Dicke Narrowing Reduction of the Doppler Contribution to a Line Width

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Abstract

In the simplest kinetic models of collisional narrowing or reduction of the Doppler contribution to a spectral line width, the narrowing process is related to the usual diffusion constant of transport theory. Dicke narrowing requires a correlation between the pre- and post-collisional absorber or emitter electric dipole moment. Pressure broadening on the other hand results from at least a partial destruction of this correlation so that in general pressure broadening and Dicke narrowing are statistically dependent on and correlated with each other. It follows that a spectroscopic diffusion constant is required. A classical phase description (which is easily converted to a semiclassical one) is used here to derive a kinetic equation for which the approximate line shape is obtained by a velocity moment method. The spectroscopic diffusion constant closely resembles the Chapman–Enskog first approximation for the diffusion constant but has mixed in an extra function (the memory) which represents the correlation between collision-induced changes of the dipole moment and velocity changes and the correlation between the pre- and post-collision electric dipole moment. Dicke narrowing can be used to obtain information about the line broadening amplitude $S_B(b, w)$ for strong velocity-changing collisions. The Galatry ('weak' collision) and 'strong' collision line-shape functions are obtained as different cutoff approximations in the velocity moment analysis. The present analysis, however, is not limited to specifically weak or strong collisions. The two line-shape formulae are shown to be virtually identical sufficiently far from the line centre and at sufficiently high densities. Convenient, approximate analytical formulae for the half-width are obtained using two different definitions.

1. Introduction

The theory of line broadening requires the calculation of a quantity $S_B(b, w)$ which is related to the partial broadening diameter b_{ij} of absorbers i colliding with perturbed j by

$$\pi b_{ij}^2 = \frac{2\pi}{\langle w_{ij} \rangle} \int_0^\infty \int w b f_{ij}(w) \, S_B(b, w) \, \mathrm{d}b \, \mathrm{d}w.$$

Here $f_{ij}(w)$ is the Maxwellian distribution of the relative velocity w and $\langle w_{ij} \rangle$ denotes the mean relative speed. The great unknown about $S_B(b, w)$ is what happens to it at small values of impact parameter b where perturbation techniques fail. One must either develop a nonperturbative theory in this region or at least make some kind of educated guess of what is to be expected. A degree of success using the latter approach has been obtained with various cutoff schemes which rely upon the second order perturbation result $S_2(b, w)$ being reobtained for large b (Anderson 1949; Ch'en and Takeo 1957; Tsao and Curnutte 1962; Murphy and Boggs 1969). The usual guiding wisdom for small b is that by certain physical arguments $S_B(b, w)$ should

tend to unity. This assumes that for strong collisions the final state is either definitively not the same as the initial absorber state or, if it is the same state, a phase randomization has occurred.

In the pressure broadening of molecular lines where large numbers of different states are energetically accessible, the above assumption is reasonable and can lead to accurate line width calculations. There are exceptions to this argument. If the number of states that are collisionally coupled is small, then in a strong collision each state will be produced with perhaps equal or comparable probabilities from any initial state. This happens for two preferentially coupled states which exhibit two-level saturation, with each state given a 50% probability of being the final state independent of the initial state. In this example S_B is equal to $\frac{1}{2}$ (Legan *et al.* 1965; Murphy and Boggs 1969; McMahon 1977a). The elastic probability can also differ from $\frac{1}{2}$ in this example due to an adiabatic saturation effect from a strong parity-conserving interaction (McMahon 1977a). If elastic collisions alone exist, then pressure broadening is entirely by phase changes. The argument that $S_B \to 1$ in strong collisions for line width calculations is again not strictly justifiable, although even there the error produced by such an assumption using perturbation and cutoff methods is not great (McMahon 1975). In those cases where $S_B(b, w)$ can be calculated from first principles, assuming for instance straight line classical paths, it is found that generally $S_B(b, w)$ oscillates as a function of b between the values of 0 and 2. In strong collisions one can only say that S_B averages to 1 due to its rapid oscillations as a function b. Oscillation effects of this kind also occur in two-level systems with strong diabatic collisional effects and persist even if M degeneracies coupled by collisions are included (McMahon 1977b).

The above discussion leads us to the idea of 'memory'. When S_B deviates from unity we refer to this as 'memory'. For $S_B < 1$ the post-collision electric dipole moment has a positive memory or a correlation with the pre-collision electric dipole moment and for $S_B > 1$ there is a negative memory or anticorrelation of the final dipole with the initial one. In classical phase models the memory is proportional to $\cos(\phi' - \phi)$ where $\phi' - \phi$ is the phase change. What do we know about the electric dipole memory present in intermolecular collisions? We know that for b large $S_B = 0$ so that a perfect pre- and post-collisional correlation exists. This correlation is reduced as b decreases towards some cutoff value b_c usually defined by $S_2(b_c, w) = 1$, where the perturbation theory fails. For $b < b_c$ the behaviour of S_B is unknown. Line broadening depends on this loss of memory in the electric dipole autocorrelation function. The pressure shift of spectral lines implies the existence of memory in absorber–perturber collisions. For instance, the classical oscillator model gives the shift in terms of odd powers of the collision-induced phase changes whereas the broadening only involves even powers. Phase-randomizing collisions ($S_B = 1$ or zero memory) contribute zero to the line shift. Line shifts have been observed even in the microwave region (Matsuura 1959; Parsons *et al.* 1972; Hewitt and Parsons 1973; Buffa *et al.* 1979) and it is possible that these shifts arise mainly from the range of b greater than b_c. This has been the assumption of theoretical attempts to reproduce the line shifts; however, they have not been successful quantitatively, even in those cases for which the shifts are the largest (Frost 1976; Frost and MacGillivray 1977; Buffa *et al.* 1979). It is possible that, in the region $b < b_c$, S_B oscillates with b and cannot be ignored in shift calculations. Can one obtain independent information about the degree of memory in the $b < b_c$ region by experimental means? We show

in the following sections that Dicke narrowing when observed is a direct consequence of residual memory in the hard collision region.

2. General Discussion of Combined Doppler and Pressure Broadening

As originally pointed out by Dicke (1953), mere motion of an ensemble of moving atoms or molecules is not sufficient for them to exhibit Doppler broadening in their spectral lines. There must also be overall progress between strongly deflecting collisions on a scale larger than the reduced wavelength $\lambda/2\pi$. For a mean free path $l \ll \lambda/2\pi$ the Doppler contribution may be significantly suppressed leaving only the collision-broadened component of the line width. But the essential point introduced in the discussion below is that the pressure broadening process tends to counteract the Dicke narrowing effect. That is, these two effects are correlated so that Dicke narrowing gives further information on the broadening process.

In a classical field representation of emitted radiation, the spectral line shape is obtained from the complex Laplace transform of the correlation function

$$\Phi_\beta(t) = \left\langle \exp\left(i \int_0^t \omega_\beta(t') \, dt'\right) \right\rangle,$$

where $\omega_\beta(t)$ denotes the angular frequency at the observer; $\omega_\beta(t)$ can be broken up into the sum $\omega_\beta(t) = \omega'_\beta(t) + \mathbf{k} \cdot \mathbf{v}(t)$ where $\omega'_\beta(t)$ denotes the angular frequency in the rest frame of the atomic or molecule emitter and $\mathbf{k} \cdot \mathbf{v}(t)$ is the Doppler contribution. The correlation function decays due to the random fluctuations in the phase $\int_0^t \omega_\beta(t') \, dt'$ from collision effects on $\omega'_\beta(t)$ and $\mathbf{v}(t)$. The decay of $\Phi_\beta(t)$ is built up from a sequence of internal phase- and velocity-changing collisions. It can also decay due to inelastic collisions where the emission frequency is switched to another spectral line. Inelastic collisions have the same effect as elastic collisions that randomize the emitter phase. Subsequent to an inelastic collision or phase-randomizing collision, the behaviour of $\mathbf{k} \cdot \mathbf{v}(t)$ for a given emitter is irrelevant to the calculation of $\Phi_\beta(t)$. In order for there to be a continuing contribution of $\omega_\beta(t)$ to the decay of $\Phi_\beta(t)$, there must be some residual correlation with the phase before the last collision. In other words, without some memory of the phase before the last collision, the effect of a velocity change on the Doppler effect is nonexistent and there is no Dicke narrowing effect.

Practically all experimental reports of a Dicke narrowing effect are for gases where the line broadening cross sections are much less than the gas kinetic cross sections of transport theory. This ensures that a high degree of phase correlation is maintained after a collision. Dicke narrowing is readily observable for hyperfine transitions where the internal degrees of freedom are very weakly coupled with the centre of mass velocity (Wittke and Dicke 1956; Arditi and Carver 1958a, 1958b; Beaty and Bender 1958; Bender and Chi 1958; Bender and Cohen 1969). The very small inelastic collision rates for H_2 led Bird (1963) to the conclusion that Dicke narrowing is important and already present in available data. This prediction was verified by Rank and Wiggins (1963). Collisional narrowing has been observed in laboratory experiments for quadrupole absorption lines of H_2 (Chackerian and Giver 1975; Reid and McKellar 1978) and electric field induced infrared absorption by H_2 (Buijs and Gush 1971) and by D_2 (McKellar and Oka 1978). Dicke narrowing of the H_2 quadrupole lines is of importance to studies of planetary atmospheres (Fink et al. 1965; Rank et al. 1966; Fink and Belton 1969; James 1969; Belton et al. 1971; Axel 1972;

Lutz 1973; Margolis 1973; Hunt and Margolis 1973). The theory of Dicke narrowing of emission and absorption lines is readily adopted to Rayleigh and Raman scattering (see e.g. Murray and Javan 1972). Collisional narrowing has been observed in Raman scattering for H_2 (Cooper *et al.* 1968, 1970; Gupta *et al.* 1972; Gupta and May 1972; Murray and Javan 1972), for HD (Gupta *et al.* 1972) and for D_2 (Gupta *et al.* 1972; Murray and Javan 1972). It has also been observed in stimulated Raman gain for H_2 (Lallemand *et al.* 1966; Owyoung 1978) and in coherent anti-Stokes Raman scattering from H_2 (De Martini *et al.* 1973; Henesian *et al.* 1976) and D_2 (Henesian *et al.* 1976; Krynetsky *et al.* 1977). A review of Raman widths and shifts has recently been given by Srivastava and Zaidi (1979).

Collisional narrowing of the spectral lines of other molecules has been observed also. Eng *et al.* (1972) have observed it for infrared absorption in H_2O binary mixtures with Ar, Xe and N_2. Sub-Doppler line widths have been observed for infrared absorption by HCl–Ar mixtures (Oka 1980) and by binary mixtures of HF with Ne and Ar (Pine 1980). All of these are for relatively high J values so that the nearest rotational level accessible by an inelastic collision requires an internal energy change greater than $k_B T$. Because inelastic collisions are relatively improbable the correlations between pre- and post-collisional electric dipole moments are significant.

There is some evidence of Dicke reduction of the Doppler effect for Rayleigh scattering from CO_2, OCS and CS_2 (Keijser *et al.* 1971). There is also evidence of Dicke narrowing in the infrared absorption lines of CH_4 (Goldring *et al.* 1968; Hubbert 1976; Hubbert and Troup 1977). CH_4 is particularly interesting because the broadening or Weisskopf diameter significantly exceeds the gas kinetic diameter. For example, the $P(7)_1$ broadening diameter is $6 \cdot 5$ Å (1 Å $\equiv 10^{-10}$ m) whereas the gas kinetic diameter calculated from the diffusion constant (Chapman and Cowling 1970, p. 267) is only $3 \cdot 9$ Å. Thus although self-broadening by CH_4 appears to follow the theory of Birnbaum (1967) with respect to the line width and its temperature dependence, the underlying cutoff assumption $S_B(b, w) = 1$ fails for impact parameters $b \leqslant 3 \cdot 9$ Å because the collisions need to be highly elastic there to produce a Dicke narrowing effect. This brings us to the potential use of collisional narrowing in the study of line broadening theory. It allows one to obtain experimental information on $S_B(b, w)$ in hard collisions with impact parameters even smaller than the Weisskopf diameter, where the perturbation techniques certainly fail.

Since the introduction of Dicke's (1953) model of diffusive narrowing of a Doppler broadened line, there have been several extensions of the theory. Nelkin and Ghatak (1964) have considered a 'strong' collision alternative to Dicke's diffusive model based on the Fokker–Planck equation ('weak' collision theory). Galatry (1961) has considered the problem of combining collisional broadening with the weak collision model whereas Gersten and Foley (1968) have done the same but using the strong collision model (where the velocity probability distribution is considered to be Maxwellian after a collision and independent of the pre-collisional velocity). These results are special cases of more formal developments based on a classical path description and Boltzmann-type kinetic equations (Rautian 1967; Rautian and Sobel'man 1967; Kol'chenko and Rautian 1968; Ward 1971; Ward *et al.* 1974). Quantum mechanical descriptions of coupled Doppler and pressure broadening have been given by Andreeva (1968), Pestov and Rautian (1969), Berman and Lamb (1970, 1971), Cattani (1970), Chappell *et al.* (1971), Smith *et al.* (1971*a*), Alekseev *et al.* (1972), Berman (1972*a*, 1972*b*, 1975, 1978) and Zaidi (1972*a*, 1972*b*).

A problem of interpretation arises when the two radiatively coupled levels give different interaction potentials with the bath molecules. The classical collision path depends on which state the absorber or emitter molecule is in. Smith *et al.* (1971*b*) have given a semiclassical description which allows for this possibility. Berman and Lamb (1970) and Berman (1975) have argued that when the interaction potential depends strongly on the energy level the classical path description of Dicke narrowing fails. A level-dependent interaction also introduces phase changes of the electric dipole moment of the absorber or emitter molecule so that line broadening by elastic collisions is inseparably related to Dicke narrowing. Our description in this paper, however, is confined to a classical path theory which assumes that energy-level-dependent classical path effects are small and that line broadening is mainly due to inelastic collisions. This should be adequate for spectroscopy that does not involve electronic excitation, although the suggestion has also been made that Dicke narrowing may be relevant to plasma diagnostics (Burgess *et al.* 1979). A comparison of semi-classical and classical results is given for completeness at the end of Section 4.

Although there are several theoretical formulations of Dicke narrowing that are rather general, actual comparisons with experiments have been confined to two extreme line shapes, namely the weak and the strong collision model line shapes (Rautian and Sobel'man 1967). The weak collision model is realistic only for light perturbers and relatively massive absorbers or emitters, whereas for the strong model to apply the perturbers need to be heavy and the absorbing or emitting molecules relatively light. Neither model is completely adequate for deriving the full line shape for real gases. Some experimental evidence exists showing that the actual line shape required must be somewhere between these two model extremes (Murray and Javan 1972; Pine 1980). One must ask then in what sense are the two model line shape formulae adequate for real gases. We consider this problem in the present paper.

The Langevin equation defines a friction coefficient ζ. From this equation the Fokker–Planck equation may be derived (Chandrasekhar 1943) and the Einstein relation $D = k_B T/m\zeta$ for the diffusion coefficient D is obtained. One can define an analogous friction coefficient for real gases even though the Langevin equation no longer holds. The coefficient ζ is then defined in terms of the appropriate velocity moment of the Boltzmann collision integral. In the first approximation the velocity distribution is only slightly shifted from the Maxwellian distribution during gas diffusion. This allows ζ to be calculated by elementary methods without simplifying restrictions on the velocity-changing kernel. By using the Einstein relation, the Chapman–Enskog first approximation for D is obtained (McMahon 1981). One would expect that our sought-after spectroscopic friction coefficient or diffusion constant can be derived in a very similar manner. These are in general not equal to the gas kinetic values. This problem plus the appropriate folding in of memory effects is considered in this paper.

One moment analysis described here leads to a line shape formula that is functionally identical with the Galatry (1961) or weak collision model. This result depends on the neglect of higher order velocity moments. A different procedure has been used by Hess (1972) which leads to a line shape formula of the strong collision form (Gersten and Foley 1968; Rautian and Sobel'man 1967). Both procedures are found to give the same expression for the spectroscopic friction coefficient η under the same simplifying approximations. Further, for sufficiently high densities or sufficiently far from the line centre the two line shapes are shown to be virtually identical, a feature

previously observed only in numerical comparisons such as that by Murray and Javan (1972). Experimental studies of hard collision memory effects using Dicke reduction of Doppler broadening should therefore be confined to pressure and frequency ranges where the two line shapes are experimentally indistinguishable or, equivalently, collision-model insensitive. Where they can be distinguished, it is generally unlikely that either line shape is perfectly adequate firstly because of the approximations made in the cutoff procedures and secondly because of the neglect of the effect of velocity-dependent broadening and friction rates on the line shape. We also neglect possible anisotropies of the line broadening and Dicke narrowing effects of the type pointed out by Gupta *et al.* (1972).

The kinetic equation appropriate to the Dicke narrowing effect in the semiclassical formulation has been given by Smith *et al.* (1971b). Because we are interested more in the details of the kinetic theory moment analysis we shall use for convenience a classical phase formalism similar to Rautian and Sobel'man (1967) and Ward *et al.* (1974) and identify the corresponding semiclassical terms at the end. In the classical phase description the absorption/emission and dispersion shapes require the calculation of $c(\omega)$ where

$$c(\omega) = \int_0^\infty \Phi(t) e^{-i\omega t} dt, \tag{1}$$

with

$$\Phi(t) = \langle \exp\{i\,\Delta\phi(t) + i\boldsymbol{k}\cdot\Delta r(t)\}\rangle, \tag{2}$$

$\Delta\phi(t)$ being a function of absorber (or emitter) angle and action variables $\boldsymbol{\alpha}(t)$ and $\boldsymbol{\beta}(t)$. One can regard $\boldsymbol{\alpha}(t)$ as being time dependent in free evolution of the internal states whereas $\boldsymbol{\beta}(t)$ changes only in collisional transitions between different degenerate states or in inelastic collisions.

3. Kinetic Theory of Coupled Internal and Translational Degrees of Freedom

The evaluation of $\Phi(t)$ can be formally represented by weighting the quantity $\exp\{i(\phi-\phi_0) + i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)\}$ over the equilibrium distribution function for the initial variables ϕ_0 and r_0 and by weighting over the Green's function coupling ϕ_0 and r_0 to ϕ and r as a function of time. Let $\boldsymbol{\Gamma} = (\boldsymbol{\alpha}, \boldsymbol{\beta})$ and $\boldsymbol{R} = (\boldsymbol{r}, \boldsymbol{v})$ be random variables where $\boldsymbol{\alpha}$ and $\boldsymbol{r}$ are the internal and external angle variables and where $\boldsymbol{\beta}$ and $\boldsymbol{v}$ are the internal and external action variables. Let the Green's function be denoted by $G(\boldsymbol{\Gamma}_0, \boldsymbol{R}_0 | \boldsymbol{\Gamma}, \boldsymbol{R}; t)$ and let us denote the internal and external equilibrium distribution functions of the absorber '1' by $F_1(\boldsymbol{\Gamma}_0)$ and $V^{-1} f_1(\boldsymbol{v}_0)$ respectively, where V is the volume of the gas sample. Then $\Phi(t)$ is given by

$$\Phi(t) = V^{-1} \iiiint \exp\{i(\phi-\phi_0) + i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)\}$$

$$\times F_1(\boldsymbol{\Gamma}_0) f_1(\boldsymbol{v}_0) G(\boldsymbol{\Gamma}_0, \boldsymbol{R}_0 | \boldsymbol{\Gamma}, \boldsymbol{R}; t)\, d\boldsymbol{\Gamma}_0\, d\boldsymbol{R}_0\, d\boldsymbol{\Gamma}\, d\boldsymbol{R}. \tag{3}$$

The equation of motion for the Green's function has the form

$$\partial G/\partial t + i\mathscr{L}_0 G + \boldsymbol{v}\cdot\nabla_r G = \delta(t)\,\delta(\boldsymbol{R}-\boldsymbol{R}_0)\,\delta(\boldsymbol{\Gamma}-\boldsymbol{\Gamma}_0) + \mathscr{D}_{11} G + \mathscr{D}_{12} G, \tag{4}$$

where $\mathscr{L}_0$ is the free flight Liouville operator for the internal degrees of freedom, $-i\boldsymbol{v}\cdot\nabla_r$ is the external Liouville operator for free flight and $\mathscr{D}_{11}$ and $\mathscr{D}_{12}$ are the

self and foreign gas collision operators respectively. The collision operators have the form

$$\mathcal{D}_{1j}G = n_j \int \dots \int bw\, F_j(\Lambda)\Big(f_j(v',w)\, K_{1j}(\xi,b,\Lambda,w;\Gamma',R';\Gamma,R)\, G(\Gamma_0,R_0\,|\,\Gamma',R';t)$$

$$-f_j(v,w)\, K_{1j}(\xi,b,\Lambda,w;\Gamma,R;\Gamma',R')\, G(\Gamma_0,R_0\,|\,\Gamma,R;t)\Big)\,\mathrm{d}\Gamma'\,\mathrm{d}R'\,\mathrm{d}\xi\,\mathrm{d}b\,\mathrm{d}\Lambda\,\mathrm{d}w\,, \quad (5)$$

where n_j is the number density, ξ is the azimuthal angle of the collision path about the axis parallel to the relative velocity w but passing through the absorber or emitter, and $f_j(v,w)$ is the normalized distribution function for the relative velocity w of 'j' bath molecules incident onto the tagged molecule '1' of velocity v. $F_j(\Lambda)$ is the normalized equilibrium distribution function for the internal angle and action variables Λ of the bath molecule, and K_{1j} is the collision kernel connecting pre-collisional and post-collisional random variables. We have $f_j(v,w) \equiv f_j(v_j)$ where $v_j = v+w$ and making the phase space transformation $\mathrm{d}v_j \to \mathrm{d}w$ when the integrations are carried out.

Equation (5) is presented in a way that obscures the fact that the internal and external degrees of freedom of the bath molecule j change in a collision. Instead the emphasis is on the change in the absorber or emitter random variables. For the purpose of later exploiting the underlying basic structure of the kernel in the setting up of the kinetic equation for $\Phi(t)$ and for the purpose of showing that equation (5) is not inconsistent with the existence of random variable changes for the bath molecule, we digress for a moment to consider the fundamental origin of K_{1j} and how for instance equation (5) is consistent with the usual Boltzmann collision integrals and the requirements of detailed balancing.

Firstly the collision is considered to take place at a particular instant t and a particular point r in space. How one may define these is described by Chapman and Cowling (1970, p. 200). Let us define the generalized random variable $X = (\xi,b,\Lambda,w;v,\Gamma)$. The random variables ξ, b and w are essentially the external angle and action variables of the bath molecule. It is not necessary to specify r_j because ξ, b and w combined with r and the molecular dynamics give r_j; similarly v_j need not be defined independently as we have $v_j = v+w$. A kernel B_{1j} may be introduced as the conditional probability that X' results from a collision at point r given X initially. In classical mechanics X' is uniquely determined by X so that in this case

$$B_{1j}(X,r,X',r') = \delta\big(X'-X'_{1j}(X)\big)\delta\big(r'-r\big). \quad (6)$$

Note that X'_{1j} is not a random variable but the deterministic result produced by the collision given X initially. In quantum mechanics, equation (6) does not hold since not only is the connection between X and X' indeterministic but one cannot generally uniquely specify both the angle and corresponding action variables simultaneously. Nevertheless a considerable resemblance between the quantum, semiclassical and classical results for the line broadening theory does exist (Baranger 1958a, 1958b; Kolb and Griem 1958). For this reason we have used the convenience of a classical angle and action description but the final resulting expressions for the memory, line width etc. may be reexpressed in more general semiclassical or quantum terms if so desired.

A general requirement of the collision integral is that it must be consistent with detailed balancing of the equilibrium distribution functions. This means that

$$F_j(\Lambda) f_j(v, w) F_1(\Gamma) f_1(v) = F_j(\Lambda'_{1j}) f_j(v'_{1j}, w'_{1j}) F_1(\Gamma'_{1j}) f_1(v'_{1j}), \qquad (7)$$

which indicates explicitly here that given any choice of the random variables Λ, Γ, v and w then detailed balancing only exists with those corresponding post-collisional variables connected by the kinematics and dynamics of the collision. Equation (7) may be written also in the form

$$F_j(\Lambda) f_j(v, w) F_1(\Gamma) f_1(v) = \int \dots \int F_j(\Lambda') f_j(v', w') F_1(\Gamma') f_1(v')$$
$$\times B_{1j}(X, r; X', r') \, dr' \, d\Lambda' \, d\Gamma' \, dw' \, dv'. \qquad (8)$$

Suppose now we reconstruct equation (5) from first principles and in so doing make, wherever possible, suitable simplifications. The collision integral consists of two parts, terms which represent collisions $X \leftrightarrows X'$ into and out of the range X of random variables. Thus we have, following the usual construction of the Boltzmann collision integral, the result

$$\mathcal{D}_{1j} G = \mathcal{D}_{1j}(+) G - \mathcal{D}_{1j}(-) G$$

$$= n_j \int \dots \int \delta(r'-r) \Bigg[b'w' F_j(\Lambda') f_j(v', w') \delta(X' - X'_{1j}(X))$$

$$\times G(\Gamma_0, R_0 \,|\, \Gamma', R'; t) - bw F_j(\Lambda) f_j(v, w) \delta(X - X_{1j}(X'))$$

$$\times G(\Gamma_0, R_0 \,|\, \Gamma, R; t) \Bigg] dX' dr' d\xi \, db \, d\Lambda \, dw. \qquad (9)$$

All variables except (R_0, Γ_0) and (R, Γ) are dummy variables and one may interchange variables in the $X' \to X$ collision term of equation (9) (that is, $\xi', b', \Lambda', w' \rightleftarrows \xi, b, \Lambda, w$). Equation (9) is found to be identical with equation (5) when we identify

$$K_{1j}(\xi, b, \Lambda, w; \Gamma, R; \Gamma', R') = \delta(r'-r) \int \dots \int \delta(X - X_{1j}(X')) \, d\xi' \, db' \, d\Lambda' \, dw'. \qquad (10)$$

Consider now G replaced by $F_1 f_1$ in equation (9). A required property of the equilibrium distribution function is $\mathcal{D}_{1j} F_1 f_1 = 0$. This follows automatically from detailed balancing applied to the square bracket in equation (9). Firstly one can replace $b'w'$ by bw by the invariance of the Liouville space volume for the collision pair (Liouville's theorem, see Chapman and Cowling 1970, p. 201). Also $\delta(X' - X'_{1j}(X)) = \delta(X - X_{1j}(X'))$ by microscopic reversibility and thus $bw \, \delta(X - X_{1j}(X))$ can be factorized out of the square bracket. This leaves inside the square bracket the term

$$F_j(\Lambda') f_j(v', w') F_1(\Gamma') f_1(v') - F_j(\Lambda) f_j(v, w) F_1(\Gamma) f_1(v),$$

with pre- and post-collisional variables coupled by the dynamics. Thus by equation (7) this bracket is zero and the usual zero collisional integral definition of the equilibrium condition is obtained.

Now to obtain an equation of motion for $\Phi(t)$ alone is not possible by direct use of equation (3) in (4). Instead one finds that one must first define $\Phi(t, \beta, v)$ for which an integral equation is obtained by utilizing (4). Now $\Phi(t)$ is defined by

$$\Phi(t) = \iint \Phi(t, \beta, v) \, \mathrm{d}\beta \, \mathrm{d}v. \tag{11}$$

The integral equation for $\Phi(t, \beta, v)$ is obtained by weighting equation (4) by the quantity $F_1(\Gamma_0) f_1(v_0) \exp\{i(\phi - \phi_0) + i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}_0)\}$ and integrating over all variables except β and v. The integral over r is no problem due to the $\delta(r' - r)$ property of K_{1j}. To define the collisional effect upon the internal phase ϕ we define in analogy with previous work (McMahon and McLaughlin 1974)

$$\iiiint \exp\{i(\phi - \phi_0)\} F_1(\Gamma) F_j(\Lambda) K_{1j}(\xi, b, \Lambda, w; \Gamma', R'; \Gamma, R) \, \mathrm{d}\alpha \, \mathrm{d}\gamma \, \mathrm{d}\Omega_\beta \, \mathrm{d}\Omega_\lambda$$

$$= \exp\{i(\phi' - \phi_0)\} F_1(\beta) F_j(\lambda) \delta(r' - r) \delta(\beta' - \beta) Q_{1j}(\xi, b, \lambda, w; \beta', v'; \beta, v), \tag{12}$$

where Ω_β and Ω_λ denote the degenerate states of the absorber and bath molecule action variables respectively and γ is the internal angle variable of the bath molecule. Q_{1j} is a combination of internal absorber adiabatic phase changes and the kernel for changes of the absorber action variables, and the $\delta(\beta' - \beta)$ factor brings out explicitly the diabatic or interruption effect of internal action changes. Only changes in the magnitude of β produce this (e.g. $\boldsymbol{\beta}$ may incorporate the angular momentum) for unless one is dealing with, say, Stark-lifted degeneracies then transitions between M degeneracies are not complete interruptions but essentially generalized phase changes. Changes in β are, of course, replaced by transitions between different quantum levels in a quantum or semiclassical theory. Equation (12) defines the essential elements of a theory of line broadening but taking into account simultaneous phase changes and velocity changes. It is equivalent to that used by Rautian and Sobel'man (1967) but brings out more explicitly the internal variables of the molecules so as to derive eventually a formula for Dicke narrowing that can be calculated from first principles if so desired.

The phase change effects arise from the $\Gamma', R' \to \Gamma, R$ kernel. The line shape problem also requires consideration of the $\Gamma, R \to \Gamma', R'$ kernel appearing in equation (5). This leads to a reduced kernel A_{1j} which is the analogue of Q_{1j}, although A_{1j} does not produce phase change effects but is merely given by

$$\iiiint F_1(\Gamma) F_j(\Lambda) K_{1j}(\xi, b, \Lambda, w; \Gamma, R; \Gamma', R') \, \mathrm{d}\alpha \, \mathrm{d}\gamma \, \mathrm{d}\Omega_\beta \, \mathrm{d}\Omega_\lambda$$

$$= F_1(\beta) F_j(\lambda) A_{1j}(\xi, b, \lambda, w; \beta, v; \beta', v'). \tag{13}$$

A_{1j} and Q_{1j} are no longer simple δ functions connecting pre- and post-collisional action variables, for even in classical mechanics once some of the internal variables are averaged one can no longer, in general, uniquely specify the end action variables from the initial ones. In this sense our purely classical description now resembles that encountered in the semiclassical and quantum approaches. A_{1j} is still essentially a conditional probability function and satisfies the unitarity property

$$\iint A_{1j}(\xi, b, \lambda, w; \beta, v; \beta', v') \, \mathrm{d}\beta' \, \mathrm{d}v' = 1. \tag{14}$$

Following through the prescription for generating the integral equation for $\Phi(t, \beta, v)$ and incorporating equations (12), (13) and (14) and the properties of the free Liouville operators, we find

$$\partial\Phi(t, \beta, v)/\partial t - i\omega_\beta\, \Phi(t, \beta, v) - i\boldsymbol{k} \boldsymbol{.} \boldsymbol{v}\, \Phi(t, \beta, v) = \delta(t)\, F_1(\beta)\, f_1(v) - R_{11}\,\Phi - R_{12}\,\Phi, \quad (15)$$

where we now have relaxation operators given by

$$R_{1j}\,\Phi = n_j \int \cdots \int b w\, F_j(\lambda)\Big(f_j(\boldsymbol{v}, \boldsymbol{w})\, \Phi(t, \beta, v)\, \delta(v' - v)$$

$$- f_j(\boldsymbol{v}', \boldsymbol{w})\, Q_{1j}(\xi, b, \lambda, \boldsymbol{w}, \beta, v'; \beta, v)\, \Phi(t, \beta, v')\Big)\, \mathrm{d}\xi\, \mathrm{d}b\, \mathrm{d}\lambda\, \mathrm{d}\boldsymbol{w}\, \mathrm{d}v'. \quad (16)$$

The $\delta(v' - v)$ appears in equation (16) because it is more convenient to replace the value of unity from equation (14) by $\int \delta(v' - v)\, \mathrm{d}v' = 1$.

We remark here that equations (1)–(3) and (11) actually represent the whole band of resolved lines. For any particular line it is only necessary to calculate $\Phi_\beta(t)$ where, defining $\Phi(t, \beta, v) = F_1(\beta)\, \Phi_\beta(t, v)$, we have

$$\Phi_\beta(t) = \int \Phi_\beta(t, v)\, \mathrm{d}\boldsymbol{v}.$$

To treat the whole band shape, when considerable overlap of neighbouring lines, if not smearing out, occurs, then the correlation function (2) must be generalized to include phase factors $\exp\{\pm i(\phi + \phi_0)\}$ and equation (12) must be extended to include phase couplings $\phi \to -\phi'$. An example of effects such as these is described for NH_3 elsewhere (McMahon and McLaughlin 1974). Analogous effects are implicit in various band shape models (*M*- and *J*-diffusion models) also and essentially represent the coupling of positive frequency lines with negative frequency lines by collisions (McMahon 1975).

It should be noted that $\Phi(t, \beta, v)$ and the relaxation operators are defined with the angular dependence of $\boldsymbol{\beta}$ integrated out (see e.g. equation 12). This amounts to the assumption that the line width, line shift and Dicke narrowing collision rates are adequately approximated by averages over the M degeneracies of the radiatively coupled levels independent of v. An explicit consideration of the M-degeneracy dependence in the problem of combined Doppler and resonance broadening (but no Dicke narrowing) has been given by Cooper and Stacey (1975) who find that the overall line shape is still very close to the single Voigt shape.

4. Collision Integral for Dicke Narrowing

Since β is fixed for any given line we shall usually drop explicit reference to it where it is convenient to do so. If collisional changes of v do not occur then there can be no Dicke effect. We have for such a model

$$Q_{1j}(\xi, b, \lambda, \boldsymbol{w}; v'; v) = \{1 - S_{1j}(\xi, b, \lambda, \boldsymbol{w})\}\, \delta(v' - v), \quad (17)$$

whereby we find $R_{1j}\,\Phi = \tau_{1j}^{-1}(v)\, \Phi(t, v)$ with the relaxation rate $\tau_{1j}^{-1}(v)$ here given by

$$\tau_{1j}^{-1}(v) = n_j \int\!\!\int\!\!\int\!\!\int b w\, F_j(\lambda)\, f_j(\boldsymbol{v}, \boldsymbol{w})\, S_{1j}(\xi, b, \lambda, \boldsymbol{w})\, \mathrm{d}\xi\, \mathrm{d}b\, \mathrm{d}\lambda\, \mathrm{d}\boldsymbol{w}. \quad (18)$$

S_{1j} is a line broadening and shift amplitude function; it does not depend upon v by Galilean invariance of the internal absorber phase change. For the same reason the direction of w is immaterial for calculating S_{1j} but $\tau_{1j}^{-1}(v)$, however, is dependent in general on v due to the velocity dependence of the distribution function of relative velocity w. Note that S_{1j} is complex, the real part governing the line width and the imaginary part governing the line shift. For this model we find

$$\Phi(t, v) = f_1(v) \exp\{(i\omega_\beta + i\mathbf{k} \cdot \mathbf{v} - \tau^{-1}(v))t\}, \qquad t \geqslant 0, \qquad (19)$$

where $\tau^{-1}(v) = \tau_{11}^{-1}(v) + \tau_{12}^{-1}(v)$. Equation (19) is the starting point of the line-shape calculations of Berman (1972c) and Ward et al. (1974) which allow for both the Doppler effect and a speed-dependent complex relaxation rate. Nienhuis (1973) also derived this as a special case in his theory incorporating deflections of the absorber or emitter; however, his velocity-change effect theory lacks generality (see Ward et al. 1974). Equation (19) is strictly valid only for straight-line path collisions. If velocity changes occur then each $\Phi(t, v)$ is coupled to all the other $\Phi(t, v')$ in an integral equation (see below). The latter coupling of different velocities has two major effects. Firstly $\tau^{-1}(v)$ is replaced by a different speed-dependent relaxation rate $\tau'^{-1}(v)$ resulting from the collisional smearing or averaging effect over different speeds. Depending on the collision effects, $\tau'^{-1}(v)$ may or may not give deviations from the Lorentzian line shape which are less pronounced than those produced by $\tau^{-1}(v)$ (assuming a negligible Doppler effect). The other effect of velocity changes exists when the Doppler effect is not negligible and is, of course, Dicke narrowing.

In the following work we are mainly interested only in Dicke deviations from the Voigt profile. Thus the theory may be applied to lines which are Lorentzians in the absence of Doppler broadening. Actually it should be more widely applicable than this because the apparent experimental deviations from the Lorentzian are very small (Netterfield et al. 1972; Luijendijk 1977) so that once the Doppler contribution to the line width is greater than several per cent the Doppler effect is the dominant deviation from the Lorentzian. Then the major effect of different veclocities being coupled should be the Dicke effect.

A case which predicts that $\tau^{-1}(v)$ is speed independent is that of dipole–dipole perturbation theory of broadening with straight-line paths. Then $\iint b\, S_{1j}\, \mathrm{d}\xi\, \mathrm{d}b$ is found to be proportional to w^{-1} so that the integrand of equation (18) is independent of w. In this case the distribution of relative speeds is irrelevant and $f_j(v, w)$ integrates out by the normalization $\int f_j(v, w)\, \mathrm{d}w = 1$. This prediction has been accurately verified by experiment with NH_3 (Netterfield et al. 1972) but He–NH_3 mixtures also give a Lorentzian line shape. This could be partly due to memory in He–NH_3 collisions leading to a reduction in the spread of speed-dependent relaxation rates due to the velocity-smearing effects mentioned earlier. Again, how much memory is present can in principle be checked experimentally by observations of the Dicke effect. The effect of speed-dependent line widths and shifts on the line shape has recently been considered by Pickett (1980).

Although we are ultimately interested in the Dicke deviations from the Voigt profile it is possible nevertheless to continue with a speed-dependent relaxation rate to extract the general form of the collision integral representing the Dicke effect. Later development leads us naturally to define the average relaxation rate τ^{-1} appropriate to the Voigt profile as follows.

$$\tau^{-1} = \int \tau^{-1}(v) f_1(v) \, dv = \tau_{11}^{-1} + \tau_{12}^{-1}. \tag{20a}$$

Using the general property

$$f_{1j}(w) = \int f_j(v, w) f_1(v) \, dv, \tag{20b}$$

where $f_{1j}(w)$ is the Maxwellian distribution function of relative velocities, we find

$$\tau_{1j}^{-1} = n_j \iiiint bw F_j(\lambda) f_{1j}(w) S_{1j}(\xi, b, \lambda, w) \, d\xi \, db \, d\lambda \, dw. \tag{20c}$$

This is the usual speed-independent rate of Lorentzian line broadening theory. The expression for τ^{-1} arises automatically when equation (19) (with τ^{-1} replacing $\tau^{-1}(v)$) is substituted into equation (15) and both sides are integrated over all v.

When velocity changes occur equation (17) must be generalized. For this case we define the memory M_{1j} such that

$$F_1(\beta) F_j(\lambda) Q_{1j}(\xi, b, \lambda, \beta, w; v'; v) = \iiiint F_1(\Gamma) F_j(\Lambda) M_{1j}(\xi, b, \Lambda, \Gamma, w)$$

$$\times \delta\left(v' - v + \frac{m_{1j}(w - w_{1j})}{m_1}\right) d\alpha \, d\gamma \, d\Omega_\beta \, d\Omega_\lambda, \tag{21a}$$

where $m_{1j} = m_1 m_j/(m_1 + m_j)$. The δ function is just momentum conservation, explicitly indicating that the post-collisional v is uniquely determined once v' and w are specified and w_{1j} is calculated from the collision dynamics. It is necessary to bring out here the fact that both internal and external dynamical variables are needed to determine uniquely the final velocity of the molecule. Thus the memory which is coupled with velocity changes cannot in general be defined with all internal phases and degeneracies integrated out, since they affect the collisional velocity change of interest in the Dicke effect. For instance, α and γ may specify the direction of a molecular dipole moment and these are relevant to the calculation of the velocity change, for example, through dipole–dipole forces etc. Again, as for S_{1j}, M_{1j} does not depend upon v due to the Galilean invariance of the phase change process.

Equation (21a) can still define $S_{1j}(\xi, b, \lambda, w)$ appropriate to line broadening theory without Doppler and Dicke effects by simply integrating over v on both sides. This gives the general relation

$$F_1(\beta) F_j(\lambda)\{1 - S_{1j}(\xi, b, \lambda, w)\} = \iiiint F_1(\Gamma) F_j(\Lambda) M_{1j}(\xi, b, \Lambda, \Gamma, w) \, d\alpha \, d\gamma \, d\Omega_\beta \, d\Omega_\lambda. \tag{21b}$$

Defining $\tau_{1j}^{-1}(v)$ as before by equation (18) and using equations (21a) and (21b) in equation (15) we find

$$\frac{\partial \Phi(t, v)}{\partial t} - \{i\omega_\beta + i\mathbf{k} \cdot \mathbf{v} - \tau^{-1}(v)\} \Phi(t, v) = \delta(t) f_1(v) + \sum_{j=1}^{2} \int N_{1j}(v', v) \Phi(t, v') \, dv', \tag{22}$$

where

$$F_1(\beta)\,N_{1j}(v',v) = n_j \int \ldots \int bw\,F_1(\Gamma)\,F_j(\Lambda)\,f_j(v',w)\,M_{1j}(\xi,b,\Lambda,\Gamma,w)$$

$$\times \left\{\delta\left(v'-v+\frac{m_{1j}(w-w_{1j})}{m_1}\right)-\delta(v'-v)\right\} d\xi\,db\,d\Lambda\,d\alpha\,d\Omega_\beta\,dw\,. \quad (23)$$

$N_{1j}(v',v)$ accounts for all velocity-change effects (it is zero when there are no velocity changes). Both the velocity-smearing effect on the relaxation rate and the Dicke narrowing effect depend on it, and equation (23) explicitly exhibits the role of memory in these two effects as already discussed qualitatively.

At this point it is relatively easy to compare equation (23) with the semiclassical theory of Smith *et al.* (1971*b*). Equation (23) has divided the relaxation parameters into a broadening and shift rate and a velocity-changing kernel which has memory effects mixed in, whereas equation (3.14) of Smith *et al.* separates out the kernel further into a pure velocity-changing part and a correlation term. The latter can be recombined for the purpose of our comparison beginning with their S-matrix expression equation (3.13). This can be specialized to $a = a'$ and $b = b'$ for isolated line broadening and shifting to read (a misprint in the sign of the correlation term has been corrected)

$$\delta_{\hat{q}\hat{q}'} - \langle aq\hat{q}\,|\,S\,|\,aq\hat{q}'\rangle\langle bq\hat{q}\,|\,S\,|\,bq\hat{q}'\rangle^* = \delta_{\hat{q}\hat{q}'}\{1 - \langle a\,|\,S_1(a,q')\,|\,a\rangle\langle b\,|\,S_1(b,q')\,|\,b\rangle^*\}$$

$$+ \langle a\,|\,S_1(a,q')\,|\,a\rangle\langle b\,|\,S_1(b,q')\,|\,b\rangle^*\{\delta_{\hat{q}\hat{q}'} - \langle\hat{q}\,|\,S_0(a,q)\,|\,\hat{q}'\rangle\langle\hat{q}\,|\,S_0(b,q)\,|\,\hat{q}'\rangle^*\}\,.$$

The product $S(a)\,S^\dagger(b)$ appears here because the shift and broadening of spectral lines are due to collision effects simultaneously from states $|a\rangle$ and $|b\rangle$ which both take part in the absorption or emission process. The first term on the right-hand side (RHS) involves no change in the relative momentum $q' = q\hat{q}' = m_{1j}w$ and leads to our speed-dependent rate $\tau_{1j}^{-1}(v)$. The term corresponding to M_{1j} is seen to be $\langle a\,|\,S_1(a,q')\,|\,a\rangle\langle b\,|\,S_1(b,q')\,|\,b\rangle^*$ on comparing with equations (18) and (21*b*). The second semiclassical S-matrix term is a product of this memory and a term representing velocity changes and so corresponds to our $N_{1j}(v',v)$ kernel of equation (23).

However, the general semiclassical theory has an additional effect not in the classical theory. Consider what energy-level-dependent classical paths can do to line broadening and Dicke narrowing. If for either level $\langle\hat{q}\,|\,S_0(c,q)\,|\,\hat{q}'\rangle = \delta_{\hat{q}\hat{q}'}$ (one interacting level) then only $\hat{q} = \hat{q}'$ contributes and there is no velocity change of the electric dipole moment and so no Dicke narrowing (Ward 1971; Ward *et al.* 1974). The semiclassical velocity-change term can be rewritten in terms of the T_0 matrix using $S_0 = 1 - 2\pi i T_0$ (Levine 1969). We find (omitting the memory factor)

$$\delta_{\hat{q}\hat{q}'} - \langle\hat{q}\,|\,S_0(a,q)\,|\,\hat{q}'\rangle\langle\hat{q}\,|\,S_0(b,q)\,|\,\hat{q}'\rangle^*$$

$$= \delta_{\hat{q}\hat{q}'}\left[2\pi i(\langle\hat{q}\,|\,T_0(a,q)\,|\,\hat{q}'\rangle - \langle\hat{q}\,|\,T_0(b,q)\,|\,\hat{q}'\rangle^*)\right.$$

$$\left. -4\pi^2 \sum_{\hat{q}''}\langle\hat{q}'\,|\,T_0(a,q)\,|\,\hat{q}''\rangle\langle\hat{q}\,|\,T_0(b,q)\,|\,\hat{q}''\rangle^*\right]$$

$$+4\pi^2 \sum_{\hat{q}''}\langle\hat{q}\,|\,T_0(a,q)\,|\,\hat{q}''\rangle\langle\hat{q}\,|\,T_0(b,q)\,|\,\hat{q}''\rangle^*(\delta_{\hat{q}\hat{q}'} - \delta_{\hat{q}''\hat{q}'})\,.$$

The first term on the RHS can be regarded as an additional contribution to the shift and broadening of a spectral line not previously identified in our classical formulation. However, this term is identically zero if the classical paths are state independent because if $T_0(a, q) = T_0(b, q)$ the term inside the square bracket is zero when $\hat{q} = \hat{q}'$ by the optical theorem (Levine 1969). The second contribution is nonzero only due to velocity changes $\hat{q}'' \neq \hat{q}$ and is the analogue of our $N_{1j}(v', v)$. Berman's (1972a, 1972b, 1975, 1978) velocity-change kernel $W_{ab}(v' \rightarrow v)$ is expressed in terms of the full T matrix. In this case the analogue of $N_{1j}(v', v)$ now depends on the quantity

$$4\pi^2 \sum_{\hat{q}''} \langle \hat{q} | T(a, q') | \hat{q}'' \rangle \langle \hat{q} | T(b, q') | \hat{q}'' \rangle^* (\delta_{\hat{q}\hat{q}'} - \delta_{\hat{q}''\hat{q}'})$$

$$= 4\pi^2 \langle a | S_1(a, q) | a \rangle \langle b | S_1(b, q) | b \rangle^*$$

$$\times \sum_{\hat{q}''} \langle \hat{q} | T_0(a, q) | \hat{q}'' \rangle \langle \hat{q} | T_0(b, q) | \hat{q}'' \rangle^* (\delta_{\hat{q}\hat{q}'} - \delta_{\hat{q}''\hat{q}'}),$$

where the RHS here is obtained from the LHS by relating T to S_1 and T_0 using $S = 1 - 2\pi i T = S_1(1 - 2\pi i T_0)$. In the semiclassical limit Berman's theory appears to be equivalent to that of Smith *et al.* (1971b) with the memory factor implicit.

5. Relation between Dicke Narrowing and Kinetic Theory of Diffusion

Generally one must solve equation (22) which requires the choice of specific collision models. In order to keep the discussion as general as possible we approximate the required solution to be of the form

$$\Phi(t, v) \approx f_1(v) \exp\{i\omega_\beta t + i\mathbf{k} \cdot \mathbf{v} J(t) - \tau'^{-1}(v) t\}, \qquad t \geqslant 0; \qquad (24a)$$

$$= 0, \qquad\qquad\qquad\qquad\qquad\qquad t < 0. \qquad (24b)$$

Equation (24a), making an analogy with equation (2), effectively assumes that there is a displacement $\Delta \bar{\mathbf{r}}(t) = \mathbf{v} J(t)$ where $J(t) \neq t$ represents the effect of free motion plus collisions. Here $\Delta \bar{\mathbf{r}}(t)$ is not the displacement $\Delta \mathbf{r}(t)$ because $\Delta \bar{\mathbf{r}}(t)$ must incorporate the effect of phase memory in defining the Doppler and Dicke effects. Introducing and calculating $J(t)$ (with a relaxation time approximation) is consistent with the Chapman and Enskog first approximation to the theory of diffusion. The value of $\tau'(v)$ generally differs from that of $\tau(v)$ due to the velocity-change smearing effect.

Firstly let us take the pressure sufficiently large to enable $\tau'(v) \mathbf{k} \cdot \mathbf{v} J(t)$ to be regarded as small so that the Doppler effect can be neglected. We arrive at the following relation for $\tau'^{-1}(v)$

$$\frac{1}{\tau'(v)} = \frac{1}{\tau(v)} - \frac{1}{f_1(v)} \sum_{j=1}^{2} \int N_{1j}(v', v) f_1(v') \, dv'. \qquad (25)$$

This relation holds for t sufficiently small otherwise the integral here has a significant time-dependent factor $\exp\{-t(\tau'^{-1}(v') - \tau'^{-1}(v))\}$. For a velocity spread of $\tau'^{-1}(v)$ which is much smaller than τ^{-1} (given by equations 20a, c), equation (25) is adequate for most of the line shape except near the line centre (corresponding to larger t). Note that the Maxwellian weighted average of $\tau'^{-1}(v)$ is still τ^{-1}.

If we substitute equation (24a) into (22) we again identify $\tau'^{-1}(v)$ as before and in addition obtain

$$i f_1(v) \mathbf{k} \cdot \mathbf{v} \left(\frac{\mathrm{d}J(t)}{\mathrm{d}t} - 1 \right) = \sum_{j=1}^{2} \int N_{1j}(v', v) f_1(v') \{ \exp(i\mathbf{k} \cdot (v' - v) J(t)) - 1 \} \, \mathrm{d}v'. \quad (26)$$

Again the spread of $\tau'^{-1}(v)$ values is ignored on the time scale of t employed here. We obtain the first approximation for $J(t)$ by solving equation (26) when the exponential on the RHS is expanded to first order only. It follows that $J(t)$ is generally a function of $\mathbf{k}$ and $\mathbf{v}$ and this velocity dependence should be retained in a theory of Dicke narrowing if one is going to incorporate the details of speed-dependent relaxation rates. If one is going to employ the averaged relaxation rate τ^{-1} then for self consistency one should also use the appropriate velocity-averaged Dicke effect. In the following we shall only deal with the averaged quantities on the assumption that speed-dependent effects are small. Self consistency also requires that

$$\int N_{1j}(v', v) f_1(v') \, \mathrm{d}v' = 0,$$

as discussed in Appendix 2.

The formal technique for deriving velocity-averaged quantities is by the appropriate moment equations. The zeroth velocity moment applied to this theory simply reproduces the relations (20a, c) for τ^{-1}. This same moment contributes zero on both sides of equation (26) to first order in $\mathbf{k}$. To find the velocity-averaged expression for $J(t)$ we suggest the first velocity moment. This is not a rigorous *a priori* procedure but, as we show below, it parallels the first approximation to the theory of the diffusion constant, which is to be expected due to the general connection that exists between diffusion and the Dicke effect as revealed by the Brownian motion model. A more formal technique due to Hess (1972) is described later. Thus working to first order in $\mathbf{k}$ we get the equation

$$\left(\frac{\mathrm{d}J}{\mathrm{d}t} - 1 \right) \int (\mathbf{k} \cdot \mathbf{v}) \mathbf{v} f_1(v) \, \mathrm{d}v = \left(\sum_{j=1}^{2} \iint \mathbf{k} \cdot (v' - v) \mathbf{v} N_{1j}(v', v) f_1(v') \, \mathrm{d}v' \, \mathrm{d}v \right) J(t). \quad (27)$$

The Boltzmann collision integral appropriate to the theory of diffusion may be obtained from equation (5) after all variables except $\mathbf{v}$ are integrated out. We also replace the Green's function by the time-dependent distribution functions $f_1(v, t)$ and we write the Boltzmann equation (assuming no density gradients) as

$$\frac{\mathrm{d}f_1(v, t)}{\mathrm{d}t} = \sum_{j=1}^{2} \int C_{1j}(v', v; t) f_1(v', t) \, \mathrm{d}v', \quad (28)$$

where

$$C_{1j}(v', v; t) = n_j \iiint\!\!\iint b w F_1(\Gamma) F_j(\Lambda) f_j(v', w; t)$$

$$\times \left\{ \delta \left(v' - v + \frac{m_{1j}(w - w_{1j})}{m_1} \right) - \delta(v' - v) \right\} \mathrm{d}\xi \, \mathrm{d}b \, \mathrm{d}\Gamma \, \mathrm{d}\Lambda \, \mathrm{d}w. \quad (29)$$

The similarity between $N_{1j}(v', v)$ and $C_{1j}(v', v; t)$ is obvious from equations (23) and (29).

The description of diffusion in terms of a diffusion constant is a velocity-averaged one, as is our single relaxation rate and velocity-averaged line-shape theory. The mutual diffusion constant may be calculated from the average momentum transfer per collision. This leads to an effective friction constant for molecular motion, and the diffusion constant is obtained from the Einstein relation. This is described in more detail elsewhere (McMahon 1981). It is only necessary here to set up the moment equation for the friction constant. Note that this moment approach is not exact but does give the dominant or first Chapman and Enskog approximation to the diffusion constant.

Consider the two gas species to be drifting with an average relative velocity $\langle v_{12} \rangle$. Choose as a convenient frame of reference the frame where gas '2' is at rest. We may use the following approximation produced by a Galilean transformation of the Maxwellian distribution,

$$f_1(v;t) \approx f_1(v) \{1 + 2\kappa_1 v \cdot \langle v_{12} \rangle\}, \qquad f_2(v,w;t) \approx f_2(v,w), \qquad \text{(30a, b)}$$

where $\kappa_1 = m_1/2k_B T$. As usual v is the velocity of the tagged '1' molecule in each case. We require to find the equation of motion for $\langle v_{12} \rangle$. From equation (30a) it is clear that the first moment is sufficient because

$$\int v f_1(v;t)\, dv = 2\kappa_1 \int v v \cdot \langle v_{12} \rangle f_1(v)\, dv = \langle v_{12} \rangle.$$

Take the first moment on both sides of equation (28). The $C_{11}(v',v;t)$ term does not contribute to the overall result on the RHS due to momentum conservation, leading to the conclusion that a collision of two identical molecules will not change their overall contribution to the average velocity. We get therefore

$$2\kappa_1 \int v v \cdot \frac{d\langle v_{12} \rangle}{dt} f_1(v)\, dv = \iint C_{12}(v',v) v f_1(v) \{1 + 2\kappa_1 v' \cdot \langle v_{12} \rangle\}\, dv'\, dv.$$

The first integral on the RHS is zero by the equilibrium condition

$$\int C_{12}(v',v) f_1(v')\, dv' = 0. \qquad \text{(31a)}$$

We then obtain

$$\frac{d\langle v_{12} \rangle}{dt} \int v v f_1(v)\, dv = \iint \langle v_{12} \rangle v' v C_{12}(v',v) f_1(v')\, dv'\, dv$$

$$= \iint \langle v_{12} \rangle (v' - v) v C_{12}(v',v) f_1(v')\, dv'\, dv. \qquad \text{(31)}$$

The introduction of $v' - v$ into the RHS is allowed because the added term depends only on v and is actually zero overall by the equilibrium condition (31a).

The similarity between equations (31) and (27) is obvious. The essential change is that $k \dot{J}(t)$ in effect replaces $\langle v_{12} \rangle$ and that both self and foreign gas collisions contribute to the collision term in equation (27). The only other difference is that the Dicke effect has a memory-weighted kernel and the constraint that β is fixed.

Equation (31) is equivalent to defining a friction coefficient $\zeta_{12}(2)$ such that,

$$d\langle v_{12}\rangle/dt = -\zeta_{12}(2)\langle v_{12}\rangle.$$

Let $\langle \boldsymbol{v}_{12}\rangle = i\langle v_{12}\rangle$ where i is a unit vector. The RHS of equation (31) leads to the result (with the appropriate changes in the dummy variables)

$$\zeta_{12}(2) = \frac{n_2 m_{12}}{k_B T}\int \ldots \int bw(\boldsymbol{i}.\boldsymbol{v})\boldsymbol{i}.(\boldsymbol{w}'-\boldsymbol{w})\,f_2(\boldsymbol{v},\boldsymbol{w})\,f_1(\boldsymbol{v})\,F_1(\Gamma)\,F_2(\Lambda)\,d\xi\,db\,d\Gamma\,d\Lambda\,d\boldsymbol{w}\,d\boldsymbol{v}$$

$$= \tfrac{4}{3}(n_2 m_{12}/m_1)\pi\sigma_{12}^2\langle w_{12}\rangle, \tag{32}$$

where $\langle w_{12}\rangle = (8k_B T/\pi m_{12})^{\frac{1}{2}}$ is the average relative speed and σ_{12} is the mutual diffusion diameter. The integral over $\boldsymbol{v}$ can be carried out to give the following relation for the diffusive cross section (see Appendix 1; also Chapman and Cowling 1970, p. 217)

$$\pi\sigma_{12}^2 = 2\sqrt{\pi}\left(\frac{m_{12}}{4k_B T}\right)^3\int \ldots \int bw(w^2 - 2ww'\cos\chi + w'^2)$$

$$\times f_{12}(\boldsymbol{w})\,F_1(\Gamma)\,F_2(\Lambda)\,d\xi\,db\,d\Gamma\,d\Lambda\,d\boldsymbol{w}$$

$$= \tfrac{1}{4}\sqrt{\pi}\int \ldots \int bg(g^2 - 2gg'\cos\chi + g'^2)\,f_{12}(\boldsymbol{g})\,F_1(\Gamma)\,F_2(\Lambda)\,d\xi\,db\,d\Gamma\,d\Lambda\,d\boldsymbol{g}, \tag{33}$$

where χ is the scattering angle, w' is the post-collisional relative speed and $g^2 = (m_{12}/2k_B T)w^2$. The Chapman and Enskog first approximation $[D_{12}]$ to the diffusion constant is obtained firstly by transforming to the laboratory frame, which gives a new friction coefficient $\zeta_{12}(0) = (n/n_2)\zeta_{12}(2)$ (McMahon 1981), with $n = n_1 + n_2$, and then using the Einstein relation $D_{12} = k_B T/(m_1\zeta_{12}(0))$. Of course, the self-diffusion coefficient D_{11} and self-diffusion diameter σ_{11} can be defined similarly by considering the relative drift of two groups of identical molecules.

In precisely the same way as for diffusion, the first moment of equation (27) leads to the equation

$$dJ(t)/dt = 1 - \eta J(t), \tag{34}$$

where the 'memory diffusive' relaxation rate $\eta = \eta_{11} + \eta_{12}$ is determined by

$$\eta_{1j} = \frac{n_j m_{1j}}{k_B T F_1(\beta)}\int \ldots \int bw(\hat{\boldsymbol{k}}.\boldsymbol{v})\hat{\boldsymbol{k}}.(\boldsymbol{w}'-\boldsymbol{w})\,M_{1j}(\xi,b,\Lambda,\Gamma,\boldsymbol{w})$$

$$\times f_2(\boldsymbol{v},\boldsymbol{w})\,f_1(\boldsymbol{v})\,F_1(\Gamma)\,F_2(\Lambda)\,d\xi\,db\,d\Lambda\,d\alpha\,d\Omega_\beta\,d\boldsymbol{w}\,d\boldsymbol{v}$$

$$= \tfrac{4}{3}(n_j m_{1j}/m_1)\pi d_{1j}^2\langle w_{1j}\rangle, \tag{35}$$

where $\langle w_{1j}\rangle = (8k_B T/\pi m_{1j})^{\frac{1}{2}}$ and $\hat{\boldsymbol{k}}$ is a unit vector. The memory diffusive diameter d_{1j} is generally defined by equation (35) but similar to σ_{12} it can be reduced by integrating over all $\boldsymbol{v}$, as described in Appendix 1. The result is

$$\pi d_{1j}^2 = \frac{\sqrt{\pi}}{2F_1(\beta)}\int \ldots \int bg^2(g - g'\cos\chi)\,M_{1j}(\xi,b,\Lambda,\Gamma,\boldsymbol{g})$$

$$\times f_{12}(\boldsymbol{g})\,F_1(\Gamma)\,F_2(\Lambda)\,d\xi\,db\,d\Lambda\,d\alpha\,d\Omega_\beta\,d\boldsymbol{g}. \tag{36}$$

It should be pointed out that d_{1j} is state dependent and we should denote it as $d_{1j}(\beta)$. Also $d_{1j}(\beta)$ is complex because M_{1j} is complex in general. Again g' differs from g in general but unlike the case of diffusion this difference only arises from changes in the internal energy of the bath molecule due to the constraint that β is fixed. When $M_{1j} = 1$ the collisions are perfectly elastic (corresponding to no pressure broadening) and when used in equation (36) $M_{1j} = 1$ defines $\sigma_{1j}(\beta)$. However, in general we can expect $|d_{1j}(\beta)| \leqslant \sigma_{1j}(\beta)$. Also $(g^2 - 2gg' \cos\chi + g'^2)$ in equation (33) can be replaced by $2g(g - g' \cos\chi)$ as shown in Appendix 1, so that there is no lack of symmetry between equations (33) and (36) when $M_{1j} = 1$. For no memory in hard velocity-deflecting collisions we have $\eta = 0$ and the usual Voigt profile is obtained.

Integrating $\Phi(t, v)$ over all v gives $\Phi(t)$ but this requires $\Phi(t, v)$ to have been calculated to sufficiently high order in k which is not the case with

$$\Phi(t, v) \approx f_1(v) \exp\{i\omega_\beta t + i\boldsymbol{k} \cdot \boldsymbol{v}(1 - e^{-\eta t})/\eta - t/\tau\}.$$

Nevertheless this equation is a sufficient starting point to obtain the final result. From the discussion in Appendix 2 we find

$$\Phi(t) = \exp\{i(\omega_\beta - \tau^{-1})t\} \exp\{-k^2(\eta t - 1 + e^{-\eta t})/2\kappa_1\eta^2\}. \tag{37}$$

Equation (37) is exactly the same form as that arising out of the weak collision model (Galatry 1961; Rautian and Sobel'man 1967). The difference is that the present analysis is not restricted to weak collisions. The essential ingredient is working only to the term linear in $\boldsymbol{k}$ and $J(t)$ on the RHS of equation (26). This is consistent with the spirit of the first approximation to the gas mutual diffusion constant which likewise assumes as a first approximation an exponential decay law for a drift velocity. For η large, equation (37) reproduces the well-known high density Lorentzian line shape with a relaxation rate $\tau^{-1} + k^2/2\kappa_1\eta$.

Another kind of cutoff procedure is obtained if we define as a first approximation

$$\int C_{12}(v', v) f_1(v', t)\, dv' = -\zeta_{12}\Big(f_1(v, t) - f_1(v)\int f_1(v', t)\, dv'\Big), \tag{38a}$$

$$\sum_{j=1}^{2} \int N_{1j}(v', v) \Phi(t, v')\, dv' = -\eta\Big(\Phi(t, v) - f_1(v)\int \Phi(t, v')\, dv'\Big). \tag{38b}$$

These are essentially integral properties of the velocity thermalizing model. If we calculate the equation for $\langle v_{12}\rangle$ as before, equation (38a) gives the same exponential decay result. If we set up the equation corresponding to (26) we find from equation (38b)

$$i f_1(v)\boldsymbol{k} \cdot \boldsymbol{v}\Big(\frac{dJ}{dt} - 1\Big) = \eta f_1(v) \int f_1(v')\Big(\exp\{i\boldsymbol{k} \cdot (v' - v) J(t)\} - 1\Big)\, dv'$$

and the moment equation to first order in $\boldsymbol{k} J(t)$ on the RHS would again ultimately lead to equation (37).

To see that equation (38b) leads to a more formal derivation for η we follow the method of Hess (1972) and denote the error in the RHS as $W[\Phi]$. The complex

Laplace transform of equation (22) in the speed-independent relaxation rate approximation is

$$(i\,\delta\omega + \tau^{-1} - i\mathbf{k}\cdot\mathbf{v})\tilde{\Phi}(\omega,\mathbf{v}) = f_1(\mathbf{v}) - \eta\left(\tilde{\Phi}(\omega,\mathbf{v}) - f_1(\mathbf{v})\int\tilde{\Phi}(\omega,\mathbf{v}')\,d\mathbf{v}'\right) - W[\Phi]$$

which leads to

$$\tilde{\Phi}(\omega,\mathbf{v}) = f_1(\mathbf{v})\left(1 + \eta\int\tilde{\Phi}(\omega,\mathbf{v}')\,d\mathbf{v}'\right)G(\omega,\mathbf{v}) - G(\omega,\mathbf{v})\,W[\Phi], \qquad (39a)$$

where

$$G(\omega,\mathbf{v}) = (i\,\delta\omega + \tau^{-1} + \eta - i\mathbf{k}\cdot\mathbf{v})^{-1}$$

and $\delta\omega = \omega - \omega_\beta$. Because $W[\Phi]$ is a linear operator, equation (39a) is easily solved by iteration. The first iteration gives

$$\Phi(\omega,\mathbf{v}) = G(\omega,\mathbf{v})\left(1 + \eta\int\Phi(\omega,\mathbf{v}')\,d\mathbf{v}'\right)\left(f_1(\mathbf{v}) - W[f_1\,G]\right) + G(\omega,\mathbf{v})\,W[GW[\Phi]].$$

$$(39b)$$

Equation (38b) is a good approximation if the effect of $W[\Phi]$ on the line shape is small. Assuming the second order correction in $W[\Phi]$ of equation (39b) to be negligible, we see that the first order correction is zero if

$$\int G(\omega,\mathbf{v})\,W[f_1\,G]\,d\mathbf{v} = 0.$$

By expanding G in powers of $\mathbf{k}\cdot\mathbf{v}$ we find that this equation gives a relation for η. From the lowest order contribution and by rewriting $W[\Phi]$ in terms of η and $N(\mathbf{v}',\mathbf{v})$ the expression obtained for η is found to be the same as the velocity weight in equation (27) except that $\mathbf{v}' - \mathbf{v}$ is replaced by $\mathbf{v}' + \mathbf{v}$ but this difference contributes zero under the same approximation

$$\int N(\mathbf{v}',\mathbf{v})\,f_1(\mathbf{v}')\,d\mathbf{v}' = 0.$$

The next contribution is from the $(\mathbf{k}\cdot\mathbf{v})^4$ power, leading to a cubic equation for η which then becomes k^2 and ω dependent. But to include this strictly requires going to the second iteration which also contributes as k^2. This point has apparently been overlooked by Hess (1972). These corrections are negligible if η is significantly less than τ^{-1} so that the deviation from the Voigt profile is not large. It is also small if $(\delta\omega)^2 + \tau^{-2} \gg \langle(\mathbf{k}\cdot\mathbf{v})^2\rangle$, either because the pressure is sufficiently high or because we only consider the line shape sufficiently far from the centre.

6. Comparison of the Two Line-shape Formulae

The line shape obtained from equation (37) has the form (Rautian and Sobel'man 1967),

$$c(\omega) = \left(i\,\delta\omega + \tau^{-1} + \frac{k^2}{2\kappa_1\eta}\right)^{-1}{}_1F_1\left[1, 1 + \left(i\,\delta\omega + \tau^{-1} + \frac{k^2}{2\kappa_1\eta}\right)\eta^{-1}; \frac{k^2}{2\kappa_1\eta^2}\right], \qquad (40a)$$

where

$$_1F_1[\alpha, \gamma; z] = 1 + \frac{\alpha}{\gamma} \frac{z}{1!} + \frac{\alpha(\alpha+1)}{\gamma(\gamma+1)} \frac{z^2}{2!} + \ldots \tag{40b}$$

is the confluent hypergeometric function. For sufficiently high densities equation (40a) reduces to the well-known Lorentzian limit where the line width is the sum of a pressure broadening part and a diffusive narrowing part inversely proportional to the density. These two contributions are correlated through the memory.

Integrating over v in equation (39b) leads to

$$c(\omega) = c_0(\omega)/\{1 - \eta\, c_0(\omega)\}, \tag{41a}$$

where

$$c_0(\omega) = \int \frac{f_1(v)}{\mathrm{i}(\delta\omega - \boldsymbol{k}\cdot\boldsymbol{v}) + (\tau^{-1} + \eta)} \, \mathrm{d}v. \tag{41b}$$

Equations (40) and (41) may be regarded as equally valid representations of the line shape, differing essentially in the cutoff hypothesis of how terms beyond the one linear in $kJ(t)$ on the RHS of equation (26) should be approximated. They give essentially the same result for sufficiently high pressures or sufficiently far from the line centre as shown below. Neither model should be regarded as specific to 'weak' or 'strong' collisions as their original derivations would suggest because both weak and strong collisions occur in the scattering formulae for η.

To see the near equivalence of these two representations let us compare equations (40) and (41) more closely. For $\eta = 0$ equation (40b) has the integral form (from equation 37)

$$c_0(\omega) = \int_0^\infty \exp\{\mathrm{i}(\delta\omega - \tau^{-1})t\} \exp(-k^2 t^2/4\kappa_1)\, \mathrm{d}t, \tag{42a}$$

whereas equation (41b) gives

$$c_0(\omega) = \left(\frac{\kappa_1}{\pi}\right)^{\frac{1}{2}} \int_{-\infty}^\infty \frac{\exp(-\kappa_1 v_z^2)}{\mathrm{i}(\delta\omega - kv_z) + \tau^{-1}}\, \mathrm{d}v_z. \tag{42b}$$

These are two equivalent representations of the Voigt line shape as can be shown by a direct mathematical transformation (Mitchell and Zemansky 1934, p. 320).

It is convenient to use a dimensionless parametrization. Let us write

$$(\kappa_1/k^2)^{\frac{1}{2}}\tau^{-1} = a(1 - M), \qquad (\kappa_1/k^2)^{\frac{1}{2}}\eta = aM, \qquad (\kappa_1/k^2)^{\frac{1}{2}}\delta\omega = x.$$

The parameter a is the dimensionless rate

$$a = (\kappa_1/k^2)^{\frac{1}{2}}(\eta + \tau^{-1}) \tag{43a}$$

and M is the effective memory, related to η and τ by

$$M = \eta\tau/(1 + \eta\tau). \tag{43b}$$

No Dicke effect corresponds to $M = 0$ (Voigt profile) and the maximal Dicke effect with perfect memory ($\tau^{-1} = 0$) corresponds to $M = 1$. That the dimensionless

relaxation rate for the line shape is $\{a(1-M)\}$ explicitly brings out the role of memory in reducing line broadening by collisions. With the definition

$$\Delta = \{ix + a(1-M) + (2aM)^{-1}\}(aM)^{-1},$$

equation (40a) becomes in dimensionless form

$$c_M(a,x) = \frac{1}{aM}\frac{1}{\Delta}{}_1F_1[1, 1+\Delta; (2a^2M^2)^{-1}]$$

$$= \frac{1}{aM}\frac{1}{\Delta}\left\{1 + \frac{1}{\Delta}\frac{1}{2a^2M^2} - \frac{1}{\Delta^2}\frac{1}{2a^2M^2}\left(1 - \frac{1}{2a^2M^2}\right) + \cdots\right.$$

$$\left. + \frac{1}{\Delta^5}\frac{1}{2a^2M^2}\left(1 - \frac{15}{2a^2M^2} + \frac{25}{4a^4M^4} - \frac{10}{8a^6M^6} + \frac{1}{16a^8M^8}\right) + \cdots\right\}.$$
$$(44)$$

This expansion is appropriate only for $M \neq 0$ and $(2a^2M^2)^{-1}$ small.

Likewise equations (41) can be written as

$$c_M(a,x) = c_0(a,x)/\{1 - aM\,c_0(a,x)\}, \qquad (45a)$$

$$c_0(a,x) = \frac{1}{\pi^{\frac{1}{2}}}\int_{-\infty}^{\infty}\frac{\exp(-y^2)}{i(x-y)+a}\,dy. \qquad (45b)$$

Set

$$i(x-y) + a = aM(\Delta + 1 - 1/2a^2M^2 - iy/aM)$$

and regard Δ as a large parameter so that an expansion of equations (45) in powers of Δ^{-1} may be made for comparison with equation (44). The complex Lorentzian integrand of equation (45b) can be expanded in powers of Δ^{-1} and y and the integrals over y carried out for each term. The result is

$$c_0(a,x) = \frac{1}{aM}\frac{1}{\Delta}\left\{1 - \frac{1}{\Delta}\left(1 - \frac{1}{2a^2M^2}\right) + \frac{1}{\Delta^2}\left(1 - \frac{3}{2a^2M^2} + \frac{1}{4a^4M^4}\right) + \cdots\right\}$$

and by equation (45a)

$$c_M(a,x) = \frac{1}{aM}\frac{1}{\Delta}\left\{1 + \frac{1}{\Delta}\frac{1}{2a^2M^2} - \frac{1}{\Delta^2}\frac{1}{2a^2M^2}\left(1 - \frac{1}{2a^2M^2}\right) + \cdots\right.$$

$$\left. + \frac{1}{\Delta^5}\frac{1}{2a^2M^2}\left(1 - \frac{13}{2a^2M^2} + \frac{25}{4a^4M^4} - \frac{10}{8a^6M^6} + \frac{1}{16a^8M^8}\right) + \cdots\right\}. (46)$$

The last displayed terms in equations (44) and (46) are the first terms in the expansions that differ and even this difference is very small. Thus equations (44) and (46) are identical out to the power Δ^{-5} so that, for most purposes, either sufficiently far into the wings or at least for a sufficiently high density the two formulations are equivalent, as already suspected from the velocity-moment analysis. Note that these expansions require $M \neq 0$. For $M = 0$ these two approaches are, of course, identical giving equations (42a) and (42b).

A different expansion of equations (41a) and (41b) is needed to compare with the formula derived by Hess (1972). This expansion is in powers of $(ix+a)^{-1}$ and gives

$$c_M(a, x) \approx \left\{ ix + a(1-M) + \tfrac{1}{2}(ix+a)^{-1} + O\big((ix+a)^{-2}\big) \right\}^{-1}.$$

Equation (46) can be rearranged to give this same expression. To follow Hess, we would then need to define a frequency-dependent spectroscopic diffusion constant which in dimensionless form would be $D(x) = \tfrac{1}{2}(ix+a)^{-1}$. Hess's formula for the effective diffusion constant here is somewhat misleading because for $x = 0$ it does not equal the correct dimensionless spectroscopic diffusion constant $D = \tfrac{1}{2}(aM)^{-1}$. In Hess's notation ω_a replaces τ^{-1} and ω_r replaces our $\tau^{-1} + \eta$ but he defines the zero frequency spectroscopic diffusion constant as $D = \tfrac{1}{2}\kappa_1/\omega_r$. However, he does not explicitly state that his definition of ω_r (his equations 47 and 48) gives $\omega_r \neq 0$ even in the absence of velocity-changing collisions. Because a true diffusion coefficient is only defined in terms of velocity changes (through the friction coefficient and the Einstein relation) Hess's definition is a matter of inappropriate nomenclature rather than a conflict with our analysis. His expansion does not in general represent Dicke narrowing because even when $\eta = 0$ (no Dicke narrowing) the general form of his expansion is not altered. It then merely represents an approximation to the Voigt profile as deviations from the Lorentzian line shape.

7. Approximate Formula for Line Width incorporating Doppler and Dicke Effects

We shall examine two line width definitions, the usual one specifying the separation in frequencies at the half-maximum points and another defined in microwave spectroscopy as the separation of the frequencies at which the slope of the line shape with frequency is a maximum (Parsons and Roberts 1965). For convenience we shall employ equations (45a) and (45b) to represent the line shape. It is not possible to obtain an exact analytical expression for the line width; however, an approximate procedure which may be used to represent the Doppler, Dicke and collision contributions more or less separately is that discussed in microwave spectroscopy by Parsons and Roberts (1965) for the case $M = 0$ (Voigt profile) with the maximum slope line width definition. Their formula is extended here to include $M \neq 0$ and the half-maximum line width definition as well. An analytical development which exploits the scale independence of equations (45a) and (45b) is used rather than their numerical method for particular line frequencies. Note that we shall approximate M as real in the following, which is reasonable if the line shift is small compared with the width. A complex M plus the Dicke effect is known to produce line asymmetry (Rautian and Sobel'man 1967). Because we want to avoid the difficulties with equations (44) and (46) when $M = 0$ we seek a new expansion of $c_M(a, x)$ in terms of the variables $X = ix+a$ and $Y = ix+a(1-M)$. Then $c_0(a, x)$ becomes

$$c_0(a, x) = \frac{1}{\pi^{\frac{1}{2}}} \int_{-\infty}^{\infty} \frac{1}{X}\left(1 - \frac{iy}{X}\right)^{-1} \exp(-y^2)\, dy = \frac{1}{X}\left(1 - \frac{1}{2X^2} + \frac{3}{4X^4} + O(X^{-6})\right)$$

$$= \left\{ X\left(1 + \frac{1}{2X^2} - \frac{1}{2X^4} + O(X^{-6})\right) \right\}^{-1}.$$

Thus we find

$$c_M(a, x) = \left[Y \left\{ 1 + \frac{1}{2XY} - \frac{1}{2X^3Y} + O\left(\frac{1}{X^5Y}\right) \right\} \right]^{-1}$$

$$= \frac{1}{Y} \left\{ 1 - \frac{1}{2XY} + \frac{1}{2X^3Y} + \frac{1}{4X^2Y^2} + O\left(\frac{1}{X^5Y}, \frac{1}{X^4Y^2}, \frac{1}{X^3Y^3}\right) \right\}. \quad (47)$$

The first term of equation (47) is a Lorentzian of dimensionless half-width $a(1-M)$ by the half-power points definition. All subsequent terms produce the Doppler and Dicke effects.

The measured dimensionless half-width x defined by the maximum slope condition (a and M real)

$$\mathrm{Re}\left(\frac{\partial^2 c_M(a, x)}{\partial x^2}\right) = -\mathrm{Re}\left(\frac{\partial^2 c_M(a, x)}{\partial X^2}\right) = 0 \quad (48)$$

leads to the solution $x = a(1-M)/3^{\frac{1}{2}}$ for the Lorentzian line shape. Let us generalize this to include the Doppler and Dicke effects on the value of x. Differentiating equation (47) twice gives

$$\frac{\partial^2 c_M(a, x)}{\partial X^2} = \frac{2}{Y^3}\left(1 - \frac{3}{2XY} - \frac{1}{X^2} - \frac{Y}{2X^3} + \frac{3}{X^3Y} + \frac{15}{4X^4} + \frac{3}{2X^2Y^2} + \frac{3Y}{X^5} + O(6)\right). \quad (49)$$

Equation (49) is accurate only at sufficiently high densities so that any solution for x will be generally wrong for zero pressure or $a = 0$. The solution to equation (49) is of the form of an expansion in powers of a^{-1}, namely

$$x^2 = \tfrac{1}{3}a^2(1-M)^2 + \lambda + \gamma a^{-2} + O(4), \quad (50)$$

where λ and γ depend on M only. Our original expansions (44) and (46) produce their best accuracy near $M = 1$. In the Lorentzian limit with strong narrowing ($M \approx 1$) we obtain from the first term of these equations

$$x^2 \approx \frac{1}{3}\left(a(1-M) + \frac{1}{2aM}\right)^2 = \frac{a^2(1-M)^2}{3} + \frac{1-M}{3M} + \frac{1}{12a^2M^2}.$$

One can guess then that for $M \approx 1$ equation (50) should lead to

$$\lambda \approx \tfrac{1}{3}(1-M), \qquad \gamma \approx \tfrac{1}{12}. \quad (51a, b)$$

To generalize for all M, equation (50) may be inserted into equation (49) and the maximum slope condition (48) applied. One simply requires the coefficient of each power of a^{-2} to be zero following an expansion of all terms into a power series in a^{-2}. This procedure is accurate only for a sufficiently small Doppler and Dicke effect but as will be seen below it can be used to extrapolate the parameters of an approximate formula applicable to quite large Doppler and Dicke effects.

The results obtained by the procedure described above are as follows.

$$\lambda = \tfrac{1}{3} N \left(1 + \tfrac{1}{3} N^2\right)^{-3} \left(1 + N + 2N^2 + 2N^3 + \tfrac{31}{27} N^4 - \tfrac{1}{27} N^5\right), \tag{52a}$$

$$\gamma = \tfrac{1}{12} \left(1 + \tfrac{1}{3} N^2\right)^{-7} \left(1 - \tfrac{2}{3} N^2 - 8N^3 - \tfrac{851}{27} N^4 - \tfrac{512}{27} N^5 + \tfrac{1420}{81} N^6 - \tfrac{848}{81} N^7\right.$$

$$\left. + \tfrac{1069}{243} N^8 - \tfrac{1472}{243} N^9 + \tfrac{74}{81} N^{10} + \tfrac{328}{243} N^{11} - \tfrac{7}{81} N^{12}\right), \tag{52b}$$

where $N = 1 - M$. For $M \to 1$ we find that equations (52a, b) reproduce equations (51a, b) as required. For M small we obtain

$$\lambda \approx 1 - \tfrac{5}{3} M + \tfrac{5}{24} M^2 + O(3), \tag{53a}$$

$$\gamma \approx -\tfrac{9}{16} \left(1 - \tfrac{2}{3} M + \tfrac{5}{2} M^2 + O(3)\right). \tag{53b}$$

The case $M = 0$, like $M = 1$, is easier to treat than the general case and has been used as an independent check on the accuracy of equations (52a) and (52b).

To find a formula which works at lower densities than does equation (50) we follow the approach of Parsons and Roberts (1965) for $M = 0$ by assuming a quadratic relation of the form $x^2 - Bx - C = 0$ such that for the parameter a large the solution satisfies equation (50) (i.e. solve for x, find x^2 and compare with equation 50). This leads to the identifications

$$B = a(1 - M)/3^{\frac{1}{2}}, \qquad C = \tfrac{1}{2}\{\lambda + (\gamma N^2 + \tfrac{3}{4} \lambda^2)/a^2 N^2\}. \tag{54a, b}$$

For calculational purposes an explicit expression for the coefficient of $a^{-2} N^{-2}$ in C is convenient. It is

$$\gamma N^2 + \tfrac{3}{4} \lambda^2 = \tfrac{1}{6} N^2 \left(1 + \tfrac{1}{3} N^2\right)^{-7} \left(1 + N + \tfrac{7}{3} N^2 + \tfrac{1}{3} N^3 - \tfrac{88}{9} N^4 - \tfrac{82}{27} N^5 + \tfrac{398}{27} N^6\right.$$

$$\left. - \tfrac{106}{81} N^7 + \tfrac{3065}{729} N^8 - \tfrac{1699}{729} N^9 + \tfrac{1427}{2187} N^{10} + \tfrac{1445}{2187} N^{11} - \tfrac{94}{2187} N^{12}\right), \tag{55a}$$

and if M is small compared with unity

$$\gamma N^2 + \tfrac{3}{4} \lambda^2 \approx \tfrac{3}{16} \left(1 - \tfrac{16}{3} M + \tfrac{239}{18} M^2 + O(3)\right). \tag{55b}$$

To compare with the earlier $M = 0$ work (Parsons and Roberts 1965) we convert back into the dimensional form to obtain the measured half-width δv from

$$\delta v - \Delta v/3^{\frac{1}{2}} = A_M/\delta v, \tag{56}$$

where Δv is the Lorentzian half-width. We find

$$\Delta v = \frac{1}{2\pi\tau} = \frac{1}{2\pi} \left(\frac{k^2}{\kappa_1}\right)^{\frac{1}{2}} a(1 - M), \qquad \delta v = \frac{1}{2\pi} \left(\frac{k^2}{\kappa_1}\right)^{\frac{1}{2}} x \tag{57a, b}$$

and

$$A_M = \frac{1}{4\pi^2} \frac{k^2}{\kappa_1} C = \frac{k_B T v_0^2}{m_1 c^2} \left\{\lambda + \left(\gamma N^2 + \frac{3\lambda^2}{4}\right) \frac{2 k_B T v_0^2}{m_1 c^2 (\Delta v)^2}\right\}, \tag{58}$$

where v_0 is the centre frequency and c is the speed of light. The pressure-dependent term in equation (58) is usually much smaller than the other term over that range of densities when the Doppler and Dicke contributions are less than about 50% of the total width. This term does not appear in the earlier numerical work and omitting

it improves the formula by eliminating the zero pressure divergence (see Fig. 2 below). Calculation of A_0 for NH_3 at 26°C and several microwave frequencies gives values within a few per cent of the numerical ones of Parsons and Roberts (1965).
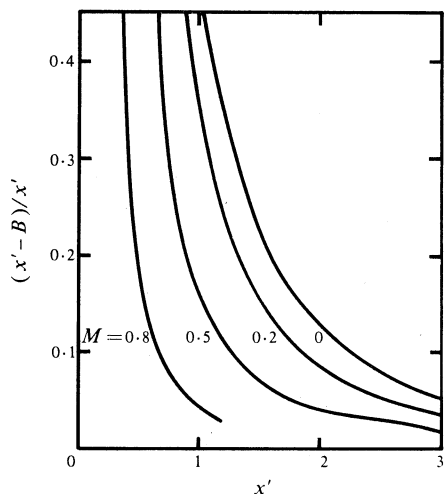

Fig. 1. Plots of the Doppler contribution as a proportion of the total line width defined by the maximum slope condition. The curves show the Dicke effect reduction of the Doppler contribution with increasing values of M.
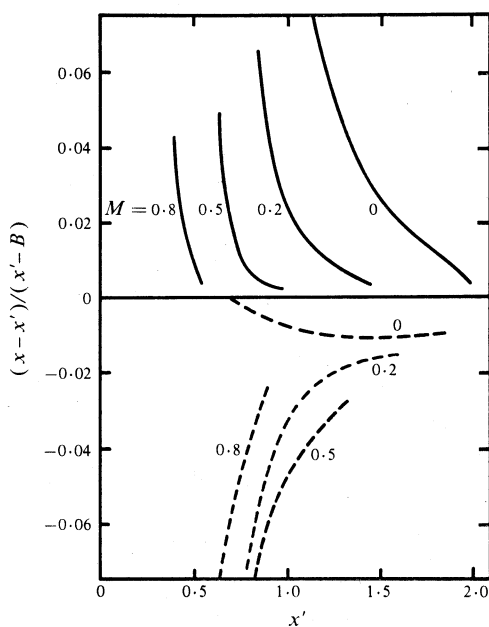

Fig. 2. Error in equation (56) shown as a proportion of the Doppler contribution to the maximum slope line width for different values of M. The full curves are for C given by equation (54b) whereas the dashed curves correspond to $C = \frac{1}{2}\lambda$. The plots extend either to $a = 10$ or to where the rounding error is intolerable because the Doppler effect becomes very small.

The expression $\delta v - \Delta v/3^{\frac{1}{2}}$ denotes the Doppler and Dicke contributions to the maximum slope half-width δv. Noting the M dependence from equations (52a) and (55a) we see that $A_M \leqslant A_0$ which corresponds to the expected Dicke reduction of the Doppler effect relative to the Voigt profile. For $M = 1$, we have $\Delta v = 0$ (no pressure broadening) and $\lambda = 0$ so that equation (56) leads to $x = (\frac{1}{12})^{\frac{1}{4}}a^{-1}$, consistent with the Lorentzian limits (extreme narrowing) for equations (44) and (46).

Despite the fact that an elementary proof of equation (56) does not seem to be possible it is nevertheless remarkably accurate up to quite large Doppler contributions to δv. Its accuracy has been tested for various M values by comparing its predicted values x with x' obtained by a numerical solution of equation (48) using $c_M(a, x)$ given by equations (45). Equation (45a) may be conveniently expressed in terms of the complex probability integral or alternatively the plasma dispersion function, both of which are tabulated (Abramowitz and Stegun 1965; Faddewa and Terent'ev 1961; Fried and Conte 1961).

Fig. 1 gives a plot of the relative contribution $(x' - B)/x'$ of the Doppler and Dicke effects to x' as a function of x' for different values of M positive and real. It is quite clear that larger M values for a given x' lead to a smaller Doppler contribution as expected. The graph shows for a value $x' \approx 1 \cdot 4$ that $M = 0 \cdot 2$ leads to roughly a 30% reduction of the Doppler effect. This is a crude estimate of what effect may exist for some weakly broadening gas mixtures in microwave pressure broadening (see Section 8).

The full curves in Fig. 2 plot $(x - x')/(x' - B)$ or the error in x obtained from equation (56) relative to the Doppler contribution. It is less than 10% in all cases over the range plotted and the error in x is less than 3% of the total half-width. The Doppler effect ranges up to 40% of the total width over the same range of x'.

The dashed curves in Fig. 2 give $(x - x')/(x' - B)$ when x is calculated as before but with the density-dependent term of equation (54b) omitted (that is, $C = \frac{1}{2}\lambda$). This avoids the low density divergence of C. For $M = 0$ the formula of Parsons and Roberts (1965) is obtained and from Fig. 2 the error in x relative to the Doppler contribution is very much reduced, dipping to only about -1% and becoming zero in the absence of collisions (corresponding to $x' = 2^{-\frac{1}{2}} = 0 \cdot 7071$). The error in x obtained now is quite tolerable for M below about $0 \cdot 15$ over the whole range of densities down to $a = 0$. For most practical purposes M should be rarely more than about $0 \cdot 2$ and the simplified quadratic relation should be sufficient.

The half-width y obtained by the half-power definition requires (M and a real)

$$\mathrm{Re}\, c_M(a, y) = \tfrac{1}{2} c_M(a, 0). \tag{59}$$

Again equation (47) can be used to get the coefficients of the solution written as

$$y^2 = a^2(1 - M)^2 + \psi + \chi a^{-2} + \dots. \tag{60}$$

The Lorentzian limit for $M \approx 1$ of equations (44) and (46) leads to

$$y^2 = \{a(1 - M) + (2aM)^{-1}\}^2$$

which produces

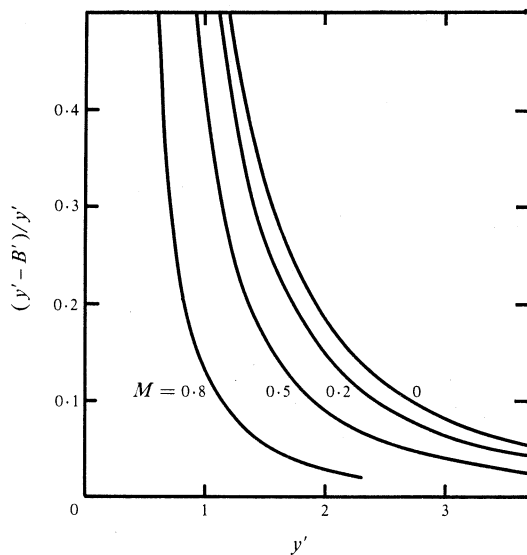$$\psi \approx 1 - M, \qquad \chi \approx \tfrac{1}{4}. \tag{61a, b}$$

Fig. 3. Relative contribution of the Doppler effect to the half-power line width for different M values, showing the Dicke reduction of the Doppler effect for each line width.
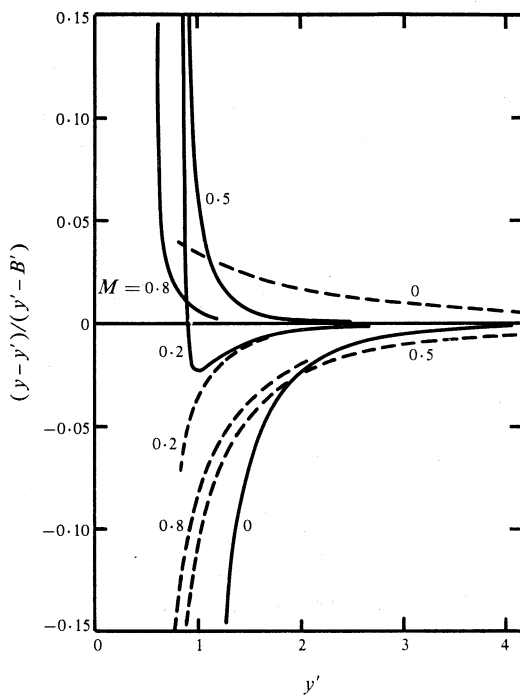

Fig. 4. Error in equation (64a) as a proportion of the Doppler contribution to the half-power line width for different M values. The full curves are for B' and C' given by equations (64b, c) whereas the dashed curves correspond to $C = \frac{1}{2}\psi$.

The general expressions obtained by this method of a^{-2} power expansion are

$$\psi = N(1+N^2)^{-1}(1+N+N^2), \tag{62a}$$

$$\chi = \tfrac{1}{4}(1+N^2)^{-3}(1-6N^2-8N^3+5N^4-12N^5-4N^7), \tag{62b}$$

which conform to the extreme narrowing limits (61a, b) as required. For M small compared with unity equations (62) become

$$\psi \approx \tfrac{3}{2}\big(1-M-\tfrac{1}{6}M^2+O(3)\big), \tag{63a}$$

$$\chi \approx -\tfrac{3}{4}\big(1-\tfrac{4}{3}M+O(3)\big). \tag{63b}$$

The new quadratic relation for y is

$$y^2 - B'y - C' = 0, \tag{64a}$$

where

$$B' = a(1-M), \qquad C' = \tfrac{1}{2}\{\psi+(\chi N^2+\tfrac{1}{4}\psi^2)/a^2N^2\}, \tag{64b, c}$$

with

$$\chi N^2 + \tfrac{1}{4}\psi^2 = \tfrac{1}{2}N^2(1+N^2)^{-3}(1+N-N^2-2N^3+\tfrac{9}{2}N^4-5N^5+\tfrac{1}{2}N^6-2N^7). \tag{65}$$

As before the accuracy of y calculated from the quadratic formula has been checked numerically. Fig. 3 gives the relative Doppler contribution $(y'-B')/y'$ to the half-width once again showing the Dicke reduction of this contribution due to a nonzero M. This reduction is due to ψ and $\chi N^2+\tfrac{1}{4}\psi^2$ in the expression for C' which decreases as M is increased. Fig. 4 plots the error in y relative to the Doppler correction both with the pressure-dependent term of equation (64c) included (full curves) and with this term omitted to avoid the $a \to 0$ divergence (that is, $C = \tfrac{1}{2}\psi$; dashed curves). The latter is generally preferable because the error in y is tolerable now over the whole density range (at least for $M \leqslant 0 \cdot 2$) as obtained before for the maximum slope widths. Note that the Dicke effect is relatively smaller for the half-power widths than the maximum slope widths. For instance, $M = 0 \cdot 2$ now near $y \approx 2 \cdot 5$ only produces approximately a 20% reduction of the Doppler effect here as opposed to the corresponding 30% previously. Note that $y = (\ln 2)^{\frac{1}{2}} \approx 0 \cdot 8326$ gives the zero pressure or fully Doppler limit. An examination of the numerical results for x' shows that over part of the density range x' can be less than $2^{-\frac{1}{2}}$ if $M \geqslant 0 \cdot 3$ roughly (similarly y' can be less than $(\ln 2)^{\frac{1}{2}}$).

Figs 1–4 are confined to M positive but there is no fundamental reason why $M < 0$ cannot occur. This corresponds to the case where the electric dipole vector after a collision is more likely to be opposite to the direction of the dipole just before the collision. Because of the correlation between the Doppler effect and pressure broadening, the line width exceeds that of the Voigt profile but no actual cases of this have so far been observed.

8. Gas Composition Dependence and Theoretical Limits of M

The basic object of Dicke narrowing observations is to find M and thereby to obtain the memory diffusive diameters d_{1j}. From equation (43b) it is clear that M

does not depend upon the gas pressure so that M may be obtained by systematic line width observations at different pressures. M does, however, change with the gas composition. By definition of the broadening diameters

$$\tau^{-1} = \sum_{j=1}^{2} n_j(\pi b_{1j}^2)\langle w_{1j}\rangle. \tag{66}$$

Combining equation (66) with (35) and (43b) we obtain

$$M/(1-M) = \tfrac{2}{3}(\alpha n_1 + \beta n_2)/(\gamma n_1 + \delta n_2), \tag{67}$$

where

$$\alpha = d_{11}^2, \qquad \beta = d_{12}^2\left(\frac{2m_2}{m_1+m_2}\right)^{\frac{1}{2}}, \qquad \gamma = b_{11}^2, \qquad \delta = b_{12}^2\left(\frac{m_1+m_2}{2m_2}\right)^{\frac{1}{2}}.$$

Also we have

$$M = \tfrac{2}{3}(\alpha n_1 + \beta n_2)/(\gamma' n_1 + \delta' n_2), \tag{68}$$

where

$$\gamma' = \gamma + \tfrac{2}{3}\alpha, \qquad \delta' = \delta + \tfrac{2}{3}\beta.$$

The line width is proportional to $\gamma n_1 + \delta n_2$. If we define $z = n_1(\gamma n_1 + \delta n_2)^{-1}$ then equation (68) becomes

$$M = \left(1 + \frac{3}{2}\frac{\delta}{\beta + z(\alpha\delta - \beta\gamma)}\right)^{-1}. \tag{69}$$

Equation (69) is appropriate to systematic observations of M at fixed total line width but changing absorber proportion in the gas. It is clear that whether M increases or decreases with z depends upon the sign of $\alpha\delta - \beta\gamma$. If self-broadening gives a much larger b_{11} than b_{12} then $\alpha\delta - \beta\gamma$ is most likely to be negative in which case the largest value of M occurs for $z = 0$, or in other words almost no absorber compared with the foreign gas perturber. The minimum value of M is when z is maximum at the value $\gamma^{-1}(n_2 = 0)$. These cases correspond to $\beta\gamma > \alpha\delta$, or equivalently

$$b_{11}^2 d_{12}^2 > b_{12}^2 d_{11}^2 (m_1 + m_2)/2m_2, \tag{70}$$

giving

$$M_{\text{max}} = (1 + \tfrac{3}{2}\delta/\beta)^{-1}, \qquad M_{\text{min}} = (1 + \tfrac{3}{2}\gamma/\alpha)^{-1}. \tag{71a, b}$$

If $\alpha\delta > \beta\gamma$, the formulae for M_{max} and M_{min} are simply interchanged. For a pure gas these two M coincide of course. Note that $M = 1$, the absolute maximal Dicke effect, requires both $\delta = 0$ and $\gamma = 0$ or no collision broadening; $M = 0$ requires $\alpha = 0$ and $\beta = 0$.

An alternative to equation (69) is obtained if we introduce the absorber composition ratio

$$R = n_1/(n_1 + n_2).$$

Since $z = R\{R(\gamma - \delta) + \delta\}^{-1}$ we find

$$M = \left(1 + \frac{3}{2}\frac{\delta + R(\gamma - \delta)}{\beta + R(\alpha - \beta)}\right)^{-1}. \tag{72}$$

Noting that $d_{1j}(\beta) \leqslant \sigma_{1j}(\beta)$ we may calculate a theoretical estimate for M_{max} by replacing $d_{1j}(\beta)$ by $\sigma_{1j}(\beta)$ in α and β and assuming that $\sigma_{1j}(\beta)$ is the gas kinetic value. This represents perfect memory in hard velocity-changing collisions. To get some idea of the upper limits consider CH_4 for which evidence of Dicke narrowing has been reported (Goldring *et al.* 1968; Hubbert and Troup 1977). Using $b_{11} = 6 \cdot 5$ Å and $\sigma_{11} = 3 \cdot 9$ Å (deduced from D_{11} for CH_4; see Chapman and Cowling 1970, p. 267), we find

$$M \leqslant \left(1 + \tfrac{3}{2}(6 \cdot 5/3 \cdot 9)^2\right)^{-1} = 0 \cdot 19.$$

The observations of Hubbert and Troup (1977) suggest $M \approx 0 \cdot 1$ so that quite a high component of adiabatic phase coherence and elastic probability needs to exist in CH_4 hard core collisions. This would mean that a high memory 'hole' exists in the $S_B(b, w)$ function for $b \leqslant \sigma_{11}$. That is, $S_B(b, w)$ has values for $b \leqslant \sigma_{11}$ somewhat smaller than it is for larger b where most of the broadening must be originating.

Dicke narrowing has not yet been observed in molecular microwave spectroscopy. An estimate for M_{max} can be obtained for the NH_3 microwave spectrum using equation (71a) with σ_{1j} gas kinetic in place of $d_{1j}(\beta)$. For pure NH_3, we have $b_{11} = 12 \cdot 5$ Å on average for the band and $\sigma_{11} \approx 4 \cdot 0$ Å, giving $M \leqslant 0 \cdot 064$. From equation (58) this is less than an 11 % reduction of the Doppler effect. With Ar, N_2, H_2 and He perturbers using the data of Morris (1971) we find broadening diameters with NH_3 of 3·8, 5·4, 3·2 and 2·0 Å respectively compared with estimated gas kinetic diameters of 3·76, 4·1, 3·11 and 2·65 Å (Chapman and Cowling 1970, p. 263). The signs of $\alpha\beta - \gamma\delta$ determining the gas composition dependence suggest that equations (70) and (71) should hold. The upper limits for M_{max} with Ar, N_2, H_2 and He are found to be 0·47, 0·32, 0·12 and 0·31 respectively. All of these would produce substantial reductions of the Doppler contribution to the line width and can be readily measured. It is at least conceivable that a high degree of elasticity may occur in these hard collisions because of the low moments of inertia for NH_3 (giving large separations of the NH_3 rotational energy levels) and because the adiabatic saturation effect (McMahon 1977a) may occur. The latter also implies the possible existence of hard collision selection rules which would enhance the probability of rotationally elastic collisions.

Fiutak and Van Kranendonk (1963) have speculated that if $S_2(\sigma_{1j}, w) < 1$ then $S_B(b, w) \approx S_2(\sigma_{1j}, w)$ for $b \leqslant \sigma_{1j}$. This gives reasonable results for Raman line broadening (Gray and Van Kranendonk 1966) but an indirect test for NH_3–He microwave broadening (Parsons *et al.* 1972) suggests better results with $S_B \approx 1$ for hard collisions. Dicke narrowing can provide an independent check of these suggestions.

9. Summary and Conclusions

This paper has been directed towards formulating an approximate theory of Dicke narrowing in a dilute gas. Special emphasis has been given to the notion of absorber or emitter phase memory following a collision which reflects the correlation between pre-collisional and post-collisional states. The Dicke effect requires both memory and absorber velocity changes together. By requiring that a parallel development must exist between the velocity moment equation for the theory of diffusion and the moment equation in the Dicke narrowing theory one is led naturally to define the memory diffusive diameters d_{1j}. An important conclusion of the present treatment

is that one should not take too seriously as far as real gases are concerned the differences in the line-shape formulae that exist between the so-called weak collision model (based on the Brownian motion theory) and the strong collision model (where the collisions thermalize the absorber or emitter velocity). In our moment analysis the two line shapes merely result from different cutoff methods. Both strong and weak collisions occur in real gases and both types of collision contribute to the Dicke narrowing memory diffusive relaxation rate η which involves an integration over all impact parameters (see equation 35). A scattering formula for η (equations 35 and 36) has been derived showing how the Dicke narrowing effect can be used to study $S_B(b, w)$ for hard collisions.

A useful parametrization of the line shape is obtained by introducing the effective memory M (equation 43b). M ranges between 0 and 1 when restricted to positive real values. $M > 0$ always leads to a Doppler effect smaller than that for the Voigt profile ($M = 0$). Dicke reductions of the Doppler effect may be, at least theoretically, as large as 30% in some cases of molecular microwave pressure and Doppler broadening. By measuring M for a range of gas compositions the values of d_{1j} may be determined from which in turn may be obtained the quantity $\langle M_{1j} \rangle$ (not to be confused with M and defined by $\langle M_{1j} \rangle \sigma_{1j}^2 = d_{1j}^2$) representing the average memory present in individual collisions. Thus by observations of the Dicke reduction of the Doppler effect one ultimately obtains information on how elastic and phase coherent hard velocity-changing collisions may be.

There are some inadequacies of the present analysis. Firstly, equations (56) and (64a) which give approximate analytical expressions for the two definitions of the line width are remarkably accurate up to quite large Doppler contributions, especially for low values of M. In view of their simplicity it would be surprising if they could not be derived from first principles rather than merely guessed using the high density limits (50) and (60) as constraints. Secondly, our line shape formulae (40a) and (41a) are not valid near the line centre at low pressures where the approximate equivalence of the 'weak' and 'strong' collision forms of the line shape fails. The weak collision representation defining $J(t)$ is generally inadequate under these conditions, which correspond to the low pressure long-time limit of $J(t)$. For instance, η can in principle be negative but then $J(t)$ diverges for $t \to \infty$. The inadequacy of this representation is closely related to the failure of the Fokker–Planck equation for time domain experiments in the long-time limit (Berman *et al.* 1975). Our time domain functions $\Phi(t)$ and $\Phi(t, v)$ introduce the functions $K(t)$ and $L(t)$ (see Appendix 2). For ηt large, $K(t) \to t/\eta$ and $L(t) \to 2t/\eta$. These functions incorporate the Dicke narrowing of the line width and properly show that this effect is inversely proportional to the density at high pressures. The alternative interpretation of ηt large is the long-time limit at low pressures. But then relaxation rates inversely proportional to the density conflict with a more detailed analysis of the theory for time domain experiments and with actual observations (Berman *et al.* 1975).

Another problem is that quantum effects on the velocity-change kernel may be important in hard core collisions. The present development only parallels the semiclassical theory which is confined to angular momentum quantum numbers $l > 1$ (Smith *et al.* 1971b) whereas $l = 0$ and $l = 1$ are possibly important for calculating hard collision (small impact parameter) S-matrix elements. There is a need to carry out a quantum mechanical moment analysis to obtain limiting approximations to the line shape when Dicke narrowing is important.

Finally, our analysis is oversimplified by omitting some of the correlations of the Doppler and Dicke narrowing effects with the collision process. One correlation occurs because the relevant collision rates in general depend on the orientations (or M degeneracy) of the molecules with respect to their relative velocity vector (see e.g. Cooper and Stacey 1975). Also it can be shown (e.g. Seidel 1979, equation 2.6) that M-dependent collision rates combined with the Doppler effect strictly invalidate use of the usual dipole autocorrelation expression for the line profile because the derivation of the autocorrelation formalism assumes an average over photon directions of propagation, independent of the absorber/emitter velocity (see Smith *et al.* 1971*a*, equation 2-12), an assumption not generally true. Our formalism is self-consistent nevertheless by assuming that M-degeneracy effects are small overall.

Acknowledgments

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Appendix 1

We consider here the essential details in deriving equations (33) and (36). It is necessary to treat only one of these and the other is readily obtained. Because of the slightly more complicated integrand we consider therefore equation (35). The integration over v can be carried out immediately, as can in fact also the integration over all orientations of w. This is not obvious at first sight and so we shall follow a path which makes it self evident.

Firstly we can imagine that the integrations over all variables except v and w have been carried out. We shall write therefore

$$\eta_{1j} = \tfrac{4}{3}(n_j m_{1j}/m_i)(\pi d_{1j}^2)\langle w_{1j}\rangle I_{1j}, \qquad (A1a)$$

where

$$I_{1j} = \frac{3k_{\mathrm B} T m_j}{4\pi d_{1j}^2 \langle w_{1j}\rangle} \iint (\hat{k} \cdot v)\hat{k} \cdot (\llbracket w' M_{1j}\rrbracket - w\llbracket M_{1j}\rrbracket) f_2(v, w) f_1(v) \, \mathrm{d}v \, \mathrm{d}w. \qquad (A1b)$$

Here the open brackets $\llbracket \; \rrbracket$ denote integration over all variables except v and w. The quantity $\llbracket M_{1j}\rrbracket$ can only depend upon the magnitude of w so that this part of the

integral can be immediately carried out for all v and directions of w. The post-collisional relative velocity w' is uniquely determined by the pre-collisional state specified by $\xi, b, \Lambda, \Gamma, w$ and v. The dependence on v comes about through momentum conservation so that w' is confined to the same plane as v and w. Of course, when $[\![w' M_{1j}]\!]$ is formed this vector must likewise be in the same plane as w and v except now $[\![w' M_{1j}]\!]$ is necessarily in the same direction as w and cannot either be correlated with v or be a function of v. The latter result follows by Galilean invariance of the collision process and v can be eliminated by a simple transformation. Furthermore, the direction of w is of no consequence for the magnitude of $[\![w' M_{1j}]\!]$ and so this term in equation (A1b) may also be integrated over all directions of w and over all v.

At this point the evaluation of equation (35) is the same as for equation (32) for diffusion theory except for the extra weight M_{1j}. At the end of the integrations over v and all directions of w one can reintroduce the explicit integrals over ξ, b, Λ and, by normalization, the directions of w to obtain equation (36). The end result is obtained either by simple inspection of the theory of diffusion result for ζ_{12} or by direct evaluation of the v and the w direction integrals.

It will be noticed that equation (33) has the quantity $g^2 - 2gg' \cos \chi + g'^2$ in the integrand (see Chapman and Cowling 1970, p. 217) in contrast to $2g(g - g' \cos \chi)$ in equation (36); however, the two are equivalent because g'^2 can be replaced by g^2 in the integrand of equation (33). This follows from energy conservation and detailed balancing. Let E_β and E_λ denote the internal energies of the absorber or emitter and the bath molecules respectively. As usual, dashed quantities will represent post-collisional variables. We have then

$$\tfrac{1}{2}m_{12} w^2 + E_\beta + E_\lambda = \tfrac{1}{2}m_{12} w'^2 + E'_\beta + E'_\lambda. \tag{A2}$$

Let X denote the set of random variables $\xi, b, \Gamma, \Lambda, w, v$. In equation (33) g' is determined by X, but it becomes an independent random variable by explicitly incorporating the equations of motion connecting X and X' by a δ function, as in equation (9). Consider the integrals

$$\iint bw \tfrac{1}{2}m_{12} w'^2 F_1(\Gamma) F_2(\Lambda) f_2(v, w) f_1(v) \delta(X' - X'_{12}(X)) \, \mathrm{d}X' \mathrm{d}X$$

$$= \iint bw\{\tfrac{1}{2}m_{12} w^2 + (E_\beta + E_\lambda) - (E'_\beta + E'_\lambda)\} F_1(\Gamma) F_2(\Lambda) f_2(v, w)$$

$$\times f_1(v) \delta(X' - X'_{12}(X)) \, \mathrm{d}X' \mathrm{d}X. \tag{A3}$$

The LHS is equivalent to the g'^2 term in equation (33). Use has been made of the property (20b). Now g'^2 can be replaced by g^2 in equation (33) if it can be shown that

$$\iint bw(E_\beta + E_\lambda) F_1(\Gamma) F_2(\Lambda) f_2(v, w) f_1(v) \delta(X' - X'_{12}(X)) \, \mathrm{d}X' \mathrm{d}X$$

$$= \iint bw(E'_\beta + E'_\lambda) F_1(\Gamma) F_2(\Lambda) f_2(v, w) f_1(v) \delta(X' - X'_{12}(X)) \, \mathrm{d}X' \mathrm{d}X. \tag{A4}$$

On the RHS, $F_1 F_2 f_2 f_1$ is equal to $F'_1 F'_2 f'_2 f'_1$ by detailed balancing (equation 7) and by the Liouville theorem for the collision pair bw can be replaced by $b'w'$. Hence the RHS is reduced to a form equivalent to the LHS except for a mere interchange

of dummy variables. Thus it is allowable to represent the integrand of equation (33) in the form used by Chapman and Cowling (1970) which is more symmetric with respect to g and g' than in equation (36). It is clear that M_{1j} spoils the above symmetrizing process for equation (36).

Appendix 2

The exponent of equation (24a) omits second order and higher powers in k and is inadequate for determining $\Phi(t)$ by direct integration over v. Nevertheless $J(t)$ has the essential physics of the Dicke effect. To see this, integrate both sides of equation (22) over all v (as usual replacing $\tau(v)$ by τ) to get the general relation

$$\frac{\partial \Phi(t)}{\partial t} - (i\omega_\beta - \tau^{-1})\Phi(t) - i\mathbf{k} \cdot \int \mathbf{v}\,\Phi(t,v)\,\mathrm{d}v = \delta(t). \tag{A5}$$

The collison term on the RHS is zero because

$$\int N_{1j}(v',v)\,\mathrm{d}v = 0.$$

One may write

$$\Phi(t) = \lim_{\chi \to 0} \int \exp(i\boldsymbol{\chi} \cdot \mathbf{v})\,\Phi(t,v)\,\mathrm{d}v \tag{A6a}$$

and

$$\int i\mathbf{v}\,\Phi(t,v)\,\mathrm{d}v = \lim_{\chi \to 0} \nabla_\chi\left(\int \exp(i\boldsymbol{\chi} \cdot \mathbf{v})\,\Phi(t,v)\,\mathrm{d}v\right). \tag{A6b}$$

The χ dependence of this transform is the same as that of equation (24a) and we write

$$\int \exp(i\boldsymbol{\chi} \cdot \mathbf{v})\,\Phi(t,v)\,\mathrm{d}v = \exp\{(i\omega_\beta - \tau^{-1})t\}\exp\left(-\frac{\chi^2}{4\kappa_1} - \frac{\boldsymbol{\chi} \cdot \mathbf{k}\,J(t)}{2\kappa_1} - \frac{k^2\,K(t)}{2\kappa_1}\right). \tag{A7}$$

The χ^2 term is easily checked from the $t = 0$ case as it is the Fourier transform of the Maxwellian distribution. The $\boldsymbol{\chi} \cdot \mathbf{k}$ term is only first order in k and so is obtainable by direct integration of equation (24a). The k^2 term of equation (A7) is not adequately given by equation (24a) alone but this is overcome by using the general constraint (A5). Combining equations (A6) and (A7) with equation (A5) we find that $J(t)$ and $K(t)$ are interrelated by

$$\mathrm{d}K(t)/\mathrm{d}t = J(t), \qquad t \geqslant 0,$$

and thus

$$K(t) = \int_0^t \frac{1 - \exp(-\eta t')}{\eta}\,\mathrm{d}t' = \frac{\eta t - 1 + \exp(-\eta t)}{\eta^2}. \tag{A8}$$

From this result the corrected version of equation (24a) is

$$\Phi(t,v) = f_1(v)\exp\{(i\omega_\beta - \tau^{-1})t\}\exp\{i\mathbf{k} \cdot \mathbf{v}\,J(t) - (k^2/4\kappa_1)L(t)\}, \tag{A9}$$

where

$$L(t) = 2K(t) - J^2(t) = \{2\eta t - 3 + 4\exp(-\eta t) - \exp(-2\eta t)\}/\eta^2. \tag{A10}$$

The above analysis shows that the expression (A10) for $L(t)$ is automatically fixed by the relaxation time approximation for $J(t)$, which can be proposed independently of any weak collision assumptions as used in the original Brownian-motion model. One can obtain $L(t)$ also by the moment technique. The inclusion of $L(t)$ in $\Phi(t, v)$ means that the LHS of equation (26) gets an extra term proportional to $f_1(v) k^2 \, dL(t)/dt$. This is second order in k and can be equated to the $k^2 J^2(t)$ term on the RHS of equation (26). Integrating both sides over all v (effectively taking the zeroth moment) gives

$$\frac{dL(t)}{dt} = (2\kappa_1/k^2) \sum_{j=1}^{2} \iint N_{1j}(v', v) \, f_1(v') \{k \cdot (v' - v)\}^2 \, dv' \, dv \, J^2(t). \qquad \text{(A11)}$$

From equation (A10) we find

$$\frac{dL(t)}{dt} = 2\frac{dK(t)}{dt} - 2J(t)\frac{dJ(t)}{dt} = -2J(t)\left(\frac{dJ(t)}{dt} - 1\right) = 2\eta \, J^2(t). \qquad \text{(A12)}$$

Equation (A12) is equivalent to (A11) provided that η is given by

$$\eta = (\kappa_1/k^2) \sum_{j=1}^{2} \iint N_{1j}(v', v) \, f_1(v') \{k \cdot (v' - v)\}^2 \, dv' \, dv. \qquad \text{(A13)}$$

This expression for η is the same as that given by equation (27) if

$$\sum_{j=1}^{2} \iint k \cdot (v - v') \, k \cdot v' \, N_{1j}(v', v) \, f_1(v') \, dv' \, dv$$

$$= - \sum_{j=1}^{2} \iint k \cdot (v - v') k \cdot v \, N_{1j}(v', v) \, f_1(v) \, dv' \, dv. \qquad \text{(A14)}$$

The $(k \cdot v')^2$ term on the LHS of equation (A14) is zero by

$$\int N_{1j}(v', v) \, dv = 0 \qquad \text{(A15a)}$$

and the $(k \cdot v)^2$ term on the RHS would be zero if it were possible to write the memory-weighted equilibrium condition

$$\int N_{1j}(v', v) \, f_1(v') \, dv' = 0. \qquad \text{(A15b)}$$

Equations (A15) guarantee the equality (A14). Equation (A15b) is not generally true. It holds in special cases, for instance, if in combination with the detailed balancing condition it happens that (consider $G \rightarrow M_{1j} F_1 f_1$ in equation 9)

$$M_{1j}(\xi, b, \Lambda, \Gamma, w) = M_{1j}(\xi'_{1j}, b'_{1j}, \Lambda'_{1j}, \Gamma'_{1j}, w'_{1j}), \qquad \beta'_{1j} = \beta.$$

It will be noticed that the LHS of equation (A15b) is the quantity that gives the velocity-smearing effect on the distribution of speed-dependent relaxation rates in equation (25). Because a single relaxation rate approximation is being used in the present theory then it is perfectly consistent to consider that equation (A15b) applies.