

Photon echoes in impulsive optical spectroscopy of phonons

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Multidimensional off resonant spectroscopy of crystals using a train of optical pulses can be effectively used to probe nuclear dynamics in solids. We predict a clear photon echo signal even in the absence of inhomogeneous broadening. This technique may be used for studying phonon dynamics in solids, in structurally frozen systems such as glasses, and in systems where the validity of the concept of phonons is not equally well established, such as liquids and gases. With this technique it is also possible to obtain information on the lifetime of phonons. We predict a long time tail of the nonlinear signal proportional to $t^{-n/5}$, where n is the order of the response function studied. © 1995 American Institute of Physics.

I. INTRODUCTION

Nonlinear optical measurements may be conveniently interpreted using nonlinear response functions and susceptibilities.¹ It is possible to compute the response functions using multiple summations over the eigenstates of the material system, which include the energy levels and their dipole matrix elements.² It is also possible to include coupling to degrees of freedom of a thermal bath through relaxation rates (T_1 and T_2 processes). The tremendous success of the optical Bloch equations in the interpretation of numerous nonlinear optical measurements involving simple few level systems demonstrates the utility of this approach. It is, however, very difficult to apply it to more complex many body systems such as neat liquids and semiconductors.³ The number of relevant states is very large and performing the multiple summations becomes an impossible task. In addition, the large number of terms in the sum over states makes it hard to develop physical intuition. Attempts to map such systems into an effective few level system, lumping all many body effects into frequency dependent non-Markovian dephasing rates are of limited success.

An alternative approach is based on a quasiparticle representation where the many-body system is mapped onto a set of coupled anharmonic oscillators.^{4,5} This provides a completely new framework for analyzing such spectroscopies in terms of spectral densities,^{6,7} rather than phenomenological T_1 and T_2 rates. It has been suggested that for short time dynamics of atomic and molecular liquids, nuclear motions are described by a system of harmonic oscillators with an electronic polarizability that depends on the nuclear configuration.⁸⁻¹⁰ Recently, Tanimura and Mukamel¹¹ showed how nonlinear optical measurements can be used to test this conjecture. They further demonstrated how higher order off resonant nonlinearities can shed light on the nature of the spectral density obtained in optical Kerr measurements and address its homogeneous and inhomogeneous character.

Several measurements have subsequently been made in order to test the predictions of this model.^{12,13}

While the model provides many useful insights, its application to specific liquids is not straightforward. This requires addressing explicitly the nature of these oscillators, the underlying inhomogeneities, and their coupling to the electronic polarizability, all of which are not readily available. In this article we calculate the off resonant response of a regular lattice of polarizable atoms with harmonic nearest neighbor interactions. This model allows a fully microscopic determination of the oscillators and their optical response. The origin of the nonlinear optical response is the dependence of the electronic polarizability on the nuclear configuration through the dipole-dipole coupling. Effects of anharmonicities and deviations from the regular lattice positions are taken into account by introducing a finite lifetime of phonons. Unlike coherent anti-Stokes Raman spectroscopy (CARS) or optical Kerr measurements,⁶ the experimental technique described here can distinguish between a static distribution of oscillators frequencies (inhomogeneous broadening) and the finite lifetime due to anharmonicities or the coupling to a heat bath with very short correlation time (homogeneous broadening). A simple semiclassical picture for the process is obtained by employing the classical Liouville equation. We calculate the classical nonlinear response function which controls electronically off resonant multipulse experiments. We further discuss the possible divergence of the nonlinear response at long times for anharmonic systems. We argue that the nonlinear response function is finite thanks to the ensemble averaging over initial conditions, which cancels possible divergences resulting from the Lyapunov exponents.

II. THE MODEL

We start with the following Hamiltonian which describes a collection of interacting atoms

$$H_T = H + H_{\text{elec}}, \quad (1)$$

with

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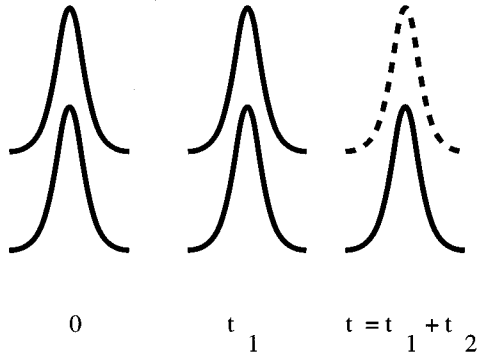


FIG. 1. Pulse sequence for an off resonant $R^{(5)}$ measurement. The system interacts with two pairs of pulses k_0 together with \tilde{k}_0 , and k_1 together with \tilde{k}_1 , and the final k_2 pulse generates the signal. The wave vector of signal follows from phase matching $k_s = k_2 + k_1 - \tilde{k}_1 + k_0 - \tilde{k}_0$.

$$H = \sum_i \frac{p_i^2}{2m} + \sum_{i < j} V(r_{ij}). \quad (2)$$

Here $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, is the distance between nuclei i and j , and $V(r)$ is the interatomic interaction. The electronic degrees of freedom are modeled as Drude oscillators and the electronic part of the Hamiltonian is given by

$$H_{\text{elec}} = \sum_i \frac{p_{x,i\alpha}^2}{2} + \sum_i \frac{\Omega^2 x_{i\alpha}^2}{2} + \frac{1}{2} \sum_{i \neq j, \alpha\beta} x_{i\alpha} T_{\alpha\beta}(\mathbf{r}_{ij}) x_{j\beta} - \sum_i E_\alpha(\mathbf{r}_i, t) x_{i\alpha}, \quad (3)$$

where $x_{i\alpha}$ denotes the α component of the 3-dimensional coordinate representing the electronic degree of freedom, and $p_{x,i\alpha}$ is the corresponding momentum.¹⁴ $E_\alpha(t)$ is the time dependent external electric field vector at particle i . We will assume that $T_{\alpha\beta}(\mathbf{r}_{ij})$ is the dipole-dipole interaction tensor

$$T_{\alpha\beta}(\mathbf{r}_{ij}) = \frac{3r_{ij,\alpha} r_{ij,\beta}}{r_{ij}^5} - \delta_{\alpha\beta} \frac{1}{r_{ij}^3}. \quad (4)$$

This form of the interaction is not essential, and the present theory applies to other forms as well.

We shall calculate the response of this model to a train of short off resonant pulses with frequencies centered around ω . We single out the contribution in which each of the pulses interacts twice (Fig. 1). The use of off resonant pulses ensures that the electronic degrees of freedom are of relevance only during the pulses. This allows us to adopt the following effective nuclear Hamiltonian

$$H_{\text{elec}}^{(\text{eff})} = \sum_{i \neq j} E_\nu^2(t) \alpha(r_{ij}), \quad (5)$$

where α is the electronic polarizability

$$\alpha(r_{ij}) = \mu^2 \langle k_0, \nu | \frac{1}{\Omega - \omega - T} + \frac{1}{-\Omega - \omega - T} | k_0, \nu \rangle, \quad (6)$$

and T is a $3N \times 3N$ matrix, with entries $T_{i\alpha, j\beta}$,

$$|k, \nu\rangle = \sum_j \exp(i\mathbf{k} \cdot \mathbf{r}_j) a_{j,\nu}^\dagger |0\rangle. \quad (7)$$

$|0\rangle$ denotes the electronic ground state in which none of the molecules is excited, and $|k, \nu\rangle$ denotes the exciton eigenstates, $a_{j,\nu}^\dagger$ is a boson operator that creates an exciton on the j th molecule polarized in the ν direction ($\nu = x, y, z$). Since the photon wave vector is very small compared with typical lattice wave vectors, we have dropped the position dependence of the electric field.

Equation (6) depends parametrically on all nuclear coordinates \mathbf{r}_{ij} as well as on the optical frequencies ω of the various pulses. Under off resonant excitation the dependence on frequency ω is weak [see Eq. (28)], we thus do not mention it explicitly.¹⁵

We consider an experiment in which $E(t)$ consists of a train of N pulses which interact with the system through the effective Hamiltonian Eq. (5). These pulses perturb the nuclear motions. The response of the system is detected with an additional off resonant probe pulse $E_f(t)$ that converts the nuclear coherence into electronic polarization and generates the signal.

All optical properties of the system can be expressed using the expectation value of the electronic dipole (the polarization) which controls the coupling with the radiation field. This in turn may be expanded in powers of the incident field. The details have been given elsewhere.¹¹ The formal expression of the polarization is

$$\langle P(t) \rangle = \sum_{j=0}^{\infty} \langle P^{(2j+1)}(t) \rangle, \quad (8)$$

where $P^{(2j+1)}(t)$ represents the polarization induced by the interaction with j pairs of pulses plus the detection pulse. We then have

$$\langle P^{(3)}(t) \rangle = E_f(t) \int_0^\infty dt_1 R^{(3)}(t_1) E^2(t-t_1), \quad (9)$$

$$\langle P^{(5)}(t) \rangle = E_f(t) \int_0^\infty dt_1 \int_0^\infty dt_2 R^{(5)}(t_2, t_1) E^2(t-t_2) \times E^2(t-t_1-t_2), \quad (10)$$

and

$$\langle P^{(7)}(t) \rangle = E_f(t) \int_0^\infty dt_1 \int_0^\infty dt_2 \int_0^\infty dt_3 R^{(7)}(t_3, t_2, t_1) \times E^2(t-t_3) E^2(t-t_3-t_2) E^2(t-t_3-t_2-t_1). \quad (11)$$

When the pulses are very short compared with the relevant nuclear dynamics timescale, the n th order optical signal integrated over time t is given by

$$S^{(2n+1)} \propto |R^{(2n+1)}(t_n, \dots, t_2, t_1)|^2, \quad (12)$$

where t_j are now the intervals between consecutive pulses. We have several time intervals at our disposal that can be varied in order to obtain information on the system.

To calculate the signal we introduce the following notation.¹⁶ We define the classical Liouville operator

$$L = \{H, \dots\}, \tag{13}$$

where $\{\dots, \dots\}$ denotes the Poisson bracket

$$\{A, B\} = \sum_i \left(\frac{\partial A}{\partial r_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial r_i} \frac{\partial A}{\partial p_i} \right), \tag{14}$$

and the interaction operator

$$\hat{\alpha} = \{\alpha, \dots\}. \tag{15}$$

In the quantum mechanical case, the Poisson brackets are replaced by commutators. The system is initially in thermal equilibrium, and is characterized by the density matrix

$$\rho_{\text{eq}} = \frac{\exp(-\beta H)}{\text{Tr} \exp(-\beta H)}. \tag{16}$$

From these definitions we find that

$$\hat{\alpha} \rho_{\text{eq}} = -\beta \alpha' \rho_{\text{eq}}, \tag{17}$$

where

$$\alpha' \equiv \{\alpha, H\}. \tag{18}$$

By treating the electronic Hamiltonian H_{elec} as a small perturbation on the system Hamiltonian H , we find the formal expressions for the response functions

$$R^{(3)}(t_1) = -\beta \langle \alpha \exp(Lt_1) \alpha' \rho_{\text{eq}} \rangle, \tag{19}$$

$$R^{(5)}(t_2, t_1) = -\beta \langle \alpha \exp(Lt_2) \hat{\alpha} \exp(Lt_1) \alpha' \rho_{\text{eq}} \rangle, \tag{20}$$

and

$$R^{(7)}(t_3, t_2, t_1) = -\beta \langle \alpha \exp(Lt_3) \hat{\alpha} \exp(Lt_2) \hat{\alpha} \exp(Lt_1) \alpha' \rho_{\text{eq}} \rangle. \tag{21}$$

The angular brackets denote the ensemble average over initial positions and velocities of the particles. The operator $\exp(Lt)$ propagates the system for a time t . To calculate it explicitly, the nuclear equations of motion have to be solved.

Alternatively we can recast these expressions in terms of correlation functions

$$R^{(3)} = -\beta \langle \alpha(t_1) \alpha'(0) \rho_{\text{eq}} \rangle, \tag{22}$$

$$R^{(5)} = -\beta \langle \alpha(t_1 + t_2) \hat{\alpha}(t_1) \alpha'(0) \rho_{\text{eq}} \rangle, \tag{23}$$

$$R^{(7)} = -\beta \langle \alpha(t_1 + t_2 + t_3) \hat{\alpha}(t_1 + t_2) \hat{\alpha}(t_1) \alpha'(0) \rho_{\text{eq}} \rangle, \tag{24}$$

where

$$\alpha(t) = \exp(-Lt) \alpha = \alpha \exp(Lt). \tag{25}$$

In a quantum mechanical formulation $\alpha(t)$ is the operator α in the Heisenberg picture.

The formal expressions derived above for the classical response functions form the basis for the applications made

in this paper. The application to an FCC solid will be made in the next section. At this point we shall consider a simpler model of a single classical oscillator with a quadratic dependence of α on its coordinate, i.e.,

$$H = \frac{1}{2m} p^2 + \frac{m\nu^2}{2} q^2, \tag{26}$$

and

$$\alpha(q) = \alpha_0 q^2, \tag{27}$$

where

$$\alpha_0 = \frac{\Omega \mu^2}{\Omega^2 - \omega^2}. \tag{28}$$

Here Ω is the transition frequency of the isolated molecule, and ω is the central frequency of the applied field.

If α were linear in q then the model would have been linear, and all nonlinear response functions would have vanished. The quadratic dependence is the simplest nontrivial form which has a nonlinear response. This model will help us gain physical insight on the various response functions. Moreover it turns out that once certain approximations are made, the response function of the FCC crystal will be expressed in terms of the response functions calculated for this simple model. We shall thus use the following results in the next section. Using Eqs. (15), (18), and (27), together with the Hamiltonian (26) we obtain

$$\alpha = \alpha_0 q^2, \tag{29}$$

$$\hat{\alpha} = 2\alpha_0 q \frac{\partial}{\partial p}, \tag{30}$$

$$\alpha' = 2\alpha_0 qp. \tag{31}$$

The response functions can now be calculated using Eqs. (22)–(25) and the solution of the equations of motion for a harmonic oscillator. We shall use the dimensionless time variable $\tau_j \equiv \nu t_j$ and obtain

$$\mathcal{R}^{(3)}(\tau_1) = \frac{1}{m\nu^2} \alpha_0^2 \sin(2\tau_1), \tag{32}$$

where $\tau_1 = \nu t_1$,

$$\begin{aligned} \mathcal{R}^{(5)}(\tau_2, \tau_1) &= \frac{\alpha_0^3}{\sqrt{\beta m^{3/2} \nu^3}} \left[\frac{3}{2} \cos(2\tau_1 - 2\tau_2) - \frac{5}{2} \cos(2\tau_1 + 2\tau_2) \right], \tag{33} \end{aligned}$$

and

$$\begin{aligned} \mathcal{R}^{(7)}(\tau_3, \tau_2, \tau_1) &= \frac{\alpha_0^4}{\beta m^2 \nu^4} \left[-\sin(2\tau_1 - 2\tau_3) + \frac{5}{2} \sin(2\tau_1 + 2\tau_3) - \frac{3}{2} \sin(\tau_1 + \tau_2 + 2\tau_3) - 3 \sin(3\tau_1 + \tau_2 + 2\tau_3) \right. \\ &\quad \left. + \sin(2\tau_1 + 2\tau_2 + 2\tau_3) - \frac{3}{2} \sin(\tau_1 + 3\tau_2 + 2\tau_3) - \frac{3}{2} \sin(3\tau_1 + 3\tau_2 + 2\tau_3) + 3 \sin(2\tau_1 + 4\tau_2 + 2\tau_3) \right]. \tag{34} \end{aligned}$$

III. THIRD ORDER RESPONSE FUNCTION OF FCC SOLIDS

We now apply the results of the previous section to a FCC solid. The nonlinearity is induced by the coupling of the polarizability to the laser fields with the nuclear coordinates as described by T . For the interaction between the nuclear and electronic degrees of freedom we use the dipole-dipole matrix T , where we assume an isotropic, harmonic interaction between a molecule and its nearest neighbors. We denote the deviation of a molecule i from its equilibrium position by q_i and expand perturbatively in q_i . We then have

$$\alpha = \alpha_1 + \alpha_2, \quad (35)$$

where the first order term is

$$\alpha_1 = \mu^2 \sum_{iaj} (\nabla_{i\alpha} T_{ij,xx}) q_{i\alpha}, \quad (36)$$

and the electric fields are taken to be linearly polarized along the x -axis. For a centrosymmetric solid, such as a FCC solid

$$\sum_j \nabla_{i\alpha} T_{ij,xx} = 0, \quad (37)$$

and therefore $\alpha_1 = 0$. The lowest nonvanishing contribution is

$$\alpha_2 = \mu^2 \sum_{iaj\beta} (\nabla_{i\alpha} \nabla_{j\beta} T_{ij,xx}) q_{i\alpha} q_{j\beta}. \quad (38)$$

Since an ideal solid is translationally invariant, it is useful to Fourier transform this to momentum (\mathbf{k}) space

$$\alpha_2 = \mu_0 \sum_k X_{xx\alpha\beta}(k) q_{k\alpha} q_{-k\beta}, \quad (39)$$

where \mathbf{k} runs over the reciprocal lattice,

$$q_{k\alpha} = \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i} q_{i\alpha} \quad (40)$$

and

$$X_{xx\alpha\beta}(k) = \sum_{ij} e^{i\mathbf{k}\cdot\mathbf{r}_{ij}} \nabla_{i,\alpha} \nabla_{j,\beta} T_{ij,xx}. \quad (41)$$

The operators $\hat{\alpha}_2$ and α'_2 follow from their defining relations Eq. (15) and Eq. (18) and are given by expressions similar to Eqs. (29)–(31). While the trace of X is zero, $\sum_\alpha X_{\alpha\alpha}(k) = 0$, we still find a signal as we are interested in traces of higher orders, such as $\text{tr} X^4(k)$.

The fifth order response function now becomes

$$\begin{aligned} R^{(5)}(t_2, t_1) = & \sum_{\mathbf{k}_2 \mathbf{k}_1 \mathbf{k}_0, \alpha} X_{\alpha_2 \alpha'_2}(k_2) X_{\alpha_1 \alpha'_1}(k_1) X_{\alpha_0 \alpha'_0}(k_0) \\ & \times \int d\Delta \mathbf{r}_{\mathbf{k}_0, \alpha_0} \int d\mathbf{v}_{\mathbf{k}_0, \alpha'_0} \Delta \mathbf{r}_{\mathbf{k}_2, \alpha_2} \\ & \times \frac{\partial}{\partial \mathbf{v}_{\mathbf{k}_2, \alpha'_2}} \exp(Lt_2) \Delta \mathbf{r}_{\mathbf{k}_1, \alpha_1} \frac{\partial}{\partial \mathbf{v}_{\mathbf{k}_1, \alpha'_1}} \\ & \times \exp(Lt_1) \Delta \mathbf{r}_{\mathbf{k}_0, \alpha_0} \mathbf{v}_{\mathbf{k}_0, \alpha'_0} \end{aligned} \quad (42)$$

with $\Delta \mathbf{r}_{\mathbf{k}_1, \alpha_1}$ is the Fourier transform, similar to Eq. (40) of the deviations of the particles from their lattice sites at $t=t_1$, and similarly $\mathbf{v}_{\mathbf{k}_1, \alpha'_1}$ is the Fourier transform of the velocities. Higher order response functions can be written in a similar way. Only the terms with $\mathbf{k}_2 = \mathbf{k}_1 = \mathbf{k}_0$ contribute for a regular lattice when the applied fields have zero wave vectors. The contributions of the various oscillators then decouple and we can use the results of the previous section. Strictly speaking, this decoupling is not rigorous, and we have used the fact that the wave vectors are finite in selecting a specific contribution to the nonlinear polarization through phase matching (see Fig. 1). Yet, for the response on a short time scale, the wave vector dependence can be neglected. The wave vector dependence can only show up on the time scale that a phonon requires to travel a distance of an optical wavelength, which is typically of the order of a nanosecond. Here we are considering a much faster response, where the typical time scale is the time it takes a phonon to move across a single unit cell, which is of the order of a picosecond. Hence, as long as the fast response is considered, the optical wave vectors can be safely set to zero.

As the relevant nonlinearity is quadratic in phonon coordinates, each interaction with the applied field as described by α_2 [Eq. (39)] corresponds to a two phonon process. The electric field wave vector is essentially zero, which implies that after an excitation two phonons with opposite wave vectors are created. Setting the wave vectors of the applied fields to zero constitutes a considerable simplification, yet Eq. (42) is still complicated as all the polarizations of the phonons (transverse and longitudinal) have to be taken into account. Since longitudinal and transverse phonons can have considerably different lifetimes and velocities it may be possible to study only the contributions of the longitudinal phonons. The sum over polarizations then collapses to a single term, and Eq. (42) can be evaluated resulting in

$$R^{(5)}(t_2, t_1) = \beta(\beta m)^{-3/2} \int d\nu Z^{(5)}(\nu) \mathcal{R}^{(5)}(\nu t_2, \nu t_1), \quad (43)$$

and

$$\begin{aligned} R^{(7)}(t_3, t_2, t_1) = & \beta(\beta m)^{-2} \int d\nu Z^{(7)}(\nu) \mathcal{R}^{(7)} \\ & \times (\nu t_3, \nu t_2, \nu t_1), \end{aligned} \quad (44)$$

where

$$Z^{(5)}(\nu) = \sum_{\mathbf{k}} \frac{[X_{\mathbf{k}\mathbf{k}}(\nu)]^3}{4\nu^3} \delta[\nu - \nu(\mathbf{k})], \quad (45)$$

and

$$Z^{(7)}(\nu) = \sum_{\mathbf{k}} \frac{[X_{\mathbf{k}\mathbf{k}}(\nu)]^4}{4\nu^4} \delta[\nu - \nu(\mathbf{k})], \quad (46)$$

with $\nu(\mathbf{k})$ the angular velocity of the phonon of wave vector \mathbf{k} . The response functions $\mathcal{R}^{(n)}$ were given by Eqs. (32)–(34).

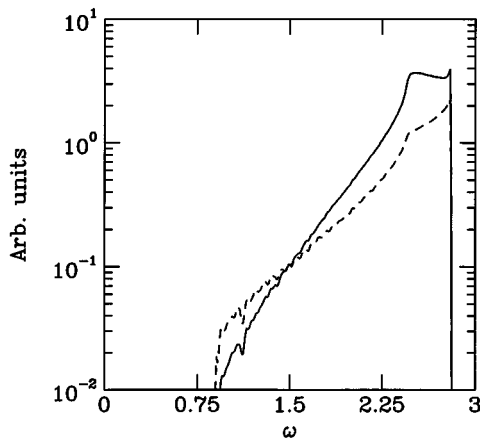


FIG. 2. The density of states (solid) and the function $Z^{(5)}(\nu)$ in arbitrary units (dashed) for a FCC solid. The frequency is expressed in terms of the Debye frequency. For organic $2 \times 10^{13} \text{ s}^{-1}$ crystals the Debye frequency is of the order of w_D .

The function $Z^{(5)}(\nu)$ for an isotropic FCC lattice with nearest neighbor interactions is presented in Fig. 2. Since for small wave vectors $\nu \propto k$ and $X(k) \propto k^2$, the function $Z^{(5)}(\nu) \propto \nu^5$ in three dimensions.

Typical time-resolved response functions are graphed in Figs. 3 and 4. The time in Figs. 3–5 is expressed in terms of the Debye period w_D^{-1} which for organic crystals is of the order of 50 fs. The most remarkable feature is the appearance of an echo in the signal. This echo is entirely due to the contribution of the first term in Eq. (33). While the echo is similar to the spin echo and the photon echo, there are some notable differences. First, the word echo is to be taken literally, since acoustic phonons are the excitations causing it. Second, we find an echo even for a perfectly ordered crystal without additional inhomogeneous broadening. That we still find an echo is due to the wave vector selection rules. Ordinarily only the $k=0$ wave vector is excited. Here, as the excitation is due to fluctuations in the dipole moments, the

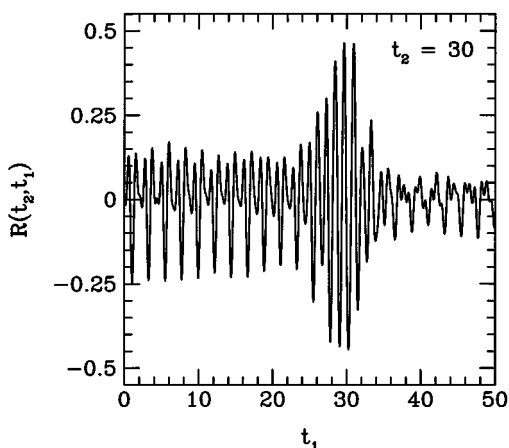


FIG. 3. A typical response as a function of time, without decay.

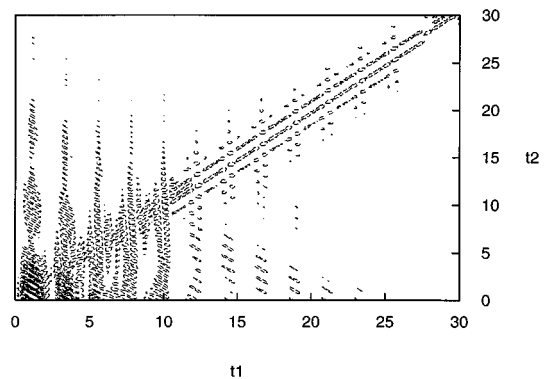


FIG. 4. Contour plot of the response function $R^{(5)}(t_2, t_1)$ as function of the two time variables. The echo signal can be clearly identified on the diagonal.

whole spectrum of wave vectors is excited with amplitudes proportional to $X(k)$. As there are four interactions, the signal depends on $X^4(k)$.

A unique property of echo experiments is that they can distinguish between different broadening processes. A commonly used distinction is between broadening due to homogeneous dephasing processes including the finite lifetime of the excitations, and pure dephasing (i.e., a frequency distribution of excited oscillators). In the echo presented in Fig. 3 only the distribution of frequencies was taken into account.

In the derivation of Eq. (33) it was assumed that the phonons have an infinite lifetime. While this is a good approximation, there will always be small anharmonicities resulting in a finite lifetime. It is well known¹⁷ that the resulting lifetime is proportional to ν^{-5} for small frequencies ν , which is of most interest for long times. For finite wave vectors there is no simple expression for the phonon lifetime and for simplicity we assume that it scales as $c\nu^{-5}$. While the exact effect on \mathcal{R} is hard to establish we will incorporate it as a simple prefactor that only depends on the frequency

$$R^{(5)}(t_2, t_1) = (\beta m)^{-2} \int d\nu Z^{(5)}(\nu) \mathcal{R}(\nu t_2, \nu t_1) \times \exp[-c\nu^5(t_2 + t_1)]. \quad (47)$$

A typical response function is given in Fig. 5. It is easy to show that the echo signal has a long time tail and decays as $R(t, t) \propto t^{-1}$. For the seventh order response function we have

$$R^{(7)}(t_3, t_2, t_1) = (\beta m)^{-2} \int d\nu Z^{(7)}(\nu) \mathcal{R}(\nu t_3, \nu t_2, \nu t_1) \times \exp[-c\nu^5(t_3 + t_2 + t_1)]. \quad (48)$$

Now the echo signal $R(t, 0, t) \propto t^{-7/5}$. An important use that can be made of this experimental setup is to establish the lifetime of phonons in liquids, or perhaps even more fundamentally: to establish the existence of phonons in liquids. The very existence of an echo could constitute a decisive point in this case. While computer simulations have demonstrated the existence of phonons in supercooled fluids,¹⁸ for ordinary liquids the case is still open.

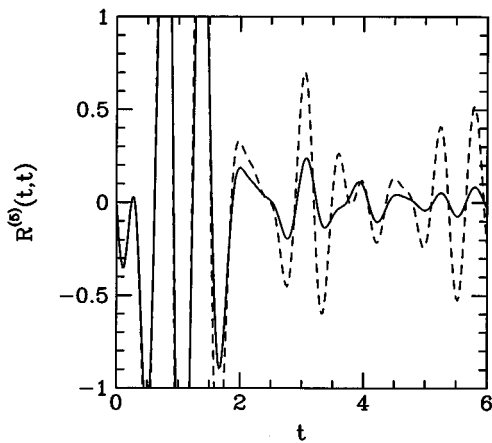


FIG. 5. The diagonal response function $R^{(5)}(t,t)$ taking into account the finite lifetime of phonons as described in the text, Eq. (47). We have used $c=0.1$ here (solid). For comparison, also the response without decay is presented (dashed).

IV. WHY ARE THE RESPONSE FUNCTIONS FINITE AT LONG TIMES?

The long-time behavior of linear response functions poses some interesting fundamental problems which even resulted in questioning their mere existence. The problem is that most dynamical systems are anharmonic, and the classical equations of motion are nonlinear. It is well established that chaotic behavior is expected under these circumstances; the separation of two trajectories with small difference in initial conditions will grow exponentially at long times. A good measure of this divergence is provided by the Lyapunov exponents. It has been argued that the response to an external field, however small, should then diverge at long times.¹⁹ If that was the case, then formally the linear response functions should diverge as well. This contradicts our common experience, since linear response functions have been computed and measured for numerous systems and found to be well behaved.

The expressions for R are more complicated than may seem at first sight as $\hat{\alpha}$ is an operator. A major difference between linear and nonlinear response is that it is not possible to eliminate the operators $\hat{\alpha}$ in the case of classical nonlinear response. As there is a derivative in the operator $\hat{\alpha}$, there is a possibility that the response function becomes very large for Hamiltonians that have positive Lyapunov exponents. Each time we make a derivative, this is equivalent to a difference between two trajectories that are slightly perturbed. At first glance the potential for divergence is therefore much larger in the nonlinear response.

The previous sections were based on the nonlinear response of a collection of harmonic oscillators with a nonlinear interaction with the field. In particular it was found that the response is bounded even though there is the possibility of divergence due to positive Lyapunov exponents.^{19,20} In this section we argue that for an integrable system the four time response function is bounded but *only because of the thermal averaging*. We shall consider an integrable system as then explicit expressions can be obtained. Calculations for

chaotic systems are much harder to perform but we believe that the same argument will hold there as well.

As a model we study the quartic potential

$$H = H_0 + E(t)r, \quad (49)$$

where $E(t)$ is the time dependent external field and

$$H_0 = \frac{p^2}{2} + r^4. \quad (50)$$

While this Hamiltonian corresponds to a one dimensional oscillator and is therefore integrable, the actual action-angle variables are not simply related to the original degrees of freedom. We find

$$H_0 = \left(\frac{3\alpha}{4} I \right)^{4/3} \quad (51)$$

with I the action and α is a numerical constant

$$\alpha = \left[8\sqrt{2}\pi \int_0^1 (1-x^4)^{-1/2} dx \right]^{-1} \approx 46.598. \quad (52)$$

In terms of the action angle variables, the solution of the equations of motion are

$$p(t) = p(\theta_0 + \dot{\theta}t, I_0), \quad r(t) = r(\theta_0 + \dot{\theta}t, I_0). \quad (53)$$

Here I_0 and θ_0 are the initial values. Explicit expressions for the functions $p(\cdot, \cdot)$ and $r(\cdot, \cdot)$ can be given in terms of elliptic functions, but they are most conveniently calculated by numerically solving the equations of motion. The solutions are periodic, with period

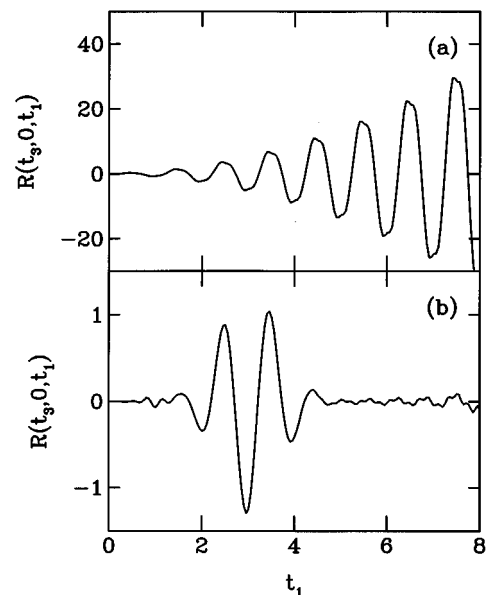


FIG. 6. The nonlinear response function $R(t_3, 0, t_1)$ for the quartic potential. In this figure $t_3=3$. In (a) the response is presented for a fixed energy ($E=1$). No echo appears, and the signal grows linearly in time. In (b) the response is graphed at temperature $T=1$. A clear echo signal appears at $t_1=3$, for other times the signal decays rapidly. Notice the difference in scales on the y-axis.

$$T = 2\pi \left(\frac{dH_0}{dI} \right)^{-1} = \frac{2\pi}{\alpha} H_0^{1/4}. \quad (54)$$

The response functions follow from the expressions of Sec. II, Eq. (24). After a straightforward, yet quite lengthy calculation we obtain

$$R^{(3)} = \beta \langle v_1 v_0 \rangle \quad (55)$$

$$R^{(5)}(t_2, t_1) = \beta^{3/2} \left\langle \frac{v_2}{E} \left[v_1 v_0 \left(\frac{1}{2} - \beta E \right) + (r_1 + v_1 t_1) r_0^3 \right] \right\rangle \quad (56)$$

and

$$\begin{aligned} R^{(7)}(t_3, t_2, t_1) = & \beta^2 \langle v_3 v_2 v_1 v_0 \rangle - \left\langle v_3 v_2 \left[\left(\frac{\beta}{E} + \frac{1}{E^2} \right) \left[\frac{v_1 v_0}{2} + (r_1 + v_1 t_1) r_0^3 \right] \right] \right\rangle + \left\langle \frac{v_3}{E^2} \left[\frac{v_2 v_1}{2} + (r_2 + v_2 t_2) r_1^3 \right] \left[v_0 \left(\frac{1}{2} - \beta E \right) \right. \right. \\ & \left. \left. + t_1 r_0^3 \right] \right\rangle + \left\langle \frac{v_3}{4E^2} (v_2 r_1 - r_2 v_1 - v_2 v_1 t_2) r_0^3 \right\rangle + \left\langle \frac{v_3}{E^2} v_1 \left(\frac{1}{2} - \beta E \right) \left(\frac{v_2 v_0}{2} + [r_2 + v_2(t_1 + t_2)] r_0^3 \right) \right\rangle \\ & \left. + \left\langle \frac{v_3}{4E^2} (r_1 + v_1 t_1) 3r_0^2 [v_2 r_0 - r_2 v_0 - v_2 v_0(t_1 + t_2)] \right\rangle, \quad (57) \end{aligned}$$

where $\langle \dots \rangle$ denotes the average over the equilibrium ensemble of r_0 and v_0 ,

$$\langle \dots \rangle = \int dr_0 \int dv_0 \exp(-\beta H_0) \dots \quad (58)$$

and $r_1 = r(t_1; r_0, v_0)$, $r_2 = r(t_1 + t_2; r_0, v_0)$, $r_3 = r(t_1 + t_2 + t_3; r_0, v_0)$, and the v 's are defined similarly. The most remarkable feature of Eqs. (56) and (57) is that in principle the response can become unbounded, and may grow linearly with time. That this growth is linear is due to the fact that we have taken an integrable model; for chaotic systems this growth will be exponential. In Fig. 6(a) we present the response function R for one particular energy. Indeed we find a signal that is increasing without bounds in time. This behavior changes dramatically when we perform the thermal averaging, as demonstrated in Fig. 6(b). The signal dephases rapidly since the oscillation period T , Eq. (54) depends on the initial energy. We believe that this dephasing applies to non-integrable systems as well. The nonlinear optical response is much more sensitive to chaotic behavior than the linear response. The design of nonlinear optical measurements that will provide a direct probe for Lyapunov exponents remains a fascinating open question.

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