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An examination of the validity of nonequilibrium molecular-dynamics simulation algorithms for arbitrary steady-state flows

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Nonlinear-response theory of nonequilibrium molecular-dynamics simulation algorithms is considered under the imposition of an arbitrary steady-state flow field. It is demonstrated that the SLLOD and DOLLS algorithms cannot be used for general flows, although the SLLOD algorithm is rigorous for planar Couette flow. Following the same procedure used to establish SLLOD as the valid algorithm for planar Couette flow [D. J. Evans and E. P. Morriss, Phys. Rev. A **30**, 1528 (1984)], it is demonstrated that the p-SLLOD algorithm is valid for arbitrary flows and produces the correct nonlinear response of the viscous pressure tensor. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2035079]

I. INTRODUCTION

Nonequilibrium molecular-dynamics (NEMD) simulations are used to determine the transport properties of fluids under the conditions of imposed gradients of velocity, concentration, or temperature.[1] For over two decades, the SLLOD algorithm has been used to determine the rheological properties of fluids for steady homogeneous planar Couette flow (PCF), which is a steady-state shear flow. It has been shown[2] that the SLLOD algorithm is correct for arbitrary shear flow strengths by comparing the stress tensor derived from the SLLOD dynamics with the one obtained from nonlinear-response theory;[3] i.e., the two were identical.

Recently, several sets of authors have turned their attention to the simulation of the rheological properties of steady-state planar elongation flow (PEF).[4–9] Two of these sets have assumed that the SLLOD algorithm, used successfully in shear flows for so long, would naturally carry over to PEF as well.[4–7] However, problems arose in these simulations in that aphysical phase transformations occurred at low strain rates due to an unavoidable numerical round-off error.[6] The final set of authors showed that the problems mentioned above were due to the use of the SLLOD algorithm in the prior simulations.[8] By using a different algorithm, called p-SLLOD, these authors demonstrated that the problems could be overcome. Although motivation for using p-SLLOD over SLLOD in PEF was given in Ref. 8, the only concrete way to demonstrate the validity of p-SLLOD (and, possibly, the inapplicability of SLLOD) in PEF is to examine the nonlinear response of these two algorithms under PEF, as in Refs. 2,3.

Thus, in this paper, we develop the nonlinear-response theory of the p-SLLOD algorithm under the imposition of an arbitrary steady-state flow field (including PEF) from two perspectives, and compare the respective results for the stress tensors at the end of the analyses. In the first perspective, which follows the analysis of Evans and Morriss,[2] we develop the nonlinear response of the system based on an analysis of the mechanical response of the canonical ensemble to the imposed flow field—see Secs. II–IV. Section II demonstrates conclusively that the SLLOD algorithm cannot be used for arbitrary flow fields, including PEF. In the second perspective, we develop the nonlinear system response through an analysis of the local equilibrium distribution, following the work of Yamada and Kawasaki.[3]

We should point out that we are precisely repeating the procedure by which SLLOD was established as the correct NEMD algorithm for PCF (Ref. 2) in order to establish that p-SLLOD (and not SLLOD) is the rigorous NEMD algorithm for PEF. We go one step further to show that p-SLLOD is the rigorous NEMD algorithm for any arbitrary flow field, reducing to SLLOD for PCF.

II. DETERMINATION OF NEMD ALGORITHM APPLICABILITY IN ARBITRARY STEADY-STATE FLOWS

The following analysis closely follows that of Evans and Morriss[2] for planar Couette flow. Herein, we adapt their analysis to arbitrary steady-state flow fields, in particular, the planar elongational flow. For PCF and PEF, the velocity gradient tensor is defined as

$$\nabla\mathbf{u}(\mathrm{PCF}) = \begin{pmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{1}$$

and

$$\nabla\mathbf{u}(\mathrm{PEF}) = \begin{pmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & -\dot{\varepsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{2}$$

Of course, in general, all components may be nonzero.

Let us focus on an initial canonical ensemble of systems described by the N-particle distribution function,

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$$f_0 = \exp(-H_0/k_BT) \Big/ \int \exp(-H_0/k_BT)d\Gamma, \tag{3}$$

where $\Gamma = (\mathbf{q}_j, \mathbf{p}_j)$ denotes phase space and

$$H_0 = \sum_{i=1}^{N} \frac{1}{2m_i}\mathbf{p}_i \cdot \mathbf{p}_i + V^{\text{fluid}}(\mathbf{q}_j). \tag{4}$$

Here, m_i is the mass of particle i. At time $t=0$, we map this distribution function to the local equilibrium distribution function,[1–3] f_1, by transforming the velocity of each particle according to

$$\dot{\mathbf{q}}_i(0^+) = \dot{\mathbf{q}}_i(0^-) + \mathbf{q}_i \cdot \nabla\mathbf{u}. \tag{5}$$

Such a system represents a canonical ensemble with an imposed strain rate, $\nabla\mathbf{u}$.

If such a system evolves adiabatically under Newton's equations, the strain rate cannot change with time.[10] The strain-rate-dependent stress tensor can be calculated by solving the Liouville equation for this system.

This derivation is simplified by noting that the exact same distribution function, f, will be obtained by calculating the response of a canonical ensemble f_0 at $t=0$ under the imposition of a fictitious strain-rate field, $\nabla\mathbf{u}(t)$, provided that the system evolves under the equations of motion,

$$\ddot{\mathbf{q}}_i = \frac{\mathbf{F}_i}{m_i} + \mathbf{q}_i \cdot \frac{d\nabla\mathbf{u}(t)}{dt}, \tag{6}$$

where $\mathbf{F}_i \equiv -\partial V^{\text{fluid}}/\partial\mathbf{q}_i$. A particle that obeys Eq. (6) will exhibit Newtonian dynamics in the absence of a time-dependent flow field. Let $\nabla\mathbf{u}(t)$ be defined in terms of a Heaviside function, $\nabla\mathbf{u}(t) = \nabla\mathbf{u}\,\Theta(t)$, so that $d\nabla\mathbf{u}(t)/dt = \nabla\mathbf{u}\,\delta(t)$. The equivalence of these two trajectories can be determined by integrating (6) in a small neighborhood around $t=0$; the result is (5). Hence we see that (6) will lead to Newtonian dynamics for $t>0$.

In what follows, it will be more convenient to deal with $6N$ first-order ordinary differential equations (ODEs) than the $3N$ system of second-order ODEs expressed by (6). Equation (6) can be transformed into

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{q}_i \cdot \nabla\mathbf{u}, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla\mathbf{u} - m_i\mathbf{q}_i \cdot \nabla\mathbf{u} \cdot \nabla\mathbf{u}. \tag{7}$$

These equations are what the present authors refer to as the p-SLLOD algorithm.[8] They stem from an original idea of Tuckerman *et al.*[11] and were further developed by Edwards and Dressler.[12] Because Eq. (7) is equivalent to Eq. (6), the p-SLLOD algorithm will generate the correct system Newtonian dynamics under the imposition of any homogeneous steady-state flow field, including both PCF and PEF. Note that we did not assume the p-SLLOD equations from the outset of our analysis, but were forced into this choice by the requirement of Newtonian dynamics.

Now let us briefly consider other NEMD algorithms, specifically, SLLOD and DOLLS.[1] First, let us examine SLLOD. The equations of motion for the SLLOD algorithm analogous to Eq. (7) are[1]

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{q}_i \cdot \nabla\mathbf{u}, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla\mathbf{u}. \tag{8}$$

Transforming these equations into the form of Eq. (6), we obtain

$$\ddot{\mathbf{q}}_i = \frac{\mathbf{F}_i}{m_i} + \mathbf{q}_i \cdot \nabla\mathbf{u} \cdot \nabla\mathbf{u} + \mathbf{q}_i \cdot \frac{d\nabla\mathbf{u}(t)}{dt}. \tag{9}$$

This equation cannot, in general, be integrated to give the Newtonian trajectories required for our physical application because Eq. (9) is not equivalent to Eq. (6). Hence the SLLOD algorithm can be used only in special cases, i.e., when the second term of the right side of Eq. (9) goes to zero, as it does in PCF (but not PEF). Note that p-SLLOD and SLLOD are equivalent in PCF.

Now let us examine the DOLLS algorithm. The equations of motion for DOLLS analogous to Eq. (7) are

$$\dot{\mathbf{q}}_i = \frac{\mathbf{p}_i}{m_i} + \mathbf{q}_i \cdot \nabla\mathbf{u}, \quad \dot{\mathbf{p}}_i = \mathbf{F}_i - \nabla\mathbf{u} \cdot \mathbf{p}_i. \tag{10}$$

Transforming to the form of Eq. (6), we find that

$$\ddot{\mathbf{q}}_i = \frac{\mathbf{F}_i}{m_i} - \frac{1}{m_i}\nabla\mathbf{u} \cdot \mathbf{p}_i + \frac{1}{m_i}\mathbf{p}_i \cdot \nabla\mathbf{u} + \mathbf{q}_i \cdot \nabla\mathbf{u} \cdot \nabla\mathbf{u} + \mathbf{q}_i \cdot \frac{d\nabla\mathbf{u}(t)}{dt}. \tag{11}$$

Again, this algorithm does not provide Newtonian trajectories for our system in general, and neither in PCF nor PEF, because Eq. (11) is not equivalent to Eq. (6).

So far, we have succeeded in demonstrating that only the p-SLLOD algorithm provides the correct Newtonian trajectories for our system in the general case, although SLLOD does so for PCF. Note that this observation implicitly provides a criterion for NEMD algorithms: the equations of motion for the algorithm must satisfy Newton's equation of motion when $d\nabla\mathbf{u}(t)/dt=0$, as can be affirmed by the appropriate transformation, described above.

III. DETERMINATION OF THE p-SLLOD INTERNAL ENERGY RATE EQUATION

Since only the p-SLLOD algorithm is applicable to PEF, we shall only consider it henceforth. According to the first of Eqs. (7), the $\mathbf{p}_i$ are recognized as peculiar momenta. Consequently, the pressure tensor can be defined as

$$\mathbf{P}V = \sum_{i=1}^{N}\left(\frac{1}{m_i}\mathbf{p}_i \cdot \mathbf{p}_i + \mathbf{q}_i \cdot \mathbf{F}_i\right), \tag{12}$$

where V is the system volume, and H_0 of Eq. (4) is recognized as the internal energy of the system. Differentiating Eq. (4) and substituting into it the p-SLLOD equations of motion, (7), give the rate equation for the internal energy,

$$\dot{H}_0 = -V\mathbf{P}:\nabla\mathbf{u} - \sum_{i=1}^{N}\mathbf{q}_i \cdot \nabla\mathbf{u} \cdot \nabla\mathbf{u} \cdot \mathbf{p}_i. \tag{13}$$

Note that $\mathbf{a}:\mathbf{b} = a_{\alpha\beta}b_{\beta\alpha}$, applying the Einstein summation over repeated indices.

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Equation (13) is not the standard rate expression for the internal energy in nonequilibrium statistical mechanics,[1] due to the second term on the right side, and begs the question why is it different and what consequences does it have? First, we will examine why it is different from the standard form, and then we will see if this nonstandard form causes a problem. Note, however, that the second term on the right side vanishes for PCF. Hence both SLLOD and p-SLLOD obey the standard form of the rate expression for internal energy in this special case.

Edwards and Dressler[12] showed that the p-SLLOD algorithm has a Hamiltonian, but only in a noncanonical framework. In other words, inserting the Hamiltonian,

$$H(\mathbf{q},\mathbf{p}) = \sum_{i=1}^{N}\left(\frac{1}{2m_i}\mathbf{p}_i\cdot\mathbf{p}_i + \mathbf{q}_i\mathbf{p}_i:(\nabla\mathbf{u})^T\right) + V^{\text{fluid}}(\mathbf{q}_j) + V^{\text{ext}}(\mathbf{q}_j), \tag{14}$$

into the noncanonical equations of motion,

$$\dot{\mathbf{q}}_i = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{q}_i} - m_i\nabla\mathbf{u}\cdot\frac{\partial H}{\partial \mathbf{p}_i} - m_i\frac{\partial H}{\partial \mathbf{p}_i}\cdot\nabla\mathbf{u}, \tag{15}$$

generates the p-SLLOD algorithm of Eq. (7). These noncanonical equations of motion, (15), were derived via a transformation from the canonical frame to the p-SLLOD framework.[12]

If one examines the Hamiltonian of Eq. (14), one sees additional terms beyond what one would normally expect to see; in particular, the Hamiltonian contains an external field potential,

$$V^{\text{ext}}(\mathbf{q}_j) = \sum_{i=1}^{N}\frac{m_i}{2}(\mathbf{q}_i\cdot\nabla\mathbf{u})^2, \tag{16}$$

which acts as another source of energy for the system. When one performs an energy balance over the system, the rate of internal energy change within the system contains not only the pressure term but also another term due to the presence of this external field. Note that the form of the rate equation, (13), is entirely consistent with the results obtained from nonequilibrium thermodynamics for systems possessing an external potential field.[13] Also note that $\dot{H}=0$ when Eq. (7) is used in this expression.

Since SLLOD and p-SLLOD are equivalent in PCF, Eq. (14) provides a Hamiltonian for SLLOD in this special case. For a long time, it was thought that the SLLOD dynamics did not have a Hamiltonian in PCF, but this was because researchers were trying to find a Hamiltonian consistent with Hamilton's canonical equations of motion instead of the noncanonical form of Eq. (15).

IV. DETERMINATION OF THE p-SLLOD VISCOUS STRESS TENSOR FROM THE LIOUVILLE EQUATION

Let us continue following the analysis of Evans and Morriss.[2] According to the discussion above, instead of studying the Newtonian evolution of f_1, we can instead examine the evolution of the canonical distribution function, f_0, under the p-SLLOD dynamics represented by Eq. (7). If we denote the Liouville operator for the p-SLLOD dynamics by L, then the distribution function at any time t is given by

$$f(t) = e^{-iLt}f_0. \tag{17}$$

Of course, this is equivalent to

$$f(t) = e^{-iL_0t}f_1, \tag{18}$$

where L_0 is the Liouville operator arising from H_0,

$$iL_0 = \sum_{i=1}^{N}\left(\frac{\mathbf{p}_i}{m_i}\cdot\frac{\partial}{\partial\mathbf{q}_i} - \frac{\partial V^{\text{fluid}}}{\partial\mathbf{q}_i}\cdot\frac{\partial}{\partial\mathbf{p}_i}\right). \tag{19}$$

The Liouville operator arising from the p-SLLOD dynamics can be found using the noncanonical Poisson bracket of Edwards and Dressler,[12]

$$iL = \sum_{i=1}^{N}\left[\left(\frac{\mathbf{p}_i}{m_i} + \mathbf{q}_i\cdot\nabla\mathbf{u}\right)\cdot\frac{\partial}{\partial\mathbf{q}_i} - \left(\frac{\partial V^{\text{fluid}}}{\partial\mathbf{q}_i} + \mathbf{p}_i\cdot\nabla\mathbf{u} + m_i\mathbf{q}_i\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}\right)\cdot\frac{\partial}{\partial\mathbf{p}_i}\right]. \tag{20}$$

Now let us substitute Eq. (3) into Eq. (17),

$$f(t) = \exp[-iLt]\exp(-H_0/k_BT)\Big/\int\exp(-H_0/k_BT)d\Gamma. \tag{21}$$

According to Evans and Morriss,[1] in the adiabatic case the distribution function propagator is the Hermitian conjugate of the phase variable propagator, so that $\exp[-iLt]$ is the negative-time phase variable propagator, $\exp[iL(-t)]$. Hence it operates on the numerator, moving time backwards in the presence of the external field, while not affecting the denominator. This implies that

$$f(t) = \exp(-H_0(-t)/k_BT)\Big/\int\exp(-H_0/k_BT)d\Gamma. \tag{22}$$

Substitution of Eq. (22) into the right-hand side of the Liouville equation,

$$\frac{\partial f(t)}{\partial t} = -iLf(t), \tag{23}$$

and then using Eq. (20), leads to

$$\frac{\partial f(t)}{\partial t} = -\left(\frac{V}{k_BT}\mathbf{P}(-t):\nabla\mathbf{u} + \frac{1}{k_BT}\sum_{i=1}^{N}\mathbf{q}_i(-t)\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}\cdot\mathbf{p}_i(-t)\right)f(t). \tag{24}$$

Of course, this same equation could have been obtained by taking the time derivative of Eq. (22) with subsequent use of Eq. (13). This equation can be integrated to give

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$$f(t) = \exp\left(-\int_0^t \left(\frac{V}{k_B T}\mathbf{P}(-s):\nabla\mathbf{u} + \frac{1}{k_B T}\sum_{i=1}^{N}\mathbf{q}_i(-s)\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}\cdot\mathbf{p}_i(-s)\right)ds\right)f_0. \quad (25)$$

Alternatively, Eq. (13) can be integrated directly,

$$H_0(-t) = H_0(0) - \int_0^t \dot{H}_0(-s)ds = H_0(0) + \int_0^t \left(\frac{V}{k_B T}\mathbf{P}(-s):\nabla\mathbf{u} + \frac{1}{k_B T}\sum_{i=1}^{N}\mathbf{q}_i(-s)\cdot\nabla\mathbf{u}\cdot\nabla\mathbf{u}\cdot\mathbf{p}_i(-s)\right)ds, \quad (26)$$

and then substituted into Eq. (22) to yield Eq. (25). Obviously, then, the nonstandard form of the internal energy rate equation, (13), is entirely consistent with the Liouville operator for the p-SLLOD dynamics, (20).

We can also solve the differential equation for the distribution function iteratively.[1,2] Let us define

$$\mathbf{Z}(\mathbf{q}_j,-s) \equiv \mathbf{P}(-s) + \frac{1}{V}\sum_{i=1}^{N}\mathbf{p}_i(-s)\mathbf{q}_i(-s)\cdot\nabla\mathbf{u}, \quad (27)$$

so that Eq. (24) becomes

$$\frac{\partial f(t)}{\partial t} = -\left(\frac{V}{k_B T}\mathbf{Z}(\mathbf{q}_j,-t):\nabla\mathbf{u}\right)f(t). \quad (28)$$

Solving this equation iteratively now yields

$$f(t) = f_0 + \sum_{n=1}^{\infty}\left(-\frac{V}{k_B T}\right)^n \nabla_\beta u_\alpha \nabla_\gamma u_\varepsilon \cdots \nabla_\xi u_\rho \times \int_0^t ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n Z_{\alpha\beta}(\mathbf{q}_j,-s_1) \times Z_{\varepsilon\gamma}(\mathbf{q}_j,-s_2)\cdots Z_{\rho\xi}(\mathbf{q}_j,-s_n)f_0. \quad (29)$$

Again, note that the Einstein summation convention applies over repeated indices. Accordingly, by defining the extra stress (viscous stress) tensor as $\Pi = \mathbf{P} - P_0\delta$ (with P_0 the equilibrium pressure), then the hydrodynamic viscous stress tensor at any time due to the imposition of a flow field at $t=0$ is given by

$$\langle\Pi(t)\rangle = \sum_{n=1}^{\infty}\left(-\frac{V}{k_B T}\right)^n \nabla_\beta u_\alpha \nabla_\gamma u_\varepsilon \cdots \nabla_\xi u_\rho \times \int_0^t ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n \langle\Pi(0) \times Z_{\alpha\beta}(\mathbf{q}_j,-s_1)Z_{\varepsilon\gamma}(\mathbf{q}_j,-s_2)\cdots Z_{\rho\xi}(\mathbf{q}_j,-s_n)\rangle_0. \quad (30)$$

Note that the angular brackets denote an average over phase space, which is a standard notation.[1–3] Of course, $\langle\Pi(0)\rangle_0 = 0$ since there is no viscous stress at equilibrium.

Equation (30) is the expression for the viscous stress tensor obtained from nonequilibrium statistical mechanics. It is analogous to the expression obtained by Evans and Morriss for the SLLOD algorithm,[2] but is not limited to PCF. We will next derive the expression for the viscous stress tensor from an independent perspective, namely, that of the nonlinear response theory of Yamada and Kawasaki.[3]

V. DETERMINATION OF THE VISCOUS STRESS TENSOR FROM NONLINEAR-RESPONSE THEORY

In this section, note that we do not assume the p-SLLOD dynamics. Yamada and Kawasaki[3] started with the local equilibrium distribution function for adiabatic flow, with only the local velocity differing from its equilibrium value. According to Mori,[14] this distribution can be written as

$$f_l = \exp(-U^{-1}H_0/k_B T) \Big/ \int \exp(-U^{-1}H_0/k_B T)d\Gamma. \quad (31)$$

In this expression, U is a "pseudocanonical" transformation operator,[3] which generates the local equilibrium distribution function from the equilibrium one. This means that the transformation is not canonical, but still conserves the volume of phase space. Consequently,

$$f_l = U^{-1}f_0. \quad (32)$$

For an arbitrary function of phase space, G,[3]

$$\langle G\rangle_l \equiv \int G f_l d\Gamma = \int U(GU^{-1}f_0)d\Gamma = \int (UG)f_0 d\Gamma \equiv \langle UG\rangle_0. \quad (33)$$

Let the local mass density, mass current density, and Hamiltonian density be defined as

$$\rho(\mathbf{q}) = \sum_{i=1}^{N} m_i\delta(\mathbf{q}_i - \mathbf{q}), \quad (34)$$

$$\mathbf{j}(\mathbf{q}) = \sum_{i=1}^{N}\mathbf{p}_i\delta(\mathbf{q}_i - \mathbf{q}), \quad (35)$$

$$H_0(\mathbf{q}) = \sum_{i=1}^{N}\frac{1}{2m_i}\mathbf{p}_i\cdot\mathbf{p}_i\delta(\mathbf{q}_i - \mathbf{q}) + V^{\text{fluid}}(\mathbf{q}_j)\delta(\mathbf{q}_i - \mathbf{q}), \quad (36)$$

so that[3]

$$\langle\rho(\mathbf{q})\rangle_l = \langle U\rho(\mathbf{q})\rangle_0 = \rho_0, \quad (37)$$

$$\langle\mathbf{j}(\mathbf{q})\rangle_l = \langle U\mathbf{j}(\mathbf{q})\rangle_0 = \rho_0\mathbf{u}(\mathbf{q}), \quad (38)$$

$$\langle H_0(\mathbf{q})\rangle_l = \langle UH_0(\mathbf{q})\rangle_0 = \langle H_0(\mathbf{q})\rangle_0 + \frac{1}{2}\rho_0\mathbf{u}(\mathbf{q})\cdot\mathbf{u}(\mathbf{q}). \quad (39)$$

Note that ρ_0 is the equilibrium mass density. Also note that the second term on the right side of Eq. (39) correlates with the external field potential of Eq. (16). Furthermore, taking the time derivative of Eq. (39) yields the Yamada and Kawasaki equivalent of Eq. (13), extra term included.

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Yamada and Kawasaki specify the transformation U as[3]

$$U\mathbf{p}_i = \mathbf{p}_i + m_i\mathbf{u}(\mathbf{q}_i), \quad U\mathbf{q}_i = \mathbf{q}_i. \tag{40}$$

Not coincidentally, this can be recognized as the noncanonical transformation that Edwards and Dressler used to derive the p-SLLOD dynamics,[12] once the velocity in Eq. (40) is identified as $\mathbf{u}(\mathbf{q}_i) \equiv \mathbf{q}_i \cdot \nabla\mathbf{u}$. Consequently, $H = UH_0$ gives the Hamiltonian of Eqs. (14) and (16) starting with the canonical Hamiltonian of Eq. (4).

For the local equilibrium distribution function of Eq. (31),

$$U^{-1}H_0(\mathbf{q}) = H_0(\mathbf{q}) + R, \tag{41}$$

where

$$R = -\int \mathbf{j}(\mathbf{q}) \cdot \mathbf{u}(\mathbf{q}) d^3q + \frac{1}{2}\int \rho(\mathbf{q})\mathbf{u}(\mathbf{q}) \cdot \mathbf{u}(\mathbf{q}) d^3q. \tag{42}$$

According to Eqs. (18), (31), (41), and (42),

$$f(t) = e^{-iL_0 t} f_l = \alpha e^{-R(-t)/k_B T} f_0, \tag{43}$$

where α is a constant. Taking the derivative of this expression yields

$$\frac{\partial f(t)}{\partial t} = \frac{\dot{R}(-t)}{k_B T} f(t). \tag{44}$$

This differential equation can be solved directly,

$$f(t) = \exp\left(\int_0^t \frac{\dot{R}(-s)}{k_B T} ds\right) f_l, \tag{45}$$

or iteratively,

$$f(t) = f_l + \sum_{n=1}^{\infty} \left(\frac{1}{k_B T}\right)^n \int_0^t ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n \dot{R}(-s_1)\dot{R}(-s_2)\cdots\dot{R}(-s_n) f_l. \tag{46}$$

Now consider the local stress tensor,

$$\mathbf{P}(\mathbf{q}) = \sum_{i=1}^{N} \left(\frac{\mathbf{p}_i\mathbf{p}_i}{m_i}\delta(\mathbf{q}_i - \mathbf{q}) + \mathbf{q}_i\mathbf{F}_i\delta(\mathbf{q}_i - \mathbf{q})\right). \tag{47}$$

The viscous part of this tensor is

$$\Pi(\mathbf{q}) = \mathbf{P}(\mathbf{q}) - P_0\delta. \tag{48}$$

Following Yamada and Kawasaki,[3] we define

$$\mathbf{P}_\nu^*(\mathbf{q}) \equiv \sum_{i=1}^{N} \left(\frac{1}{m_i}[\mathbf{p}_i - m_i\mathbf{u}(\mathbf{q}_i)][\mathbf{p}_i - m_i\mathbf{u}(\mathbf{q}_i)]\delta(\mathbf{q}_i - \mathbf{q}) + \mathbf{q}_i\mathbf{F}_i\delta(\mathbf{q}_i - \mathbf{q})\right) - P_0\delta. \tag{49}$$

Clearly then,

$$U\mathbf{P}_\nu^*(\mathbf{q}) = \mathbf{P}(\mathbf{q}) - P_0\delta = \Pi(\mathbf{q}), \quad U^{-1}\mathbf{P}(\mathbf{q}) = \mathbf{P}_\nu^*(\mathbf{q}) + P_0\delta. \tag{50}$$

Consequently, we can write

$$\langle\Pi(t)\rangle = \langle\mathbf{P}_\nu^*(0)\rangle_1 + \sum_{n=1}^{\infty} \left(\frac{1}{k_B T}\right)^n \int_0^t ds_1 \int_0^{s_1} ds_2 \ldots \int_0^{s_{n-1}} ds_n \times \langle\mathbf{P}_\nu^*(0)\dot{R}(-s_1)\dot{R}(-s_2)\cdots\dot{R}(-s_n)\rangle_1. \tag{51}$$

In view of Eqs. (33) and (50),

$$\langle\mathbf{P}_\nu^*(0)\rangle_1 = \langle U\mathbf{P}_\nu^*(0)\rangle_0 = \langle\mathbf{P}(0)\rangle_0 - P_0\delta = \langle\Pi(0)\rangle_0, \tag{52}$$

so that Eq. (51) becomes

$$\langle\Pi(t)\rangle = \sum_{n=1}^{\infty} \left(\frac{1}{k_B T}\right)^n \int_0^t ds_1 \int_0^{s_1} ds_2 \cdots \int_0^{s_{n-1}} ds_n \langle\Pi(0)U[\dot{R}(-s_1)\dot{R}(-s_2)\cdots\dot{R}(-s_n)]\rangle_0. \tag{53}$$

Note that the U in this expression applies to the whole term inside the rectangular brackets. Also recall that $\langle\Pi(0)\rangle_0 = 0$. The time, t, in the above equation is chosen such that it is much greater than the microscopic time scale of the dynamics, but much less than the relaxation time of the macroscopic hydrodynamics.[3] This ensures that the local equilibrium distribution follows exact dynamics while allowing proper averages to be obtained.

Lastly, we need to calculate $\dot{R}$. According to Eq. (42), this quantity is

$$\dot{R} = -\int \frac{d\mathbf{j}(\mathbf{q})}{dt} \cdot \mathbf{u}(\mathbf{q}) d^3q + \frac{1}{2}\int \frac{d\rho(\mathbf{q})}{dt}\mathbf{u}(\mathbf{q}) \cdot \mathbf{u}(\mathbf{q}) d^3q. \tag{54}$$

Using the balance equations[3]

$$\frac{d\rho}{dt} = -\nabla \cdot \mathbf{j}, \quad \frac{d\mathbf{j}}{dt} = -\nabla \cdot \mathbf{P}, \tag{55}$$

Eq. (54) becomes

$$\dot{R} = \int \nabla \cdot \mathbf{P} \cdot \mathbf{u} d^3q - \frac{1}{2}\int \nabla \cdot \mathbf{j}\mathbf{u} \cdot \mathbf{u} d^3q. \tag{56}$$

Applying integration by parts to the above expression finally yields (neglecting surface contributions)

$$\dot{R} = -\int \mathbf{P}:\nabla\mathbf{u} d^3q + \int \mathbf{u}\mathbf{j}:\nabla\mathbf{u} d^3q. \tag{57}$$

From Eqs. (47) and (49),

$$\mathbf{P} = P_0\delta + \mathbf{P}_\nu^* + \mathbf{u}\mathbf{j} + \mathbf{j}\mathbf{u} - \rho\mathbf{u}\mathbf{u}. \tag{58}$$

Consequently, Eq. (57) becomes

$$\dot{R} = -\int (\mathbf{P}_\nu^*:\nabla\mathbf{u} + P_0\delta + \mathbf{j}\mathbf{u}:\nabla\mathbf{u} - \rho\mathbf{u}\mathbf{u}:\nabla\mathbf{u}) d^3q, \tag{59}$$

and hence

$$U\dot{R} = -\int (\mathbf{P}:\nabla\mathbf{u} + \mathbf{j}\mathbf{u}:\nabla\mathbf{u}) d^3q \equiv -\int \mathbf{Z}(\mathbf{q}):\nabla\mathbf{u} d^3q. \tag{60}$$

With this expression, Eq. (53) for the hydrodynamic viscous stress tensor becomes

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$$\langle \Pi(t) \rangle = \sum_{n=1}^{\infty} \left(\frac{-1}{k_B T} \right)^n \nabla_\beta u_\alpha \nabla_\gamma u_\varepsilon \cdots \nabla_\xi u_\rho \int_0^t ds_1 \int d^3 q^1 \int_0^{s_1} ds_2 \int d^3 q^2 \cdots \int_0^{s_{n-1}} ds_n \int d^3 q^n \langle \Pi(0) Z_{\alpha\beta}(\mathbf{q}^1, -s_1) Z_{\varepsilon\gamma}(\mathbf{q}^2, -s_2) \cdots Z_{\rho\xi}(\mathbf{q}^n, -s_n) \rangle_0. \quad (61)$$

Equation (61) can be compared directly with Eq. (30), and it is thus recognized that the two expressions are identical. Hence the nonlinear response is the same in both perspectives, and therefore the p-SLLOD algorithm will yield the appropriate rheological properties under the imposition of an arbitrary steady-state flow field. Also note that the nonstandard form of the internal energy rate equation, (13), was used to derive Eq. (30), and is thus essential in obtaining the correct nonlinear system response; had the standard form been used for this expression, the correct nonlinear response would not have been generated.

VI. CONCLUSION

While it had been demonstrated via NEMD simulation that p-SLLOD removed the problems SLLOD encountered in the simulation of PEF,[8] there had been lacking a widely accepted theoretical basis for this choice of algorithm. By repeating the procedure by which SLLOD was established as the correct NEMD algorithm for PCF,[2] we have now established that p-SLLOD (and not SLLOD) is the rigorous NEMD algorithm for PEF. We have also shown that p-SLLOD is the rigorous NEMD algorithm for any arbitrary flow field, reducing to SLLOD for PCF. We have shown that the form of the internal energy for p-SLLOD is consistent with both continuum nonequilibrium thermodynamics and nonequilibrium statistical mechanics. We have shown that the form of the viscous stress tensor is consistent with nonequilibrium statistical mechanics and nonlinear-response theory.

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[1] D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Academic, New York, 1990).
[2] D. J. Evans and G. P. Morriss, Phys. Rev. A **30**, 1528 (1984).
[3] T. Yamada and K. Kawasaki, Prog. Theor. Phys. **38**, 1031 (1967).
[4] B. D. Todd and P. J. Daivis, Phys. Rev. Lett. **81**, 1118 (1998).
[5] B. D. Todd and P. J. Daivis, Comput. Phys. Commun. **117**, 191 (1999).
[6] B. D. Todd and P. J. Daivis, J. Chem. Phys. **112**, 40 (2000).
[7] A. Baranyai and P. T. Cummings, J. Chem. Phys. **110**, 42 (1999).
[8] C. Baig, B. J. Edwards, D. J. Keffer, and H. D. Cochran, J. Chem. Phys. **122**, 114103 (2005).
[9] C. Baig, B. J. Edwards, D. J. Keffer, and H. D. Cochran, J. Chem. Phys. **122**, 184906 (2005).
[10] D. J. Evans, Phys. Rev. A **23**, 2622 (1981).
[11] M. E. Tuckerman, C. J. Mundy, S. Balasubramanian, and M. L. Klein, J. Chem. Phys. **106**, 5615 (1997).
[12] B. J. Edwards and M. Dressler, J. Non-Newtonian Fluid Mech. **96**, 163 (2001).
[13] M. Dressler, B. J. Edwards, and H. C. Öttinger, Rheol. Acta **38**, 2028 (1999).
[14] H. Mori, Phys. Rev. **112**, 1829 (1958).

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