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A reversible problem in non-equilibrium thermodynamics: Hamiltonian evolution equations for non-equilibrium molecular dynamics simulations

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Abstract

The reversible contribution to contemporary theories of non-equilibrium thermodynamics is reviewed as a methodology for attacking difficult, conservative problems in complex fluid dynamics. Several examples of past successes are discussed, and a new application is addressed: non-equilibrium molecular dynamics (NEMD) simulations. NEMD simulations of fluids are generally based on either a DOLLS or SLLOD tensor algorithm. The former is always considered to be a Hamiltonian system, but not particularly useful in high strain rate flow simulations, while the latter is considered not to be a Hamiltonian system, but much more practical and accurate in flow simulations. We demonstrate herein using non-canonical transformations of the particle momenta of the system that the SLLOD equations, when written in terms of appropriate non-canonical variables, *are* completely Hamiltonian, whereas the DOLLS equations *are not* so. A modified set of DOLLS equations in terms of the non-canonical variables which again is completely Hamiltonian is also derived. Both algorithms then lead to a phase space distribution function which is canonical in both the coordinates and momenta.

Keywords: Non-equilibrium molecular dynamics (NEMD) simulations; Hamiltonian system; SLLOD equation; DOLLS equation

1. Introduction

In the past, non-equilibrium thermodynamicists essentially studied only thermodynamics. They did not pay much attention to the reversible or conservative effects that occurred simultaneously with the irreversible or dissipative ones that really aroused their interest. To be sure, they did incorporate reversible convection mechanisms into their dynamical evolution equations, but these devices were always assumed as known a priori and plugged into the appropriate evolution equations in the appropriate places, in much the same way as one hangs paper clothes on a cardboard doll. Usually, this worked out all right, because the

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systems that concerned the investigators were fairly simple, at least relative to the complex materials that are exciting interest these days. This action was a very reasonable thing to do because classical continuum mechanics was in its glory days, and promised wonderful models for any conservative dynamical system. To extend these results to dissipative thermodynamic systems, it seemed like the obvious thing to do was to tack the dissipative terms onto the conservative equations. Even so, the past decade, with the help of contemporary non-equilibrium thermodynamics, has witnessed a fair number of dynamical models being laid bare and dissected upon the examination table, revealing all manner of physical deformities. Many of the mechanical inconsistencies and thermodynamic limitations of these dynamical models are actually associated with the *reversible*, as opposed to irreversible, system dynamics, i.e. the part that was *assumed* rather than *derived*. No one is to blame for these lapses; it just so happens that to describe all of the interesting dynamical problems in nature, the obvious thing does not work. Indeed, only recently has the realization set in that, for general dynamical systems, the reversible contributions to the dynamics must be *derived* at the same time as the dissipative ones in order to guarantee a fully consistent dynamical model.

Throughout this special issue of *Journal of Non Newtonian Fluid Mechanics*, the reader is introduced to various forms of a unified theory of non-equilibrium thermodynamics that describes *both* reversible and irreversible processes on an equal footing; however, most of the contributions presented herein focus primarily on the dissipative contributions to the system thermodynamics. In this article, ergo, we wish to focus on the reversible contributions to said subject, and to see what happens when we *derive* reversible dynamics, rather than assume them. Several such cases from the literature are discussed in the following section, and then, in subsequent sections, a new example is examined where deriving reversible dynamics leads to an amelioration of some computational cataracts associated with non-equilibrium molecular dynamics simulations.

2. Reversible dynamics in non-equilibrium thermodynamics

Contemporary theories of non-equilibrium thermodynamics are concerned with more than just dissipative phenomena. It is now obvious that the reversible processes, undergone by a dynamical system simultaneously with the irreversible ones, cannot be so cavalierly neglected during model development as in the past. Both types of processes are interwoven into the dynamic material response, and both must be described within a common modelling framework in order to derive a consistent set of evolution equations for the system dynamics. This new thermodynamic framework has been described in various forms throughout the current volume, so the present authors adopt without ceremony a simple form, given by the single-generator bracket equation,

$$\frac{\mathrm{d}F}{\mathrm{d}t} = \{F, H\} + [F, H]. \tag{1}$$

In this equation, F is an arbitrary function (or functional, as the case may be) of the system variables, H is the Hamiltonian or energy function, and the French and square brackets represent the Poisson and dissipative operators, respectively. Each bracket operator has its own inherent properties, as required by mechanics or thermodynamics, for describing reversible or irreversible phenomena. It may, thus, seem that each bracket is independent of the other, and this is essentially correct; however, both brackets account for common terms in the dynamical evolution equations that result from their construction. For instance,

the hydrodynamic stress tensor appearing in the Cauchy momentum equation can manifest both reversible and irreversible contributions. Since the dissipative contribution to Eq. (1) has already been discussed and analyzed extensively in the other contributions, we focus instead on the reversible system representation through the Poisson bracket.

The Poisson bracket boasts some fundamental mathematical properties, all of which have been known for approximately 175 years. (Writing Poisson brackets for dynamical systems is nothing new, only their transformations into non-canonical forms and subsequent combinations with similarly expressed dissipative brackets is.) The first property of the Poisson bracket is its bilinearity in F and H. Although not particularly enlightening, it does act to restrict severely the mathematically allowable functionality of non-canonical forms of this operator. If one follows the procedure of deriving a non-canonical Poisson bracket from one with the canonical form, this property should always take care of itself. The second property of the Poisson bracket is its antisymmetry with respect to an interchange of F and H. This property ensures, among other things, that the conservation law of energy is upheld; however, it does not place much of a restriction on the form of the Poisson bracket. A third property of the Poisson bracket is that it satisfies the Jacobi identity,

$$\{\{G, F\}, H\} + \{\{F, H\}, G\} + \{\{H, G\}, F\} = 0, \tag{2}$$

where G is another arbitrary function, similar to F. This property guarantees the time/structure invariance of the reversible dynamics, and it acts as a very severe restriction on the allowed functionality of this operator, as described below.

Now the question that we wish to address is the following: what does the non-canonical Poisson bracket and its associated properties allow us to do in the new thermodynamic framework that we could not have done with the old methodology? Three benefits have sprung up so far (more to come?), and each is described in turn below, with specific examples discussed where the advantage was exploited to greater gain. The first benefit stems directly from the Jacobi identity: by requiring that the non-canonical Poisson bracket used to describe any reversible system dynamics satisfies this relationship, we obtain very severe restrictions on allowable dynamic behavior in complicated flow problems. The second benefit comes from the antisymmetry of the Poisson bracket: this requires a coupling between the macroscopic balance laws and constitutive evolutions equations for any dynamical system, resulting in a minimization of requisite parameters. The third benefit arises from using a generator, H, to describe the total energy of any given material. The form of the non-canonical Poisson bracket is invariant of the exact functional form of the Hamiltonian, and hence additional effects may be added to H, and hence the governing dynamical equations, without much extra effort. Ergo, known models for various systems can be improved and extended to more general (or more specific, as the case may be) situations. We shall now elaborate on each of these three advantages.

The first benefit, arising from the Jacobi identity, has manifested itself in two different applications thus far. One is for deriving constraints on closure approximations, and the other is for determining between several plausible alternatives for polymeric fluid reptation models without the independent alignment approximation.

In [1], the time-structure invariance of the non-canonical Poisson bracket was used to derive constraints on closure approximations. In many areas of physics, time evolution equations for moments of distributions are expressed in terms of higher-order moments. Closure approximations are then introduced, usually in an ad hoc fashion, to reduce the higher-order moments to functions of the lower-order ones. Unfortunately, very little physical guidance is available for determining accurate closure approximations

from the infinitely many possibilities. However, it turns out that, by re-expressing the evolution equations for the lower-order moments in terms of a non-canonical Poisson bracket, one can require satisfaction of the Jacobi identity as a further restriction on the forms of these closure approximations. Indeed, this identity places very severe restrictions on the allowed functionality of these approximations, drastically weeding out inappropriate possibilities.

The Jacobi identity was also used in [2] to distinguish between multiple alternatives for a polymer reptation model without the independent alignment approximation. The original Doi–Edwards model made use of the so-called 'independent alignment assumption,' which led to several inconsistencies with experimental data. (It is not necessary to know what is meant by 'independent alignment' for the present discussion. The interested reader may refer to [3] for details.) Hence, several models without this assumption have been derived over the past two decades. In [2], three different possibilities for convection-diffusion equations without independent alignment were investigated: one from the literature, originally proposed by Doi and Edwards [3], and two proposed by the authors themselves. By expressing the convection-diffusion equations for the distribution function corresponding to these three model possibilities in the forms of non-canonical Poisson brackets, checks of the Jacobi identity could be made. These checks ruled out two of the possibilities, leaving only one thermodynamically consistent reptation model without the independent alignment assumption; however, it is possible that other viable alternatives, which were not tested, may exist.

The second benefit arises through the antisymmetry property of the non-canonical Poisson bracket, which requires coupling between the various phenomena occurring in separate evolution equations for the system variables. The literature contains many examples of dynamic models which contain many more parameters than necessary because this property has not been recognized or tested. Many dynamical models even contain internally inconsistent evolution equations for the system variables. We shall now discuss examples of each kind of problem.

With regard to the redundant parameter problem, in 1962, G.L. Hand published a seminal work on the dynamics of anisotropic fluids [4], which has been cited over three hundred times since then. Hand's theory is expressed in terms of an expansion for the evolution equation for an internal structural variable, with a large number of parameters, and also an expansion for the stress tensor, also with a large number of parameters. But did you know that Hand's theory possesses twice as many parameters as it actually needs? If one re-expresses his equations in terms of a non-canonical, antisymmetric Poisson bracket, it becomes apparent immediately that the same parameters must appear in both the stress constitutive equation and the evolution equation for the structural variable.

With regard to the problem of internal consistency mentioned above, the past decade has seen several interesting cases where the antisymmetric non-canonical Poisson bracket has laid bare inconsistencies between stress tensors and evolution equations, which go well beyond the presence of redundant parameters. Consider the polymer reptation model mentioned above with respect to the problem associated with independent alignment. Not only was the modification of the convection-diffusion equation proposed by Doi and Edwards found to be inconsistent with the notion of a non-canonical Poisson bracket, but also the stress tensor used by Doi and Edwards in conjunction with this convection-diffusion equation was inconsistent. This was discovered in [2] during the re-expression of the reptation model alternatives without independent alignment in the forms of non-canonical Poisson brackets. The antisymmetry property of the Poisson bracket dictated the form of the stress tensor that must be associated with the one consistent alternative of the three that were proposed. The work in [2] was later extended to incorporate anisotropic tube sections in [5], and again the antisymmetry property of the corresponding Poisson

bracket dictated the form of the stress tensor associated with the new convection-diffusion equation for this model.

Other examples of this internal consistency problem have also been discovered. The first such discovery came in [6], where re-expression of Doi's liquid crystal model [7] in the form of a Poisson bracket demonstrated that Doi's stress tensor was incompatible with his evolution equation for the second-rank order parameter tensor. This action also dictated a different stress tensor that was consistent with the evolution equation. Furthermore, recent work examining non-isothermal macroscopic models for polymeric liquids has revealed inconsistencies in a large number of papers devoted to this topic, as described therein [8]. To name just one example, the much exalted theory of *Rational Thermodynamics* was shown to contain the same sort of inconsistency between the total stress constitutive equation and the sacrosanct macroscopic balance laws postulated by this theory.

The third benefit arises from using a generator, H, to dictate the dynamics of any given system through its insertion into the Poisson bracket. Since the form of the non-canonical Poisson bracket is invariant of the exact functional form of the Hamiltonian, with respect to its variable arguments, additional effects may be added to H to produce easily any model improvements or extensions one desires. For instance, one study extended results for bulk flows of incompressible polymeric liquids to incorporate surface effects [9] by adding an additional term to the Hamiltonian which accounted for the decrease in available chain conformations to polymer molecules located near the surface. This additional term then manifested itself in both the evolution equation for the conformation tensor as well as the in the stress tensor. In [10], the second-rank order parameter tensor theory of Doi was extended to cover additional phenomena associated with inhomogeneous director fields, applied external fields, and rotational effects through the addition of several new terms to the Hamiltonian. This theory is still the only complete model of liquid crystalline materials in terms of a second-rank tensor, despite numerous subsequent attempts by competitors to usurp its status. Another example has appeared recently [11], where the Doi–Ohta model for multiphase fluids was extended to handle in a basic fashion phenomena close to the nucleation threshold, such as off-critical spinodal decomposition.

It should now be apparent that some practical advantages ensue from using Poisson brackets to describe the reversible contributions to dynamical system responses. When coupled with a similarly expressed thermodynamic representation of the irreversible contributions, a powerful tool is forged which cannot help but to alter the efficacy and utility of contemporary modelling procedures, as the above examples clearly demonstrate. In the remainder of this article, we offer one more new example of this thesis by studying how reversible, non-canonical Poisson brackets can help to eliminate some questionable methodology from computer simulations of molecular dynamics.

3. A new application: non-equilibrium molecular dynamics simulations

Over the past decade, non-equilibrium molecular dynamics (NEMD) simulations have become a sophisticated tool for explaining dynamical phenomena far from equilibrium, in particular, for exploring the behavior of fluids under the application of a flow field. Let us consider a system of N discrete particles with coordinates, $\{\boldsymbol{q}'_i, \ldots, \boldsymbol{q}'_N\} \equiv \{\boldsymbol{q}'\}$, momenta, $\{\boldsymbol{p}'_1, \ldots, \boldsymbol{p}'_N\} \equiv \{\boldsymbol{p}'\}$, and an interaction potential $V'(\boldsymbol{q}'_1, \ldots, \boldsymbol{q}'_N) \equiv V'\{\boldsymbol{q}'\}$. This system is subjected to an external flow field, $\boldsymbol{\nabla u}$, which is taken as a constant. Phase space, $\boldsymbol{\Gamma}'$, is then the union of the sets of coordinates and momenta mentioned above.

The DOLLS tensor algorithm for NEMD simulations was developed by Hoover [12] and Hoover et al. [13] by postulating ad hoc an extended Hamiltonian for this system,

$$H'(\boldsymbol{q}', \boldsymbol{p}') = \sum_{i=1}^{N} \left(\frac{1}{2m_i} \boldsymbol{p}_i' \cdot \boldsymbol{p}_i' + \boldsymbol{q}_i' \boldsymbol{p}_i' : \boldsymbol{\nabla u} \right) + V'(\boldsymbol{q}'), \tag{3}$$

where m_i is the mass of the i-th particle and $\boldsymbol{a}$:$\boldsymbol{b}$ denotes the product $a_{ij}b_{ij}$, summing over repeated indices. Assuming that the variables $\boldsymbol{q}'$ and $\boldsymbol{p}'$ obey Hamiltonian eqations [13],

$$\dot{\boldsymbol{q}}_i' = \frac{\partial H'}{\partial \boldsymbol{p}_i'}, \qquad \dot{\boldsymbol{p}}_i' = -\frac{\partial H'}{\partial \boldsymbol{q}_i'}, \tag{4}$$

the evolution equations for these variables are found to be

$$\dot{\boldsymbol{q}}_i' = \frac{\boldsymbol{p}_i'}{m_i} + \boldsymbol{q}_i' \cdot \boldsymbol{\nabla u}, \qquad \dot{\boldsymbol{p}}_i' = \boldsymbol{F}_i' - \boldsymbol{\nabla u} \cdot \boldsymbol{p}_i', \tag{5}$$

where $\boldsymbol{F}_i' = -\partial V'/\partial \boldsymbol{q}_i'$, $\boldsymbol{a} \cdot \boldsymbol{\nabla u} = a_j \nabla_j u_i$, and $\boldsymbol{\nabla u} \cdot \boldsymbol{a} = \nabla_i u_j a_j$. These equations can be associated with a Poisson bracket bearing canonical form,

$$\{F', H'\} = \sum_{i=1}^{N} \left(\frac{\partial F'}{\partial \boldsymbol{q}_i'} \cdot \frac{\partial H'}{\partial \boldsymbol{p}_i'} - \frac{\partial H'}{\partial \boldsymbol{q}_i'} \cdot \frac{\partial F'}{\partial \boldsymbol{p}_i'} \right), \tag{6}$$

where F' is an arbitrary function of $\{\boldsymbol{q}'\}$ and $\{\boldsymbol{p}'\}$. This set of equations is thus considered to be a Hamiltonian system in the literature on this subject, e.g. [12–15].

The importance of a Hamiltonian system is that the Hamiltonian, such as that of Eq. (3), provides a conserved quantity in the absense of time-dependent boundary conditions. Thus, it can be used as a check on the stability of a numerical integration scheme [15]. It also allows the derivation of the corresponding phase space distribution function, $f(\boldsymbol{\Gamma}')$ [15]. For the Hamiltonian of Eq. (3), one has [15]

$$f \sim \exp\left(-\frac{1}{k_B T} \left[\sum_{i=1}^{N} \left\{ \frac{1}{2m_i} (\boldsymbol{p}_i' + m_i \boldsymbol{q}_i' \cdot \boldsymbol{\nabla u})^2 - \frac{m_i}{2} (\boldsymbol{q}_i' \cdot \boldsymbol{\nabla u})^2 \right\} + V'(\boldsymbol{q}') \right] \right). \tag{7}$$

This equation is canonical in the 'lab' momenta, but not in the coordinates [15], which is less than ideal. (We use 'canonical' in this sense to denote that the distribution function maintains the form, in terms of the Hamiltonian, of $f \sim \exp(-H/k_B T)$ under an appropriate transformation, such as that of Eq. (13).) Furthermore, it is known that the DOLLS algorithm only gives reasonable flow behavior in the limit of linear strain rates [14].

In order to overcome these deficiencies, the SLLOD algorithm was developed [14]. The evolution equations for the variables of this algorithm are

$$\dot{\boldsymbol{q}}_i' = \frac{\boldsymbol{p}_i'}{m_i} + \boldsymbol{q}_i' \cdot \boldsymbol{\nabla u}, \qquad \dot{\boldsymbol{p}}_i' = \boldsymbol{F}_i' - \boldsymbol{p}_i' \cdot \boldsymbol{\nabla u}, \tag{8}$$

where the momentum equation was obtained ad hoc by using the transpose of the velocity gradient tensor in the product on the right-hand side of Eq. (5). In the literature on this subject, these equations are taken as not being derivable from a Hamiltonian, e.g. [14,15]. Nevertheless, they seem to give an exact

description of shear flow arbitrarily far from equilibrium [14], and even though the system presumably has no Hamiltonian, an ad hoc distribution function can be obtained which is canonical in both the momenta and coordinates [14]:

$$f \sim \exp\left(-\frac{1}{k_B T}\left[\sum_{i=1}^{N}\frac{1}{2m_i}(\boldsymbol{p}_i' + m_i \boldsymbol{q}_i' \cdot \boldsymbol{\nabla u})^2 + V'(\boldsymbol{q}')\right]\right). \tag{9}$$

Hence, the SLLOD algorithm has advantages over the DOLLS algorithm, but apparently lacks the benefit of having a Hamiltonian dynamics in terms of a conserved quantity like Eq. (3).

Considerable effort has recently been expended in order to find a conserved quantity for the thermostatted SLLOD equations [15]. To accomplish this objective, an additional variable with a prescribed time evolution was inserted into the DOLLS Hamiltonian. This allowed dH'/dt, as expanded through its constituent variables using the chain rule, to vanish.

4. Examination of the DOLLS and SLLOD equations using a non-canonical transformation of the particle momenta

In the preceding section, we denoted the coordinates and momenta with primes to emphasize that the variables $\{\boldsymbol{q}'\}$ and $\{\boldsymbol{p}'\}$ can alternatively be considered as non-canonical variables, in contrast to the usual procedure. This point has not been noted nor exploited in the past, and we now wish to do so. Even if one works in terms of non-canonical variables, it is very important to maintain the integrity of the Hamiltonian system, as expressed through the Poisson bracket. This bracket structure, whether it is canonical or non-canonical, is apparently a universal property of the reversible dynamics of all physical systems. This statement has been verified for many physical systems over the past 20 years; many examples are compiled in [16–18]. However, this point was not exploited in the development of the algorithms described in the preceding section.

If we consider a discrete particle system, in the absense of a flow field, then the system is Hamiltonian in terms of the canonical variables, $\{\boldsymbol{q}\}$ and $\{\boldsymbol{p}\}$. The Hamiltonian for the system is

$$H(\boldsymbol{q}, \boldsymbol{p}) = \sum_{i=1}^{N}\frac{1}{2m_i}\boldsymbol{p}_i \cdot \boldsymbol{p}_i + V(\boldsymbol{q}), \tag{10}$$

and the dynamics are described by the canonical Poisson bracket expression,

$$\frac{dF}{dt} = \{F, H\} = \sum_{i=1}^{N}\left(\frac{\partial F}{\partial \boldsymbol{q}_i}\cdot\frac{\partial H}{\partial \boldsymbol{p}_i} - \frac{\partial H}{\partial \boldsymbol{q}_i}\cdot\frac{\partial F}{\partial \boldsymbol{p}_i}\right). \tag{11}$$

The evolution equations for the canonical variables are then

$$\dot{\boldsymbol{q}}_i = \frac{\partial H}{\partial \boldsymbol{p}_i} = \frac{1}{m_i}\boldsymbol{p}_i, \qquad \dot{\boldsymbol{p}}_i = -\frac{\partial H}{\partial \boldsymbol{q}_i} = -\frac{\partial V}{\partial \boldsymbol{q}_i} = \boldsymbol{F}_i. \tag{12}$$

The Poisson bracket in Eq. (11) is bilinear, antisymmetric (thus implying a conserved quantity, H), and satisfies the Jacobi identity. All Poisson bracket structures should possess these three properties whether they are canonical or non-canonical.

The canonical Hamiltonian system described above is the starting point for a consistent analysis, as it represents the most secure expression of the system dynamics. If one wishes to alter the Hamiltonian by addition of a supplemental external potential, in this case due to a flow field, one must be careful that the functional form of the Hamiltonian is not affected. Otherwise, the canonical form of Hamilton's equations becomes invalid.

For the present problem, it is desired to obtain a Hamiltonian of the form of Eq. (3), but this represents the addition to the canonical Hamiltonian of a new external potential with a different functional form than $V(\boldsymbol{q})$. Thus, the Hamiltonian equations corresponding to the new problem become non-canonical, and should most appropriately be expressed through a non-canonical Poisson bracket. Hence, in order to maintain mechanical consistency, the Poisson bracket of Eq. (11) must be transformed into a non-canonical bracket through an appropriate non-canonical transformation of the system variables in order to ensure the preservation of the Poisson structure within the system. There are many possibilities for this non-canonical variable transformation. If we are interested in obtaining the Hamiltonian of Eq. (3), then a valid transformation producing the required result is

$$\boldsymbol{p}_i \rightarrow \boldsymbol{p}_i' + m_i \boldsymbol{q}_i' \cdot \boldsymbol{\nabla u}, \qquad \boldsymbol{q}_i \rightarrow \boldsymbol{q}_i'. \tag{13}$$

The motivation for this transformation is that $\boldsymbol{p}_i{}'$ quantifies the momentum of the particle relative to the carrying fluid as measured relative to the origin of the coordinate system once the velocity profile has been linearized with respect to the same position. Substitution of this transformation into the canonical Hamiltonian, Eq. (10), produces the Hamiltonian of Eq. (3), where

$$V'(\boldsymbol{q}') = V(\boldsymbol{q}') + \sum_{i=1}^{N} \frac{m_i}{2} (\boldsymbol{q}_i' \cdot \boldsymbol{\nabla u})^2. \tag{14}$$

In order to see more clearly why the variable transformations of Eq. (13) are appropriate for this problem, let us consider momentarily the corresponding Lagrangian problem, with the Lagrangian, $L(\boldsymbol{q}, \dot{\boldsymbol{q}})$. In most textbooks, the Lagrangian is defined as [16,19]

$$L = \sum_{i=1}^{N} \frac{m_i}{2} \dot{\boldsymbol{q}}_i \cdot \dot{\boldsymbol{q}}_i - Q(\boldsymbol{q}), \tag{15}$$

where $Q(\boldsymbol{q})$ is the system interaction potential function. When a flow field is introduced into the Lagrangian, similarly to Eq. (3), this quantity no longer has the simple form of Eq. (15). It now possesses the form

$$L = \sum_{i=1}^{N} \frac{m_i}{2} \dot{\boldsymbol{q}}_i \cdot \dot{\boldsymbol{q}}_i - Q(\boldsymbol{q}, \dot{\boldsymbol{q}}), \tag{16}$$

where the potential Q now depends not only on $\{\boldsymbol{q}\}$ but also on $\{\dot{\boldsymbol{q}}\}$. The reader should pause here to understand fully this point because it is the most important one of this article. In the original derivations of NEMD algorithms, even though the Lagrangian was never explicitly considered, it was implicitly taken as possessing the form of (15) rather than the more appropriate (some might say 'correct') form of (16).

For the problem at hand, $Q = V(\boldsymbol{q}) + Z(\boldsymbol{q}, \dot{\boldsymbol{q}})$, where $Z = \sum_{i=1}^{N} m_i \boldsymbol{q}_i \dot{\boldsymbol{q}}_i : \boldsymbol{\nabla u}$. Nevertheless, Lagrange's equations of motion, as derived from Hamilton's principle of least action [16,19], remain invariant of form:

$$\frac{\partial L}{\partial \boldsymbol{q}_i} - \frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial L}{\partial \dot{\boldsymbol{q}}_i} \right) = 0. \tag{17}$$

The corresponding Hamiltonian problem is obtained by taking the Legendre transformation of the Lagrangian, thus defining $\{\boldsymbol{p}'\}$ as

$$\boldsymbol{p}_i' \equiv \frac{\partial L}{\partial \dot{\boldsymbol{q}}_i} = m_i \dot{\boldsymbol{q}}_i - \frac{\partial Z}{\partial \dot{\boldsymbol{q}}_i}. \tag{18}$$

Consequently,

$$\boldsymbol{p}_i' = \boldsymbol{p}_i - m_i \boldsymbol{q}_i \cdot \boldsymbol{\nabla u}, \tag{19}$$

which is the transformation of Eq. (13). The Hamiltonian is then given by

$$H'(\boldsymbol{q}', \boldsymbol{p}') = \sum_{i=1}^{N} \frac{1}{m_i} \boldsymbol{p}_i' \cdot \boldsymbol{p}_i - L\left(\boldsymbol{q}, \frac{\boldsymbol{p}}{m}\right). \tag{20}$$

Solving Eq. (19) for $\{\boldsymbol{p}\}$ and inserting the result in the above expression (along with $\{\boldsymbol{q}\}=\{\boldsymbol{q}'\}$) gives the Hamiltonian of Eq. (3) with V' given by Eq. (14). It is thus now clear why the transformation of Eq. (13) must be performed in order to obtain the proper Poisson bracket for the system dynamics. It is also clear that the bracket of Eq. (6) is not consistent with the Hamiltonian of Eq. (3) in the non-canonical representation described above, and cannot be expected to generate the proper system dynamics when the system is expressed in terms of non-canonical variables. Hence, the DOLLS algorithm, written in terms of non-canonical variables, is *not completely Hamiltonian*, although it does still possess a conserved quantity, Eq. (3). What we mean by this is that, although derivable from a Poisson bracket of canonical Hamiltonian form, the DOLLS algorithm is not a *complete* Hamiltonian problem because the connection with the underlying Lagrangian problem, via a Legendre transformation, has been severed, as previously explained. This probably explains why it encounters difficulties at high strain rates, and definitely explains why it produces a phase space distribution function that is non-canonical in the coordinates. (Indeed, Hamilton, Jacobi, Poisson, and their contemporaries might not have considered the DOLLS algorithm as being Hamiltonian at all, since it bears no underlying Lagrangian connection. Neither do the present authors. Although it may be possible to express a set of evolution equations in the form of Hamilton's canonical equations of motion (4), it is debatable whether or not this should be sufficient reason to label the system as 'Hamiltonian.' However, in order to avoid unrest, we make the distinction of a 'completely Hamiltonian' system, as defined above.)

Let us proceed by transforming the canonical Poisson bracket of Eq. (11) to its non-canonical counterpart using the transformation of Eq. (13). This can be accomplished with the mappings

$$\begin{aligned}
\frac{\partial F}{\partial \boldsymbol{q}_i} &= \frac{\partial F'}{\partial \boldsymbol{p}_i'} \cdot \frac{\partial \boldsymbol{p}_i'}{\partial \boldsymbol{q}_i} + \frac{\partial F'}{\partial \boldsymbol{q}_i'} \cdot \frac{\partial \boldsymbol{q}_i'}{\partial \boldsymbol{q}_i} = -m_i \boldsymbol{\nabla u} \cdot \frac{\partial F'}{\partial \boldsymbol{p}_i'} + \frac{\partial F'}{\partial \boldsymbol{q}_i'}, \\
\frac{\partial F}{\partial \boldsymbol{p}_i} &= \frac{\partial F'}{\partial \boldsymbol{p}_i'} \cdot \frac{\partial \boldsymbol{p}_i'}{\partial \boldsymbol{p}_i} + \frac{\partial F'}{\partial \boldsymbol{q}_i'} \cdot \frac{\partial \boldsymbol{q}_i'}{\partial \boldsymbol{p}_i} = \frac{\partial F'}{\partial \boldsymbol{p}_i'},
\end{aligned} \tag{21}$$

and similarly for H. Substituting these mappings into the canonical Poisson bracket of Eq. (11), one obtains the non-canonical Poisson bracket

$$\{F', H'\} = \sum_{i=1}^{N} \left[\frac{\partial F'}{\partial \boldsymbol{q}_i'} \cdot \frac{\partial H'}{\partial \boldsymbol{p}_i'} - \frac{\partial H'}{\partial \boldsymbol{q}_i'} \cdot \frac{\partial F'}{\partial \boldsymbol{p}_i'} - m_i \boldsymbol{\nabla u} : \left(\frac{\partial H'}{\partial \boldsymbol{p}_i'} \frac{\partial F'}{\partial \boldsymbol{p}_i'} - \frac{\partial F'}{\partial \boldsymbol{p}_i'} \frac{\partial H'}{\partial \boldsymbol{p}_i'} \right) \right]. \tag{22}$$

This expression is bilinear, antisymmetric, and satisfies the Jacobi identity. Although it is not necessary for a non-canonical Poisson bracket to produce an incompressible phase space in the non-canonical variables [18], this one does so. A more intuitively enlightening re-expression of this bracket can be written using the vorticity, $\boldsymbol{w} \equiv \boldsymbol{\nabla} \times \boldsymbol{u}$, as

$$\{F'H'\} = \sum_{i=1}^{N} \left[\frac{\partial F'}{\partial \boldsymbol{q}'_i} \cdot \frac{\partial H'}{\partial \boldsymbol{p}'_i} - \frac{\partial H'}{\partial \boldsymbol{q}'_i} \cdot \frac{\partial F'}{\partial \boldsymbol{p}'_i} - m_i \boldsymbol{w} \cdot \left(\frac{\partial H'}{\partial \boldsymbol{p}'_i} \times \frac{\partial F'}{\partial \boldsymbol{p}'_i} \right) \right]. \tag{23}$$

This form more clearly demonstrates the antisymmetry of the bracket and the close relationship of the algorithm to the local fluid rotation. The evolution equations for the non-canonical variables can now be written down taking H' as Eqs. (3) and (14):

$$\dot{\boldsymbol{q}}'_i = \frac{\boldsymbol{p}'_i}{m_i} + \boldsymbol{q}'_i \cdot \boldsymbol{\nabla} \boldsymbol{u}, \qquad \dot{\boldsymbol{p}}'_i = \hat{\boldsymbol{F}}'_i - \boldsymbol{p}'_i \cdot \boldsymbol{\nabla} \boldsymbol{u}, \tag{24}$$

where

$$\hat{\boldsymbol{F}}'_i \equiv \boldsymbol{F}_i - m_i \boldsymbol{q}'_i \cdot \boldsymbol{\nabla} \boldsymbol{u} \cdot \boldsymbol{\nabla} \boldsymbol{u} = -\frac{\partial V(\boldsymbol{q}')}{\partial \boldsymbol{q}'_i} - m_i \boldsymbol{q}'_i \cdot \boldsymbol{\nabla} \boldsymbol{u} \cdot \boldsymbol{\nabla} \boldsymbol{u}. \tag{25}$$

Note that $\hat{\boldsymbol{F}}'_i$ is not equivalent to $-\partial V'(\boldsymbol{q}')/\partial \boldsymbol{q}'_i$. It is quite remarkable that the DOLLS Hamiltonian, Eq. (3), actually leads to a set of equations which is almost identical to the SLLOD equations! However, from Eqs. (24) and (25), it is evident that there is a correction to the traditional SLLOD equations which can dominate the system response at high strain rates but effectively disappear at low ones. One must wonder, then, how the SLLOD equations can give an exact description of shear flow at arbitrarily high strain rates [14]. The answer is that for a shear flow field, only one component of $\boldsymbol{\nabla} \boldsymbol{u}$ is non-zero, say $\nabla_2 u_1$. For this flow field, the quadratic term vanishes and one is left with $\hat{\boldsymbol{F}}'_i = -\partial V(\boldsymbol{q}')/\partial \boldsymbol{q}'_i$, thus producing exactly the traditional form of the SLLOD equations for shear flow. However, for extensional or mixed flow fields, this quadratic contribution is non-vanishing, and must be included in the momenta equations in order to obtain a Hamiltonian set of evolution equations.

As mentioned in Section 1, Tuckerman et al. [15] have proposed a conserved quantity for the thermostatted SLLOD equations by incorporating an additional variable into the system description. Such a device (the additional variable) now appears unnecessary, but shows up in their analysis as a factor which essentially mimics the effects of the non-canonical transformation proposed herein. Note that the same quadratic term as the one appearing above was also necessary in [15] to provide a conserved quantity for the thermostatted system. Thus, we have derived the algorithm of [15] by an independent and more logical methodology without the need of an additional dynamic variable.

This demonstrates that the SLLOD equations for shear flow *are Hamiltonian*, in contrast to the usual assertion in the literature, but that the variables of the problem must be interpreted as non-canonical ones. The non-canonical Hamiltonian of Eqs. (3) and (14) is a conserved quantity for the system for a general flow field. Also, H' leads directly to the distribution function,

$$f \sim \exp\left(-\frac{1}{k_B T} \left[\sum_{i=1}^{N} \frac{1}{2m_i} (\boldsymbol{p}'_i + m_i \boldsymbol{q}'_i \cdot \boldsymbol{\nabla} \boldsymbol{u})^2 + V(\boldsymbol{q}') \right] \right). \tag{26}$$

Notice that this distribution is not exactly the same as the one of Eq. (9), since in that expression one finds $V'(\boldsymbol{q}')$ instead of $V(\boldsymbol{q}')$. However, in prior work the $V'(\boldsymbol{q}')$ in Eq. (9) has always been equivalent to $V(\boldsymbol{q}')$ since the variables $\{\boldsymbol{q}'\}$ and $\{\boldsymbol{p}'\}$ were taken as the canonical sets $\{\boldsymbol{q}\}$ and $\{\boldsymbol{p}\}$, thus producing, ironically, the correct result!

Now let us examine the implications of choosing a different non-canonical transformation than the one of Eq. (13), say

$$\boldsymbol{p}_i \to \boldsymbol{p}_i' + m_i \boldsymbol{\nabla u} \cdot \boldsymbol{q}_i', \qquad \boldsymbol{q}_i \to \boldsymbol{q}_i'. \tag{27}$$

In this case, the non-canonical Hamiltonian is

$$H'(\boldsymbol{q}', \boldsymbol{p}') = \sum_{i=1}^{N} \left(\frac{1}{2m_i} \boldsymbol{p}_i' \cdot \boldsymbol{p}_i' + \boldsymbol{p}_i' \boldsymbol{q}_i' : \boldsymbol{\nabla u} \right) + V'(\boldsymbol{q}'), \tag{28}$$

where

$$V'(\boldsymbol{q}') = V(\boldsymbol{q}') + \sum_{i=1}^{N} \frac{m_i}{2} (\boldsymbol{\nabla u} \cdot \boldsymbol{q}_i')^2. \tag{29}$$

A similar mapping to that of Eq. (21) leads to another non-canonical Poisson bracket,

$$\{F', H'\} = \sum_{i=1}^{N} \left[\frac{\partial F'}{\partial \boldsymbol{q}_i'} \cdot \frac{\partial H'}{\partial \boldsymbol{p}_i'} - \frac{\partial H'}{\partial \boldsymbol{q}_i'} \cdot \frac{\partial F'}{\partial \boldsymbol{p}_i'} - m_i \boldsymbol{\nabla u} : \left(\frac{\partial F'}{\partial \boldsymbol{p}_i'} \frac{\partial H'}{\partial \boldsymbol{p}_i'} - \frac{\partial H'}{\partial \boldsymbol{p}_i'} \frac{\partial F'}{\partial \boldsymbol{p}_i'} \right) \right]. \tag{30}$$

This bracket is bilinear, antisymmetric, and satisfies the Jacobi identity. It also results in an incompressible phase space. The corresponding equations of motion are

$$\dot{\boldsymbol{q}}_i' = \frac{\boldsymbol{p}_i'}{m_i} + \boldsymbol{\nabla} u \cdot \boldsymbol{q}_i', \qquad \dot{\boldsymbol{p}}_i = \hat{\boldsymbol{F}}_i' - \boldsymbol{\nabla u} \cdot \boldsymbol{p}_i', \tag{31}$$

where

$$\hat{\boldsymbol{F}}_i' \equiv \boldsymbol{F}_i - m_i \boldsymbol{\nabla u} \cdot \boldsymbol{\nabla u} \cdot \boldsymbol{q}_i', = -\frac{\partial V(\boldsymbol{q}_i')}{\partial \boldsymbol{q}_i'} - m_i \boldsymbol{\nabla u} \cdot \boldsymbol{\nabla u} \cdot \boldsymbol{q}_i'. \tag{32}$$

Again, note that $\hat{\boldsymbol{F}}_i' \neq -\partial V'(\boldsymbol{q}_i')/\partial \boldsymbol{q}_i'$. This set of equations is similar to the DOLLS equations except for two points. The first is that again there is a quadratic correction to the force vector. The second is that the evolution equations for the coordinates in Eq. (31) involve the transpose of $\boldsymbol{\nabla u}$ as compared to Eq. (5). Hence, the above system of equations represents an alternate Hamiltonian algorithm for NEMD simulations. Again, the quadratic correction to the force vector vanishes for shear flows. Furthermore, since H' is a conserved quantity for this system, the distribution function is given by

$$f \sim \exp\left(-\frac{1}{k_B T} \left[\sum_{i=1}^{N} \frac{1}{2m_i} (\boldsymbol{p}_i' + m_i \boldsymbol{\nabla u} \cdot \boldsymbol{q}_i')^2 + V(\boldsymbol{q}') \right] \right), \tag{33}$$

which is canonical in both momenta and coordinates. However, in the case of the transformation of Eq. (27), one lacks a clear physical interpretation, as was available for the prior transformation, Eq. (13). This might explain why such an algorithm has not found any applications in NEMD computations to date.

5. Summary

In this article, we began by pointing out numerous advantages that could be gained by using a non-canonical Poisson bracket to express the reversible system dynamics of materials. Examples were reviewed where these advantages helped uncover new insights regarding dynamical models. After this review, we examined non-canonical variable transformations, and in so doing have demonstrated that the DOLLS tensor algorithm of NEMD simulations is not completely Hamiltonian since its inherent variables should be interpreted as non-canonical. This is so because the effective potential function in the DOLLS Hamiltonian depends on the particle momenta as well as coordinates. Hence the canonical form of Hamilton's equations, used in the DOLLS derivation involving canonical variables, is not necessarily the most appropriate choice for describing the system dynamics, as indicated by the algorithm's poor performance at high strain rates and its non-canonical distribution function. In contrast to popular belief, the SLLOD equations for shear flows are Hamiltonian once the variables are interpreted as being non-canonical. For general flow fields, the SLLOD momentum equations must each be supplemented by a term which is quadratic in the strain rate, although this quadratic term vanishes for pure shear flows. An alternate set of Hamiltonian evolution equations in terms of non-canonical variables was developed which is similar in spirit to the DOLLS equations, but lacking a thorough physical justification. Both algorithms then produce local equilibrium distribution functions which are canonical in both the particle momenta and coordinates.

6. A clear, concise, memorizable, penetrant overview of the main message

In order to guarantee that a computational algorithm possesses all of the desired properties for NEMD simulations, one should proceed in the derivation via a *completely Hamiltonian technique*, such as is defined and described in this article.

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