PHYSICAL REVIEW A VOLUME 12, NUMBER 3 SEPTEMBER 1975

# Kinetic theory of spectral line broadening

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(Received 16 December 1974)

Recent developments in the kinetic theory of time correlation functions are applied to the problem of describing spectral line broadening in a fluid. The width and shift operator of Fano's formulation for dipole radiation is expressed in terms of the solution to a few-body problem, involving the shielded interaction of a single perturber with the radiating atom. No approximations are required in this reformulation, and previous theories of neutral and Stark broadening are shown to result from systematic small-parameter expansions to low order. A plasma-parameter expansion is suggested for the Stark-broadening case under usual experimental conditions, resulting in complete shielding of the atom-perturber interaction.

## I. INTRODUCTION

In the past decade a number of fruitful results have been obtained in the area of spectral line broadening with the application of new methods developed in many-body physics and nonequilibrium statistical mechanics.[1] Among these methods are projection-operator equations, Green's-function techniques, and cluster expansions. These results are of two types: (1) improved quantitative predictions of line shapes obtained by deriving new and tractable equations, and (2) improved understanding of existing equations by obtaining them from well-defined approximations to a specific theoretical formulation. Each type has played a role in developing present theories that are both predictive and descriptive. In this spirit, the work presented below is an application of recent developments in the kinetic theory of linear response and transport in fluids to the line-broadening problem. The motivation and derivation for these formally exact results are presented here, along with a discussion of the appropriate expansions leading to previously derived expressions for the line-shape function and suggestions for improvement. In a subsequent paper, application of these results to line broadening in dense fluids and plasmas will be described.

The problem of predicting the line-shape function for, say, dipole radiation from an atom in a fluid (neutral gas or plasma), is complex not only because of the atomic structure of the radiating atom, but also because of the many-body nature of the environment. The advantage of a kinetic-theory approach to such a problem is that it yields a reduction of the description to that of a few-body problem. For example, the Boltzmann-type equation for neutral pressure broadening[2] requires only calculation of the scattering of a single perturber and the atom. While this is still a difficult chore in general, it is relatively simple compared to treating a large number of perturbers at once. One of the shortcomings of most kinetic descriptions is their limitation to weakly interacting or dilute systems. In addition, even for experimental conditions of sufficiently low density where usual kinetic-theory results should hold, the *ad hoc* assumptions often introduced in the derivation of kinetic equations are not easily assessed and systematic corrections are difficult to formulate. For this reason the low-density results are often better understood in the context of other more complex many-body approaches (e.g., binary-collision expansion of the width and shift operator[3]). These latter approaches have their own disadvantages in that the full many-body problem must be confronted at an early stage in the analysis. Here, we wish to describe how a kinetic-theory approach may be used to effect the reduction to a few-body problem without the above-mentioned *ad hoc* assumptions, and extract without approximation the essential few-body ingredients of the line-shape function. The many-body aspects are retained in a form for which simple approximation leads to good results even in lowest order; for example, such approximations will (i) include all initial equilibrium correlations between atom and perturbers, (ii) be "unified" in the sense that the result is applicable over the whole frequency range, and (iii) be asymptotically exact for high frequencies. Property (i) means that this reduction to a few-body problem, which does not require the low-density or weak-coupling approximations, provides the potential for describing dense and strongly interacting systems. The advantages of reformulating the problem to provide a more suitable starting point have already been appreciated in Fano's work[4] and the subsequent projection-operator formulations[5] which demonstrate that better results are obtained from simple approximations to the width and shift operator than can be obtained easily from direct approximation

of the line-shape function. The reformulation here provides an explicit expression for the width and shift operator itself in terms of few-body operators before initiating any many-body analysis. As mentioned, in this form even the simplest descriptions lead to sophisticated descriptions of the line shape.

The formalism presented here is a direct application to line broadening of the recent work of Mazenko[6] on time correlation functions for fluids. The relationship of kinetic theory to the line-broadening problem is well known, and has recently been applied with considerable success by Voslamber.[7] The connection with this latter work will be noted below, and is discussed in the conclusion.

## II. GENERAL THEORY

### A. The kinetic equation

The main structure of the intensity of dipole radiation from an atom immersed in a surrounding fluid is contained in the line-shape function,[8]

$$I(\omega) = \pi^{-1}\,\mathrm{Re}\int_0^\infty dt\, e^{i\omega t}\langle \vec{d}\cdot\vec{d}(t)\rangle, \tag{2.1}$$

where $\langle\cdots\rangle$ denotes an equilibrium ensemble average for the system of radiating atom and fluid, and $\vec{d}$ is the atomic dipole operator. For clarity of presentation we do not include here the Doppler broadening, so that the average extends only over internal states of the atom. However, it is straightforward to include this in the same manner as in Ref. 2. The dipole autocorrelation function occurring in the integrand of Eq. (2.1) may be expressed in terms of atomic operators by first performing the average over the fluid subspace:

$$\begin{aligned}\langle \vec{d}\cdot\vec{d}(t)\rangle &= \mathrm{Tr}\,\vec{d}\cdot\vec{d}(t)\rho \\ &= \mathrm{Tr}_a\vec{d}\cdot[\mathrm{Tr}_f\rho\vec{d}(-t)], \\ \langle d\cdot d(t)\rangle &= \mathrm{Tr}_a\vec{d}\cdot\vec{F}(t).\end{aligned} \tag{2.2}$$

Here $\rho$ is the equilibrium density matrix for the atom and fluid. The subscripts $a$ and $f$ denote, respectively, traces over atomic and fluid subspaces. Also $\vec{F}(t)$ is related to the average dipole operator $\vec{D}$ at time $t$ by

$$\begin{aligned}\vec{F}(t) &= f(a)\vec{D}(t), \\ \vec{D}(t) &= f(a)^{-1}\mathrm{Tr}_f\rho\vec{d}(-t),\end{aligned} \tag{2.3}$$

where $f(a)$ is the atomic density matrix,

$$f(a) = \mathrm{Tr}_f\rho. \tag{2.4}$$

The equilibrium coupling of the atom and fluid is retained implicitly through the definition of $f(a)$. Equation (2.2) shows that to determine $I(\omega)$ it is sufficient to calculate the average dipole operator $\vec{D}(t)$, or equivalently $\vec{F}(t)$, in the atomic subspace rather than the many-body dipole operator $\vec{d}(t)$. In the kinetic-theory method an equation for $\vec{F}(t)$ is obtained; the solution to this equation then determines $I(\omega)$ through Eqs. (2.2) and (2.1). The difficulty with this approach lies in the fact that $\vec{F}(t)$ satisfies the first equation of an infinite hierarchy (the BBGKY hierarchy[9]) and some means of closure of this set must be devised. A set of functions satisfying this hierarchy is defined by

$$n^s\vec{F}^{(s)}(a;1,\ldots,s;t) = [N!/(N-s)!]\,\mathrm{Tr}_{s+1,\ldots,N}\rho\vec{d}(-t), \tag{2.5}$$

where $n = N/\Omega$ is the fluid density and the trace extends over the subspace of particles $s+1,\ldots,N$. The atomic operator $\vec{F}(a;t)$, defined by Eqs. (2.3), is the $s=0$ member of this set. Direct differentiation of Eq. (2.5) leads to the above-mentioned hierarchy, the first two equations of which are

$$\frac{\partial}{\partial t}\vec{F}(a;t) + iL(a)\vec{F}(a;t) + n\,\mathrm{Tr}_1 iL_1(a,1)\vec{F}^{(1)}(a;1;t) = 0, \tag{2.6a}$$

$$\frac{\partial}{\partial t}\vec{F}^{(1)}(a;1;t) + iL(a,1)\vec{F}^{(1)}(a;1;t) + n\,\mathrm{Tr}_2[iL_1(a,1) + iL_2(1,2)]\vec{F}^{(2)}(a;1,2;t) = 0. \tag{2.6b}$$

The various Liouville operators are defined, for arbitrary operators $O$, by

$$\begin{aligned}L(a;1,\ldots,s)O &\equiv [H(a,1,\ldots,s),O], \\ L_1(a,1)O &\equiv [V_1(a,1),O], \\ L_2(1,2)O &\equiv [V_2(1,2),O],\end{aligned} \tag{2.7}$$

and $H(a;1,\ldots,s)$ is the Hamiltonian for $s$ particles and the atom. $V_1(a,i)$ and $V_2(i,j)$ are, respectively, the interaction potential for the atom with the $i$th perturber and the interaction potential between the $i$th and $j$th perturbers. Equation (2.6a) for $\vec{F}$ depends on $\vec{F}^{(1)}$; Eq. (2.6b) for $\vec{F}^{(1)}$ depends on $\vec{F}^{(2)}$, etc. A closed equation for $\vec{F}(a;t)$ will be obtained using the linear dependence of these functions on the dipole operator $\vec{d}$. To describe how this closure may be made, we first note from Eq. (2.5) that at $t=0$,

$$\vec{F}^{(s)}(a;1,\ldots,s;t=0) = f^{(s)}(a;1,\ldots,s)\vec{d}, \tag{2.8}$$

where $f^{(s)}(a;1,\ldots,s)$ are the equilibrium reduced density matrices,

$$n^s f^{(s)}(a;1,\ldots,s) = [N!/(N-s)!]\,\mathrm{Tr}_{s+1,\ldots,N}\rho. \tag{2.9}$$

Then, using the Liouville representation for $d(-t)$,

$$\vec{\mathrm{d}}(-t) = e^{-iL(a;1,\ldots,N)t}\vec{\mathrm{d}}, \tag{2.10}$$

Eq. (2.5) may be written for $t \neq 0$ in the compact form,

$$\vec{\mathbf{F}}^{(s)}(a;1,\ldots,s;t) = U(a;1,\ldots,s;t) \times f^{(s)}(a;1,\ldots,s)\vec{\mathrm{d}}, \tag{2.11}$$

$$U(a;1,\ldots,s;t) \equiv [N!/n^s(N-s)!] \times \mathrm{Tr}_{s+1,\ldots,N}\rho e^{-iL(a;1,\ldots,N)t} \times [f^{(s)}(a;1,\ldots,s)]^{-1}, \tag{2.12}$$

or, using Eq. (2.8),

$$\vec{\mathbf{F}}^{(s)}(a;1,\ldots,s;t) = U(a;1,\ldots,s;t) \times \vec{\mathbf{F}}^{(s)}(a;1,\ldots,s;t=0). \tag{2.13}$$

Therefore, $U(a;1,\ldots,s;t)$ is the time-development operator in the subspace of the atom and the $s$ perturbers. Furthermore, it is clear from the definition (2.12) that $U$ is a linear operator. Before proceeding, we note that it is actually the Laplace transform of $\vec{\mathbf{F}}(a;t)$ that is required for the line-shape function [Eq. (2.1)], and it will be convenient to consider as well the Laplace transformed $\vec{\mathbf{F}}^{(s)}$. Denoting the transform of a function or operator $g(t)$ by $\hat{g}(\omega)$,

$$\hat{g}(\omega) \equiv \int_0^\infty dt\, e^{i\omega t} g(t),$$

then Eq. (2.13) gives

$$\hat{\vec{\mathbf{F}}}^{(s)}(a;1,\ldots,s;\omega) = \hat{U}(a;1,\ldots,s;\omega) \times \vec{\mathbf{F}}^{(s)}(a;1,\ldots,s;t=0), \tag{2.14}$$

$$\hat{\vec{\mathbf{F}}}(a;\omega) = \hat{U}(a;\omega) f(a)\vec{\mathrm{d}}. \tag{2.15}$$

This result may be formally inverted for $\vec{\mathrm{d}}$ and substituted into (2.14) for general $s$ so that

$$\hat{\vec{\mathbf{F}}}^{(s)}(a;1,\ldots,s;\omega) = \hat{K}'(a;1,\ldots,s;\omega)\vec{\mathbf{F}}(a;\omega), \tag{2.16}$$

$$\hat{K}'(a;1,\ldots,s;\omega) \equiv \hat{U}(a;1,\ldots,s;\omega) \times f^{(s)}(a;1,\ldots,s) f^{-1}(a)\hat{U}^{-1}(a;\omega). \tag{2.17}$$

Noting that $\hat{K}'(a;1,\ldots,s;\omega=\infty)$ is nonzero, it is convenient to rewrite Eq. (2.16) as

$$\hat{\vec{\mathbf{F}}}^{(s)}(a;1,\ldots,s;\omega) = \hat{K}'(a;1,\ldots,s;\omega=\infty)\hat{\vec{\mathbf{F}}}(a;\omega) + \hat{K}(a;1,\ldots,s;\omega)\hat{\vec{\mathbf{F}}}(a;\omega), \tag{2.18}$$

where

$$\hat{K}(a;1,\ldots,s;\omega) \equiv \hat{K}'(a;1,\ldots,s;\omega) - \hat{K}'(a;1,\ldots,s;\omega=\infty) = \hat{U}(a;1,\ldots,s;\omega) \times f^{(s)}(a;1,\ldots,s) f^{-1}(a)\hat{U}^{-1}(a;\omega) - f^{(s)}(a;1,\ldots,s) f^{-1}(a). \tag{2.19}$$

A kinetic equation for $\vec{\mathbf{F}}(a;t)$ follows by inverting the transform in Eq. (2.18) and substituting into the first equation of the hierarchy, (2.6a):

$$\frac{\partial}{\partial t}\vec{\mathbf{F}}(a;t) + iL(a)\vec{\mathbf{F}}(a;t) = B\vec{\mathbf{F}}(a;t) + \int_0^t d\tau\, M(t-\tau)\vec{\mathbf{F}}(a;\tau), \tag{2.20}$$

with

$$B \equiv -n\,\mathrm{Tr}_1 iL_1(a,1) f^{(2)}(a,1) f^{-1}(a), \tag{2.21}$$

$$M(t) = -n\,\mathrm{Tr}_1 iL_1(a,1) K(a;1;t). \tag{2.22}$$

Equation (2.20) is a closed equation for $\vec{\mathbf{F}}(a;t)$ although the operator $M(t)$ is not as simple as the operators occurring in the hierarchy. Furthermore, from the definitions (2.19) and (2.22) the second term on the right-hand side of Eq. (2.20) vanishes at $t \to 0$, so that $[B - iL(a)]$ may be considered a generator of time translations that is exact in the short-time limit; i.e., Eq. (2.20) with the neglect of the last term on the right is an asymptotically exact kinetic equation for short times. Such an approximation leads to a quite simple result for the line-shape function that is exact in the far wings. Further investigation shows, however, that this result is not applicable to the present experimental range so that contributions from $M$ must be retained. It is apparent from Eq. (2.21) that $B$ is a mean field, or Hartree-Fock type of term. It will be shown that $M$ is of second order, or higher, in the atom-fluid interaction and represents collisional effects that require finite times. For this reason $M$ will be referred to as the "collision operator."

### B. The collision operator $M$

The formal definition of the Laplace transform of $M$ is readily identified from Eqs. (2.22):

$$\hat{M}(\omega) \equiv -n\,\mathrm{Tr}_1 iL_1(a,1)\hat{K}(a;1;\omega). \tag{2.23}$$

To expose the structure of $\hat{M}(\omega)$, an equation for $\hat{K}$ will first be obtained and then substituted into Eq. (2.23). The idea here, due to Mazenko, is to make use of a formal closure of the second equation of the hierarchy in much the same way as that used to get the kinetic equation (2.20). To do this, we take the Laplace transform of the second equation of the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy to get

$$[-i\omega + iL(a,1)]\hat{\vec{F}}^{(1)}(a;1;\omega) + n\,\mathrm{Tr}_2 iL(a,2)\hat{\vec{F}}^{(2)}(a;1,2;\omega) = f^{(1)}(a;1)\vec{d}. \tag{2.24}$$

Then, recognizing that $\hat{F}^{(s)}(a;1,\ldots,s;\omega)$ and $\hat{K}(a;1,\ldots,s;\omega)$ are related by Eq. (2.18), an equation for $\hat{K}(a;1;\omega)$ may be obtained

$$[-i\omega + iL(a,1)]\hat{K}(a;1;\omega) - f^{(1)}(a,1)f^{-1}(a)n\,\mathrm{Tr}_2 iL_1(a,2)\hat{K}(a;2;\omega)$$
$$+ n\,\mathrm{Tr}_2[iL_1(a,2) + iL_2(1,2)]\hat{K}(a;1,2;\omega) = -f^{(1)}(a,1)i\mathcal{L}(a,1)f^{-1}(a). \tag{2.25}$$

The effective atom-perturber interaction operator $i\mathcal{L}(a,1)$ is defined by

$$i\mathcal{L}(a,1) = iL_1(a,1) + [f^{(1)}(a,1)]^{-1}n\,\mathrm{Tr}_2[f^{(2)}(a;1,2) - f^{(1)}(a;1)f^{-1}(a)f^{(1)}(a;2)]iL_1(a,2). \tag{2.26}$$

Equation (2.25) is equivalent to the second equation of the BBGKY hierarchy; it is not a closed equation for $\hat{K}(a;1;\omega)$ since it is coupled to $\hat{K}(a;1,2;\omega)$. However, a closure relation expressing $\hat{K}(a;1,2;\omega)$ in terms of $\hat{K}(a;1;\omega)$ is obtained by noting that $\hat{K}(a;1;\omega)$ and $\hat{K}(a;1,2;\omega)$ may be written in the form [see Eqs. (A4) and (A6) of Appendix A]

$$\hat{K}(a;1;\omega) = G(a;1;\omega)iL_1(a,1)f^{-1}(a),$$
$$\hat{K}(a;1,2;\omega) = G(a;1,2;\omega)iL_1(a,1)f^{-1}(a), \tag{2.27}$$

where $G(a;1;\omega)$ and $G(a;1,2;\omega)$ are defined by Eqs. (A5) and (A7). Then,

$$\hat{K}(a;1,2;\omega) = G(a;1,2;\omega)G^{-1}(a;1;\omega)\hat{K}(a;1;\omega). \tag{2.28}$$

This is the desired closure relation. Use of Eq. (2.28) in (2.25) gives the kinetic equation for $\hat{K}(a;1;\omega)$

$$[-i\omega + iL(a,1) + iV(a;1;\omega)]\hat{K}(a;1;\omega) = -f^{(1)}(a,1)i\mathcal{L}(a,1)f^{-1}(a), \tag{2.29}$$

where

$$iV(a;1;\omega) = -f^{(1)}(a,1)f^{-1}(a)n\,\mathrm{Tr}iL_1(a,2)P_{12} + n\,\mathrm{Tr}_2[iL_1(a,2) + iL_2(1,2)]G(a;1,2;\omega)G^{-1}(a;1;\omega). \tag{2.30}$$

This kinetic equation may be solved for $\hat{K}(a;1;\omega)$ and substituted into (2.23) to give the desired form for the collision operator.

In summary, the line-shape function, as given by Eqs. (2.10), (2.2), (2.20), (2.23), and (2.29) is

$$I(\omega) = \pi^{-1}\,\mathrm{Re}\,\mathrm{Tr}_a\vec{d}[-i\omega + iL(a) - B - \hat{M}(\omega)]^{-1}f(a)\vec{d}, \tag{2.31}$$

$$\hat{M}(\omega) = n\,\mathrm{Tr}_1 iL_1(a,1)[-i\omega + iL(a,1) + iV(a;1;\omega)]^{-1}f^{(1)}(a,1)i\mathcal{L}(a,1)f(a)^{-1} \tag{2.32}$$

and where $B$ and $\mathcal{L}$ are defined, respectively, by Eqs. (2.21) and (2.26). Equations (2.31) and (2.32) are the main results of this paper. The collision operator $\hat{M}(\omega)$ has been expressed without approximations in terms of a one perturber-atom scattering problem and an effective interaction $V(a;1;\omega)$. As will be demonstrated in the next sections, the most important contributions from $V(a;1;\omega)$ are contained in $V(a;1;\omega=\infty)$ for which an explicit form is obtained. Of course, it is possible to display more completely the structure of $V(a;1;\omega)$ itself by repeating the above analysis using the third equation of the hierarchy. This will not be required here.

## III. SMALL-PARAMETER EXPANSIONS

The line-shape function given by (2.30) and (2.31) is exact and in a form suitable for approximation; only the operator $\hat{M}(\omega)$ causes any difficulty in the calculation, and that through its dependence on the formal operator $V(a;1;\omega)$. However, even if $V(a;1;\omega)$ is neglected entirely one is still left with a description of pressure broadening that is an improvement over the usual Boltzmann-impact result in that it (i) describes both the impact ($\omega \to 0$) and quasistatic ($\omega \to \infty$) limits and (ii) includes correlations [through $\mathcal{L}(a,1)$] between atom and perturber. Thus, in this form the crudest approximation to the theory leads to very good results; hence it may be expected that systematic approximations to the line-shape function can be generated through expansions of $V(a;1;\omega)$ and $\mathcal{L}(a,1)$. [In this way properties (i) and (ii) may be preserved in any order approximation.] An important point with regard to (i) is that strong collisions are always represented in each approximation through the presence of $L_1(a,1)$ in the denominator of the expression for $\hat{M}(\omega)$ [Eq. (2.31)]. Such theories have been termed "unified." Before describing the

expansions of $V(a;1;\omega)$ and $\mathfrak{L}(a,1)$, it is convenient to write $V(a;1;\omega)$ as

$$iV(a;1;\omega) = iV(a;1;\omega=\infty) + i\Delta(a;1;\omega), \tag{3.1}$$

where Eq. (3.1) defines $\Delta(a;1;\omega)$. The separation of the high-frequency limit from the remainder is useful because $V(a;1;\omega=\infty)$ has a relatively simple structure, and most of the low-order contributions come entirely from $V(a;1;\omega=\infty)$. The form of $V(a;1;\omega=\infty)$ may be identified from Eq. (2.29):

$$iV(a;1;\omega=\infty) = -f^{(1)}(a,1)f^{-1}(a)n\,\mathrm{Tr}_2 iL_1(a,2)P_{12} + n\,\mathrm{Tr}_2[iL_1(a,2)+iL_2(1,2)][G(a;1,2;\omega)G^{-1}(a;1;\omega)]_{\omega=\infty}. \tag{3.2}$$

The operator $[G(a;1,2;\omega)G^{-1}(a;1;\omega)]_{\omega=\infty}$ may be written as

$$[i\omega G(a;1,2;\omega)]_{\omega=\infty}[i\omega G(a;1;\omega)]^{-1}_{\omega=\infty}$$

where [see Eqs. (A8) and (A9) of Appendix A]

$$[i\omega G(a;1;\omega)]_{\omega=\infty} = f^{(1)}(a;1) + n\,\mathrm{Tr}_2[f^{(2)}(a;1,2) - f^{(1)}(a;1)f^{-1}(a)f^{(1)}(a;2)]P_{12}, \tag{3.3}$$

$$[i\omega G(a;1,2;\omega)]_{\omega=\infty} = f^{(2)}(a;1,2)(1+P_{12}) + n\,\mathrm{Tr}_3[f^{(3)}(a;1,2,3) - f^{(2)}(a;1,2)f^{-1}(a)f^{(1)}(a;3)]P_{13}. \tag{3.4}$$

The important point here is that the operator $iV(a;1;\omega=\infty)$ is linear in the interactions $L_1$ and $L_2$, and otherwise depends on the perturbers only through low-order equilibrium distribution functions $f^{(s)}$. Furthermore, it also follows from Eq. (2.29) that $i\Delta(a;1;\omega)$ is second order in these interactions. This separation of $iV(a;1;\omega)$ into its high-frequency part and $i\Delta(a;1;\omega)$ is similar to the separation of the interaction term in the kinetic equation for $\vec{F}(a;\omega)$ into the terms with $B$ and $\hat{M}(\omega)$, respectively. Analogous to the latter case, $iV(a;1;\omega=\infty)$ may be considered as a mean-field contribution for the atom and a perturber colliding in the presence of the remaining perturbers, while $i\Delta(a;1;\omega)$ describes genuine multiple perturber collision effects. It is now straightforward to consider some results obtained by expanding $iV(a;1;\omega)$ and $\mathfrak{L}(a,1)$ in the various parameters available. Only the lowest-order results will be given, rather than a discussion of the general structure.

### A. Density expansion

If the perturbers form a low-density gas, and if the range of interaction among perturbers is not too large (e.g., excluding Coulomb forces) a density expansion of $iV(a;1;\omega)$ may be appropriate:

$$iV(a;1;\omega) = iV^{(0)}(a;1;\omega) + niV^{(1)}(a;1;\omega) + \cdots,$$

$$i\mathfrak{L}(a;1) = i\mathfrak{L}^{(0)}(a;1) + ni\mathfrak{L}^{(1)}(a;1) + \cdots.$$

It is readily seen from Eqs. (2.29) and (2.25) that $iV^{(0)}(a;1;\omega)=0$ and $i\mathfrak{L}^{(0)}(a;1) = iL_1(a,1)$; so to lowest order in the density, the line-shape function is

$$I^{(0)}(\omega) = \pi^{-1}\,\mathrm{Re}\,\mathrm{Tr}_a\vec{d}[-i\omega + iL(a) - M^{(0)}(\omega)]^{-1}f(a)\vec{d}, \tag{3.5}$$

$$M^{(0)}(\omega) = n\,\mathrm{Tr}_1 iL_1(a,1)[-i\omega + iL(a,1)]^{-1} \times f_0^{(1)}(a,1)iL_1(a,1)f(a)^{-1}. \tag{3.6}$$

Here $f_0^{(1)}$ is the low-density limit of $f^{(1)}$ and use has been made of the fact that $B$ does not contribute to this order. The results (3.5) and (3.6) are similar (although not identical[10]) to the unified theory of pressure broadening[2] and is seen here to result from the low-density limit to $iV(a;1;\omega)$ and $i\mathfrak{L}(a,1)$. It is also the leading term in the density expansion of $\hat{M}(\omega)$ itself, as is well known. It is not very profitable to pursue the corrections to the lowest order in the density as there appear to be nonanalyticities like $n^2\ln n$ in subsequent orders. An alternative suggestion for dense fluids will be given elsewhere.

### B. Expansion in the interaction

For a weakly coupled fluid (small momentum transfer), a direct expansion of $iV(a;1;\omega)$ and $i\mathfrak{L}(a,1)$ may be considered. If we introduce coupling constants $\lambda_1$ and $\lambda_2$ for the atom-perturber and perturber-perturber interactions, respectively, then

$$\begin{aligned} iV(a;1;\omega) &= iV^{(0,0)}(a;1;\omega) + \lambda_1 iV^{(1,0)}(a;1;\omega) \\ &\quad + \lambda_2 iV^{(0,1)}(a;1;\omega) + \cdots, \\ i\mathfrak{L}(a;1;\omega) &= i\mathfrak{L}^{(0,0)}(a,1) + \lambda_1 i\mathfrak{L}^{(1,0)}(a;1) \\ &\quad + \lambda_2 i\mathfrak{L}^{(0,1)}(a;1) + \cdots. \end{aligned} \tag{3.7}$$

Equations (2.29) and (2.25) show immediately that $iV^{(0,0)} = i\mathfrak{L}^{(0,0)} = i\mathfrak{L}^{(0,1)} = 0$. Furthermore, since $\Delta(a;1;\omega)$ in Eq. (3.1) is of second order, $iV^{(1,0)}$ and $iV^{(0,1)}$ may be determined from (3.2). The results to first order are

$$i\mathfrak{L}^{(1,0)} = iL_1(a,1), \quad iV^{(1,0)} = 0, \quad iV^{(0,1)} = H(1),$$

where $H(1)$ is the Vlasov operator,

$$H(1) \equiv n\,\mathrm{Tr}_2 iL_2(1,2)f(1)P_{12}.$$

The line-shape function to lowest order in this expansion is therefore,

$$I^{(0)}(\omega)=\pi^{-1}\,\mathrm{Re}\,\mathrm{Tr}_a\vec{d}[-i\omega+iL(a)+B^{(0)}-M^{(0)}(\omega)]^{-1}\times f(a)\vec{d}, \tag{3.8}$$

$$M^{(0)}(\omega)=n\,\mathrm{Tr}_1 L_1(a,1)[-i\omega+iL(a,1)+H(1)]^{-1}\times f(a)f(1)L_1(a,1)f^{-1}. \tag{3.9}$$

This result is similar to that of the density expansion except for the presence of the Vlasov operator $H(1)$. This is important if the perturbers interact through long-range forces as in a plasma since the mean field of the background distorts the straight-line motion of the perturbers between collisions. However, the expansion in the perturber-perturber interaction is not suitable for a plasma, except for "soft" collisions. A more suitable expansion parameter is the plasma parameter $(nL_D^3)^{-1}$, where $L_D$ is the Debye length, and is typically of the order of $10^{-2}$ for most present experimental conditions. In Sec. IV the operator $\hat{M}(\omega)$ is expressed in a form suitable for the introduction of an expansion in the atom-perturber interaction and the plasma parameter.

## IV. PLASMA LINE BROADENING

Typically in plasma-line-broadening theories the ions are essentially static over most of the line profile, and their effect is treated approximately through the introduction of an ion microfield distribution. This separate treatment of the ions and electrons will not be made explicitly in the following, with the understanding that the free-atom Liouville operator $iL(a)$ may be generalized to include an ion microfield contribution. To introduce a suitable systematic approximation scheme based on the atom-perturber interaction and the plasma parameter, the width and shift operator will be expressed in the suggestive form of an effective binary-collision operator. It is shown in Appendix B that the collision operator $\hat{M}(\omega)$ given by Eq. (2.32) is of the form,

$$\hat{M}(\omega)=n\,\mathrm{Tr}_1 iL_1(a,1)f^{(1)}(a,1)\times[-i\omega+iL(a)+iL(1)+i\mathfrak{L}(a,1)+C(a;1;\omega)]^{-1}\times i\mathfrak{L}(a,1)f^{-1}(a). \tag{4.1}$$

The essential point of Eq. (4.1) is the observation that the operator $iV(a;1;\omega)$ contains a term $i\mathfrak{L}(a,1)$. The remainder, denoted by $C(a;1;\omega)$, is defined in Appendix B and contains Vlasov-like mean-field operators and the multiple collision effects of $\Delta(a;1;\omega)$ [see Eq. (3.1)]. A generalized binary-collision operator, or $T$ matrix, may be defined as

$$T(a;1;\omega)f^{(1)}(a;1)R_0(a;1;\omega)=iL_1(a,1)f^{(1)}(a,1)\times R(a;1;\omega), \tag{4.2}$$

where

$$R(a;1;\omega)=[-i\omega+iL(a)+iL(1)+i\mathfrak{L}(a,1)+C(a;1;\omega)]^{-1},$$

$$R_0(a;1;\omega)=[-i\omega+iL(a)+iL(1)+C(a;1;\omega)]^{-1}.$$

Use of the identity $R=R_0-Ri\mathfrak{L}R_0$ in (4.2) yields

$$Tf^{(1)}=iL_1f^{(1)}-Tf^{(1)}R_0i\mathfrak{L}. \tag{4.3}$$

Iteration of this equation shows that $T$ consists of a sum of terms each representing a sequence of interactions represented by $i\mathfrak{L}$ (except for the first one), with propagation between interactions represented by $R_0$. The effect of the surrounding fluid on the atom-perturber collision is twofold; the interaction $iL_1(a,1)$ is replaced by the shielded interaction, $i\mathfrak{L}(a,1)$, and the "free" motion of atom and perturber is replaced by propagation $R_0$ in the background of the surrounding fluid. The utility of this $T$ operator may be seen by writing the total width and shift operator, $B+\hat{M}(\omega)$, given by Eqs. (2.21) and (4.1), as

$$B+\hat{M}(\omega)=-n\,\mathrm{Tr}_1[iL_1(a,1)f^{(1)}(a,1)-iL_1(a,1)f^{(1)}(a,1)R(a;1;\omega)\times i\mathfrak{L}(a,1)]f^{-1}(a). \tag{4.4}$$

Use of Eqs. (4.2) and (4.3) give the desired result,

$$[B+\hat{M}(\omega)]=-n\,\mathrm{Tr}_1 T(a;1;\omega)f^{(1)}(a,1)f^{-1}(a). \tag{4.5}$$

This is of the same form as the binary-collision approximation, with the two-body scattering operator replaced by $T(a;1;\omega)$ and the initial correlation of atom and perturber included through $f^{(1)}(a,1)$. The result (4.5) is exact and holds both for quantum systems and in the classical limit.

Approximate forms for $T(a;1;\omega)$ may be obtained by expanding $i\mathfrak{L}(a,1)$ and $R_0(a;1;\omega)$. Here, these quantities will be calculated to lowest order in the atom-perturber interaction and the plasma parameter. In the following, classical mechanics is used to represent usual experimental conditions. For quantum systems there is, in addition to the plasma parameter, another dimensionless parameter characterizing the degeneracy. To lowest order in this expansion, one finds, for an arbitrary atomic operator $y(a)$,

$$\mathfrak{L}^{(0)}(a,1)y(a)=[V_s(a,1),y(a)], \tag{4.6}$$

$$V_s(a,1)=V(a,\vec{r}_1)+n\int d\vec{r}_2\,[g(\vec{r}_1-\vec{r}_2)-1]V(a,\vec{r}_2), \tag{4.7}$$

where $V_s(a,1)$ is the shielded potential and $g(\vec{r})$ is the Debye-Hückel radial distribution function.[11] Similarly, to lowest order $R_0$ is given by

$$R_0^{(0)}(a;1;\omega) = [-i\omega + iL(a) + iL(1) + \tilde{H}(1)]^{-1}, \quad (4.8)$$

where $\tilde{H}(1)$ is the Vlasov operator defined by Eq. (B9) of Appendix B. Equation (4.8) shows that to lowest order the propagator in the $T$ operator is simply the free propagator modified by the background through the mean Vlasov field of all the other perturbers. The resulting approximation to $T$ yields a width and shift operator, to lowest order,

$$[B + \hat{M}(\omega)]^{(0)} = -n \int d\vec{p}_1\, d\vec{r}_1\, T^{(0)}(a;1;\omega) f^{(1)}(a;1) f^{-1}(a)$$

or

$$[B + \hat{M}(\omega)]^{(0)} = B + n \int d\vec{r}_1\, d\vec{p}_1\, iL_1(a,1) f^{(1)}(a,1)[-i\omega + iL(a) + iL(1) + \tilde{H}(1) + i\mathcal{L}^{(0)}(a,1)]^{-1} i\mathcal{L}^{(0)}(a,1) f^{-1}(a). \quad (4.9)$$

The second term is essentially the result of Voslamber, with one significant difference. The interaction operator in the denominator of this term is the shielded interaction, $i\mathcal{L}^{(0)}(a,1)$, rather than the "bare" interaction, $iL_1(a,1)$. As shown by Voslamber, the effect of the Vlasov operator is to dynamically shield the remaining bare interaction, so Eq. (4.9) represents a binary-collision operator with *all* interactions shielded.

The result is found to be

$$\hat{M}^{(0)}(\omega) = n \int \frac{d\vec{k}}{(2\pi)^3} \frac{d\vec{k}'}{(2\pi)^3} i\mathcal{L}(a;k;\omega)\, \mathcal{G}(k,k';\omega)\, i\mathcal{L}^{(0)}(a;k) f^{-1}(a), \quad (4.10)$$

with

$$\mathcal{G}(\vec{k},\vec{k}';\omega) = \int d\vec{r}_1\, d\vec{p}_1\, e^{i\vec{k}\cdot\vec{r}_1} f(a,1)[-i\omega + iL(a) + iL(1) + i\mathcal{L}^{(0)}(a;1)]^{-1} e^{-i\vec{k}'\cdot\vec{r}_1}, \quad (4.11)$$

$$i\mathcal{L}(a;\vec{k};\omega) = \int \frac{dk'}{(2\pi)^3} iL_1(a,\vec{k}')\epsilon^{-1}(\vec{k}',\vec{k};\omega) \quad (4.12)$$

and $\epsilon^{-1}(\vec{k}',\vec{k};\omega)$ is a generalized dielectric function that reduces, to lowest order in the atomic-perturber interaction, to the usual dielectric function $\epsilon(k,\omega - L(a))$. Thus $\mathcal{L}(a;\vec{k};\omega)$ is a dynamically shielded interaction. The results, (4.9) and (4.10), are equivalent, although the latter shows explicitly that all interactions are shielded.

## V. DISCUSSION

The line-shape function $I(\omega)$ has been expressed in terms of the solution to an effective two-body atom-perturber collision problem using kinetic theory. The main results, Eqs. (2.32) or (4.5), are exact and valid for both classical and quantum mechanics. Some of the advantages of this formulation are that (i) the two-body nature of the collision operator is displayed explicitly and separated from the more complicated many-body effects *before* any approximations are introduced; (ii) the initial static correlations of the atom and fluid are included through low-order equilibrium distribution functions such as $f^{(1)}(a,1)$; (iii) the atom-perturber interaction occurs through $i\mathcal{L}(a,1)$ shielded by the equilibrium distribution functions; (iv) the simplest approximation to the effective binary-collision operator $T^{(0)}(a;1;\omega)$ is unified, fully shielded, and the leading term in a systematic expansion procedure; (v) the exact formulation is sufficiently general to provide the framework for discussion of more complex line structure and to suggest phenomenological descriptions of such problems. An example of this last advantage is the prediction of line spectra from atoms in dense fluids which, as mentioned above, will be discussed elsewhere.

It was noted in the last section that the approximate collision operator obtained from expansion in the atom-perturber interaction and plasma parameter differs from the theory of Voslamber mainly by the appearance of $i\mathcal{L}(a,1)$ instead of $iL_1(a,1)$ in the denominator of the integrand in Eq. (4.9). This difference may be traced to the uniform application of the plasma-parameter expansion of the fluid properties rather than an expansion in the perturber-perturber interaction. It is interesting to see how this result provides justification for the assumptions of Smith, Cooper, and Vidal in their unified theory.[5] The latter is essentially the low-density result, Eq. (3.6), applied to a plasma by assuming the charged perturbers behave as "quasiparticles" with short-ranged inter-

action. To see that this assumption is justified, consider the results (4.10)–(4.12) with the dielectric function $\epsilon^{-1}(k,k';\omega)$ approximated by neglecting its dependence on $L_1(a,1)$. Then it is easily shown that

$$\lim_{\omega\to 0} \mathfrak{L}(a;k;\omega) \to \mathfrak{L}^{(0)}(a;1).$$

So, with this estimate for $\mathfrak{L}(a;k;\omega)$, Eq. (4.10) becomes

$$\hat{M}^{(0)}(\omega) \to n \int d\vec{p}_1\, d\vec{r}_1\, i\mathfrak{L}^{(0)}(a;1) f(a,1) \times [-i\omega + iL(a) + iL(1) + i\mathfrak{L}^{(0)}(a;1)]^{-1} \times i\mathfrak{L}^{(0)}(a,1) f^{-1}(a). \tag{5.1}$$

This is just the low-density result (3.6) with the actual atom-perturber interaction replaced by the shielded interaction $i\mathfrak{L}^{(0)}$. In this sense, Eq. (5.1) represents the collision operator for an atom in the presence of a noninteracting gas of "quasiparticles" that interact with the atom through the shielded potential given in (4.7); this is precisely the assumption of Smith, Cooper, and Vidal. The effect of the frequency dependence of the shielding in $i\mathfrak{L}(a;k;\omega)$ on the line shape is presently under study for the Lyman-$\alpha$ line, and will be presented elsewhere.


## ACKNOWLEDGMENTS

Two of the authors (C.F.H. and J.W.D.) are grateful to the Lawrence Livermore Laboratory, where part of this work was carried out, for the hospitality shown them.


## APPENDIX A: PROOF OF EQUATIONS (2.27)

In this Appendix, it will be indicated how the operators $\hat{K}(a;1;\omega)$ and $\hat{K}(a;1,2;\omega)$ may be written in the form given by Eqs. (2.27), and identify the operators $G(a;1;\omega)$ and $G(a;1,2;\omega)$. Since the proof is similar for the two cases, the operator $\hat{K}(a;1;\omega)$ will be analyzed, and only the results for $\hat{K}(a;1,2;\omega)$ will be quoted. From Eqs. (2.17) and (2.19),

$$\begin{aligned}\hat{K}(a;1;\omega) &= \hat{U}(a;1;\omega) f^{(1)}(a,1) f^{-1}(a) \hat{U}^{-1}(a;\omega) - f^{(1)}(a,1) f^{-1}(a) \\ &= [(N/n)\,\mathrm{Tr}_{2,\ldots,N}\,\rho R(\omega)][\mathrm{Tr}_{1,\ldots,N}\,\rho R(\omega)]^{-1} - f^{(1)}(a,1) f^{-1}(a).\end{aligned} \tag{A1}$$

Here $R(\omega)$ is the resolvent operator, $R(\omega) = (-i\omega + iL)^{-1}$. Using the identity

$$R(\omega) = [1 - R(\omega) iL](-i\omega)^{-1},$$

Eq. (A1) may be written, after some algebra, as

$$\begin{aligned}\hat{K}(a;1;\omega) &= \hat{U}(a;1;\omega) f^{(1)}(a,1) f^{-1}(a) \hat{U}^{-1}(a;\omega) \times \mathrm{Tr}_{1,\ldots,N}\,\rho R(\omega) \sum_{\alpha=1}^{N} iL_1(a,\alpha) f^{-1}(a) \\ &\quad - (N/n)\,\mathrm{Tr}_{2,\ldots,N}\,\rho R(\omega) \sum_{\alpha=1}^{N} iL_1(a,\alpha) f^{-1}(a).\end{aligned} \tag{A2}$$

Use has been made of the fact that the domain of operation of $\hat{K}(a;1;\omega)$ is the atomic subspace. Introducing the permutation operator $P$,

$$P = 1 + \sum_{\alpha=1}^{N} P_{1\alpha}, \tag{A3}$$

Eq. (A2) may be written in the desired form,

$$\hat{K}(a;1;\omega) = G(a;1;\omega) iL_1(a,1) f^{-1}(a), \tag{A4}$$

$$G(a;1;\omega) = \hat{U}(a;1;\omega) f^{(1)}(a,1) f^{-1}(a) \hat{U}^{-1}(a;\omega) \times \mathrm{Tr}_{1,\ldots,N}\,\rho R(\omega) P - (N/n)\,\mathrm{Tr}_{2,\ldots,N}\,\rho R(\omega) P. \tag{A5}$$

Similarly $\hat{K}(a;1,2;\omega)$ is found to be

$$\hat{K}(a;1,2;\omega) = G(a;1,2;\omega) iL_1(a,1) f^{-1}(a), \tag{A6}$$

$$G(a;1,2;\omega) = \hat{U}(a;1,2;\omega) f^{(2)}(a;1,2) f^{-1}(a) \hat{U}^{-1}(a,\omega) \times \mathrm{Tr}_{1,\ldots,N}\,\rho R(\omega) P - [N(N-1)/n^2]\,\mathrm{Tr}_{3,\ldots,N}\,\rho R(\omega) P. \tag{A7}$$

Equations (A4) and (A6) are the desired Eq. (2.27) of Sec. II. The formal operators $G(a;1;\omega)$ and $G(a;1,2;\omega)$ simplify considerably in the high-frequency limit,

$$\lim_{\omega\to\infty} G(a;1;\omega) \to -(i\omega)^{-1}\{f^{(1)}(a,1) f^{-1}(a)\,\mathrm{Tr}_{1,\ldots,N}\,\rho P - [N/n]\,\mathrm{Tr}_{2,\ldots,N}\,\rho P\}$$

or

$$\lim_{\omega\to\infty} G(a;1;\omega) \to (i\omega)^{-1}\{f^{(1)}(a,1) + n\,\mathrm{Tr}_2[f^{(2)}(a;1,2) - f^{(1)}(a,1) f^{-1}(a) f^{(1)}(a,2)] P_{12}\}. \tag{A8}$$

Similarly,

$$\lim_{\omega\to\infty} G(a;1,2;\omega) \to (i\omega)^{-1}\{f^{(2)}(a;1,2)(1 + P_{12}) + n\,\mathrm{Tr}_3[f^{(3)}(a;1,2,3) - f^{(2)}(a;1,2) f^{-1}(a) f^{(1)}(a;3)] P_{13}\}. \tag{A9}$$

## APPENDIX B: PROOF OF EQUATION (4.1)

The general expression for the collision operator $\hat{M}(\omega)$ [Eq. (2.32)] can be put in a form where the atom-perturber interaction appears in the denominator of the trace as the shielded interaction $i\mathfrak{L}(a,1)$. It is convenient to rewrite Eq. (2.32) as

$$\hat{M}(\omega) = n\,\mathrm{Tr}_1 iL_1(a,1) f(a,1) R(a,1;\omega) i\mathfrak{L}(a,1) f^{-1}(a), \tag{B1}$$

where

$$R(a,1;\omega) = [f^{(1)}(a,1)]^{-1}[-i\omega + iL(a,1) + iV(a;1;\omega)]^{-1} f^{(1)}(a,1) = [-i\omega + i\tilde{L}(a,1) + i\tilde{V}(a;1;\omega)]^{-1}. \tag{B2}$$

Here the tilde over an operator $\mathcal{O}$ means $\tilde{\mathcal{O}} \equiv [f^{(1)}(a,1)]^{-1}\mathcal{O} f^{(1)}(a,1)$. Consider now $i\tilde{L}(a,1) + i\tilde{V}(a;1;\omega)$, using the definitions (3.1) and (3.2),

$$i\tilde{L}(a,1) + i\tilde{V}(a,1;\omega) = i\tilde{L}(a,1) + [f^{(1)}(a,1)]^{-1} n\,\mathrm{Tr}_2[iL_1(a,2) + iL_2(1,2)][G(a;1;2;\omega)G^{-1}(a;1;\omega)]_{\omega=\infty}[f(a,1)]$$
$$- f^{-1}(a) n\,\mathrm{Tr}_2 iL_1(a,2) P_{12} f^{(1)}(a,1) + i\tilde{\Delta}(a;1;\omega). \tag{B3}$$

Inspection of (3.3) and (3.4) shows that the second and third terms in (B3) may be written as the sum of a multiplicative operator and integral operator,

$$[f^{(1)}(a,1)]^{-1} n\,\mathrm{Tr}_2[iL_1(a,2) + iL_2(1,2)] f^{(2)}(a;1,2) + n\,\mathrm{Tr}_2\lambda(a;1,2)P_{12}, \tag{B4}$$

where $\lambda(a;12)$ denotes the kernel of the integral operator. Equation (B3) then becomes

$$i\tilde{L}(a,1) + i\tilde{V}(a;1;\omega) = i\tilde{L}(a,1) + [f^{(1)}(a,1)]^{-1} n\,\mathrm{Tr}_2[iL_1(a,2) + iL_2(1,2)]\ f^{(2)}(a;1,2) + n\,\mathrm{Tr}_2\lambda(a;1,2)P_{12} + i\tilde{\Delta}(a;1;\omega). \tag{B5}$$

The first two terms in (B5) may be transformed using the second equation of the equilibrium BBGKY hierarchy to give

$$i\tilde{L}(a,1) + i\tilde{V}(a;1;\omega) = iL(a) + iL(1) + i\mathfrak{L}(a,1) + C(a;1;\omega), \tag{B6}$$

with

$$C(a;1;\omega) = f^{-1}(a) n\,\mathrm{Tr}_2 f^{(1)}(a,2) iL_1(a,2) + [f^{(1)}(a,1)]^{-1} n\,\mathrm{Tr}_2 f^{(2)}(a;1,2) iL_2(1,2) + n\,\mathrm{Tr}_2\lambda(a;1,2)P_{12} + i\tilde{\Delta}(a;1;\omega). \tag{B7}$$

This is the desired result, Eq. (4.1) of the text. The contributions from $C(a;1;\omega)$ are of a different nature than the others in (B6). The leading term of (B7) is simply related to the operator $B$ defined by Eq. (2.21) and represents a mean-field effect of the plasma due to initial correlations. The second and third terms are modified Vlasov operators giving mean-field effects on the free motion of the perturber. Finally, the last term contains all the multiple collision effects.

To lowest order in the atom-perturber interaction, the first two terms in (B7) vanish and the second two become, to lowest order in the atom-perturber interaction and the plasma parameter,

$$C^{(0)}(a;1;\omega) = \tilde{H}(1), \tag{B8}$$

where $\tilde{H}(1)$ is a Vlasov operator

$$\tilde{H}(1) \equiv f^{-1}(1) n \int d\vec{r}_2\, d\vec{p}_1\, iL_2(1,2) f(1) f(2) P_{12}. \tag{B9}$$

*Research supported in part by a grant from the Division of Sponsored Research of the University of Florida.

†Research supported in part by a grant from the American Gas Association.

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