# Dielectric response, nonlinear-optical processes, and the Bloch–Maxwell equations for polarizable fluids

#### Shaul Mukamel, Zhifang Deng, and Jonathan Grad

Department of Chemistry, University of Rochester, Rochester, New York 14627

Received October 19, 1987; accepted November 23, 1987

Reduced equations of motion, which generalize the Bloch-Maxwell equations to polarizable fluids with intermolecular interactions, are derived. Local-field effects are analyzed using the solvable limiting case of a perfect crystal. The dielectric function  $\epsilon(\mathbf{k}, \omega)$  and the nonlinear susceptibility  $\chi^{(3)}$  are explicitly evaluated for a model system. Two four-wave mixing techniques, which provide a direct probe for transport processes, are analyzed: the transient grating and its frequency-domain analog. A unified picture is provided for transport phenomena, cascading, and polariton effects.

# 1. INTRODUCTION

Nonlinear spectroscopic techniques, particularly four-wave mixing (4WM) processes, provide important tools for monitoring the dynamics of molecular electronic and vibrational excited states in condensed phases.<sup>1-6</sup> The most common 4WM techniques include transient grating,<sup>7-10</sup> stationary<sup>5,11,12</sup> and time-resolved<sup>13-19</sup> coherent Raman spectroscopy, hole burning,<sup>20,21</sup> and photon echoes.<sup>22-25</sup> Considerable theoretical effort was devoted toward calculating the nonlinear susceptibilities of dilute absorbers that do not interact with one another but do interact with a thermal bath. Such single-absorber models can be used in the interpretation of nonlinear-optical experiments performed on low-concentration impurities in mixed crystals,<sup>24,26</sup> glasses,<sup>20</sup> and dilute solutions.<sup>27-30</sup> The resulting nonlinear susceptibilities depend on the frequencies of the various fields  $(\omega_i)$  but do not depend explicitly on the wave vectors  $(\mathbf{k}_i)$ . The nonlinear process itself depends on the wave vectors through the phase-matching condition but not through the nonlinear susceptibility. In perfect molecular crystals, where the absorbers do interact, the nonlinear susceptibilities depend explicitly on wave vectors.<sup>3,9,10,31,32</sup> In these cases, it is possible to use translational invariance and to use the exact eigenstates of the crystal toward the calculation of nonlinear susceptibilities. The situation is more complicated, however, for molecules in solution, mixed crystals, or glasses. In these cases the system is disordered, and interactions among the absorbers can be significant, leading to various transport, energy-transfer, and relaxation processes. Much of this information is contained in the wave-vector dependence of the nonlinear susceptibilities. Because the exact manybody eigenstates of disordered systems are not readily available, an approximate theoretical framework needs to be developed for the calculation of nonlinear-optical processes in disordered media. Considerable attention was given recently to studies of 4WM processes in interacting absorbers. The transient-grating (TG) technique was used to study excitonic motion in a wide variety of systems, including molecular crystals,<sup>3,7,26</sup> ionic crystals,<sup>8</sup> and solutions.<sup>7</sup> Loring and Mukamel<sup>9,10</sup> studied the exciton motion in a perfect crystal by using the Haken-Strobl model. Several 4WM experiments were performed in an attempt to observe the Anderson transition.<sup>33–35</sup> The possibility of using the photon-echo experiment to investigate the excited-state dynamics of interacting absorbers in disordered systems was considered by several authors.<sup>36–38</sup>

In this paper we consider the linear (dielectric) and the nonlinear-optical response of a fluid of interacting polarizable molecules. Our approach is based on the derivation of reduced equations of motion (REM) for a set of relevant molecular variables.<sup>39</sup> The REM are expanded perturbatively in the intermolecular interactions. Our REM generalize the conventional Bloch-Maxwell equations<sup>40</sup> to include explicitly transport processes and intermolecular interactions. The resulting nonlinear susceptibilities are therefore both frequency and wave-vector dependent. In Section 2 we define the nonlinear-optical processes and susceptibilities. In Section 3 we introduce general formal definitions for the lowest nonlinear susceptibilities,  $\chi^{(2)}$  and  $\chi^{(3)}$ , representing three-wave mixing and 4WM, respectively. Localfield and cascading effects are discussed. In Section 4 we specialize to a simple model of a polarizable fluid consisting of interacting two-level systems. Using projection-operator techniques, we derive the generalized Bloch-Maxwell equations that include the effects of intermolecular interactions. In Section 5 we analyze the linear response and the dielectric function predicted by our REM. There are several options for defining the local field by properly modifying the intermolecular interactions. To clarify this point, we derive in Appendix A the dielectric constant  $\epsilon(\mathbf{k}, \omega)$  for a perfect crystal of interacting absorbers, including an arbitrary intermolecular interaction  $J_0(\mathbf{r})$ . That function is used to analyze the proper choice of the local-field corrections. In Section 6 we present explicit examples of 4WM processes (i.e., the TG and its frequency-domain analog) in which intermolecular interactions play a significant role. Finally, in Section 7 we summarize and analyze our results.

# 2. NONLINEAR RESPONSE FUNCTIONS AND SUSCEPTIBILITIES

In this section we introduce the notation and the basic definitions and dynamic variables to be used throughout this paper. Consider an electromagnetic field  $E(\mathbf{r}, t)$  propagating in a nonlinear infinite optical medium. It satisfies the Maxwell equation<sup>41-43</sup>

$$\nabla \times \nabla \times E = -\frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} - \frac{4\pi}{c^2} \frac{\partial^2 P}{\partial t^2}.$$
 (1)

Here P is the polarization in the medium. For an isotropic medium we can separate the transverse and longitudinal parts of  $E(\mathbf{r}, t)$  and  $P(\mathbf{r}, t)$ , and the transverse parts are related by the wave equation

$$\nabla^2 E - \frac{1}{c^2} \frac{\partial^2 E}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 P}{\partial t^2}.$$
 (2)

In Eq. (2) and in the remainder of this paper, E and P will denote the transverse part of the Maxwell field and the polarization, respectively. We shall adopt a complete microscopic description of the material system and shall assume that it consists of interacting neutral molecules whose density matrix is  $\rho(t)$ . We further assume that the intermolecular interactions do not allow for charge transfer, which is usually the case when the intermolecular separation is sufficiently large. We thus allow for the formation of Frenkel excitons but not for Wannier excitons. The polarization operator can be expressed as a sum of single-molecule operators, i.e.,<sup>42,43</sup>

$$\hat{P}(\mathbf{r}) = \sum_{j=1}^{\infty} (-1)^{j-1} \nabla^{j-1} \sum_{m} \mu_m^{(j)} \delta(\mathbf{r} - \mathbf{r}_m).$$
(3)

Here the index *m* runs over the molecules.  $r_m$  is the center of mass of the *m*th molecule,  $\mu_m^{(j)}$  is its *j*th multipole, and we are using a tensor notation. The first (j = 1) term in Eq. (3) is the dipole operator

$$\hat{P}(\mathbf{r}) = \sum_{m} \mu_{m} \delta(\mathbf{r} - \mathbf{r}_{m}), \qquad (4)$$

where  $\mu_m \equiv \mu_m^{(1)}$  is the dipole operator of the *m*th molecule. In this paper we adopt the dipole approximation and use Eq. (4). The polarization  $P(\mathbf{r}, t)$  is the expectation value of the polarization operator

$$P(\mathbf{r}, t) \equiv \mathrm{Tr}[\hat{P}(\mathbf{r})\rho(t)], \qquad (5)$$

where  $\rho(t)$  is the complete many-body density matrix of the material system, which evolves in time following the Liouville equation

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -iL\rho - iL_{\mathrm{int}}\rho. \tag{6}$$

Here L is the Liouville operator, defined as

$$LA = \frac{1}{\hbar} [H, A], \tag{7a}$$

$$L_{\rm int}A = \frac{1}{\hbar} [H_{\rm int}, A], \qquad (7b)$$

where H is the total Hamiltonian for the material system and  $H_{\text{int}}$  is the radiation-matter interaction, which in the dipole approximation assumes the form

$$H_{\rm int} = -\sum_{m} \mu_m E_L(\mathbf{r}_m, t).$$
(8)

 $E_L$  is the local field acting on the *m*th molecule and  $\mu_m$  is its dipole operator. As noted by Lorentz,  $E_L$  in general is different from the Maxwell field E, which is the average field in the medium.<sup>41-49</sup> We shall assume that  $E_L$  and E are related by a formula of the form

$$E_L(\mathbf{r},t) = E(\mathbf{r},t) + \frac{4\pi}{3} \int d\mathbf{r}' \eta(\mathbf{r}-\mathbf{r}') P(\mathbf{r}',t), \qquad (9a)$$

or, on transforming to  $\mathbf{k}$ ,  $\omega$  space,

$$E_L(\mathbf{k},\omega) = E(\mathbf{k},\omega) + \frac{4\pi}{3} \eta(\mathbf{k}) P(\mathbf{k},\omega).$$
(9b)

Throughout this paper we shall adopt the following definition of a Fourier transform:

$$A(\mathbf{k},\omega) = \int d\mathbf{r} \int dt \, \exp(i\omega t - i\mathbf{k} \cdot \mathbf{r}) A(\mathbf{r},t), \qquad (10a)$$

$$A(\mathbf{r},t) = \frac{1}{(2\pi)^4} \int d\mathbf{k} \int d\omega \, \exp(-i\omega t + i\mathbf{k} \cdot \mathbf{r}) A(\mathbf{k},\omega).$$
(10b)

The choice of  $\eta(\mathbf{k})$  depends on the nature of the system. The local field accounts for part of the intermolecular interactions. The form of  $\eta(\mathbf{k})$  is therefore intimately connected with the nature of the material Hamiltonian H. In principle we could have included in Eq. (9a) a convolution over space and time, letting  $\eta$  depend on **r** and t. In Eq. (9b) this generalization amounts to replacing  $\eta(\mathbf{k})$  by  $\eta(\mathbf{k}, \omega)$ . We shall show in Section 5 that Eqs. (9) provide an adequate definition for the local field for point dipoles in a cubic lattice. In that case, Eqs. (9) hold in the long-wavelength  $\mathbf{k}$  $\rightarrow$  0 limit, provided that we eliminate the dipole-dipole interactions in the Hamiltonian H [Eqs. (7)] and we set  $\eta(\mathbf{k})$ =  $1.^{41,44,46-49}$  For extended charge distributions,  $\eta(\mathbf{k})$  is usually less than one.<sup>3</sup> For metals<sup>50</sup> or free excitons.<sup>31,32</sup> we usually take  $\eta(\mathbf{k}) = 0$ , i.e., the local field is assumed to be the same as the Maxwell field. In the remainder of this section and in Sections 3 and 4 we shall assume that  $\eta(\mathbf{k})$  is known since it may be calculated from a detailed knowledge of the microscopic charge distribution. A procedure for calculating  $\eta(\mathbf{k})$  and constructing the Hamiltonian H in a systematic way that avoids overcounting of intermolecular interactions is developed in Section 5. Equations (2)-(6) and (9) provide a closed set of equations that permit us, in principle, to solve simultaneously for the density matrix of the material system  $(\rho)$  and for the electromagnetic field E. These equations are still too complicated since they contain the entire material many-body density matrix. The main goal of this paper is to develop an appropriate reduced description toward the approximate evaluation of the polarization [Eq. (5)] for nonlinear-optical processes. We shall now introduce the nonlinear response functions that will be calculated later. They are defined by expanding  $P(\mathbf{r}, t)$  in a power series in  $E_L(\mathbf{r}, t)$ , i.e.,

$$P(\mathbf{r}, t) = \int_{0}^{\infty} dt_{1} \int d\mathbf{r}_{1} R^{(1)}(\mathbf{r} - \mathbf{r}_{1}, t_{1}) E_{L}(\mathbf{r}_{1}, t - t_{1}) + \int_{0}^{\infty} dt_{1} \int_{0}^{\infty} dt_{2} \int d\mathbf{r}_{1} \int d\mathbf{r}_{2} R^{(2)}(\mathbf{r} - \mathbf{r}_{1}, \mathbf{r} - \mathbf{r}_{2}, t_{1}, t_{2}) \times E_{L}(\mathbf{r}_{1}, t - t_{1} - t_{2}) E_{L}(\mathbf{r}_{2}, t - t_{2}) + \int_{0}^{\infty} dt_{1} \int_{0}^{\infty} dt_{2} \int_{0}^{\infty} dt_{3} \int d\mathbf{r}_{1} \int d\mathbf{r}_{2} \int d\mathbf{r}_{3} \times R^{(3)}(\mathbf{r} - \mathbf{r}_{1}, \mathbf{r} - \mathbf{r}_{2}, \mathbf{r} - \mathbf{r}_{3}, t_{1}, t_{2}, t_{3}) \times E_{L}(\mathbf{r}_{1}, t - t_{1} - t_{2} - t_{3}) E_{L}(\mathbf{r}_{2}, t - t_{2} - t_{3}) \times E_{L}(\mathbf{r}_{3}, t - t_{3}) + \dots,$$
(11)

where we assumed that the electromagnetic field interacts with the system at times  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ , and we have introduced the time variables  $t_1 = \tau_2 - \tau_1$ ,  $t_2 = \tau_3 - \tau_2$ , and  $t_3 = t - \tau_3$  to denote the intervals between successive radiation-matter interactions. We can write the polarization in the **k**,  $\omega$ domain as

$$P(\mathbf{k}, \omega) = \hat{R}^{(1)}(\mathbf{k}\omega)E_{L}(\mathbf{k}, \omega)$$

$$+ \int d\omega_{1} \int d\omega_{2} \int d\mathbf{k}_{1} \int d\mathbf{k}_{2}\hat{R}^{(2)}(\mathbf{k}_{1}\omega_{1}, \mathbf{k}_{2}\omega_{2})$$

$$\times E_{L}(\mathbf{k}_{1}, \omega_{1})E_{L}(\mathbf{k}_{2}, \omega_{2})\delta(\omega - \omega_{1} - \omega_{2})\delta(\mathbf{k} - \mathbf{k}_{1} - \mathbf{k}_{2})$$

$$+ \int d\omega_{1} \int d\omega_{2} \int d\omega_{3} \int d\mathbf{k}_{1} \int d\mathbf{k}_{2} \int d\mathbf{k}_{3}$$

$$\times \hat{R}^{(3)}(\mathbf{k}_{1}\omega_{1}, \mathbf{k}_{2}\omega_{2}, \mathbf{k}_{3}\omega_{3})$$

$$\times E_{L}(\mathbf{k}_{1}, \omega_{1})E_{L}(\mathbf{k}_{2}, \omega_{2})E_{L}(\mathbf{k}_{3}, \omega_{3})$$

$$\times \delta(\omega - \omega_{1} - \omega_{2} - \omega_{3})\delta(\mathbf{k} - \mathbf{k}_{1} - \mathbf{k}_{2} - \mathbf{k}_{3}) + \dots$$
(12)

Here  $R^{(n)}$  is the nonlinear response function to *n*th order in  $E_L$ .  $\hat{R}^{(n)}$  are related to  $R^{(n)}$  by a simple Fourier transformation:

$$\hat{R}^{(1)}(\mathbf{k}\omega) = \int d\mathbf{r} \int_0^\infty dt \times \exp(i\omega t - i\mathbf{k}\cdot\mathbf{r})R^{(1)}(\mathbf{r},t),$$
(13a)

$$\hat{R}^{(2)}(\mathbf{k}_{1}\omega_{1}, \mathbf{k}_{2}\omega_{2}) = \int d\mathbf{r}_{1} \int d\mathbf{r}_{2} \int_{0}^{\infty} dt_{1} \int_{0}^{\infty} dt_{2}$$

$$\times \exp[i\omega_{1}t_{1} + i(\omega_{1} + \omega_{2})t_{2} - i\mathbf{k}_{1} \cdot \mathbf{r}_{1}$$

$$- i\mathbf{k}_{2} \cdot \mathbf{r}_{2}]R^{(2)}(\mathbf{r}_{1}, \mathbf{r}_{2}, t_{1}, t_{2}), \quad (13b)$$

$$\begin{split} \hat{R}^{(3)}(\mathbf{k}_{1}\omega_{1},\mathbf{k}_{2}\omega_{2},\mathbf{k}_{3}\omega_{3}) &= \int d\mathbf{r}_{1} \int d\mathbf{r}_{2} \int d\mathbf{r}_{3} \int_{0}^{\infty} dt_{1} \int_{0}^{\infty} dt_{2} \int_{0}^{\infty} dt_{3} \\ &\times \exp[i\omega_{1}t_{1} + i(\omega_{1} + \omega_{2})t_{2} \\ &+ i(\omega_{1} + \omega_{2} + \omega_{3})t_{3} \\ &- i\mathbf{k}_{1} \cdot \mathbf{r}_{1} - i\mathbf{k}_{2} \cdot \mathbf{r}_{2} - i\mathbf{k}_{3} \cdot \mathbf{r}_{3}] \\ &\times R^{(3)}(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},t_{1},t_{2},t_{3}). \end{split}$$
(13c)

The microscopic calculation of  $R^{(n)}$  and  $\hat{R}^{(n)}$  is the main goal of the present paper. Once  $R^{(n)}$  and  $\hat{R}^{(n)}$  are evaluated, Eqs. (12) can be substituted into Eqs. (2) and (9), and a closed

equation for the Maxwell field E can be obtained.  $R^{(n)}$  or  $\hat{R}^{(n)}$  thus contain the complete microscopic information necessary for the calculation of any nonlinear-optical experiment. Finally, it will be useful to expand the polarization P in powers of the Maxwell field E rather than the local field  $E_L$ . We thus define

$$P(\mathbf{r}, t) = P^{(1)}(\mathbf{r}, t) + P_{\rm NL}(\mathbf{r}, t),$$
(14a)

where  $P^{(1)}$  is to first order in E and  $P_{NL}$  represents the nonlinear contribution to the polarization

$$P_{\rm NL}(\mathbf{r},t) = P^{(2)}(\mathbf{r},t) + P^{(3)}(\mathbf{r},t) + \dots$$
 (14b)

We further introduce the frequency and wave-vector-dependent dielectric function  $\epsilon(\mathbf{k}, \omega)$ 

$$P^{(1)}(\mathbf{k},\omega) = \frac{\epsilon(\mathbf{k},\omega) - 1}{4\pi} E(\mathbf{k},\omega).$$
(15)

Combining Eqs. (2), (14), and (15) results in

$$\nabla^2 E(\mathbf{r}, t) - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \int_0^\infty \mathrm{d}t_1 \int \mathrm{d}\mathbf{r}_1 \epsilon(\mathbf{r} - \mathbf{r}_1, t_1) E(\mathbf{r}_1, t - t_1)$$
$$= \frac{4\pi}{c^2} \frac{\partial^2 P_{\mathrm{NL}}(\mathbf{r}, t)}{\partial t^2}, \quad (16)$$

which may be recast in  $\mathbf{k}$ ,  $\omega$  space as

$$[c^{2}k^{2} - \omega^{2}\epsilon(\mathbf{k},\omega)]E(\mathbf{k},\omega) = 4\pi\omega^{2}P_{\mathrm{NL}}(\mathbf{k},\omega), \qquad (17)$$

where  $k = |\mathbf{k}|$ . In the following sections we shall use the definitions and the formal relations introduced here to develop a microscopic theory for the linear and the nonlinear-optical response of molecular fluids.

## 3. THREE-WAVE AND FOUR-WAVE MIXING INCLUDING LOCAL-FIELD AND CASCADING CORRECTIONS

In Section 2 we introduced the nonlinear response functions  $R^{(n)}$  and their Fourier transforms  $\hat{R}^{(n)}$  [Eqs. (11)–(13)], which carry the complete microscopic information required for the description of any nonlinear-optical process in the medium. The response functions may be obtained by solving the Liouville equation for the material system [Eq. (6)], treating  $E_L$  as an external perturbation, and expanding the material density matrix in powers of  $E_L$ . It should be emphasized that the calculation of  $R^{(n)}$  can be made by using Eq. (6) alone, and we do not need to consider the Maxwell equations [Eq. (2)] at this stage. The calculation of the nonlinearoptical signal requires, however, the solution of the Maxwell equation [Eq. (16)] for  $E(\mathbf{r}, t)$ . To this end, we need to expand  $E_L$  in a power series in E and recast the expansion [Eqs. (11) and (12)] in terms of E. When this expansion is substituted into Eq. (16), we obtain a closed (nonlinear) equation for E. We shall now consider a stationary experiment in which we have a few relevant modes of the radiation field. We shall then expand E,  $E_L$ , and P in a discrete Fourier series, i.e.,

$$E_{L}(\mathbf{r}, t) = \sum_{j} [E_{L}(\mathbf{k}_{j}, \omega_{j}) \exp(i\mathbf{k}_{j} \cdot \mathbf{r} - i\omega_{j}t) + E_{L}^{*}(\mathbf{k}_{j}, \omega_{j})$$
$$\times \exp(-i\mathbf{k}_{i} \cdot \mathbf{r} + i\omega_{j}t)], \qquad (18a)$$

$$E(\mathbf{r}, t) = \sum_{j} [E(\mathbf{k}_{j}, \omega_{j}) \exp(i\mathbf{k}_{j} \cdot \mathbf{r} - i\omega_{j}t) + E^{*}(\mathbf{k}_{j}, \omega_{j})$$
$$\times \exp(-i\mathbf{k}_{j} \cdot \mathbf{r} + i\omega_{j}t)], \qquad (18b)$$

$$P(\mathbf{r}, t) = \sum_{j} [P(\mathbf{k}_{j}, \omega_{j}) \exp(i\mathbf{k}_{j} \cdot \mathbf{r} - i\omega_{j}t) + P_{j}^{*}(\mathbf{k}_{j}, \omega_{j})$$
$$\times \exp(-i\mathbf{k}_{j} \cdot \mathbf{r} + i\omega_{j}t)].$$
(18c)

The present notation is different from the continuous transforms used earlier, i.e.,  $E_L(\mathbf{r}, t)$  and  $E_L(\mathbf{k}, \omega)$  are not related by Eqs. (10). We shall first introduce the microscopic susceptibilities  $(\alpha, \beta, \gamma, \ldots)$  defined as

$$P(\mathbf{r}, t) = \sum_{j} \alpha(\mathbf{k}_{j}\omega_{j})E_{L}(\mathbf{k}_{j}, \omega_{j})\exp(i\mathbf{k}_{j} \cdot \mathbf{r} - i\omega_{j}t)$$

$$+ \sum_{j \ge n} \beta(\mathbf{k}_{j}\omega_{j}, \mathbf{k}_{n}\omega_{n})E_{L}(\mathbf{k}_{j}, \omega_{j})E(\mathbf{k}_{n}, \omega_{n})$$

$$\times \exp[i(\mathbf{k}_{j} + \mathbf{k}_{n}) \cdot \mathbf{r} - i(\omega_{j} + \omega_{n})t]$$

$$+ \sum_{j \ge n \ge m} \gamma(\mathbf{k}_{j}\omega_{j}, \mathbf{k}_{n}\omega_{n}, \mathbf{k}_{m}\omega_{m})$$

$$\times E_{L}(\mathbf{k}_{j}\omega_{j})E_{L}(\mathbf{k}_{n}, \omega_{n})E_{L}(\mathbf{k}_{m}\omega_{m})$$

$$\times \exp[i(\mathbf{k}_{j} + \mathbf{k}_{n} + \mathbf{k}_{m}) \cdot \mathbf{r} - i(\omega_{j} + \omega_{n} + \omega_{m})t] + \dots$$
(19)

Comparing Eq. (19) with Eq. (11) and using Eq. (18a) results , in

$$\alpha(\mathbf{k}_{j}\omega_{j}) = \hat{R}^{(1)}(\mathbf{k}_{j}\omega_{j}), \qquad (20a)$$

$$\beta(\mathbf{k}_{j}\omega_{j},\mathbf{k}_{n}\omega_{n}) = \sum_{[j,n]} \hat{R}^{(2)}(\mathbf{k}_{j}\omega_{j},\mathbf{k}_{n}\omega_{n}), \qquad (20b)$$

$$\gamma(\mathbf{k}_{j}\omega_{j}, \mathbf{k}_{n}\omega_{n}, \mathbf{k}_{m}\omega_{m}) = \sum_{\{j,n,m\}} \hat{R}^{(3)}(\mathbf{k}_{j}\omega_{j}, \mathbf{k}_{n}\omega_{n}, \mathbf{k}_{m}\omega_{m}).$$
(20c)

 $\hat{R}^{(2)}(\mathbf{k}_{j}\omega_{j}, \mathbf{k}_{n}\omega_{n})$  represents a nonlinear process in which the system interacts first with the  $\mathbf{k}_{j}$  field and later with the  $\mathbf{k}_{n}$  field [Eq. (13)]. The sum  $\{j, n\}$  in Eq. (20b) is over the two permutations of j and n and represents the fact that the interaction with the two fields can occur in all possible orders in time.<sup>6</sup> Similarly the sum  $\{j, n, m\}$  in Eq. (20c) is over the six permutations of j, n, m. We further note that we have included in Eq. (19) only the  $\mathbf{k}_{j} + \mathbf{k}_{n}$  or  $\mathbf{k}_{j} + \mathbf{k}_{n} + \mathbf{k}_{m}$  Fourier components of  $P(\mathbf{r}, t)$ . In fact, the possible Fourier components are all choices of signs in  $\pm \mathbf{k}_{j} \pm \mathbf{k}_{n}$  or  $\pm \mathbf{k}_{j} \pm \mathbf{k}_{m} \pm \mathbf{k}_{m}$ . These Fourier components may be obtained from Eq. (19) by changing one (or more)  $\mathbf{k}_{j}$  and  $\omega_{j}$  to  $-\mathbf{k}_{j}$  and  $-\omega_{j}$  and replacing  $E_{L}(\mathbf{k}_{j}, \omega_{j})$  by  $E_{L}^{*}(\mathbf{k}_{j}, \omega_{j})$ . For brevity we did not write all these possibilities explicitly.

At this point we introduce the molecular susceptibilities that relate the polarization  $P(\mathbf{r}, t)$  to the Maxwell field, i.e.,

$$P(\mathbf{r},t) = P^{(1)}(\mathbf{r},t) + P^{(2)}(\mathbf{r},t) + P^{(3)}(\mathbf{r},t) + \dots, \qquad (21a)$$

$$P^{(1)}(\mathbf{r},t) = \sum_{j} \chi^{(1)}(-\mathbf{k}_{j} - \omega_{j}, \mathbf{k}_{j}\omega_{j})E_{j}(\mathbf{k}_{j}, \omega)\exp(i\mathbf{k}_{j}\cdot\mathbf{r} - i\omega_{j}t),$$
(21b)

$$P^{(2)}(\mathbf{r}, t) = \sum_{j \ge n} \chi^{(2)}(-\mathbf{k}_j - \mathbf{k}_n - \omega_j - \omega_n; \mathbf{k}_j \omega_j, \mathbf{k}_n \omega_n)$$
$$\times E(\mathbf{k}_j, \omega_j) E(\mathbf{k}_n, \omega_n)$$
$$\times \exp[i(\mathbf{k}_j + \mathbf{k}_n) \cdot \mathbf{r} - i(\omega_j + \omega_n)t], \qquad (21c)$$

$$P^{(3)}(\mathbf{r}, t) = \sum_{j \ge n \ge m} \chi^{(3)}(-\mathbf{k}_j - \mathbf{k}_n - \mathbf{k}_m - \omega_j - \omega_n - \omega_m;$$
  
 
$$\times \mathbf{k}_j \omega_j, \mathbf{k}_n \omega_n, \mathbf{k}_m \omega_m) E(\mathbf{k}_j, \omega_j) E(\mathbf{k}_n, \omega_n) E(\mathbf{k}_m, \omega_m)$$
  
 
$$\times \exp[i(\mathbf{k}_j + \mathbf{k}_n + \mathbf{k}_m) \cdot \mathbf{r} - i(\omega_j + \omega_n + \omega_m)].$$
  
(21d)

 $\chi^{(1)}$  is the ordinary (linear) susceptibility and is responsible for the dielectric properties of the medium when the incoming fields are weak.  $\chi^{(2)}$  describes three-wave mixing (e.g., second-harmonic generation), and  $\chi^{(3)}$  is responsible for  $4\text{WM}.^{1-6} \chi^{(2)}$  can have any of the Fourier components  $\pm \mathbf{k}_j \pm \mathbf{k}_n$ ;  $\chi^{(3)}$  can have the Fourier components  $\pm \mathbf{k}_j \pm \mathbf{k}_n \pm \mathbf{k}_m$ . In Eqs. (21) [as for Eq. (19)] we have written explicitly only the components with the pluses. All other components may be obtained by changing one (or more)  $\mathbf{k}_j$  and  $\omega_j$  to  $-\mathbf{k}_j$  and  $-\omega_j$  and by changing  $E(\mathbf{k}_j, \omega_j)$  to  $E^*(\mathbf{k}_j, \omega_j)$ . We are now in a position to express the susceptibilities  $\chi^{(n)}$  [Eqs. (21)] in terms of the microscopic susceptibilities  $\alpha, \beta, \gamma$  [Eqs. (20)]. To that end, we first combine Eqs. (9b), (14a), and (15) and recast the local field in the form

$$E_L(\mathbf{k},\omega) = S(\mathbf{k},\omega)E(\mathbf{k},\omega) + \frac{4\pi}{3}\eta(\mathbf{k})P_{\rm NL}(\mathbf{k},\omega), \qquad (22a)$$

where

$$S(\mathbf{k},\omega) = \frac{3+\eta(\mathbf{k})[\epsilon(\mathbf{k},\omega)-1]}{3}$$
(22b)

and  $P_{NL}(\mathbf{k},\omega)$  is given by Eq. (14b). The linear polarization is given by

$$P^{(1)}(\mathbf{k},\omega) = \chi^{(1)}(-\mathbf{k}-\omega;\mathbf{k}\omega)E(\mathbf{k},\omega), \qquad (23a)$$

where

$$\chi^{(1)}(-\mathbf{k}-\omega;\mathbf{k}\omega) = \alpha(\mathbf{k}\omega)S(\mathbf{k},\omega) = \frac{\epsilon(\mathbf{k},\omega)-1}{4\pi}.$$
 (23b)

For second-order nonlinear processes we assume two incoming fields:  $\mathbf{k}_1\omega_1$  and  $\mathbf{k}_2\omega_2$ . The nonlinear polarization is then given by

$$P^{(2)}(\mathbf{k},\,\omega) = \chi^{(2)}(-\mathbf{k}-\omega;\,\mathbf{k}_1\omega_1,\,\mathbf{k}_2\omega_2)E(\mathbf{k}_1,\,\omega_1)E(\mathbf{k}_2,\,\omega_2),$$
(24a)

where

$$\chi^{(2)}(-\mathbf{k} - \omega; \mathbf{k}_1 \omega_1, \mathbf{k}_2 \omega_2) = \beta(\mathbf{k}_1 \omega_1, \mathbf{k}_2 \omega_2)$$
$$\times S(\mathbf{k}_1, \omega_1) S(\mathbf{k}_2, \omega_2) S(\mathbf{k}, \omega) \quad (24b)$$

and

$$\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2; \, \omega = \omega_1 + \omega_2. \tag{24c}$$

For third-order nonlinear processes we introduce three incoming fields:  $\mathbf{k}_1\omega_1$ ,  $\mathbf{k}_2\omega_2$ , and  $\mathbf{k}_3\omega_3$ . We then get for the polarization at  $\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ 

$$P(\mathbf{k}, \omega) = \gamma(\mathbf{k}_{1}\omega_{1}, \mathbf{k}_{2}\omega_{2}, \mathbf{k}_{3}\omega_{3})E_{L}(\mathbf{k}_{1}, \omega_{1})E_{L}(\mathbf{k}_{2}, \omega_{2})E_{L}(\mathbf{k}_{3}, \omega_{3})$$

$$+ \beta(\mathbf{k}_{1} + \mathbf{k}_{2}\omega_{1} + \omega_{2}, \mathbf{k}_{3}\omega_{3})E_{L}(\mathbf{k}_{1} + \mathbf{k}_{2}, \omega_{1} + \omega_{2})E_{L}(\mathbf{k}_{3}, \omega_{3})$$

$$+ \beta(\mathbf{k}_{1} + \mathbf{k}_{3}\omega_{1} + \omega_{3}, \mathbf{k}_{2}\omega_{2})E_{L}(\mathbf{k}_{1} + \mathbf{k}_{3}, \omega_{1} + \omega_{3})E_{L}(\mathbf{k}_{2}, \omega_{2})$$

$$+ \beta(\mathbf{k}_{2} + \mathbf{k}_{3}\omega_{2} + \omega_{3}, \mathbf{k}_{1}\omega_{1})E_{L}(\mathbf{k}_{2} + \mathbf{k}_{3}, \omega_{2} + \omega_{3})E_{L}(\mathbf{k}_{1}, \omega_{1})$$

$$+ \alpha(\mathbf{k}, \omega)E_{L}(\mathbf{k}, \omega). \qquad (25)$$

By substituting Eq. (22a) into Eq. (25) and collecting terms to third order in E, we get

$$P^{(3)}(\mathbf{k}, \omega) = \chi^{(3)}(-\mathbf{k} - \omega; \mathbf{k}_1\omega_1, \mathbf{k}_2\omega_2, \mathbf{k}_3\omega_3)E(\mathbf{k}_1, \omega_1)$$
$$\times E(\mathbf{k}_2, \omega_2)E(\mathbf{k}_3, \omega_3), \qquad (26a)$$

where

$$\chi^{(3)}(-\mathbf{k} - \omega; \mathbf{k}_1\omega_1, \mathbf{k}_2\omega_2, \mathbf{k}_3\omega_3) = [\gamma(\mathbf{k}_1\omega_1, \mathbf{k}_2\omega_2, \mathbf{k}_3\omega_3) + \beta(\mathbf{k}_1\omega_1, \mathbf{k}_2\omega_2)\beta(\mathbf{k}_1 + \mathbf{k}_2\omega_1 + \omega_2, \mathbf{k}_3\omega_3)Q(\mathbf{k}_1 + \mathbf{k}_2, \omega_1 + \omega_2) + \beta(\mathbf{k}_1\omega_1, \mathbf{k}_3\omega_3)\beta(\mathbf{k}_1 + \mathbf{k}_3\omega_1 + \omega_3, \mathbf{k}_2\omega_2)Q(\mathbf{k}_1 + \mathbf{k}_3, \omega_1 + \omega_3) + \beta(\mathbf{k}_2\omega_2, \mathbf{k}_3\omega_3)\beta(\mathbf{k}_2 + \mathbf{k}_3\omega_2 + \omega_3, \mathbf{k}_1\omega_1)Q(\mathbf{k}_2 + \mathbf{k}_3, \omega_2 + \omega_3) \times S(\mathbf{k}_1, \omega_1)S(\mathbf{k}_2, \omega_2)S(\mathbf{k}_3, \omega_3)S(\mathbf{k}, \omega),$$
(26b)

with

$$\mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3, \qquad \omega = \omega_1 + \omega_2 + \omega_3, \tag{26c}$$

$$Q(\mathbf{k},\omega) = \frac{4\pi}{3} \eta(\mathbf{k}) S(\mathbf{k},\omega), \qquad (26d)$$

and  $k = |\mathbf{k}|$ . From Eqs. (26), we see that the low-order nonlinear processes ( $\beta$ ) contribute to the higher-order nonlinear process  $\chi^{(3)}$ . This effect is called cascading.<sup>3,48</sup> Let us examine Eq. (26b) more carefully. The first term in Eq. (26b) represents the nonlinear process by which three waves,  $\mathbf{k}_1\omega_1$ ,  $\mathbf{k}_2\omega_2$ , and  $\mathbf{k}_3\omega_3$ , mix to generate a new wave  $\mathbf{k}\omega$ . The second term in Eq. (26b) represents the nonlinear process whereby two waves,  $\mathbf{k}_1\omega_1$  and  $\mathbf{k}_2\omega_2$ , mix to generate a wave  $\mathbf{k}'$  $= \mathbf{k}_1 + \mathbf{k}_2$ ,  $\omega' = \omega_1 + \omega_2$ , and this generated wave mixes further with the third wave,  $\mathbf{k}_3\omega_3$ , to generate the final wave with wave vector  $\mathbf{k} = \mathbf{k}' + \mathbf{k}_3$  and frequency  $\omega = \omega' + \omega_3$ . The last two terms in Eq. (26b) represent the same sequence of events with all possible permutations of the three fields.

# 4. THE BLOCH-MAXWELL EQUATIONS FOR A POLARIZABLE FLUID

We consider a nonlinear-optical medium consisting of polarizable molecules (absorbers) distributed randomly in a solvent.<sup>49-54</sup> We denote the static pair distribution function of the absorbers by g(r).<sup>53-55</sup> We shall be interested in transitions between two electronic states of the molecules. These states are well separated from other electronic levels; thus each molecule may be described as a two-level system with transition energy  $\hbar\Omega$ . The transition dipole matrix element between these two states will be denoted  $\mu$ . The molecules are coupled further by intermolecular interactions. We assume that the transition energies of the molecules are sufficiently different from those of the solvent that there is no solvent-absorber resonant interaction. The material Hamiltonian is taken to be<sup>9,10</sup>

$$H = H_0 + H_1 + H_2, (27a)$$

with

$$H_0 = \hbar \ \Omega \sum_m a_m^{\dagger} a_m, \tag{27b}$$

$$H_1 = \frac{\hbar}{2} \sum_{n,m} \overline{J}(r_n - r_m)(a_m + a_m^{\dagger})(a_n + a_n^{\dagger}), \qquad (27c)$$

and

$$H_2 = \hbar \sum_m \Delta_m(t) a_m^{\dagger} a_m, \qquad (27d)$$

and the radiation-matter interaction [Eq. (8)] in this case assumes the form

$$H_{\rm int} = -\mu \sum_{m} (a_m^{\dagger} + a_m) E_L(\mathbf{r}_m, t).$$
<sup>(28)</sup>

Here  $a_m^{\dagger}$  and  $a_m$  are the creation and annihilation operators for the electronic excitation on the *m*th molecule located at  $r_m$ . They satisfy the Fermi anticommutation relations, i.e.,<sup>31</sup>

$$\{a_m^{\dagger}, a_n\} \equiv a_m^{\dagger} a_n + a_n a_m^{\dagger} = \delta_{m,n} + 2a_m^{\dagger} a_n (1 - \delta_{m,n}).$$
(29)

The total intermolecular interaction between molecules nand m will be denoted  $J_0(r_n - r_m)$ . In Eq. (27b),  $\overline{J}(r_n - r_m)$  is a modified interaction that should be chosen consistently with the local-field factor  $\eta(\mathbf{k})$  to avoid the overcounting of intermolecular interactions. This point will be discussed in detail in Section 5.  $\hbar\Delta_m(t)$  is a stochastic modulation of the energy of site m and is assumed to be a Gaussian-Markov process with

$$\langle \Delta_m(t) \rangle = 0, \tag{30}$$

$$\langle \Delta_m(t_1)\Delta_n(t_2)\rangle = \hat{\Gamma}\delta_{mn}\delta(t_1 - t_2). \tag{31}$$

The angle brackets in Eqs. (30) and (31) indicate an average over the stochastic fluctuations. The summations in Eqs. (27) and (28) are over all molecules, and  $E_L(\mathbf{r}_m, t)$  in Eq. (28) is the local electric field [Eq. (9)]. Equations (30) and (31) represent an ideal homogeneous line-broadening mechanism whereby level fluctuations on different sites are uncorrelated, and the time scale for solvent motions is short compared with  $\hbar$  divided by the magnitude of level fluctuations. An additional broadening mechanism, which is dominant in low-temperature glasses, viscous solvents, polymers, and molecular crystals, corresponds to the opposite extreme of inhomogeneous broadening in which the solvent configurations are static on the time scale corresponding to  $\hbar$  divided by the linewidth. This mechanism is not included in the present paper. A discussion of the range of applicability of the present model and its limitations and possible extensions will be given in Section 7.

To calculate the optical response of the system, we start at  $t = -\infty$  and assume that the system is in thermal equilibrium with respect to its Hamiltonian H (without the radiation field), i.e.,

$$\rho(-\infty) = \exp(-\beta H) / \operatorname{Tr} \exp(-\beta H), \qquad (32)$$

where  $\beta = (KT)^{-1}$ . The many-body density matrix of the system then evolves in time according to the Liouville equation

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -iL\rho - iL_{\mathrm{int}}\rho. \tag{33}$$

We shall also define a Liouville-space matrix element,<sup>30</sup> i.e.,

$$\langle \langle A|L|B \rangle \rangle = \operatorname{Tr}(A^{\dagger}LB). \tag{34}$$

The Liouville equation [Eq. (33)] describes the dynamics of the disordered system. In this paper we derive REM that will allow us to solve Eq. (33) approximately and calculate the polarization [Eq. (5)]. The REM are derived in the following steps. We first define a set of operators, whose expectation values are of interest. In our case we choose a complete set of single-body operators:

$$A_0 = 1, \tag{35a}$$

$$A_1(\mathbf{r}) = \sum_m a_m^{\dagger} a_m \delta(\mathbf{r} - \mathbf{r}_m), \qquad (35b)$$

$$A_2(\mathbf{r}) = \sum_m a_m^{\dagger} \delta(\mathbf{r} - \mathbf{r}_m), \qquad (35c)$$

$$A_3(\mathbf{r}) = \sum_m a_m \delta(\mathbf{r} - \mathbf{r}_m).$$
(35d)

The expectation values of these operators will be denoted

$$\sigma_i(\mathbf{r}) \equiv \langle \operatorname{Tr}[A_i^{\dagger}(\mathbf{r})\rho(t)] \rangle \qquad i = 0, \dots 3,$$
(36)

where Tr represents a trace over the internal degrees of freedom and an average over the random configurations. By definition  $\sigma_0 = 1$ .  $\sigma_1(\mathbf{r})$  is the excited-state population at position  $\mathbf{r}$ , and  $\sigma_2(\mathbf{r})$  and  $\sigma_3(\mathbf{r})$  represent the polarization at position  $\mathbf{r}$ . We further denote

$$P(\mathbf{r}) = \mu[\sigma_2(\mathbf{r}) + \sigma_3(\mathbf{r})], \qquad (37a)$$

$$V(\mathbf{r}) = i\mu[\sigma_2(\mathbf{r}) - \sigma_3(\mathbf{r})], \qquad (37b)$$

$$W(\mathbf{r}) = \sigma_1(\mathbf{r}). \tag{37c}$$

The only material variable necessary for solving the Maxwell equations [Eq. (2)] for the radiation field is the polarization  $P(\mathbf{r})$ . The other variables  $V(\mathbf{r})$  and  $W(\mathbf{r})$  are included to obtain a simple, reduced description of the system.

We next introduce a complementary set of operators:

$$\overline{A}_0 = \rho_0, \tag{38a}$$

$$\overline{A}_1 = \sum_m a_m^{\dagger} \rho_0 a_m \delta(\mathbf{r} - \mathbf{r}_m), \qquad (38b)$$

$$\overline{A}_2 = \sum_m a_m^{\dagger} \rho_0 \delta(\mathbf{r} - \mathbf{r}_m), \qquad (38c)$$

$$\overline{A}_3 = \sum_m \rho_0 a_m \delta(\mathbf{r} - \mathbf{r}_m), \qquad (38d)$$

where  $\rho_0 = |0\rangle \langle 0|$  is the ground state of the disordered system in which all molecules are in their ground state. In addition, we define the scalar product of our variables

$$S_{i\mathbf{r},j\mathbf{r}'} \equiv \langle\!\langle A_i(\mathbf{r}) | \overline{A}_j(\mathbf{r}') \rangle\!\rangle. \tag{39a}$$

Using Eqs. (35), (38), and (39), we have

$$S_{0,0} \equiv \langle \langle A_0 | A_0 \rangle = 1,$$
  

$$S_{0,1\mathbf{r}} \equiv \langle \langle A_0 | \overline{A}_1(\mathbf{r}) \rangle = 1,$$
  

$$S_{i\mathbf{r},i\mathbf{r}'} \equiv \langle \langle A_i(\mathbf{r}) | \overline{A}_i(\mathbf{r}') \rangle = \delta(\mathbf{r} - \mathbf{r}'), \quad i = 1, 2, 3; (39b)$$

all other matrix elements of S not specified in Eqs. (39) are zero. We next introduce the projection operator

$$\overline{P} = \iint \mathbf{dr} \mathbf{dr'} \sum_{ij} |\overline{A}_i(\mathbf{r}) \rangle S_{i\mathbf{r},j\mathbf{r}'}^{-1} \langle \langle A_j(\mathbf{r}') |$$
(40)

and the complementary projection  $\overline{Q} = 1 - \overline{P}$ . The density matrix can now be partitioned as

$$\rho(t) = \overline{P}\rho(t) + \overline{Q}\rho(t), \qquad (41)$$

where

$$\overline{P}\rho(t) = \iint \mathbf{drdr'} \sum_{ij} |\langle\!\langle \overline{A}_i(\mathbf{r}) \rangle\!\rangle S_{i\mathbf{r},j\mathbf{r}'}^{-1} \langle\!\langle A_j(\mathbf{r}') | \rho(t) \rangle\!\rangle.$$
(42)

Using standard projection-operator techniques,<sup>39</sup> we can derive the REM for  $\sigma_j(\mathbf{r}, t)$ . The REM can be written formally as

$$\frac{\mathrm{d}\sigma_{j}(\mathbf{r},t)}{\mathrm{d}t} = -i\langle\langle A_{j}(\mathbf{r})|\overline{P}L(t)\overline{P}|\rho(t)\rangle\rangle -\int_{-\infty}^{t}\mathrm{d}\tau\langle\langle A_{j}(\mathbf{r})|\overline{P}L(t)\overline{Q}K(t,\tau)L(\tau)\overline{P}|\rho(\tau)\rangle\rangle,$$
(43a)

with

$$K(t, \tau) = \exp_{+}\left[-i \int_{\tau}^{t} \mathrm{d}\tau_{1} L(\tau_{1}) \overline{Q}\right], \qquad (43b)$$

where  $\exp_+$  stands for the positive time-ordered exponential, i.e.,

$$K(t, \tau) = 1 - i \int_{\tau}^{t} d\tau_1 L(\tau_1) \overline{Q} + (-i)^2 \int_{\tau}^{t} d\tau_1 \int_{\tau}^{\tau_1} d\tau_2 L(\tau_1) \overline{Q} L(\tau_2) \overline{Q} + \dots$$
(43c)

The significance of the projection operator  $\overline{P}$  [Eq. (40)] is as follows. Given the expectation values of the dynamic variables of interest  $\sigma_j(\mathbf{r}, t)$ , we construct an approximate density matrix  $\overline{P}\rho(t)$ . We require that the expectation values of our relevant operators  $A_j(\mathbf{r})$ , calculated using the exact  $(\rho)$  and approximate  $(\overline{P}\rho)$  density matrices, be the same, i.e.,

$$\langle\!\langle A_j(\mathbf{r})|\rho(t)\rangle\!\rangle = \langle\!\langle A_j(\mathbf{r})|\overline{P}\rho(t)\rangle\!\rangle = \sigma_j(\mathbf{r},t).$$
(44)

The actual density matrix at time t is given by  $\overline{P}\rho(t)$  and the correction term  $\overline{Q}\rho(t)$  [Eq. (41)]. The first term on the right-hand side of Eq. (43a) is a mean-field term obtained assuming that  $\overline{P}\rho(t) = \rho(t)$ . The second term represents fluctuations [the fact that actually  $\overline{P}\rho(t) \neq \rho(t)$ ]. We have calculated the first term exactly and the second term to second order in  $H_1$  and to zeroth order in  $H_{\text{int}}$ . The resulting equations are

$$\frac{\mathrm{d}P(\mathbf{r},t)}{\mathrm{d}t} = \Omega V(\mathbf{r},t) - \Gamma P(\mathbf{r},t), \tag{45a}$$

$$\frac{\mathrm{d}V(\mathbf{r},t)}{\mathrm{d}t} = -\Omega P(\mathbf{r},t) - \Gamma V(\mathbf{r},t) - 2C \int \mathrm{d}\mathbf{r}' J(\mathbf{r}-\mathbf{r}') P(\mathbf{r}',t)$$

$$-2\overline{\mu^2}E_L(\mathbf{r},t)[2W(\mathbf{r},t)-C], \qquad (45b)$$

$$\frac{\mathrm{d}W(\mathbf{r},t)}{\mathrm{d}t} = -\gamma W(\mathbf{r},t) + \frac{1}{\hbar} E_L(\mathbf{r},t) V(\mathbf{r},t) - 2C \int_{-\infty}^t \mathrm{d}\tau \exp[-2\Gamma(t-\tau)] \times \left\{ \int \mathrm{d}\mathbf{r}' T(\mathbf{r}-\mathbf{r}') [W(\mathbf{r},\tau) - W(\mathbf{r}',\tau)] \right\}, \quad (45c)$$

$$\nabla^2 E(\mathbf{r},t) - \frac{1}{c^2} \frac{\partial^2 E(\mathbf{r},t)}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 P(\mathbf{r},t)}{\partial t^2}, \quad (45d)$$

$$E_L(\mathbf{r}, t) = E(\mathbf{r}, t) + \frac{4\pi}{3} \int d\mathbf{r}' \eta(\mathbf{r} - \mathbf{r}') P(\mathbf{r}', \tau). \qquad (45e)$$

Here we have introduced the following definitions:

$$\overline{\mu^2} = \mu^2 / \hbar, \tag{46a}$$

$$J(\mathbf{r}) = \overline{J}(\mathbf{r})g(\mathbf{r}), \tag{46b}$$

$$T(\mathbf{r}) = \overline{J}^2(\mathbf{r})g(\mathbf{r}), \qquad (46c)$$

$$\Gamma = \frac{1}{2} \left( \gamma + \hat{\Gamma} \right). \tag{46d}$$

 $\gamma^{-1}$  is the lifetime (radiative or nonradiative) of the electronically excited state,  $\Gamma$  is the total dephasing rate of the transition, and *C* is the number of molecules per unit volume. Equations (45) are the basic REM that couple the material variables *P*, *V*, and *W* with the local field  $E_L$  and the Maxwell field *E*. These basic REM should be solved simultaneously for these five quantities. If we set  $J(\mathbf{r}) = 0$ , Eqs. (45) reduce to the ordinary Bloch-Maxwell equations in which intermolecular interactions are not incorporated.<sup>40</sup> Equations (45) can be used to study the nonlinear-optical properties of disordered systems in the presence of transport. The nonlinear susceptibilities calculated from Eqs. (45) will be explicitly wave-vector (k) dependent. It will be convenient to rewrite Eqs. (45) in k space as

$$\frac{\mathrm{d}P(\mathbf{k},t)}{\mathrm{d}t} = \Omega V(\mathbf{k},t) - \Gamma P(\mathbf{k},t), \qquad (47a)$$

$$\frac{\mathrm{d}V(\mathbf{k},t)}{\mathrm{d}t} = -\left[\Omega + 2CJ(\mathbf{k})\right]P(\mathbf{k},t) - \Gamma V(\mathbf{k},t)$$

$$-2\overline{\mu^2} \int \mathrm{d}\mathbf{k}' E_L(\mathbf{k}',t) [2W(\mathbf{k}-\mathbf{k}',t)$$

 $-C\delta(\mathbf{k}-\mathbf{k}')],$ 

$$\frac{\mathrm{d}W(\mathbf{k},t)}{\mathrm{d}t} = -\gamma W(\mathbf{k},t) + (1/\hbar) \int \mathrm{d}\mathbf{k}' E_L(\mathbf{k}',t) V(\mathbf{k}-\mathbf{k}',t) - 2C[T(\mathbf{k}=0) - T(\mathbf{k})] \times \int_{-\infty}^t \mathrm{d}\tau \, \exp[-2\Gamma(t-\tau)] W(\mathbf{k},\tau), \qquad (47c)$$

where  $T(\mathbf{k})$  is given by the Fourier transform of  $T(\mathbf{r})$  [Eq. (46c)], i.e.,

$$T(\mathbf{k}) = \int d\mathbf{r} T(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}). \qquad (47d)$$

# 5. THE LINEAR SUSCEPTIBILITY AND THE DIELECTRIC FUNCTION

In this section we derive the linear susceptibility and the dielectric function, using the REM obtained in Section 4. For a perfect lattice and in the absence of disorder, it is possible to obtain the dielectric function independently by diagonalizing the entire radiation-matter Hamiltonian following the procedure of Hopfield.<sup>56</sup> The detailed derivation is given in Appendix A. The result allows us to explore the proper definition of the local field and to define  $\eta(\mathbf{k})$  in a way that is consistent with this solution.

The linear polarization in the frequency domain is given by Eq. (15), where  $E(\mathbf{k}, \omega)$  is the averaged field in the medium. By solving Eqs. (47) to first order of the field, we obtain the linear polarization, which is proportional to the local field. We then define the effective linear susceptibility [Eq. (19)] as

$$P^{(1)}(\mathbf{k},\omega) = \alpha(\mathbf{k}\omega)E_L(\mathbf{k},\omega) + \dots$$
(48)

The dielectric function  $\epsilon(\mathbf{k}, \omega)$  is defined as [see Eq. (21b)]

$$P^{(1)}(\mathbf{k},\omega) = \chi^{(1)}(-\mathbf{k}-\omega;\mathbf{k}\omega)E(\mathbf{k},\omega), \qquad (49a)$$

with

$$\chi^{(1)}(-\mathbf{k}-\omega;\mathbf{k}\omega) \equiv \frac{\epsilon(\mathbf{k},\omega)-1}{4\pi}.$$
 (49b)

When we ignore the nonlinear polarization  $P_{\rm NL}$  in Eq. (22a), we further have

$$E_L(\mathbf{k},\omega) = \frac{3+\eta(\mathbf{k})[\epsilon(\mathbf{k},\omega)-1]}{3} E(\mathbf{k},\omega).$$
(50)

Equations (48)-(50) result in

$$\chi^{(1)}(-\mathbf{k},\omega;\mathbf{k},\omega) = \frac{\alpha(\mathbf{k}\omega)}{1 - 4\pi\eta(\mathbf{k})\alpha(\mathbf{k}\omega)/3}$$
(51)

and

(47b)

$$\frac{[\epsilon(\mathbf{k},\omega)-1]}{3+\eta(\mathbf{k})[\epsilon(\mathbf{k},\omega)-1]} = \frac{4\pi}{3} \alpha(\mathbf{k}\omega).$$
(52)

In Eqs. (51) and (52) we have expressed  $\chi^{(1)}$  and  $\epsilon$  in terms of the microscopic response function  $\alpha(\mathbf{k}\omega)$ , which can be obtained by solving Eqs. (47) to linear order in  $E_L(\mathbf{k}, t)$ . Our linearized equations are obtained by setting  $W(\mathbf{r}) = 0$  in Eqs. (47), resulting in

$$\frac{\mathrm{d}P(\mathbf{k},t)}{\mathrm{d}t} = \Omega V(\mathbf{k},t) - \Gamma P(\mathbf{k},t), \qquad (53a)$$

$$\frac{\mathrm{d}V(\mathbf{k},t)}{\mathrm{d}t} = -[\Omega + 2CJ(\mathbf{k})]P(\mathbf{k},t) - \Gamma V(\mathbf{k},t) + 2\overline{\mu^2}CE_L(\mathbf{k},t).$$
(53b)

By solving Eqs. (53) and using Eq. (48), we obtain

$$\alpha(\mathbf{k}\omega) = \frac{2C\overline{\mu^2}\Omega}{(-i\omega+\Gamma)^2 + \Omega[\Omega + 2CJ(\mathbf{k})]}.$$
 (54)

Equation (54) together with Eq. (52) results in

$$\epsilon(\mathbf{k},\omega) = 1 + \frac{8\pi C\mu^2 \Omega}{(-i\omega + \Gamma)^2 + \Omega[\Omega + 2CJ(\mathbf{k}) - 8\pi\eta(\mathbf{k})C\overline{\mu^2}/3]}.$$
(55)

At this stage we reiterate that the forms of the intermolecular interaction J(k) [Eq. (47)] and the local-field correction  $\eta(\mathbf{k})$  are related. The local field [Eq. (9)] takes into account part of the intermolecular interactions. Therefore  $J(\mathbf{k})$  and  $\eta(\mathbf{k})$  should be defined consistently to account for intermolecular interactions and to avoid overcounting. To gain some insight on this issue, we derive in Appendix A the expression for  $\epsilon(\mathbf{k}, \omega)$  for a special case of the present model in which the molecules occupy a perfect cubic lattice and have an intermolecular interaction  $J_0(\mathbf{r})$  [Eq. (A5)]. This model is solvable by using the method first employed by Hopfield.<sup>56</sup> The final result [Eq. (A20)] is

$$\epsilon(\mathbf{k},\omega) = 1 + \frac{8\pi C \mu^2 \Omega}{(-i\omega + \Gamma)^2 + \Omega[\Omega + 2CJ_0(\mathbf{k})]}.$$
 (56)

We are now in a position to address the issue of what systematic choice of  $J(\mathbf{k})$  and  $\eta(\mathbf{k})$  in our formulation will make the resulting  $\epsilon(\mathbf{k}, \omega)$  [Eq. (55)] identical to the crystal result [Eq. (56)].  $J(\mathbf{k}), J_0(\mathbf{k})$ , and  $\eta(\mathbf{k})$  have to satisfy the relation

$$J(\mathbf{k}) = J_0(\mathbf{k}) + \frac{4\pi\overline{\mu 2}}{3} \eta(\mathbf{k}).$$
(57)

One possible choice that can be made for  $J(\mathbf{k})$  and for  $\eta(\mathbf{k})$  is

$$J(\mathbf{k}) = 0, \tag{58a}$$

$$\eta(\mathbf{k}) = -3J_0(\mathbf{k})/(4\pi\mu^2).$$
 (58b)

For the special case of dipole-dipole interaction we have<sup>56,57</sup>

$$\hbar J_d(\mathbf{r}) = \frac{\mu^2}{|\mathbf{r}|^3} - \frac{3(\mu \cdot \mathbf{r})^2}{|\mathbf{r}|^5}.$$
 (59a)

In the long-wavelength limit ( $\mathbf{k} \rightarrow 0$ ) we then have<sup>56–58</sup>

$$J_d(\mathbf{k}) = -4\pi \overline{\mu^2}/3, \qquad \mathbf{k} \to 0.$$
 (59b)

For this case  $\eta(\mathbf{k}) = 1$ . The local field with  $\eta(\mathbf{k}) = 1$  thus takes properly into account the dipole-dipole interactions. A common phenomenological way to incorporate local-field effects in nonlinear-optical processes<sup>4,47</sup> is based on the Lorentz-Lorenz equation and corresponds to choosing  $\eta(\mathbf{k}) =$ 1. The present derivation shows that this procedure takes into account the long-wavelength  $(\mathbf{k} \rightarrow 0)$  contribution of the dipolar interaction  $J_d(\mathbf{k})$ . If this procedure is adopted,  $J(\mathbf{k})$ in Eq. (55) should be defined as the total interaction  $J_0(\mathbf{k})$ minus the long-range dipolar interaction, i.e.,

$$J(\mathbf{k}) = J_0(\mathbf{k}) - J_d(\mathbf{k}), \tag{60a}$$

$$\eta(\mathbf{k}) = 1. \tag{60b}$$

Otherwise  $J_d(\mathbf{k})$  is counted twice. It should be emphasized that Eq. (57) and the choices [Eqs. (58) or (60)] guarantee that the linear optical properties, as given by  $\epsilon(\mathbf{k}, \omega)$ , obtained from the REM, agree with Hopfield's result [Eq. (56)]. The applicability of these relations to nonlinear optics is an interesting open problem.

### 6. SOLUTION OF REDUCED EQUATIONS OF MOTION FOR FOUR-WAVE MIXING: THE TRANSIENT GRATING AND ITS STEADY-STATE ANALOG

In this section we solve our REM [Eqs. (47)] for some special cases. We first note that for the two-level model presented in Section 4,  $\beta$  and  $\chi^{(2)}$  vanish. We shall therefore focus on 4WM and  $\chi^{(3)}$ . In this case Eqs. (26) assume the form

$$\chi^{(3)}(-\mathbf{k}_{s}-\omega_{s};\mathbf{k}_{1}\omega_{1},\mathbf{k}_{2}\omega_{2},\mathbf{k}_{3}\omega_{3})$$
  
=  $\gamma(\mathbf{k}_{1}\omega_{1},\mathbf{k}_{2}\omega_{2},\mathbf{k}_{3}\omega_{3})S(\mathbf{k}_{1},\omega_{1})S(\mathbf{k}_{2},\omega_{2})S(\mathbf{k}_{3},\omega_{3})S(\mathbf{k}_{s},\omega_{s}).$   
(61a)

A 4WM process involves the interaction of three incoming laser fields with wave vectors  $\mathbf{k}_1$ ,  $\mathbf{k}_2$ , and  $\mathbf{k}_3$  and frequencies  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$ , respectively, with the nonlinear medium. A coherently generated signal with wave vector  $\mathbf{k}_s$  and frequency  $\omega_s$  is then detected, where

$$\mathbf{k}_s = \pm \mathbf{k}_1 \pm \mathbf{k}_2 \pm \mathbf{k}_3, \tag{61b}$$

and

$$\omega_s = \pm \omega_1 \pm \omega_2 \pm \omega_3. \tag{61c}$$

Equations (61) imply that  $\mathbf{k}_s$  and  $\omega_s$  are given by any linear combination of the incoming wave vectors and frequencies. The various types of 4WM processes differ by the particular choices  $\mathbf{k}_s$  and  $\omega_s$  [i.e., the particular choice of signs in Eqs. (61)].<sup>6</sup> They also differ according to the temporal characteristics of the incoming fields. In one limit the incoming fields (and the signal field) are stationary. In the opposite limit the incoming fields are infinitely short pulses, resulting in an ideal time-domain 4WM. In this section we shall discuss two examples of 4WM techniques: the TG and its steady-state analog. Both examples provide a sensitive probe for transport processes<sup>9,10</sup> through the wave-vector dependence of the nonlinear response function  $R^{(3)}$  and the nonlinear susceptibility  $\chi^{(3)}$ . We shall consider a lattice model in which the molecules occupy a fraction  $f = Ca^3$  of the lattice sites, where a is the lattice spacing, and the interaction  $J(\mathbf{r})$  is equal to J for nearest neighbors and is zero otherwise.9,10

### A. Transient Grating

We shall first consider a time-domain 4WM process, the transient grating (TG), which is commonly used for the direct measurement of transport processes in disordered systems. In a TG experiment, the sample initially interacts with a pair of simultaneous laser pulses with wave vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$ . After a delay period T, the sample is probed by a third pulse with the wave vector  $\mathbf{k}_1$ , and a coherent signal with wave vector  $\mathbf{k}_s = 2\mathbf{k}_1 - \mathbf{k}_2$  is detected.<sup>7-9</sup> This TG signal, measured as a function of the delay time between excitation and probe, will decay, owing to the excited-state lifetime and to exciton motion that occurs over distances that are large compared with the grating wavelength. Therefore, by measuring the generated TG signal as a function of the decay time T, we can monitor directly the dynamics of excitations in the medium. We assume that the in-

coming fields are short enough to be described by a  $\delta$  function but are long enough to make the rotating-wave approximation valid. In this case the time-dependent incoming field is given by

$$E(\mathbf{r}, t) = [E_1 \exp(i\mathbf{k}_1\mathbf{r}) + E_1 \exp(-i\mathbf{k}_1\mathbf{r}) + E_2 \exp(i\mathbf{k}_2\mathbf{r}) + E_2 \exp(-i\mathbf{k}_2\mathbf{r})]\delta(t) + [E_1 \exp(i\mathbf{k}_1\mathbf{r}) + E_1 \exp(-i\mathbf{k}_1\mathbf{r})]\delta(t - T).$$
(62)

 $P(\mathbf{k}_s, t)$  may be found by substituting Eq. (62) into Eqs. (47) and by solving Eqs. (47) perturbatively to third order in E. We shall ignore the local-field corrections (setting  $E = E_L$ ) and invoke the rotating-wave approximation<sup>40</sup> whereby high-frequency components of the polarization are neglected. The transient signal  $I(\mathbf{k}_s, t)$  (omitting proportionality and geometric factors) for  $t \ge T$  is then given by

$$I(\mathbf{k}_{s}, t) = |P(\mathbf{k}_{s}, t)|^{2}.$$
(63)

Equation (63) is simplified considerably when the excitation motion is incoherent, i.e.,  $\hat{\Gamma} \gg J$ . In this case the transport of excitations can be described by a simple diffusion equation and we get

$$I(\mathbf{k}_{s}, T) \propto \exp[-2\gamma T - 2D(\mathbf{k}_{1} - \mathbf{k}_{2})^{2}T], \qquad (64)$$

where D is the excitation diffusion constant

$$D = \frac{(Ca^3)J^2a^2}{\hat{\Gamma}}.$$
 (65)

This result is identical to the result of Loring and Mukamel [Eq. (3.20) of Ref. 10]. A plot of log  $I(\mathbf{k}_s, T)$  versus  $(\mathbf{k}_1 - \mathbf{k}_2)^2 T$  will yield D directly in this case.<sup>7-10</sup>

## **B.** Extra Resonances in Degenerate Four-Wave Mixing: Steady-State Analog of the Transient Grating

The possibility of probing transport processes by using frequency-domain 4WM was explored by Loring and Mukamel.<sup>9,10</sup> Using Green-function techniques, they derived expressions for the frequency- and wave-vector-dependent  $\chi^{(3)}$ for the Haken–Strobl model. Extra resonances, which are the frequency-domain analog of the TG, in degenerate 4WM were then predicted. Extra resonances permit the direct probe of transport by using a steady-state 4WM experiment. We shall now repeat that calculation by using the present REM. We consider a 4WM experiment in which the disordered medium is irradiated by two stationary incoming fields,  $\mathbf{k}_1$  and  $\mathbf{k}_2$ , and a stationary signal is generated at the direction  $\mathbf{k}_s = 2\mathbf{k}_1 - \mathbf{k}_2$  with the frequency  $\omega_s = 2\omega_1 - \omega_2$ . Within the rotating-wave approximation, the signal (omitting proportionality and geometrical factors) is given by

$$I(\mathbf{k}_s, \omega_s) = |P(\mathbf{k}_s, \omega_s)|^2, \tag{66a}$$

$$P(\mathbf{k}_{s}, \omega_{s}) = E_{1}^{2} E_{2} \chi^{(3)}(-\mathbf{k}_{s} - \omega_{s}; \mathbf{k}_{1}\omega_{1}, \mathbf{k}_{1}\omega_{1}, -\mathbf{k}_{2} - \omega_{2}), \quad (66b)$$

$$\chi^{(3)}(-\mathbf{k}_s - \omega_s; \mathbf{k}_1\omega_1, \mathbf{k}_1\omega_1, -\mathbf{k}_2 - \omega_2) = \gamma(\mathbf{k}_1\omega_1, \mathbf{k}_1\omega_1, -\mathbf{k}_2 - \omega_2)S^2(\mathbf{k}_1, \omega_1)S(\mathbf{k}_2, \omega_2)S(\mathbf{k}_s, \omega_s),$$
(66c)

$$\mathbf{k}_s = 2\mathbf{k}_1 - \mathbf{k}_2,\tag{66d}$$

$$\omega_s = 2\omega_1 - \omega_2. \tag{66e}$$

 $\gamma$  can be obtained by solving Eqs. (47) to second order in  $E_1$  and to first order in  $E_2$ .

When  $\hat{\Gamma} \gg J$ , the transport of excitations is diffusive. Within the rotating-wave approximation we get

$$I(\mathbf{k}_s, \omega_s) \propto \frac{\Gamma \hat{\Gamma}}{(\omega_1 - \omega_2)^2 + [\gamma + D(\mathbf{k}_1 - \mathbf{k}_2)^2]^2}.$$
 (67)

In this case the degenerate 4WM signal has a single resonance at  $\omega_1 = \omega_2$ , and its width consists of a **k**-independent (lifetime) part  $\gamma$  and a contribution from transport processes that is proportional to  $(\mathbf{k}_1 - \mathbf{k}_2)^2$ .

These results are similar to those obtained by Loring and Mukamel<sup>10</sup> for the exactly solvable Haken-Strobl model. The agreement between our results obtained using the approximate REM [Eq. (47)] and those obtained for the exactly solvable model<sup>10</sup> supports the validity of the present REM. Relations (64) and (67) were derived for incoherent transport, where  $\hat{\Gamma} \gg J$ . When this condition does not hold, the transport becomes partially or totally coherent. The transient grating signal will then decay in a more complicated oscillatory form. In the frequency domain, the extra resonance [relation (67)] will be split into two lines, whose splitting, intensity, and width reflect the nature of the excitation motion. This behavior was analyzed in detail earlier.<sup>10</sup> In concluding this section we compare the TG and its steady-state analog. In general, these two experiments carry different information regarding the disordered system. For example, in the stationary 4WM experiment the generated coherent signal contains information about population transport as well as the transport of the polarization P. On the other hand, the time-resolved TG experiment contains only information regarding the transport of populations W. Only under the condition whereby Eqs. (64) and (67) hold do both experiments measure the transport of population and contain precisely the same information. In this case both signals are related by a single Fourier transform.<sup>9,10</sup>

### 7. DISCUSSION

In this paper we developed REM that can be used for the calculation of the frequency- and wave-vector-dependent dielectric function  $\epsilon(\mathbf{k}, \omega)$  as well as nonlinear-optical processes and nonlinear susceptibilities  $\chi^{(2)}, \chi^{(3)}$ , etc. in polarizable fluids. The present formalism applies to a broad range of condensed-phase optical media, including polarizable liquids, solutions, pure and mixed molecular crystals, polymers, and glasses. In the model presented in Section 4 [Eq. (31)] we included only the simplest line-broadening mechanism, i.e., homogeneous broadening in which the solvent motions are infinitely fast compared with  $\hbar$  divided by the linewidth (or by the magnitude of level fluctuations). Line broadening is, however, not always homogeneous. The solvent time scale can be comparable with  $\hbar$  divided by the linewidth. In that case our REM [Eqs. (47)] should be modified to include additional memory corresponding to a non-Markovian description of the line broadening.<sup>30</sup> The other extreme of inhomogeneous broadening, in which the solvent is static on the relevant time scale, is of great importance in low-temperature glasses, polymers, viscous fluids, and disordered solids. A proper treatment of inhomogeneous broadening is straightforward in principle, although it

may be quite tedious in practice. The molecules should be divided into groups, depending on their solvent environment. Each group should have its own polarization, and the total polarization is the sum of contributions from the various groups. In practice, this generalization implies that we may still use REM of the form of Eqs. (47) but with more dynamic variables corresponding to the various groups of molecules. This procedure becomes tedious for broad continuous distributions of solvent configurations, which require the introduction of many additional variables. The present REM [Eqs. (47)] apply to solutions and to mixed molecular crystals at sufficiently high temperatures such that the bath motions are fast. The present formalism incorporates explicitly and systematically effects of transport (spatial dispersion), local-field corrections, cascading, and the propagation of the electromagnetic fields. Effects of polaritons are naturally incorporated when we solve Eq. (45d) for the propagation of the electromagnetic field. The present equations generalize the Bloch-Maxwell equations,40 which do not include spatial dispersion. They provide a unified and convenient starting point for the microscopic description of molecular nonlinear-optical processes.

In Section 2 we introduced the basic model. The optical medium is assumed to consist of randomly distributed interacting molecules with the static pair distribution function g(r).<sup>55</sup> We further assumed that the intermolecular distances are sufficiently large that electron tunneling and charge-transfer processes can be ignored. The molecules can thus exchange excitations but not charges. Using molecular crystal terminology,<sup>31</sup> we consider Frenkel excitons. We then introduced the linear and nonlinear response functions  $R^{(n)}$  [Eq. (11)] and  $\hat{R}^{(n)}$  [Eq. (12)]. The three dynamic variables of interest are the Maxwell field  $E(\mathbf{r}, t)$ , the local field  $E_L(\mathbf{r}, t)$ , which actually acts on the molecules, and the polarization field  $P(\mathbf{r}, t)$ , which is the expectation value of the polarization operator  $\hat{P}(r)$  [Eq. (3)]. The polarization operator may be expressed as an infinite sum of charge multipoles,<sup>42,43</sup> and the leading term in that sum is the dipole operator. Because the material system actually interacts with  $E_L$ , we can assume that  $E_L$  is given and can define a set of material response functions  $\alpha$ ,  $\beta$ ,  $\gamma$ ... [Eq. (19)].

In Section 3 we introduced these functions, which can be calculated using a perturbative expansion of the material equations alone (i.e., without using the Maxwell equations), and related them to the actual susceptibilities  $\chi^{(2)}$ ,  $\chi^{(3)}$ , etc.  $\chi^{(2)}$  describes the simplest nonlinear-optical processes involving three-wave mixing (e.g., second-harmonic generation), whereas  $\chi^{(3)}$  describes 4WM, coherent anti-Stokes Raman spectroscopy, transient grating, etc.). Transport (spatial dispersion), local-field, and cascading corrections appear naturally when our expansion is used. The effects of transport are reflected in the explicit wave-vector dependence of the nonlinear susceptibilities and response functions. Local-field effects are controlled by the parameter  $\eta(\mathbf{k})$ , whose value is discussed in Section 5.  $\eta(\mathbf{k}) = 0$  implies no local-field corrections, and  $\eta(\mathbf{k}) = 1$  results in the Clausius-Mosotti, Lorentz-Lorenz equation and the local-field corrections, as introduced by Bedeaux and Bloembergen.<sup>47</sup> Cascading implies that lower-order nonlinear processes affect the higher nonlinear processes. We note that the cascading terms are of higher order in density C of the material system and can be ignored if the density is sufficiently low.

In Section 4 we derived the REM, which permit the microscopic calculation of the molecular response functions and susceptibilities. We adopted a two-level model for the absorbers and introduced a set of operators  $A_j(\mathbf{r})$  [Eqs. (35)], which constitute a complete set of single-body operators. These operators form the basis for our reduced description of the system in which we follow only the expectation values of these operators. Our chosen relevant variables carry much less information than the information contained in the entire many-body density matrix of the interacting disordered system. The level of description is adequate, however, for the treatment of nonlinear-optical processes. Our relevant dynamic variables are the polarization varibles  $P(\mathbf{r}, t)$  and  $V(\mathbf{r}, t)$  and the excited-state population  $W(\mathbf{r}, t)$  [Eqs. (37)].

Using projection-operator techniques, we derived the formally exact REM [Eq. (43a)]. The second term on the righthand side of Eq. (43a) is the relaxation kernel. On expanding the kernel to second order in the intermolecular interactions and to zero order in the electromagnetic field, we obtained our final REM. Because the ensemble-averaged system is translationally invariant, it is convenient to write these equations in **k** space. Our final generalized Bloch-Maxwell equations [Eqs. (47)] are for the variables  $P(\mathbf{k}, t)$ ,  $V(\mathbf{k}, t), W(\mathbf{k}, t), E(\mathbf{k}, t)$ , and  $E_L(\mathbf{k}, t)$ , and they constitute the main formal result of this paper.

The problem of nonlinear-optical processes in disordered systems with interacting absorbers received some theoretical attention. Warren and Zewail<sup>36</sup> and Root and Skinner<sup>37</sup> used the methods of moments and the cumulant expansion with respect to the intermolecular interaction to calculate the photon-echo signal in a disordered system. The density expansion method was used by Loring et al.38 to obtain photon echoes in impurity crystals with inhomogeneous broadening. Unlike the present theory, these treatments do not include the effects of transport and local-field corrections. Takagahara<sup>62</sup> derived equations of motion to study the dephasing relaxation of excitonic polaritons in perfect These equations allow for spatial dispersion crystals. through the propagation of coherences (P and V) but do not contain the transport of population (W). In addition, these equations do not include the local-field corrections.

The first application of our REM was made in Section 5. where we calculated the linear susceptibility  $\chi^{(1)}(-\mathbf{k} - \omega)$ ;  $\mathbf{k}\omega$ ) and the dielectric function  $\epsilon(\mathbf{k},\omega)$ . The linear susceptibility is related directly to the absorption spectrum of the medium and to the propagation of weak electromagnetic fields in the medium (reflection, refraction, and polariton effects). A special case of the present model is that of a perfect crystal of polarizable molecules. We assumed an arbitrary intermolecular interaction  $J_0(\mathbf{r})$  (including both short- and long-range dipole-dipole interactions). We further introduced a coupling with a thermal bath, which causes dephasing.  $\epsilon(\mathbf{k}, \omega)$  for this model may be calculated by using the method of Hopfield.<sup>56</sup> This calculation, which does not rely on our REM [Eqs. (47)] and does not require the introduction of a local field, is carried out in Appendix A. That calculation [Eq. (56)] is then used to analyze our REM and to discuss the proper choice of the local-field corrections. Strictly speaking, the local-field corrections arise from the intermolecular interactions. Our equations contain explicitly the intermolecular interactions  $J(\mathbf{r})$  as well as the local-field correction, which is controlled by the (yet unspecified) parameter  $\eta(\mathbf{k})$ . The problem is how to choose  $\eta(\mathbf{k})$  and  $J(\mathbf{k})$  in a consistent manner so that intermolecular interactions are properly incorporated and to avoid double counting of intermolecular interactions. Possible choices of  $J(\mathbf{k})$  and  $\eta(\mathbf{k})$  were discussed [Eqs. (57), (58), and (60)]. None of these procedures is exact for nonlinear optics. The conventional procedures<sup>4,47</sup> for the incorporation of local-field corrections are, therefore, approximate in nature.

In Section 6 we used our REM to calculate explicitly nonlinear-optical processes that are sensitive to transport processes. For our two-level model of Section 5,  $\beta$  and  $\chi^{(2)}$ vanish. Therefore the simplest relevant nonlinear-optical process is 4WM, as given by  $\chi^{(3)}$ . We focused on two 4WM techniques: the TG and its steady-state analog. Both techniques use only two incoming fields with wave vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$  and probe the signal at  $\mathbf{k}_s = 2\mathbf{k}_1 - \mathbf{k}_2$ . In the TG technique the incident fields and the signal are pulsed. The variation of the signal with the time delay T between pulses and its variation with  $\mathbf{k}_1 - \mathbf{k}_2$  provide a direct probe for transport. It was predicted<sup>9,10</sup> by using the Haken-Strobl model that a frequency-domain degenerate 4WM should contain extra resonances, which are transport induced and carry the same information as the TG. Using our REM, we showed that the same conclusion holds for a disordered fluid as well.

## APPENDIX A: THE DIELECTRIC FUNCTION FOR A PERFECT CRYSTAL WITH INTERACTING ABSORBERS

In this appendix we calculate the frequency- and wave-vector-dependent dielectric function  $\epsilon(\mathbf{k}, \omega)$  for a simplified model. The material Hamiltonian is taken to be given by Eqs. (27) and (28), except that the molecules are now located on a perfect lattice, and there is no disorder. In addition, we treat the radiation field quantum mechanically. We write the entire radiation-matter Hamiltonian and diagonalize this Hamiltonian. In this appendix we basically follow Hopfield's derivation<sup>56</sup> but generalize the Hamiltonian to include an arbitrary intermolecular interaction instead of the dipole-dipole interaction used by Hopfield. Consider the Hamiltonian for the system and the radiation field

$$H = H_{\rm p} + H_{\rm e} + H_{\rm pe} + H_{\rm ee}.\tag{A1}$$

Here  $H_p$  is the photon Hamiltonian,  $H_e$  is the exciton Hamiltonian,  $H_{pe}$  is the photon–exciton interaction, and  $H_{ee}$  represents the exciton–exciton interaction. We further have

$$H_{\rm p} = \hbar \sum_{\bf k} \omega_{\bf k} b_{\bf k}^{\dagger} b_{\bf k}, \tag{A2}$$

$$H_{\rm e} = \hbar\Omega \sum_{m} a_m^{\dagger} a_m, \tag{A3}$$

$$H_{\rm pe} = -\frac{e}{Mc} \sum_{m} \mathbf{A}(\mathbf{r}_m) \cdot p(\mathbf{r}_m) + \frac{e^2}{2Mc^2} \sum_{m} \mathbf{A}(r_m) \cdot \mathbf{A}(\mathbf{r}_m),$$
(A4)

$$H_{ee} = \frac{\hbar}{2} \sum_{n,m} J_0(\mathbf{r}_n - \mathbf{r}_m)(a_n^{\dagger} + a_n)(a_m^{\dagger} + a_m), \qquad (A5)$$

with  $A(\mathbf{r}_m)$  being the vector potential,

1

$$\mathbf{A}(\mathbf{r}_m) = \sum_{\mathbf{k},\epsilon} \left(\frac{2\pi\hbar c^2}{V\omega_{\mathbf{k}}}\right)^{1/2} \epsilon [b_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}_m) + b_{\mathbf{k}}^{\dagger} \exp(-i\mathbf{k} \cdot \mathbf{r}_m)], \qquad (A6)$$

$$p(\mathbf{r}_m) = -\frac{i\mu M\Omega}{e} (a_m - a_m^{\dagger}), \qquad (A7a)$$

where  $\epsilon$  is the polarization of the photon and  $\mu$  is the dipole moment defined by

$$\boldsymbol{\mu} = e\langle 0 | \mathbf{r} | n \rangle. \tag{A7b}$$

In the derivation of Eq. (A7a) we used the relation

$$\langle n'|p|n\rangle = -iM\omega_{nn'}\langle n'|\mathbf{r}|n\rangle.$$
 (A7c)

In Eq. (A6) V is the volume of the medium, M is the mass of electron,  $\mu$  is the electronic dipole moment operator for a single molecule,  $a_m^{\dagger}(a_m)$  is the creation (annihilation) operator for an exciton on the m molecule, and  $b_k^{\dagger}(b_k)$  is the creation (annihilation) operator for the kth mode of the radiation field. By introducing the Fourier transform

$$a_{\mathbf{k}}^{\dagger} = \frac{1}{\sqrt{N}} \sum_{m} \exp(i\mathbf{k} \cdot \mathbf{r}_{m}) a_{m}^{\dagger},$$
 (A8)

$$a_{\mathbf{k}} = \frac{1}{\sqrt{N}} \sum_{m} \exp(-i\mathbf{k} \cdot \mathbf{r}_{m}) a_{m}, \tag{A9}$$

we may recast  $H_{pe}$  and  $H_{ee}$  in the form

$$H_{\rm pe} = \sum_{\mathbf{k}} \left[ i \left( \frac{N2\hbar\pi c}{V|\mathbf{k}|} \right)^{1/2} \frac{\Omega}{c} \mu (a_{\mathbf{k}} b_{\mathbf{k}}^{\dagger} - a_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + a_{\mathbf{k}} b_{-\mathbf{k}} - a_{\mathbf{k}}^{\dagger} b_{-\mathbf{k}}^{\dagger}) + \frac{2\pi N}{c|\mathbf{k}|V} \Omega \mu^2 (b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + b_{\mathbf{k}} b_{\mathbf{k}}^{\dagger} + b_{\mathbf{k}}^{\dagger} b_{-\mathbf{k}}^{\dagger} + b_{\mathbf{k}} b_{-\mathbf{k}}) \right], \quad (A10)$$

$$H_{\rm ee} = N \frac{\hbar}{2} \sum_{\mathbf{k}} J_0(\mathbf{k}) (a_{\mathbf{k}}^{\dagger} a_{-\mathbf{k}}^{\dagger} + a_{\mathbf{k}} a_{-\mathbf{k}} + a_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} + a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}}), \tag{A11}$$

where  $J_0(\mathbf{k})$  is the discrete Fourier transform of  $J(\mathbf{r})$ , i.e.,

$$J_0(\mathbf{k}) = \frac{1}{N} \sum_m \exp(i\mathbf{k} \cdot \mathbf{r}_m) J_0(\mathbf{r}_m). \tag{A12}$$

The normal modes of the Hamiltonian H will now be expressed in terms of a new set of creation and annihilation operators. Because the Hamiltonian H is invariant under translation, it is sufficient to consider a single wave vector  $\mathbf{k}$ . We therefore look for normal modes of the form

$$A_{\mathbf{k}} = wb_{\mathbf{k}} + xa_{\mathbf{k}} + yb_{-\mathbf{k}}^{\dagger} + za_{-\mathbf{k}}^{\dagger},$$
 (A13)

so that

$$A_{\mathbf{k}}(t) = A_{\mathbf{k}}(0)\exp(-i\omega t). \tag{A14}$$

On substitution of Eqs. (A13) and (A14) in the Heisenberg equations of motion

$$\dot{A}_{\mathbf{k}} = (i/\hbar)[H, A_{\mathbf{k}}], \tag{A15}$$

we obtain the following matrix equation:

1

$$\begin{bmatrix} c|\mathbf{k}| + 2D & -iR & -2D & -iR \\ iR & \Omega + \alpha - i\Gamma & -iR & -\alpha \\ 2D & -iR & -c|\mathbf{k}| - 2D & -iR \\ -iR & \alpha & iR & -\Omega - \alpha - i\Gamma \end{bmatrix} \begin{bmatrix} w \\ x \\ y \\ z \end{bmatrix} = \omega \begin{bmatrix} w \\ x \\ y \\ z \end{bmatrix}, \quad (A16)$$

where

$$R = \left[\frac{2\pi N}{\hbar V |\mathbf{k}| c}\right]^{1/2} \mu \Omega, \qquad (A17)$$

$$D = \frac{2\pi N \Omega \mu^2}{\hbar c |\mathbf{k}| V},\tag{A18}$$

$$\alpha = NJ_0(\mathbf{k}). \tag{A19}$$

In Eq. (A16) we have introduced a phenomenological dephasing width  $\Gamma$  [Eq. (46d)]. We have further used the approximation  $[a_k, a_k^{\dagger}] = 0$ , which is valid when the total number of excitations is much less than the total number of the molecules in the medium,<sup>31</sup> and we have further used the *f*-sum rule. Equation (A16) can be recast in the form

$$\epsilon(\mathbf{k},\omega) \equiv \frac{c^2 k^2}{\omega^2} = 1 + \frac{8\pi C \overline{\mu^2} \Omega}{(-i\omega + \Gamma)^2 + \Omega^2 + 2C J_0(\mathbf{k}) \Omega} \times [1 - (\Gamma/\omega)^2 + 2i(\Gamma/\omega)], \quad (A20)$$

where C = N/V is the density of the molecules and  $\overline{\mu^2} = \mu^2/\hbar$ . Since usually  $\Gamma/\omega \ll 1$ , we can neglect the correction terms inside the square bracket in Eq. (A20), setting

$$1 - (\Gamma/\omega)^2 + 2i(\Gamma/\mu)^2 \approx 1.$$
 (A20a)

Equation (A20) together with Eq. (A20a) is used in Section 5 [Eq. (56)].

Suppose that  $J_0(\mathbf{k})$  consists of the dipole-dipole interaction

$$\hbar J_0(\mathbf{r}_n - \mathbf{r}_m) = \frac{\mu^2}{|\mathbf{r}_n - \mathbf{r}_m|^3} - \frac{3[\mu \cdot (\mathbf{r}_n - \mathbf{r}_m)]^2}{|\mathbf{r}_n - \mathbf{r}_m|^5}$$
(A21)

and in k space<sup>56,57</sup>

$$\hbar J_0(\mathbf{k}) = \frac{4\pi}{3} \left[ \frac{3(\boldsymbol{\mu} \cdot \mathbf{k})^2}{k^2} - \mu^2 \right] + J_d'(\mathbf{k}), \tag{A22}$$

where  $J_{d'}(\mathbf{k})$  is the part of the dipole–dipole interaction with  $\mathbf{k} \neq 0$ . For transverse modes  $\mu \cdot \mathbf{k} = 0$  since the polarization of the field is always perpendicular to its wave vector. We then have<sup>56,57</sup>

$$J_0(\mathbf{k}=0) = -4\pi\mu^2/3.$$
 (A23)

Substituting this equation into Eq. (A20) together with Eq. (A20a), we have

$$\epsilon(\mathbf{k}=0,\omega) = 1 + \frac{8\pi C \overline{\mu^2} \Omega}{(-i\omega + \Gamma)^2 + \Omega^2 - 8\pi C \overline{\mu^2} \Omega/3} \cdot \quad (A24)$$

Equation (A24) can be recast in the Clausius-Mosotti form

$$\frac{\epsilon(0,\,\omega)-1}{\epsilon(0,\,\omega)+2} = \frac{4\pi}{3} C\alpha_0(\omega),\tag{A25}$$

where

$$\alpha_0(\omega) = 2\overline{\mu^2}\Omega[(-i\omega + \Gamma)^2 + \Omega^2]^{-1}$$
 (A26)

is the polarizability of a single absorber. More generally, we can define

$$\eta(\mathbf{k}) = -3J(\mathbf{k})(4\pi\mu^2). \tag{A27}$$

Equation (A20) then assumes the form

$$\epsilon(\mathbf{k},\omega) = 1 + \frac{8\pi C\mu^2 \Omega}{(-i\omega + \Gamma)^2 + \Omega^2 - 8\pi \overline{\mu^2} C\Omega \eta(\mathbf{k})/3}, \quad (A28)$$

which can be rearranged in the form

$$\frac{\epsilon(\mathbf{k},\omega)-1}{3+\eta(\mathbf{k})[\epsilon(\mathbf{k},\omega)-1]} = \frac{4\pi}{3} C\alpha_0(\omega).$$
(A29)

For dipole-dipole interactions at  $\mathbf{k} = 0$ ,  $\eta(\mathbf{k}) = 1$ , and Eq. (A29) reduces to Eq. (A25).

#### ACKNOWLEDGMENTS

We wish to thank E. Wolf and J. Knoester for most stimulating discussions. The support of the National Science Foundation, the U.S. Office of Naval Research, the U.S. Army Research Office, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Shaul Mukamel is a Camille and Henry Dreyfus Teacher-Scholar.

# REFERENCES

- 1. N. Bloembergen, Nonlinear Optics (Benjamin, New York, 1965).
- 2. P. N. Butcher, Nonlinear Optical Phenomena (Ohio U. Press, Athens, Ohio, 1965).
- C. Flytzanis, in *Quantum Electronics*, H. Rabin and C. L. Tang, eds. (Academic, New York, 1975), Vol. I, p. 1.
- 4. Y. R. Shen, The Principles of Nonlinear Optics (Wiley, New York, 1984).
- 5. S. A. J. Druet and J. P. E. Taran, Prog. Quantum Electron. 7, 1 (1981).
- 6. S. Mukamel and R. F. Loring, J. Opt. Soc. Am. B 3, 595 (1986).
- M. D. Fayer, Ann. Rev. Phys Chem. 33, 63 (1982); D. R. Lutz, K.
   A. Nelson, C. R. Gochanour, and M. D. Fayer, Chem. Phys. 58, 325 (1981); K. A. Nelson, R. Casalegno, R. J. D. Miller, and M.
   D. Fayer, J. Chem. Phys. 77, 1144 (1982); T. S. Rose, R. Righini, and M. D. Fayer, Chem. Phys. Lett. 106, 13 (1984).
- J. K. Tyminski, R. C. Powell, and W. K. Zwicker, Phys. Rev. B 29, 6074 (1984).
- 9. R. F. Loring and S. Mukamel, J. Chem. Phys. 83, 4353 (1985).
- 10. R. F. Loring and S. Mukamel, J. Chem. Phys. 84, 1228 (1986).
- 11. N. Bloembergen, H. Lotem, and R. T. Lynch, Indian J. Pure

Appl. Phys. 16, 151 (1978); A. R. Bogdan, M. W. Downer, and N. Bloembergen, Phys. Rev. A 24, 623 (1981); L. J. Rothberg and N. Bloembergen, Phys. Rev. A 30, 820 (1984).

- J. R. Andrews and R. M. Hochstrasser, Chem. Phys. Lett. 82, 381 (1981); J. R. Andrews, R. M. Hochstrasser, and H. P. Trommsdorff, Chem. Phys. 62, 87 (1981).
- 13. N. Bloembergen, Am. J. Phys. 35, 989 (1967).
- A. Laubereau and W. Kaiser, Rev. Mod. Phys. 50, 607 (1978); W.
   Zinth, H.-J. Polland, A. Laubereau, and W. Kaiser, Appl. Phys.
   B 26, 77 (1981); S. M. George, A. L. Harris, M. Berg, and C. B.
   Harris, J. Chem. Phys. 80, 83 (1984).
- 15. R. F. Loring and S. Mukamel, J. Chem. Phys. 83, 2116 (1985).
- I. I. Abram, R. M. Hochstrasser, J. E. Kohl, M. G. Semack, and D. White, J. Chem. Phys. 71, 153 (1979); F. Ho, W. S. Tsay, J. Trout, S. Velski, and R. M. Hochstrasser, Chem. Phys. Lett. 97, 141 (1983); S. Velsko, J. Trout, and R. M. Hochstrasser, J. Chem. Phys. 79, 2114 (1983).
- E. L. Chronister and D. D. Dlott, J. Chem. Phys. 79, 5286 (1984);
   C. L. Schosser and D. D. Dlott, J. Chem. Phys. 80, 1394 (1984).
- B. H. Hesp and D. A. Wiersma, Chem. Phys. Lett. **75**, 423 (1980);
   D. P. Weitekamp, K. Duppen, and D. A. Wiersma, Phys. Rev. A **27**, 3089 (1983).
- A. M. Weiner, S. DeSilvestri, and E. P. Ippen, J. Opt. Soc. Am. B 2, 654 (1985).
- G. J. Small, in Modern Problems in Condensed Matter Sciences, V. M. Agranovich and A. A. Maradudin, eds. (North-Holland, Amsterdam, 1983), Vol. 4.
- R. W. Olson, H. W. H. Lee, F. G. Patterson, M. D. Fayer, R. M. Shelby, D. P. Burum, and R. M. Macfarlane, J. Chem. Phys. 77, 2283 (1982).
- I. D. Abella, N. A. Kurnit, and S. R. Hartmann, Phys. Rev. 141, 391 (1966); S. R. Hartmann, IEEE J. Quantum Electron. QE-4, 802 (1968); T. W. Mossberg, R. Kachru, A. M. Flusberg, and S. R. Hartmann, Phys. Rev. A 20, 1976 (1979).
- R. W. Olson, F. G. Patterson, H. W. H. Lee, and M. D. Fayer, Chem. Phys. Lett. 78, 403 (1981).
- W. H. Hesselink and D. A. Wiersma, in Modern Problems in Condensed Matter Sciences, V. M. Agranovich and A. A. Maradudin, eds. (North-Holland, Amsterdam, 1983), Vol. 4, p. 249.
- 25. R. F. Loring and S. Mukamel, Chem. Phys. Lett. 114, 425 (1985).
- G. J. Small, in Spectroscopy and Excitation Dynamics of Condensed Molecular Systems, V. M. Agranovich and R. M. Hochstrasser, eds. (North-Holland, New York, 1983), p. 515; T. C. Caau, C. K. Johnson, and G. J. Small, J. Phys. Chem. 89, 2984 (1985).
- M. D. Levenson, Introduction to Nonlinear Laser Spectroscopy (Academic, New York, 1982); J. J. Song, J. H. Lee, and M. D. Levenson, Phys. Rev. A 17, 1439 (1978).
- 28. R. Trebino and A. E. Siegman, J. Chem. Phys. 79, 3621 (1983).
- 29. T. Yajima and H. Souma, Phys. Rev. A 17, 309 (1978); T. Yajima, H. Souma, and Y. Ishida, Phys. Rev. A 17, 324 (1978).
- S. Mukamel, Phys. Rep. 93, 1 (1982); Phys. Rev. A 28, 3480 (1983); V. Mizrahi, Y. Prior, and S. Mukamel, Opt. Lett. 8, 145 (1983); R. Boyd and S. Mukamel, Phys. Rev. A 29, 1973 (1984).
- A. S. Davydov, Theory of Molecular Excitons (Plenum, New York, 1971).
- 32. V. M. Agranovich and V. L. Ginzburg, Crystal Optics with

Spatial Dispersion and Excitons (Springer-Verlag, Berlin, 1984).

- 33. J. Koo, L. R. Walker, and S. Geschwind, Phys. Rev. Lett. 35, 1669 (1975).
- 34. S. Chu, H. M. Gibbs, and A. Passner, Phys. Rev. B 24, 7162 (1981).
- P. E. Jessop and A. Szabo, Phys. Rev. Lett. 45, 1712 (1980); Phys. Rev. B 26, 420 (1982).
- 36. W. S. Warren and A. H. Zewail, J. Chem. Phys. 78, 2279 (1983).
- 37. L. Root and J. L. Skinner, J. Chem. Phys. 81, 5310 (1984).
- R. F. Loring, H. C. Andersen, and M. D. Fayer, J. Chem. Phys. 81, 5395 (1984).
- For a review, see B. J. Berne, in *Statistical Mechanics*, B. J. Berne, ed. (Plenum, New York, 1977), Part B, Chap. V.
- M. Sargent, M. O. Scully, and W. E. Lamb, Laser Physics (Addison-Wesley, London, 1974).
- 41. M. Born and E. Wolf, *Principles of Optics*, 4th ed. (Pergamon, Oxford, 1970), Sec. 2.4.
- 42. P. Mazur, Adv. Chem. Phys. 1, 309 (1958).
- S. R. De Groot, The Maxwell Equations (North-Holland, Amsterdam, 1969).
- J. Van Kranendonk and J. E. Sipe, in *Progress in Optics*, E. Wolf, ed. (North-Holland, Amsterdam, 1977), Vol. 15, p. 245.
- 45. H. A. Lorentz, *The Theory of Electrons* (Dover, New York, 1952).
- 46. M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Oxford, London, 1954).
- 47. D. Bedeaux and N. Bloembergen, Physica 69, 67 (1973).
- G. R. Meredith, J. Chem. Phys. 77, 5863 (1982); Phys. Rev. B 24, 5522 (1981).
- C. J. F. Bottcher, Theory of Electric Polarization (Elsevier, Amsterdam, 1973), Vol. I; C. J. F. Bottcher and P. Bordewijk, Theory of Electric Polarization (Elsevier, Amsterdam, 1978), Vol. II.
- 50. D. Pines and P. Nozieres, The Theory of Quantum Liquids (Benjamin, New York, 1966).
- D. E. Sullivan and J. M. Deutch, J. Chem. Phys. 64, 3870 (1976);
   S. A. Adelman and J. M. Deutch, Adv. Chem. Phys. 31, 103 (1975).
- 52. R. L. Fulton, Mol. Phys. 29, 405 (1975).
- J. S. Hoye and G. Stell, J. Chem. Phys. 61, 562 (1974); 75, 5133 (1981).
- 54. M. J. Thompson, K. S. Schweizer, and D. Chandler, J. Chem. Phys. 76, 1128 (1982).
- 55. J. P. Hansen and I. R. MacDonald, *Theory of Simple Liquids* (Academic, New York, 1976).
- 56. J. J. Hopfield, Phys. Rev. 112, 1555 (1958); 182, 945 (1969).
- 57. M. H. Cohen and F. Keefer, Phys. Rev. 99, 1128 (1955).
- 58. R. F. Loring and S. Mukamel, J. Chem. Phys. 87, 1272 (1987).
- G. R. Fleming, Chemical Applications of Ultrafast Spectroscopy (Oxford U. Press, 1986).
- 60. D. J. Williams, Nonlinear Optical Properties of Organic and Polymeric Materials, ACS Symposium Series 233 (American Chemical Society, Washington, D.C., 1983).
- Y. Masumoto, S. Shionoya, and T. Takagahara, Phys. Rev. Lett. 51, 923 (1983).
- 62. T. Takagahara, Phys. Rev. B 31, 8171 (1983).