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Planar mixed flow and chaos: Lyapunov exponents and the conjugate-pairing rule

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In this work we characterize the chaotic properties of atomic fluids subjected to planar mixed flow, which is a linear combination of planar shear and elongational flows, in a constant temperature thermodynamic ensemble. With the use of a recently developed nonequilibrium molecular dynamics algorithm, compatible and reproducible periodic boundary conditions are realized so that Lyapunov spectra analysis can be carried out for the first time. Previous studies on planar shear and elongational flows have shown that Lyapunov spectra organize in different ways, depending on the character of the defining equations of the system. Interestingly, planar mixed flow gives rise to chaotic spectra that, on one hand, contain elements common to those of shear and elongational flows but also show peculiar, unique traits. In particular, the influence of the constituent flows in regards to the conjugate-pairing rule (CPR) is analyzed. CPR is observed in homogeneously thermostatted systems whose adiabatic (or unthermostated) equations of motion are symplectic. We show that the component associated with the shear tends to selectively excite some of those degrees, and is responsible for violations in the rule. © 2011 American Institute of Physics. [doi:10.1063/1.3567095]

I. INTRODUCTION

A novel method for arbitrarily long simulations of planar mixed flow (PMF) has recently been developed,1 combining the SLLOD equations of motion for planar shear (PSF) and elongational (PEF) flows with compatible and reproducible periodic boundary conditions (PBCs). Previous attempts with algorithms for simulating this type of flow existed in the literature,2 but lacked the possibility of maintaining steady states for times compatible with an evaluation of Lyapunov exponents. This is a necessary condition when trying to investigate the chaotic properties of nonequilibrium flows, given that Lyapunov exponents are the preferred means for the quantitative characterization of chaos and are strictly defined in the limit of infinite simulation times.

A dynamical system is generally defined to be chaotic if at least one of its Lyapunov exponents is positive. These exponents measure the average rate of expansion or contraction of the distance between infinitesimally displaced phase space trajectories, and their calculation for several smooth and continuous fluid models, either for equilibrium or nonequilibrium steady states, has been very successful. The literature contains many examples where flows of theoretical and industrial interest have been characterized in terms of their Lyapunov spectra, in a multitude of thermodynamic ensembles.2,3,8 Recently, the authors have also explored in some detail the appearance of these spectra for typical inhomogeneous, confined flows.9

It is well-known that the study of Lyapunov exponents is fruitful not only in analyzing relations between dynamical instabilities and the geometry of the phase space,10,11 but also because it contains a link with statistical mechanics. In particular, for the most commonly used homogeneous thermostatted systems in nonequilibrium steady states, the rate of entropy production can be related to the sum over the Lyapunov exponents and then to the transport coefficients,12–14 even when nonlinear processes are far from equilibrium.5,7 The relationship between the entropy production and phase space compression (or the sum of the Lyapunov exponents) is discussed in detail in Ref. 14.

In this regard, the satisfaction of the so-called conjugate-pairing rule (CPR) for a given flow can facilitate the evaluation of transport coefficients through Lyapunov exponents, by substituting the computation of all sums with just a couple of exponents. In fact, when held, the CPR states that if the Lyapunov exponents are ordered from the largest to the smallest (λ1 > λ2 ... > λM), where M is the phase space dimension of the system, the sums of the ordered couples (λn + λM+1−n, n = 1, M/2) are a constant.7,13,15 We note that determination of the transport coefficients from the Lyapunov exponents is much more computationally demanding than determining them directly from the flux (approximately M times more). If CPR is obeyed this computational effort can be reduced to determination of just two exponents, irrespective of the phase space dimension of the system.

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we have studied it is still more efficient to use the flux for this calculation, however the relationship is of fundamental importance.

It is well-established that equilibrium Hamiltonian systems always obey the CPR and the couples sum to zero due to the symplectic character of the equations. As each Lyapunov exponent refers to expansion or contraction in a particular direction of the phase space, their sum describes the evolution of the entire hypervolume. Thus equilibrium Hamiltonian systems, being volume preserving, show exponents that sum to zero. In nonequilibrium homogeneous systems, necessary conditions for CPR to hold have been discussed in a number of works. Although the necessary and sufficient conditions for a system to obey CPR are not known, it has been found that if the unthermostated equations of motion are symplectic, and a standard homogeneous thermostat (Gaussian or Nosé–Hoover) is applied to all particles, then the system will obey the CPR. These systems are referred to as $\mu$-symplectic.

In the case of PMF studied in this paper, the two basic flows that are present in the equations of motion, i.e., PEF and PSF, have opposing trends in terms of conjugate-pairing. When formulated with the use of the well-known non-Hamiltonian SLLOD equations of motion in conjunction with appropriate PBCs, PSF displays non-negligible deviations from the CPR, which tend to increase with the increase in shear rate. On the other hand, SLLOD PEF equations with compatible and reproducible PBCs (Ref. 22) have been shown to respect conjugate-pairing due to the Hamiltonian nature of the unthermostated equations of motion.

The present work tries to address two questions. First, a characterization of Lyapunov spectra for PMF is proposed, and the link between exponents and transport coefficients, in this case viscosity, is established. Second, an analysis of the CPR in terms of the underlying PSF and PEF is carried out, showing how the differences in simplicity between the flows influence the divergences from conjugate-pairing. To do so, in Sec. II we first introduce the equations of motion for PMF and derive the expression for viscosity based on the Lyapunov exponents, where we also give a brief description of the algorithm and the methods we used for calculating the exponents. Next, results for the exponents in a combination of flow rates are presented, investigating the differences and analogies with previously established results for the constitutive flows, PSF and PEF. Finally, a brief discussion concludes the paper.

II. THE ALGORITHM FOR MIXED FLOW

This is the first time to our knowledge that chaotic properties for PMF can be analyzed, since previously employed algorithms were capable of producing finite time simulations only. This was due to the particles in the cell box being subjected to an irreversible deformation, so that simulations needed to be stopped as soon as the box length in the contracting direction shrank to less than the effective atomic diameter. For the study of nonequilibrium mechanical properties such as viscosity, repetitions of the whole simulation were sufficient to improve statistics. However, for Lyapunov spectra computation, a run of arbitrary length is necessary: as we will show in Sec. III, Lyapunov exponents are properly defined in the infinite time limit. The algorithm for mixed flow used herein allows for this, since the simulation box, similarly to what has already been done for PEF, deforms according to the streamlines of the flow (see Fig. 1) and is mapped back into its initial shape after a fixed time. This assures the absence of discontinuities in the calculated physical properties.

Let us now briefly outline the algorithm for PMF (we consider a two-dimensional system), a detailed explanation of which can be found in Ref. 1. We consider a velocity gradient of the form

$$\mathbf{V} = \begin{pmatrix} \dot{\varepsilon} & 0 \\ \dot{\gamma} & -\dot{\varepsilon} \end{pmatrix},$$

where the expanding/contracting directions are, respectively, along the $x$ and $y$ axes, with elongational field strength $\dot{\varepsilon}$, and shear gradient $\dot{\gamma}$ along the $y$ direction only. Using results from lattice theory, it can be shown that, for the velocity gradient $\mathbf{V}$ in Eq. (1), it is possible to choose a set of basis vectors $\mathbf{l}_i$, with $i = 1, 2$, such that the lattice $\mathbf{L}_i$ they generate is both compatible and reproducible under PMF. Compatibility warrants the existence of a minimum distance between lattice points that is never less than the interatomic particle interaction distance, whereas reproducibility implies that the displacement of the lattice points in space is identical to the initial displacement after a fixed amount of time. These conditions are both necessary to ensure no spurious effects are introduced into the dynamics.

We can now use the lattice basis vectors to generate our cell box

$$\mathbf{I}_1 = (\cos \theta - \frac{\dot{\gamma}}{2\dot{\varepsilon}} \sin \theta, \sin \theta),$$

$$\mathbf{I}_2 = (-\sin \theta - \frac{\dot{\gamma}}{2\dot{\varepsilon}} \cos \theta, \cos \theta),$$

where $\theta$ is the angle between the simulation box basis vector along the $x$ direction and the extension direction for PEF (see Fig. 1). Only certain values of $\theta$ give reproducible lattices, and we choose, for our simulations, the value of $\theta \approx 31.7^\circ$, already used in the literature. The simulation box evolves according to the streamlines of the flow

$$x(t) = \frac{\dot{\gamma}}{\dot{\varepsilon}} y(0) \sinh(\dot{\varepsilon} t) + x(0) \exp(\dot{\varepsilon} t),$$

$$y(t) = -y(0) \exp(-\dot{\varepsilon} t),$$

and is reproducible after a period of time $\tau_p$, i.e., when the system has experienced a so-called “Hencky” strain of $\varepsilon_p = \dot{\varepsilon} \tau_p = \ln(\lambda)$, $\lambda$ is the eigenvalue of the velocity gradient tensor due to PEF components only, so that $\mathbf{L}_i(t = \tau_p) = \exp(\mathbf{V} \mathbf{L}_i(0)) = \mathbf{L}_i(0)$ (see Fig. 1).

For particle dynamics, the equivalent version of the SLLOD equations of motion for PMF is used. The general expression for SLLOD with an arbitrary velocity gradient is

$$\mathbf{q}_i(t) = \frac{\mathbf{p}_i(t)}{m} + \mathbf{q}_i \cdot \nabla \mathbf{u},$$

$$\mathbf{p}_i(t) = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{u}.$$
For pure elongation (PEF) and pure shear (PSF) respectively, these equations become

\[
\begin{align*}
\dot{q}_i &= \frac{p_i}{m_i} + \dot{\varepsilon}(x_i \hat{x} - y_i \hat{y}), \\
\dot{p}_i &= F_i - \dot{\varepsilon}(p_{xi} \hat{x} - p_{yi} \hat{y}), \\
\dot{q}_v &= \frac{p_v}{m_v} + \dot{\gamma} y \hat{x}, \\
\dot{p}_v &= F_v - \dot{\gamma} p_{yi} \hat{x}.
\end{align*}
\]  

(6)

We note that Eqs. (6) and (7) do not in general conserve total momentum and center of mass unless appropriate initial conditions, in which both quantities are set to zero, are used. This choice, employed in this work, does not affect the physics of the system, but the presence or not of conserved properties in phase space is reflected in the Lyapunov exponents and will be discussed in Sec. IV. Also note that because of finite precision numerics, errors in the evaluation of the total momentum would grow exponentially for Eq. (6), therefore a rescaling is required each time step\textsuperscript{27} to keep it constant. However, this does not affect the chaotic properties.\textsuperscript{6} It is clear that in PMF, with \( \mathbf{V} \mathbf{u} \) as in Eq. (1), the two contributions linearly combine. If we couple them to an isokinetic Gaussian thermostat, we are left with

\[
\begin{align*}
\dot{q}_i &= \frac{p_i}{m_i} + \dot{\varepsilon}(x_i \hat{x} - y_i \hat{y}) + \dot{\gamma} y_i \hat{x}, \\
\dot{p}_i &= F_i - \dot{\varepsilon}(p_{xi} \hat{x} - p_{yi} \hat{y}) - \dot{\gamma} p_{yi} \hat{x} - \xi p_i, \\
\dot{q}_v &= \frac{p_v}{m_v} + \dot{\gamma} y \hat{x}, \\
\dot{p}_v &= F_v - \dot{\gamma} p_{yi} \hat{x}.
\end{align*}
\]  

(8)

where

\[
\xi = \sum_{i=1}^{N}(F_i \cdot p_i - \dot{\varepsilon}(p_{xi}^2 - p_{yi}^2) - \dot{\gamma} p_{yi} p_{xi}).
\]  

(9)

We choose a Gaussian thermostat for consistency with previous work on Lyapunov exponents\textsuperscript{4,7,8,13,15,17} and to facilitate a direct comparison between results. Clearly the choice of the thermostat has no large influence on mechanical properties, but does affect the Lyapunov spectra of the system to some degree.\textsuperscript{6,23} As already noted, even though the unthermostated SLLOD equations for PEF, Eq. (6), are Hamiltonian, the SLLOD equations for PMF inherit the non-Hamiltonian character from PSF, Eq. (7), and this will be reflected in the behavior of the Lyapunov exponents.

From the relation between the heat production rate per unit volume and the second scalar invariant (II) of the strain rate tensor \( II = \dot{\gamma} : \dot{\gamma} \), Hounkonnou \textit{et al.}\textsuperscript{28} derived a general expression for the viscosity of an isotropic fluid undergoing isochoric flow:

\[
\eta = (\sigma : \dot{\gamma})/(\dot{\gamma} : \dot{\gamma}).
\]  

(10)

where \( \sigma \) is the stress tensor and \( \dot{\gamma} \) is the strain rate tensor. It is thus possible to obtain a formula for viscosity for PMF that can be expressed in terms of PSF and PEF viscosities. Since \( II = 2\dot{\gamma}^2 \) for PSF and \( II = 8\dot{\gamma}^2 \) for PEF, it turns out that

\[
\eta_{\text{mixed}} = \frac{-2\dot{\varepsilon} P_{xx} + 2\dot{\varepsilon} P_{xy} - 2\dot{\gamma} P_{xy}}{8\dot{\varepsilon}^2 + 2\dot{\gamma}^2} = \frac{(8\dot{\varepsilon}^2 \eta_{\text{PEF}} + 2\dot{\gamma}^2 \eta_{\text{PSF}})}{8\dot{\varepsilon}^2 + 2\dot{\gamma}^2},
\]  

(11)

where

\[
\eta_{\text{PEF}} = \frac{P_{xy} - P_{xx}}{4\dot{\varepsilon}}, \quad \eta_{\text{PSF}} = -\frac{P_{xy}}{\dot{\gamma}}.
\]  

(12)

PMF viscosity is therefore a linear combination of the pure flow viscosities weighted by the inverse of the second scalar invariant, i.e., \( II_{\text{PMF}} = 2\dot{\gamma}^2 + 8\dot{\varepsilon}^2 \). From this expression it is clear that the elongational field contributes for a factor of 4 to \( II \), more than pure shear, and this will be taken into account when we select the mixed flow rates for our analysis of exponents.

Finally, the system we study in this work is a two-dimensional atomic fluid interacting by a smooth repulsive potential, via the Weeks–Chandler–Anderson potential (WCA).\textsuperscript{29,30} This is a truncated and shifted form of the
Lennard-Jones (LJ) potential:

\[ \Phi_{\text{WCA}} = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] + \epsilon, & r_{ij} \leq 2^{\frac{1}{6}} \sigma, \\ 0, & r_{ij} > 2^{\frac{1}{6}} \sigma, \end{cases} \tag{13} \]

where \( r_{ij} = |\mathbf{q}_i - \mathbf{q}_j| \), with \( \mathbf{q}_i \) being the laboratory position of particle \( i \), \( \sigma \) is the value of \( r_{ij} \) for which the LJ interaction potential is zero, and \( \epsilon \) is the well-depth of the LJ potential. In the following, all the physical units are expressed in reduced units, where the unit mass is the particle mass \( m \), the unit energy is the parameter \( \epsilon \), and the unit length is \( \sigma \). In our work we set \( \epsilon = \sigma = m = 1 \). For consistency with previous studies on pure shear and elongational flows, the same system specifications are used: 32 particles, at a density \( \rho = 0.3 \) and at a temperature \( T = 1.0 \). Simulations have been performed at different state points, depending on the values of field strengths \( \dot{\epsilon} \) and \( \dot{\gamma} \), and ordered according to the second scalar invariant of the strain rate tensor \( (I_1 = 2, 4, 8, 10, 16) \). The values of \( \dot{\epsilon} \) and \( \dot{\gamma} \) are selected so that \( I_{P_{\text{PMF}}} \) specified is reproduced to at least five decimal places, as reported in Table I, however in the figures, their values are rounded to two decimal places. Equations are integrated via a fourth order Gear predictor-corrector method, with a time step \( \Delta t = 0.001 \). An initial simulation time of \( 5 \times 10^6 \) time steps was carried out to ensure that the system had reached a steady state, which was then followed by data production for \( 6 \times 10^6 \) time steps. Results for exponents and sums are averaged over 10 independent runs.

III. LYAPUNOV EXPONENTS AND THE CONJUGATE-PAIRING RULE

The measurement of chaos in dynamical systems quantitatively characterizes the concept of sensitivity to initial conditions introduced by Lorenz.\(^{31}\) Essentially, if a system subjected to small perturbations evolves toward a state considerably different from the initial one, this indicates the presence of chaos. Lyapunov exponents describe the rate of exponential growth or contraction of nearby phase space trajectories, and the presence of a positive exponent indicates that the system is chaotic.

The evolution of a point in phase space for a system of \( N \) particles can be written as

\[ \dot{\mathbf{\Gamma}}(t) = \mathbf{G}(\mathbf{\Gamma}, t), \tag{14} \]

where \( \mathbf{\Gamma}(t) = [\mathbf{q}_1(t), \ldots, \mathbf{q}_N(t), \mathbf{p}_1(t), \ldots, \mathbf{p}_N(t)]^T \). If we define a displacement vector \( \delta \mathbf{\Gamma} \) between two points and we take the vanishing limit \( \delta \mathbf{\Gamma} \to 0 \), we can solve its evolution in the tangent space

\[ \delta \dot{\mathbf{\Gamma}}(t) = \mathbf{T} \cdot \delta \mathbf{\Gamma}, \tag{15} \]

where \( \mathbf{T} \) is the stability or Jacobian matrix \( \mathbf{T} \equiv \partial \dot{\mathbf{\Gamma}} / \partial \mathbf{\Gamma} \).

A practical definition of the Lyapunov exponents is given by

\[ \lambda^i = \lim_{t \to \infty} \lim_{\delta \Gamma \to 0} \frac{1}{t} \ln \left( \frac{|\delta \mathbf{\Gamma}(t)|}{|\delta \mathbf{\Gamma}(0)|} \right), \tag{16} \]

where \( |\delta \mathbf{\Gamma}(t)| \) is the length of the \( i \)th orthogonal displacement vector at time \( t \), and \( i = 1, \ldots, 4N \) in two dimensions. Benettin et al.\(^{32,33}\) used this definition to implement a "classic" algorithm that can be adapted to nonequilibrium molecular dynamics (NEMD), which is the method we use in this paper.

As mentioned above, an important link between dynamical systems theory and nonequilibrium statistical mechanics is the relation between Lyapunov spectra and transport coefficients in fluids. In particular, it has been shown\(^{13}\) that the viscosity described by the SLLOD equations of motion can be expressed in terms of the sum of its Lyapunov exponents (for a review, also see Ref. 5). As discussed in Ref. 6, this relationship becomes a proportionality between the viscosity and the sum of the Lyapunov exponents in the thermodynamic limit; furthermore, if the system respects the CPR only the knowledge of the maximum and minimum exponents is required. The relationship between the sum of the Lyapunov exponents and the viscosity has already been tested in previous works for simple fluids under shear and elongational flows\(^{6,13}\) and we now extend it to PMF. It is worth noting that the proof for this relation was first derived for PSF SLLOD equations, Eq. (7), for an isokinetic system in the thermodynamic limit.\(^{13}\) The same result applies to isokinetic systems.

For PSF and PEF we have, respectively,

\[ \eta_{\text{PSF}}(\dot{\gamma}) = -\frac{k_B T_{SS}}{\dot{\gamma}^2 V} \sum_{i=1}^{4N} \lambda^i, \tag{17} \]

\[ \eta_{\text{PEF}}(\dot{\epsilon}) = -\frac{k_B T_{SS}}{4\dot{\epsilon}^2 V} \sum_{i=1}^{4N} \lambda^i, \tag{18} \]

where \( V \) is the cell box volume, \( k_B \) is the Boltzmann constant, and \( T_{SS} \) is the temperature at the steady state. Using Eq. (11) we derive the following expression for PMF:

\[ \eta_{\text{PMF}}(\dot{\epsilon}, \dot{\gamma}) = -\frac{k_B T_{SS}}{(4\dot{\epsilon}^2 + \dot{\gamma}^2) V} \sum_{i=1}^{4N} \lambda^i, \tag{19} \]

which, as said, is exact in the limit of large \( N \). Comparing viscosity values from NEMD runs, we will see that the above equation for PMF is already satisfactory when \( N = 32 \).

IV. RESULTS

Let us now present and discuss the results for Lyapunov spectra, according to different values of \( I_1 \). Throughout the paper, we define the exponent pair index as \( M/2 - 1 + n \), where \( M \) is the phase space dimension and \( n \) is the Lyapunov exponent index, such that it is maximum for the maximal (in absolute value) Lyapunov exponents. Before showing the spectra, we remark that particles in nonequilibrium steady flows generally give rise to six trivial exponents. These are omitted from the plots, since they are not to be considered when evaluating the CPR. They are however considered when calculating the results presented in Table I. The origin of these exponents for PSF and PEF has been explained at length in a previous paper,\(^{6}\) therefore we only present a brief explanation.
TABLE I. Summary of the results for PEF, PSF, and PMF, ordered according to $I$. The system is composed of 32 particles at a density $\rho = 0.3$ and temperature $T = 1.0$. $\lambda_{\text{max}}$ and $\lambda_{\text{min}}$ are the maximum and minimum Lyapunov exponents, respectively, $\sum \lambda_i$ is the sum of the whole spectra, $D_{\text{KY}}$ is the Kaplan–Yorke dimension, $\eta_{\text{NEMD}}$ and $\eta_{\text{Lyap}}$ are the viscosities computed using NEMD and the Lyapunov exponents relation, respectively, $(\xi)$ is the time average of the Gaussian multiplier. The errors, in brackets, are twice the standard error of the mean of ten independent runs. When uncertainties are of the order of $10^{-4}$ for $\eta_{\text{NEMD}}$ and $\eta_{\text{Lyap}}$, they have not been indicated.

<table>
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<th>$I$</th>
<th>$\dot{\gamma}$</th>
<th>$\dot{\varepsilon}$</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\lambda_{\text{min}}$</th>
<th>$\sum \lambda_i$</th>
<th>$D_{\text{KY}}$</th>
<th>$\eta_{\text{NEMD}}$</th>
<th>$\eta_{\text{Lyap}}$</th>
<th>$(\xi)$</th>
<th>$\sum \lambda_i; \lambda_i &gt; 0$</th>
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<td>115.1 (0.1)</td>
<td>0.248</td>
<td>0.258 (0.002)</td>
<td>0.430 (0.001)</td>
<td>63.2 (0.1)</td>
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<td>-25.2 (0.2)</td>
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<tr>
<td>10.0</td>
<td>1.0</td>
<td>2112 (0.004)</td>
<td>-3.564 (0.004)</td>
<td>-92.8 (0.2)</td>
<td>97.1 (0.1)</td>
<td>0.168</td>
<td>0.175</td>
<td>1.463 (0.002)</td>
<td>63.2 (0.1)</td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>2.0</td>
<td>2194 (0.003)</td>
<td>-4.258 (0.004)</td>
<td>-131.0 (0.3)</td>
<td>90.8 (0.1)</td>
<td>0.149</td>
<td>0.154</td>
<td>2.067 (0.002)</td>
<td>58.9 (0.1)</td>
<td></td>
</tr>
</tbody>
</table>
Their numerical value can be obtained exactly in the low density limit, when the interatomic forces become negligible and the particle dynamics just follows the streamlines. Practically this means solving the evolution of displacements given by $\delta q$ and $\delta p$ according to the underlying SLLOD equations of motion neglecting $F_i$ terms. Because we are dealing with dense systems and high force fields, the potential energy cannot be ignored, therefore the exact value of these exponents is sometimes hard to determine. Five of the six trivial exponents result from properties conserved by the dynamics (temperature, center of mass, and total momentum). Displacements orthogonal to the isokinetic constraint hypersurface give exponents of value 0 (PSF) or close to zero (PEF). Displacements in $q_i$ result in two exponents of value 0 for PSF and of value $\hat{\gamma}$ and $-\hat{\gamma}$ for PEF; and displacement in $p_i$ gives two exponents of value $-\langle \xi \rangle$ for PSF and $\hat{\gamma} - \langle \xi \rangle$ and $-\hat{\gamma} - \langle \xi \rangle$ for PEF. Here $\langle \xi \rangle$ is the average value of the Gaussian constraint multiplier for the flow considered. In both cases there is an additional exponent due to displacements in the direction of flow, which is nonzero due to the nonautonomous nature of the equations of motion (the box boundaries change in time). Consideration of Eq. (8) shows that the trivial exponents for PMF will have the same form as those for PEF due to the dominating exponential growth along the expanding and contracting directions.

In Figs. 2(a) and 2(b) we plot the Lyapunov spectra and the ordered pair sum, respectively, for pure elongation, pure shear, and three rates of mixed flow, all characterized by $II = 2$. For PMF, two systems have a dominant elongation contribution. This is also true for Figs. 3(a) and 3(b). As expected, the spectra for PSF look qualitatively different from PEF, the coupled exponents show in fact a larger separation for PEF. It is interesting that PMF spectra show a transition between the two pure flows, according to which flow geometry is dominant ($\hat{\gamma} > e$ or $e > \hat{\gamma}$). In the two cases when $\hat{\gamma}$ is higher, PMF spectra almost completely overlap with PEF spectra, while when $\hat{\gamma}$ is higher, the spectrum sits in between PEF and PSF spectra. Clearly, this reflects the stronger contribution of the elongational component in the total balance of $II$, which is four times larger than the corresponding component for shear.

Looking at the maximum exponents in Table I, we can notice that pure shear flow is consistently smaller. This result needs a careful interpretation. In fact, even if it could suggest that PSF is less chaotic than PEF, and to certain extent PMF, we need to consider the heat dissipation, also consistently smaller for PSF. The PSF lower average exponent sum and lower average thermostat multiplier with respect to PEF and PMF (also reflected in the values of the Kaplan–Yorke dimension and Kolmogorov–Sinai entropy) could be due to the approximation of the heat production rate per unit volume, i.e., the $II$ (obtained by macroscopic continuum mechanics considerations) could be not exactly reproduced in these small systems by the average of the thermostat multiplier. If the equivalence between $II$ and heat production rate were exact, the values of the average thermostat multiplier would also be identical for all flows. However, if we now consider the maximum exponents for pure PSF at $\hat{\gamma} = 2.0$ and PMF at $\hat{\gamma} = 1.0$ and $\epsilon = 0.5$, we see that the former is smaller. This time $II$ and the heat dissipation for PSF are two times that of PMF, therefore even if the maximal exponents values are too close for definitive conclusions to be made, this is an indicator that the exponents respond differently to the two flows.

In general, the action of each separate flow on the degrees of freedom of the system does not appear homogeneous. This can also be confirmed, in a more general way, by looking at the rest of the spectra in Fig. 2(a). The exponents with maximal absolute values are known to be associated with the fastest events happening in the system (i.e., particle collisions), whereas the smaller couples are indicative of global and delocalized aspects of the dynamics. If we consider only the positive half of the spectra, we can see that exponents for PSF are always below those for PMF for low couple numbers, similarly, PMF exponents are below PEF exponents. As we move toward larger exponent pair indices, the differences between PSF, PMF, and PEF drastically diminish. All this shows that the collective particle behavior of planar shear is markedly different from planar elongation and both seem to provide a lower and upper limit, respectively, for planar mixed flow depending on the ratio of the fields. Collisions instead, being mostly controlled by state variables as temperature and density, are less sensitive to the type of flow considered at small and high values of $II$ [see also Figs. 3(a) and 3(b)], and seem to occur with similar frequencies and energy exchanges in all the flows.

The ordered pair sum in Fig. 2(b) looks qualitatively analogous for PEF and PMF, and different from PSF. Sums for PEF and PMF share the same trend, and their average absolute value increases as the elongational/shear component is increased/decreased. This suggests that the CPR is only sensitive to the value of the strain rate, and not the value of $II$. However, the fact that deviations from CPR are smaller in
PMF with respect to PSF and more sensitive to the value of the strain rate is not surprising, as it is the shear flow that is responsible for the deviations. These irregularities, which show a distinctive kink for low pair indices, are in fact the expected deviations from CPR for non-Hamiltonian shear-SLLOD. Note that the small deviations from CPR in PEF are due to pathological sums tend to occur both at one third and two thirds of the spectrum, rather than concentrate at its ends or in the middle. This indicates that the way inhomogeneous dissipation takes place in PSF, and therefore PMF, shows that less dissipation is produced by couples of exponents associated with collective particles dynamics and vice versa for couples of exponents associated with short time-scale dynamics. As said, this imbalance is also evident in the spectra in Figs. 2(a) and 2(b).

If we now inspect Figs. 3(a) and 3(b) where \( II = 8 \), we can better appreciate how qualitatively different the spectra are. In particular, notice how for PEF and PMF, around pair index 25, a jump divides the bell-shaped spectra into two parts: one with a slightly different slope than PSF, and the other, at small pair indices, with a much smoother parabolic end. PEF and PMF have similar spectra, as in Fig. 2. Note that the differences between exponents of pure shear, mixed, and pure elongational flows remain large and constant for a longer part of the spectrum than those in Fig. 2(a), where \( II \) is smaller. This indicates that differences among flows increase as \( II \) is increased, and they tend to persist over a larger range of time scales. Only fast collisions (i.e., the end of the spectrum) are relatively insensitive to the type of flow considered. The degree of similarity between PSF and PEF, instead, does not seem to be affected overall by changes in \( II \).

From Fig. 3(b), it is now clear that CPR does not hold for shear-SLLOD while much smaller deviations exist for PEF, whose sums display once more very strong similarities and satisfy CPR within less than 1%. An interesting fact that is more evident in Fig. 3(b) is that the non-Hamiltonian character in PMF due to PSF has a quantitative influence on the quality of conjugate-pairing for PMF. The initial part of the kink that PSF displays for the sums of lower index is in fact mimicked by the shear dominated PMF: as we increase the rate of \( \dot{\gamma} \), a jump appears. Its amplitude depends directly on the value of the rate, making the divergence from CPR higher when the shear component is made larger. Also, the asymmetry between low and high pair numbers in Fig. 3(b) with respect to the average value of the sums is more prominent for stronger shear rates in PMF.

To better understand the effect of \( \dot{\gamma} \) over the sums for PMF, in Fig. 4 we plot the difference between the ordered pair sum and the expected CPR value, computed as \( \left( \sum \lambda_i \right)/2N \) for different fields. We can clearly see how an increase in \( \dot{\gamma} \) pushes deviations in the CPR to higher values, up to about 4% when the shear rate is doubled. Instead, when the weight of elongation is increased, keeping \( \dot{\gamma} = 1.0 \), the conjugate-pairing does not worsen. Interestingly, the most pathological sums tend to occur both at one third and two thirds of the spectrum, rather than concentrate at its ends or in the middle. This indicates that the way inhomogeneous dissipation takes place in PSF, and therefore PMF, shows that less dissipation is produced by couples of exponents associated with collective particles dynamics and vice versa for couples of exponents associated with short time-scale dynamics. As said, this imbalance is also evident in the spectra in Figs. 2(a) and 2(b).

In Figs. 5(a), 5(b), 6(a) and 6(b) we compare PMF with \( \dot{\gamma} = 2.0 \) and \( \dot{\gamma} = 1.0 \) with PSF with \( \dot{\gamma} = 2 \) and PEF with \( \dot{\gamma} = 1 \). The \( II \) for PSF and PEF are the same, but lower than that of PMF. This will result in a significantly different conjugate pair sum for PMF due to the much higher heat dissipation, and therefore to aid the comparison, the spectra in Fig. 5(b) are shifted so that they are all centered about 0. From an analysis of Fig. 5(b) we see that PMF and PEF are nearly overlapping for low pair indices up to about 15, where the arms of the spectra for PMF separate from those of pure elongation. This shows that the elongational component dominates the collective dynamics in PMF even when the shear component generates similar heat dissipation, whereas larger effects tend to appear in high indices: at large \( II \), collisions in PMF are quantitatively affected by the presence of a \( \dot{\gamma} \neq 0 \). Figure 5(a) shows that this change is not absolute, since the differences between maximal exponents for PEF and PMF are small, but rather a relative effect with respect to CPR, i.e., with respect to the average dissipation of all degrees of
freedom in the system. This increase in the importance of collisions in the distribution of energy events in the system may indicate either that collisions are more frequent and/or that the energy exchanged per particle is larger. Finally, in Figs. 6(a) and 6(b), the contribution to violations in CPR due to the non-Hamiltonian character of the shear component in PMF are, once again, directly evident. In Fig. 6(b), similarly to what is already observed in Fig. (4), at constant $\dot{\gamma}$ the deviation from the expected CPR does not change with changes in $\dot{\varepsilon}$.

Finally, from Table I, we can observe that PMF viscosities, obtained using the sum of all Lyapunov exponents, are in good agreement with the NEMD viscosities, the accuracy of which has already been tested in Ref. 1.

V. CONCLUSIONS

In this work we analyzed the chaotic structure of planar mixed flow, a linear combination of planar elongation flow and planar shear flow. We concentrated our attention on the compliance of PMF to the conjugate-pairing rule. Since the equations of motion for PMF are non-Hamiltonian, due to PSF contribution (also non-Hamiltonian), a breaking of conjugate-pairing rule is expected. The most interesting point in this regard is the quantitative dependence of the Hamiltonian character to the shear rate. The higher the value of $\dot{\gamma}$, the larger the non-Hamiltonian contribution, and therefore a worse abidance of the CPR. The elongation component is however important in determining the degree of chaoticity of the system. Also from a qualitative point of view, PMF spectra resemble PEF spectra’s shape, suggesting a similar phase space distribution function. The collective behavior of the particles is mainly due to the flow streamlines. The streamlines of PMF and PEF are qualitatively similar, in fact the only action of the shear flow in PMF is to change the angle between the expansion and contraction axes, leaving the elongational field along them the same.