A simple, direct derivation and proof of the validity of the SLLOD equations of motion for generalized homogeneous flows

Peter J. Daivis[a)]
Applied Physics, School of Applied Sciences, RMIT University, G.P.O. Box 2476 V, Melbourne, Victoria 3001, Australia

B. D. Todd[b)]
Centre for Molecular Simulation, Swinburne University of Technology, P.O. Box 218, Hawthorn, Victoria 3122, Australia

(Received 11 August 2005; accepted 13 March 2006; published online 16 May 2006)

We present a simple and direct derivation of the SLLOD equations of motion for molecular simulations of general homogeneous flows. We show that these equations of motion (1) generate the correct particle trajectories, (2) conserve the total thermal momentum without requiring the center of mass to be located at the origin, and (3) exactly generate the required energy dissipation. These equations of motion are compared with the *g*-SLLOD and *p*-SLLOD equations of motion, which are found to be deficient. Claims that the SLLOD equations of motion are incorrect for elongational flows are critically examined and found to be invalid. It is confirmed that the SLLOD equations are, in general, non-Hamiltonian. We derive a Hamiltonian from which they can be obtained in the special case of a symmetric velocity gradient tensor. In this case, it is possible to perform a canonical transformation that results in the well-known DOLLS tensor Hamiltonian. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2192775]

I. INTRODUCTION

The SLLOD equations of motion[1] are the acknowledged standard set of first order linear differential equations that enable one to perform nonequilibrium molecular dynamics (NEMD) simulations of homogeneous planar shear flow. They have been implemented for simple and complex fluids and have been central to some spectacularly successful studies of the shear rheology of fluids from first principles. The SLLOD equations of motion are usually written in the form of two first order differential equations:

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{u},$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i^{\phi} - \mathbf{p}_i \cdot \nabla \mathbf{u}, \tag{1}$$

where m_i, $\mathbf{r}_i$, and $\mathbf{p}_i$ represent the mass, position, and *thermal* momentum, respectively, of particle i, $\mathbf{F}_i^{\phi}$ represents the total force due to *intermolecular potentials* of all other particles on particle i, and $\nabla \mathbf{u}$ represents the velocity gradient tensor. A thermostating mechanism is also required in order for these equations to generate a steady state, but the thermostats are not the subject of this paper and will therefore be omitted.

Simulations of elongational flow—a much more complex flow geometry—were first performed in the mid-1980s by Heyes[2] who implemented a simple NEMD technique based on deformation of the simulation cell for a Lennard-Jones fluid, and then later by Evans and Heyes[3] who implemented the SLLOD equations of motion. Work in this field then languished for several years because of the inherent finiteness of the simulation caused by the contraction of at least one of the lengths of the simulation box. This means that more interesting and industrially relevant fluids, such as alkanes or polymers, could not be studied due to their long relaxation times compared with the short finite simulation time available. In the mid-1990s Baranyai and Cummings[4] and Todd and Daivis[5] revived interest in this problem by devising several new algorithms to simulate elongational flows for longer or indefinite times. A solution to this problem was finally applied to molecular dynamics simulations of planar elongational flow by Todd and Daivis,[6] and independently by Baranyai and Cummings,[7] who implemented a new set of periodic boundary conditions that allowed for simulations of unrestricted duration. These boundary conditions were based on the set of reproducible lattices derived by Kraynik and Reinelt.[8]

At about this time, Tuckerman *et al.*[9] suggested that the SLLOD equations of motion were incorrect when applied to elongational flow. They proposed an alternative set of equations given by

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{u},$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i^{\phi} - \mathbf{p}_i \cdot \nabla \mathbf{u} - m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u}, \tag{2}$$

which they called the *g*-SLLOD (or "generalized" SLLOD) equations. These equations differ from the original SLLOD equations in that an additional term proportional to the particle position is included in the force equation. The additional term is zero for shear flow but nonzero for elongation. Thus,

[a)]Author to whom correspondence should be addressed. Electronic mail: peter.daivis@rmit.edu.au
[b)]Electronic mail: btodd@swin.edu.au

g-SLLOD is the same as SLLOD for shear, but different for elongation.

Soon after they were proposed, the g-SLLOD equations were criticized for a number of shortcomings, including generation of an incorrect distribution function. This was followed by a more general discussion on the formulation of statistical mechanics for systems with non-Hamiltonian and noncanonical equations of motion,[10] and many questions remain unresolved. We do not intend to discuss these more general issues here. While simulations of elongational flow using the SLLOD equations of motion continued with more refined algorithmic improvements[11–13] and incorporated the study of more complex molecular systems,[14,15] it is clear that some doubts remain over the validity of either the SLLOD or g-SLLOD equations of motion for simulating elongational flow. The debate has again been opened very recently by Edwards and co-workers,[16–18] who maintain that the g-SLLOD equations are the correct equations to use for elongational flow. They call their implementation p-SLLOD (for "proper" SLLOD), but, despite the fact that they were obtained by different methods, the p-SLLOD and g-SLLOD equations of motion are identical.

Our intention in writing this paper has been to remove these doubts by presenting a simple and clear derivation of the equations of motion for molecular simulations of flows with homogeneous velocity gradients. In what follows we will show that the SLLOD equations of motion are indeed the correct equations of motion to use for all types of generalized homogeneous flow. We will do this by carefully deriving the SLLOD equations for generalized flow fields in Sec. II and showing that these equations are completely consistent with Newton's equations of motion. We will specifically examine planar shear and planar elongational flows. The relationship of SLLOD to the system Hamiltonian for shear and elongational flows will then be discussed in Sec. III. In Sec. IV we point out several crucial deficiencies in the g-SLLOD equations which were not discussed in the previous Comment[10] on the paper in which the g-SLLOD equations of motion were first proposed.[9] Finally, in Sec. V we discuss the periodic boundary conditions that must be used in conjunction with the SLLOD algorithm, and offer concluding remarks in Sec. VI.

II. DERIVATION OF THE SLLOD ALGORITHM

Our aim in this section is to demonstrate that for arbitrary homogeneous flows, the SLLOD equations of motion are identical to Newton's equations of motion for a fluid in the presence of an external force. Let $\mathbf{G}(\mathbf{r},t)$ be an external body force density (i.e., the force per unit volume) applied to a fluid of infinite extent at the laboratory position $\mathbf{r}$ and time t. If ρ is the fluid density, $\mathbf{u}$ is the fluid streaming velocity, and $\mathbf{P}$ is the pressure tensor, then the local, instantaneous equation of motion can be expressed as[1,19]

$$\frac{\partial \mathbf{J}(\mathbf{r},t)}{\partial t} = -\nabla\cdot\mathbf{P}(\mathbf{r},t) - \nabla\cdot[\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)] + \mathbf{G}(\mathbf{r},t), \tag{3}$$

where $\mathbf{J}(\mathbf{r},t)=\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)=\Sigma_i m_i\mathbf{v}_i\delta(\mathbf{r}-\mathbf{r}_i)$ is the local instantaneous momentum density, the body force $\mathbf{G}(\mathbf{r},t)$ is given by

$$\mathbf{G}(\mathbf{r},t) = \sum_i \mathbf{F}_i^e\delta(\mathbf{r}-\mathbf{r}_i), \tag{4}$$

where $\mathbf{F}_i^e$ is the external force on particle i, and the index i ranges over all molecules in the fluid. To express this in terms of the wave vector $\mathbf{k}$, one takes the Fourier transform of Eq. (3) to obtain

$$\frac{\partial \tilde{\mathbf{J}}(\mathbf{k},t)}{\partial t} = i\mathbf{k}\cdot\tilde{\mathbf{P}}(\mathbf{k},t) + i\mathbf{k}\cdot[\widetilde{\rho\mathbf{u}\mathbf{u}}(\mathbf{k},t)] + \tilde{\mathbf{G}}(\mathbf{k},t). \tag{5}$$

Here the tilde above a quantity represents its Fourier transform and $\tilde{\mathbf{J}}(\mathbf{k},t)$ represents the Fourier transform of the local momentum density. This equation immediately shows that the time dependence of the zero wave vector component of the momentum density is completely determined by the external body force. The equation of motion for the zero wave vector component of the momentum density is

$$\frac{d}{dt}\sum_i m_i\mathbf{v}_i = \sum_i \mathbf{F}_i^e, \tag{6}$$

where m_i is the mass of molecule i, and $\mathbf{v}_i$ is the laboratory frame velocity of molecule i. We now define the peculiar, or thermal, velocity $\mathbf{c}_i$ for molecule i, with a change of variable such that

$$\mathbf{v}_i = \mathbf{c}_i + \mathbf{u}(\mathbf{r}_i)\Theta(t) = \mathbf{c}_i + \mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t),$$

$$\sum_i m_i\mathbf{c}_i = 0, \quad \frac{d}{dt}\sum_i m_i\mathbf{c}_i = 0, \tag{7}$$

in which the first line is valid for a homogeneous velocity gradient and line two expresses the condition that the total thermal momentum and its derivative are both zero. It is assumed that they are maintained at these values by the equations of motion, i.e., that the thermal component of the momentum is conserved.

It is assumed here that the velocity gradient is applied as a step function at time $t=0$, where the Heaviside step function is defined as

$$\Theta(t) = \begin{cases} 0, & t<0 \\ 1, & t>0. \end{cases} \tag{8}$$

We now demonstrate that the SLLOD equations of motion emerge naturally when we insist that the zero wave vector momentum obeys Eq. (6) and that the peculiar or thermal velocity satisfies Eq. (7).

Taking the time derivative of the zero wave vector momentum gives

$$\frac{d}{dt}\sum_i m_i\mathbf{v}_i = \frac{d}{dt}\sum_i m_i[\mathbf{c}_i + \mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t)]$$

$$= \frac{d}{dt}\sum_i m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t),$$

where we have used the fact that the thermal momentum is conserved to obtain the second line. Taking the derivative of the product inside the sum, substituting Eq. (7) for the velocity, and using the fact that the mean value of the thermal momentum is zero, we obtain

$$\frac{d}{dt}\sum_i m_i\mathbf{v}_i = \sum_i \left[m_i\mathbf{v}_i\cdot\nabla\mathbf{u}\Theta(t) + m_i\mathbf{r}_i\cdot\frac{d}{dt}(\nabla\mathbf{u}\Theta(t))\right]$$

$$= \sum_i [m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}\Theta(t) + m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\delta(t)]. \quad (9)$$

In obtaining the last line of Eq. (9) we have used the property that the total peculiar momentum is conserved and the product of the step function with itself is just the step function. In an actual computer simulation, finite precision numerics and discretization error in the solution of the ordinary differential equations mean that conservation of thermal momentum may not be strictly achieved, though Eq. (9) is formally correct. This will be discussed in Sec. IV. Comparing the right hand sides of Eqs. (6) and (9), we see that the sum of the external forces over all particles is given by the right hand side of Eq. (9). If we insist that the equations of motion are spatially homogeneous, i.e., that they have the same functional form for every particle in the system, then the external force acting on each particle that is required to generate the correct zero wave vector momentum density, subject to the condition that the total peculiar momentum and its derivative are zero at all times, is given by

$$\mathbf{F}_i^{\text{ext}} = m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\delta(t) + m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}\Theta(t). \quad (10)$$

From this one can identify the total external force per molecule as consisting of two components: an impulse force at time $t=0$ at the moment the field is applied, and an additional term that is zero before the application of the field and a constant multiplied by the molecule's laboratory position afterwards. This expression for the external force is the only one that gives the same equations of motion for each particle and simultaneously satisfies Eqs. (6) and (7) while specifically excluding terms of the form $m_i\mathbf{c}_i\cdot\nabla\mathbf{u}\Theta(t)$ whose sum is zero and therefore cannot contribute to the zero wave vector component of the momentum density or the total external force.

In Newtonian form, the full equations of motion are

$$\mathbf{F}_i = m_i\frac{d\mathbf{v}_i}{dt}, \quad (11)$$

where the total force on molecule i is the sum of internal (intermolecular) and external forces given by

$$\mathbf{F}_i = \mathbf{F}_i^{\phi} + \mathbf{F}_i^{\text{ext}}. \quad (12)$$

The external force is given by Eq. (10).

The SLLOD equations of motion are not usually expressed in the Newtonian form given above. Instead, a change of variable is performed, in which we define the peculiar or thermal velocity by

$$\dot{\mathbf{r}}_i = \mathbf{c}_i + \mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t). \quad (13)$$

If we now substitute this expression for the velocity into Newton's second law [Eq. (11)], and then insert the forces given by Eq. (12) into the left hand side of Eq. (11) and make the peculiar velocity the subject of the equation, we obtain a first order differential equation for the peculiar velocity,

$$m_i\dot{\mathbf{c}}_i = \mathbf{F}_i^{\phi} - m_i\mathbf{c}_i\cdot\nabla\mathbf{u}\Theta(t). \quad (14)$$

Equations (13) and (14) are just the first order version of the SLLOD equations of motion, identical to Eq. (1) when we define the peculiar momentum as $\mathbf{p}_i = m_i\mathbf{c}_i$. Normally these are written without the explicit inclusion of the step function, which we have included here for greater clarity. It is important to appreciate that we have solved for the *laboratory position* and the *thermal velocity*. Both of these quantities are calculated relative to the laboratory reference frame, since the definition of $\mathbf{c}_i$ *exclusively* involves quantities referred to the laboratory frame. If we had used a moving reference frame, the streaming velocity would be zero. This is clearly *not* the case in the SLLOD equations of motion, which explicitly include a nonzero streaming velocity.

We now consider two specific types of flow: planar shear and planar elongational. If the desired velocity gradient corresponds to simple planar shear with flow in the x direction and gradient in the y direction, then we have

$$\nabla\mathbf{u} = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (15)$$

where $\dot{\gamma} = \partial u_x/\partial y$ is the magnitude of the velocity gradient. For planar shear flow $\nabla\mathbf{u}\cdot\nabla\mathbf{u}=0$ and so the external force described by Eq. (10) only consists of the impulse term. The flow is generated by the impulse at $t=0$ and, because the system is infinite in extent (the use of periodic boundary conditions ensures this), the impulse will result in a persistent zero wave vector momentum current for all times thereafter without the need for a constant driving external field at $t>0$. This must necessarily be the case because there is no zero wave vector acceleration of the system of particles in planar shear flow after the impulse, as shown by Eq. (9). [Equation (3) shows that we do not need to consider the effect of stresses, because they occur at first order, not zero order, in wave vector.]

In the case of planar elongational flow, with expansion in the x direction, contraction in the y direction, and no field in the z direction, the velocity gradient tensor is

$$\nabla\mathbf{u} = \begin{pmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (16)$$

in which case

$$\nabla \mathbf{u} \cdot \nabla \mathbf{u} = \begin{pmatrix} \dot{\varepsilon}^2 & 0 & 0 \\ 0 & \dot{\varepsilon}^2 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{17}$$

where $\dot{\varepsilon}$ is the elongation rate. In this case the external force described by Eq. (10) has the initial impulse, as with planar shear flow, but in addition has a term proportional to the laboratory position of the molecule. In particular, the form for the individual components is

$$\begin{aligned} F_{i,x}^{\text{ext}} &= m_i \dot{\varepsilon} x_i \delta(t) + m_i \dot{\varepsilon}^2 x_i \Theta(t), \\ F_{i,y}^{\text{ext}} &= -m_i \dot{\varepsilon} y_i \delta(t) + m_i \dot{\varepsilon}^2 y_i \Theta(t), \\ F_{i,z}^{\text{ext}} &= 0. \end{aligned} \tag{18}$$

For planar elongation an impulse force alone is insufficient to sustain an indefinite flow. An additional external force proportional to the laboratory position must apply at all times to every molecule. The signature of this external force is that it must induce a zero wave vector component of the acceleration of the fluid. This acceleration is observed as the hyperbolic streaming velocity profile, in which both the magnitude and direction of the velocity of a small element of fluid continually change with time, unlike in shear flow for which they remain constant.

It is important to appreciate that Eqs. (11) and (14) are equivalent ways of expressing Newton's second law and are completely general for homogeneous flows. The *g*-SLLOD equations of motion instead introduce an additional term, $-m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u}$, into Eq. (14). This in turn actually *negates* the influence of the necessary nonimpulsive external force required to sustain an elongational flow indefinitely. The observation that simulations using *g*-SLLOD do, in fact, continue to flow is a consequence of implementing them with a coupled thermostat and boundary conditions that are consistent with the desired flow through the definition of the peculiar velocity, Eq. (13), and the evolution of the periodic boundaries, which is also essentially given by Eq. (13) (see Sec. V). As we will show later, the boundary conditions do not exert a force on the particles unless their streaming motion is incompatible with the motion of the boundaries. In addition, the thermostat interprets any deviations from the assumed velocity profile as heat and compensates by applying an additional force to the molecules, which in turn serves to sustain the velocity gradient specified by the definition of the peculiar velocity [Eq. (13)]. Thus, it is possible to induce the desired flow, even when the equations of motion are inconsistent with the flow, as they are in the case of *g*-SLLOD.

III. RELATIONSHIP TO HAMILTONIAN MECHANICS

The question now arises: can these equations be derived from a Hamiltonian, and what relationship do they have to the Hamiltonian description? If a Hamiltonian containing a standard potential energy function exists, then we should be able to write the external force on the right hand side of the Newtonian form of the SLLOD algorithm [Eq. (10)] as the gradient of a potential. This can immediately be checked by calculating the curl of the external force, since a potential energy exists only if $\nabla \times \mathbf{F}^e = 0$. Examining the external force terms, we see that if the impulse force can be expressed as the gradient of a potential, it must satisfy

$$\begin{aligned} \frac{\partial}{\partial \mathbf{r}_i} \times \mathbf{r}_i \cdot \nabla \mathbf{u} &= \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \dfrac{\partial}{\partial x_i} & \dfrac{\partial}{\partial y_i} & \dfrac{\partial}{\partial z_i} \\ \mathbf{r}_i \cdot \nabla u_x & \mathbf{r}_i \cdot \nabla u_y & \mathbf{r}_i \cdot \nabla u_z \end{vmatrix} \\ &= \mathbf{i}\left(\frac{\partial u_z}{\partial y} - \frac{\partial u_y}{\partial z}\right) - \mathbf{j}\left(\frac{\partial u_z}{\partial x} - \frac{\partial u_x}{\partial z}\right) \\ &\quad + \mathbf{k}\left(\frac{\partial u_y}{\partial x} - \frac{\partial u_x}{\partial y}\right) = 0. \end{aligned} \tag{19}$$

This condition is clearly satisfied if the velocity gradient tensor is symmetric. Thus, for planar shear it is not satisfied, whereas for planar elongational flow it is. For planar elongational flow the potential energy associated with the impulsive external force is

$$\begin{aligned} V &= -\int \mathbf{F} \cdot d\mathbf{r}_i = -\delta(t) m_i \int \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot d\mathbf{r}_i \\ &= -\frac{m_i \dot{\varepsilon}}{2}(x_i^2 - y_i^2)\delta(t). \end{aligned} \tag{20}$$

For the nonimpulsive external force term we see that

$$\begin{aligned} &\frac{\partial}{\partial \mathbf{r}_i} \times \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} \\ &= \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ \dfrac{\partial}{\partial x_i} & \dfrac{\partial}{\partial y_i} & \dfrac{\partial}{\partial z_i} \\ \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla u_x & \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla u_y & \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla u_z \end{vmatrix} \\ &= \mathbf{i}\left(\frac{\partial \mathbf{u}}{\partial y} \cdot \nabla u_z - \frac{\partial \mathbf{u}}{\partial z} \cdot \nabla u_y\right) - \mathbf{j}\left(\frac{\partial \mathbf{u}}{\partial x} \cdot \nabla u_z - \frac{\partial \mathbf{u}}{\partial z} \cdot \nabla u_x\right) \\ &\quad + \mathbf{k}\left(\frac{\partial \mathbf{u}}{\partial x} \cdot \nabla u_y - \frac{\partial \mathbf{u}}{\partial y} \cdot \nabla u_x\right), \end{aligned} \tag{21}$$

which is zero if the velocity gradient tensor is symmetric. This condition is satisfied for all types of elongational flow, and it is irrelevant for shear flow, since the nonimpulsive external force term is then zero.

Therefore, the potential energy corresponding to this part of the external force is zero for shear flow, while for planar elongational flow it is

$$\begin{aligned} V &= -\int \mathbf{F} \cdot d\mathbf{r}_i = -\Theta(t) m_i \int \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} \cdot d\mathbf{r}_i \\ &= -\frac{m_i \dot{\varepsilon}^2}{2}(x_i^2 - y_i^2)\Theta(t). \end{aligned} \tag{22}$$

Thus we see that a Hamiltonian description for the SLLOD equations of motion does not exist for planar shear flow, but does exist for planar elongational flow. It will, in fact, exist for all types of elongational flow.

The general form of the Hamiltonian for flows with a symmetric velocity gradient tensor is

$$H(\mathbf{r}^N,\mathbf{p}'^N,t) = \phi(\mathbf{r}^N) + K(\mathbf{p}'^N) + V(\mathbf{r}^N,t), \tag{23}$$

where ϕ is the intermolecular potential energy, K is the kinetic energy, and V is the potential energy due to the external field, which is given by

$$V(\mathbf{r}^N,t) = -\frac{1}{2}\sum m_i(\mathbf{r}_i\cdot\nabla\mathbf{u})^2\Theta(t) - \frac{1}{2}\sum m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\cdot\mathbf{r}_i\delta(t). \tag{24}$$

Here, the conjugate momentum $\mathbf{p}'$ is related to the velocity by the usual definition from classical mechanics, $\mathbf{p}_i' = \partial L/\partial\dot{\mathbf{r}}_i = m_i\dot{\mathbf{r}}$, consistent with the system Lagrangian. When this Hamiltonian is used with Hamilton's equations of motion, the resulting equations of motion are the same as Eq. (12), except that the velocity gradient in the impulse term of the external force is now only the symmetric part of the velocity gradient. This is totally consistent with our previous discussion in which we found that a Hamiltonian only exists for flows with a symmetric velocity gradient tensor. Further, it is easily shown that if we perform a canonical transformation such that

$$\mathbf{q}_i = \mathbf{r}_i,$$
$$\mathbf{p}_i = \mathbf{p}' - m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t), \tag{25}$$

with a generating function for the canonical transformation[20] given by

$$F(\mathbf{r}^N,\mathbf{p}^N,t) = \sum\mathbf{r}_i\cdot\mathbf{p}_i + \frac{1}{2}\sum m_i(\mathbf{r}_i\cdot\nabla\mathbf{u})^2\Theta(t), \tag{26}$$

then we obtain the Hamiltonian in terms of the new variables as

$$H_{\mathrm{DOLLS}}(\mathbf{q}^N,\mathbf{p}^N,t) = H + \frac{\partial F}{\partial t} = \phi(\mathbf{q}^N) + \sum\frac{\mathbf{p}_i^2}{2m_i} + \sum\mathbf{q}_i\cdot\nabla\mathbf{u}\cdot\mathbf{p}_i\Theta(t), \tag{27}$$

which is the DOLLS tensor Hamiltonian.[21] This results in the well-known DOLLS equations of motion, which, we now see can only be applied for symmetric velocity gradients, in which case it is equivalent to the SLLOD algorithm. An important point here is that the explicit time dependence of the Hamiltonian (which has been neglected by Baig *et al.*[17]) must be taken into account in order to obtain correct results.

IV. MOMENTUM CONSERVATION AND ENERGY DISSIPATION

The SLLOD equations of motion conserve the total thermal momentum of the system. This is easily seen by summing over all molecules in Eq. (14) and is valid for any type of homogeneous flow, including shear and elongation. Note that this is a separate issue to the phenomenon observed by Todd and Daivis,[12] in which they found that *numerical* simulations of elongational flow via the SLLOD algorithm exhibited an inherent instability in the total thermal momentum which was nevertheless controllable. The source of this instability is due entirely to finite precision numerics and does not result from a flaw in the SLLOD algorithm, as has been asserted recently by Baig *et al.*[17] We have previously demonstrated that the effect of uncorrected numerical error in the thermal momentum can be analyzed for the case of planar elongational flow as follows. The equation of motion for the thermal momentum given by the SLLOD equations of motion is $\dot{\mathbf{P}} = -\mathbf{P}\cdot\nabla\mathbf{u}$, where $\mathbf{P} = \Sigma_i m_i\mathbf{c}_i$ is the total peculiar momentum of the system. If we allow the initial value of the total thermal momentum to be nonzero, contradicting the exact equations of motion, but allowing for a small *numerical* error, the equation of motion for the thermal momentum can be solved for each Cartesian component with Eq. (16) to give[12]

$$P_x(t) = P_x(0)\exp(-\dot{\varepsilon}t),$$
$$P_y(t) = P_y(0)\exp(\dot{\varepsilon}t). \tag{28}$$

Clearly if we set the components of the initial thermal momentum identically equal to zero and we solve the equations of motion without introducing any numerical error, the evolution of the system will always result in zero total thermal momentum at all times. Since the complete elimination of discretization and truncation errors in numerical computation is impossible there will always be numerical errors in the momentum. Because any nonzero error in total initial momentum in the y direction grows exponentially in time, ultimately this can cause serious problems for the simulation if it remains uncorrected. Fortunately, this numerical error is easily corrected by periodically subtracting the mean y component of the peculiar momentum from each particle, by adding proportional feedback to correct the momentum, or by adding a constraint to prevent it from growing.[12] Interestingly, it has recently been suggested[22,23] that fluctuations may be an inherently chaotic source of instability for elongational flows in general, and work is continuing to explore this microscopic connection. No such problem will occur in the x direction because now the total momentum is forced to converge exponentially to zero. We have previously also shown that no such problem occurs in shear flow, which explains why numerical simulations of planar shear are always stable.[12]

The g-SLLOD equations differ from the SLLOD equations only in the force equation, so that the equations of motion for the first moment of the positions $\mathbf{Q} = \Sigma_i m_i\mathbf{r}_i$ and the total peculiar momentum $\mathbf{P} = \Sigma_i\mathbf{p}_i$ are

$$\dot{\mathbf{Q}} = \mathbf{P} + \mathbf{Q}\cdot\nabla\mathbf{u},$$
$$\dot{\mathbf{P}} = -\mathbf{P}\cdot\nabla\mathbf{u} - \mathbf{Q}\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}. \tag{29}$$

Using the first of these equations, the second can be written as

$$\dot{\mathbf{P}} = -\dot{\mathbf{Q}}\cdot\nabla\mathbf{u}, \tag{30}$$

which can be directly integrated to give

$$\mathbf{P}(t) = \mathbf{P}(0) - [\mathbf{Q}(t) - \mathbf{Q}(0)] \cdot \nabla \mathbf{u}. \tag{31}$$

The initial value problem can be solved explicitly by taking the derivative of the first line of Eq. (29), substituting the second line of Eq. (29) into it, and integrating twice with respect to time, giving

$$\mathbf{Q}(t) = \mathbf{Q}(0) + \dot{\mathbf{Q}}(0)t = \mathbf{Q}(0) + \mathbf{Q}(0) \cdot \nabla \mathbf{u} t, \tag{32}$$

which results in the expression for the total thermal momentum derived by Baig *et al.*[17]

$$\mathbf{P}(t) = \mathbf{P}(0) - [\mathbf{P}(0) + \mathbf{Q}(0) \cdot \nabla \mathbf{u}] \cdot \nabla \mathbf{u} t. \tag{33}$$

For shear flow $\nabla \mathbf{u} \cdot \nabla \mathbf{u} = 0$ so the equations of motion conserve thermal momentum. However, for elongational flow, $\nabla \mathbf{u} \cdot \nabla \mathbf{u} \neq 0$ and so the equations of motion will not conserve thermal momentum instantaneously unless the center of mass is located at the origin, $\Sigma_i m_i \mathbf{r}_i = 0$. This condition can be arbitrarily *chosen* as an initial condition for the simulation, but it is not physically *required* in the same way that the thermal momentum must satisfy $\mathbf{P} = \Sigma_i m_i \mathbf{c}_i = 0$. The requirement of a special choice for the origin in the *g*-SLLOD algorithm violates the property of translational invariance that a periodic system would be expected to possess. This requirement is not shared by the SLLOD equations of motion.

g-SLLOD has another serious problem associated with it, namely, it generates the wrong energy dissipation. The aim of a synthetic-force nonequilibrium molecular dynamics algorithm is to *replace* the boundary conditions that are responsible for generating macroscopic fluxes with synthetic forces in the equations of motion. These synthetic forces should have, as their sole result, the production of the appropriate dissipative flux, so that the link with linear response theory becomes explicit and analytically tractable. Therefore, it is crucial that the rate of change of internal energy should only consist of a bilinear expression involving the appropriate flux and synthetic force.

The SLLOD equations of motion are known to generate the correct rate of energy dissipation. This is obtained by taking the time derivative of the total internal energy $E = \Sigma_i 1/2 m_i \mathbf{c}_i^2 + 1/2 \Sigma_i \Sigma_j \phi_{ij}(r_{ij})$, using the equations of motion and standard manipulations, and is found to be[1,24]

$$\dot{E}^{\mathrm{SLLOD}} = -V\mathbf{P}^T : \nabla \mathbf{u} = \begin{cases} -VP_{xy}\dot{\gamma} & \text{planar shear} \\ -V\dot{\varepsilon}(P_{xx} - P_{yy}) & \text{planar elongation,} \end{cases} \tag{34}$$

where $\mathbf{P}$ is the pressure tensor. The rate of change of the internal energy given by the *g*-SLLOD equations of motion is

$$\dot{E}^{g\text{-SLLOD}} = -V\mathbf{P}^T : \nabla \mathbf{u} - \left(\sum_i m_i \mathbf{c}_i \mathbf{r}_i \right) \cdot \nabla \mathbf{u} : \nabla \mathbf{u}. \tag{35}$$

This gives the same dissipation rate as the SLLOD equations of motion for shear, but for planar elongation it is incorrect, since it is known from hydrodynamics that the rate of internal energy generation by viscous processes is given by $-V\mathbf{P}^T : \nabla \mathbf{u}$ for *all* flows. While the extra term in Eq. (35) might become negligible in the thermodynamic limit, Eq. (35) has the disadvantage that the energy balance equation is no longer satisfied exactly and instantaneously, as it is when the SLLOD equations of motion are applied. This means that the work done by the external field will not correspond exactly to the energy removed by the internal energy constraint force in a constant internal energy simulation. Furthermore, because the application of linear response theory requires that the correct dissipation be generated by the equations of motion, the *g*-SLLOD equations of motion will not give the correct linear response for small systems and the magnitude of the error will not be easy to quantify.

V. PERIODIC BOUNDARY CONDITIONS

The first simulations of elongational flow were performed by direct deformation of the simulation box.[2] The introduction of equations of motion that allowed a flow to be induced by an explicit external force, rather than by direct deformation of the simulation box, had major benefits. One of these was that the nonequilibrium response of the system could be analyzed mathematically using linear and nonlinear response theories.[1] It follows from this that if we want our mathematical analysis to be correct, no other external forces than those explicitly imposed on the system should be included. Therefore, it is essential that the periodic boundary conditions should not impose a force on the system. The way to achieve this is to allow the simulation box to evolve according to the kinematics of the induced flow. Let $\mathbf{L}$ represent one of the vectors defining the vertices of the simulation box. If $\mathbf{L}$ is to evolve with the flow, it must obey

$$\dot{\mathbf{L}} = \mathbf{L} \cdot \nabla \mathbf{u} \Theta(t), \tag{36}$$

and the acceleration of the box vertex must therefore be given by

$$\ddot{\mathbf{L}} = \mathbf{L} \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} \Theta(t) + \mathbf{L} \cdot \nabla \mathbf{u} \delta(t). \tag{37}$$

This is identical to the acceleration of a noninteracting particle with no thermal momentum given by the SLLOD equations of motion, as can easily be shown by setting the peculiar velocity to zero and then taking the time derivative of Eq. (7). However, it is not consistent with the acceleration calculated from the *g*-SLLOD equations of motion, $\ddot{\mathbf{r}}_i = \mathbf{r}_i \cdot \nabla \mathbf{u} \delta(t)$ which lacks the first term of Eq. (37). Thus, we observe that if these boundary conditions were applied in conjunction with the *g*-SLLOD equations of motion (in the absence of a thermostat), they would be inconsistent with the flow induced by those equations of motion. In the presence of a thermostat, the thermostat itself would apply a force on the particles to induce the desired flow unless a profile unbiased thermostat[1] was used. We will consider a simple example that exhibits the problem explicitly. Imagine a noninteracting particle with an initial velocity of zero. At time $t = 0$, the external field is applied. With properly formulated equations of motion, this particle's motion at subsequent times should be solely determined by the external force that generates the flow. In this case, the equation of motion given by the SLLOD equations of motion would be

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = m_i \mathbf{r}_i \cdot \nabla \mathbf{u}\, \delta(t) + m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} \Theta(t)$$

$$= \frac{d}{dt}(m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \Theta(t)). \tag{38}$$

Integrating this gives the expected particle velocity, $\mathbf{u}(t) = \mathbf{r}_i \cdot \nabla \mathbf{u} \Theta(t)$. As shown by Tuckerman *et al.*[9] [their Eq. (22)], the *g*-SLLOD equations of motion lack the second term in the external force. In *g*-SLLOD dynamics, the external force only provides an initial acceleration through the delta function term, but it is zero thereafter, and the trajectory of a noninteracting particle with zero peculiar momentum will then be a simple straight line by Newton's first law. This means that the particle trajectory generated by the *g*-SLLOD equations of motion will be incorrect if this term is nonzero. Specifically, the *g*-SLLOD equations of motion generate incorrect trajectories for extensional flows. We must then ask, what provides the force required to generate the flow observed in simulations of elongational flow performed with the *g*-SLLOD equations of motion? The answer must be that it is provided by the periodic boundary conditions and the thermostat. This is unsatisfactory, since the correct application of response theory requires that the flow should be generated by a force that can be expressed in analytical form and appears explicitly in the equations of motion.

VI. CONCLUSIONS

The discussion that we have presented makes it clear that the SLLOD equations of motion correctly generate the desired zero wave vector velocity gradient and particle trajectories in a homogeneous flow simulation. We have also explicitly confirmed the often-stated fact that, in their most general form, these equations of motion cannot be derived from a Hamiltonian, due to the lack of a suitable potential function to represent the effect of the external field on the particles. It might be thought that the introduction of a velocity-dependent generalized potential might make it possible to place these equations in Hamiltonian form.[16] However, since the external force terms in Eq. (10) only depend on the positions, this is clearly not an option. The only alternative seems to be to introduce a generalized force into the Lagrangian equations of motion, resulting in noncanonical Hamiltonian equations of motion, nullifying the advantages of a Hamiltonian description.

Finally, it is appropriate to consider the distribution function and nonlinear response that result from the application of SLLOD dynamics to a system of particles. The form of Eq. (10) makes it clear that the first effect of propagation with the SLLOD equations of motion is to instantaneously add a streaming component to the particle velocities so as to create an initial local equilibrium distribution function. This initial condition is often used in theoretical treatments of nonequilibrium statistical mechanics.[25] The procedure used by Yamada and Kawasaki[25] to obtain the nonlinear shear response was to begin with an initial local equilibrium distribution function and then propagate the system with Newton's equations of motion. In the case of planar shear flow, this means that the total force on each atom is simply the sum of the intermolecular forces acting on that particle, since the second term in Eq. (10) is zero for shear flow. For elongational flow the situation is different, and the second term in the external force must be included, therefore the Liouville operator and propagator must be modified. This immediately invalidates the recent extension of Yamada and Kawasaki's nonlinear response theory to general flows attempted by Edwards *et al.*[26] Evans and Morriss[27] have previously demonstrated the equivalence of the nonlinear response of a system in planar shear flow under SLLOD dynamics and that of a system with an initial local equilibrium distribution function propagated with Newtonian dynamics, as derived by Yamada and Kawasaki.[25] Since it has already been shown that SLLOD dynamics also generates the correct velocity gradient for elongational flows, it is obvious that propagation of an initial equilibrium distribution function with the SLLOD propagator will generate the correct nonequilibrium distribution function for any homogeneous flow. In fact, the generalization of nonlinear response theory to a general, homogeneous velocity gradient tensor has already been tested for steady and oscillatory elongational flow with excellent results.[24,28]

VII. COMMENTS ON "A VALIDATION OF THE *p*-SLLOD EQUATIONS OF MOTION FOR HOMOGENEOUS STEADY-STATE FLOWS"[29]

The following article by Edwards *et al.*[29] presents criticisms of our article and states the arguments in support of their view that the *p*-SLLOD equations of motion are preferable to the SLLOD equations of motion for molecular dynamics simulations of flows with homogeneous velocity gradients. We would like to add the following comments in response to their article.

(1) In their Sec. I, Edwards *et al.* state that the NEMD algorithm based on the SLLOD equations of motion is "artificial" and that the *p*-SLLOD algorithm is "natural" because the former contains an external force and the latter does not. While we agree that NEMD algorithms do contain artificial forces (in the sense that they do not exist in nature), we disagree with the implication that this invalidates these algorithms. On the contrary, we believe that the ability to generate the desired nonequilibrium flux with terms that appear explicitly in the equations of motion is a great advantage, because it allows us to simulate systems with nonequilibrium fluxes in translationally invariant, homogeneous systems with periodic boundary conditions. In addition, the existence of explicit terms in the equations of motion that generate the flow allows us to apply linear and nonlinear response theories, providing the most convincing validation of the equations of motion, as shown long ago by Evans and Morriss.[27]

(2) Edwards *et al.* state further that the only forces acting on the particles in the central simulation box in a *p*-SLLOD algorithm simulation are intermolecular forces, which sum to zero, but that this sum is nonzero for all other simulation boxes. This cannot possibly be true in a system with periodic boundary conditions, be-

cause the intermolecular forces are functions only of the positions, which are periodic. This periodicity ensures that the sum of the intermolecular forces must be zero for every image of the central simulation box.

(3) The *p*-SLLOD equations of motion are identical to the *g*-SLLOD equations, which were proposed in 1997 by Tuckerman *et al.*[9] The claim by Edwards *et al.* that the *p*-SLLOD equations of motion do not contain an external force is in disagreement with the analysis of Tuckerman *et al.*, who have shown that there is an impulse force at the time the velocity gradient is applied (usually taken as $t=0$) in the *g*-SLLOD equations of motion when they are expressed in terms of the laboratory frame acceleration.

(4) In their Sec. III, Edwards *et al.* make a spurious comparison between experimental elongational flow, which is obviously driven by boundary conditions, and NEMD simulations of homogeneous flow in an infinite periodic system with the SLLOD equations of motion. Our view is that in NEMD simulations using the SLLOD equations of motion on an infinitely periodic system, the total boundary stress on the simulation box is zero if the periodic boundary conditions are formulated correctly (so as to evolve with the flow) and the time derivative of the zero wave vector momentum density can only be nonzero if there is an applied body force. This is why we are able to use Eq. (5) to analyze the flow. In the case of homogeneous shear, only a delta function force is required, whereas for elongational flow, an additional force is needed, as we have shown in our Eq. (10). This surprising situation occurs because the zero wave vector momentum of the system never decays once it has been established in an infinite system undergoing planar shear.[1] The same is not true for elongational flows.

(5) The claim by Edwards *et al.* in their Sec. III following Eq. (10) that our derivation of the expression for the external force acting on each particle is not rigorous appears to be based on a misunderstanding of our derivation. We use two physical assumptions to arrive at our expression for the external force. First, we express the total external force on the system of particles in terms of the desired independent variables, the position, and the peculiar momentum and then eliminate terms whose sum is equal to zero because they cannot contribute to the external force. This gives our Eq. (9), which is the sum of the external forces on each particle. Second, we insist that the equations of motion are the same for every particle in the system. This gives our Eq. (10). The discussion by Edwards *et al.* misinterprets our derivation by implying that a term that sums to zero and thus contributes a total external force of zero at all times should be included in the external force for each particle.

(6) Equation (III.11) of Edwards *et al.* incorrectly identifies the external force on each particle as the mass times the time derivative of the streaming component of the velocity of that particle.

(7) The analysis following Eq. (III.13) of Edwards *et al.* is misleading, because the velocity that is desired in this instance is the one that exists immediately after the application of the velocity gradient. This means we must take the limit as ε approaches zero in their Eq. (III.13), giving the expected result that the velocities are incremented by the local streaming velocity.

(8) The analysis of the energy balance for the SLLOD equations of motion in Sec. VI of their paper contains the misleading statement that the effect of the external force has been neglected in arriving at their Eq. (VI.4). This is clearly incorrect because the full form of the SLLOD equations of motion [their Eq. (VI.2)] has been used to obtain it. Our view is that since the SLLOD equations of motion give the desired rate of work by the velocity gradient, shown by their Eq. (VI.3), this is simply a further argument in favor of the SLLOD equations and against the *p*-SLLOD equations of motion, which do not share this property.

(9) Edwards *et al.* state in their Sec. VII that "the Yamada and Kawasaki derivation was performed for a general, homogeneous steady-state flow field." However, Yamada and Kawasaki make no claims that their derivation is valid for general homogeneous flows, and their specific results are all for planar shear flow.

We believe that we have addressed most of the main points of difference between our two points of view, but there remain many detailed points on which we have refrained from commenting.

[1] D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Academic, London, 1990).
[2] D. M. Heyes, Chem. Phys. **98**, 15 (1985).
[3] M. W. Evans and D. M. Heyes, Mol. Phys. **69**, 241 (1990).
[4] A. Baranyai and P. T. Cummings, J. Chem. Phys. **103**, 10217 (1995).
[5] B. D. Todd and P. J. Daivis, J. Chem. Phys. **107**, 1617 (1997).
[6] B. D. Todd and P. J. Daivis, Phys. Rev. Lett. **81**, 1118 (1998).
[7] A. Baranyai and P. T. Cummings, J. Chem. Phys. **110**, 42 (1999).
[8] A. M. Kraynik and D. A. Reinelt, Int. J. Multiphase Flow **18**, 1045 (1992).
[9] M. E. Tuckerman, C. J. Mundy, S. Balasubramanian and M. L. Klein, J. Chem. Phys. **106**, 5615 (1997).
[10] D. J. Evans, D. J. Searles D. J., Wm. G. Hoover, C. G. Hoover, B. L. Holian, H. A. Posch, and G. P. Morriss, J. Chem. Phys. **108**, 4351 (1998); Much of this debate is reviewed in G. S. Ezra, J. Math. Chem. **35**, 29 (2004).
[11] B. D. Todd and P. J. Daivis, Comput. Phys. Commun. **117**, 191 (1999).
[12] B. D. Todd and P. J. Daivis, J. Chem. Phys. **112**, 40 (2000).
[13] M. L. Matin, P. J. Daivis and B. D. Todd, Comput. Phys. Commun. **151**, 35 (2003).
[14] M. L. Matin, P. J. Daivis, and B. D. Todd, J. Chem. Phys. **113**, 9122 (2000); **115**, 5338 (2001).
[15] P. J. Daivis, M. L. Matin, and B. D. Todd, J. Non-Newtonian Fluid Mech. **111**, 1 (2003).
[16] B. J. Edwards and M. Dressler, J. Non-Newtonian Fluid Mech. **96**, 163 (2001).
[17] C. Baig, B. J. Edwards, D. J. Keffer, and H. D. Cochran, J. Chem. Phys. **122**, 114103 (2005).
[18] C. Baig, B. J. Edwards, D. J. Keffer, and H. D. Cochran, J. Chem. Phys. **122**, 184906 (2005).
[19] S. R. de Groot and P. Mazur, *Non-equilibrium Thermodynamics* (Dover, New York, 1984).
[20] H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, MA, 1980).
[21] W. G. Hoover, D. J. Evans, R. B. Hickman, A. J. C. Ladd, W. T. Ashurst, and B. Moran, Phys. Rev. A **22**, 1690 (1980).

[22] T. A. Hunt and B. D. Todd, Mol. Phys. **101**, 3445 (2003).
[23] B. D. Todd, Mol. Simul. **31**, 411 (2005).
[24] B. D. Todd, Phys. Rev. E **56**, 6723 (1997).
[25] T. Yamada and K. Kawasaki, Prog. Theor. Phys. **38**, 1031 (1967).
[26] B. J. Edwards, C. Baig, and D. J. Keffer, J. Chem. Phys. **123**, 114106 (2005).
[27] D. J. Evans and G. P. Morriss, Phys. Rev. A **30**, 1528 (1984).
[28] B. D. Todd, Phys. Rev. E **58**, 4587 (1998).
[29] B. J. Edwards, C. Baig, and D. J. Keffer, J. Chem. Phys. **124**, 194104 (2006), following paper.