Pair correlations, cascading, and local-field effects in nonlinear optical susceptibilities

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A formalism is developed for evaluating the effects of pair correlations on cascading of the nonlinear susceptibilities of fluid dielectrics. The corresponding correlative and nonlinear alterations of the usual local-field corrections are determined. These corrections to the nonlinear susceptibilities when the polarization density is expanded in terms of the effective linear field are found to be significantly different from results previously reported in the literature. The consequences of the considerable field dependence of the susceptibility expansions on the local-field corrections and the cascading are pointed out, and a detailed comparison is made to previous work. A simple model (β media), in which only the second-order molecular polarizabilities are nonzero, is introduced in order to isolate the roles of the pair correlations and the intermediate electromagnetic propagators on the parts of the macroscopic third-order susceptibilities that result solely from cascading. In β media the exact macroscopic third-order susceptibilities are expressed in terms of so-called irreducible cascading coefficients, which are multidimensional multiple integrals involving known quantities. This model is extended to include intrinsic linear and third-order polarizabilities and the effects of pair correlations in the local-field-correction factors.

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I. INTRODUCTION

The effects of pair correlations on the linear and nonlinear dielectric properties of fluids have been investigated extensively from a number of points of view [1–4]. Some indications of their influence on nonlinear optical susceptibilities have also been observed [5]. For example, Levine and Bethea [6] found that pair correlations can be significant in associating liquid mixtures and it has also been shown that they lead to a twofold error in the measured second-order susceptibility in liquid nitrobenzene [7–9].

Pair correlations can affect any nonlocal phenomenon, particularly cascading, which is the generation of higher-order nonlinear dielectric effects by means of lower-order ones. For example, in noncentrosymmetric media, with nontrivial $\chi^{(2)}$, contributions to $\chi^{(3)}$ arising from cascading have been observed [10–17]. Because of nonlocality there is some ambiguity in isolating "intrinsic" higher-order effects from those arising from cascading [15–17]. Also, since it represents one way in which the collective response of the medium differs from the simple additivity of the isolated responses of its constituents, cascading comprises part of the problem of local-field corrections [13,18].

We should contrast our work with the approach advocated by Meredith [15–17], where the effects of cascading from points throughout the medium can sometimes be represented in terms of a cascading operator that acts locally upon the fields. This approach was formalized by Meredith and co-workers [19–22] in a generalization of the traditional [23–26] local-field argument correct through third order, but it is not specific enough to allow the identification of the effects of pair correlations.

It has been shown that dipolar molecules exhibit enhanced third-order optical nonlinearities [27,28], and dense incorporation of such molecules in polymers and polymer liquid crystals may lead to nonlinear-optical materials of practical interest. It is of central importance, then, to obtain estimates of the effects of pair correlations on cascading in dense dipolar materials. Although pair correlations and cascading have been discussed previously, see, e.g., [29], no previous treatments, to the authors' knowledge, have brought these concepts together as required for this promising class of materials. Since no previous treatment is entirely suitable for practical calculations of this kind, we undertake this problem here. This paper develops a formalism for investigating pair-correlation contributions to cascading in dipolar fluids.

We establish how cascading is manifested in three different ways of organizing the macroscopic susceptibility expansion, how it depends on the correlations for various modelings of the microscopic properties of the fluid, and how it is tied in with a proper treatment of the local-field problem for nonlinear media. The level of interest in these questions and our discovery of several important corrections to previous work has led us to present the formalism we require for model calculations and analysis of experiments. The theoretical and experimental applications of this formalism are planned to be reported separately.

II. ALTERNATIVE MACROSCOPIC SUSCEPTIBILITIES

The signal generated by an externally applied field $\mathbf{E}_{ex}$ in a nonlinear medium is often studied in terms of a background linear field $\mathbf{E}_L$ rather than either $\mathbf{E}_{ex}$ or the full macroscopic electric field $\mathbf{E}$. It is known that there are significant differences among these three fields in the handling of the constitutive-relation, wave-propagation, statistical averaging, and local-field problems [12]. In this section we obtain nontrivial corrections to previous results that are crucial for the calculation of local-field cascading.

We consider the field $\mathbf{E}$ in a nonmagnetic dipolar medium in thermal equilibrium that is related to the polarization density $\mathbf{P}$ by

$$\mathbf{E}=\mathbf{E}_{\rm ex}-\mathbf{F}\cdot(\mathbf{P}) , \tag{2.1}$$

where $\mathbf{E}_{\rm ex}$ satisfies Maxwell's equations with $\mathbf{P}=0$. In $x\equiv(\mathbf{x},t)$ space the components of this equation are

$$E^i(\mathbf{x},t)=E^i_{\rm ex}(\mathbf{x},t) -\sum_j \int d^3x'dt'F^{ij}(\mathbf{x}-\mathbf{x}';t-t')P^j(\mathbf{x}',t') , \tag{2.2}$$

where $i,j=1,2,3$. See Ref. [30] regarding some of our notational conventions. Although its precise structure is irrelevant for the analysis in this section, the nonlocal second-rank tensor $\mathbf{F}(\mathbf{x};t)$ is the kernel of the differential operator

$$(4\pi/c^2)\left\{\nabla\nabla-\left[\nabla^2-\left[\frac{1}{c^2}\right]\frac{\partial^2}{\partial t^2}\right]\right\}^{-1}\frac{\partial^2}{\partial t^2} . \tag{2.3}$$

The inverse in (2.3) is defined by the outgoing-wave condition along with a consistent treatment of the singularity at the origin [31,32]. In $k\equiv(\mathbf{k},\omega)$ space Eq. (2.1) becomes

$$\mathbf{E}(\mathbf{k},\omega)=\mathbf{E}_{\rm ex}(\mathbf{k},\omega)-\mathbf{F}(\mathbf{k},\omega)\cdot(\mathbf{P}(\mathbf{k},\omega)) , \tag{2.4}$$

where the outgoing-wave ($+i0$) propagator is

$$\mathbf{F}(\mathbf{k},\omega)=4\pi[k^2-(\omega/c+i0)^2]^{-1}[\mathbf{kk}-\mathbf{U}(\omega^2/c^2)] , \tag{2.5}$$

with the tensor notations $\mathbf{kk}=(k_ik_j)$ and $\mathbf{U}=(\delta_{ij})$.

We suppose that $\mathbf{P}$ can be expanded in powers of either $\mathbf{E}_{\rm ex}$ or $\mathbf{E}$:

$$\mathbf{P}=\boldsymbol{\gamma}^{(1)}\cdot(\mathbf{E}_{\rm ex})+\boldsymbol{\gamma}^{(2)}\cdot(\mathbf{E}_{\rm ex})^{\otimes 2}+\boldsymbol{\gamma}^{(3)}\cdot(\mathbf{E}_{\rm ex})^{\otimes 3}+\cdots , \tag{2.6}$$

$$\mathbf{P}=\boldsymbol{\chi}^{(1)}\cdot(\mathbf{E})+\boldsymbol{\chi}^{(2)}\cdot(\mathbf{E})^{\otimes 2}+\boldsymbol{\chi}^{(3)}\cdot(\mathbf{E})^{\otimes 3}+\cdots , \tag{2.7}$$

where $(\mathbf{V})^{\otimes n}$ denotes the nth-order direct product of the vector $\mathbf{V}$. Using a truncated form of the expansion (2.6) in Eq. (2.1) one obtains an explicit solution of the wave-propagation problem in the nonlinear medium. A similar truncation of (2.7) when inserted into Eq. (2.1) yields a nonlinear integral equation for $\mathbf{E}$ that can be solved approximately by systematically replacing $\mathbf{E}$ in $\mathbf{P}$ by a known field, such as one finds with the expansion (2.6) when $\mathbf{E}_{\rm ex}$ is regarded as the known field. If the linear field

$$\mathbf{E}_L\equiv\mathbf{E}_{\rm ex}-\mathbf{F}\cdot(\boldsymbol{\chi}^{(1)}\cdot(\mathbf{E}_L)) \tag{2.8}$$

is taken as the known field, only the nonlinear effects are treated perturbatively and one has the constitutive relation

$$\mathbf{P}=\boldsymbol{\xi}^{(1)}\cdot(\mathbf{E}_L)+\boldsymbol{\xi}^{(2)}\cdot(\mathbf{E}_L)^{\otimes 2}+\boldsymbol{\xi}^{(3)}\cdot(\mathbf{E}_L)^{\otimes 3}+\cdots . \tag{2.9}$$

It is convenient to obtain a nested set of dependencies wherein the $\xi^{(n)}$'s are expressed in terms of the $\chi^{(n)}$'s, which, in turn, are expressed in terms of the $\gamma^{(n)}$'s. These relationships are used for identifying cascading for statistical averaging and for analyzing the local-field problem [12,14,33,34]. They are obtained by a method that we illustrate next by expressing the $\chi^{(n)}$'s in terms of the $\gamma^{(n)}$'s for $n\le 3$.

If we truncate the expansion (2.6) at third order and then replace each factor of $(\mathbf{E}_{\rm ex})$ by $[\mathbf{E}+\mathbf{F}\cdot(\mathbf{P})]$, we obtain a nonlinear integral equation for $\mathbf{P}$ whose linear kernel we invert to obtain

$$\mathbf{P}=\boldsymbol{\Gamma}\cdot(\boldsymbol{\gamma}^{(1)}\cdot(\mathbf{E})+\boldsymbol{\gamma}^{(2)}\cdot(\mathbf{E}+\mathbf{F}\cdot(\mathbf{P}))^{\otimes 2} +\boldsymbol{\gamma}^{(3)}\cdot(\mathbf{E}+\mathbf{F}\cdot(\mathbf{P}))^{\otimes 3}) , \tag{2.10}$$

where

$$\boldsymbol{\Gamma}=(\mathbf{U}-\boldsymbol{\gamma}^{(1)}\cdot\mathbf{F})^{-1} . \tag{2.11}$$

The iterative solution of (2.10) yields an infinite power series in $\mathbf{E}$ whose coefficients are the exact $\chi^{(n)}$'s for $n\le 3$, but for $n>3$ correspond to the approximation $\gamma^{(n)}=0$ for $n>3$.

On comparing Eqs. (2.7) and (2.10) we see that

$$\boldsymbol{\chi}^{(1)}=\boldsymbol{\Gamma}\cdot\boldsymbol{\gamma}^{(1)}=\boldsymbol{\gamma}^{(1)}\cdot\boldsymbol{\Gamma}^t , \tag{2.12}$$

where

$$\boldsymbol{\Gamma}^t\equiv(\mathbf{U}-\mathbf{F}\cdot\boldsymbol{\gamma}^{(1)})^{-1} , \tag{2.13}$$

so that

$$\boldsymbol{\Gamma}=(\mathbf{U}+\boldsymbol{\chi}^{(1)}\cdot\mathbf{F}) , \tag{2.14}$$

$$\boldsymbol{\Gamma}^t=(\mathbf{U}+\mathbf{F}\cdot\boldsymbol{\chi}^{(1)}) . \tag{2.15}$$

Upon further iteration of (2.10) we find that

$$\boldsymbol{\chi}^{(2)}\cdot=\boldsymbol{\Gamma}\cdot(\boldsymbol{\gamma}^{(2)}\cdot(\boldsymbol{\Gamma}^t\cdot)^{\otimes 2}) , \tag{2.16}$$

where the free dots define the tensor product contractions, viz.,

$$\boldsymbol{\chi}^{(2)}\cdot(\mathbf{E})^{\otimes 2}=\boldsymbol{\Gamma}\cdot(\boldsymbol{\gamma}^{(2)}\cdot(\boldsymbol{\Gamma}^t\cdot\mathbf{E})^{\otimes 2}) . \tag{2.17}$$

The expression one obtains for $\chi^{(3)}$ in terms of the $\gamma^{(n)}$'s, with $n\le 3$, divides into two parts:

$$\boldsymbol{\chi}^{(3)}=\boldsymbol{\chi}^{(3)}_{\rm int}+\boldsymbol{\chi}^{(3)}_{\rm cas} , \tag{2.18}$$

$$\boldsymbol{\chi}^{(3)}_{\rm int}\cdot\equiv\boldsymbol{\Gamma}\cdot(\boldsymbol{\gamma}^{(3)}\cdot(\boldsymbol{\Gamma}^t\cdot)^{\otimes 3}) , \tag{2.19}$$

$$\boldsymbol{\chi}^{(3)}_{\rm cas}\equiv\sum_m \boldsymbol{\chi}^{(2)}\cdot\{\mathbf{F}_\epsilon\cdot\boldsymbol{\chi}^{(2)}\}_m , \tag{2.20}$$

that we call the *intrinsic* and the *cascading* parts of $\chi^{(3)}$, respectively [35]. The rank-three tensors $\boldsymbol{\chi}^{(2)}\cdot\{\mathbf{F}_\epsilon\cdot\boldsymbol{\chi}^{(2)}\}_m$, with $m=1,2$ are defined by

$$\boldsymbol{\chi}^{(2)}\cdot\{\mathbf{F}_\epsilon\cdot\boldsymbol{\chi}^{(2)}\}_1\cdot(\mathbf{E})^{\otimes 3}\equiv\boldsymbol{\chi}^{(2)}\cdot(\mathbf{F}_\epsilon\cdot(\boldsymbol{\chi}^{(2)}\cdot(\mathbf{E})^{\otimes 2}))(\mathbf{E}) , \tag{2.21}$$

$$\boldsymbol{\chi}^{(2)}\cdot\{\mathbf{F}_\epsilon\cdot\boldsymbol{\chi}^{(2)}\}_2\cdot(\mathbf{E})^{\otimes 3}\equiv\boldsymbol{\chi}^{(2)}\cdot(\mathbf{E})(\mathbf{F}_\epsilon\cdot(\boldsymbol{\chi}^{(2)}\cdot(\mathbf{E})^{\otimes 2})) . \tag{2.22}$$

Here $\mathbf{F}_\epsilon$ is the dipole propagator in the linear medium that is expressed in terms of the dielectric-constant tensor $\boldsymbol{\epsilon}[\equiv\mathbf{U}+4\pi\boldsymbol{\chi}^{(1)}]$ as

$$\mathbf{F}_\epsilon = 4\pi(4\pi\mathbf{F}^{-1}+\epsilon-\mathbf{U})^{-1} . \tag{2.23}$$

It is evident that $\chi^{(3)}_{\rm cas}$ is a macroscopic third-order susceptibility built up out of successive second-order processes connected by a wave propagating in the linear medium [Fig. 1]. However, pair correlations enter into $\chi^{(3)}_{\rm cas}$ only through their influence on the macroscopic $\chi^{(1)}$ and $\chi^{(2)}$, rather than from the microscopic cascading between molecules that is statistically averaged as with $\gamma^{(3)}_{\rm cas}$ in Sec. III.

Let us next rewrite Eq. (2.7) as

$$\mathbf{P}=\chi^{(1)}\cdot(\mathbf{E})+\mathbf{P}_{\rm NL}[\mathbf{E}] , \tag{2.24}$$

where, e.g., to third order,

$$\mathbf{P}_{\rm NL}[\mathbf{E}]=\chi^{(2)}\cdot(\mathbf{E})^{\otimes 2}+\chi^{(3)}\cdot(\mathbf{E})^{\otimes 3} . \tag{2.25}$$

From Eqs. (2.1) and (2.8) we find that

$$\mathbf{E}=\mathbf{E}_{\rm L}-\mathbf{F}_\epsilon\cdot(\mathbf{P}_{\rm NL}[\mathbf{E}]) . \tag{2.26}$$

Equation (2.26) does not allow us to eliminate $\mathbf{E}$ in favor of $\mathbf{E}_L$ in (2.24), except iteratively, in contrast to the transition $\mathbf{E}_{\rm ex}\rightarrow\mathbf{E}$. Using (2.26) in the linear part of (2.24) we obtain

$$\mathbf{P}=\chi^{(1)}\cdot(\mathbf{E}_{\rm L})+(\mathbf{\Gamma}^{-1})\cdot\mathbf{P}_{\rm NL}[\mathbf{E}] . \tag{2.27}$$

On the other hand, as an alternative to (2.24), and corresponding to (2.9), we can write

$$\mathbf{P}=\xi^{(1)}\cdot(\mathbf{E}_{\rm L})+\mathbf{P}_{\rm NL}\{\mathbf{E}_{\rm L}\} . \tag{2.28}$$

The *exact* equivalence of (2.27) and (2.28) leads to the identity

$$(\xi^{(1)}-\chi^{(1)})\cdot(\mathbf{E}_{\rm L})=(\mathbf{\Gamma}^{-1})\cdot(\mathbf{P}_{\rm NL}[\mathbf{E}])-\mathbf{P}_{\rm NL}\{\mathbf{E}_{\rm L}\} , \tag{2.29}$$

Since by (2.26) $\mathbf{E}$ and $\mathbf{E}_{\rm L}$ differ only by nonlinear terms, we infer from (2.29) that

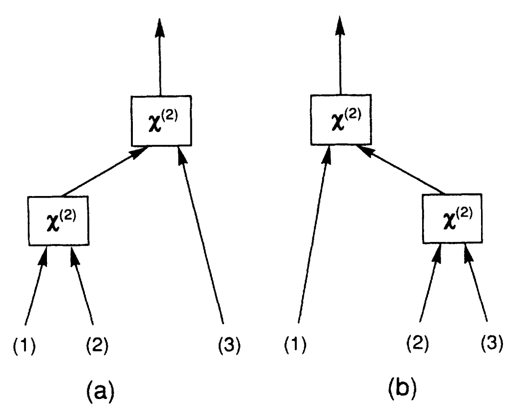

FIG. 1. Graphical representations of the third-order cascading terms $\chi^{(2)}\cdot\{F_\epsilon\cdot\chi^2\}_m$. The external lines depict incoming and outgoing waves, while the intermediate line represents the propagator $\mathbf{F}_\epsilon$ in the linear medium; the square boxes refer to the wave mixing generated by $\chi^{(2)}$. The numbering is such that the top box corresponds to the formal functional dependences $\chi^{(2)}(1+2+3;1+2,3)$ for $m=1$, and $\chi^{(2)}(1+2+3;1,2+3)$ for $m=2$.

$$\xi^{(1)}=\chi^{(1)} , \tag{2.30}$$

which agrees with the results of Refs. [12, 14], and

$$\mathbf{P}_{\rm NL}\{\mathbf{E}_{\rm L}\}=(\mathbf{\Gamma}^{-1})\cdot(\mathbf{P}_{\rm NL}[\mathbf{E}]) , \tag{2.31}$$

which does not, cf. Eqs. (2.29) and (2.30) of [12], but which is crucial for the correct treatment of the nonlinear local-field and cascading problems in the $\mathbf{E}_{\rm L}$ formalism.

Equations (2.25), (2.26), and (2.31) lead us to the expansion

$$\mathbf{P}_{\rm NL}\{\mathbf{E}_{\rm L}\}=(\mathbf{\Gamma}^{-1})\cdot(\chi^{(2)}\cdot(\mathbf{E}_{\rm L})^{\otimes 2}+[\chi^{(3)}-\chi^{(3)}_{\rm cas}]\cdot(\mathbf{E}_{\rm L})^{\otimes 3}+\cdots) , \tag{2.32}$$

which, upon using Eqs. (2.9) and (2.31) imply that

$$\xi^{(2)}=(\mathbf{\Gamma}^{-1})\cdot(\chi^{(2)}) \tag{2.33}$$

and

$$\xi^{(3)}=(\mathbf{\Gamma}^{-1})\cdot(\chi^{(3)}{}_{\rm int}) . \tag{2.34}$$

The susceptibilities (2.33) and (2.34) differ from the results obtained in Refs. [12] and [14] by the multiplicative factor $\mathbf{\Gamma}^{-1}$. This factor results from the difference between the linear kernels of the integral equations for $\mathbf{P}$ as obtained in the $\mathbf{E}$ or $\mathbf{E}_{\rm L}$ formalisms. Equations (2.33) and (2.34) are needed for a consistent treatment of the local-field problem in terms of $\mathbf{E}_{\rm L}$.

Another striking feature of the $\mathbf{E}_{\rm L}$ formalism is the cancellation of the third-order term $\chi^{(3)}_{\rm cas}$ that appears in the $\mathbf{E}_{\rm L}$ formalism. Therefore, the cascading in this picture is entirely implicit in the intrinsic susceptibility $\chi^{(3)}_{\rm int}$ appearing in (2.19) and so can be isolated from other effects only within specific models. We see then that the identification of cascading is strongly dependent on how one chooses to organize the power series for $\mathbf{P}$ in terms of the various fields. For example, parts of the purely second-order terms in the $\mathbf{E}$ formalism get promoted to third-order cascading terms in the $\mathbf{E}_{\rm L}$ formalism because of the second-order difference between these two fields. Those cascading terms then exactly cancel terms that arise because of the differences, in all except the lowest order, between the fields $\mathbf{E}$ and $\mathbf{E}_{\rm ex}$. Thus $\chi^{(3)}_{\rm cas}$ disappears entirely in the $\mathbf{E}_{\rm L}$ case. The corrected susceptibilities (2.33) and (2.34) are required for the quantitative evaluation of the third-order cascading signals in terms of $\mathbf{E}_{\rm L}$.

III. MICROSCOPIC MODEL

Statistical correlations in a model of the linear dielectric properties of a collection of nonpolar molecules in thermodynamical equilibrium were studied in detail by Bedeaux and Mazur [31]. The same model was extended to the nonlinear case by Bedeaux and Bloembergen [12], but cascading was considered only in the uncorrelated limit. We apply this model to the nonlinear case to identify the correlative part of the polarization arising from cascading in each of the three ways of organizing the susceptibility expansion considered in Sec. II. Our treatment of the $\mathbf{E}_{\rm L}$ formalism yields new results in both the uncorrelated and the correlated cases.

The model of Bedeaux and Mazur consists of a collection of N identical molecules at positions $\mathbf{R}_i$ and with orientations $\mathbf{\Omega}_i$, with $i=1,2,\ldots,N$. It is assumed that each molecule responds to an electric field as a fixed-point dipole, but that it has no permanent dipole moment [36]. Macroscopic observables are calculated by statistical averaging over the molecular positions and orientations with the neglect of any dynamical changes in $\mathbf{R}_i$ and $\mathbf{\Omega}_i$ that might occur during the interaction with the electric field. The molecular susceptibilities $\boldsymbol{\alpha}^{(n)}$, $n=1,2,3,\ldots$, are assumed to be local, time invariant, and, in general, orientation dependent.

The molecular dipole moment $\mathbf{p}_{\rm mol}(\mathbf{x},\mathbf{\Omega},t)$ generated in response to the local field $\mathbf{E}_{\rm LF}(\mathbf{x},t)$ is

$$\mathbf{p}_{\rm mol}(\mathbf{x},\mathbf{\Omega},t)=\int dt'\boldsymbol{\alpha}^{(1)}(\mathbf{\Omega},t-t')\cdot[\mathbf{E}_{\rm LF}(\mathbf{x},t')]+\mathbf{n}[\mathbf{E}_{\rm LF}]\ , \tag{3.1}$$

where, suppressing the time integrations,

$$\mathbf{n}[\mathbf{E}_{\rm LF}]=\boldsymbol{\alpha}^{(2)}(\mathbf{\Omega})\cdot(\mathbf{E}_{\rm LF})^{\otimes 2}+\boldsymbol{\alpha}^{(3)}(\mathbf{\Omega})\cdot(\mathbf{E}_{\rm LF})^{\otimes 3}+\cdots\ . \tag{3.2}$$

The local field at $(\mathbf{R}_i,t)$, which is a function of all of the variables $\{N\}\equiv(\mathbf{R}_1,\mathbf{\Omega}_1,\ldots,\mathbf{R}_N,\mathbf{\Omega}_N)$, is the sum of $\mathbf{E}_{\rm ex}$, the dipole radiation from the other molecules, and the self-field [31]:

$$\mathbf{E}_{\rm LF}(\mathbf{R}_i,t;\{N\})=\mathbf{E}_{\rm ex}(\mathbf{R}_i,t)-\sum_j\int dt'\{\mathbf{F}(\mathbf{R}_i-\mathbf{R}_j;t-t')(1-\delta_{ij})+\delta_{ij}\tfrac{1}{2}[\mathbf{F}(0;t-t')-\mathbf{F}^{\dagger}(0;t-t')]\}\cdot\mathbf{p}_{\rm mol}(\mathbf{R}_j,\mathbf{\Omega}_j,t')\ , \tag{3.3}$$

where † denotes Hermitian conjugation.

If we note that the total dipole-moment density is given by

$$\mathbf{P}_0(\mathbf{x},\mathbf{\Omega},t;\{N\})=\rho(\mathbf{x},\mathbf{\Omega};\{N\})\mathbf{p}_{\rm mol}(\mathbf{x},\mathbf{\Omega},t)\ , \tag{3.4}$$

where the particle density is

$$\rho(\mathbf{x},\mathbf{\Omega};\{N\})=\sum_{i=1}^{N}\delta(\mathbf{x}-\mathbf{R}_i)\delta(\mathbf{\Omega}-\mathbf{\Omega}_i)\ , \tag{3.5}$$

then (3.3) can be rewritten compactly as

$$\mathbf{E}_{\rm LF}(\mathbf{x},t;\{N\})=\mathbf{E}_{\rm ex}(\mathbf{x},t)-\int d^3x'dt'd\mathbf{\Omega}'\mathbf{H}(\mathbf{x}-\mathbf{x}';t-t')\cdot(\mathbf{P}_0(\mathbf{x}',\mathbf{\Omega}',t';\{N\}))\ . \tag{3.6}$$

Here $\mathbf{H}$ is the short-distance-modified propagator [31]

$$\begin{aligned}\mathbf{H}(\mathbf{x}-\mathbf{x}';t-t')&\equiv\mathbf{F}(\mathbf{x}-\mathbf{x}';t-t'),\quad |\mathbf{x}-\mathbf{x}'|>a\ ,\\ &\equiv\tfrac{1}{2}[\mathbf{F}(\mathbf{x}-\mathbf{x}';t-t')-\mathbf{F}^{\dagger}(\mathbf{x}-\mathbf{x}';t-t')]\ ,\\ &\qquad |\mathbf{x}-\mathbf{x}'|<a\ ,\end{aligned} \tag{3.7}$$

where the limit $a\to 0+$ is taken after all integrations have been completed. The representation-independent form of Eq. (3.6) is

$$\mathbf{E}_{\rm LF}=\mathbf{E}_{\rm ex}-\mathbf{H}\cdot(\mathbf{P}_0)\ , \tag{3.8}$$

where the dot operation has been extended to include the intermediate integration over the orientation, and we have suppressed the dependence on $\{N\}$.

Using Eqs. (3.1), (3.4), and (3.8) we obtain an integral equation for $\mathbf{P}_0$ [12]:

$$\mathbf{P}_0=\rho\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{E}_{\rm ex})-\rho\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{H}\cdot(\mathbf{P}_0))+\rho\mathbf{n}[\mathbf{E}_{\rm ex}-\mathbf{H}\cdot(\mathbf{P}_0)]\ . \tag{3.9}$$

The macroscopic polarization density $\mathbf{P}(\mathbf{x},\mathbf{\Omega},t)$ is the statistical average

$$\mathbf{P}(\mathbf{x},\mathbf{\Omega},t)=\left[\prod_i(1/\Omega)\int d\mathbf{\Omega}_i(1/V)d^3R_i\right]\times F_N(\{N\})\mathbf{P}_0(\mathbf{x},\mathbf{\Omega},t;\{N\})\ , \tag{3.10}$$

where $F_N(\{N\})$ is the N-particle distribution function, V is the volume, and Ω is 4π (linear molecule) or $8\pi^2$ (otherwise). Because of correlations the statistical average of (3.9) does not yield an integral equation for $\mathbf{P}\equiv\langle\mathbf{P}_0\rangle$. However, if we iterate (3.9) up to some order in $\mathbf{E}_{\rm ex}$ and then ensemble average, we can use the methods of Sec. II to obtain the $\chi^{(n)}$'s and $\xi^{(n)}$'s in terms of the statistically averaged $\gamma^{(n)}$'s.

The inversion of the linear part of Eq. (3.9) brings in the linear factor

$$\mathbf{K}_0\equiv(\mathbf{U}+\rho\boldsymbol{\alpha}^{(1)}\cdot\mathbf{H})^{-1}=(\mathbf{U}-\gamma_0^{(1)}\cdot\mathbf{H})\ , \tag{3.11}$$

so that upon iterating the higher-order terms we get

$$\mathbf{P}_0=\gamma_0^{(1)}\cdot(\mathbf{E}_{\rm ex})+\gamma_0^{(2)}\cdot(\mathbf{E}_{\rm ex})^{\otimes 2}+\gamma_0^{(3)}\cdot(\mathbf{E}_{\rm ex})^{\otimes 3}\ , \tag{3.12}$$

with

$$\gamma_0^{(1)}=\mathbf{K}_0\cdot(\rho\boldsymbol{\alpha}^{(1)})\ , \tag{3.13}$$

$$\gamma_0^{(2)}\cdot=\mathbf{K}_0\cdot(\rho\boldsymbol{\alpha}^{(2)}\cdot(\mathbf{K}_0^t\cdot)^{\otimes 2})\ , \tag{3.14}$$

$$\gamma_0^{(3)}=[\gamma_0^{(3)}]_{\rm int}+[\gamma_0^{(3)}]_{\rm cas}\ , \tag{3.15}$$

and

$$[\gamma_0^{(3)}]_{\rm int}\cdot=\mathbf{K}_0\cdot(\rho\boldsymbol{\alpha}^{(3)}\cdot(\mathbf{K}_0^t\cdot)^{\otimes 3})\ , \tag{3.16}$$

$$[\gamma_0^{(3)}]_{\rm cas}=-\sum_m\gamma_0^{(2)}\cdot\{\mathbf{H}_K\cdot\gamma_0^{(2)}\}_m\ , \tag{3.17}$$

$$\mathbf{K}_0^t \equiv (\mathbf{U}+\mathbf{H}\cdot\rho\boldsymbol{\alpha}^{(1)})^{-1} = (\mathbf{U}-\mathbf{H}\cdot\boldsymbol{\gamma}_0^{(1)}) , \tag{3.18}$$

$$\mathbf{H}_K \equiv (\mathbf{K}_0^t)^{-1}\cdot\mathbf{H} = \mathbf{H}\cdot(\mathbf{K}_0)^{-1} . \tag{3.19}$$

The ensemble average of Eq. (3.12) yields (2.6) with

$$\boldsymbol{\gamma}^{(n)} \equiv \langle \boldsymbol{\gamma}_0^{(n)} \rangle . \tag{3.20}$$

Then $\boldsymbol{\chi}^{(1)}$, $\boldsymbol{\chi}^{(2)}$, and $\boldsymbol{\chi}^{(3)}$ are given in terms of the $\boldsymbol{\gamma}^{(n)}$ by Eqs. (2.12), (2.16), and (2.18)–(2.20), respectively. Also, $\boldsymbol{\xi}^{(2)}$ and $\boldsymbol{\xi}^{(3)}$ are obtained from Eqs. (2.33) and (2.34), respectively. If we call

$$\boldsymbol{\gamma}_{\rm int}^{(3)} \equiv \langle [\boldsymbol{\gamma}_0^{(3)}]_{\rm int} \rangle , \tag{3.21a}$$

$$\boldsymbol{\gamma}_{\rm cas}^{(3)} \equiv \langle [\boldsymbol{\gamma}_0^{(3)}]_{\rm cas} \rangle , \tag{3.21b}$$

then $\boldsymbol{\xi}^{(3)}$ decomposes into terms representing the intrinsic and cascaded third-order susceptibilities

$$\boldsymbol{\xi}^{(3)} = \boldsymbol{\xi}_{\rm int}^{(3)} + \boldsymbol{\xi}_{\rm cas}^{(3)} , \tag{3.22}$$

$$\boldsymbol{\xi}_{\rm int}^{(3)}\cdot = \boldsymbol{\gamma}_{\rm int}^{(3)}\cdot(\boldsymbol{\Gamma}^t\cdot)^{\otimes 3} , \tag{3.23a}$$

$$\boldsymbol{\xi}_{\rm cas}^{(3)}\cdot = \boldsymbol{\gamma}_{\rm cas}^{(3)}\cdot(\boldsymbol{\Gamma}^t\cdot)^{\otimes 3} . \tag{3.23b}$$

Thus we see that in this microscopic model the cascading contribution is indeed recovered in the $\mathbf{E}_L$-field formalism; see the discussion following Eq. (2.34).

IV. β MEDIA

To identify irreducible cascading coefficients, we study cascading under circumstances where it can be isolated from other effects by specializing the model of Sec. III to the artificial case in which [37]

$$\boldsymbol{\alpha}^{(n)}(\boldsymbol{\Omega}) = 0, \quad n \neq 2 \ (\beta \text{ media}) . \tag{4.1}$$

When (4.1) applies, Eq. (3.9) reduces to

$$\mathbf{P}_0 = \rho\boldsymbol{\alpha}^{(2)}\cdot(\mathbf{E}_{\rm ex} - \mathbf{H}\cdot(\mathbf{P}_0)^{\otimes 2}) , \tag{4.2}$$

a single iteration of which gives $\mathbf{P}_0$ through third order in $\mathbf{E}_{\rm ex}$,

$$\mathbf{P}_0 = \rho\boldsymbol{\alpha}^{(2)}\cdot(\mathbf{E}_{\rm ex})^{\otimes 2} - \sum_m \rho[\boldsymbol{\alpha}^{(2)}\cdot\{\mathbf{H}\cdot\rho\boldsymbol{\alpha}^{(2)}\}_m]\cdot(\mathbf{E}_{\rm ex})^{\otimes 3} . \tag{4.3}$$

The ensemble average of Eq. (4.3) is

$$\mathbf{P} = \boldsymbol{\gamma}^{(2)}\cdot(\mathbf{E}_{\rm ex})^{\otimes 2} + \boldsymbol{\gamma}^{(3)}\cdot(\mathbf{E}_{\rm ex})^{\otimes 3} , \tag{4.4}$$

where

$$\boldsymbol{\gamma}^{(2)} \equiv \langle \rho \rangle \boldsymbol{\alpha}^{(2)} , \tag{4.5}$$

and

$$\boldsymbol{\gamma}^{(3)} \equiv -\sum_m \langle \rho[\boldsymbol{\alpha}^{(2)}\cdot\{\mathbf{H}\cdot\rho\boldsymbol{\alpha}^{(2)}\}_m] \rangle . \tag{4.6}$$

For β media $\boldsymbol{\xi}^{(n)}$ and $\boldsymbol{\gamma}^{(n)}$ are identical for all n.

In β media the susceptibilities $\boldsymbol{\chi}^{(2)}$ and $\boldsymbol{\gamma}^{(2)}$ are also identical:

$$\boldsymbol{\chi}^{(2)}(\mathbf{x},\boldsymbol{\Omega}) = \boldsymbol{\gamma}^{(2)}(\mathbf{x},\boldsymbol{\Omega}) = (\rho_0/\Omega)F_1(\mathbf{x},\boldsymbol{\Omega})\boldsymbol{\alpha}^{(2)}(\boldsymbol{\Omega}) , \tag{4.7}$$

where $\rho_0 = N/V$ and $F_1(\mathbf{x},\boldsymbol{\Omega})$ is the one-particle distribution function [4]. For a uniform liquid of density ρ_0, we have

$$\boldsymbol{\chi}^{(2)}(\boldsymbol{\Omega}) = (\rho_0/\Omega)f_1(\boldsymbol{\Omega})\boldsymbol{\alpha}^{(2)}(\boldsymbol{\Omega}) , \tag{4.8}$$

where $f_1(\boldsymbol{\Omega})$ is the normalized orientational distribution function

$$\int d\boldsymbol{\Omega}\, f_1(\boldsymbol{\Omega}) = 1 . \tag{4.9}$$

The orientational average of $\boldsymbol{\chi}^{(2)}(\boldsymbol{\Omega})$ is then

$$\boldsymbol{\chi}_{\rm av}^{(2)} \equiv (1/\Omega)\int d\boldsymbol{\Omega}\, \boldsymbol{\chi}^{(2)}(\boldsymbol{\Omega}) . \tag{4.10}$$

Next we consider the statistically averaged third-order terms. We see from (4.6) that the intrinsic third-order term

$$\boldsymbol{\chi}_{\rm int}^{(3)} = \boldsymbol{\gamma}^{(3)} \tag{4.11}$$

is actually a sum of two cascading terms involving two-particle correlations. This is in contrast to the noncorrelative "cascading" term

$$\boldsymbol{\chi}_{\rm cas}^{(3)} = \sum_m \boldsymbol{\gamma}^{(2)}\cdot\{\mathbf{F}\cdot\boldsymbol{\gamma}^{(2)}\}_m \tag{4.12}$$

that arises in passing between the $\mathbf{E}_{\rm ex}$ and the $\mathbf{E}$ pictures. Summing these two contributions, we get

$$\boldsymbol{\chi}^{(3)} = \sum_m \mathbf{X}_m , \tag{4.13}$$

where

$$\mathbf{X}_m = -\langle \rho\boldsymbol{\alpha}^{(2)}\cdot\{\mathbf{H}\cdot\rho\boldsymbol{\alpha}^{(2)}\}_m \rangle + \boldsymbol{\gamma}^{(2)}\cdot\{\mathbf{F}\cdot\boldsymbol{\gamma}^{(2)}\}_m . \tag{4.14}$$

Equations (4.6) and (4.14) involve the density-density correlation function [38]

$$\begin{aligned}\langle \rho(\mathbf{x},\boldsymbol{\Omega};\{N\})\rho(\mathbf{y},\boldsymbol{\Omega}';\{N\}) \rangle &= (\rho_0/\Omega)^2 F_2(\mathbf{x},\boldsymbol{\Omega};\mathbf{y},\boldsymbol{\Omega}') \\ &\quad + (\rho_0/\Omega)\delta(\mathbf{x}-\mathbf{y})\delta(\boldsymbol{\Omega}-\boldsymbol{\Omega}')F_1(\mathbf{x},\boldsymbol{\Omega}) .\end{aligned} \tag{4.15}$$

In the uncorrelated (unc) limit F_2 factorizes and so

$$\begin{aligned}\langle \rho(\mathbf{x},\boldsymbol{\Omega};\{N\})\rho(\mathbf{y},\boldsymbol{\Omega}';\{N\}) \rangle_{\rm unc} &= (\rho_0/\Omega)^2 F_1(\mathbf{x},\boldsymbol{\Omega})F_1(\mathbf{y},\boldsymbol{\Omega}') \\ &\quad + (\rho_0/\Omega)\delta(\mathbf{x}-\mathbf{y})\delta(\boldsymbol{\Omega}-\boldsymbol{\Omega}')F_1(\mathbf{x},\boldsymbol{\Omega}) .\end{aligned} \tag{4.16}$$

The pair-correlation function, which is defined by

$$g_2(\mathbf{x},\boldsymbol{\Omega};\mathbf{y},\boldsymbol{\Omega}') = F_2(\mathbf{x},\boldsymbol{\Omega};\mathbf{y},\boldsymbol{\Omega}') - F_1(\mathbf{x},\boldsymbol{\Omega})F_1(\mathbf{y},\boldsymbol{\Omega}') , \tag{4.17}$$

vanishes in the uncorrelated limit.

In the average (4.6) the δ functions in (4.16) yield a self-correlative term that is omitted in the identification

$$\langle \rho\boldsymbol{\alpha}^{(2)}\cdot\{\mathbf{H}\cdot\rho\boldsymbol{\alpha}^{(2)}\}_m \rangle_{\rm unc} \equiv \boldsymbol{\gamma}^{(2)}\cdot\{\mathbf{H}\cdot\boldsymbol{\gamma}^{(2)}\}_m . \tag{4.18}$$

This leads to the decomposition of $\boldsymbol{\chi}^{(3)}$ into its uncorrelated and correlated (cor) parts,

$$\boldsymbol{\chi}^{(3)} = \boldsymbol{\chi}^{(3)}{}_{\rm unc} + \boldsymbol{\chi}_{\rm cor}^{(3)} , \tag{4.19}$$

where

$$\chi^{(3)}_{\rm unc}=\sum_m \gamma^{(2)}\cdot\{\mathbf{G}\cdot\gamma^{(2)}\}_m ,\qquad (4.20)$$

$$\chi^{(3)}_{\rm cor}=-\sum_m \langle[\rho(\{N\})\alpha^{(2)}-\gamma^{(2)}]\cdot\{\mathbf{H}\cdot(\rho(\{N\})\alpha^{(2)}-\gamma^{(2)})\}_m\rangle ,\qquad (4.21)$$

and in the limit $a\to 0+$,

$$\mathbf{G}\equiv\mathbf{F}-\mathbf{H}=(4\pi/3)\mathbf{U} .\qquad (4.22)$$

In β media both $\chi^{(3)}_{\rm unc}$ and $\chi^{(3)}_{\rm cor}$ arise solely from cascading. However, as we see next $\chi^{(3)}_{\rm cor}\neq 0$ only when $g_2\neq 0$, so unlike $\chi^{(3)}_{\rm unc}$, it is nonlocal and responsive to molecular correlations.

As a consequence of Eqs. (4.5) and (4.22) one finds from (4.20) the local structure

$$\chi^{(3)}_{\rm unc}(\mathbf{\Omega}|\mathbf{x};x_1,x_2,x_3)=(4\pi/3)(\rho_0/\Omega)^2\left[\prod_{i=1}^{3}\delta(\mathbf{x}-\mathbf{x}_i)\right]F_1(\mathbf{x},\mathbf{\Omega})\times\int dt'd\mathbf{\Omega}'F_1(\mathbf{x},\mathbf{\Omega}')\,\mathbf{A}(\mathbf{\Omega},\mathbf{\Omega}'|t,t_1,t_2,t_3;t') ,\qquad (4.23)$$

where

$$\mathbf{A}=\alpha^{(2)}(\mathbf{\Omega}|t;t',t_3)\cdot\{\mathbf{U}\cdot\alpha^{(2)}(\mathbf{\Omega}'|t';t_1,t_2)\}_1+\alpha^{(2)}(\mathbf{\Omega}|t;t_1,t')\cdot\{\mathbf{U}\cdot\alpha^{(2)}(\mathbf{\Omega}'|t';t_2,t_3)\}_2 ,\qquad (4.24)$$

and now the $\{\cdots\}_m$ notation refers only to tensor contractions. For a uniform liquid $F_1(\mathbf{x},\mathbf{\Omega})\to f_1(\mathbf{\Omega})$ and so the spatial Dirac δ functions in (4.23) give rise to an overall momentum-conserving δ function in $\mathbf{k}$ space, which we ignore, along with a factor $\delta(\omega-\sum_j\omega_j)$ representing energy conservation resulting from time invariance, which we also ignore, when we write down the Fourier component of $\chi^{(3)}_{\rm unc}$ in k space:

$$\chi^{(3)}_{\rm unc}(\mathbf{\Omega}|-\omega;\omega_1,\omega_2,\omega_3)=(4\pi/3)f_1(\mathbf{\Omega})(\rho_0/\Omega)^2\times\int d\mathbf{\Omega}'f_1(\mathbf{\Omega}')\mathbf{a}(\mathbf{\Omega},\mathbf{\Omega}'|-\omega;\omega_1,\omega_2,\omega_3) ,\qquad (4.25)$$

where

$$\mathbf{a}=\alpha^{(2)}(\mathbf{\Omega}|-\omega;\omega_1+\omega_2,\omega_3)\cdot\{\mathbf{U}\cdot\alpha^{(2)}(\mathbf{\Omega}'|-\omega_1-\omega_2;\omega_1,\omega_2)\}_1+\alpha^{(2)}(\mathbf{\Omega}|-\omega;\omega_1,\omega_2+\omega_3)\cdot\{\mathbf{U}\cdot\alpha^{(2)}(\mathbf{\Omega}'|-\omega_2-\omega_3;\omega_2,\omega_3)\}_2 .\qquad (4.26)$$

The nonlocality and the g_2 dependence of $\chi^{(3)}_{\rm cor}$ are manifested in its x-space representation:

$$\chi^{(3)}_{\rm cor}(\mathbf{\Omega}|x;x_1,x_2,x_3)=-(\rho_0/\Omega)^2\int dt'dt''d\mathbf{\Omega}'[g_2(\mathbf{x},\mathbf{\Omega};\mathbf{x}_1,\mathbf{\Omega}')\delta(\mathbf{x}-\mathbf{x}_3)\delta(\mathbf{x}_1-\mathbf{x}_2)\alpha^{(2)}(\mathbf{\Omega}|t;t',t_3)\cdot\{\mathbf{H}(\mathbf{x}-\mathbf{x}_1,t'-t'')\cdot\alpha^{(2)}(\mathbf{\Omega}'|t'';t_1,t_2)\}_1$$
$$+g_2(\mathbf{x},\mathbf{\Omega};\mathbf{x}_2,\mathbf{\Omega}')\delta(\mathbf{x}-\mathbf{x}_1)\delta(\mathbf{x}_2-\mathbf{x}_3)\alpha^{(2)}(\mathbf{\Omega}|t;t_1,t')\cdot\{\mathbf{H}(\mathbf{x}-\mathbf{x}_2,t'-t'')\cdot\alpha^{(2)}(\mathbf{\Omega}'|t'';t_2,t_3)\}_2],\qquad (4.27)$$

where, for simplicity, we have omitted the self-correlative part of (4.21). Translational invariance implies that when g_2 and $\mathbf{H}$ appear together in (4.27), they depend on the same coordinate pairs, which presents the possibility of mutual enhancements of the propagator and correlation-function contributions to $\chi^{(3)}_{\rm cor}$.

The nonlocality implies a nontrivial wave-vector dependence in the Fourier transformation of $\chi^{(3)}_{\rm cor}$. Here we obtain, ignoring the overall $\mathbf{k}$-space δ-function factor,

$$\chi^{(3)}_{\rm cor}(\mathbf{\Omega}|-k;k_1,k_2,k_3)=-(\rho_0/\Omega)\mathbf{b}(\mathbf{\Omega}|-\omega;\omega_1,\omega_2,\omega_3)-(\rho_0/\Omega)^2\int d\mathbf{\Omega}'d^3q\,\mathbf{c}(\mathbf{q},\mathbf{\Omega},\mathbf{\Omega}'|-k;k_1,k_2,k_3) ,\qquad (4.28)$$

with the self-correlative term given by

$$\mathbf{b}=\alpha^{(2)}(\mathbf{\Omega}|-\omega;\omega_1+\omega_2,\omega_3)\cdot\{\mathbf{h}(\omega_1+\omega_2)\cdot\alpha^{(2)}(\mathbf{\Omega}|-\omega_1-\omega_2;\omega_1,\omega_2)\}_1+\alpha^{(2)}(\mathbf{\Omega}|-\omega;\omega_1,\omega_2+\omega_3)\cdot\{\mathbf{h}(\omega_2+\omega_3)\cdot\alpha^{(2)}(\mathbf{\Omega}|-\omega_2-\omega_3;\omega_2,\omega_3)\}_2 ,\qquad (4.29)$$

where $\mathbf{h}(\omega)=-i(4/3)(\omega/c)^3\mathbf{U}$ is the Fourier transform of $\mathbf{H}(0,t)$, and where

$$\mathbf{c}\equiv g_2(\mathbf{\Omega},\mathbf{\Omega}',\mathbf{k}_1+\mathbf{k}_2-\mathbf{q})\alpha^{(2)}(\mathbf{\Omega}|-\omega;\omega_1+\omega_2,\omega_3)\cdot\{\mathbf{h}(\mathbf{q},\omega_1+\omega_2)\cdot\alpha^{(2)}(\mathbf{\Omega}'|-\omega_1-\omega_2;\omega_1,\omega_2)\}_1$$
$$+g_2(\mathbf{\Omega},\mathbf{\Omega}',\mathbf{k}_2+\mathbf{k}_3-\mathbf{q})\alpha^{(2)}(\mathbf{\Omega}|-\omega;\omega_1,\omega_2+\omega_3)\cdot\{\mathbf{h}(\mathbf{q},\omega_2+\omega_3)\cdot\alpha^{(2)}(\mathbf{\Omega}'|-\omega_2-\omega_3;\omega_2,\omega_3)\}_2 .\qquad (4.30)$$

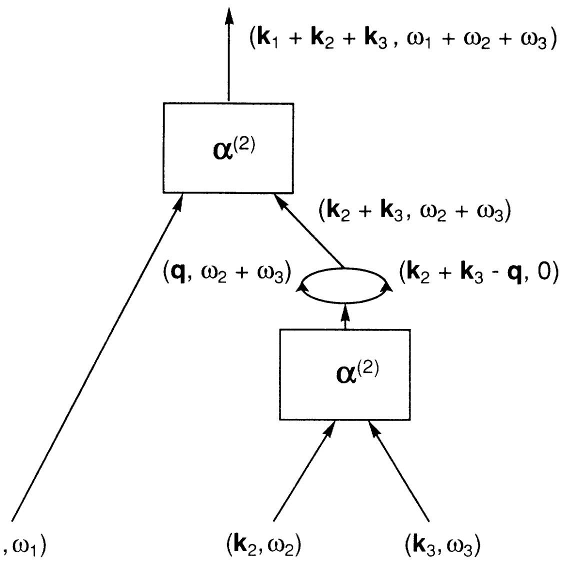

FIG. 2. Graphical representations of a correlated third-order cascading term Eq. (4.28) in wave-vector and frequency space. The external lines represent waves that are mixed by the hyperpolarizabilities $\boldsymbol{\alpha}^{(2)}$ depicted by the rectangular boxes. One arc on the loop attached to the intermediate line corresponds to the propagator $\mathbf{h}(\mathbf{q},\omega_2+\omega_3)$ between two spatial points correlated by the function g_2, which carries momentum $\mathbf{k}_2+\mathbf{k}_3-\mathbf{q}$, but no energy, and represented by the other arc of the loop. An integration over all of the virtual loop momenta $\mathbf{q}$ is implied.

Here $\mathbf{h}(\mathbf{k},\omega)$ is the Fourier transform of $\mathbf{H}(\mathbf{x},t)$, viz.,

$$\mathbf{h}(\mathbf{k},\omega)\equiv\int d^3x\,dt\,e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega t)}\mathbf{H}(\mathbf{x},t)\ , \tag{4.31}$$

whose explicit form is given in [31]. Using translational invariance we have

$$g_2(\boldsymbol{\Omega},\boldsymbol{\Omega}',\mathbf{k})\equiv\int d^3x\,e^{-i\mathbf{k}\cdot\mathbf{x}}g_2(\mathbf{x},\boldsymbol{\Omega};0,\boldsymbol{\Omega}')\ . \tag{4.32}$$

A k-space graphical interpretation of the non-self-correlative terms entering into Eq. (4.28) is shown in Fig. 2. In contrast to Fig. 1, the intermediate propagation line in Fig. 2 contains a "bubble" subgraph representing the effects of the molecular interactions.

In β media the susceptibility $\xi^{(3)}$ is equal to $\gamma^{(3)}$ and is given by Eqs. (4.28)–(4.30), but with g_2 replaced by the two-particle distribution function F_2. Using (4.17) we see that this leads to a different, propagator-dependent uncorrelated limit than $\chi^{(3)}_{\rm unc}$ [cf. Eq. (5.16b)]; however, $\xi^{(3)}_{\rm cor}$ and $\chi^{(3)}_{\rm cor}$ are identical.

For more realistic media, with $\boldsymbol{\alpha}^{(1)}\neq 0$ and where the effects of the $\boldsymbol{\alpha}^{(n)}$ for $n>1$ are a small perturbation on the linear behavior, the generalizations of Eqs. (4.27) and (4.28) are of such complexity that their exact evaluation is typically not practical, except when the effects of correlations on the *linear behavior* are small. Estimates of the cascading can be made within a more comprehensive picture (Sec. V) using the *irreducible cascading coefficients* defined by (4.25) and (4.28), or their counterparts for $\gamma^{(3)}$, with the conventional uncorrelated linear local-field factors appended in the usual way [11,14,23–25]. Even this is no trivial endeavor. The first step is the computation of the irreducible cascading coefficients for representative parametrizations of the pair-correlation function, second-order hyperpolarizabilities $\boldsymbol{\alpha}^{(2)}$, and ranges of thermodynamic conditions. This work, which involves the evaluation of a large number of multidimensional integrals using Monte Carlo techniques, is planned to be reported elsewhere.

The major result of this section is the identification of irreducible cascading coefficients that depend only on the one- and two-particle distribution functions in addition to the second-order hyperpolarizabilities and electromagnetic propagators. These coefficients provide a means for estimating limits on the magnitude of two-particle correlations in association with possible near-field enhancements on the cascading arising from the propagator $\mathbf{H}$.

V. GENERAL MEDIA

The linear polarizability ($\boldsymbol{\alpha}^{(1)}$) affects the polarization directly and indirectly through local-field corrections to the nonlinear contributions. These effects complicate the extensions of the β media model in which the nonlinear (cascading) effects due to correlations are handled exactly. We carry out the extension to $\boldsymbol{\alpha}^{(n)}\neq 0$ for $n\leq 3$ in several stages.

A. Uncorrelated media

The complicating feature of the ensemble-averaged susceptibilities $\gamma^{(n)}$, $\chi^{(n)}$, and $\xi^{(n)}$ is the occurrence of the "inside" local-field factors $\mathbf{K}_0$ and $\mathbf{K}_0^t$, cf. Eqs. (3.11)–(3.19). The "outside" local-field factors $\boldsymbol{\Gamma}$ and $\boldsymbol{\Gamma}^t$ given by Eqs. (2.11) and (2.13), respectively, are themselves defined in terms of ensemble-averaged quantities, but otherwise present no difficulties.

In the uncorrelated limit $\mathbf{K}_0$ and $\mathbf{K}_0^t$ also present no problems [12,14]. We can see this by neglecting all correlations in the ensemble average of Eq. (3.9), which yields

$$\mathbf{P}_{\rm unc}=\langle\rho\rangle[\boldsymbol{\alpha}^{(1)}\cdot(\langle\mathbf{E}_{\rm LF}\rangle_{\rm unc})+\boldsymbol{\alpha}^{(2)}\cdot(\langle\mathbf{E}_{\rm LF}\rangle_{\rm unc})^{\otimes 2}+\boldsymbol{\alpha}^{(3)}\cdot(\langle\mathbf{E}_{\rm LF}\rangle_{\rm unc})^{\otimes 3}]\ , \tag{5.1}$$

which is correct to third order in an expansion in terms of the uncorrelated local-field

$$\langle\mathbf{E}_{\rm LF}\rangle_{\rm unc}=\mathbf{E}+\mathbf{G}\cdot(\mathbf{P}_{\rm unc})\ . \tag{5.2}$$

Therefore, to third order in $\mathbf{E}$ we have

$$\mathbf{P}_{\rm unc}=\boldsymbol{\chi}^{(1)}_{\rm unc}\cdot(\mathbf{E})+\boldsymbol{\chi}^{(2)}_{\rm unc}\cdot(\mathbf{E})^{\otimes 2}+\boldsymbol{\chi}^{(3)}_{\rm unc}\cdot(\mathbf{E})^{\otimes 3}\ , \tag{5.3}$$

where the first-order susceptibility is given by the Clausius-Mossotti relation

$$\boldsymbol{\chi}^{(1)}_{\rm unc}\cdot=\mathbf{f}_\epsilon\cdot(\langle\rho\rangle\boldsymbol{\alpha}^{(1)}\cdot)=\langle\rho\rangle\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{f}_\epsilon\cdot)\ , \tag{5.4a}$$

$$\mathbf{f}_\epsilon\equiv(\mathbf{U}-\langle\rho\rangle\boldsymbol{\alpha}^{(1)}\cdot\mathbf{G})^{-1}=(\mathbf{U}-\mathbf{G}\cdot\langle\rho\rangle\boldsymbol{\alpha}^{(1)})^{-1}\ . \tag{5.4b}$$

The usual form of Lorentz local-field correction

$$\mathbf{f}_\epsilon=\tfrac{1}{3}(\boldsymbol{\epsilon}_{\rm unc}+2\mathbf{U}) \tag{5.5}$$

is recovered in terms of the uncorrelated dielectric tensor

$$\boldsymbol{\epsilon}_{\rm unc}\equiv\mathbf{U}+4\pi\boldsymbol{\chi}^{(1)}_{\rm unc}\ . \tag{5.6}$$

The higher-order susceptibilities are

$$\chi^{(2)}_{\rm unc}\cdot=\mathbf{f}_\epsilon\cdot(\langle\rho\rangle\boldsymbol{\alpha}^{(2)}\cdot(\mathbf{f}_\epsilon\cdot)^{\otimes 2})\ , \tag{5.7}$$

as in β media Eq. (4.7) except for the local-field corrections, and

$$\chi^{(3)}_{\rm unc}=(\chi^{(3)}_{\rm unc})_{\rm int}+(\chi^{(3)}_{\rm unc})_{\rm cas}\ , \tag{5.8}$$

where we introduce the notation [39]

$$(\chi^{(3)}_{\rm unc})_{\rm int}\cdot\equiv\mathbf{f}_\epsilon\cdot(\langle\rho\rangle\boldsymbol{\alpha}^{(3)}\cdot(\mathbf{f}_\epsilon\cdot)^{\otimes 3})\ , \tag{5.9}$$

$$(\chi^{(3)}_{\rm unc})_{\rm cas}\equiv\sum_m\chi^{(2)}_{\rm unc}\cdot\{\mathbf{G}_\epsilon\cdot\chi^{(2)}_{\rm unc}\}_m\ , \tag{5.10}$$

$$\mathbf{G}_\epsilon\equiv4\pi(\epsilon_{\rm unc}+2\mathbf{U})^{-1}\ . \tag{5.11}$$

We see that $(\chi^{(3)}_{\rm unc})_{\rm cas}$, which is the local-field-corrected form of (4.20), survives in the β media limit, while $(\chi^{(3)}_{\rm unc})_{\rm int}$ does not.

It is important to see how the preceding results for $\chi^{(3)}$ follow directly as the uncorrelated limits of Eqs. (2.12), (2.16), (2.18)–(2.20), and (3.20) rather than indirectly from Eq. (5.1). This is shown in the Appendix and provides the basis of our analysis of correlations.

Using the effective linear field $\mathbf{E}_{\rm L}(1)$ in the uncorrelated limit defined by

$$\mathbf{E}_{\rm L}(1)=\mathbf{E}_{\rm ex}-\mathbf{F}\cdot(\chi^{(1)}_{\rm unc}\cdot(\mathbf{E}_{\rm L}(1))\ , \tag{5.12}$$

we obtain in place of (5.3)

$$\mathbf{P}_{\rm unc}=\chi^{(1)}_{\rm unc}\cdot(\mathbf{E}_{\rm L}(1))+\xi^{(2)}_{\rm unc}\cdot(\mathbf{E}_L(1))^{\otimes 2}+\xi^{(3)}_{\rm unc}\cdot(\mathbf{E}_{\rm L}(1))^{\otimes 3}\ , \tag{5.13}$$

where, in disagreement with the results of [12, 14], cf. Eqs. (3.20)–(3.22) of [12],

$$\xi^{(2)}_{\rm unc}\cdot=(\mathbf{K}_0)_{\rm unc}\cdot(\langle\rho\rangle\boldsymbol{\alpha}^{(2)}\cdot(\mathbf{f}_\epsilon\cdot)^{\otimes 2})\ , \tag{5.14}$$

$$\xi^{(3)}_{\rm unc}=(\xi^{(3)}_{\rm unc})_{\rm int}+(\xi^{(3)}_{\rm unc})_{\rm cas}\ , \tag{5.15}$$

$$(\xi^{(3)}_{\rm unc})_{\rm int}\cdot=(\mathbf{K}_0)_{\rm unc}\cdot(\langle\rho\rangle\boldsymbol{\alpha}^{(3)}\cdot(\mathbf{f}_\epsilon\cdot)^{\otimes 3})\ , \tag{5.16a}$$

$$(\xi^{(3)}_{\rm unc})_{\rm cas}=-\sum_m\xi^{(2)}_{\rm unc}\cdot\{\mathbf{H}_\epsilon\cdot\chi^{(2)}_{\rm unc}\}_m\ . \tag{5.16b}$$

The factor $(\mathbf{K}_0)_{\rm unc}$ and the propagator $\mathbf{H}_\epsilon$ are defined in the Appendix. It is clear that $\xi^{(2)}_{\rm unc}$ and $(\xi^{(3)}_{\rm unc})_{\rm cas}$ are the local-field-corrected β media limit forms of $\xi^{(2)}_{\rm unc}$ and $\xi^{(3)}_{\rm unc}$, respectively.

Third-order term (5.16b) represents the contribution of the cascading over and above the linear background when there are no correlations. Because of the absence of local-field-correction factors to the outgoing-wave parts of the susceptibilities (5.14)–(5.16) and the different form of cascading manifested in Eq. (5.16b) as compared to Eq. (5.10), there are significant differences between the nonlinear susceptibilities $\chi^{(n)}$ and $\xi^{(n)}$ for $n\geq2$.

The uncorrelated limit permits the direct assessment of the propagator and linear local-field effects on the cascading. On the other hand, in the β media model the role of the propagators and the pair correlations is clearly delinated, but the linear local-field effects are absent. A hybrid of the two models is to ignore correlations in the linear local-field factors $\mathbf{K}_0$, $\mathbf{K}_0^t$, $\boldsymbol{\Gamma}$, and $\boldsymbol{\Gamma}^t$, thereby removing them from the ensemble averaging, and thus ascribing all correlative effects solely to the irreducible cascading functions.

Generally, it is necessary to assess the role of correlations on all of the factors that involve linear susceptibilities appearing in the $\chi^{(n)}$'s and the $\xi^{(n)}$'s to see how such a hybrid model is embedded in a more general approach. Despite the enormous literature concerning the effects of correlations upon linear dielectric properties, we are not aware of any systematic techniques for dealing with the linear factors arising in the local-field and cascading problems as we have developed them in Sec. III. The method we consider next (linear media) is especially designed for application to local-field corrections in the nonlinear case (nonlinear media).

B. Linear media

We use the linear form of Eq. (3.9) to study $\chi^{(1)}$:

$$\mathbf{P}^{(1)}_0=\rho\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{E}_{\rm ex})-\rho\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{H}\cdot(\mathbf{P}^{(1)}_0))\ . \tag{5.17}$$

We replace (5.17) by a hierarchy of integral equations corresponding to a density expansion of $\mathbf{P}^{(1)}_0$ in terms of the variance $\Delta\rho[\equiv\rho-\langle\rho\rangle]$:

$$\mathbf{P}^{(1)}_0(1)=\rho\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{E}_{\rm ex})-\langle\rho\rangle\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{H}\cdot(\mathbf{P}^{(1)}_0(1)))\ , \tag{5.18a}$$

$$\mathbf{P}^{(1)}_0(p+1)=-\langle\rho\rangle\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{H}\cdot(\mathbf{P}^{(1)}_0(p+1)))-\Delta\rho\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{H}\cdot(\mathbf{P}^{(1)}_0(p)))\ , \tag{5.18b}$$

where

$$\mathbf{P}^{(1)}_0=\sum_p\mathbf{P}^{(1)}_0(p)\ . \tag{5.19}$$

Thus the polarization of the linear medium is

$$\mathbf{P}^{(1)}=\sum_p\mathbf{P}^{(1)}(p)\ , \tag{5.20}$$

in terms of the statistical averages

$$\mathbf{P}^{(1)}(p)\equiv\langle\mathbf{P}^{(1)}_0(p)\rangle\ , \tag{5.21}$$

with a corresponding expansion for the electric field in the medium, namely,

$$\mathbf{E}_{\rm L}=\sum_p\mathbf{E}_{\rm L}(p)\ , \tag{5.22}$$

$$\mathbf{E}_{\rm L}(1)=\mathbf{E}_{\rm ex}-\mathbf{F}\cdot(\mathbf{P}^{(1)}(1))\ , \tag{5.23a}$$

$$\mathbf{E}_{\rm L}(p)=-\mathbf{F}\cdot(\mathbf{P}^{(1)}(p)),\quad p\geq2\ . \tag{5.23b}$$

We can now develop a correlative expansion of $\mathbf{P}^{(1)}$. From (5.18a) we find that

$$\mathbf{P}^{(1)}(1)=(\mathbf{K}_0)_{\rm unc}\cdot(\langle\rho\rangle\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{E}_{\rm ex}))\ . \tag{5.24}$$

Thus in the uncorrelated limit we have

$$\mathbf{P}^{(1)}(1)=\chi^{(1)}_{\rm unc}\cdot(\mathbf{E}_{\rm L}(1))\ . \tag{5.25}$$

Generally, we can write

$$\chi^{(1)}=\chi^{(1)}_{\rm unc}+\chi^{(1)}_{\rm cor}\ , \tag{5.26}$$

where the lowest-order contributions to $\chi^{(1)}_{\rm cor}$ are generated by the sum

$$\mathbf{P}_0^{(1)}(2)+\mathbf{P}_0^{(1)}(3)=-(\mathbf{K}_0)_{\text{unc}}\cdot(\mathbf{C}_0^{(1)}\cdot(\mathbf{K}_0^t)_{\text{unc}}\cdot(\mathbf{E}_{\text{ex}})) , \quad (5.27)$$

$(\mathbf{K}_0^t)_{\text{unc}}$ is defined in the Appendix, and

$$\mathbf{C}_0^{(n)}\equiv\Delta\rho\boldsymbol{\alpha}^{(1)}\cdot(\mathbf{H}\cdot((\mathbf{K}_0)_{\text{unc}}\cdot(\Delta\rho\boldsymbol{\alpha}^{(n)}))) . \quad (5.28a)$$

If we call

$$\mathbf{C}^{(n)}=\langle\mathbf{C}_0^{(n)}\rangle , \quad (5.28b)$$

then

$$\mathbf{P}^{(1)}(2)+\mathbf{P}^{(1)}(3)=-(\mathbf{K}_0)_{\text{unc}}\cdot(\mathbf{C}^{(1)}\cdot(\mathbf{K}_0^t)_{\text{unc}}\cdot(\mathbf{E}_{\text{ex}})) , \quad (5.29)$$

so we see that to lowest order in the correlations

$$\boldsymbol{\gamma}^{(1)}=(\mathbf{K}_0)_{\text{unc}}\cdot(\langle\rho\rangle\boldsymbol{\alpha}^{(1)}-\mathbf{C}^{(1)}\cdot(\mathbf{K}_0^t)_{\text{unc}}) , \quad (5.30)$$

$$\boldsymbol{\Gamma}=(\boldsymbol{\Gamma})_{\text{unc}}-\mathbf{f}_\epsilon\cdot\mathbf{C}^{(1)}\cdot f_\epsilon\cdot\mathbf{F} \quad (5.31)$$

and therefore

$$\boldsymbol{\chi}_{\text{cor}}^{(1)}\cdot=-\mathbf{f}_\epsilon\cdot\mathbf{C}^{(1)}\cdot\mathbf{f}_\epsilon . \quad (5.32)$$

The significance of Eqs. (5.4), (5.26), and (5.32) is that they represent the solution of the linear local-field problem, correct to first order in the correlations. As part of the solution of that problem we see from (2.15) and (5.32) that

$$\boldsymbol{\Gamma}^t=\boldsymbol{\Gamma}_{\text{unc}}^t-[(\mathbf{K}_0^t)_{\text{unc}}]^{-1}\cdot(\mathbf{D}^{(1)}) , \quad (5.33)$$

where

$$\mathbf{D}^{(1)}\equiv\mathbf{f}_\epsilon\cdot\mathbf{F}\cdot(\mathbf{K}_0)_{\text{unc}}\cdot\mathbf{C}^{(1)}\cdot\mathbf{f}_\epsilon \quad (5.34a)$$

$$=-(\mathbf{K}_0^t)_{\text{unc}}\cdot\mathbf{F}\cdot\boldsymbol{\chi}_{\text{cor}}^{(1)} . \quad (5.34b)$$

Thus in the linear case, pair correlations enter in through $\mathbf{C}^{(1)}$, which has an integral representation analogous to those for the irreducible cascading coefficients including the dependence on the propagator $\mathbf{H}$.

C. Nonlinear media

In this subsection the various linear local-field-correction factors are considered only up to the lowest-order correlative corrections, but the nonlinear correlations associated with cascading are treated exactly. Besides the factors $\boldsymbol{\Gamma}$ and $\boldsymbol{\Gamma}^t$, linear effects enter into the nonlinear parts of the polarization through the inside factors $\mathbf{K}_0$ and $\mathbf{K}_0^t$. Since $\mathbf{K}_0$ always appears in conjunction with $\rho\boldsymbol{\alpha}^{(n)}$, the pertinent quantity for $n\geq2$ is

$$\mathbf{K}_0\cdot\rho\boldsymbol{\alpha}^{(n)}=(\mathbf{K}_0)_{\text{unc}}\cdot(\rho\boldsymbol{\alpha}^{(n)}-\mathbf{C}_0^{(n)}-\tilde{\mathbf{H}}^{(1)}\cdot(\mathbf{K}_0)_{\text{unc}}\cdot\langle\rho\rangle\boldsymbol{\alpha}^{(n)}) , \quad (5.35)$$

while the $\mathbf{K}_0^t$ factor leads to the expression:

$$\mathbf{K}_0^t=(\mathbf{K}_0^t)_{\text{unc}}\cdot(\mathbf{U}-\mathbf{H}^{(1)}\cdot(\mathbf{K}_0^t)_{\text{unc}}) , \quad (5.36)$$

where

$$\tilde{\mathbf{H}}^{(1)}\cdot\equiv(\Delta\rho\boldsymbol{\alpha}^{(1)}-C_0^{(1)})\cdot\mathbf{H}\cdot , \quad (5.37a)$$

$$\mathbf{H}^{(1)}\cdot\equiv\mathbf{H}\cdot(\Delta\rho\boldsymbol{\alpha}^{(1)}-\mathbf{C}_0^{(1)})\cdot . \quad (5.37b)$$

Using Eqs. (5.35) and (5.36), in conjunction with Eq. (3.14), we obtain a decomposition of $\gamma_0^{(2)}$ into a part that does not vanish in the limit of β media and a part that does, viz.,

$$\boldsymbol{\gamma}_0^{(2)}=\boldsymbol{\gamma}_0^{(2)}[\beta]+\boldsymbol{\gamma}_0^{(2)}[\beta_0] , \quad (5.38)$$

$$\boldsymbol{\gamma}_0^{(2)}[\beta]\cdot\equiv(\mathbf{K}_0)_{\text{unc}}\cdot\rho\boldsymbol{\alpha}^{(2)}\cdot((\mathbf{K}_0^t)_{\text{unc}}\cdot)^{\otimes2} , \quad (5.39)$$

$$\boldsymbol{\gamma}_0^{(2)}[\beta_0]\cdot\equiv-(\mathbf{K}_0)_{\text{unc}}\cdot\mathbf{S}_0^{(2)}\cdot((\mathbf{K}_0^t)_{\text{unc}}\cdot)^{\otimes2} , \quad (5.40)$$

respectively. Here $\beta_0(\beta)$ refers to a term that is zero (nonzero) in the β media limit. For $n\geq2$, we have introduced the correlation-dependent quantities

$$\mathbf{S}_0^{(n)}\cdot\equiv\mathbf{C}_0^{(n)}\cdot-\tilde{\mathbf{H}}^{(1)}\cdot(\mathbf{K}_0)_{\text{unc}}\cdot\langle\rho\rangle\boldsymbol{\alpha}^{(n)}\cdot+\mathbf{R}_0^{(n)}\cdot , \quad (5.41)$$

$$\mathbf{R}_0^{(n)}\cdot\equiv(\rho\boldsymbol{\alpha}^{(n)}-\tilde{\mathbf{H}}^{(1)}\cdot(\mathbf{K}_0)_{\text{unc}}\cdot\langle\rho\rangle\boldsymbol{\alpha}^{(n)})\cdot$$
$$((\mathbf{K}^{(1)}\cdot)(\mathbf{U}\cdot)^{\otimes(n-1)}-(\mathbf{K}^{(1)}\cdot)^{\otimes2}(\mathbf{U}\cdot)^{\otimes(n-2)}+\not{h}) , \quad (5.42)$$

$$\mathbf{K}^{(1)}\cdot\equiv(\mathbf{K}_0^t)_{\text{unc}}\cdot\mathbf{H}^{(1)}\cdot , \quad (5.43)$$

and $\not{h}$ refers in (5.42) to the sum of all other possible orderings of the direct products of the tensor $\mathbf{K}^{(1)}$ and the $(n-1)$ factors of $\mathbf{U}$, etc. We use the same notation in connection with other tensors.

Calling

$$\mathbf{S}^{(n)}\equiv\langle\mathbf{S}_0^{(n)}\rangle , \quad (5.44)$$

we have then

$$\boldsymbol{\gamma}^{(2)}\cdot=(\boldsymbol{\gamma}^{(2)})_{\text{unc}}\cdot-(\mathbf{K}_0)_{\text{unc}}\cdot\mathbf{S}^{(2)}\cdot((\mathbf{K}_0^t)_{\text{unc}}\cdot)^{\otimes2} , \quad (5.45)$$

where

$$(\boldsymbol{\gamma}^{(2)})_{\text{unc}}\cdot\equiv\langle\boldsymbol{\gamma}_0^{(2)}[\beta]\cdot\rangle . \quad (5.46)$$

The term $\mathbf{S}^{(2)}$, which vanishes in both the uncorrelated and the β media limits, has an integral representation similar to that of the irreducible cascading coefficients when terms of order $(\Delta\rho)^3$ and higher are dropped.

As in the linear case we can now write

$$\boldsymbol{\chi}^{(2)}=\boldsymbol{\chi}_{\text{unc}}^{(2)}+\boldsymbol{\chi}_{\text{cor}}^{(2)} , \quad (5.47)$$

where the first-order correction from the correlations is

$$\boldsymbol{\chi}_{\text{cor}}^{(2)}\cdot=-\mathbf{f}_\epsilon\cdot[\langle\rho\rangle\boldsymbol{\alpha}^{(2)}\cdot((\mathbf{D}^{(1)}\cdot)(\mathbf{f}_\epsilon\cdot)+(\mathbf{f}_\epsilon\cdot)(\mathbf{D}^{(1)}\cdot))+(\mathbf{S}^{(2)}+\mathbf{C}^{(1)}\cdot(\mathbf{K}_0^t)_{\text{unc}}\cdot\mathbf{F}\cdot\mathbf{f}_\epsilon\cdot\langle\rho\rangle\boldsymbol{\alpha}^{(2)})\cdot(\mathbf{f}_\epsilon\cdot)^{\otimes2}] . \quad (5.48)$$

Similarly, we have

$$\xi^{(2)}=\xi_{\text{unc}}^{(2)}+\xi_{\text{cor}}^{(2)} , \quad (5.49)$$

with

$$\xi_{\text{cor}}^{(2)}\cdot=-(\mathbf{K}_0)_{\text{unc}}\cdot[\langle\rho\rangle\boldsymbol{\alpha}^{(2)}\cdot((\mathbf{D}^{(1)}\cdot)(\mathbf{f}_\epsilon\cdot)+(\mathbf{f}_\epsilon\cdot)(\mathbf{D}^{(1)}\cdot))+\mathbf{S}^{(2)}\cdot(\mathbf{f}_\epsilon\cdot)^{\otimes2}] . \quad (5.50)$$

The expressions (5.48) and (5.50) both arise from the local-field corrections to $\langle\rho\rangle\alpha^{(2)}$ from first-order correlative effects; they vanish in the β media limit.

Next, with the use of Eqs. (3.16), (5.35), and (5.36), we find that

$$\gamma^{(3)}_{\rm int}\cdot \equiv \langle [\gamma_0^{(3)}]_{\rm int}\cdot\rangle = (\gamma^{(3)}_{\rm int})_{\rm unc}\cdot - (\mathbf{K}_0)_{\rm unc}\cdot\mathbf{S}^{(3)}\cdot((\mathbf{K}_0^t)_{\rm unc}\cdot)^{\otimes 3}\ , \quad (5.51)$$

to first order in the correlations, where

$$(\gamma^{(3)}_{\rm int})_{\rm unc}\cdot = (\mathbf{K}_0)_{\rm unc}\cdot(\langle\rho\rangle\alpha^{(3)}\cdot((\mathbf{K}_0^t)_{\rm unc}\cdot)^{\otimes 3})\ . \quad (5.52)$$

The correlations are treated exactly in the cascading part of $\gamma^{(3)}$ apart from the linear local-field factors as we see from the expression [cf. Eq. (3.17)]

$$\gamma^{(3)}_{\rm cas} \equiv \langle \gamma_0^{(3)}]_{\rm cas}\rangle = \gamma^{(3)}[\beta] + \gamma^{(3)}_{\rm cas}[\beta_0]\ . \quad (5.53)$$

Here

$$\gamma^{(3)}[\beta] \equiv -\sum_m \langle \gamma_0^{(2)}[\beta]\cdot\{\mathbf{H}\cdot\rho\alpha^{(2)}((\mathbf{K}_0^t)_{\rm unc}\cdot)^{\otimes 2}\}_m\rangle \quad (5.54)$$

is the part of $\gamma^{(3)}$ that reduces to $\xi^{(3)}$ in the β media limit; it is a sum of tensor products of the two types of irreducible cascading coefficients introduced in Sec. IV with various uncorrelated linear local-field factors. Also we have defined

$$\gamma^{(3)}_{\rm cas}[\beta_0]\cdot \equiv -\sum_m \langle \gamma_0^{(2)}\cdot\{\mathbf{H}_K\cdot\gamma_0^{(2)}\cdot\}_m - \gamma_0^{(2)}[\beta]\cdot\{(\mathbf{H}_K)_{\rm unc}\cdot\gamma_0^{(2)}[\beta]\cdot\}_m\rangle\ . \quad (5.55)$$

We can now analyze the correlative structure of $\chi^{(3)}$. Let us decompose the intrinsic part of $\chi^{(3)}$ into unc and cor parts

$$\chi^{(3)}_{\rm int} = (\chi^{(3)}_{\rm int})_{\rm unc} + (\chi^{(3)}_{\rm int})_{\rm cor}\ , \quad (5.56)$$

where

$$(\chi^{(3)}_{\rm int})_{\rm unc}\cdot = (\mathbf{\Gamma})_{\rm unc}\cdot(\gamma^{(3)}_{\rm unc}\cdot((\mathbf{\Gamma}^t)_{\rm unc}\cdot)^{\otimes 3})\ , \quad (5.57)$$

with

$$\gamma^{(3)}_{\rm unc} = (\gamma^{(3)}_{\rm int})_{\rm unc} + (\gamma^{(3)}[\beta])_{\rm unc}\ , \quad (5.58)$$

and $(\gamma^{(3)}[\beta])_{\rm unc}$ is the uncorrelated part of (5.54). Thus the part of $(\chi^{(3)}_{\rm int})_{\rm unc}$ that survives in the β media limit is

$$(\chi^{(3)}_{\rm int}[\beta])_{\rm unc}\cdot \equiv (\mathbf{\Gamma})_{\rm unc}\cdot(\gamma^{(3)}[\beta]_{\rm unc}\cdot((\mathbf{\Gamma}^t)_{\rm unc}\cdot)^{\otimes 3})\ . \quad (5.59)$$

Next, after some rearrangement, we find that

$$\begin{aligned}(\chi^{(3)}_{\rm int})_{\rm cor}\cdot = {} & (\mathbf{\Gamma})_{\rm unc}\cdot((\gamma^{(3)}[\beta])_{\rm cor} + \gamma^{(3)}_{\rm cas}[\beta_0])\cdot((\mathbf{\Gamma}^t)_{\rm unc}\cdot)^{\otimes 3} - \mathbf{f}_\epsilon\cdot\mathbf{S}^{(3)}\cdot(\mathbf{f}_\epsilon\cdot)^{\otimes 3} \\ & -(\mathbf{\Gamma})_{\rm unc}\cdot(\gamma^{(3)}_{\rm unc}\cdot([(\mathbf{\Gamma}^t)_{\rm unc}\cdot]^{\otimes 2}([(\mathbf{K}_0^t)_{\rm unc}]^{-1}\cdot\mathbf{D}^{(1)}\cdot)+\not{p})) \\ & -\mathbf{f}_\epsilon\cdot\mathbf{C}^{(1)}\cdot(\mathbf{K}_0^t)_{\rm unc}\cdot\mathbf{F}\cdot(\chi^{(3)}_{\rm int})_{\rm unc}\cdot\ ,\end{aligned} \quad (5.60)$$

where $(\gamma^{(3)}[\beta])_{\rm cor}$ is the correlated part of (5.54). The terms in (5.60) involving the tensors $\gamma^{(3)}[\beta]_{\rm cor}$ and $\gamma^{(3)}_{\rm cas}[\beta_0]$ represent contributions to the cascading that depend upon the pair correlations. The rest of the terms on the right-hand side of Eq. (5.60), except the part of $(\chi^{(3)}_{\rm int})_{\rm cor}$ that survives in the β media limit, viz.,

$$\chi^{(3)}_{\rm int}[\beta]_{\rm cor}\cdot \equiv (\mathbf{\Gamma})_{\rm unc}\cdot(\gamma^{(3)}[\beta]_{\rm cor}\cdot((\mathbf{\Gamma}^t)_{\rm unc}\cdot)^{\otimes 3})\ , \quad (5.61)$$

are due to correlative effects from the linear factors $\mathbf{\Gamma}$, $\mathbf{\Gamma}^t$, $\mathbf{K}_0$, and $\mathbf{K}_0^t$ that correct the third-order polarizabilities. Thus if the molecular third-order polarizabilities are less important than those of second order, then $\chi^{(3)}_{\rm int}$ consists of just the local-field-corrected cascading terms.

A similar analysis can be carried out with the cascading part of $\chi^{(3)}$, namely,

$$\chi^{(3)}_{\rm cas} = (\chi^{(3)}_{\rm cas})_{\rm unc} + (\chi^{(3)}_{\rm cas})_{\rm cor}\ , \quad (5.62)$$

where

$$(\chi^{(3)}_{\rm cas})_{\rm unc} \equiv \chi^{(3)}_{\rm cas}[\beta] = \sum_m \chi^{(2)}_{\rm unc}\cdot\{(\mathbf{F}_\epsilon)_{\rm unc}\cdot\chi^{(2)}_{\rm unc}\}_m\ , \quad (5.63)$$

$$(\chi^{(3)}_{\rm cas})_{\rm cor} \equiv \chi^{(3)}_{\rm cas}[\beta_0] = \sum_m [\chi^{(2)}_{\rm unc}\cdot\{(\mathbf{F}_\epsilon)_{\rm cor}\cdot\chi^{(2)}_{\rm unc}\}_m + \chi^{(2)}_{\rm cor}\cdot\{(\mathbf{F}_\epsilon)_{\rm unc}\cdot\chi^{(2)}_{\rm unc}\}_m + \chi^{(2)}_{\rm unc}\cdot\{(\mathbf{F}_\epsilon)_{\rm unc}\cdot\chi^{(2)}_{\rm cor}\}_m]\ , \quad (5.64)$$

$$(\mathbf{F}_\epsilon)_{\rm unc} = [\mathbf{f}_\epsilon\cdot]^{-1}(\mathbf{K}_0^t)_{\rm unc}\cdot\mathbf{F} = \mathbf{F}\cdot(\mathbf{K}_0)_{\rm unc}\cdot[\mathbf{f}_\epsilon]^{-1}\ , \quad (5.65)$$

$$(\mathbf{F}_\epsilon)_{\rm cor} = -(\mathbf{F}_\epsilon)_{\rm unc}\cdot\chi^{(1)}_{\rm cor}\cdot(\mathbf{F}_\epsilon)_{\rm unc} = \mathbf{F}\cdot(\mathbf{K}_0)_{\rm unc}\cdot\mathbf{C}^{(1)}\cdot(\mathbf{K}_0^t)_{\rm unc}\cdot\mathbf{F}\ . \quad (5.66)$$

We can now identify the β media limit parts of $\chi^{(3)}$:

$$\chi^{(3)}[\beta] \equiv \chi^{(3)}_{\rm int}[\beta] + \chi^{(3)}_{\rm cas}[\beta]\ , \quad (5.67)$$

where $\chi^{(3)}_{\rm int}[\beta]$ is the sum of (5.59) and (5.61).

The susceptibilities $\xi^{(3)}$ with corrections due to correlations follow immediately. One finds that

$$\xi^{(3)}=\xi^{(3)}_{\rm unc}+\xi^{(3)}_{\rm cor} , \qquad (5.68)$$

where $\xi^{(3)}_{\rm unc}$ is defined by Eqs. (5.15) and (5.16) and the correlative part is

$$\xi^{(3)}_{\rm cor}\cdot=(\gamma^{(3)}[\beta]_{\rm cor}+\gamma^{(3)}_{\rm cas}[\beta_0])\cdot((\mathbf{\Gamma}^t)_{\rm unc}\cdot)^{\otimes 3}-\gamma^{(3)}_{\rm unc}\cdot([(\mathbf{\Gamma}^t)_{\rm unc}\cdot]^{\otimes 2}([(\mathbf{K}^t_0)_{\rm unc}]^{-1}\cdot\mathbf{D}^{(1)}\cdot)+\not{h}) . \qquad (5.69)$$

Finally, we group together all of the terms in $\xi^{(3)}$ that can be associated with cascading:

$$\xi^{(3)}_{\rm cas}\cdot\equiv(\gamma^{(3)}[\beta]+\gamma^{(3)}_{\rm cas}[\beta_0])\cdot((\mathbf{\Gamma}^t)_{\rm unc}\cdot)^{\otimes 3}-\gamma^{(3)}[\beta]_{\rm unc}\cdot([(\mathbf{\Gamma}^t)_{\rm unc}\cdot]^{\otimes 2}([(\mathbf{K}^t_0)_{\rm unc}]^{-1}\cdot\mathbf{D}^{(1)}\cdot)+\not{h}) . \qquad (5.70)$$

For the sake of consistency it is important to note that [cf. Ref. [39] and Eq. (A9)]

$$(\xi^{(3)}_{\rm cas})_{\rm unc}\cdot\equiv(\gamma^{(3)}[\beta]_{\rm unc})\cdot((\mathbf{\Gamma}^t)_{\rm unc}\cdot)^{\otimes 3} ,$$
$$=(\xi^{(3)}_{\rm unc})_{\rm cas}\cdot , \qquad (5.71)$$

where $(\xi^{(3)}_{\rm unc})_{\rm cas}$ is from (5.16b) and $\gamma^{(3)}[\beta]_{\rm unc}$ is the uncorrelated part of (5.54).

Equation (5.70) is the major result of this paper. It incorporates all of our new results on local-field and correlative corrections along with our analysis of β media. Since, as Bloembergen and co-workers [12, 14] have argued, the $\mathbf{E}_{\rm L}$-based susceptibilities $\xi^{(n)}$, $n\geq 2$ can be conveniently associated with the nth order signals in a nonlinear dielectric, Eq. (5.70) represents a definitive starting point for the quantitative analysis of the effects of pair correlations on cascading in dielectric fluids.

VI. SUMMARY AND CONCLUSIONS

We have presented a detailed development of cascading from several points of view. Our major objectives were to clarify the relationship between the seemingly different characterizations of this phenomenon that have appeared in the literature and to determine the dependence of cascading on pair correlations.

The susceptibility formalism is investigated by comparing expansions of the polarization with respect to the external, macroscopic, and linearly modified fields. Each of these expansions is particularly relevant for different applications and examples are given in each case. The identifications of cascading and local-field effects are shown to depend significantly on the choice of expansion of the polarization.

Cascading in its simplest context is investigated by means of the model of β media in which there is no linear molecular polarizability and only second-order hyperpolarizabilities. This leads to the identification of irreducible cascading coefficients that depend only on the one- and two-particle distribution functions along with various singularity-regulated electromagnetic propagators. The detailed numerical investigation of these coefficients should provide valuable insight as to the magnitudes of cascading in various materials and its dependence on pair correlations, the near- and far-zone electric fields, the density, and the temperature.

General media are studied using a microscopic model for calculating the macroscopic polarization in terms of the microscopic hyperpolarizabilities from first to third order. A systematic approach is developed for calculating the lowest-order pair-correlation effects on the susceptibilities, and, in particular, on the cascading. The modifications due to pair correlations of the usual linear local-field corrections are found.

The connection of cascading to the method of local-field corrections is established. This is done by recognizing that cascading consists of the terms that are usually ignored in correcting the third- and higher-order hyperpolarizabilities for local-field effects. When this correction procedure is carried out consistently, cascading terms appear naturally.

The relative contribution of the correlative cascading terms is most easily seen by considering the results of Sec. IV dealing with β media. One need compare the value of the intrinsic (scalar) $\chi^{(3)}$ with those of both the correlated and uncorrelated contributions. We can roughly approximate these as:

$$(\chi^{(3)}_{\rm int})_{\rm unc}\approx(\rho/\Omega)\alpha^{(3)} ,$$
$$(\chi^{(3)}_{\rm cas})_{\rm unc}\approx(\rho/\Omega)^2(\alpha^{(2)})^2 ,$$
$$(\chi^{(3)}_{\rm cas})_{\rm cor}\approx-(\rho/\Omega)^2(\alpha^{(2)})^2 g_2 h .$$

For a typical organic molecule possessing a large value of $\alpha^{(2)}$ of 10^{-28} esu and an $\alpha^{(3)}$ of 10^{-34} esu at a density of $10^{22}/{\rm cm}^3$, all three terms will be of comparable magnitude. The propagator h will be of order unity, and in materials of interest, so too will g_2. Both cascading contributions will be most apparent at high density due to the $(\rho/\Omega)^2$ dependence. This dependence, of course, could be employed to separate the cascading contributions to third-order processes. The sign difference implies that the correlated and uncorrelated parts tend to cancel. This can be explored by measuring a dense, large-$\alpha^{(2)}$ material in temperature regimes where the correlations are rapidly varying.

The results of this paper provide a basis for the quantitative numerical and experimental study of pair-correlation contributions to linear and nonlinear susceptibilities including cascaded processes in the third-order susceptibility. Pair-correlated cascaded processes may make significant contributions to third-order nonlinearities in dense dipolar material. Since such materials are already of interest due to enhanced intrinsic third-order nonlinearities, these studies may have important practical implications. Work in this direction is now in progress and is planned to be reported elsewhere. Additionally, experimental work to study pair-correlations contributions to cascaded nonlinearities is in progress and is also planned to be reported elsewhere.

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APPENDIX

We establish how the $\chi^{(n)}_{\rm unc}$'s follow directly from the uncorrelated limit of the ensemble-averaged susceptibilities. To do this we require the identities

$$(\mathbf{\Gamma})_{\rm unc}\cdot(\mathbf{K}_0)_{\rm unc}=(\mathbf{K}_0^t)_{\rm unc}\cdot(\mathbf{\Gamma}^t)_{\rm unc}=\mathbf{f}_\epsilon \ , \tag{A1}$$

$$(\mathbf{K}_0)_{\rm unc}\equiv(\mathbf{U}+\langle\rho\rangle\boldsymbol{\alpha}^{(1)}\cdot\mathbf{H})^{-1} \ , \tag{A2}$$

$$(\mathbf{K}_0^t)_{\rm unc}\equiv(\mathbf{U}+\mathbf{H}\cdot\langle\rho\rangle\boldsymbol{\alpha}^{(1)})^{-1} \ , \tag{A3}$$

$$(\mathbf{\Gamma})_{\rm unc}\equiv(\mathbf{U}-\boldsymbol{\gamma}^{(1)}_{\rm unc}\cdot\mathbf{F})^{-1} \ , \tag{A4}$$

$$(\mathbf{\Gamma}^t)_{\rm unc}\equiv(\mathbf{U}-\mathbf{F}\cdot\boldsymbol{\gamma}^{(1)}_{\rm unc})^{-1} \ , \tag{A5}$$

and

$$\boldsymbol{\gamma}^{(1)}_{\rm unc}\equiv(\mathbf{K}_0)_{\rm unc}\cdot\langle\rho\rangle\boldsymbol{\alpha}^{(1)} \ . \tag{A6}$$

For example, from Eqs. (2.12) and (3.20) we have

$$\boldsymbol{\chi}^{(1)}_{\rm unc}=(\mathbf{\Gamma})_{\rm unc}\cdot\boldsymbol{\gamma}^{(1)}_{\rm unc}=\boldsymbol{\gamma}^{(1)}_{\rm unc}\cdot(\mathbf{\Gamma}^t)_{\rm unc} \ , \tag{A7}$$

which with (A4) and (A6) yields (5.4a). Equation (5.7) is obtained in much the same manner from Eqs. (2.16) and (3.20), but the recovery of Eqs. (5.8)–(5.10) requires the identity

$$\begin{aligned}\mathbf{H}_\epsilon&\equiv(\mathbf{F}_\epsilon)_{\rm unc}-\mathbf{G}_\epsilon\\&=(\mathbf{f}_\epsilon)^{-1}\cdot(\mathbf{K}_0^t)_{\rm unc}\cdot(\mathbf{H}_K)_{\rm unc}\cdot(\mathbf{K}_0)_{\rm unc}\cdot(\mathbf{f}_\epsilon)^{-1} \ ,\end{aligned} \tag{A8}$$

where $(\mathbf{H}_K)_{\rm unc}$ is the uncorrelated limit of (3.19).

We note that an important consequence of (A1) and (A8) is the consistency condition

$$(\boldsymbol{\chi}^{(3)}_{\rm unc})_{\rm cas}\cdot=(\boldsymbol{\chi}^{(3)}_{\rm cas})_{\rm unc}\cdot+(\mathbf{\Gamma})_{\rm unc}\cdot((\boldsymbol{\gamma}^{(3)}_{\rm cas})_{\rm unc}\cdot((\mathbf{\Gamma}^t)_{\rm unc}\cdot)^{\otimes 3}) \ , \tag{A9}$$

where $(\boldsymbol{\chi}^{(3)}_{\rm unc})_{\rm cas}$ is defined by Eq. (5.10) and the second term on the right-hand side is the uncorrelated part of $\chi^{(3)}_{\rm int}$ that can be identified with cascading. This should be contrasted with the consistency condition (5.71).

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[30] Equations (2.1) and (2.2) illustrate our conventions for the contractions of tensor indices with respect to vectors. Generally, the component-free form of any Cartesian tensor, including a vector, is denoted by boldface; a dot indicates successive contractions with respect to a sequence of vectors that are each enclosed in parentheses; nested parentheses around contracted vectors represent sequential dot operations; and in x space the dot also includes the operation of an intermediate space-time integration when the tensor has an operator character such as **F**.

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[36] The extensions to include more than one species of particle and possibly polar molecules are necessary to encompass many interesting physical situations. If the polarizabilities are simply additive, additional species are easily accommodated into the formalism as applied to uniform mixtures with an additional index that we have chosen to suppress for the sake of simplicity. On the other hand, the inclusion of polar molecules in more complicated.

[37] We express our thanks to M. Kuzyk for several discussions concerning this model.

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