Conjugate-pairing rule and thermal-transport coefficients

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It has recently been shown by Evans, Cohen, and Morriss [Phys. Rev. A **42**, 5990 (1990)] that bulk thermal-transport coefficients can be calculated from the maximal Lyapunov exponents by using the conjugate-pairing rule. In the present paper we use computer simulation to explore the validity of the rule under conditions which are more general than those used in the derivation by Evans, Cohen, and Morriss. We show that the existence of a *steady* state for dissipative dynamics and the satisfaction of the condition known as the adiabatic incompressibility of phase space (i.e., area preserving in the absence of a thermostat) are insufficient for the rule to hold. We also show that the linear field-induced shift of the Lyapunov exponents with respect to the exponent index, is among the nonequilibrium molecular-dynamics algorithms, apparently peculiar to the SLLOD algorithm (so named because of its close relationship to the Dolls tensor algorithm) for shear flow.

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I. INTRODUCTION

The Lyapunov spectra for nonequilibrium steady states generated by various nonequilibrium molecular-dynamics (NEMD) algorithms have been obtained numerically for some years [2,3]. These spectra are of interest in characterizing the fractal character of nonequilibrium distribution functions in phase space and the contraction of the phase-space dimensionality in nonequilibrium steady states. However, Lyapunov spectra are of more than merely geometrical interest. Recently we have proved some important relations between the Lyapunov exponents and the numerical values of thermal-transport coefficients.

If one orders the Lyapunov exponents in terms of size, one can define conjugate pairs by grouping the largest with the smallest, the second largest with the second smallest, etc. Regardless of whether a system is at equilibrium or not, and regardless of whether a system is subject to an external field, if the motion of the system is generated from a Hamiltonian, the sum of all the Lyapunov exponents is equal to zero and the sum of each conjugate pair is also zero [4].

If a system is subject to an external dissipative field and each degree of freedom in the system is thermostatted, the sum of the Lyapunov exponents becomes negative and equal to the phase-space-compression factor [5,6]. Since the mid-1970s people have used nonequilibrium molecular-dynamics computer simulation to calculate the transport properties of statistical-mechanical systems. NEMD is efficient and realistic. For example, using the "Evans" heat-flow NEMD algorithm [6], one can calculate the thermal conductivity of model liquid argon close to its triple point with greater precision than it can be measured experimentally.

In order to create a nonequilibrium *steady* state, computer simulators employ one of two families of mathematical thermostats: the Nosé-Hoover thermostat or the so-called Gaussian thermostat [6]. The heat generated in the simulated system from the work done on it by the external field, is removed by a thermostat which constrains the total peculiar kinetic energy or the total internal energy. In the Nosé-Hoover thermostat it is only the time average of these quantities which is held constant. In the Gaussian thermostats these quantities are made constants of the motion.

The fact that the phase-space-compression factor is equal to the sum of the Lyapunov exponents [5,6] means that the exponents are also related to the transport coefficients of the system. From a practical point of view, such a relationship is not very useful because it is extraordinarily difficult to calculate all the Lyapunov exponents. For an N-particle three-dimensional system, it requires performing $6N$ molecular-dynamics simulations, each of which involve $6N$ first-order differential equations.

In a recent work [1], hereafter referred to as I, Evans, Cohen, and Morriss showed that if in the absence of thermostatting (so-called *adiabatic* condition), the eigenvalues of the stability matrix appear in zero-sum conjugate pairs, then, when a Gaussian thermostat is applied to the system, the arithmetic mean of every conjugate pair of Lyapunov exponents is negative and independent of the particular pair number. This rule is called the conjugate-pairing rule.

It is thus possible to evaluate the phase-space-compression factor and consequently the transport coefficients by knowing just one pair of Lyapunov exponents, preferably the smallest one and the largest one, because they are the easiest ones to compute.

It is easy to show that this adiabatic eigenvalue struc-

ture is present if the adiabatic equations of motion can be derived from a Hamiltonian. This is the case for many but not all NEMD thermal-transport algorithms [6] (e.g., the Dolls tensor for the limiting zero-shear viscosity and the color-conductivity algorithms for computing the self- and mutual-diffusion coefficients of fluids and fluid mixtures). This eigenvalue structure is also present in the SLLOD algorithm (so named because of its close relationship to the Dolls tensor algorithm) [6] for calculating the nonlinear viscosity coefficients of fluids which are far from equilibrium. This is in spite of the fact that the SLLOD algorithm cannot be derived from a Hamiltonian. It is worth pointing out that the SLLOD algorithm, unlike the Dolls algorithm, is the exact dynamics for a shearing fluid not only in the linear regime but also in the nonlinear regime [6].

It is not known whether the above-mentioned adiabatic eigenvalue structure is a necessary condition for the conjugate-pairing rule to hold. For example, a more general necessary condition that had been tentatively proposed [7] is that the conjugate-pairing rule should hold for systems in which the adiabatic motion is phase-space preserving (this condition is known as the adiabatic incompressibility of phase space or AIΓ [6]) and which come to a steady state under thermostatting. This conjecture is related to the time-invariance properties of steady states.

In this paper we show that this conjecture is incorrect. We do this by calculating the Lyapunov spectrum for the "Evans" algorithm for the thermal conductivity of fluids. The adiabatic equations of motion for this algorithm are not derivable from a Hamiltonian but the algorithm does satisfy AIΓ. The simulations show that the conjugate-pairing rule does not hold for this system.

We also calculate Lyapunov spectra for most of the other NEMD simulation algorithms showing that the conjugate-pairing rule is observed when the conditions for the conjugate-pairing rule proved by Evans, Cohen, and Morriss hold.

II. THEORY AND METHOD

A. Equations of motion for NEMD algorithms

The systems of interest consist of N particles of mass m. The volume of the system is V. The position coordinates and the momenta of particle i are denoted by $\mathbf{q}_i$ and $\mathbf{p}_i$, respectively, and $\mathbf{q}_{ij}=\mathbf{q}_j-\mathbf{q}_i$ is the distance vector between particle i and particle j. The pair-interaction energy between these particles is Φ_{ij} and the force exerted on particle i by particle j is $\mathbf{F}_{ij}$.

We have studied four types of algorithms for dynamical systems: the Dolls tensor and the SLLOD equations of motion for planar Couette flow, the color-conductivity algorithm for the self-diffusion coefficient, and the "Evans" heat-flow algorithm. These algorithms are now standard techniques in molecular dynamics and the reader is referred to a recent text [6] for details. The Dolls tensor equations for shear flow are given by

$$\begin{aligned}\dot{\mathbf{q}}_i&=\frac{\mathbf{p}_i}{m}+\mathbf{i}\gamma y_i\ ,\\ \dot{\mathbf{p}}_i&=\mathbf{F}_i-\mathbf{j}\gamma p_{xi}-\alpha\mathbf{p}_i\ ,\end{aligned}\tag{1}$$

where $\mathbf{i}$ and $\mathbf{j}$ are the unit vectors in the x and y directions, respectively, $\gamma=\partial u_x/\partial y$ is the shear rate, and α is the Gaussian thermostat multiplier. In the isokinetic version of the algorithm, where the total kinetic energy $\sum_i p_i^2/2m$ is held constant, α is given by

$$\alpha=\frac{\sum_{i=1}^{N}\mathbf{F}_i\cdot\mathbf{p}_i-\gamma p_{xi}p_{yi}}{\sum_{i=1}^{N}\mathbf{p}_i^2}\ .\tag{2}$$

If the total internal energy is a constant of the motion, one has

$$\alpha=-\gamma\frac{\sum_{i=1}^{N}\left[F_{xi}\cdot y_i+\frac{p_{xi}p_{yi}}{m}\right]}{\frac{1}{m}\sum_{i=1}^{N}\mathbf{p}_i^2}=-\gamma\frac{P_{xy}V}{\frac{1}{m}\sum_{i=1}^{N}\mathbf{p}_i^2}\ ,\tag{3}$$

where P_{xy} is the xy element of the pressure tensor P:

$$\mathsf{P}V=\sum_{i=1}^{N}\frac{\mathbf{p}_i\mathbf{p}_i}{m}-\tfrac{1}{2}\sum_{i,j}^{N}\mathbf{q}_{ij}\mathbf{F}_{ij}\ .\tag{4}$$

The SLLOD equations of motion are almost the same as the above equations, except that the equation for the time derivative of the momentum is different:

$$\dot{\mathbf{p}}_i=\mathbf{F}_i-\mathbf{i}\gamma p_{yi}-\alpha\mathbf{p}_i\ .\tag{5}$$

In these two algorithms the shear viscosity η is calculated from the constitutive relation

$$\eta=\frac{-\langle P_{xy}\rangle}{\gamma}\ .\tag{6}$$

Both of these algorithms are correct in the limit of zero-shear rate. For finite shear rates, the SLLOD equations are exact but the Dolls tensor algorithm leads to incorrect predictions of the thermophysical properties [6].

The (adiabatic) Dolls tensor equations can be derived from a Hamiltonian,

$$H_{\text{Dolls}}=H_0+\gamma\sum_{i=1}^{N}y_ip_{xi}\ ,\tag{7}$$

where H_0 is the sum of the peculiar kinetic energy and the potential energy. There is no Hamiltonian which generates the SLLOD equations of motion [6].

Under adiabatic conditions both SLLOD and Dolls dynamics have eigenvalues of their respective stability matrices (see Sec. II B) that occur in zero-sum conjugate pairs. However, a major difference between the two dynamics is that at an arbitrary point in phase space, the eigenvalues of the SLLOD stability matrix have *no* explicit dependence on the strain rate.

These two shear-flow algorithms must be implemented together with the Lees-Edwards shearing periodic bound-

ary conditions [8,6]. The proof of the conjugate-pairing rule given by Evans *et al.* refers only to an *isolated* dynamical system. NEMD computer simulations are usually carried out under periodic boundary conditions (for recent exceptions see Refs. [9,10]). For shearing systems we employ the time-dependent, nonorthogonal, Lees-Edwards periodic boundary conditions. The proof of the conjugate-pairing rule for SLLOD dynamics refers to the SLLOD equations of motion but not to the time-dependent Lees-Edwards periodic boundary conditions [1] which tell the N interacting particles which comprise the system where their external neighbors are at any given instant. Under Lees-Edwards periodic boundary conditions these external neighbors are shifted periodic images of the system particles [6]. The magnitude of this shift or displacement is a function of the unit-cell size, the strain rate, and the time. This latter fact has important consequences for the Lyapunov spectrum of shearing systems.

One can always argue that since we are interested in *bulk* thermophysical properties we take the large system limit of the results of NEMD simulations. If the system is made sufficiently large, the influence of these boundary conditions will affect only the dynamics of "surface" particles, and hence their influence should diminish as the system becomes larger.

The third system we examined was the color-conductivity algorithm for the self-diffusion constant. The equations of motion are

$$\begin{aligned}
&\dot{\mathbf{q}}_i=\frac{\mathbf{p}_i}{m}\ ,\\
&\dot{\mathbf{p}}_i=\mathbf{F}_i+c_i\mathbf{F}_D-\alpha\left[\mathbf{p}_i-\frac{2c_i\mathbf{J}_1}{N}\right]\ ,\\
&\mathbf{J}_1=\sum_{i=1}^{N/2}\mathbf{p}_i\ .
\end{aligned}\tag{8}$$

In these equations the particles are divided into two different fictitious species. The particles 1 through $N/2$ constitute species 1 and the others constitute species 2. The particles are given a color charge c_i which is equal to $+1$ for $1\le i\le N/2$ and -1 for $N/2<i\le N$. The variable $\mathbf{F}_D$ is the color field. The color current of species 1 is $\mathbf{J}_1$. The system is studied in the centre of momentum frame $\mathbf{J}_2=-\mathbf{J}_1$. The thermostat multiplier α is given by

$$\alpha=\frac{\sum_{i=1}^{N}\left[\mathbf{p}_i-\frac{2c_i\mathbf{J}_1}{N}\right]\cdot\mathbf{F}_i}{\sum_{i=1}^{N}\left[\mathbf{p}_i-\frac{2c_i\mathbf{J}_1}{N}\right]^2}\ .\tag{9}$$

The mass current of the either species is subtracted from the momenta to prevent the thermostat from interpreting induced mass currents as heat.

The adiabatic equations of motion of this algorithm can be derived from a Hamiltonian,

$$H_{\text{color}}=H_0-\sum_{i=1}^{N}c_i\mathbf{q}_i\cdot\mathbf{F}_D\ ,\tag{10}$$

and the color conductivity $L(F_D)$ defined by its constitutive relation,

$$L(F_D)=\frac{\langle J_1\rangle}{NF_D}\ ,\tag{11}$$

where $J_1=|\mathbf{J}_1|$ and $F_D=|\mathbf{F}_D|$, are related, in the zero color-field limit, to the self-diffusion coefficient D:

$$D=\lim_{F_D\to 0}k_BL(F_D)\ .\tag{12}$$

Finally, the "Evans" heat-flow algorithm was investigated. The equations of motion in the center-of-momentum frame are

$$\begin{aligned}
&\dot{\mathbf{q}}_i=\frac{\mathbf{p}_i}{m}\ ,\\
&\dot{\mathbf{p}}_i=\mathbf{F}_i+\left[\mathsf{S}_i-\frac{1}{N}\mathsf{S}\right]\cdot\mathbf{F}_Q-\alpha\mathbf{p}_i\ ,\\
&\mathsf{S}_i=\frac{1}{2}\left[\frac{\mathbf{p}_i^2}{m}+\sum_{j=1}^{N}\Phi_{ij}\right]\mathsf{I}-\frac{1}{2}\sum_{j=1}^{N}\mathbf{q}_{ij}F_{ij}\ ,\\
&\mathsf{S}=\sum_{i=1}^{N}\mathsf{S}_i\ .
\end{aligned}\tag{13}$$

In (13), $\mathbf{F}_Q$ is the heat field and I is the second-rank unit tensor. The Gaussian thermostatting multiplier is

$$\alpha=\frac{\sum_{i=1}^{N}\mathbf{p}_i\cdot\left[\mathbf{F}_i+\left[\mathsf{S}_i-\frac{1}{N}\mathsf{S}\right]\cdot\mathbf{F}_Q\right]}{\sum_{i=1}^{N}\mathbf{p}_i^2}\ .\tag{14}$$

The adiabatic form of these equations of motion (13) cannot be derived from a Hamiltonian, but they do satisfy AIΓ:

$$\frac{\partial}{\partial\Gamma}\cdot\dot{\Gamma}^{\text{ad}}=\sum_i\frac{\partial}{\partial\mathbf{q}_i}\cdot\dot{\mathbf{q}}_i^{\text{ad}}+\frac{\partial}{\partial\mathbf{p}_i}\cdot\dot{\mathbf{p}}_i^{\text{ad}}=0\ .\tag{15}$$

The thermal conductivity of the fluid is calculated from the constitutive relation

$$\lambda=\lim_{F_Q\to 0}\frac{\langle J_Q\rangle}{TF_Q}\ ,\tag{16}$$

where $J_Q=|\mathbf{J}_Q|$, $F_Q=|\mathbf{F}_Q|$, and $\mathbf{J}_Q$ is the heat-flux vector [10]:

$$\mathbf{J}_Q\mathbf{V}=\sum_{i=1}^{N}\frac{\mathbf{p}_i}{m}\left[\frac{\mathbf{p}_i^2}{2m}+\frac{1}{2}\sum_{j=1}^{N}\Phi_{ij}\right]-\frac{1}{2}\sum_{i,j}^{N}\mathbf{q}_{ij}\mathbf{p}_i\cdot\mathbf{F}_{ij}\ .\tag{17}$$

It is worth remarking that there is a related algorithm for heat flow due to Gillan and Dixon [11] which is not tested in this paper. Because the Gillan-Dixon algorithm violates AIΓ and momentum conservation, the Gillan-Dixon algorithm was not of interest (AIΓ is known to be a necessary condition for the conjugate-pairing rule to hold).

B. Lyapunov exponents

Each of the equations of motion discussed so far can formally be written as

$$\dot{\mathbf{\Gamma}}=\mathbf{G}(\mathbf{\Gamma},t)\ , \tag{18}$$

where $\mathbf{\Gamma}$ is the phase-space vector consisting of the position coordinates and the momenta of all N particles in the system. The two shear-flow algorithms (1) and (5) are nonautonomous in the sense that in (18), $\mathbf{G}$ is an explicit function of time. For both the other algorithms, $\mathbf{G}$ is only implicitly dependent on time thus the color conductivity and the heat-flow algorithm are autonomous.

We can define a distance vector $\boldsymbol{\delta}_1=\mathbf{\Gamma}_1-\mathbf{\Gamma}_0$ between two phase-space vectors $\mathbf{\Gamma}_1$ and $\mathbf{\Gamma}_2$. If the length of the distance vector goes to zero it becomes a tangent vector whose equation of motion is

$$\dot{\boldsymbol{\delta}}_1=\left.\frac{\partial \mathbf{G}}{\partial \mathbf{\Gamma}}\right|_{\mathbf{\Gamma}=\mathbf{\Gamma}_0}\cdot\boldsymbol{\delta}_1\equiv \mathsf{T}\cdot\boldsymbol{\delta}_1\ , \tag{19}$$

where T is the stability or Jacobian matrix of the equations of motion. The largest, i.e., most positive, Lyapunov exponent $\lambda_{\max}$ can be obtained as a limit [4]

$$\lambda_{\max}=\lambda_1=\lim_{t\to\infty}\frac{1}{2t}\ln\frac{\delta_1^2(t)}{\delta_1^2(0)}\ , \tag{20}$$

where $\delta_i=|\boldsymbol{\delta}_i|$. The ith Lyapunov exponent $i=1,2,\ldots,6N$ can be calculated by following a tangent vector $\boldsymbol{\delta}_i$, constrained to be orthogonal to the tangent vectors $\boldsymbol{\delta}_j$, i.e., $\boldsymbol{\delta}_i\cdot\boldsymbol{\delta}_j=0$, $j=1,2,\ldots,i-1$. The equation of motion for $\boldsymbol{\delta}_i$ is

$$\dot{\boldsymbol{\delta}}_i=\mathsf{T}\cdot\boldsymbol{\delta}_i-\sum_{j=1}^{i-1}\zeta_{ij}\boldsymbol{\delta}_j\ . \tag{21}$$

The multiplier ζ_{ij} is determined from the differential form of the orthogonality constraint

$$\dot{\boldsymbol{\delta}}_i\boldsymbol{\delta}_j+\boldsymbol{\delta}_i\dot{\boldsymbol{\delta}}_j=0 \tag{22}$$

and is

$$\zeta_{ij}=\frac{\boldsymbol{\delta}_i\cdot\mathsf{T}\cdot\boldsymbol{\delta}_j+\boldsymbol{\delta}_j\cdot\mathsf{T}\cdot\boldsymbol{\delta}_i}{\delta_j^2}\ . \tag{23}$$

Note that the equations of motion of the tangent vectors $1,2,\ldots,i-1$ are not affected by the equations of motion for $\boldsymbol{\delta}_i$. The tangent vector equations form a hierarchical set. The ith Lyapunov exponent is then defined from the limit

$$\lambda_i=\lim_{t\to\infty}\frac{1}{2t}\ln\frac{\delta_i^2(t)}{\delta_i^2(0)}\ . \tag{24}$$

This scheme is essentially the Benettin *et al.* [12] method with their iterative Gram-Schmidt orthogonalization procedure replaced by a continuous-constraint-multiplier orthogonalization. The Benettin method is inconvenient because the tangent vectors grow or shrink exponentially with time, requiring periodic rescaling [12]. For this reason we use a continuous rescaling method, proposed originally by Hoover and Posch [13] and independently by Goldhirsch *et al.* [14]. We give a considerably simplified sketch of the proof, by Goldhirsch, that the Lyapunov exponents so obtained are simple time averages of the tangent forces required to maintain these length constraints.

Consider an orthogonal set of infinitesimal tangent vectors $\{\boldsymbol{\delta}_i^c\}$ whose lengths are constant. This length constraint implies

$$\boldsymbol{\delta}_i^2=\text{const}\ ,\quad i=1,2,\ldots,6N \tag{25}$$

and therefore

$$\boldsymbol{\delta}_i^c\cdot\dot{\boldsymbol{\delta}}_i^c=0\ ,\quad i=1,2,\ldots,6N\ . \tag{26}$$

The equations of motion for the length-constrained tangent vectors are

$$\dot{\boldsymbol{\delta}}_i^c=\mathsf{T}\cdot\boldsymbol{\delta}_i^c-\sum_{j=1}^{i-1}\zeta_{ij}\boldsymbol{\delta}_j^c-\zeta_{ii}\boldsymbol{\delta}_i^c \tag{27}$$

with

$$\zeta_{ii}=\frac{\boldsymbol{\delta}_i^c\cdot\mathsf{T}\cdot\boldsymbol{\delta}_i^c}{(\delta_i^c)^2} \tag{28}$$

and

$$\zeta_{ij}=\frac{\boldsymbol{\delta}_i^c\cdot\mathsf{T}\cdot\boldsymbol{\delta}_j^c+\boldsymbol{\delta}_j^c\cdot\mathsf{T}\cdot\boldsymbol{\delta}_i^c}{(\delta_i^c)^2}\ . \tag{29}$$

These equations of motion are the same as Eq. (21) apart from the constraint multipliers ζ_{ii}. Fixing the length of the vectors $\boldsymbol{\delta}_j$, for $j<i$ does not affect $\boldsymbol{\delta}_i$ because only the direction, but not the magnitude, of the $\boldsymbol{\delta}_j$'s affects the solution of Eq. (27). In order to derive a relationship between the multiplier ζ_{ii} and the Lyapunov exponents we rewrite Eq. (27) as

$$\begin{aligned}\dot{\boldsymbol{\delta}}_i^c&=\mathsf{T}\cdot\boldsymbol{\delta}_i^c-\sum_{j=1}^{i-1}\zeta_{ij}\boldsymbol{\delta}_j^c-\zeta_{ii}\boldsymbol{\delta}_i^c\\&=\left[\mathsf{T}-\sum_{j=1}^{i-1}\zeta_{ij}\frac{\boldsymbol{\delta}_j^c\boldsymbol{\delta}_i^c}{(\delta_i^c)^2}-\zeta_{ii}\mathsf{I}\right]\cdot\boldsymbol{\delta}_i^c=(\mathsf{T}'-\zeta_{ii}\mathsf{I})\cdot\boldsymbol{\delta}_i^c\ ,\end{aligned} \tag{30}$$

where

$$\mathsf{T}'\equiv\mathsf{T}-\sum_{j=1}^{i-1}\zeta_{ij}\frac{\boldsymbol{\delta}_j^c\boldsymbol{\delta}_i^c}{(\delta_i^c)^2} \tag{31}$$

and I is the unit matrix. The solution of this equation is

$$\begin{aligned}\boldsymbol{\delta}_i^c(t)&=\exp_L\left[\int_0^t[\mathsf{T}'(s)-\zeta_{ii}(s)\mathsf{I}]ds\right]\cdot\boldsymbol{\delta}_i(0)\\&=\boldsymbol{\delta}_i(t)\exp\left[-\int_0^t\zeta_{ii}(s)ds\right]\ ,\end{aligned} \tag{32}$$

which gives the following expression for the length of the constrained tangent vector:

$$[\delta_i^c(t)]^2=\delta_1^2(t)\exp\left[\int_0^t-2\zeta_{11}(s)ds\right]\ . \tag{33}$$

The operator $\exp_L$ is the left-ordered exponential. Since the norm of $\boldsymbol{\delta}_i^c(t)$ is constant

$$\lim_{t\to\infty}\frac{1}{2t}\ln\frac{[\delta_i^c(t)]^2}{[\delta_i(0)]^2}$$
$$=0=\lim_{t\to\infty}\frac{1}{2t}\ln\left[\frac{\delta_i^2(t)}{\delta_i^2(0)}\exp(-2t\bar{\xi}_{ii})\right]$$
$$=\lim_{t\to\infty}\left[\frac{1}{2t}\ln\left[\frac{\delta_i^2(t)}{\delta_i^2(0)}\right]-\bar{\xi}_{ii}\right]=\lambda_i-\bar{\xi}_{ii}\ . \tag{34}$$

Therefore

$$\lambda_i=\bar{\xi}_{ii}\equiv\lim_{t\to\infty}\frac{1}{t}\int_0^t\xi_{ii}(s)ds \tag{35}$$

and the ith Lyapunov exponent is simply the time average of the multiplier used to keep the ith tangent vector fixed in length.

The Lyapunov exponents are also the logarithms of eigenvalues of the matrix [4]

$$\Lambda=\lim_{t\to\infty}[\mathbf{M}^\dagger(t)\mathbf{M}(t)]^{1/2t}\ , \tag{36}$$

where $\mathbf{M}(t)$ is the propagator of the unconstrained tangent vectors, i.e.,

$$\mathbf{M}(t)\equiv\exp_L\int_0^t ds\ \mathsf{T}(s) \tag{37}$$

and $\mathbf{M}^\dagger$ is the Hermitian adjoint of $\mathbf{M}$.

The equations given above require the solution of equations of motion for the variables T, $\boldsymbol{\delta}_1$, $\boldsymbol{\delta}_2$, etc. However we prefer to solve a finite difference approximation to (27) where the tangent vector $\boldsymbol{\delta}_i$ is approximated by the $\Gamma_i-\Gamma_0$ vector and $\mathsf{T}\cdot\boldsymbol{\delta}_i$ is replaced by $\mathbf{G}(\Gamma_i)-\mathbf{G}(\Gamma_0)$. This gives the following equations of motion for the ith tangent vector:

$$\dot{\Gamma}_i-\dot{\Gamma}_0=\mathbf{G}(\Gamma_i)-\mathbf{G}(\Gamma_0)-\sum_{j=1}^{i-1}\zeta_{ij}(\Gamma_j-\Gamma_0)-\zeta_{ii}(\Gamma_i-\Gamma_0)\ . \tag{38}$$

The off-diagonal multipliers ζ_{ij} become

$$\zeta_{ij}=\frac{(\Gamma_i-\Gamma_0)\cdot[\mathbf{G}(\Gamma_j)-\mathbf{G}(\Gamma_0)]+(\Gamma_j-\Gamma_0)\cdot[\mathbf{G}(\Gamma_i)-(\mathbf{G}(\Gamma_0)]}{(\Gamma_j-\Gamma_0)\cdot(\Gamma_j-\Gamma_0)} \tag{39}$$

and the diagonal multipliers ζ_{ii}, the time average of which are Lyapunov exponents, become

$$\zeta_{ii}=\frac{(\Gamma_i-\Gamma_0)\cdot[\mathbf{G}(\Gamma_i)-\mathbf{G}(\Gamma_0)]}{(\Gamma_i-\Gamma_0)\cdot(\Gamma_i-\Gamma_0)}\ . \tag{40}$$

In I it was shown that if the eigenvalues of the stability matrix of the *adiabatic* equations of motion occurred in conjugate pairs of equal magnitude but opposite signs, then the Lyapunov exponents of the *isothermal* or *isoenergetic* equations of motion appear in conjugate pairs whose sums are all the same. This is called the conjugate-pairing rule. When the adiabatic equations of motion can be derived from a Hamiltonian, the eigenvalues of the stability matrix can be arranged in such pairs. This is also the case for the adiabatic SLLOD equations of motion. As mentioned in the Introduction, it is not known whether this eigenvalue structure is a *necessary* condition for the conjugate-pairing rule to hold.

There are some further quite general remarks that can be made regarding the nature of the Lyapunov spectra for the NEMD algorithms considered here. Because each of the algorithms preserves the total peculiar momentum there are two zero Lyapunov exponents that result from each Cartesian component of the momentum. The first of these zero exponents corresponds to the momentum sum and the second to the position of the center of mass, for each Cartesian component. In addition there is another zero exponent resulting from the nonholonomic thermostatting constraint.

In the Appendix we discuss, in relation to statistical-mechanical systems, Haken's [15] proof that autonomous systems [i.e., $\mathbf{G}(\Gamma,t)=\mathbf{G}(\Gamma)$] possess an additional zero exponent. This means that for autonomous systems such as heat flow and color conductivity, there is an even number of nonzero Lyapunov exponents. However, if the dynamics is nonautonomous, as in the shearing systems [16], there is no additional zero exponent, leaving an odd number of nonzero exponents (i.e., one exponent is *unpaired).*

C. Technical details

The particles we have simulated interact via a WCA potential

$$u(r)=\begin{cases}4\varepsilon\left[\dfrac{\sigma^{12}}{r^{12}}-\dfrac{\sigma^6}{r^6}\right]+\varepsilon\ , & r<r_c\\ 0\ , & r\geq r_c\end{cases} \tag{41}$$

which is a Lennard-Jones potential truncated at its minimum and shifted to remove the discontinuity in the energy. The parameters σ and ε are the zero and the depth of the minimum of the original Lennard-Jones potential, respectively, and r is the scalar distance between the two interacting particles. The cutoff distance beyond which the pair potential is equal to zero, r_c is equal to $2^{1/6}\sigma$. The mass and the Lennard-Jones diameter σ of the particles have been set equal to 1. The energy unit is ε and the time unit is $\tau=\sigma(m/\varepsilon)^{1/2}$. All the values of the Lyapunov exponents and conjugate sums reported in this work are given in units of τ^{-1}.

The equations of motion were solved using a fourth-

order Runge-Kutta method with a time step 0.001τ. The tangent vectors were approximated by distance vectors of length 0.0001. It has been shown by Morriss [17] that this length is sufficiently small not to distort the Lyapunov exponents. The tangent vectors are rescaled about every fiftieth time step in order to maintain the lengths and the orthogonality. The simulation-run lengths were 1600τ and the error bars of the different averages have been obtained by the dividing the run into four equal parts and calculating the standard deviation of the subaverages.

It may seem an unnecessary complication to solve the tangent dynamics for a finite phase separation rather than solving the linearized dynamics. However, the solution for finite separations can be made very efficient by sharing neighbor lists among the $6N$ simulations.

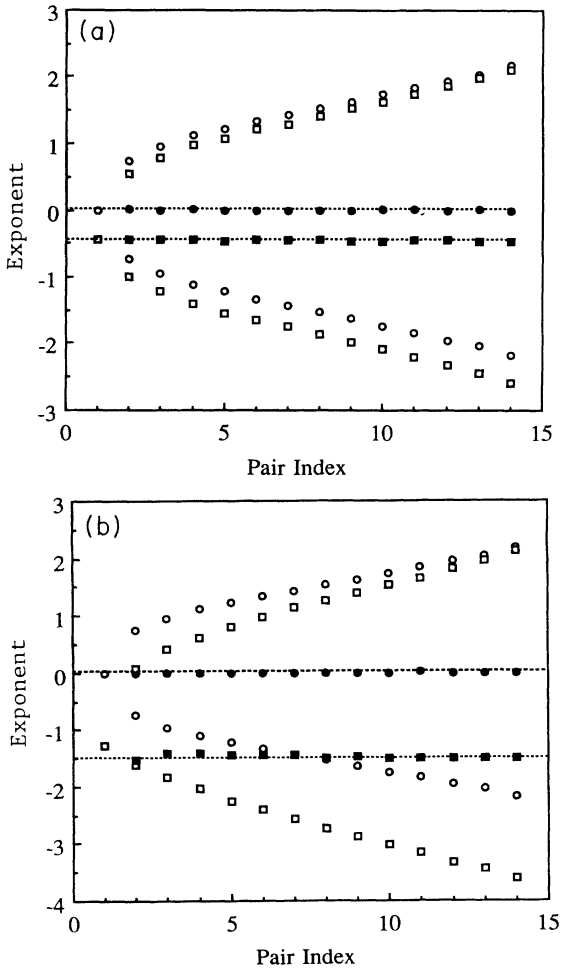

FIG. 1. (a) Conjugate pairs of Lyapunov exponents are denoted by open symbols and the sums of the conjugate pairs are denoted by solid symbols. The circles depict equilibrium results and the squares depict nonequilibrium results. The pair index is largest for the maximal Lyapunov exponents and decrements by 1 for each subsequent conjugate pair. The unpaired exponent is assigned a pair index of 1. The system is studied under SLLOD dynamics with reduced shear rate $\gamma\tau=1.0$. The Lyapunov exponents and the conjugate sums are given in units of τ^{-1}. (b) The same as in (a), but the reduced shear rate has been increased to 2.0.

III. CALCULATIONS, RESULTS, AND DISCUSSION

We calculated Lyapunov spectra for each of the NEMD algorithms discussed above. We simulated a two-dimensional WCA fluid consisting of eight particles. The reduced density $n\sigma^2$ was equal to 0.40 and the reduced temperature k_BT/ε was equal to 1.00.

The first system that we studied was a shearing fluid subject to Couette flow under the SLLOD equations of motion [(1) and (5)]. The Lyapunov exponents of this system for the reduced shear rate $\gamma\tau=1.0$ is shown in Fig. 1(a). In accord with the predictions of the conjugate-pairing rule, the sums of the conjugate pairs are constant. The value of the unpaired exponent, for this nonautonomous system, is equal to the sum of the conjugate pairs.

At a reduced shear rate of 2.0, the sum of the conjugate pairs is apparently not exactly the constant. However, the deviation which is essentially confined to the unpaired exponent is barely distinguishable above the statistical noise. Checks were carried out using higher-accuracy, shorter-time-step stimulations but the weak "turnup" of the unpaired exponent persisted. The largest exponent seems to be almost independent of the shear rate. It is very close to the equilibrium value even at the highest shear rate.

At very high shear rates these systems form a nonergodic "string phase [6]." The existence of this high-shear-rate string phase is known to be an artifact which results from the combined influence of the Gaussian thermostat and the periodic boundary conditions. At very high shear rates a particle can stream across the simulation cell in a time so short that lateral diffusion is insignificant. The particles can minimize the entropy production by traveling in tubes or "strings." If the system was not periodic this tendency would be greatly re-

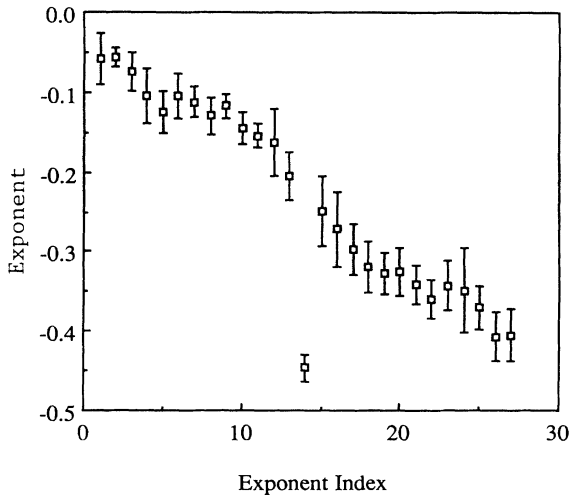

FIG. 2. The shift of the SLLOD exponents away from the equilibrium value $\lambda(\gamma\tau=1,i)-\lambda(\gamma\tau=0,i)$ in units of τ^{-1}, for a reduced shear rate of 1.0 as a function of the exponent index. In this figure the exponent index is defined by setting the largest exponent number to 1, the second largest number to 2, etc.

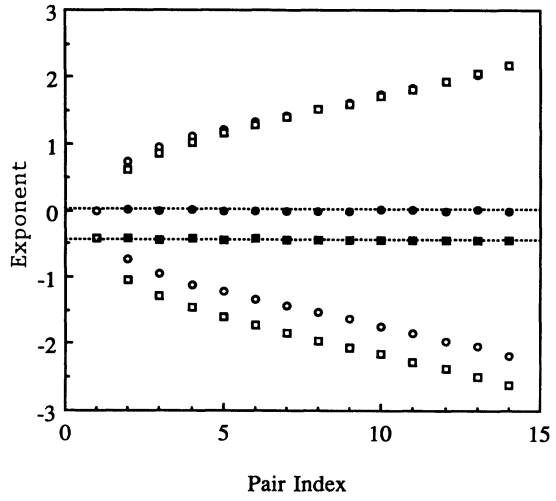

FIG. 3. The same as Fig. 1(a) but the Dolls tensor equations of motion have been applied instead of the SLLOD equations.

duced. It is possible that these small, barely distinguishable deviations, principally of the unpaired exponent, are related to the existence of this nonergodic string phase. An unavoidable and unfortunate result of the proximity of the string phase is that the equations of motion (27) for the tangent vectors become more and more stiff as the shear rate increases and the string phase transition is approached.

In Fig. 2 we have plotted the difference between the Lyapunov exponents of the nonequilibrium shearing system and the corresponding equilibrium system at zero shear rate as a function of the exponent index. (The index of the exponent is defined by calling the largest exponent number 1, the second largest number 2, etc.) The data are consistent with the hypothesis that the shear-induced shift of the Lyapunov exponents is a linear function of the exponent index.

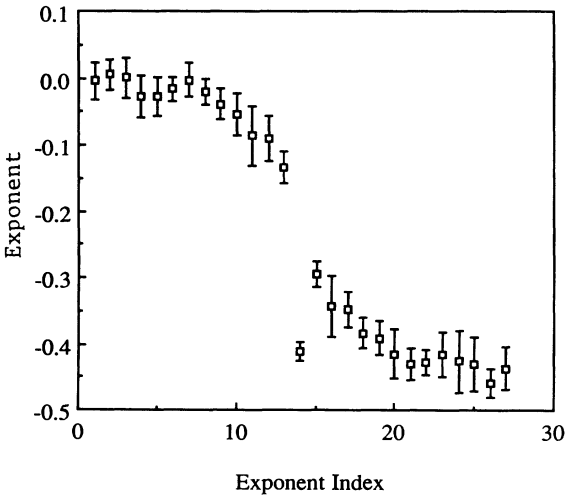

FIG. 4. The same as Fig. 2 but the nonequilibrium system has been created by applying the Dolls equation of motion.

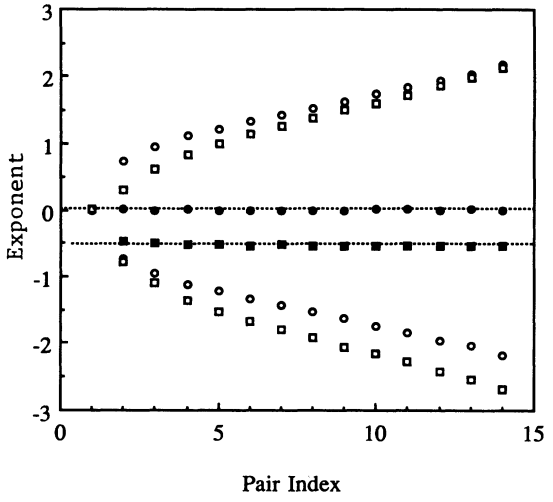

FIG. 5. The same as Fig. 1(a) but the nonequilibrium system is created by applying the color-conductivity algorithm with a reduced color field of 1.5. Note that away from equilibrium, one of the Lyapunov exponents remains at zero.

The next system that we examined was also a Couette flow, but one driven by the Dolls equations of motion (1). The Lyapunov spectra of this system for a reduced shear rate of 1.0 is shown in Fig. 3. The SLLOD and the Dolls conjugate sums virtually coincide, although some of the exponents are slightly different. The conjugate-pairing rule is satisfied and the unpaired exponent is equal to the conjugate sum.

In Fig. 4 the shift of the Dolls tensor Lyapunov exponents from their equilibrium values is plotted as a function of the exponent index. It is fairly obvious that this is not a linear function as was apparently the case for SLLOD dynamics. One can thus rule out the possibility that the satisfaction of the conjugate-pairing rule implies

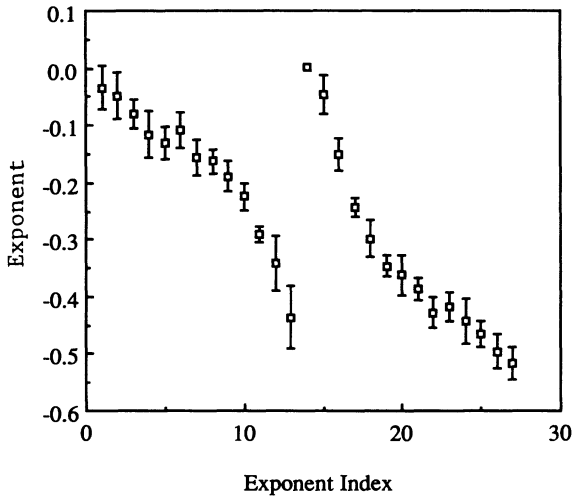

FIG. 6. The same as Fig. 2 but the nonequilibrium system has been created by using the color-field equations of motion with a color field of 1.5.

that the exponent shift should be a linear function of the exponent index.

The Lyapunov exponents of a system subject to a color field (8) are shown in Fig. 5. The color field is equal to 1.5. The adiabatic equations of motion can be derived from a Hamiltonian, so we expect that the conjugate-pairing rule should be valid; this is seen to be the case.

A difference between a color-conductivity spectrum and a Couette-flow spectrum is that in the former case the "unpaired" exponent is zero. This is because, unlike the shear-flow algorithms, the color-conductivity algorithm is autonomous [16].

In Fig. 6 we have plotted the shift of the Lyapunov exponents away from the equilibrium value. Again it is obvious that it is not a linear function. Since the eigenvalues of the stability matrix for color conductivity have (like SLLOD) no explicit dependence on the applied field, this aspect of the dynamics can be ruled out as contributing to the apparent linear exponent shift observed for SLLOD dynamics.

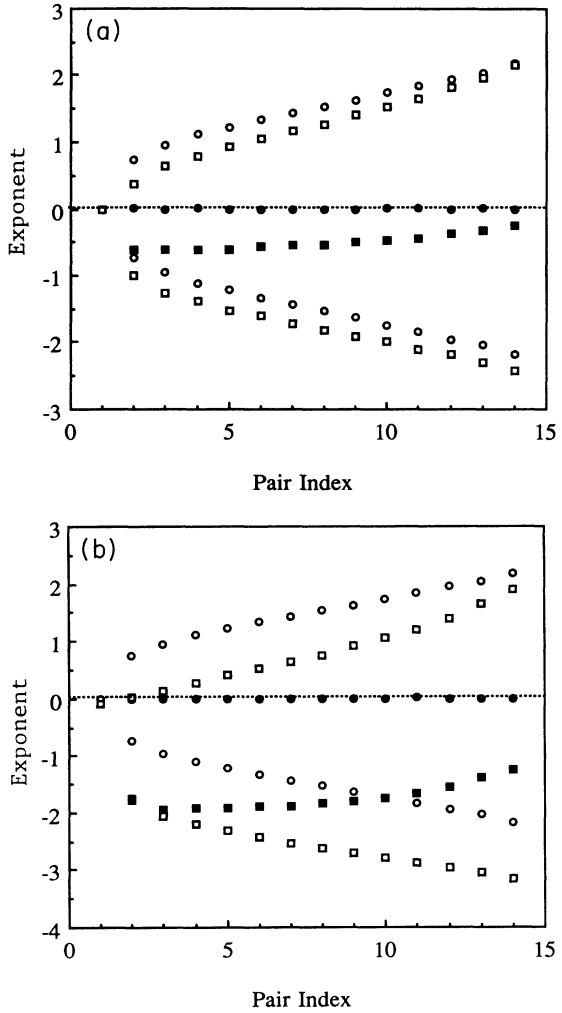

FIG. 7. (a) The same as Fig. 1(a) but the Evans thermal-conductivity algorithm with a heat field of 0.5 has been applied instead of the SLLOD equations. The conjugate-pairing rule is not satisfied in this case, so no straight line can be drawn through the sums of the conjugate pairs. Note that away from equilibrium, one of the Lyapunov exponents remains at zero. (b) The same as Fig. 7(a) but the heat field has been increased to 1.0. Note that the unpaired exponent is less than zero and that largest exponent in conjugate pair number 2 is equal to zero.

The eigenvalues of the adiabatic stability matrices for the algorithms discussed so far occur in zero-sum conjugate pairs. This is a sufficient condition for the conjugate-pairing rule to hold. However, the Lyapunov exponents are not the eigenvalues of the stability matrix, but rather are the eigenvalues of the Λ matrix (36). It is possible that there may exist a less restrictive, necessary condition for the conjugate-pairing rule. It might be suggested that a necessary condition would be that the equations of motion satisfy $A\Gamma\Gamma$ and that the Lyapunov spectra be obtained for a *steady* state.

In order to test this conjecture we have calculated the Lyapunov exponents of a system whose dynamics is governed by the "Evans" heat-flow algorithm (13). The adiabatic equations of motion of this algorithm cannot be derived from a Hamiltonian but they do satisfy $A\Gamma\Gamma$. In Fig. 7 we show the Lyapunov exponents for two heat fields, $F_Q=0.5$ and $F_Q=1.0$. It is obvious that the conjugate-pairing rule does not hold for this system. When the field increases, the positive exponents decrease and become negative, even though at least one exponent is always equal to zero. As mentioned above this is a very general property of autonomous systems. At low heat fields the unpaired exponent vanishes, but when F_Q increases this exponent becomes negative and a *different* positive exponent becomes equal to zero.

IV. CONCLUSION

We have calculated the Lyapunov spectra generated by various NEMD equations of motion. The purpose of this investigation has been to explore the necessary conditions for the conjugate-pairing rule to hold. Sufficient conditions for the conjugate-pairing rule are that the system is thermostated by a Gaussian thermostat applied to all degrees of freedom, and the eigenvalues of the adiabatic stability matrix occur in zero-sum conjugate pairs.

This rule is useful because it makes it possible to calculate the phase-space-compression factor and thereby the transport coefficients, by knowing just one pair of exponents. It is easy to show the rule is valid for any NEMD algorithm whose adiabatic equations of motion are derivable from a Hamiltonian. The color-conductivity and SLLOD algorithms fall into this class and our data verify that they satisfy the conjugate-pairing rule. The SLLOD algorithm is not derivable from a Hamiltonian but it does have the requisite adiabatic eigenvalue structure that is known to lead to the conjugate-pairing rule. Again our numerical data support this.

The main difference between the Couette-flow spectra and the color-conductivity spectrum is that for color conductivity there is always one zero exponent. The reason for this is that the color-conductivity equations of motion and boundary condition are autonomous, whereas the Lees-Edwards periodic boundary conditions employed in

shear-flow algorithms make the system nonautonomous [15,16].

Another property that we have studied for these three algorithms is the field-induced shift of the exponents as a function of exponent index. The data for the SLLOD algorithm suggests that this shift is a linear function of the index. However, *none* of the other algorithms displays such a linear dependence. We know of no explanation for this effect, but it is clear that since both the color-conductivity and the SLLOD algorithms have the property that their local stability-matrix eigenvalues are both independent of the applied external field, this property is ruled out as the origin of the linear shift in the Lyapunov exponents which is observed for SLLOD.

Finally, we evaluated the Lyapunov spectrum of the Evans heat-flow algorithm. This algorithm satisfies AIΓ but the eigenvalues of the local adiabatic stability matrix do not appear in conjugate pairs of equal size nor with opposite signs. We found that the sums of the conjugate pairs were all negative but of unequal magnitude. Satisfaction of AIΓ is thus *not* a sufficient condition for the conjugate-pairing rule to hold.

A final remark is pertinent regarding heat flow and the thermal-conductivity coefficient. One should not regard the failure of the conjugate-pairing rule for the "Evans" heat-flow algorithm as implying that there is something peculiar about thermal-conduction processes. The "Evans" algorithm provides the most efficient method presently known for calculating the limiting zero-field thermal conductivity [18]. However it is quite straightforward to construct (vastly) less efficient algorithms for calculating the thermal conductivity which do satisfy the conjugate-pairing rule. The most obvious dynamics for this purpose are generated by the following Hamiltonian:

$$H = H_0 + \mathbf{F}_Q \cdot \sum_i \mathbf{q}_i (e_i - \bar{e}) \ , \tag{42}$$

where e_i is the contribution to the total internal energy made by i, and $\bar{e}$ is the instantaneous mean of $\{e_i\}$. Although valid in principle, this algorithm is unsuitable in practice because, being incompatible with periodic boundary conditions, it requires the simulation of *huge* systems to reduce the N dependence of the results.

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APPENDIX

The existence of at least one zero Lyapunov exponent in an autonomous system has been proved by Haken [15]. Here we present a simplified version of that proof, as it applies to statistical-mechanical systems. Consider the equations of motion

$$\dot{\Gamma} = \mathbf{G}(\Gamma, t) \ . \tag{A1}$$

Differentiation with respect to time gives

$$\ddot{\Gamma} = \frac{\partial \mathbf{G}}{\partial \Gamma} \cdot \dot{\Gamma} + \frac{\partial \mathbf{G}}{\partial t} \ . \tag{A2}$$

When the equations of motion are autonomous, which is the case for the color-conductivity and the heat-flow algorithms but not the Couette-flow algorithms, the term $\partial \mathbf{G}/\partial t$ vanishes and we have

$$\ddot{\Gamma} = \frac{\partial \mathbf{G}}{\partial \Gamma} \cdot \dot{\Gamma} \ . \tag{A3}$$

From Eq. (19) we see that $d\Gamma/dt$ is a tangent vector, with the corresponding Lyapunov exponent

$$\lambda = \lim_{t \to \infty} \frac{1}{2t} \ln \frac{\dot{\Gamma}^2(t)}{\dot{\Gamma}^2(0)} \ . \tag{A4}$$

This exponent is zero if $d\Gamma/dt$ is bounded or at least grows at a slower than exponential rate. In the systems examined in this work we have

$$[\dot{\Gamma}(t)]^2 = \sum_{i=1}^{N} \dot{\mathbf{q}}_i^2 + \sum_{i=1}^{N} \dot{\mathbf{p}}_i^2 \ . \tag{A5}$$

This is a function of the phase variables. By definition, in a steady state the average of such a function does not change with time. Thus the numerator in (A4) does not grow or shrink with time and the limit is consequently equal to zero.

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