Microscopic theory of photoacoustic pulse generation. II. Solids

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The nonlinear-response theory of acoustic pulse generation by linear spectroscopy developed in an earlier paper [Phys. Rev. A 29, 1453 (1984)] is extended to the case of solids. Viscoelastic equations for the dynamics of the fluctuations are obtained by explicitly including the stress tensor into the macroscopic description of the system, as well as correlation-function forms for the coupling constants linking the incident optical pulse to the local stress relaxation. Since transverse waves propagate in solids, absorption-driven transverse shear waves are obtained and their properties are discussed.

I. INTRODUCTION

In the preceding paper in this series[1] (hereafter referred to as I), the generation of the photoacoustic pressure pulse in liquids was considered from a microscopic point of view. Specifically, response theory to quadratic order in an external electric field of the form

$$\vec{E}_{\rm ext}(\vec{r},t)\equiv\vec{e}(\vec{r},t)e^{i(\omega_{\rm inc}t-\vec{k}\cdot\vec{r})}+\text{c.c.}\ , \tag{1.1}$$

was used (c.c. denotes the complex conjugate of the preceding terms). The field amplitude was allowed to be space and time dependent in order to account for any modulation of the incident beam.

In addition to the usual expression for the sound generated by the adiabatic expansion of the fluid upon absorption of the light,[2] several new terms were obtained. In general the new terms have a different pulse time dependence. Significantly, one of them has a dependence on the polarization of the incident light which is totally absent in the phenomenological theory. They arise from any coherent aspect of the force being exerted on the fluid molecules in the absorption process. In other words, if upon absorption of light, the molecule polarizes or has some other geometry change in a specific direction (related to the incident optical polarization), then the resulting sound field should reflect this direction to some extent. A mechanism based solely on heating will not have any polarization dependence in an isotropic medium to quadratic order in the applied field.

In this paper the analysis of I will be extended to the case of solids. In solids there are two kinds of sound, i.e., transverse and longitudinal, with two different sound speeds. Only the latter is present in fluids, the transverse modes are diffusive. As will be shown, the possibility of transverse sound leads to a new type of photoacoustic signal which is qualitatively different from that predicted by the phenomenological theory or by the microscopic theory presented in I.

In Sec. II the method used in I is outlined and the necessary results are summarized. In Sec. III the method is extended to solids. In Sec. IV the elastic response of a solid is discussed as it pertains to the photoacoustic pulse generation. Section V contains an analysis of the photoacoustic pulse and the last section summarizes and discusses the results.

II. SUMMARY OF PREVIOUS RESULTS

In I and here, the system is taken to be governed by the Hamiltonian

$$\begin{aligned}H_T&=H-\vec{\mu}(\vec{r},t)*\vec{E}_{\rm ext}(\vec{r},t)\\&\equiv H+H_1(t)\ ,\end{aligned} \tag{2.1}$$

where $\vec{\mu}(\vec{r},t)$ is the dipole moment density and H is the Hamiltonian in the absence of the external electric field $\vec{E}_{\rm ext}$. The symbol $*$ is used to denote a dot product and an integration over $\vec{r}$. The evolution of the system is governed by the quantum Liouville equation, which can be solved perturbatively in $\vec{E}_{\rm ext}$, and the result used to compute the average of any observable, e.g., B. To quadratic order, this procedure yields

$$\begin{aligned}\langle B(t)\rangle_{\rm ne}=\langle B\rangle&-\int_{-\infty}^{t}dt_1\frac{\langle[B(t-t_1),\vec{\mu}(\vec{r})]\rangle}{i\hbar}*\vec{E}(\vec{r},t_1)\\&+\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2\frac{\langle[[B(t-t_1),\vec{\mu}(\vec{r}_1)],\vec{\mu}(\vec{r}_2,t_2-t_1)]\rangle}{(i\hbar)^2}**\vec{E}(\vec{r}_2,t_2)\vec{E}(\vec{r}_1,t_1)+O(E^3)\ ,\end{aligned} \tag{2.2}$$

where the notation $\langle\ \rangle_{ne}$ and $\langle\ \rangle$ are used to denote a nonequilibrium and equilibrium average, respectively. In addition, it was assumed that the system was in equilibrium in the infinite past. Subsequently, use was made of the existence of three very different time scales: the fastest was the period of the incident light, next was the time scale characterizing the "fast" processes in the fluid (i.e., the collision or dipole moment relaxation times), and finally there were the time scales which characterize the "slow" (e.g., hydrodynamic) motions of the fluid as well as the modulation of the incident light (it is assumed that the optical modulation is slower than the dipole moment relaxation time). The large difference between the first two and the third allows the nonlocality in time and space in $\vec{e}(\vec{r},t)$ to be dropped. The fact that the measurements are being carried out using a slow response-time detector (e.g., a piezoelectric crystal) allows the term linear in the external electric field to be dropped; it will oscillate at the frequency of the incident light. Thus Eq. (2.2) was rewritten as

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

$$\times:[e^{i\omega_{inc}t'}\vec{e}^{\,*}(\vec{r}\,',t_1)\vec{e}(\vec{r}\,',t_1)+\text{c.c.}]\ , \tag{2.3}$$

where $\delta B\equiv B-\langle B\rangle$.

The separation of time scales between the fast and slow motions of the system was exploited by using the following identity:[3]

$$\underline{A}(\vec{k},t)=\underline{G}(\vec{k},t)\cdot\underline{A}(\vec{k},t=0)+\int_0^t dt'\underline{G}(\vec{k},t-t')\cdot\dot{\underline{A}}_D(\vec{k},t')\ , \tag{2.4}$$

where $\underline{G}(\vec{k},t)$ is the propagator which describes the macroscopic evolution of $\underline{A}(\vec{k},t)$ and $\dot{\underline{A}}_D(\vec{k},t)$ is referred to as the dissipative or microscopic part of the rate of charge of A. In I only densities of conserved variables were considered and dissipative currents appeared instead of $\dot{\underline{A}}_D$. Equation (2.4) can be viewed as a definition of the dissipative variables. Alternately they can be defined in terms of time correlation functions using projection-operator techniques.[3] Physically, they represent the parts of the exact microscopic equations of motion governing $\underline{A}(\vec{k},t)$ not described by the macroscopic equations. Thus, providing the correct macroscopic equations are known, the dissipative variables should evolve on fast time scales and correlations involving them should decay quickly in time. Specifically, using Eq. (2.4) in Eq. (2.2) for $B=A$ gave

$$\underline{a}(\vec{k},t)=\int_{-\infty}^{t}dt_1\underline{G}(\vec{k},t-t_1)[\underline{\Omega}^{ij}(\vec{k};\omega_{inc})+\underline{\Omega}^{ji}(\vec{k};-\omega_{inc})]S^{ji}(\vec{k},t_1)\ , \tag{2.5}$$

where repeated indices are henceforth summed, and

$$S^{ji}(\vec{k},t)\equiv\frac{c}{2\pi}\int d\vec{r}\,e^{i\vec{k}\cdot\vec{r}}[e^j(\vec{r},t)]^*e^i(\vec{r},t) \tag{2.6}$$

and

$$\underline{\Omega}^{ij}(\vec{k};\omega_{inc})\equiv\underline{\Omega}^{ij}_R(\vec{k};\omega_{inc})+\underline{\Omega}^{ij}_D(\vec{k};\omega_{inc})\ . \tag{2.7}$$

The reversible and dissipative parts of Ω are defined by

$$\underline{\Omega}^{ij}_R(\vec{k};\omega_{inc})\equiv\frac{2\pi}{c(i\hbar)^2V}\int_0^{\infty}dt'e^{i\omega_{inc}t'}\langle[[\underline{A}(\vec{k}),\mu^i(-\tfrac{1}{2}\vec{k})],\mu^j(-\tfrac{1}{2}\vec{k},-t')]\rangle \tag{2.8}$$

and

$$\underline{\Omega}^{ij}_D(\vec{k};\omega_{inc})\equiv\frac{2\pi}{c(i\hbar)^2V}\int_0^{\infty}dt\int_0^{\infty}dt'e^{i\omega_{inc}t'}\langle[[\dot{\underline{A}}_D(\vec{k},t),\mu^i(-\tfrac{1}{2}\vec{k})],\mu^j(-\tfrac{1}{2}\vec{k},-t')]\rangle\ , \tag{2.9}$$

respectively (V is the system's volume and c is the speed of light). Note that the trace of $\overleftrightarrow{S}(\vec{r},t)$ is the incident optical intensity. The remainder of I was concerned with the analysis of the specific forms of the propagators and correlation functions for fluids.

III. SOLIDS

It must be stressed that the manipulations which lead to Eq. (2.5) are not specific to fluids. Equation (2.5) will be valid as long as the various separation of time-scale as-

sumptions hold. Clearly the assumption which is not always under control is the separation between the system's fast and slow motions. In fluids the slow variables are densities of conserved quantities. In particular, this means that their characteristic time is inversely proportional to the wave vector of the mode (which can be taken to be as small as desired). On the other hand, in solids there are slow nonconserved modes.

The solid is characterized by extremely slow stress relaxation rates. This is responsible for the observed elastic behavior of solids. However, it is obvious that any mechanical quantity whose evolution depends on large-scale translational motion of the molecules comprising the solid is apt to evolve on a slow time scale. In contrast, quantities which depend on the velocities of the molecules or on functions of their positions which change on microscopic distances (e.g., the interatomic forces) should in general evolve on faster time scales. This is not to say that such quantities exhibit only fast motions; there will always be some slow component. Here it is assumed that all slow motions can be expressed as a linear combination of the slow variables whose averages specify the macroscopic viscoelastic state of the system [at least for the purposes of calculating the averages in Eq. (2.5)].

In the usual treatments of the elastic behavior of solids, the elastic state of the system is assumed to be determined in terms of the strain field.[4] Unfortunately, unless an equilibrium lattice is assumed, strain is not easily defined microscopically. On the other hand, in the linear regime stress and strain are proportional (Hooke's law) and the well-defined stress tensor can be used in place of the strain. As will be shown below, the addition of the stress to the set of variables, $\underline{A}(\vec{r},t)$, results in a correct macroscopic description of the elastic response of the solid.

The stress tensor is well-defined microscopically and does not require the introduction of an equilibrium lattice, harmonic forces, etc. In Fourier representation, the stress tensor is defined as[5]

$$\overleftrightarrow{\tau}(\vec{k},t)=\sum_j\left[\frac{(\vec{p}_j-\frac{1}{2}\hbar\vec{k})e^{i\vec{k}\cdot\vec{r}_j}(\vec{p}_j+\frac{1}{2}\hbar\vec{k})}{m_j}+\frac{1}{2}\sum_{j'\neq j}\vec{r}_{jj'}\vec{F}_{jj'}\frac{1-e^{-i\vec{k}\cdot\vec{r}_{jj'}}}{i\vec{k}\cdot\vec{r}_{jj'}}\right], \tag{3.1}$$

where m_j, $\vec{p}_j$, and $\vec{F}_{jj'}$ are the mass of the jth particle, momentum, and force j' exerts on j, respectively. The Fourier transform is defined by

$$f_{\vec{k}}\equiv\int d\vec{r}\,f(\vec{r})e^{i\vec{k}\cdot\vec{r}}\,.$$

Note the appearance of the terms explicitly depending on $\hbar$ in the kinetic part of the stress. In addition, note that some care must be taken when considering the Hermitian conjugate of the Fourier transform of an operator. The Fourier-transform variable $i\vec{k}$ should not be included when the Hermitian conjugate is taken. This is equivalent to letting $\vec{k}\rightarrow-\vec{k}$ after Hermitian conjugation.

The other slow variables are the mass density, energy density, and momentum density, hereafter denoted as $N(\vec{r},t)$, $H(\vec{r},t)$, and $\vec{P}(\vec{r},t)$, respectively. They have their usual definitions. The set of slow variables will be denoted collectively by

$$\underline{A}(\vec{r},t)\equiv[N(\vec{r},t),H(\vec{r},t),\vec{P}(\vec{r},t),\overleftrightarrow{\Pi}(\vec{r},t)]\,,$$

where $\overleftrightarrow{\Pi}(\vec{r},t)$ is the nonhydrostatic part of the stress [cf. Eq. (3.3) below]. Note that, unlike theories of harmonic solids, the density is an independent variable, due to the existence of (extremely slow) defect diffusion processes.

In order to use Eqs. (2.5)—(2.9) the microscopic equations of motion for the elastic variables must be given. For the conserved variables these are

$$\dot{N}(\vec{r},t)=-\vec{\nabla}\cdot\vec{P}(\vec{r},t)\,, \tag{3.2a}$$

$$\dot{\vec{P}}(\vec{r},t)=-\vec{\nabla}\cdot\overleftrightarrow{\tau}(\vec{r},t)\,, \tag{3.2b}$$

and

$$\dot{H}(\vec{r},t)=-\vec{\nabla}\cdot\vec{J}_H(\vec{r},t)\,, \tag{3.2c}$$

where $\vec{J}_H(\vec{r},t)$ is the energy current, defined in the usual way. The stress tensor is nonconserved and has a microscopic form for its time derivative which is complicated and not particularly illuminating.

The inclusion of the stress tensor into the set of macroscopic variables has been performed in many situations and a variety of techniques have been used to derive the macroscopic equations of motion.[6] It is convenient to decompose the stress into the hydrostatic part $\overleftrightarrow{p}_h$ and the viscoelastic part $\overleftrightarrow{\Pi}$ (i.e., $\overleftrightarrow{\tau}\equiv\overleftrightarrow{p}_h+\overleftrightarrow{\Pi}$). The hydrostatic pressure is defined by its Fourier transform,

$$\overleftrightarrow{p}_h(\vec{k},t)\equiv\langle\overleftrightarrow{\tau}_{\vec{k}}\tilde{\underline{A}}_{-\vec{k}}\rangle\cdot\langle\tilde{\underline{A}}_{\vec{k}}\tilde{\underline{A}}_{-\vec{k}}\rangle^{-1}\cdot\tilde{\underline{A}}(\vec{k},t)\,, \tag{3.3}$$

where the tilde on $\underline{A}$ is used to denote the subset of $\underline{A}$ corresponding to the conserved densities. Note that for small wave vectors

$$\overleftrightarrow{p}_h\sim\overleftrightarrow{1}\left[\left(\frac{\partial p_h}{\partial n}\right)N(\vec{k},t)+\left(\frac{\partial p_h}{\partial h}\right)H(\vec{k},t)\right]+O(k^2)$$

and the coefficients in Eq. (3.3) can be expressed as partial derivatives of the hydrostatic pressure with respect to density and energy density. This definition has the consequence that the viscoelastic part of the stress is orthogonal to the slow variables in the sense that $\langle\overleftrightarrow{\Pi}_{\vec{k}}\tilde{\underline{A}}_{-\vec{k}}\rangle=0$.

The equations of motion for the mass and momentum densities follow trivially upon averaging Eqs. (3.2a) and (3.2b). Those for the viscoelastic part of the stress and the energy density need a constitutive law to relate the energy current and stress rate of change to the slow variables. This can be obtained from projection-operator techniques or by using response theory. For example, in Ref. 6(c), the following equations of motion (isotropy or cubic symmetry was assumed) were obtained:

$$\dot{\pi}^{ij}(\vec{r},t)=-\omega^{ijkl}\pi^{kl}(\vec{r},t)-C^{ijkl}\frac{\partial v^k(\vec{r},t)}{\partial x^l} \tag{3.4a}$$

and

$$\dot{h}(\vec{r},t)=-\vec{\nabla}\cdot[\rho h_s\vec{v}(\vec{r},t)-\overleftrightarrow{\lambda}\cdot\vec{\nabla}T(\vec{r},t)]\,, \tag{3.4b}$$

where repeated indices are summed. The fields $\vec{v}(\vec{r},t)$ and $T(\vec{r},t)$ are the velocity and temperature, respectively, and are defined in terms of the densities of the conserved variables in the same way as in an equilibrium system. The parameters h_s, λ, $\overleftrightarrow{\omega}$, and $\overleftrightarrow{C}$ are the specific enthalpy, thermal conductivity, stress relaxation rates, and elastic constants, respectively. They have their usual microscopic definitions,[6,7] e.g.,

$$\lambda \equiv \int_0^\infty \frac{dt}{k_B T^2 V} \langle \vec{I}_{H,T}(t) \vec{I}_{H,T}(0) \rangle \ , \tag{3.5a}$$

and

$$C^{ijkl} \equiv \frac{\langle \Pi_T^{ij} \Pi_T^{kl} \rangle}{V k_B T} \ , \tag{3.5b}$$

etc., where the subscript T is used to denote the total or $k=0$ value of the subscripted quantity. Note that components of the various tensors are not all independent; time-reversal symmetry and the rotational symmetry of the solid relates them. For example, in isotropic systems or in systems with cubic symmetry[8]

$$C^{ijkl} = C_1(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \tfrac{2}{3}\delta_{ij}\delta_{kl}) + C_2 \delta_{ij}\delta_{kl} \ , \tag{3.6a}$$

$$\omega^{ijkl} = \omega_1(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \tfrac{2}{3}\delta_{ij}\delta_{kl}) + \omega_2 \delta_{ij}\delta_{kl} \ , \tag{3.6b}$$

and

$$\lambda^{ij} = \lambda \delta_{ij} \ , \tag{3.6c}$$

where δ_{ij} is a Kronecker delta. In writing Eqs. (3.4a) and (3.4b), terms containing more than first gradients have been omitted and these should be unimportant for acoustic phenomena. Equations (3.4a) and (3.4b) are sometimes referred to as the Maxwell relaxation equations for a viscoelastic medium.[3]

The most important consequence of adding the stress tensor to the set of slow variables is the appearance of two propagating transverse modes, in addition to the usual longitudinal ones. Fortunately, the dynamics of the longitudinal and transverse modes decouple, thereby greatly simplifying the calculation.

IV. THE MACROSCOPIC DYNAMICS OF THE SOLID

As was mentioned above, the calculation of the Green's function is greatly simplified due to the fact that the longitudinal and transverse modes decouple. For what follows, an isotropic solid or cubic crystal is considered. This simplifies the calculation without loosing any of the physical content. In particular, the forms of the coefficients as given by Eqs. (3.6a)—(3.6c) will be used in all of the subsequent manipulations.

The macroscopic dynamics of the solid is determined by Eqs. (3.2a) and (3.2b) and (3.4a) and (3.4b). In matrix notation these can be written as

$$\frac{\partial \underline{a}(\vec{r},t)}{\partial t} = \underline{M} \cdot \underline{a}(\vec{r},t) \ ,$$

where M is the differential operator corresponding to the equations of motion. Fourier transforming the macroscopic equations of motion in time and space allows the defining equation for the Green's function to be written as

$$(i\omega - \underline{M}_{\vec{k}}) \cdot \underline{G}(\vec{k},\omega) = \underline{\mathbb{1}} \ . \tag{4.1}$$

The calculation of the Green's function is simplified by decomposing the stress into its longitudinal and transverse parts, i.e.,

$$\begin{aligned} \vec{\tau}(\vec{k},t) = \overleftrightarrow{1} \Bigg[\left[\frac{\partial p_h}{\partial n} \right] n(\vec{k},t) + \left[\frac{\partial p_h}{\partial h} \right] h(\vec{k},t) \\ + \tfrac{1}{3} \mathrm{Tr} \overleftrightarrow{\pi}(\vec{k},t) \Bigg] + \overleftrightarrow{\pi}^{ll}(\vec{k},t) + \overleftrightarrow{\pi}^{lt}(\vec{k},t) \\ + \overleftrightarrow{\pi}^{tl}(\vec{k},t) + \overleftrightarrow{\pi}^{tt}(\vec{k},t) \ , \end{aligned} \tag{4.2}$$

where

$$\overleftrightarrow{\pi}^{ll}(\vec{k},t) \equiv \hat{k}\hat{k} \cdot [\overleftrightarrow{\pi}(\vec{k},t) - \tfrac{1}{3}\mathrm{Tr}\overleftrightarrow{\pi}(\vec{k},t)] \cdot \hat{k}\hat{k} \ , \tag{4.3a}$$

$$\begin{aligned} \overleftrightarrow{\pi}^{tt}(\vec{k},t) \equiv (\overleftrightarrow{1} - \hat{k}\hat{k}) \cdot [\overleftrightarrow{\pi}(\vec{k},t) \\ - \tfrac{1}{3}\overleftrightarrow{1}\mathrm{Tr}\overleftrightarrow{\pi}(\vec{k},t)] \cdot (\overleftrightarrow{1} - \hat{k}\hat{k}) \ , \end{aligned} \tag{4.3b}$$

and

$$\begin{aligned} \overleftrightarrow{\pi}^{lt}(\vec{k},t) &\equiv \hat{k}\hat{k} \cdot [\overleftrightarrow{\pi}(\vec{k},t) - \tfrac{1}{3}\overleftrightarrow{1}\mathrm{Tr}\overleftrightarrow{\pi}(\vec{k},t)] \cdot (\overleftrightarrow{1} - \hat{k}\hat{k}) \\ &\equiv [\overleftrightarrow{\pi}^{tl}(\vec{k},t)]^T \ . \end{aligned} \tag{4.3c}$$

The symbol $\hat{}$ is used to denote a unit vector. These definitions, when used in Eqs. (3.4a) and (3.4b) together with (3.6a) and (3.6b), show that the calculation of the Green's function [or matrix, cf. Eq. (4.1)] can be split into a number of blocks. These are the fully transverse block (tt), which contains $\overleftrightarrow{\pi}^{tt}(\vec{k},t)$; the transverse blocks (lt or tl), which are made up of $\vec{p}^{\,t}(\vec{k},t)$ and $\overleftrightarrow{\pi}^{lt}(\vec{k},t)$ [$\vec{p}^{\,t}(\vec{k},t)$ is the transverse momentum]; and finally, the longitudinal block (ll), which comprises $n(\vec{k},t)$, $h(\vec{k},t)$, $p^l(\vec{k},t)$, $\mathrm{Tr}\overleftrightarrow{\pi}(\vec{k},t)$, and $\mathrm{Tr}\overleftrightarrow{\pi}^{ll}(\vec{k},t)$ [$p^l(\vec{k},t)$ is the longitudinal momentem].

The simplest block is the fully transverse one. From Eqs. (3.4a) and (3.6a) and (3.6b) it follows that

$$\overleftrightarrow{\pi}^{tt}(\vec{k},t) = -2\omega_1 \overleftrightarrow{\pi}^{tt}(\vec{k},t) - \tfrac{2}{3}(\overleftrightarrow{1} - \hat{k}\hat{k}) c_t^2 i k p^l(\vec{k},t) \ , \tag{4.4}$$

where the transverse sound speed is defined by $c_t^2 \equiv C_1/\rho$. The general solution to Eq. (4.4) has two terms. The first is $\exp(-\omega_1 t)\overleftrightarrow{\pi}^{tt}(\vec{k},t=0)$. This represents a very slow mode of the system (recall that $\omega_i \to 0$ in solids) and is completely unimportant for acoustics. The second term only involves the longitudinal momentum, which does not depend on the tt components of $\overleftrightarrow{\pi}$. Thus Fourier transforming in time and setting ω_1 to zero shows (for the acoustic modes) that

$$G_{\overleftrightarrow{\pi}^{tt},\underline{A}}(\vec{k},\omega) \sim -\tfrac{2}{3} c_t^2 (\overleftrightarrow{1} - \hat{k}\hat{k}) k G_{p^l,\underline{A}}(\vec{k},\omega)/\omega \ . \tag{4.5}$$

The next simplest contribution comes from the lt block. From Eqs. (3.2b), (3.4a), and (3.6) it follows that

$$\dot{\vec{p}}^{\,t}(\vec{k},t) = i\vec{k} \cdot \overleftrightarrow{\pi}^{lt}(\vec{k},t) \tag{4.6a}$$

and

$$\overleftrightarrow{\pi}^{lt}(\vec{k},t)=-2\omega_1\overleftrightarrow{\pi}^{lt}(\vec{k},t)+c_t^2 i\vec{k}\,\vec{p}^{\,t}(\vec{k},t)\ . \tag{4.6b}$$

The associated Green's function is easily shown to be

$$\underline{G}^{lt}(\vec{k},\omega)=\frac{\begin{bmatrix}(i\omega+2\omega_1)(\overleftrightarrow{1}-\hat{k}\hat{k}) & i\vec{k}\\ i\vec{k}(\overleftrightarrow{1}-\hat{k}\hat{k})c_t^2 & i\omega\hat{k}(\overleftrightarrow{1}-\hat{k}\hat{k})\hat{k}\end{bmatrix}}{k^2c_t^2-\omega^2+2i\omega\omega_1}\ . \tag{4.7}$$

As will become clear below, only the stress-stress element of the lt Green's function is needed. By inverting all Fourier transforms, dropping ω_1 and going to the acoustic far field, this element can be written as

$$G_{\overleftrightarrow{\pi}^{lt},\overleftrightarrow{\pi}^{lt}}(\vec{r},t)\sim-\frac{\hat{r}(\overleftrightarrow{1}-\hat{r}\hat{r})\hat{r}}{4\pi r}\delta'(r-c_t t)+O(r^{-2})\ , \tag{4.8}$$

where $\delta(x)$ is the δ function.

Finally, the longitudinal variables must be considered. These are defined as

$$\underline{A}^{l}(\vec{k},t)\equiv[N(\vec{k},t),H(\vec{k},t),\hat{k}\cdot\vec{P}(\vec{k},t),\mathrm{Tr}\overleftrightarrow{\pi}(\vec{k},t),\hat{k}\hat{k}:[\overleftrightarrow{\pi}(\vec{k},t)-\tfrac{1}{3}\mathrm{Tr}\overleftrightarrow{\pi}(\vec{k},t)]]\ .$$

There are five longitudinal modes. Two of them propagate and the rest are diffusive. The latter contain the heat mode, as well as two which describe longitudinal stress relaxation [i.e., as related to the parameters ω_i, $i=1,2$ in Eq. (3.4a)]. On the time scale of relevance to photoacoustic detection, these nonpropagating modes can be ignored.

Using Eq. (3.4a) it follows that the longitudinal modes satisfy

$$(i\omega-\underline{M}^{\,l}_{\vec{k},\omega})\underline{A}^{l}(\vec{k},\omega)=0\ , \tag{4.9}$$

where

$$\underline{M}^{\,l}_{\vec{k},\omega}\equiv\begin{bmatrix}0 & 0 & ik & 0 & 0\\ 0 & 0 & ikh_s & 0 & 0\\ ik\left[\frac{\partial p_h}{\partial n}\right] & ik\left[\frac{\partial p_h}{\partial h}\right] & 0 & \frac{ik}{3} & ik\\ 0 & 0 & 3ikC_2/\rho & -3\omega_2 & 0\\ 0 & 0 & ik\frac{4}{3}C_1/\rho & 0 & -2\omega_1\end{bmatrix}\ , \tag{4.10}$$

where the thermal conductivity has been neglected, as was discussed above.

For the problem at hand, the full longitudinal propagator is not needed. The various detectors respond to forces exerted on their surfaces. These are equal to the normal components of the stress tensor at the detector. By using Eqs. (4.2), (4.4), and (4.10), the propagating part of the stress can be reexpressed as

$$\begin{aligned}\overleftrightarrow{\tau}(\vec{k},\omega)=&\overleftrightarrow{1}\omega_{\vec{k}}[p^l(\vec{k},\omega)-p^l(\vec{k},t=0)]\\ &+\overleftrightarrow{\pi}^{lt}(\vec{k},\omega)+\overleftrightarrow{\pi}^{tl}(\vec{k},\omega)\\ &+\frac{2c_t^2kp^l(\vec{k},\omega)}{\omega}(\hat{k}\hat{k}-\overleftrightarrow{1})\ .\end{aligned} \tag{4.11}$$

Aside from the lt components, only the longitudinal momentum appears. Moreover, from Eqs. (4.9) and (4.10),

$$[(i\omega-\underline{M}^{\,l}_{k})^{-1}]_{p^l,\underline{A}^l}=-i\frac{\left[\left[\frac{\partial p_h}{\partial n}\right],\left[\frac{\partial p_h}{\partial h}\right],\frac{\omega}{k},\frac{1}{3},1\right]}{(\omega^2-k^2c_l^2)}\ , \tag{4.12}$$

where the longitudinal sound speed is defined by

$$c_l\equiv\left[\left[\frac{\partial p_h}{\partial n}\right]+h_s\left[\frac{\partial p_h}{\partial h}\right]+\frac{(\frac{4}{3}C_1+C_2)}{\rho}\right]^{1/2}\ . \tag{4.13}$$

The stress propagator can now be obtained simply by substituting Eq. (4.12) for $p^l(\vec{k},\omega)$ in Eq. (4.11). Moreover, only the couplings to the energy and π are needed. For these, inverting the Fourier transforms in the far field gives

$$G_{\overleftrightarrow{\tau},H}(\vec{r},t)\sim-\left[\frac{\partial p_h}{\partial h}\right]\frac{\delta'(r-c_l t)}{4\pi r}\left[\overleftrightarrow{1}+2\left[\frac{c_t}{c_l}\right]^2(\hat{r}\hat{r}-\overleftrightarrow{1})\right] \tag{4.14a}$$

and

$$G_{\overleftrightarrow{\tau},\overleftrightarrow{\Pi}}(\vec{r},t)\sim-\frac{\delta'(r-c_l t)}{4\pi r}\left[\overleftrightarrow{1}+2\left[\frac{c_t}{c_l}\right]^2(\hat{r}\hat{r}-\overleftrightarrow{1})\right]\hat{r}\hat{r}-\frac{\delta'(r-c_t t)}{4\pi r}(\hat{r}\overleftrightarrow{1}\hat{r}+\hat{e}_i\hat{r}\hat{e}_i\hat{r}+\hat{e}_i\hat{r}\hat{r}\hat{e}_i+\hat{r}\hat{e}_i\hat{r}\hat{e}_i-4\hat{r}\hat{r}\hat{r}\hat{r})\ , \tag{4.14b}$$

where $\hat{e}_i$, $i=1,2,3$, are the usual Cartesian unit vectors. In obtaining this last result, Eq. (4.8) was used.

Thus once the forms for the various optical stress coupling constants are known, it is a simple matter to use Eq. (4.13) in (2.5) to compute the observed stress response.

V. THE PHOTOACOUSTIC PULSES

The coupling of the mechanical and optical processes is contained in the $\underline{\Omega}_{R,D}$ coefficients defined in Sec. II. As was the case in I, the reversible coefficients can all be calculated explicitly. In fact the number, energy, and momentum components are exactly equal to those discussed in I, i.e.,

$$\Omega^{ij}_{R,N}=0\ , \tag{5.1}$$

$$\Omega^{ij}_{R,\vec{P}}(\vec{k};\omega_{\rm inc})+\Omega^{ji}_{R,\vec{P}}(\vec{k};-\omega_{\rm inc})=i\vec{k}\epsilon(\omega_{\rm inc})\delta_{ij}+O(k^3)\ , \tag{5.2}$$

and

$$\Omega^{ij}_{R,H}(\vec{k};\omega_{\rm inc})+\Omega^{ji}_{R,H}(\vec{k};-\omega_{\rm inc})=\alpha(\omega_{\rm inc})\delta_{ij}+O(k^2)\ , \tag{5.3}$$

where

$$\alpha(\omega_{\rm inc})=\frac{4\pi\omega_{\rm inc}}{i\hbar cV}\int_0^\infty dt\,\sin(\omega_{\rm inc}t)\langle[\vec{\mu}_T,\vec{\mu}_T(t)]\rangle$$
$$=\frac{4\pi\omega_{\rm inc}}{i\hbar cV}\int_{-\infty}^\infty dt\,\sin(\omega_{\rm inc}t)\langle\vec{\mu}_T\vec{\mu}_T(t)\rangle\ , \tag{5.4a}$$

is the absorption coefficient and

$$\epsilon(\omega_{\rm inc})\equiv\frac{4\pi}{i\hbar cV}\int_0^\infty dt\,\cos(\omega_{\rm inc}t)\langle[\mu^x_T(t),\mu^x_T]\rangle \tag{5.4b}$$

is the derivative of $\alpha(\omega_{\rm inc})/\omega_{\rm inc}$. As was the case in I, ϵ will be extremely small and will make a negligible contribution; henceforth it is omitted. This is the reason why couplings to the momentum were not needed in Sec. IV.

The coupling to the stress tensor is new. Using Eqs. (2.8) and (3.1) gives

$$[\overleftrightarrow{\tau}_{\vec{k}},\vec{\mu}_{(-1/2)\vec{k}}]/i\hbar=\tfrac{1}{2}i\sum_j e^{(i\vec{k}\cdot\vec{r}_j)/2}(\vec{k}\,\vec{p}_j+\vec{p}_j\vec{k}$$
$$+\tfrac{1}{2}\hbar k^2)\ . \tag{5.5}$$

The last term on the right-hand side of the equation is nonclassical. As long as long-wavelength sound is considered, the stress component of $\underline{\Omega}^{ij}_k$ is at least $O(k^2)$, since the average resulting from using Eq. (5.5) in (2.8) can be written as $\vec{k}$ times the average of a third-rank tensor function of $\vec{k}$ (in systems with inversion symmetry, this must be at least proportional to one power of k). As was the case in I, terms of this order are neglected, resulting in no new contribution at the reversible level.

The form of $\Omega^{ij}_D(\vec{k},\omega)$ coefficients is easily obtained. Unlike the case in I, the dissipative part of the momentum current vanishes, since the exact stress tensor has been included in the set of variables. (For a similar reason, the dissipative mass current vanishes.) Moreover, while the dissipative energy current is nonzero, the resulting coupling coefficient can be written as $\vec{k}$ times a third-rank tensor. In systems with inversion symmetry, averages of third-rank tensor functions of $\vec{k}$ must be proportional to at least one power of $\vec{k}$, thereby making the energy contribution $O(k^2)$. Note that this sort of argument implicitly assumes that the correlations are nonsingular as $k\to 0$.

Hence only the coupling to the dissipative stress needs to be considered. From Eq. (2.9) this becomes

$$\underline{\Omega}^{ij}_{D,\Pi^{mn}}(\vec{k};\omega_{\rm inc})+\underline{\Omega}^{ji}_{D,\Pi^{mn}}(\vec{k};-\omega_{\rm inc})=\frac{4\pi}{c(i\hbar)^2V}\int_0^\infty dt\int_0^\infty dt'\cos(\omega_{\rm inc}t')\langle[[\dot{\Pi}^{mn}_{D,T}(t),\mu^i_T],\mu^j_T(-t')]\rangle+O(k^2) \tag{5.6a}$$

$$\equiv\xi_1(\omega_{\rm inc})(\delta_{im}\delta_{jn}+\delta_{in}\delta_{jm}-\tfrac{2}{3}\delta_{ij}\delta_{mn})+\xi_2(\omega_{\rm inc})\delta_{ij}\delta_{mn}\ , \tag{5.6b}$$

where the last equality holds for systems with cubic or isotropic rotational symmetry and with a symmetric microscopic stress tensor. Note that, should the system not possess inversion symmetry, then the correction to Eq. (5.6a) can be $O(k)$, although in this event many other new couplings must be considered.

It is now straightforward to combine Eqs. (2.5) (in the coordinate representation), (4.14a), (4.14b), (5.3), and (5.6b) to obtain the far-field stress response. The result is

$$\langle\overleftrightarrow{\tau}(\vec{r},t)\rangle_{\rm ne}=\int_{-\infty}^t dt'\int\frac{d\vec{r}'}{4\pi|\vec{r}-\vec{r}'|}\left[\frac{\delta(|\vec{r}-\vec{r}'|-c_l(t-t'))}{c_l}\left[\overleftrightarrow{1}+2\left[\frac{c_t}{c_1}\right]^2(\hat{\kappa}\hat{\kappa}-\overleftrightarrow{1})\right]\right.$$
$$\times\left\{\left[\left[\frac{\partial p_h}{\partial h}\right]\alpha(\omega_{\rm inc})+\xi_2(\omega_{\rm inc})\right]\overleftrightarrow{1}+2\xi_1(\omega_{\rm inc})(\hat{\kappa}\hat{\kappa}-\tfrac{1}{3}\overleftrightarrow{1})\right\}$$
$$+\frac{2\xi_1(\omega_{\rm inc})\delta(|\vec{r}-\vec{r}'|-c_t(t-t'))}{c_t}$$
$$\left.\times(\hat{\kappa}\overleftrightarrow{1}\hat{\kappa}+\hat{e}_i\hat{\kappa}\hat{e}_i\hat{\kappa}+\hat{e}_i\hat{\kappa}\hat{\kappa}\hat{e}_i+\hat{\kappa}\hat{e}_i\hat{\kappa}\hat{e}_i-4\hat{\kappa}\hat{\kappa}\hat{\kappa}\hat{\kappa})\right]\vdots\dot{\vec{S}}(\vec{r}',t')\ , \tag{5.7}$$

where $\hat{\kappa}$ denotes the unit vector $\vec{r}-\vec{r}'$ and the derivative on the δ function was transferred to $\overleftrightarrow{S}$ by integrating by parts in time ($\dot{\overleftrightarrow{S}}$ is the time derivative of $\overleftrightarrow{S}$). If the measurements are carried out at distances large compared with *all* dimensions of the incident beam (e.g., a point source), then Eq. (5.7) can be simplified further by dropping r' with respect to r and using the δ function to eliminate the time integration. Equation (5.7) thus becomes

$$\langle \overleftrightarrow{\mathcal{T}}(\vec{r},t)\rangle_{\rm ne}=\frac{1}{4\pi c_1^2 r}\left[\left[\overleftrightarrow{\mathbb{1}}+2\left[\frac{c_t}{c_l}\right]^2(\hat{r}\hat{r}-\overleftrightarrow{\mathbb{1}})\right]\left\{\left[\left[\frac{\partial p_h}{\partial h}\right]\alpha(\omega_{\rm inc})+\xi_2(\omega_{\rm inc})\right]\overleftrightarrow{\mathbb{1}}\right.\right.$$
$$\left.+2\xi_1(\omega_{\rm inc})(\hat{r}\hat{r}-\tfrac{1}{3}\overleftrightarrow{\mathbb{1}})\right\}:\int d\vec{r}'\dot{\overleftrightarrow{S}}(\vec{r}',t-|\vec{r}-\vec{r}'|/c_l)$$
$$+\frac{2\xi_1(\omega_{\rm inc})c_l^2}{c_t^2}(\hat{r}\overleftrightarrow{\mathbb{1}}\hat{r}+\hat{e}_i\hat{r}\hat{e}_i\hat{r}+\hat{e}_i\hat{r}\hat{r}\hat{e}_i+\hat{r}\hat{e}_i\hat{r}\hat{e}_i-4\hat{r}\hat{r}\hat{r}\hat{r}):\int d\vec{r}'\dot{\overleftrightarrow{S}}(\vec{r}',t-|\vec{r}-\vec{r}'|/c_t)\Bigg]. \tag{5.8}$$

Note that there are now two different retardation times due to the fact that the transverse and longitudinal sound speeds are different. From Eq. (4.13), it follows that $c_l^2\geq\frac{4}{3}c_t^2$.

Unfortunately, most experiments are carried out using extended sources. In order to see the experimental ramifications more clearly, assume that the incident light beam is a uniform cylinder of radius R with Gaussian temporal profile and linear polarization, i.e.,

$$\overleftrightarrow{S}(\vec{r},t)=\begin{cases}\vec{n}\,\vec{n}\dfrac{I_0(t)}{\pi R^2}, & r_\perp\leq R\\ 0, & \text{otherwise}\end{cases} \tag{5.9a}$$

where

$$I_0(t)\equiv\frac{E_0 e^{-(t/\tau_p)^2}}{\pi^{1/2}\tau_p}, \tag{5.9b}$$

$\vec{n}$ 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, $E_0(t)$ is the energy in the incident pulse, and τ_p is the pulse time. As long as the measurements are carried out far from the beam soon after the pulse arrives [specifically, $r_\perp\gg R$, $\tau_p c_{l,t}$ and $r_\perp/c_{l,t}-t\sim O(\tau_p)$], Eq. (5.9a) can be used in (5.8) to rewrite the latter as

$$\langle \overleftrightarrow{\mathcal{T}}(\vec{r},t)\rangle_{\rm ne}=\frac{1}{2\pi c_l(c_l t+r_\perp)^{1/2}}\left[\overleftrightarrow{\mathbb{1}}+2\left[\frac{c_t}{c_l}\right]^2(\hat{r}_\perp\hat{r}_\perp-\overleftrightarrow{\mathbb{1}})\right]$$
$$\times\left\{\left[\left[\frac{\partial p_h}{\partial h}\right]\alpha(\omega_{\rm inc})+\xi_2(\omega_{\rm inc})\right]+2\xi_1(\omega_{\rm inc})[(\hat{r}_\perp\cdot\hat{n})^2-\tfrac{1}{3}]\right\}F_l(r_\perp,t)$$
$$+\frac{\xi_1(\omega_{\rm inc})\hat{n}\cdot\hat{r}_\perp}{\pi c_t(c_t t+r_\perp)^{1/2}}(\hat{r}_\perp\hat{n}+\hat{n}\hat{r}_\perp-2\hat{r}_\perp\hat{r}_\perp)F_t(r_\perp,t), \tag{5.10}$$

where

$$F_{l,t}(\vec{r},t)\equiv\int_{r'_\perp\leq R}\frac{d\vec{r}'_\perp}{\pi R^2}\int_{-\infty}^{t-|\vec{r}_\perp-\vec{r}'_\perp|/c_{l,t}}dt'\frac{\dot{I}_0(t')}{[c_{l,t}(t-t')-|\vec{r}_\perp-\vec{r}'_\perp|]^{1/2}}. \tag{5.11}$$

This integral has the same form as those considered for fluids. It can be simplified in two limits. The first is the thin beam limit, i.e., $R\ll\tau_p c_{l,t}$. As was shown in I, in the thin beam limit [cf. Eq. (4.11a) and Fig. 1 in I]

$$F_{l,t}\sim-\frac{E_0 2^{1/4}e^{-x^2/2}}{2(\tau_p^3 c_{l,t})^{1/2}}[2^{3/2}xD_{-1/2}(-2^{1/2}x)$$
$$-D_{-3/2}(-2^{1/2}x)], \tag{5.12}$$

where $x=(t-r_\perp/c_{l,t})/\tau_p$ and D_ν is the parabolic cylinder function. This function will result in a compression pulse followed by a rarefaction pulse at the detector.

In the thick-beam limit, the observed pulse shape is determined by the acoustic propagation times across the beam (i.e., $R/c_{t,l}$) and not by the optical pulse time. It is not too difficult to approximately evaluate the integrals appearing in Eq. (5.11). For the purpose of this discussion, suffice it to note that $F_{l,t}\propto E_0 c_{l,t}/R^{3/2}$ and is in-

dependent of τ_p. Further discussion of Eq. (5.10) is deferred to the next section.

VI. DISCUSSION

In this paper, the methods of I were used to examine photoacoustic pulse generation in solids. While the general expressions should be valid for solids of arbitrary symmetry, the discussion here has been restricted to isotropic or cubic systems. This greatly simplifies the algebraic manipulations without losing any important physical consequences.

As was the case in fluids, terms other than those generated by the adiabatic expansion of the solid were obtained, although as in I, only two new coefficients were obtained in isotropic systems. From Eqs. (5.10)—(5.12) it is easy to imagine a number of experimental configurations which can measure $\xi_1(\omega_{\rm inc})$ since use can be made of the propagating nature of the transverse modes. They will arrive at the detector after the longitudinal ones and will exert forces perpendicular to the propagation direction. In contrast to what was obtained in I, the temporal profile of the pulses will all be the same. This will complicate any measurement of $\xi_2(\omega_{\rm inc})$.

Unlike the case in fluids, there are some experiments on photoacoustic pulse generation in solids,[9] although absorption measurements have not been carried out. These measurements have been analyzed in terms of the phenomenological theory of Ref. 10 and in terms of an adiabatic expansion model similar to that used in Ref. 2. The expressions obtained here can be used to write microscopic expressions for the parameters used in the phenomenological approaches. From Eq. (2.5) it follows that the macroscopic fields satisfy

$$\frac{\partial \underline{a}(\vec{k},t)}{\partial t}=\underline{M}_k\cdot\underline{a}(\vec{k},t)+[\underline{\Omega}^{ij}(\vec{k};\omega_{\rm inc}) +\underline{\Omega}(\vec{k};-\omega_{\rm inc})]S^{ji}(\vec{k},t)\ . \quad (6.1)$$

Using the explicit forms of the equations for motion [cf. Eqs. (3.4a) and (3.4b)] and for the $\underline{\Omega}$ coefficients [cf. Eqs. (5.3) and (5.6a) and (5.6b)] in Eq. (6.1) gives

$$\dot{\pi}^{ij}(\vec{r},t)=-\omega^{ijkl}\pi^{kl}(\vec{r},t)-C^{ijkl}\frac{\partial v^k(\vec{r},t)}{\partial x^l} +\xi^{ijkl}(\omega_{\rm inc})S^{kl}(\vec{r},t) \quad (6.2a)$$

and

$$\dot{h}(\vec{r},t)=-\vec{\nabla}\cdot[\rho h_s\vec{v}(\vec{r},t)+\vec{\lambda}\cdot\vec{\nabla}T(\vec{r},t)] +\alpha(\omega_{\rm inc})S^{ii}(\vec{r},t)\ . \quad (6.2b)$$

These equations are correct to first order in gradients. If the stress relaxation coefficients are set to zero and the result used in Eq. (3.2b), then macroscopic equations equivalent to those discussed in Refs. 9 and 10 are obtained, along with microscopic forms for the ξ^{ijkl} parameters (sometimes referred to as Pockel's elasto-optic coefficients). It must be stressed, however, that the nature of the phenomena for absorption measurements is potentially quite different.

Keeping the ω_i coefficients results in equations which are applicable to viscoelastic continua and in the limit of large ω_i, these will yield expressions equivalent to those obtained in I. For intermediate values of the stress relaxation constants, the resulting expressions can be applied to viscoelastic media (e.g., supercooled liquids) where absorption spectroscopy should yield information concerning the local stress relaxation and dynamics.

The usual elasto-optical effect usually refers to the coupling between the collective dielectric and elastic responses of a solid. On the other hand, in absorption spectroscopy a single particle is involved and thus any observed sound (especially the transverse modes) is a measure of the interaction between the absorber and its local environment. It is clear that this is not restricted to single component crystals. Any probe molecule could be used.

In summary, as was the case in I, the pressure pulse can be generated by nonthermal means, resulting in a response which depends on the polarization of the incident light. Unfortunately, an estimate for the magnitude of the coefficients in these new terms for absorption spectroscopy is not yet available, although work which should remedy this is in progress. Nonetheless, the sound associated with the new terms lends itself to a variety of sensitive detection schemes and should be observable.

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