PHYSICAL REVIEW
LETTERS

VOLUME 78 17 FEBRUARY 1997 NUMBER 7

Nonlinear Response for Time-dependent External Fields

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(Received 4 November 1996)

We generalize nonlinear response theory for autonomous systems so that it describes the response of classical many-body systems to large time-dependent external fields. Our formalism represents the first practical application of response theory to such problems. Our expressions for the nonlinear time-dependent response are tested against nonequilibrium molecular dynamics computer simulation. The relation of our results to known special cases (time-dependent linear response and time-independent nonlinear response) is discussed. [S0031-9007(97)02384-3]

PACS numbers: 02.70.Ns, 05.20.–y, 61.20.Ja, 61.20.Lc

When a sufficiently weak time-dependent external field perturbs a classical N-particle system, and only the linear response need be considered, the Green-Kubo formula [1] and the linear response theory [1,2] can be applied. For the time-independent fields, the general nonlinear response can be found using either of the two equivalent methods, Kawasaki response formula [3] or the transient time-correlation function (TTCF) approach [4]. There have been attempts to develop a formalism for treatment of nonlinear response to time-dependent fields [5], which parallels the quantum mechanical perturbation methods and makes use of the time-ordered exponentials for the definition of propagators. However, the resulting expressions are so complex that no one has yet succeeded in testing them against either laboratory or even computer experiments.

In this Letter we describe an entirely new approach to the treatment of nonlinear nonautonomous systems. Our approach is based on the definition of an extended phase space in which the system becomes autonomous. This allows the computationally efficient TTCF method to be applied. We discuss the relation of our results to known special cases (time-dependent linear response and time-independent nonlinear response).

The algorithm corresponding to this extended phase space TTCF formalism is tested using computer simulation of a very simple system of two colored disks interacting with a color sensitive, time-dependent, external field. We compare the response of field induced changes in the hydrostatic pressure to that predicted by our theory. The changes in the hydrostatic pressure are an entirely nonlinear effect. The results provide an emphatic validation of the theory.

Somewhat surprisingly our extended TTCF approach enables the calculation of these time-dependent effects with greater computational efficiency than direct observation. This improved efficiency is apparent even in the presence of very strong applied fields.

We consider a general isokinetic N-particle system subject to a time-dependent external field which is introduced at $t = 0$. The equations of motion of such a system are

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i/m + \mathbf{C}_i(\mathbf{\Gamma})F_e(t)\,, \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{D}_i(\mathbf{\Gamma})F_e(t) - \alpha\mathbf{p}_i\,, \end{aligned} \tag{1}$$

where the Gaussian thermostat multiplier α, given by

$$\alpha = \frac{\sum_i \mathbf{F}_i \cdot \mathbf{p}_i/m}{\sum_i \mathbf{p}_i^2/m} + \frac{\sum_i \mathbf{D}_i \cdot \mathbf{p}_i/m}{\sum_i \mathbf{p}_i^2/m} F_e\,, \tag{2}$$

constrains the peculiar kinetic energy $K = \sum_i \mathbf{p}_i^2/2m$ to be a constant of motion. The state of the system can be represented by a point in the phase space $\mathbf{\Gamma}$ spanned by $[\mathbf{q}_i, \mathbf{p}_i\ (i = 1, \ldots, N)]$. We assume that the external field is periodic in time, so that $F_e(t + T_e) = F_e(t)$.

For $t \leq 0$, the external field is zero and the system is assumed to be at equilibrium. The time-independent

equilibrium phase space probability distribution of the isokinetic system is

$$f_0(\mathbf{\Gamma}) = \frac{\exp[-\beta U(\mathbf{\Gamma})]\delta(K(\mathbf{\Gamma}) - K_0)}{\int d\mathbf{\Gamma} \exp[-\beta U(\mathbf{\Gamma})]\delta(K(\mathbf{\Gamma}) - K_0)}, \quad (3)$$

where U is the potential energy of the system, $K_0 = dN/2\beta$ is the kinetic energy, $\beta = 1/k_B T$ where T is the temperature, k_B the Boltzmann constant, and d is the Cartesian dimensionality of the system.

After the time-dependent external field starts acting upon the system (at $t \geq 0$), the phase space probability distribution changes from $f_0(\mathbf{\Gamma})$ towards a periodic long time nonequilibrium distribution $f_\infty = f_\infty(\mathbf{\Gamma}, t) = f_\infty(\mathbf{\Gamma}, t + T_e)$.

Therefore a nonautonomous system features two different types of time dependence. The first one arises from the approach to the long time distribution through a sequence of transient states, which is analogous to the case of autonomous systems. The second type of time dependence arises from the fact that the long time distribution itself is time dependent.

This complex picture [5], can be simplified by incorporating a new variable

$$\varphi(t) = \varphi + \omega t, \quad (4)$$

which is directly proportional to time, into the equations of motion (1)

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i/m + \mathbf{C}_i(\mathbf{\Gamma})F_e(\varphi), \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{D}_i(\mathbf{\Gamma})F_e(\varphi) - \alpha \mathbf{p}_i, \\ \dot{\varphi} &= \omega. \end{aligned} \quad (5)$$

The new variable φ is the generalization of the "phase angle" of the sine or cosine functions. The *linear* time dependence of this additional phase space coordinate is essential for the development of the extended TTCF algorithm, because it enables one to reach exactly the prescribed values of φ after a given number of time steps. The state of the system can now be represented by a point in *extended* phase space $\mathbf{\Gamma}' = (\mathbf{\Gamma}, \varphi) = (\mathbf{q}_i, \mathbf{p}_i, \varphi;\ i = 1, \ldots, N)$. Because of the periodicity of the external field F_e, it is sufficient to consider values of φ in the range $\varphi \in [0, \omega T_e]$.

For systems governed by (5), the equilibrium extended phase space distribution $f_0'(\mathbf{\Gamma}')$ is uniform in φ, $f_0'(\mathbf{\Gamma}')d\mathbf{\Gamma}' = [f_0(\mathbf{\Gamma})/\omega T_e]d\mathbf{\Gamma}d\varphi$.

For systems where the long time macroscopic averages are not sensitively dependent on the initial phase $\mathbf{\Gamma}' = (\mathbf{\Gamma}, \varphi)$, the long time distribution $f_\infty'(\mathbf{\Gamma}')$ will be time independent, but dependent on φ. This is analogous to the approach to a unique steady state in autonomous systems. The only time dependence comes from the change of $f_0'(\mathbf{\Gamma}')$ to $f_\infty'(\mathbf{\Gamma}')$ when the external field $F_e(\varphi)$ is applied. Clearly this lack of sensitivity to the initial phase will eventually break down if the external field is sufficiently strong. We do not consider such systems here.

Let us consider a phase variable $B(\mathbf{\Gamma})$ which is a function of $\mathbf{\Gamma}$, and which by definition does not explicitly depend on time, or therefore on the additional phase space coordinate φ. Although $B(\mathbf{\Gamma})$ is solely a function of $\mathbf{\Gamma}$, we can see from the equations of motion (5) that the phase $\mathbf{\Gamma}$ that the system evolves to at time t, namely $\mathbf{\Gamma}(t)$, is a function of the initial *extended* phase $\mathbf{\Gamma}' = (\mathbf{\Gamma}, \varphi)$. Thus it is more revealing to write $B(t) = B(\mathbf{\Gamma}(t; \mathbf{\Gamma}, \varphi))$. In order to know the value of a phase function at time t, in addition to the elapsed time, we need to specify the initial phase vector $\mathbf{\Gamma}$ and the initial phase angle φ of the external field.

The average over extended phase space of B, taken at time t, is

$$\begin{aligned} \langle B(t)\rangle' &= \int d\mathbf{\Gamma}' f'(\mathbf{\Gamma}', t) B(\mathbf{\Gamma}) \\ &= \int d\mathbf{\Gamma}' f'(\mathbf{\Gamma}', 0) B(\mathbf{\Gamma}(t; \mathbf{\Gamma}')) \\ &= \int d\mathbf{\Gamma}' f_0'(\mathbf{\Gamma}') B(\mathbf{\Gamma}(t; \mathbf{\Gamma}, \varphi)) \\ &= \int d\mathbf{\Gamma} d\varphi \, \frac{f_0(\mathbf{\Gamma})}{\omega T_e} B(\mathbf{\Gamma}(t; \mathbf{\Gamma}, \varphi)), \end{aligned} \quad (6)$$

in the Schrödinger and Heisenberg pictures, respectively. As the equilibrium distribution $f_0'(\mathbf{\Gamma}')$ is known and given by (3), it is simpler to use the Heisenberg picture. Using the definition of the dissipative flux J [6],

$$\beta \sum_i [\mathbf{C}_i(\mathbf{\Gamma}) \cdot \mathbf{F}_i - \mathbf{D}_i(\mathbf{\Gamma}) \cdot \mathbf{p}_i/m] \equiv \beta J(\mathbf{\Gamma}),$$

and the adiabatic incompressibility of phase space condition [6] (AI$\mathbf{\Gamma}$), one can show that since

$$\begin{aligned} \langle B[\mathbf{\Gamma}(t; \varphi(t) = \varphi_P)]\rangle &= \langle B(\mathbf{\Gamma}(t))\delta(\varphi(t) - \varphi_P)\rangle' \\ &= d\mathbf{\Gamma}' f_0'(\mathbf{\Gamma}') B(\mathbf{\Gamma}(t; \mathbf{\Gamma}, \varphi)) \\ &\quad \times \delta(\varphi - \varphi_P + \omega t), \end{aligned} \quad (7)$$

averages taken over the standard phase space $\mathbf{\Gamma}$ for a particular value of $\varphi = \varphi_P$ at time t are given by

$$\begin{aligned} \langle B[\mathbf{\Gamma}(t; \varphi(t) = \varphi_P)]\rangle = \langle B[\mathbf{\Gamma}(0; \varphi(0) = \varphi_P)]\rangle - \beta \int_0^t ds F_e(\varphi_P - \omega s) \\ \times \langle B[\mathbf{\Gamma}(s; \varphi(s) = \varphi_P)] J[\mathbf{\Gamma}(0; \varphi(0) = \varphi_P - \omega s)]\rangle. \end{aligned} \quad (8)$$

The average value $\langle B(\mathbf{\Gamma}(t); \varphi(t) = \varphi_P)\rangle$ in (8) means the average over all values of the phase $\mathbf{\Gamma}$, at the time t, for a particular chosen constant value φ_P of the phase angle at time t, $\varphi(t)$; $\varphi(t) = \varphi_P$. If all possible values of φ_P from the interval $[0, \omega T_e]$ are substituted into (8), the dependence of $\langle B(\mathbf{\Gamma}(t); \varphi(t) = \varphi_P)\rangle$ on φ_P at the time t can be found. It should be pointed out that this dependence cannot be obtained by direct calculations from a set of trajectories starting from the **single** initial value of $\varphi(0)$. Such a set could only give the value of $\langle B(\mathbf{\Gamma}(t); \varphi(t) = \varphi_0 + \omega t)\rangle$ at the time t, $\langle B(\mathbf{\Gamma}(t + \delta t); \varphi(t) = \varphi_0 + \omega(t + \delta t))\rangle$ at the time $t + \delta t$, etc. It should also be observed that in the integrals on both sides of (8) $\varphi(s)$ is a constant equal to φ_P. However, as the time s changes, trajectories which contribute to the correlation function at some particular value of s change. For different times s they start at different initial values of $\varphi_0 = \varphi_P - \omega s$. Therefore, in order to find the evolution of $\langle B(\mathbf{\Gamma}(t); \varphi(t) = \varphi_P)\rangle$ for the chosen value of $\varphi(t) = \varphi_P$, we need to know the behavior of trajectories with **all** possible initial $\varphi(0)$ at all previous times.

The expression (8) is the general expression for the nonlinear response to a time-dependent external field. For time-independent fields, there is no φ dependence in the distribution function, and all extended phases that differ only in the extended phase space coordinate φ become identical, so that (8) reduces to the TTCF formula for autonomous systems [1]. The linear time-dependent response formula [1], applicable in the low amplitude and high frequency limit, is obtained from (8) if the equilibrium correlation function is substituted for the transient correlation in the integrand of (8).

This formalism is illustrated by the example of nonequilibrium molecular dynamics simulation of a system of two disks with periodic boundary conditions, subject to a time-dependent color field [7].

The interaction $\mathbf{F}_i$ between disks is characterized by the WCA (Weeks-Chandler-Anderson) potential [8]. In this work the effective diameter of the disks σ, the depth of the potential well of the corresponding Lennard-Jones potential ε, and the particle mass m are all set to unity.

The disks differ by color labels, $c_i = (-1)^i$, $i = 1, 2$, which determine the interaction of each disk with the external color field $F_c(t)$ acting in the x direction. We assume a sinusoidal time dependence of the color field for $t > 0$, $F_c(t) = F_0 \sin(\varphi_0 + \omega t)$.

The additional coordinate φ is defined from (4) so that the equations of motion for $t > 0$ in *extended* phase space $\mathbf{\Gamma}' = (\mathbf{q}_i, \mathbf{p}_i, \varphi), i = 1, 2$ are

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i/m\,, \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + \mathbf{i}c_i F_0 \sin\varphi - \alpha \mathbf{p}_i\,, \\ \dot{\varphi} &= \omega\,, \end{aligned} \tag{9}$$

with the thermostatting term α given by (3).

In this system the dissipative flux is given by $J = \sum_{i=1,2} c_i \dot{x}_i$, and the response of the hydrostatic pressure P,

$$P = \frac{1}{2}(P_{xx} + p_{yy}) = \frac{1}{2V}\left\langle \sum_{i=1}^{N} \left(\frac{p_{xi}^2 + p_{yi}^2}{m} + x_i F_{xi} + y_i F_{yi} \right) \right\rangle, \tag{10}$$

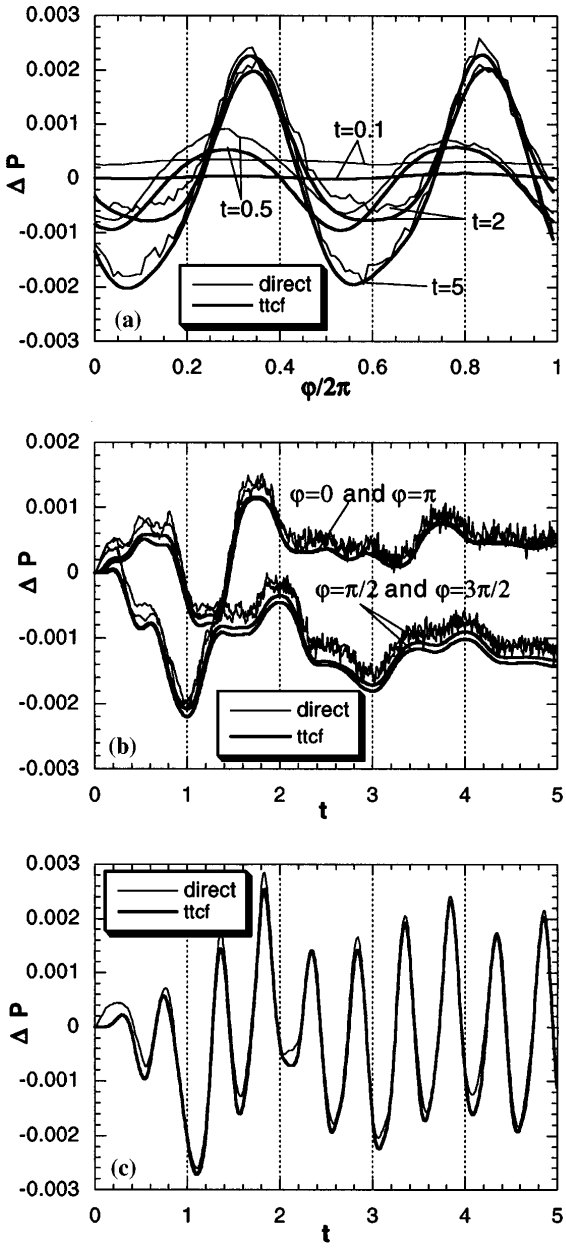

FIG. 1. The direct simulation and TTCF results for the pressure in the periodic color field. Both the direct simulation and the TTCF results show that the pressure oscillates with twice the frequency of the color field. The amplitude of the pressure oscillations changes in time from zero to the final value. (a) Pressure as a function of φ at different times. (b) Pressure at a constant value of φ. (c) Pressure as a function of time for $\varphi(0) = 0$.

to a sinusoidal color field was monitored as a function of the angle φ and time t. The response was calculated from (8) with B replaced by P.

The simulations were done at a density $\rho = N/V = 0.396850$ and at a temperature $T = 1.0$, using the fourth-order Runge-Kutta method of integration of the equations of motion (9) with a time step of $\delta t = 0.002$.

The simulations were carried out for $2 \times 50\,000$ initial phases from the isokinetic equilibrium ensemble, for each of the 100 initial values of $\varphi(0)$, and for a time $0 < t < 5$. From each starting phase $\mathbf{\Gamma} = (\mathbf{q}_i, \mathbf{p}_i)$, an additional starting point was generated using the time-reversal mapping $\mathbf{M}^T(\mathbf{\Gamma}) = (\mathbf{q}_i, -\mathbf{p}_i)$, in order to improve the statistics and to reduce the systematic error. This additional starting phase point ensures that the average initial current is identically zero.

The equilibrium correlation function under the time integral in (8), $\langle P(t)J_x(0)\rangle$, vanishes at all times, and therefore in the linear approximation the pressure is just equal to its equilibrium value. However, for strong fields the pressure oscillates with twice the frequency of the external field (since it is even under $\mathbf{M}^T$). The pressure shift is a strictly nonlinear effect and therefore provides a powerful test of our theory. In Fig. 1 are shown the results obtained by the direct simulation and the time-dependent TTCF method. Since the effect is very small, the direct simulation data are very noisy and therefore there is still some disagreement at early times. At late times, the agreement between the two sets of calculations is excellent. This agreement is all the more remarkable because of the complex shape of the response curves and the fact that these responses are entirely nonlinear. The chance of accidental agreement, particularly in Fig. 1(b), must be negligible.

In Fig. 1(b) we see the response for $\varphi(t) = 0, \pi$ and for $\varphi(t) = \pi/2, 3\pi/2$. By symmetry the response in each of these pairs should be identical. The disparity gives a reasonable estimate of the statistical uncertainty in the TTCF and the direct response curves. Although the direct and the extended TTCF curves are computed from the same number of simulation time steps, the extended TTCF curves always have a smaller variance. This is somewhat surprising given that the field amplitude is so large (TTCF methods will always be more efficient than direct methods at sufficiently small fields). We believe that this improvement in efficiency is related to the fact that in Eq. (8) the response at a given time and specified phase angle is computed from an ensemble average of trajectory responses which span the initial phase angle distribution. This cross phase averaging results in superior efficiency.

It is hoped that this development of a tractable nonlinear response theory for nonautonomous systems will open the way to studying a wide variety of nonlinear time-dependent phenomena [9].

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