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A validation of the *p*-SLLOD equations of motion for homogeneous steady-state flows

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A validation of the *p*-SLLOD equations of motion for nonequilibrium molecular dynamics simulation under homogeneous steady-state flow is presented. We demonstrate that these equations generate the correct center-of-mass trajectory of the system, are completely compatible with (and derivable from) Hamiltonian dynamics, satisfy an appropriate energy balance, and require no fictitious external force to generate the required homogeneous flow. It is also shown that no rigorous derivation of the SLLOD equations exists to date. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2192776]

I. OPENING REMARKS

Molecular dynamics simulations, either at equilibrium or away from it, are inherently artificial. For example, a *NVT* simulation in the canonical ensemble would incorporate a thermostat, which is a mathematical equation that dissipates thermal energy in the simulation box in a manner that is not congruent with what is actually happening in the real material. A nonequilibrium molecular dynamics (NEMD) simulation of a flowing material is also inherently artificial, not just because of the algorithm that produces the external flow field, but also with respect to the thermostat, barostat, etc. If one could perform the simulation exactly as in experiment, one would need neither a NEMD algorithm nor a thermostat. One would need only boundary conditions and Newton's equations of motion. If that were the case, there would be no need to debate anything, because science is completely objective and the proper (classical) equations of motion are well known to everyone.

The problem arises because we cannot do the simulation the way that the experiment is performed. We must artificially induce the proper flow field and thermostat the system. We thus have to insert some artwork into the simulation, and hope that this artwork makes the simulation mimic the experiment very closely, so that the simulated physical quantities are in agreement with those measured in actual experiments. The problem is that the art is subjective, not objective. Consequently, the outcome is possibly not unique. Different subjective points of view can produce very different outcomes for describing exactly the same object.

It is highly possible that there can be multiple NEMD algorithms for general flows. How do we know if a particular algorithm is a good one or not; i.e., whether or not simulated physical properties agree with experimentally measured values? We hope that we can directly compare the two. If the experimental data are available, that would be possible. For NEMD simulations, that is usually not possible. Therefore, we need some objective criteria for determining whether a particular algorithm can be reasonably expected to give simulated physical properties that agree with experimental values.

For planar Couette flow (PCF), this issue was apparently resolved years ago with respect to the DOLLS and SLLOD algorithms. But who is to say that another, equivalent or possibly better, algorithm for shear flow does not exist? In the case of planar elongational flow (PEF), there are two algorithms that have been proposed for simulating physical systems, called SLLOD and *p*-SLLOD. These algorithms essentially inject subjectivity into the scientific problem where there should be none. This is unavoidable at present. We must then try to revert to objective criteria to determine if one or both of these algorithms is likely to generate correct physical properties.

That is the point where we now stand. There are two groups of researchers who have seemingly different criteria for determining which algorithm is better for determining the structural and rheological properties of fluids under PEF. It is certainly within the realm of possibility that SLLOD and *p*-SLLOD are equally good for PEF simulations, although that is not our opinion at present. This article presents a discussion of NEMD algorithms for the purpose of beginning to establish which criteria are essential, or at least the most important, for a proper algorithm to meet.

Let us begin by considering the experiment that we are trying to mimic with the simulation; i.e, an elongational flow of a particular material. In elongational flow, the fluid stretches in at least one direction, and compresses in at least one direction. This experiment is usually entirely boundary driven. For one example, imagine grasping a rubber band by the ends and pulling the ends apart. Under the assumption of a negligible gravitational effect, the only external forces are applied at the ends of the band, yet the matter in the interior of the band will translate and deform. How does the material know to do this? The answer is, of course, Newton's equation of motion applied to each microscopic particle in the band,

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$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i^{\phi}, \tag{1.1}$$

where m_i is the mass of the particle, $\mathbf{r}_i$ is its position, and $\mathbf{F}_i^{\phi}$ is the force which the particle experiences due to the presence of all the other particles in the band. This equation is unquestionable. The effects of the boundary are transferred into the material through the interparticle forces, and through this way only. There is no additional external force required to act on each and every interior particle to induce the proper flow field, only the forces on those particles which are part of the boundary.

Of course, we cannot simulate the whole band, so we attempt to simulate only a small portion of it, say one interior material (or fluid) element composed of many microscopic particles. Thus the simulation box can be conceptually thought of as an element in the sense of continuum mechanics. If this element is stationary in space relative to the laboratory coordinate system, or if it is translating with a constant velocity relative to it (as in PCF), then there is no force on the element. In this case, Newton's third law tells us that $\mathbf{F}_{\text{net}}^{\phi}=\Sigma_i \mathbf{F}_i^{\phi}=0$; that is, all the interparticle forces in the element sum to zero, and the net force on the element is zero.

In PEF, as shown below, only the fluid element located at the origin of the coordinate system is stationary in space. All of the other fluid elements are experiencing a net acceleration as they translate and deform as the band is stretched. This means that for all other elements, $\mathbf{F}_{\text{net}}^{\phi} \neq 0$, thus explaining how the interparticle forces impose the macroscopic flow field induced by the boundary conditions. This example reveals clearly what the physical situation is during the actual elongational flow experiment. The dynamics of the material are completely described by the imposed boundary conditions and Eq. (1.1). Nothing else is necessary.

In principle, we have all we need to perform an NEMD simulation of a flowing material. In practice, however, we run into well-known problems associated with the finite size of the simulation system,[1] as well as the problems associated with the artificial production of heat (i.e, the thermostat effect). Hence the NEMD algorithms mentioned above are introduced into the simulation methodology to mimic the effects of the flow field on the particles in the simulation box. The *p*-SLLOD and SLLOD algorithms have two very different philosophies with regard to how this mimicry should be conducted.

The philosophy of *p*-SLLOD is to mimic the equations of motion of the actual experiment as closely as possible; i.e., to insist that Eq. (1.1) is satisfied for each particle in the simulation box. Boundary conditions are then used to drive the flow, just as in the actual experiment. All effects of these boundary conditions are then felt on each particle through the interparticle force applied to it, just as in the actual experiment.

For SLLOD, the philosophy is to add another term into Eq. (1.1), which artificially drives the flow,

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i^{\phi} + \mathbf{F}_i^{\text{ext}}, \tag{1.2}$$

where $\mathbf{F}_i^{\text{ext}}$ is an applied external force, acting on each particle within the material. This is not the same as in the actual experiment. In the experiment, there is no external force on each particle. Therefore, philosophically, SLLOD is artificial in this respect, whereas *p*-SLLOD is quite natural. Of course, in PCF, $\mathbf{F}_i^{\text{ext}}=0$, and the two philosophies coincide, but in PEF, this is not the case.

II. A DISCUSSION OF THE *p*-SLLOD EQUATIONS OF MOTION FROM A BOUNDARY-DRIVEN PERSPECTIVE

We will now demonstrate that the correct experimental equations of motion, Eq. (1.1), without an external force, are enough to generate the boundary-driven *p*-SLLOD algorithm. When we say "boundary driven," we mean that no external force is necessary to generate the macroscopic flow, only the proper forms of the equations of motion for the particle positions and momenta, as well as their associated simulated boundary conditions.

We want to write down the equations of motion in terms of the positions and momenta of all the particles in the simulation box. We require that these evolution equations satisfy Eq. (1.1), because these are the experimentally relevant equations for boundary-driven flow. We do not have any choice for the evolution equation for the position of a particle; this is dictated by the imposed flow field. For a homogeneous flow field, which is imposed at time $t=0$, the equation of motion for the position of a particle is simply

$$\frac{d\mathbf{r}_i}{dt} = \frac{\mathbf{p}_i}{m_i} + \mathbf{u}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{u} \Theta(t), \tag{2.1}$$

where $\mathbf{u}_i \equiv \mathbf{r}_i \cdot \nabla \mathbf{u} \Theta(t)$ is the local streaming velocity of the flow field and $\Theta(t)$ is the Heaviside function. Equation (2.1) is thus merely a coordinate transformation of the particle velocity in the laboratory frame into a coordinate system that translates with the local streaming velocity of the flow. In this framework, the $\mathbf{p}_i$ are often called "thermal" or "peculiar" momenta.

Now that we have an equation for the evolution of the particle, and a requirement that Eq. (1.1) is satisfied, we can derive uniquely an evolution equation for the particle momentum. This is achieved by taking the time derivative of Eq. (2.1), and substituting the result into Eq. (1.1). The result of this procedure is

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i^{\phi} - \mathbf{p}_i \cdot \nabla \mathbf{u} \Theta(t) - m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} \Theta(t) - m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \delta(t). \tag{2.2}$$

Equations (2.1) and (2.2) constitute the time-dependent *p*-SLLOD equations of motion for the particle dynamics under the imposition of a homogeneous flow field. Thus we see clearly that the *p*-SLLOD equations are indeed compatible with the experimentally valid equations of motion, (1.1), which contain no fictitious external forces.

III. COMMENTS ON THE SIMPLE AND DIRECT DERIVATION OF THE SLLOD EQUATIONS OF MOTION BY DAIVIS AND TODD

Daivis and Todd[2] have claimed to have provided a derivation of the SLLOD equations of motion using a fictitious external force, as in Eq. (1.2). However, the expression used for the external force used in their derivation is incorrect. This is demonstrated in this section of the article. Furthermore, a derivation for the proper set of equations of motion is performed using the correct expression for the external force, and the ensuing result is not the SLLOD equations for motion.

Let us begin by following the procedure of Daivis and Todd.[2] Let $\mathbf{G}(\mathbf{r},t)$ be an external force density applied to the fluid at position $\mathbf{r}$ and time t. The equation of motion for the momentum density, $\mathbf{J}$, is

$$\frac{\partial \mathbf{J}(\mathbf{r},t)}{\partial t} = -\nabla \mathbf{P}(\mathbf{r},t) - \nabla[\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)] + \mathbf{G}(\mathbf{r},t), \tag{3.1}$$

where ρ is the fluid density, $\mathbf{u}$ is the streaming velocity, and $\mathbf{P}$ is the pressure tensor. The momentum density and the external force can be viewed microscopically as

$$\mathbf{J}(\mathbf{r},t) = \rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t) = \sum_i m_i \mathbf{v}_i \delta(\mathbf{r} - \mathbf{r}_i), \tag{3.2}$$

$$\mathbf{G}(\mathbf{r},t) = \sum_i \mathbf{F}_i^{\text{ext}} \delta(\mathbf{r} - \mathbf{r}_i), \tag{3.3}$$

respectively, where $\mathbf{v}_i$ is the laboratory velocity of a particle.

Now before we continue, let us make an important point derived from experimental evidence: the external force in Eq. (3.1) is unnecessary to the drive flow, elongational or not. Only boundary conditions are required, as many experiments have demonstrated. Thus, when $\mathbf{G}=0$, Eq. (3.1) does indeed describe the elongational flow.

Now let us continue by writing Eq. (3.1) as a Fourier series. For a generic vectorial quantity, the Fourier series representation is

$$\mathbf{A} = \sum_{\mathbf{k}} \mathbf{A}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{3.4}$$

where the $\mathbf{A}_{\mathbf{k}}$ are coefficients and the summation extends over all possible values of the wave vector, $\mathbf{k}$.[3] Hence the dynamical expression (3.1) can be expressed as a Fourier series by

$$\frac{\partial}{\partial t}\left(\sum_{\mathbf{k}} \mathbf{J}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\right) = -\sum_{\mathbf{k}} i\mathbf{k}\cdot\mathbf{P}_k e^{i\mathbf{k}\cdot\mathbf{r}} - \sum_{\mathbf{k}} i\mathbf{k}\cdot\mathbf{T}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} + \sum_{\mathbf{k}} \mathbf{G}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{3.5}$$

where $\mathbf{T} \equiv \rho\mathbf{uu}$. This expression can be decomposed into a set of equations, one for each possible value of the wave vector,

$$\frac{\partial \tilde{\mathbf{J}}(\mathbf{k},t)}{\partial t} = -i\mathbf{k}\cdot\tilde{\mathbf{P}}(\mathbf{k},t) - i\mathbf{k}\cdot\tilde{\mathbf{T}}(\mathbf{k},t) + \tilde{\mathbf{G}}(\mathbf{k},t), \tag{3.6}$$

where a tilde denotes the Fourier transform of the respective quantity. Thus, any flow can be described by a superposition of wave equations, one for each possible value of $\mathbf{k}$, whether or not an external force is present.

It is clear from Eq. (3.6) that no external force is necessary to drive the flow, only boundary conditions. Daivis and Todd[2] focus on the zero-wave-vector component of the momentum density, and correctly note that this component predicts a constant zero-wave-vector momentum density, regardless of the type of flow. They therefore argue that an external force must be inserted into the system to drive an elongational flow, despite the fact that the other wave vector components are perfectly capable of driving the flow without an external force, and that no such force is necessary in the experiment. Thus they artificially force the zero-wave-vector component of the momentum density to do something in their derivation which it is not doing in the actual experiment: it is clear in the experiment that $\mathbf{G}_{\mathbf{k}}=0$, which implies that the zero-wavevector component of the momentum density is truly constant. Setting $\mathbf{G}=0$ in Eq. (3.1) does not prevent the fluid from undergoing elongational flow in the least.

Despite this paradox, let us continue with the analysis of Daivis and Todd. According to Eq. (3.6), the equation of motion for the zero-wave-vector component of the momentum density is[2]

$$\frac{d}{dt}\sum_i m_i \mathbf{v}_i = \sum_i \mathbf{F}_i^{\text{ext}}. \tag{3.7}$$

Using the transformation of Eq. (2.1), for exactly the same reasoning, the left side of this equation can be evaluated as

$$\frac{d}{dt}\sum_i m_i \mathbf{v}_i = \frac{d}{dt}\sum_i [\mathbf{p}_i + m_i \mathbf{r}_i \cdot \nabla \mathbf{u}\Theta(t)] = \frac{d}{dt}\sum_i m_i \mathbf{r}_i \cdot \nabla \mathbf{u}\Theta(t), \tag{3.8}$$

wherein the second line results from the first by recognizing that $\Sigma_i \mathbf{p}_i = 0$. By applying the time derivative inside the summation, this equation becomes

$$\begin{aligned}\frac{d}{dt}\sum_i m_i \mathbf{v}_i &= \sum_i \left[m_i \mathbf{v}_i \cdot \nabla \mathbf{u}\Theta(t) + m_i \sum_i \mathbf{r}_i \cdot \frac{d}{dt}(\nabla \mathbf{u}\Theta(t)) \right] \\ &= \sum_i [\mathbf{p}_i + m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u}\Theta(t) + m_i \mathbf{r}_i \cdot \nabla \mathbf{u}\delta(t)] \\ &= \sum_i [m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u}\Theta(t) + m_i \mathbf{r}_i \cdot \nabla \mathbf{u}\delta(t)] \\ &= \sum_i \mathbf{F}_i^{\text{ext}},\end{aligned} \tag{3.9}$$

where the second equality in the third line arises from Eq. (3.7). Using this expression, Daivis and Todd assign the external force on particle i as

$$\mathbf{F}_i^{\text{ext}} = m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} \Theta(t) + m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \delta(t), \tag{3.10}$$

but this is clearly not a rigorous derivation of the external force. They have assumed in the assignation of Eq. (3.10) that, in terms of generic quantities, $\Sigma_i(A_i+B_i)=\Sigma_i X_i$ implies that $A_i+B_i=X_i$ for each value of i, and, more specifically, that $\Sigma_i X_i=0$ implies that $X_i=0$ for each i. (Specifically, they have assumed that $\Sigma_i \mathbf{p}_i=0$ implies that $\mathbf{p}_1=\mathbf{p}_2=\cdots=0$.) These are clearly not rigorous expressions. An example that illustrates this problem is provided in Appendix A.

In order to continue with this analysis in a scientific fashion, we need to find a rigorous method to derive the external force. From the discussion surrounding Eq. (2.1), an apparent and obvious candidate for the external force is simply to use Newton's equation, force equals mass times acceleration, on the velocity in that expression. In this case,

$$\mathbf{F}_i^{\text{ext}} = m_i \frac{d\mathbf{u}_i}{dt} = m_i \frac{d[\mathbf{r}_i \cdot \nabla \mathbf{u} \Theta(t)]}{dt}, \tag{3.11}$$

however, we need to demonstrate that this external force, when substituted into Eq. (3.7), does indeed generate the exact Newtonian dynamics necessary for an NEMD simulation.

This demonstration can be accomplished as follows. Let us consider what we are actually trying to do in an NEMD simulation. At $t=0$, we map the equilibrium distribution onto a local equilibrium distribution by transforming the velocity of each particle according to

$$\mathbf{v}_i(\varepsilon) = \mathbf{v}_i(0^-) + \mathbf{r}_i \cdot \nabla \mathbf{u}, \tag{3.12}$$

where ε is an arbitrary but positive constant, approximately equal to zero. Note that we have only changed the velocity, and not the particle position, which is possible because the two are independent quantities. Inserting the force of Eq. (3.11) into the expression for the zero-wave-vector component of the momentum density, Eq. (3.7), and then integrating, one finds exactly Eq. (3.12), thus proving that Eq. (3.11) is indeed the rigorous definition of the external force. Note that if we take the Daivis and Todd expression for the external force of Eq. (3.10) and perform the appropriate time integration, we obtain

$$\mathbf{v}_i(\varepsilon) = \mathbf{v}_i(0^-) + \varepsilon \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} + \mathbf{r}_i \cdot \nabla \mathbf{u}. \tag{3.13}$$

This mapping is not consistent with the Newtonian dynamics and demonstrates that this expression for the external force (3.10) does not generate exactly the Newtonian dynamics. Since ε is a very small parameter, the effect of the additional term is probably negligible, except possibly for systems with a large number of particles.

Now we continue the analysis of Daivis and Todd, but using the rigorous external force expression of Eq. (3.11). The full equations of motion are

$$m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i^{\phi} + \mathbf{F}_i^{\text{ext}}. \tag{3.14}$$

Evaluating the derivative in Eq. (3.11), we find that

$$\mathbf{F}_i^{\text{ext}} = \mathbf{p}_i \cdot \nabla \mathbf{u} \Theta(t) + m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} \Theta(t) + m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \delta(t). \tag{3.15}$$

Substitution of this expression and Eq. (2.1) into Eq. (3.14) then yields

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i^{\phi}. \tag{3.16}$$

Note that performing a summation of Eq. (3.15) over all particles yields the third line of Eq. (3.9), thus illustrating explicitly the ambiguity of the Daivis and Todd derivation of the external force; i.e., the sum of Eqs. (3.10) and (3.15) both give the same result.

Equation (3.16) is a very interesting equation when viewed from several perspectives. First, it is obviously not the SLLOD expression, which has an additional factor of $-\mathbf{p}_i \cdot \nabla \mathbf{u} \Theta(t)$ on the right side of Eq. (3.16). Thus we have demonstrated that the derivation of Daivis and Todd, when performed rigorously, does not generate SLLOD dynamics. Thus there remains to date no rigorous derivation of the SLLOD equations of motion. Second, the form of this expression is exactly that which would be expected from experimental considerations; i.e., the evolution of the particle momentum is solely determined by the interparticle forces. Eq. (3.16) is therefore fully compatible with the experimental equation for the zero-wave-vector component of the momentum density, since for this wave vector component (in which the interparticle terms vanish) the momentum density is a constant. Third, Eqs. (3.14) and (3.16) duly satisfy the principle of material frame indifference, essentially meaning that the inverse of the transformation which led from the first to the second will also lead back from the second to the first. Fourth, by comparing Eq. (3.16) with the corresponding expression of p-SLLOD, Eq. (2.2), it is evident that the p-SLLOD version of this equation contains the negative of the external force of Eq. (3.15). This makes sense in that the p-SLLOD equations of motion do not contain the fictitious external force. Therefore, in order to obtain the particle momentum evolution equation for boundary-driven p-SLLOD from the rigorous external-force algorithm's momentum evolution equation of (3.16), one simply has to subtract off exactly that which was artificially applied in the first place.

IV. A DERIVATION OF THE *p*-SLLOD EQUATIONS OF MOTION USING A NONCANONICAL COORDINATE TRANSFORMATION

Now we shall provide a mathematically and physically rigorous derivation of the p-SLLOD equations of motion. We do so in the vein of Edwards and Dressler,[4] following earlier work of Tuckerman *et al.*[5] We omit superfluous detail, and focus only on the salient points for the present article. The starting point is Eq. (1.1), in the laboratory frame of reference,

$$m_i \frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i^{\phi}. \tag{4.1}$$

There is no doubt that this is the correct set of evolution equations to describe the process under consideration (i.e.,

macroscopic flow), and that no external force is needed to drive the flow, only boundary conditions. These dynamics can be expressed in Hamiltonian form as

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i'}{m_i}$$
$$\dot{\mathbf{p}}_i' = \mathbf{F}_i^{\phi}. \tag{4.2}$$

Here, $\mathbf{p}_i'$ denotes the particle momentum with respect to the laboratory frame. It is well known that this set of equations is canonical, and possesses a canonical Hamiltonian, given by

$$H'(\mathbf{r},\mathbf{p}') = \sum_i \frac{\mathbf{p}_i' \cdot \mathbf{p}_i'}{2m_i} + V(\mathbf{r}). \tag{4.3}$$

where $V(\mathbf{r})$ is the potential energy due to the particles. Equation (4.2) can be derived from this expression using the canonical Poisson bracket.[6–8] The Hamiltonian thus represents the total energy of the system, which in this case is equivalent to the internal energy of the system. Note that the time derivative of Eq. (4.3) is zero,

$$\frac{dH'}{dt} = \sum_i \left(\frac{\mathbf{p}_i' \cdot \dot{\mathbf{p}}_i'}{m_i} + \frac{\partial V}{\partial \mathbf{r}_i} \cdot \dot{\mathbf{r}}_i \right) = 0, \tag{4.4}$$

given Eq. (4.2) and the realization that $-\partial V/\partial \mathbf{r}_i = \mathbf{F}_i^{\phi}$. Hence energy is conserved in the laboratory framework.

Under flow, the boundary conditions dictate the deformation of the material, as transferred throughout the material via the interparticle forces. We wish to calculate the pressure tensor under this flow, however, we need to do so in a codeformational framework, as noted by Oldroyd.[9] In other words, we need to introduce the peculiar momenta which are assigned to the framework that translates with the fluid element represented by the simulation box. This is not difficult to do, as we simply have to transform the laboratory particle momentum to the peculiar momentum in exactly the same way as Eq. (2.1),

$$\mathbf{p}_i' \rightarrow \mathbf{p}_i + m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \Theta(t). \tag{4.5}$$

(Note that this transformation is noncanonical; i.e., it will not preserve the canonical structure of Hamilton's equations of motion.[4]) Substituting this expression into the laboratory framework equations of (4.2) then gives the equations of motion in the peculiar framework,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i \cdot \nabla \mathbf{u} \Theta(t)$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i^{\phi} - \mathbf{p}_i \cdot \nabla \mathbf{u} \Theta(t) - m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \Theta(t) - m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \delta(t). \tag{4.6}$$

These are the time-dependent *p*-SLLOD equations discussed in Sec. II. As noted in that section, combining these expressions to eliminate the particle momentum leads directly back to Newton's equation, (4.1). This is a necessary requirement for the set of dynamical equations of (4.6) since this form of Newton's equation (also known as the Euler-Lagrange equation) is known to be invariant of the reference frame in which it is expressed.[6–8]

Now let us examine the Hamiltonian with respect to the peculiar reference frame. Applying the transformation of Eq. (4.5) to the Hamiltonian of Eq. (4.3) yields

$$H(\mathbf{r},\mathbf{p}) = \sum_i \left(\frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i} + \mathbf{p}_i \cdot (\mathbf{r}_i \cdot \nabla \mathbf{u}) \Theta(t) + \frac{m_i}{2} (\mathbf{r}_i \cdot \nabla \mathbf{u}) \cdot (\mathbf{r}_i \cdot \nabla \mathbf{u}) \Theta(t) \right) + V(\mathbf{r}). \tag{4.7}$$

This is the Hamiltonian in the peculiar reference frame, expressed in terms of the noncanonical variable set, $(\mathbf{r},\mathbf{p})$. It remains the total energy of the system, as well as the internal energy; the transformation did not alter this fact. Taking the time derivative of this expression, and substituting in the equations for motion, (4.6), then yields, after a laborious calculation,

$$\frac{dH}{dt} = 0. \tag{4.8}$$

For all t, the energy of the system in the peculiar framework is conserved, as would be expected from the principle of material frame indifference:[8] the scalar Hamiltonian should remain the same regardless of the reference frame in which it is expressed. It is thus clear that the transformation of Eq. (4.5) has not altered any of the physics present in the original set of equations, (4.2), and has merely changed the frame of reference to the peculiar one, wherein the pressure tensor must be calculated.

We postpone further discussion of the energy rate equation until Sec. VI. First, let us examine the dynamics of the system as whole; i.e., from the perspective of the simulation box as a representation of a fluid element of a bulk material.

V. DYNAMICS OF THE TOTAL MOMENTUM AND THE FIRST MOMENT OF POSITIONS

In simulations with the *p*-SLLOD equations of motion under PEF,[10,11] the first moment of the positions, $\mathbf{Q} \equiv \Sigma_i m_i \mathbf{r}_i$, is set at the origin of the coordinate system of the simulation. Daivis and Todd[2] state that this choice is arbitrary. This is not true. The choice is one of convenience, not necessity, as we shall demonstrate below—see Sec. V C. Daivis and Todd also state that the *p*-SLLOD equations of motion do not generate the correct trajectory of the first moment under elongational flow. This statement is also shown to be false. In this section, we examine the dynamics of the first moment and the total momentum of the system of both the *p*-SLLOD and SLLOD equations of motion. We also investigate the dynamics of the same quantities for the equations of motion derived under a rigorous expression for the external force.

A. The *p*-SLLOD equations of motion

For *p*-SLLOD dynamics, the equations of motion for the first moment and total momentum, $\mathbf{P} \equiv \Sigma_i \mathbf{p}_i$, are

$$\dot{\mathbf{Q}} = \mathbf{P} + \mathbf{Q} \cdot \nabla \mathbf{u}$$
$$\dot{\mathbf{P}} = \mathbf{F}_{\text{net}}^{\phi} - \mathbf{P} \cdot \nabla \mathbf{u} - \mathbf{Q} \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u}, \tag{5.1}$$

wherein Newton's third law was used: $\Sigma_i \mathbf{F}_i^{\phi} = \mathbf{F}_{\text{net}}^{\phi}$. In Ref. 10, $\mathbf{F}_{\text{net}}^{\phi}$ was taken as zero, for reasons explained below. In this case, the solution to this set of two, coupled, first order, ordinary differential equations is[10]

$$\mathbf{Q}(t) = \mathbf{Q}(0) + [\mathbf{P}(0) + \mathbf{Q}(0) \cdot \nabla \mathbf{u}]t$$
$$\mathbf{P}(t) = \mathbf{P}(0) - [\mathbf{P}(0) + \mathbf{Q}(0) \cdot \nabla \mathbf{u}] \cdot \nabla \mathbf{u} t. \tag{5.2}$$

Now we need to impose the physical requirement that the total momentum of the system vanishes at all times. For a general nonvanishing velocity gradient, it is clear from the above expression that for the momentum to vanish at all times, it is necessary that $\mathbf{Q}(0)=0$. Furthermore, it is evident that for this value of $\mathbf{Q}(0)$, $\mathbf{Q}(t)=0$ for all $t \geqslant 0$. We will discuss the reason for this below.

In PCF, the last term on the right-hand side of the second equation of (5.2) vanishes. In this case, $\mathbf{Q}(0)=0$ is not required, and the first equation of (5.2) tells us that the first moment then follows the trajectory

$$\begin{pmatrix} Q_1(t) \\ Q_2(t) \\ Q_3(t) \end{pmatrix} = \begin{pmatrix} Q_1(0) + Q_2(0)\dot{\gamma}t \\ Q_2(0) \\ Q_3(0) \end{pmatrix}, \tag{5.3}$$

when $\mathbf{P}(0)=0$. Here, $\dot{\gamma}$ is the shear rate, with flow in the 1 direction and the gradient in the 2 direction. This is indeed the correct trajectory for PCF, regardless of the location of the origin of the simulation coordinate system. Hence a fluid element will translate with uniform velocity in the 1 direction, but will not do so in the other two directions. Eq. (5.3) fully complies with the zero-wave-vector equation for the momentum density in the absence of an external field.

For a general velocity gradient tensor, the correct trajectory of a fluid element, $\mathbf{Z}$, is dictated by the equation of change for a contravariant, first-rank tensor,[9]

$$\dot{\mathbf{Z}} = \mathbf{Z} \cdot \nabla \mathbf{u}. \tag{5.4}$$

Note that Eq. (5.3) is compatible with this expression. For PEF, the solution to this equation is

$$\begin{pmatrix} Z_1(t) \\ Z_2(t) \\ Z_3(t) \end{pmatrix} = \begin{pmatrix} Z_1(0)e^{\dot{\varepsilon}t} \\ Z_2(0)e^{-\dot{\varepsilon}t} \\ Z_3(0) \end{pmatrix}. \tag{5.5}$$

Here, $\dot{\varepsilon}$ is the elongation rate, with extension in the 1 direction and compression in the 2 direction. Comparing Eqs. (5.2) and (5.5), we see immediately that the *p*-SLLOD equations do indeed generate the correct trajectory of the first moment under PEF if and only if $\mathbf{Q}(t)=0$ for all $t \geqslant 0$, which is the case when $\mathbf{Q}(0)=0$ and $\mathbf{P}(0)=0$ according to Eq. (5.2).

The reason for the requirement that $\mathbf{Q}(t)=0$ is evident from the following remarks. Note that in the case of $\mathbf{Q}(0) \neq 0$, Eqs. (5.2) dictate that the total momentum does not vanish, in general, indicating a net center-of-mass motion of the system. This is due to the fact that the starting assumption of $\Sigma_i \mathbf{F}_i^{\phi}=0$ under PEF is only valid when $\mathbf{Q}(t)=0$, as discussed in Sec. I. Otherwise, there is a net force on the fluid, $\mathbf{F}_{\text{net}}^{\phi} \equiv \Sigma_i \mathbf{F}_i^{\phi} \neq 0$, which is why the material deforms in the actual experiment. If we knew $\mathbf{F}_{\text{net}}^{\phi}$, then we could derive a generalized version of Eq. (5.2) valid for all values of $\mathbf{Q}(0)$; however, an appropriate expression for this quantity was not apparent to us in the past. By setting the center of mass of the particles at the origin of the coordinate system, the problem of determining $\mathbf{F}_{\text{net}}^{\phi}$ was avoided. We will resolve this issue in a separate subsection (Sec. V C), below.

Now let us discuss the practical implementation of the *p*-SLLOD equations in a PEF simulation. It is now obvious that the origin of the simulation coordinate system should coincide with the center of mass of the particles. All this means is that the simulation box corresponds to the fluid element located at the origin of the local kinematics. Thus we have chosen our simulation coordinate system such that the most convenient reference frame for the simulation is achieved; this is common practice in scientific calculations, both analytical and numerical.

When implementing the simulation, one must deal with the finite numerical precision issue. At the beginning of the simulation, we cannot set $\mathbf{Q}(0)=0$ exactly, but only approximately. According to Eqs. (5.2), this small error in $\mathbf{Q}$ will grow linearly with time. Furthermore, when we apply the Kraynik-Reinelt boundary conditions at each time period, there arises an unavoidable jump discontinuity in $\mathbf{Q}$ due to the changes in the particle positions.[10] Therefore, in a *p*-SLLOD PEF simulation, we rezero $\mathbf{Q}$ after each application of the periodic Kraynik-Reinelt boundary conditions. This shift of the coordinate system has absolutely no effect on the particle dynamics or the interparticle forces, and so cannot upset the physical reality of the simulation.

B. The SLLOD equations of motion

Now let us perform the same analysis for the SLLOD equations of motion. The SLLOD equations of motion for the first moment and total momentum are

$$\dot{\mathbf{Q}} = \mathbf{P} + \mathbf{Q} \cdot \nabla \mathbf{u}$$
$$\dot{\mathbf{P}} = -\mathbf{P} \cdot \nabla \mathbf{u}. \tag{5.6}$$

Note that in the SLLOD approach, the flow is entirely driven by the fictitious external field, and $\mathbf{F}_{\text{net}}^{\phi}$ is assumed to vanish. In PCF, the solution to this set of equations is exactly the same as for *p*-SLLOD,

$$\mathbf{Q}(t) = \begin{pmatrix} Q_1(0) + P_1(0)t + Q_2(0)\dot{\gamma}t \\ Q_2(0) + P_2(0)t \\ Q_3(0) + P_3(0)t \end{pmatrix}$$
$$\mathbf{P}(t) = \begin{pmatrix} P_1(0) - P_2(0)\dot{\gamma}t \\ P_2(0) \\ P_3(0) \end{pmatrix}. \tag{5.7}$$

Consequently, in SLLOD, the first moment also follows the correct trajectory regardless of the origin of the coordinate system under PCF.

In PEF, the solution to equation set (5.6) is

$$\mathbf{Q}(t) = \begin{pmatrix} Q_1(0)e^{\dot{\varepsilon}t} + \frac{1}{2\dot{\varepsilon}}P_1(0)(e^{\dot{\varepsilon}t} - e^{-\dot{\varepsilon}t}) \\ Q_2(0)e^{-\dot{\varepsilon}t} + \frac{1}{2\dot{\varepsilon}}P_2(0)(e^{\dot{\varepsilon}t} - e^{-\dot{\varepsilon}t}) \\ Q_3(0) + P_3(0)t \end{pmatrix}$$

$$\mathbf{P}(t) = \begin{pmatrix} P_1(0)e^{-\dot{\varepsilon}t} \\ P_2(0)e^{\dot{\varepsilon}t} \\ P_3(0) \end{pmatrix}. \tag{5.8}$$

When $\mathbf{P}(0)=0$, these equations show that the total momentum is conserved and that the center of mass of the system follows the correct trajectory for PEF of Eq. (5.5), regardless of the value of $\mathbf{Q}(0)$. Thus, in principle, the SLLOD equations of motion are perfect in this regard.

In simulation practice, however, there is the problem of finite numerical precision to be considered. As mentioned above, $\mathbf{P}(0)$ cannot be exactly zeroed in a computational simulation. As noted by Todd and Daivis,[12] Eq. (5.8) implies exponential growth in the two components of the total momentum, giving rise to aphysical phase transformations under some conditions. In order to avoid this problem, Todd and Daivis rezero the two components of the total momentum at each time step; however, this will clearly perturb the particle dynamics to some degree. Furthermore, it is also evident from Eq. (5.8) that two components of the first moment will also grow exponentially, thus upsetting the correct center-of-mass trajectory, unless it too is periodically readjusted. In the case where $\mathbf{Q}(0)=0$, this periodic readjustment is easy to implement. When $\mathbf{Q}(0)\neq 0$, it is more complicated because the value of $\mathbf{Q}$ must be set to the value it would have at the current time step according to [Eq. (5.5)].

In light of the above remarks, the *p*-SLLOD equations of motion offer an advantage over the SLLOD equations. Since the finite precision errors cannot be eliminated from the simulation, they must be dealt with, and preferably in the most noninvasive way possible. In *p*-SLLOD, the errors grow linearly in time, and the particle dynamics are not disturbed during the rezeroing of the center of mass. Hence the aphysical phase transition observed by Todd and Daivis[12] can be overcome without perturbing the system.[10] In SLLOD, the errors grow exponentially in time, and the rezeroing of the total momentum can alter the deterministic particle dynamics in unforeseen ways.

C. The *p*-SLLOD equations of motion with a nonzero net force

At the time Ref. 10 was published, we did not know how to determine $\mathbf{F}_{\text{net}}^{\phi}$ in an unambiguous fashion. Here we resolve this issue, and examine the consequences of this action. We start again in the laboratory framework, where the equations of motion are unquestionable; they are Eq. (4.2). Summing over all particles, the equations of motion for the first moment and total momentum are

$$\begin{aligned} \dot{\mathbf{Q}} &= \mathbf{P}' \\ \dot{\mathbf{P}}' &= \mathbf{F}_{\text{net}}^{\phi}. \end{aligned} \tag{5.9}$$

When $\mathbf{F}_{\text{net}}^{\phi}=0$, $\mathbf{P}'(t)=\mathbf{P}'(0)$ and $\mathbf{Q}(t)=\mathbf{P}'(0)t+\mathbf{Q}(0)$, and when $\mathbf{P}'(0)=0$, $\mathbf{Q}(t)=\mathbf{Q}(0)$ for all values of $t\geqslant 0$.

When $\mathbf{F}_{\text{net}}^{\phi}\neq 0$, a force acts on the system and acceleration of the fluid element occurs. In this case, $\mathbf{P}'(t)$ is not constant in time. In this case, the dynamics of the first moment are dictated by the evolution equation for a contravariant, first-rank tensor,[9]

$$\dot{\mathbf{Q}} = \mathbf{Q}\cdot\nabla\mathbf{u}. \tag{5.10}$$

We need to find the expression for $\mathbf{F}_{\text{net}}^{\phi}$ that produces this equation for the first moment.

Comparing Eq. (5.10) with the first line of Eq. (5.9), we observe that

$$\mathbf{P}' = \mathbf{Q}\cdot\nabla\mathbf{u}. \tag{5.11}$$

Taking the time derivative of this equations gives

$$\dot{\mathbf{P}}' = \dot{\mathbf{Q}}\cdot\nabla\mathbf{u} = \mathbf{Q}\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}, \tag{5.12}$$

wherein the second equality was obtained via Eq. (5.10). Comparing Eq. (5.12) with the second line of Eq. (5.9), we find that

$$\mathbf{F}_{\text{net}}^{\phi} = \mathbf{Q}\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}. \tag{5.13}$$

Thus we have determined the net force in the laboratory reference frame.

Now we need to determine the correct equations of motion for $\mathbf{Q}$ and $\mathbf{P}$ in the peculiar reference frame. Since the net force depends only on $\mathbf{Q}$, and since we are not transforming this quantity, the force will not be affected. The appropriate transformation is

$$\mathbf{P}' = \mathbf{P} + \mathbf{Q}\cdot\nabla\mathbf{u}, \tag{5.14}$$

which implies that

$$\dot{\mathbf{P}}' = \dot{\mathbf{P}} + \dot{\mathbf{Q}}\cdot\nabla\mathbf{u}. \tag{5.15}$$

Substituting this last expression into Eq. (5.12) yields

$$\dot{\mathbf{P}} + \dot{\mathbf{Q}}\cdot\nabla\mathbf{u} = \mathbf{F}_{\text{net}}^{\phi}. \tag{5.16}$$

The equation of change for $\dot{\mathbf{Q}}$ has to be consistent with Eq. (5.15), and is given by

$$\dot{\mathbf{Q}} = \mathbf{P} + \mathbf{Q}\cdot\nabla\mathbf{u}. \tag{5.17}$$

Substituting this expression into Eq. (5.16) then gives

$$\dot{\mathbf{P}} = \mathbf{F}_{\text{net}}^{\phi} - \mathbf{P}\cdot\nabla\mathbf{u} - \mathbf{Q}\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}, \tag{5.18}$$

which is the *p*-SLLOD evolution equation for the total momentum of the system, as per Eq. (5.1). However, we see now that it can be reduced, using Eq. (5.13), to

$$\dot{\mathbf{P}} = -\mathbf{P}\cdot\nabla\mathbf{u}. \tag{5.19}$$

Comparing this expression with Eq. (5.6) of the SLLOD dynamics, we see that the two are identical. Thus the *p*-SLLOD equations of motion exhibit exactly the same dynamics of the

total system as the SLLOD equations of motion. Hence it is apparent now that the correct trajectory of $\mathbf{Q}(t)$ is indeed generated by the *p*-SLLOD equations of motion for all values of t and for all choices of $\mathbf{Q}(0)$; however, for avoiding the issue of finite numerical precision in simulation practice, $\mathbf{Q}(0)=0$ is still the most convenient choice—see the discussion in the preceding subsection (Sec. V B).

In the article of Daivis and Todd,[2] an example is given with regard to the evolution of the simulation box which is claimed to show that the *p*-SLLOD equations of motion are inconsistent with the prescribed deformation. This statement is based on a misunderstanding of the net force acting in the *p*-SLLOD system of equations. Since the conclusions from this specific example simply reiterate the more general discussion already presented, we have included the specific analysis in Appendix B for interested readers.

D. The rigorous external force equations of motion

Before leaving this issue, let us examine the alternate set of equations of motion dictated by the rigorous force determination of Sec. III. In this case, in view of Eq. (3.16), the evolution equations for the first moment and total momentum are

$$\dot{\mathbf{Q}} = \mathbf{P} + \mathbf{Q}\cdot\nabla\mathbf{u}$$
$$\dot{\mathbf{P}} = 0, \tag{5.20}$$

since, as in SLLOD, $\Sigma_i \mathbf{F}_i^{\phi}=0$ in this reference system. In PCF, the solution to this set of equations is

$$\mathbf{Q}(t) = \begin{pmatrix} Q_1(0) + P_1(0)t + Q_2(0)\dot{\gamma}t + \frac{1}{2}P_2(0)\dot{\gamma}t^2 \\ Q_2(0) + P_2(0)t \\ Q_3(0) + P_3(0)t \end{pmatrix}$$
$$\mathbf{P}(t) = \begin{pmatrix} P_1(0) \\ P_2(0) \\ P_3(0) \end{pmatrix}. \tag{5.21}$$

Again, when $\mathbf{P}(0)=0$, the correct dynamics for PCF are generated regardless of the initial value of $\mathbf{Q}$.

For PEF, the solution to Eq. (5.20) is

$$\mathbf{Q}(t) = \begin{pmatrix} Q_1(0)e^{\dot{\varepsilon}t} + \frac{1}{\dot{\varepsilon}}P_1(0)e^{\dot{\varepsilon}t} - \frac{1}{\dot{\varepsilon}}P_1(0) \\ Q_2(0)e^{-\dot{\varepsilon}t} - \frac{1}{\dot{\varepsilon}}P_2(0)e^{-\dot{\varepsilon}t} + \frac{1}{\dot{\varepsilon}}P_2(0) \\ Q_3(0) + P_3(0)t \end{pmatrix}$$
$$\mathbf{P}(t) = \begin{pmatrix} P_1(0) \\ P_2(0) \\ P_3(0) \end{pmatrix}. \tag{5.22}$$

These equations also generate the correct dynamics in PEF for the center-of-mass trajectory, regardless of the initial value of $\mathbf{Q}$ when $\mathbf{P}(0)=0$. Note, however, that there will be no exponential growth of the total momentum due to finite numerical precision in a computational simulation. Only the center of mass needs to be adjusted, thus insuring that the particle dynamics are unaffected by this process.

VI. THE RATE EQUATION OF THE INTERNAL ENERGY

Daivis and Todd[2] state that the *p*-SLLOD equations of motion violate the energy balance of the simulation system, effectively implying a violation of the first law of thermodynamics. This statement is demonstrated to be false in this section. Indeed, given that the equations of motion in the laboratory frame, Eqs. (4.2), conserve energy, and that the equations of motion in the peculiar frame, (4.6), do as well (see Sec. IV), it is hard to imagine that this statement could be correct. This erroneous conclusion is based on the supposition that the *p*-SLLOD equations of motion arise from the presence of an external force, as in SLLOD. Therefore, let us first examine the SLLOD equations of motion, and then look at the *p*-SLLOD equations.

According to the SLLOD equations, the internal energy of the system is quantified by the expression

$$E^{\text{int}}(\mathbf{r},\mathbf{p}) = \sum_i \frac{\mathbf{p}_i\cdot\mathbf{p}_i}{2m_i} + V(\mathbf{r}). \tag{6.1}$$

Taking the time derivative of this equation, and substituting in the SLLOD equations of motion,

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i\cdot\nabla\mathbf{u}$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i^{\phi} - \mathbf{p}_i\cdot\nabla\mathbf{u}, \tag{6.2}$$

we obtain

$$\frac{dE^{\text{int}}}{dt} = -V^t\Pi^T:\nabla\mathbf{u}, \tag{6.3}$$

wherein the instantaneous pressure tensor is defined as

$$\Pi \equiv \frac{1}{V^t}\sum_i \left(\frac{\mathbf{p}_i\mathbf{p}_i}{m_i} + \mathbf{r}_i\mathbf{F}_i^{\phi}\right), \tag{6.4}$$

and V^t is the total volume of the simulation box. Equation (6.3) is a balance on the internal energy of the system, and thus is an expression of the first law of thermodynamics. The quantity on the right side of this equation is the energy dissipation rate, caused by the degradation of the internal energy due to the work done by the viscous forces (per unit time) imposed on the system by the macroscopic flow. Note that the effect of the external force on the time rate of change of the total energy of the system has not been considered in the above analysis. Of course, if the external force was included in the energy balance, then the total energy (internal plus the potential energy of the field) should be conserved.

Now let us examine the *p*-SLLOD algorithm. In *p*-SLLOD, we have already noted that the total energy of the system, H, is conserved—see Eq. (4.8) of Sec. IV. This is in full compliance with the first law of thermodynamics. To dissect the issue further, let us split the total energy into two components,

$$H_0(\mathbf{r},\mathbf{p}) = \sum_i \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i} + V(\mathbf{r})$$

$$H_1(\mathbf{r},\mathbf{p}) = H - H_0, \tag{6.5}$$

where H is the Hamiltonian of Eq. (4.7). Let us examine the dynamics of each part of this expression.

It is apparent that H_0 has the identical form as the internal energy of Eq. (6.1), although it is not the internal energy in the *p*-SLLOD framework. In *p*-SLLOD, there is no external force, and all energy is internal. Recall that the *p*-SLLOD equations of motion in the peculiar frame are completely compatible with the experimentally valid equations of motion in the laboratory reference frame, where it is obvious that all energy is internal. So despite the fact that H_0 has no special meaning in *p*-SLLOD, let us continue with the analysis.

Taking the time derivative of H_0, and then substituting in the time-independent *p*-SLLOD equations of motion, yields

$$\frac{dH_0}{dt} = -V^t \Pi^T : \nabla \mathbf{u} - \sum_i \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} \cdot \mathbf{p}_i$$

$$= -V^t \Pi^T : \nabla \mathbf{u} - \dot{\mathbf{W}}_{\text{net}}. \tag{6.6}$$

In this expression, we have taken note of the similarity between the second term on the right side of the first equality and Eq. (5.13) to come to the realization that this term represents the work (per unit time) required to drive the flow in the system. Its definition therefore involves force multiplied by velocity, or

$$\dot{\mathbf{W}}_{\text{net}} \equiv \sum_i m_i \mathbf{r}_i \cdot \nabla \mathbf{u} \cdot \nabla \mathbf{u} \cdot \frac{\mathbf{p}_i}{m_i}. \tag{6.7}$$

Hence we see that the proper energy balance for H_0 contains not only the energy dissipation caused by the viscous forces, but also the dissipation due to the rate of work done on the system by the net force exerted on the fluid element by the flow. This is in complete agreement with the first law of thermodynamics. Of course, an energy balance on H_1 yields the equal but opposite result, and hence the total internal energy of the system is conserved.

VII. NONLINEAR RESPONSE THEORY

Forty years ago, long before the advent of the fictitious force algorithms for NEMD simulation (DOLLS and SLLOD), Yamada and Kawasaki[13] developed a rigorous theory for the nonlinear dynamical response of a system of particles using exactly the noncanonical transformation subsequently used in the *p*-SLLOD derivation,[4] Eq. (4.5). Nowhere in this theory does there appear an external force, and, indeed, as described above, it is evident that the transformation of Eq. (4.5) does not require one to generate an arbitrary steady-state flow. The Yamada and Kawasaki derivation was performed for a general, homogeneous, steady-state flow field. Evans and Morriss[14] used this theory as the standard for validating the SLLOD equations of motion under PCF. Edwards *et al.*[15] have applied the same standard to PEF, and have shown that the correct nonlinear response of the system under PEF is provided by the *p*-SLLOD, and not the SLLOD, equations of motion. Indeed, the SLLOD equations of motion do not generate the requisite exact Newtonian dynamics necessary for the theory of Yamada and Kawasaki to be applicable—see Eq. (3.13).

Daivis and Todd[2] call this result into question, stating that an external force is required to generate the flow under PEF, but as we have seen in Sec. V above, this is unnecessary. Indeed, the application of an external force was never implied in the theory of Yamada and Kawasaki.[13] In order to accommodate the fictitious external force necessary to drive the flow under SLLOD dynamics, Daivis and Todd suggest modifying the Liouville operator.[2] This seems to be a very unnatural perturbation of the Yamada and Kawasaki theory. Despite claims that the correct Newtonian dynamics will thus obviously be generated, until a rigorous mathematical and physical analysis is put forward, we view this idea as speculative.

VIII. CONCLUDING REMARKS

In view of our remarks in the opening section of this article, we offer our opinion on which criteria should be used to judge the validity and practicality of NEMD algorithms for flowing materials.

(1) The equations of motion should be derived from an unquestionable source. The *p*-SLLOD equations are directly derivable from Lagrangian and Hamiltonian mechanics,[4] as summarized in Sec. IV. The SLLOD equations were introduced in a purely *ad hoc* manner, and, as described in Sec. III have not been derived in a valid and rigorous fashion to date.
(2) Since no external force is present in the actual experiment, one should not be required to perform the NEMD simulation. Again, *p*-SLLOD satisfies this requirement, whereas SLLOD does not.
(3) The algorithm should satisfy a basic energy balance over the system, in accordance with the first law of thermodynamics. Both algorithms satisfy this criterion.
(4) The correct trajectory of the center of mass, with respect to the imposed flow, should be generated by the equations of motion. Both algorithms meet this requirement, in principle, but it is better to deal with numerical precision issues through adjusting the first moment periodically rather than the total momentum.
(5) The system should have a conserved Hamiltonian, be it canonical or noncanonical, under an arbitrary flow. The *p*-SLLOD equations satisfy this criterion, whereas SLLOD does not.
(6) The equations of motion should generate the correct and exact nonlinear dynamical response of the system. Again, the *p*-SLLOD equations have been shown to satisfy rigorously this criterion for arbitrary homogeneous flows,[15] whereas no rigorous analysis yet exists for SLLOD.

Given that the *p*-SLLOD equations of motion satisfy all of the above-stated criteria, we will continue to refer to them as "proper-SLLOD," thus indicating our belief that they do

indeed represent a valid and practical algorithm for implementation of arbitrary steady-state flows in molecular dynamics simulations. Furthermore, we have chosen this name to emphasize that *p*-SLLOD is not an synthetic force algorithm, and, in this sense, is fundamentally different than what the authors of Ref. 2 refer to as "GSLLOD."

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APPENDIX A: AN EXAMPLE DISCUSSING THE UNPHYSICAL ASSUMPTION OF DAIVIS AND TODD

In the article of Daivis and Todd,[2] the authors determine the external force acting on each particle by eliminating any forces that do not contribute to the sum of the external forces—see the discussion surrounding Eq. (3.9) in the main body of this article. In this appendix, we present an example which demonstrates the lack of rigor in this assumption.

Consider a system composed of two particles. Let each particle be acted on by two forces, such that $\mathbf{f}_1$ and $\mathbf{F}_1$ act on the first particle, and $\mathbf{f}_2$ and $\mathbf{F}_2$ act on the second. Let us say that $\mathbf{f}_1=-\mathbf{f}_2\neq 0$, but that no relationship exists between $\mathbf{F}_1$ and $\mathbf{F}_2$. According to Newton's second law, the resultant forces on the particles are given by

$$\mathbf{F}_1^{\text{net}}=\mathbf{f}_1+\mathbf{F}_1$$
$$\mathbf{F}_2^{\text{net}}=\mathbf{f}_2+\mathbf{F}_2. \tag{A.1}$$

The sum of the forces in this system is then given by

$$\sum_{i=1}^{2}\mathbf{F}_i^{\text{net}}=\sum_{i=1}^{2}\mathbf{f}_i+\sum_{i=1}^{2}\mathbf{F}_i=\sum_{i=1}^{2}\mathbf{F}_i, \tag{A2}$$

where the second equality occurs since $\Sigma_{i=1}^{2}\mathbf{f}_i=0$. Daivis and Todd argue that the forces on the particles that do not contribute to the sum of the forces, Eq. (A2), do not contribute to the net forces on the particles. If one makes this assumption, then Eq. (A2) leads to

$$\mathbf{F}_1^{\text{net}}=\mathbf{F}_1$$
$$\mathbf{F}_2^{\text{net}}=\mathbf{F}_2, \tag{A.3}$$

which contradicts Eq. (A1), and is clearly incorrect. *Quod erat demonstratum*.

APPENDIX B: EVOLUTION OF THE SIMULATION BOX

In the paper of Daivis and Todd,[2] an example is used to illustrate that the SLLOD equations of motion, and not the *p*-SLLOD, were compatible with the expected evolution of the simulation box when the interparticle forces vanish. This result is not surprising, since the *p*-SLLOD algorithm does not have any forces under such a condition. In this appendix, we take a close look at this example and show that the inconsistency with *p*-SLLOD is as expected. Furthermore, by applying a rigorous analysis, we show that the example is not consistent with the SLLOD equations of motion, and does not result in Newtonian dynamics.

As described by Daivis and Todd,[2] the simulation box must evolve according to the kinematics of the induced flow. If $\mathbf{L}$ represents one of the vectors defining the vertices of the simulation box, then it must obey the dynamical relation

$$\dot{\mathbf{L}}=\mathbf{L}\cdot\nabla\mathbf{u}\Theta(t). \tag{B1}$$

The acceleration of this quantity is then given by

$$\ddot{\mathbf{L}}=\mathbf{L}\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}\Theta(t)+\mathbf{L}\cdot\nabla\mathbf{u}\delta(t). \tag{B2}$$

Before continuing, let us take note of one important fact. In the actual experiment, the equations describing the motion of the particles are irrefutable: they are Newton's equations, $m_i\ddot{\mathbf{r}}_i=\mathbf{F}_i^{\phi}$. Therefore, if the interparticle forces all vanish, then the real material does not deform according to Eq. (B1). This is because the boundary cannot impose forces on the atoms that are not in contact with it. Consequently, the case of noninteracting particles, discussed hereafter, is pathological for elongational or shear flow. In order to get any flow at all under such a condition, one must impose an external field, which is neither necessary nor even present in the actual experiment. If the real material does not deform according to Eq. (B1) for noninteracting particles, then we should not require our NEMD equations of motion to do so for this case. In the case of vanishing thermal momenta used as an example by Daivis and Todd,[2] both SLLOD and *p*-SLLOD give the same dynamical equation for the position vector, $\dot{\mathbf{r}}_i=\mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t)$, which is exactly Eq. (B1). However, in *p*-SLLOD, the coupled set of dynamical equations only enforces this deformation when the interparticle forces are present. In SLLOD, the deformation is imposed regardless of the presence of interparticle forces, which is in contrast to the actual physics of the real process.

Now according to the SLLOD algorithm, for noninteracting particles, the evolution equation for a particle's momentum is

$$\frac{d\mathbf{p}_i}{dt}=-\mathbf{p}_i\cdot\nabla\mathbf{u}\Theta(t). \tag{B3}$$

Note that Daivis and Todd set the $\mathbf{p}_i=0$ in their analysis, but we do not use this unnecessary requirement here. Substituting the time derivative of Eq. (2.1) for $\dot{\mathbf{p}}_i$ into the above expression, we obtain

$$m_i\ddot{\mathbf{r}}_i=m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}\Theta(t)+m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\delta(t). \tag{B4}$$

Comparison of this expression with Eq. (B2) demonstrates that the SLLOD equations of motion are indeed compatible with the evolution of the simulation box.

Daivis and Todd next state that the *p*-SLLOD equations of motion are inconsistent with the acceleration expression of Eq. (B2), but this is not correct. They base this claim on the form of the acceleration for (time-independent) *p*-SLLOD, which is

$$m_i\ddot{\mathbf{r}}_i = m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\,\delta(t). \tag{B5}$$

However, one must realize that this expression is for noninteracting particles; i.e., when $\mathbf{F}_i^{\phi}=0$. In the actual experiment, the flow is realized solely through the application of boundary conditions, which enter the equations of motion for the material (i.e., Newton's equations, $m_i\ddot{\mathbf{r}}_i=\mathbf{F}_i^{\phi}$) through the interparticle forces, $\mathbf{F}_i^{\phi}$. In a real experiment, if $\mathbf{F}_i^{\phi}=0$ and a velocity impulse of the form indicated by Eq. (B5) is applied to the system, then the particles will beginning translating with constant velocities according to the nature of the impulse. This can be seen by integrating Eq. (B5),

$$m_i\frac{d\mathbf{r}_i}{dt} = \int_{0^-}^{\varepsilon} m_i(\mathbf{r}_i\cdot\nabla\mathbf{u})_0\,\delta(t)dt = m_i(\mathbf{r}_i\cdot\nabla\mathbf{u})_0\Theta(t). \tag{B6}$$

This is the expected constant particle momentum, where $\mathbf{r}_i\cdot\nabla\mathbf{u}$ is taken at time $t=0$. There is absolutely no inconsistency of the *p*-SLLOD expression, Eq. (B5), with this physical reality.

For the time-dependent *p*-SLLOD equations of motion, Eq. (B5) is simply $m_i\ddot{\mathbf{r}}_i=0$. In this case, the particle momenta are again constants, and having removed the external impulse force from the equation, we recover the experimentally valid form of the zero-wave-vector equation of the momentum density.

In view of the above arguments, it is clear that the deformation of the simulation box using the *p*-SLLOD equations of motion is accomplished in the same way as in the actual experiment; i.e., through the boundary conditions as transferred into the material through the interparticle forces. There is no physical reason why the equations of motion should contain *a priori* information about the deformation of the simulation box any more than they should contain *a priori* information about which type of flow is going to be induced at the instant the flow is applied.

From a physical point of view, it is actually the SLLOD expression, Eq. (B4), which is inconsistent with reality, since, in the actual experiment, no external forces are required to induce elongational flow, only boundary conditions. The example given in Sec. V of Ref. 2 is not relevant to the experiments under consideration, because the external force applied in this case acts on all of the particles for $t\geqslant 0$. This is not what happens in a real elongation experiment. The time-dependent *p*-SLLOD equations of motion operate without the imposition of an external force field, since one is not required in the real experiment; therefore, if one devises an example incorporating an external force, the *p*-SLLOD equations of motion are bound to give an unrealistic result.

Now let us look even closer at the example of Daivis and Todd in Sec. V of their paper.[2] According to their example, a force $m_i d[\mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t)]/dt$ is imposed for $t\geqslant 0$, where $\mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t)$ is the imposed velocity. Let us perform this analysis in general by incorporating the interparticle forces. The equations of motion for the particles, according to Newton, are thus

$$m_i\frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i^{\phi} + m_i\frac{d[\mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t)]}{dt}. \tag{B7}$$

Note that if the velocities $(\mathbf{r}_i\cdot\nabla\mathbf{u})$ in the force expressions are held constant, then Eq. (B5) is recovered. Using the product rule of differentiation on the right-hand side of Eq. (B7), we see that

$$m_i\frac{d^2\mathbf{r}_i}{dt^2} = \mathbf{F}_i^{\phi} + m_i\mathbf{r}_i\cdot\nabla\mathbf{u}\,\delta(t) + m_i\dot{\mathbf{r}}_i\cdot\nabla\mathbf{u}\Theta(t). \tag{B8}$$

So far, we have not used the SLLOD equations of motion, only Newton's equation (force equals mass time acceleration). Now let us see if Eq. (B8) corresponds to the SLLOD equations of motion. According to SLLOD, the equations of motion for the particle positions and momenta are

$$\dot{\mathbf{p}}_i = \mathbf{F}_i^{\phi} - \mathbf{p}_i\cdot\nabla\mathbf{u}\Theta(t), \quad \dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t). \tag{B9}$$

Taking the time derivative of the second equation, and substituting into the result the first equation, yields

$$\ddot{\mathbf{r}}_i = \frac{\mathbf{F}_i^{\phi}}{m_i} - \frac{1}{m_i}\mathbf{p}_i\cdot\nabla\mathbf{u}\Theta(t) + \dot{\mathbf{r}}_i\cdot\nabla\mathbf{u}\Theta(t) + \mathbf{r}_i\cdot\nabla\mathbf{u}\,\delta(t). \tag{B10}$$

Replacing $\dot{\mathbf{r}}_i$ in this equation with the second expression of Eq. (B9) then gives

$$\ddot{\mathbf{r}}_i = \frac{\mathbf{F}_i^{\phi}}{m_i} + \mathbf{r}_i\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}\Theta(t) + \mathbf{r}_i\cdot\nabla\mathbf{u}\,\delta(t). \tag{B11}$$

This is not the same as Newton's expression, Eq. (B8), except in the case when $\dot{\mathbf{r}}_i=\mathbf{r}_i\cdot\nabla\mathbf{u}$; however, in this case the second part of Eq. (B9) reduces to $\mathbf{p}_i=0$, and the first part implies that $\mathbf{F}_i^{\phi}=0$ at all times in the SLLOD algorithm. [Note that the two lines of Eq. (38) in Ref. 2 are not equivalent, in general; i.e., when $\mathbf{p}_i\neq 0$.] Thus the example of Daivis and Todd only works for noninteracting particles. Therefore, we are forced to conclude that the SLLOD equations of motion are, in general, inconsistent with Newton's equation. The reason is obvious from Sec. III, the SLLOD equations of motion are incompatible with the imposed external force.

In Sec. III it was shown that the correct form of the equations of motion for a system with an imposed external force are

$$\dot{\mathbf{p}}_i = \mathbf{F}_i^{\phi}, \quad \dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{r}_i\cdot\nabla\mathbf{u}\Theta(t). \tag{B12}$$

Again taking the time derivative of the second equation, and substituting into the result the first equation, we find that

$$\ddot{\mathbf{r}}_i = \frac{\mathbf{F}_i^{\phi}}{m_i} + \dot{\mathbf{r}}_i\cdot\nabla\mathbf{u}\Theta(t) + \mathbf{r}_i\cdot\nabla\mathbf{u}\,\delta(t). \tag{B13}$$

This is indeed Eq. (B8). These results are confirmed by noting that with this set of equations of motion, (B12), $\dot{\mathbf{p}}_i=0$, so that the time derivative of the second part of Eq. (B12) directly gives Eq. (B2) when interparticle forces and the ther-

mal velocities vanish in the case suggested by Daivis and Todd.[2] Thus we see that when the external force is taken into account correctly, the appropriate equations of motion are indeed obtained.

In summary, this example has demonstrated that the *p*-SLLOD equations of motion are not, in general, compatible with an external force, which is to be expected since they were not derived under the imposition of an external force. There was no need to do so, since the external force is not present in a typical experimental elongational flow. The *p*-SLLOD equations rely on the boundary conditions to generate the proper flow field.

This example also showed that the SLLOD equations of motion do not, in general, generate the correct Newtonian equations of motion under an imposed external field, as also described in preceding sections of this article. Since SLLOD requires a sustained external field to generate elongational flow, whereas *p*-SLLOD does not, this would seem to point to a definite advantage of the latter over the former; the *p*-SLLOD equations of motion are correct when a sustained external force is absent, but the SLLOD equations are incorrect when one is present.

[1] D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Academic, London, 1990).
[2] P. J. Daivis and B. D. Todd, J. Chem. Phys. **124**, 194103 (2006), preceding paper.
[3] L. D. Landau and E. M. Lifshitz, *The Classical Theory of Fields* (Pergamon, Oxford, 1962).
[4] B. J. Edwards and M. Dressler, J. Non-Newtonian Fluid Mech. **96**, 163 (2001).
[5] M. E. Tuckerman, C. J. Mundy, S. Balasubramanian, and M. L. Klein, J. Chem. Phys. **106**, 5615 (1997).
[6] C. Lanczos, *The Variational Principles of Mechanics* (University of Toronto Press, Toronto, 1970).
[7] H. Goldstein, *Classical Mechanics* (Addison-Wesley, Reading, MA, 1980).
[8] A. N. Beris and B. J. Edwards, *Thermodynamics of Flowing Systems* (Oxford University Press, New York, 1994).
[9] J. G. Oldroyd, Proc. R. Soc. London, Ser. A **200**, 523 (1950).
[10] C. Baig, B. J. Edwards, D. J. Keffer, and H. D. Cochran, J. Chem. Phys. **122**, 114103 (2005).
[11] C. Baig, B. J. Edwards, D. J. Keffer, and H. D. Cochran, J. Chem. Phys. **122**, 184906 (2005).
[12] B. D. Todd and P. J. Daivis, J. Chem. Phys. **112**, 40 (2000).
[13] T. Yamada and K. Kawasaki, Prog. Theor. Phys. **38**, 1031 (1967).
[14] D. J. Evans and G. P. Morriss, Phys. Rev. A **30**, 1528 (1984).
[15] B. J. Edwards, C. Baig, and D. J. Keffer, J. Chem. Phys. **123**, 114106 (2005).