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Irreversible dynamics, Onsager-Casimir symmetry, and an application to turbulence

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Irreversible contributions to the dynamics of nonequilibrium systems can be formulated in terms of dissipative, or irreversible, brackets. We discuss the structure of such irreversible brackets in view of a degeneracy implied by energy conservation, where we consider different types of symmetries of the bracket corresponding to the Onsager and Casimir symmetries of linear irreversible thermodynamics. Slip and turbulence provide important examples of antisymmetric irreversible brackets and offer guidance for the more general modeling of irreversible dynamics without entropy production. Conversely, turbulence modeling could benefit from elucidating thermodynamic structure. The examples suggest constructing antisymmetric irreversible brackets in terms of completely antisymmetric functions of three indices. Irreversible brackets without well-defined symmetry properties can arise for rare events, causing big configurational changes.

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I. INTRODUCTION

An efficient and illuminating way of formulating the dynamics of mixed reversible and irreversible systems is given by the evolution equation [1–3]

$$\frac{dA}{dt} = \{A,E\} + [A,S], \tag{1}$$

where A is an arbitrary element from an algebra of classical observables. The energy E and the entropy S are particular observables from the same algebra. Moreover, the algebra of observables needs to be equipped with a Poisson bracket $\{.,.\}$ and a irreversible bracket $[.,.]$. A Poisson bracket is antisymmetric, has a derivation structure (with a product rule for each argument), and satisfies the Jacobi identity (which expresses the time-structure invariance of this bracket [4]). The structure and properties of Poisson brackets are very well understood (see, for example, Refs. [5–7]). It is the goal of the present paper to offer a thorough discussion of the structure of irreversible brackets, which should support future thermodynamic modeling activities.

The two terms on the right-hand side of Eq. (1) represent the reversible contribution to dynamics generated by the energy by means of a Poisson bracket and the irreversible contribution generated by the entropy via a dissipative or irreversible bracket, respectively. Equation (1) is henceforth referred to as GENERIC ("general equation for the nonequilibrium reversible-irreversible coupling") and may be considered as the fundamental evolution equation of nonequilibrium thermodynamics, going far beyond linear irreversible thermodynamics [8,9]. Our goal for this work can hence be reformulated as a deeper understanding of the structure of irreversible dynamics and the relevant thermodynamic properties.

A. Some details on GENERIC

Classical observables are functions or functionals of the independent variables x chosen to define a nonequilibrium thermodynamic system. The Poisson and irreversible brackets in the fundamental equation (1) can then be expressed in terms of the Poisson and friction matrices L and M, respectively:

$$\{A,B\} = \frac{\delta A}{\delta x} L \frac{\delta B}{\delta x}, \tag{2}$$

and

$$[A,B] = \frac{\delta A}{\delta x} M \frac{\delta B}{\delta x}, \tag{3}$$

where L and M are allowed to depend on x. Because x typically contains position-dependent fields, such as the local mass, momentum, and energy densities of hydrodynamics, the independent variables are usually labeled by continuous (position) labels in addition to discrete ones (labeling the different fields). A matrix multiplication hence implies not only summations over discrete indices but also integrations over continuous labels, and $\delta/\delta x$ typically implies functional rather than partial derivatives. The occurrence of derivatives leads to the derivation character of the brackets defined in Eqs. (2) and (3). The symmetry of the brackets is contained in the symmetry properties of the matrices L and M. Whereas L is always antisymmetric, M is usually assumed to be symmetric. However, much more needs to be said about the symmetry properties of M in the following.

By applying Eq. (1) with the representations (2) and (3) to the independent system variables as observables, we obtain the evolution equation

$$\frac{dx}{dt} = L\frac{\delta E}{\delta x} + M\frac{\delta S}{\delta x}. \tag{4}$$

In the GENERIC framework for isolated systems [1–3], Eq. (4) is supplemented by the complementary degeneracy requirements

$$L\frac{\delta S}{\delta x} = 0, \tag{5}$$

and

$$M\frac{\delta E}{\delta x} = 0, \tag{6}$$

which further clarify the splitting into reversible and irreversible dynamics. The requirement that the entropy gradient $\delta S/\delta x$ is in the null space of L in Eq. (5) expresses the

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reversible nature of the L contribution to the dynamics: the functional form of the entropy is such that it cannot be affected by any operator generating reversible dynamics. The requirement that the energy gradient $\delta E/\delta x$ is in the null space of M in Eq. (6) expresses the conservation of the total energy in a closed system by the M contribution to the dynamics.

By means of the chain rule and the degeneracy requirement (5), we obtain the entropy evolution equation

$$\frac{dS}{dt} = \frac{\delta S}{\delta x} M \frac{\delta S}{\delta x} = [S,S]. \tag{7}$$

By assuming that the matrix M and hence the irreversible bracket is positive semidefinite, we obtain a strong formulation of the second law of beyond-equilibrium thermodynamics. The friction matrix M hence characterizes the irreversible system behavior, typically in terms of transport coefficients and relaxation times. Only the symmetric part of the matrix M contributes to the entropy production (7).

In view of the occurrence of energy and entropy as generators in the fundamental evolution equations (1) and (4), GENERIC may be referred to as a double-generator framework. Also in the single-generator framework of nonequilibrium thermodynamics [10], a dissipation bracket closely related to the dissipative or irreversible bracket of GENERIC occurs. The precise relationship between the single- and double-generator frameworks has been elaborated in several papers [11–13].

The GENERIC evolution equation (4) has been justified by means of the projection-operator formalism [14–19]. The resulting explicit recipe for calculating the friction matrix by statistical mechanics is given by the Green-Kubo formula

$$M_{jk} = \frac{1}{k_{\mathrm{B}}} \int_0^{\tau} \langle [\mathcal{Q} i\mathcal{L}\Pi_k][\mathcal{Q} e^{i\mathcal{L}u} i\mathcal{L}\Pi_j] \rangle_x du, \tag{8}$$

where $\mathcal{L}$ is the Liouville operator, $\mathcal{Q}$ is the projection operator on the fast (or fluctuating) part of a microscopic observable, Π_j is the microscopic observable corresponding to x_j, that is, $\langle \Pi_j \rangle_x = x_j$, and $\langle \ldots \rangle_x$ is the nonequilibrium ensemble average, for example, evaluated with a generalized microcanonical or canonical ensemble characterized by the macroscopic averages x. The observable $\mathcal{Q} i\mathcal{L}\Pi_k$ may be interpreted as the fluctuating part of the time-derivative of Π_k and the Green-Kubo formula hence expresses the matrix M as a time integral of the decaying correlation function of such time derivatives. The Green-Kubo formula gives the only GENERIC building block that involves dynamic properties; the statistical mechanics expressions for E, S, and L involve only static information. Our goal behind investigating the structure of friction matrices can hence be rephrased as the search for a deeper understanding of dynamic system or material properties.

B. Applications

The GENERIC framework has been used to discuss a variety of applications and has revealed a large number of new insights through the thermodynamic modeling approach. A review of these applications has recently been given in Ref. [20]. Because the review article [20] is not easily accessible, we summarize here the most important and some more recent applications. The present discussion of the nature of the irreversible bracket should facilitate future applications.

In addition to many famous applications of linear irreversible thermodynamics, a number of applications of nonlinear irreversible thermodynamics have been compiled in Appendix E of Ref. [3]. Those advanced applications are from the fields of complex fluids (reptation model for entangled linear polymers [21–25], responsive particle dynamics model for entangled melts [26], pompon model for branched polymers [27,28], polymer blends [29–34], colloidal suspensions [35–37], and two-phase systems [38–41]), relativistic hydrodynamics [42–46], discrete formulations of hydrodynamics for simulations [47–50], and thermodynamically guided simulations [51–60] (see also the review article [61] offering "four lessons and a caveat" for good simulations in the context of nonequilibrium statistical mechanics).

Several basic transport phenomena have been generalized to the nonlinear regime. For example, diffusion through polymeric and nanocomposite membranes has been modeled by means of the GENERIC framework [62,63]. Also, a comprehensive discussion of the multiscale thermodynamics and mechanics of heat flow goes beyond linear irreversible thermodynamics [64]. Thermodynamics has also contributed to the understanding of gas flow in the smallest of channels, as in microfluidics, and of aerodynamics of satellites and space stations in the outer limits of our atmosphere [65–67].

Whereas the original development of nonequilibrium thermodynamics has mainly been pushed in the context of complex fluids, the general framework is by no means restricted to fluids. Also, crystallization phenomena, including polymer crystallization, have been better understood with the help of the methods of modern nonequilibrium thermodynamics and statistical mechanics [68–75]. Plasticity and viscoplastic solids are further topics in which important issues have been clarified by means of thermodynamics [76–82]. By combining thermodynamics with a thoughtful characterization of the microstructure, valuable insight into continuum damage mechanics has been gained [83]. Structural glasses are another challenging problem in physics and materials science for which nonequilibrium phenomena are widely believed to play an important role. In this context, the shear-transformation-zone model [84,85] has been revisited [86], and promising new ways to approach this long-standing challenge are suggested by the GENERIC framework [87–90]. The geometric structure of the GENERIC framework suggests a natural generalization to describe dissipative quantum systems [91–95].

Most of the applications of nonequilibrium thermodynamics deal with the modeling of bulk systems. To solve the resulting bulk equations one typically needs boundary conditions. The usefulness of linear irreversible thermodynamics for obtaining boundary conditions has been shown by Waldmann in his famous 1967 article [96]. Brenner and Ganesan [97] asked the very deep question "Are conditions at a boundary 'boundary conditions'?" Nonequilibrium thermodynamics actually provides the powerful language for expressing the physics at the boundary consistently [98,99], thus going well beyond the mathematics of boundary conditions. An illustrative example is provided by the thermodynamic formulation of wall slip [100]. Within linear irreversible thermodynamics, a general description of the dynamics of interfaces has been developed by Bedeaux and coworkers [101–103]. The main challenge is to generalize the concept of local equilibrium, which is known to be a key ingredient to the nonequilibrium thermodynamics of bulk systems, to lower-dimensional interfaces [104–106]. The analysis of the fully nonlinear thermodynamic behavior of complex interfaces within modern nonequilibrium thermodynamics is a very active field of research [107–112].

II. SYMMETRIC IRREVERSIBLE BRACKETS

In view of the degeneracy requirement (6), the friction matrix and hence the irreversible bracket has to know about energy. More precisely, the irreversible bracket must depend on the gradient $\delta E/\delta x$. A simple way of accomplishing symmetry and degeneracy is by writing

$$[A,B] = \zeta_{\alpha\beta,\mu\nu} \frac{\delta A}{\delta x_\alpha} \frac{\delta E}{\delta x_\beta} \frac{\delta B}{\delta x_\mu} \frac{\delta E}{\delta x_\nu}, \tag{9}$$

where we have used Einstein's summation convention (actually, indices occurring twice imply summations over discrete labels and integrations over continuous labels). The antisymmetry properties

$$\zeta_{\alpha\beta,\mu\nu} = -\zeta_{\beta\alpha,\mu\nu} = -\zeta_{\alpha\beta,\nu\mu} \tag{10}$$

take care of the degeneracy requirement (6), whereas the symmetry property

$$\zeta_{\alpha\beta,\mu\nu} = \zeta_{\mu\nu,\alpha\beta} \tag{11}$$

implies the symmetry of the irreversible bracket. A natural way of implementing the symmetry properties (10) and (11) is obtained by assuming the factorization

$$\zeta_{\alpha\beta,\mu\nu} = \Lambda^m_{\alpha\beta} D_{mn} \Lambda^n_{\mu\nu}, \tag{12}$$

with the antisymmetric matrices

$$\Lambda^m_{\alpha\beta} = -\Lambda^m_{\beta\alpha}, \tag{13}$$

and the symmetric matrix

$$D_{mn} = D_{nm}. \tag{14}$$

The size of the matrix D_{mn} depends on the number of relevant dissipative processes and does not need to coincide with the size of the vector of the independent system variables x_α. The representation (9) of the irreversible bracket, with the corresponding symmetry properties or the factorization (12), provides an explicit functional form for the anticipated dependence of the irreversible bracket on the energy gradient.

A. Some justifications

Of course, symmetry and degeneracy constraints alone do not lead to an unambiguous functional form of the irreversible bracket. However, the particularly simple functional form proposed in Eq. (9) with the factorization (12) has been found in a number of previous modeling attempts. Most obvious is this structure in previous formulations of relativistic hydrodynamics (see Eq. (5.142) of Ref. [3]) and interfacial transport phenomena (see Eq. (35) of [107] or Eqs. (27) and (28) of Ref. [112]).

A more formal motivation may be found in the Green-Kubo formula (8). The two factors $i\mathcal{L}\Pi_k$ and $i\mathcal{L}\Pi_j$ represent Poisson brackets expressing the microscopic Hamiltonian dynamics and hence antisymmetric structures involving energy; the antisymmetry behind these two factors is reflected in the antisymmetry of the two factors Λ in Eq. (12). Exactly the same kind of argument has been used to introduce dissipation into quantum systems by formulating the quantum generalization of the irreversible bracket as the canonical correlation of two commutators [91,92].

B. A previous factorization

Edwards [11] observed that many friction matrices can be factorized in the form

$$M = CDC^T, \tag{15}$$

where the matrix D contains all the dynamic system information, whereas the matrix C is considered as a mechanical component. If D is symmetric and positive semidefinite, these properties are inherited by M.

The factorization (15) plays a central role in establishing the relationship between GENERIC and linear irreversible thermodynamics, as has been elaborated in Sec. 3.1.1 of Ref. [3]. It can moreover be used to introduce the concept of force-flux pairs even in the nonlinear domain. Similar to a diagonalization, Eq. (15) brings out the essence of a friction matrix; D might actually be diagonal with transport coefficients and relaxation times as diagonal elements, but it could also contain off-diagonal elements describing physical cross effects. As pointed out before, the size of the quadratic matrix D is given by the number of dissipative processes in a system (on which linear irreversible thermodynamics is focused), whereas the size of the quadratic friction matrix M matches the length of the vector x (which is central to GENERIC). The matrix C describes how the the various system variables in the list x participate in the various dissipative processes.

Equation (15) is an immediate consequence of our more explicit assumption (12). We actually have

$$C_{\alpha m} = \Lambda^m_{\alpha\beta} \frac{\delta E}{\delta x_\beta}, \tag{16}$$

that is, similar to reversible dynamics, the columns of the matrix C are generated by antisymmetric matrices from the energy gradient. The matrices C have been given for a number of transport and relaxation processes in Secs. 2.3.2, 3.1.2, and 4.2.3 of Ref. [3]. In all cases it can be verified that they can be expressed in the form (16) where, when present, the label m represents a spatial index or a pair of spatial indices. The freedom of using forms of the matrix C more general than the one proposed in Eq. (16), for example, nonlinear in the energy gradient, indeed does not seem to be required in applications. We thus obtain a further strong justification of our fundamental assumption (9) with the factorization assumption (12) through many physically relevant examples.

The considerations of Sec. 3.1.1 of Ref. [3] combined with Eq. (16) imply that the thermodynamic driving forces X_n associated with the dissipative processes n can be expressed as

$$X_n = \Lambda^n_{\alpha\beta} \frac{\delta E}{\delta x_\alpha} \frac{\delta S}{\delta x_\beta}. \tag{17}$$

Whereas the thermodynamic forces X_n are usually introduced within the framework of linear irreversible thermodynamics, the elegant formula (17) holds within the more general GENERIC framework and hence also for nonlinear applications.

III. ANTISYMMETRIC IRREVERSIBLE BRACKETS

We have so far focused on symmetric irreversible brackets. This symmetry is a generalization of the Onsager symmetry of linear irreversible thermodynamics [8] to nonlinear problems. In his celebrated papers, Onsager derived the symmetry from microscopic time-reversal behavior [113,114]. Casimir [115] later showed that also antisymmetric behavior can occur, depending on the time-reversal properties of the various independent variables. Also in the nonlinear generalization provided by GENERIC, the symmetry properties of friction matrices have been inferred from microscopic time-reversal behavior, based on the Green-Kubo formula (8) (see, for example, Sec. 3.2.1 of Ref. [3] and references therein).

According to Eq. (7), antisymmetric friction matrices or the corresponding irreversible brackets do not contribute to the entropy production. Entropy production is a sufficient but not a necessary condition for irreversibility. The term "friction" may hence be misleading for irreversible processes without entropy production (dissipation). This is actually the reason why we switched from the usual term "dissipative bracket" to the more general term "irreversible bracket" throughout this paper. It might actually be even more appropriate to refer to it as the "Grmela bracket." In the summer of 1983, Miroslav Grmela first introduced the idea of such brackets to formulate irreversible dynamics at a research conference in the mathematical sciences on fluids and plasmas in Boulder, Colorado, USA [116]. In the following year, three seminal papers on his idea appeared in Phys. Lett. A [117–119].

Switching from symmetric to antisymmetric irreversible brackets is possible by introducing a minus sign into Eqs. (11) and (14). However, there is an even simpler representation of antisymmetric irreversible brackets, requiring only one factor of $\delta E/\delta x$ instead of the two factors in (9):

$$[A,B] = \xi_{\alpha\beta\gamma} \frac{\delta A}{\delta x_\alpha} \frac{\delta B}{\delta x_\beta} \frac{\delta E}{\delta x_\gamma}, \tag{18}$$

where $\xi_{\alpha\beta\gamma}$ is a completely antisymmetric function of its three indices. The complete antisymmetry of $\xi_{\alpha\beta\gamma}$ implies both degeneracy and antisymmetry of the bracket (18). The corresponding irreversible contribution to the time evolution is given by

$$\left(\frac{dx_\alpha}{dt}\right)_{\text{irr}} = \xi_{\alpha\beta\gamma} \frac{\delta S}{\delta x_\beta} \frac{\delta E}{\delta x_\gamma}. \tag{19}$$

Experience should tell us whether the representation (9), with a minus sign in Eqs. (11) and (14), or the representation (18) is more appropriate in the antisymmetric case. In view of the bilinear versus linear dependence on the energy gradient and the associated difference in index structure, these representations are fundamentally different. Because the representation (18) is not associated with a Green-Kubo formula, the calculation of the coefficients $\xi_{\alpha\beta\gamma}$ characterizing the nondissipative irreversible behavior from statistical mechanics is an open problem deserving further investigation.

A. Slip

In modeling the flow behavior of polymer solutions and melts by rheological constitutive equations, convected time derivatives play an important role. A very general form of a convected derivative is known as the Gordon-Schowalter derivative [see, for example, Eq. (5.8) of Ref. [120], Eqs. (6.3–49) of Ref. [121], or Eq. (2.93) of Ref. [3]]:

$$\frac{\mathcal{D}\boldsymbol{c}}{\mathcal{D}t} = \frac{\partial \boldsymbol{c}}{\partial t} + \boldsymbol{v} \cdot \frac{\partial \boldsymbol{c}}{\partial \boldsymbol{r}} - \boldsymbol{\kappa} \cdot \boldsymbol{c} - \boldsymbol{c} \cdot \boldsymbol{\kappa}^T + \frac{\xi}{2}(\boldsymbol{c} \cdot \dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}} \cdot \boldsymbol{c}), \tag{20}$$

where $\boldsymbol{c} = \boldsymbol{c}(\boldsymbol{r},t)$ is a time-dependent tensor field, $\boldsymbol{v}$ is the convecting velocity field, the components of the velocity gradient tensor $\boldsymbol{\kappa}$ are given by $\kappa_{jk} = \partial v_j/\partial r_k$, $\dot{\boldsymbol{\gamma}} = \boldsymbol{\kappa} + \boldsymbol{\kappa}^T$ is the symmetrized velocity gradient tensor, and ξ is known as the slip parameter. In addition to the partial time derivative, we have the spatial translation of the tensor with the flow field and the full or partial deformation rate tensor mixing the various tensor components of $\boldsymbol{c}$. The parameters $\xi = 0$ and $\xi = 2$ correspond to upper and lower convected behavior, respectively, which can be understood as reversible dynamics. For any intermediate slip parameter ξ, the Gordon-Schowalter derivative cannot be represented by Hamiltonian dynamics (the natural candidate for a Poisson bracket does not satisfy the Jacobi identity).

It seems natural to think of "slip" as an irreversible phenomenon that does not lead to entropy production. A representation of slip in terms of an antisymmetric friction matrix has indeed been given in Eq. (4.68) of Ref. [3]. We here show that this antisymmetric friction matrix is of the simple form given in Eq. (18).

We focus on the independent variables involved in slip phenomena, $x = (\boldsymbol{M}(\boldsymbol{r}),\epsilon(\boldsymbol{r}),\boldsymbol{c}(\boldsymbol{r}))$, where $\boldsymbol{M}(\boldsymbol{r})$ is the momentum density, $\epsilon(\boldsymbol{r})$ is the nonconfigurational internal energy density, and $\boldsymbol{c}(\boldsymbol{r})$ is our tensorial structural variable characterizing the state of a polymeric liquid. The energy and entropy gradients are given by

$$\frac{\delta E}{\delta x} = \begin{pmatrix} \boldsymbol{v} \\ 1 \\ \partial \epsilon_{\text{c}}/\partial \boldsymbol{c} \end{pmatrix}, \tag{21}$$

and

$$\frac{\delta S}{\delta x} = \begin{pmatrix} 0 \\ 1/T \\ \partial s_{\text{c}}/\partial \boldsymbol{c} \end{pmatrix}, \tag{22}$$

where ϵ_{c} and s_{c} are the configurational contributions to the internal energy and entropy densities. The friction matrix contains six nonzero entries which are all obtained by permutations of the single element

$$\begin{aligned}\xi_{M_j(\boldsymbol{r}),\epsilon(\boldsymbol{r}'),c_{kl}(\boldsymbol{r}'')} &= \frac{\xi T(\boldsymbol{r}')}{2}\delta(\boldsymbol{r}'-\boldsymbol{r}'')\frac{\partial\delta(\boldsymbol{r}-\boldsymbol{r}')}{\partial r'_n}\\ &\quad\times[c_{jl}(\boldsymbol{r}')\delta_{kn}+\delta_{jl}c_{kn}(\boldsymbol{r}')+c_{kj}(\boldsymbol{r}')\delta_{nl}+\delta_{kj}c_{nl}(\boldsymbol{r}')],\end{aligned} \tag{23}$$

with the proper minus signs for odd permutations. The δ functions express the locality of the slip effect; the derivative is required to produce velocity gradient tensors. In view of the complicated index structure, it here is actually more convenient to label ξ by $x_\alpha, x_\beta, x_\gamma$ rather than α, β, γ. We still need to verify the expression (23). In evaluating Eq. (19) for the tensor variable, only one term contributes to the time evolution and we obtain

$$\left(\frac{d\boldsymbol{c}}{dt}\right)_{\text{irr}} = -\frac{\xi}{2}(\boldsymbol{c}\cdot\dot{\boldsymbol{\gamma}}+\dot{\boldsymbol{\gamma}}\cdot\boldsymbol{c}), \tag{24}$$

which is consistent with the slip contribution in the definition (20) of the Gordon-Schowalter derivative. For the time evolution of the momentum density, we obtain two contributions which can be combined into

$$\left(\frac{d\boldsymbol{M}}{dt}\right)_{\text{irr}} = -\frac{\partial}{\partial\boldsymbol{r}}\cdot 2\xi\boldsymbol{c}\cdot\left(\frac{\partial\epsilon_{\text{c}}}{\partial\boldsymbol{c}}-T\frac{\partial s_{\text{c}}}{\partial\boldsymbol{c}}\right). \tag{25}$$

We hence recover the known contribution to the stress tensor associated with slip.

A more detailed comparison shows that we cannot only reproduce the known contribution to the evolution equations associated with slip [122,123], but the entire friction matrix given in Eq. (4.68) of Ref. [3]. We hence have a first example in favor of the representation (18) of antisymmetric dissipation brackets.

B. Turbulence

Three-dimensional turbulence is one of the most challenging problems in classical physics. Key issues are the theoretical understanding of the energy-cascade mechanism and of deviations from the classical Kolmogorov theory [124]. In particular, there exists a whole spectrum of anomalous scaling exponents for different correlation functions which are not predicted by the Kolmogorov theory (intermittency of the energy cascade; see Ref. [125] and references therein). We are hence faced with two reasons for trying to find a reduced set of equations that can reproduce the energy-cascade mechanism of the Navier-Stokes equation: (i) Solving the full Navier-Stokes equation at very large Reynolds numbers is an extremely demanding numerical problem so that simulations over a wide range of scales and the calculation of scaling exponents are difficult and would benefit enormously from simplified numerics. (ii) Finding a smaller set of equations exhibiting the same features as the full Navier-Stokes equation would bring out the essence of the energy cascade and hence provide understanding in a very deep way.

A promising idea for a reduced description of the energy cascade in turbulent flows is given by shell models. The most popular shell model is the so-called GOY model going back to Glezder, Ohkitani, and Yamada [126,127]. This model is based on a number of velocity modes u_n as independent variables,

$$x = (u_0, u_1, \ldots, u_N), \tag{26}$$

where each u_n is a complex number and the corresponding wave numbers k_n are chosen in geometric progression,

$$k_n = k_0\lambda^n, \tag{27}$$

with a shell spacing parameter or intershell ratio λ, usually taken as 2. The idea is to drive only the lowest, large-scale modes, say u_0, by an external force and to observe the energy cascade resulting from the coupling of only a few successive modes.

Because energy irreversibly cascades down from larger to smaller scales, but entropy is not produced until the very small scales are reached, we make an attempt to implement the coupling of the velocity modes by an antisymmetric friction matrix. In other words, turbulence provides an important intuitive example of an irreversible process without entropy production. In accordance with an observation by M. Mungan sketched in Sec. II of Ref. [128], we use an irreversible bracket of the form (18) with

$$\xi_{n\,n+1\,n+2} = \Xi_n \text{ for } n = 0, \ldots, N-2. \tag{28}$$

Each term couples three successive modes and represents six contributions to the irreversible bracket corresponding to the permutations of n, $n+1$, and $n+2$. To complete the construction of the coupled evolution equations, we need to define energy and entropy. The usual expression for the energy in shell models is

$$E = \frac{1}{2}\sum_{n=0}^{N}|u_n|^2, \tag{29}$$

where $|u_n|^2 = u_n u_n^*$ and the asterisk indicates complex conjugation. For simplicity, we choose also the entropy as a quadratic function,

$$S = \sum_{n=0}^{N} s_n|u_n|^2, \tag{30}$$

where we expect the parameters $|s_n|$ to increase with n because higher-wave-number oscillations should lead to a bigger loss of entropy. We can now write out the evolution equations (19) to obtain

$$\begin{aligned}\left(\frac{du_n}{dt}\right)_{\text{irr}} &= \tilde{\Xi}_n\left(1-\frac{s_{n+1}}{s_{n+2}}\right)u_{n+1}^*u_{n+2}^*\\ &\quad-\tilde{\Xi}_{n-1}\left(1-\frac{s_{n-1}}{s_{n+1}}\right)u_{n-1}^*u_{n+1}^*\\ &\quad+\tilde{\Xi}_{n-2}\left(\frac{s_{n-1}}{s_n}-\frac{s_{n-2}}{s_n}\right)u_{n-1}^*u_{n-2}^*,\end{aligned} \tag{31}$$

where we have introduced $\tilde{\Xi}_n = \Xi_n s_{n+2}/2$ (if the subscript of a variable u^* is outside the range $0, \ldots, N$, the corresponding term is absent). These equations become particularly simple if we make the natural choice $s_n = s_0 q^{-n}$ with $|q| < 1$. With

$\hat{\Xi}_n = (1-q)\tilde{\Xi}_n$, we finally arrive at

$$\left(\frac{du_n}{dt}\right)_{\text{irr}} = \hat{\Xi}_n u^*_{n+1} u^*_{n+2} - (1+q)\hat{\Xi}_{n-1} u^*_{n-1} u^*_{n+1} + q\,\hat{\Xi}_{n-2} u^*_{n-1} u^*_{n-2}. \tag{32}$$

By choosing $\hat{\Xi}_n = ik_n$ we recover the usual form of the coupling terms of the GOY model. A viscous term $-\nu k_n^2 u_n$ with dynamic viscosity ν, which leads to significant entropy production only at small scales, needs to be added to Eq. (32). This term could be incorporated into the GENERIC formulation by including the internal energy into the list of independent system variables.

Shell models with positive and negative ratio q have been considered in the literature (see discussion on p. 448 of Ref. [125] and references therein). For an entropy, it is natural to expect all terms in Eq. (30) to be of the same sign, that is $q > 0$ (actually with $s_0 < 0$). However, the usual interpretation of the two quadratic invariants of the evolution equation (32), that is, in the absence of viscous dissipation and external forcing, is as energy and helicity rather than as energy and entropy. For our thermodynamic formulation of the energy cascade as an irreversible mechanism within the GENERIC framework, the interpretation as entropy is more natural. For keeping the essential features of the energy-cascade mechanism of the full Navier-Stokes equation, however, helicity is very important. It is hence desirable to keep the proper roles of both entropy and helicity. However, the alternating sign between even and odd modes is not really a natural way of implementing helicity. More appropriately, shell models have been constructed on the basis of a helical decomposition of the Navier-Stokes equation in Fourier space in Ref. [129], where two shell variables $u_n^\pm$ carrying positive and negative helicity for each wave number k_n have been introduced. Moreover, a connection between a positive second invariant and enstrophy in two-dimensional turbulence has been made in Ref. [129]. The setting with two shell variables hence seems to be promising for implementing both entropy and helicity as invariants.

Because shell models arise from significant coarse graining of the Navier-Stokes equation, the thermodynamic modeling approach suggests new forms of entropy and irreversibility emerging in shell models, having no counterparts on the full hydrodynamic level. Deeper understanding of turbulence through coarse graining may actually be identified with the search for the proper forms of the emerging entropy and irreversible bracket contributions (in the same way as entropy, entropy production, and transport coefficients emerge from the coarse graining of molecular dynamics). It is natural to expect that the new type of entropy should favor smooth velocity fields by imposing a price to pay for large-wave-number modes or vorticity. One should not hesitate to refer to such unusual terms as new forms of entropy rather than to invent new terms like enstrophy; the defining characteristic of entropy in nonequilibrium thermodynamics is its role in generating irreversible dynamics. The new form of irreversibility arising in the passage from the Navier-Stokes equation to shell models is associated with the energy cascade; whereas the viscous damping is inherited from the Navier-Stokes equation, the contribution (32) emerges from further coarse graining. Its antisymmetric character leads to irreversibility without entropy production as a hallmark of the energy cascade. Making full use of such thermodynamic concepts and ideas should be helpful in the further development of shell models.

IV. NONSYMMETRIC IRREVERSIBLE BRACKETS

In the preceding sections, we considered the symmetric and antisymmetric irreversible brackets corresponding to Onsager and Casimir symmetry. Let us now briefly address the question whether there can be irreversible brackets that are neither symmetric nor antisymmetric. The answer to this question is "yes." The existence of nonsymmetric irreversible brackets may be surprising because Onsager or Casimir symmetry are commonly believed to be the only alternatives allowed by microscopic time-reversal properties. For the entropy production, only the symmetric part matters.

A nonsymmetric irreversible bracket has actually been found in the context of Boltzmann's equation for rarified gases. A first intuitive investigation of the GENERIC structure of Boltzmann's equation had led to the identification of a symmetric friction matrix [130], based on the desired equation of motion. When later the friction matrix was calculated in a straightforward manner by means of statistical mechanics [131] (see also Sec. 7.2.4 of Ref. [3]), it turned out that there exists a more natural nonsymmetric friction matrix.

Coupled chemical reactions have recently been identified as another situation in which we should expect nonsymmetric irreversible brackets or friction matrices [132] (the problem arises in guaranteeing positive-definiteness in the nonlinear case, based on bilinear rather than quadratic forms). However, a direct calculation of this nonsymmetric bracket from statistical mechanics has not been achieved yet. Such an explicit calculation would be important because, as we have learned from the example of Boltzmann's equation, the identification of friction matrices from evolution equations does not lead to unique answers (for a discussion of the nonuniqueness of phenomenological building blocks of GENERIC, see p. 85 of Ref. [3]; on the other hand, statistical mechanics can provide unique building blocks).

What is the cause of the loss of Onsager-Casimir symmetry? There are two fundamentally different situations in which we obtain the slow variables that nonequilibrium thermodynamics deals with: many small events or rare big events. On the one hand, many independent small kicks accumulating according to the central limit theorem are typical of diffusion processes. On the other hand, the collisions between particles in rarified gases are rare events and these collisions lead to big changes of the particle momenta; the duration of a collision is very short compared to the time between collisions. Or, chemical reactions result when a system escapes from one local minimum of energy to another one by passing an energy barrier; the escape time, which was discussed in a classical paper by Kramers [133], can be very large, but the actual escape process happens in a short time. In both examples, nothing happens for a long time and eventually a big change happens within a short time. This seems to be the situation in which nonsymmetric irreversible brackets arise. One then also needs to reconsider the fluctuation-dissipation theorem (see, for example, Secs. 1.2.5 and 6.3.3 of Ref. [3]) because fluctuations are expected to be governed by Poissonian rather than Gaussian behavior.

A convenient reformulation of the Green-Kubo formula (8) for the case of rare big events is given by

$$M_{jk} = \frac{1}{k_{\rm B}} \langle [\mathcal{Q} i \mathcal{L} \Pi_k] e^{i\mathcal{L}\tau} \Pi_j \rangle_x, \tag{33}$$

in which the time integration has been carried out. The result looks less symmetric than in Eq. (8), but the two versions of the Green-Kubo formula are actually equivalent. The intermediate timescale τ should be large compared to the duration of a collision or transition, but small compared to the time between such big events. For the case of Boltzmann's equation, the actual calculation of a nonsymmetric friction matrix in Ref. [3] has indeed been based on Eq. (33).

Note that also Eq. (8) is less symmetric than it might appear at first sight. This is a consequence of the fact that the evolution operator changes the nonequilibrium ensemble used for performing the average. Equilibrium ensembles depend on conserved variables only, whereas nonequilibrium ensembles depend on slow variables and hence evolve slowly. Formally, this effect is expected to be negligible for a small ratio of fast to slow timescales but, in the case of rare big events, such a formal argument could be invalid because the changes on the fast timescale (duration of a big event) are the same as on the slow timescale (time between big events).

V. SUMMARY AND CONCLUSIONS

We have discussed the structure of the irreversible brackets and the equivalent friction matrices which play an important role in describing irreversible time evolution in nonequilibrium thermodynamics. For symmetric irreversible brackets, the representation (9) with the factorization (12) and the proper symmetry properties should be very useful in thermodynamic modeling efforts. For antisymmetric irreversible brackets, which imply irreversibility without entropy production, the examples of slip and turbulence suggest that we should not just change the symmetries in the representation (9), (12), but rather rely on the simpler representation (18). Moreover, we suggest that irreversible brackets that are neither symmetric nor antisymmetric may arise in situations of rare events causing big configurational changes.

Going beyond phenomenological modeling efforts, the proposed representations might also be useful when evaluating friction matrices from the Green-Kubo formula; that is, by statistical mechanics. For the symmetric case, one could focus on evaluating the factors in Eq. (12). For the antisymmetric case, the calculation of slip coefficients, the parameters of shell models for the turbulent energy cascade, and similar irreversible (but not dissipative) material properties by statistical mechanics still needs to be elaborated.

Our results for symmetric irreversible brackets could also have an impact on modeling irreversible time evolution in terms of dissipation potentials (see Refs. [134,135] and references therein; for a detailed comparison between symmetric irreversible brackets and dissipation potentials, see Ref. [136]). Finally, the further development of shell models for the turbulent energy cascade might benefit from a thermodynamic framework for modeling irreversible dynamics in the antisymmetric case where irreversibility is not accompanied by entropy production.

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[1] M. Grmela and H. C. Öttinger, Phys. Rev. E **56**, 6620 (1997).

[2] H. C. Öttinger and M. Grmela, Phys. Rev. E **56**, 6633 (1997).

[3] H. C. Öttinger, *Beyond Equilibrium Thermodynamics* (Wiley, Hoboken, 2005).

[4] B. J. Edwards and H. C. Öttinger, Phys. Rev. E **56**, 4097 (1997).

[5] V. I. Arnold, *Mathematical Methods of Classical Mechanics*, 2nd ed. (Springer, New York, 1989).

[6] J. E. Marsden, *Lectures on Mechanics* (Cambridge University Press, Cambridge, 1992).

[7] J. E. Marsden and T. S. Ratiu, *Introduction to Mechanics and Symmetry*, Texts in Applied Mathematics Vol. 17, 2nd ed. (Springer, New York, 1999).

[8] S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland, Amsterdam, 1951).

[9] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, 2nd ed. (Dover, New York, 1984).

[10] A. N. Beris and B. J. Edwards, *The Thermodynamics of Flowing Systems* (Oxford University Press, New York, 1994).

[11] B. J. Edwards, J. Non-Equilib. Thermodyn. **23**, 301 (1998).

[12] B. J. Edwards, A. N. Beris, and H. C. Öttinger, J. Non-Equilib. Thermodyn. **23**, 334 (1998).

[13] A. N. Beris, J. Non-Newtonian Fluid Mech. **96**, 119 (2001).

[14] H. C. Öttinger, Phys. Rev. E **57**, 1416 (1998).

[15] R. Zwanzig, Phys. Rev. **124**, 983 (1961).

[16] H. Mori, Prog. Theor. Phys. **33**, 423 (1965).

[17] H. Mori, Prog. Theor. Phys. **34**, 399 (1965).

[18] B. Robertson, Phys. Rev. **144**, 151 (1966).

[19] H. Grabert, *Projection Operator Techniques in Nonequilibrium Statistical Mechanics* (Springer, Berlin, 1982).

[20] H. C. Öttinger, Dyna **79/175E**, 122 (2012).

[21] H. C. Öttinger and A. N. Beris, J. Chem. Phys. **110**, 6593 (1999).

[22] H. C. Öttinger, J. Non-Newtonian Fluid Mech. **89**, 165 (2000).

[23] H. C. Öttinger, J. Rheol. (Melville, NY, U. S.) **43**, 1461 (1999).

[24] J. Fang, M. Kröger, and H. C. Öttinger, J. Rheol. (Melville, NY, U. S.) **44**, 1293 (2000).

[25] H. Eslami and M. Grmela, Rheol. Acta **47**, 399 (2008).

[26] T. Savin, W. J. Briels, and H. C. Öttinger, Rheol. Acta **52**, 23 (2013).

[27] H. C. Öttinger, Rheol. Acta **40**, 317 (2001).

[28] J. van Meerveld, J. Non-Newtonian Fluid Mech. **108**, 291 (2002).

[29] N. J. Wagner, H. C. Öttinger, and B. J. Edwards, AIChE J. **45**, 1169 (1999).

[30] M. Grmela, M. Bousmina, and J.-F. Palierne, Rheol. Acta **40**, 560 (2001).

[31] M. Dressler and B. J. Edwards, Rheol. Acta **43**, 257 (2004).

[32] J. F. Gu and M. Grmela, Phys. Rev. E **78**, 056302 (2008).

[33] J. F. Gu, M. Grmela, and M. Bousmina, Phys. Fluids **20**, 043102 (2008).

[34] A. Jelić, P. Ilg, and H. C. Öttinger, Phys. Rev. E **81**, 011131 (2010).

[35] N. J. Wagner, J. Non-Newtonian Fluid Mech. **96**, 177 (2001).

[36] M. Grmela, A. Aït-Kadi, and P. G. Lafleur, J. Chem. Phys. **109**, 6973 (1998).

[37] M. Keshtkar, M.-C. Heuzey, P. J. Carreau, M. Rajabian, and C. Dubois, J. Rheol. (Melville, NY, U. S.) **54**, 197 (2010).

[38] M. Hütter, Phys. Rev. E **64**, 011209 (2001).

[39] M. Hütter, J. Non-Equilib. Thermodyn. **27**, 349 (2002).

[40] P. Español, J. Chem. Phys. **115**, 5392 (2001).

[41] P. Español and C. Thieulot, J. Chem. Phys. **118**, 9109 (2003).

[42] H. C. Öttinger, Physica A (Amsterdam, Neth.) **259**, 24 (1998).

[43] H. C. Öttinger, Physica A (Amsterdam, Neth.) **254**, 433 (1998).

[44] H. C. Öttinger, Phys. Rev. D **60**, 103507 (1999).

[45] P. Ilg and H. C. Öttinger, Phys. Rev. D **61**, 023510 (1999).

[46] H. C. Öttinger, Physica A (Amsterdam, Neth.) **387**, 4560 (2008).

[47] P. Español, M. Serrano, and H. C. Öttinger, Phys. Rev. Lett. **83**, 4542 (1999).

[48] M. Serrano and P. Español, Phys. Rev. E **64**, 046115 (2001).

[49] P. Español and M. Revenga, Phys. Rev. E **67**, 026705 (2003).

[50] M. Ellero, P. Español, and E. G. Flekkøy, Phys. Rev. E **68**, 041504 (2003).

[51] M. Kröger, J. Ramírez, and H. C. Öttinger, Polymer **43**, 477 (2002).

[52] V. G. Mavrantzas and H. C. Öttinger, Macromolecules (Washington, DC, U.S.) **35**, 960 (2002).

[53] V. A. Harmandaris, V. G. Mavrantzas, D. N. Theodorou, M. Kröger, J. Ramírez, H. C. Öttinger, and D. Vlassopoulos, Macromolecules (Washington, DC, U.S.) **36**, 1376 (2003).

[54] M. Kröger, Phys. Rep. **390**, 453 (2004).

[55] H. C. Öttinger, J. Non-Newtonian Fluid Mech. **120**, 207 (2004).

[56] M. Kröger and H. C. Öttinger, J. Non-Newtonian Fluid Mech. **120**, 175 (2004).

[57] P. Ilg, H. C. Öttinger, and M. Kröger, Phys. Rev. E **79**, 011802 (2009).

[58] P. Ilg and M. Kröger, J. Rheol. (Melville, NY, U.S.) **55**, 69 (2011).

[59] P. Ilg, M. Hütter, and M. Kröger, Phys. Rev. E **83**, 061713 (2011).

[60] C. Baig, V. G. Mavrantzas, and H. C. Öttinger, Macromolecules (Washington, DC, U.S.) **44**, 640 (2011).

[61] H. C. Öttinger, MRS Bull. **32**, 936 (2007).

[62] Q. Liu and D. De Kee, Rheol. Acta **44**, 287 (2005).

[63] Q. Liu and D. De Kee, J. Non-Newtonian Fluid Mech. **131**, 32 (2005).

[64] M. Grmela, G. Lebon, and C. Dubois, Phys. Rev. E **83**, 061134 (2011).

[65] H. C. Öttinger, Phys. Rev. Lett. **104**, 120601 (2010).

[66] H. Struchtrup and M. Torrilhon, Phys. Rev. Lett. **105**, 128901 (2010).

[67] H. C. Öttinger, Phys. Rev. Lett. **105**, 128902 (2010).

[68] J. Mukherjee, S. Wilson, and A. N. Beris, J. Non-Newtonian Fluid Mech. **120**, 225 (2004).

[69] M. Hütter, J. Non-Newtonian Fluid Mech. **120**, 55 (2004).

[70] M. Hütter, G. C. Rutledge, and R. C. Armstrong, Phys. Fluids **17**, 014107 (2005).

[71] M. Hütter, J. Non-Equilib. Thermodyn. **31**, 73 (2006).

[72] J. van Meerveld, M. Hütter, and G. W. M. Peters, J. Non-Newtonian Fluid Mech. **150**, 177 (2008).

[73] J. Mukherjee and A. N. Beris, J. Comp. Theor. Nanosci. **7**, 726 (2010).

[74] C. Baig and B. J. Edwards, Europhys. Lett. **89**, 36003 (2010).

[75] C. Baig and B. J. Edwards, J. Non-Newtonian Fluid Mech. **165**, 992 (2010).

[76] M. Hütter, M. Grmela, and H. C. Öttinger, Rheol. Acta **48**, 769 (2009).

[77] M. Hütter and T. A. Tervoort, J. Non-Newtonian Fluid Mech. **152**, 45 (2008).

[78] M. Hütter and T. A. Tervoort, J. Non-Newtonian Fluid Mech. **152**, 53 (2008).

[79] H. C. Öttinger, J. Non-Newtonian Fluid Mech. **165**, 1005 (2010).

[80] A. Mielke, Continuum Mech. Thermodyn. **23**, 233 (2011).

[81] M. Hütter and L. C. A. van Bremen, J. Appl. Polym. Sci. **125**, 4376 (2012).

[82] M. Hütter and B. Svendsen, Continuum Mech. Thermodyn. **24**, 211 (2012).

[83] M. Hütter and T. A. Tervoort, Acta Mech. **201**, 297 (2008).

[84] M. L. Falk and J. S. Langer, Phys. Rev. E **57**, 7192 (1998).

[85] J. S. Langer, Phys. Rev. E **73**, 041504 (2006).

[86] A. M. Luo and H. C. Öttinger, Phys. Rev. E **89**, 022137 (2014).

[87] H. C. Öttinger, Phys. Rev. E **74**, 011113 (2006).

[88] E. Del Gado, P. Ilg, M. Kröger, and H. C. Öttinger, Phys. Rev. Lett. **101**, 095501 (2008).

[89] M. Mosayebi, E. Del Gado, P. Ilg, and H. C. Öttinger, Phys. Rev. Lett. **104**, 205704 (2010).

[90] M. Mosayebi, E. Del Gado, P. Ilg, and H. C. Öttinger, J. Chem. Phys. **137**, 024504 (2012).

[91] H. C. Öttinger, Europhys. Lett. **94**, 10006 (2011).

[92] H. C. Öttinger, Phys. Rev. A **82**, 052119 (2010).

[93] H. C. Öttinger, Phys. Rev. A **86**, 032101 (2012).

[94] J. Flakowski, M. Schweizer, and H. C. Öttinger, Phys. Rev. A **86**, 032102 (2012).

[95] M. Osmanov and H. C. Öttinger, Int. J. Thermophys. **34**, 1255 (2013).

[96] L. Waldmann, Z. Naturforsch. A **22**, 1269 (1967).

[97] H. Brenner and V. Ganesan, Phys. Rev. E **61**, 6879 (2000).

[98] H. C. Öttinger, Phys. Rev. E **73**, 036126 (2006).

[99] A. N. Beris and H. C. Öttinger, J. Non-Newtonian Fluid Mech. **152**, 2 (2008).

[100] H. C. Öttinger, J. Non-Newtonian Fluid Mech. **152**, 66 (2008).

[101] D. Bedeaux, A. M. Albano, and P. Mazur, Physica A (Amsterdam, Neth.) **82**, 438 (1976).

[102] D. Bedeaux, Adv. Chem. Phys. **64**, 47 (1986).

[103] A. M. Albano and D. Bedeaux, Physica A (Amsterdam, Neth.) **147**, 407 (1987).

[104] E. Johannessen and D. Bedeaux, Physica A (Amsterdam, Neth.) **330**, 354 (2003).

[105] E. Johannessen, J. Gross, and D. Bedeaux, J. Chem. Phys. **129**, 184703 (2008).

[106] K. S. Glavatskiy and D. Bedeaux, Phys. Rev. E **79**, 031608 (2009).

[107] H. C. Öttinger, D. Bedeaux, and D. C. Venerus, Phys. Rev. E **80**, 021606 (2009).

[108] L. M. C. Sagis, Adv. Colloid Interface Sci. **153**, 58 (2010).

[109] L. M. C. Sagis, Physica A (Amsterdam, Neth.) **389**, 1993 (2010).

[110] L. M. C. Sagis, Rev. Mod. Phys. **83**, 1367 (2011).

[111] T. Savin, K. S. Glavatskiy, S. Kjelstrup, H. C. Öttinger, and D. Bedeaux, Europhys. Lett. **97**, 40002 (2012).

[112] L. M. C. Sagis and H. C. Öttinger, Phys. Rev. E **88**, 022149 (2013).

[113] L. Onsager, Phys. Rev. **37**, 405 (1931).

[114] L. Onsager, Phys. Rev. **38**, 2265 (1931).

[115] H. B. G. Casimir, Rev. Mod. Phys. **17**, 343 (1945).

[116] M. Grmela, in *Fluids and Plasmas: Geometry and Dynamics*, Contemporary Mathematics Vol. 28, edited by J. E. Marsden (American Mathematical Society, Providence, 1984), pp. 125–132.

[117] A. N. Kaufman, Phys. Lett. A **100**, 419 (1984).

[118] P. J. Morrison, Phys. Lett. A **100**, 423 (1984).

[119] M. Grmela, Phys. Lett. A **102**, 355 (1984).

[120] R. G. Larson, *Constitutive Equations for Polymer Melts and Solutions*, Butterworths Series in Chemical Engineering (Butterworths, Boston, 1988).

[121] P. J. Carreau, D. C. R. De Kee, and R. P. Chhabra, *Rheology of Polymeric Systems* (Hanser, Munich, 1997).

[122] P. Wapperom and M. A. Hulsen, J. Rheol. (Melville, NY, U.S.) **42**, 999 (1998).

[123] H. C. Öttinger, Rev. Mex. Fís. **48**, Supl. 1, 220 (2002).

[124] A. N. Kolmogorov, Proc. R. Soc. London, Ser. A **434**, 9 (1991).

[125] L. Biferale, Annu. Rev. Fluid Mech. **35**, 441 (2003).

[126] E. B. Gledzer, Sov. Phys. Dokl. **18**, 216 (1973).

[127] M. Yamada and K. Ohkitani, J. Phys. Soc. Jpn. **56**, 4210 (1987).

[128] L. Kadanoff, D. Lohse, J. Wang, and R. Benzi, Phys. Fluids **7**, 617 (1995).

[129] R. Benzi, L. Biferale, R. M. Kerr, and E. Trovatore, Phys. Rev. E **53**, 3541 (1996).

[130] H. C. Öttinger, J. Non-Equilib. Thermodyn. **22**, 386 (1997).

[131] H. C. Öttinger, J. Non-Equilib. Thermodyn. **27**, 105 (2002).

[132] D. Bedeaux, S. Kjelstrup, and H. C. Öttinger, J. Chem. Phys. **141**, 124102 (2014).

[133] H. A. Kramers, Physica **7**, 284 (1940).

[134] M. Grmela, Adv. Chem. Eng. **39**, 75 (2010).

[135] M. Grmela, J. Non-Newtonian Fluid Mech. **165**, 980 (2010).

[136] M. Hütter and B. Svendsen, Continuum Mech. Thermodyn. **25**, 803 (2013).