbf{j}$ (McCourt *et al.* 1990). The order of the approximation to the solution depends upon the number of terms taken in the expansion. Based on experience for monatomic systems, the lowest-order approximation is expected to be sufficiently accurate to describe adequately most of the transport properties of polyatomic gases.

As for the monatomic case the essential information about the processes contributing to the macroscopic observables is given by the reduced matrix elements of the linearized collision operator. They can be simply related to quantities called effective cross sections (McCourt *et al.* 1990, McCourt 1992a). The effective cross-sections

$$\mathfrak{S}\begin{pmatrix} p\,q\,s\,t & A \\ p'q's't' & B \end{pmatrix}_{12},$$

represent the collisional coupling between microscopic tensor polarizations which depend in general upon the reduced molecular velocity $\mathbf{W}$ and the rotational angular momentum $\mathbf{j}$. The indices p, p' and q, q' denote the tensorial ranks in $\mathbf{W}$ and $\mathbf{j}$ respectively, while s, s' and t, t' denote the highest powers in W^2 and j^2, where $W=|\mathbf{W}|$ and $j=|\mathbf{j}|$, respectively that occur in the microscopic polarization (McCourt *et al.* 1990). The indices A, B and 1, 2 separately refer to two molecules partaking in the collision. To avoid unnecessary labelling the notation for the effective cross-sections for interactions of like molecules is condensed to

$$\mathfrak{S}\begin{pmatrix} p\,q\,s\,t \\ p'q's't' \end{pmatrix},$$

in the rest of the paper. Cross-sections for which primed and unprimed indices are different are termed production or coupling cross-sections, since they describe the effects of coupling of different polarizations. If the unprimed and primed indices are the same, the notation for the effective cross-section is further condensed to $\mathfrak{S}(pqst)$. Such cross-sections are known as relaxation cross-sections since they describe the decay of various $(pqst)$ polarizations.

Although the kinetic theory of polyatomic gases has been primarily developed to describe the transport properties the definition of the effective cross-section is such that it encompasses a much wider range of phenomena. In particular, relaxation and optical phenomena such as vibrational and rotational relaxation in the gas, pressure broadening of microwave, infrared, Raman and depolarized Rayleigh lines, gas phase nuclear magnetic resonance (NMR) and light birefringence can all be described in terms of the effective cross-sections. Furthermore, other processes such as sub-Doppler or optical relaxation experiments can be described with cross sections (McCaffery 1992) which can be related to the effective cross-sections arising out of the kinetic theory of polyatomic gases (Liu and Dickinson 1990b). The effective cross-sections thus provided a unifying description of a number of phenomena. There is therefore, in principle, the possibility that different macroscopic observables can be related to each other through an analysis of the appropriate effective cross-sections. In turn, the effective cross-sections should provide some insight into microscopic processes. Moreover, the effective cross-sections provide the opportunity of testing the internal consistency among different macroscopic properties and thereby the reliability of experiments. Hence, it is important to identify the independent effective cross-sections, to establish general relationships among them and to consider how can they be obtained from measurements of experimental observables.

3.1. *Macroscopic observables and effective cross-sections*

In this review we concentrate attention upon those effective cross-sections that govern processes relating to the transport of mass, momentum and energy in gases.

For a pure gas characterised by a single intermolecular pair potential, there are a number of exact relationships between the cross-sections which can be derived completely generally. For example, the effective cross-sections $\mathfrak{S}(0000)$ and $\mathfrak{S}(1000)$ can be shown to be identically zero using the conservation of mass and momentum. It also follows directly from conservation of energy that there is a set of dependent cross-sections related to each other by

$$\mathfrak{S}\begin{pmatrix}0010\\ pqst\end{pmatrix}=-\left(\frac{5}{3}\right)^{1/2}r\mathfrak{S}\begin{pmatrix}0001\\ pqst\end{pmatrix},\tag{1}$$

where $r^2=2C_{\text{int}}/5k_B$, C_{int} is the molecular isochoric heat capacity and k_B is Boltzmann's constant. Also, relationships involving cross-sections describing independent phenomena can be obtained. For example, the cross-section governing the bulk viscosity, $\mathfrak{S}(0001)$ and those describing the translational and internal energy coupling are related by

$$\mathfrak{S}(0001)=-\frac{6}{5r}\mathfrak{S}\begin{pmatrix}1010\\ 1001\end{pmatrix}=\frac{3}{5r^2}\mathfrak{S}(0010).\tag{2}$$

Similarly, there is a relationship between the cross-section for the translational energy flux $\mathfrak{S}(1010)$ and the bulk, $\mathfrak{S}(0001)$ and shear, $\mathfrak{S}(2000)$ viscosity cross-sections

$$\mathfrak{S}(1010)=\frac{2}{3}\mathfrak{S}(2000)+\frac{25}{18}r^2\mathfrak{S}(0001).\tag{3}$$

For the production cross-sections governing the influence of field effects on transport properties there is a relationship

$$\mathfrak{S}\begin{pmatrix}2000\\ 0200\end{pmatrix}=5^{1/2}\mathfrak{S}\begin{pmatrix}1200\\ 1010\end{pmatrix}.\tag{4}$$

A number of exact relationships (McCourt *et al.* 1990) also exist between the cross-sections describing similar processes occurring in mixtures, but they will not be dealt with here. For the purposes of this work it is sufficient to show that some of the phenomena are interrelated and that information on one can be obtained from the other as equations (1–4) show. In addition to exact relationships there are a number of approximate relationships between the cross-sections which have been obtained using the distorted wave Born approximation to describe the encounter between the molecules (Snider 1974). The accuracy of these approximate relationships is not presently known very well so that computational test must be conducted before any conclusions about their usefulness can be made.

In order to obtain experimental information on the behaviour of the effective cross-sections, it is important to describe how they are related to the macroscopic observables and how easily the necessary information can be extracted.

3.2. *Field-free transport properties*

In the lowest-order approximation of the kinetic theory the field free viscosity of a pure gas, $\eta(T)$ is given by

$$\eta(T)=\frac{k_BT}{\bar{c}_r}\frac{1}{\mathfrak{S}(2000)},\tag{5}$$

where the average relative thermal velocity, $\bar{c}_r$ is

$$\bar{c}_r=4(k_BT/\pi m)^{1/2}.\tag{6}$$

T is the temperature and m the mass of the molecule. Hence the effective cross-section $\mathfrak{S}(2000)$ can easily be obtained from the experimental measurements of viscosity. The thermal conductivity, on the other hand, being associated with the transport of energy through the gas, is greatly affected by the presence of internal degrees of freedom. Using the two flux approach and the traditional expansion vectors (Mason and Monchick 1962, McCourt *et al.* 1990) the thermal conductivity is in the lowest-order approximation given as the sum of two contributions

$$\lambda(T)=\lambda_{\mathrm{tr}}(T)+\lambda_{\mathrm{int}}(T), \tag{7}$$

where the translational part is

$$\lambda_{\mathrm{tr}}=\frac{5k_{\mathrm{B}}^2T}{2m\bar{c}_{\mathrm{r}}}\left[\frac{\mathfrak{S}(1001)-r\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix}}{\mathfrak{S}(1010)\mathfrak{S}(1001)-\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix}^2}\right], \tag{8}$$

and the internal part is

$$\lambda_{\mathrm{int}}=\frac{5k_{\mathrm{B}}^2T}{2m\bar{c}_{\mathrm{r}}}\left[\frac{r^2\mathfrak{S}(1010)-r\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix}}{\mathfrak{S}(1010)\mathfrak{S}(1001)-\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix}^2}\right]. \tag{9}$$

The expressions (8, 9) contain three cross-sections, two of which

$$\mathfrak{S}(1010) \quad \text{and} \quad \mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix},$$

can be eliminated using equation (3) and equation (2) in favour of other, experimentally accessible, cross-sections $\mathfrak{S}(2000)$ and $\mathfrak{S}(0001)$. The first one can be obtained from the shear viscosity measurements while the second is related to the bulk viscosity, $\eta_{\mathrm{V}}(T)$, by

$$\eta_{\mathrm{V}}(T)=\frac{k_{\mathrm{B}}C_{\mathrm{int}}}{C_{\mathrm{v}}^2}\,\frac{k_{\mathrm{B}}T}{\bar{c}_{\mathrm{r}}\mathfrak{S}(0001)}, \tag{10}$$

where C_{v} is the isochoric heat capacity. There are now two ways to proceed to obtain a set of consistent effective cross-sections for a given molecule (Millat and Wakeham 1989, Millat, Vesovic and Wakeham 1989). For this purpose one can either use the heat capacity, viscosity, thermal conductivity and bulk viscosity measurements (Millat, Mustafa, Ross, Wakeham and Zalaf 1987) or instead of the bulk viscosity one can, if they are available, use thermal transpiration data which are a direct measure of the translational part of the thermal conductivity (Millat *et al.* 1988). Such an analysis, supplemented by including the effects of spin polarization on the thermal conductivity, has been performed for a number of gases (Millat and Wakeham 1989, Millat *et al.* 1989) to produce a consistent set of effective cross-sections relating to the field free transport properties. An analysis of this kind provides one example of a check on the internal consistency of experimental data.

A different measure of internal energy relaxation can be established by defining the diffusion coefficient for internal energy (Mason and Monchick 1962, Maitland *et al.* 1981) in terms of the cross-section $\mathfrak{S}(1001)$

$$D_{\mathrm{int}}=\frac{k_{\mathrm{B}}T}{nm\bar{c}_{\mathrm{r}}}\,\frac{1}{[\mathfrak{S}(1001)-0{\cdot}5\mathfrak{S}(0001)]}, \tag{11}$$

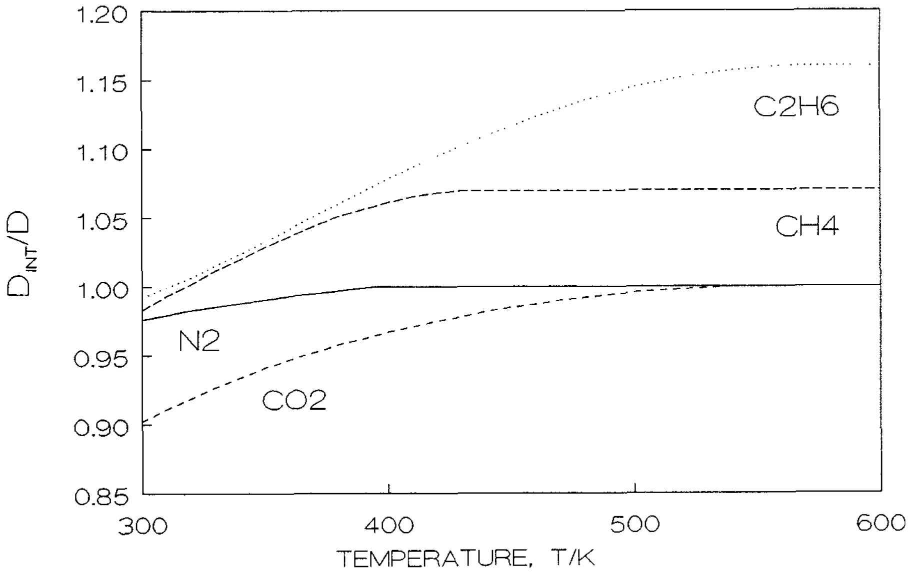

Figure 1. Ratio of D_{int}/D for several gases.

where n is the number density. The ratio of the internal energy diffusion coefficient to that of the self diffusion coefficient, D_{int}/D, can be then related to the viscosity through the kinetic theory and is given by

$$\frac{D_{\text{int}}}{D}=\frac{5}{6A^*}\frac{nmD_{\text{int}}}{\eta}, \tag{12}$$

where A^* is cross-section ratio (Maitland *et al.* 1981) weakly dependent on the intermolecular potential. Figure 1 shows the behaviour of this ratio as a function of temperature for the number of gases for which a set of consistent effective cross-sections has been obtained. Values of D_{int}/D smaller than unity imply that the internal energy transport through the gas is slower than that of the molecules themselves. For nitrogen and carbon dioxide which behave as rigid rotors at these temperatures D_{int}/D reaches unity asymptotically at high temperatures whereas for the other two molecules, where the vibrational degrees of freedom are important, the asymptotic value lies above unity. Although there is a theoretical justification based on the distorted wave Born approximation (Moraal and Snider 1971) for the rigid rotor result there is so far no explanation for the behaviour of methane and ethane systems.

Recently, an alternative expression for the thermal conductivity of a pure gas has been derived (Thijsse, 't Hoft, Coombe, Knaap and Beenakker 1979). It is based on a total flux approach using a different set of the expansion vectors in the kinetic theory solution of the Boltzmann-like equation and results in the following expression for the thermal conductivity

$$\lambda(T)=\frac{5k_B^2T}{2m\bar{c}_r}\frac{(1+r^2)}{\mathfrak{S}(10E)}\frac{1}{F_T}, \tag{13}$$

where F_T is given by

$$F_T=1-\frac{\mathfrak{S}\begin{pmatrix}10E\\10D\end{pmatrix}^2}{\mathfrak{S}(10E)\mathfrak{S}(10D)}. \tag{14}$$

This expression is equivalent to the one given in equations (7–9) and hence there exist (Thijsse *et al.* 1979, McCourt *et al.* 1990) linear relationships between the cross-sections

$$\mathfrak{S}(10E),\ \mathfrak{S}(10D),\ \mathfrak{S}\begin{pmatrix}10E\\10D\end{pmatrix}\quad\text{and}\quad\mathfrak{S}(1010),\ \mathfrak{S}(1001),\ \mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix}.$$

These relationships made it possible to evaluate the F_T term together with the individual cross-section from a set of consistent experimental data. The results (Millat *et al.* 1989, Wakeham and Vesovic 1992) indicate that for all practical purposes F_T can be taken as unity. Hence, just as for the monatomic systems, only one cross-section is needed to describe the thermal conductivity with the difference that in the case of polyatomic molecules the cross-section $\mathfrak{S}(10E)$ incorporates both the effects of the translational and internal energy flux.

3.3. *Field effects on transport properties*

The analysis of SBE data provides information on a large number of effective cross-sections. As we have seen before the SBE depends on the interplay between the precessional motion characterised by the frequency ω which is proportional to the magnetic field strength B and the collisional change of the polarization characterized by a relaxation time τ inversely proportional to pressure P. The experimental measurements of the SBE are always presented as functions of the B/P ratio and hence it is useful to introduce the precession angle ξ for a given polarization as the product of precessional frequency ω and the relaxation time τ.

So far the theoretical studies have been limited to systems involving linear and symmetric top molecules (McCourt *et al.* 1990) and since the analysis for both systems follow similar route we shall discuss only the analysis of SBE data for linear molecules.

The viscomagnetic effects of the linear molecules are relatively straightforward to analyse. The precession angle, ξ, for the leading polarization (0200), is related to the strength of the magnetic field, B by

$$\xi=\omega\tau=\frac{|\mathbf{g}|\mu_{\mathrm{N}}k_{\mathrm{B}}T}{\hbar\bar{c}_{\mathrm{r}}\mathfrak{S}(0200)}\frac{B}{P},\tag{15}$$

where μ_{N} is the nuclear magneton, and the $\mathbf{g}$ is the rotational $\mathbf{g}$-tensor (McCourt *et al.* 1990, Hermans 1992). It can be shown (McCourt *et al.* 1990) that at the value of B/P for which the precession angle ξ equals unity the longitudinal change in viscosity reaches half of its saturation value while the transverse effect attains its maximum value. Hence, the effective cross-section $\mathfrak{S}(0200)$ can be determined from experimental data by determining, for example, the strength of the magnetic field at which the decrease in the longitudinal shear viscosity coefficient attains half of its saturation value. The magnitude of the observed viscosity change, ψ, is given by

$$\psi=\frac{\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix}^2}{\mathfrak{S}(2000)\mathfrak{S}(0200)}.\tag{16}$$

Since both $\mathfrak{S}(2000)$ and $\mathfrak{S}(0200)$ are experimentally accessible, evaluation of the magnitude of the production cross-section

$$\left|\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix}\right|,$$

is easy. However the sign has to be determined from some other experiment. This can be done by measuring the flow birefringence coefficient (Van Houten and Beenakker 1985) which is proportional to the cross-section

$$\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix},$$

so the sign can be determined.

For symmetric top molecules a slightly more complicated analysis of the experimental data is required. Such an analysis has been performed and the values of a number of effective cross-sections are available (van Houten *et al.* 1985, Hermans 1992).

The analysis of the thermal conductivity SBE is more complicated, by analogy with the field free thermal conductivity, because of the larger number of cross-sections that describe this effect. Nevertheless, by using the exact relationships, obtaining some cross-sections from other experimental data and using both the total and two flux approach it is possible to obtain all of the effective cross-sections of interest (McCourt *et al.* 1990). It is worth pointing out that, as for viscomagnetic phenomena, the sign of the production cross-sections has to be determined independently.

Thus, in the lowest-order approximation, it is possible to derive consistent values of effective cross-sections from experimentally measured properties. The higher-order approximations for polyatomic gases have been worked out for some of the cases (Maitland, Mustafa and Wakeham 1983, McCourt *et al.* 1990). There have been few analyses of experimental data using these expresssions. Although for the field free transport properties some of the data has been analysed using the monatomic higher-order correction factors, the influence of the higher-order terms can only be assessed computationally and will be discussed briefly later on.

The effective cross-section for a particular polarization can be viewed as conveying information about the processes that contribute to the macroscopic observable in question. It is useful to examine some of the experimental trends observed between cross-sections for a number of different molecules. In order to compare different systems it is important to eliminate system dependent effects. One of the ways of achieving this is to introduce a dimensionless scaled cross-section $\mathfrak{S}^*$ (Thijsse 1978, Thijsse *et al.* 1979, McCourt *et al.* 1990) defined by

$$\mathfrak{S}^* = \frac{\mathfrak{S}}{(\alpha/\epsilon_0)^{2/3}}, \tag{17}$$

where α is the average polarizability and ϵ_0 is the permitivity of free space. A very thorough analysis of experimental trends using this concept has already been presented (Thijsse 1978, Thijsse *et al.* 1979, McCourt *et al.* 1990) so that, in this review, we shall limit our discussion to summarizing some of the findings for non-polar and weakly polar molecules.

For the systems studied so far the value of $\mathfrak{S}^*(2000)$ is approximately constant, of the order of $4{\cdot}6 \pm 0{\cdot}5$. The $\mathfrak{S}^*(0200)$ cross-section has been found to be generally smaller although of the same magnitude. The production cross-section

$$\mathfrak{S}^*\begin{pmatrix}2000\\0200\end{pmatrix},$$

on the other hand, is typically an order of magnitude smaller than $\mathfrak{S}^*(2000)$. The rotational relaxation cross-section, $\mathfrak{S}^*(0001)$ is, for most systems smaller, than

$\mathfrak{S}^*(0200)$. The difference can reach an order of magnitude for molecules with small moments of inertia or for molecules whose intermolecular potentials are weakly anisotropic.

Figure 2 shows the observed correlation between

$$\mathfrak{S}^*\begin{pmatrix}2000\\0200\end{pmatrix} \quad \text{and} \quad \mathfrak{S}^*(0200),$$

cross-sections at 300 K (McCourt *et al.* 1990). Most of the molecules seem to fall on a straight line with the exception of molecules with a large rotational level splitting (small moments of inertia) which seem to fall below the line. The intuitive reason for this behaviour is not obvious. It is hoped that advances in computation will throw some light on the dominant processes affecting each cross-section and thus enable this and similar trends (Thijsse 1978, McCourt *et al.* 1990) to be understood.

3.4. *Transport properties of mixtures*

For binary mixtures of gases the kinetic theory is also well developed, but because each binary interaction contributes roughly the same number of the cross-sections to the property the accuracy with which any particular effective cross-sections can be determined from the experimental data is decreased. For instance, the expression for the field free binary mixture viscosity in the lowest approximation, is given by

$$\eta_{\text{mix}} = -\begin{vmatrix} H_{11} & H_{12} & x_1 \\ H_{21} & H_{22} & x_2 \\ x_1 & x_2 & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{vmatrix}, \tag{18}$$

$$H_{ii} = \frac{x_i^2}{\eta_{ii}} + \frac{2x_ix_j}{\eta_{ij}} y_i^2 y_j^2 \left(\frac{5}{3A_{ij}^*} + \frac{m_j}{m_i}\right), \tag{19}$$

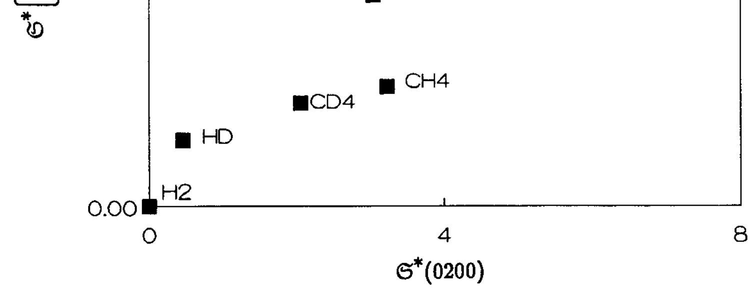

Figure 2. Correlation between

$$\mathfrak{S}^*\begin{pmatrix}2000\\0200\end{pmatrix} \quad \text{and} \quad \mathfrak{S}^*(0200),$$

for several gases.

and for $i \neq j$

$$H_{ij} = -\frac{2x_i x_j}{\eta_{ij}} y_i^2 y_j^2 \left(\frac{5}{3A_{ij}^*} - 1\right), \tag{20}$$

where x_i, m_i and y_i^2 are the mole fraction, the molecular mass and the molecular mass ratio, $y_i^2 = m_i/(m_1 + m_2)$, respectively of species i while η_{ii} is the viscosity of the pure species i. The interaction viscosity, which arises as the result of the unlike interactions, is given by

$$\eta_{ij} = \frac{k_B T}{\bar{c}_r} \frac{2y_2^4}{\mathfrak{S}_\eta^{(2)}}. \tag{21}$$

Hence, to evaluate the single cross-section characteristic of the unlike interaction, $\mathfrak{S}_\eta^{(2)}$, one needs much more experimental information than was necessary for the pure gas. The situation for the other transport properties is either similar or worse.

4. Calculation of effective cross-sections

The foregoing discussion makes it clear that the effective cross-sections have an essential role in the description of near-equilibrium phenomena in gases. Thus, the evaluation of these cross-sections for prescribed intermolecular pair potential has in the last fifteen years, become a dominant theme in the study of such phenomena. There are two main motivations for such studies. On the one hand they provide the means to probe the ability of a particular intermolecular potential to describe a series of the macroscopic properties and thereby improve our knowledge of intermolecular potentials. On the other hand such calculations can improve our insight into those microscopic processes that contribute most of particular macroscopic observables. For example, it may be that certain phenomena are dominated by the occurrence of a particular kind of a molecular collision process or that the corresponding macroscopic observable is affected rather strongly by specific changes in anisotropy of the intermolecular potential in a local region of molecular separations. That such simplifications should arise from the evident complexity of the multitude of collisional processes that occur in a dilute gas is indicated by the experimental observation of some simple relationships among cross-sections that are not apparent from the formal theory. It is also possible that other such relationships exist, as yet undetected, all of which would permit the evaluation of some macroscopic observables from others. Such relationships and, indeed, the role of the intermolecular potential in determining the effective cross-sections constitute the underlying physics of the subject of near equilibrium phenomena, but the algebraic complexity of the topic currently inhibits an understanding and hence exploitation of them.

The same complexity makes the computation of the cross-sections time consuming and expensive. Thus, initial studies concentrated upon simple molecular models such as rough spheres and spherocylinders where progress could be made analytically or with a small amount of computational effort. Unfortunately, such simple models have pathological features, that are not typical of real molecular systems, which render them useless for detailed analysis. The computation of effective cross-sections for realistic molecular models is therefore unavoidable and the development of accurate, reliable, fast and efficient means of accomplishing the calculations has been the preoccupation in the field for a number of years. This period of development of the methodology is now coming to an end and the advent of very fast computers has now paved the way for implementation. Consequently the remainder of this section is devoted to a review of the developmental phase culminating in a summary of the current 'best practice' and of the results to date.

4.1. *Methods of computation*

The kinetic theory of polyatomic gases is based on a quantum mechanical description of the gas, so it would be most natural to evaluate the effective cross-sections using a full quantum mechanical formalism. This implies that a complete calculation of the scattering of two molecules is necessary. For a number of simple cases, namely atom–diatom and diatom–diatom encounters, the scattering problem has been solved formally and the results can be expressed in terms of scattering amplitude matrices, **S** (Arthurs and Dalgarno 1960, Takayanagi 1965). These **S** matrices contain all the dynamical information about the binary encounter and each effective cross-section can be related to them (McCourt *et al.* 1990). For the same, relatively simple cases of atom–diatom and diatom–diatom collisions all of the required expressions are available. For the purposes of further discussion here it is useful to present the relationship linking the atom–rigid rotor effective cross-section, $\mathfrak{S}_\eta^{(2)}$, governing the interaction viscosity in an atom–diatom gas mixture to the **S** matrix

$$\mathfrak{S}_\eta^{(2)}=\frac{4\,y_2^4}{15Z_{\mathrm{rot}}}\int_0^\infty \mathrm{d}X\,X^3\exp(-X)\bar{\sigma}_\eta^{(2)}, \tag{22}$$

$$\bar{\sigma}_\eta^{(2)}=\sum_j (E_k/E)^2\sum_{j'}(E'_k/E)\sigma_\eta^{(2)}(jj'|E), \tag{23}$$

$$\begin{aligned}\sigma_\eta^{(2)}(jj'|E)=\frac{\pi}{k^2}&\sum_{J_1J_2}\sum_{l_1l'_1}\sum_{l_2l'_2}(-)^{j+j'}(2J_1+1)(2J_2+1)\\&\times[(2l_1+1)(2l'_1+1)(2l_2+1)(2l'_2+1)]^{1/2}\\&\times\begin{pmatrix}l_2 2 l_1\\000\end{pmatrix}\begin{pmatrix}l'_2 2 l'_1\\000\end{pmatrix}\begin{Bmatrix}J_1\,l_1\,j\\l_2\,J_2\,2\end{Bmatrix}\begin{Bmatrix}J_1\,l'_1\,j'\\l'_2\,J_2\,2\end{Bmatrix}\\&\times[\delta_{jj'}\delta_{l_1l'_1}\delta_{l_2l'_2}-S^{J_2}_{j'l'_2\,jl_2}(E)S^{J_1*}_{j'l'_1\,jl_1}(E)],\end{aligned} \tag{24}$$

where E is the total energy of the system, E_k is the relative kinetic energy of the colliding pair, $X=E/k_{\mathrm{B}}T$, Z_{rot} is the rotational partition function, l, j and J are the orbital, rotational and the total angular momentum quantum numbers, k is the wave number while the bracketed quanties $(\because)$ and $\{\because\}$ are $3-j$ and $6-j$ coefficients respectively (Brink and Satchler 1975).

Equations (22–24) embody all the statistical information about the binary encounters which determine the interaction viscosity cross-section. The result is presented here in the total-J representation (Liu, McCourt, Fitz and Kouri 1979) which is particularly suited for quantum mechanical calculations, having advantages for both exact dynamical calculations and approximate procedures. It has been found useful to perform all the computations at constant total energy for two reasons. The first reason is simply one of convenience because the **S** matrices are always evaluated at specific total energy. The second reason is that quantum calculations performed in this way can be compared with classical results directly without the use of any approximate quantization procedure such as 'binning'.

The principal disadvantage of the full quantum approach is the enormity of the actual calculation. In order to obtain the S matrices one has to solve a set of N close coupled equations, where N is the number of coupled channels (Bernstein 1979, Hutson and Green 1985). For atom–rigid rotor, at each total energy, there are usually $(j_{\max}+1)^2$ channels where $j_{\max}$ is the highest rotor state included in the basis set used to expand the scattering function (Bernstein 1979). Although there exist computer algorithms which can efficiently tackle this problem (Hutson and Green 1985), the computer time increases approximately with N^3 and, very quickly, the solution becomes computationally too expensive and time consuming. Moreover, the evaluation of the cross-section itself is computational intensive. For example, the non-zero $6-j$ coefficients for the case of viscosity are those for which J_2 can take values between J_1-2 and J_1+2. The structure of equation (24) implies that in each summation two S matrices, usually with different total angular momentum quantum numbers, will be simultaneously sampled. Thus for optimum speed of execution of the summation at least five S matrices should reside in the computer memory simultaneously. For calculations involving more than just five or six open channels this leads either to large computer memory requirements or to a very fast and efficient method of exchanging the S matrices in computer memory (McCourt, Vesovic, Wakeham, Dickinson and Mustafa 1991). Even so, as the energy of the encounter increases and with it the number of open channels, the time spent evaluating equations (22–24) rapidly becomes comparable to the time required for solving the scattering problem. Thus, even future increases in the execution speed of computers are soon overtaken by even a modest increase in N. Furthermore, the intricate interdependence among the terms of equations (23, 24) and the coupled structure of the equations describing scattering process are such that parallel processing does not alleviate the situation. Not surprisingly, therefore, close-coupled calculations (CC) have only been performed for hydrogen isotopes and encounters of He with small rigid rotors (McCourt *et al.* 1990) and it seems that for the foreseeable future the evaluation of effective cross-sections by fully quantum mechanical techniques will remain computationally impossible for heavier molecules.

As a result, the search for approximate methods which could reduce the number of coupled channels has been an enduring feature of the kinetic theory in the last decade. Two dynamical approximations have been most commonly used. One of them, the centrifugal sudden approximation (CSA), is based on replacing the angular momentum operator $\mathbf{L}^2$ in the close coupled equations by its eigenvalue $\bar{l}(\bar{l}+1)$, where $\bar{l}$ is an arbitrary orbital momentum quantum number which needs to be specified (Bernstein 1979). The substitution is based upon the hypothesis that for large relative kinetic energies the features of the centrifugal potential are unimportant. This replacement partially uncouples the close coupled equations and allows the S matrices to be evaluated much more easily. Particular choices of the parameter $\bar{l}$ also lead to a considerable simplification of the formulae for the effective cross-sections. For example for $\bar{l}=l$, the initial quantum number, equation (24) simplifies to

$$\sigma_\eta^{(2)}(jj'|E)=\frac{\pi}{k^2}\sum_{l_1l_2}\sum_{\lambda}(2l_1+1)(2l_2+1)\begin{pmatrix}l_2 2 l_1\\000\end{pmatrix}^2 \times[\delta_{jj'}-S_{j'jl_2\lambda}(E)S^*_{j'jl_1\lambda}(E)], \tag{25}$$

where $S_{j'jl_2\lambda}$ is the CS approximation to the S^J matrix element (Bernstein 1979, Liu *et al.* 1979). The averaging over the states is now much simpler and computationally more rapidly carried out. Different choices of parameter $\bar{l}$ lead to different CSA expressions. The three most common choices are the initial value, l, the final value, l', and the average value, $(l+l')/2$. While the first two choices simplify the calculations considerably they suffer from not preserving the time reversal symmetry (Kouri, Heil and Shimoni 1976, Bernstein 1979). This drawback can manifest itself in giving the erroneous values for some of the cross-sections. On the other hand using the average l labelling leads to the more complicated formulation of equation (25). Nevertheless it is still computationally cheaper than the full CC calculation, since the computational effort involved in the dynamical calculations to obtain CSA S matrix is similar for all $\bar{l}$ choices.

Owing to its physical basis the CSA successfully describes encounters for which the kinetic energies are considerably larger than the height of the centrifugal barrier. However, because the effective cross-sections are weighted averages over enormous number of such encounters in which the importance of this particular encounter is not known *a priori*, it is difficult to say for what effective cross-sections CSA is going to work well. Thus, insight into this problem can only be obtained by comparing effective cross-sections calculated with CS approximation for different anisotropic potentials with the equivalent CC calculations and is therefore inhibited by a lack of the latter.

A further simplification of the CC method can be achieved if CSA is combined with an energy sudden (ES) approximation. The operator $\mathbf{j}^2$ is then replaced by its eigenvalue $\bar{j}(\bar{j}+1)$, where $\bar{j}$ is an arbitrary rotational quantum number which needs to be specified, or equivalently the wave-number k^2 is replaced everywhere by $\bar{k}^2$. The resulting approximation is known as the infinite order sudden approximation (IOSA) (Bernstein 1979). The IOSA approach is based on two underlying physical assumptions. First, it is supposed that the dynamics of the collision are determined essentially during the time when the molecules are the near the distance of the closest approach. The evidence for this is mainly based on the study of transport properties of monatomic gases where such a behaviour has been observed (Maitland *et al.* 1981). The time the molecules spend near the distance of the closest approach is small compared with the rotational or vibrational period of the molecules and it is likely that the molecules will not appreciably change their relative orientation during the encounter. Thus IOSA assumes that the encounter takes place at fixed relative orientation. Second, it is assumed that, on average, the energy transferred between translational and internal modes is much smaller than the average kinetic energy. This is really the energy sudden part of the approximation which greatly simplifies the statistics of the encounter.

The IOSA has the advantage of completely uncoupling the CC set of equation (Bernstein 1979). The scattering problem is then reduced to scattering at a fixed orientation of two molecules for the orbital parameter $\bar{l}$. Since this is the same as the collision of two structureless particles the S matrix can be replaced in favour of the phase shifts which are simply related to the intermolecular potential for the fixed orientation (Child 1974). In its simplest form, when $\bar{l}=l$ or $\bar{l}=l'$, the $\bar{j}$ is chosen as either initial or a final j and summations over j are not bounded, IOSA (Parker and Pack 1978) is equivalent to the classical approximation of Mason and Monchick (MM) (Monchick and Mason 1961, Mason and Monchick 1962). So far as the viscosity cross-section is concerned application of the MM/IOS approximation to equations (22–24) leads for an atom rigid rotor system to the result

$$\mathfrak{S}_\eta^{(2)}=\frac{1}{2}\int_{-1}^{1} \mathrm{d}\cos\gamma\, \mathfrak{S}_\eta^{(2)}(\gamma), \tag{26}$$

$$\mathfrak{S}_{\eta}^{(2)}(\gamma)=\frac{4\,y_2^4}{15}\int_0^\infty \mathrm{d}X\,X^3\exp(-X)\,\sigma_{\eta}^{(2)}(\gamma), \tag{27}$$

$$\sigma_{\eta}^{(2)}(\gamma)=\frac{6\pi}{k^2}\sum_l\frac{(l+1)(l+2)}{(2l+3)}\sin^2[\eta_l(\gamma)-\eta_{l+2}(\gamma)], \tag{28}$$

where γ is the angle between the atom–diatom line of centres and the diatom axis and $\eta(\gamma)$ is the phase shift obtained from the intermolecular potential at the fixed orientation. The evaluation of the $\mathfrak{S}_{\eta}^{(2)}$ cross-section is straightforward and is only slightly more demanding of computer time than for the atom–atom case. It is worth pointing out that the simplicity is retained even when the complexity of the system increases beyond that of the atom–rigid rotor system. The only difference is that the angle averaging in equation (26) has to be performed over all the angles of orientation of the colliding pair rather than one.

The analysis of the viscosity and the diffusion cross sections within IOSA indicates (Goldflam, Kouri and Green 1977, Parker and Pack 1978, Vesovic 1982) that these cross-sections are not determined solely by elastic scattering from the ground rotational state, but involve additional information on inelastic processes.

For the rotational relaxation cross-section $\mathfrak{S}(0001)$ where the energy weighting is entirely based on the difference in energy between the rotational states MM/IOSA fails dramatically predicting a value of zero. It is thus expected that MM/IOSA will not successfully predict similar cross-sections. For some of the cross-sections, in particular production cross-sections a better approximation can be achieved by taking $\bar{k}^2$ as the average of the initial and final k^2 (Sachs and Bowmann 1980). Although the resulting equations are more complicated then equations (26–28), the additional computational effort in solving them is small.

Although from the computational point of view the CSA and MM/IOSA are much more rapid than the full CC calculation, both of the approximate methods introduce rather gross simplifications to the dynamics of the encounter and can thus give erroneous values for some, but not all, cross-sections.

Notwithstanding the fact that the rigorous evaluation of the effective cross-sections requires a quantum mechanical treatment, under certain circumstances, a classical mechanical evaluation is legitimate. Those circumstances are when the molecular mass of the species involved is large, when the rotational energy spacing is small and when purely quantum phenomena such as tunnelling and interference can be neglected. Indeed there exists a full classical kinetic theory of gases (Curtiss 1981, Curtiss and Tonsager 1985). Since the circumstances under which classical mechanics is adequate are quite often realized this approach offers some attractions. In fact, it is usual to work with a classical limit of the quantum expressions (Marcus 1972, Miller 1974, Liu and Dickinson 1990a) rather than with the classical expressions themselves because it is then easier to compare the quantum and classical results at the intermediate stages, but this is a matter of choice rather than one of principle. In this case the atom–rigid rotor $\mathfrak{S}_{\eta}^{(2)}$ cross-section is given by

$$\mathfrak{S}_{\eta}^{(2)}=\frac{y_2^4}{40}\int_0^\infty \mathrm{d}X\,X^4\exp(-X)\,\bar{\sigma}_{\eta}^{(2)}, \tag{29}$$

$$\bar{\sigma}_{\eta}^{(2)}=\frac{2}{\pi}\int_{-1}^{1}\mathrm{d}w\int_0^\infty b\,\mathrm{d}b\int_{-1}^{1}\mathrm{d}\cos\gamma\int_0^{2\pi}\mathrm{d}\beta\int_0^{2\pi}\mathrm{d}\varphi$$

$$\times\left(\frac{E_k}{E}\right)^2\left(\frac{E'_k}{E}\right)\left[\left(\frac{E_k}{E'_k}\right)-(\hat{\mathbf{V}}\cdot\hat{\mathbf{V}}')^2-\frac{1}{6}\left(\frac{E_k}{E'_k}\right)\left(1-\frac{E'_k}{E_k}\right)^2\right], \tag{30}$$

where $w=(E_r-E_k)/E$, E_r is the rotational energy of the diatom, b is the impact parameter and the angles γ, β and φ are related to the initial orientation of rotor axis, relative velocity, $\mathbf{V}$ and rotor angular momementum, j. The preferred means of evaluating the resulting multi-dimensional integral of equation (30) is by use of a Monte Carlo method (Porter and Raff 1976) although some workers (Dickinson and Lee 1985) have successfully employed quadratures. At the given total energy the initial values of the relative velocity, the rotational and orbital angular momentum and the corresponding angles are chosen randomly. Then the classical Hamiltonian equations of motion are integrated along a trajectory to their final post-collisional values. The process is then repeated for sufficient initial choices to lead to convergence of the integrals. Virtually all the computational effort in such classical trajectory (CT) calculations goes into solving the Hamiltonian equations of motion, and thus evaluating the trajectories, while only a very small effort is then involved in evaluating the multidimensional integral of equation (30). This is in contrast to the CC calculation where, at least for high energies, the effort of evaluating the collision dynamics and of evaluating the cross-sections from S matrices is of a similar order of magnitude. The advantage of the classical trajectory (CT) approach is that the number of trajectories does not increase with increasing total energy, in fact it shows a marked decrease. This is fortunate since it is expected that each system behaves more classically as the energy increases and hence it would seem that the CT are computationally easiest in the region where they are expected to be most accurate. Unfortunately, the convergence rate of the classical trajectory calculations is very slow, varying as $N_t^{1/2}$ where the N_t is the number of trajectories employed. Thus while it is possible to obtain rough estimates of effective cross-sections using a small number of trajectories such cross-sections are of limited use because the precision of the results is poorer than is attainable from experimental determination. Although some CT calculations have been performed for the simplest atom–diatom system, with a precision comparable with that of experiment, CT calculations are not as yet performed on the routine basis required for systematic investigations. In principle CT calculations, unlike CC calculations, can easily take advantage of parallel processing which should lead to significant improvements in the speed of execution.

Although each of the methods outlined above treats the statistics and the dynamics of the binary encounters differently there are a few general points which pertain to all of them. The first point arises from the energy averaging of equations (22, 27 or 29) to obtain the effective cross-sections at a given temperature. The most common approach is to evaluate the integral by the Clenshaw–Curtis algorithm combined with Chebycheff interpolation formula (O'Hara and Smith 1970). This quadrature has the advantage over the more obvious Laguerre quadrature that its pivot points are independent of temperature and hence the evaluation of the energy dependent cross-section has to be performed only once at a predetermined set of total energies. Recently, a new integration scheme has been suggested (Thachuk and McCourt 1990) whereby Laguerre quadrature is used to evaluate the integral together with a method to interpolate between the cross-section evaluated at the set values of the total energy. In principle, both methods are based on the same underlying approach, but the second method has a much greater flexibility in recalculating the integrand at the pivot points and hence estimating the error involved. If the integrand is well-behaved very accurate results can be achieved with only a few pivot points.

A second point of some significance for quantum calculation concerns the question of resonances. If one of the energy pivot points is inadvertently chosen to coincide with the resonance energy then the effective cross-section can be greatly over estimated. However, the issue is more general since while it is desirable to obviate this practical difficulty the question remains of how greatly such resonances affect the value of the final cross-section. It is convenient to deal with the second point first since it established the context for the practical resolution of the problem.

Hutson and McCourt (1984) and Hutson (1987) have investigated the role of resonances in the transport and relaxation cross-sections of the H_2–Ar system. Six cross-sections were studied, namely

$$\mathfrak{S}(2000),\ \mathfrak{S}(1000),\ \mathfrak{S}(0200),\ \mathfrak{S}\begin{pmatrix}0200\\2000\end{pmatrix},\ \mathfrak{S}(0001),$$

and linewidth cross-section. The results indicated that the effect of the resonances is small for the transport cross-sections, $\mathfrak{S}(1000)$ and $\mathfrak{S}(2000)$ but for the relaxation and linewidth cross-sections the resonance region can contribute up to 30% of the integrand at temperatures below 100 K. As the temperature increases the resonance effects decrease rapidly and become negligible near room temperature. The reason for such a strong temperature dependence can be attributed to the energy weighting of the integrand. The form of the integrand of equations (22 or 27) is such that an increase in temperature pushes the sampling towards high energies and hence reduces the contribution from the low energy part where the resonances occur. The conclusions of the above studies are in broad agreement with the findings of Koehler and Schaefer (1983b, c) who have reported that for para H_2–H_2 the effect of resonances is significant for the $\mathfrak{S}(0200)$ cross-section only below 200 K. No explicit studies have been performed for heavier systems, but it is worth pointing out that for the He–N_2 system the effect of resonances even for relaxation cross-sections was negligible at 100 K (McCourt *et al.* 1991). It thus appears that for most systems the effect is of small practical significance.

Nevertheless, the proper allowance of the resonances should be made in thermal averages whenever possible and two ways of minimizing the errors incurred owing to the presence of the resonances have been developed. The first is to split the integral in two parts such that all the resonant behaviour is contained in the low-energy part. Quadratures with a different number of pivot points can then be used to evaluate the two integrals separately. Second, it is possible to increase the number of pivot points at the low energies which would then allow the use of spline or some other interpolation procedure to map the behaviour of the integrand in the region where it is changing rapidly because of resonances.

For some other cross-sections such as the production cross-sections a further difficulty arises because these cross-sections can be either positive or negative. This property then manifests itself in a slow convergence of the summation over the total angular momentum number in the close coupled calculations or as oscillations of the integrand as a function of the angles β and φ and the impact parameter, b of equation (30) in the classical trajectory calculations. Since, both positive and negative contributions of similar magnitude contribute to these cross-sections the numerical round-off error is inevitably larger than for other cross-sections. Furthermore, only for the production cross-sections are the diagonal (elastic) and off-diagonal (inelastic) elements in j–j' of similar magnitude. Hence, cancellation will also occur when performing the rotational quantum number averaging. This makes production cross-sections very hard to calculate accurately. This problem can only be overcome by increasing the accuracy of the evaluation of the S matrices or evaluating a large number of extra classical trajectories. As a routine check of the adequacy of sampling one should always perform calculations for both

$$\mathfrak{S}\begin{pmatrix} p\,q\,s\,t \\ p'q's't' \end{pmatrix} \quad \text{and} \quad \mathfrak{S}\begin{pmatrix} p'q's't' \\ p\,q\,s\,t \end{pmatrix},$$

cross-sections, since theoretically they should differ by no more than their sign.

4.2. *Atom–diatom effective cross-sections*

The encounters of an atom with a homonuclear diatom represent the simplest system for which the phenomena discussed above can be studied. In fact, almost all of the knowledge and insight gained about the collisional behaviour of the polyatomic systems has been acquired by investigating the atom–diatom case. Furthermore, to render problems tractable, in all the calculations performed so far, the diatom has been taken to be a rigid rotor. From the theoretical and the experimental viewpoint this is a very unfortunate set of circumstances. First, these calculations do not allow a direct comparison of the results of the calculations with experiments, at least for transport properties. This is because the cross-sections of such systems are necessarily for the unlike interactions in binary mixtures and as such are embedded in the theoretical formulations (McCourt *et al.* 1990; section 3.4) for the property itself. A comparison is only possible if all the cross-sections for the like interactions are known. Nevertheless, if some accuracy is sacrificed and quantities relating to the like interactions are obtained from the experiment, it is possible to make indirect comparisons.

A number of studies has been performed for a variety of systems with the independent aim of testing the applicability of approximate methods of calculation or of testing different intermolecular potential models. The systems studied can be broadly classified into the interactions of He, Ne and Ar with either H_2 or HD, or with N_2 and O_2. The fulfilment of the first aim requires as a starting point a set of essentially exact close coupled calculations for a prescribed intermolecular pair potential to use as a benchmark against which to judge the approximate results. Extensive CC calculations have been performed for HD–He (Kohler and Schaefer 1983a, b, c, Schaefer and Kohler 1985, Liu, McCourt and Dickinson 1989, Liu, Dickinson and McCourt 1990), H_2–Ar (Maitland, Mustafa and Wakeham 1987b) and N_2–He (Maitland, Mustafa, Wakeham and McCourt 1987a, McCourt *et al.* 1991) and the results have subsequently been compared with MM/IOSA, CSA, and CT calculations.

Figure 3 shows the deviations between the ‘exact’ CC (McCourt *et al.* 1991) calculations and the MM/IOSA (Maitland *et al.* 1987a), CSA (Gianturco, Serna and Sanna 1991) and CT (Dickinson and Lee 1986) calculations for the interaction viscosity cross section, $\mathfrak{S}_{\eta}^{(2)}$ for He–N_2 as a function of temperature. It can be seen that the CT calculations are within ±1·5% of CC results at 100 K and the difference decreases rapidly to become negligible at 300 K. The CSA calculations also yield the viscosity relatively well over the whole temperature range, while MM/IOS is remarkably accurate for such a simple calculation. Similar behaviour has been found for H_2–Ar and He–HD systems. In fact, for the other cross-sections describing field independent transport properties similar trends are observed although, the difference between the three calculation schemes is larger, and only CT calculations are within 1% of the exact results, while MM/IOS approximation overestimates for example the $\mathfrak{S}(1000)$ and $\mathfrak{S}(1001)$ cross-sections by 3–4% at 300 K (Maitland *et al.* 1987a).

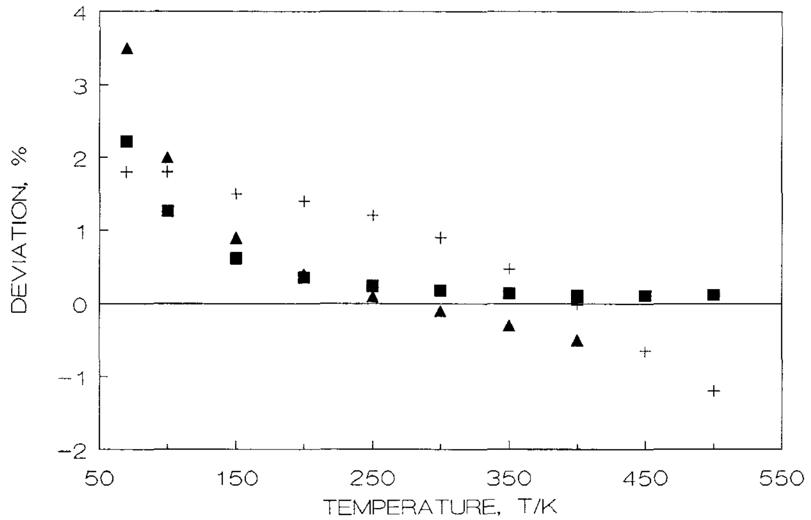

Figure 3. Deviations of the $\mathfrak{S}_{\eta}^{(2)}$ cross-section for the He–N_2 system obtained by approximate methods from CC results: ▲ MM/IOSA; + CSA; ■ CT.

Not enough calculations have been performed using CSA to judge its usefulness unequivocally. Its predictions, in general, for field independent transport properties are better than MM/IOSA predictions but worse than classical trajectory calculations. Recently, the corrected centrifugal sudden approximation (CCSA) has been used (Thachuk and McCourt 1990) to calculate the cross-sections for He–H_2 system. In order to get the best results the average l labelling scheme was adopted. The results show that CCSA can evaluate field independent transport properties with an accuracy that is only slightly worse than is obtained using CT. This is significant because, although average l labelled CCSA calculations take much longer than MM/IOSA calculations they are still computationally cheaper than CT calculations. Future studies on the He–N_2 system (McCourt 1992b) are intended to shed more light on the use of CCSA as the routine way of evaluating field independent transport properties.

The CT calculations have come out of these studies as the most accurate replacement for CC calculations. Even in the most stringent test of evaluating He–HD field free transport properties (Liu *et al.* 1989, Liu *et al.* 1990a) the deviations do not exceed ±2% at 100 K.

At first sight it might be surprising that all the three methods predict field independent transport properties so well given the quantal nature of some of the systems studied and the gross simplifications introduced to the dynamics in some cases. However, these results seem to support the notion that field independent transport properties are dominated by elastic contributions. This does not imply, as is sometimes believed, that accurate values of viscosity, diffusion and the thermal conductivity can be obtained by using only the spherical part of the full anisotropic surface. On the contrary, it has been shown for He–CO_2 (Parker and Pack 1978, Vesovic 1982) that calculations based only on the spherical part of the intermolecular potential underestimate the viscosity and diffusion cross-sections by as much as 20–30%. Of course it is valid to assert that there must exist a spherically symmetric potential function that leads to the same viscosity and diffusion cross-sections as the full anisotropic potential. However the spherically symmetric potential differs substantially from the unweighted spherical average of the full potential (Maitland, Mustafa, Vesovic and Wakeham 1986, Vesovic and Wakeham 1987).

Effective cross-sections governing relaxation properties like rotational relaxation, pressure broadening of the depolarized Rayleigh line or Senftleben–Beenakker effects are, by their nature, more influenced by inelastic collisions (McCourt *et al.* 1990). As such they are much more difficult to evaluate accurately than the cross-sections governing the field free transport properties. For instance, the IOSA method is at best accurate to 20% (Wong, McCourt and Dickinson 1989), while for worse cases, errors of an order of magnitude have been observed (Liu, McCourt, Fitz and Kouri 1981, Wong *et al.* 1989). It is therefore not accurate enough for the evaluation of relaxation cross-sections that govern SBE or the broadening of the DPR line.

Figure 4 shows the deviations of the results for $\mathfrak{S}(0200)$ and $\mathfrak{S}_{DPR}$ cross-sections obtained by the 'exact' CC (McCourt *et al.* 1991) calculations, those computed by initial l labelled CSA (Gianturco *et al.* 1991) and CT (Dickinson and Lee 1986) for He–N_2 as a function of temperature. For the $\mathfrak{S}(0200)$ cross-sections both schemes overestimate the cross-section at low temperatures by ±5%, but the CT deviations decrease rapidly to less than 0·5% by 500 K while CSA results exhibit no such improvement.† For the $\mathfrak{S}_{DPR}$ cross-section neither scheme seems to be able to predict it to better than 3% and at low temperatures CT predictions are very much worse.

It is instructive to examine why there is such a difference in the prediction of these two cross-sections, specially since it is known that they depend on the same state to state cross-section $\sigma_T(jj'|E)$. The $\mathfrak{S}(0200)$ (also denoted $\mathfrak{S}_T$) cross-section determines the strength of the magnetic field at which the decrease in the longitudinal viscosity

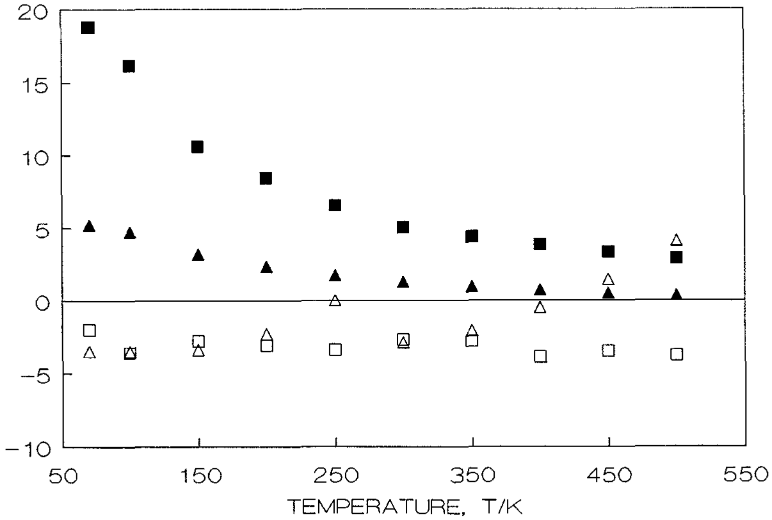

Figure 4. Deviations of the $\mathfrak{S}(0200)$ and $\mathfrak{S}_{DPR}$ cross-sections for the He–N_2 system obtained by approximate methods from CC results: $\mathfrak{S}(0200)$: △ CSA; ▲ CT; $\mathfrak{S}_{DPR}$: □ CSA; ■ CT.

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† This trend for CSA might be spurious (Gianturco *et al.* 1991) since the energy dependent cross-section evaluated by CSA had to be extrapolated to higher energies to facilitate the energy integration and this might have led to larger uncertainty in the cross-sections above 300 K.

coefficient in the magnetic field attains half of its saturation value while $\mathfrak{S}_{\mathrm{DPR}}$ is a measure of the collisional reorientation of the rotation angular momentum which gives rise to the pressure broadening of the DPR line. Both cross-sections are given by

$$\mathfrak{S}_Y=\frac{1}{Z_{\mathrm{rot}}N_Y}\int_0^\infty \mathrm{d}X\, X\exp(-X)\,\bar{\sigma}_Y(E), \tag{31}$$

$$\bar{\sigma}_Y(E)=\sum_j d_Y(j)(E_k/E)\sum_{j'} d_Y(j')\,\sigma_T(jj'|E), \tag{32}$$

$$N_T=\frac{1}{Z_{\mathrm{rot}}}\sum_j d_T^2(j)\exp(-E_j/k_{\mathrm{B}}T), \tag{33}$$

$$N_{\mathrm{DPR}}=\frac{1}{Z_{\mathrm{rot}}}\sum_j d_{\mathrm{DPR}}^2(j)\exp(-E_j/k_{\mathrm{B}}T), \tag{34}$$

$$d_{\mathrm{DPR}}=4d_T/[(2j+3)(2j-1)], \tag{35}$$

$$d_T=j(2j+1)(j+1)(2j-1)(2j+3)/6, \tag{36}$$

where Y in equations (31, 32) either refers to T or DPR and E_j is the rotational energy of the level j. The calculations have shown (Liu *et al.* 1989, McCourt *et al.* 1991) that while $\bar{\sigma}_{\mathrm{DPR}}$ increases approximately as $E^{1/2}$, $\bar{\sigma}_T$ increases approximately $E^{5/2}$. Thus the peak in the integrand for the thermal average is approximately at $3{\cdot}5k_{\mathrm{B}}T$ for $\mathfrak{S}(0200)$ and at $1{\cdot}5k_{\mathrm{B}}T$ for $\mathfrak{S}_{\mathrm{DPR}}$ which implies that the major contribution to $\mathfrak{S}_{\mathrm{DPR}}$ will come from a much lower energy range than for $\mathfrak{S}(0200)$. Furthermore, although a large number of rotational channels is accessible in N_2 the structure of N_{DPR} is such that it favours low j values so that taking the classical limit of N_{DPR} for CT calculations is only accurate at high temperatures (McCourt *et al.* 1991). So, although both cross-sections are influenced by the same inelastic processes, the different energy and N_Y weighting leads to relatively poor estimate of $\mathfrak{S}_{\mathrm{DPR}}$ cross-sections using CT calculations and to a smaller extent the CS approximation. This particular case therefore provides one example of the use of the computation of the cross-sections to elucidate the different nature of the two cross-sections. Improvement in CT predictions of $\mathfrak{S}_{\mathrm{DPR}}$ can be achieved by evaluating N_{DPR} from equation (34) and not replacing it by its classical limit.

If the calculations are done on a more quantal system than He–N_2 a different trend concerning the ability of CT and CSA to predict relaxation cross-sections $\mathfrak{S}(0200)$ and $\mathfrak{S}_{\mathrm{DPR}}$ emerges. The CT calculations for He–HD (Liu *et al.* 1989) indicate that even at 300 K both cross-sections are overestimated by 30%. Furthermore, the rotational relaxation cross section, $\mathfrak{S}(0001)$, which for He–N_2 has been predicted within 2% at 300 K, is for the He–HD system overestimated by 25%. Although, the other relaxation cross-sections namely $\mathfrak{S}(1100)$ and $\mathfrak{S}(1200)$ are predicted (Liu *et al.* 1990) within 3% at similar temperatures these results confirm intuition that for systems with only a few open rotational channels CT should not be used. On the other hand the most recent results for CCSA (Thachuk and McCourt 1990) indicate that for He–H_2 system the relaxation cross-sections mentioned above are all predicted within 1–2%. Hence, based on these studies, it seems best to use average l labelled CCSA at low temperatures and for systems where only a few rotational channels are opened. For more classical systems and at higher temperatures CT is to be preferred. It is worth noting that both CCSA an CT in the regions where they are recommended allow evaluation of the effective relaxation cross-sections better than they are known experimentally.

The production cross-sections mainly appear in the description of effect of the field on transport properties and flow birefringence (McCourt *et al.* 1990). As already mentioned their structure is different from other effective cross-sections and hence they are much more prone to cancellation errors. Since their accuracy is strongly influenced by the dynamics of the encounter most approximate quantum mechanical methods fail to predict them properly. However for the systems studied so far CT predictions have been very successful. For the

$$\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix},$$

cross-section for the He–N_2 system the deviations of CT calculations from CC results decrease from 4% at 100 K to 0·5% at 300 K (McCourt *et al.* 1991). In a more quantal He–HD system at 300 K

$$\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix},\ \mathfrak{S}\begin{pmatrix}1200\\1000\end{pmatrix},\ \mathfrak{S}\begin{pmatrix}1200\\1010\end{pmatrix}\ \text{and}\ \mathfrak{S}\begin{pmatrix}1200\\1001\end{pmatrix},$$

cross-sections have all been predicted within 15%.

One of the ways of improving the accuracy of the calculations of any cross-sections at low temperatures and for systems where only a few rotational channels are opened is to perform so called 'hybrid calculations' (Liu *et al.* 1989). This involves performing CC calculations at low energies where they are reasonable cheap and where CT calculations are time consuming and inaccurate. At high energies CT calculations are performed. These two sets of supplementary information take advantage of accuracy and computational ease of CC calculations at low and CT calculations at high energies leading to superior predictions overall. Judging by the studies carried out so far this scheme is as accurate as a full quantal treatment for most of the effective cross-sections concerned provided that the switch from quantal to classial mechanics is made at an appropriate total energy. The choice of energy depends on both the anisotropy of the intermolecular surface and the number of available rotational channels. At present the information obtained from the few systems studied is insufficient to make even a guess at the switching energy and how to determine it.

The reasonable agreement for field independent transport properties between the MM/IOSA calculation procedure and the exact results encourages the examination of its usefulness for routine calculations for testing proposed intermolecular potential models against experimental data. However, based upon the results of the comparison with CC calculations it seems prudent at present to confine the comparison to the viscosity cross-section because for both the thermal conductivity and diffusion the inaccuracies of the MM/IOSA results exceed these of the experimental data by an order of magnitude (Maitland *et al.* 1987a, Wong *et al.* 1989, McCourt *et al.* 1991). On the other hand the other studies (Corey, McCourt and Maitland 1987, Gianturco, Venangi and Dickinson 1988a, b) indicate that at least for coarse screening of the proposed potentials against experimental viscosity data the MM/IOSA is sufficiently accurate. Nevertheless, it is advisable to issue caveats concerning the use of such procedures because the conclusions in accuracy are based on a studies of a limited set of systems. Thus, for example Gianturco, Venanzi and Dickinson (1990) have reported that the errors in using MM/IOSA calculation increase with increasing mass of the atom which is, perhaps, counter intuitive. Similar caveats apply with much less force to the use of CT calculations for the same sort of study and there is most definitely strong evidence to suggest that this calculational method can be used for the fine tuning of intermolecular potentials.

A large amount of work has been performed on analysing and refining the inert gas–H_2, HD, N_2 and O_2 potentials (Dickinson and Heck (1990), Gianturco *et al.* (1990), McCourt *et al.* (1990), Wong, McCourt and Casavecchia (1990), Benveneti *et al.* (1991), and references therein). Although, these potentials are still not as accurately known as those of the inert gases (Aziz 1984) they yield reasonable agreement with the majority of experimental data. The intermolecular pair potentials are, of course, a topic in their own right. However, from the point of view of the present discussion, it is more relevant to consider the sensitivity of various cross-sections to the features of the potential surface. This is of paramount importance for two reasons. First it would enrich our understanding of what, if any, are the dominant microscopic process that contribute to specific macroscopic observables. Second it could allow tuning of special features of the potential to particular cross-sections. Knowledge in this area is still qualitative, but it is known that the cross-sections that govern field free transport properties are not especially sensitive to the particular features of the anisotropy of the intermolecular surface but rather to its averaged value. On the other hand, cross-sections that govern relaxation phenomena are sensitive to the anisotropy of the potentials studied so far and usually to the anisotropy of the repulsive wall (McCourt *et al.* 1990). The greatest sensitivity to the anisotropy should be exhibited by the production cross-sections, at least if the results of the distorted-wave Born approximation are taken as a guide (McCourt *et al.* 1990). However the results of the more exact calculations (Wong *et al.* 1989, Gianturco *et al.* 1990) do not seem to support this conclusion.

The temperature dependence of different cross-sections can also provide very useful information. The structure of the final integral over the total energy in equations (22, 27 or 29) is such that for the cross-sections at a particular temperature the main contribution arises from a relatively narrow range of total energies. Hence at each temperature each cross-section provides a ‘window’ on the potential. As the temperature is increased the ‘window’ moves up the intermolecular potential towards higher energies. This idea was exploited very successfully to examine the influence of intermolecular potential on the transport properties of monatomic gases and eventually led to an inversion procedure whereby the potential could be determined directly from transport properties (Maitland *et al.* 1981, Vesovic 1982). At present, for polyatomic systems no sensitivity analysis has been attempted to study how the relaxation and production cross-section sample the intermolecular potential surface. One of the main reasons for this is the purely computational one, discussed earlier, that CT calculations cannot be performed on a routine basis with sufficient accuracy owing to the sheer magnitude of the task. The most recent developments in computational techniques and computers promise to alleviate this situation.

A number of clear and relatively simple relationships between different cross-sections for pure gases have been observed experimentally. Because of the complexity of some of the relationships between the transport properties of gas mixtures and the cross-sections for the like and unlike interactions that enter them and because of the limited number of systems studied, it is at present difficult to draw any conclusions concerning the trends among the atom–diatom effective cross-sections. However, some of the trends with temperature, observed for He–HD and He–H_2, are interesting. For example, it has been found that above 100 K the $\mathfrak{S}(0200)$ cross-section for He–HD decreases with temperature (Liu *et al.* 1989) whereas for He–H_2 the opposite behaviour with temperature has been observed (Thachuk and McCourt 1990).

The evaluation of higher-order approximations to any of the transport properties of gases or gas mixtures requires very many more effective cross-sections than does the first-order theory. The fact that for the CC method such an increase in the number of cross-sections adds formidably to the already prohibitively large computational task has inhibited any examination of these higher-order evaluations. Now, that CT and MM/IOSA methods have gained acceptance there have been two recent studies which have both analysed the second-order correction in the spherical limit for the field free transport properties (Gianturco and Venanzi 1989, Wong *et al.* 1990). Both studies indicate that the correction term is small, of the order 1% at most. Hence, this correction can in future be roughly estimated without an adverse effect on the calculation of the field-free transport property in question.

4.3. *Ion–molecule effective cross-sections*

In principle, the calculations of the cross-sections that govern the mobility and the diffusion coefficients of ions moving in trace amounts through molecular gases under the influence of the electrostatic field should not be more difficult than the atom–molecule calculations. In practice, however, the calculation of ion–molecule effective cross-sections proves computationally much more demanding for two reasons. First, the ion–molecule potentials are of much longer range than their atom–molecule counterparts, and hence their long-range tail falls off more slowly with separation. Thus, it takes more computational effort to solve the dynamics of the scattering. Secondly, the experimental data covers a wide range of E/n, the ratio of the electric field strength, E, to the gas number density, n. This means that the energy integrations require many more energy pivot points, further increasing the computational effort. As a result, very few computational studies have been carried out for these systems and then only for the ion–rigid rotor system. No CC calculations have been carried out so far but, in a recent study, Viehland (1992) has used CT to evaluate the ion mobility and the diffusion cross-sections for the Li^+–N_2 system. The computational effort in obtaining a precision of 1% in the cross sections involved about 3 million trajectories at 23 energies. This is more than an order of magnitude larger than the effort required for the analogous atom–diatom calculation (Gianturco *et al.* 1990). Since there are no direct comparisons with CC results for the ion–diatom system it is difficult to assess how accurate the CT calculation is. For ion–atom systems it is known that the effective cross-sections show similar behaviour to those of atom–atom transport cross-sections (Viehland and Kumar 1989). Furthermore, the structure of ion–diatom cross-sections has similarities with the structure of the cross-sections that govern field free transport properties and it is likely that the elastic contributions will dominate. There is, therefore, some indirect evidence that the results for the field free transport properties for atom–diatom systems can be useful in establishing CT as an accurate calculational method for ion–diatom cross-sections. Comparison with experiment indicates reasonable agreement except at low E/n ratios where the collisions at low energies contribute most. This discrepancy may be due to inaccuracies in the long-range part of the potential or to increasing errors in CT at the lowest energies and further work is necessary to resolve the two possibilities. Taking into account the fact that most of the computational time with the CT method was spent evaluating low-energy collisions it might be advantageous to apply a hybrid scheme using CC at the very lowest energies and CT at higher energies as in the preferred scheme for neutral systems.

4.4. *Diatom–diatom effective cross-sections*

The studies carried out so far on diatom–diatom systems can be separated into two categories. First the studies of the H_2–H_2 effective cross-sections for which the calculations by CC method are, in principle, simple and secondly those for other systems where little has yet been done.

The large rotational spacing of H_2 has made it the obvious choice for diatom–diatom studies. Full CC calculations have been performed (Kohler and Schaefer 1983b, c) on a realistic anisotropic potential surface (Schaefer and Meyer 1979). At the time of their work it was not possible to include more than two states owing to the computational complexity, so that only calculations on para H_2 have been performed (Kohler and Schaefer 1983b, c) including only one rotational state, although the calculations were performed for two potential surfaces. It was thus possible to separate the contributions from different transitions to the final effective cross-section and compare the influence of change in anisotropy.

Very thorough discussion of the results has been presented both by the original authors (Kohler and Schaefer 1983b, c) and by McCourt *et al.* (1990) so only its main conclusions will be summarized here. It was found, as expected, that the cross-sections that govern field free transport properties are nearly totally determined by elastic collisions. Unfortunately, the cross-section that governs the self diffusion process has not been reported and although the $\mathfrak{S}(1001)$ cross-section was found to be mainly determined by elastic $(0,2)\to(0,2)$ transition no conclusions could be drawn about the D_{int}/D ratio which would have been very useful for the thermal conductivity analysis. Some of the cross-sections that govern field effects, namely $\mathfrak{S}(1200)$ and $\mathfrak{S}(0200)$ were also found to be insensitive to inelastic collisions or the anisotropy of the potential. The results for $\mathfrak{S}(0200)$ are very surprising since it is known from atom–diatom studies that this cross-section is strongly anisotropy dependent. It seems likely (McCourt *et al.* 1990) that for the case of hydrogen the major contributions to $\mathfrak{S}(0200)$ at low temperatures came from the long-range tail of the potential and from around separations where the potential is zero. The potentials tested in this work had very similar anisotropy in both of these regions and this might have lead coincidently to the small difference in a values for $\mathfrak{S}(0200)$ between the two potentials (McCourt *et al.* 1990). Such a result illustrates the dangers of drawing general conclusions on the basis of a small set of results for one system and reinforces the need for more systematic studies on a range of systems.

The rotational relaxation cross-section $\mathfrak{S}(0001)$ is solely determined by inelastic collisions and it was found to be strongly anisotropy dependent. The production cross-sections were also found to be strongly influenced by the anisotropy. For this particular system for example it was found that

$$\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix},$$

is more sensitive to the anisotropy than for instance the cross-section

$$\mathfrak{S}\begin{pmatrix}1200\\1001\end{pmatrix},$$

associated with the production of Kagan polarization (McCourt *et al.* 1990). Although these calculations have proved useful in elucidating the behaviour of the effective cross-sections of hydrogen molecules and further refining the intermolecular potential of hydrogen they are of limited value for furthering our knowledge of effective cross-sections of other molecular species. The reasons for this are numerous. The highly quantal nature of the hydrogen interaction does not yield easily to any other calculations apart from those of full close coupled ones. Hence, no judgment on the performance of CT or approximate calculations is possible. Furthermore, in the particular calculations performed only one rotational level was open so it is difficult to generalize the behaviour of the cross-sections to the other systems, where the interaction of a large number of rotational channels may produce different trends. Finally, the hydrogen intermolecular potential is only weakly anisotropic so that it is difficult to judge the influence of anisotropy of the potential surface on the effective cross-sections.

For all the other diatomic systems the results of computations are very much more limited. Although theoretical formulations exist (McCourt *et al.* 1990), there is adequate experimental data and a number of reasonable potential surfaces are available (van der Avoird 1992) the complexity and the cost of calculations has, until the last few years, presented insuperable difficulties. The full quantal calculation is simply still impossible and is very likely to remain so for the foreseeable future. The success of CT calculations for the atom–diatom case encourages the belief that this may be the way forward. Unfortunately, even for two rigid rotors this proves to be an expensive computational undertaking, especially if the accuracy of the calculation is to be maintained at the level achieved for the atom–diatom system (better than 1%). There are, at the moment a few such studies underway, but so far only three calculations have been carried out (Turfa, Knaap, Thijsse and Beenakker 1982, Nyeland, Poulson and Billing 1984, Turfa, Connor, Thijsse and Beenakker 1985). They were all performed on the N_2–N_2 system for realistic intermolecular potentials but either for a limited number of effective cross-sections or at one temperature. Turfa *et al.* (1982) only calculated the rotational relaxation cross-section $\mathfrak{S}(0001)$, whereas Nyeland *et al.* (1984) performed calculations for the cross-sections governing mainly field free transport properties. Subsequently, Turfa *et al.* (1985) calculated a number of effective cross-sections but only at 293 K. Owing to the large computational effort required a smaller number of trajectories than desirable to achieve high accuracy were included. Furthermore, to reduce the number of energy pivot points needed and hence reduce the computational effort Nyeland *et al.* (1984) applied a linear interpolation formula $\ln[\sigma(E)]$ against $\ln[E]$ to perform energy integration for their cross-sections. Although certainly justified on 5–10% accuracy this procedure is questionable if cross-sections of very high accuracy are sought. Thus, the final cross-sections are deemed to be accurate to 5%. Since the primary objective of the work of Nyeland *et al.* (1984) was to compare the results for two potential surfaces the accuracy was adequate in this particular case. However a comparison of CT results with other approximate schemes such as MM/IOSA (McLaughlin, Rigby, Vesovic and Wakeham 1986) for the same potential surfaces shows that a more accurate CT calculation is necessary. This is certainly borne out by figure 5 which shows a comparison between CT and MM/IOSA calculations (McLaughlin *et al.* 1986) in the form of deviations from the experimental values (Cole and Wakeham 1985).

The calculation of the rotational relaxation cross-section $\mathfrak{S}(0001)$ (Turfa *et al.* 1982) also produced a surprising result. Their calculations indicated that the contribution of the second-order Chapman–Cowling term to this cross-section amounts to 17%. This result is not supported either by calculations on hydrogen or by rough sphere calculations which are known to overestimate the effect of higher-order terms.

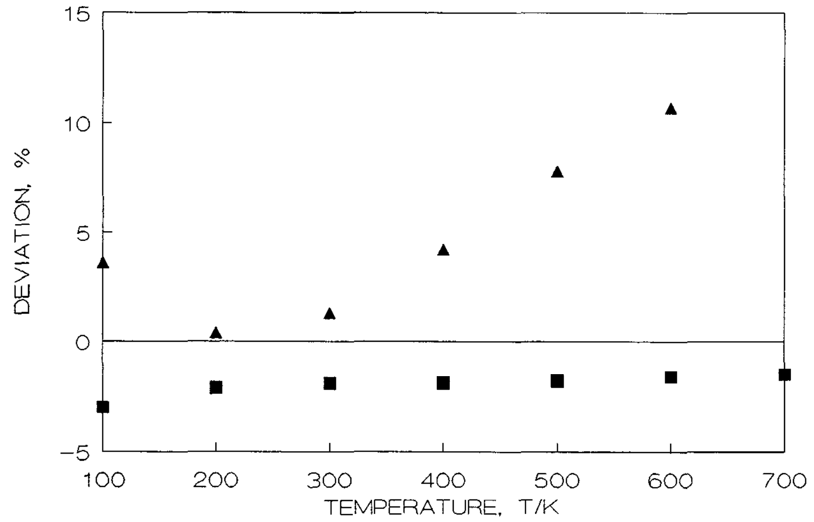

Figure 5. Deviations of the 𝔖(2000) cross-section for the N_2–N_2 system from the experimental values: ▲ CT; ■ MM/IOSA.

However, there are some indications based on experiment (Van den Oord, de Lignie, Beenakker and Korving 1988) that the polynomials in rotational energy used in the solution of the Boltzmann like equation might be more slowly converging than the Sonine expansion in terms of translational energy. Since, 𝔖(0001) is only dependent on the expansion in the rotational energy there is at least the possibility that the second-order terms are larger than previously thought (McCourt 1992a). If this proves to be the case, and again only new and more accurate CT calculation can clarify this situation, much of the information on 𝔖(0001) cross-sections obtained from the experimental rotational relaxation data would have to be reanalysed. Furthermore, there would be reason to reexamine possibility of smaller effects for some other relaxation and production cross-sections.

No CSA and only a few MM/IOSA calculations have been performed for diatom–diatom systems. The viscosity cross-section 𝔖(2000) have been examined using MM/IOSA either to roughly screen the potentials (Ling and Rigby 1984), compare with experiment (Freire and Rodriguez 1988) or as input for tests of an inversion procedure (Maitland, Mustafa, Vesovic and Wakeham 1986). All these tests seem indirectly to support MM/IOSA for evaluation of at least the 𝔖(2000) cross-section, but the final test must await the results of the more accurate CT calculations and clarification of the results presented in figure 5.

Although CT have been more or less accepted as the tool to study the behaviour of the effective cross-section for diatom–diatom systems, there remains one additional complication to be considered, namely vibrational degrees of freedom. For most simple molecules the translational to vibrational energy state changes are large and therefore only a few vibrational channels will be accessible at the temperatures of interest. In such a situation CT calcualtions will not be able to predict accurately effective cross-sections. Thus CT would have to be supplemented with a quantum description of the vibrational degrees of freedom. Such a semi-classical theory has been developed and has been used for scattering of atom–diatom, diatom–diatom and polyatomic molecules (Billing 1984, 1992). Furthermore there has been one attempt to evaluate

N_2–N_2 field free transport properties (Nyeland and Billing 1988). The results were inconclusive since, contrary to intuition, the inclusion of vibrational degrees of freedom considerably decreased the value of the effective cross-sections.

In a relatively short time the computation of effective cross-sections has advanced considerably by virtue of the development of new algorithms and the increased speed of computers. There is now a broad agreement that the method of choice for the majority of systems is that of CT supplemented, when necessary, by CC calculations at low energy. For a number of atom–diatom systems knowledge of the effective cross-sections and how to calculate them has led to advances in the knowledge of the intermolecular potentials of those systems. For para hydrogen at least it has been possible to discover how different transitions influence different cross-sections and eventually to understand how the different macroscopic phenomena can be explained in terms of microscopic changes. For other molecule–molecule systems the necessary calculations are becoming possible. Such computational studies are essential to provide insight into those experimental observations for which an explanation is still lacking and indeed to provide the motivation for any further experimental study.

5. Conclusions

This review has attempted to demonstrate that the effective cross-sections of the kinetic theory of gases provide a unifying formulation for the description of many of the macroscopic phenomena observed in the dilute non-uniform gases. There is, for a number of effective cross-sections, a wealth of experimental information available and, in some cases it is possible to use this information in conjunction with the kinetic theory to describe a series of diverse phenomena.

More generally, however, the review has shown that the field of study of effective cross-sections stands at the threshold of a new era when it will be dominated by calculations. The methodology and hardware for the performance of such calculations is now in place and it remains to carry out systematic studies towards a well defined objective. The ultimate goal must be the elucidation of the physics of the microscopic processes that determine particular macroscopic observables. Thus, the role of calculation should be the study of carefully selected systems with a view to identifying which, if any, of special types of binary molecular collisions dominate particular cross-sections and whether particular features of the intermolecular potential are preeminent in determining the effects of these collisions. Incidental objectives should include answers to questions arising from experimental observations such as the correlation found between the production and relaxation cross-sections governing the viscomagnetic effects for simple molecules. Such insight will not be gained by a superficial study of a wide variety of different molecular systems, but rather by a detailed study of a few. There is, as yet, no general agreement on the ideal systems for such a study because the merits of individual cases have hitherto been determined largely by the practicability of the calculation. Now that this barrier has almost been removed consensus on the systems of greatest significance should be established as a high priority.

In this paper we have adopted the definition of the irreducible basis tensors given by McCourt *et al.* (1990). Some of the tensors differ in sign from those used in earlier literature (Freziger and Kaper 1972) and hence some of the production cross-sections have a different sign in the two conventions. Thus, equations (2), (8) and (9) are sometimes given in the literature with a plus sign in front of the production cross-section

$$\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix}.$$

The reader is referred to Millat *et al.* (1987, 1989).

The recent CCSA study of effective cross-sections for the He–N_2 system (McCourt 1992b) has shown that in general CCSA does not improve the accuracy of CSA results using either the final *l* or average *l* labelling schemes. Thus, it seems, based on the results from He–N_2, that CCSA is best for systems where only a few rotational channels are open.

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