

# An atomistic approach to general equation for the nonequilibrium reversible–irreversible coupling

Juan José de Pablo<sup>a,\*</sup>, Hans Christian Öttinger<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering and Rheology Research Center, University of Wisconsin, Madison, WI 53706, USA

<sup>b</sup> ETH Zürich, Department of Materials, Institute of Polymers, and Swiss F.I.T Rheocenter, CH-8092 Zürich, Switzerland

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## Abstract

Focusing on the atomistic approach to the general equation for the nonequilibrium reversible–irreversible coupling (GENERIC) framework of nonequilibrium thermodynamics, we first summarize the atomistic expressions for the inputs of this framework as previously derived by standard projection-operator methods. We then review to what extent GENERIC can be derived from atomistic principles. In the context of hydrodynamics, we illustrate how one can actually evaluate the atomistic expressions. This example shows what steps are involved in such calculations, and in which direction the formalism needs to be generalized in order to obtain a powerful tool for atomistic calculations for nonequilibrium systems of practical importance. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Within the general equation for the nonequilibrium reversible–irreversible coupling (GENERIC) framework, the time-evolution of any isolated thermodynamic system is given in the form

$$\frac{dx}{dt} = L(x) \cdot \frac{\delta E(x)}{\delta x} + M(x) \cdot \frac{\delta S(x)}{\delta x}, \quad (1)$$

where  $x$  represents a set of independent state variables required for a complete description of a given nonequilibrium system and ‘ $\cdot$ ’ denotes the standard scalar product. In this framework of nonequilibrium thermodynamics, the functionals  $E$  and  $S$  represent the total energy and entropy expressed in terms of the state variables  $x$ , and  $L$  and  $M$  are certain matrices. The two contributions to the time-evolution of  $x$  generated by the energy  $E$  and the entropy  $S$  in Eq. (1) are called the reversible and irreversible contributions, respectively. Unless  $x$  contains all the particle momenta and positions, we refer to a coarse-grained

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\* Corresponding author. Tel.: +1-608-262-7727; fax: +1-608-262-5434.

E-mail address: depablo@engr.wisc.edu (J.J. de Pablo).

description of the system of interest. As  $x$  typically contains position-dependent fields, such as local mass, momentum and energy densities, the state variables are usually labeled by continuous (position) labels in addition to discrete ones. A matrix multiplication, often referred to as the application of a linear operator, hence implies not only summations over discrete labels but also integrations over continuous labels, and  $\delta/\delta x$  typically implies functional, rather than partial derivatives. The compact notation and the physical significance of all the GENERIC building blocks should become entirely clear in the subsequent sections, when the formalism is applied to Hamilton's equations of motion and to hydrodynamics.

The properties of the GENERIC building blocks  $E$ ,  $S$ ,  $L$  and  $M$ , which will be discussed from an atomistic perspective in detail below, were originally deduced by considering the compatibility of two levels of description [1] and by studying a number of specific examples [2]. These properties constitute the basis for the predictive power of nonequilibrium thermodynamics.

There exists an alternative formulation of Eq. (1) in terms of brackets rather than operators. More precisely, if one introduces the Poisson bracket associated with the operator  $L(x)$ ,

$$\{A, B\} = \frac{\delta A}{\delta x} \cdot L(x) \cdot \frac{\delta B}{\delta x}, \quad (2)$$

and the dissipative bracket associated with  $M(x)$ ,

$$[A, B] = \frac{\delta A}{\delta x} \cdot M(x) \cdot \frac{\delta B}{\delta x}, \quad (3)$$

for arbitrary functionals  $A, B$  of the state variables  $x$ , then Eq. (1) can be rewritten in the equivalent form

$$\frac{dA}{dt} = \{A, E\} + [A, S], \quad (4)$$

where, again,  $A$  is an arbitrary functional of the state variables  $x$ . While the operator and bracket formulations are fully equivalent, in discussing the various properties of the GENERIC building blocks it may be advantageous to work with one or the other representation.

The key innovation in the GENERIC framework is the use of two separate generators for the reversible and irreversible dynamics. This innovation is of crucial importance when treating systems without local equilibrium states, such as systems described by Boltzmann's kinetic equation [3]. That example also serves to illustrate that, in spite of the linear appearance of the fundamental equation (1), the formalism is not limited to the linear response regime. The unrestricted functional dependence of  $L(x)$  and  $M(x)$  on  $x$  rather allows for the description of systems far from equilibrium (it is the fully nonlinear Boltzmann equation that can be treated, not only its linearization). While nonequilibrium dynamics had traditionally been expressed in terms of a single generator [4], the two-generator idea, which leaves more flexibility in the choice of variables, allows us not only to treat systems without a local temperature variable, but also to formulate the properties of the building blocks in an elegant, symmetric way.

Before we focus on the atomistic approach to GENERIC we give a brief review of the work on relations to other formalisms and new applications. The relationship between GENERIC and the single-generator bracket formalism originally proposed by Grmela [5,6] and further developed by Beris and Edwards [4] was studied in particular detail [2,7,8]. The single-generator bracket formalism was identified as a special case of GENERIC, where its double-generator concept is more powerful because it can handle

systems without a global or local temperature variable. Knowing that the bracket formalism is a special case of GENERIC, the entire wealth of insights and results compiled for the bracket formalism [4] can immediately be taken over. In particular, the classical theory of linear irreversible thermodynamics is established as a special case of GENERIC.

The relationship between GENERIC and the matrix model of Jongschaap et al. [9] is important because the matrix model was designed for describing driven systems, whereas the former framework is formulated for isolated systems. A separation of a subsystem and its environment is necessary in order to obtain the equations of the matrix model from GENERIC [10]. The comparison of GENERIC to the modern formulation of classical irreversible thermodynamics developed by Muschik et al. [11] shows that one of the degeneracy requirements of GENERIC has a counterpart in what is known as Liu's technique, which plays an important role in constructing admissible equations in the context of classical nonequilibrium thermodynamics based on balance equations. Finally, comments on the relationship between rational thermodynamics and GENERIC can be found in [12].

A number of new results has been produced by the GENERIC formulation of nonequilibrium thermodynamics. We here mention only the new insights into reptation models without independent alignment and with anisotropic tube cross-sections, convective constraint release and chain stretching [13–16], an analysis of the pom–pom model of multiply branched polymers [17], a modification of the Doi–Ohta model for multiphase flow [18], an analysis of equations for colloidal suspensions [19], and new ways of producing equations for discrete hydrodynamics [20]. Moreover, the applicability of GENERIC to relativistic systems has been established. Covariant hydrodynamic equations of the GENERIC form were proposed [21,22], even a generally covariant version of the formalism was developed [23], and the implications for cosmological models were explored [24]. This list is incomplete; a more systematic review of relationships and applications can be found in [25].

In this paper, we focus on the atomistic approach to GENERIC. We summarize the atomistic expressions for the building blocks  $E$ ,  $S$ ,  $L$  and  $M$ . These expressions are the counterpart of the formulas for thermodynamic potentials in terms of partition functions in equilibrium thermodynamics; they, therefore, are of great importance for practical applications of nonequilibrium thermodynamics. We discuss in detail which properties of  $E$ ,  $S$ ,  $L$  and  $M$  can be derived rigorously or motivated heuristically from the atomistic expressions. In other words, we review to what extent GENERIC can be derived from atomistic principles, where the assumption of a wide separation of time scales between the slow thermodynamic variables  $x$  and the fast, eliminated variables needs to be made. In the context of hydrodynamics, we illustrate how one can actually evaluate the atomistic expressions for the GENERIC building blocks. This example shows how exceedingly lengthy such calculations are even for simple systems, and in which direction the formalism needs to be generalized in order to obtain a powerful tool for atomistic calculations for nonequilibrium systems of practical importance.

## 2. Atomistic expressions for $E$ , $S$ , $L$ and $M$

Atomistic expressions for the building blocks  $E$ ,  $S$ ,  $L$  and  $M$  were previously derived by projection-operator techniques [26]. The standard tool of projection-operators (see, for example, [27,28]) was used in a microcanonical variant of the form used in [29]. Since all the details of the projection-operator derivation are worked out in [26,29], here we only need to compile the final atomistic expressions. An alternative approach to coarse-graining is discussed in this issue [30].

The starting-point for classical atomistic calculations is the purely reversible, classical time-evolution equation

$$\frac{dz}{dt} = L_0 \cdot \frac{\delta E_0(z)}{\delta z}, \quad (5)$$

which represents Hamilton's equations of motion for the  $6N$  position coordinates and momenta of all the  $N$  particles in a system,  $z=(\mathbf{r}_i, \mathbf{p}_i)$ ,  $i=1, \dots, N$ ; here  $E_0(z)$  is the atomistic Hamiltonian, and the antisymmetric matrix  $L_0$  (defining the canonical Poisson bracket of classical mechanics) does not depend on  $z$ . In view of the discrete nature of the state variables, for Hamilton's equations of motion, the  $\delta$  symbol actually indicates partial rather than functional differentiations.

The relevant thermodynamic variables  $x$  of the coarse-grained description can be obtained as phase space functions  $\Pi$  from the atomistic variables  $z$ , that is,  $x=\Pi(z)$ . It is crucial for the application of the projection-operator method that a clear separation of time scales exists: the time-evolution of  $x$  (and all functions of  $x$ ) is assumed to be much slower than that of all the other variables in the system. With this assumption, one obtains the following expressions for the GENERIC building blocks, which can be made plausible even without resorting to a rather formal projection-operator derivation. If, in a given problem, there is no separation of time scales then one cannot expect to find a consistent coarse-grained description of the problem.

### 2.1. Energy

In the GENERIC approach it is assumed that the total energy of the system  $E$  can be expressed in terms of the relevant state variables  $x$  or, in equations,

$$E(x) = E(\Pi(z)) = E_0(z). \quad (6)$$

If a phase space function is constant on the inverse images of the coarse-grained configurations, as expressed in Eq. (6), then we call it available on the coarse-grained level. Since the total energy must be available on any level of description, the energy of a coarse-grained state  $x$  can thus be obtained from any atomistic configuration consistent with  $x$ .

### 2.2. Entropy

In the microcanonical setting of the projection-operator derivation of GENERIC, the entropy is obtained by assigning equal probabilities to all atomistic configurations and counting the configurations consistent with a given thermodynamic state  $x$ ,

$$S(x) = k_B \ln \int \delta(\Pi(z) - x) dz. \quad (7)$$

Eq. (7) corresponds to a natural generalization of the Gibbs entropy formula from equilibrium thermodynamics.

There is, however, a fundamental problem with the application of Eq. (7). If one uses the state variables  $x'$  instead of  $x$ , where we assume that the transformation is one-to-one so that all states are labeled equivalently by  $x$  or  $x'$ , then one obtains

$$S'(x') = S(x(x')) + k_B \ln \left| \frac{\partial x(x')}{\partial x'} \right|. \quad (8)$$

The surprising term involving the logarithm of the Jacobian indicates a problem with the proper counting of states. While an overall rescaling of volume elements in the coarse-grained state space would only lead to an irrelevant constant contribution to the entropy, local nonuniformities in the parametrization of the coarse-grained state space could lead to difficulties. If a proper reference parametrization,  $x_{\text{ref}}$  of the coarse-grained state space is known, one should actually change the entropy definition (7) into

$$S(x) = k_B \left\{ \ln \left[ \int \delta(\Pi(z) - x) dz \right] - \ln \left| \frac{\partial x_{\text{ref}}(x)}{\partial x} \right| \right\}, \quad (9)$$

so that one obtains the more natural transformation law

$$S'(x') = S(x(x')). \quad (10)$$

We will return to this problem of *correct counting* several times in this article. Heuristically, the problem can be seen as follows: for a proper counting of atomistic states one needs to assign a certain volume in phase space to the submanifold associated with a given thermodynamic state or, in other words, one needs to assign a certain thickness to the submanifold in order to obtain a nonzero measure for it. The natural idea of a uniform thickness, however, is not invariant under nonlinear transformations. Actually, the same problem occurs in the special case of equilibrium thermodynamics. In the microcanonical approach to equilibrium thermodynamics, however, one typically assigns a thickness by specifying a fixed ‘energy window’ while keeping the other extensive variables at fixed values, which corresponds to selecting reference variables. As at equilibrium, this correct counting problem can be avoided by using a generalized canonical instead of microcanonical approach [31].

It should be noted that it is important to know the functional form of the entropy in terms of the chosen state variables  $x$ , and that the entropy defined in Eqs. (7) and (9) depends on the level of coarse-graining. The more atomistic configurations are mapped into a thermodynamic state, the larger is the entropy, so that an increasing amount of entropy occurs in any step of coarse-graining (there is no entropy on the atomistic level).

### 2.3. Poisson operator

In the atomistic expression for the Poisson operator or matrix,

$$L(x) = \exp \left\{ -\frac{S(x)}{k_B} \right\} \int \frac{\delta \Pi(z)}{\delta z} \cdot L_0 \cdot \frac{\delta \Pi(z)}{\delta z} \delta(\Pi(z) - x) dz, \quad (11)$$

the matrix  $L_0$  is to be contracted from both sides with the  $z$  in the denominator of the transformation matrix  $\delta \Pi(z)/\delta z$ , which maps the Poisson operator from the atomistic configuration space to the coarse-grained state space. The integral involving the  $\delta$  function divided by the total number of states corresponds to an average over all atomistic states  $z$  consistent with the coarse-grained state  $x$ .

### 2.4. Friction matrix

The friction matrix  $M(x)$  is obtained as,

$$M(x) = \frac{1}{k_B} \exp \left\{ -\frac{S(x)}{k_B} \right\} \int_0^\tau dt \delta(\Pi(z) - x) [\dot{x}_0(z) - \dot{x}_1(x)] [\dot{x}_0(z(t)) - \dot{x}_1(x)] dz, \quad (12)$$

where

$$\dot{x}_0(z) = \frac{\delta \Pi(z)}{\delta z} \cdot L_0 \cdot \frac{\delta E_0(z)}{\delta z}, \quad (13)$$

$$\dot{x}_1(x) = \exp \left\{ -\frac{S(x)}{k_B} \right\} \int \dot{x}_0(z) \delta(\Pi(z) - x) dz, \quad (14)$$

and the trajectory  $z(t)$  in Eq. (12) is the solution of the time-evolution equation (5) with the initial condition  $z(0)=z$ , and  $\tau$  is a time scale large enough for the time-integral to converge and small enough for  $x$  to be still considered as independent of time (such an intermediate time scale must exist as a consequence of the previously mentioned assumption of clearly separated time scales for slow and fast variables).

While  $\dot{x}_0$  is a state variable that varies on a rapid, atomistic time scale,  $\dot{x}_1$  depends only on  $x=\Pi(z)$  and hence has a much slower time-evolution. Thus,  $\dot{x}_0 - \dot{x}_1$  describes fluctuation effects. Eq. (12), which holds for general nonequilibrium systems, even in coarse-grained configurations  $x$  far away from equilibrium, has the form of the Green–Kubo expressions for transport coefficients known from linear response theory. Here we did not extend the time integral in Eq. (12) to infinity because then it would be necessary to consider the slow time-evolution of  $\dot{x}_1$  in the second factor.

The explicit occurrence of the intermediate time scale  $\tau$  in Eq. (12) points to an important limitation of the coarse-grained theory: one cannot apply the coarse-grained theory in any meaningful way to dynamic phenomena that occur on time scales of order  $\tau$  or shorter. The relaxation phenomena described by  $M$  must be associated with relaxation times larger than  $\tau$ . The transport phenomena appropriately described by  $M$  must take place on time scales large compared to  $\tau$  because otherwise the time integrals for the corresponding transport coefficients would not even be converged. For example, the momentum balance equation should not be applied at flow rates as high as  $1/\tau$ , where one should keep in mind that  $\tau$  is supposed to be large compared to the time scale of atomic motions. After these comments, frequently made statements like ‘even simple fluids are non-Newtonian if the shear rate is sufficiently high’ must be considered as highly questionable for structureless fluids; if inverse shear rates of the order of atomic time scales are considered, then the concept of the transport coefficient viscosity is no longer meaningful, and one cannot really speak about a shear-rate dependent viscosity. For structureless fluids, the breakdown of the concept of viscosity occurs at shear rates that are not sufficiently high for seeing any non-Newtonian behavior.

The identity

$$\dot{x}_1(x) = L(x) \cdot \frac{\delta E(x)}{\delta x}, \quad (15)$$

which is obtained from Eqs. (6) and (11) and the chain rule, shows that  $\dot{x}_1(x)$  describes the reversible contribution to the slow motion. It might be useful in employing simulation techniques (e.g. molecular dynamics) for determining  $M$  from Eq. (12).

## 2.5. Clarifying notation

It should be noted that  $\Pi(z)$  occurs in two fundamentally different ways in the atomistic expressions (6), (7), (11) and (12). If  $\Pi(z)$  occurs inside a  $\delta$  function, it corresponds to the counting of or averaging over atomistic configurations consistent with the coarse-grained variables  $x$ . All other occurrences of

$\Pi(z)$  describe the transformation from atomistic to coarse-grained quantities for a given atomistic state  $z$ . In the context of hydrodynamics, we shall realize that the latter type of occurrence can be handled by straightforward analytical calculations, whereas the proper counting and averaging is a difficult problem to be approached by heuristic arguments or numerical calculations. For a clearer separation of these two different types of occurrence of  $\Pi(z)$ , we introduce the following notation for the averaging over all atomistic configurations  $z$  consistent with the coarse-grained variables  $x$ ,

$$\langle \cdots \rangle_x = \exp \left\{ -\frac{S(x)}{k_B} \right\} \int \cdots \delta(\Pi(z) - x) dz. \quad (16)$$

Note that this average has no effect on quantities that depend on  $z$  only through  $x=\Pi(z)$ . With this definition, Eqs. (11) and (12) can be rewritten as

$$L(x) = \left\langle \frac{\delta \Pi(z)}{\delta z} \cdot L_0 \cdot \frac{\delta \Pi(z)}{\delta z} \right\rangle_x \quad (17)$$

and

$$M(x) = \frac{1}{k_B} \left\langle \int_0^\tau dt [\dot{x}_0(z) - \dot{x}_1(x)] [\dot{x}_0(z(t)) - \dot{x}_1(x)] \right\rangle_x, \quad (18)$$

where

$$\dot{x}_1(x) = \langle \dot{x}_0(z) \rangle_x = L(x) \cdot \frac{\delta E(x)}{\delta x}. \quad (19)$$

Eq. (17) emphasizes the above-mentioned fact that  $L(x)$  is obtained by transformation of  $L_0$ , where the necessity of averaging is a consequence of the fact that the transformation is not one-to-one but coarse-graining. Also, the Green–Kubo formula behind Eq. (18) becomes evident from the appearance of that expression.

## 2.6. Some comments

In the fundamental Eq. (1) for the state variables  $x$ , fluctuations are not taken into account. As a major advantage, the projection-operator formalism employed here actually provides equations for these fluctuations because one works on the level of configurational distribution functions,  $f(x)$ , in order to capture the slow dynamics of all functions of  $x$  [26,29]. The precise form of the fluctuations is given by a *fluctuation-dissipation theorem* of the second kind [32]. The proper description of fluctuations requires the correct counting of atomistic configurations, which was already identified as a problem in connection with the atomistic expression for the entropy. It should also be noted that, in view of the transformation rules for stochastic differential equations [33], nonlinear transformations of the time-evolution equations with noise can lead to additional systematic effects (of order  $k_B$ ).

The atomistic expressions for the GENERIC building blocks given in this section are derived within a generalized microcanonical ensemble. As in equilibrium thermodynamics, the microcanonical ensemble is most natural for establishing the fundamental recipes of statistical mechanics, but certainly not the most convenient for practical calculations. For example, studying the ideal gas, i.e. the simplest possible system, the conservation of energy in the microcanonical ensemble couples all particles in the combinatorial evaluation of the entropy. By going to the canonical ensemble, one achieves the physically natural and much simpler situation that only decoupled integrals for each of the noninteracting particles need to be

evaluated. Analogous simplifications are needed also in nonequilibrium statistical mechanics, and the analysis presented in this paper is actually meant to initiate future work in that direction.

The above expressions for the GENERIC building blocks were derived from Hamilton's equations of motion, that is, from the most microscopic classical level of description. The building blocks for any two levels of description of a system were related in Section 4 of [26]. A derivation of the fundamental Eq. (1) from a quantum mechanical description of the atomistic system has been offered recently [31]. However, as this derivation is based on a generalized canonical ensemble, it does not provide a proper description of statistical fluctuations.

### 3. Properties of generic building blocks

We can now discuss some implications of the atomistic expressions (6), (7), (17) and (18) for the building blocks of GENERIC. It turns out that most of the properties formulated in the original papers [1,2] can be derived from these expressions, and the remaining ones can be made plausible.

#### 3.1. Transformation behavior

Having discussed the transformation behavior of the entropy in the preceding section, we next determine how the remaining building blocks of GENERIC transform under a one-to-one transformation  $x \rightarrow x'$ . From Eq. (6) we immediately obtain

$$E'(x') = E(x(x')). \quad (20)$$

One can verify that the operators  $L$  and  $M$  transform as follows:

$$L'(x') = \frac{\partial x'}{\partial x} \cdot L(x(x')) \cdot \frac{\partial x'}{\partial x}, \quad (21)$$

$$M'(x') = \frac{\partial x'}{\partial x} \cdot M(x(x')) \cdot \frac{\partial x'}{\partial x}, \quad (22)$$

where  $L'$ ,  $M'$  are the Poisson operators and the friction matrix in the coordinates  $x'$ ,  $\partial x'/\partial x$  is the transformation matrix (here to be considered as a function of  $x'$ ), and  $L$  and  $M$  are to be contracted from both sides with the  $x$  in the denominator of the transformation matrix. To derive Eq. (22), one needs to assume that the coarse-grained configurations do not change on the time scale  $\tau$ . As an example of a transformation  $x \rightarrow x'$  we mention the transition from hydrodynamics in the energy representation to hydrodynamics in the entropy representation (see [2]). The knowledge of the transformation behavior is very useful because, in many cases, it may be convenient to use different sets of variables in developing the reversible and irreversible contributions to the time-evolution, so that a transformation is required before the results can be added. Transformations can be very useful also for simplifying the check of the Jacobi identity to be discussed below.

#### 3.2. Symmetry properties

In the GENERIC framework [1,2], it is required that the matrix  $L$  be antisymmetric, and that  $M$  be symmetric. These symmetry properties are important for the construction of  $L$  and  $M$ , and hence for the



predictive power of the formalism. According to Eq. (17), the antisymmetry of  $L$  follows immediately from the antisymmetry of  $L_0$ .

The formal expression (18) for  $M$  is symmetric, provided that the atomistic time-evolution is reversible, that is, for  $\dot{x}_0(z(-t)) = -\dot{x}_0(z(t))$  (the minus sign for quantities with even parity needs to be introduced because we consider the rate of change of these quantities, which have the opposite parity). In order to recognize the symmetry of  $M$  one should keep in mind that, on a time scale  $\tau$  short compared to the slow time-evolution, an atomistic configuration  $z(t)$  is consistent with a coarse-grained state variable  $x$  if, and only if, the initial condition  $z$  is consistent with  $x$ . For state variables with odd parity under time reversal, that is, for components with  $\dot{x}_0(z(-t)) = \dot{x}_0(z(t))$ , coupled to components with even parity, we find antisymmetric contributions to the friction matrix  $M$  so that, in general, we expect  $M$  to be *Onsager–Casimir symmetric*. Note that these (anti)symmetry properties are only found when the sign of those components of  $x$  corresponding to quantities with odd parity is reversed. For example, for hydrodynamics, the coupling term between momentum density or velocity (odd parity) and internal energy (even parity) is expected to be antisymmetric; however, these components are proportional to the velocity, so that they can be classified as symmetric when the sign of the velocity in the  $M$  matrix is not reversed [2]. For a related discussion, a recent article [34] is recommended.

In order to avoid problems with antisymmetric contributions to  $M$  corresponding to irreversible dynamics without entropy production, in previous papers we assumed that a sufficiently detailed level of description has been chosen. An odd parity under time reversal of a certain quantity contributing to the friction matrix can always be changed into an even parity by going to a more detailed inertial description, because the time derivative of a quantity with odd parity possesses even parity, and friction affects the highest order derivatives (see the problems caused by the transition from an inertial to a noninertial level of description discussed in [35]; the slip effect expressed in the Schowalter derivative is a typical example of an antisymmetric contribution to the friction matrix  $M$ ). In conclusion, the Onsager–Casimir symmetry of  $M$  can be traced back to the symmetry of the time correlation function in Eq. (18).

The original derivation of Onsager’s reciprocity relations had been for the relaxation of spatially homogeneous deviations from equilibrium. The linear-irreversible-thermodynamics postulation of analogous reciprocity relations for the constitutive equations relating the fluxes to the gradients of the intensive variables responsible for such fluxes has repeatedly been criticized in the literature [36,37]. Since the friction matrix  $M$  unifies the description of relaxation and transport processes, the derivation of  $M$  by the projection-operator method and the study of its symmetry properties under time reversal actually generalizes Onsager’s work from relaxation to transport processes. Furthermore, assumptions about being close to equilibrium need not be made in the projection-operator derivation of  $M$ ; in particular, a temperature variable does not arise in the microcanonical version of this derivation. This is in contrast to the canonical formulation of [29], where a global temperature variable occurs in the entropy expression and in the averages (16) (suggesting that one is close to a global equilibrium state).

### 3.3. Degeneracy requirements

In the GENERIC framework, Eq. (1) is supplemented by the complementary degeneracy requirements

$$L(x) \cdot \frac{\delta S(x)}{\delta x} = 0 \quad (23)$$

and

$$M(x) \cdot \frac{\delta E(x)}{\delta x} = 0. \quad (24)$$

The requirement that the gradient  $\delta S/\delta x$  be in the null-space of  $L$  in Eq. (23) expresses the reversible nature of the  $L$ -contribution to the dynamics: the functional form of the entropy is such that it cannot be affected by the operator generating the reversible dynamics. The requirement that the gradient  $\delta E/\delta x$  be in the null-space of  $M$  in Eq. (24) implies the conservation of the total energy by the  $M$ -contribution to the dynamics.

The degeneracy requirement (24) is an immediate consequence of the identity  $\dot{x}_0(z) \cdot \delta E(x)/\delta x = 0$  for  $x=\Pi(z)$  which, in turn, follows from Eqs. (6) and (13) and the anti-symmetry of  $L_0$ . In favor of the degeneracy requirement (23), we can offer the following heuristic argument (a more rigorous derivation can be given within a generalized canonical approach [31]): since the projection should be such that, on microscopic time scales,  $\Pi(z)=\Pi(z')$  if and only if  $\Pi(z(t))=\Pi(z'(t))$ , and since the microscopic time-evolution preserves volume in phase space, we expect

$$\frac{dS(\Pi(z))}{dt} = -\frac{\delta E_0(z)}{\delta z} L_0 \frac{\delta S(\Pi(z))}{\delta z} = 0. \quad (25)$$

This leads to

$$\frac{\delta E(x)}{\delta x} L(x) \frac{\delta S(x)}{\delta x} = 0, \quad (26)$$

for arbitrary functionals  $E(x)$  and hence to Eq. (23). Note that, if the degeneracy requirement (23) is fulfilled for some choice of coarse-grained state variables  $x$ , the transformation law (8) for the entropy would lead to a violation of the degeneracy requirement in the transformed state variable  $x'$  by a term of order  $k_B$ . The degeneracy requirement (23) may thus be considered as a necessary condition for the correct counting in the macroscopic state space. We finally mention that the degeneracy requirement (23) has important implications, such as the stress tensor expressions resulting from the time-evolution of the structural variables for complex fluids.

### 3.4. Positive-semidefiniteness of $M$

The positive-semidefinite character of the matrix  $M$ , which can be thought of as the second law of nonequilibrium thermodynamics, is not immediately obvious from Eq. (18). However, the Fokker–Planck equation for the configurational distribution function in the coarse-grained state space derived by the projection-operator method [26] is meaningful if, and only if,  $M$  is positive-semidefinite; a violation of this condition would lead to physically unacceptable properties of the fluctuating forces. Again, the clear separation of time scales is crucial for the argumentation because it allows us to treat the eliminated degrees of freedom as noise having the natural physical properties of fluctuations.

### 3.5. Jacobi identity

The Jacobi identity for the bracket associated with the  $L$ -matrix [1,2],

$$\{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0, \quad (27)$$

for arbitrary functionals  $A$ ,  $B$ , and  $C$ , has not yet been derived from the atomistic expression for  $L$ . The mathematical problem is that the  $L$  operator (17) and hence the Poisson bracket  $\{\cdot, \cdot\}$  defined in Eq. (2) involve an average  $\langle \cdots \rangle_x$ , so that the nested brackets in the Jacobi identity imply products of averages, which cannot be obtained by averaging the Jacobi identity for the canonical Poisson bracket given by  $L_0$ . The Jacobi identity imposes severe restrictions on the formulation of convection mechanisms [13–15] and of moment closure approximations [38].

Since the Jacobi identity, which expresses the time-structure invariance of the reversible dynamics [38], is of great importance for the predictive power of the GENERIC framework, we here sketch the arguments that might eventually lead to a rigorous proof of this identity on the coarse-grained level. In [2], it was explained that the construction of an  $L$  operator satisfying the Jacobi identity can be based on the representation of space transformation on the state space of a nonequilibrium system. If, for a given infinitesimal generator of a space transformation  $\tilde{\mathbf{v}}(\mathbf{r})$ , we introduce the weighted total momentum

$$G_0(z) = \sum_{i=1}^N \mathbf{p}_i \cdot \tilde{\mathbf{v}}(\mathbf{r}_i), \quad (28)$$

in the atomistic state space, then  $-L_0(\delta G_0/\delta z)$  for particle  $i$  has the space and velocity components  $\tilde{\mathbf{v}}(\mathbf{r}_i)$  and  $-\nabla \tilde{\mathbf{v}}(\mathbf{r}_i) \cdot \mathbf{p}_i$ , respectively, which describe the translation of the particle position and the lower-convected rotation of the particle momentum under space transformations. If  $L_0$  had not been known in advance, this representation of space transformations could have been used to construct it because the same Poisson operator is used for generating local space transformations from  $G_0$  and for generating reversible time translations from  $E_0$ .

We next make the crucial assumption that the quantity  $G_0$  defined in Eq. (28) is available on the coarse-grained level, that is,

$$G_0(z) = G(\Pi(z)) = G(x). \quad (29)$$

This assumption for the weighted total momentum, which is analogous to Eq. (6) for the total energy, is natural for all complex fluids because we expect the momentum density  $\mathbf{u}(\mathbf{r})$  to be among the state variables  $x$ , so that

$$G(x) = \int \mathbf{u}(\mathbf{r}) \cdot \tilde{\mathbf{v}}(\mathbf{r}) d^3r. \quad (30)$$

With the assumption (29), Eq. (17) leads to

$$L(x) \cdot \frac{\delta G(x)}{\delta x} = \left\langle \frac{\delta \Pi(z)}{\delta z} \cdot L_0 \cdot \frac{\delta G_0(z)}{\delta z} \right\rangle_x. \quad (31)$$

Eq. (31) implies that the atomistic expression (17) for the  $L$  operator occurs in generating the space transformations on the coarse-grained state space that are naturally obtained by projecting and averaging the action of space transformations on the atomistic configuration space. Assuming that any  $L$  operator occurring in generating a group of space transformations from  $G$  on a coarse-grained state space satisfies the Jacobi identity (we are not aware of a rigorous group theoretical proof of this plausible assumption), the rather mild condition of the availability of the weighted total momentum on a coarse-grained level of description would lead to an atomistic derivation of the Jacobi identity.

Furthermore, Eq. (31) shows how coarse-grained Poisson operators can be obtained from atomistic simulations. In particular, no dynamic simulations are needed for constructing  $L$  operators. One rather needs to generate an ensemble of atomistic configurations consistent with a coarse-grained state  $x$ ;  $L$  is then constructed from an ensemble average of the action of space transformations on the atomistic configurations. In several important cases, one can directly find the coarse-grained  $L$  operators or Poisson brackets (see, e.g. [39–41], Chapter 5 of [4], and below).

### 3.6. Further properties

If the projection  $x=\Pi(z)$  from the atomistic configuration space to a coarse-grained state space is known, the formulas (6), (7), (17) and (18) give unique expressions for the building blocks of GENERIC. However, if one is working on the coarse-grained level only, for a given set of time-evolution equations, not even the separation of reversible and irreversible contributions is unique. For example, for given  $E$ ,  $S$ ,  $L$ ,  $M$ , and an arbitrary constant  $c$ , one can replace  $L$  and  $M$  by [42]

$$L' = (1 - c)L, \quad (32)$$

$$M' = \left( \frac{\delta S}{\delta x} \cdot M \cdot \frac{\delta S}{\delta x} \right)^{-1} \left( cL \cdot \frac{\delta E}{\delta x} + M \cdot \frac{\delta S}{\delta x} \right) \left( -c \frac{\delta E}{\delta x} \cdot L + \frac{\delta S}{\delta x} \cdot M \right), \quad (33)$$

without changing the time-evolution equation or the GENERIC structure. In particular, one can always choose a vanishing Poisson operator, and one can always construct a friction matrix  $M'$  of rank one that accounts for the irreversible time-evolution.

If one would like to obtain a unique formulation on the coarse-grained level, further properties of the GENERIC building blocks need to be found. In view of the above remarks, one would presumably need to formulate a minimum property for the irreversible contribution in order to uniquely separate the reversible and irreversible contributions. Further conditions for splitting each of these contributions into two building blocks might be necessary. For example, the rank of the friction matrix should be related to the number of transport and relaxation processes described by it, and to the scalar, vector, or tensor nature of the corresponding state variables.

## 4. Example: from atomistic to hydrodynamic level

We would now like to find equations of motion for coarse-grained variables  $x$  at the level of hydrodynamics. We explicitly construct such variables as phase-space functions  $\Pi$  of the atomistic variables  $z$ , i.e.  $x=\Pi(z)$ . In the discussion that follows, we use a notation in which we keep track of the  $N$  particles through a Latin subscript, of the three Cartesian components through a Greek subscript, and of the positions and momenta through a column vector, so that all  $6N$  degrees of freedom of  $z$  in the atomistic description are resolved explicitly.

The transition from the atomistic level to the level of hydrodynamics illustrates a quite general paradox: we start with a finite number of degrees of freedom, namely the particle positions and momenta, and we end up with the infinite number of degrees of freedom of the hydrodynamic fields. The coarse-grained level of description thus has more degrees of freedom than the atomistic one. Of course, there is a natural way out of this paradox, which would occur for any coarse-grained description using field variables. These

fields should be assumed to be sufficiently smooth, and one should not try to resolve any information below a characteristic length scale  $l$ , which clearly should be larger than the characteristic inter-particle distance. Quite surprisingly, the analysis of simulation data shows that the hydrodynamic description works successfully down to lengths  $l$  of only a few, say five, inter-particle distances [43]. We here assume that the range of particle interactions is smaller than  $l$ . Once one realizes that the hydrodynamic fields can be represented by a discretization on the length scale  $l$ , it becomes clear that the coarse-grained level of description indeed uses fewer state variables than the atomistic description, as anticipated.

In conclusion, the occurrence of a scale  $l$  points to another limitation of the coarse-grained level of description, in addition to the one indicated by the time scale  $\tau$ . While the latter limitation applies to all coarse-grained theories, the former one applies only to the coarse-grained theories that employ fields as state variables. Significant variations of the fields on the length scale  $l$  are clearly meaningless. For example, significant differences in velocity should not occur on the length scale  $l$ , and hence certainly not on the atomistic length scale.

#### 4.1. Projection to hydrodynamic variables

The projected fields to be used on the hydrodynamic level are given by the mass density, the momentum density, and the internal energy density field, respectively, i.e.  $x=(\rho(\mathbf{r}), \mathbf{u}(\mathbf{r}), \epsilon(\mathbf{r}))$ . In the smoothed representation employed here, the density field is defined by

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

where  $m_i$  is the mass of particle  $i$ , and where  $f$  is a smooth, differentiable function whose precise identity need not be specified here. One can think of  $f$  as a smoothed  $\delta$  function, where the range over which  $f$  differs from zero is of the order of  $l$ , and thus small compared to macroscopic distances. The sum in Eq. (34) runs over all  $N$  particles in the system. Similarly, the momentum density field is defined as

$$\mathbf{u}(\mathbf{r}) = \sum_{i=1}^N \mathbf{p}_i f(\mathbf{r}_i - \mathbf{r}). \quad (35)$$

The velocity field  $\mathbf{v}(\mathbf{r})$  is defined by  $\mathbf{u}(\mathbf{r}) = \rho(\mathbf{r})\mathbf{v}(\mathbf{r})$ . Finally, the internal energy density field is defined by

$$\epsilon(\mathbf{r}) = \sum_{i=1}^N \left( \frac{1}{2} m_i \left[ \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right]^2 + \frac{1}{2} \sum_{j=1}^N \phi_{ij}(\mathbf{r}_{ij}) \right) f(\mathbf{r}_i - \mathbf{r}), \quad (36)$$

where  $\phi_{ij}$  is a function of  $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$  (it is convenient to set  $\phi_{ii} = 0$ ). For the forces acting on particle  $i$  as a result of interactions with other particles, we write

$$\mathbf{F}_i = \sum_{j=1}^N \mathbf{F}_{ij} = - \sum_{j=1}^N \frac{\partial}{\partial \mathbf{r}_i} \phi_{ij}. \quad (37)$$

Eqs. (34)–(36) define the abstract projection  $\Pi$  of the previous sections for the transition from the atomistic to the hydrodynamic level of description.

For the forthcoming analysis of the transformation from the atomistic to the hydrodynamic description, it is also necessary to determine the derivatives of these fields with respect to the atomistic variables  $\mathbf{z}$ . We find the following derivatives of the density field,

$$\frac{\delta \rho(\mathbf{r})}{\delta z_{i\beta}} = \begin{pmatrix} -m_i \frac{\partial}{\partial r_\beta} f(\mathbf{r}_i - \mathbf{r}) \\ 0 \end{pmatrix}, \quad (38)$$

the momentum density field,

$$\frac{\delta u_\gamma(\mathbf{r})}{\delta z_{i\beta}} = \begin{pmatrix} -p i_\gamma \frac{\partial}{\partial r_\beta} f(\mathbf{r}_i - \mathbf{r}) \\ \delta_{\gamma\beta} f(\mathbf{r}_i - \mathbf{r}) \end{pmatrix}, \quad (39)$$

and the internal energy density field,

$$\frac{\delta \epsilon(\mathbf{r})}{\delta z_{i\beta}} = \begin{pmatrix} -\frac{1}{2} m_i \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right)^2 \frac{\partial}{\partial r_\beta} f(\mathbf{r}_i - \mathbf{r}) - \frac{1}{2} \sum_j \phi_{ij} \frac{\partial}{\partial r_\beta} f(\mathbf{r}_i - \mathbf{r}) \\ + \frac{1}{2} \sum_j f(\mathbf{r}_j - \mathbf{r}) \frac{\partial}{\partial r_{i\beta}} \phi_{ji} + \frac{1}{2} \sum_j f(\mathbf{r}_i - \mathbf{r}) \frac{\partial}{\partial r_{i\beta}} \phi_{ij} \\ \left( \frac{p_{i\beta}}{m_i} - v_\beta(\mathbf{r}) \right) f(\mathbf{r}_i - \mathbf{r}) \end{pmatrix}. \quad (40)$$

Note that also  $\mathbf{v}(\mathbf{r})$  depends on  $\mathbf{z}$ ; however, the corresponding contribution to Eq. (40) vanishes.

#### 4.2. Energy and entropy

With these definitions, it is now a straightforward calculation to show that the total energy  $E_0$ ,

$$E_0 = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{i,j=1}^N \phi_{ij}(\mathbf{r}_{ij}) \quad (41)$$

is available on the hydrodynamic level,

$$E = \int \left( \frac{1}{2} \frac{\mathbf{u}(\mathbf{r})^2}{\rho(\mathbf{r})} + \epsilon(\mathbf{r}) \right) d^3 r. \quad (42)$$

The availability of energy on the hydrodynamic level is a direct consequence of the fact that we introduced the internal energy as all the energy not associated with the overall flow, that is, as the sum of the kinetic energy of all motions with respect to the center-of-mass velocity and of all the interaction energies. We expect the introduction of a macroscopically unresolved internal energy to be a useful step in more general statistical treatments of the flow behavior of complex fluids.

As indicated before, the construction of the total entropy  $S$  by counting states is much less straightforward; at this point we can only offer heuristic arguments. We expect to obtain the total entropy by adding up the contributions of small boxes, say of the size of order  $l$ . Due to the coarse-graining assumption, there

are many particles in each box, while there are no significant variations of velocity over its dimensions. If we count the number of states in a reference system moving with the local fluid velocity, then we recover the equilibrium result. It is hence natural to write the total entropy as

$$S = \int s(\rho(\mathbf{r}), \epsilon(\mathbf{r})) d^3r, \quad (43)$$

where the entropy density  $s$  is the same function of the mass density  $\rho$  and the internal energy density  $\epsilon$  as at equilibrium. In particular, we can hence introduce the local equilibrium values of the temperature, the chemical potential and the pressure in the same way as in equilibrium thermodynamics. The correct counting problem for the entropy is simply reduced to the corresponding problem at equilibrium.

### 4.3. Poisson operator

We now evaluate the Poisson operator (17) by means of the expressions (34)–(36) for  $\delta\Pi/\delta z$ . We arrange our results in a  $3 \times 3$  matrix for the mass, momentum, and internal energy components. The mass–mass and energy–energy components of the antisymmetric Poisson operator vanish immediately for symmetry reasons. The remaining components are discussed below.

#### 4.3.1. Mass–energy

The component of the Poisson operator (17) associated with the mass density  $\rho(\mathbf{r})$  and the internal energy density  $\epsilon(\mathbf{r}')$  is given by

$$L_{\rho\epsilon} = \left\langle \sum_{i,i',\beta,\beta'} \begin{pmatrix} -m_i \frac{\partial}{\partial r_\beta} f(\mathbf{r}_i - \mathbf{r}) \\ 0 \end{pmatrix} \delta_{ii'} \delta_{\beta\beta'} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} \cdots \\ \left( \frac{p_{i'\beta'}}{m_{i'}} - v_{\beta'}(\mathbf{r}') \right) f(\mathbf{r}_{i'} - \mathbf{r}') \end{pmatrix} \right\rangle_x, \quad (44)$$

which can be simplified to

$$L_{\rho\epsilon} = - \left\langle \sum_{i,\beta} (p_{i\beta} - m_i v_\beta(\mathbf{r}')) f(\mathbf{r}_i - \mathbf{r}') \frac{\partial}{\partial r_\beta} f(\mathbf{r}_i - \mathbf{r}) \right\rangle_x. \quad (45)$$

We now need to employ an argument that is crucial for the successful atomistic evaluation of the Poisson operator of hydrodynamics: as  $f$  is a smoothed version of the  $\delta$  function, smeared out over dimensions  $l$  small compared to macroscopic distances, we can consider the functions  $f$  in Eq. (45) as  $\delta$  functions to obtain

$$L_{\rho\epsilon} = - \left\langle \sum_{i,\beta} (p_{i\beta} - m_i v_\beta(\mathbf{r}')) f(\mathbf{r}_i - \mathbf{r}') \frac{\partial}{\partial r_\beta} \delta(\mathbf{r}' - \mathbf{r}) \right\rangle_x. \quad (46)$$

By means of Eqs. (34) and (35), we then find that  $L_{\rho\epsilon}$  vanishes.

#### 4.3.2. Mass–momentum

The component of the Poisson operator (17) associated with the mass density  $\rho(\mathbf{r})$  and the momentum density  $\mathbf{u}(\mathbf{r}')$  is given by

$$L_{\rho u} = - \left\langle \sum_{i=1}^N m_i f(\mathbf{r}_i - \mathbf{r}') \frac{\partial}{\partial \mathbf{r}} f(\mathbf{r}_i - \mathbf{r}) \right\rangle_x. \quad (47)$$

By the arguments previously used for the mass–energy component we obtain

$$L_{\rho u} = - \left\langle \sum_{i=1}^N m_i f(\mathbf{r}_i - \mathbf{r}') \right\rangle_x \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}} = \rho(\mathbf{r}') \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} . \quad (48)$$

The occurrence of the mass density, which is among the coarse-grained state variables  $x$ , in the pointed brackets makes the averaging unnecessary. This result coincides with the one given in Eq. (21) of [2].

#### 4.3.3. Momentum–momentum

When we apply Eq. (17) to the components of the momentum density field we find

$$L_{uu} = \left\langle \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} \sum_{i=1}^N \mathbf{p}_i f(\mathbf{r}_i - \mathbf{r}) - \sum_{i=1}^N \mathbf{p}_i f(\mathbf{r}_i - \mathbf{r}') \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}} \right\rangle_x. \quad (49)$$

After substitution of Eq. (35), again only coarse-grained quantities occur in the average, and we find

$$L_{uu} = \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} \mathbf{u}(\mathbf{r}) + \mathbf{u}(\mathbf{r}') \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} . \quad (50)$$

#### 4.3.4. Energy–momentum

For the energy–momentum component of the  $L$  matrix we write

$$\begin{aligned} L_{\epsilon u} = & \epsilon(\mathbf{r}') \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} + \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} \cdot \left\langle \sum_{i=1}^N \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right) \mathbf{p}_i f(\mathbf{r}_i - \mathbf{r}) \right\rangle_x \\ & - \left\langle \frac{1}{2} \sum_{i,j=1}^N [f(\mathbf{r}_i - \mathbf{r}) + f(\mathbf{r}_j - \mathbf{r})] \mathbf{F}_{ij} f(\mathbf{r}_i - \mathbf{r}') \right\rangle_x. \end{aligned} \quad (51)$$

In terms of the fluctuating kinetic stress contribution,

$$\boldsymbol{\sigma}_k(\mathbf{r}, z) = \sum_{i=1}^N m_i \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right) \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right) f(\mathbf{r}_i - \mathbf{r}), \quad (52)$$

one of the building blocks occurring in Eq. (51) can be rewritten as

$$\left\langle \sum_{i=1}^N \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right) \mathbf{p}_i f(\mathbf{r}_i - \mathbf{r}) \right\rangle_x = \langle \boldsymbol{\sigma}_k(\mathbf{r}, z) \rangle_x. \quad (53)$$

By exchanging summation indices, the last term in Eq. (51) can be rewritten as

$$\sum_{i,j=1}^N [f(\mathbf{r}_i - \mathbf{r}) + f(\mathbf{r}_j - \mathbf{r})] \mathbf{F}_{ij} f(\mathbf{r}_i - \mathbf{r}') = \sum_{i,j=1}^N f(\mathbf{r}_i - \mathbf{r}) \mathbf{F}_{ij} [f(\mathbf{r}_i - \mathbf{r}') - f(\mathbf{r}_j - \mathbf{r}')]. \quad (54)$$



Assuming a short range of particle interactions, we further develop the term  $f(\mathbf{r}_i - \mathbf{r}') - f(\mathbf{r}_j - \mathbf{r}')$  by means of a first-order Taylor expansion, which gives

$$\sum_{i,j=1}^N f(\mathbf{r}_i - \mathbf{r}) \mathbf{F}_{ij} [f(\mathbf{r}_i - \mathbf{r}') - f(\mathbf{r}_j - \mathbf{r}')] = \frac{\partial}{\partial \mathbf{r}'} \cdot \sum_{i,j=1}^N \mathbf{r}_{ij} \mathbf{F}_{ij} f(\mathbf{r}_i - \mathbf{r}) f(\mathbf{r}_i - \mathbf{r}'). \quad (55)$$

After introducing the direct interaction contribution to the stress tensor,

$$\boldsymbol{\sigma}_\phi(\mathbf{r}, z) = -\frac{1}{2} \sum_{i,j=1}^N \mathbf{r}_{ij} \mathbf{F}_{ij} f(\mathbf{r}_i - \mathbf{r}), \quad (56)$$

and the total stress tensor

$$\boldsymbol{\sigma}(\mathbf{r}, z) = \boldsymbol{\sigma}_\kappa(\mathbf{r}, z) + \boldsymbol{\sigma}_\phi(\mathbf{r}, z), \quad (57)$$

we obtain the final result

$$L_{\epsilon u} = \epsilon(\mathbf{r}') \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} + \frac{\partial \delta(\mathbf{r} - \mathbf{r}')}{\partial \mathbf{r}'} \cdot \langle \boldsymbol{\sigma}(\mathbf{r}, z) \rangle_x. \quad (58)$$

#### 4.3.5. General form of $L$

After including all terms derived in previous sections, and taking into account the antisymmetry requirement, the matrix  $L(x)$  of hydrodynamics is found to be of the form

$$L = \begin{pmatrix} 0 & \rho(\mathbf{r}') \frac{\partial \delta}{\partial \mathbf{r}'} & 0 \\ \rho(\mathbf{r}) \frac{\partial \delta}{\partial \mathbf{r}'} & \mathbf{u}(\mathbf{r}') \frac{\partial \delta}{\partial \mathbf{r}'} + \frac{\partial \delta}{\partial \mathbf{r}'} \mathbf{u}(\mathbf{r}) & \epsilon(\mathbf{r}) \frac{\partial \delta}{\partial \mathbf{r}'} + \frac{\partial \delta}{\partial \mathbf{r}'} \cdot \langle \boldsymbol{\sigma}(\mathbf{r}', z) \rangle_x \\ 0 & \epsilon(\mathbf{r}') \frac{\partial \delta}{\partial \mathbf{r}'} + \frac{\partial \delta}{\partial \mathbf{r}'} \cdot \langle \boldsymbol{\sigma}(\mathbf{r}, z) \rangle_x & 0 \end{pmatrix}, \quad (59)$$

where the symbol  $\delta$  implies  $\delta(\mathbf{r} - \mathbf{r}')$ . This expression coincides with the one given in Eq. (21) of [2], provided that  $\langle \boldsymbol{\sigma}(\mathbf{r}, z) \rangle_x = p(\mathbf{r}) \mathbf{1}$ , which actually follows from the degeneracy requirement (23) generally derived from the atomistic expressions.

One might consider using a higher-order Taylor expansion in Eq. (55) for constructing an improved theory. Then, however, higher-order derivatives would occur in  $L_{u\epsilon}$  and the degeneracy requirement (23) might not be satisfied for the entropy expression obtained from the local-equilibrium assumption.

One can alternatively derive the  $L$  operator of hydrodynamics from Eq. (31). After using Eq. (28) to rewrite that equation in the general form

$$L \cdot \frac{\delta G}{\delta x} = \left\langle \sum_{i,\beta,\beta'} \frac{\delta \Pi}{\delta z_{i,\beta}} \cdot \begin{pmatrix} \delta_{\beta\beta'} \\ -p_{i\beta'} \frac{\partial}{\partial \mathbf{r}_{i\beta}} \end{pmatrix} \tilde{v}_{\beta'} \right\rangle_x, \quad (60)$$

the second column of the  $L$  operator can actually be calculated more directly after inserting Eqs. (38)–(40).

#### 4.4. Rapidly fluctuating quantities

As a first step towards evaluating the friction matrix, we next consider the rapidly fluctuating quantities introduced in Eq. (13).

##### 4.4.1. Mass

For the density, we write

$$\dot{\rho}_0(\mathbf{r}, z) = \sum_{i,i',\beta,\beta'} \begin{pmatrix} -m_i \frac{\partial}{\partial r_\beta} f(\mathbf{r}_i - \mathbf{r}) \\ 0 \end{pmatrix} \delta_{i'i} \delta_{\beta\beta'} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} -F_{i'\beta'} \\ \frac{p_{i'\beta'}}{m_{i'}} \end{pmatrix}, \quad (61)$$

which, according to the definition (35), can be rewritten as

$$\dot{\rho}_0(\mathbf{r}, z) = - \sum_{i=1}^N \frac{\partial}{\partial \mathbf{r}} \cdot f(\mathbf{r}_i - \mathbf{r}) \mathbf{p}_i = - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}(\mathbf{r}) \rho(\mathbf{r}). \quad (62)$$

Note that  $\dot{\rho}_0(\mathbf{r}, z)$  turns out to depend only on the slow variables  $x$  so that we obtain

$$\Delta \dot{\rho}_0(\mathbf{r}, z) = \dot{\rho}_0(\mathbf{r}, z) - \langle \dot{\rho}_0(\mathbf{r}, z) \rangle_x = 0. \quad (63)$$

##### 4.4.2. Momentum

Similarly, for the rapid fluctuations of the momentum density we obtain

$$\dot{\mathbf{u}}_0(\mathbf{r}, z) = - \frac{\partial}{\partial \mathbf{r}} \cdot \sum_{i=1}^N \frac{1}{m_i} \mathbf{p}_i \mathbf{p}_i f(\mathbf{r}_i - \mathbf{r}) + \sum_{i=1}^N \mathbf{F}_i(\mathbf{r}_i - \mathbf{r}). \quad (64)$$

This equation can be cast in a more convenient form by replacing  $\mathbf{p}_i$  in the first term by  $m_i[(\mathbf{p}_i/m_i) - \mathbf{v}(\mathbf{r})]$ , and by including the resulting compensating terms,

$$- \frac{\partial}{\partial \mathbf{r}} \cdot \left[ \sum_{i=1}^N m_i \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v} \right) \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v} \right) f(\mathbf{r}_i - \mathbf{r}) + \sum_{i=1}^N m_i \left( \frac{\mathbf{p}_i}{m_i} \mathbf{v} + \mathbf{v} \frac{\mathbf{p}_i}{m_i} - \mathbf{v} \mathbf{v} \right) f(\mathbf{r}_i - \mathbf{r}) \right]. \quad (65)$$

With Eq. (35), we then obtain after some rearrangements

$$\dot{\mathbf{u}}_0(\mathbf{r}, z) = - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}(\mathbf{r}) \mathbf{u}(\mathbf{r}) - \frac{\partial}{\partial \mathbf{r}} \cdot \boldsymbol{\sigma}_k(\mathbf{r}, z) + \sum_{i=1}^N \mathbf{F}_i f(\mathbf{r}_i - \mathbf{r}). \quad (66)$$

By means of an expansion attributed to Kirkwood, the last term in Eq. (66) can also be expressed as a divergence. Physically such a reformulation is natural because, according to Newton's third law, the interaction forces on the particles balance so that only effects due to small displacements of the order of the range of interaction are left over. If we assume that the potential energy of the system can be decomposed into pair contributions  $\phi_{ij}$ , we can expand the symmetrized expression

$$\sum_{i=1}^N \mathbf{F}_i f(\mathbf{r}_i - \mathbf{r}) = \frac{1}{2} \sum_{i,j=1}^N \mathbf{F}_{ij} [f(\mathbf{r}_i - \mathbf{r}) - f(\mathbf{r}_j - \mathbf{r})], \quad (67)$$

in order to obtain

$$\sum_{i=1}^N \mathbf{F}_i f(\mathbf{r}_i - \mathbf{r}) = -\frac{\partial}{\partial \mathbf{r}} \cdot \boldsymbol{\sigma}_\phi(\mathbf{r}, z). \quad (68)$$

The direct interaction contribution to the stress tensor,  $\boldsymbol{\sigma}_\phi(\mathbf{r}, z)$ , was defined in Eq. (56). We thus obtain the final result

$$\dot{\mathbf{u}}_0(\mathbf{r}, z) = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}(\mathbf{r}) \mathbf{u}(\mathbf{r}) - \frac{\partial}{\partial \mathbf{r}} \cdot \boldsymbol{\sigma}(\mathbf{r}, z). \quad (69)$$

Note that the same stress tensor  $\boldsymbol{\sigma}(\mathbf{r}, z)$ , the average of which previously occurred in the Poisson operator (59), occurs also in the fluctuating momentum. The reason for this is that the state variable  $\epsilon$  describes the nonkinetic part of the total energy, so that the  $\epsilon$  column of the  $L$  operator in Eq. (17) is closely related to the rapidly fluctuating quantity (19).

The first term in Eq. (69) possesses slow dynamics, so that it does not contribute to  $\Delta \dot{\mathbf{u}}_0(\mathbf{r}, z) = \dot{\mathbf{u}}_0(\mathbf{r}, z) - \langle \dot{\mathbf{u}}_0(\mathbf{r}, z) \rangle_x$ . We hence obtain

$$\Delta \dot{\mathbf{u}}_0(\mathbf{r}, z) = -\frac{\partial}{\partial \mathbf{r}} \cdot \Delta \boldsymbol{\sigma}(\mathbf{r}, z), \quad (70)$$

with the following fluctuations in the stress tensor,

$$\Delta \boldsymbol{\sigma}(\mathbf{r}, z) = \boldsymbol{\sigma}(\mathbf{r}, z) - p(\mathbf{r}) \mathbf{1}. \quad (71)$$

#### 4.4.3. Internal energy

For the internal energy, we find

$$\begin{aligned} \dot{\epsilon}_0(\mathbf{r}, z) = & -\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}(\mathbf{r}) \epsilon(\mathbf{r}) - \frac{\partial \mathbf{v}(\mathbf{r})}{\partial \mathbf{r}} : \boldsymbol{\sigma}_k(\mathbf{r}, z) \\ & - \frac{\partial}{\partial \mathbf{r}} \cdot \sum_{i=1}^N \left[ \frac{1}{2} m_i \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right)^2 f(\mathbf{r}_i - \mathbf{r}) + \frac{1}{2} \sum_{j=1}^N \phi_{ij} f(\mathbf{r}_i - \mathbf{r}) \right] \\ & \times \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right) + \frac{1}{2} \sum_{i,j=1}^N [f(\mathbf{r}_i - \mathbf{r}) - f(\mathbf{r}_j - \mathbf{r})] \mathbf{F}_{ij} \cdot \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \cdot \sum_{i=1}^N \mathbf{F}_i f(\mathbf{r}_i - \mathbf{r}). \end{aligned} \quad (72)$$

After another Taylor expansion of  $f(\mathbf{r}_i - \mathbf{r}) - f(\mathbf{r}_j - \mathbf{r})$  and using Eq. (68), we finally obtain

$$\dot{\epsilon}_0(\mathbf{r}, z) = -\frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{v}(\mathbf{r}) \epsilon(\mathbf{r}) - \frac{\partial \mathbf{v}(\mathbf{r})}{\partial \mathbf{r}} : \boldsymbol{\sigma}(\mathbf{r}, z) - \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{j}(\mathbf{r}, z), \quad (73)$$

with the heat-flux vector

$$\begin{aligned} \mathbf{j}(\mathbf{r}, z) = & \sum_{i=1}^N \left[ \frac{1}{2} m_i \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right)^2 f(\mathbf{r}_i - \mathbf{r}) + \frac{1}{2} \sum_{j=1}^N \phi_{ij} f(\mathbf{r}_i - \mathbf{r}) \right] \\ & \times \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right) - \frac{1}{2} \sum_{i,j=1}^N \mathbf{r}_{ij} \mathbf{F}_{ij} f(\mathbf{r}_i - \mathbf{r}) \cdot \left( \frac{\mathbf{p}_i}{m_i} - \mathbf{v}(\mathbf{r}) \right). \end{aligned} \quad (74)$$

The first term in Eq. (73) possesses slow dynamics, so that it does not contribute to  $\Delta\dot{\epsilon}_0(\mathbf{r}, z) = \dot{\epsilon}_0(\mathbf{r}, z) - \langle \dot{\epsilon}_0(\mathbf{r}, z) \rangle_x$ . We find

$$\Delta\dot{\epsilon}_0(\mathbf{r}, z) = -\frac{\partial \mathbf{v}(\mathbf{r})}{\partial \mathbf{r}} : \Delta \boldsymbol{\sigma}(\mathbf{r}, z) - \frac{\partial}{\partial \mathbf{r}} \cdot \Delta \mathbf{j}(\mathbf{r}, z), \quad (75)$$

with the following fluctuations in the heat flux,

$$\Delta \mathbf{j}(\mathbf{r}, z) = \mathbf{j}(\mathbf{r}, z) - \langle \mathbf{j}(\mathbf{r}, z) \rangle_x. \quad (76)$$

#### 4.5. Friction matrix

After incorporating the result (63), we can now write the  $M$  matrix for hydrodynamics in the form

$$M = \frac{1}{k_B} \int_0^\tau \begin{pmatrix} 0 & 0 & 0 \\ 0 & \langle \Delta \dot{\mathbf{u}}_0(\mathbf{r}, z) \Delta \dot{\mathbf{u}}_0(\mathbf{r}', z(t)) \rangle_x & \langle \Delta \dot{\mathbf{u}}_0(\mathbf{r}, z) \Delta \dot{\epsilon}_0(\mathbf{r}', z(t)) \rangle_x \\ 0 & \langle \Delta \dot{\epsilon}_0(\mathbf{r}, z) \Delta \dot{\mathbf{u}}_0(\mathbf{r}', z(t)) \rangle_x & \langle \Delta \dot{\epsilon}_0(\mathbf{r}, z) \Delta \dot{\epsilon}_0(\mathbf{r}', z(t)) \rangle_x \end{pmatrix} dt, \quad (77)$$

where the fluctuations  $\Delta \dot{\mathbf{u}}_0(\mathbf{r}, z)$  and  $\Delta \dot{\epsilon}_0(\mathbf{r}, z)$  are given in terms of the fluctuations of stresses and heat flux by Eqs. (70) and (75). We illustrate the further evaluation of  $M$  for the contribution resulting from the fluctuations in the heat flux,  $\Delta \mathbf{j}(\mathbf{r}, z)$

$$M = \frac{1}{k_B} \left\langle \frac{\partial}{\partial \mathbf{r}'} \frac{\partial}{\partial \mathbf{r}} : \int_0^\tau \Delta \mathbf{j}(\mathbf{r}, z) \Delta \mathbf{j}(\mathbf{r}', z(t)) dt \right\rangle_x. \quad (78)$$

In order to recover the usual result for hydrodynamics (see Eq. (27) of [2]),

$$M_{\epsilon\epsilon}^{(j)} = \frac{\partial}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}'} \lambda T^2 \delta(\mathbf{r} - \mathbf{r}'), \quad (79)$$

where  $\lambda$  is the thermal conductivity, we need to assume that the correlation of the fluctuations in the heat flux vanishes if the distance between  $\mathbf{r}$  and  $\mathbf{r}'$  is large compared to  $l$ , and that the thermal conductivity tensor is isotropic,

$$\frac{1}{k_B T^2} \left\langle \int_0^\tau \int \Delta \mathbf{j}(\mathbf{r}, z) \Delta \mathbf{j}(\mathbf{r}', z(t)) dt d^3 r' \right\rangle_x = \lambda \mathbf{1}. \quad (80)$$

Eq. (80) is the Green–Kubo formula that expresses the thermal conductivity as the integral of time-dependent heat-flux correlations (cf. Eqs. (2.119) and (8.32) of [44] or (6.58) and (6.62) of [45]), which can depend on the hydrodynamic variables (at position  $\mathbf{r}$ ). One could also try to derive nonlocal corrections from Eq. (78) [46], where one must make sure that the higher-order approximations do not violate the degeneracy or positive-semidefiniteness conditions.

One can similarly evaluate the contribution to the  $M$  matrix resulting from  $\Delta \boldsymbol{\sigma}(\mathbf{r}, z)$ , where all the nonzero components of  $M$  in Eq. (77) will be affected. One then finds the Green–Kubo formulas for the shear and bulk viscosities. The contribution resulting from correlations between  $\Delta \boldsymbol{\sigma}(\mathbf{r}, z)$  and  $\Delta \mathbf{j}(\mathbf{r}, z)$  is usually assumed to be zero. This assumption can be justified by the Curie principle, or by symmetry arguments for the odd moments in velocity space.

## 5. Approach to nonequilibrium simulations

An atomistic understanding of specific nonequilibrium systems requires computer simulations. Even in the relatively simple case of hydrodynamics, the reliable evaluation of the transport coefficients, such as the thermal conductivity in Eq. (80), in terms of atomistic interactions requires simulations. We, therefore, offer some general comments on the role of computer simulations in understanding nonequilibrium systems, which hopefully might guide future developments in the field.

Many molecular dynamics simulations (see, e.g. contributions in [47,48]) are similar in spirit to laboratory experiments in the following sense: a certain nonequilibrium situation, such as a flow field, is imposed on an atomistic system, and macroscopic informations, such as stresses, are extracted directly. Traditionally, no attempt has been made to extract the behavior of a complete set of coarse-grained state variables, which then would determine the stresses (of course, finding a set of state variables that allow one the consistent description of a nonequilibrium system is a major challenge).

In contrast, the approach to simulations suggested by the equations and considerations of this paper is focused directly on the coarse-grained description of a system. The choice of state variables and their identification in terms of atomistic quantities (i.e. the definition of the projector) are the fundamental steps of this approach, after which the four building blocks of nonequilibrium thermodynamics,  $E$ ,  $S$ ,  $L$  and  $M$ , are fully determined by explicit atomistic expressions. All kinds of properties of experimental interest are then obtained from the coarse-grained GENERIC description of the system. This approach is, hence, fundamentally different from the usual analysis of specific problems, for example by nonequilibrium molecular dynamics simulations in shear flow.

Focusing on obtaining the building blocks  $E$ ,  $S$ ,  $L$  and  $M$  from simulations has the advantage that, even in approximate representations of the simulation results, the structure of nonequilibrium thermodynamics is respected automatically, including subtle issues such as the ‘second law’. In many cases, an a priori understanding of the system of interest allows one to suggest a certain functional form of the building blocks  $E$ ,  $S$ ,  $L$  and  $M$ , so that only some remaining parameters need to be determined from atomistic simulations. Ideally, atomistic simulations should therefore be targeted on determining the free parameters in well-established, coarse-grained levels of description. This is particularly true when one considers the fact that nonequilibrium molecular dynamics simulations can only be carried out for shear rates that are several orders of magnitude above those realizable in the laboratory, and that typical relaxation times for complex fluids are significantly longer than most simulation times. A sound understanding of the coarse-grained target level is hence the most important prerequisite for the outline simulation strategy. Of course, simulations can also be used to analyze the validity of the assumed target level. This is conceptually different from simulating specific nonequilibrium situations and ‘measuring’ experimentally observable quantities, possibly with the idea of subsequently extracting certain constitutive equations, as is typically done with experimental data.

### 5.1. Energy and entropy

For specific systems, the generators energy and entropy can be evaluated by the same simulation methods established in equilibrium thermodynamics—not surprisingly, in view of the key role played by a combination of just these two quantities at equilibrium. For complex fluids this can be useful because highly efficient Monte-Carlo simulation methods have been developed to sample the configuration space of complex fluids, thereby avoiding the dynamic bottlenecks that prevail in such systems. Since the energy is

usually known on the atomistic level, the evaluation of energy from a representative atomistic configuration is straightforward. Much more difficult is the counting problem involved in finding the entropy from Eq. (7) or (9). For example, Monte-Carlo methods were employed for calculating the entropy [49,50] in the context of polymer crystallization in fiber spinning. In general, it might be much more convenient to pass from the generalized microcanonical ensemble used for the fundamental developments of the previous paper [26] to a generalized canonical ensemble, analogous to the one used in the projection-operator approach to quantum systems [31]. Such a recommendation, however, assumes that at least a local equilibrium temperature can be introduced, so that one can carry out a Legendre transformation, just as in the equilibrium case.

One of the most serious challenges facing nonequilibrium simulations of complex fluids such as polymers is that the relaxation times associated with large-scale conformational transitions (e.g. the decay of the end-to-end distance autocorrelation function) are much longer than the duration of a typical molecular dynamics simulation [51–57]. If the initial configuration of a simulated system is that corresponding to equilibrium, it is therefore unrealistic to expect a conventional molecular dynamics simulation to reach a steady state corresponding to the fully relaxed, nonequilibrium state of the system. This challenge has long been recognized and, in a few isolated instances, researchers have tried to apply Monte-Carlo techniques to sample the configurations of polymeric molecules in homogeneous flow fields. Unfortunately, such efforts have in general been limited to dilute solutions and potential flow fields [58–60]. The attempt to conduct Monte-Carlo, as opposed to molecular dynamics simulations, has been fueled by recent advances in the simulation of complex fluids [61–65]. Some of these advances have led to dramatic improvements in the sampling of the equilibrium configuration space of complex fluids in arbitrary fields and, in some cases, have reduced the computational demands of polymer simulations by several orders of magnitude.

Recently, Mavrantzas and Theodorou [66] have proposed a novel approach in which a condensed, many-molecule system is subject to an orienting field. These authors derive a probability distribution function for a statistical-mechanical ensemble in which such a field is one of the intensive variables; Monte-Carlo simulations are then performed in that ensemble, thereby leading to fully-relaxed, representative samples of the molecules in that ensemble. The rationale for that work is as follows: the authors postulate that, in the presence of a deforming field, the Helmholtz free energy of a system of macromolecules is a function not only of temperature and density, but also of a conformation tensor. In their case, such a tensor is expressed in terms of the end-to-end distance of the molecules. (Note that the molecules studied in [66] are not entangled; a Rouse-like representation of the system is therefore sufficient. As discussed below, an alternative description in terms of long-polymer melt models would have been necessary had the polymers been entangled.) In the language of GENERIC, the relevant thermodynamic variables are therefore temperature, density and a conformation tensor. Having postulated such a list of variables, the tensorial deforming field conjugate to the conformation tensor is identified by means of conventional thermodynamic manipulations. A Legendre transform is subsequently performed to arrive at a convenient thermodynamic potential (the nonequilibrium analog of the Gibbs free energy); the microscopic probability distribution function for the ensemble leading to that potential can then be written as a function of the molecules' spatial coordinates, and efficient Monte-Carlo techniques can be implemented to conduct simulations in that ensemble. While the exact correspondence between the orienting field and particular values of a flow field (e.g. an elongation rate) must necessarily be derived from dynamic simulations [66,67], the work of Mavrantzas and Theodorou is significant in that it constructs a purely thermodynamic framework to generate representative, atomistic configurations of a complex fluid subject to elongation.

The work of Mavrantzas and Theodorou has so far been limited to unentangled macromolecules subject to elongation. It would now be worthwhile to consider the more complex case of entangled polymers, where the coarse-grained description of the system is not as well established as in the unentangled regime, and where the definition of an entanglement itself is nontrivial [68,69]. It would also be worthwhile to consider the use of alternative simulation methodologies, such as the hyper-parallel tempering Monte-Carlo technique, which offer the possibility of calculating directly the free energy of a deformed fluid as a function of deformation [70,71].

## 5.2. Poisson operator and friction matrix

While the Poisson operator  $L$  expresses kinematics, we believe that its evaluation should not require dynamic simulation techniques. A possible evaluation scheme can be based on Eq. (31), which can be implemented as follows. Assume that we have generated an atomistic configuration, and we apply a small space transformation by moving the particles and rotating their momenta. If we evaluate the corresponding change in the coarse-grained variables resulting through the projection from the atomistic space transformation, then Eq. (31) tells us that, by averaging over an ensemble of atomistic configurations consistent with a coarse-grained state, we obtain the action of the space transformation on the coarse-grained state space. Such representations allow us to identify the Poisson operator [2]. If a priori information about the structure of  $L$  is available and only a few parameters are left to be found, one can choose particularly convenient coarse-grained states for determining these parameters, or one can further average Eq. (31). As an example, we mention the determination of the two parameters ( $\alpha$  and  $\beta$ ) occurring in a model for the anisotropic tube cross-sections that arise in the reptation theory for melts of linear polymers [14,15].

The friction matrix  $M$  is the only building block whose determination requires dynamic simulation techniques. If we start on the atomistic level, Eq. (18) (or simplified versions like Eq. (80)) tells us that we need to create an ensemble of atomistic configurations  $z$  consistent with a given coarse-grained state  $x$ . Those configurations  $z$  need to be evolved in time according to Hamilton's equations of motion, and an ensemble average of the integral of the time-dependent correlations must then be evaluated. The time-evolution needs to be followed only over the time scale  $\tau$  on which the coarse-grained nonequilibrium state does not change. Nonequilibrium molecular dynamics simulations should be based on such considerations, or equivalent reformulations. For example, one could imagine the simulation of a very long trajectory in time, for which a certain coarse-grained nonequilibrium state is artificially maintained over many  $\tau$  by some control mechanism in such a way that, over the time interval  $\tau$ , the modification of Hamilton's equations of motion by the control mechanism can be shown to be negligibly small. A perturbation theory of control mechanisms, such as thermostats or methods for imposing velocity gradients, maybe in connection with finite-size scaling analysis, would shed some light on existing schemes in nonequilibrium molecular dynamics. Again, a priori information about the structure of the friction matrix would allow us to choose particularly convenient coarse-grained states for determining the remaining parameters, or to further average Eq. (18). This procedure is similar to the evaluation of model parameters in existing simulations (see, e.g. [67]). If the friction matrix is known to be independent of  $x$ , then equilibrium molecular dynamics simulations are sufficient for determining the dynamic material properties.

If we wish to determine a friction matrix on a coarse-grained level from some intermediate rather than the atomistic level of description, then we need to resort to Brownian dynamics rather than molecular dynamics simulations. The corresponding generalization of Eq. (18) was discussed in Section 4 of [26]. An example of such a situation would be the derivation of constitutive equations for polymeric liquids for

the level of continuum mechanics, based on mechanical polymer models using beads, springs and rods.

The determination of the building blocks  $E$ ,  $S$ ,  $L$  and  $M$  on a suitable coarse-grained target level should not only guide computer simulations but also kinetic theory calculations. By focusing on the building blocks, one can avoid redundant calculations and inconsistent approximations while keeping the full GENERIC structure.

## 6. Conclusions and outlook

After briefly reviewing the GENERIC formalism of nonequilibrium thermodynamics, we have summarized the atomistic expressions for its building blocks  $E$ ,  $S$ ,  $L$  and  $M$ , as previously derived by standard projection-operator methods for a generalized microcanonical ensemble (see the basic formulas (6), (7), (17) and (18)). These expressions are the counterpart of the formulas for thermodynamic potentials in terms of partition functions in equilibrium thermodynamics and, hence, they are of great importance for practical applications of nonequilibrium thermodynamics. Certain ambiguities in the entropy expression have been pointed out. In an attempt to base the GENERIC framework on a separation-of-time-scales assumption, we have discussed in detail which properties of  $E$ ,  $S$ ,  $L$  and  $M$  can be derived rigorously or motivated heuristically from the atomistic expressions. The Onsager–Casimir symmetry of the friction matrix has been discussed in some detail. A full proof of the Jacobi identity, which expresses the time-structure invariance of the reversible dynamics, is still missing, but a promising approach to the problem has been outlined.

In the context of hydrodynamics, we have illustrated how one can actually evaluate the atomistic expressions for the GENERIC building blocks. The limitations of coarse-grained levels with field variables have been elaborated, the role of Taylor expansions has been revealed, and the Green–Kubo formulas for the transport coefficients have been reproduced. Finally, we have offered a number of remarks on desirable simulation procedure for nonequilibrium systems, clearly distinguishing between systematic *coarse-graining by simulation techniques* on the one hand and *computer experiments* on the other hand. In particular, we have pointed out the need for developing proper ensemble techniques, and we have described a promising simulation approach to the determination of Poisson operators based on the coarse-graining of the action of space transformations on the state space (where Eq. (31) is the fundamental starting point).

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