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The Kawasaki distribution function for nonautonomous systems

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We describe a time-dependent generalization of the Kawasaki form of nonlinear response theory, and verify the validity of our expressions against direct molecular dynamics computer simulations.
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The microstate of a classical N-particle system is represented by a point in phase space spanned by coordinates and momenta of all constituent particles, $\mathbf{\Gamma}=\mathbf{\Gamma}(\mathbf{q},\mathbf{p})$. Assuming ergodicity, the macroscopic quantities of interest such as energy density, pressure or heat flux can be calculated from an ensemble (or phase space) average of some *phase function* $B(\mathbf{\Gamma})$. B is a function of phase $\mathbf{\Gamma}$ only, and not, for example, of time or of the external field.

The ensemble average $\langle B\rangle$ can be calculated from

$$\langle B\rangle=\int d\mathbf{\Gamma}\; B(\mathbf{\Gamma}(t))f(\mathbf{\Gamma},0)=\int d\mathbf{\Gamma}\; B(\mathbf{\Gamma})f(\mathbf{\Gamma},t), \quad (1)$$

in Heisenberg and Schrödinger pictures, respectively, where f is the phase space probability distribution describing the probability of observing the system in a differential phase volume $\mathbf{\Gamma}$, $\mathbf{\Gamma}+d\mathbf{\Gamma}$.

If we assume that the system is in equilibrium for $t\leqslant 0$ and is perturbed by a constant external field F_e for $t>0$, the phase space distribution function changes from its equilibrium form $f(\mathbf{\Gamma},0)$, valid for $t\leqslant 0$, to a different form $f(\mathbf{\Gamma},t)$ at time t, approaching the steady state distribution function $f(\mathbf{\Gamma},\infty)$ as $t\to\infty$. The ensemble average (1) changes continuously in time from the equilibrium value $\langle B(0)\rangle$, through transient values $\langle B(t)\rangle$ approaching the steady state value $\langle B(\infty)\rangle$, because the phase space probability density changes.

When F_e does not depend on time, evaluation of the change in $\langle B\rangle$ can be approached from either of the two ''pictures'' in Eq. (1). One method involves writing the equation of motion for $\langle B(t)\rangle$ using the Heisenberg form in Eq. (1) and solving it. The result is the transient time-correlation function (TTCF) expression [1] for the change $\langle B(t)\rangle$-$\langle B(0)\rangle$, which is a nonlinear analog of the Green-Kubo equilibrium time-correlation function. An alternative approach, pioneered by Yamada and Kawasaki [2], is to derive a closed expression for the perturbed distribution function $f(\mathbf{\Gamma},t)$ by solving the Liouville equation for the perturbed system, and to evaluate $\langle B(t)\rangle$ using the Schrödinger picture.

The derivations of both theories specifically require that the equations of motion of constituent particles do not depend explicitly on time, and therefore cannot be applied to nonautonomous systems. For a general time-dependent field there is no steady state in the long time limit. However, if the explicit time dependence in the perturbed equations of motion is periodic, the time dependence of $\langle B\rangle$ will also be periodic in the long time limit. We recently showed [3] that the TTCF formalism can be generalized to describe the response of such time-periodic systems by introducing the concept of an *extended phase space*. The same concept can be used to derive the Kawasaki distribution for time-periodic fields.

The general equations of motion for an N-particle system in a time-dependent external field are

$$\dot{\mathbf{q}}_i=\frac{\mathbf{p}_i}{m}+\mathbf{C}_i(\mathbf{\Gamma})F_e(t), \quad \dot{\mathbf{p}}_i=\mathbf{F}_i+\mathbf{D}_i(\mathbf{\Gamma})F_e(t)-\alpha\mathbf{p}_i, \quad (2)$$

where α is a constraint multiplier, thermostat or ergostat, used to extract the heat produced in the system by the dissipative external field, usually the Gaussian isokinetic [4] or Nosé-Hoover [5] thermostat. It is assumed that the external field is periodic in time with the period of T_e, so that $F_e(t+T_e)=F_e(t)$.

The explicit time dependence in Eq. (2) can be avoided by incorporating a new variable, $\varphi(t)=\varphi(0)+\omega t$, proportional to time, into Eq. (2). The new variable φ is the generalization of the ''phase angle'' of the trigonometric functions. The system (3) does not contain explicit time dependence, but has one additional equation,

$$\begin{aligned}\dot{\mathbf{q}}_i&=\frac{\mathbf{p}_i}{m}+\mathbf{C}_i(\mathbf{\Gamma})F_e(\varphi),\\ \dot{\mathbf{p}}_i&=\mathbf{F}_i+\mathbf{D}_i(\mathbf{\Gamma})F_e(\varphi)-\alpha\mathbf{p}_i, \quad \dot{\varphi}=\omega.\end{aligned} \quad (3)$$

The state of the system in the external field at any time is completely represented by the phase $\mathbf{\Gamma}$ and the additional coordinate φ, i.e., by a point $\mathbf{\Gamma}'=(\mathbf{q},\mathbf{p},\varphi)$ in an extended phase space, spanned by the coordinates $\mathbf{q}$, momenta $\mathbf{p}$, and the phase angle φ. Equations (3) are autonomous, and in fact have the same form as the constant field equations. Therefore the system (3) has a well defined steady state under the same circumstances as a system in constant field.

Although the value of B itself does not depend on φ explicitly, in the presence of the external field $\mathbf{\Gamma}(t)$ depends on the initial $\varphi(0)$. Therefore we shall write $B(\mathbf{\Gamma}')$ for the sake of generality and observe the evolution of the extended phase space functions. The value of $B(\mathbf{\Gamma}')$ can change in time only because of the change of extended phase,

$$\dot{B}(\mathbf{\Gamma}')=\dot{\mathbf{\Gamma}}'\cdot\frac{\partial B(\mathbf{\Gamma}')}{\partial\mathbf{\Gamma}'}=iL'(\mathbf{\Gamma}')B(\mathbf{\Gamma}'),\tag{4}$$

where $iL'(\mathbf{\Gamma}')$ is the extended phase space p Liouvillean. The formal solution of Eq. (4) can be written in terms of the extended phase space p propagator, $\exp[iL'(\mathbf{\Gamma}')t]$, so that

$$B(\mathbf{\Gamma}'(t))=\exp[iL'(\mathbf{\Gamma}')t]B(\mathbf{\Gamma}'(0)).$$

The equilibrium extended phase space distribution function is independent of φ, and therefore $f'(\mathbf{\Gamma}',0)d\mathbf{\Gamma}'=(1/\omega T_e)f(\mathbf{\Gamma},0)d\mathbf{\Gamma}\,d\varphi$. The perturbation $F_e[\varphi(t)]$ starts at $t=0$ and as time progresses, the φ dependence of the extended phase space distribution function $f'(\mathbf{\Gamma}',t)$ becomes more apparent. Since the number of ensemble members in extended phase space is conserved, the change in f' can be described by the extended phase space Liouville equation,

$$\left.\frac{\partial f'}{\partial t}\right|_{\mathbf{r}'}=-\left[\left(\frac{\partial}{\partial\mathbf{\Gamma}'}\cdot\dot{\mathbf{\Gamma}}'\right)+\dot{\mathbf{\Gamma}}'\cdot\frac{\partial}{\partial\mathbf{\Gamma}'}\right]f'\equiv-iL'(\mathbf{\Gamma}')f',\tag{5}$$

and the Liouvilleans and the extended phase space f and p propagators can be defined in a manner analogous to their definitions in conventional phase space. The operator on the right hand side of Eq. (5), $-iL'(\mathbf{\Gamma}')$, is the extended phase space f Liouvillean. The first term in the brackets in the f Liouvillean is the extended phase space compression factor $\Lambda'(\mathbf{\Gamma})$, which does not depend on φ because there is no compression in the φ direction. The second term is the extended phase space p Liouvillean.

Since $-iL'(\mathbf{\Gamma}')$ is not explicitly time dependent, the formal solution of Eq. (5) can be written as

$$\begin{aligned}f'(\mathbf{\Gamma}',t)&=\exp[-iL'(\mathbf{\Gamma}')t]f'(\mathbf{\Gamma}',0)\\&=\exp\left[-\int_0^t ds\;\Lambda'(\mathbf{\Gamma}(-s))\right]\\&\quad\times\exp[-iL'(\mathbf{\Gamma}')t]f'(\mathbf{\Gamma}',0),\end{aligned}\tag{6}$$

where $\exp[-iL'(\mathbf{\Gamma}')t]$ is the extended phase space f propagator. The expression on the far right side of Eq. (6) is obtained by Dyson decomposition.

Let us now consider a canonical ensemble of systems obeying Hamiltonian equations of motion in equilibrium. For such a system $\Lambda'(\mathbf{\Gamma})\equiv 0$, and the exponent in the f propagator becomes $-iL'(\mathbf{\Gamma}')t=-iL'(\mathbf{\Gamma}')t=iL'(\mathbf{\Gamma}')(-t)$. The initial equilibrium extended phase space distribution function is canonical and independent of φ,

$$f'(\mathbf{\Gamma},\varphi,0)=\frac{e^{-\beta H_0(\mathbf{\Gamma}')}}{\omega T_e\int d\mathbf{\Gamma}\;e^{-\beta H_0(\mathbf{\Gamma})}},$$

where $H_0=\Sigma_i\mathbf{p}_i^2/2m+U(\mathbf{q})$ is the unperturbed Hamiltonian of the system, $U(\mathbf{q})$ is the interaction potential, and $\beta=1/k_BT$, where k_B is the Boltzmann constant and T is the temperature of the system. The external field $F_e(\varphi)$ starts to act upon the system at $t=0$. The above expression for H_0 does not depend on φ, and $f'(\mathbf{\Gamma},\varphi,0)$ is uniform in φ. However, because the extended phase space points with the same initial $\mathbf{\Gamma}(0)$ and different initial $\varphi(0)$ follow different trajectories according to the equations of motion which contain the field $F_e(\varphi)$, leading to different $\mathbf{\Gamma}(t)$ and $\varphi(t)$, we write $H_0(\mathbf{\Gamma}')$ in the exponent of the numerator. In the denominator, the φ dependence has been integrated out.

Substituting the canonical distribution into Eq. (6) we obtain the extended phase space distribution function at time t,

$$\begin{aligned}f'(\mathbf{\Gamma},\varphi,t)&=e^{iL'(-t)}\frac{e^{-\beta H_0(\mathbf{\Gamma}')}}{\omega T_e\int d\mathbf{\Gamma}\;e^{-\beta H_0(\mathbf{\Gamma})}}\\&=\frac{e^{-\beta H_0[\mathbf{\Gamma}'(-t)]}}{\omega T_e\int d\mathbf{\Gamma}e^{-\beta H_0(\mathbf{\Gamma})}}\\&=\exp\left(-\beta\int_0^t ds\;J[\mathbf{\Gamma}(-s)]F_e[\varphi(-s)]\right)\\&\quad\times f'(\mathbf{\Gamma}',0),\end{aligned}\tag{7}$$

where the dissipative flux J is defined in terms of the adiabatic (i.e., unthermostatted) rate of change of the internal energy H_0, as $\dot{H}_0^{\mathrm{ad}}\equiv-J(\mathbf{\Gamma})F_e(\varphi)$. Equation (7) is the generalized Kawasaki distribution function in time-dependent fields.

Adiabatic systems are generally not of great interest because the applied field causes them to heat up, and a steady state can never be reached. Dissipative systems following the equations of the form (3), where α is the Gaussian or Nosé-Hoover thermostat or ergostat, are more interesting. In the case of autonomous systems it has been shown [6,7] that for Gaussian or Nosé-Hoover isokinetic systems, the expression for the perturbed phase space distribution function still satisfies Eq. (7), except that all time propagation [e.g., $J(\mathbf{\Gamma}(t))$] is understood to be generated in the presence of the thermostat [4].

The ensemble average of a phase function at time t is determined using the Heisenberg picture. It should be mentioned that only the hyperplane $\varphi(t)$, which is the solution of the last equation in Eq. (3), is the ergodically consistent representation of the system at time t. In order to obtain the time-dependent response to a well-defined field (which starts at a defined value φ_0), we have to evaluate the exponential

correction (7) to the equilibrium distribution function on different φ planes at different times.

Our results are tested by nonequilibrium molecular dynamics simulation of a system of two disks with periodic boundary conditions, subject to a time-dependent color field [8]. 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 $F_e=F_0\sin(\varphi_0+\omega t)$ acting in the x direction. The equations of motion for $t>0$ in *extended* phase space are

$$\dot{\mathbf{q}}_i=\frac{\mathbf{p}_i}{m},\quad \dot{\mathbf{p}}_i=\mathbf{F}_i+\mathbf{i}c_iF_0\sin\varphi-\alpha\mathbf{p}_i,\quad \dot{\varphi}=\omega.$$

The interaction $\mathbf{F}_i$ between disks is characterized by the WCA (Weeks-Chandler-Andersen) potential [9], and the system is thermostatted using the Gaussian thermostat α,

$$\alpha=\frac{\sum_{i=1,2}(\mathbf{F}_i+\mathbf{i}c_iF_c)\mathbf{p}_i}{\sum_{i=1,2}\mathbf{p}_i^2}.$$

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 amplitude and frequency of the color field are chosen to be $F_0=4$ and $\omega=2\pi$.

The dissipative flux is given by $J=\Sigma_i c_i\dot{x}_i$, and we observed the time-dependent response of the hydrostatic pressure,

$$B\equiv P=\frac{1}{2}(P_{xx}+P_{yy})$$

$$=\frac{1}{2V}\left\langle\sum_{i=1}^{N}\left(\frac{p_{xi}^2+p_{yi}^2}{m}+x_iF_{xi}+y_iF_{yi}\right)\right\rangle.$$

The simulations were done at the density $\rho=N/V=0.396\,850$ and at the temperature $T=1.0$, using the fourth-order Runge-Kutta method of integration of the equations of motion with a time step of $\delta t=0.002$. The simulations were carried out for $2\times650\,000$ 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 point ensures that the average initial dissipative flux is identically zero.

Figure 1 shows different views of the pressure response in extended phase space using direct simulation and the time-dependent Kawasaki formula. In Fig. 1(a) all trajectories start at the same φ_0 and are followed for five periods of the color field. Figure 1(b) shows the development of the response $P(\varphi(t))$ with time. In the linear approximation the pressure is just equal to its equilibrium value, but for strong fields it oscillates with twice the frequency of the external field, since it is even under $\mathbf{M}^T$. At early times the response is very weak and increases in amplitude and changes its form

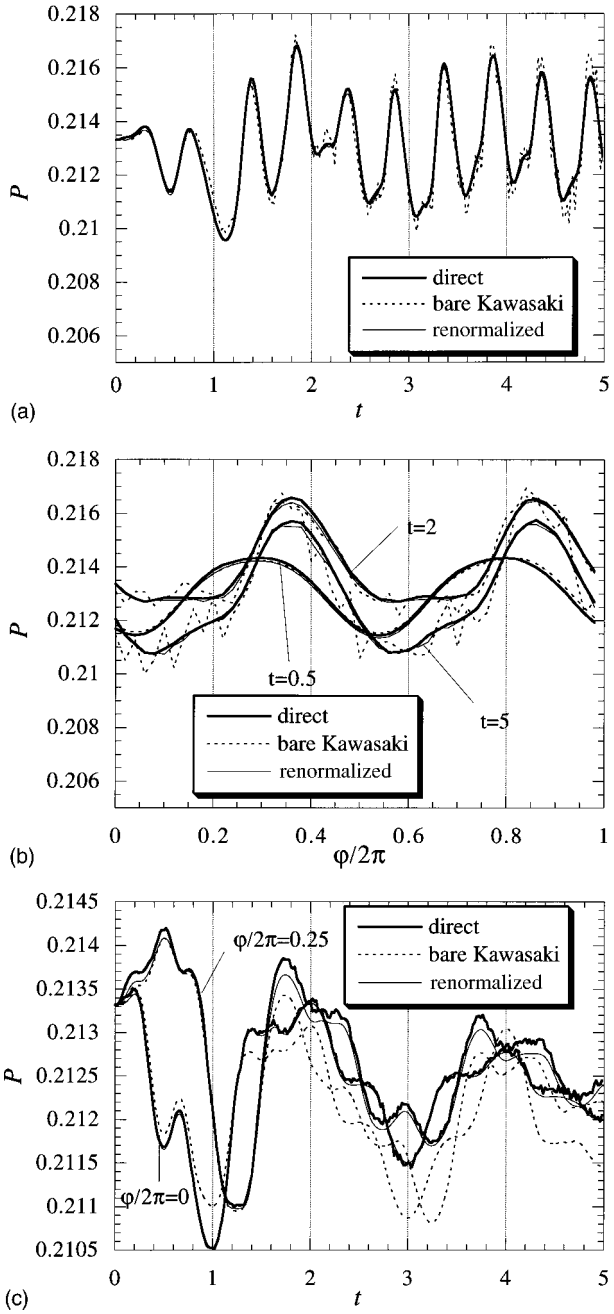

FIG. 1. The direct simulation and Kawasaki results for the pressure in the periodic color field. Both the direct simulation and the Kawasaki results show that the pressure oscillates with twice the frequency of the color field. The amplitude of the pressure oscillations changes in time from zero to the final value. The correspondence between direct simulation and the renormalized Kawasaki method is so good that it is difficult to distinguish the two respective curves on the scale of these graphs. The bare Kawasaki results are correct only at early times.

in time. Time evolution of the pressure response for five periods of color field for two different angles is shown in Fig. 1(c). Although there is no final steady state in the conventional phase space for time-periodic systems, there is a ''steady state response'' for each value of φ. This figure shows the *approach* to this ''steady state'' for $\varphi/2\pi=0$ and $\varphi/2\pi=0.25$.

Initially, for about one period, the direct and Kawasaki

results (called ''bare Kawasaki'' in the figures) show very good agreement. After that the ''bare Kawasaki'' results show increasing fluctuations, because the errors due to incomplete sampling are amplified exponentially in Eq. (7). The distribution function (7) can also be explicitly normalized at each time t,

$$f_r'(\mathbf{\Gamma}',t)=\frac{\exp(-\beta\int_0^t ds\ J[\mathbf{\Gamma}(-s)]F_e[\varphi(-s)])f'(\mathbf{\Gamma}',0)}{\int d\mathbf{\Gamma}'\ \exp(-\beta\int_0^t ds\ J[\mathbf{\Gamma}(-s)]F_e[\varphi(-s)])}. \tag{8}$$

The renormalized form (referred to as ''renormalized Kawasaki'' in the figures) gives better simulation results since the additional factor in the denominator attenuates the large fluctuations. It can be shown that the renormalization factor in Eq. (8) becomes exactly unity in the case of perfect sampling [4].

In this paper we have described a time-dependent generalization of the Kawasaki form of nonlinear response theory. For a two-particle thermostatted system which responds to a strong time-dependent color field, our expressions agree with direct computation. This numerical agreement was obtained for the color field induced changes in the hydrostatic pressure. This check is particularly convincing for at least two reasons. First, the induced pressure changes is an intrinsically nonlinear effect. Thus there is no possibility of a strong linear component of response masking a possibly weak nonlinear component. Secondly, because of the small system size (just two particles) and the oscillatory nature of the applied field, the response curves are quite complex in shape. This means that the chance of ''accidental'' agreement between theory and experiment is exceedingly remote.

Since our calculations have verified the validity of the time-dependent Kawasaki theory for a system of just two particles, it is clear that there is no need to take the thermodynamic limit in order for it to be applicable.

The generalized Kawasaki theory describes the change in the equilibrium phase space distribution function some time t after the time-periodic field has been applied, by tracing backwards in time the phase space volume elements which come to given phase points following the new equations of motion containing the field. Since the expression for the distribution function is exponential in form, the computer simulation errors (caused mainly by incomplete sampling of phase space) increase exponentially, making this method computationally much more expensive than the direct simulation of the nonlinear response. However, when applied to time-independent systems, it has proven useful in deriving fundamental exact fluctuation relations for nonequilibrium steady states. We hope that the same might be true for the time-dependent generalization of the Kawasaki formula.

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