

## Equivalence of thermostatted nonlinear responses

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(Received 26 October 1992)

In this paper we show that, in general, both steady-state averages and time correlation functions computed under Gaussian isokinetic dynamics, Gaussian isoenergetic dynamics, or Nosé-Hoover thermostats are all equal. This result is true even in the far-from-equilibrium nonlinear regime as long as the system is mixing and the quantities involved are local and not trivially related to constants of the motion. We provide computer-simulation results that support this theoretical prediction.

PACS number(s): 05.70.Ln, 03.40.Gc, 02.50.-r, 51.10.+y

### I. INTRODUCTION

Consider an  $N$ -particle system of structureless particles with coordinates,  $\mathbf{q}_1, \mathbf{q}_2, \dots$ , and peculiar momenta,  $\mathbf{p}_1, \mathbf{p}_2, \dots$ , and a potential energy,  $\Phi(\mathbf{q}_1, \mathbf{q}_2, \dots)$ . In 1984 we established [1] that the linear thermostatted response of a phase function  $B(\Gamma) = B(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{p}_1, \mathbf{p}_2, \dots)$ , to an external perturbing field  $F_e$  can usually [2] be written in a Kubo form,

$$\lim_{F_e \rightarrow 0} \langle B(t_\iota) \rangle = -\beta \int_0^t dx \langle J(0) B(s_{,0}) \rangle F_e, \quad (1)$$

where the dissipative flux  $J$  is defined in terms of the adiabatic (i.e., unthermostatted) derivative of the internal energy,  $H_0 = \sum_i \mathbf{p}_i^2 / 2m + \Phi(\mathbf{q}_1, \mathbf{q}_2, \dots)$ ,

$$\left. \frac{dH_0}{dt} \right|^{ad} \equiv -J(\Gamma) F_e, \quad (2)$$

and where  $\beta = 1/k_B T$  is the Boltzmann factor for the ensemble whose average is denoted  $\langle \rangle$ .

In Eq. (1) the subscript  $\iota$  for the time arguments  $t, s$  denotes the form of the thermostat used to extract the heat produced in the system by the dissipative external field. The most common reversible, deterministic thermostats that have been studied include the following [3]: the Gaussian isokinetic thermostat ( $\iota = K$ ), Gaussian isoenergetic thermostat ( $\iota = E$ ), and the usual Nosé-Hoover thermostat ( $\iota = NHK$ ), which employs an integral feedback mechanism based on the peculiar kinetic energy. In this paper we shall also introduce a variant of the Nosé-Hoover thermostat that is based on an internal energy feedback equation ( $\iota = NHE$ ). In Eq. (1) the zero subscript for the time argument  $s$  denotes that the external field  $F_e$  is set to zero. If there is no zero subscript on a time argument [as is the case for  $t$  in (1)], it is understood that the time generation proceeds in the presence of the external field  $F_e$ .

The equations of motion for each of these thermostats ( $\iota = K, E, NHK, \text{ and } NHE$ ) can be written in the form [3]

$$\begin{aligned} \dot{\mathbf{q}}_i &= \mathbf{p}_i / m + C_i F_e, \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + D_i F_e - \alpha_i \mathbf{p}_i, \end{aligned} \quad (3)$$

where it is assumed that the momenta  $\mathbf{p}_i$  are peculiar and are measured with respect to the local streaming velocity of the position of particle  $i$ . The forms of these equations of motion can be derived from Gauss's Principle of Least Constraint [3]. For  $\iota = K, E, NHK$ , and  $NHE$  all that changes is the expression for the thermostating multiplier  $\alpha$ . In the two cases we shall give most detailed consideration to,  $\iota = K$  and  $E$ , we have

$$\alpha_K = \frac{\sum_{i=1}^N \mathbf{F}_i \cdot \mathbf{p}_i / m + F_e D_i \cdot \mathbf{p}_i / m}{\sum_{i=1}^N \mathbf{p}_i^2 / m} \quad (4)$$

and

$$\alpha_E = \frac{\mathbf{F}_e \cdot \sum_{i=1}^N D_i \mathbf{p}_i / m - \mathbf{F}_i C_i}{\sum_{i=1}^N \mathbf{p}_i^2 / m}. \quad (5)$$

In words, Eq. (1) simply states that the thermostatted linear response ( $\lim_{F_e \rightarrow 0}$ ) of a phase function  $B$  is related to the time integral of a thermostatted equilibrium ( $F_e = 0$ ) time correlation function which correlates the phase function  $B$  to the dissipative flux which is generated by the perturbing external field.

In 1983 we showed [4] that in the thermodynamic limit, equilibrium time correlation functions evaluated under Gaussian isothermal dynamics are identical to the corresponding equilibrium time correlation functions evaluated under Newtonian dynamics. Later in the same year Evans and Holian [5] showed that Nosé-Hoover thermostatted dynamics ( $NHK$ ) also leaves equilibrium time correlation functions unchanged in the thermodynamic limit.

When this equivalence of thermostatted equilibrium time correlation functions is combined with the results of thermostatted linear-response theory summarized in (1), we observe that at the same thermodynamic state point the linear thermostatted response is independent of the nature of the thermostat. These results, however, only relate to the linear-response regime where  $F_e \rightarrow 0$ . From

a practical point of view it has been known for some time that even in the nonlinear regime computed averages and time correlation functions are remarkably insensitive to the form of the thermostat.

Recently Liem, Brown, and Clarke [6] performed accurate comparisons of the viscosity and the nonequilibrium equation of state of systems which are thermostatted homogeneously (as described above) with corresponding results for systems which are thermostatted by conduction to thermal boundaries. They compared the results of homogeneous thermostatted shear flow with results from simulations of Couette flow between atomistically modeled walls. They found that within the estimated statistical uncertainties of their calculations ( $\pm 2\%$ ), the homogeneously sheared and thermostatted results agreed with the inhomogeneous simulations. It is worth pointing out that these comparisons were carried out reasonably far from the linear regime. In fact, at their highest shear rates the viscosity is some 20% smaller than the extrapolated zero shear value.

Somewhat earlier, in 1985 we presented [7] a comparison of soft-sphere viscosities obtained homogeneously using Gaussian isothermal, Gaussian isoenergetic, and Nosé-Hoover thermostats. Again, all of these results agreed with each other within estimated uncertainties ( $\pm 2\%$ ). This comparison was carried out far into the nonlinear regime where the viscosity is 30% smaller than its limiting Newtonian value.

In the present paper we sketch a proof of the thermostat independence of both steady-state averages and steady-state time correlation functions in the nonlinear regime. We also provide numerical data that support these predictions.

## II. THEORY

### A. Steady-state averages

Consider two noncommuting operators  $\mathcal{A}$  and  $\mathcal{B}$ . A Dyson equation [3] giving an exact relation between the resolvents of these operators can be written as

$$e^{(\mathcal{A}+\mathcal{B})t} = e^{\mathcal{A}t} + \int_0^t dt_1 e^{\mathcal{A}t_1} \mathcal{B} e^{(\mathcal{A}+\mathcal{B})(t-t_1)}. \quad (6)$$

We now choose

$$\mathcal{A} + \mathcal{B} \equiv iL_K, \quad \mathcal{A} \equiv iL_E, \quad (7)$$

where  $iL_K$  is the Gaussian isokinetic Liouvillean and  $iL_E$  the Gaussian isoenergetic  $p$  Liouvillean, which describes the thermostatted and field-dependent motion of an arbitrary phase function  $B$ ,

$$B(\Gamma(t_i)) = e^{iL_i t_i} B(\Gamma(0)), \quad i = K, E, \quad (8)$$

where  $\Gamma = (\mathbf{q}_1, \dots, \mathbf{q}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)$ . From Eq. (3) the Liouville operators can be written as [3]

$$iL_i = \dot{\Gamma}_i \cdot \frac{\partial}{\partial \Gamma}. \quad (9)$$

The only difference between the isokinetic and the isoenergetic Liouvillians is in the form of the thermostating phase function  $\alpha$ ,

$$iL_K - iL_E = -(\alpha_K - \alpha_E) \sum_{i=1}^N \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \equiv i\delta L. \quad (10)$$

Recursive substitution into the Dyson equation (6) gives

$$\begin{aligned} e^{iL_K t} &= e^{iL_E t} + \int_0^t dt_1 e^{iL_E t_1} i\delta L e^{iL_K(t-t_1)} \\ &= e^{iL_E t} + \int_0^t dt_1 e^{iL_E t_1} i\delta L \left[ e^{iL_E(t-t_1)} + \int_0^{t-t_1} dt_2 e^{iL_E t_2} i\delta L e^{iL_K(t-t_1-t_2)} \right] \\ &= e^{iL_E t} + \int_0^t dt_1 e^{iL_E t_1} i\delta L e^{iL_E(t-t_1)} + \int_0^t dt_1 \int_0^{t-t_1} dt_2 e^{iL_E t_1} i\delta L e^{iL_E t_2} i\delta L e^{iL_E(t-t_1-t_2)} + \dots \end{aligned} \quad (11)$$

It is frequently convenient to use the short-hand notation [3]

$$\Rightarrow = \{ \rightarrow + \rightarrow \Delta \rightarrow + \dots \}, \quad (12)$$

where

$$e^{iL_K t} \equiv \Rightarrow, \quad e^{iL_E t} = \rightarrow \quad \text{and} \quad i\delta L \equiv \Delta, \quad (13)$$

and where arrow chains denote convolutions.

Without loss of generality, consider the difference between the steady-state averages of an arbitrary *extensive* phase function  $A(\Gamma)$ . We assume that the two systems (i.e., the isokinetic and isoenergetic thermostatted systems) are at the same nonequilibrium state point. To ensure this, we assume the two systems have the same values for the number of particles  $N$ , the volume  $V$ , the

external field  $F_e$ , and the same steady-state-average value of the phase-space compression factor [3]  $\Lambda$ ,

$$\frac{d}{dt} \ln f(\Gamma, t) \equiv -\Lambda(\Gamma(t)). \quad (14)$$

For E, K, NHK, and NHE thermostatted systems this implies that the average values of the thermostating multipliers are identical, since for these systems  $\Lambda(t_i) = -3N\alpha(t_i)$ . So in particular for isoenergetic and isokinetic thermostatted systems we have

$$\lim_{t \rightarrow \infty} \langle \alpha(t_K) \rangle - \langle \alpha(t_E) \rangle = 0. \quad (15)$$

The difference in the nonlinear thermostatted response of a canonical ensemble average of an arbitrary local, extensive phase function  $A(\Gamma)$  is therefore

$$\begin{aligned}
\langle A(t_K) \rangle - \langle A(t_E) \rangle &= \int d\Gamma f_c(\Gamma) (e^{iL_K t} - e^{iL_E t}) A \\
&= \int d\Gamma f_c(\Gamma) \left[ \int_0^t dt_1 e^{iL_E t_1} \delta L e^{iL_E(t-t_1)} \right. \\
&\quad \left. + \int_0^t dt_1 \int_0^{t-t_1} dt_2 e^{iL_E t_1} \delta L e^{iL_E t_2} \delta L e^{iL_E(t-t_1-t_2)} + \dots \right] A. \quad (16)
\end{aligned}$$

(A local, extensive phase function  $A(\Gamma)$  can by definition be written as a sum,  $\sum_{i=1}^N A_i(\Gamma)$  and  $\lim_{|\mathbf{q}_i - \mathbf{q}_j| \rightarrow \infty} \langle A_i A_j \rangle = 0$  [3,7].)

It is convenient to define a new phase function  $B'(t)$  in the following manner:

$$B'(t) \equiv \sum \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} B(t). \quad (17)$$

From this definition it is clear [3], that if  $B$  is extensive, so too is  $B'$ . From Eq. (10)

$$i\delta L e^{iL_E(t-s)} A = -\delta\alpha \sum_{i=1}^N \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} A(t_E - s_E) \equiv -\delta\alpha A'(t_E - s_E). \quad (18)$$

Substituting this result into (16), we see that

$$\begin{aligned}
\langle A(t_K) \rangle - \langle A(t_E) \rangle &= \int d\Gamma f_c(\Gamma) \left[ -\int_0^t dt_1 e^{iL_E t_1} \delta\alpha A'(t-t_1) \right. \\
&\quad \left. + \int_0^t dt_1 \int_0^{t-t_1} dt_2 e^{iL_E t_1} \delta\alpha \delta\alpha'(t_{E2}) A''(t_E - t_{E1}) - \dots \right], \quad (19)
\end{aligned}$$

where  $A''$  is defined recursively in terms of  $\delta\alpha$  and  $A'$ ,

$$\delta\alpha'(s_{E2}) A''(t_E - t_{E1}) \equiv \sum_i \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} \delta\alpha(t_{E2}) A'(t_E - t_{E1}). \quad (20)$$

From (20) and (19) we see that

$$\langle A(t_K) \rangle - \langle A(t_E) \rangle = -\int_0^t dt_1 \langle \delta\alpha(t_{E1}) A'(t_E) \rangle + \int_0^t dt_1 \int_0^{t-t_1} dt_2 \langle \delta\alpha(t_{E1}) \delta\alpha'(t_{E2} + t_{E1}) A''(t_E) \rangle + \dots \quad (21)$$

Now there are two very important properties of the primed variables. Firstly, as already mentioned, if  $A$  is extensive, so too are  $A'$ ,  $A''$ , . . . Likewise  $\alpha$ ,  $\alpha'$ , and  $\alpha''$  are local, intensive variables. Secondly, in the long-time limit  $A'$  and  $A''$  and  $\delta\alpha$ ,  $\delta\alpha'$ , and  $\delta\alpha''$  have zero means. This can be proved quite easily.

From its definition (17) we see that

$$\begin{aligned}
\langle B'(t_i) \rangle &= \int d\Gamma f_c(\Gamma) \sum_i \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} B(t_i) = -\int d\Gamma B(t_i) \sum_i \frac{\partial}{\partial \mathbf{p}_i} \cdot [\mathbf{p}_i f_c(\Gamma)] \\
&= -3N \langle B(t_i) \rangle - \int d\Gamma B(t) \sum_i \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} f_c(\Gamma) = -3N \langle B(t_i) \rangle + \frac{\beta}{m} \int d\Gamma B(t) \sum_i \mathbf{p}_i^2 f_c(\Gamma) \\
&= 2\beta \langle B(t_i) \Delta K(0) \rangle. \quad (22)
\end{aligned}$$

Assuming that the variable  $B$  is not a trivial function of either of the constants of motion, the kinetic or the internal energy, and assuming that the system is *mixing* [8],

$$\lim_{t \rightarrow \infty} \langle B'(t_i) \rangle = 0, \quad i = E, K. \quad (23)$$

Similarly, one can show that

$$\lim_{t_1, t_2 \rightarrow \infty} \langle \delta\alpha'(t_{i1}) A''(t_{i2}) \rangle = 0. \quad (24)$$

Returning to Eq. (21) we see that in the long-time limit, the difference in averages of  $A$  computed under isoenergetic and isokinetic thermostats can be expressed as time integrals of correlation functions of zero-mean variables. Further, since  $A'$ ,  $A''$ , . . . are extensive while  $\delta\alpha$ ,  $\delta\alpha'$ , . . . are intensive, it follows that in the long-time limit the

difference  $\langle A(t_K) \rangle - \langle A(t_E) \rangle$  is intensive and therefore becomes insignificant compared to  $\langle A(t_E) \rangle$  in the large system limit. (In deriving this result we use the fact that the average of products of zero-mean, local, extensive variables is itself extensive—see p. 4071 of Ref. [7]).

## B. Steady-state averages

We now consider the thermostat dependence of *steady-state* time correlation functions,  $\lim_{t \rightarrow \infty} \int d\Gamma f_c A(t) B(t+s)$ , of extensive phase functions  $A$  and  $B$ . Without loss of generality, we assume that under the isokinetic thermostat the steady-state means of both  $A$  and  $B$  are zero. Using the Dyson equation (6) we see that

$$\begin{aligned}
\langle A(t_K)B(t_K + \tau_K) \rangle &= \int d\Gamma f_c(e^{iL_K t} A)(e^{iL_K(t+\tau)} B) \\
&= \int d\Gamma f_c[(\{\rightarrow + \rightarrow \Delta \rightarrow + \dots\})_t A] \\
&\quad \times [(\{\rightarrow + \rightarrow \Delta \rightarrow + \dots\})_{t+\tau} B], \tag{25}
\end{aligned}$$

where the indices to the parentheses around the Dyson expanded propagators denote the total time each expansion works through. The operators within each of the two expansions  $t$  and  $t+\tau$  only operate on the phase functions  $A$  and  $B$ , respectively. Writing out the first few terms of the Dyson equation expansion, we see that

$$\begin{aligned}
\langle A(t_K)B(t_K + \tau_K) \rangle &= \langle A(t_E)B(t_E + \tau_E) \rangle + \int d\Gamma f_c[(\rightarrow \Delta \rightarrow)_t A][(\rightarrow)_{t+\tau} B] + \int d\Gamma f_c[(\rightarrow)_t A][(\rightarrow \Delta \rightarrow)_{t+\tau} B] \\
&\quad + \int d\Gamma f_c[(\rightarrow \Delta \rightarrow)_t A][(\rightarrow \Delta \rightarrow)_{t+\tau} B] + \dots \tag{26}
\end{aligned}$$

We note that from the results of Sec. II A, since  $A$  and  $B$  have zero steady-state means under the isokinetic thermostat they also must be zero-mean variables under the isoenergetic thermostat.

We now consider the second term on the right-hand side of (26):

$$\begin{aligned}
\int d\Gamma f_c[(\rightarrow \Delta \rightarrow)_t A][(\rightarrow)_{t+\tau} B] &= \int_0^{t+\tau} ds \int d\Gamma f_c B(t_E + \tau_E) e^{iL_E s} i\delta L e^{iL_E(t-s)} A \\
&= - \int_0^{t+\tau} ds \int d\Gamma f_c B(t_E + \tau_E) \delta\alpha(s_E) A'(t_E) = O(1), \text{ as } t_E \rightarrow \infty. \tag{27}
\end{aligned}$$

In deriving the last equality we have again assumed the system is mixing [8] and that there is no trivial relation between the variables  $B$ ,  $\delta\alpha$ , and  $A'$  and either of the constants of the motion. Clearly, the third term on the right-hand side of (26) is also  $O(1)$ . The fourth term on the right-hand side of (26) can be expanded as

$$\begin{aligned}
\int d\Gamma f_c[(\rightarrow \Delta \rightarrow)_t A][(\rightarrow \Delta \rightarrow)_{t+\tau} B] &= \int_0^t ds_1 \int_0^{t+\tau} ds_2 \int d\Gamma f_c(e^{iL_E s_1} i\delta L e^{iL_E(t-s_1)} A)(e^{iL_E s_2} i\delta L e^{iL_E(t-s_2)} B) \\
&= \int_0^t ds_1 \int_0^{t+\tau} ds_2 \int d\Gamma f_c \delta\alpha(s_{1E}) A'(t_E) \delta\alpha(s_{2E}) B'(t_E + \tau_E) \\
&= \int_0^t ds_1 \int_0^{t+\tau} ds_2 \langle \delta\alpha(s_{1E}) \delta\alpha(s_{2E}) A'(t_E) B'(t_E + \tau_E) \rangle \\
&= O(1/N) \text{ as } t_E, \tau_E \rightarrow \infty. \tag{28}
\end{aligned}$$

It is clear that the same methods can be used to conclude that higher-order terms in (26) are at least of  $O(1)$  and can therefore be ignored in the large system limit. This concludes our proof of the equivalence of steady-state time correlation functions computed under Gaussian isoenergetic and Gaussian isothermal thermostats.

### C. Nosé-Hoover thermostats

It is straightforward to extend the proof in Sec. II A to encompass the equivalence of Nosé-Hoover (NHK and NHE) averages as well. The equations of motion for the NHK and NHE thermostats are identical to (3) with the addition that the thermostating multiplier must be considered as an additional phase-space variable, since it satisfies an equation of motion. For the usual NHK thermostat we have, instead of (4) or (5),

$$\frac{d\alpha_{\text{NHK}}}{dt} = \left[ \left| \frac{\sum p_i^2/2m}{3Nk_B T/2} \right| - 1 \right] / \tau^2, \tag{29}$$

while for the energy equivalent, NHE, we have

$$\frac{d\alpha_{\text{NHE}}}{dt} = \left[ \frac{H_0}{\langle H_0 \rangle} - 1 \right] / \tau^2. \tag{30}$$

Thus,  $6N$ -dimensional phase space must be augmented to at least  $6N+1$  dimensions:  $\Gamma^* \equiv \Gamma, \alpha_{\text{NHK}}$  or  $\Gamma, \alpha_{\text{NHE}}$ .

The difference in the NHK and isokinetic Liouvilleans considered in this augmented phase space is

$$\begin{aligned}
i\delta L &= iL_{\text{NHK}} - iL_E \\
&= -(\alpha_{\text{NHK}} - \alpha_E) \sum \mathbf{p}_i \cdot \frac{\partial}{\partial \mathbf{p}_i} - \dot{\alpha}_{\text{NHK}} \frac{\partial}{\partial \alpha_{\text{NHK}}}. \tag{31}
\end{aligned}$$

The last term in this equation has no effect on phase variables  $A(\Gamma)$  and  $B(\Gamma)$ , since these variables are not functions of  $\alpha_{\text{NHK}}$ . The phase-space compression factor is

$$\Lambda_{\text{NHK}} = -3N\alpha_{\text{NHK}}. \tag{32}$$

So we see immediately that if the nonequilibrium steady-state point is defined by the variables  $N$ ,  $V$ ,  $F_e$ , and  $\langle \Lambda \rangle$ , the analog of Eq. (15) also holds in this case, namely

$$\lim_{t \rightarrow \infty} \langle \alpha(t_{\text{NHK}}) \rangle - \langle \alpha(t_K) \rangle = 0. \tag{33}$$

From this point on the equivalence proof is formally identical to that given above for the equivalence of isoenergetic and isokinetic steady-state averages. It is also clear the proof can easily be extended to cover the NHE thermostat.

### III. CALCULATIONS

In order to provide numerical support of the proof of the equivalence of the different kinds of thermostats, we simulated a WCA fluid subject to a Couette strain field. The equations of motion for this system are [3]

$$\begin{aligned}\dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m} + \mathbf{n}_x \gamma y_i, \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \mathbf{n}_x \gamma P_{yi} - \alpha \mathbf{p}_i,\end{aligned}\quad (34)$$

where  $\mathbf{n}_x$  is the unit vector in the  $x$  direction and  $\gamma = \partial u_x / \partial y$  is the strain rate. In the absence of thermostats, these equations give an exact description of adiabatic planar Couette flow [3].

The expressions for  $\alpha$  depend on the particular choice of thermostat. The Gaussian isokinetic and isoenergetic  $\alpha$ 's [Eqs. (4) and (5)] become

$$\alpha_K = \frac{\sum_{i=1}^N (\mathbf{F}_i \cdot \mathbf{p}_i - \gamma P_{xi} P_{yi})}{\sum_{i=1}^N \mathbf{p}_i^2} \quad (35)$$

and

$$\alpha_E = \frac{-\gamma \sum_{i=1}^N (p_{xi} p_{yi} - y_i F_{xi})}{\sum_{i=1}^N \mathbf{p}_i^2} = \frac{-\gamma V P_{xy}}{\sum_{i=1}^N \mathbf{p}_i^2}, \quad (36)$$

where  $P_{xy}$  is the  $xy$  element of the pressure tensor [3]. The Nosé-Hoover  $\alpha$ 's are given by Eqs. (29) and (30).

A WCA potential is a Lennard-Jones potential that has been truncated at its minimum and shifted to make it continuous:

$$u(r) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + \epsilon, & r < 2^{1/6} \sigma \\ 0, & r \geq 2^{1/6} \sigma. \end{cases} \quad (37)$$

The results reported here are given in reduced units. The length unit is  $\sigma$ , the energy unit is  $\epsilon$ , and the time unit is  $t_0 = \sigma(m/\epsilon)^{1/2}$ , where  $m$  is the mass of the particle. The equations of motion have been solved by a fourth-order gear predictor-corrector method with a time step of  $0.002t_0$ .

We chose a state point with a reduced density  $n\sigma^3 = 0.8442$ , a reduced temperature  $k_B T/\epsilon = 0.722$ , and a reduced shear rate  $\gamma t_0 = 1.0$ . We performed two  $20000t_0$  long simulations for a 108-particle system and four  $1000t_0$  long simulations for a 2048-particle system.

In the small system we compared the pressure tensor  $P$ , the temperature  $T$ , the internal energy  $H_0$ , the  $\alpha$ 's and the self-diffusion tensor  $D$  for a Gaussian isokinetic system and a Gaussian isoenergetic system. In the isoenergetic simulation the internal energy was set equal to the average internal energy from the isokinetic simulation.

From the theory presented in Sec. II A the differences in the averages of the phase functions for the pressure, energy, and the  $\alpha$ 's should all be at least of order  $1/N$ . The self-diffusion tensor for a shearing fluid has recently been shown [9] to be the time integral of steady-state time cross-correlation functions of the various Cartesian components of the peculiar velocity [ $\mathbf{p}_i/m$  in (34)]. Thus a comparison of the diffusion tensors computed under different thermostats tests the predictions of the theory

TABLE I. Comparison of thermostat for 108 WCA particles ( $\gamma t_0 = 1$ ,  $k_B T/\epsilon \approx 0.722$ ,  $n\sigma^3 = 0.8442$ ).

Property	Gaussian const $H_0$	Gaussian const $T$
$\alpha$	$0.998 \pm 0.002$	$0.989 \pm 0.002$
$P_{xy}$	$1.785 \pm 0.003$	$1.786 \pm 0.003$
$P_{xx}$	$7.181 \pm 0.004$	$7.182 \pm 0.005$
$P_{yy}$	$7.205 \pm 0.004$	$7.207 \pm 0.002$
$P_{zz}$	$6.833 \pm 0.001$	$6.832 \pm 0.005$
$D_{xx}$	$0.0625 \pm 0.0003$	$0.0627 \pm 0.0003$
$D_{yy}$	$0.0581 \pm 0.0005$	$0.0582 \pm 0.0004$
$D_{zz}$	$0.0524 \pm 0.0002$	$0.0525 \pm 0.0002$
$\eta_-$	$0.012 \pm 0.003$	$0.012 \pm 0.002$
$\eta_0$	$0.180 \pm 0.001$	$0.180 \pm 0.001$

given in Sec. II B.

In Table I we compare the various properties of the isokinetic and the isothermal 108-particle systems. The viscosity coefficients  $\eta_0$  and  $\eta_-$  are defined as  $-[P_{zz} - (P_{xx} + P_{yy})/2]/2\gamma$  and  $-(P_{xx} - P_{yy})/2\gamma$ . All the properties except the  $\alpha$ 's agree very well within estimated statistical uncertainties. For  $\eta_-$  this is not a very convincing test, since the error bars are  $\sim 25\%$ . However, the larger relative bars for  $\eta_-$  are simply due to the rather small difference between  $P_{xx}$  and  $P_{yy}$ . For the other properties the relative errors are about 0.5% or less. We omitted the off-diagonal elements of the self-diffusion tensor because they are zero within error bars of 0.001. Although the  $\alpha$ 's do not agree within the estimated statistical uncertainties, they do agree to  $O(1/N) = 0.01$  as predicted by theory.

The velocity autocorrelation functions whose Cartesian elements form the self-diffusion tensor are thermostat independent to within absolute errors bars of  $\pm 0.003$ . In Fig. 1 we show a typical comparison of steady-state velocity autocorrelation functions.

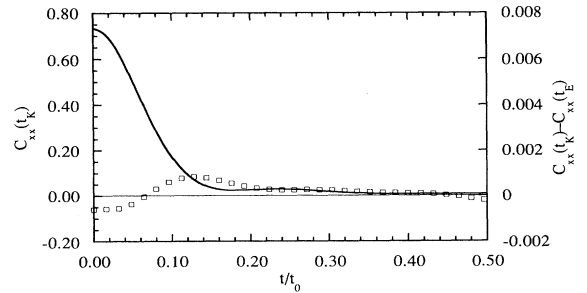


FIG. 1. In this graph we show the steady-state peculiar velocity autocorrelation function  $C_{xx}(t_i) = \langle p_x(t_i) p_x(0) \rangle / m^2$ ,  $i = K$ , computed for the 108-particle WCA system described in the text. The squares show, after expansion by a factor of 100, the differences  $C_{xx}(t_E) - C_{xx}(t_K)$  between this correlation function and that computed at the corresponding times under the isoenergetic thermostat. The differences between these results are of the same size as the estimated statistical uncertainties in the correlation functions themselves,  $\pm 0.001$ .

TABLE II. Comparison of thermostat for 2048 WCA particles ( $\gamma t_0=1$ ,  $k_B T/\epsilon \approx 0.722$ ,  $n\sigma^3=0.8442$ ). NH denotes Nosé-Hoover. For Nosé-Hoover thermostats,  $\tau=3.3$  in the isothermal case and 2.0 in the isoenergetic case.

Property	Gaussian const $T$	NH const $T$	Gaussian const $H_0$	NH const $H_0$
$\alpha$	0.990±0.001	0.990±0.002	0.992±0.001	0.987±0.001
$P_{xy}$	1.808±0.001	1.808±0.003	1.811±0.001	1.805±0.002
$P_{xx}$	7.226±0.002	7.226±0.004	7.232±0.003	7.226±0.003
$P_{yy}$	7.269±0.003	7.272±0.008	7.274±0.001	7.270±0.002
$P_{zz}$	6.912±0.002	6.910±0.003	6.912±0.003	6.913±0.001
$\eta_-$	0.021±0.002	0.023±0.005	0.021±0.002	0.022±0.002
$\eta_0$	0.168±0.002	0.170±0.002	0.171±0.002	0.168±0.001

We performed four simulations for a 2048-particle system to compare all four different thermostats. The results are shown in Table II. Here all the properties also agree within an error of  $\pm 0.5\%$ , including the  $\alpha$ 's. Note also that there are small but statistically significant differences between the properties of the large system and the small system. The magnitude of all the elements of the pressure tensor and  $\eta_-$  increase slightly. The value of  $\eta_0$  changes by some 5%. The  $N$  dependence of  $\eta_0$  has been noted before [10]. In spite of this  $N$  dependence, for a given  $N$  there is good agreement between estimates obtained for this sensitive property using each of the different thermostats.

#### IV. DISCUSSION

We have shown that for mixing [8] systems where the variables  $A, A', \dots, B, B', \dots, \alpha, \alpha', \dots$  have no trivial relations to the constants of the motion, steady-state time averages  $\langle A \rangle$  and  $\langle B \rangle$  and steady-state time correlation functions  $\langle A(0)B(t) \rangle$  formed under E, K, NHK, and NHE thermostats are identical in the large system limit. This is true even far into the nonlinear regime as long as the system retains the mixing property as required in Eq.

(22). One should not think that these results imply that the thermostat independence of both steady state averages and time correlation functions is observed for *all* thermostats.

We recently introduced  $\mu$  thermostats [11], in which the thermostatted equation of motion for the peculiar momenta reads

$$\dot{p}_{\delta i} = F_{\delta i} + D_i F_{e\delta} - \alpha_\mu \frac{P_{\delta i}}{|p_{\delta i}|} |p_{\delta i}|^\mu, \quad \delta = x, y, z. \quad (38)$$

For these thermostats, the phase-space compression factor is

$$\Lambda = -\alpha_\mu \mu \sum_{\delta=x}^z \sum_{i=1}^N |p_{\delta i}|^{\mu-1}. \quad (39)$$

Now the difference between the  $p$  Liouvillean of the  $\mu$  and the isokinetic thermostat is such that the variables that correspond to  $\delta\alpha$  and  $A'$  no longer have zero means in the steady state defined by the values of  $N$ ,  $V$ ,  $F_e$ , and  $\langle \Lambda \rangle$ . Thus both steady-state averages and time correlation functions differ under  $\mu$  and isokinetic thermostats. This has recently been observed in computer simulations [11].

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