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CORRELATION EFFECTS IN THE THEORY OF COMBINED DOPPLER AND PRESSURE BROADENING—I. CLASSICAL THEORY*

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Abstract—A classical Fourier amplitude theory of combined Doppler and pressure broadening in the impact approximation is developed which treats phase changes due to translation and collision on an equal basis. Radiator motion is accounted for properly by including speed dependence in the collision frequency and velocity dependence in the distribution function for phase shifts and final velocities as the result of a collision. The resulting theory is shown to be equivalent to a previous kinetic equation formulation of the problem. The one-perturber and classical analogue of the quantum one-interacting-level approximations are derived. In the latter case, a simple expression for the line shape in terms of speed dependent width and shift functions is obtained without approximation. Correlation effects are investigated by means of model speed dependent width and shift functions calculated for an inverse power interaction using straight line trajectories. The model shows no departure from a Voigt profile for the r^{-3} interaction and for the r^{-6} and r^{-12} interactions the resulting profile is narrower in the core than the Voigt and in general asymmetric. Analysis of correlated profiles as Voigt profiles is shown under some conditions to lead to non-linear density dependence in the width and shifts resulting in extrapolation anomalies and to significant errors in temperatures inferred from Doppler widths. Results are compared with previous work.

1. INTRODUCTION

FUNDAMENTAL to an understanding of spectral line shapes is the problem of combining the effects of various phenomena that influence the line profile. The present work is concerned primarily with the combined influence of radiator–perturber collisions and radiator translational motion[1–10] in the context of foreign gas broadening of optical transitions in neutral radiators.

As is well known the translational motion of a radiator produces frequency shifts due to the Doppler effect and we may quasi-classically describe collisions as producing phase changes in the emitted radiation. Traditionally, one has assumed that these broadening mechanisms are statistically independent so that the line profile is described by a convolution integral (GRIEM,[11] p. 101),

$$I(\omega) = \int_{-\infty}^{\infty} I_D(\omega')I_P(\omega-\omega')\,\mathrm{d}\omega', \tag{1.1}$$

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where $I_D(\omega)$ and $I_P(\omega)$ are pure Doppler and pure pressure broadening profiles respectively and ω is the angular frequency measured from the unperturbed frequency. Most calculations have treated the Doppler effect in the approximation that collisions do not alter the radiator trajectory in which case $I_D(\omega)$ is Gaussian:

$$I_D(\omega) = \frac{1}{\sqrt{\pi}\,\omega_D} e^{-(\omega/\omega_D)^2}, \tag{1.2}$$

$$\omega_D = \kappa\tilde{v}_M = \frac{\omega_0}{c}\left(\frac{2kT}{M}\right)^{1/2}. \tag{1.3}$$

Here ω_0 is the unperturbed atomic transition frequency of interest for radiators of mass M at temperature T, $\boldsymbol{\kappa}$ is the propagation vector of the emitted radiation and $\tilde{v}_M$ is the most probable radiator speed. Pressure broadening theories for which the isolated line and impact approximations are appropriate[12,13] lead to Lorentzian profiles characterized by width Γ ($2\Gamma = FWHM$) and shift Δ:

$$I_P(\omega) = \frac{1}{\pi}\frac{\Gamma}{(\omega-\Delta)^2+\Gamma^2}. \tag{1.4}$$

When Gaussian and Lorentzian profiles are used in (1.1), $I(\omega)$ is referred to as a Voigt profile.

Two decades ago, DICKE[30] pointed out that collisions could lead to narrowing and a change in character of the Doppler profile from Gaussian to Lorentzian but with significant effects only when the mean free path between collisions is small compared to the wavelength of the emitted radiation. In an extension of Dicke's work, GALATRY[14] treated a radiator undergoing collisions as a particle in Brownian motion but assumed statistical independence in the treatment of combined Doppler and pressure broadening. Theories incorporating a simple type of statistical dependence first appeared in the work of RAUTIAN and SOBEL'MAN[15] and GERSTEN and FOLEY.[16] Independently,both groups of authors developed what we call the "correlated strong collision model" which assumes that the post-collision distribution of radiator velocities is always Maxwellian (strong collision model) and that phase shifts and velocity changes are uncorrelated except that both occur in the *same* collision. Gersten and Foley used a conventional line broadening argument (which we generalize) adapted specifically to the correlated strong collision model whereas Rautian and Sobel'man developed a general kinetic equation formalism of combined Doppler and pressure broadening and derived the model as a special case. All authors have worked in the context of classical Fourier amplitude (CFA) theory which obtains the line profile from a Fourier analysis of the emitted (classical) radiation. In the absence of a more fundamental theory of correlation effects, MIZUSHIMA[17,18] and EDMONDS[19] have introduced *ad hoc* modifications in the Voigt profile. Essentially they assume that the width parameter of the Voigt profile may depend on radiator speed and then attempt a calculation of this dependence.

In general, correlation effects appear to enter the problem in three ways that stem from one basic fact: the velocity distribution important for collision processes is the distribution of perturber velocities *relative* to the radiator. For a moving radiator, the perturber gas appears to be streaming past it with mean velocity opposite that of the radiator resulting in a relative perturber velocity distribution which depends on radiator velocity. Consequently, the collision frequency, the distribution of phase shifts in a collision and the distribution of radiator velocity *changes* in a collision all depend on radiator speed or velocity.

In a series of papers we formulate a general CFA theory of combined Doppler and pressure broadening, establish its validity conditions and investigate departures from Voigt behavior produced by correlation effects. In this paper the general theory is developed in the impact approximation using methods familiar in line broadening theory. Phase changes in the emitted radiation due to translational motion are treated on an equal basis with phase shifts due to collisions and the velocity dependence of the collision frequency and the distribution function for phase and velocity changes is taken into account. After showing that the resulting theory is exactly equivalent to the kinetic equation formalism of Rautian and Sobel'man, two useful approximations are developed: the one-perturber approximation and the CFA analogue of the quantum mechanical one interacting level (OIL) approximation (also called the "no lower state interaction" approximation). We conclude by exhibiting the effects of correlation on representative line profiles calculated in the OIL approximation for simple inverse power law interaction potentials and compare our results to previous work.

This leaves unsettled the question of validity conditions. For *conventional* pressure broadening theory, BARANGER[20] has derived the classical theory as a limit of the isolated line, adiabatic, quantum impact theory and this result has been implicitly assumed in previous extensions of classical theory to the problem of combined Doppler and pressure broadening. With the advent of quantum theories of combined Doppler and pressure broadening in the work of SMITH *et al.*[21,22] (hereafter denoted SCCD) and BERMAN and LAMB[8,9] a proper treatment of validity conditions is now possible. This has already been done in part by SCCD who show that in the limit of radiator mass much greater than perturber mass the general theory goes over to the conventional theory to which Baranger's argument applies. However, for arbitrary perturber/radiator mass ratios the question of validity conditions requires a tedious derivation of the semi-classical limit of the quantum one-perturber approximation and is therefore deferred to a second paper. There we will show that for arbitrary perturber/radiator mass ratios the classical theory derived here is valid only for the case of *identical* radiator–perturber interaction in both radiating levels or the case of interaction in *only one level* (OIL case). Moreover, in the OIL case quantum theory indicates that JWKB scattering phase shifts should be used in place of the conventional classical phase shift (integral of the interaction potential along the scattering trajectory). The relationship between these phase shifts has been discussed by RECK[23] and will be further developed in the second paper of this series.

The OIL calculations presented in this paper use the conventional phase shift calculated along straight line trajectories and consequently serve as *model* calculations. However, in comparison with conventional results calculated under the same assumptions, we believe the model accurately reflects the nature and magnitude of correlation effects that may be expected in optical transitions for which the OIL approximation is appropriate.

2. SPEED DEPENDENT COLLISION FREQUENCY

Careful velocity averaging plays a distinctive role in the treatment of combined Doppler and pressure broadening and accordingly we begin with a brief review. Consider a system of radiators (mass M) and perturbers (mass m) described by Maxwellian velocity distributions $f_M(\mathbf{v})$ and $f_m(\mathbf{v})$ where for example

$$f_M(\mathbf{v}) = \left(\frac{M}{2\pi kT}\right)^{3/2} e^{-Mv^2/2kT} \tag{2.1}$$

Then the average value of any velocity dependent properly $A(\mathbf{v})$ of an *isolated* radiator is given by

$$\bar{A} = \int A(\mathbf{v}) f_M(\mathbf{v})\, \mathrm{d}^3 v. \tag{2.2}$$

A more interesting situation occurs when we consider properties depending on the *relative* velocity $\mathbf{v}_R$ of two *interacting* particles as for example a scattering or reaction cross section. Let $B(\mathbf{v}_R)$ be such a property for an interacting radiator–perturber system and neglect collisions between radiators. Then two types of average B properties may be considered: the average resulting from those collisions in which the radiator always enters with velocity $\mathbf{v}$ which we denote by $\bar{B}_{\mathrm{I}}(\mathbf{v})$ and the average resulting from all possible radiator–perturber collisions which we denote by $\bar{B}_{\mathrm{II}}$. To perform these averages we introduce the relative collision frequency $\nu_c(\mathbf{v}_R\,;\mathbf{v})$ defined so that $\nu_c(\mathbf{v}_R\,;\ \mathbf{v})\,\mathrm{d}^3 v_R$ is the frequency of collisions with perturbers which have a velocity $\mathbf{v}_R$ to $\mathbf{v}_R + \mathrm{d}^3 v_R$ relative to a radiator with velocity $\mathbf{v}$. Then the collision frequency for a radiator with velocity $\mathbf{v}$ is given by

$$\nu_c(\mathbf{v}) = \int \nu_c(\mathbf{v}_R\,;\mathbf{v})\, \mathrm{d}^3 v_R \tag{2.3}$$

and the mean collision frequency for a radiator is

$$\nu_c = \int \nu_c(\mathbf{v}) f_M(\mathbf{v})\, \mathrm{d}^3 v. \tag{2.4}$$

In terms of these collision frequencies, we may express our averages as

$$\bar{B}_{\mathrm{I}}(\mathbf{v}) = \frac{1}{\nu_c(\mathbf{v})} \int \nu_c(\mathbf{v}_R\,;\mathbf{v}) B(\mathbf{v}_R)\, \mathrm{d}^3 v_R, \tag{2.5}$$

$$\bar{B}_{\mathrm{II}} = \frac{1}{\nu_c} \int \nu_c(\mathbf{v}) f_M(\mathbf{v}) \bar{B}_{\mathrm{I}}(\mathbf{v})\, d^3 v. \tag{2.6}$$

In obtaining $\bar{B}_{\mathrm{II}}$ one requires the probability that a radiator has velocity $\mathbf{v}$ to $\mathbf{v} + \mathrm{d}^3 v$ *in a collision* which is $[\nu_c(\mathbf{v})/\nu_c] f_M(\mathbf{v})\, \mathrm{d}^3 v$.

Our discussion so far rests on the assumption that a collision is a well defined event which is unfortunately not generally the case. To circumvent this difficulty we introduce a collision sphere(24,25) of radius R about the radiator and define collision frequencies in terms of those encounters with distance of closest approach less than or equal to R. To calculate $\nu_c(\mathbf{v}_R\,;\mathbf{v})$ consider the number of collisions $\Delta N(\mathbf{v}_R\,;\ \mathbf{v})\,\mathrm{d}^3 v_R$ in time Δt with relative velocity $\mathbf{v}_R$ to $\mathbf{v}_R + \mathrm{d}^3\mathbf{v}_R$ which is given by the perturber density times the volume of perturber gas colliding with the radiator in time Δt at speed v_R times the probability of a perturber having relative velocity $\mathbf{v}_R$ to $\mathbf{v}_R + \mathrm{d}^3\mathbf{v}_R$. Since the radiator is moving with velocity $\mathbf{v}$ the appropriate relative velocity distribution for the perturber gas is a displaced Maxwellian, $f_m(\mathbf{v} + \mathbf{v}_R)$. Thus

$$\Delta N(\mathbf{v}_R\,;\mathbf{v})\, \mathrm{d}^3 v_R = n\pi R^2 v_R \Delta t f_m(\mathbf{v} + \mathbf{v}_R)\, \mathrm{d}^3 v_R$$

where n is the perturber density. Dividing by Δt and passing to the limit $\Delta t \to 0$ gives the relative collision frequency $\nu_c(\mathbf{v}_R\,;\mathbf{v})$. By expressing all collision frequencies in terms of the mean collision frequency we can delete explicit reference to R from our formalism. Carrying out the indicated integrations in (2.3) and (2.4) gives

$$\nu_c(\mathbf{v}_R\,;\,\mathbf{v}) = \nu_c f_m(\mathbf{v} + \mathbf{v}_R)v_R/\bar{v}_R, \tag{2.7}$$

$$\nu_c(v) = \nu_c\,\omega_c(v/\tilde{v}_M\,;\,m/M), \tag{2.8}$$

$$\nu_c = n\pi R^2\bar{v}_R, \tag{2.9}$$

where $\bar{v}_R = (8kT/\pi\mu)^{1/2}$ is the mean relative speed, $\tilde{v}_M = (2kT/M)^{1/2}$ is the most probable radiator speed and

$$\omega_c(x;\,\lambda) = (1+\lambda)^{-1/2}\left[\frac{\sqrt{\pi}}{4}\frac{1}{\sqrt{\lambda}x}(1+2\lambda x^2)\Phi(\sqrt{\lambda}x) + \tfrac{1}{2}e^{-\lambda x^2}\right]. \tag{2.10}$$

Here $\Phi(z)$ is the error function (GRADSHTEYN and RYZHIK,[61] No. 8.250.1, p. 930)

$$\Phi(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-t^2}\,\mathrm{d}t \tag{2.11}$$

and we have introduced the reduced mass $\mu = mM/(m+M)$. As expected, $\nu_c(v)$ depends only on radiator *speed* and we have adjusted our notation accordingly. Notice that $\omega_c(x;\,\lambda)$ is simply a dimensionless collision frequency with radiator speed x expressed in units of the most probable radiator speed $\tilde{v}_M$. Using (2.5) and (2.7) in (2.6) and introducing the reduced mass Maxwell distribution gives

$$\bar{B}_{\mathrm{II}} = \frac{1}{\bar{v}_R}\int v_R f_\mu(\mathbf{v}_R)B(\mathbf{v}_R)\,\mathrm{d}^3v_R \tag{2.12}$$

which is the familiar velocity average in line broadening theory.

3. GENERAL THEORY

A. *The correlation function*

We adopt the usual classical model (BORN and WOLF,[26] pp. 90–98; ROSSI,[27] pp. 348–366) in which the radiator is treated as an oscillating dipole with unperturbed frequency ω_0. The Fourier analysis of the radiation emitted by an ensemble of such oscillators leads to an expression for the line shape in terms of a correlation function.[1,4,14–16,28–31]

In previous treatments of combined Doppler and pressure broadening we note that some authors (GERSTEN and FOLEY;[16] BEN-REUVEN[31]) have assumed that a moving dipole oscillates at its Doppler shifted frequency. Another point of view assumes that a moving dipole oscillates at its unperturbed frequency and to lowest order in v/c the Doppler shift is then a retardation effect brought about by the finite speed of light. However, a careful treatment[32] of retardation effects in the correlation function leads in the nonrelativistic limit to the usual results:

$$I(\omega) = \frac{1}{\pi}\,Re\int_0^\infty c(s)e^{i\omega s}\,\mathrm{d}s, \tag{3.1}$$

$$c(s) = \langle e^{-i\zeta(s)}\rangle, \tag{3.2}$$

$$\zeta(s) = \eta(s) + \boldsymbol{\kappa}\cdot[\mathbf{R}(s) - \mathbf{R}(0)], \tag{3.3}$$

$$c(-s) = c^*(s). \tag{3.4}$$

Here $I(\omega)$ is the line profile normalized to unity, ω is measured from the unperturbed frequency, $c(s)$ is the correlation function and $\langle\cdots\rangle$ denotes an ensemble average over the perturbers. The total phase shift in time s, $\zeta(s)$, is the sum of the phase shift due to collisions, $\eta(s)$, and the phase shift due to translational motion given by $\boldsymbol{\kappa}\cdot[\mathbf{R}(s)-\mathbf{R}(0)]$ where $\boldsymbol{\kappa}$ is the propagation vector of the emitted radiation and $\mathbf{R}(s)$ is the position vector of the oscillator. As is customary, we have made the adiabatic approximation by taking constant amplitudes for each oscillator (COOPER,[13] p. 246) and have excluded the so-called "negative resonance" or VAN VLECK–WEISSKOPF term[29] (negligible for optical transitions) by requiring $c(-s) = c^*(s)$.

B. The ensemble average

The average over the phase shifts and velocity changes produced by collisions is performed as a Poisson process. The collisions are regarded as instantaneous events randomly distributed in time with frequency $\nu_c(v)$ where v is the speed of the radiator. The probability of free propagation at speed v for a time interval t followed by a collision between t and $t+\mathrm{d}t$ is given by

$$P_c(v, t)\,\mathrm{d}t = \nu_c(v)\exp[-\nu_c(v)t]\,\mathrm{d}t \tag{3.5}$$

where $\exp[-\nu_c(v)t]$ is the probability that no collision occurs during an interval t. The phase shift in the classical oscillator induced by the jth collision will be denoted by ϕ_j, the radiator velocity after the jth collision will be $\mathbf{v}_j$ and the time interval following the jth collision will be Δ_j. The total phase shift in the emitted radiation due to a sequence of n collisions in time s is therefore given by

$$\zeta(s;\phi_1,\ldots\phi_n,\mathbf{v}_0,\ldots\mathbf{v}_n) = \boldsymbol{\kappa}\cdot\mathbf{v}_0\Delta_0 + \sum_{j=1}^{n}(\phi_j + \boldsymbol{\kappa}\cdot\mathbf{v}_j\Delta_j), \tag{3.6}$$

$$s = \sum_{j=0}^{n}\Delta_j \tag{3.7}$$

where $\mathbf{v}_0$ is the initial radiator velocity. The probability that the jth collision induces the phase change ϕ_j and a velocity change from $\mathbf{v}_{j-1}$ to $\mathbf{v}_j$ is denoted by $G(\phi_j, \mathbf{v}_j; \mathbf{v}_{j-1})\,\mathrm{d}\phi_j\,\mathrm{d}^3v_j$.

The probability that a phase change ζ in the emitted radiation will occur in an interval of time s due to a sequence of n collisions may now be given by $P_n(\zeta, s)\,\mathrm{d}\zeta$ where

$$\begin{aligned} P_n(\zeta, s) = &\int\cdots\int \mathrm{d}^3v_0\cdots\mathrm{d}^3v_n \int\cdots\int \mathrm{d}\phi_1\cdots\mathrm{d}\phi_n \int_0^\infty\cdots\int_0^\infty \mathrm{d}\Delta_0\cdots\mathrm{d}\Delta_n \\ &\times\delta\Big(s-\sum_{j=0}^{n}\Delta_j\Big)\delta\Big[\zeta-\boldsymbol{\kappa}\cdot\mathbf{v}_0\Delta_0-\sum_{j=1}^{n}(\phi_j+\boldsymbol{\kappa}\cdot\mathbf{v}_j\Delta_j)\Big] \\ &\times\exp[-\nu_c(v_n)\Delta_n]\Big[\prod_{j=0}^{n-1}P_c(v_j,\Delta_j)G(\phi_{j+1},\mathbf{v}_{j+1};\mathbf{v}_j)\Big]f_M(\mathbf{v}_0). \end{aligned} \tag{3.8}$$

Notice that the probability function for the time interval Δ_n following the nth collision is given by $\exp[-\nu_c(v_n)\Delta_n]$ rather than $P_c(v_n, \Delta_n)$ because this interval is not terminated by a collision. The probability for a phase change ζ due to all possible collision processes in time interval s is then given by

$$P(\zeta, s) = \sum_{n=0}^{\infty}P_n(\zeta, s) \tag{3.9}$$

$$P_0(\zeta, s) = \int d^3v_0 \int_0^\infty d\Delta_0\, \delta(s - \Delta_0)\delta(\zeta - \boldsymbol{\kappa} \cdot \mathbf{v}_0\, \Delta_0)\exp[-\nu_c(v_0)\Delta_0] f_M(\mathbf{v}_0). \tag{3.10}$$

The correlation function (3.2) is now

$$c(s) = \int e^{-i\zeta} P(\zeta, s)\, d\zeta \tag{3.11}$$

$$= \int d^3v_0\, f_M(\mathbf{v}_0)\exp\{-[\nu_c(v_0) + i\boldsymbol{\kappa} \cdot \mathbf{v}_0]s\}$$

$$\times \left[1 + \sum_{n=1}^{\infty} \frac{1}{n!} \int d\phi_1 \int d^3v_1 \int_0^s d\Delta_1\, \nu_c(v_0) G(\phi_1, \mathbf{v}_1; \mathbf{v}_0)\exp(-i\phi_1)\right.$$

$$\times \exp\{-[\nu_c(v_1) - \nu_c(v_0) + i\boldsymbol{\kappa} \cdot (\mathbf{v}_1 - \mathbf{v}_0)]\Delta_1\} \times \cdots \times \int d\phi_n \int d^3v_n \int_0^s d\Delta_n \nu_c(v_{n-1})$$

$$\left. \times\, G(\phi_n, \mathbf{v}_n; \mathbf{v}_{n-1})\exp(-i\phi_n)\exp\{-[\nu_c(v_n) - \nu_c(v_0) + i\boldsymbol{\kappa} \cdot (\mathbf{v}_n - \mathbf{v}_0)]\Delta_n\}\right] \tag{3.12}$$

where we have performed the Δ_0-integration using

$$\int_0^\infty \cdots \int_0^\infty d\Delta_0 \cdots d\Delta_n\, \delta\left(s - \sum_{j=0}^n \Delta_j\right) \prod_{j=0}^n \exp\{-[\nu_c(v_j) + i\boldsymbol{\kappa} \cdot \mathbf{v}_j]\Delta_j\}$$

$$= \exp\{-[\nu_c(v_0) + i\boldsymbol{\kappa} \cdot \mathbf{v}_0]s\} \frac{1}{n!} \int_0^s \cdots \int_0^s d\Delta_1 \cdots d\Delta_n$$

$$\times \prod_{j=1}^n \exp\{-[\nu_c(v_j) - \nu_c(v_0) + i\boldsymbol{\kappa} \cdot (\mathbf{v}_j - \mathbf{v}_0)]\Delta_j\} \tag{3.13}$$

which expresses the fact that the δ-function constrains the $\Delta_0 \cdots \Delta_n$ integrations to an n-dimensional shell in $(n + 1)$-dimensional space. The remaining $\Delta_0 \cdots \Delta_n$ integrations are trivial but not helpful and consequently we regard (3.12) as a formal solution to the problem.

The only way in which our treatment of the ensemble average differs from that given by GERSTEN and FOLEY[16] is in the use of a speed dependent collision frequency and a general distribution function for the phase shifts and velocity changes in a collision. In place of $G(\phi, \mathbf{v}; \mathbf{v}_0)$ Gersten and Foley use $g(\phi) f_M(\mathbf{v})$ where $g(\phi)$ is the phase shift distribution from conventional pressure broadening theory; the only correlation in such a theory stems from the fact that phase and velocity changes occur in the same collision. By using $G(\phi, \mathbf{v}; \mathbf{v}_0)$ we allow for correlation between phase and velocity changes in a collision and the dependence of the distribution function on radiator velocity.

C. *Properties of* $G(\phi, \mathbf{v}; \mathbf{v}_0)$

To evaluate the G-function we assume elastic scattering by a potential for which there exists a unique relation between impact parameter and scattering angle. In the Appendix we show that

$$G(\phi, \mathbf{v}; \mathbf{v}_0) = \frac{4n}{\nu_c(v_0) w^2} \int d^3v_R\, v_R\, f_m(\mathbf{v}_0 + \mathbf{v}_R) \hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}} \sigma(\Theta, v_R)$$

$$\times\, \delta\left(w - \frac{2\mu}{M} \mathbf{v}_R \cdot \hat{\mathbf{w}}\right) \delta[\phi - \phi(\Theta, v_R)], \tag{3.14}$$

$$\mathbf{w} = \mathbf{v} - \mathbf{v}_0, \tag{3.15}$$

$$\Theta = \pi - 2\cos^{-1}\hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}}, \tag{3.16}$$

$$\phi(\Theta, v_R) = \phi[\rho(\hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}}, v_R), v_R]. \tag{3.17}$$

The integration variable $\mathbf{v}_R$ is the velocity of the perturber *relative* to the initial radiator velocity $\mathbf{v}_0$, $\mathbf{w}$ is the velocity change vector, $\sigma(\Theta, v_R)$ is the center of mass differential scattering cross section, $\phi(\rho, v_R)$ is the phase shift in a collision with impact parameter ρ, $\rho(\hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}}, v_R)$ is the impact parameter as a function of scattering angle and relative speed as determined by classical mechanics, n is the perturber density, μ is the reduced mass and ^ denotes unit vector.

One may verify that $G(\phi, \mathbf{v}; \mathbf{v}_0)$ is correctly normalized to unity and that in the limit of scattering only in the forward direction

$$G(\phi, \mathbf{v}; \mathbf{v}_0) \to \delta(\mathbf{v} - \mathbf{v}_0)g(\phi; v_0) \tag{3.18}$$

where

$$\begin{aligned} g(\phi; v_0) &= \int G(\phi, \mathbf{v}; \mathbf{v}_0)\, \mathrm{d}^3 v \\ &= \frac{2\pi n}{\nu_c(v_0)} \int_0^\infty \mathrm{d}\rho\rho \int \mathrm{d}^3 v_R\, v_R\, f_m(\mathbf{v}_0 + \mathbf{v}_R)\delta[\phi - \phi(\rho, v_R)]. \end{aligned} \tag{3.19}$$

The interpretation of $g(\phi; v_0)$ is that it gives the distribution of phase shifts in a collision irrespective of the velocity change and as the notation indicates, it depends only on radiator speed. Using (2.6) we obtain the distribution of phase shifts in a collision averaged over all possible collisions

$$\begin{aligned} g(\phi) &= \frac{1}{\nu_c} \int \nu_c(v_0) f_M(\mathbf{v}_0) g(\phi; v_0)\, \mathrm{d}^3 v_0 \\ &= \frac{2\pi n}{\nu_c} \int_0^\infty \mathrm{d}\rho\rho \int \mathrm{d}^3 v_R\, v_R\, f_\mu(\mathbf{v}_R)\delta[\phi - \phi(\rho, v_R)] \end{aligned} \tag{3.20}$$

which is recognized as the phase shift distribution function of conventional CFA pressure broadening theory.

Finally, we note two symmetry relations: time reversal invariance

$$G(\phi, -\mathbf{v}; -\mathbf{v}_0) = G(\phi, \mathbf{v}; \mathbf{v}_0) \tag{3.21}$$

and detailed balance

$$\nu_c(v_0) f_M(\mathbf{v}_0) G(\phi, \mathbf{v}; \mathbf{v}_0) = \nu_c(v) f_M(\mathbf{v}) G(\phi, \mathbf{v}_0; \mathbf{v}). \tag{3.22}$$

The interpretation is that the frequency of collisions making phase change ϕ and velocity change $\mathbf{v}_0 \to \mathbf{v}$ is equal to the frequency of collisions making the same phase shift and the velocity change $\mathbf{v} \to \mathbf{v}_0$.

D. Kinetic equation formalism

The first task in deriving a kinetic equation is to express our theory in terms of the probability per unit time per particle (=transition rate per particle) for the process of interest This is just the collision frequency times the probability in a collision for the process of interest. Consequently the transition rate per radiator for a phase change ϕ and a velocity change $\mathbf{v}_0 \to \mathbf{v}$ is

$$A(\phi, \mathbf{v}; \mathbf{v}_0) = \nu_c(v_0) G(\phi, \mathbf{v}; \mathbf{v}_0). \tag{3.23}$$

Next we define the distribution function $f(\mathbf{r}, \mathbf{v}, t)$ for $t \geq 0$ as follows:

$$
\begin{aligned}
f(\mathbf{r}, \mathbf{v}, t) = \frac{1}{(2\pi)^4} \int \mathrm{d}^3 k \int_{-\infty}^{\infty} \mathrm{d}\omega e^{-i(\omega t - \boldsymbol{\kappa} \cdot \mathbf{r})} \frac{f_M(\mathbf{v})}{\nu_c(v) - i(\omega - \boldsymbol{\kappa} \cdot \mathbf{v})} \\
\times \left[1 + \sum_{n=1}^{\infty} \int \mathrm{d}\phi_1 \int \mathrm{d}^3 v_1 \frac{\exp(-i\phi_1) A(\phi_1, \mathbf{v}_1; \mathbf{v})}{\nu_c(v_1) - i(\omega - \boldsymbol{\kappa} \cdot \mathbf{v}_1)} \right. \\
\left. \times \cdots \times \int \mathrm{d}\phi_n \int \mathrm{d}^3 v_n \frac{\exp(-i\phi_n) A(\phi_n, \mathbf{v}_n; \mathbf{v}_{n-1})}{\nu_c(v_n) - i(\omega - \boldsymbol{\kappa} \cdot \mathbf{v}_n)} \right].
\end{aligned}
\tag{3.24}
$$

The interpretation of $f(\mathbf{r}, \mathbf{v}, t)$ rests on establishing the connection between our work and that of Rautian and Sobel'man. Then it follows that $f(\mathbf{r}, \mathbf{v}, t)$ gives the distribution of positions and velocities at time t for a radiator initially at the origin with a Maxwellian velocity distribution. One may verify that $f(\mathbf{r}, \mathbf{v}, t)$ satisfies the correct initial condition

$$
f(\mathbf{r}, \mathbf{v}, 0) = f_M(\mathbf{v}) \delta(\mathbf{r}) \tag{3.25}
$$

and that the correlation function may be expressed as

$$
c(s) = \int \mathrm{d}^3 v \int \mathrm{d}^3 r e^{-i\boldsymbol{\kappa} \cdot \mathbf{r}} f(\mathbf{r}, \mathbf{v}, s). \tag{3.26}
$$

Now we consider the equation that $f(\mathbf{r}, \mathbf{v}, t)$ satisfies. In view of the divergent initial condition we may not differentiate (3.24) under the integral sign at $t = 0$ so we limit ourselves to $t > 0$. Then one obtains

$$
\begin{aligned}
\left[\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right] f(\mathbf{r}, \mathbf{v}, t) = -\nu_c(v) f(\mathbf{r}, \mathbf{v}, t) \\
+ \frac{1}{(2\pi)^4} \int \mathrm{d}^3 \kappa \int_{-\infty}^{\infty} \mathrm{d}\omega [\nu_c(v) - i(\omega - \boldsymbol{\kappa} \cdot \mathbf{v})] e^{-i(\omega t - \boldsymbol{\kappa} \cdot \mathbf{r})} \frac{f_M(\mathbf{v})}{\nu_c(v) - i(\omega - \boldsymbol{\kappa} \cdot \mathbf{v})} \\
\times \sum_{n=1}^{\infty} \int \mathrm{d}\phi_1 \int \mathrm{d}^3 v_1 \frac{\exp(-i\phi_1) A(\phi_1, \mathbf{v}_1; \mathbf{v})}{\nu_c(v_1) - i(\omega - \boldsymbol{\kappa} \cdot \mathbf{v}_1)} \times \cdots \times \int \mathrm{d}\phi_n \int \mathrm{d}^3 v_n \\
\times \frac{\exp(-i\phi_n) A(\phi_n, \mathbf{v}_n; \mathbf{v}_{n-1})}{\nu_c(v_n) - i(\omega - \boldsymbol{\kappa} \cdot \mathbf{v}_n)}.
\end{aligned}
\tag{3.27}
$$

where we have added and subtracted a $\nu_c(v) f(\mathbf{r}, \mathbf{v}, t)$ term on the right-hand side. The Maxwell distribution $f_M(\mathbf{v})$ can be brought under the $\mathbf{v}_1$-integral and use made of the detailed balance relation (3.22) to obtain

$$
\begin{aligned}
\left[\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right] f(\mathbf{r}, \mathbf{v}, t) = -\nu_c(v) f(\mathbf{r}, \mathbf{v}, t) \\
+ \frac{1}{(2\pi)^4} \int \mathrm{d}^3 \kappa \int_{-\infty}^{\infty} \mathrm{d}\omega e^{-i(\omega t - \boldsymbol{\kappa} \cdot \mathbf{r})} \int \mathrm{d}\phi_1 \int \mathrm{d}^3 v_1 \exp(-i\phi_1) \frac{f_M(\mathbf{v}_1) A(\phi_1, \mathbf{v}; \mathbf{v}_1)}{\nu_c(v_1) - i(\omega - \boldsymbol{\kappa} \cdot \mathbf{v}_1)} \\
\times \left[1 + \sum_{n=2}^{\infty} \int \mathrm{d}\phi_2 \int \mathrm{d}^3 v_2 \frac{\exp(-i\phi_2) A(\phi_2, \mathbf{v}_2; \mathbf{v}_1)}{\nu_c(v_2) - i(\omega - \boldsymbol{\kappa} \cdot \mathbf{v}_2)} \right. \\
\left. \times \cdots \times \int \mathrm{d}\phi_n \int \mathrm{d}^3 v_n \frac{\exp(-i\phi_n) A(\phi_n, \mathbf{v}_n; \mathbf{v}_{n-1})}{\nu_c(v_n) - i(\omega - \boldsymbol{\kappa} \cdot \mathbf{v}_n)} \right].
\end{aligned}
\tag{3.28}
$$

Next we relabel dummy integration variables:

$$\mathbf{v}_1 \to \mathbf{v}'$$
$$\phi_1 \to \phi$$
$$(\phi_n, \mathbf{v}_n) \to (\phi_{n-1}, \mathbf{v}_{n-1}) \qquad \text{for} \quad n = 2, 3 \cdots.$$

Then the orders of integration are interchanged and we obtain finally the desired equation for $f(\mathbf{r}, \mathbf{v}, t)$:

$$\left[\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla\right] f(\mathbf{r}, \mathbf{v}, t) = -\nu_c(v) f(\mathbf{r}, \mathbf{v}, t) + \int \mathrm{d}\phi \int \mathrm{d}^3 v' e^{-i\phi} A(\phi, \mathbf{v}, \mathbf{v}') f(\mathbf{r}, \mathbf{v}', t). \tag{3.29}$$

This result has the form of a kinetic equation and is in fact *exactly* equivalent to equations (5.5), (5.16) and (5.17) of Rautian and Sobel'man. Note that the $A(\mathbf{v}_0, \mathbf{v}, \phi)$of Rautian and Sobel'man which means exactly the same as the $A(\phi, \mathbf{v}; \mathbf{v}_0)$ of this work has the order of its velocity variables *opposite* to our convention. Similar results hold for related functions such as the $\tilde{A}$ of Rautian and Sobel'man equation (5.17). Also our distribution function, $f(\mathbf{r}, \mathbf{v}, t)$ corresponds to the $\tilde{f}(\mathbf{r}, \mathbf{v}, t)$ of Rautian and Sobel'man. Thus we have obtained their general kinetic equation formalism using a more conventional approach to the pressure broadening problem. Alternatively, one may regard our work as a formal solution to the Rautian and Sobel'man kinetic equation. Both points of view are constructive as each formalism suggests its own approximations. For example, the one-perturber approximation developed in Section 5 follows naturally from our formalism. Similarly, the GALATRY(14) and DICKE(30) results follow naturally from the Kinetic equation as developed by RAUTIAN and SOBEL'MAN.(15) We conclude this section by noting that Doppler and pressure broadening have been treated in a consistent fashion in a generalized CFA theory.

4. ELEMENTARY SOLUTION

The conventional Voigt profile may be obtained as an illustrative example of the formalism. We assume a constant mean collision frequency, unperturbed trajectories and the usual distribution of phase shifts (3.20):

$$\nu_c(v_0) \to \nu_c \tag{4.1a}$$

$$G(\phi, \mathbf{v}; \mathbf{v}_0) = g(\phi)\delta(\mathbf{v} - \mathbf{v}_0). \tag{4.1b}$$

With these assumptions in (3.12), the velocity integrals are trivial, the Δ-integrals all contribute an s factor and we obtain

$$\begin{aligned} c(s) &= \int \mathrm{d}^3 v_0 \, f_M(\mathbf{v}_0) \exp[-(\nu_c + i\boldsymbol{\kappa} \cdot \mathbf{v}_0)s] \sum_{n=0}^{\infty} \frac{1}{n!} \left(\nu_c s \int \mathrm{d}\phi g(\phi) e^{-i\phi}\right)^n \\ &= \exp\left[-\nu_c s \int \mathrm{d}\phi g(\phi)(1 - e^{-i\phi})\right] \int \mathrm{d}^3 v_0 \, f_M(\mathbf{v}_0) \exp[-i\boldsymbol{\kappa} \cdot \mathbf{v}_0 s] \\ &= \exp[-(\Gamma + i\Delta)s] \exp(-\omega_D{}^2 s^2/4) \end{aligned} \tag{4.2}$$

where we have used the normalization of $g(\phi)$ to unity and made the familiar definitions of width and shift:

$$\Gamma + i\Delta = \nu_c \int \mathrm{d}\phi g(\phi)(1 - e^{-i\phi}) \tag{4.3}$$

$$= 2\pi n \int_0^{\infty} \mathrm{d}\rho \rho \int \mathrm{d}^3 v_R \, v_R \, f_\mu(\mathbf{v}_R)\{1 - \exp[-i\phi(\rho, v_R)]\}. \tag{4.4}$$

The fact that the correlation function is a *product* of Doppler and pressure correlation functions means that the two broadening mechanisms are *statistically independent*. Use of (4.2) in (3.1) gives a Voigt profile

$$I_V(\omega) = \frac{\Gamma}{\pi^{3/2}\omega_D}\int_{-\infty}^{\infty}\frac{\exp[-(\omega'/\omega_D)^2]}{(\omega-\omega'-\Delta)^2+\Gamma^2}\,d\omega'. \tag{4.5}$$

5. ONE-PERTURBER APPROXIMATION

This approximation treats the correlation function under the condition that one collision occurs on the average during times of interest. One can show (BARANGER,[12] p. 530; COOPER[33]) that for any profile satisfying the conditions of the impact approximation there is a region in the wings for which the one-perturber approximation is valid. Mathematically we assume $v_c s \ll 1$ for times of interest s and expand the correlation function to first order in $v_c s$. The resulting line profile will be valid for $\omega \gg v_c$.

The correlation function has already been written as a sum of terms corresponding to the number of collisions in an interval of time. Retaining only the first two terms in (3.12) and expanding, we obtain

$$\begin{aligned} c(s) &= \int d^3v_0\, f_M(\mathbf{v}_0)\exp(-i\boldsymbol{\kappa}\cdot\mathbf{v}_0 s)[1 - v_c(v_0)s + \cdots] \\ &\quad\times\left[1 + \int d\phi\int d^3v\int_0^s d\Delta v_c(v_0)G(\phi,\mathbf{v};\mathbf{v}_0)\exp(-i\phi)\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{v}-\mathbf{v}_0)s] + \cdots\right] \\ &= \int d^3v_0\, f_M(\mathbf{v}_0)\exp(-i\boldsymbol{\kappa}\cdot\mathbf{v}_0 s) \\ &\quad\times\left[1 - v_c(v_0)s + \int d\phi\int d^3v\, v_c(v_0)G(\phi,\mathbf{v};\mathbf{v}_0)\exp(-i\phi)\frac{1-\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{v}-\mathbf{v}_0)s]}{i\boldsymbol{\kappa}\cdot(\mathbf{v}-\mathbf{v}_0)} + \cdots\right]. \end{aligned} \tag{5.1}$$

This is the one-perturber result which we can now write in a form that will prove convenient for later comparison with quantum theory. We define a function $\mathscr{F}$ by the expression

$$\frac{1-\exp[-i\boldsymbol{\kappa}\cdot(\mathbf{v}-\mathbf{v}_0)s]}{i\boldsymbol{\kappa}\cdot(\mathbf{v}-\mathbf{v}_0)s} = 1 + \mathscr{F}[\boldsymbol{\kappa}\cdot(\mathbf{v}-\mathbf{v}_0)s] \tag{5.2}$$

and use the normalization of $G(\phi, \mathbf{v}; \mathbf{v}_0)$, (3.14) and (3.19) to write

$$\begin{aligned} c(s) &= \int d^3v_0\, f_M(\mathbf{v}_0)\exp(-i\boldsymbol{\kappa}\cdot\mathbf{v}_0 s)\Big\{1 - v_c(v_0)s\int d\phi\, g(\phi; v_0)(1-e^{-i\phi}) \\ &\quad + v_c(v_0)s\int d\phi\int d^3v\, G(\phi,\mathbf{v};\mathbf{v}_0)e^{-i\phi}\mathscr{F}[\boldsymbol{\kappa}\cdot(\mathbf{v}-\mathbf{v}_0)s]\Big\} \end{aligned} \tag{5.3}$$

$$\begin{aligned} &= \int d^3v_0\, f_M(\mathbf{v}_0)\exp(-i\boldsymbol{\kappa}\cdot\mathbf{v}_0 s) \\ &\quad\times\Bigg[1 - 2\pi n s\int_0^{\infty} d\rho\rho\int d^3v_R\, v_R f_m(\mathbf{v}_0+\mathbf{v}_R)\{1-\exp[-i\phi(\rho, v_R)]\} \\ &\quad + 4ns\int d^3v\frac{1}{w^2}\int d^3v_R\, v_R f_m(\mathbf{v}_0+\mathbf{v}_R)\hat{\mathbf{v}}_R\cdot\hat{\mathbf{w}}\sigma(\Theta, v_R) \\ &\quad\times\exp[-i\phi(\Theta, v_R)]\mathscr{F}(\boldsymbol{\kappa}\cdot\mathbf{w}s)\delta\left(w - \frac{2\mu}{M}\mathbf{v}_R\cdot\hat{\mathbf{w}}\right)\Bigg]. \end{aligned} \tag{5.4}$$

Notice that the terms in these equations may be interpreted physically: the unit term in the square brackets is the collisionless Doppler term, the second term is a generalized pressure broadening term which contains some correlation effects because of its dependence on radiator speed and the third term contains additional correlation effects which cannot easily be separately identified as due to radiator motion or perturbations of phase. It is a distinctive feature of the one-perturber approximation that these various factors are additive.

6. ONE-INTERACTING-LEVEL (OIL) APPROXIMATION

As one may surmise from the name, the OIL approximation has its basis in a quantum mechanical treatment and from a purely classical point of view is difficult to interpret. In fact, a simple classical *interpretation* only appears possible when both upper and lower states scatter in the same direction.[8,9,21] At this point we simply assert that the classical analogue of the quantum OIL approximation is obtained by adopting the G-function

$$G(\phi, \mathbf{v}; \mathbf{v}_0) = g(\phi, v_0)\delta(\mathbf{v} - \mathbf{v}_0) \tag{6.1}$$

where $g(\phi, v_0)$ is given in (3.19). This will be justified in a future paper by comparison of (6.4) and (6.5) with the results of a fully quantum mechanical OIL theory[21] in the adiabatic semiclassical limit. Alternatively (6.1) may be substituted into (3.29) and the result compared with the appropriate limit of equation (17) given by BERMAN.[62] In retrospect we can argue that (6.1) may represent in a classical sense the fact that the quantum mechanical OIL approximation can be expressed entirely in terms of forward scattering amplitudes.[21] Still, the naive classical interpretation of (6.1) is that no scattering of the radiator takes place in a collision and this runs counter to the intuitive picture of how things should happen.

Using (6.1) in (3.12) leads to

$$\begin{aligned} c(s) &= \int d^3v_0\, f_M(\mathbf{v}_0)\exp\{-[\nu_c(v_0) + i\boldsymbol{\kappa}\cdot\mathbf{v}_0]s\} \\ &\quad\times \sum_{n=0}^{\infty}\frac{1}{n!}\left[\nu_c(v_0)s\int d\phi\, g(\phi; v_0)\exp(-i\phi)\right]^n \qquad (6.2) \\ &= \int d^3v_0\, f_M(\mathbf{v}_0)\exp(-i\boldsymbol{\kappa}\cdot\mathbf{v}_0 s) \\ &\quad\times \exp\left\{-\nu_c(v_0)s\int d\phi\, g(\phi; v_0)[1 - \exp(-i\phi)]\right\}, \qquad (6.3) \\ &= \int d^3v_0\, f_M(\mathbf{v}_0)\exp(-i\boldsymbol{\kappa}\cdot\mathbf{v}_0 s)\exp\{-[\Gamma(v_0) + i\Delta(v_0)]s\} \qquad (6.4) \end{aligned}$$

where we have used the normalization of $g(\phi; v_0)$ to unity and introduced speed dependent width and shift functions defined by

$$\Gamma(v_0) + i\Delta(v_0) = \nu_c(v_0)\int d\phi\, g(\phi; v_0)(1 - e^{-i\phi}). \tag{6.5}$$

The interpretation of these quantities as the width and shift for a radiator with speed v_0 is substantiated by the observation that the average of $\Gamma(v_0)$ and $\Delta(v_0)$ over all radiator velocities gives the width and shift functions of conventional theory: using (3.20) and (4.3) one easily shows that

$$\int d^3v_0\, f_M(\mathbf{v}_0)[\Gamma(v_0) + i\Delta(v_0)] = \Gamma + i\Delta. \tag{6.6}$$

In (6.4) we see that contributions to the correlation function from motional and pressure broadening do not enter in a statistically independent fashion.

The line shape which follows from (3.1) and (6.4) is given by

$$I_{\mathrm{OIL}}(\omega) = \frac{1}{\pi} \int \mathrm{d}^3 v_0 \, f_M(\mathbf{v}_0) \frac{\Gamma(v_0)}{[\omega - \Delta(v_0) - \boldsymbol{\kappa} \cdot \mathbf{v}_0]^2 + \Gamma^2(v_0)} \tag{6.7}$$

which may be interpreted as the Maxwell average of the velocity dependent Doppler shifted pressure broadened profile that would describe emission in the direction $\boldsymbol{\kappa}$ from an ensemble of radiators with velocity $\mathbf{v}_0$. This expression was obtained implicitly by SCCD [see equations (2.20), (3.1), (5.3), and (9.3) of Ref. (21)] and explicitly by BERMAN[34] [see equations (1a), (4a) and (4b)].

Performing the angular integrations in (6.7) and using the fact that $\Gamma(v_0)$ and $\Delta(v_0)$ are even functions as can be established from equations (6.5), (2.10) and (3.21) gives

$$I_{\mathrm{OIL}}(\omega) = \frac{2}{\pi^{3/2} \omega_D \tilde{v}_M{}^2} \int_{-\infty}^{\infty} \mathrm{d}v_0 \, v_0 \exp[-(v_0/\tilde{v}_M)^2] \arctan\left[\frac{\kappa v_0 - \omega + \Delta(v_0)}{\Gamma(v_0)}\right]. \tag{6.8}$$

Integrating by parts and defining $\omega' = \kappa v_0$ leads to a general expression for the line shape in the OIL approximation:

$$I_{\mathrm{OIL}}(\omega) = \frac{1}{\pi^{3/2}\omega_D} \int_{-\infty}^{\infty} \exp[-(\omega'/\omega_D)^2] \frac{\Gamma(\omega'/\kappa)}{[\omega - \Delta(\omega'/\kappa) - \omega']^2 + \Gamma^2(\omega'/\kappa)} W(\omega'; \omega) \, \mathrm{d}\omega' \tag{6.9}$$

$$W(\omega'; \omega) = 1 + \frac{\mathrm{d}}{\mathrm{d}\omega'} \Delta(\omega'/\kappa) + \frac{\omega - \Delta(\omega'/\kappa) - \omega'}{\Gamma(\omega'/\kappa)} \frac{\mathrm{d}}{\mathrm{d}\omega'} \Gamma(\omega'/\kappa). \tag{6.10}$$

Comparison with the Voigt profile in (4.5) suggests an interpretation of the OIL profile as a 'weighted convolution' of a Doppler distribution with a generalized pressure broadening distribution. Clearly the OIL profile reduces to a Voigt profile in the limit of constant width and shift functions.

To investigate the symmetry of the OIL profile we may use the fact that for a profile to be symmetric there must exist a center frequency ω_c such that

$$I(\omega) = I(-\omega + 2\omega_c). \tag{6.11}$$

But from (6.9) by transforming $\omega' \to -\omega'$ and noticing that the derivative of an even function is odd one can show that

$$I_{\mathrm{OIL}}(-\omega + 2\omega_c) = \frac{1}{\pi^{3/2}\omega_D} \int_{-\infty}^{\infty} \exp[-(\omega'/\omega_D)^2 \frac{\Gamma(\omega'/\kappa)}{[\omega - 2\omega_c + \Delta(\omega'/\kappa) - \omega']^2 + \Gamma^2(\omega'/\kappa)}$$

$$\times \left\{1 - \frac{\mathrm{d}}{\mathrm{d}\omega'} \Delta(\omega'/\kappa) + \frac{\omega - 2\omega_c + \Delta(\omega'/\kappa) - \omega'}{\Gamma(\omega'/\kappa)} \frac{\mathrm{d}}{d\omega'} \Gamma(\omega'/\kappa)\right\} \mathrm{d}\omega'. \tag{6.12}$$

Thus the condition for symmetry is that

$$\frac{\mathrm{d}}{d\omega'} \Delta(\omega'/\kappa) = 0 \tag{6.13}$$

in which case ω_c is expressed in terms of the *constant* shift function as $\omega_c = \Delta$. In general, this result means that the OIL profile is *asymmetric* except when the shift function is vanishingly small. In passing we note that the asymmmetry of the OIL profile depends on the speed dependence of the shift function whereas the asymmetry found by RAUTIAN and SOBEL'MAN[15] (p. 714) in their correlated string collision model (phase shifts and velocity changes uncorrelated except both occur in the same collision) depends only on a non-zero shift function which may be taken as a constant.

7. INVERSE POWER LAW MODEL CALCULATIONS

A. *Width and shift functions*

From (3.19) and (6.5) we have

$$\Gamma(v_0) + i\Delta(v_0) = 2\pi n \int_0^\infty \mathrm{d}\rho\rho \int \mathrm{d}^3 v_R\, v_R\, f_m(\mathbf{v}_0 + \mathbf{v}_R)\{1 - \exp[-i\phi(\rho, v_R)]\}. \tag{7.1}$$

Notice that the only difference between (7.1) and the expression for the width and shift functions of conventional theory given in (4.4) is in the perturber velocity distributions. Here the displaced Maxwell distribution takes into account the motion of the radiator.

The problem is now to calculate $\phi(\rho, \mathbf{v}_R)$ explicitly. For this we use a model that is standard in conventional CFA theory (FOLEY,[35] p. 620; MARGENAU and LEWIS,[25] p. 590): we assume that $\phi(\rho, v_R)$ may be expressed in terms of the radiator–perturber interaction potential $V(\mathbf{r})$ and the classical trajectory $\mathbf{r}(t)$ as

$$\phi(\rho, v_R) = \frac{1}{\hbar} \int_{-\infty}^{\infty} V[\mathbf{r}(t)]\, \mathrm{d}t \tag{7.2}$$

and we evalute this expression assuming *straight line trajectories* for a *spherically symmetric interaction* that varies as the inverse qth power of the radiator–perturber separation. Writing

$$V(r) = \frac{\text{const}}{r^q} \tag{7.3}$$

we have

$$\phi(\rho, v_R) = \frac{\text{const}}{\hbar} \int_{-\infty}^{\infty} \frac{\mathrm{d}t}{(\rho^2 + v_R{}^2 t^2)^{q/2}} \tag{7.4}$$

$$= \frac{\alpha}{v_R\, \rho^{q-1}} \tag{7.5}$$

where α depends on q and the strength of the interaction. The utility of this model is twofold: when the broadening is dominated by distant collisions so that straight line trajectories are a good approximation for most collisions of interest the model turns out to be equivalent to a semi-classical limit of the full quantum theory and even when this is not the case the model permits us to consider the *changes* in the line profile that result from a general formulation of the combined Doppler and pressure broadening problem in the OIL approximation as compared with the conventional CFA line profile derived under the same assumptions.

Using (7.5) in (7.1) and (4.4) one may show by a somewhat tedious calculation (WARD,[32] p. 143) that

$$\frac{\Gamma(v_0)}{\Gamma} = \frac{\Delta(v_0)}{\Delta} = \beta(v_0/\tilde{v}_M\,;\, \lambda, q). \tag{7.6}$$

$$\beta(x_0\,;\lambda, q) = (1+\lambda)^{-[(q-3/2q-2)]}M\left(-\frac{q-3}{2q-2}, \frac{3}{2}, -\lambda x_0{}^2\right). \tag{7.7}$$

Here $\beta(x_0\,;\lambda, q)$ is just the *dimensionless width and shift function* in terms of the dimensionless radiator speed x_0 introduced in (2.10) and the perturber/radiator mass ratio $\lambda = m/M$. $M(a, b, z)$ is the confluent hypergeometric function defined by the series (ABROMOWITZ and STEGUN,[36] p. 504)

$$M(a, b, z) = 1 + \frac{az}{b} + \frac{a(a+1)}{b(b+1)}\frac{z^2}{2!} + \frac{a(a+1)(a+2)}{b(b+1)(b+2)}\frac{z^3}{3!} + \cdots. \tag{7.8}$$

Notice that the shift-to-width ratio is independent of radiator speed and is identical to the usual result for shifts all of one sign[35]

$$\frac{|\Delta(v_0)|}{\Gamma(v_0)} = \frac{|\Delta|}{\Gamma} = \tan\left(\frac{\pi}{q-1}\right). \tag{7.9}$$

The result that $\Gamma(v_0)$ and $\Delta(v_0)$ have the same velocity and mass dependence is somewhat surprising. This is not a general feature of the theory but rather depends on the existence of a transformation of variables which separates the ρ and $\mathbf{v}_R$-integrals in (7.1). Such a transformation is not available for a general potential and its availability for the straight line trajectory inverse power potential is what makes the model tractable.

Turning now to the form of $\beta(x_0\,;\lambda, q)$ for specific types of interaction we find from (7.7) and (7.8) that for resonance broadening ($q = 3$),

$$\beta(x_0\,;\lambda, 3) \equiv 1. \tag{7.10}$$

In other words the spatial dependence of the r^{-3} interaction in our model exactly compensates for the speed and mass dependence of $g(\phi;\, v_0)$, $v_c(v_0)$ and $\phi(\rho, v_R)$ so as to yield a result *unchanged* from the conventional CFA impact theory treatment of this interaction. We conclude that the Voigt profile exactly describes the r^{-3} interaction under the conditions of the OIL approximation to the CFA theory and our model $g(\phi;\, v_0)$ function.

Owing to the relatively long range of the r^{-3} interaction, meaning that distant collisions contribute significantly to the broadening, this result is expected to be generally valid for the usual impact theories of resonance broadening using an r^{-3} interaction and is consistent with existing experimental data on the resonance lines ($^2P_{1/2}$, $^2P_{3/2} \to {}^2S_{1/2}$) of K and Cs. LEWIS, REBBECK and VAUGHAN[37] have recently measured resonance broadening of the K resonance lines by extracting the Lorentzian (resonance broadened) components from an analysis of the observed profiles in terms of Voigt profiles. Their work uses the *core* of the observed profile where impact theory is valid and they point out that the results are in agreement with observations by CHEN and PHELPS[38] on the *far wings* of Cs resonance lines where statistical theories should apply. This is taken[37] as indicative of the velocity independence of resonance broadening, though admittedly the test is not very sensitive ($\pm 25\%$).

Encouraging as this result is, we must point out that simple impact theories based on the r^{-3} interaction may not provide an adequate treatment of resonance broadening. In experiments on resonance broadening in the noble gases, KUHN *et al.*[2,3,39,40] have observed that the pressure width apparently depends nonlinearly on density at low pressures where resonance broadening and natural broadening are comparable. A number of authors have considered deviations from the r^{-3} interaction[41–43] and their effect on the radiative width of the excited atom.[44–46] Other authors[47,48] have suggested that excitation transfer may affect the profile by introducing an "effective statistical dependence" between Doppler and pressure broadening (excitation transfer occurs without change in phase but results in a different velocity for the excited atom). Neither of these effects is included within the model CFA–OIL theory presented here. One concludes that our work is restricted to the regime where radiative width is negligible and excitation transfer between atoms with appreciably different velocities is unimportant.

The other cases which we consider are for $q = 6$ and $q = 12$. Series and asymptotic expansions can be developed from the properties of $M(a, b, z)$:

$$\beta(x_0\,;\lambda, q) = \begin{cases} (1+\lambda)^{-3/10}\left(1 + \frac{1}{5}\lambda x_0^2 - \frac{7}{250}\lambda^2 x_0^4 + \cdots\right)[q=6] & (7.11a) \\ (1+\lambda)^{-9/22}\left(1 + \frac{3}{11}\lambda x_0^2 - \frac{39}{1210}\lambda^2 x_0^4 + \cdots\right)[q=12] & (7.11b) \end{cases}$$

$$\beta(x_0\,;\lambda, q) \sim \begin{cases} \sqrt{\pi}\,\frac{(1+\lambda)^{-3/10}(\lambda x_0^2)^{3/10}}{2\Gamma(9/5)}\left(1 + \frac{6}{25\lambda x_0^2} + \frac{21}{1250\lambda^2 x_0^4} + \cdots\right)[q=6] & (7.12a) \\ \sqrt{\pi}\,\frac{(1+\lambda)^{-9/22}(\lambda x_0^2)^{9/22}}{2\Gamma(21/11)}\left(1 + \frac{45}{121\lambda x_0^2} + \frac{585}{58564\lambda^2 x_0^4} + \cdots\right)[q=12]. & (7.12b) \end{cases}$$

The $\Gamma(9/5)$ and $\Gamma(21/11)$ in (7.12) are gamma functions (ABRAMOWITZ and STEGUN,[36] p. 255).

Figure 1 shows $\beta(x_0\,;\lambda, q)$ for several values of λ and $q = 6$, 12. For purposes of interpretation note that 71 per cent of the radiators have $0{\cdot}5 \le x_0 \le 1{\cdot}5$. We observe that the speed dependence of the width and shift is greatest in the massive perturber–light radiator case as expected and more severe for $q = 12$ than for $q = 6$.

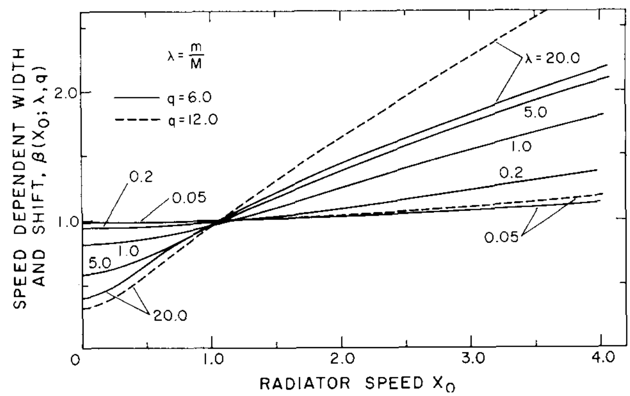


Fig. 1. Dimensionless speed dependent width and shift function for the r^{-6} and r^{-12} interaction. The radiator speed x_0 is in units of the most probable radiator speed and $\lambda = m/M$.

B. Line profile

At this point it is convenient to introduce dimensionless frequency variables with ω_D as the unit of frequency. Rather than change the notation for ω, Γ, Δ, we will use a tilde on the line profile symbol to remind the reader that frequencies are expressed in units of the Doppler width: $\omega_D I(\omega) \to \tilde{I}(\omega)$

From (7.6) and (6.8) or (6.9) we can derive a number of equivalent expressions for the model OIL profile. Writing β for $\beta(t;\, \lambda,\, q)$ we have:

$$\tilde{I}_{\mathrm{OIL}}(\omega) = \frac{1}{\pi^{3/2}} \int_{-\infty}^{\infty} \mathrm{d}t \exp(-t^2) \frac{\Gamma\beta}{(\omega - \Delta\beta - t)^2 + \Gamma^2\beta^2} \left[1 + (\omega - t)\frac{\mathrm{d}}{\mathrm{d}t}\log\beta\right] \tag{7.13}$$

$$= \frac{2}{\pi^{3/2}} \int_{-\infty}^{\infty} \mathrm{d}t\, t \exp(-t^2) \arctan\left(\frac{t - \omega + \Delta\beta}{\Gamma\beta}\right) \tag{7.14}$$

$$= \frac{1}{2\sqrt{\pi}} + \frac{2}{\pi^{3/2}} \int_{0}^{\infty} \mathrm{d}t\, t \exp(-t^2) \arctan\left[\frac{t^2 - \Gamma^2\beta^2 - (\omega - \Delta\beta)^2}{2t\Gamma\beta}\right] \tag{7.15}$$

$$= \tilde{I}_V(\omega) + \frac{2}{\pi^{3/2}} \int_{0}^{\infty} \mathrm{d}t\, t \exp(-t^2) \times \arctan\left\{\frac{2(1-\beta)\Gamma t[t^2 - \omega^2 + \beta(\Gamma^2 + \Delta^2)]}{4\beta\Gamma^2 t^2 + [t^2 - \beta^2\Gamma^2 - (\omega - \Delta\beta)^2][t^2 - \Gamma^2 - (\omega - \Delta)^2]}\right\}. \tag{7.16}$$

Equation (7.13) follows from (6.9) and shows the structure of the weight function (6.10) for our model; (7.14) follows from (6.8). Equation (7.15) has been given by BERMAN,[34] (equation 13) and follows from (7.14) by considering the even part of the integrand in (7.14) and using an identity relating the arctangents of z and z^{-1}. The last expression involves the difference between $\tilde{I}_{\mathrm{OIL}}(\omega)$ and the Voigt profile $\tilde{I}_V(\omega)$ where (7.15) and its Voigt profile analogue ($\beta \equiv 1$) have been used. Although it looks messy, (7.16) has one of the better behaved integrands and forms the basis of our numerical work.

An example of an OIL profile for the r^{-6} interaction is shown in Fig. 2 where the shift

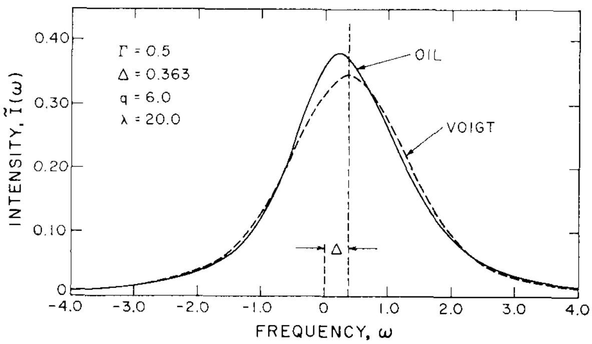


Fig. 2. Comparison of Voigt and model CFA–OIL profiles for non-vanishing shift.

to width ratio has been chosen in accord with (7.9). Generally we may characterize the OIL profile as having a greater maximum intensity and being narrower in the core with slightly broader wings than the corresponding Voigt profile. Additionally, when $\Delta \neq 0$ the OIL profile is asymmetric and shifted *in the direction of* Δ *by an amount less than* Δ. All of these features (with the exception of the wing behavior) are apparent in Fig. 2.

To discuss the wings we will use an asymptotic expansion of the one perturber approximation to the OIL profile analogous to the corresponding expansion of the Voigt profile.

Using (6.1) and (6.5) in (5.3) leads to the one-perturber OIL correlation function. When this is substituted into (3.1) an asymptotic expansion in powers of ω^{-1} leads to (WARD,[32] p. 101ff).

$$\tilde{I}_{\mathrm{OIL}}(\omega) \sim \frac{\Gamma}{\pi\omega^2} + \frac{4\Gamma}{\pi^{3/2}\omega^4} \int_0^{\infty} t^4 e^{-t^2} \beta(t; \lambda, q)\, \mathrm{d}t. \tag{7.17}$$

For $\beta \equiv 1$ this reduces to the familiar expansion of the Voigt profile[49]

$$\tilde{I}_V(\omega) \sim \frac{\Gamma}{\pi\omega^2} + \frac{3\Gamma}{2\pi\omega^4}. \tag{7.18}$$

Although the OIL expansion lacks the algebraic simplicity of the Voigt expansion, the integral in (7.17) is very well behaved numerically and the expansion provides a simple means of analyzing the OIL wing. As might be expected, the two expansions make very nearly the same error in approximating their respective profiles.

8. COMPARISON WITH VOIGT PROFILE

A number of methods of comparison are possible. For example, we could examine the fractional difference between Voigt and OIL profiles as a function of frequency. However, we feel a more interesting comparison results if we analyze OIL profiles *as if they were Voigt profiles*. This method of comparison mimics the procedures used in the interpretation of low pressure foreign gas broadening to date.

We adopt the point of view that the parameters Γ, Δ and ω_D which characterize both the OIL and Voigt profiles are theoretical quantities related to the interaction potential by (4.4) in the case of Γ and Δ and to the temperature by (1.3) in the case of ω_D. The problem in analyzing line profiles is to deduce these parameters and thereby make inferences concerning the potential and/or the conditions under which the line was formed. However, if the actual profile is an OIL profile which is analyzed in terms of a Voigt profile, one obtains parameters Γ', Δ' and ω_D' characteristic of some kind of best fit but not necessarily related to the interaction potential or the temperature. The differences between the best fit parameters (primed) and the true parameters represent the kind of errors one may make in assuming a Voigt profile and accordingly we investigate the ratios Γ'/Γ, Δ'/Δ and ω_D'/ω_D under a variety of conditions.

Although we believe the results which follow serve clearly to delineate the kinds of errors and the conditions under which they occur when correlation effects are ignored and analysis is made in terms of Voigt profiles, we emphasize that the present work is based on the one-interacting-level assumption and is tied to a particular model for the interaction potential (inverse power) and the way in which this interaction produces phase changes (classical straight line trajectory approximation). Moreover the ratios Γ'/Γ and ω_D'/ω_D depend on what criteria are applied in fitting the Voigt profile as we shall discuss below. Finally, we discuss briefly the effect of instrumental width which enters the OIL profile in a non-trivial manner and may mask correlation effects.

A. Core analysis

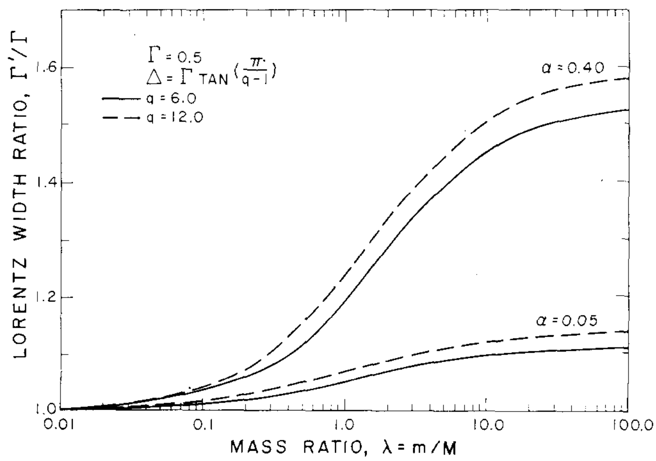
For the core of the line (frequencies within several HWHM of line center) at least two methods have been used to fit Voigt profiles to experimental data: fit the half maximum width[40,50] and full Voigt analysis.[2,40,50] The former method is useful when $\Gamma \gg 1$

(dimensionless frequency variables) or when *a priori* knowledge of the temperature can be assumed and is the method used by BERMAN[34] in analyzing the fit of Voigt profiles to OIL profiles (SDVP in his nomenclature) for the r^{-12} interaction. In the general case one wants to obtain both Γ and ω_D and this requires 'full Voigt analysis', that is, the width of the Voigt profile is required to fit the experimental profile at two different fractions of the profile maximum.[2,51–53] Clearly the parameters Γ' ω_D' which result from this procedure will be independent of what fractions are chosen for the fits only when the experimental profile is Voigt and systematic variations in Γ' or ω_D' with choice of fitting points provide a sensitive test of deviations from Voigt behavior. In applications of this method it is customary to chose the FWHM as one of the fitting points and various fractions α of maximum intensity for the other fitting point. In the present analysis we have chosen $\alpha = 0{\cdot}4$, $0{\cdot}3$, $0{\cdot}2$, $0{\cdot}1$ and $0{\cdot}05$ although our figures show only the $\alpha = 0{\cdot}4$ and $0{\cdot}05$ cases for simplicity; the other three cases fall between the extremes at nearly equally spaced intervals.

We should also note that this fitting procedure is based on fits of the *full* widths at various fractions of maximum intensity and consequently minimizes the effects of profile asymmetry. Indeed, we have analyzed OIL profiles for $\Delta = 0{\cdot}0$ and $\Delta = \Gamma \tan[\pi/(q-1)]$ and find that asymmetry has very little effect on either of the ratios Γ'/Γ or ω'/ω_D; at most the differences would just barely show in the figures and are omitted for clarity. The parameter Δ' is of course the frequency at which the maximum of the OIL profile occurs.

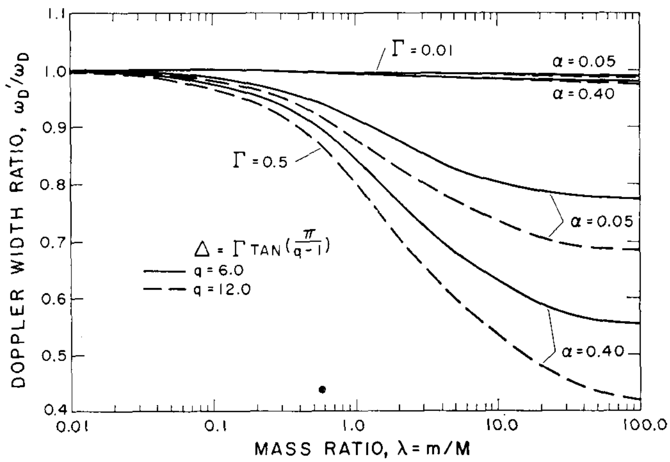
Figure 3 shows the variations in Γ'/Γ, ω_D'/ω_D and Δ'/Δ as a function of perturber/radiator mass ratio, $\lambda = m/M$, for representative values of Γ. In Fig. 3(a) the ratio Γ'/Γ for $\Gamma = 0{\cdot}01$ is omitted because it reaches a value of $1{\cdot}6$ at $\lambda \approx 1{\cdot}0$ for the $q = 12$, $\alpha = 0{\cdot}40$ case (see Fig. 4). The extreme cases of $\alpha = 0{\cdot}4$ and $0{\cdot}05$ serve to indicate the level of sensitivity required to detect departures from Voigt behavior. As an example, for $\Gamma = 0{\cdot}5$, $\lambda = 1{\cdot}0$, the difference in Γ'/Γ at $\alpha = 0{\cdot}4$ and $0{\cdot}05$ is $0{\cdot}14$ so one would need width determinations better than 10 per cent to begin observing any correlation effects.

It is also encouraging to note that the ratios are not especially strong functions of the choice of power in the interaction potential. Although this probably limits the utility of correlation effects as a probe of the interaction potential, it is a welcomed result in the context of the present work where only the simplest model potentials have been considered.

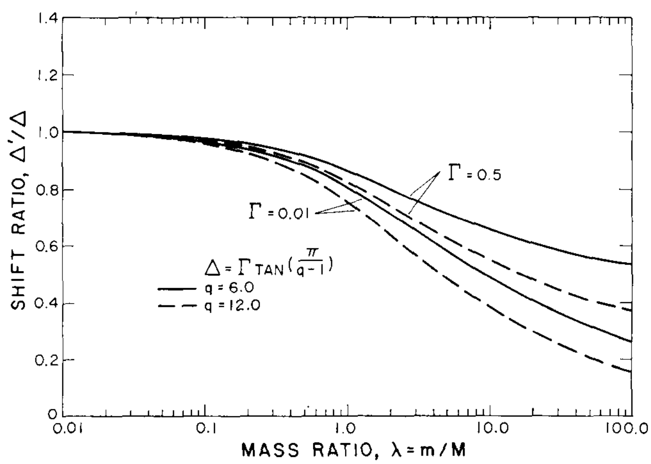


(a)

Fig. 3



(b)



(c)

Fig. 3. Ratio of fit parameters (primed) to the true parameters as a function of perturber/radiator mass ratio $\lambda = m/M$ for the r^{-6} and r^{-12} interaction potentials. Full Voigt analysis is used with fitting points at the half maximum and the α-function of maximum intensity. (a) Γ'/Γ; (b) ω_D'/ω_D; (c) Δ'/Δ.

This strengthens the expectation that the inverse power model serves to adequately delimit the scope of correlation effects. Still a word of caution is in order. HINDMARSH, PETFORD and SMITH[54] have investigated conventional theory for the case of a Lennard–Jones (12-6) potential and found results surprisingly different from either the r^{-6} or r^{-12} interactions. The nature of correlation effects for the Lennard–Jones (12-6) potential is currently under investigation.

In Fig. 4 we show the dependence of Γ'/Γ and ω_D'/ω_D on Γ for the case $\lambda = 20{\cdot}0$. Again the ratios are not especially significant functions of q except for the Doppler ratio near $\Gamma = 1{\cdot}0$. Note that for some $\Gamma \gtrsim 1$ the fitting procedure fails to yield a physical solution

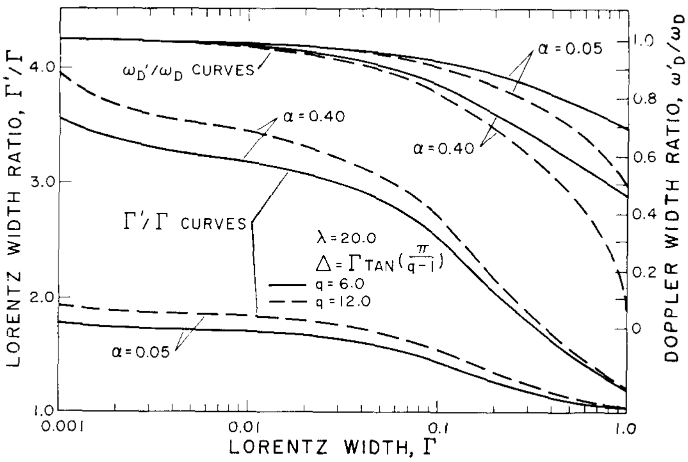


Fig. 4. Ratio of fit parameters (primed) to the true parameters as a function of width parameter Γ for the r^{-6} and r^{-12} interaction potentials and the perturber/radiator mass ratio $\lambda = 20$. Since Γ is linearly proportional to perturber density, the figure shows the density behavior (on a log scale) of the ratios Γ'/Γ and ω_D'/ω_D.

for the Voigt parameters; in Fig. 4 this is apparent in the ω_D'/ω_D ratio for the $\alpha = 0{\cdot}40$, $q = 12{\cdot}0$ case. Also the increased negative slope of Γ'/Γ for $\Gamma \lesssim 0{\cdot}005$ is a real effect and we suspect that for some Γ sufficiently small the slope diverges signifying that the fit equations again no longer possess physical solutions. Although such a divergence occurs in a region of no physical interest (possibly at $\Gamma = 0$), it would be the analogue of what is apparent in the ω_D'/ω_D ratio for larger Γ.

For any given radiator–perturber system, Γ is directly proportional to perturber density so that Fig. 4 may be interpreted as the density behavior of the Γ'/Γ and ω_D'/ω_D ratios. The behavior is more or less what one might expect, namely, *correlation effects lead to significant errors in the parameter that plays a minor role in the characterization of the profile.* Thus for small Γ, Doppler effects dominate the profile and residual correlation effects are interpreted as anomalous behavior of the Lorentzian component. As Γ increases, Doppler effects play a progressively less important role in determining the profile and correlation effects lead to increased errors in the Doppler width and decreased errors in the Lorentzian width.

The rather large Γ'/Γ ratios for $\Gamma \lesssim 0{\cdot}1$ suggest that experiments may easily detect correlation effects with favorable perturber/radiator mass ratios. However, small Γ corresponds to low pressure and for many systems the region $\Gamma \lesssim 0{\cdot}1$ remains experimentally difficult or altogether inaccessible. Moreover, the actual difference between OIL and Voigt profiles for $\Gamma \lesssim 0{\cdot}1$ is everywhere less than a few per cent (because Doppler broadening dominates the profile) which gives some estimate of the signal to noise requirements in an experiment. Figure 5 shows the fractional difference $[\tilde{I}_V(\omega) - \tilde{I}_{\rm OIL}(\omega)]/\tilde{I}_V(\omega)$ for the case $\lambda = 20{\cdot}0$ and a range of Γ values. For $\Gamma \lesssim 0{\cdot}1$ full Voigt analysis with $0{\cdot}05 \lesssim \alpha \lesssim 0{\cdot}4$ uses that part of the profile corresponding to frequencies in the range $1{\cdot}0 \lesssim \omega \lesssim 2{\cdot}0$.

Experiments have traditionally been interpreted in terms of plots of width and shift vs perturber density, n, and summarized in terms of the broadening and shift constant and the shift to width ratio, Γ/n, Δ/n and Δ/Γ respectively. Figures 6(a) and (b) show plots of Γ'

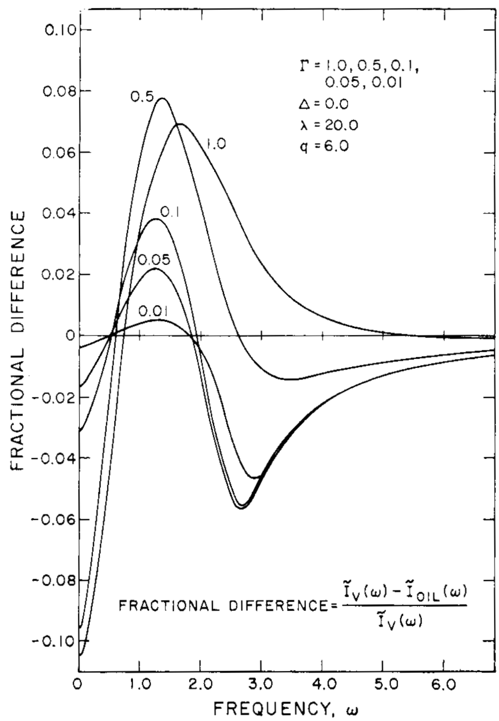
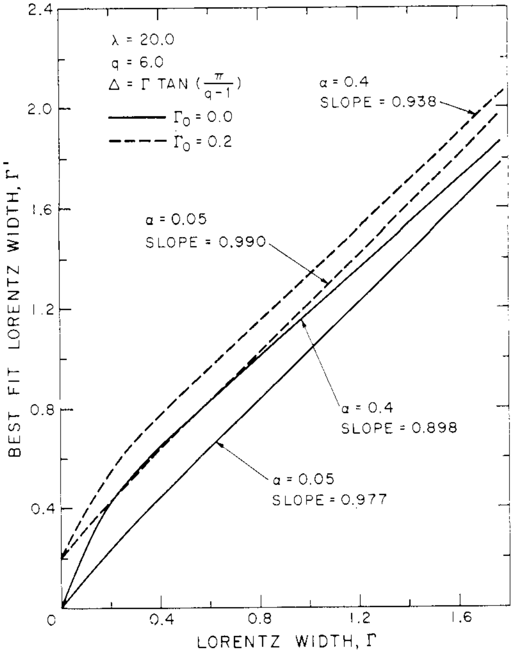


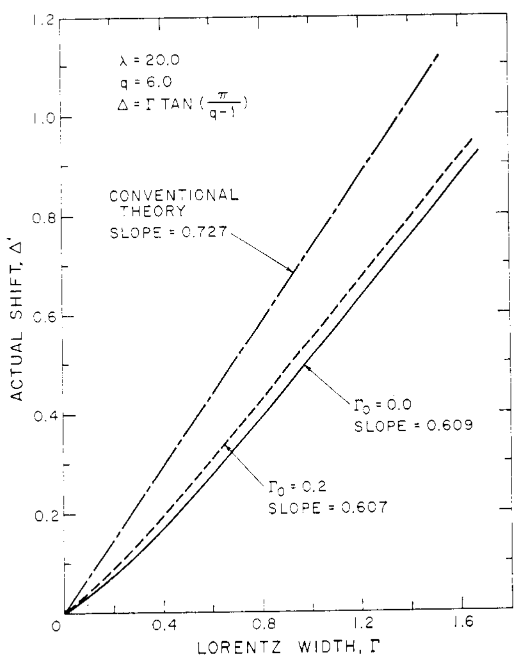
Fig. 5. Fractional difference between the Voigt and model OIL profiles as a function of frequency from line center for the r^{-6} interaction and perturber/radiator mass ratio $\lambda = 20{\cdot}0$. Since both profiles are symmetric in the $\Delta = 0{\cdot}0$ case only positive frequencies are shown.

and Δ' vs Γ (proportional to n) for $\lambda = 20$ and $q = 6$ and thereby indicate the density behavior as it would normally be encountered when full Voigt analysis is applied to OIL profiles. Again the difference between the $\alpha = 0{\cdot}4$ and $0{\cdot}05$ curves indicates the level of sensitivity required in an experiment to detect correlation effects. If we use the slopes from the linear portion of the curves and take an average slope of 0·94 for the Γ' vs Γ curve we obtain broadening constant, shift constant and shift to width ratio 6, 16 and 11 per cent *smaller* than predicted by conventional theory. These are not appreciable changes and the case $\lambda = 20{\cdot}0$ is rather extreme. In fact the variation of ω_D'/ω_D with density (Fig. 6c) may be a more experimentally accessible indicator of correlation effects and we caution that experiments which rely on temperature determinations from ω_D in the $\Gamma \sim 1$ region to infer perturber densities may be susceptible to systematic error; the fitted Doppler width ω_D' is smaller than the true Doppler width resulting in temperatures ($T \sim \omega_D{}^2$) *lower* than the true temperatures.

We should also note that the non-linear variation of Γ' with density will lead to errors if natural or instrument widths are obtained from extrapolations to zero density based on the linear portion of the curve. The amount and even the *sign* of the error will depend on the method of Voigt analysis applied to the profile as is clear from a comparison of Fig. 6(a) with Fig. 3 given by Berman.[34] (The SDVP width parameter $W_{ab}'(r)$ used by Berman is $\Gamma\beta(1; \lambda, q) \simeq \Gamma$ since $\beta(1; \lambda, q) \simeq 1$ independent of λ and q.) The relation between the Lorentz parameters deduced by the two methods is easy to see qualitatively. Let Γ_B' denote the

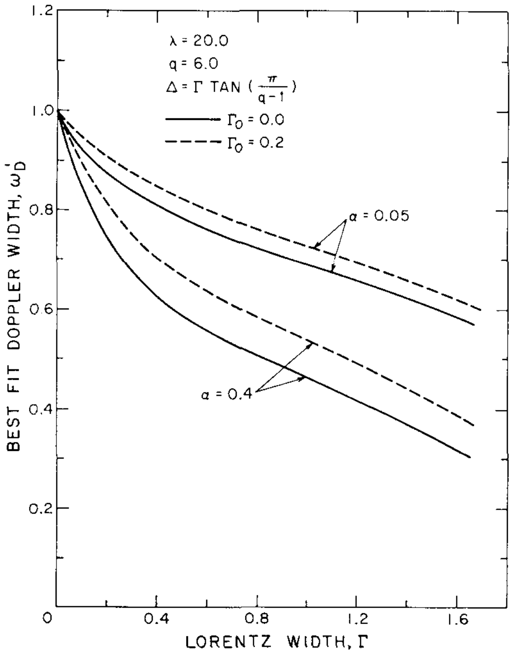

λ = 20.0
q = 6.0
Δ = Γ TAN (π/(q-1))
Γ0 = 0.0
Γ0 = 0.2
α = 0.4
SLOPE = 0.938
α = 0.05
SLOPE = 0.990
α = 0.4
SLOPE = 0.898
α = 0.05
SLOPE = 0.977
BEST FIT LORENTZ WIDTH, Γ'
LORENTZ WIDTH, Γ
2.4
2.0
1.6
1.2
0.8
0.4
0
0.4
0.8
1.2
1.6

(a)


λ = 20.0
q = 6.0
Δ = Γ TAN (π/(q-1))
CONVENTIONAL THEORY
SLOPE = 0.727
Γ0 = 0.0
SLOPE = 0.609
Γ0 = 0.2
SLOPE = 0.607
ACTUAL SHIFT, Δ'
LORENTZ WIDTH, Γ
1.2
1.0
0.8
0.6
0.4
0.2
0
0.4
0.8
1.2
1.6

(b)

Fig. 6



(c)

Fig. 6. Fit parameters as a function of Γ (proportional to perturber density) for the case of an r^{-6} interaction with perturber/radiator mass ratio $\lambda = 20{\cdot}0$. The figures show the non-linear density dependence and concomitant extrapolation errors as they would normally be encountered. Also shown is the extent to which convolution of an OIL profile with a Lorentzian ($HWHM = \Gamma_0$) may mask correlation effects when full Voigt analysis is applied. The Lorentzian parameter Γ_0 is in general the sum of natural and instrumental widths with the latter usually dominant; $\Gamma_0 = 0{\cdot}0$ of course corresponds to an OIL profile as given by (7.13) (natural width neglected). (a) Γ'; (b) Δ'; (c) ω_D'.

dimensionless Lorentz parameter obtained by requiring that a Voigt profile using the *correct* Doppler width, ω_D, fit an OIL profile at the FWHM (Berman's method). Since the OIL profile is slightly narrower at the FWHM point than the corresponding Voigt profile, Γ_B' will be smaller than the true Lorentz parameter Γ. However, when a full Voigt analysis is applied to approximately the same region of the profile ($\alpha = 0{\cdot}4$) we find that the Doppler width ω_D' of the best fit (Voigt) profile is *smaller* than the true Doppler parameter so that Γ' must be greater than Γ. Since both Γ' and Γ_B' approach Γ at low densities, we see that full Voigt analysis will yield curves of width vs density with negative curvature and positive extrapolation errors while Berman's method yields curves with positive curvature and negative extrapolation errors. Similarly, we note that the non-linear variation of shift with density will yield an extrapolation at zero density and here the result is unambiguous.

Figure 5 also permits a somewhat different characterization of correlation effects on the basis of where in the profile they appear. What we observe is that when Γ is large the OIL wings approach Voigt behavior and deviations, though sizeable, are confined to the central part of the OIL profile. This is because as Γ gets large the Doppler core and hence correlation effects are confined to a smaller region of the profile. The opposite occurs in the limit $\Gamma \rightarrow 0$. Then the pressure and correlation part of the OIL profile behaves increasingly like a delta function with the result that in the central region of the OIL profile the convolution integral (7.13) samples only the collisionless Doppler factor $\exp(-t^2)$ which gives essentially a Voigt profile. Residual correlation effects appear in the wing where pressure and Doppler effects make approximately equal contributions [this occurs at $\omega \approx 2{\cdot}0$ for $\Gamma = 0{\cdot}01$ on the basis of HUMMER[49] equation (2.6)] to the profile and the far wing goes over to Voigt behavior.

B. Wing analysis

This discussion applies to that region in the line wing at frequencies greater than several HWHM from line center where an impact or one perturber theory is still applicable. Here the asymptotic expansions (7.17) or (7.18) provide a good description of the profile and by fitting these expansions to the wing we can determine the parameter Γ approximately. This method of analysis is applicable to a wide range of Γ if ω_D is known *a priori* or to $\Gamma \lesssim 0{\cdot}1$ in which case ω_D is determined from the FWHM by treating the core as a pure Gaussian. Letting $2\omega_{1/2}$ be the FWHM, we have $\omega_D' = \omega_{1/2}/(\log 2)^{1/2}$. Figure 7(a) shows the fractional error made in ω_D' as a function of Γ with the interesting result that smaller errors are made when OIL profiles with larger q and λ are analyzed this way. This reflects the fact that OIL profiles are slightly narrower in the core than Voigt profiles as previously noted.

Knowing ω_D (or its approximation ω_D') we can proceed to fit an asymptotic expansion to the OIL profile wing. We consider two cases: in the Voigt-wing-fit case the asymptotic Voigt wing (7.18) is fitted to the OIL profile resulting in the width

$$\Gamma' = \frac{\pi\omega^2 \tilde{I}_{\mathrm{OIL}}(\omega)}{[1 + (2/3\omega^2)]} \tag{8.1}$$

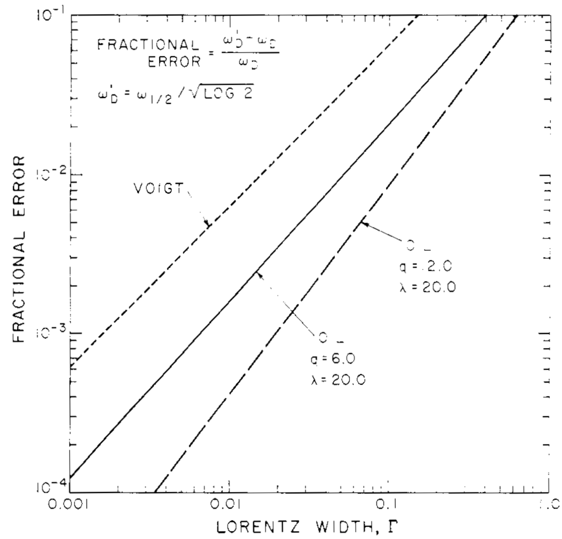
whereas in the OIL-wing-fit case the asymptotic OIL wing (7.17) is fitted to the OIL profile resulting in the width

$$\Gamma' = \frac{\pi\omega^2 \tilde{I}_{\mathrm{OIL}}(\omega)}{\left[1 + \dfrac{4}{\sqrt{\pi}\,\omega^2}\displaystyle\int_0^\infty t^4 \exp(-t^2)\beta(t;\lambda,q)\,\mathrm{d}t\right]}. \tag{8.2}$$

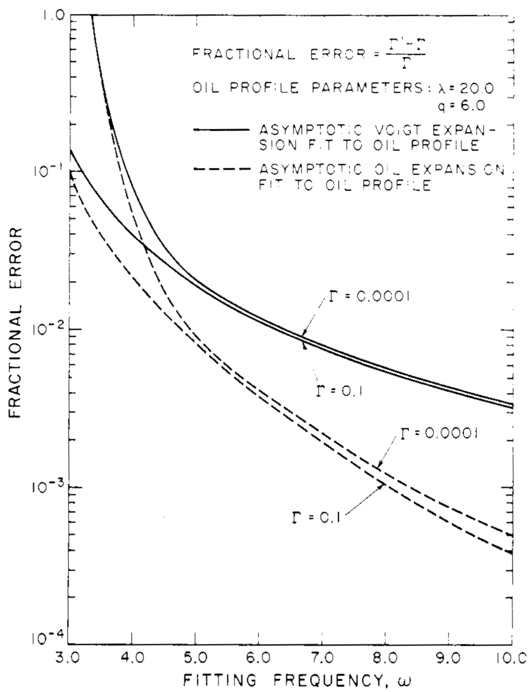
In Figure 7(b) we plot the fractional error $(\Gamma' - \Gamma)/\Gamma$ for both cases as a function of ω for $\Gamma = 0{\cdot}1$ and $\Gamma = 0{\cdot}0001$. Only fits to an OIL profile with $q = 6{\cdot}0$ have been shown for clarity; in the region $\omega \geq 5{\cdot}0$ the *fractional* errors for fits to an OIL profile with $q = 12{\cdot}0$ are approximately 25 per cent greater for the Voigt-wing-fit case and 10 per cent greater for the OIL-wing-fit case. As λ decreases the Voigt-wing-fit curves move down towards the OIL-wing-fit curves which move down slightly (about 10 per cent) to the limiting case defined by fitting the asymptotic Voigt wing to a Voigt profile. We see that the errors incurred in the Voigt-wing-fit case are quite respectable and such a procedure may be entirely adequate in practice. We conclude that Doppler width determinations based on the FWHM of the OIL profile are in fact better than those from the corresponding Voigt profile, that the OIL wing is largely Voigt is character and that analysis of OIL profiles based on the FWHM and the asymptotic Voigt wing expression will lead to errors of less than 1 per cent in ω_D and Γ under a wide variety of conditions. We stress that the errors incurred depend on where in the wings the fit is made and that the asymptotic expansion fits are unreliable for frequencies less than about five Doppler (half) widths from line center.

C. Instrumental width

One may often approximate an instrumental profile by a Voigt profile[2,55,56] in which case the convolution of a Voigt line profile and the instrument profile is again a Voigt



(a)



(b)

Fig. 7. Fractional errors incurred in determination of profile parameters using the FWHM for ω_D' and asymptotic wing expansions for Γ'. The case of perturber/radiator mass ratio $\lambda = 20{\cdot}0$ is shown. (a) Fractional error $(\omega_D' - \omega_D)/\omega_D$ as a function of Γ when ω_D' is determined from the HWHM $= \omega_{1/2}$ of an OIL profile according to $\omega_D' = \omega_{1/2}/\sqrt{\log 2}$. (b) Fractional error $(\Gamma' - \Gamma)/\Gamma$ as a function of frequency from line center (in units of the Doppler width ω_D which is assumed to be known exactly) at which Voigt or OIL asymptotic wing expansions are applied.

profile and the problem of deconvolution is reduced to algebra by the theorem[51] on additivity of Lorentzian widths and additivity of squares of Gaussian widths. When the spectral profile is not Voigt, the convolution or deconvolution problem is more difficult and in this section we consider briefly the convolution of an OIL profile with Lorentzian and Voigt instrumental profiles.

We consider first the case of convolution with a Lorentzian with FWHM given by $2\Gamma_0$ which in general is the sum of the natural width and the Lorentzian instrumental width. Typically natural width is negligible and we shall refer to Γ_0 as simply instrumental width. From inspection of (4.2) and (6.4) we see that the convolution of Lorentzian and OIL profiles is again an OIL profile with total speed dependent width $\Gamma_{tot}(v)$ given by

$$\Gamma_{tot}(v) = \Gamma_0 + \Gamma(v). \tag{8.3}$$

This is equivalent to the replacement $\Gamma\beta \rightarrow \Gamma_0 + \Gamma\beta$ in (7.13)–(7.15) but *not* in (7.16) where cancellation has occurred between the Voigt and OIL integrands. Not surprisingly, the effect of a Lorentzian instrumental profile is to increase the Voigt character of the resulting OIL profile as is shown in Fig. 6 for the extreme case of $\lambda = 20$ and the relatively modest instrumental width $\Gamma_0 = 0{\cdot}2$ (dimensionless variables). In the presence of instrumental width the error in the broadening constant deduced from the linear portion of the Γ' vs Γ curve is reduced from about 6 per cent to about 3 per cent whereas the shift constant remains relatively unchanged although the extrapolation anomaly in the shift is appreciably reduced. The Doppler widths ω_D' obtained from a full Voigt analysis are also improved in the presence of the Lorentzian instrumental width although in this case the sizeable correlation effects are not substantially altered.

We have also considered the convolution of OIL and Voigt profiles in which case the resulting profile is no longer an OIL profile and the convolution must be performed numerically. For the case of a Voigt instrumental profile with Lorentzian parameter $\Gamma_0 = 0{\cdot}2$ and Gaussian parameter $\omega_0 = 0{\cdot}2$ we find little change from the case of a pure Lorentzian with $\Gamma_0 = 0{\cdot}2$ when full Voigt analysis is applied: Γ' and Δ' are increased by $\lesssim 1$ per cent in absolute value and the slopes (Γ' and Δ' as a function of Γ) are changed negligibly. The Doppler widths ω_D' are of course increased but when the instrumental component ω_0 is subtracted according to the additivity of squares theorem, the corrected Doppler widths are $\lesssim 1$ per cent greater than for the case of a pure Lorentzian instrumental profile.

More generally the problem of instrumental width is particular to each experiment and it does not seem appropriate to pursue the problem further in this paper. We have raised the question to see what effects might be expected and we conclude that instrumental width tends to mask correlation effects when full Voigt analysis is applied to the resulting profiles and that small Lorentzian components are much more significant than small Gaussian components.

9. PREVIOUS WORK

A. Theory

Previous theoretical efforts to account for correlation between Doppler and pressure broadening consist chiefly of the correlated strong collision (CSC) model due to RAUTIAN and SOBEL'MAN[15] and GERSTEN and FOLEY[16] and the *ad hoc* modifications of the Voigt profile by MIZUSHIMA[17,18] and EDMONDS.[19]

In the CSC model one assumes a constant collision frequency ν_c and adopts the G-function $g(\phi)f_M(\mathbf{v})$ where $g(\phi)$ is given by (3.20) and the post-collision velocity distribution is Maxwellian. Then the line profile may be expressed in terms of the complex error function. However, it is unclear what status should be accorded the CSC model as far as the problem of Doppler-pressure correlation effects is concerned. We noted in the introduction that for arbitrary perturber/radiator mass ratios one can show that CFA theory is valid only for identical interaction in both levels or for interaction in only one level. In the former case correlation effects disappear because the phase shifts all vanish (although collisions still modify the Doppler profile) and in the latter (OIL) case we have used an exact form of the G-function (based on correspondence with quantum theory) which clearly incorporates rather different collision physics than the CSC model G-function. Consequently we regard similarities in the strong collision and OIL profiles as mostly the result of accident or fortune and are not surprised to find significant differences as for example the fact that the peak of the asymmetric CSC model profile is shifted by more than Δ whereas for OIL profiles the shift is less than Δ.

The first problem to arise in any attempt at quantitative comparison of the OIL and CSC models is to choose the collision frequency ν_c for the CSC model. One expects that $\nu_c \sim \Gamma$ since departures from Voigt behavior (correlation effects) are small and for $\Delta = 0$ the choice $\nu_c = \Gamma$ reduces the CSC model to a Voigt profile *exactly*. On the other hand, the CSC model has no explicit dependence on the perturber/radiator mass ratio λ so that ν_c has to compensate for variations in λ. It turns out that the choice of ν_c as a function of λ can be settled unambiguously[32] by equating the asymptotic expansion of the one-perturber approximation to the CSC model,

$$\tilde{I}(\omega) \sim \frac{\Gamma}{\pi\omega^2} + \frac{\nu_c + 2\Gamma}{2\pi\omega^4}, \tag{9.1}$$

to the asymptotic OIL wing given by (7.17). The result for the r^{-6} interaction is that $1{\cdot}0 \lesssim \nu_c/\Gamma \lesssim 1{\cdot}6$ as λ ranges from 0 to ∞. With ν_c chosen in this manner we find fractional differences between the CSC and OIL model profiles ($q = 6$ case) of $\lesssim 1$ per cent for $\Delta = 0{\cdot}0$ and $\Gamma \lesssim 0{\cdot}5$ and significantly larger fractional differences for $\Delta \neq 0$. Unfortunately the asymptotic OIL wings are nearly Voigt in character and consequently do not provide a sensitive criterion for the λ dependence of either the OIL profile itself or the CSC model collision frequency as the following example illustrates. For the case $\Delta = 0{\cdot}0$, $\lambda = 20{\cdot}0$ and $\Gamma = 1{\cdot}0$ the 'optimum' collision frequency based on the asymptotic wing criterion is $\nu_c = 1{\cdot}57$ which results in agreement between the OIL and CSC models of about 5 per cent for $|\omega| \lesssim 2{\cdot}0$ and $\lesssim 1$ per cent over the rest of the profile out to $|\omega| \approx 8{\cdot}0$. However, use of $\nu_c = 2{\cdot}2$ for this case reduces the fractional differences in the core by a factor of 10 with no significant loss over the rest of the profile. In general, however, the CSC and OIL models are different (especially when $\Delta \neq 0$) because the basic physics is different and we do not believe parameter manipulation should obscure this fact.

In the *ad hoc* theories of Mizushima and Edmonds both authors begin by generalizing the Voigt profile (4.5) with the replacement $\Gamma \rightarrow \Gamma(v)$ so that the profile they consider is given by

$$\tilde{I}_{V'}(\omega) = \frac{1}{\pi^{3/2}} \int_{-\infty}^{\infty} \mathrm{d}t \exp(-t^2) \frac{\Gamma\beta}{(\omega - t)^2 + \Gamma^2\beta^2} \tag{9.2}$$

where we have written β for $\beta(t;\lambda, q)$ as previously. Comparison with (6.9) or (7.13) shows that this procedure approximates the "convolution weight function" given in (6.10) by unity. For the straight line trajectory–inverse power law interaction model (also used by Mizushima and Edmonds) this amounts to requiring

$$(\omega - t)\frac{\mathrm{d}}{\mathrm{d}t}\log \beta(t; \lambda, q) \ll 1 \tag{9.3}$$

which from the properties of the confluent hypergeometric function (7.8) one can show is satisfied for λt small. Since values of $|t| \sim 1$ are important the condition is essentially that λ be small. Consequently the basic Mizushima–Edmonds line profile is a *massive radiator approximation* which is also the limit of small correlation effects.

It is worth noting that the starting point for Berman's derivation of the OIL profile (SDVP profile) is the replacement $\Gamma \rightarrow \Gamma(v)$ (along with $\Delta \rightarrow \Delta(v)$) in a formula for the Voigt profile exactly equivalent to and only slightly different in form from the conventional formula used by Mizushima and Edmonds (see BERMAN,[34] equation 1a). The lesson is that the deceptively simple replacement $\Gamma \rightarrow \Gamma(v)$ and $\Delta \rightarrow \Delta(v)$ is a delicate matter that must be informed by fundamental theory which of course BERMAN has done.[8,9]

In the calculation of the speed dependent width Mizushima and Edmonds proceed differently. Edmonds considers natural, Stark and Van der Waals broadening as well as macroscopic turbulence and we shall illustrate his method for a general r^{-q} potential in the absence of macroscopic turbulence. First he calculates the mean relative speed as a function of radiator speed:*

$$\langle v_R(v)\rangle = \int |\mathbf{v}' - \mathbf{v}|\, f_m(\mathbf{v}')\, \mathrm{d}^3v' \tag{9.4}$$

$$= \bar{v}_R\, \omega_c(v/\tilde{v}_M\,; \lambda). \tag{9.5}$$

Next he notices that the width of conventional line broadening theory assuming *straight line paths* and an r^{-q} potential may be expressed as

$$\Gamma = (\mathrm{const}) n \bar{v}_R^{[(q-3)/(q-1)]} \tag{9.6}$$

from which Edmonds obtains his expression for the speed dependent width by the replacement $\bar{v}_R \rightarrow \langle v_R(v)\rangle$:

$$\Gamma_E(v) = \Gamma \beta_E(v/\tilde{v}_M;\, \lambda, q), \tag{9.7}$$

$$\beta_E(x;\, \lambda, q) = [\omega_c(x;\, \lambda)]^{[(q-3)/(q-1)]} \tag{9.8}$$

where $\beta_E(x; \lambda, q)$ has the interpretation a dimensionless width function; Edmonds does not consider the effect of line shift. In general $\beta_E(x; \lambda, q)$ approximates the behavior of $\beta(x; \lambda, q)$ and from the series expansion of (2.10) one has

$$\beta_E(x; \lambda, q) = \begin{cases} (1+\lambda)^{-3/10}\left(1 + \dfrac{\lambda x^2}{5} - \dfrac{1}{30}\lambda^2 x^4 + \cdots\right)[q = 6] & (9.9\mathrm{a}) \\[2ex] (1+\lambda)^{-9/22}\left(1 + \dfrac{3}{11}\lambda x^2 - \dfrac{43}{1210}\lambda^2 x^4 + \cdots\right)[q = 12]. & (9.9\mathrm{b}) \end{cases}$$

Comparison with (7.11) shows that $\beta_E(x; \lambda, q)$ is an excellent approximation to $\beta(x; \lambda, q)$ for the small λ region in which (9.2) is valid.

* [The (−) signs in Edmond's equation (10) should be replaced by (+) signs; on the basis of his discussion, these are probably typographical errors.]

MIZUSHIMA[17] works in the language of isolated line adiabatic quantum line broadening theory, but his method may just as easily be cast in the language of CFA theory where it is perhaps a little more transparent. He derives an expression for the speed dependent width and shift including correct velocity averaging which is equivalent to (7.1) and then assumes small phase shifts so that

$$1 - \exp[-i\phi(\rho, v_R)] \approx i\phi(\rho, v_R) + \tfrac{1}{2}\phi^2(\rho, v_R) \tag{9.10}$$

is a reasonable approximation. Using straight line trajectories for an r^{-q} potential leads to [α comes from (7.5)]

$$\Gamma_M(v) = n\pi\alpha^2 \int_0^\infty d\rho\rho^{(3-2q)} \int d^3v_R \frac{1}{v_R} f_m(\mathbf{v} + \mathbf{v}_R). \tag{9.11}$$

A similar treatment of conventional theory leads to an expression for Γ and allows us to express Mizushima's results in the form*

$$\Gamma_M(v) = \Gamma\beta_M(v/\tilde{v}_M\,;\lambda) \tag{9.12}$$

$$\beta_M(x;\lambda) = \tfrac{1}{2}\sqrt{\pi}(1+\lambda)^{1/2}\Phi(\sqrt{\lambda}x)/\sqrt{\lambda}x \tag{9.13}$$

where $\Phi(z)$ is the error function (2.11) and Mizushima's dimensionless shift function $\beta_M(x;\lambda)$ is *independent of the inverse power of the interaction potential.* To the same approximation, the *shift is independent of speed.* Comparison of Fig. 1 with Fig. 3 of Mizushima's 1967 paper shows that $\beta_M(x;\lambda)$ seriously misrepresents the speed dependence of the speed dependent width. Only for small λ does $\beta_M(x;\lambda)$ behave approximately as $\beta(x;\lambda,q)$ (both being approximately unity) but this is just the condition under which the modified Voigt profile (9.2) properly includes correlation effects. Nonetheless, Mizushima applies his theory to the case $\lambda = 1$ and these results must be regarded as suspect.

B. Experiment

We have examined some of the recent experimental literature to see if there is any evidence of correlation effects. To date the interaction between theory and experiment has been justifiably concerned with the problem of interaction potential[57] and most if not all work has been carried out for systems with $\lambda \lesssim 2$. Not surprisingly we find no direct evidence.

In the experiments of SMITH[55] and VAUGHAN and SMITH[50] on Kr broadened by He, Ne, Ar, and Kr no departures from linearity in the density dependence of the width and shift were found and Vaughan and Smith report no asymmetries. However, the Smith experiment suffers from a large and difficult spectrographic instrument profile and on the basis of our simulation of the Vaughan and Smith experiment we would not expect any observable departures from linear density dependence or obvious asymmetries; essentially $\lambda \lesssim 1$ is just too small.

In an experiment by MCCARTAN and HINDMARSH[56] on the broadening of the K resonance line λ4047 Å by Kr ($\lambda = 2{\cdot}14$) the density dependence of width and shift is reported as

* Actually $\beta_M(x;\lambda)$ differs from Mizushima's equation (11) of his 1971 paper[18] (which corrects equation (13) of his 1967 paper[17]) by a factor of $\sqrt{2}$ which comes about by using the *reduced mass* Maxwell distribution in the expression for Γ of conventional theory (see our equation 4.4); Mizushima apparently uses the perturber mass Maxwell distribution. The ordinate in Fig. 3 of the 1967 paper should be multiplied by $\sqrt{2}$. Mizushima considers mainly the case $\lambda = 1$ but our dependence on the mass ratio λ corrects equation (35) of his 1967 paper.

"satisfactorily linear" but both show extrapolation anomalies at zero density. The method of Voigt analysis is not specified and we note simply that the very small extrapolation anomaly in the broadening constant is qualitatively what would be expected in a Berman type analysis (fit of half maximum width). The larger anomaly in the shift vs density curve is ascribed to a shift in the emission line relative to which the shift was measured. However, we estimate that as much as 20 per cent of the observed anomaly may be due to correlation effects.

In a more recent experiment on the broadening of the Ca resonance line λ4227 Å by He, Ne, Ar, Kr and Xe, SMITH[58] has observed asymmetries and non-linear density behavior in the broadening and shift constants for Ar, Kr and Xe perturbers. These results are ascribed to breakdown of the impact approximation although this is not obviously the case for the densities and region of profile examined. Correlation effects were not considered but are not ruled out and the experimental results should perhaps be re-evaluated with this in mind.

10. SUMMARY

A classical Fourier amplitude theory of line broadening in the impact approximation has been developed which accounts for radiator motion by including speed dependence in the collision frequency and velocity dependence in the distribution function (G-function) for collisional phase shifts and velocity changes; the work is equivalent to the general kinetic equation theory of Rautian and Sobel'man. We have derived the one-perturber approximation which serves as the starting point for asymptotic wing expansions and, in conjunction with the one-perturber quantum theory of combined Doppler and pressure broadening, permits an investigation of the validity conditions of the classical theory to be reported in a future paper. The classical OIL approximation corresponding to the quantum mechanical one-interacting-level approximation was introduced and in this case the general theory was reduced to a single integration for the line shape provided the speed dependent width and shift functions are known. Correlation effects in the OIL approximation were extensively investigated by means of model speed dependent width and shift functions. The model assumed an inverse power interaction potential and evaluated the classical phase shift using straight line trajectories. Conventional impact theory for this model leads to Voigt profiles and correlation effects were studied in terms of departure from Voigt behavior. For the case of an r^{-3} potential the model leads to Voigt profiles just as with conventional theory. However, resonance broadening is a more complicated phenomenon involving exchange of excitation which the present theory does not consider so that the applicability of this result remains open to question. Our main concern was with foreign gas broadening and here we found that correlation effects are relatively insensitive to choice of power in the interaction potential (r^{-6} or r^{-12}) which suggests that the simple model adequately displays the range and behavior of correlation effects.

Generally we may characterize the model OIL profiles as being slightly narrower in the core than corresponding Voigt profiles and with nearly Voigt wings. Except when the shift parameter Δ is vanishingly small, the OIL profile is asymmetric and has maximum intensity shifted by an amount less than the corresponding Voigt profile. Considerable attention was given to the question of errors in the width, shift and Doppler parameters (Γ', Δ' and ω_D') that result if OIL profiles are analyzed as Voigt profiles. When $\Gamma \lesssim 0{\cdot}1$ we find that an analysis based on using the FWHM value to determine ω_D' and a fit of the asymptotic Voigt wing expansion at frequencies greater than $5\omega_D'$ to determine Γ' leads to errors of $\lesssim 1$ per cent. When full Voigt analysis is employed, correlation effects were found to lead to the following kinds of behavior: dependence of Γ' and ω_D' on choice of fitting points, non-linear density dependence in Γ' and Δ' with concomittant extrapolation anomalies at zero density, and significant variations in ω_D' which may result in systematic errors in density if temperatures are inferred from ω_D'. All correlation effects are functions of the perturber/radiator mass ratio λ and systems with $\lambda \geq 5$ will probably have to be used in experimental investigations. Also close attention will have to be given to the problem of instrumental profile which tends to mask correlation effects when conventional methods of analysis are used.

With the possible exception of systematic errors in the density, correlation effects do not seem to have affected previous work on line broadening primarily because only $\lambda \lesssim 2$ systems have been extensively investigated. Also the broadening constant (slope of linear region of width vs density curve) turns out to be rather insensitive to correlation effects, especially in the presence of a Lorentzian component to the instrumental profile. The conclusion is that correlation between Doppler and pressure broadening warrants further theoretical work (more general potentials and removal of OIL restriction) and careful experimental investigation but the results are not likely to significantly alter either the kind of information available from line broadening studies or the means of obtaining that information.

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APPENDIX

To derive the distribution function for collisional phase and velocity changes we first consider a collision in the frame of reference where the radiator is initially at rest and the perturber is incident with velocity $\mathbf{u}_0$ along the z axis. The perturber scatters with a final velocity $\mathbf{u}$ in the direction θ and the radiator recoils with a final velocity $\mathbf{v}$ making an angle ψ the z axis. Conservation of energy and momentum leads to (MARION,[59] p. 325)

$$v = \frac{2\mu}{M} u_0 \cos\psi \tag{A1}$$

where μ is the reduced mass of the radiator–perturber system. The relation between radiator recoil angle ψ and the center of mass scattering angle Θ is given simply by (MARION,[59] p. 322)

$$2\psi = \pi - \Theta. \tag{A2}$$

Consequently the probability for a recoil angle ψ can be expressed in terms of the probability for scattering through an angle Θ in the center of mass frame. This probability is simply the ratio of the differential center of mass scattering cross section to the total elastic cross section. Unfortunately, in classical scattering theory, the total cross section is in general undefined (MARION,[58] p. 334; GOLDSTEIN,[60] p. 85) so we introduce an interaction sphere of radius R outside of which the potential is assumed to vanish. This results in a total cross section $\sigma_t = \pi R^2$.

With this definition of σ_t the probability of radiator recoil with velocity $\mathbf{v}$ is

$$P(\mathbf{v}; \mathbf{u}_0)\, d^3v = -\frac{1}{\sigma_t}\sigma(\Theta, u_0)\sin\Theta\, d\Theta\, d\phi_{CM}\delta\left(v - \frac{2\mu}{M}u_0\cos\psi\right)dv$$

$$= \frac{4}{\sigma_t v^2}\delta\left(v - \frac{2\mu}{M}u_0\cos\psi\right)\sigma(\pi - 2\psi, u_0)\cos\psi$$

$$\times v^2 \sin\psi\, dv\, d\psi\, d\phi_v$$

$$= \frac{4}{\sigma_t v^2}\delta\left(v - \frac{2\mu}{M}\mathbf{u}_0\cdot\hat{\mathbf{v}}\right)\sigma(\pi - 2\cos^{-1}\hat{\mathbf{u}}_0\cdot\hat{\mathbf{v}}, u_0)\hat{\mathbf{u}}_0\cdot\hat{\mathbf{v}}\, d^3v. \tag{A3}$$

Here $\sigma(\Theta, u_0)$ is the center of mass differential scattering cross section with relative speed dependence introduced explicitly, the minus sign was introduced because of the opposite sign conventions on Θ and ψ, the center of mass azimuthal scattering angle ϕ_{CM} is related to the rest frame azimuthal recoil angle ϕ_v by an uninteresting constant and the transformation $\Theta \to \psi$ follows from (A2).

Now the joint probability $P(\phi, \mathbf{v}; \mathbf{u}_0)\, d\phi\, d^3v$, for a phase change ϕ and a radiator recoil velocity $\mathbf{v}$ in a collision with the radiator initially at rest and the perturber incident with velocity $\mathbf{u}_0$ is just

$$P(\phi, \mathbf{v}; \mathbf{u}_0)\, d\phi\, d^3v = P(\mathbf{v}; \mathbf{u}_0)\, d^3v\, P(\phi/\mathbf{v}; \mathbf{u}_0)\, d\phi \tag{A4}$$

where $P(\phi/\mathbf{v}; \mathbf{u}_0)\, d\phi$ is the conditional probability for a phase change ϕ subject to the condition of a recoil velocity $\mathbf{v}$. The phase change in a collision is assumed to depend only on impact parameter and relative speed, $\phi = \phi(\rho, v_R)$, so that $P(\phi/\mathbf{v}; \mathbf{u}_0)\, d\phi$ can be expressed in terms of still another conditional probability distribution. Let $w(\rho/\mathbf{v}; \mathbf{u}_0)\, d\rho$ be the probability of an impact parameter ρ subject to the condition of radiator recoil with velocity $\mathbf{v}$. Then

$$P(\phi/\mathbf{v}; \mathbf{u}_0) = \int_0^\infty d\rho\, w(\rho/\mathbf{v}; \mathbf{u}_0)\delta[\phi - \phi(\rho, u_0)] \tag{A5}$$

and

$$P(\phi, \mathbf{v}; \mathbf{u}_0) = \frac{4}{\sigma_t v^2}\delta\left(v - \frac{2\mu}{M}\mathbf{u}_0\cdot\hat{\mathbf{v}}\right)\sigma(\pi - 2\cos^{-1}\hat{\mathbf{u}}_0\cdot\hat{\mathbf{v}}, u_0)\hat{\mathbf{u}}_0\cdot\hat{\mathbf{v}}$$

$$\times \int_0^\infty d\rho w(\rho/\mathbf{v}; \mathbf{u}_0)\delta[\phi - \phi(\rho, u_0)]. \tag{A6}$$

This essentially solves the problem for perturbers incident with velocity $\mathbf{u}_0$ in the rest frame of the radiator. Let $P(\phi, \mathbf{v}; \mathbf{v}_0, \mathbf{v}_R)\, d\phi\, d^3v$ be the probability of a phase change ϕ and a new radiator velocity $\mathbf{v}$ in a collision event where the radiator initially has velocity $\mathbf{v}_0$ and the perturber initially has velocity $\mathbf{v}_R$ relative to the radiator. Then $P(\phi, \mathbf{v}; \mathbf{v}_0, \mathbf{v}_R)$ follows from (A6) by the replacements: $\mathbf{u}_0 \to \mathbf{v}_R$ and $\mathbf{v} \to \mathbf{v} - \mathbf{v}_0$. Hence

$$P(\phi, \mathbf{v}; \mathbf{v}_0, \mathbf{v}_R) = \frac{4}{\sigma_t w^2}\delta\left(w - \frac{2\mu}{M}\mathbf{v}_R\cdot\hat{\mathbf{w}}\right)\sigma(\pi - 2\cos^{-1}\hat{\mathbf{v}}_R\cdot\hat{\mathbf{w}}, v_R)$$

$$\times \hat{\mathbf{v}}_R\cdot\hat{\mathbf{w}}\int_0^\infty d\rho w(\rho/\mathbf{w}; \mathbf{v}_R)\delta[\phi - \phi(\rho, v_R)] \tag{A7}$$

where the velocity change vector, $\mathbf{w}$, has been defined as

$$\mathbf{w} = \mathbf{v} - \mathbf{v}_0 . \tag{A8}$$

The quantity of interest, $G(\phi, \mathbf{v}; \mathbf{v}_0)$ is just the average of $P(\phi, \mathbf{v}; \mathbf{v}_0, \mathbf{v}_R)$ over all collisions in which the radiator has velocity $\mathbf{v}_0$. From (2.5), (2.7) and (2.9) we have:

$$G(\phi, \mathbf{v}; \mathbf{v}_0) = \frac{1}{\nu_c(v_0)} \int \nu_c(\mathbf{v}_R ; \mathbf{v}_0) P(\phi, \mathbf{v}; \mathbf{v}_0, \mathbf{v}_R)\, \mathrm{d}^3 v_R \tag{A9}$$

$$\nu_c(\mathbf{v}_R ; \mathbf{v}_0) = n\sigma_t v_R f_m(\mathbf{v}_0 + \mathbf{v}_R) \tag{A10}$$

$$\nu_c(v_0)G(\phi, \mathbf{v}; \mathbf{v}_0) = \frac{4n}{w^2} \int \mathrm{d}^3 v_R v_R f_m(\mathbf{v}_0 + \mathbf{v}_R)\delta\left(w - \frac{2\mu}{M} \mathbf{v}_R \cdot \hat{\mathbf{w}}\right) \sigma(\pi - 2 \cos^{-1}\hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}}, v_R)$$
$$\times\, \hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}} \int_0^\infty \mathrm{d}\rho\, w(\rho/\mathbf{w}; \mathbf{v}_R)\delta[\phi - \phi(\rho, v_R)]. \tag{A11}$$

This is the general result. To obtain (3.14) we consider the case where there is a unique relation between impact parameter and scattering angle. This will be true of repulsive interactions and approximately true of realistic interatomic potentials under conditions appropriate to many line broadening problems. Then for azimuthally symmetric scattering

$$w(\rho/\mathbf{w}; \mathbf{v}_R) = \delta[\rho - \rho(\hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}}, v_R)] \tag{A12}$$

where the function $\rho(\hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}}, v_R)$ giving the impact parameter corresponding to recoil angle $\cos^{-1} \hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}}$ at relative speed v_R is given by classical scattering theory (MARION,[59] p. 329; GOLDSTEIN,[60] p. 73). The ρ-integral in (A11) may be performed immediately giving (3.14).

The normalization condition may be verified by relatively straightforward integration of (3.14). The forward scattering limit is defined by a differential scattering cross section of the form

$$\sigma(\Theta, v_R) = \frac{\sigma_t}{2\pi}\, \delta(\cos \Theta - 1) \tag{A13}$$

in which case there is no longer a unique relation between impact parameter and scattering angle so that (A11) must be used with

$$w(\rho/\mathbf{w}; \mathbf{v}_R)\, \mathrm{d}\rho = \frac{2\pi\rho\, \mathrm{d}\rho}{\sigma_t}. \tag{A14}$$

From (A13) we have

$$\frac{4}{w^2}\, \hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}}\sigma(\pi - 2 \cos^{-1}\hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}}, v_R)\delta\left(w - \frac{2\mu}{M} \mathbf{v}_R \cdot \hat{\mathbf{w}}\right) = \frac{\sigma_t}{2\pi w^2}\, \delta(\hat{\mathbf{v}}_R \cdot \hat{\mathbf{w}})\delta(w)$$
$$= \sigma_t \delta(\mathbf{w}) \tag{A15}$$

and (3.18), (3.19) follow in a straightforward manner.

The time reversal symmetry relation (3.21) is easy but it appears that the detailed balance relation (3.22) requires evaluation of some of the integrations in (3.14). Put the $\mathbf{v}_R$-space z axis along $\hat{\mathbf{w}}$ and let $\mathbf{v}_0$ have spherical coordinates (v_0, θ_0, ϕ_0) so that

$$\mathbf{v}_R \cdot \mathbf{v}_0 = v_R v_0[\cos \theta_0 \cos \theta_R + \sin \theta_0 \sin \theta_R \cos(\phi_R - \phi_0)]. \tag{A16}$$

Then

$$G(\phi, \mathbf{v}; \mathbf{v}_0) = \frac{4n}{v_c(v_0)w^2} f_m(\mathbf{v}_0) \int_0^\infty \mathrm{d}v_R\, v_R{}^3 \exp(-mv_R{}^2/2kT)$$
$$\times \int_0^\pi \mathrm{d}\theta_R \sin\theta_R \cos\theta_R\, \sigma(\pi - 2\theta_R, v_R)\exp(-mv_0 v_R \cos\theta_0 \cos\theta_R/kT)$$
$$\times\, \delta\left(w - \frac{2\mu v_R}{M}\cos\theta_R\right)\delta\{\phi - \phi[\rho(\cos\theta_R, v_R), v_R]\}$$
$$\times \int_0^{2\pi} \mathrm{d}\phi_R \exp[-mv_0 v_R \sin\theta_0 \sin\theta_R \cos(\phi_R - \phi_0)/kT]. \tag{A17}$$

The ϕ_R-integral may be expressed in terms of the modified Bessel function $I_0(x)$ (GRADSHTEYN and RYZHIK,[61] No. 8.431.3, p. 958) and the v_R-integral may be performed with the first delta function provided the θ_R-integration is restricted to $0 \le \theta_R \le \pi/2$. Defining $z = (\cos\theta_R)^{-1}$ we obtain

$$G(\phi, \mathbf{v}; \mathbf{v}_0) = \frac{8\pi n w}{v_c(v_0)}\left(\frac{M}{2\mu}\right)^4 f_m(\mathbf{v}_0)\exp(-mM\mathbf{v}_0\cdot\mathbf{w}/2\mu kT)\int_1^\infty \mathrm{d}z z \exp(-mM^2w^2z^2/8\mu^2kT)$$
$$\times\, \sigma\left(\pi - 2\cos^{-1}\frac{1}{z}, \frac{Mwz}{2\mu}\right)$$
$$\times\, I_0\left(\frac{mM|\mathbf{v}_0\times\mathbf{w}|}{2\mu kT}\sqrt{z^2-1}\right)\delta\left(\phi - \phi\left[\rho\left(\frac{1}{z}, \frac{Mwz}{2\mu}\right), \frac{Mwz}{2\mu}\right]\right). \tag{A18}$$

The integrand is insensitive to the sign of $\mathbf{w}$ and from the identity

$$(M+m)v_0{}^2 + \frac{mM}{\mu}\mathbf{v}_0\cdot(\mathbf{v}-\mathbf{v}_0) = (M+m)v^2 + \frac{mM}{\mu}\mathbf{v}\cdot(\mathbf{v}_0-\mathbf{v}) \tag{A19}$$

we obtain

$$f_M(\mathbf{v}_0)f_m(\mathbf{v}_0)\exp(-mM\mathbf{v}_0\cdot\mathbf{w}/2\mu kT) = f_M(\mathbf{v})f_m(\mathbf{v})\exp(+mM\mathbf{v}_0\cdot\mathbf{w}/2\mu kT). \tag{A20}$$

The detailed balance condition (3.22) follows immediately.