

## Microscopic theory of photoacoustic pulse generation. III. Excited-state polarization transfer to the solvent

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A molecular expression for the polarization-dependent part of the photoacoustic signal in gases is derived [see D. Ronis, *Phys. Rev. A* **29**, 2125 (1984)]. The effect is found to be proportional to the viscosity  $\eta$ , the absorption coefficient  $\alpha(\omega)$ , and the branching ratio for anisotropic versus isotropic energy transfer to the translational degrees of the solvent. The branching ratio is given in terms of the inelastic scattering cross sections for the excited species.

### I. INTRODUCTION

In the first two papers in this series<sup>1,2</sup> various aspects of the generation of an acoustic pulse in a photoacoustic spectroscopic experiment were considered. In particular, the acoustic pressure or stress resulting from the absorption of light in liquids<sup>1</sup> and solids<sup>2</sup> was related to the microscopic properties of the absorber and the rest of the system via nonlinear-response theory; this gave correlation-function expressions for the parameters governing the acoustic pulse generation.

In liquids, subsequent analysis of the correlation functions showed that in addition to the usual photoacoustic signal, i.e., the part due to adiabatic expansion of the solvent,<sup>3</sup> a new component was obtained. Moreover, unlike the adiabatic expansion signal, the new part depends on the polarization of the exciting light. Intuitively, this new component is due to energy relaxation processes which occur before the excited molecule rotationally relaxes, and in addition, should be a probe of the anisotropy of the cross sections governing the energy transfer to the solvent. This is in contrast with a linewidth measurement which contains both isotropic and anisotropic contributions.

In the thin-beam limit, the polarization dependent part of the acoustic pressure,  $\delta p_{\text{pol}}(\mathbf{r}, t)$ , at position  $\mathbf{r}$  and time  $t$  could be written as<sup>1</sup>

$$\delta p_{\text{pol}}(\mathbf{r}, t) = \frac{2\Lambda_1(\cos^2\theta - \frac{1}{3})}{\pi c_s} \times \int_{-\infty}^{t-r/c_s} dt' \frac{\ddot{I}_0(t')}{[c_s^2(t-t')^2 - r_1^2]^{1/2}}, \quad (1.1)$$

where  $c_s$  is the adiabatic sound speed,  $\theta$  is the angle between the observation and the polarization directions,  $r_1$  is the distance between the beam and the detector, and  $I_0(t)$  is the incident power. Of central importance is the parameter  $\Lambda_1$ ; it characterizes the coupling between the absorption process and the stress exerted on the solvent and it is defined by

$$\Lambda_1 \equiv \frac{4\pi n_a}{c(i\hbar)^2} \int_0^\infty dt \int_0^\infty dt' \cos(\omega t') \times \langle \langle [\tau_T^{xy}(t), \mu_1^x], \mu_1^y(-t') \rangle \rangle, \quad (1.2)$$

where  $n_a$  is the absorber number density,  $c$  is the speed of light,  $\omega$  is the frequency of the light,  $\mu_1^j$  is the  $j$ th component of the dipole moment operator for the absorber molecule,  $[, ]$  denotes a commutator,  $\langle \rangle$  denotes an equilibrium average, and  $\tau_T(t)$  is the symmetric part of the stress tensor at time  $t$ .

In this paper, we will derive an expression for  $\Lambda_1$  in terms of the inelastic scattering cross sections in gases. Before beginning, we note that isotropy allows us to rewrite Eq. (1.2) as

$$\Lambda_1 \equiv \frac{2\pi n_a}{c(i\hbar)^2} \int_0^\infty dt \int_0^\infty dt' \cos(\omega t') \times \langle \langle [\tau_T^{xx-yy}(t), \mu_1^x], \mu_1^x(-t') \rangle \rangle, \quad (1.3)$$

where

$$\tau_T^{xx-yy}(t) \equiv \tau_T^{xx}(t) - \tau_T^{yy}(t); \quad (1.4)$$

as it turns out, this form for  $\Lambda_1$  results in a physically more intuitive expression (cf. Sec. IV).

In the next section, we examine the low-density forms of the operators appearing in Eq. (1.3), introduce a tetradic operator notation, and write down a naive density expansion obtained by use of the binary collision expansion. In order to simplify the notation, we treat the absorber as an impurity and ignore any internal structure of the solvent particles. In Sec. III various divergences associated with multiple collision processes are eliminated. We thereby obtain dressed propagators for the translational

motion of the system and for the internal dynamics of the absorber. In the former instance, we find that the translation motion is governed by Boltzmann and Boltzmann-Lorentz propagation, whereas the absorber degrees of freedom are described by propagation under a Boltzmann-Bloch equation. Section IV discusses

relaxation-time approximations for the dressed propagators. For the translational degrees of freedom, this can be viewed as a Bhatnagar-Gross-Krook<sup>4</sup> (BGK) approximation, while for the absorber degrees of freedom, the well-known Bloch-equation picture results.<sup>5</sup>

As we will see,

$$\Lambda_1 \propto n_a \frac{\eta}{2k_B T} \alpha(\omega) \left[ \int d\mathbf{p}_f d\mathbf{p}_i \frac{(p_{f,x}^2 - p_{f,y}^2)}{\gamma_b m_r \hbar \omega_{a,b}} \sigma(|\mathbf{p}_i, b\rangle \rightarrow |\mathbf{p}_f, a\rangle) \frac{|\mathbf{p}_i|}{m_r} \phi_r(\mathbf{p}_i) \right], \quad (1.5)$$

where  $\eta$  is the solvent viscosity,  $\omega_{a,b}$  is the transition frequency,  $\alpha(\omega)$  is the absorption coefficient,  $\sigma(|\mathbf{p}_i, b\rangle \rightarrow |\mathbf{p}_f, a\rangle)$  is the inelastic cross section for a solvent-absorber collision in which the initial and final relative momenta and absorber internal state are  $|\mathbf{p}_i, b\rangle$  and  $|\mathbf{p}_f, a\rangle$ , respectively (we denote the ground state by  $a$ ),  $m_r$  is the reduced mass for the absorber-solvent collision pair,  $\gamma_b^{-1}$  is the lifetime of the  $|b\rangle$  state, and finally,  $\phi_r(\mathbf{p}_i)$  is a Boltzmann distribution characterizing the distribution of relative initial momenta. Note that  $\sigma$  contains an energy-conserving  $\delta$  function  $\delta((p_f^2 - p_i^2)/m_r - \hbar\omega_{a,b})$ . Most of the factors appearing in Eq. (1.5) have fairly obvious origins; the viscosity, however, does not and will be discussed below.

## II. DENSITY EXPANSION: PRELIMINARY REMARKS

The type of correlation function contained in Eq. (1.3) is qualitatively different from those encountered in line-shape theories.<sup>6</sup> Unlike the absorption coefficient, it can be positive or negative, and depends on the correlation between events at three time points. In order to see which dynamical events are important, we will consider the low-density behavior of the coefficient.

In the low-density limit, it is very unlikely to find particles close together. It is therefore reasonable to expect that terms in the correlation function which explicitly depend on the interparticle potentials will not contribute to leading order in density. This is not to say that the potential is unimportant; when particles collide their momenta and internal states are modified and these changes persist for long times. As will be shown below, the kinetic effects of the interparticle interactions result in a singular density dependence and thereby force a resummation of any naive density expansion. The explicit potential terms result in next-order density corrections. This situation is completely analogous to that which occurs in the density expansion

of transport coefficients.<sup>7-9</sup>

Dropping any explicit potential dependence allows us to write

$$\vec{\tau}_T(t) \sim \sum_j \frac{\mathbf{p}_j \mathbf{p}_j}{m_j} \left[ \sum_{\alpha} |\alpha\rangle \langle \alpha| \right] \quad (2.1)$$

and

$$\rho_{eq} \sim \prod_{i=1}^{N+1} \phi_i(\mathbf{p}_i) \frac{\left[ \sum_{\alpha} |\alpha\rangle \langle \alpha| e^{-\beta E_{\alpha}} \right]}{q_A}, \quad (2.2)$$

where, from here on, the center-of-mass parts of all operators are given in the momentum representation; i.e., in terms of the states

$$|\mathbf{p}_j, \alpha\rangle \equiv \frac{\exp(i\mathbf{p}_j \cdot \mathbf{r}_j / \hbar)}{V} |\alpha\rangle. \quad (2.3)$$

In addition, in order to simplify the notation we henceforth omit the absorber internal-degrees-of-freedom unit operator when no confusion will result. Note that to lowest order in density, the density matrix is diagonal in the momentum representation. In Eq. (2.2),  $E_{\alpha}$  is the energy of internal state  $|\alpha\rangle$  (the internal ground-state energy was set to zero),  $q_A$  is the partition function for the internal degrees of freedom, and  $\phi_i(\mathbf{p}_i)$  is the Boltzmann distribution for the center-of-mass degrees of freedom of the  $i$ th particle; i.e.,

$$\phi_i(\mathbf{p}_i) \equiv \frac{e^{-\beta p_i^2 / 2m_i}}{(2\pi m_i k_B T)^{3/2} V}. \quad (2.4)$$

For what follows, we assume that the thermal populations of the excited internal states are negligible. Should this not be the case, only trivial modifications of the theory presented below will be necessary. Moreover, we have assumed that the absorber is infinitely dilute. Thus [cf. Eq. (3.21a) of paper I],

$$\Lambda_1 = \frac{2\pi n_a}{c(i\hbar)^2} \int_0^{\infty} dt \int_0^{\infty} dt' \cos(\omega t') \left\langle \left[ \left[ \frac{N[\mathbf{p}_2 \mathbf{p}_2]^{xx-yy}}{m} + \frac{[\mathbf{p}_1 \mathbf{p}_1]^{xx-yy}}{M} \right] (t), \mu_1^x \right], \mu_1^x(-t') \right\rangle, \quad (2.5)$$

where  $N$ ,  $m$ ,  $M$  and quantities subscripted by 2 correspond to the number of bath particles, mass of a bath particle, mass of the absorber, and any one bath particle, respectively. Henceforth, we use the superscript  $xx - yy$  to denote the difference between the  $xx$  and  $yy$  components of a tensor [cf. Eq. (1.4)]. At this point it is more convenient to adopt a tetradic operator notation,<sup>7-11</sup> and we rewrite Eq. (2.5) as

$$\Lambda_1 = \frac{\pi n_a}{c} \lim_{\epsilon \rightarrow 0^+} \text{Tr} \left[ \left[ \frac{N[\mathbf{p}_2 \mathbf{p}_2]^{xx-yy}}{m} + \frac{[\mathbf{p}_1 \mathbf{p}_1]^{xx-yy}}{M} \right] G(\epsilon) \tilde{\mu}_x [G(i\omega) + G(-i\omega)] \tilde{\mu}_x \rho_{eq} \right], \quad (2.6)$$

where

$$\tilde{\mu}_i \equiv \frac{[\mu_1^i, ]}{i\hbar}, \quad i = x, y, z \quad (2.7)$$

$$G(\epsilon) \equiv \frac{1}{\epsilon + iL}, \quad (2.8)$$

$$iL \equiv \frac{i}{\hbar} [H, ], \quad (2.9)$$

and Tr denotes a trace over both the translational and internal degrees of freedom. In obtaining Eq. (2.6) we have used the fact that the trace is invariant to cyclic permutation of the operators. In the momentum representation Eq. (2.6) becomes

$$\begin{aligned} \Lambda_1 = \frac{\pi n_a}{c} \lim_{\epsilon \rightarrow 0^+} \sum & \left[ \frac{N[\mathbf{p}_2 \mathbf{p}_2]^{xx-yy}}{m} + \frac{[\mathbf{p}_1 \mathbf{p}_1]^{xx-yy}}{M} \right] G^{\alpha, \alpha; \gamma, \beta}(\mathbf{p}^{N+1}, \mathbf{p}^{N+1} | \mathbf{p}'^{N+1}, \mathbf{p}''^{N+1}; \epsilon) \tilde{\mu}_x^{\gamma, \beta; \delta, \sigma} \\ & \times [G^{\delta, \sigma; \zeta, \xi}(\mathbf{p}'^{N+1}, \mathbf{p}''^{N+1} | \mathbf{p}'''^{N+1}, \mathbf{p}''''^{N+1}; i\omega) \\ & + G^{\delta, \sigma; \zeta, \xi}(\mathbf{p}'^{N+1}, \mathbf{p}''^{N+1} | \mathbf{p}'''^{N+1}, \mathbf{p}''''^{N+1}; -i\omega)] \tilde{\mu}_x^{\zeta, \xi; a, a} \prod_{i=1}^{N+1} \phi_i(\mathbf{p}_i'''). \end{aligned} \quad (2.10)$$

The summations in Eq. (2.10) are over all momenta and internal states of the absorber. It should also be noted that we have assumed that the temperature is sufficiently low so as to be able to ignore the thermally populated excited states; this assumption can be relaxed at the expense of a somewhat more complicated notation.

A naive density expansion of  $\Lambda_1$  can be obtained by using the binary collision expansion<sup>12</sup> for the propagators in Eq. (2.6); i.e., we write

$$\begin{aligned} G(\epsilon) = G_0(\epsilon) - \sum_{\substack{i,j \\ i < j}} G_0(\epsilon) T_{i,j}(\epsilon) G_0(\epsilon) \\ + \sum'_{\substack{i,j,k,l \\ i < j, k < l}} G_0(\epsilon) T_{i,j}(\epsilon) G_0(\epsilon) T_{k,l}(\epsilon) G_0(\epsilon) - \dots, \end{aligned} \quad (2.11)$$

where  $G_0(\epsilon)$  is the tetradic propagator for the noninteracting system (i.e.,  $[\epsilon + iL_0]^{-1}$ ),  $T_{i,j}(\epsilon)$  is the tetradic binary collision operator (cf. Sec. IV) and the prime on the sum indicates that all consecutive pairs of interacting particles must be different. A number of useful properties of  $G_0$  and  $T_{i,j}$  have been worked out in the literature<sup>7-11</sup> and are listed in Appendix A.

As was mentioned above, the density expansion of Eqs. (2.6) or (2.10) is complicated by the fact that the states of the particles remain correlated for very long times at low

density. This manifests itself in singular dependence in the propagators, and forces us to resum the naive density expansion.

### III. DENSITY EXPANSION: RESUMMATION

That the naive density expansion needs resummation is easily seen from the leading order terms obtained when the binary collision expansion, Eq. (2.11), is inserted in Eq. (2.10). Since the leftmost free propagator is diagonal [cf. Eq. (A.1)] it diverges as  $\epsilon^{-1}$  as  $\epsilon \rightarrow 0^+$ . In addition, the rightmost free propagator will diverge as  $\omega$  approaches the transition frequency (for the moment, we ignore the natural linewidth). This situation is analogous to what occurs in the density expansions of transport coefficients<sup>7</sup> or of the collision-induced linewidth,<sup>10</sup> and similar resummation techniques can be applied. For what follows we use the procedure developed by Bartis and Oppenheim<sup>8</sup> and by Albers and Oppenheim.<sup>9</sup>

From Eq. (A.2), it is clear that any term containing binary collision operators referring to  $n$  particles will be  $O(n_B^n)$  in the naive density expansion when the  $n$  particles are chosen in all possible ways. The strategy of the resummation procedure is to find the most divergent (in  $\epsilon$  or  $\omega$ ) terms at a given order in density, and then, if possible, to resum these terms. The next density corrections are found by resumming the next most divergent terms at any order in density, and so on.

Fortunately, it is not too difficult to identify the most

divergent terms. Consider the following sequences of binary collision operators

$$G_0(\epsilon)T_{2,3}(\epsilon)G_0(\epsilon)T_{2,4}(\epsilon)G_0(\epsilon) \quad (3.1a)$$

and

$$G_0(\epsilon)T_{2,3}(\epsilon)G_0(\epsilon)T_{2,4}(\epsilon)G_0(\epsilon)T_{2,3}(\epsilon)G_0(\epsilon). \quad (3.1b)$$

Both sequences involve the same number of particles and therefore contribute to the same order in density. However, by virtue of the momentum conservation rules for the  $T$  operators [cf. Eq. (A.3)], it is easy to see that the first sequence will not contain any intermediate momentum integrations whereas the second will. The first sequence will have an  $\epsilon^{-3}$  divergence; the second will be less divergent [in fact it diverges like  $\epsilon^{-2}$  in three spatial dimensions and like  $\epsilon^{-2}\ln(\epsilon)$  in two dimensions<sup>13</sup>], and thus it is unimportant to leading order in density. Generalizing this to more complicated collision sequences, we conclude that the most divergent ones are those in which an additional particle is involved for every  $T$  operator. These are sometimes referred to as the factorizable collisions.<sup>8</sup>

There are, however, two complications. The first is the fact that the sequence of collisions can start with one bath particle and end with a binary collision operator not involving that particle at all; e.g., as is the case in the following sequence:

$$G_0(\epsilon)T_{2,3}(\epsilon)G_0(\epsilon)T_{2,4}(\epsilon)G_0(\epsilon)T_{4,5}(\epsilon)G_0(\epsilon). \quad (3.2)$$

The standard way in which this problem is overcome is by introducing a tetradic particle-label-permutation operator,<sup>13(a)</sup>  $P_{i,j}$ ; it interchanges the state labels pertaining to particles  $i$  and  $j$  in any operator on which it acts. Thus Eq. (3.2) can be rewritten as

$$G_0(\epsilon)T_{2,3}(\epsilon)G_0(\epsilon)T_{2,4}(\epsilon)P_{2,4}G_0(\epsilon)T_{2,5}(\epsilon)G_0(\epsilon). \quad (3.3)$$

The general form of these terms is therefore

$$n_B^{s-3}G_0(\epsilon) \prod_{j=3}^s [-V T_{2,j}(\epsilon)(1 + P_{2,j})G_0(\epsilon)], \quad (3.4)$$

where we have put in the bath density dependence explicitly. Since the added particle in the factorizable collision sequences appears only once, the trace over its momenta and its action on its momentum distribution can be performed immediately. We thereby introduce the bath linearized quantum Boltzmann collision operator,<sup>9</sup>  $L_B$ , defined by

$$L_B(2,\epsilon) \equiv \sum_{\mathbf{p}_3, \mathbf{p}'_3} VT_{2,3}(\mathbf{p}_2, \mathbf{p}_3; \mathbf{p}'_2, \mathbf{p}_3 | \mathbf{p}_2'', \mathbf{p}_3'; \mathbf{p}_2''', \mathbf{p}_3'; \epsilon) \times (1 + P_{2,3})\phi_3(\mathbf{p}'_3) \quad (3.5)$$

and replace the sequence of collisions shown in Eq. (3.4) by  $G_0(\epsilon)[-n_B L_B(2,\epsilon)G_0(\epsilon)]^{s-3}$ . Clearly this is just one term in an operator geometric series which can be summed to give

$$\frac{1}{\epsilon + iL_0 + n_B L_B(2,\epsilon)}. \quad (3.6)$$

In addition to the collisions between the bath particles just considered, we must also include the collisions with the absorber (i.e., particle 1). The absorber appears in two ways: first, one of the terms in the stress tensor explicitly depends on the momentum of the absorber, and second, one must allow for the possibility of collisions with the absorber and the gas particles.

The explicit absorber momentum term can be treated in exactly the same manner as the terms considered above. The only difference lies in the fact that only one absorber is present, and hence, the type of terms which involve exchange of particle labels are absent. Thus, by introducing the absorber Boltzmann-Lorentz collision operator,

$$L_A(\epsilon) \equiv \sum_{\mathbf{p}_3, \mathbf{p}'_3} VT_{1,3}(\mathbf{p}_1, \mathbf{p}_3; \mathbf{p}'_1, \mathbf{p}_3 | \mathbf{p}_1'', \mathbf{p}_3'; \mathbf{p}_1''', \mathbf{p}_3'; \epsilon) \times \phi_3(\mathbf{p}'_3), \quad (3.7)$$

we see that the relevant resummed propagator is

$$\frac{1}{\epsilon + iL_0 + n_B L_A(\epsilon)}. \quad (3.8)$$

Note that  $L_A$  is responsible for the various  $T_1$  and  $T_2$  processes observed in the pressure broadened line shape.

The fact that the bath particle referred to in the stress tensor can collide with the absorber is included by considering the following sequences of collisions: First, there are the factorizable binary collisions between the special bath particle (i.e., particle 2) and other bath particles which led to Eq. (3.6). However, some collision sequences will contain a collision between particle 2 and the absorber; this correlates their dynamics. Subsequently, both the absorber and particle 2 suffer uncorrelated binary collisions with the other bath particles in all possible orders. It is easy to show that this last type of collision sequence results in another geometric series, and the net result is the following propagator for particle 2:

$$\frac{1}{\epsilon + iL_0 + n_B L_B(2,\epsilon)} \left[ 1 - T_{1,2}(\epsilon) \frac{1}{\epsilon + iL_0 + n_B L_B(2,\epsilon) + n_B L_A(\epsilon)} \right]. \quad (3.9)$$

Note that only one collision between the special bath particle and the absorber need be considered; any sequence in which they recollide will involve at least one intermediate momentum integration, and thereby results in a weaker  $\epsilon$  divergence. As was explained above, such events are unimportant to leading order in density.

We are now in a position to rewrite Eq. (2.6) by using the appropriate resummed propagators for the  $G(\epsilon)$ ; i.e., Eqs.

(3.6) and (3.9). The result is

$$\Lambda_1 = \frac{\pi n_a}{c} \lim_{\epsilon \rightarrow 0+} [ I(i\omega) + I(-i\omega) + J(i\omega) + J(-i\omega) ], \quad (3.10)$$

where

$$I(\pm i\omega) \equiv \text{Tr} \left[ \frac{N[\mathbf{p}_2 \mathbf{p}_2]^{xx-yy}}{m} \frac{1}{\epsilon + iL_0 + n_B L_B(2, \epsilon)} \times \left[ 1 - T_{1,2}(\epsilon) \frac{1}{\epsilon + L_0 + n_B L_B(2, \epsilon) + n_B L_A(\epsilon)} \right] \tilde{\mu}_x G(\pm i\omega) \tilde{\mu}_x \rho_{eq} \right] \quad (3.11)$$

and

$$J(\pm i\omega) \equiv \text{Tr} \left[ \frac{[\mathbf{p}_1 \mathbf{p}_1]^{xx-yy}}{M} \frac{1}{\epsilon + iL_0 + n_B L_A(\epsilon)} \tilde{\mu}_x G(\pm i\omega) \tilde{\mu}_x \rho_{eq} \right]. \quad (3.12)$$

The last  $N$ -body propagator [i.e.,  $G(\pm i\omega)$ ] in Eqs. (3.11) and (3.12) can be expressed in terms of the Boltzmann-Lorentz collision operator. In general, keeping all sequences of factorizable collisions would result in a propagator of the form

$$\frac{1}{\pm i\omega + iL_0 + n_B L_B(2, \pm i\omega) + n_B L_A(\pm i\omega)}. \quad (3.13)$$

However, in both Eqs. (3.11) and (3.12),  $G(\pm i\omega)$  acts only on the equilibrium distribution for particle 2 as far as its action on particle 2's degrees of freedom, and since this is the equilibrium solution to the linearized Boltzmann equation, the result is zero. Consequently, only the part of the propagator pertaining to the absorber degrees of

freedom need be kept, and we take

$$G(\pm i\omega) \sim [\pm i\omega + iL_0 + n_B L_A(\pm i\omega)]^{-1}, \quad (3.14)$$

for the purposes of calculating  $I(\pm i\omega)$  and  $J(\pm i\omega)$ . Note that this propagator is exactly what appears in the low-density theories of the line shape.<sup>10,14</sup> Finally, by noting that

$$\sum_{\alpha} \tilde{\mu}_i^{\alpha, \alpha; \beta, \gamma} = 0, \quad i = x, y, z \quad (3.15)$$

and that  $L_B$  is diagonal in the absorber degrees of freedom, we can drop the term not containing the 1-2 collision operator in  $I(\pm i\omega)$ . Equation (3.11) is thereby rewritten as

$$I(\pm i\omega) \equiv -n_B \text{Tr} \left[ \frac{[\mathbf{p}_2 \mathbf{p}_2]^{xx-yy}}{m} \frac{1}{\epsilon + iL_0 + n_B L_B(2, \epsilon)} V T_{1,2}(\epsilon) \times \frac{1}{\epsilon + iL_0 + n_B L_B(2, \epsilon) + n_B L_A(\epsilon)} \tilde{\mu}_x G(\pm i\omega) \tilde{\mu}_x \rho_{eq} \right]. \quad (3.16)$$

From the  $\epsilon \rightarrow 0+$  limit, we see that the magnitude of  $\Lambda_1$  scales like  $n_a/n_B$  (providing we neglect the radiative linewidth) and is therefore independent of the overall density in the system. This is analogous to what is found for the leading-order density dependence of the viscosity and thermal conductivity. We will discuss this point more fully below.

In order to evaluate the functions  $I(\pm i\omega)$  and  $J(\pm i\omega)$ , it is necessary to solve a set of coupled quantum Boltzmann and Boltzmann-Lorentz equations. In general, this cannot be carried out exactly, and we will use some of the standard approximations from line-shape theory and the kinetic theory of gases in order to obtain analytic expressions for  $\Lambda_1$ .

#### IV. THE RELAXATION-TIME APPROXIMATION AND THE BLOCH EQUATION

The functions  $I(\pm i\omega)$  and  $J(\pm i\omega)$  introduced in the previous section correspond to slightly different processes. Both contain the excitation dynamics; i.e., the factors of  $\tilde{\mu}_i$  which give the coupling to the radiation field, and the propagator  $G(\pm i\omega)$  which contains the absorption line shape [cf. Eq. (3.14)]. However, what happens after the excited state is prepared differs in the two functions. In  $I(\pm i\omega)$ , a bath particle inelastically collides with the excited absorber, converts the excitation energy into translational energy and then propagates away from the collision under the action of the linearized Boltzmann propagator.

It is the stress component of the momentum so transferred which is responsible for any observed acoustic pulse. On the other hand, in  $J(\pm i\omega)$ , after excitation, the absorber wanders about the fluid under the action of a Boltzmann-Lorentz propagator which now includes coupling between the internal and translational degrees of freedom. As we shall see below, when one of the bath collisions leads to deexcitation, there is a concomitant recoil of the absorber which creates sound. We will refer to these two processes as being direct or recoil, respectively.

We first consider the function  $I(\pm i\omega)$ . The adjoint of the leftmost propagator in Eq. (3.16) only acts on the translational degrees of freedom of the bath particle. In general this requires us to choose a model for the bath-bath scattering process. However, in the kinetic theory of gases, Boltzmann equations are commonly solved via basis-set expansion techniques (e.g., using Sonine polynomials<sup>15</sup>). In particular,  $[\mathbf{p}_2\mathbf{p}_2]^{xx-yy}$  is one of the expansion functions. Thus in the one-Sonine-polynomial approximation,

$$n_B \frac{[\mathbf{p}_2\mathbf{p}_2]^{xx-yy}}{m} \frac{1}{\epsilon + iL_0 + n_B L_B(2, \epsilon)} \sim \text{Tr} \left[ n_B \frac{[\mathbf{p}_2\mathbf{p}_2]^{xx-yy}}{m} \frac{1}{\epsilon + iL_0 + n_B L_B(2, \epsilon)} \right. \\ \left. \times \frac{[\mathbf{p}_2\mathbf{p}_2]^{xx-yy}}{m} \phi_2(\mathbf{p}_2) \right] \frac{[\mathbf{p}_2\mathbf{p}_2]^{xx-yy}}{m(k_B T)^2} \quad (4.1a)$$

$$\sim \frac{\eta}{k_B T} \frac{[\mathbf{p}_2\mathbf{p}_2]^{xx-yy}}{m}, \quad (4.1b)$$

where  $\eta$  is the shear viscosity of the bath. Note that this approximation is exact for a number of classical scattering models; namely, the Maxwell potential and the BGK or other relaxation time models.<sup>4</sup> By using Eq. (4.1b), we rewrite Eq. (3.16) as

$$I(\pm i\omega) \sim - \frac{\eta}{k_B T} \text{Tr} \left[ \frac{[\mathbf{p}_2\mathbf{p}_2]^{xx-yy}}{m} V T_{1,2}(\epsilon) \frac{1}{\epsilon + iL_0 + n_B L_B(2, \epsilon) + n_B L_A(\epsilon)} \tilde{\mu}_x G(\pm i\omega) \tilde{\mu}_x \rho_{eq} \right]. \quad (4.2)$$

Finally, by repeating the argument following Eq. (3.13) we can omit the bath parts of the remaining propagators in Eq. (4.2) which becomes

$$I(\pm i\omega) \sim - \frac{\eta}{k_B T} \text{Tr} \left[ \frac{[\mathbf{p}_2\mathbf{p}_2]^{xx-yy}}{m} V T_{1,2}(\epsilon) \phi_2(\mathbf{p}_2) \frac{1}{\epsilon + iL_0 + n_B L_A(\epsilon)} \right. \\ \left. \times \tilde{\mu}_x \frac{1}{\pm i\omega + iL_0 + n_B L_A(\epsilon)} \tilde{\mu}_x |a\rangle \langle a| \phi_1(\mathbf{p}_1) \right] \quad (4.3)$$

where we have used Eq. (3.14) and the low-density form of the equilibrium density matrix.

The relaxation approximation can also be applied to the propagator appearing in the recoil term,  $J(\pm i\omega)$ . However, two important differences must be noted. First, the collision operators which appear in Eq. (3.12) are Boltzmann-Lorentz collision operators and as such yield diffusive translational motion for the absorber. Hence, in a relaxation time approximation, the relevant transport coefficient will be the diffusion constant (or self-diffusion constant in one-component systems). Usually, the diffusion constant is quite small. A second point which can be noted is that it is the kinetic energy anisotropy of the absorber relative to that of the solvent particle which carries away the energy which governs the relative importance of  $I(\pm i\omega)$  and  $J(\pm i\omega)$ . This will scale like the

mass ratio,  $m/M$ ; hence, the recoil term will be small if the absorber is much heavier than the bath particle. Either or both of these conditions can be arranged in an experiment, and thus we will not analyze  $J(\pm i\omega)$  further.

Only propagators which appear in usual line-shape theories remain in  $I(\pm i\omega)$ , cf. Eq. (4.3). However, unlike usual line-shape theories, it is the correlation with the translational degrees of freedom which is important here. Nonetheless, we can still make a relaxation time approximation for the propagators which govern the internal dynamics of the absorber. That is, we calculate them within the context of the Bloch equation.<sup>5</sup> Having said this, we proceed by inserting complete sets of internal states on both sides of the leftmost propagator in Eq. (4.3). We thereby obtain

$$\begin{aligned}
I(\pm i\omega) \sim & -\frac{\eta}{k_B T} \text{Tr} \left\{ \frac{[\mathbf{P}_2 \mathbf{P}_2]^{xx-yy}}{m} V T_{1,2}(\epsilon) \phi_2(\mathbf{p}_2) \sum_{\alpha} |\alpha\rangle\langle\alpha| \frac{1}{\epsilon + iL_0 + n_B L_A(\epsilon)} \right. \\
& \times \sum_{\beta} |\beta\rangle\langle\beta| \tilde{\mu}_x \frac{1}{\pm i\omega + iL_0 + n_B L_A(\epsilon)} \\
& \left. \times \tilde{\mu}_x |a\rangle\langle a| \phi_1(\mathbf{p}_1) \right\}. \quad (4.4)
\end{aligned}$$

The largest acoustic signal should arise from the coherent transfer of the absorber's internal energy to the translational motion of particle 2; i.e., the  $T_{1,2}$  which appears in Eq. (4.4) must be associated with population relaxation to the ground state  $|a\rangle$ . By retaining only this contribution, we find that

$$\begin{aligned}
I(\pm i\omega) \sim & -\frac{\eta}{k_B T} \text{Tr} \left\{ \frac{[\mathbf{P}_2 \mathbf{P}_2]^{xx-yy}}{m} V T_{1,2}^{b,b;a,a}(\epsilon) \phi_2(\mathbf{p}_2) |b\rangle\langle b| \frac{1}{\epsilon + iL_0 + n_B L_A(\epsilon)} |b\rangle\langle b| \right. \\
& \left. \times \tilde{\mu}_x \frac{1}{\pm i\omega + iL_0 + n_B L_A(\epsilon)} \tilde{\mu}_x |a\rangle\langle a| \phi_1(\mathbf{p}_1) \right\}. \quad (4.5)
\end{aligned}$$

We have also used the fact that at the resonance frequency,  $\tilde{\mu}_x [\pm i\omega + iL_0 + n_B L_A(\epsilon)]^{-1} \tilde{\mu}_x |a\rangle\langle a|$  leaves the absorber in the  $|b\rangle\langle b|$  state,<sup>14</sup> thereby eliminating the second sum over internal states. Indeed, the associated tetradic matrix element is simply related to the complex line-shape function,  $\alpha_C$ ; i.e.,

$$\alpha_C(\pm i\omega) = \left[ \tilde{\mu}_x \frac{1}{\pm i\omega + iL_0 + n_B L_A(\epsilon)} \tilde{\mu}_x \right]^{b,b;a,a} \sim \frac{|\mu_{a,b}|^2}{\hbar^2} \left[ \frac{1}{\pm i\omega + i\omega_{a,b} + \gamma} + \frac{1}{\pm i\omega - i\omega_{a,b} + \gamma} \right], \quad (4.6)$$

where  $\gamma$  is the linewidth and  $\mu_{a,b}$  is the dipole moment matrix element for the  $a,b$  transition. The linewidth  $\gamma$  can be written as

$$\gamma = \frac{1}{2} (\gamma_a + \gamma_b) + \tilde{\Gamma}.$$

Here  $\gamma_a$  and  $\gamma_b$  are the inverse lifetimes of the  $|a\rangle$  and  $|b\rangle$  states, respectively, and  $\tilde{\Gamma}$  is the proper dephasing width arising from processes which modulate the transition frequency,  $\omega_{a,b}$ , without affecting the lifetime.

The middle factor in Eq. (4.5) is the lifetime of the state  $|b\rangle$ ; i.e.,

$$\left[ \frac{1}{\epsilon + iL_0 + n_B L_A(\epsilon)} \right]^{b,b;b,b} \equiv \gamma_b^{-1}. \quad (4.7)$$

Note that  $\gamma_b^{-1}$  represents the total lifetime of the  $|b\rangle$  state ( $T_1$  processes) which can be either radiative or non-radiative in nature. In addition, when radiative effects can be ignored,<sup>11,14</sup>

$$\begin{aligned}
\gamma_b \sim & n_B \sum_{\beta(\neq b)} \int d\mathbf{p}_f d\mathbf{p}_i \sigma(|\mathbf{p}_i, b\rangle \rightarrow |\mathbf{p}_b, \beta\rangle) \\
& \times \frac{|\mathbf{p}_i|}{m_r} \phi(p_i). \quad (4.8)
\end{aligned}$$

We also define

$$\Gamma^{(2)} \equiv \text{Tr} \left[ \frac{[\mathbf{P}_2 \mathbf{P}_2]^{xx-yy}}{2m \hbar \omega_{a,b}} V T_{1,2}^{b,b;a,a}(\epsilon) \phi_2(\mathbf{p}_2) \phi_1(\mathbf{p}_1) \right]. \quad (4.9)$$

Finally, it should be noted that in deriving Eqs. (4.6) and (4.7), we have ignored the coupling between the absorber's internal degrees of freedom and its translational ones which may be induced through interactions with other bath particles (e.g., "3," etc.). This becomes rigorous when the absorber is infinitely massive.

Upon combining Eqs. (4.6)–(4.9) and (3.10) we obtain

$$\begin{aligned}
\Lambda_1 = & -\frac{2\pi n_a |\mu_{a,b}|^2 \eta \hbar \omega_{a,b} \Gamma^{(2)}}{ck_B T \hbar^2 \gamma_b} \\
& \times \left[ \frac{2\gamma}{(\omega - \omega_{a,b})^2 + \gamma^2} + \frac{2\gamma}{(\omega + \omega_{a,b})^2 + \gamma^2} \right]. \quad (4.10)
\end{aligned}$$

In the rotating-wave approximation, we neglect the second (antiresonant) term in the large parentheses in Eq. (4.10); this is an excellent approximation for optical or infrared transitions.

All that remains is to relate the tetradic matrix elements appearing in the definitions of  $\Gamma^{(0)}$  and  $\Gamma^{(2)}$  to the cross sections describing the scattering of a bath particle from the absorber. This problem has been considered in the literature,<sup>10,11,14</sup> and we note that

$$\begin{aligned}
& T_{1,2}^{b,b;a,a}(\{\mathbf{p}_{1,f}, \mathbf{p}_{2,f}\}, \{\mathbf{p}_{1,f}, \mathbf{p}_{2,f}\} | \{\mathbf{p}_{1,i}, \mathbf{p}_{2,i}\}, \{\mathbf{p}_{1,i}, \mathbf{p}_{2,i}\}) \\
& = (2\pi)^6 \delta(\mathbf{p}_{1,i} + \mathbf{p}_{2,i} - \mathbf{p}_{1,f} - \mathbf{p}_{2,f}) \sigma(|\mathbf{p}_{r,i}, b\rangle \rightarrow |\mathbf{p}_{r,f}, a\rangle) \frac{|\mathbf{p}_i|}{m_r} \quad (4.11)
\end{aligned}$$

in the momentum representation. The subscript  $r$  signifies a relative momentum and  $\sigma$  is the cross section. When this is used in Eq. (4.9), and going over to center of mass and relative momenta in the integrations, we find

$$\begin{aligned}
\Gamma^{(2)} &= \int d\mathbf{p}_f d\mathbf{p}_i \frac{[\mathbf{p}_{x,f}^2 - \mathbf{p}_{y,f}^2]}{2m_r \hbar \omega_{a,b}} \\
&\times \sigma(|\mathbf{p}_i, b\rangle \rightarrow |\mathbf{p}_f, a\rangle) \frac{|\mathbf{p}_i|}{m_r} \phi_r(p_i). \quad (4.12)
\end{aligned}$$

Equation (4.10) has a simple physical interpretation. We express the coefficient of the anisotropic photoacoustic signal as a product of three factors

$$\Lambda_1 = -\chi_1 \chi_2 \alpha(\omega), \quad (4.13)$$

where

$$\alpha(\omega) \equiv \frac{4\pi n_a |\mu_{a,b}|^2 \hbar \omega_{a,b}}{c \hbar^2} \frac{\gamma}{(\omega - \omega_{a,b})^2 + \gamma^2}, \quad (4.14)$$

$$\chi_1 \equiv \frac{\Gamma^{(2)}}{\gamma_b}, \quad (4.15)$$

and

$$\chi_2 \equiv \frac{\eta}{k_B T}. \quad (4.16)$$

$\alpha(\omega)$  is the absorption coefficient and represents the rate of energy absorption from the radiation field.  $\Gamma^{(2)}$  gives the rate of anisotropic collisional deactivation of the excited absorber; it actually equals the difference in the rate of kinetic energy release in the  $x$  and  $y$  directions, scaled to the transition energy, which arises from the anisotropy of the excited absorber-bath interaction. Since  $\gamma_b^{-1}$  is the total lifetime of the  $|b\rangle$  state (both radiative and nonradiative),  $\chi_1$  represents the quantum yield for anisotropic deactivation versus all decay processes. The parameter  $\chi_2$  is a measure of the stress relaxation time for the solvent; the longer the induced anisotropic stress survives, the

more sound generated. Finally, it should be noted that for systems where the radiative lifetime of the  $|b\rangle$  state can be ignored with respect to the collisional lifetime, we will have  $\gamma_b \propto n_B$  and thus the product  $n_a \chi_1 \chi_2$  will be independent of the overall pressure of the system (recall that the viscosity of a dilute gas is independent of the pressure).

The generation of the photoacoustic signal may be viewed as an excitation process followed by two competing anisotropic and isotropic deactivation processes with rates  $\Gamma^{(2)}$  and  $\gamma'_b$ , respectively. Thus Eq. (4.13) can be understood in terms of the kinetic scheme shown in Fig. 1. Here

$$\gamma_b = \gamma'_b + \Gamma^{(2)}$$

and

$$\chi_1 = \frac{\Gamma^{(2)}}{\gamma'_b + \Gamma^{(2)}}$$

is the branching ratio for the anisotropic and isotropic decay. Processes such as rotational relaxation will contribute to  $\gamma'_b$  and thereby reduce  $\chi_1$ . Moreover, since rotational relaxation is usually much more efficient than vibrational relaxation, we expect  $\chi_1$  to be small.

## V. DISCUSSION

We have derived a relationship between the coefficient of the anisotropic photoacoustic signal and the anisotropic parts of the inelastic cross section governing relaxation of the excited state. While the derivation assumed a dilute gas, it is clear from the discussion at the end of the previous section that anisotropic photoacoustic signal in solids and liquids should still be proportional to the branching ratio for anisotropic versus isotropic processes in the relaxation [cf. Eq. (4.13)]. It must be emphasised that a simple line-shape measurement does not differentiate between these two processes, and hence, even though the anisotropic part of the photoacoustic signal will probably be

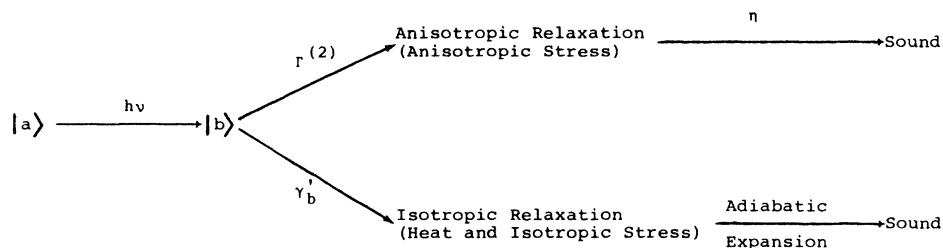


FIG. 1. Pictorial representation of the kinetic scheme governing the anisotropic energy transfer to the solvent.



small, it will provide some new information concerning the nature of the absorber-bath interaction.

The new contribution to the photoacoustic signal depends on the direction of polarization of the incident light.<sup>1,2</sup> Moreover, in pulsed experiments, the incident-pulse time dependence<sup>1</sup> and acoustic-pulse time profile<sup>1,2</sup> of the anisotropic contribution are different than those associated with the adiabatic expansion of the solvent. Hence, a variety of sensitive differential measurements (e.g., acoustic ellipsometry) can be used in order to study this effect.

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#### APPENDIX A

We note the following useful properties of the operators appearing in the binary collision expansion

$$G_0(1,2;3,4;\epsilon) = \frac{\Delta(1,3)\Delta(2,4)}{\epsilon + i[E(1) - E(3)]} \quad (\text{A1})$$

where the notation 1,2, etc., represents sets of quantum numbers (both momentum and internal) for the noninteracting system,  $E(1)$  is the energy of the noninteracting system in state 1, and  $\Delta(1,2)$  is a Kronecker- $\delta$  in the system quantum numbers in states 1 and 2. In addition,

$$T_{i,j}(1,2;3,4;\epsilon) \propto V^{-1} \quad (\text{A2})$$

as  $V \rightarrow \infty$ . Finally,

$$\begin{aligned} T_{i,j}(1,2;3,4;\epsilon) \propto & \Delta(\mathbf{p}_1^{N-2} - \mathbf{p}_3^{N-2})\Delta(\mathbf{p}_2^{N-2} - \mathbf{p}_4^{N-2}) \\ & \times \Delta(\mathbf{p}_{i,1} + \mathbf{p}_{j,1} - \mathbf{p}_{i,3} - \mathbf{p}_{j,3}) \\ & \times \Delta(\mathbf{p}_{i,2} + \mathbf{p}_{j,2} - \mathbf{p}_{i,4} - \mathbf{p}_{j,4}), \quad (\text{A3}) \end{aligned}$$

which is merely a statement of momentum conservation. The reader is referred to Refs. 7–10 for proofs of these relations.

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