PHYSICAL REVIEW E, VOLUME 65, 061102

Generalized Langevin equation approach to higher-order classical response: Second-order-response time-resolved Raman experiment in CS_2

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(Received 30 November 2001; published 12 June 2002)

A simple, systematic generalized Langevin equation approach for calculating classical nonlinear response functions is formulated and discussed. The two-time Poisson brackets appearing at second and higher order are rendered tractable by a physically motivated approximation. The method is used to calculate the fifth order (second order response) Raman response of liquid CS_2. Agreement with simulation is good, but the simplicity of the theoretical expression suggests that the path to obtaining qualitatively new information about liquids with the fifth order experiment is uncertain. Further applications of the basic approach are suggested.

DOI: 10.1103/PhysRevE.65.061102 PACS number(s): 05.20.−y, 78.47.+p, 61.20.Lc

I. INTRODUCTION

Quantum response functions are averages of nested commutators of variables at different times [1,2]. The perturbing Hamiltonian H' is a product of an interaction dynamical variable and the external fields. The observable that is calculated has the latest time argument, and the interaction variable appears at each time the external fields act. One route to the classical limit is replacing the commutators with Poisson brackets. The linear response is easily reexpressed as a time correlation function, but Poisson brackets of variables at different times cannot be avoided in higher order.

Recently there has been great theoretical [2–10] and experimental [11–14] effort directed towards the fifth order Raman experiment in liquids. The perturbation is the interaction of a pair of pulsed electric fields with the total system polarizability tensor $\mathbf{\Pi}$,

$$H' = E_a \Pi^{ab} E_b, \tag{1}$$

where a and b are the polarization directions. ''Fifth order'' refers to the four pulses in the two factors of H' appearing in second order response, and the fifth pulse that probes the response, the nonequilibrium refractive index. The pulse pairs act at times zero and t_1, the probe at $t_1 + t_2$. The refractive index is also an element of $\mathbf{\Pi}$ and so

$$R^{(5)}(t_1,t_2) = \langle [[\Pi^{ab}(t_1+t_2),\Pi^{cd}(t_1)],\Pi^{ef}(0)] \rangle, \tag{2}$$

with directions a–e determined by the experimental geometry. The Poisson bracket for any variables A and B, in units such that mass $m=1$ and energy is in Kelvin, is

$$[A,B] = \sum_{i=1}^{3N} \left(\frac{dA}{dx_i}\frac{dB}{dv_i} - \frac{dB}{dx_i}\frac{dA}{dv_i} \right), \tag{3}$$

where x and v are atomic positions and velocities, and the index i denotes both atom number and Cartesian direction. The brackets in $R^{(5)}$ require the derivatives of Π at later times with respect to coordinates at time zero; we use Π to indicate an unspecified element of $\mathbf{\Pi}$. Little theory exists for dealing with such objects, but they must be mastered if the fifth and higher-order experiments are to yield any information about liquids.

The original motivation for the Tanimura-Mukamel fifth order experiment [3,11] rests upon a normal mode picture. If vibrational intermolecular modes exist in liquids, at least at short to intermediate times, then the third order (linear) response function $R^{(3)}(t)$, a familiar time correlation function, receives contributions from all the modes. This constitutes inhomogeneous broadening, which cannot be distinguished from mode lifetime effects in $R^{(3)}(t)$. The idea was that in fifth order the two pulse pairs separated by t_1 would select modes of period t_1, which could then be probed to determine homogeneous decay only. The signature of well defined modes is an echo in $R^{(5)}$ at $t_1 = t_2$. Tanimura and Mukamel [3] gave a theory based on the [15] quantum multi mode Brownian oscillator model, in which the ''system'' mode, representing vibrational motion coupled to the polarizability, is coupled to damped bath oscillators. Their approach has some similarities to the classical theory developed herein, but there are also some obvious differences; it will be interesting to work out the relation of the two appoaches.

A discussions of modes in liquids naturally suggests [16,17] instantaneous normal modes (INM), and an INM calculation of $R^{(5)}$ was given by Saito and Ohmine (SO) [2]. In both CS_2 and water they found strong echos in a first approximation which were washed out in a more complete calculation. The problem is that Π is a nonlinear function of the normal coordinates and can provide enough mode mixing that the experiment does *not* pick out modes with a single frequency. Keyes and Fourkas [6] gave the first completely consistent INM theory and presented a general INM approach to more complicated dynamical quantities, e.g., nonlinear response functions. Ma and Stratt [8] found that INM did predict an echo in liquid Xe, but a computer simulation had no echo and decayed very quickly, over a few hundred femtoseconds. These authors have recently attempted to add anharmonicity to the harmonic INM theory to provide the evident damping of the harmonic modes.

INM calculations of $R^{(5)}$ are straightforward because the harmonic oscillator equations yield simple, explicit expressions for $x(t)$ and $v(t)$ in terms of $x(0)$ and $v(0)$. Thus, a

Poisson bracket of form $[\Pi(t),\Pi(0)]$ presents no special difficulty; $\Pi(t)$ is expanded as a Taylor series in the normal coordinates $q_\alpha(t)=\Sigma_{i=1}^{3N}e(\alpha,i)x_i(t)$, $x_i(t)$ is expressed in terms of all $\{x(0),v(0)\}$, and the derivatives in Eq. (3) with respect to $x_i(0)$ and $v_i(0)$ are easily evaluated. The polarizability is a function of the instantaneous positions only. In general, however, the time-dependent brackets create an enormous theoretical difficulty. There exists no systematic framework for generating approximations to $R^{(5)}$. Contrast this to the situation for time correlation functions with a single time argument, where one finds a host of techniques to choose from. Perhaps the greatest flexibility (sometimes unfortunately) is provided [18–20] by the generalized Langevin equation (GLE). The GLE describes the time evolution of dynamical variables A obeying Newton's equations, expressed formally with the Liouville operator $dA/dt=i\mathcal{L}A$. However, the components of time-dependent brackets do *not* follow Liouvillian dynamics; $(d/dt)(dA(t)/dx(0))=(d/dx(0))i\mathcal{L}A(t)$, and $i\mathcal{L}$ does not commute with $d/dx(0)$.

The matrix $d(\{x(t),v(t)\})/d(\{x(0),v(0)\})$ obeys its own equation governed by the "dynamical matrix," the instaneous Hessian, and this may potentially be used as the starting point for a GLE-like theory of correlations involving the *t*-dependent brackets. Denny and Reichman [9] have given a calculation of $R^{(5)}$ in Xe which circumvents the brackets altogether, and also gives good agreement with simulation. In atomic fluids, to leading order in the dipole-induced dipole expansion, $\mathbf{\Pi}$ can be expressed with a product of density operators and so the commutators in the quantum $R^{(5)}$ expand to yield four time-ordered quantum correlations of six density operators. Making a Gaussian approximation on the quantum correlations and expressing the resulting correlations of two density operators as classical density correlations with a quantum correction, an eminently simple classical limit is obtained without ever introducing Poisson brackets. This approach is very promising, although so far it requires the special form of $\mathbf{\Pi}$ in atomic fluids.

While some progress has been made, the current theories of $R^{(5)}$ are disjoint. It is not possible to calculate $R^{(n)}, n\geqslant 5$, with the same ease and systematic framework afforded by the GLE for familiar two-variable, one-time correlation functions. Thus we now give a theory of classical nonlinear response functions based upon the GLE.

II. GENERALIZED LANGEVIN EQUATION APPROACH TO NONLINEAR RESPONSE

A. Basic ideas

The GLE for a set of variables $\{A\}$ is

$$\frac{dA_\alpha(t)}{dt}=\int_0^t ds\, M_{\alpha\beta}(t-s)A_\beta(s)+I_\alpha(t) \tag{4}$$

with the solution

$$A_\alpha(t)=G_{\alpha\beta}(t)A_\beta(0)+\int_0^t ds\, G_{\alpha\beta}(t-s)I_\beta(s), \tag{5}$$

where the propagator $G(t)$ is the solution to the homogeneous equation, I is the random force, and

$$M(t)=(\langle\dot{A}A^*\rangle\delta(t)-\langle I(t)I^*(0)\rangle)\langle AA^*\rangle^{-1}. \tag{6}$$

The equilibrium averages $\langle\rangle$, M and G are matrices, and A and I are vectors, in the space of the dynamical variables. We will omit the indices where the usage seems evident, and sums over repeated indices are implicit. Different derivations give different expressons for the random force. In Mori's formalism [18] it evolves via the projected operator $(1-P)i\mathcal{L}$, $I(t)=e^{(1-P)i\mathcal{L}t}I(0)$, where $1-P$ projects orthogonal to $\{A\}$ and its complement P projects onto $\{A\}$; $PB=\langle BA^*\rangle\langle AA^*\rangle^{-1}A$. In the approach [19,20] of Oppenheim and co-workers $I(t)$ follows true dynamics and P is defined with the matrix M. In either case, a crucial property of the random force, which indeed expresses in part what is meant by "random," is $\langle I(t)A^*(0)\rangle=0, t\geqslant 0$. It follows that the matrix of correlation functions, $C(t)\equiv\langle A(t)A^*(0)\rangle$, obeys

$$C_{\alpha\beta}(t)=G_{\alpha\gamma}(t)\langle A_\gamma A^*_\beta\rangle. \tag{7}$$

The most careful, systematic use of the GLE is based on the idea that, since the random force is orthogonal to $A(0)$, it must lack any property poesessed by the $\{A\}$. Oppenheim and co-workers have argued accordingly [19,20] that when $\{A\}=\{Q\}$, where $\{Q\}$ is the set of *all multilinear products* of the hydrodynamic conserved variables, $I(t)$ must be "fast," decaying on a molecular time scale, and all explicit slow time dependence is contained in the first term on the right-hand side (RHS) of Eq. (5). It is also possible to use the GLE to construct correlation functions which, though approximate, possess a specified number of terms in the exact short-time expansion. In addition an enormous number of uncontrolled, but often useful, theories have been based upon *ad hoc* choices of $\{A\}$ and modeling of the random force correlation.

Since the third-order (linear) response function reduces to an ordinary correlation function, the GLE may be used without difficulty to predict and interpret conventional spectra. Indeed, it is a cornerstone of such research. The situation is far less clear, however, for more complicated dynamical quantities. Consider a correlation of three variables with (by time translation invariance) two time arguments, $C(t_2,t_1)\equiv\langle A(t_1+t_2)A(t_1)A^*(0)\rangle$, which is *far simpler* than the average of nested time-dependent brackets in Eq. (2). One might begin by expressing the two time-dependent variables with the solution of the GLE, Eq. (5). A sum of terms containing zero, one, and two random forces results. When seeking the long time behavior of $C(t_2,t_1)$ one is tempted to simply discard the random forces as fast variables. This is valid for the one-force terms. However, Schramm and Oppenheim showed [20] that a product $I(s)I(s')$ *behaved as a hydrodynamic slow variable* for $s\sim s'$. In evaluating $C(t_2,t_1)$ with the GLE both random forces are integrated over the interval $(0,t_1)$, and an important slow contribution arises from $t_1\geqslant s\sim s'\geqslant 0$.

Given the power of the GLE, it is compelling to apply it to $R^{(5)}$. Substituting Eq. (5) into Eq. (2), a desirable result immediately emerges; the first term on the RHS of Eq. (5) expresses the time-dependent variables in terms of their zero-time values, allowing evaluation of the Poisson brackets. However, brackets also appear now of random forces at different times. The work of Schramm and Oppenheim [20] on the simpler two-time correlation indicates that these brackets cannot be neglected. Perhaps an extension of their work can be formulated for the problem at hand. However, we will now take another tack, to rewrite $R^{(5)}$ such that the random forces *can*, to a good approximation, be ignored. The intractable contributions arise from a product of random forces which have similar time arguments; so, keep the forces well separated in time. Time-translational invariance is easily demonstrated for the quantum Heisenberg representation of $R^{(5)}$. Subtracting t_1 from the time argument of each variable and then taking the classical limit

$$R^{(5)}(t_1,t_2)=\langle[[\Pi^{ab}(t_2),\Pi^{cd}(0)],\Pi^{ef}(-t_1)]\rangle. \tag{8}$$

We will now use the GLE to propagate Π^{ab} forward from zero to t_2 and Π^{ef} backward from zero to $-t_1$, and their random forces cannot overlap except for $s\sim s'\sim 0$. Consequently, the random force contribution to Eq. (8) should be negligible at long time; this argument, applied to two-time correlations, is due to van Zon and Schofield [21]. For a good short time theory we will construct a GLE with random forces that vanish at short time, effectively eliminating the remaining "overlap."

The indicated procedure immediately yields

$$\begin{aligned}R^{(5)}(t_1,t_2)&=G_{\pi\alpha}(t_2)G_{\pi\beta}(-t_1)\langle[[A_\alpha,\Pi],A_\beta]\rangle\\&=\left(\frac{-1}{T}\right)G_{\pi\alpha}(t_2)G_{\pi\beta}(-t_1)\langle[A_\alpha,\Pi]\dot{A}_\beta\rangle,\end{aligned} \tag{9}$$

where the second equality is obtained with partial integration and the properties of the equilibrium distribution function; it is understood that Π^{ab} is on the left and Π^{ef} on the right, and energy is in Kelvin. We will use the second equality for actual calculations, defining the coupling coefficients $c^{(5)}_{\alpha\beta}$ as

$$c^{(5)}_{\alpha\beta}=\langle[A_\alpha,\Pi]\dot{A}_\beta\rangle. \tag{10}$$

Equation (9) represents an extraordinary simplification, with time-dependent brackets eliminated altogether. Similar results are easily obtained for higher-order response functions. To complete the approach we choose as a basis set Π and its time derivatives up to the nth derivative, for the nth approximation to the theory. When the time derivatives are included in the basis set they appear explicitly in the first, systematic term on the RHS of the solution of the GLE, Eq. (5), and this term will express the exact time expansion out to the nth power. So long as that truncation of the expansion is accurate the random force must be zero. By increasing n we can increase the interval around zero of vanishing random force and satisfy the condition of no overlap better and better. For the same reason the nth approximation, denoted $R^{(5)}_n$, reproduces the exact [6] time expansion to the nth order in combined powers of t_1 and t_2. Note that calculating a conventional time correlation function with this basis set reproduces the time expansion out to the $(2n)$th power.

The tensorial nature of $\mathbf{\Pi}$ causes a further complication. A GLE representation of $\Pi^{ab}(t)$ based on our idea should include all the irreducible tensorial components of $\Pi^{ab}(t)$ and its derivatives. For, e.g., $\Pi^{zz}(t)$ that means both the trace (isotropic) and second-rank (anisotropic) parts enter separately, and in the nth approximation $\{A\}$ contains $2(n+1)$ variables. In this paper for simplicity we will treat $\Pi^{ab}(t)$ and its derivatives as single variables. The anisotropic polarizability is much larger than the isotropic polarizability in the model to be used in our calculations on CS_2, the [22] point atomic polarizability approximation including first-order intermolecular dipole-induced dipole terms. Using the smaller basis set will make little difference for polarizations where both $\Pi^{ab}(t_2)$ and $\Pi^{ef}(-t_1)$ are dominated by the larger second rank part. This includes "fully polarized" $zzzzzz$ and "depolarized" $xzxzxz$ but definitely not $zzzzmm$, as the "magic angle" polarization is explicitly chosen to enhance the contribution of the isotropic polarizability.

B. Zero, first, and second order approximations

There is no zero order theory; with Π as the only variable the coupling coefficient $c^{(5)}_{\pi\pi}$ contains $[\Pi,\Pi]=0$ and $R^{(5)}_0=0$. In general, $c^{(5)}_{\pi\beta}=0$. The first approximation corresponds to the basis set $\{\Pi,\dot{\Pi}\}$. The theory is sensitive to polarization through $c^{(5)}_{\alpha\beta}$ and through the different propagators which represent different components of $\mathbf{\Pi}$ in the GLE; the fifth-order signal has [4,5,10,11,13] a strong polarization dependence. Consider now some properties of $c^{(5)}_{\alpha\beta}$. A quantity must be even in the velocities to have a nonzero average. The operations d/dt and $[,]$ in $c^{(5)}_{\alpha\beta}$ each reverse the velocity parity, which thus remains identical to that of the product $A_\alpha A_\beta$. The polarizability Π is even (function of positions only) and each successive derivative reverses the parity. It follows that (also using $c^{(5)}_{\pi\alpha}=0$) the first approximation has one contribution

$$R^{(5)}_1(t_2,t_1)=\left(\frac{-1}{T}\right)c^{(5)}_{\dot{\pi}\dot{\pi}}G_{\pi\dot{\pi}}(t_2)G_{\pi\dot{\pi}}(-t_1). \tag{11}$$

The averages required for $c^{(5)}_{\alpha\beta}$ may be expressed straightforwardly, albeit tediously in some cases, with the techniques described in Ref. [6]. There is no difficulty with $c^{(5)}_{\dot{\pi}\dot{\pi}}$,

$$c^{(5)}_{\dot{\pi}\dot{\pi}}=T(\langle\Pi''_{ij}\Pi'_i\Pi'_j\rangle+\langle\Pi'_i\Pi''_{ij}\Pi'_j\rangle), \tag{12}$$

where Π'_i can denote either the derivative with respect to the ith atomic or molecular position or the ith INM normal coordinate. Our approach will be to express the propagators in terms of the computationally convenient correlation functions $C_{\alpha\beta}(t)$ with Eq. (7). We will not attempt a GLE approximation to $C_{\alpha\beta}(t)$ but take the viewpoint that, if we used the exact M matrix we would obtain the exact correlation function. The GLE is employed to express $R^{(5)}$ in terms of conventional correlation functions, not to calculate them. At first approximation the relation between G and C is simple since the matrix $\langle AA^*\rangle$ is diagonal,

$$G_{\pi\dot{\pi}}(t)=C_{\pi\dot{\pi}}(t)/\langle(\dot{\Pi})^2\rangle. \tag{13}$$

Combining these results and noting that $G_{\pi\dot{\pi}}(t)$ is an odd function of t,

$$R_1^{(5)}(t_2,t_1)=(\langle\Pi''_{ij}\Pi'_i\Pi'_j\rangle+\langle\Pi'_i\Pi''_{ij}\Pi'_j\rangle)\times\frac{C_{\pi\dot{\pi}}(t_2)C_{\pi\dot{\pi}}(t_1)}{\langle(\dot{\Pi})^2\rangle^2}. \tag{14}$$

The remarkable aspect of Eq. (14) is that, since the third-order response $R^{(3)}(t)$ is $(1/T)C_{\pi\dot{\pi}}(t)$, we have the result

$$R_1^{(5)}(t_2,t_1)\propto R^{(3)}(t_2)R^{(3)}(t_1). \tag{15}$$

Equation (15) is a remarkably good approximation, in much better agreement with simulation than INM for [10,7] CS_2 and [8] Xe. The peak in $R^{(3)}(t)$ provides a good estimate for the distance from the origin of the peak in $R^{(5)}(t_2,t_1)$. In a recent simulation paper SO [10] write "the peak maxima of R_{zzzzzz}, R_{yzzzyz}, and R_{zzmmzz} are all located at (~ 0.1 ps, ~ 0.1 ps), which is slightly shifted from the peak maximum position, ~ 0.14 ps, of the third order response functions ...." Our theory shows the fundamental underpinning of this observation. Although $R_1^{(5)}$ is not the whole story by far, we do *roughly* expect that $R^{(5)}$ will relax on the time scale of $R^{(3)}$ (somewhat faster in CS_2). Unfortunately, the implications are negative for the utility of the fifth order experiment. It is necessary [11,13] to remove the strong "cascade" from the experimental signal to isolate $R^{(5)}$. The cascade is expressed as a product of two $R^{(3)}$, and now $R^{(5)}$ itself is seen to be, approximately, a product of two $R^{(3)}$.

In Xe [8] $R^{(3)}$ peaks at a little over 0.20 ps and $R^{(5)}_{zzzzzz}$ near (0, 0.30), that is, strongly skewed towards the t_2 axis. There is a fundamental t_1,t_2 asymmetry in $R^{(5)}$ which is missed in the symmetric $R_1^{(5)}$. At $t_2=0$ [Eq. (8)] $R^{(5)}$ contains a same-time $[\Pi,\Pi]=0$ and vanishes on the t_1 axis; however, it need not vanish away from the origin on the t_2 axis. Our first approximation cannot describe, beyond getting a rough estimate of the distance of the peak from the origin, a system where the asymmetry is pronounced. On the other hand, in CS_2 $R^{(5)}_{zzzzzz}$ is [10] sufficiently symmetric that $R_1^{(5)}$ is a reasonable description. Of course we must include the asymmetry, an essential feature, and this can be found in the second approximation with the basis set $\{\Pi,\dot{\Pi},\ddot{\Pi}\}$. When used to calculate the correlation function alone [26] this basis produces a rich description, with the capability of describing either rotational diffusion or the solidlike librations plus large reorientational jumps found in supercooled liquids.

The nonzero couplings are $c^{(5)}_{\dot{\pi}\dot{\pi}}$ [Eq. (12)], $c^{(5)}_{\ddot{\pi}\pi}$, and $c^{(5)}_{\ddot{\pi}\ddot{\pi}}$,

$$c^{(5)}_{\ddot{\pi}\pi}=-2T\langle\Pi''_{ij}\Pi'_i\Pi'_j\rangle, \tag{16}$$

$$c^{(5)}_{\ddot{\pi}\ddot{\pi}}=6T^2(\langle\Pi'''_{ijk}\Pi'_j\Pi''_{ik}\rangle+\langle\Pi''_{ij}\Pi''_{jk}\Pi''_{ik}\rangle)-2T\left\langle\Pi''_{ij}\Pi'_j\Pi'_k\frac{dF_k}{dr_i}\right\rangle, \tag{17}$$

where F_k is the force on coordinate k. The coefficients grow in complexity according to the total number of time derivatives in the subscripts. Both $c^{(5)}_{\dot{\pi}\dot{\pi}}$ and $c^{(5)}_{\ddot{\pi}\pi}$ have two derivatives and similar expressions, proportional to averages of three factors of Π containing a total of four position derivatives. Such averages determine the contribution to the INM theory that SO [2] named $R^{(5,1)}$. Accordingly, let the sum of all contributions to $R_2^{(5)}$ with $2m$ time derivatives in the coefficients be denoted $R^{(5)}_{2,m}$. Then $R_2^{(5)}=R^{(5)}_{2,1}+R^{(5)}_{2,2}$ and $R^{(5)}_{2,1}$ is related to $R^{(5,1)}$. More spatial derivatives enter $R^{(5)}_{2,2}$ and, through dF_k/dr_i, the first sign [6,8] of what would be anharmonicity in an INM picture. Of course, unlike INM, the exact correlation functions we use to express $R_2^{(5)}$ are fully anharmonic.

Expressing the propagators in terms of the correlation functions now requires a small amount of algebra; the matrix $\langle AA^*\rangle$ is no longer diagonal since $\langle\Pi\ddot{\Pi}\rangle\neq 0$. The result is

$$\begin{aligned}R^{(5)}_{2,1}(t_2,t_1)&=\left[(\langle\Pi''_{ij}\Pi'_i\Pi'_j\rangle+\langle\Pi'_i\Pi''_{ij}\Pi'_j\rangle)\frac{C_{\pi\dot{\pi}}(t_2)C_{\pi\dot{\pi}}(t_1)}{\langle(\dot{\Pi})^2\rangle^2}\right]\\&\quad+\left[\frac{2\langle\Pi''_{ij}\Pi'_i\Pi'_j\rangle}{[1-(\omega_1^2/\omega_2^2)]^2}\left(\frac{\omega_1^2C_{\pi\pi}(t_2)-C_{\dot{\pi}\dot{\pi}}(t_2)}{\langle\ddot{\Pi}^2\rangle}\times\frac{C_{\pi\pi}(t_1)-\dfrac{1}{\omega_2^2}C_{\dot{\pi}\dot{\pi}}(t_1)}{\langle\Pi^2\rangle}\right)\right],\end{aligned} \tag{18}$$

$$R^{(5)}_{2,2}(t_2,t_1)=\frac{-c^{(5)}_{\ddot{\pi}\ddot{\pi}}}{T[1-(\omega_1^2/\omega_2^2)]^2}\times\left(\frac{\omega_1^2C_{\pi\pi}(t_2)-C_{\dot{\pi}\dot{\pi}}(t_2)}{\langle\ddot{\Pi}^2\rangle}\times\frac{\omega_1^2C_{\pi\pi}(t_1)-C_{\dot{\pi}\dot{\pi}}(t_1)}{\langle\ddot{\Pi}^2\rangle}\right), \tag{19}$$

where $\omega_1^2=\langle\dot{\Pi}^2\rangle/\langle\Pi^2\rangle$ and $\omega_2^2=\langle\ddot{\Pi}^2\rangle/\langle\dot{\Pi}^2\rangle$. In the remainder of the paper we will discuss $R^{(5)}_{2,1}$, which SO [2] found to be dominant in INM theory. For that reason, and for others to be explained below, $R^{(5)}_{2,1}$ is a plausible approximation. There is actually some [4] evidence that $R^{(5)}_{2,2}$ is significant. Its evaluation requires some averages which, while nothing like a time-dependent Poisson bracket, are computationally difficult and will be presented in future work. The aim here is to demonstrate our theory with the simplest full-featured approximation.

The first square bracket on the RHS of Eq. (18) is just $R_1^{(5)}$, symmetric in (t_1,t_2) as described previously. To this is added the second square bracket, from the $(\pi,\ddot{\pi})$ coupling, which is quite different. It is easy to verify that the correct, exact time expansion of $R^{(5)}$ to second order results. The t_2 dependence of the second bracket, via $G_{\pi\ddot{\pi}}(t_2)$, is a combination of $C_{\pi\pi}(t_2)$ and $G_{\dot{\pi}\dot{\pi}}(t_2)$ which vanishes at $t_2=0$; the quadratic and higher terms in the time expansion remain. On the other hand, the t_1 dependence, via $G_{\pi\pi}(t_1)$, is a combination in which the t_1^2 terms cancel, leaving the $t_1=0$ value and the quadratic and higher terms in the expansion nonzero. Thus we obtain the essential asymmetry; $R_{2,1}^{(5)}$ is zero on the t_1 axis but nonzero on the t_2 axis, and

$$R_{2,1}^{(5)}(t_2,0)=\frac{2\langle\Pi''_{ij}\Pi'_i\Pi'_j\rangle}{1-(\omega_1^2/\omega_2^2)}\,\frac{\omega_1^2C_{\pi\pi}(t_2)-C_{\dot{\pi}\dot{\pi}}(t_2)}{\langle\ddot{\Pi}^2\rangle}. \quad (20)$$

Varying the polarizations changes the relative values of averages $\langle\Pi''_{ij}\Pi'_i\Pi'_j\rangle$ and $\langle\Pi'_i\Pi''_{ij}\Pi'_j\rangle$, and thus polarization dependence arises from different admixtures of the two distinctly different time dependences. Different polarizations also introduce different time correlations. For $R_{zzzzzz}^{(5)}$ and $R_{xzxzxz}^{(5)}$, which we expect are well described by the smaller basis set (lacking separate irreducible components), the correlations are all the same, the averages are identical, and the shape of the response function may be written down without evaluating them,

$$R_{2,1}^{(5)}(t_2,t_1)\propto\frac{C_{\pi\dot{\pi}}(t_2)C_{\pi\dot{\pi}}(t_1)}{\langle(\dot{\Pi})^2\rangle^2}+\frac{1}{[1-(\omega_1^2/\omega_2^2)]^2}\times\left(\frac{\omega_1^2C_{\pi\pi}(t_2)-C_{\dot{\pi}\dot{\pi}}(t_2)}{\langle\ddot{\Pi}^2\rangle}\times\frac{C_{\pi\pi}(t_1)-\frac{1}{\omega_2^2}C_{\dot{\pi}\dot{\pi}}(t_1)}{\langle\Pi^2\rangle}\right). \quad (21)$$

III. CALCULATIONS AND COMPARISON WITH SIMULATION AND EXPERIMENT

Here we evaluate Eq. (21) as an approximation to $R_{zzzzzz}^{(5)}$. The various same-time averages and correlation functions may all be obtained from the ordinary Π^{zz} correlation, $C_{\pi\pi}(t)$. The other correlation functions needed, $C_{\pi\dot{\pi}}(t)$ and $C_{\dot{\pi}\dot{\pi}}(t)$, are obtained by numerically differentiating $C_{\pi\pi}(t)$. The equilibrium average $\langle\Pi^2\rangle$ is just the zero-time polarizability correlation, and the other constants $\langle\dot{\Pi}^2\rangle$ and $\langle\ddot{\Pi}^2\rangle$ are calculated by nonlinear fits to the short time expansion of $C_{\pi\pi}(t)$.

MD simulations are performed on 108 molecules at 293 K and a density of 1.26 g/cm^3, corresponding to room temperature, and $P=1$ atm. The length of a trajectory is 1.2 ns. Our molecular model for CS_2 is [23] a three-site flexible potential, and the velocity-Verlet version [23,24] of the multiple-time step algorithm is used at constant NVE.

The total system polarizability $\mathbf{\Pi}$ is calculated [22] with the point atomic polarizability approximation. Each C or S atom has a point polarizability chosen to give the correct gas phase isolated-molecular polarizability. The dipole-induced dipole (DID) problem is solved keeping all intramolecular terms and intermolecular interactions to first order. It is not too difficult to treat the entire DID problem exactly, but the first-order approximation should be adequate for our purpose.

Our polarizability model greatly overestimates the sensitivity of $\mathbf{\Pi}$ to the symmetric stretch, superimposing spurious fast oscillations on the slower intermolecular decay of $C_{\pi\pi}(t)$. This defect can be corrected [24] with the Applequist-Quicksall [25] model, but here we use a simpler procedure. The orientation of the molecule is obtained from the MD simulation, and the polarizability is calculated for a system of equilibrium-geometry molecules in the indicated orientations. Figure 1 shows the third order response function $C_{\pi\dot{\pi}}(t)$ obtained with this scheme; no oscillations are visible.

Figure 2 presents our prediction for the 2D Raman *zzzzzz* spectrum, in the second approximation $R_{2,1}^{(5)}$ and using Eq. (21). Some features are seen more clearly in a contour plot, Fig. 3. The result is in reasonable agreement with the simulation of SO [10]. Although $R_{2,1}^{(5)}$ vanishes along the t_1 axis but not the t_2 axis the contours are still fairly symmetric, all as found by SO [10]. The peak position is (0.13,0.19), roughly on the time scale of the peak in $R^{(3)}$ at 0.13 ps and somewhat longer than that of SO [10] (0.1,0.1). SO [10] and Kauffman *et al.* [14] (for a different polarization) find a node along the t_2 axis and we do not. Considering that we have made several approximations to our general theory for the simplest reasonable first calculation of $R^{(5)}$ the results must be considered very encouraging. They are far better than [2] INM and, it must be stressed, there *is* currently no other theory for molecular liquids.

IV. DISCUSSION AND FUTURE DIRECTIONS

We have proposed a method for reducing higher-order response functions containing time-dependent Poisson brack-

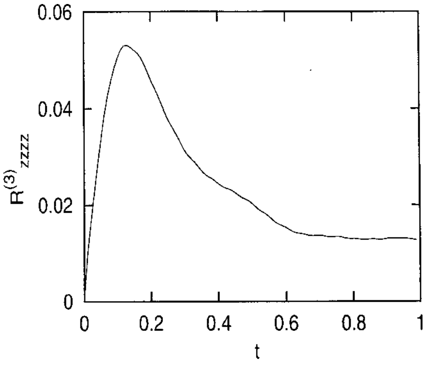

FIG. 1. Third order response $R_{zzzz}^{(3)}$ (arbitrary units) vs *t* (ps).

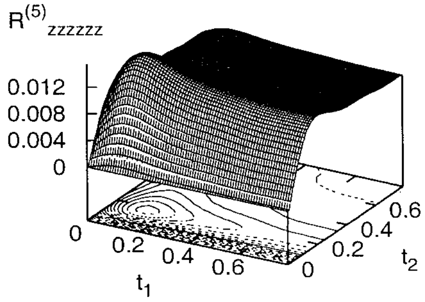

FIG. 2. Fifth order *zzzzzz* response $R^{(5)}_{2,1}$ (arbitrary units) vs t (ps). Function vanishes on t_1 axis.

ets to sums of ordinary correlation functions. Since little theory exists for brackets $[A(t),B(0)]$, and since they are also computationally challenging, this is a major simplification. Good agreement between simulation and the simple second order theory for liquid CS_2 supports our ideas. We believe that the fourth order theory [27], with the exact time expansion out to t^4 [6] and, as all versions of this theory, well behaved at long times, will be quite accurate. Since the peak is at short times it must be largely formed by positive t^2 and negative t^4 terms, and a theory which has these exactly cannot be too far off. Of course we first want to evaluate $R^{(5)}_{2,2}$, which contains the exact $t_1^2 t_2^2$ quartic coefficient, and to treat the different irreducible tensorial components. The latter are essential for magic angle polarizations. In sum, with the theory easily reproducing the correct time scale of the response, further refinements should fill in the details.

Other developments of the basic theme are possible. The essential step is using the GLE to handle the time-dependent Poisson bracket. We have expressed both $\Pi(t_2)$ and $\Pi(-t_1)$ with the GLE, but it is possible to use it only once to obtain an expression which is in that sense less approximate. Equation (8) may be rewritten two ways so that there is one t-dependent bracket of $\Pi(0)$ and either $\Pi(t_2)$ or $\Pi(-t_1)$. Substituting the systematic part of Eq. (5) for the latter we obtain

$$R^{(5)}(t_1,t_2)=\left(\frac{-1}{T}\right)G_{\pi\alpha}(-t_1)\times\left\langle \Pi(t_2)\left([\Pi,\dot{A}_\alpha]-\frac{1}{T}\dot{\Pi}\dot{A}_\alpha\right)\right\rangle=\left(\frac{-1}{T}\right)G_{\pi\alpha}(t_2)\langle[A_\alpha,\Pi]\dot{\Pi}(-t_1)\rangle. \quad (22)$$

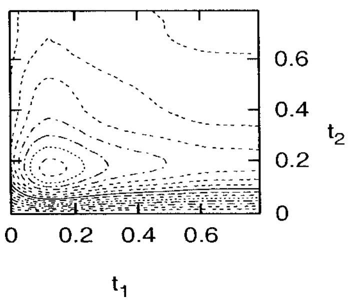

FIG. 3. Contour plot of fifth order *zzzzzz* response $R^{(5)}_{2,1}$. Function vanishes on t_1 axis.

Equation (22) introduces some unusual time correlation functions, but they are still computationally convenient conventional quantities with one time argument and are not comparable in difficulty with time-dependent brackets. We will [27] evaluate Eq. (22) by simulating these new t_2 or t_1-dependent functions.

It was originally hoped that the fifth order experiment would provide information about liquids unavailable from the many, well understood third order experiments. If $R^{(5)}$ can be represented with correlations of the polarizability and its time derivatives, plus equilibrium averages of same-time Poisson brackets, that hope cannot be realized. In fact, the time correlations arising in our theory can all be expressed as time derivatives of the garden-variety Π correlation function, hardly exciting new data. Is there any possibility of finding something novel? Perhaps. Very recent simulations [10] and experiments [14] on CS_2 show nodal lines for some polarizations. These are not reproduced by the current theory and may represent new phenomenon, although we will certainly try to explain them in future versions.

We have been somewhat cavalier with the random force. Our basis set is not the multilinear hydrodynamic basis $\{Q\}$ [19,20], but one selected for short to intermediate time polarizability dynamics. Thus we may have discarded some interesting slow behavior of the brackets of the random forces, visible in the *long time* behavior of $R^{(5)}$. It appears that $R^{(5)}$ mostly decays in a few hundred fs, so a long-time measurement will be difficult, but may be essential for the viability of the technique.

The slow behavior of $R^{(5)}$ may be obtained with the method [19,20] of Oppenheim and co-workers So long as the $\{Q\}$ are included $I(t)$ will be fast, its time-dependent brackets should follow the behavior deduced by Scramm and Oppenheim [20] for a product of random forces, and Eq. (9) should contain the slow optical response. One possibility is to simply combine the $\{Q\}$ with the Π-derivative basis set. To strictly focus on long time, one may project Π onto the $\{Q\}$ [20],

$$\Pi(t)=M_{\pi\ell}Q^{\ell}(t)+I_{\pi}(t), \quad (23)$$

where $Q^{\ell}(t)$ is an ℓth order hydrodynamic product variable and the index ℓ also serves as shorthand for variable identity and all the wave vectors. Calculations of $R^{(5)}$ so far have used the total polarizability but most generally the three factors are $\Pi^{ab}_{\mathbf{k_1}+\mathbf{k_2}}\Pi^{cd}_{-\mathbf{k_1}}\Pi^{ef}_{-\mathbf{k_2}}$. Wave vector must also be considered when coupling to hydrodynamics so let the wave vectors be considered implicit, as with tensor indices. The arguments that led to Eq. (9) then yield

$$R^{(5)}(t_1,t_2)=\left(\frac{-1}{T}\right)M_{\pi\ell}M_{\pi\ell'}G_{\ell n}(t_2)G_{\ell' m}(-t_1)\times\langle[Q^n,\Pi]\dot{Q}^m\rangle. \quad (24)$$

All that is required to evaluate Eq. (24), given what is already known [19,20] about multilinear hydrodynamics, is $M_{\pi\ell}$. The linear coupling to the momentum density is well understood [28]. Evaluation of the nonlinear couplings [29] will allow a determination of the long time behavior of $R^{(5)}$ [27], and an answer to the question of whether qualitatively new information can be obtained from the fifth order Raman effect in liquids.

ACKNOWLEDGMENTS

This work was supported by NSF Grant No. CHE0090975 and has benefited from discussions with Professor Irwin Oppenheim and Professor Minhaeng Cho.

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