

## Microscopic theory of photoacoustic pulse generation

David Ronis

*Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138*

(Received 26 August 1983)

Nonlinear-response theory to quadratic order in the external electric field is used to derive correlation-function expressions for the hydrodynamic disturbances caused by the absorption of light in linear spectroscopy. For relatively low-frequency sound, this treatment is shown to give the phenomenological expression for the pressure generated by adiabatic expansion of the solvent. In addition, two new terms are obtained. These represent the direct coupling between the dynamics of the absorbers and the local microscopic stress. One of these terms has a dependence on the polarization of the incident light which is totally absent in the phenomenological theory. A photoacoustic experiment is suggested which can measure this new effect.

### I. INTRODUCTION

Photoacoustic spectroscopy has proved to be a very sensitive detection method.<sup>1</sup> The phenomenological theory of photoacoustic pulse generation is extremely simple; the absorbed light adiabatically expands the fluid, thereby generating sound. For many applications, any coupling between the absorbed light and modes other than those leading to adiabatic expansion, if present, should be unimportant, since only relative measurements are being made. On the other hand, in many cases absolute intensity measurements are needed (e.g., as in the recent application of the photoacoustic effect to the measurement of various heats of reaction in solution,<sup>2</sup> in the photo-calorimetric studies of reaction intermediates in membranes,<sup>3</sup> and in measurements of photochemical quantum yields<sup>4</sup>). Any couplings to other modes of the solvent must be understood insofar as they effect the partitioning of the absorbed optical energy between acoustic and nonacoustic modes. At present, the experiments are calibrated using well understood standards and it is then assumed that the partitioning for the system under study will be the same.

At present, the phenomenological theory of photoacoustic pulse generation assumes that all the energy goes into sound through the adiabatic expansion of the solvent. For example, no couplings, hydrodynamic or otherwise, to shear, entropy, or other modes are allowed. In this work, these assumptions are reexamined from a microscopic viewpoint.

In Sec. II, nonlinear-response theory<sup>5</sup> is used to derive a general expression for the response of average properties of the system to quadratic order in the external electric field. The system is treated quantum mechanically and the coupling to the external field is treated in the dipole approximation. Moreover, no solvent polarization (local-field) corrections are considered. If they are important, they can be included phenomenologically. Section II also contains a summary of the manipulations leading to the well-known correlation function expression for the absorbed energy,<sup>6,7</sup> as well as some simplifications of the

general quadratic term resulting from the expected short-range character of the dipole-dipole correlations.

In Sec. III, the expression worked out in Sec. II is analyzed for the hydrodynamic response of the system, i.e., for the behavior of the mass, momentum, and energy densities. For sufficiently long-wavelength sound, an expansion in wave vector yields four types of terms: one proportional to the absorbed intensity, one electrostrictive in nature, and two which represent the direct coupling between the motion of the dipoles and the local stress in the solvent. Significantly, one of the latter generates a disturbance which depends on the polarization of the incident light.

Detailed expressions for the response of the pressure are derived in Sec. IV. The incident beam is modeled as a thin cylinder and the detection is assumed to occur in the acoustic far field using a point detector. Of the three types of terms obtained in Sec. III, the first is shown to correspond exactly to the usual phenomenological expression.<sup>1</sup> For the remaining two terms, the polarization dependence of one of them is used to suggest an experiment which should directly measure the coupling to the microscopic solvent stress field. Section V contains a summary and discussion.

### II. NONLINEAR COUPLING TO THE EXTERNAL FIELD

In this work, the system is assumed to be subjected to an external electric field of the form

$$\vec{E}(\vec{r}, t) \equiv e^{i(\omega t - \vec{k} \cdot \vec{r})} \vec{e}(\vec{r}, t) + \text{c.c.}, \quad (2.1)$$

where c.c. is used to denote the complex conjugate of the preceding terms,  $\omega$  and  $\vec{k}$  are the frequency and wave vector of the incident light, respectively, and  $\vec{e}(\vec{r}, t)$  is the space- and time-modulated electric field amplitude. In what follows, geometric optics is assumed for the incident light, which means that the modulation lengths and times are large compared to the wavelength of light and  $\omega^{-1}$ , respectively. In fact, the modulation time is further restricted to be longer than the characteristic microscopic

decay time for the optical processes under consideration, typically 1–100 ps.

By assuming the dipole approximation for the coupling to the external field<sup>8</sup> and neglecting local-field effects (this should be valid for low-polarizability solvents), the Hamiltonian for the system  $H_T$  can be written as

$$H_T = H - \vec{\mu}(\vec{r}, t) * \vec{E}(\vec{r}, t) \equiv H + H_1(t), \quad (2.2)$$

where  $H$  is the Hamiltonian in the absence of the electric field,  $H_1(t)$  is the perturbation,

$$\vec{\mu}(\vec{r}, t) \equiv \sum_j \delta(\vec{r} - \vec{R}_j(t)) \vec{\mu}_j(t) \quad (2.3)$$

is the dipole moment density operator, and the symbol  $*$  is used to denote a dot product and integration over the field point  $\vec{r}$ . In Eq. (2.3),  $\vec{R}_j$  is the center-of-mass position of the  $j$ th molecule and  $\vec{\mu}_j$  is its dipole moment. Note, the molecular dipole moment operator is Hermitian and commutes with the center-of-mass degrees of free-

dom.

The system's density matrix  $\rho$  satisfies the quantum Liouville equation

$$\begin{aligned} \frac{\partial \rho(t)}{\partial t} &= \frac{1}{i\hbar} [H + H_1(t), \rho(t)] \\ &\equiv -i[L + L_1(t)]\rho(t), \end{aligned} \quad (2.4)$$

where  $[\dots, \dots]$  is the commutator and  $L$  ( $L_1$ ) is the tetradic Liouville operator corresponding to  $H$  ( $H_1$ ). The formal solution to Eq. (2.4) is

$$\rho(t) = T_+ \exp \left[ -i \int_{-\infty}^t d\tau [L + L_1(\tau)] \right] \rho_{\text{eq}}, \quad (2.5)$$

where it has been assumed that the system was in equilibrium in the infinite past, with equilibrium density matrix  $\rho_{\text{eq}}$ , and  $T_+$  is a positive time-ordering operator. In response theory, the right-hand side of Eq. (2.5) is expanded in powers of the perturbing Hamiltonian. The well-known result is

$$\begin{aligned} \rho(t) &= \rho_{\text{eq}} + \int_{-\infty}^t dt_1 \frac{[\rho_{\text{eq}}, \vec{\mu}(\vec{r}, t_1 - t)]}{i\hbar} * \vec{E}(\vec{r}, t_1) \\ &+ \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 e^{-iL(t-t_1)} \frac{[[\rho_{\text{eq}}, \vec{\mu}(\vec{r}_2, t_2 - t_1)], \vec{\mu}(\vec{r}_1)]}{(i\hbar)^2} * \vec{E}(\vec{r}_1, t_1) \vec{E}(\vec{r}_2, t_2) + O(E^3), \end{aligned} \quad (2.6)$$

where

$$\vec{\mu}(\vec{r}, t) = \exp \left[ \frac{iHt}{\hbar} \right] \vec{\mu}(\vec{r}) \exp \left[ -\frac{iHt}{\hbar} \right]. \quad (2.7)$$

Equation (2.6) is an expansion for the full  $N$ -body density matrix of the system; as such, it can be expected to give reasonable results only when used to compute the average of few-body operators. Fortunately, this is the case here. Denoting the operator whose average is desired by  $B$  and using Eq. (2.6) gives

$$\begin{aligned} \langle B(t) \rangle_{\text{nc}} &= \langle B \rangle - \int_{-\infty}^t dt_1 \frac{\langle [B(t-t_1), \vec{\mu}(\vec{r})] \rangle}{i\hbar} * \vec{E}(\vec{r}, t_1) \\ &+ \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \frac{\langle [[B(t-t_1), \vec{\mu}(\vec{r}_1)], \vec{\mu}(\vec{r}_2, t_2 - t_1)] \rangle}{(i\hbar)^2} * \vec{E}(\vec{r}_2, t_2) \vec{E}(\vec{r}_1, t_1) + O(E^3), \end{aligned} \quad (2.8)$$

where  $\langle \dots \rangle_{\text{nc}}$  and  $\langle \dots \rangle$  denote a nonequilibrium and equilibrium average, respectively. In obtaining Eq. (2.8), the identity

$$\text{Tr}(A[B, C]) = \text{Tr}(B[C, A]),$$

for any operators  $A, B, C$ , was used.

The term linear in the external field is the usual linear-response expression. It is completely unimportant for photoacoustic pulse generation. It is linear in the electric field and will oscillate at the frequency of the incident light (i.e.,  $\omega \approx 10^{15} \text{ sec}^{-1}$ ). The modulation of the incident light will not modify this in any essential way as long as it is slow. On the other hand, the photoacoustic signal is usually detected by a microphone or piezoelectric crystal; these will not respond to disturbances which vary on the time scale of light and hence, the leading-order pho-

toacoustic disturbance will arise from the quadratic term. Similar arguments can be used to show that the photoacoustic signal only depends on the terms even in the external field, since these are the only ones which can generate low-frequency disturbances.

There is, however, one aspect of the linear response which is important, namely, the total power being dissipated by the system. This is a well-known result and is a specific example of the fluctuation dissipation theorem.<sup>7</sup> The power dissipated by the system,  $P(\omega)$ , to leading order in  $E$  is given by

$$P(\omega) = \frac{\partial \vec{E}(\vec{r}, t)}{\partial t} * \int_0^\infty dt_1 \frac{\langle [\vec{\mu}(\vec{r}, t_1), \vec{\mu}(\vec{r}')] \rangle}{i\hbar} * \vec{E}(\vec{r}', t_1), \quad (2.9)$$

which when combined with Eq. (2.1) and omitting all

high-frequency terms, can be rewritten as

$$P(\omega) = -2\omega \int_0^\infty dt' \sin(\omega t') \frac{\langle [\vec{\mu}_T(t'), \vec{\mu}_T] \rangle}{i\hbar V} \\ \times \int d\vec{r} |e(\vec{r}, t)|^2. \quad (2.10)$$

The volume of the system is denoted by  $V$  and the total dipole moment is denoted by  $\vec{\mu}_T$ . In writing Eq. (2.10), use was made of the fact that the system is translationally and rotationally invariant, and that the correlation length and time of  $\langle [\vec{\mu}(\vec{r}, t), \vec{\mu}(\vec{0}, 0)] \rangle$  are small compared with the wavelength of light and modulation length and time scales. This should be an excellent approximation, given the short lifetime of the dipole-dipole correlation function.

A rough estimate of the correlation length can be obtained when the correlation between different absorbers can be neglected (e.g., a dilute or weak coupling limit). In such cases, the correlation between different points in the system is established through factors of the form  $\delta(\vec{r} - \vec{r}' - \vec{R}_j(0) + \vec{R}_j(t))$ , cf. Eq. (2.3). An estimate for the distance traveled by the absorber during the dipole correlation-function lifetime can be obtained by assuming free streaming (gases) or diffusive (liquids) motion. The former gives a much larger correlation length, but nonetheless, is only  $O(10^{-6} \text{ cm})$  for lifetimes in the picoseconds; in liquids, the diffusive estimate gives  $O(1-10 \text{ \AA})$ . Note that isotropy implies that the correlation function on the right-hand side of Eq. (2.10) is diagonal with respect to its Cartesian indices.

$S(\vec{r}, t)$ , the incident optical energy flux along the incident wave vector at position  $\vec{r}$  (i.e., the Poynting vector), in geometric optics is given by

$$S(\vec{r}, t) = \frac{c}{2\pi} |e(\vec{r}, t)|^2,$$

where  $c$  is the speed of light. With this, the absorption coefficient  $\alpha(\omega)$ , defined by  $P(\omega) = \alpha(\omega) \int d\vec{r} S(\vec{r}, t)$ , becomes

$$\alpha(\omega) = \frac{4\pi\omega}{i\hbar c V} \int_0^\infty dt \sin(\omega t) \langle [\vec{\mu}_T, \vec{\mu}_T(t)] \rangle, \\ = \frac{4\pi\omega}{i\hbar c V} \int_{-\infty}^\infty dt \sin(\omega t) \langle \vec{\mu}_T \cdot \vec{\mu}_T(t) \rangle, \quad (2.11)$$

this being the usual result.

The quadratic term can be simplified somewhat by making use of the expected short-range correlation properties of the correlation function. As was the case with the linear term, it is reasonable to assume that the dipole moment densities (or the various commutators of them) will yield nonzero averages only if  $|\vec{r}_1 - \vec{r}_2|$  and  $|t_1 - t_2|$  are small with respect to the length and time scales which characterize the wavelength of light or the modulation. In order to exploit this property, the spatial integration variables are changed from  $\vec{r}_1$  and  $\vec{r}_2$  to  $\vec{r}' \equiv \frac{1}{2}(\vec{r}_1 + \vec{r}_2)$  and  $\vec{r}_{12} \equiv \vec{r}_1 - \vec{r}_2$  in the two spatial integrations in the quadratic term in Eq. (2.8). Next, Eq. (2.1) is used in the quadratic response term. Of the resulting four terms, two are high frequency (i.e., double harmonics of the light) and can be dropped. Finally, expanding the electric field amplitudes and  $e^{-i\vec{k} \cdot \vec{r}_{12}}$  (which vary on long space and time scales) in Taylor series about  $t_1 - t_2 = 0$  and  $\vec{r}_{12} = 0$  and keeping the lowest-order terms allows Eq. (2.8) to be rewritten as

$$\langle \delta B(t) \rangle_{\text{ne}} = \int_{-\infty}^t dt_1 \int_0^\infty dt' \int d\vec{r}_{12} d\vec{r}' \frac{\langle [[B(t-t_1), \vec{\mu}(\vec{r}' + \frac{1}{2}\vec{r}_{12})], \vec{\mu}(\vec{r}' - \frac{1}{2}\vec{r}_{12}, -t')] \rangle}{(i\hbar)^2} \\ \times [e^{i\omega t'} \vec{e}^*(\vec{r}', t_1) \vec{e}(\vec{r}', t_1) + \text{c.c.}]. \quad (2.12)$$

The linear term has been dropped pursuant to the discussion given above.  $\delta B$  is henceforth used to denote the deviation of  $B$  from its equilibrium average value and the superscript  $*$  denotes the complex conjugate. Note, that at this stage, unlike the case of the absorbed power, it cannot be concluded that the quadratic term depends only on  $|e(\vec{r}, t)|^2$ . In fact, as will be seen below, it does not.

It must be stressed that the approximations which transformed Eq. (2.8) into (2.12) are completely analogous to those which allowed Eq. (2.9) to be reexpressed as Eq. (2.10). Their validity depends only on the large separation of time and length scales between the dipole density correlations and the properties of the incident light. In fact, the weakest of these assumptions is the restriction that the correlation length be small with respect to the wavelength of light. While this should hold due to the fact that the spectroscopy (i.e., ir, visible, etc.) is essentially a single-particle probe, expressions valid for much shorter-wavelength light can be obtained by restoring the factors

of  $e^{-i\vec{k} \cdot \vec{r}_{12}}$  to the integrands of Eqs. (2.12) and (2.11). Up to this point, the discussion has not depended on the precise form of  $B$ . For photoacoustic measurements,  $B$ 's corresponding to specific combinations of the hydrodynamic variables are probed. These are considered in Sec. III.

### III. RESPONSE OF THE HYDRODYNAMIC VARIABLES

The detector in photoacoustic spectroscopy measures the instantaneous pressure (momentum flux) at a specific point in the system. Since the time and length scales involved in this measurement are long, macroscopic expressions relating the pressure to the hydrodynamic variables can be used (e.g., the Navier-Stokes expression for the stress tensor). Hence, all that is actually required are the instantaneous values of the hydrodynamic variables in the vicinity of the microphone. The hydrodynamic variables

are the densities of the conserved properties of the system, i.e., the energy, mass, and momentum densities. These will be denoted by  $H(\vec{r}, t)$ ,  $M_i(\vec{r}, t)$ , and  $\vec{P}(\vec{r}, t)$ , where  $i$  labels the components, respectively, or collectively by  $\underline{A}(\vec{r}, t)$ . The nonequilibrium average deviation of these quantities from their equilibrium values will be denoted by lower case letters, e.g.,  $h(\vec{r}, t)$ , or collectively by  $\underline{a}(\vec{r}, t)$ . The microscopic definitions of these quantities are well known.<sup>7,9</sup> What makes the hydrodynamic variables relevant to long-time processes is the fact that they all satisfy continuity equations of the form

$$\frac{\partial a(\vec{r}, t)}{\partial t} = -\vec{\nabla} \cdot \vec{J}(\vec{r}, t), \quad (3.1)$$

$$\underline{W}^{ij}(\vec{r} - \vec{r}'; t; \omega) \equiv \frac{2\pi}{c(i\hbar)^2} \int_0^\infty dt' \int_V d\vec{r}_1 e^{i\omega t'} \langle [[\underline{A}(\vec{r}, t), \mu^i(\vec{r}' + \frac{1}{2}\vec{r}_{12})], \mu^j(\vec{r}' - \frac{1}{2}\vec{r}_{12}, -t')] \rangle, \quad (3.3)$$

$$S^{ji}(\vec{r}, t) \equiv \frac{c}{2\pi} [e^j(\vec{r}, t)]^* e^i(\vec{r}, t), \quad (3.4)$$

and where, henceforth, repeated indices are to be summed. Note that translational invariance implies that  $\underline{W}$  is a function of  $\vec{r} - \vec{r}'$ . In addition, the trace of  $S^{ij}$  is the incident energy flux.

The spatial integral on the right-hand side of Eq. (3.2) is a convolution; hence, the subsequent analysis can be simplified by introducing spatial Fourier transforms, e.g.,

$$\underline{A}(\vec{k}, t) \equiv \int_V d\vec{r} e^{i\vec{k} \cdot \vec{r}} \underline{A}(\vec{r}, t). \quad (3.5)$$

Equation (3.2) thus becomes

$$\underline{a}(\vec{k}, t) = \int_{-\infty}^t dt_1 [\underline{W}^{ij}(\vec{k}, t - t_1, \omega) + \underline{W}^{ji}(\vec{k}, t - t_1, -\omega)] S^{ji}(\vec{k}, t). \quad (3.6)$$

From Eq. (3.3) and translational invariance,

$$\underline{W}^{ij}(\vec{k}, t, \omega) = \frac{2\pi}{c(i\hbar)^2 V} \int_0^\infty dt' e^{i\omega t'} \langle [[\underline{A}(\vec{k}, t), \mu^i(-\frac{1}{2}\vec{k})], \mu^j(-\frac{1}{2}\vec{k}, -t')] \rangle. \quad (3.7)$$

There are two types of motion contained in  $\underline{W}$ : the fast motions associated with the absorption and other microscopic processes, and the relatively slow motions associated with the photoacoustic pulse propagation to the detector. The latter are characterized by small  $k$ 's and long times in Eq. (3.6). In order to make the separation of time scales more explicit, note the following projection operator identity:<sup>7,10</sup>

$$\underline{A}(\vec{k}, t) = \underline{G}(\vec{k}, t) \underline{A}(\vec{k}, t=0) + \int_0^t dt' \underline{G}(\vec{k}, t - t') i\vec{k} \cdot \vec{I}(\vec{k}, t'), \quad (3.8)$$

where  $\underline{G}(\vec{k}, t)$  is the hydrodynamic propagator and  $\vec{I}(\vec{k}, t)$  is the random or dissipative current. In the language of projection operators, the dissipative currents are orthogonal to the space of slow variables and therefore represent

where  $\vec{I}(\vec{r}, t)$  refers collectively to the microscopic fluxes of energy  $\vec{J}_E(\vec{r}, t)$ , mass  $\vec{J}_i(\vec{r}, t)$ , and momentum  $\vec{T}(\vec{r}, t)$  (stress tensor). Again, the microscopic definitions of the fluxes are well known<sup>7,9</sup> and will not be repeated here.

From Eq. (2.12) it follows that

$$\underline{a}(\vec{r}, t) = \int_{-\infty}^t dt_1 \int_V d\vec{r}' [\underline{W}^{ij}(\vec{r} - \vec{r}'; t - t_1; \omega) + \underline{W}^{ji}(\vec{r} - \vec{r}'; t - t_1; -\omega)] \times S^{ji}(\vec{r}', t_1), \quad (3.2)$$

where

the fast motions of the system. This, of course, depends on a correct identification of the complete set of slow variables. Here it has been *assumed* that the hydrodynamic variables are the only relevant slow quantities in the problem. The dissipative currents should thus have correlations which decay on microscopic length and time scales. The propagator, strictly speaking, is defined in terms of the hydrodynamic variable time-correlation functions, although for long-wavelength phenomena it can be obtained phenomenologically (see below).

Using Eq. (3.8) in (3.7) allows the latter to be rewritten as

$$\underline{W}^{ij}(\vec{k}, t, \omega) = \underline{W}_R^{ij}(\vec{k}, t, \omega) + \underline{W}_D^{ij}(\vec{k}, t, \omega), \quad (3.9)$$

where the reversible and dissipative parts of  $\underline{W}$  are defined by

$$\underline{W}_R^{ij}(\vec{k}, t, \omega) \equiv \underline{G}(\vec{k}, t) \frac{2\pi}{c(i\hbar)^2 V} \int_0^\infty dt' e^{i\omega t'} \langle [[\underline{A}(\vec{k}), \mu^i(-\frac{1}{2}\vec{k})], \mu^j(-\frac{1}{2}\vec{k}, -t')] \rangle, \quad (3.10)$$

and

$$\underline{W}_D^{ij}(\vec{k}, t, \omega) \equiv \frac{2\pi}{c(i\hbar)^2 V} \int_0^t dt_1 \underline{G}(\vec{k}, t - t_1) \int_0^\infty dt' e^{i\omega t'} \langle [[i\vec{k} \cdot \vec{I}(\vec{k}, t_1), \mu^i(-\frac{1}{2}\vec{k})], \mu^j(-\frac{1}{2}\vec{k}, -t')] \rangle, \quad (3.11)$$

respectively.

Note that the time-correlation functions in Eqs. (3.10) and (3.11) have their time dependence associated with some microscopic quantity, i.e., the dipole moment densities or dissipative currents. As such, they should decay on microscopic time scales, with a concomitant microscopic correlation length. Since photoacoustic spectroscopy probes only long time and wavelength acoustic phenomena, the time-correlation functions on the right-hand sides of Eqs. (3.10) and (3.11) can be expanded into Taylor series in the wave vector (i.e., into a series in  $k\lambda_s$ , where  $\lambda_s$  is some small length). This is analogous to the expansion of Selwyn and Oppenheim<sup>11</sup> in their treatment of generalized hydrodynamics. As with all such expansions, there is the question of convergence, a question which is

beyond the scope of this paper.

First consider the reversible part of  $\underline{W}$ . It is easily shown that the dipole moment density commutes with all of the mass densities. The commutator with the momentum density is easily shown to equal

$$[\vec{P}_{\vec{k}}, \vec{\mu}_{-\frac{1}{2}\vec{k}}] = -\hbar\vec{k}\vec{\mu}_{\frac{1}{2}\vec{k}}.$$

Finally, for the coupling to the energy density, the resulting correlation function is a rank 2 tensor and thus must be an even function of  $\vec{k}$  in a system with inversion symmetry. Moreover, the  $k=0$  limit of the energy density is simply the total Hamiltonian of the system. Thus Eq. (3.10) becomes

$$\begin{aligned} \underline{W}_{\gamma,R}^{ij}(\vec{k},t,\omega) = & \frac{2\pi}{c(i\hbar)^2V} \int_0^\infty dt' e^{i\omega t'} \{ G_{\gamma,H}(\vec{k},t) \langle [[H, \mu_T^i], \mu_T^j(-t')] \rangle \\ & - G_{\gamma,p^n}(\vec{k},t) \hbar k^n \langle [\mu_T^i, \mu_T^j(-t')] \rangle \} + O((k\lambda_s)^2). \end{aligned} \quad (3.12)$$

Of course,

$$i\hbar \frac{\partial \vec{\mu}_T(t)}{\partial t} = [\vec{\mu}_T(t), H], \quad (3.13)$$

which when used in Eq. (3.12), using the fact that the equilibrium distribution is stationary in time, and integrating by parts gives

$$\underline{W}_{\gamma,R}^{ij}(\vec{k},t,\omega) = \frac{2\pi}{c i \hbar V} \int_0^\infty dt' e^{i\omega t'} [i\omega G_{\gamma,H}(\vec{k},t) + G_{\gamma,p^n}(\vec{k},t) i k^n] \langle [\mu_T^x(t'), \mu_T^x] \rangle \delta_{ij} + O((k\lambda_s)^2), \quad (3.14)$$

where  $\delta_{ij}$  is the Kronecker delta. (It is due to the fact that the system is isotropic.) Using Eqs. (3.14) and (2.11) gives

$$\underline{W}_{\gamma,R}^{ij}(\vec{k},t,\omega) + \underline{W}_{\gamma,R}^{ji}(\vec{k},t,-\omega) = [G_{\gamma,H}(\vec{k},t)\alpha(\omega) + G_{\gamma,p^n}(\vec{k},t) i k^n \epsilon(\omega)] \delta_{ij} + O((k\lambda_s)^2), \quad (3.15)$$

where

$$\epsilon(\omega) \equiv \frac{4\pi}{i\hbar c V} \int_0^\infty dt \cos(\omega t) \langle [\mu_T^x(t), \mu_T^x] \rangle \quad (3.16)$$

is the derivative of  $\alpha(\omega)/\omega$ . When Eq. (3.15) is used in conjunction with Eq. (3.2), it follows that the response due to the first term in the reversible part of the motion depends only on the absorbed power. In fact, as will be shown below, this term is exactly what the phenomenological theories of photoacoustic pulse generation would predict. Before showing this, however, the dissipative part will be examined. The term in  $\epsilon(\omega)$  will vanish at the absorption maxima. Roughly speaking, it represents the dis-

turbance generated electrostrictively and should be very small. In fact, it can be shown, cf. Eq. (4.10) below, that this term is  $O((\omega\tau_p)^{-1})$ , where  $\tau_p$  is the pulse time.

The response excited via the coupling between the dissipative currents and the dipole moment densities is explicitly proportional to  $k$ , cf. Eq. (3.11). Since a simple form for the reversible terms could be obtained only to  $O((k\lambda_s)^2)$ , it is sufficient to consider the leading order behavior of  $\underline{W}_D$ . From Eq. (3.11) it follows that

$$\underline{W}_D^{ij}(\vec{k},t,\omega) = \frac{2\pi}{c(i\hbar)^2V} \int_0^t dt_1 \underline{G}(\vec{k},t) \int_0^\infty dt' e^{i\omega t'} i\vec{k} \cdot \langle [[\vec{I}_T(t_1), \mu_T^i], \mu_T^j(-t')] \rangle + O((k\lambda_s)^2), \quad (3.17)$$

where in obtaining this last expression, the  $t_1$  dependence of  $G$  was neglected, since it comes in with extra factors of  $k$ , cf. Eq. (3.1). Also the limit of the  $t_1$  integration was extended to  $\infty$ , as the integrand should decay on a microscopic time scale. The correlation function on the right-hand side of Eq. (3.17) is much more complicated than that which appeared in the reversible terms. Nonetheless, for systems with inversion symmetry, it is easy to see that the couplings to the dissipative energy and mass currents vanish, since the associated correlations involve the average of a third-rank tensor, which will average to zero. Thus Eq. (3.17) becomes

$$\underline{W}_{\gamma,D}^{ij}(\vec{k},t,\omega) = \frac{2\pi}{c(i\hbar)^2V} \int_0^\infty dt_1 G_{\gamma,\vec{P}}(\vec{k},t) \int_0^\infty dt' e^{i\omega t'} i\vec{k} \cdot \langle [[\vec{I}_{\vec{P},T}(t_1), \mu_T^i], \mu_T^j(-t')] \rangle + O((k\lambda_s)^2), \quad (3.18)$$

where  $\vec{\Gamma}_{\vec{P},T}$  is the  $k=0$  limit of the dissipative part of the stress tensor. Since the correlation function is the average of a fourth-rank tensor in an isotropic system, Eq. (3.18) can be rewritten as

$$\begin{aligned} \underline{W}_{\gamma,D}^{ij}(\vec{k},t,\omega) = & [G_{\gamma,pi}(\vec{k},t)ik^j + G_{\gamma,pj}(\vec{k},t)ik^i - \frac{2}{3}\delta_{ij}G_{\gamma,pn}ik^n]\Lambda_1 \\ & + [G_{\gamma,pn}(\vec{k},t)ik^n]\Lambda_2\delta_{ij} + [G_{\gamma,pi}(\vec{k},t)ik^j - G_{\gamma,pj}(\vec{k},t)ik^i]\Lambda_3, \end{aligned} \quad (3.19)$$

where

$$\Lambda_1 \equiv \frac{2\pi}{c(i\hbar)^2V} \int_0^\infty dt_1 \int_0^\infty dt' e^{i\omega t'} \langle [[I_{\vec{P},T}^{xy,s}(t_1), \mu_T^x], \mu_T^y(-t')] \rangle + O((k\lambda_s)^2), \quad (3.20a)$$

$$\Lambda_2 \equiv \frac{2\pi}{9c(i\hbar)^2V} \int_0^\infty dt_1 \int_0^\infty dt' e^{i\omega t'} \langle [[I_{\vec{P},T}^{ii}(t_1), \mu_T^i], \mu_T^i(-t')] \rangle + O((k\lambda_s)^2), \quad (3.20b)$$

and

$$\Lambda_3 \equiv \frac{2\pi}{c(i\hbar)^2V} \int_0^\infty dt_1 \int_0^\infty dt' e^{i\omega t'} \langle [[I_{\vec{P},T}^{yx,a}(t_1), \mu_T^x], \mu_T^y(-t')] \rangle + O((k\lambda_s)^2), \quad (3.20c)$$

where the superscripts  $a$  and  $s$  denote the asymmetric and symmetric parts of  $\vec{\Gamma}$ , respectively. The  $\Lambda$  coefficients represent the dissipative coupling to between the external field and the local stress in the solvent. Of the three terms, only  $\Lambda_2$  will generate a response which is proportional to the incident power, although the absorption coefficient does not fall out exactly, as was the case with the reversible terms. The terms in  $\Lambda_1$  are qualitatively new. They generate a response which in general depends coherently on the polarizations of the incident fields. Finally, the terms in  $\Lambda_3$  arise from nonspherically symmetric interactions. They do not couple to the (longitudi-

nal) acoustic modes and are not considered further. The remaining parts of  $\underline{W}_D^{ij}$  are explicitly symmetric in  $ij$ , cf. Eq. (3.19); thus when they are combined with Eqs. (3.9) and (3.6) the net result will be to take twice the real part of the  $\Lambda$  coefficients [i.e., to replace the factors of  $e^{i\omega t'}$  by  $2\cos(\omega t')$  in Eqs. (3.20a) and (3.20b)]. It is henceforth assumed that this has been carried out and the same notation, i.e.,  $\Lambda_{1,2}$  will be used for the coefficient of the result.

In the limits of high dilution or weak interabsorber coupling, the correlation between different dipoles can be neglected and Eqs. (3.20a) and (3.20b) can be rewritten as

$$\Lambda_1 = \frac{4\pi n_a}{c(i\hbar)^2} \int_0^\infty dt_1 \int_0^\infty dt' \cos(\omega t') \langle [[I_{\vec{P},T}^{xy,s}(t_1), \mu_1^x], \mu_1^y(-t')] \rangle + O((k\lambda_s)^2) \quad (3.21a)$$

and

$$\Lambda_2 = \frac{4\pi n_a}{9c(i\hbar)^2} \int_0^\infty dt_1 \int_0^\infty dt' \cos(\omega t') \langle [[I_{\vec{P},T}^{ii}(t_1), \mu_1^i], \mu_1^i(-t')] \rangle + O((k\lambda_s)^2), \quad (3.21b)$$

where  $n_a$  is the absorber number density and  $\vec{\mu}_1$  corresponds to the dipole moment of any single absorber. In addition, pursuant to the preceding discussion, Eqs. (3.21a) and (3.21b) have been written in a form which can be directly used in Eq. (3.6). Similarly, the absorption coefficient can be written as the absorber number density times a single-particle absorption coefficient [cf. Eq. (2.11)].

Note that the fact that the dissipative stress is evaluated at  $k=0$  leads to some well-known simplifications. Specif-

ically, the  $x$ - $y$  components become equal to the corresponding components of the stress tensor, i.e.,

$$\vec{\tau}_T = \sum_j \left[ \frac{\vec{P}_j \vec{P}_j}{m_j} + \frac{1}{2} \sum_{j' (\neq j)} \vec{r}_{j,j'} \vec{F}_{j,j'} \right], \quad (3.22)$$

where  $\vec{F}_{j,j'}$  is the force  $j$  exerts on  $j'$  (pairwise additivity is assumed).

Combining Eqs. (3.19), (3.15), (3.9), and (3.6) gives

$$\begin{aligned} a_\gamma(\vec{k},t) = & \int_{-\infty}^t dt_1 \{ G_{\gamma,H}(\vec{k},t-t_1)\alpha(\omega) + ik^n G_{\gamma,pn}(\vec{k},t-t_1)[\Lambda_2 + \epsilon(\omega)] \} S(\vec{k},t_1) \\ & + [G_{\gamma,pi}(\vec{k},t-t_1)ik^j + G_{\gamma,pj}(\vec{k},t-t_1)ik^i - \frac{2}{3}\delta_{ij}G_{\gamma,pn}(\vec{k},t-t_1)ik^n]\Lambda_1 S^{ji}(\vec{k},t_1) + O((k\lambda_s)^2). \end{aligned} \quad (3.23)$$

In Sec. IV, a specific experimental configuration which should allow  $\Lambda_1$  to be measured is proposed and analyzed.

#### IV. THE PHOTOACOUSTIC EXPERIMENT

Equation (3.23) is a general expression for the response of the system to quadratic order in the external fields. All that needs to be done in order to compare with the experiment is to write out the various elements of the propagators and carry out the algebra. In what follows, it is assumed that the photoacoustic experiment measures the instantaneous deviation of the hydrostatic pressure from equilibrium, i.e.,

$$\delta p_h(\vec{k}, t) \equiv \Xi_{M_i} m_i(\vec{k}, t) + \Xi_H h(\vec{k}, t), \quad (4.1)$$

where

$$\Xi_{M_i} \equiv \left[ \frac{\partial p_h}{\partial m_i} \right]_{m_j \neq i, h}, \quad (4.2a)$$

$$\Xi_H \equiv \left[ \frac{\partial p_h}{\partial h} \right]_{m_j} = \frac{c_s^2 \gamma_T}{c_p}, \quad (4.2b)$$

and  $c_s$ ,  $\gamma_T$ , and  $c_p$  are the adiabatic sound speed, thermal-expansion coefficient, and specific heat at constant pressure, respectively. Thus from Eq. (3.23) it follows that

$$G_{p_h, \gamma}(\vec{k}, t) \equiv \Xi_{M_i} G_{M_i, \gamma}(\vec{k}, t) + \Xi_H G_{H, \gamma}(\vec{k}, t), \quad \gamma = H, \vec{P} \quad (4.3)$$

is needed. This is not too difficult a task if use is first made of the fact that hydrodynamics does not couple longitudinal and transverse modes (the pressure belongs to the former class) and if the length and time scales of the acoustics are chosen to be sufficiently fast so as to be able to ignore purely diffusive modes. That is, the diffusive modes will not have time to reach the detector. Here the longitudinal diffusive modes are the entropy and mass diffusion modes. The purely longitudinal response, cf., Eqs. (4.3) and (3.23) can be written as

$$\delta p_h(\vec{r}, t) = \frac{1}{2\pi} \int_{-\infty}^{t-r/c_s} dt' \frac{\left[ \frac{c_s \gamma_T \alpha(\omega)}{c_p} \dot{I}_0(t') + \frac{\epsilon(\omega) + \Lambda_2 + 4\Lambda_1 [(\hat{n} \cdot \hat{r}_1)^2 - \frac{1}{3}]}{c_s} \ddot{I}_0(t') \right]}{[c_s^2(t-t')^2 - r_1^2]^{1/2}}, \quad (4.7)$$

where the overdot denotes a time derivative.

The first term in the integrand of Eq. (4.7) is exactly what was obtained by Patel and Tam<sup>1</sup> and arises from the adiabatic expansion of the fluid on absorption of light. The two terms in  $\Lambda$  are new. As mentioned above, they arise from the direct coupling of the molecular dipole mo-

$$\begin{aligned} \delta p_h(\vec{k}, t) = & \int_{-\infty}^t dt_1 \{ G_{p_h, H}(\vec{k}, t-t_1) \alpha(\omega) \\ & + ik G_{p_h, P}^{\parallel}(\vec{k}, t-t_1) [\Lambda_2 + \epsilon(\omega)] \} \\ & \times S(\vec{k}, t_1) + 2ik G_{p_h, P}^{\parallel}(\vec{k}, t-t_1) \Lambda_1 \\ & \times (\hat{k} \hat{k} - \frac{1}{3} \mathbb{I}) : \vec{S}(\vec{k}, t_1), \end{aligned} \quad (4.4)$$

where the superscript  $\parallel$  on the propagator denotes the part corresponding to the longitudinal velocity and where  $k$  is a unit vector in the  $\vec{k}$  direction. The low-wave-vector form of the propagators is well known and for example is given in Appendix A of Ref. 12 (note that the notation is somewhat different). The propagators are thus

$$G_{p_h, H}(\vec{k}, t) = \frac{c_s^2 \gamma_T}{c_p} \cos(kc_s t) e^{-k^2 \Gamma_s t} \quad (4.5a)$$

and

$$G_{p_h, P}^{\parallel}(\vec{k}, t) = ic_s \sin(kc_s t) e^{-k^2 \Gamma_s t}, \quad (4.5b)$$

where  $\Gamma_s$  is the sound damping constant. For what follows, it is assumed that the distance to the detector is small enough so that damping can be neglected in the acoustic propagation.

The photoacoustic experiment measures the acoustic signal generated by an extended source. The incident beam is usually modeled by an infinite cylinder of radius  $R$  along the  $z$  direction;<sup>1</sup> thus

$$\vec{S}(\vec{r}, t) = \begin{cases} \vec{n} \vec{n} \frac{I_0(t)}{\pi R^2}, & r_{\perp} < R \\ 0, & \text{otherwise} \end{cases} \quad (4.6)$$

where  $\vec{n}$  is the polarization direction of the incident light (it of course must lie in the  $x$ - $y$  plane), the subscript  $\perp$  denotes the projection onto the  $x$ - $y$  plane and  $I_0(t)$  is the incident power. For the moment, the time dependence of  $I_0(t)$  will be left unspecified, except for the fact that it be a pulse with characteristic time  $\tau_p$ . With this incident beam profile, Eqs. (4.6) and (4.5) can be used in Eq. (4.4) to compute the pressure response. In order to simplify the calculation, it is assumed that the measurement is performed in the acoustic far field and that the incident beam is very thin (specifically,  $r_{\perp} \gg R$  and  $R \ll c_s \tau_p$ ). The details are contained in Appendix A and the pressure response is

ment to the local stress. Roughly speaking, the relationship between the new and old terms is analogous to that between the reversible and dissipative terms in the hydrodynamic equations (e.g., the sound speed versus the viscosities). It is probably the case that the new terms are small. However, the term in  $\Lambda_1$  is qualitatively new; it de-

pends on the polarization of the incident light. Thus a differential measurement of the photoacoustic pulses generated from light with polarization pointing toward and perpendicular to the detector would measure the  $\Lambda_1$  term directly.

In order to facilitate comparison with experiment, the time integrals in Eq. (4.7), will be evaluated for a pulse which is Gaussian in time;<sup>1</sup> specifically,

$$\delta p_h(\vec{r}, t) = -\frac{E_0}{2\pi(2r_1 c_s \tau_p^3)^{1/2}} \left[ \frac{c_s \gamma_T \alpha(\omega)}{2c_p} f_1[(t-r_1/c_s)/\tau_p] - \frac{3\{\epsilon(\omega) + \Lambda_2 + 4\Lambda_1[(\hat{n} \cdot \hat{r}_1)^2 - \frac{1}{3}]\}}{c_s \tau_p} f_2[(t-r_1/c_s)/\tau_p] \right], \quad (4.10)$$

where

$$\begin{aligned} f_1(x) &\equiv \frac{4}{\pi^{1/2}} \int_{-\infty}^x dt \frac{te^{-t^2}}{(x-t)^{1/2}} \\ &= 2^{1/4} e^{-x^2/2} [2^{3/2} x D_{-1/2}(-2^{1/2}x) \\ &\quad - D_{-3/2}(-2^{1/2}x)] \end{aligned} \quad (4.11a)$$

and

$$\begin{aligned} f_2(x) &\equiv \frac{2}{3\pi^{1/2}} \int_{-\infty}^x dt \frac{(2t^2-1)e^{-t^2}}{(x-t)^{1/2}} \\ &= \frac{2^{3/4}}{6} e^{-x^2/2} [3D_{-5/2}(-2^{1/2}x) \\ &\quad - 4xD_{-3/2}(-2^{1/2}x) \\ &\quad - (2x^2+1)D_{-1/2}(-2^{1/2}x)], \end{aligned} \quad (4.11b)$$

where  $D_\nu(x)$  is a parabolic cylinder function.<sup>13</sup> Equation (4.11a) gives the standard expression for the time dependence of the response due to a Gaussian pulse. Equation (4.11b) is new. For  $x \gg 1$ ,  $f_1(x)$  and  $f_2(x)$  decay like  $x^{-3/2}$  and  $x^{-5/2}$ , respectively. Both functions are plotted in Fig. 1. Note the appearance of a compression pulse at  $-0.4\tau_p$  followed by a rarefaction pulse at  $1.3\tau_p$  associated with  $f_1$ . This phenomena has been noticed before,<sup>1</sup> although the times for the compression and rarefaction differ slightly from those reported here. Similar behavior is exhibited by  $f_2$ , although the extrema are at slightly different times. Finally, note that the new terms have a different pulse time dependence than the usual ones; they are larger for shorter pulses.

## V. DISCUSSION

The main result of this work is contained in Eqs. (4.7) and (4.10). In addition to the usual photoacoustic signal, two new effects have been predicted. The one which should be most readily accessible to experiment should be the coupling to the shear stress fluctuations via  $\Lambda_1$ , since a different symmetry is involved. The coupling to  $\Lambda_2$ , while

$$I_0(t) \equiv \frac{E_0}{\pi^{1/2} \tau_p} e^{-(t/\tau_p)^2}, \quad (4.8)$$

where  $E_0$  is the energy in the pulse. Moreover, since  $r_1 \approx c_s t$ , then

$$[c_s(t-t')^2 - r_1^2]^{1/2} \approx (2r_1)^{1/2} [c_s(t-t') - r_1]^{1/2}. \quad (4.9)$$

This allows Eq. (4.7) to be rewritten as

not having any polarization dependence, has, cf. Eq. (4.10), a different dependence on the pulse time. This fact might allow the effects associated with simple absorption and  $\Lambda_2$  to be extracted separately.

Unfortunately, an estimate for the new coefficients  $\Lambda_{1,2}$  is not available and it is possible that they will be very small. In addition, their magnitude is very likely to depend strongly on the type of processes under study, i.e., simple absorption spectroscopy will probably have smaller values of  $\Lambda$  than some highly polarization-dependent photochemical reaction (although to be fair, it is not clear if this theory is valid in the latter case). Finally, for dilute gases,  $\Lambda_2$  will be an order of density smaller than  $\Lambda_1$  for the same reason that the bulk viscosity is smaller than the shear viscosity in gases. The question of their magnitude aside, the new terms become more important for shorter duration pulses. Again, this is analogous to the relative importance of the reversible and dissipative terms in the hydrodynamic equations.

In this work, a quantum-mechanical formulation has been used. Clearly, none of the assumptions concerning the length and time scales is likely to depend seriously on whether classical or quantum mechanics is used. Thus the

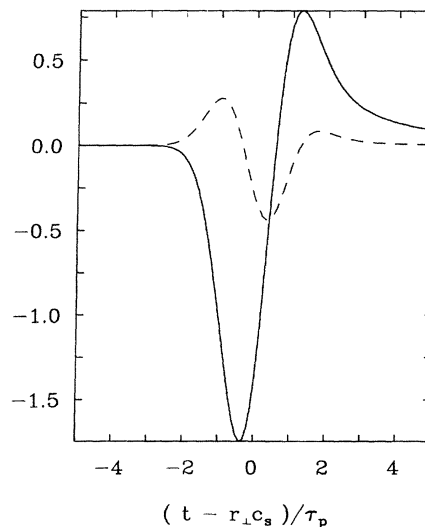


FIG. 1. Functions  $f_1$  (—) and  $f_2$  (---) used in Eq. (4.10).



final expression for the new coefficients can be converted to a classical one simply by replacing  $[\dots, \dots]/i\hbar$  by the Poisson bracket. Of course, a better approximation would be to treat the mechanics of the dipole semiclassically and the remaining degrees of freedom classically. This should result in coefficients which, at worst, should be amenable to (classical) numerical simulation. This direction is currently under study.

Clearly what is needed is an experiment. If the new terms are observable, then they will yield more direct information concerning the coupling of the internal motions of molecules (at least as described by their dipole moments) and the solvent (via the local microscopic stress). In addition, the magnitude of such couplings must be understood if photoacoustic detection techniques are to be used, without extensive calibration, for absolute intensity measurements.

#### ACKNOWLEDGMENTS

I thank Kevin Peters, Bill Klemperer, and Rob Coalson for many useful discussions. A portion of this work was supported by the National Science Foundation under Grant No. CHE-83-02423.

#### APPENDIX

In this appendix, the manipulations which lead to Eq. (4.7) are described. The most difficult term is that in  $\Lambda_1$ . The integrals are most easily performed in the coordinate representation. From Eqs. (4.4) and (4.5b) it follows that the required propagator is

$$\frac{2}{\pi^2 R^2 c_s} \int_{-\infty}^t dt' \int_0^R r' dr' \int_0^{2\pi} d\phi \frac{[(\vec{r}-\vec{r}')_{\perp}(\vec{r}-\vec{r}')_{\perp} - \frac{1}{3}\vec{1} | \vec{r}-\vec{r}' |_{\perp}^2]:\hat{n}\hat{n}\Theta(c_s(t-t') - |\vec{r}_1 - \vec{r}'_1|)}{|\vec{r}-\vec{r}' |_{\perp}^2 [c_s^2(t-t')^2 - |\vec{r}-\vec{r}'_{\perp}|^2]^{1/2}} \ddot{I}_0(t'), \quad (\text{A3})$$

where  $\Theta$  is the Heaviside step function. In the far field,  $r_{\perp} \gg R$  and thus Eq. (A3) can be approximated by

$$\frac{2(\hat{r}_1 \hat{r}_1 - \frac{1}{3}\vec{1}):\hat{n}\hat{n}}{\pi c_s} \int_{-\infty}^{t-r_1/c_s} dt' \frac{\ddot{I}_0(t')}{[c_s^2(t-t')^2 - r_1^2]^{1/2}}. \quad (\text{A4})$$

$$\begin{aligned} & -2c_s \int \frac{d\vec{k}}{(2\pi)^3} e^{-i\vec{k}\cdot\vec{r}} k \sin(kc_s t) (\hat{k}\hat{k} - \frac{1}{3}\vec{1}) \\ & = \frac{c_s}{\pi r} (\hat{r}\hat{r} - \frac{1}{3}\vec{1}) \left[ \delta''(r-c_s t) - \frac{3}{r} \delta'(r-c_s t) \right. \\ & \quad \left. + \frac{3}{r^2} \delta(r-c_s t) \right], \end{aligned} \quad (\text{A1})$$

where terms in  $\delta(r+c_s t)$  have been dropped. This propagator is doubly contracted and convolved in space and time with  $\vec{S}(\vec{r}, t)$ , cf. Eq. (4.6). The derivatives on the  $\delta$  functions are moved to  $S$  by integrating by parts in time, thereby giving

$$\begin{aligned} & \frac{1}{\pi^2 R^2 c_s} \int_{-\infty}^t dt' \int_{r'_1 \leq R} d\vec{r}' \frac{\delta(|\vec{r}-\vec{r}'| - c_s(t-t'))}{|\vec{r}-\vec{r}'|^3} \\ & \quad \times [(\vec{r}-\vec{r}')(\vec{r}-\vec{r}') - \frac{1}{3}\vec{1}]:\hat{n}\hat{n} \\ & \quad \times \left[ \ddot{I}_0(t') + \frac{3\dot{I}_0(t')}{(t-t')} + \frac{3I_0(t')}{(t-t')^2} \right]. \end{aligned} \quad (\text{A2})$$

In the acoustic far field,  $t \approx r/c_s$  is large compared with the pulse duration time; hence, the last two terms in the integrand in Eq. (A2) can be dropped. The spatial integration is performed in cylindrical coordinates and the  $\delta$  function is eliminated in the  $z$  integration. Equation (A2) is thus rewritten as

Multiplying Eq. (A4) by  $\Lambda_1$  gives the corresponding term in Eq. (4.7). The remaining two terms are obtained in an analogous fashion.

<sup>1</sup>For a recent review, see C. K. N. Patel and A. C. Tam, *Rev. Mod. Phys.* **53**, 517 (1981).

<sup>2</sup>See, e.g., L. J. Rothberg, J. D. Simon, M. Bernstein, and K. S. Peters, *J. Am. Chem. Soc.* **105**, 3464 (1983); M. Bernstein, J. D. Simon, and K. S. Peters, *Chem. Phys. Lett.* **100**, 241 (1983).

<sup>3</sup>H. Garity, S. R. Caplan, and D. Cahen, *Biophys. J.* **37**, 405 (1982).

<sup>4</sup>J. N. Demas and G. A. Crosby, *J. Phys. Chem.* **75**, 991 (1971).

<sup>5</sup>See, e.g., D. Ronis and I. Oppenheim, *Physica (Utrecht)* **86A**, 475 (1977), and references therein.

<sup>6</sup>R. Gordon, *Adv. Magn. Reson.* **3**, 1 (1968).

<sup>7</sup>D. Forster, *Hydrodynamics, Fluctuations, Broken Symmetry*

*and Correlation Functions* (Benjamin, New York, 1975).

<sup>8</sup>E. U. Condon and G. H. Shortly, *The Theory of Atomic Spectra* (Cambridge University, Cambridge, England, 1964).

<sup>9</sup>See, e.g., J. H. Irving, R. W. Zwanzig, and J. G. Kirkwood, *J. Chem. Phys.* **19**, 1173 (1951).

<sup>10</sup>B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976), Chaps. 11 and 12.

<sup>11</sup>Ph. A. Selwyn and I. Oppenheim, *Physica (Utrecht)* **54**, 161 (1971).

<sup>12</sup>D. Ronis, I. Procaccia, and I. Oppenheim, *Phys. Rev. A* **19**, 1324 (1979).

<sup>13</sup>I. S. Gradshteyn and I. M. Ryzhik, *Tables of Integrals, Series and Products*, 4th ed. (Academic, New York, 1980).