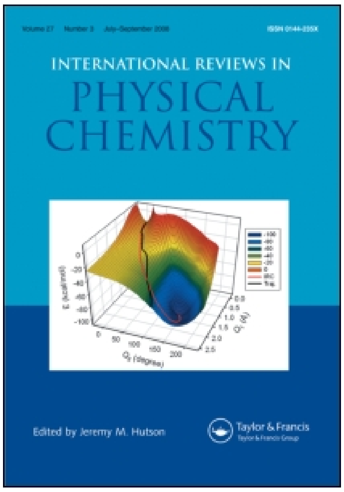

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Vibrational energy transfer in fluids

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Vibrational energy transfer in fluids

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A review of several of the available theories of vibrational energy transfer (VET) in the gas and liquid phases is presented. First the classical theory of gas phase VET mainly due to Landau and Teller, to Jackson and Mott and to Zener is developed in some detail. Next the Schwartz–Slawsky–Herzfeld theory, a framework for analysing VET data based on the classical theory, is outlined. Experimental tests of the classical theory and theoretical critiques of its assumptions are then described. Next a brief review of the modern *ab-initio* quantum approach to gas phase VET rates, taking as an example the work of Banks, Clary and Werner, is given. Theories of VET at elevated densities are then discussed. The isolated binary collision model is reviewed and a new molecular approach to the density, temperature and isotope dependences of vibrational energy relaxation rates, due to Adelman and co-workers, is outlined.

1. Introduction

Vibrational energy transfer (VET) in gases and liquids is a phenomenon of particular importance because it provides a relatively simple prototype for chemical reaction dynamics. Recent advances in both laser spectroscopy techniques and computer simulation capability have generated renewed interest and activity in the field. The goal is to develop a comprehensive understanding of VET that extends over wide ranges of temperatures, densities and system types. In particular, a theoretical framework which permits interpretation of qualitative trends is desired.

VET divides into two processes: (1) vibrational energy relaxation (VER), in which the oscillator undergoes a transition from an excited state to a less excited state with energy being transferred from the relaxing mode to the surrounding fluid; and (2) vibrational excitation, in which the reverse process occurs. As the rates for these two processes are related by detailed balance (see § 2.4.2), a knowledge of one determines the other.

Early experimental measurements of VET involved ultrasonic absorption and dispersion. The basis of this method, first pointed out by Herzfeld and Rice (1928), is the slow rate of VET which results in an absorption of acoustic waves. A major drawback of this technique is the available frequency range which restricts the accessible relaxation times to the nanosecond regime. Thorough reviews of the ultrasound method are available in the standard monographs by Herzfeld and Litovitz (1959) and Cottrell and McCoubrey (1961).

A variety of laser spectroscopy techniques capable of measuring an enormous range of vibrational lifetimes have supplanted the traditional ultrasound probes. These laser techniques employ a two-stage operation: the sample is first excited by a pump pulse tuned to the appropriate frequency, and the time evolution of the vibrational population is then monitored by a probe pulse. A common procedure involves infrared absorption by the sample followed by laser-induced fluorescence detection. A useful summary of laser methods relevant to the measurement of VET rates is given by Chesnoy and Gale (1984).

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The major focus of this review is the theoretical description of VET. The outline of the remainder of this paper is as follows. In § 2, we review the classical theories of gas phase VET developed by Zener (1931a, b, 1933), Jackson and Mott (1932), Landau and Teller (1936), Takayanagi (1963, 1965), Herzfeld and Litovitz (1959), as well as others (for example Cottrell and McCoubrey 1961). In § 3, we discuss modern theories of gas phase VET which employ *ab-initio* potential energy surfaces (PESs) and sophisticated quantum scattering methodologies. Singled out for description is the paper by Banks *et al.* (1986) which provides a representative example of work in this area. Section 4 summarizes the isolated binary collision (IBC) model, currently the most widely used model for liquid phase VET. Finally, in § 5, a brief synopsis of a new approach to gas and liquid phase VET, based on the work of our group, is presented.

We note that the scope of this paper leads to inevitable overlap with the content of other reviews. Section 2 on gas phase VET differs from, but makes significant contact with, § 19 and chapter 7 of Herzfeld and Litovitz (1959), chapter 6 of Cottrell and McCoubrey (1961), and the reviews by Takayanagi (1963, 1965). The greatest overlap is with the survey by Rapp and Kassal (1969). The material in § 4 on the IBC model overlaps the reviews by Chesnoy and Gale (1984, 1988), by Oxtoby (1981a, b) and by Harris *et al.* (1990).

2. The classical theory of gas phase vibrational energy transfer

Even in the ideal gas (binary collision) regimen, the problem of developing accurate algorithms for the evaluation of VET rates is difficult requiring the use of state-of-the-art PESs and advanced dynamical methods.

Such sophistication was, of course, not possible before the availability of modern computers and thus the earliest treatments of VET (Zener 1931a, b, 1933, Jackson and Mott 1932, Landau and Teller 1936) were based on crude one-dimensional interaction potentials and highly simplified collisional models. Since these early treatments, as well as the well known Schwartz–Slawsky–Herzfeld (SSH) (1952) theory (Herzfeld and Litovitz 1959) which emerged from them, are closely interrelated, for convenience we shall refer to these treatments collectively as the 'classical theory' of gas phase VET.

The classical theory remains of interest for at least two reasons: (1) much of the essential physics of VET (e.g. the role of collision time and mass effects and the crucial importance of the repulsive forces) is easily identified and discussed within the context of the classical theory; and (2) Some of the results of the classical theory, for example Landau–Teller plots, are still widely used in the experimental VET literature.

For these reasons, we present a brief review of the classical theory. Our goal is to give an easy-to-read synopsis which emphasizes these aspects of the theory which are of greatest contemporary interest. Thus we make no attempt at completeness either in the development of the theory or in the citation of the relevant literature. Comprehensive reviews of the theory, with very extensive lists of references, are available elsewhere (Herzfeld and Litowitz 1959, Cottrell and McCoubrey 1961, Takayanagi 1963, 1965, Rapp and Kassal 1969).

We begin with a brief overview of the theory and synopsis of the contents of this section.

2.1. *Overview of the classical theory*

The development of the collision theory of molecular energy transfer processes commenced in the earliest days of quantum mechanics (Kallmann and London 1929, 1930, Oldenberg 1931, Rice 1931a, b, Zener 1931a, b). Interest soon focused on VET, perhaps because the possibility of measuring VET rates by sound absorption experiments had been pointed out by Herzfeld and Rice (1928).

It was soon realized (Kallmann and London 1929, 1930) that because of the strength of molecular interactions the Born approximation was unsuitable for molecular collision processes. More useful zeroth-order approximations were suggested by Mott (1931) and Zener (1931b) who introduced the semiclassical (SC) method (§ 2.3.2) and by Zener (1931a) who introduced the distorted-wave approximation (DWA) (§ 2.3.4).

Zener additionally introduced the collinear atom–harmonic oscillator repulsive exponential potential model (figure 1) which is the basis of the earliest treatments of VET. This collinear model was first solved exactly by Jackson and Mott (1932) within the DWA (§ 2.3.4). Zener (1933) then solved the collinear model exactly within the first-order perturbation theory SC approximation (§ 2.3.2). Here, Zener (1933) also made two other important contributions. (1) He found a close relationship (§ 2.3.5) between his SC solution and the Jackson–Mott DWA result; and (2) he gave the first clear discussion of the importance of the adiabatic parameter $\omega_0\tau_c$ (where ω_0 is the oscillator frequency and τ_c is the collision time) and of the reduced mass of the collision partners in determining the VET efficiency.

The next important development came with the work of Landau and Teller (1936) who presented an approximate classical mechanical solution (§ 2.3.1) of the collinear model. In their paper Landau and Teller also (1) developed an approximate method (§ 2.4.3) for performing the Boltzmann average required to evaluate the thermal rate constants $k(T)$ for the collinear model (this method yields the widely used $\ln[k(T)] \propto T^{-1/3}$ Landau–Teller rate formula); and (2) developed a relationship equation (2.71 *b*) between the VER time T_1 and the collisional rate constant $k_{0,1}(T)$ for the $v=0 \rightarrow v=1$ vibrational transition.

The next developments came in the 1950s when Takayanagi, Herzfeld and co-workers, and others, extended the theory to three-dimensional scattering (§ 2.4.4). This work is thoroughly reviewed in the book by Herzfeld and Litovitz (1959) and in the articles by Takayanagi (1963, 1965).

Finally all this work was synthesized into a practical prescription for analysing VET data, the SSH theory, by Herzfeld and his collaborators (see, e.g. Herzfeld and Litowitz 1959). The SSH theory and some experimental tests (Cottrell and McCoubrey 1961, Millikan and White 1963) are reviewed in §§ 2.4.4 and 2.5. A critique of the classical theory based on the work of Widom (1962), Shin (1964, 1965), Kelley and Wolfsberg (1966), Mies (1965), and Secrest and Johnson (1966) is given in § 2.6.

2.2. *The collinear atom–harmonic diatom collision model*

We begin by specifying the model collision problem which is the basis of the classical VET theory.

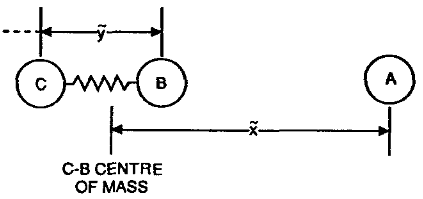

Figure 1. Model collision system analysed by Landau and Teller (1936), Zener (1933) and Jackson and Mott (1932). Atom of mass m_A collides collinearly with a harmonic diatom with atomic masses m_B and m_C and with circular frequency ω_0.

2.2.1. *Specification of the model problem*

We consider a collinear collision between an atom A with a diatomic molecule BC which is oriented (figure 1) so that atoms A and B strike one another. The masses and coordinates of the three atoms will be denoted respectively by m_A, m_B and m_C, and x_A, x_B and x_C. The diatom BC is assumed to be a harmonic oscillator with circular frequency ω_0.

The problem is best formulated in terms of the following generalized coordinates: the centre-of-mass coordinate of the system given by

$$X=\frac{m_A x_A+m_B x_B+m_C x_C}{m_A+m_B+m_C}; \tag{2.1 a}$$

the relative coordinate which is the displacement of atom A from the centre $\bar{x}_{BC}$ of mass of BC given by

$$\tilde{x}=x_A-\bar{x}_{BC}; \tag{2.1 b}$$

the internuclear separation of BC given by

$$\tilde{y}=x_B-x_C. \tag{2.1 c}$$

In the classical theory the total potential $V_T(x_A, x_B, x_C)$ is assumed to be of site–site (or 'dumb-bell') form (Mies 1965), that is

$$V_T(x_A, x_B, x_C)=w_{AB}(x_A, x_B)+w_{AC}(x_A, x_C)+w_{BC}(x_B, x_C) \tag{2.2}$$

where w_{AB}, etc., are site–site potentials. The BC site–site potential is just the harmonic potential of the diatom, that is

$$w_{BC}(x_B, x_C)=U(\tilde{y})\equiv\tfrac{1}{2}\mu_0\omega_0^2(\tilde{y}-\tilde{y}_{eq})^2, \tag{2.3}$$

where $\tilde{y}_{eq}$ is the equilibrium value of the oscillator coordinate $\tilde{y}$ and where the reduced mass μ_0 of BC is given by

$$\mu_0=\frac{m_B m_C}{m_B+m_C}. \tag{2.4}$$

Given the orientation of the diatom depicted in figure 1, during the interaction $w_{AB}\gg w_{AC}$. Thus w_{AC} is assumed to be negligible and the interaction potential $V_I=V_T-w_{BC}$ is taken as

$$V_I=w_{AB}(x_A, x_B)\equiv V_{AB}(x_A-x_B). \tag{2.5}$$

However, using the definition of $\bar{x}_{BC}$, namely

$$\bar{x}_{BC}=\frac{m_B x_B+m_C x_C}{m_B+m_C}, \tag{2.6}$$

it follows from equations (2.1 *b*) and (2.1 *c*) that $x_A-x_B=\tilde{x}-\lambda\tilde{y}$ where

$$\lambda=\frac{m_C}{m_B+m_C}. \tag{2.7}$$

Thus the interaction potential is given by

$$V_I=V_{AB}(\tilde{x}-\lambda\tilde{y}). \tag{2.8}$$

Given equations (2.2), (2.3), (2.5), and (2.8), it folows that the total potential is given by

$$V_T=U(\tilde{y})+V_{AB}(\tilde{x}-\lambda\tilde{y}). \tag{2.9}$$

Note that V_T in equation (2.9) is independent of the centre-of-mass coordinate X. Consequently we may work in a centre-of-mass rest frame in which the collision dynamics depends only on the coordinates $\tilde{x}$ and $\tilde{y}$. The energy E of the system is therefore the sum of the initial oscillator energy $E_{o,i}$ and the initial relative kinetic energy

$$E_i=\tfrac{1}{2}\mu\tilde{v}_i^2, \tag{2.10}$$

where $\tilde{v}_i$ is the initial relative velocity and where the reduced mass μ of the system is given by

$$\mu=\frac{m_A(m_B+m_C)}{m_A+m_B+m_C}. \tag{2.11}$$

2.2.2. *Reduced variable description of Secrest and Johnson*

Secrest and Johnson (1966) have shown that with an appropriate choice of reduced quantities the model problem can be further simplified. Specifically (referring to equations 2.12 and figure 2) it can be rigorously converted into the collision of a fictitious atom of mass m and coordinate x off a fictitious atom of unit mass and coordinate y, the latter being harmonically bound, with unit circular frequency, to a rigid wall. This conversion significantly aids in the comprehension of VET dynamics.

Secrest and Johnson (1966) introduce the following reduced quantities (our notation differs slightly from theirs):

$$y=\left(\frac{\mu_0\omega_0}{\hbar}\right)^{1/2}(\tilde{y}-\tilde{y}_{eq}), \tag{2.12a}$$

$$x=\left(\frac{\mu_0\omega_0}{\hbar}\right)^{1/2}\lambda^{-1}(\tilde{x}-\lambda\tilde{y}_{eq}), \tag{2.12b}$$

$$\varepsilon=(\hbar\omega_0)^{-1}E, \tag{2.12c}$$

$$V(x-y)=(\hbar\omega_0)^{-1}V_{AB}(\tilde{x}-\lambda\tilde{y}), \tag{2.12d}$$

$$m=\frac{m_Am_C}{m_B(m_A+m_B+m_C)}. \tag{2.12e}$$

Note that ε and $V(x-y)$ are the energy and interaction potential, respectively, of the system measured in units of the vibrational level spacing of BC, $\hbar\omega_0$.

2.2.3. *Linear expansion of the interaction potential*

Note that the coordinate y defined in equation (2.12a) is a dimensionless displacement of BC from vibrational equilibrium. In the classical theory it is assumed

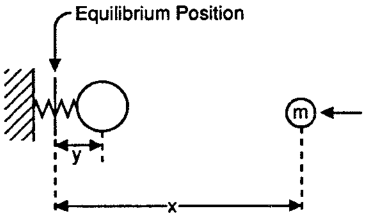

Figure 2. Fictitious atom–oscillator collision system. An 'atom' of mass $m=[m_B(m_A+m_B+m_C)]^{-1}m_Am_C$ collides with a fictitious bound harmonic oscillator with unit mass and unit circular frequency. The fictitious system may be derived from the real collision system in figure 1 by the transformation (equations 2.12) of Secrest and Johnson.

that during the collision the vibrational displacement of BC is sufficiently small that the following linear order expansion of $V(x-y)$ is valid:

$$V(x-y)\approx V(x)-yF(x), \tag{2.13 a}$$

where

$$F(x)\equiv-\left(\frac{\partial V(x-y)}{\partial y}\right)_{y=0}=V'(x). \tag{2.13 b}$$

2.2.4. *The repulsive exponential interaction potential*

The collision time arguments of Zener (1933) mentioned earlier suggested that the energy transfer dynamics were dominated by the steep repulsive wall of the interaction potential. (In modern language (Adelman *et al.* 1933a–c) the Fourier components of the vibrational force $F[x(t)]$ at the high frequencies important for VET are dominated by the repulsive wall since near the wall $F[x(t)]$ varies most rapidly in the time domain.) Because of the assumed importance of the wall a purely repulsive interaction potential

$$V_{AB}(\tilde{x}-\lambda\tilde{y})=\tilde{A}\exp\left(-\frac{\tilde{x}-\lambda\tilde{y}}{L}\right), \tag{2.14}$$

was employed in the most important early treatments of VET.

The corresponding repulsive exponential form for the reduced potential $V(x-y)$ follows from equations (2.12) and (2.14), as

$$V(x-y)=A\exp[-\alpha(x-y)], \tag{2.15}$$

where $A=(\hbar\omega)^{-1}\tilde{A}$ and where

$$\alpha=\lambda L^{-1}\left(\frac{\hbar}{\mu_0\omega_0}\right)^{1/2}. \tag{2.16}$$

Comparing equations (2.13) and (2.15) yields the following linear order expansion of the repulsive exponential potential:

$$V(x-y)=A\exp(-\alpha x)-yF(x), \tag{2.17}$$

where

$$F(x)=-\alpha A\exp(-\alpha x). \tag{2.18}$$

2.3. *Approximate solutions of the collinear collision model*

We next summarize approximate classical, SC and quantum solutions of the collinear collision model.

2.3.1. *Classical mechanics: the treatment of Landau and Teller*

We begin with the approximate classical mechanical treatment of Landau and Teller (1936).

Our starting point is the following exact expression for the total energy E of the system:

$$E=\tfrac{1}{2}\mu\dot{\tilde{x}}^2(t)+\tfrac{1}{2}\mu_0\dot{\tilde{y}}^2(t)+\tfrac{1}{2}\mu_0\omega_0^2(\tilde{y}-\tilde{y}_{eq})^2+V_{AB}[\tilde{x}(t)-\lambda\tilde{y}(t)]. \tag{2.19 a}$$

Transforming to the reduced variables of equations (2.12), equation (2.19 *a*) may be rewritten in dimensionless form as (cf. figure 2)

$$\varepsilon=\frac{E}{\hbar\omega_0}=\tfrac{1}{2}m\dot{x}^2(\tau)+\tfrac{1}{2}\dot{y}^2(\tau)+\tfrac{1}{2}y^2(\tau)+V[x(\tau)-y(\tau)], \tag{2.19 b}$$

where $\tau\equiv\omega_0 t$ and where $\dot{x}(\tau)\equiv \mathrm{d}x(\tau)/\mathrm{d}\tau$ and $\dot{y}(\tau)\equiv \mathrm{d}y(\tau)/\mathrm{d}\tau$.

In the treatment of Landau and Teller (1936) the potential in equation (2.17) is employed and the effects of oscillator motion on the dynamics of the incident atom are neglected since the oscillator is kept at equilibrium during the collision. These approximations permit an analytical treatment of the energy transfer dynamics. Within these approximations the reduced classical equations of motion become

$$m\frac{\mathrm{d}^2x(\tau)}{\mathrm{d}\tau^2}=F[x(\tau)] \tag{2.20 a}$$

and

$$\frac{\mathrm{d}^2y(\tau)}{\mathrm{d}\tau^2}=-y(\tau)-F[x(\tau)], \tag{2.20 b}$$

where $F(x)$ is defined in equation (2.18).

The Landau–Teller (1936) result, equation (2.37), for the energy transfer $\Delta\varepsilon_{\mathrm{LT}}$, is obtained by solving equations (2.20) in two steps. First equation (2.20 *a*) is solved to obtain $x(\tau)$ and, hence, $F[x(\tau)]$. Second, using this result for $F[x(\tau)]$, equation (2.20 *b*) is solved to obtain $\Delta\varepsilon_{\mathrm{LT}}$.

To perform the first step, we begin with the energy conservation expression

$$\varepsilon_{\mathrm{i}}\equiv\frac{E_{\mathrm{i}}}{\hbar\omega}=\tfrac{1}{2}m\dot{x}^2(\tau)+V[x(\tau)]. \tag{2.21}$$

In equation (2.21), E_{i} is defined in equation (2.10) and

$$V(x)=A\exp(-\alpha x). \tag{2.22}$$

From equations (2.21) and (2.22) it follows that

$$\frac{\mathrm{d}\tau}{\mathrm{d}x(\tau)}=[\dot{x}(\tau)]^{-1}=\left(\frac{m}{2\varepsilon_{\mathrm{i}}}\right)^{1/2}\left(1-\frac{A\exp[-\alpha x(\tau)]}{\varepsilon_{\mathrm{i}}}\right)^{-1/2},$$

or equivalently

$$\tau-\tau_0=\left(\frac{m}{2\varepsilon_{\mathrm{i}}}\right)^{1/2}\int_{x_0}^{x(\tau)}\frac{\mathrm{d}x}{[1-(A/\varepsilon_{\mathrm{i}})\exp(-\alpha x)]^{1/2}}, \tag{2.23}$$

where x_0 and τ_0 will be specified later. To perform the integration in equation (2.23) we define a new variable u by

$$u^{-2}=\frac{A}{\varepsilon_{\mathrm{i}}}\exp(-\alpha x). \tag{2.24}$$

Equation (2.23) may then be rewritten as

$$\tau-\tau_0=\alpha^{-1}\left(\frac{2m}{\varepsilon_{\mathrm{i}}}\right)^{1/2}\int_{u_0}^{u(\tau)}\frac{\mathrm{d}u}{(u^2-1)^{1/2}},$$

which upon integration yields

$$\tau-\tau_0=\alpha^{-1}\left(\frac{2m}{\varepsilon_i}\right)^{1/2}\{\cosh^{-1}[u(\tau)]-\cosh^{-1}u_0\}.$$

The above equation may be inverted to give

$$u(\tau)=\cosh\left[\alpha\left(\frac{\varepsilon_i}{2m}\right)^{1/2}(\tau-\tau_0)+\cosh^{-1}u_0\right]. \tag{2.25}$$

We next specify x_0 and τ_0. We take x_0 to be the classical turning point of $x(\tau)$ and τ_0 to be the time at which the atom reaches x_0. From equations (2.21) and (2.22) it then follows that x_0 is determined by the equation

$$\varepsilon_i=V[x(\tau_0)]=V[x_0]=A\exp(-\alpha x_0). \tag{2.26}$$

Comparing equations (2.24) and (2.26) then yields

$$u_0^{-2}=\frac{A}{\varepsilon_i}\exp(-\alpha x_0)=1. \tag{2.27}$$

Hence $u_0=1$ and $\cosh^{-1}u_0=0$. Moreover we are free to choose the time origin so that $\tau_0=0$. With these simplifications, equation (2.25) reduces to

$$u(\tau)=\cosh\left[\alpha\left(\frac{\varepsilon_i}{2m}\right)^{1/2}\tau\right]. \tag{2.28}$$

Comparing equations (2.18), (2.24) and (2.28) then yields the required result for $F[x(\tau)]$:

$$F[x(\tau)]=-\alpha\varepsilon_i\,\mathrm{sech}^2\left[\alpha\left(\frac{\varepsilon_i}{2m}\right)^{1/2}\tau\right], \tag{2.29}$$

where

$$\varepsilon_i=\tfrac{1}{2}mv_i^2. \tag{2.30}$$

We next turn to the determination of the energy transfer. We begin by solving equation (2.20 *b*) to yield

$$y(\tau)=\cos(\tau-\tau_i)\,y(\tau_i)-\sin(\tau-\tau_i)\,\dot{y}(\tau_i)+\int_{\tau_i}^{\tau}\sin(\tau-\tau')\mathscr{F}(\tau')\,d\tau', \tag{2.31}$$

where

$$\mathscr{F}(\tau)\equiv-F[x(\tau)]=\alpha\varepsilon_i\,\mathrm{sech}^2(\tfrac{1}{2}\alpha v_i\tau), \tag{2.32}$$

where $\tau_i=-\infty$ is the time at which the collision commences, and where we have used equations (2.29) and (2.30) to obtain equation (2.32). The collisional energy transfer to the oscillator is

$$\Delta\varepsilon=\varepsilon_{f,0}-\varepsilon_{i,0}=\tfrac{1}{2}[\dot{y}^2(\infty)+y^2(\infty)]-\tfrac{1}{2}[\dot{y}^2(\tau_i)+y^2(\tau_i)]. \tag{2.33}$$

This energy transfer may be evaluated from equations (2.31) and (2.33). A brief calculation which uses the fact that $\mathscr{F}(-\tau)=\mathscr{F}(\tau)$ yields

$$\Delta\varepsilon=\eta_0+\text{terms linear in } y(\tau_i) \text{ and } \dot{y}(\tau_i), \tag{2.34}$$

where

$$\eta_0=\frac{1}{2}\left|\int_{-\infty}^{\infty}\exp(i\tau)\mathscr{F}(\tau)\,d\tau\right|^2. \tag{2.35}$$

The Landau–Teller energy transfer $\Delta\varepsilon_{\mathrm{LT}}$ is defined as the mean of $\Delta\varepsilon$ over the uniform distribution of initial oscillator phases. The phase-averaged values of $y(\tau_{\mathrm{i}})$ and $\dot{y}(\tau_{\mathrm{i}})$ are, however, zero. Thus it follows from equation (2.34) that

$$\Delta\varepsilon_{\mathrm{LT}}=\eta_0. \tag{2.36}$$

Using equation (2.32) in equation (2.35) and performing the Fourier transform yields the following expression for $\Delta\varepsilon_{\mathrm{LT}}$:

$$\Delta\varepsilon_{\mathrm{LT}}=\frac{2\pi^2m^2}{\alpha^2}\operatorname{cosech}^2\left(\frac{\pi}{\alpha v_{\mathrm{i}}}\right). \tag{2.37}$$

Equation (2.37) gives the energy transfer of the fictitious system in figure 2. The energy transfer of the real system in figure 1 may be obtained from equation (2.37) using the transformations given earlier. The result is

$$\Delta E_{\mathrm{LT}}=\hbar\omega_0\,\Delta\varepsilon_{\mathrm{LT}}=\frac{2\pi^2\omega_0^2L^2\mu^2\lambda^2}{\mu_0}\operatorname{cosech}^2\left(\frac{\pi\omega_0L}{\tilde{v}_{\mathrm{i}}}\right), \tag{2.38}$$

where the initial relative velocity $\tilde{v}_{\mathrm{i}}$ is defined in equation (2.10). For typical collision energies, $\pi\omega_0L/\tilde{v}\gg 1$, equation (2.38) becomes

$$\Delta E_{\mathrm{LT}}=\frac{8\pi^2\omega_0^2L^2\mu^2\lambda^2}{\mu_0}\exp\left(-\frac{2\pi\omega_0L}{\tilde{v}_{\mathrm{i}}}\right). \tag{2.39}$$

Note that the collision time $\tau_{\mathrm{c}}\approx L/\tilde{v}_{\mathrm{i}}$. Thus equation (2.39) shows that ΔE_{LT} is an exponentially decreasing function of the adiabatic parameter $\omega_0\tau_{\mathrm{c}}$. This behaviour is in accord with the qualitative arguments of Zener (1933) mentioned earlier. Similar arguments were also presented by Landau and Teller (1936).

2.3.2. *Semiclassical mechanics: the first-order solution of Zener*

Within the SC approximation, the relative motion of the system is evaluated using classical mechanics while the collisional transition probabilities of its internal degrees of freedom are computed from the time-dependent Schrödinger equation.

We next summarize Zener's (1933) SC solution of the collinear atom–harmonic diatom collision problem. Zener's treatment is a SC analogue of the classical Landau–Teller (1936) calculation. Thus, within Zener's theory, the classical motion of the relative coordinate occurs in the repulsive exponential field produced by the fixed oscillator while the vibrational transition probabilities are evaluated using the linearized potential equation (2.17). The time-dependent Schrödinger equation for the vibrational motion thus (in reduced units) takes the following form:

$$\mathrm{i}\frac{\partial\psi(y,\tau)}{\partial\tau}=\left(-\frac{1}{2}\frac{\partial^2}{\partial y^2}+\frac{1}{2}y^2+V_0(y,\tau)\right)\psi(y,\tau), \tag{2.40}$$

where the interaction potential is given by

$$V_0(y,\tau)=-yF[x(\tau)]=y\mathscr{F}(\tau), \tag{2.41}$$

where $\mathscr{F}(\tau)$ is given in equation (2.32).

For simplicity, when discussing vibrational excitation, we shall assume that the diatom is initially in its ground ($v=0$) vibrational state. Thus we shall focus on the probabilities for the $v=0\rightarrow v=n$ transitions. Following Zener (1933), we shall evaluate these transition probabilities via a first-order perturbation solution of equation (2.40) and hence assume that the weak-coupling limit, $V_0(y,\tau) \ll \frac{1}{2}y^2$, holds.

Applying standard first-order time-dependent perturbation theory (for example Cohen-Tannoudji *et al.* 1977) to equations (2.40) and (2.41) yields the following result for the transition probability $p_{0,n}(\varepsilon)$:

$$p_{0,n}(\varepsilon) = |\langle \phi_n | y | \phi_0 \rangle|^2 \left| \int_{-\infty}^{\infty} \exp(\mathrm{i}\tau) \mathscr{F}(\tau)\, \mathrm{d}\tau \right|^2, \tag{2.42 a}$$

where the functions $\{\phi_n(y)\}$ are the stationary-state vibrational wavefunctions of the diatom. These satisfy the following Schrödinger equation:

$$\left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}y^2} + \frac{1}{2}y^2 \right) \phi_n(y) = \varepsilon_{0,n} \phi_n(y), \tag{2.43}$$

where

$$\varepsilon_{0,n} = n + \tfrac{1}{2}, \qquad n = 0, 1, 2, \ldots. \tag{2.44}$$

Evaluating the harmonic matrix element $\langle \phi_n | y | \phi_0 \rangle$ in equation (2.42 *a*) and using equation (2.35) yields the required result for the transition probability:

$$p_{0,n}(\varepsilon) = \delta_{n,1} \eta_0. \tag{2.42 b}$$

Equation (2.42 *b*) shows that, within the present treatment, only single quantum transitions are allowed. To complete the calculation we evaluate η_0 for the repulsive exponential interaction. Comparison of equation (2.36) and (2.37) yields

$$\eta_0 = \frac{2\pi^2 m^2}{\alpha^2} \operatorname{cosech}^2 \left(\frac{\pi}{\alpha v_i} \right). \tag{2.45}$$

Equations (2.42 *b*) and (2.45) are equivalent to the result of Zener (1933).

2.3.3. *Comparison of classical and semiclassical treatment*

Following Takayanagi (1963) and Rapp and Kassal (1969), we next compare the results of the Landau–Teller and the Zener treatments. To do this we evaluate the collisional energy transfer ΔE to the oscillator from the Zener transition probabilities $p_{0,n}(\varepsilon)$.

We note that, if a transition $v = 0 \rightarrow v = n$ is made, the energy transfer to the oscillator is, from equation (2.44), $\Delta\varepsilon_{0,n} - \varepsilon_{0,n} - \varepsilon_{0,0} = n$. Thus the energy transfer averaged over an ensemble of collisions each with energy ε is

$$\Delta\varepsilon = \sum_{n=1}^{\infty} \Delta\varepsilon_{0,n} p_{0,n}(\varepsilon) = \sum_{n=1}^{\infty} n p_{0,n}(\varepsilon). \tag{2.46}$$

Comparing equations (2.42 *b*) and (2.46) then yields the Zener energy transfer $\Delta\varepsilon_{\mathrm{Zener}}$ as

$$\Delta\varepsilon_{\mathrm{Zener}} = \eta_0. \tag{2.47}$$

However, comparing equations (2.36) and (2.47) gives $\Delta\varepsilon_{\mathrm{Zener}} = \Delta\varepsilon_{\mathrm{LT}}$. Thus the Landau–Teller and the Zener energy transfers are identical.

2.3.4. *Quantum mechanics: the distorted-wave solution of Jackson and Mott*

We next turn to the DWA treatment of Jackson and Mott (1932).

We begin with the time-independent Schrödinger equation for the collision system which, in reduced variables, is

$$\left(-\frac{1}{2m}\frac{\partial^2}{\partial x^2}-\frac{1}{2}\frac{\partial^2}{\partial y^2}+\frac{1}{2}y^2+V(x-y)\right)\Psi(x,y)=\varepsilon\Psi(x,y). \tag{2.48}$$

We next describe the DWA. Since complete developments of the DWA are available in standard textbooks (for example Messiah 1966) we shall limit ourselves here to a brief synopsis. As before, we shall restrict ourselves to the $v=0\rightarrow v=n$ transitions. For these transitions, energy conservation, together with equations (2.44), yields the following results for the initial and final relative kinetic energies:

$$\varepsilon_{\mathrm{i}}\equiv\tfrac{1}{2}\kappa_0^2=\varepsilon-\tfrac{1}{2},\quad \varepsilon_{\mathrm{f}}\equiv\tfrac{1}{2}\kappa_n^2=\varepsilon-(n+\tfrac{1}{2}). \tag{2.49}$$

We further note that the system wavefunction may be exactly expanded as

$$\Psi(x,y)=\sum_{n'=0}^{\infty}\phi_{n'}(y)F_{n'}(x), \tag{2.50}$$

where the functions $\phi_{n'}(y)$ are the harmonic oscillator eigenfunctions of equation (2.43) and where the $F_{n'}(x)$ are scattering wavefunctions for asymptotic relative kinetic energies $\frac{1}{2}\kappa_{n'}^2=\varepsilon-(n'+\frac{1}{2})$.

An infinite set of coupled differential equations for the scattering wavefunctions $F_{n'}(x)$ (the standard 'close-coupled' equations) may be straightforwardly derived from equations (2.48) and (2.50). Determination of the $F_{n'}(x)$, by solution of these equations, gives $\Psi(x,y)$ from equation (2.50) and hence the transition probabilities $p_{0,n}(\varepsilon)$.

The DWA may be regarded as an approximate decoupling of the infinite set of equations. For the present purposes, it is sufficient to note that within the DWA the transition probabilities $p_{0,n}(\varepsilon)$ may be evaluated from the solutions $F_{n'}^{(0)}(x)$ of fully decoupled versions of the original equations. Specifically, the $F_{n'}^{(0)}(x)$ satisfy

$$\left(-\frac{1}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+V(x)\right)F_{n'}^{(0)}(x)=\tfrac{1}{2}\kappa_{n'}^2F_{n'}^{(0)}(x). \tag{2.51}$$

The DWA transition probabilities are then given by

$$p_{0,n}(\varepsilon)=\frac{2\pi m^2}{\kappa_n\kappa_0}|A|^2, \tag{2.52}$$

where

$$A=\int_{-\infty}^{\infty}\mathrm{d}x\int_{-\infty}^{\infty}\mathrm{d}y\,[F_n^{(0)}(x)\phi_n(y)\,\Delta V(x,y)\,F_0^{(0)}(x)\Phi_0(y)], \tag{2.53}$$

and where

$$\Delta V(x,y)=V(x-y)-V(x). \tag{2.54}$$

Note that, as in the Landau–Teller (1936) and Zener (1933) treatments, the DWA solution is expressed in terms of the elastic scattering off a fixed oscillator. However, in contrast with the earlier treatments, the DWA includes the effects of energy conservation (since $F_0^{(0)}(x)$ describes scattering with the relative kinetic energy ε_{i} while $F_n^{(0)}(x)$ describes scattering with the relative kinetic energy ε_{f}). We shall return to this point later.

Given this outline of the DWA, we next turn to the treatment of Jackson and Mott (1932). This treatment is based on the linearized potential of equations (2.17) and (2.18). For this potential, $\Delta V(x,y)$, defined in equation (2.54), becomes

$$\Delta V(x,y)=\alpha A\exp(-\alpha x)\,y. \tag{2.55}$$

Comparison of equations (2.52), (2.53) and (2.55) then yields

$$p_{0,n}(\varepsilon)=\frac{2\pi m^2}{\kappa_0\kappa_n}\alpha^2A^2|\langle\phi_n|y|\phi_0\rangle|^2\left|\int_{-\infty}^{\infty}F_n^{(0)}(x)\exp(-\alpha x)F_0^{(0)}(x)\,\mathrm{d}x\right|^2. \tag{2.56}$$

To complete the calculation, we must solve equation (2.51) (subject to appropriate boundary conditions) for $V(x)=A\exp(-\alpha x)$ to obtain $F_0^{(0)}(x)$ and $F_n^{(0)}(x)$ and then perform the integral in equation (2.56). Jackson and Mott (1932) show this calculation can be carried out analytically to yield (in our notation)

$$p_{0,n}(\varepsilon)=\frac{8\pi^2m^2}{\alpha^2}\frac{\sinh(\pi q_0)\sinh(\pi q_n)}{[\cosh(\pi q_0)-\cosh(\pi q_n)]^2}\delta_{n,1}, \tag{2.57}$$

where

$$q_n\equiv\frac{2\kappa_n m^{1/2}}{\alpha}. \tag{2.58}$$

2.3.5. *Zener's comparison of the first-order semiclassical and distorted-wave transition probabilities*

Zener (1933) pointed out that a close relation exists between his first-order SC result for the transition probability, equation (2.42 *b*), and the corresponding Jackson–Mott (1932) result, equation (2.57). We next briefly review his argument.

To establish the connection, we specialize the Jackson–Mott result to the classical limit for the relative motion. This limit holds if $\pi q_{0(n)}\gg 1$. In this limit, $\sinh(\pi q_{0(n)})=\cosh(\pi q_{0(n)})=\frac{1}{2}\exp(\pi q_{0(n)})$ and the Jackson–Mott formula reduces as follows:

$$\lim_{\pi q_{0(n)}\gg 1}[p_{0,n}(\varepsilon)]=\delta_{n,1}\frac{8\pi^2m^2}{\alpha^2}\frac{\exp(\pi q_0)\exp(\pi q_n)}{[\exp(\pi q_0)-\exp(\pi q_n)]^2}$$

$$=\delta_{n,1}\frac{2\pi^2m^2}{\alpha^2}\left(\frac{\exp[\frac{1}{2}\pi(q_0-q_n)]-\exp[-\frac{1}{2}\pi(q_0-q_n)]}{2}\right)^{-2}.$$

It then follows from the above equation and equation (2.58) that

$$\lim_{\pi q_{0(n)}\gg 1}[p_{0,n}(\varepsilon)]=\delta_{n,1}\frac{2\pi^2m^2}{\alpha^2}\operatorname{cosech}^2\left[\frac{\pi m^{1/2}(\kappa_0-\kappa_n)}{\alpha}\right]. \tag{2.59}$$

However,

$$\kappa_0-\kappa_n=\frac{\kappa_0^2-\kappa_n^2}{\kappa_0+\kappa_n}=n\left[\tfrac{1}{2}(\kappa_0+\kappa_n)\right]^{-1},$$

where the final equality follows from equation (2.49). Using the above expression, equation (2.59) may be rewritten as (since $n=1$ for the allowed transition)

$$\lim_{\pi q_{0(n)}\gg 1}[p_{0,n}(\varepsilon)]=\delta_{n,1}\frac{2\pi^2m^2}{\alpha^2}\operatorname{cosech}^2\left(\frac{\pi m^{1/2}}{\alpha\frac{1}{2}(\kappa_0+\kappa_1)}\right). \tag{2.60}$$

Finally defining the initial and final relative velocities by (cf. equations 2.30 and 2.49)

$$\varepsilon_{\mathrm{i}}=\tfrac{1}{2}\kappa_0^2=\tfrac{1}{2}mv_{\mathrm{i}}^2, \quad \varepsilon_{\mathrm{f}}=\tfrac{1}{2}\kappa_1^2=\tfrac{1}{2}mv_{\mathrm{f}}^2, \tag{2.61}$$

equation (2.60) may be re-expressed as

$$\lim_{\pi q_{0(n)}\gg 1}\,[p_{0,n}(\varepsilon)]=\delta_{n,1}\frac{2\pi^2m^2}{\alpha^2}\operatorname{cosech}^2\left(\frac{\pi}{\alpha\bar{v}}\right), \tag{2.62}$$

where

$$\bar{v}=\tfrac{1}{2}(v_{\mathrm{i}}+v_{\mathrm{f}}). \tag{2.63}$$

Note that $\bar{v}$ is the mean of the initial and final velocities.

Equation (2.62) is the SC limit of the Jackson–Mott (1932) DWA result. Note that it bears a strong resemblance to Zener's (1933) SC result, which from equations (2.42 *b*) and (2.45) is

$$p_{0,n}(\varepsilon)=\delta_{n,1}\frac{2\pi^2m^2}{\alpha^2}\operatorname{cosech}^2\left(\frac{\pi}{\alpha v_{\mathrm{i}}}\right). \tag{2.64}$$

Equations (2.62) and (2.64) differ only in that the SC result involves the initial velocity v_{i} while the DWA result involves the symmetrical velocity $\bar{v}$. This difference reflects the fact that only the DWA treatment accounts for energy conservation.

For $\varepsilon_{\mathrm{i}}=\frac{1}{2}mv_{\mathrm{i}}^2\gg 1$, the initial relative kinetic energy is much greater than the energy transferred to the oscillator and, hence, $v_{\mathrm{f}}\approx v_{\mathrm{i}}$. Thus, in the high-energy limit, the Jackson–Mott and Zener expressions for $p_{0,n}(\varepsilon)$ become identical, and all three simple theories (Landau and Teller 1936, Zener 1933, Jackson and Mott 1932) yield identical results for the energy transfer to the oscillator.

This completes our review of the zeroth-order dynamical treatments.

2.4. *A framework of analysing vibrational energy transfer data*

We next provide a synopsis of the efforts that have been made to convert the results of the zeroth-order treatments into a framework for analysing VET data. A comprehensive review of this work is given in section 19 and chapter 117 of the book by Herzfeld and Litovitz (1959).

In this discussion we express all results in terms of the real variables of the collision system. Thus, for example, the DWA result for $p_{0,1}(\varepsilon)$, given in reduced variables in equations (2.62) and (2.63), will be re-expressed as

$$p_{0,i}(\tilde{v}_i)\equiv p_{0,1}(\varepsilon)=\frac{2\pi^2\omega_0^2L^2\mu^2\lambda^2}{\hbar\omega_0\mu_0}\operatorname{cosech}^2\left(\frac{\pi\omega_0L}{w}\right), \tag{2.65}$$

where w is defined by

$$w=\tfrac{1}{2}(\tilde{v}_{\mathrm{i}}+\tilde{v}_{\mathrm{f}}), \tag{2.66}$$

and where $\tilde{v}_{\mathrm{i}}$ and $\tilde{v}_{\mathrm{f}}$ are the initial and final relative velocities defined, as in equation (2.10), by

$$\tfrac{1}{2}\mu\tilde{v}_{\mathrm{i(f)}}^2=E_{\mathrm{i(f)}}. \tag{2.67}$$

Note that $\tilde{v}_{\mathrm{i}}$ and $\tilde{v}_{\mathrm{f}}$ are related (by energy conservation) by

$$\tfrac{1}{2}\mu\tilde{v}_{\mathrm{i}}^2=\tfrac{1}{2}\mu\tilde{v}_{\mathrm{f}}^2+\hbar\omega_0. \tag{2.68}$$

We next turn to the definition of the thermal rate constant $k_{0,1}(T)$ for the $v=0\rightarrow v=1$ excitation.

2.4.1. *The thermal rate constant* $k_{0,1}(T)$

To define $k_{0,1}(T)$, we first define the thermal transition probability $p_{0,1}(T)$ by

$$p_{0,1}(T) \equiv \int_0^\infty P(\tilde{v}_i) p_{0,1}(\tilde{v}_i)\, d\tilde{v}_i, \tag{2.69}$$

where $P(\tilde{v}_i)$ is the Maxwell velocity distribution function. The rate constant is then defined as

$$k_{0,1}(T) = Z(T) p_{0,1}(T), \tag{2.70}$$

where $Z(T)$ (available from the kinetic theory of gases) is the total number of A + BC collisions that a BC molecule experiences per second.

2.4.2. *The Landau–Teller theory of the relaxation time* T_1

Landau and Teller (1936) have developed an expression for the VER time T_1 of the collinear collision system. Their result is

$$T_1^{-1} = k_{1,0}(T) - k_{0,1}(T), \tag{2.71 a}$$

where $k_{0,1}(T)$ is the rate constant for excitation, defined in equation (2.70), and where $k_{1,0}(T)$ is the rate constant for the inverse ($v = 1 \rightarrow v = 0$) de-excitation process. Since $k_{1,0}(T)$ is determined in terms of $k_{0,1}(T)$ by detailed balance as

$$k_{1,0}(T) = \exp\left(\frac{\hbar\omega_0}{k_B T}\right) k_{0,1}(T), \tag{2.72}$$

the following alternative forms for T_1:

$$T_1^{-1} = k_{0,1}(T)\left[\exp\left(\frac{\hbar\omega_0}{k_B T}\right) - 1\right] \tag{2.71 b}$$

and

$$T_1^{-1} = k_{1,0}(T)\left[1 - \exp\left(-\frac{\hbar\omega_0}{k_B T}\right)\right], \tag{2.71 c}$$

are also valid.

Equation (2.71 *b*) permits evaluation of T_1 from $k_{0,1}(T)$ and hence, ultimately, from the DWA result equation (2.65). Equation (2.71 *c*) shows that for typical ω_0, except at elevated temperatures, T_1^{-1} is essentially identical with the de-excitation rate constant $k_{1,0}(T)$.

We next discuss the method of derivation of equations (2.71) and (2.72). Since the actual derivation of Landau and Teller (1936) is somewhat involved, we shall outline here a similar but simpler derivation, valid for a two-state 'oscillator' with energy levels $E_0 = \frac{1}{2}\hbar\omega_0$ and $E_1 = \frac{3}{2}\hbar\omega_0$. This two-level problem has also been discussed by Herzfeld and Litovitz (1959) and Rapp and Kassal (1969).

Let $n_0(t)$ and $n_1(t)$ be the number density of 'oscillators' in the ground state and excited state respectively at time t. Denote the corresponding equilibrium number densities by $n_{0,\mathrm{eq}}$ and $n_{1,\mathrm{eq}}$.

Consider the excess vibrational energy relative to equilibrium:

$$\Delta E(t) \equiv \tfrac{1}{2}\hbar\omega_0[n_0(t) - n_{0,\mathrm{eq}}] + \tfrac{3}{2}\hbar\omega_0[n_1(t) - n_{1,\mathrm{eq}}]. \tag{2.73}$$

Our goal is first to show that $\Delta E(t)$ decays according to an exponential relaxation law, namely

$$\frac{\mathrm{d}[\Delta E(t)]}{\mathrm{d}t} = -T_1^{-1}\,\Delta E(t), \tag{2.74}$$

and second to relate the relaxation time T_1 in equation (2.74) to the rate constants $k_{0,1}(T)$ and $k_{1,0}(T)$.

To proceed further we assume, following Landau and Teller (1936), that $n_0(t)$ and $n_1(t)$ obey simple rate equations, namely

$$\frac{\mathrm{d}n_0(t)}{\mathrm{d}t} = k_{1,0}(T)n_1(t) - k_{0,1}(T)n_0(t) \tag{2.75 a}$$

and

$$\frac{\mathrm{d}n_1(t)}{\mathrm{d}t} = k_{0,1}(T)n_0(t) - k_{1,0}(T)n_1(t). \tag{2.75 b}$$

At equilibrium, $\mathrm{d}n_0(t)/\mathrm{d}t = \mathrm{d}n_1(t)/\mathrm{d}t = 0$ and either of equations (2.75) yields

$$k_{0,1}(T)n_{0,\mathrm{eq}} = k_{1,0}(T)n_{1,\mathrm{eq}}, \tag{2.76}$$

a result which is the basis of the detailed balance condition equation (2.72). A second consequence of equations (2.75) is that $\mathrm{d}[n_0(t)+n_1(t)]/\mathrm{d}t = 0$ or equivalently that

$$n_0(t)+n_1(t) = n_{0,\mathrm{eq}} + n_{1,\mathrm{eq}}. \tag{2.77}$$

Using equations (2.76) and (2.77) to eliminate $n_0(t)$ and $n_{0,\mathrm{eq}}$ from equation (2.75 *b*) then yields

$$\frac{\mathrm{d}n_1(t)}{\mathrm{d}t} = -[k_{0,1}(T)+k_{1,0}(T)][n_1(t) - n_{1,\mathrm{eq}}]. \tag{2.78}$$

Moreover, using equation (2.77), equation (2.73) becomes

$$\Delta E(t) = \hbar\omega_0[n_1(t) - n_{1,\mathrm{eq}}]. \tag{2.79}$$

It then follows immediately from equations (2.78) and (2.79) that

$$\frac{\mathrm{d}[\Delta E(t)]}{\mathrm{d}t} = -[k_{0,1}(T)+k_{1,0}(T)]\,\Delta E(t). \tag{2.80}$$

Equation (2.80) is identical in form with the required result equation (2.74). Moreover, as required, the relaxation time is determined in terms of rate constants, that is

$$T_1^{-1} = k_{1,0}(T) + k_{0,1}(T). \tag{2.81}$$

(Note that the two-state system result for T_1, equation (2.81), differs from the harmonic oscillator result, equation (2.71 *a*). The difference is, however, only significant at high temperatures.)

2.4.3. *Determination of the temperature dependence of T_1 by the Landau–Teller thermal averaging procedure*

We next determine the temperature dependence of T_1. Our procedure is to determine $k_{0,1}(T)$ from equations (2.65), (2.69) and (2.70) and then to evaluate T_1 from equation (2.71 *b*). This requires the evaluation of the thermal average in equation (2.69), which defines $p_{0,1}(T)$ in terms of $p_{0,1}(\tilde{v}_i)$. We perform this thermal average by Laplace integration following Landau and Teller (1936). The justification for this asymptotic integration is that $P(\tilde{v}_i)$ and $p_{0,1}(\tilde{v}_i)$ are rapidly decreasing and rapidly increasing functions, respectively of $\tilde{v}_i$ and thus one expects the integrand in equation (2.69) to be sharply peaked at a 'most effective' collision velocity v^*.

In their original calculation, Landau and Teller ignored energy conservation and thus set $\tilde{v}_i=\tilde{v}_f=w$. This approximation is valid (see equation 2.68) in the high-energy limit $E_i=\frac{1}{2}\mu\tilde{v}_i^2 \gg \hbar\omega_0$. To illustrate the Landau–Teller procedure, we first perform the thermal average in this high-energy limit. Then, following Herzfeld, we extend the calculation to include a first correction for energy conservation. We thus, initially, approximate equation (2.65) by

$$p_{0,1}(\tilde{v}_i)\approx\frac{2\pi^2\omega_0^2L^2\mu^2\lambda^2}{\hbar\omega_0\mu_0}\operatorname{cosech}^2\left(\frac{\pi\omega_0L}{\tilde{v}_i}\right). \tag{2.82}$$

In their calculation, Landau and Teller additionally assume the limit $\omega_0\tau_c\approx\pi\omega_0L/\tilde{v}_i\gg 1$ obtains. Then equation (2.82) further simplifies to (cf. equation 2.39)

$$p_{0,1}(\tilde{v}_i)\approx\frac{8\pi^2\omega_0^2L^2\mu^2\lambda^2}{\hbar\omega_0\mu_0}\exp\left(-\frac{2\pi\omega_0L}{\tilde{v}_i}\right). \tag{2.83}$$

The Laplace evaluation of $p_{0,1}(T)$ is now straightforward. Using the explicit form

$$P(\tilde{v}_i)=\left(\frac{\mu}{2\pi k_BT}\right)^{1/2}\exp\left(-\frac{1}{2}\frac{\mu\tilde{v}_i^2}{k_BT}\right), \tag{2.84}$$

equations (2.69) and (2.83) yield (the superscript 0 indicates $E_i\gg\hbar\omega$)

$$p_{0,1}^{(0)}(T)=\left(\frac{\mu}{2\pi k_BT}\right)^{1/2}\frac{8\pi^2\omega_0^2L^2\mu^2\lambda^2}{\hbar\omega_0\mu_0}I(T), \tag{2.85}$$

where

$$I(T)=\int_0^\infty \exp[-A(\tilde{v}_i)]\,d\tilde{v}_i, \tag{2.86}$$

with

$$A(\tilde{v}_i)=\frac{1}{2}\frac{\mu\tilde{v}_i^2}{k_BT}+\frac{2\pi\omega_0L}{\tilde{v}_i}. \tag{2.87}$$

Within the Laplace method, $A(\tilde{v}_i)$ is approximated by the quadratric order expansion $A(\tilde{v}_i)\approx A(v^*)+\frac{1}{2}A''(v^*)(\tilde{v}_i-v^*)^2$, where v^* is determined by the condition $A'(v^*)=0$ or equivalently, using equation (2.87),

$$\frac{\mu v^*}{k_BT}=\frac{2\pi\omega_0L}{(v^*)^2}. \tag{2.88}$$

Solving equation (2.88) yields

$$v^*=\left(\frac{2\pi\omega_0Lk_BT}{\mu}\right)^{1/3}. \tag{2.89}$$

Next using the quadratic expansion of $A(\tilde{v}_i)$, equation (2.86) may be integrated to yield

$$I(T)=\left(\frac{2\pi}{A''(v^*)}\right)^{1/2}\exp[-A(v^*)]. \tag{2.90}$$

$A(v^*)$ and $A''(v^*)$ in equation (2.90) may be evaluated from equations (2.87)–(2.89) as

$$A(v^*)=\frac{3}{2}\frac{\mu(v^*)^2}{k_BT}=\frac{3}{2}\left(\frac{4\pi^2\omega_0^2L^2\mu}{k_B}\right)^{1/3}T^{-1/3} \tag{2.91 a}$$

and

$$A''(v)=\frac{3\mu}{k_BT}. \tag{2.91 b}$$

Comparing equations (2.85), (2.90) and (2.91) then yields the Landau–Teller result

$$p^{(0)}_{0,1}(T)=A\exp\left(-\frac{a}{T^{1/3}}\right), \tag{2.92}$$

where

$$a=\frac{3}{2}\left(\frac{4\pi^2\omega_0^2L^2\mu}{k_B}\right)^{1/3} \tag{2.93}$$

and

$$A=\left(\frac{1}{3}\right)^{1/2}\frac{8\pi^2\omega_0^2L^2\mu^2\lambda^2}{\hbar\omega_0\mu_0}. \tag{2.94}$$

Note that equation (2.92) exhibits the familiar Landau–Teller $\ln P\propto T^{-1/3}$ temperature dependence.

The Landau–Teller result, equation (2.92), since it neglects conservation of energy, is invalid unless the temperature is sufficiently high that $\frac{1}{2}\mu(v^*)^2\gg\hbar\omega_0$. We next describe the introduction by Herzfeld and Litovitz (1959) of a correction for energy conservation.

We thus begin with the 'exact' form for $p_{0,1}(\tilde{v}_i)$ (equation 2.65), which includes the effects of energy conservation. Specializing equation (2.65) to the limit $\omega_0\tau_c\gg 1$ yields (cf. equation 2.83)

$$p_{0,1}(\tilde{v}_i)\approx\frac{8\pi^2\omega_0^2L^2\mu^2\lambda^2}{\hbar\omega_0\mu_0}\exp\left(-\frac{2\pi\omega_0L}{w}\right), \tag{2.95}$$

where w is defined in equation (2.66). We next turn to the energy conservation condition, equation (2.68), which may be rewritten as

$$\tilde{v}_f=\tilde{v}_i\left(1-\frac{2\hbar\omega_0}{\mu\tilde{v}_i^2}\right)^{1/2}. \tag{2.96}$$

For excitation $E_i=\frac{1}{2}\mu v_i^2\geqslant\hbar\omega_0$ which equals the threshold energy. Thus the following power series expansion of equation (2.96) holds:

$$\tilde{v}_f=\tilde{v}_i\left[1-\frac{\hbar\omega_0}{\mu\tilde{v}_i^2}+\frac{1}{2}\left(\frac{\hbar\omega_0}{\mu\tilde{v}_i^2}\right)^2+\dots\right]. \tag{2.97}$$

Within the Landau–Teller treatment it is assumed that $\tilde{v}_f=\tilde{v}_i$. Herzfeld and Litovitz include the first correction term in equation (2.97) and thus take

$$\tilde{v}_f\approx\tilde{v}_i-\frac{\hbar\omega_0}{\mu\tilde{v}_i}. \tag{2.98}$$

Equation (2.98) implies the following approximation for the symmetrized velocity w defined in equation (2.66), $w=\tilde{v}_i-\frac{1}{2}\hbar\omega_0/\mu\tilde{v}_i$. Hence

$$w^{-1}=\tilde{v}_i^{-1}\left(1-\frac{\hbar\omega_0}{2\mu\tilde{v}_i^2}\right)^{-1}\approx\tilde{v}_i^{-1}\left(\frac{\hbar\omega_0}{2\mu\tilde{v}_i^2}\right).$$

Using this last result in equation (2.95) yields the Herzfeld–Litovitz approximation for the transition probability:

$$p_{0,1}(\tilde{v}_i)\approx p_{0,1}^{(0)}(\tilde{v}_i)\exp\left[-\frac{2\pi\omega_0 L}{\tilde{v}_i^2}\left(\frac{\hbar\omega_0}{2\mu\tilde{v}_i}\right)\right], \tag{2.99}$$

where $p_{0,1}^{(0)}(\tilde{v}_i)$ is the Landau–Teller expression given in equation (2.83). The Herzfeld–Litovitz approximation to the thermal transition probability $p_{0,1}(T)$ may be obtained by combining equations (2.69) and (2.99) and then using Laplace integration to perform the thermal average. This yields

$$p_{0,1}(T)=p_{0,1}^{(0)}(T)\exp\left[-\frac{2\pi\omega_0 L}{(v^*)^2}\left(\frac{\hbar\omega_0}{2\mu v^*}\right)\right], \tag{2.100}$$

where the Landau–Teller result $p_{0,1}^{(0)}(T)$ is defined in equations (2.92)–(2.94). Finally using equation (2.88), equation (2.100) simplifies to

$$p_{0,1}(T)=p_{0,1}^{(0)}(T)\exp\left(-\frac{\hbar\omega_0}{2k_B T}\right). \tag{2.101}$$

Given equation (2.101) it is now straightforward to obtain an expression for the VER time T_1. Comparing equations (2.70), (2.71 *b*), (2.92) and (2.101) yields

$$T_1^{-1}=A(T)\exp\left(-\frac{a}{T^{1/3}}+\frac{b}{T}\right), \tag{2.102}$$

where

$$A(T)\equiv AZ(T)\left[1-\exp\left(-\frac{\hbar\omega_0}{k_B T}\right)\right], \tag{2.103}$$

and where

$$b=\frac{\hbar\omega_0}{2k_B}. \tag{2.104}$$

Note that the inclusion of energy conservation by Herzfeld and Litovitz modifies the Landau–Teller $T^{-1/3}$ exponent by introducing a correction term b/T with a T^{-1} temperature dependence.

2.4.4. *The Schwartz–Slawsky–Herzfeld theory*

We next briefly describe the SSH theory (Schwartz *et al.* 1952) which is a practical framework for analysing VET data based on the fundamental theory reviewed here. To obtain this framework, SSH provided simple ways (1) to include the effect of attractive forces; (2) to choose the interaction potential parameters; and (3) to include effects arising from the non-collinear nature of the collisions.

To include attractive forces, the repulsive exponential interaction potential of equation (2.14) was modified by adding a constant of magnitude $-\mathscr{E}$, where $\mathscr{E}$ is the Lennard-Jones well depth of the collision system. This yields a modified potential of the form

$$U_{\exp}(\tilde{x})=A\exp\left(-\frac{\tilde{x}}{L}\right)-\mathscr{E}. \tag{2.105}$$

This modification changes the T_1 expression in equation (2.102) to the following expression:

$$T_1^{-1}=A(T)\exp\left(-\frac{a}{T^{1/3}}+\frac{b}{T}+\frac{c}{T}\right), \tag{2.106}$$

where

$$c=\frac{\mathscr{E}}{k_B}. \tag{2.107}$$

The method of choosing the interaction potential parameter $\mathscr{E}$ was just mentioned. To choose the repulsion parameter L, SSH fitted the potentials $U_{\mathrm{exp}}(\bar{x})$ to Lennard-Jones potentials (Hirschfelder *et al.* 1954) derived from viscosity measurements. They suggested two simple methods for making the fits. Both methods yielded

$$\frac{\sigma}{L}\approx 17\text{–}20 \tag{2.108}$$

for a range of molecules, where σ is the Lennard-Jones diameter of the system.

Three-dimensional collision effects were introduced via approximate procedures reviewed in detail by Takayanagi (1963, 1965). Since these methods are somewhat complex, they will not be further described here. The net effect of including these three-dimensional effects is to modify the pre-exponential factor $A(T)$ in equation (2.106) but to leave the exponential unchanged. The final result of the SSH theory, including the three-dimensional corrections, is given by equations (62.16) and (64.25) in the book by Herzfeld and Litovitz (1959).

2.5. *Experimental tests of the classical theory*

We next briefly discuss some of the experimental tests of the classical theory. We begin with the correlation of Millikan and White (1963).

2.5.1. *The Millikan–White correlation*

The Landau–Teller (1936) prediction of the temperature dependence of T_1 is (set $b=0$ in equation 2.102)

$$\ln T_1=\frac{a}{T^{1/3}}-\ln[A(T)], \tag{2.109}$$

where, from equation (2.93),

$$a=\frac{3}{2}\left(\frac{4\pi^2\omega_0^2L^2\mu}{k_B}\right)^{1/3}. \tag{2.110}$$

Millikan and White tested the Landau–Teller prediction by logarithmically plotting a large number of experimental results for T_1 against $T^{-1/3}$. They found good linear plots for 12 simple energy transfer systems over a temperature range from room temperature to several thousand kelvins.

While confirming the $\ln T_1 \propto T^{-1/3}$ prediction, they did not confirm the Landau–Teller prediction (see equation 2.110) that the parameter $a\propto\omega_0^{2/3}L^{2/3}\mu^{1/3}$. Instead the corresponding parameter in their correlation has an $\omega_0^{4/3}\mu^{1/2}$ dependence.

2.5.2. *Tests of the Schwartz–Slawsky–Herzfeld theory*

We next turn to specific tests of the SSH theory. Such tests have been performed by Schwartz *et al.* (1952), McCoubrey *et al.* (1961), Dickens and Ripamonte (1961), Tanczos (1956), Herzfeld and Litovitz (1959) as well as others. A good discussion of the results of these comparisons is given on pp. 158–164 of the book by Cottrell and McCoubrey (1961). We shall restrict ourselves here to a summary of their main points. These are as follows.

(1) The energy conservation and attractive force corrections to the Landau–Teller result for T_1 (the terms $b/T + c/T$ in the exponent of equation 2.106), must be included in order that the exponential repulsion parameters L required to fit the VET data be in reasonable agreement with those obtained from viscosity measurements.

(2) For a number of diatomic and triatomic systems, the relaxation times computed from the SSH theory are in rough order-of-magnitude agreement with experiments.

2.6. *Critique of the classical theory*

We next give a discussion, based on results available in the literature, of the validity of several of the key assumptions of the classical theory. We begin with a synopsis of the work of Widom (1962) and Shin (1964, 1965).

2.6.1. *The analysis of Widom and of Shin*

The analysis of Widom (1962) and Shin (1964, 1965) permits one to examine the following question. How strongly is the SSH form of the temperature dependence of T_1 tied to the form of the interaction potential? In particular, is the Landau–Teller $T^{-1/3}$ temperature dependence a consequence of the assumed repulsive exponential interaction potential or does it have more general validity?

Widom and Shin evaluated the exponential contribution to the DWA matrix element appearing in equation (2.56) in the SC (Wentzel–Kramers–Brillouin) limit using a procedure due to Landau (1932). Within this formulation the analysis which leads to equation (2.102), could be extended to potentials other than the repulsive exponential potential. In particular, analytical results for the high-temperature expansion of $\ln T_1$ were obtained for the Morse and Lennard-Jones potentials.

From the present standpoint, the main results obtained by Widom and by Shin are as follows.

(1) For all potentials studied, the leading term in the high-temperature expansion of $\ln T_1$ is very similar to the Landau–Teller term.

(2) For all potentials studied an energy conservation term *identical* with the bT^{-1} term appearing in equation (2.106) is found.

(3) The higher-order correction terms in the $\ln T_1$ expansion are specific to the potential and may differ significantly from the attractive force term $\mathscr{E}/k_B T$ proposed by SSH.

2.6.2. *Mies' test of the model potential*

Mies (1965), using the He–H_2 system as a prototype, examined a number of the main assumptions of classical VET theory. His basic procedure was to compare results predicted by the model potential utilized in the classical theory with corresponding results computed from a He + H_2 Hartree–Fock potential (Krauss and Mies 1965). The model potential in question is equation (2.9), with $V_{AB}(\tilde{x} - \lambda\tilde{y})$ approximated by a linearized repulsive exponential, with range parameter L determined from viscosity potentials, and with $U(\tilde{y})$ taken as harmonic as in equation (2.3).

Some of the main conclusions of Mies (1966) are as follows.

(1) Viscosity potentials, since they are sensitive to glancing collisions which do not adequately probe the repulsive wall of the potential, provide a very poor basis for VET studies. (This point has also been made by other workers, such as Rapp and Kassal 1969.) For example, for the He–H_2 system, transport measurements yield $L = 0{\cdot}14$–$0{\cdot}17$ Å while the value of L obtained by fitting a repulsive exponential to the Hartree–Fock potential of Krauss and Mies (1965) is $L = 0{\cdot}28$ Å.

(2) The model potential if determined in the standard manner (Herzfeld and Litovitz 1959) contains no information about the vibrational coordinate dependence of the real potential. Thus the model potential can lead to very poor results for the vibrational force $F(x)$ defined in equation (2.13 *b*). It is this vibrational force, however, which determines the energy transfer within the Landau–Teller (1936) and Zener (1933) treatments.

(3) The neglect of anharmonic effects and the linearization of the interaction potential can lead to serious errors in the evaluation of DWA matrix elements.

These results of Mies (1966) are summarized in the table and figure 3. In particular from the table, it is evident that the DWA transition probabilities using the standard assumptions of the SSH theory (case F) are orders of magnitude larger than the 'exact' DWA transition probabilities (case A).

2.6.3. *The Kelly–Wolfsberg–Secrest–Johnson tests of the dynamical approximations*

The study of Mies (1965), while providing useful information concerning the validity of the potential model used in the classical theory, provides no information about the validity of its dynamical approximations. This is because Mies' calculations are all made within the DWA framework.

Tests of the dynamical approximations are, however, available in the literature. Specifically the exact collinear atom–diatom classical trajectory studies of Kelley and Wolfsberg (1966) permit a test of the Landau–Teller (1936) model. Similarly, the

Table 1. Distorted-wave VET probabilities $p_{0,1}(\varepsilon)$ for collinear He–H_2 collisions. Case A: exact Morse oscillator results computed from a Hartree–Fock (Krauss and Mies 1965) interaction potential. Case B: same as case A, except the interaction potential is a site–site repulsive exponential fit (equations 2.9 and 2.14) to the Hartree–Fock potential. Case C: same as case B, except the oscillator is harmonic and the interaction potential is linearized as in equation (2.13). Case F: same as case C except the exponential repulsion parameter L is obtained from viscosity potentials. Case F corresponds to the standard SSH theory. (Reproduced from table I 5 of Mies (1965).)

	$P_{0,1}(\varepsilon)$	
Case	$\varepsilon = 1{\cdot}5$	$\varepsilon = 3{\cdot}0$
A	7·24(−8)	9·34(−5)
B	3·50(−7)	1·39(−4)
C	3·99(−5)	2·62(−2)
F	1·38(−2)	6·77(−1)

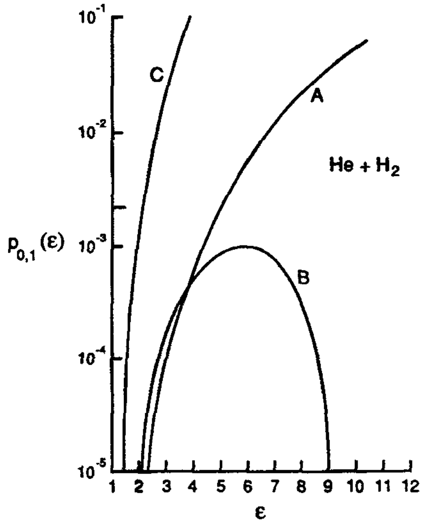

Figure 3. Energy dependence of the $v=0\rightarrow v=1$ transition probabilities $p_{0,1}(\varepsilon)$ calculated by Mies for cases A–C specified in table 1. (Reproduced from figure 5 of Mies (1965).)

corresponding exact quantum calculations of Secrest and Johnson (1966) permit a complementary test of the Jackson–Mott (1932) model.

One of the most important points brought out by these exact calculations is that the simple theories can seriously overestimate energy transfer because they neglect oscillator deformation. Moreover, this overestimation due to neglect of deformation can be severe even when the energy transfer is very small. Thus, for example, the DWA can break down very badly even at low collision energies.

As one would expect from figure 2, this type of breakdown becomes increasingly severe as the mass parameter m increases. For example, Kelley and Wolfsberg (1966) find for their model system 4 ($m_A=2$ and $m_B=m_C=24$), for which $m=0{\cdot}04$, that the ratio R_{CM} of Landau–Teller energy transfer ΔE_{LT} to exact classical energy transfer ΔE_{CM} equals 1·07. In contrast, for their model system 26 ($m_A=12$, $m_B=1$ and $m_C=13$), for which $m=6$, R falls in the approximate range 10^2–10^5. At low energies, the results of Kelley and Wolfberg may be summarized by the empirical relation

$$R_{CM}=\frac{\Delta E_{LT}}{\Delta E_{CM}}=\exp(1{\cdot}685m). \qquad (2.111)$$

Secrest and Johnson (1966) found an analogous empirical relation valid at low energies, namely

$$R_{QM}=\frac{\Delta E_{JM}}{\Delta E_{CM}}=\exp(1{\cdot}685m). \qquad (2.112)$$

where R_{QM} is the ratio of the Jackson–Mott (1932) energy transfer to exact quantum energy transfer. Secrest and Johnson also find (their figure 7) the expected breakdown of the DWA at high energies due to the failure of first-order perturbation theory.

2.7. *Concluding remarks*

The classical theory is, in essence, an asymptotic theory aimed at describing high-energy VET processes for which the energy transfer may be parametrized in terms of a few quantities which characterize the repulsive wall of the potential. Thus it is clearly unsuitable for the low-temperature regime as shown, for example, experimentally by Losert *et al.* (1988). However, even at high temperatures, difficulties remain. The dynamical approximations of the theory, for instance, are most questionable at high energies. For example, as discussed by Rapp and Kassal (1969), at high T the 'most effective' collision energies, about $\frac{1}{2}\mu(v^*)^2$, are often so large that the DWA is invalid.

In summary our belief is that the classical theory, because of both the crudity of its potential energy function model (e.g. table 1) and of its dynamical and statistical approximations, is unsuitable as a framework for analysing VET data. Its main value today is pedagogical.

3. Modern theories of gas phase vibrational energy transfer

We next turn to modern techniques for computing VET rates based on *ab-initio* PESs and advanced quantum collisional methods. While implementation of these techniques has been performed by a number of workers (for example Schinke and Diercksen 1985, Schwenke 1988, Schwenke and Truhlar 1988, Cacciatore and Billing 1992 and Kolesnick and Billing 1993), here we focus on a particularly excellent example of this rigorous quantum approach due to Banks *et al.* (1986). These workers determine the de-excitation rate constants $k_{1,0}(T)$ for molecular nitrogen by He isotopes at temperatures <300 K. Their methods illustrate the state of the art in the theory of gas phase VET and thus differ sharply from the relatively primitive procedures reviewed in §2.

The procedure of Banks *et al.* (1986) consists of the following steps.

Step 1. *Determination of the PES.* Points on the He–N_2 PES were computed using the coupled electron pair (CEPA) electron correlation method. The PES, in addition to being determined as a function of the atom–diatom centre-of-mass separation and the orientation of the diatom, was also determined as a function of the diatom internuclear separation. (As emphasized in §2.6.2, this inclusion of internuclear separation dependence is necessary since otherwise the PES is not expected to reproduce accurately the vibrational forces.) Specifically, the PES was computed at three values of the internuclear separation, the equilibrium bond length and the two most probable separations in the $v=1$ state. The *ab-initio* PES, in order that it be suitable for the collisional calculations, was then fitted to an analytical expression.

Step 2. *Evaluation of cross-sections.* Using this *ab-initio* PES, state-to-state rotational–vibrational cross-sections were evaluated using the highly accurate centrifugal sudden approximation (CSA) scattering method. (Two less rigorous treatments of the collision dynamics were for purposes of comparison also implemented.)

Step 3. *Evaluation of the rate constant.* The final step consists of performing rigorous Boltzmann averages over the state-to-state cross-sections to obtain the $v=1 \rightarrow v=0$ rate constant $k_{1,0}(T)$.

These evaluations led to rate constants which compare well with experiments (Banks *et al.* 1986). What is particularly encouraging was the ability of the CEPA–CSA method to reproduce the observed variations in the rate constants with temperature, which were approximately two orders of magnitude.

4. The isolated binary collision model

The theories of VET discussed so far assume binary collision dynamics and thus are restricted to low-density gases. We conclude this review with a brief discussion of theories which apply at elevated densities, particularly liquid phase densities.

It is important to note that most of the simple energy-transfer systems liquefy only at cryogenic temperatures. Consequently for these systems, in the liquid phase, vibrational excitation occurs at a negligibly slow rate (since collisions with incident energy which exceeds the threshold energy $\hbar\omega_0$ are very rare at low temperatures) and experimental studies of VET are restricted to VER. Additionally, the assumptions which underlie classical VET theory (§2) are singularly inappropriate in the low-temperature regime. Thus, to treat VER in liquids, new theories based on assumptions tailored to the physics of the low-temperature regime are required.

The currently most widely used theory of VER in dense fluids is the IBC model. The IBC model was developed by Herzfeld and Litovitz (1959), Davis and Oppenheim (1972) and Delalande and Gale (1979), as well as others. A comprehensive review of the IBC model had been provided by Chesnoy and Gale (1984). Useful shorter summaries (Oxtoby 1981a, b, Harris *et al.* 1990) are also available.

The problem of developing theories of liquid phase VER is difficult since the process is mediated by many-body interactions. Within the IBC, much of this difficulty is bypassed by assuming that the collisions which determine T_1 may be approximated (Herzfeld 1962) by isolated binary encounters and thus treated by the methods of gas phase scattering theory. Given this hypothesis, the observed large enhancement in VER rates in the liquid, relative to the gas phase, is attributed solely to the greater frequency of collisions in the liquid. These assumptions lead directly to the following IBC model form for the liquid phase rate constant $k_{\text{liq}}(T,\rho)\equiv k_{1,0}(T)\approx T_1^{-1}$:

$$k_{\text{liq}}(T,\rho)=P(T)\nu_{\text{liq}}(T,\rho), \tag{4.1}$$

where $P(T)$ is the gas phase relaxation probability per collision and $\nu_{\text{liq}}(T,\rho)$ is the liquid phase collision frequency.

We mention in passing that the IBC model has been the subject of continuing controversy (for example Fixman 1961, Zwanzig 1961, Velsko and Oxtoby 1980 and Dardi and Cukier 1991). Since this controversy has often been reviewed in the literature (for example, Harris *et al.* 1990) we shall not discuss it further here.

Despite the controversy over the theoretical foundations of the IBC model, the factorized form of the rate constant given in equation (4.1) has a very strong empirical foundation (for example Chesnoy and Gale 1984, 1988). The IBC model was originally introduced (Herzfeld and Litovitz 1959, pp. 407–417, especially table 95.1) to explain the fact that while, individually, the liquid and gas phase values of T_1^{-1} vary greatly, as one changes system and thermodynamic state, their ratio varies over a much narrower range and, moreover, is of the same order of magnitude as the ratio of the density of the liquid to that of the gas. This experimental fact motivated the IBC model form for $k_{\text{liq}}(T,\rho)$ (equation 4.1).

In early formulations of the IBC approach (Herzfeld and Litovitz 1959), ν_{liq} was approximated using semiempirical cell models, for example the model proposed by Madigosky and Litovitz (1961). These cell models have, however, been superseded by more realistic models for ν_{liq} based on the solute–solvent pair correlation function (Davis and Oppenhein 1972, Delalande and Gale 1979, Chesnoy 1984). These pair correlation models assume firstly that the solute and solvent molecules are spherical and secondly that VER is localized in the repulsive part of the solute–solvent potential at a critical radius R^*.

These assumptions yield the current form of the IBC rate expression (Davis and Oppenheim 1972)

$$k_{\text{liq}}(T, \rho) = \rho \frac{g_{\text{liq}}(R^*)}{g_{\text{gas}}(R^*)} k_{\text{gas}}(T), \tag{4.2}$$

where $g_{\text{liq}}(R)$ is the spherical molecule liquid phase solute–solvent pair correlation function and $g_{\text{gas}}(R)$ is the corresponding gas phase function and where $k_{\text{gas}}(T)$ is the gas phase rate constant. A practical method for implementing equation (4.2), due to Delalande and Gale (1979), is widely used to interpret the density dependence of observed VER rates. This method is described in detail by Chesnoy and Gale.

5. A molecular theory of liquid phase vibrational energy relaxation

Because of the primitive nature of the assumptions (spherical molecules, and energy transfer localized at the collision radius R^*) underlying the current form of the IBC model, it is unlikely that this model will provide a generally satisfactory basis for the interpretation of observed VER rates. This point is illustrated, for example, by the work of Chatelet *et al.* (1983) who applied the IBC model to the interpretation of the density dependence of T_1 for molecular hydrogen (a system for which the standard IBC assumptions seem relatively reasonable). They found that, to fit the IBC expression (equation 4.2) to experiment, a significantly temperature-dependent Lennard–Jones diameter is required.

In this section we summarize a new first-principles theory of fluid phase VER developed by our research group (Adelman and Stote 1988, Adelman *et al.* 1991, Adelman *et al.* 1993a–c). This theory which is based on the physical principles (Adelman 1983, Adelman *et al.* 1993a, b) of our theory of chemical reaction dynamics in liquids is, we believe, likely to give a far better account of the temperature, density and isotope dependences of VER rates than that provided by the available (Chesnoy and Gale 1984, 1988) IBC models. A detailed, but non-mathematical account of the theory, as well as many references to the experimental VET literature are available in Adelman *et al.* 1993b).

The assumptions behind the present theory, described in detail elsewhere (Adelman *et al.* 1993a, b), are tailored to fit the physics of the low-temperature regime, where the energy relaxation dynamics (because of Boltzmann weight factors) is dominated by low-energy collisions. Thus, while some of the results of the present theory resemble those of the classical theory, the physical picture and assumptions underlying the present theory are radically different from those of classical VET theory.

The basis of the present theory is the following expression for the relaxation time T_1 (Oxtoby 1981a, b, Adelman and Stote 1988, Adelman *et al.* 1993a–c);

$$T_1 = \beta^{-1}(\omega_1), \tag{5.1}$$

where $\beta(\omega)$ is the friction kernel of the relaxing solute normal mode and where ω_1 is its liquid phase frequency.

We evaluate $\beta(\omega)$ within our partial clamping model (Adelman 1984, 1987), which assumes that the excursions of the relaxing mode are restricted to small amplitudes. (Note that this small-amplitude assumption is very different from the fixed-oscillator assumption of classical VET theory. The small-amplitude assumption is reasonable if low-energy collisions dominate the energy relaxation dynamics.) Within the partial clamping model, the friction kernel is given by

$$\beta(\omega)=(k_BT)^{-1}\int_0^\infty \langle\tilde{\mathcal{F}}(t)\tilde{\mathcal{F}}\rangle_0\cos(\omega t)\,\mathrm{d}t, \tag{5.2}$$

where $\langle\tilde{\mathcal{F}}(t)\tilde{\mathcal{F}}\rangle_0$ is the autocorrelation function of the fluctuating generalized force exerted by the solvent on the coordinate of the relaxing solute mode conditional that this coordinate is fixed at its equilibrium value.

The present theory may be implemented via a molecular dynamics simulation in which the relaxing solute mode is fixed at equilibrium while all other degrees of freedom of the solution are allowed to move freely subject to this single constraint. Such constrained molecular dynamics implementations of the present theory have been reported elsewhere (Adelman and Stote 1988, Whitnell *et al.* 1992, Benjamin and Whitnell 1993). Alternatively the theory may be implemented by analytical procedures. We next describe the analytical approach focusing, for simplicity, on the prototype case of a diatom relaxing in a monatomic solvent. (Molecular solvents have been discussed elsewhere (Adelman *et al.* 1993a–c).)

This analytical approach is based on the fact that, if ω_l is sufficiently large, an approximate form for $\beta(\omega)$ which realistically describes only its high-frequency wings suffices. These wings, however, depend only on the short-time part of $\langle\tilde{\mathcal{F}}(t)\tilde{\mathcal{F}}\rangle_0$ which may be approximated (Adelman *et al.* 1993a–c) by the following Gaussian model:

$$\langle\tilde{\mathcal{F}}(t)\tilde{\mathcal{F}}\rangle_0=\langle\tilde{\mathcal{F}}^2\rangle_0\exp\left[-\tfrac{1}{2}\langle\omega^2\rangle t^2\right], \tag{5.3}$$

where

$$\langle\omega^2\rangle=\frac{\langle\dot{\tilde{\mathcal{F}}}^2\rangle_0}{\langle\tilde{\mathcal{F}}^2\rangle_0}. \tag{5.4}$$

A comparison of equations (5.1)–(5.3) yields the desired result for T_1:

$$T_1=\frac{2k_BT}{\langle\tilde{\mathcal{F}}^2\rangle_0}\left(\frac{\langle\omega^2\rangle}{2\pi}\right)^{1/2}\exp\left(\frac{1}{2}\frac{\omega_l^2}{\langle\omega^2\rangle}\right). \tag{5.5}$$

To evaluate T_1 from equations (5.4) and (5.5) we require expressions for ω_1, $\langle\dot{\tilde{\mathcal{F}}}^2\rangle_0$ and $\langle\tilde{\mathcal{F}}^2\rangle_0$. The required expressions have been derived elsewhere (Adelman and Stote 1988, Adelman *et al.* 1993a–c). We note here that the expressions permit evaluation of T_1 from molecular properties and from the solute–solvent site–site interaction potentials and equilibrium pair correlation functions. The latter may be evaluated as solutions to fluid phase integral equations.

The theory therefore provides a practicable (Adelman *et al.* 1991) *first-principles* evaluation of the liquid phase rate constant $k(T,\rho)$. (In contrast, the IBC model is semiempirical since this model requires as input the experimental gas phase rate constant.)

The molecular theory has been applied (Adelman *et al.* 1991) to model Lennard-Jones solutions designed to simulate molecular iodine in fluid xenon at $T=298$ K and molecular bromine in fluid argon at $T=295$ and 1500 K. The rate constants $k(T,\rho)\equiv T_1^{-1}$ were computed as functions of density, from densities ranging from the ideal gas to the dense fluid regime. For the Br_2–Ar solutions, the rates display superlinear deviations from the low-density extrapolations which are qualitatively similar to those found experimentally (Chesnoy and Gale 1984, 1988) for simple fluids.

For the I_2–Xe solution the molecular theory predicts a 'non-classical' sublinear deviation in the density dependence of the rate constant.

In addition to providing a computational algorithm for T_1, the theory provides qualitative insights. For example, the theory provides a molecular basis for the IBC hypothesis (see equation 4.2) that $k(T, \rho)$ may be factorized into density-independent and density-dependent contributions. This factorization results from the fact (Adelman *et al.* 1991) that $\langle\omega^2\rangle$, defined in equation (5.4), is found to be nearly independent of density over the whole range studied. As a consequence it follows from equation (5.5), from the definition $k(T, \rho) \equiv T_1^{-1}$, and from the fact that ω_1 is also nearly independent of density, that

$$k(T,\rho) \doteq \langle\mathcal{F}^2\rangle_0 \lim_{\rho\to 0}\left(\frac{\langle\mathcal{F}^2\rangle_0}{\rho}\right)^{-1} k_{\text{gas}}(T), \tag{5.6}$$

where $\rho k_{\text{gas}}(T) \equiv \lim_{\rho\to 0}[k(T,\rho)]$. Note that, if one makes the formal correspondence $\langle\mathcal{F}^2\rangle_0 \leftrightarrow \rho g(R^*)$, then the molecular theory result, equation (5.6), and the IBC result, equation (4.2), become identical.

Despite this formal similarity, the rate expressions in equations (4.2) and (5.6) predict significantly different isothermal density dependences. The difference arises because, in contrast with the IBC model, within the molecular theory the anisotropy of the solute molecule is treated realistically and the collisions are not assumed to be localized at a critical radius R^*. As importantly, the factorized form of equation (5.6) emerges as a consequence of a fundamental molecular level analysis (Adelman *et al.* 1993a–c) while the factorized form of equation (4.2) derives from the basic IBC hypothesis equation (4.1).

We finally note that realistic implementations of the present theory, based on PESs of the type described by Banks *et al.* (1986), are currently under way.

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