

Nonlinear Response of Classical Dynamical Systems to Short Pulses

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Valuable insight into the nonlinear dynamics of a system can be gleaned from its response to a single intense short pulse. We derive expressions for the corresponding nonlinear response functions and show that the fluctuation-dissipation theorem may be extended beyond the linear response limit to an arbitrary pulse intensity. As an illustrative example, we calculate response functions up to 11th order for the regular Lorentz gas in two dimensions.

Key Words : Chaos, Classical statistical mechanics, Nonlinear spectroscopy

Introduction

The dynamics of condensed matter systems are often studied experimentally by perturbing the sample with an external field $E(t)$ (or a sequence of fields) and recording its relaxation back to equilibrium. From such a response information about the microscopic dynamics of the system can be extracted. If we use the observable B to monitor the evolution of the system, the n -th order response to an arbitrary perturbation can be succinctly written as

$$B^{(n)}(t) = \int_0^t d\tau_n \int_0^{\tau_n} d\tau_{n-1} \cdots \int_0^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \cdots E(\tau_2) E(\tau_1) \times S^{(n)}(t, \tau_n, \tau_{n-1}, \dots, \tau_2, \tau_1), \quad (1)$$

where the n -th order response function $S^{(n)}(t, \tau_n, \tau_{n-1}, \dots, \tau_2, \tau_1)$ depends on the dynamics of the system, on how the system couples to the external perturbation and also on the variable B selected to follow the system's time evolution. For a system evolving classically according to Newton's equations of motion, the nonlinear response function can be obtained from perturbation theory:

$$S^{(n)}(t, \tau_n, \tau_{n-1}, \dots, \tau_2, \tau_1) = (-1)^n \int dx B(x) e^{-iL_0(t-\tau_n)} \times \{A, e^{-iL_0(\tau_n-\tau_{n-1})} \{ \cdots, e^{-iL_0(\tau_2-\tau_1)} \{A, \rho_{eq}\} \} \cdots \}. \quad (2)$$

Here ρ_{eq} is the equilibrium phase space distribution of the system, $A(x)$ is the phase space variable appearing in the field-matter coupling $H'(x,t) = -E(t)A(x)$ and L_0 is the classical Liouville operator of the unperturbed system.

Calculation of nonlinear response functions for classical many-body systems requires evaluation of stability matrices describing the time evolution of small displacements in phase space.¹⁻³ Although such stability matrices can be obtained from molecular dynamics simulations, they cause severe

numerical problems; due to the fast, exponential growth of stability matrix elements, averages depending on stability matrices converge very slowly and nonlinear response functions can be calculated only for short times. The response to a single pulse of arbitrary magnitude, however, is an exception. This response may be recast in the form of a combination of correlation functions and does not depend on the stability matrix. In that respect, we obtain a generalization to arbitrary order of the fluctuation dissipation theorem,⁶⁻⁸ which rigorously connects the observable linear response function $S^{(1)}(t)$ with an equilibrium correlation function of the unperturbed system (see Eq. 12): Purely equilibrium simulations are enough, no additional information is necessary for computing the response and the numerical simulation is then straightforward.

The n -th order response function to a single short pulse acting on the system at time $t = 0$ is

$$S^{(n)}(t) = (-1)^n \int dx B(x) e^{-iL_0 t} \{A, \cdots \{A, \rho\} \cdots\} \quad (3)$$

when we propagate the density matrix, *i.e.*, when we operate in the "Schrödinger representation". Alternatively we can propagate the operators, *i.e.*, in the "Heisenberg representation".^{1,2} The response function then assumes the form

$$S^{(n)}(t) = \langle \{A, \cdots \{A, B(t)\} \cdots\} \rangle. \quad (4)$$

Here, $B(t) \equiv B e^{-iL_0 t} \equiv e^{iL_0 t} B$.

The Poisson bracket on the right hand side of equation (3) can be written as

$$\{A, \cdots \{A, \rho\} \cdots\} = \sum_{j=1}^n \beta^j D_j^{(n)} \rho, \quad (5)$$

where the phase space functions $D_j^{(n)}$ are obtained by repeated application of the Poisson bracket. The first few of these functions are

$$D_1^{(1)} = -\dot{A}, \quad (6)$$

$$D_1^{(2)} = -\{A, \dot{A}\}, \quad D_2^{(2)} = \dot{A}^2, \quad (7)$$

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$$D_1^{(3)} = -\{A, \{A, A\}\}, D_2^{(3)} = 3A\{A, A\}, D_3^{(3)} = -A^3. \quad (8)$$

Here, $\hat{A} \equiv L_0 A$. Using Eq. (5) we can then recast Eq. (3) in the form

$$S^{(n)}(t) = (-1)^n \sum_{j=1}^n \beta^j \langle B(t) D_j^{(n)} \rangle. \quad (9)$$

The response functions to a single short perturbation become especially simple and easy to interpret if the observable A is one of the phase space variables. So, let us assume that $A = x_1$ and denote this variable $q \equiv x_1$ and its conjugate momentum p . Then, the single pulse response function of order n in the Heisenberg picture assumes the form

$$S^{(n)} = \left\langle \frac{\partial^n B(t)}{\partial p^n(0)} \right\rangle. \quad (10)$$

The partial derivatives in the above equation can be easily evaluated with the following recursion formula corresponding to an integration by parts:

$$\begin{aligned} \left\langle p^k(0) \frac{\partial^n B(t)}{\partial p^n(0)} \right\rangle &= C \int dp \exp(-\beta p^2/2m) p^k \frac{\partial^n B(t)}{\partial p^n} \\ &= -C \int dp \frac{\partial}{\partial p} [\exp(-\beta p^2/2m) p^k] \frac{\partial^{n-1} B(t)}{\partial p^{n-1}} \\ &= \frac{\beta}{m} \left\langle p^{k+1}(0) \frac{\partial^{n-1} B(t)}{\partial p^{n-1}(0)} \right\rangle - k \left\langle p^{k-1}(0) \frac{\partial^{n-1} B(t)}{\partial p^{n-1}(0)} \right\rangle. \end{aligned} \quad (11)$$

Here, C is a normalization constant. Repeated application of this recursion formula yields nonlinear response functions to arbitrary order:

$$S^{(1)}(t) = \gamma C_t^1, \quad (12)$$

$$S^{(2)}(t) = \gamma^2 C_t^2 - \gamma C_t^0, \quad (13)$$

$$S^{(3)}(t) = \gamma^3 C_t^3 - 3\gamma^2 C_t^1, \quad (14)$$

$$S^{(4)}(t) = \gamma^4 C_t^4 - 6\gamma^3 C_t^2 + 3\gamma^2 C_t^0, \quad (15)$$

$$S^{(5)}(t) = \gamma^5 C_t^5 - 10\gamma^4 C_t^3 + 15\gamma^3 C_t^1, \quad (16)$$

$$S^{(6)}(t) = \gamma^6 C_t^6 - 15\gamma^5 C_t^4 + 45\gamma^4 C_t^2 - 15\gamma^3 C_t^0, \quad (17)$$

$$S^{(7)}(t) = \gamma^7 C_t^7 - 21\gamma^6 C_t^5 + 105\gamma^5 C_t^3 - 105\gamma^4 C_t^1, \quad (18)$$

$$S^{(8)}(t) = \beta^8 C_t^8 - 28\gamma^7 C_t^6 + 210\gamma^6 C_t^4 - 420\gamma^5 C_t^2 + 105\gamma^4 C_t^0, \quad (19)$$

$$S^{(9)}(t) = \gamma^9 C_t^9 - 36\gamma^8 C_t^7 + 378\gamma^7 C_t^5 - 1260\gamma^6 C_t^3 + 945\gamma^5 C_t^1, \quad (20)$$

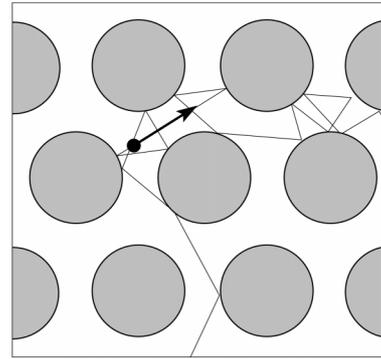


Figure 1. The Lorentz gas consists of a point particle moving through an infinite periodic array of hard scatterers in two dimensions. When the particle collides with a scatterer it is reflected elastically, *i.e.*, its velocity component normal to the scatterer surface is inverted. Here we imagine that the moving particle carries a unit charge and that the perturbation is a short pulse of strength E accelerating the particle in x -direction.

$$S^{(10)}(t) = \gamma^{10} C_t^{10} - 45\gamma^9 C_t^8 + 630\gamma^8 C_t^6 - 3150\gamma^7 C_t^4 + 4725\gamma^6 C_t^2 - 945\gamma^5 C_t^0, \quad (21)$$

$$S^{(11)}(t) = \gamma^{11} C_t^{11} - 55\gamma^{10} C_t^9 + 990\gamma^9 C_t^7 - 6930\gamma^8 C_t^5 + 17325\gamma^7 C_t^3 - 10395\gamma^6 C_t^1, \quad (22)$$

where $\gamma \equiv \beta/m$ and $C_t^n \equiv \langle p^n(0) B(t) \rangle$. Higher order response functions can be evaluated analogously. The first equation in the hierarchy, Eq. (12), is known as the fluctuation dissipation theorem.⁶⁻⁸

As an illustrative example, we have calculated the response of the Lorentz gas⁴ to short pulses. This model, shown in Figure 1, consists of a point particle of mass m with momentum p moving in a plane through an infinite regular array of circular scatterers with radius R arranged on a triangular lattice with lattice constant a . When the particle collides with a scatterer it is reflected elastically, *i.e.*, its velocity component normal to the scatterer surface changes sign. Between collisions the particle moves on a straight line with constant velocity. Due to the collisions of the particle with the convex (and therefore dispersing) surface of the scatterer the dynamics is strongly chaotic.⁵

Throughout, we study a system in which the scatterer density is $\rho = 4/5\rho_0$, where ρ_0 is the close packed density at which the scatterers are in contact. At this particular density $\rho = (1/2\sqrt{3})R^{-2}$ and the lattice constant is $a = \sqrt{5}R$. Since at $\rho = 4/5\rho_0$ the horizon is finite, *i.e.*, the particle can fly freely only for finite distances, the motion of the particle is strictly diffusive. Initial conditions of the moving particle are assumed to follow a canonical distribution, *i.e.*, positions $\mathbf{r} \equiv \{r_x, r_y\}$ are homogeneously distributed in the area not occupied by the scatterers and momenta $\mathbf{p} \equiv \{p_x, p_y\}$ are distributed according to $P(p) \propto \exp\{-\beta(p_x^2 + p_y^2)/2m\}$. All results are presented in dimensionless units with $\beta = 1$, $R = 1$ and $m = 1$.

Nonlinear response functions from order 1 to 11 obtained

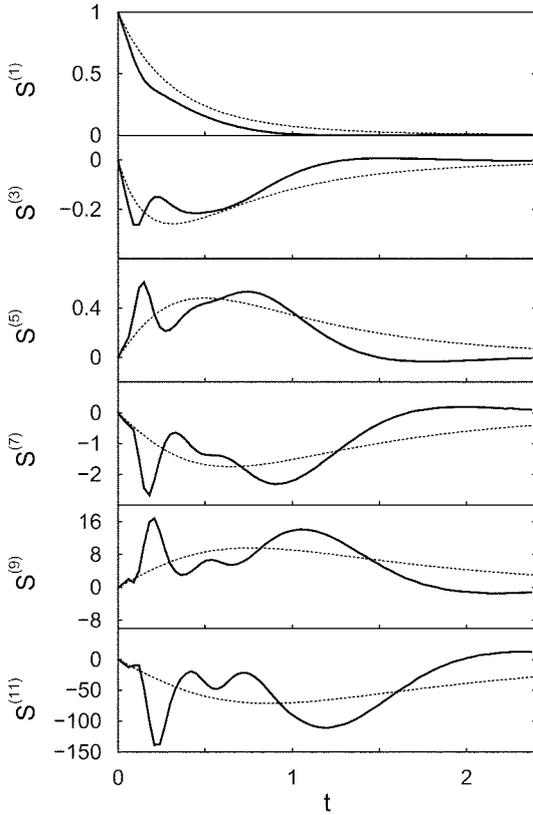


Figure 2. Response functions $S^{(1)}(t)$ to $S^{(11)}(t)$ to a single short pulse acting on the Lorentz gas depicted in Fig. 1 (all response functions of even order vanish due to symmetry). The response functions shown in the figure were obtained from correlation functions calculated as averages over 2×10^9 trajectories initiated at canonically distributed initial conditions and for a density of $\rho = (4/5)\rho_0$ where ρ_0 is the close packed density. The average time between collisions is $\tau = 0.474$ in the units described in the main text.

numerically for the Lorentz gas using Eqs. (12) to (22) are shown in Figure 2 as thick lines. Since all even n response functions vanish by symmetry, only the odd n response functions are depicted. The thin lines denote results for a stochastic model to be discussed later. While the first order response decays almost monotonically, the nonlinear response functions acquire additional features. The first characteristic feature appears at approximately half the average time between collisions which is $\tau = 0.474$ at the density studied here. As one proceeds to higher order the response functions begin to display oscillatory behavior which becomes more pronounced with increasing order. The exact physical origin of this behavior remains to be explained in detail.

An interesting observation is that for systems with hard interactions, such as the Lorentz gas, canonical nonlinear response functions to arbitrary order can be written in terms of simple microcanonical autocorrelation functions. To see this, we write the correlation function $C^{(n)}(t) = \langle p_x^n(0)p_x(t) \rangle$ as the canonical average:

$$C^{(n)}(t) = \frac{\beta}{2\pi mA} \int d\mathbf{r} d\mathbf{p} \exp[-\beta U(\mathbf{r})] \times \exp(-\beta \mathbf{p}^2/2m) p_x^n p_x(\mathbf{r}, \mathbf{p}, t), \quad (23)$$

where $U(\mathbf{r})$ is the potential energy of the system and \mathbf{r} and \mathbf{p} specify the position and the momentum of the moving particle, respectively. The integration over space extends over the unit cell of the triangular scatterer lattice and A is the area in the unit cell not occupied by a scatterer. The above expression can be simplified by noting that initial conditions differing only in the magnitude of the momentum but not in its direction yield identical trajectories in configuration space. Integration over all momentum directions then yields:

$$C^{(n)}(t) = \frac{\beta}{m} \int dp \exp(-\beta p^2/2m) p^{n+2} C_{\text{mc}}^{(n)}(tp/m), \quad (24)$$

where $p = |\mathbf{p}|$ and $C_{\text{mc}}^{(n)}(t) = \langle p_x^n(0)p_x(t)/p^2 \rangle_{\text{mc}}$ is a microcanonical correlation function. Since for a system with hard interactions

$$\langle p_x^n(0)p_x(t)/p^2 \rangle_{\text{mc}} = \langle p_x^n/p \rangle_{\text{mc}} \langle p_x(0)p_x(t)/p^2 \rangle_{\text{mc}} \quad (25)$$

and if n even

$$\langle p_x^n/p \rangle_{\text{mc}} = \begin{cases} 0 & \text{if } n \text{ even} \\ n!/(n+1)!! & \text{if } n \text{ odd} \end{cases} \quad (26)$$

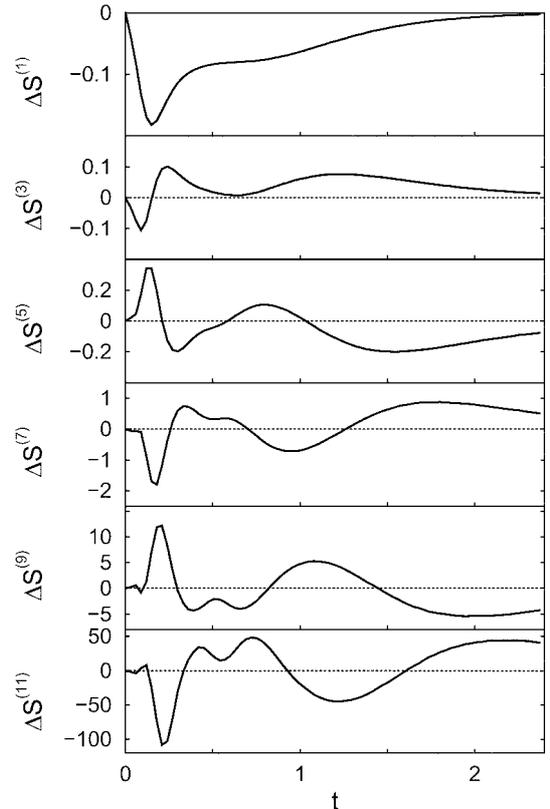


Figure 3. Deviation $\Delta S^{(i)} \equiv S^{(i)}(t) - S_{\text{sto}}^{(i)}(t)$ of the response functions $S^{(1)}(t)$ to $S^{(11)}(t)$ from the response functions predicted by the exponential model discussed in the main text. Since the exponential model is based on the assumption that subsequent collisions are uncorrelated, any non-vanishing deviation $\Delta S^{(i)}(t)$ is due to correlated collisions of the moving particle with the scatterers.

the correlation function $C^{(n)}(t)$ can be finally written as

$$C^{(n)}(t) = \frac{n!!}{(n+1)!!} \frac{\beta}{m} \int dp \exp(-\beta p^2/2m) p^{n+2} \times \langle p_x(0) p_x(tp/m)/p^2 \rangle_{mc}, \quad (27)$$

for odd order. For even order, $C^{(n)}(t)$ vanishes. From these correlation functions response functions can be calculated using expressions (12) to (22).

This relation between canonical and microcanonical correlation functions allows us to analyze the information content of the nonlinear response functions shown in Figure 2 using a stochastic model lacking correlations. In this model we assume that subsequent collisions of the moving particle with the scatterers are uncorrelated and that times between collisions are distributed exponentially with an average collision time of τ (Poisson process). We furthermore assume that at each collision the particle's velocity is randomized such that all memory of the incoming velocity is lost (strong collisions). In this case

$$C^{(n)}(t) = \frac{n!!}{(n+1)!!} \frac{\beta}{m} \int dp \exp(-\beta p^2/2m) p^{n+2} \exp(-t/\tau), \quad (28)$$

for odd order. Thus the only parameter in this model is the average time between collisions, τ . Response functions up to 11th order are shown in Figure 2 as thin dotted lines for an average collision time of $\tau = 0.591$ which is the collision

time at $\rho = (4/5)\rho_0$ for a particle with unit speed. The deviations $\Delta S^{(i)}(t) \equiv S^{(i)}(t) - S_{\text{sto}}^{(i)}(t)$ of the response functions $S^{(1)}(t)$ to $S^{(11)}(t)$ of the Lorentz gas from the corresponding response functions $S_{\text{sto}}^{(1)}(t)$ to $S_{\text{sto}}^{(11)}(t)$ predicted by the stochastic model are shown in Figure 3. By construction, the stochastic model neglects all correlations between subsequent collisions. Any non-vanishing value of the deviation $\Delta S^{(i)}(t)$ must be therefore attributed to correlated collision sequences. The signature of such correlated events is clearly visible in higher order response functions shown in Figure 2. Higher order response functions should therefore be capable of serving as sensitive probes for correlated cooperative motion in molecular systems.

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References

1. Dellago, C.; Mukamel, S. *Phys. Rev. Lett. E* **2003**, *67*, 035205(R).
2. Dellago, C.; Mukamel, S. *J. Chem. Phys.* **2003**, in print.
3. Mukamel, S.; Khidekel, V.; Chernyak, V. *Phys. Rev. E* **1996**, *53*, R1-R4.
4. Machta, J.; Zwanzig, R. *Phys. Rev. Lett.* **1983**, *50*, 1959.
5. Dellago, C.; Posch, H. A. *Phys. Rev. E* **1995**, *52*, 2401.
6. Onsager, L. *Phys. Rev.* **1931**, *37*, 405; *Phys. Rev.* **1931**, *38*, 2265.
7. Callen, H. B.; Welton, T. A. *Phys. Rev.* **1951**, *83*, 34.
8. Kubo, R. *Rep. Progr. Phys.* **1966**, *29*, 255.