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Dynamics and thermodynamics of complex fluids. II. Illustrations of a general formalism

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For a number of well-known time-evolution equations for nonequilibrium systems we extract a common structure from these equations, referred to as a general equation for the nonequilibrium reversible-irreversible coupling (GENERIC). This fundamental structure is determined by four building blocks, two ‘‘potentials’’ (total energy and entropy) and two ‘‘matrices.’’ We illustrate for various examples how three of the four building blocks can be determined in a rather straightforward manner so that, within our GENERIC approach to nonequilibrium dynamics, understanding of a given nonequilibrium system is reduced to determining a single ‘‘metric matrix,’’ or friction matrix, either empirically or by more microscopic considerations. In formulating nonisothermal polymer kinetic theories, we show how the general structure provides a clear distinction between spring potentials of energetic and entropic origins in the various time-evolution equations. [S1063-651X(97)06112-6]

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I. INTRODUCTION

We here consider a number of examples of time-evolution equations for nonequilibrium systems, some of them in great detail. Most of the equations are not new: Only the way of formulating these equations is different [1]. We show for the various examples that the time-evolution equations can be written in the form

$$\frac{dx}{dt} = L\frac{\delta E}{\delta x} + M\frac{\delta S}{\delta x}, \tag{1}$$

where x represents a set of independent variables required for a complete description of the nonequilibrium system, E and S are the total energy and entropy expressed in terms of the state variables x, and L and M are certain linear operators (or matrices). Since x typically contains position-dependent fields, such as mass, momentum, and energy densities, the state variables are usually labeled by continuous (position) labels in addition to discrete ones. A matrix multiplication, or 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.

Equation (1) is supplemented by the complementary degeneracy requirements

$$L\frac{\delta S}{\delta x} = 0 \tag{2}$$

and

$$M\frac{\delta E}{\delta x} = 0. \tag{3}$$

The requirement that the gradient $\delta S/\delta x$ is in the null space of L in Eq. (2) 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 $\delta E/\delta x$ is in the null space of M in Eq. (3) expresses the conservation of the total energy by the M contribution to the dynamics. 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. In this paper the crucial role played in our general formalism by the degeneracy requirements (2) and (3) is underlined by carefully elaborating their implications.

Further general properties of L and M are discussed most conveniently in terms of the two brackets

$$\{A,B\} = \left\langle \frac{\delta A}{\delta x}, L\frac{\delta B}{\delta x} \right\rangle, \tag{4}$$

$$[A,B] = \left\langle \frac{\delta A}{\delta x}, M\frac{\delta B}{\delta x} \right\rangle, \tag{5}$$

where $\langle\ ,\ \rangle$ denotes the scalar product and A,B are sufficiently regular real-valued functions on the state space. In terms of these brackets, Eq. (1) and the chain rule lead to the following time-evolution equation of an arbitrary function A in terms of the two separate generators E and S:

$$\frac{dA}{dt} = \{A,E\} + [A,S]. \tag{6}$$

The further conditions for L can now be stated as the antisymmetry property

$$\{A,B\} = -\{B,A\} \tag{7}$$

and the Jacobi identity

$$\{A,\{B,C\}\}+\{B,\{C,A\}\}+\{C,\{A,B\}\}=0, \tag{8}$$

where C is an arbitrary sufficiently regular real-valued function on the state space. These properties are well known from the Poisson brackets of classical mechanics and they capture the essence of reversible dynamics (the state space has the structure of a Poisson manifold [2]). In particular, the Jacobi identity expresses the time invariance of the Poisson bracket. Important implications of the Jacobi identity for moment closure approximations have been elaborated recently [3]. At least when the state space is finite dimensional, the Jacobi identity can be formulated directly in terms of the antisymmetric matrix L (see p. 28 of [2]),

$$\sum_l \left(L^{il}\frac{\partial L^{jk}}{\partial x^l}+L^{jl}\frac{\partial L^{ki}}{\partial x^l}+L^{kl}\frac{\partial L^{ij}}{\partial x^l}\right)=0. \tag{9}$$

Further properties of M can be formulated in terms of the symmetry condition

$$[A,B]=[B,A] \tag{10}$$

and the non-negativeness condition

$$[A,A]\geqslant 0. \tag{11}$$

This non-negativeness condition, together with the requirement that $\delta S/\delta x$ lie in the null space of L (implying $\{S,E\}=0$), guarantees that the entropy is a nondecreasing function of time

$$\frac{dS}{dt}\geqslant 0. \tag{12}$$

The properties (10) and (11) imply the symmetry and the positive semidefiniteness of M; we hence refer to M as a metric matrix (although it is of contravariant rather than covariant nature; a covariant inverse, however, does not exist due to the degeneracy of M). From a physical point of view, M may be regarded as a friction matrix.

While the structure of the fundamental time-evolution equation (1) and the importance of all the conditions for L and M have been explained and motivated in more depth in the preceding paper [1], referred to as paper I in the following, the details of the notation and the implications of the postulated structure will become more obvious when considering the examples below. Also some limitations of Eq. (1) have been pointed out in paper I: All variables neglected on the chosen level of description need to evolve on a much faster time scale than the variables x and, for example, the equations governing the time evolution of externally forced systems that generate complex patterns need not possess the postulated structure. For example, the Burnett equations [4] provide a counterexample violating the symmetry conditions (cf. the discussion of the Onsager-Casimir relations in paper I). Paper I and the present paper are written such that they can be read in either order, depending on whether one prefers to start from a more abstract consideration of levels of description (paper I) or from concrete and typical examples of nonequilibrium systems (this paper).

The skeptical reader might and actually should ask: What is the *benefit of reformulating various time-evolution equations* in the form of Eq. (1)? Do we gain any *additional insight*, or is this, at best, just an esthetically nice but useless exercise? Of course, the proper answer to these questions is important not only for motivating the reader, but also for revealing the full possible significance of this and the preceding paper. We hence wish to spend some time on answering these questions by a simple analogy.

Consider the equilibrium thermodynamics of a gas, to be described by the independent variables T (absolute temperature), V (volume), and N (number of particles). Note that identifying the proper variables required for a complete description of the system under consideration is always the first fundamental problem of thermodynamics. (Unfortunately, we are taught to see or used to seeing this as a trivial choice between well-known lists of appropriate state variables for gases, mixtures, magnetic systems, etc.) If the caloric equation of state for the energy $E=E(T,V,N)$ and the thermodynamic equations of state for the entropy $S=S(T,V,N)$, pressure $p=p(T,V,N)$, and chemical potential $\mu=\mu(T,V,N)$ are known, one has a complete description of the system. Is there any additional insight to be gained from reformulating these equations of state, by recognizing a deeper structure underlying these equations? Any reader familiar with the most basic ideas of thermodynamics [4,5] will immediately give a strongly affirmative answer to this question: Yes, there is a lot to be gained; the essence of thermodynamics actually is the identification of the unifying structure behind the various equations of state.

More precisely, by specifying the proper thermodynamic potential for the variables T,V,N, which is the Helmholtz free energy $F(T,V,N)$, all the above-mentioned equations of state can be obtained by taking partial derivatives. All information about the particular system is contained in a single thermodynamic potential F. From this structure of thermodynamics, certain consistency conditions (Maxwell relations) arise for the various equations of state (conditions such as ‘‘if E is independent of V then p must be linear in T’’ are certainly not immediately obvious and much more fundamental than even the most successful empirical or microscopically derived equations of state). By recognizing the fundamental role of thermodynamic potentials we obtain a much more compact and transparent description of the system. We can reproduce all the equations of state and we automatically satisfy all the consistency equations for these equations [6].

The formulation of thermodynamics in terms of thermodynamic potentials incorporates, and is actually guided by and based on, the celebrated fundamental laws of thermodynamics. The *proper formulation of the equations* is synonymous with the *deepest insight* into thermodynamics. Listing all the equations of state is good enough for *understanding a particular system*; however, *understanding thermodynamics* means identifying the structure of the equations. This successful identification of the structure behind thermodynamics is also very important when calculating thermodynamic properties from a more microscopic approach: No separate (and possibly inconsistent) calculations for each equation of state are required, but only a single calculation of a thermodynamic potential is needed (via the partition functions of statistical mechanics); a consistent set of equations of state is then derived from the thermodynamic potential.

As should be clear now by analogy, the proposed general time-evolution equation (1), if successful, would provide a deep understanding of nonequilibrium thermodynamics in the above spirit. We hence refer to Eq. (1) as the general equation for the nonequilibrium reversible-irreversible coupling (GENERIC). Only two ''potentials'' or generators (E and S) and two ''matrices'' or linear operators (L and M) need to be determined in order to specify the full time-evolution equations. We refer to the GENERIC (1) together with the requirements (2), (3), and (7)–(11) as the GENERIC structure. The GENERIC time evolution is proposed for nonequilibrium systems that, if not driven by external forces, approach thermodynamic equilibrium.

Writing well-known successful equations for nonequilibrium systems in the form (1) is the essential step for validating the proposed structure of nonequilibrium thermodynamics. The separate but similar occurrence of the two generators E and S in the reversible and irreversible terms of the GENERIC (1), which, together with the mutual degeneracy requirements, is the key innovation of the proposed formalism, leads to a deeper and more complete understanding of the role of entropy than can be gained in equilibrium thermodynamics.

A number of consistency conditions are implied by the proposed form of Eqs. (1)–(3) (including the Maxwell relations of equilibrium thermodynamics and the Onsager-Casimir relations of nonequilibrium thermodynamics [4]). As in equilibrium thermodynamics, the predictive power of the nonequilibrium formalism is based on these general consistency conditions extracted from many observations. Since there exists vast experience with the form of the energy E and the entropy S in equilibrium thermodynamics and since we will illustrate how the matrix L (or ''Poisson operator'') can be constructed in a rather straightforward manner, the formulation of dynamic equations for nonequilibrium systems can focus on the determination of M (the friction matrix, which has the properties of a ''metric matrix''). Calculations based on more microscopic models need to provide only an expression for M and not for all the terms in the time-evolution equations. In summary, a general formalism for nonequilibrium systems should provide the following: (i) a unified framework for empirical (macroscopic and mesoscopic) modeling, (ii) consistency conditions as the most fundamental predictions, and (iii) recipes for going from more microscopic to more macroscopic levels of description.

It is very important that the reader think critically about the above motivation and that he or she keeps the fundamental importance of our goal in mind while we are reformulating various known time-evolution equations for nonequilibrium systems in the form of the GENERIC (1). We first present detailed discussions of the reformulations of classical hydrodynamics (Sec. II) and a nonisothermal kinetic theory of polymeric fluids (Sec. III). As an example of the predictive power implied by the GENERIC structure of the time-evolution equations we then propose a more detailed polymer kinetic theory for heat transport (Sec. IV); we obtain further insight regarding the role of spring potentials of energetic and entropic origin. Finally, we comment on the reformulation of other well-known theories, such as extended irreversible thermodynamics, the bracket formalism of Beris and Edwards, and various additional effects considered in polymer kinetic theory, within our formalism (Sec. V).

II. CLASSICAL HYDRODYNAMICS

A. Time-evolution equations

We choose the following fields as independent variables for classical hydrodynamics: the mass density $\rho(\boldsymbol{r})$, the momentum density $\boldsymbol{u}(\boldsymbol{r})$, and the internal energy density $\epsilon(\boldsymbol{r})$. The momentum density field is closely related to the velocity field $\boldsymbol{v}(\boldsymbol{r})$, namely, by

$$\boldsymbol{u}(\boldsymbol{r})=\rho(\boldsymbol{r})\boldsymbol{v}(\boldsymbol{r}). \tag{13}$$

The time evolution of the mass density $\rho=\rho(\boldsymbol{r},t)$ is given by the equation of continuity

$$\frac{\partial\rho}{\partial t}=-\frac{\partial}{\partial\boldsymbol{r}}\cdot(\boldsymbol{v}\rho). \tag{14}$$

The time evolution of the momentum density $\boldsymbol{u}=\boldsymbol{u}(\boldsymbol{r},t)$ is given by the Navier-Stokes equation

$$\frac{\partial\boldsymbol{u}}{\partial t}=-\frac{\partial}{\partial\boldsymbol{r}}\cdot(\boldsymbol{v}\boldsymbol{u})-\frac{\partial}{\partial\boldsymbol{r}}p-\frac{\partial}{\partial\boldsymbol{r}}\cdot\boldsymbol{\tau}, \tag{15}$$

where p is the pressure, and we assume Newton's expression for the stress tensor in terms of velocity gradients, the viscosity η, and the dilatational viscosity (or second viscosity) κ,

$$\begin{aligned}\boldsymbol{\tau}=&-\eta\left[\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}+\left(\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}\right)^T\right]\\&-\left(\kappa-\frac{2}{3}\eta\right)\frac{\partial}{\partial\boldsymbol{r}}\cdot\boldsymbol{v}\boldsymbol{1}.\end{aligned} \tag{16}$$

External forces have been neglected in the Navier-Stokes equation (15).

The time evolution of $\epsilon=\epsilon(\boldsymbol{r},t)$ is given by the internal energy equation

$$\frac{\partial\epsilon}{\partial t}=-\frac{\partial}{\partial\boldsymbol{r}}\cdot(\boldsymbol{v}\epsilon)-p\frac{\partial}{\partial\boldsymbol{r}}\cdot\boldsymbol{v}-\frac{\partial}{\partial\boldsymbol{r}}\cdot\boldsymbol{j}^q-\boldsymbol{\tau}:\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}, \tag{17}$$

where we assume Fourier's expression for the heat flux $\boldsymbol{j}^q$ in terms of the temperature gradient and the thermal conductivity λ,

$$\boldsymbol{j}^q=-\lambda\frac{\partial}{\partial\boldsymbol{r}}T. \tag{18}$$

If the equilibrium equations of state $p=p(\rho,\epsilon)$ and $T=T(\rho,\epsilon)$ are known and if we make the ''local equilibrium assumption'' that the pressure and temperature fields can be obtained from these equilibrium relations by inserting the local mass and internal energy densities, then Eqs. (14)–(18) constitute a closed set of time-evolution equations. These are the well-known equations of classical hydrodynamics (see, e.g., Sec. 88 of [7] or Secs. 1.1 and 1.2 of [8]). The irreversible contributions to the dynamics are those involving the stress tensor $\boldsymbol{\tau}$ and the heat flux $\boldsymbol{j}^q$ in Eqs. (15) and (17); all the other terms in Eqs. (14), (15), and (17) constitute reversible contributions. In other words, the reversible contributions in Eqs. (14), (15), and (17) are obtained by setting $\eta=\kappa=\lambda=0$. We discuss the reformulation of the reversible and irreversible contributions to the time-evolution equations of hydrodynamics separately.

B. Reversible dynamics

In order to specify the reversible contribution to the general time-evolution equation (1) we need to define both the energy E as a function of x and the matrix L. For classical hydrodynamics, the list of independent state variables x is chosen as $(\rho(\boldsymbol{r}),\boldsymbol{u}(\boldsymbol{r}),\epsilon(\boldsymbol{r}))$. In other words, x is a vector with five components ($\boldsymbol{u}$ is a vector field), each of which is labeled by a further continuous variable $\boldsymbol{r}$. We hence need to define the energy E as a functional of the hydrodynamic fields $(\rho(\boldsymbol{r}),\boldsymbol{u}(\boldsymbol{r}),\epsilon(\boldsymbol{r}))$ and $\delta E/\delta x$ is to be interpreted as a collection of five functional derivatives.

The total energy can naturally be obtained by adding and integrating kinetic and internal energy densities over the entire volume of the flow system,

$$E=\int\left[\frac{1}{2}\,\frac{\boldsymbol{u}(\boldsymbol{r})^2}{\rho(\boldsymbol{r})}+\epsilon(\boldsymbol{r})\right]d^3r. \tag{19}$$

By taking functional derivatives with respect to the hydrodynamic fields we obtain, after using Eq. (13),

$$\frac{\delta E}{\delta x}=\begin{pmatrix}\dfrac{\delta}{\delta\rho(\boldsymbol{r})}\\[2ex] \dfrac{\delta}{\delta\boldsymbol{u}(\boldsymbol{r})}\\[2ex] \dfrac{\delta}{\delta\epsilon(\boldsymbol{r})}\end{pmatrix}E(\rho,\boldsymbol{u},\epsilon)=\begin{pmatrix}-\dfrac{1}{2}\boldsymbol{v}(\boldsymbol{r})^2\\[1ex] \boldsymbol{v}(\boldsymbol{r})\\[1ex] 1\end{pmatrix}. \tag{20}$$

External forces, such as gravity (characterized by a constant acceleration vector $\boldsymbol{g}$), can be incorporated by simply adding the corresponding potential energy, that is, $-\int\rho(\boldsymbol{r})\boldsymbol{g}\cdot\boldsymbol{r}d^3r$ for gravity, to the total energy (19).

The matrix L, or Poisson operator, of the general framework for classical hydrodynamics has two discrete indices (running from 1 to 5) and two further labels (corresponding to positions in space). We more explicitly denote it by $\boldsymbol{L}^{(S)}(\boldsymbol{r},\boldsymbol{r}')$, where the superscript (S) on the 5×5 matrix $\boldsymbol{L}$ indicates that entropy is taken as the underlying thermodynamic potential, that is, internal energy appears among the independent variables. A multiplication with $\boldsymbol{L}$ implies not only a matrix multiplication with a 5×5 matrix but also a three-dimensional integration over $\boldsymbol{r}'$. The explicit form of the matrix $\boldsymbol{L}$ for hydrodynamics is

$$\boldsymbol{L}^{(S)}(\boldsymbol{r},\boldsymbol{r}')=\begin{pmatrix}0 & \rho(\boldsymbol{r}')\dfrac{\partial\delta}{\partial\boldsymbol{r}'} & 0\\[2ex] \rho(\boldsymbol{r})\dfrac{\partial\delta}{\partial\boldsymbol{r}'} & \boldsymbol{u}(\boldsymbol{r}')\dfrac{\partial\delta}{\partial\boldsymbol{r}'}+\dfrac{\partial\delta}{\partial\boldsymbol{r}'}\boldsymbol{u}(\boldsymbol{r}) & \epsilon(\boldsymbol{r})\dfrac{\partial\delta}{\partial\boldsymbol{r}'}+\dfrac{\partial\delta}{\partial\boldsymbol{r}'}p(\boldsymbol{r}')\\[2ex] 0 & \epsilon(\boldsymbol{r}')\dfrac{\partial\delta}{\partial\boldsymbol{r}'}+\dfrac{\partial\delta}{\partial\boldsymbol{r}'}p(\boldsymbol{r}) & 0\end{pmatrix}, \tag{21}$$

where $\delta=\delta(\boldsymbol{r}-\boldsymbol{r}')$ is Dirac's delta function of $\boldsymbol{r}-\boldsymbol{r}'$. By multiplying the right-hand side of Eq. (20), using $\boldsymbol{r}'$ instead of $\boldsymbol{r}$ in that equation, with the right-hand side of Eq. (21), and integrating over $\boldsymbol{r}'$ one can verify explicitly that all the reversible contributions to the time-evolution equations of classical hydrodynamics are obtained, that is, Eqs. (14)–(18) with $\eta=\kappa=\lambda=0$.

The actual calculation can be simplified by observing that, as mentioned above, multiplication with the Poisson operator $\boldsymbol{L}^{(S)}(\boldsymbol{r},\boldsymbol{r}')$ implies both a matrix multiplication and an integration over $\boldsymbol{r}'$. After an integration by parts, the integration over $\boldsymbol{r}'$ can be performed due to the occurrence of δ functions in all the matrix elements of $\boldsymbol{L}^{(S)}(\boldsymbol{r},\boldsymbol{r}')$. Instead of a matrix with generalized functions as matrix elements we then obtain an equivalent matrix, the elements of which are differential operators (the derivatives act on all terms to the right of them):

$$\boldsymbol{L}^{(S)}(\boldsymbol{r})=-\begin{pmatrix}0 & \dfrac{\partial}{\partial\boldsymbol{r}}\rho(\boldsymbol{r}) & 0\\[2ex] \rho(\boldsymbol{r})\dfrac{\partial}{\partial\boldsymbol{r}} & \left[\dfrac{\partial}{\partial\boldsymbol{r}}\boldsymbol{u}(\boldsymbol{r})+\boldsymbol{u}(\boldsymbol{r})\dfrac{\partial}{\partial\boldsymbol{r}}\right]^T & \epsilon(\boldsymbol{r})\dfrac{\partial}{\partial\boldsymbol{r}}+\dfrac{\partial}{\partial\boldsymbol{r}}p(\boldsymbol{r})\\[2ex] 0 & \dfrac{\partial}{\partial\boldsymbol{r}}\epsilon(\boldsymbol{r})+p(\boldsymbol{r})\dfrac{\partial}{\partial\boldsymbol{r}} & 0\end{pmatrix}. \tag{22}$$

We will repeatedly use this kind of simplified notation throughout this paper.

While the verification of the proper form of the Poisson operator (21) for classical hydrodynamics is straightforward, its form may at first sight appear rather arbitrary. Beris and Edwards present a derivation of the Poisson bracket (4) equivalent to the Poisson operator (21) from a variational principle of classical mechanics (see Secs. 5.1–5.3 of [9] and [10]; the pioneering original publications are [11–14]). A straightforward construction of the expression (21) based on the representation of the continuous group of space transformations on the space of hydrodynamic fields will be given at the end of this section, where also a number of other procedures for constructing Poisson operators are summarized.

C. Irreversible dynamics

In order to specify the irreversible contribution to the general time-evolution equation (1) we must define both the entropy S as a function of x, and the metric matrix M. For classical hydrodynamics, a very natural expression for the entropy is obtained by the local equilibrium assumption

$$S=\int s(\rho(\boldsymbol{r}),\epsilon(\boldsymbol{r}))d^3r, \tag{23}$$

where the function $s(\rho,\epsilon)$ expresses the relationship between the densities of entropy, mass, and internal energy at equilibrium. By taking functional derivatives with respect to the hydrodynamic fields we obtain

$$\frac{\delta S}{\delta x}=\begin{pmatrix} -\dfrac{\mu(\boldsymbol{r})}{T(\boldsymbol{r})} \\ \mathbf{0} \\ \dfrac{1}{T(\boldsymbol{r})} \end{pmatrix}, \tag{24}$$

where the local temperature T is defined by

$$T(\boldsymbol{r})=\left(\frac{\partial s(\rho,\epsilon)}{\partial\epsilon}\right)^{-1} \tag{25}$$

and the local chemical potential μ per unit mass by

$$\frac{\mu(\boldsymbol{r})}{T(\boldsymbol{r})}=-\frac{\partial s(\rho,\epsilon)}{\partial\rho}, \tag{26}$$

both being functions of $\boldsymbol{r}$ because they are evaluated at $\rho(\boldsymbol{r}),\epsilon(\boldsymbol{r})$.

In order to reproduce the equations of hydrodynamics we introduce the metric matrix M,

$$\boldsymbol{M}^{(S)}(\boldsymbol{r},\boldsymbol{r}')=\begin{pmatrix} 0 & 0 & 0 \\ 0 & \left(\dfrac{\partial}{\partial\boldsymbol{r}'}\dfrac{\partial}{\partial\boldsymbol{r}}+\mathbf{1}\dfrac{\partial}{\partial\boldsymbol{r}'}\cdot\dfrac{\partial}{\partial\boldsymbol{r}}\right)\eta T\delta+2\dfrac{\partial}{\partial\boldsymbol{r}}\dfrac{\partial}{\partial\boldsymbol{r}'}\hat{\kappa}T\delta & \dfrac{\partial}{\partial\boldsymbol{r}}\cdot\eta T\dot{\boldsymbol{\gamma}}\delta+\dfrac{\partial}{\partial\boldsymbol{r}}\hat{\kappa}T\mathrm{tr}\dot{\boldsymbol{\gamma}}\delta \\ 0 & \dfrac{\partial}{\partial\boldsymbol{r}'}\cdot\eta T\dot{\boldsymbol{\gamma}}\delta+\dfrac{\partial}{\partial\boldsymbol{r}'}\hat{\kappa}T\mathrm{tr}\dot{\boldsymbol{\gamma}}\delta & \dfrac{1}{2}\eta T\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}}\delta+\dfrac{\partial}{\partial\boldsymbol{r}}\cdot\dfrac{\partial}{\partial\boldsymbol{r}'}\lambda T^2\delta+\dfrac{1}{2}\hat{\kappa}T(\mathrm{tr}\dot{\boldsymbol{\gamma}})^2\delta \end{pmatrix}, \tag{27}$$

where $\delta=\delta(\boldsymbol{r}-\boldsymbol{r}')$, the transport coefficient $\hat{\kappa}$ is a combination of the viscosity η and the dilatational viscosity κ,

$$\hat{\kappa}=\frac{\kappa}{2}-\frac{\eta}{3}, \tag{28}$$

and the tensor $\dot{\boldsymbol{\gamma}}$ is the symmetrized velocity gradient tensor

$$\dot{\boldsymbol{\gamma}}(\boldsymbol{r})=\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}(\boldsymbol{r})+\left[\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}(\boldsymbol{r})\right]^T. \tag{29}$$

While verifying that $M\partial S/\partial x$ reproduces all the irreversible terms in Eqs. (15) and (17) is straightforward, the detailed motivation for writing the metric matrix for hydrodynamics in the form (27) may not be so obvious. In view of Eq. (24), only the last column of M in Eq. (27) actually contributes to the irreversible dynamics. The last row is then fixed by the symmetry requirement $\boldsymbol{M}^{(S)}(\boldsymbol{r},\boldsymbol{r}')=\boldsymbol{M}^{(S)}(\boldsymbol{r}',\boldsymbol{r})^T$. Crucial for constructing $\boldsymbol{M}^{(S)}(\boldsymbol{r},\boldsymbol{r}')$ is actually the element in the lower right corner, which describes the energy dissipation. The other nonvanishing block in the last row is determined by the requirement that $\delta E/\delta x$ lies in the null space of M,

$$M\frac{\delta E}{\delta x}=\int \boldsymbol{M}^{(S)}(\boldsymbol{r},\boldsymbol{r}')\cdot\begin{pmatrix} -\dfrac{1}{2}\boldsymbol{v}(\boldsymbol{r}')^2 \\ \boldsymbol{v}(\boldsymbol{r}') \\ 1 \end{pmatrix} d^3r'=\mathbf{0}. \tag{30}$$

Then the other nonvanishing block in the last column is determined by symmetry. Finally, the determination of the central block of M again requires the assumption (30).

The matrix M in Eq. (27) has all the properties formulated in the Introduction. It is symmetric [see Eq. (10)] and can be verified to be positive semidefinite [see Eq. (11)], so that we may call M a metric matrix and $\delta E/\delta x$ lies in the null space of M [see Eq. (3)]. We just realized that these properties are very important for obtaining a unique expression for the matrix M of classical hydrodynamics. The matrix elements of M for classical hydrodynamics are proportional to η, $\hat{\kappa}$, and λ, so that its relation to dissipative material properties and irreversible dynamics should be obvious. This observation justifies the term ''friction matrix'' for M.

The positive-semidefinite nature of the matrix $\boldsymbol{M}^{(S)}(\boldsymbol{r},\boldsymbol{r}')$ can be shown by writing it in the form

$$\int \boldsymbol{B}^{(S)}(\boldsymbol{r},\boldsymbol{r}'') \cdot \boldsymbol{B}^{(S)}(\boldsymbol{r}',\boldsymbol{r}'')^T d^3r'' = 2k_\mathrm{B}\boldsymbol{M}^{(S)}(\boldsymbol{r},\boldsymbol{r}'), \quad (31)$$

where k_B is Boltzmann's constant. This identity can be verified explicitly for the lower triangular matrix

$$\boldsymbol{B}^{(S)}(\boldsymbol{r},\boldsymbol{r}') = \begin{pmatrix} 0 & 0 & 0 \\ 2\frac{\partial}{\partial r_j}\sqrt{\hat{\kappa} k_\mathrm{B} T}\,\delta & \left(\delta_{jk}\frac{\partial}{\partial r_l} + \delta_{jl}\frac{\partial}{\partial r_k}\right)\sqrt{\eta k_\mathrm{B} T}\,\delta & 0 \\ \mathrm{tr}\dot{\boldsymbol{\gamma}}\sqrt{\hat{\kappa} k_\mathrm{B} T}\,\delta & \dot{\gamma}_{kl}\sqrt{\eta k_\mathrm{B} T}\,\delta & \frac{\partial}{\partial r_k}\sqrt{2\lambda k_\mathrm{B} T^2}\,\delta \end{pmatrix}, \quad (32)$$

where, again, $\delta = \delta(\boldsymbol{r}-\boldsymbol{r}')$. In the middle row, the subscript j labels the rows corresponding to the components of the momentum vector. The indices k and l in the middle column correspond to an index pair to be summed over if $\boldsymbol{B}^{(S)}(\boldsymbol{r},\boldsymbol{r}')$ is multiplied with another matrix or column vector from the right. According to the fluctuation-dissipation theorem of paper I, the matrix (32) characterizes the fluctuations to be added to the equations of hydrodynamics; the resulting stochastic partial differential equations coincide with those occurring in the standard theory of fluctuating hydrodynamics where, however, $T = T(\boldsymbol{r})$ here is the local-equilibrium temperature defined in Eq. (25) (see Chap. IX of [7] and [15]).

Another important cross relationship between the reversible and irreversible dynamics, stated in Eq. (2), remains to be checked for classical hydrodynamics:

$$L\frac{\delta S}{\delta x} = \boldsymbol{L}^{(S)}(\boldsymbol{r}) \cdot \begin{pmatrix} -\dfrac{\mu(\boldsymbol{r})}{T(\boldsymbol{r})} \\ \boldsymbol{0} \\ \dfrac{1}{T(\boldsymbol{r})} \end{pmatrix} = \boldsymbol{0}. \quad (33)$$

By using the explicit expression (22) for $\boldsymbol{L}^{(S)}(\boldsymbol{r})$ we find the alternative formulation

$$\frac{\partial}{\partial \boldsymbol{r}}\left(\frac{\epsilon(\boldsymbol{r}) - \mu(\boldsymbol{r})\rho(\boldsymbol{r}) - T(\boldsymbol{r})s(\boldsymbol{r}) + p(\boldsymbol{r})}{T(\boldsymbol{r})}\right) = \boldsymbol{0}. \quad (34)$$

In view of our definitions for p, T, s, and μ, this latter form of the condition follows immediately from the Gibbs-Duhem equation for the local equilibrium system.

A more general explicit calculation shows that the gradient of a functional of the form $\int f(\rho(\boldsymbol{r}),\epsilon(\boldsymbol{r}))d^3r$ is in the null space of the Poisson operator L if and only if

$$f - \rho\frac{\partial f}{\partial \rho} - (\epsilon + p)\frac{\partial f}{\partial \epsilon} = \text{const}. \quad (35)$$

The fact that $\delta S/\delta x$ is in the null space of L follows from the Gibbs-Duhem equation, which can be written in the form

$$s = \rho\frac{\partial s}{\partial \rho} + (\epsilon + p)\frac{\partial s}{\partial \epsilon}. \quad (36)$$

Further solutions of Eq. (35) are constants ($f = \text{const}$) and the mass density ($f = \rho$). The gradient of the total mass

$$\frac{\delta}{\delta x}\int \rho(\boldsymbol{r})d^3r = \begin{pmatrix} 1 \\ \boldsymbol{0} \\ 0 \end{pmatrix} \quad (37)$$

is actually in the null space of both L and M. Of course, this property simply expresses the conservation of mass.

The matrix elements of $\boldsymbol{M}^{(S)}(\boldsymbol{r},\boldsymbol{r}')$ are generalized functions, that is, the derivatives act only on the functions in the matrix elements. As previously observed for the Poisson operator $\boldsymbol{L}^{(S)}(\boldsymbol{r},\boldsymbol{r}')$, we can simplify notation and calculations by introducing a matrix $\boldsymbol{M}^{(S)}(\boldsymbol{r})$, the elements of which are differential operators (that is, the derivatives act on all terms to the right of them and all integrations have already been performed):

$$\boldsymbol{M}^{(S)}(\boldsymbol{r}) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\left(\frac{\partial}{\partial \boldsymbol{r}}\eta T\frac{\partial}{\partial \boldsymbol{r}} + \boldsymbol{1}\frac{\partial}{\partial \boldsymbol{r}}\cdot\eta T\frac{\partial}{\partial \boldsymbol{r}}\right)^T - 2\frac{\partial}{\partial \boldsymbol{r}}\hat{\kappa}T\frac{\partial}{\partial \boldsymbol{r}} & \frac{\partial}{\partial \boldsymbol{r}}\cdot\eta T\dot{\boldsymbol{\gamma}} + \frac{\partial}{\partial \boldsymbol{r}}\hat{\kappa}T\mathrm{tr}\dot{\boldsymbol{\gamma}} \\ 0 & -\eta T\dot{\boldsymbol{\gamma}}\cdot\frac{\partial}{\partial \boldsymbol{r}} - \hat{\kappa}T\mathrm{tr}\dot{\boldsymbol{\gamma}}\frac{\partial}{\partial \boldsymbol{r}} & \frac{1}{2}\eta T\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}} - \frac{\partial}{\partial \boldsymbol{r}}\cdot\lambda T^2\frac{\partial}{\partial \boldsymbol{r}} + \frac{1}{2}\hat{\kappa}T(\mathrm{tr}\dot{\boldsymbol{\gamma}})^2 \end{pmatrix}. \quad (38)$$

At this point, the reader should pause and think about the implications of the GENERIC structure for the familiar example of hydrodynamics. Of course, we know too much about hydrodynamics, so that we cannot gain any new insight. The concrete and important implications of the rather formal complementary degeneracy requirements (2) and (3) should, however, be fully appreciated. Equation (2) implies the Gibbs-Duhem equation for the local equilibrium system and Eq. (3) implies that the form of the energy dissipation determines the entire metric matrix and hence the structure of the stress tensor.

D. Construction of the Poisson operator from group theory

In the GENERIC formulation (1) of time-evolution equations for nonequilibrium systems, four building blocks are required. For classical hydrodynamics we have seen that the expressions for the energy E and the entropy S are very natural. Formulating the metric matrix M corresponds to postulating the constitutive equations of Newton and Fourier, which can be justified empirically or by more microscopic calculations. What can be said about the construction of the Poisson operator L? So far, we have identified L by rewriting the well-known time-evolution equations of hydrodynamics within our formalism. It is the purpose of this section to show how L can be constructed in a rather straightforward and more general manner by arguments from group theory.

The basic idea is that L should express only kinematic effects, while all the interactions and inertial effects come in through the total energy. The pure kinematics of the systems studied in this paper are expected to be closely related to space transformations and we hence consider actions of the group of space transformations on the state space for the system of interest. Such actions are the key to the construction of the kinematics accounted for by Poisson operators.

There is one requirement for L that might be expected to bring in some physics beyond pure kinematics: the degeneracy requirement that the gradient of entropy should be in the null space of L. For classical hydrodynamics, this thermodynamic requirement enters L only through the pressure and we have already realized that it corresponds to the Gibbs-Duhem equation. The pressure occurs very naturally when considering the behavior of the internal energy density under volume-changing space transformations.

In order to construct a natural action of the group of space transformations on the state space of hydrodynamics $H^{(S)}=\{(\rho(\boldsymbol{r}),\boldsymbol{u}(\boldsymbol{r}),\epsilon(\boldsymbol{r}))\}$, we first consider the transformation behavior of a scalar density field such as the mass density $\rho(\boldsymbol{r})$. Let us describe an infinitesimal space transformation by

$$\boldsymbol{r}\rightarrow\boldsymbol{r}+t\boldsymbol{v}(\boldsymbol{r}), \tag{39}$$

where t is a small parameter and the vector field $\boldsymbol{v}(\boldsymbol{r})$ generates the infinitesimal transformation. If t is interpreted as (infinitesimally short) time, $\boldsymbol{v}(\boldsymbol{r})$ formally corresponds to a velocity field. For a scalar field, the natural action of an infinitesimal space transformation would be that the transformed field is obtained by evaluating the original field at the position $\boldsymbol{r}-t\boldsymbol{v}(\boldsymbol{r})$. For a scalar density field, also the effect of volume changes as described by the Jacobian of the transformation (39), or its inverse, has to be taken into account,

$$\rho(\boldsymbol{r})\rightarrow\rho(\boldsymbol{r}-t\boldsymbol{v}(\boldsymbol{r}))\left|\mathbf{1}-t\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}(\boldsymbol{r})\right|. \tag{40}$$

For small t, the Jacobian can be expressed in terms of the trace of $\partial\boldsymbol{v}/\partial\boldsymbol{r}$ and we thus obtain to first order in t

$$\rho(\boldsymbol{r})\rightarrow\rho(\boldsymbol{r})-t\frac{\partial}{\partial\boldsymbol{r}}\cdot[\boldsymbol{v}(\boldsymbol{r})\rho(\boldsymbol{r})]. \tag{41}$$

Equation (41) expresses the canonical action of the infinitesimal space transformation (39) on a scalar density field. As a next step, we consider the transformation behavior of a vector density field such as $\boldsymbol{u}(\boldsymbol{r})$. More precisely, $\boldsymbol{u}(\boldsymbol{r})$ is a covariant vector density field. A vector field cannot simply be evaluated at the position $\boldsymbol{r}-t\boldsymbol{v}(\boldsymbol{r})$, but needs to be properly convected according to the gradient of $\boldsymbol{v}(\boldsymbol{r})$, so that convected derivatives occur (see, e.g., Appendix D.2 of [16] or pp. 106–107 of [17]; in geometrical terms, these correspond to Lie derivatives [18]). We hence obtain the following canonical action of the infinitesimal space transformation (39) on a covariant vector density field:

$$\boldsymbol{u}(\boldsymbol{r})\rightarrow\boldsymbol{u}(\boldsymbol{r})-t\left\{\frac{\partial}{\partial\boldsymbol{r}}\cdot[\boldsymbol{v}(\boldsymbol{r})\boldsymbol{u}(\boldsymbol{r})]+\left[\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}(\boldsymbol{r})\right]\cdot\boldsymbol{u}(\boldsymbol{r})\right\}. \tag{42}$$

Equations (41) and (42) are expressions of pure kinematics in the sense that the scalar or vector density field character completely determines the behavior under space transformations. This simplicity is related to the conservation of mass and momentum. If we turn to the internal energy density field $\epsilon(\boldsymbol{r})$, this contribution to energy is not conserved. This observation is related to the fact that volume changes lead to a change of internal energy, where thermodynamic information enters through the pressure field. We hence formulate the following modification of Eq. (41) as the canonical action of the infinitesimal space transformation (39) on $\epsilon(\boldsymbol{r})$:

$$\epsilon(\boldsymbol{r})\rightarrow\epsilon(\boldsymbol{r})-t\left\{\frac{\partial}{\partial\boldsymbol{r}}\cdot[\boldsymbol{v}(\boldsymbol{r})\epsilon(\boldsymbol{r})]+p(\boldsymbol{r})\frac{\partial}{\partial\boldsymbol{r}}\cdot\boldsymbol{v}(\boldsymbol{r})\right\}. \tag{43}$$

With Eqs. (41)–(43) we know how the infinitesimal space transformation (39) acts on arbitrary functionals of $(\rho(\boldsymbol{r}),\boldsymbol{u}(\boldsymbol{r}),\epsilon(\boldsymbol{r}))$, that is, on arbitrary functions defined on the state space $H^{(S)}$ of hydrodynamics.

We now assume that the operator L generates the transformations (41)–(43) in the following sense:

$$\begin{pmatrix} -\dfrac{\partial}{\partial \boldsymbol{r}}\cdot[\boldsymbol{v}(\boldsymbol{r})\rho(\boldsymbol{r})] \\ -\dfrac{\partial}{\partial \boldsymbol{r}}\cdot[\boldsymbol{v}(\boldsymbol{r})\boldsymbol{u}(\boldsymbol{r})]-\left[\dfrac{\partial}{\partial \boldsymbol{r}}\boldsymbol{v}(\boldsymbol{r})\right]\cdot\boldsymbol{u}(\boldsymbol{r}) \\ -\dfrac{\partial}{\partial \boldsymbol{r}}\cdot[\boldsymbol{v}(\boldsymbol{r})\epsilon(\boldsymbol{r})]-p(\boldsymbol{r})\dfrac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{v}(\boldsymbol{r}) \end{pmatrix}$$

$$=\int \boldsymbol{L}^{(S)}(\boldsymbol{r},\boldsymbol{r}')\cdot\begin{pmatrix} \dfrac{\delta G}{\delta\rho(\boldsymbol{r}')} \\ \dfrac{\delta G}{\delta\boldsymbol{u}(\boldsymbol{r}')} \\ \dfrac{\delta G}{\delta\epsilon(\boldsymbol{r}')} \end{pmatrix} d^3r', \tag{44}$$

where

$$G=\int \boldsymbol{u}(\boldsymbol{r})\cdot\boldsymbol{v}(\boldsymbol{r})d^3r \tag{45}$$

is a bilinear functional of the covariant vector field $\boldsymbol{u}(\boldsymbol{r})$ and the contravariant vector field $\boldsymbol{v}(\boldsymbol{r})$ that is closely related to the kinetic energy and hence to kinematics. The linearity of G in $\boldsymbol{v}(\boldsymbol{r})$ is crucial in order to obtain an operator L that is independent of the infinitesimal space transformation $\boldsymbol{v}(\boldsymbol{r})$. One should note the well-known crucial role of momentum in the generating functional for space transformations (45): For a translation independent of position, G is the projection of the total momentum on the shift vector $\boldsymbol{v}$; for position-dependent space transformations, the momentum density is weighted by $\boldsymbol{v}(\boldsymbol{r})$. Equations (44) and (45) constitute the precise formulation of the idea that the action of infinitesimal space transformations and pure kinematics should be related.

From Eq. (44) we conclude that the Poisson operator has a matrix representation of the form

$$\boldsymbol{L}^{(S)}(\boldsymbol{r},\boldsymbol{r}')=\begin{pmatrix} * & \rho(\boldsymbol{r}')\dfrac{\partial\delta(\boldsymbol{r}-\boldsymbol{r}')}{\partial\boldsymbol{r}'} & * \\ * & \boldsymbol{u}(\boldsymbol{r}')\dfrac{\partial\delta(\boldsymbol{r}-\boldsymbol{r}')}{\partial\boldsymbol{r}'}+\dfrac{\partial\delta(\boldsymbol{r}-\boldsymbol{r}')}{\partial\boldsymbol{r}'}\boldsymbol{u}(\boldsymbol{r}) & * \\ * & \epsilon(\boldsymbol{r}')\dfrac{\partial\delta(\boldsymbol{r}-\boldsymbol{r}')}{\partial\boldsymbol{r}'}+\dfrac{\partial\delta(\boldsymbol{r}-\boldsymbol{r}')}{\partial\boldsymbol{r}'}p(\boldsymbol{r}) & * \end{pmatrix}. \tag{46}$$

Only the center column of $\boldsymbol{L}^{(S)}(\boldsymbol{r},\boldsymbol{r}')$ is fixed by Eq. (44). The center row is determined by the antisymmetry requirement on the Poisson operator. If the four corner elements are set equal to zero because they are irrelevant to the kinematics and because the gradient of the entropy then turns out to lie in the null space of the Poisson operator, we arrive at the previously given expression (21) for the Poisson operator for hydrodynamics.

The formulation of L for hydrodynamics becomes somewhat simpler if the state space $H^{(E)}=\{(\rho(\boldsymbol{r}),\boldsymbol{u}(\boldsymbol{r}),s(\boldsymbol{r}))\}$ is used instead of $H^{(S)}$. The simplification results from the assumption that the gradient of the entropy must lie in the null space of the Poisson operator, which corresponds to assuming that $s(\boldsymbol{r})$ is a scalar density field. The corresponding Poisson operator is then given by

$$\boldsymbol{L}^{(E)}(\boldsymbol{r},\boldsymbol{r}')=\begin{pmatrix} 0 & \rho(\boldsymbol{r}')\dfrac{\partial\delta}{\partial\boldsymbol{r}'} & 0 \\ \rho(\boldsymbol{r})\dfrac{\partial\delta}{\partial\boldsymbol{r}'} & \boldsymbol{u}(\boldsymbol{r}')\dfrac{\partial\delta}{\partial\boldsymbol{r}'}+\dfrac{\partial\delta}{\partial\boldsymbol{r}'}\boldsymbol{u}(\boldsymbol{r}) & s(\boldsymbol{r})\dfrac{\partial\delta}{\partial\boldsymbol{r}'} \\ 0 & s(\boldsymbol{r}')\dfrac{\partial\delta}{\partial\boldsymbol{r}'} & 0 \end{pmatrix}, \tag{47}$$

where $\delta=\delta(\boldsymbol{r}-\boldsymbol{r}')$. Using $s(\boldsymbol{r})$ as an independent variable in constructing the Poisson operator for hydrodynamics is thus very advantageous. However, when polymer solutions are considered in Sec. III, the total rather than the solvent entropy is conserved by the reversible time evolution, so that the use of $s(\boldsymbol{r})$ as a state variable is less advantageous. On the other hand, by using $\epsilon(\boldsymbol{r})$ as a state variable for polymer solutions one can very intuitively couple the polymer and solvent dynamics through the osmotic pressure.

One can summarize the above procedure for constructing L as follows. We are interested in the Poisson bracket that allows us to determine the reversible time evolution from a given energy function. Since we have a more direct understanding of space transformations rather than of time propagations, we consider the behavior of the state variables under space transformations together with the corresponding generator (momentum). By relating space transformations and momentum, we obtain information about the appropriate Poisson bracket or L operator.

There are a number of alternative procedures for determining L. One possibility is based on a close relationship between the Lie group structure and the Poisson structure (the state variables are regarded as elements of the dual of a Lie algebra). We refer interested readers to [2] and, in particular, to [19], where important examples are worked out explicitly (in Sec. 4).

In another alternative approach to constructing L, the state variables are regarded as elements of a space that is reduced in size (by the Marsden-Weinstein reduction [2]) from a larger space on which the Poisson kinematics is canonical. For example, in the context of hydrodynamics, the Poisson kinematics in the Lagrangian description is canonical. The Eulerian description can be obtained from the Lagrangian description as a Marsden-Weinstein reduction. Variations on this method have been developed in [9,10,14]. Alternatively, the state variables can be obtained by a projection operator from state variables in a more microscopic state space in which the Poisson kinematics is known. While this method is very useful, there is, however, no guarantee for success because problems with closing the equations may occur.

In some cases it may be useful to look for a one-to-one relation with another state space whose Poisson kinematics is known. In such a case the transformation (31) of paper I relates the two Poisson operators L. This is, for example, the procedure that we can use to derive the Poisson kinematics of the Eulerian hydrodynamics in the entropy representation (21) from the energy representation (47). Finally, also methods developed originally in quantum mechanics have been employed to derive the Poisson kinematics in [13].

The formulation of the Poisson operator is quite straightforward when the state variables x are densities of conserved quantities. For example, the operator L of hydrodynamics merely expresses the conservation laws. State variables related to conserved or extensive quantities are particularly convenient also in constructing suitable energy and entropy expressions. In general, however, we leave the nature of the state variables unspecified.

III. NONISOTHERMAL KINETIC THEORY OF POLYMERIC FLUIDS

As a next step we cast a nonisothermal kinetic theory model of polymeric fluids into our general framework. Encouraged by our experience with classical hydrodynamics, we do not start from the known equations of motion for obtaining the four building blocks in the fundamental equation (1). We directly formulate expressions for the energy and entropy, we construct the Poisson operator by means of group theory, and we modify the metric matrix of classical hydrodynamics in a rather suggestive manner, which is checked to be consistent with the general requirements. The time-evolution equations implied by the resulting four building blocks of our formalism will then be written down explicitly and compared to the known equations of polymer kinetic theory. Again, we do not obtain new equations, but the reader should learn to appreciate the implications of the GENERIC structure and the general procedure. Of course, the dumbbell model considered here is only a very crude approximation to polymeric fluids. A related but different approach to the same problem can be found in [20].

A. Independent variables, energy, and entropy

We choose the following fields as independent variables for a dumbbell kinetic theory of a dilute polymer solution: the mass density $\rho(\boldsymbol{r})$ of solution, the momentum density $\boldsymbol{u}(\boldsymbol{r})$ of the solution, the internal energy density of solvent $\epsilon(\boldsymbol{r})$, and the configurational distribution function $\psi(\boldsymbol{r},\boldsymbol{Q})$, where $\boldsymbol{Q}$ is interpreted as a dumbbell configuration vector. For a dilute polymer solution, the mass and momentum densities of the solvent and the solution coincide, whereas the large polymer molecules can contribute significantly to stress and internal energy.

The total energy is obtained by adding the kinetic energy and the solvent and polymer potential energy contributions,

$$E=\int\left[\frac{1}{2}\,\frac{\boldsymbol{u}(\boldsymbol{r})^2}{\rho(\boldsymbol{r})}+\epsilon(\boldsymbol{r})+\int V(Q)\,\psi(\boldsymbol{r},\boldsymbol{Q})d^3Q\right]d^3r, \tag{48}$$

where $V(Q)$ is the interaction potential between the beads of a dumbbell (potential of the ‘‘connector or spring force’’). In many cases, the spring force is assumed to be of entropic origin. Within our framework, it is natural to trace back carefully the energetic and entropic origin of interactions. While in equilibrium thermodynamics (and in the bracket formalism [9]) only a combination of energy and entropy effects occurs in the fundamental free energy, energy and entropy play clearly distinct roles in our present nonequilibrium theory. In a nonisothermal situation, a spring potential of entropic origin $V^{(S)}(\boldsymbol{r},Q)$ would actually depend through temperature on position. More precisely, we assume that for potentials of purely entropic origin the ratio $S^{(V)}(Q)=V^{(S)}(\boldsymbol{r},Q)/T(\boldsymbol{r})$ is independent of $\boldsymbol{r}$. While true interaction potentials should be incorporated into Eq. (48), the classical entropic spring must be included in the entropy

$$S=\int\left\{s(\rho(\boldsymbol{r}),\epsilon(\boldsymbol{r}))-\int\psi(\boldsymbol{r},\boldsymbol{Q})\left[\frac{V^{(S)}(\boldsymbol{r},Q)}{T(\boldsymbol{r})}+k_{\mathrm{B}}\ln\psi(\boldsymbol{r},\boldsymbol{Q})\right]d^3Q\right\}d^3r. \tag{49}$$

While $s(\rho,\epsilon)$ is to be interpreted as the solvent entropy, the $\psi\ln\psi$ term is clearly associated with the dumbbell translational and configurational entropy, and the entropic potential $V^{(S)}(\boldsymbol{r},Q)$ accounts for entropic effects on the much finer level of polymer segments that have been eliminated in coarse graining to the dumbbell level. For later use, we write down the functional derivatives of E and S with respect to the independent variables $x=(\rho(\boldsymbol{r}),\boldsymbol{u}(\boldsymbol{r}),\epsilon(\boldsymbol{r}),\psi(\boldsymbol{r},\boldsymbol{Q}))$:

$$\frac{\delta E}{\delta x}=\begin{pmatrix}-\frac{1}{2}\boldsymbol{v}(\boldsymbol{r})^2\\ \boldsymbol{v}(\boldsymbol{r})\\ 1\\ V(Q)\end{pmatrix} \tag{50}$$

and

$$\frac{\delta S}{\delta x}=\begin{pmatrix}-\dfrac{\mu(\boldsymbol{r})}{T(\boldsymbol{r})}\\ \boldsymbol{0}\\ \dfrac{1}{T(\boldsymbol{r})}\\ -\dfrac{V^{(S)}(\boldsymbol{r},Q)}{T(\boldsymbol{r})}-k_{\mathrm{B}}\ln\psi(\boldsymbol{r},\boldsymbol{Q})-k_{\mathrm{B}}\end{pmatrix}. \tag{51}$$

B. Construction of the Poisson operator

As the state space for our nonisothermal kinetic theory of a dilute polymer solution we use $\{(\rho(\boldsymbol{r}),\boldsymbol{u}(\boldsymbol{r}),\epsilon(\boldsymbol{r}),\psi(\boldsymbol{r},\boldsymbol{Q}))\}$. The action of space transformations on $\rho(\boldsymbol{r})$ and $\boldsymbol{u}(\boldsymbol{r})$ is still given by Eqs. (41) and (42), respectively. However, the pressure term in the transformation of the internal energy density should be modified due to the presence of osmotic pressure,

$$\epsilon(\boldsymbol{r})\rightarrow\epsilon(\boldsymbol{r})-t\left\{\frac{\partial}{\partial\boldsymbol{r}}\cdot[\boldsymbol{v}(\boldsymbol{r})\epsilon(\boldsymbol{r})]+[p(\boldsymbol{r})+\Pi(\boldsymbol{r})]\frac{\partial}{\partial\boldsymbol{r}}\cdot\boldsymbol{v}(\boldsymbol{r})\right\}, \tag{52}$$

where

$$\Pi(\boldsymbol{r})=2k_{\mathrm{B}}T(\boldsymbol{r})\int\psi(\boldsymbol{r},\boldsymbol{Q})d^3Q \tag{53}$$

is the osmotic pressure due to the presence of the beads. The solvent temperature is given by the expression in Eq. (25).

The quantity $2\int \psi(\boldsymbol{r},\boldsymbol{Q})d^3Q$ corresponds to the bead number density (this statement actually clarifies the normalization of ψ).

The occurrence of osmotic pressure in Eq. (52) is related to entropy effects; it is essential for ensuring that the gradient of entropy lies in the null space of the Poisson operator, that is, for satisfying the degeneracy requirement (2). However, the conservation of the spring contribution to entropy under the reversible dynamics has not yet been taken into account. This can be done by further modifying Eqs. (52) and (53) in the following manner:

$$\epsilon(\boldsymbol{r})\to\epsilon(\boldsymbol{r})-t\left\{\frac{\partial}{\partial\boldsymbol{r}}\cdot[\boldsymbol{v}(\boldsymbol{r})\epsilon(\boldsymbol{r})]+[p(\boldsymbol{r})\boldsymbol{1}+\boldsymbol{\Pi}(\boldsymbol{r})]:\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}(\boldsymbol{r})\right\}, \tag{54}$$

where

$$\boldsymbol{\Pi}(\boldsymbol{r})=\int\psi(\boldsymbol{r},\boldsymbol{Q})\left[2k_{\mathrm{B}}T(\boldsymbol{r})\boldsymbol{1}-\boldsymbol{Q}\frac{\partial V^{(S)}(\boldsymbol{r},Q)}{\partial\boldsymbol{Q}}\right]d^3Q \tag{55}$$

is the *osmotic pressure tensor*. The osmotic pressure tensor in Eq. (54) provides the thermodynamic coupling of solvent and polymers in the reversible dynamics of a polymer solution. Its presence is dictated by the requirement that the gradient of the entropy must lie in the null space of the Poisson operator.

Finally, the transformation behavior of the configurational distribution function $\psi(\boldsymbol{r},\boldsymbol{Q})$ is determined by the requirements that ψ is a scalar density in $\boldsymbol{r}$ and that $\boldsymbol{Q}$ is transported as a contravariant vector. These requirements can be formulated as

$$\psi(\boldsymbol{r},\boldsymbol{Q})\to\psi(\boldsymbol{r},\boldsymbol{Q})-t\left\{\frac{\partial}{\partial\boldsymbol{r}}\cdot[\boldsymbol{v}(\boldsymbol{r})\psi(\boldsymbol{r},\boldsymbol{Q})]+\frac{\partial}{\partial\boldsymbol{Q}}\cdot\left[\left(\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}(\boldsymbol{r})\right)^T\cdot\boldsymbol{Q}\psi(\boldsymbol{r},\boldsymbol{Q})\right]\right\}. \tag{56}$$

With the transformation behavior of all the state variables at hand, the Poisson operator can now be identified in exactly the same way as for hydrodynamics. However, $\boldsymbol{L}(\boldsymbol{r},\boldsymbol{Q},\boldsymbol{r}',\boldsymbol{Q}')$ is now a bigger matrix, where the new components associated with ψ even have an additional label $\boldsymbol{Q}$ (matrix multiplication implies integration over $\boldsymbol{Q}'$ also):

$$\boldsymbol{L}(\boldsymbol{r},\boldsymbol{Q},\boldsymbol{r}',\boldsymbol{Q}')=\begin{pmatrix} * & \rho(\boldsymbol{r}')\dfrac{\partial\delta}{\partial\boldsymbol{r}'} & * & * \\ * & \boldsymbol{u}(\boldsymbol{r}')\dfrac{\partial\delta}{\partial\boldsymbol{r}'}+\dfrac{\partial\delta}{\partial\boldsymbol{r}'}\boldsymbol{u}(\boldsymbol{r}) & * & * \\ * & \epsilon(\boldsymbol{r}')\dfrac{\partial\delta}{\partial\boldsymbol{r}'}+\dfrac{\partial\delta}{\partial\boldsymbol{r}'}\cdot[p(\boldsymbol{r})\boldsymbol{1}+\boldsymbol{\Pi}(\boldsymbol{r})] & * & * \\ * & \psi(\boldsymbol{r}',\boldsymbol{Q})\dfrac{\partial\delta}{\partial\boldsymbol{r}'}+\dfrac{\partial}{\partial\boldsymbol{Q}}\left[\psi(\boldsymbol{r},\boldsymbol{Q})\boldsymbol{Q}\cdot\dfrac{\partial\delta}{\partial\boldsymbol{r}'}\right] & * & * \end{pmatrix}. \tag{57}$$

The second row of the Poisson operator is obtained from the second column and the antisymmetry requirement. When the remaining components are chosen to be zero then it can be verified that the gradient of the total entropy (51) indeed is contained in the null space of the Poisson operator. The polymer contributions to the entropy and the osmotic pressure tensor are tuned such that only the Gibbs-Duhem equation (36) for the solvent is needed for verifying the degeneracy requirement (2). Our final expression for the Poisson operator is, after once more carrying out $\boldsymbol{r}'$ integrations,

$$\boldsymbol{L}(\boldsymbol{r},\boldsymbol{Q},\boldsymbol{Q}')=-\begin{pmatrix} 0 & \dfrac{\partial}{\partial\boldsymbol{r}}\rho(\boldsymbol{r}) & 0 & 0 \\ \rho(\boldsymbol{r})\dfrac{\partial}{\partial\boldsymbol{r}} & \left[\dfrac{\partial}{\partial\boldsymbol{r}}\boldsymbol{u}(\boldsymbol{r})+\boldsymbol{u}(\boldsymbol{r})\dfrac{\partial}{\partial\boldsymbol{r}}\right]^T & \epsilon(\boldsymbol{r})\dfrac{\partial}{\partial\boldsymbol{r}}+\dfrac{\partial}{\partial\boldsymbol{r}}p(\boldsymbol{r})+\dfrac{\partial}{\partial\boldsymbol{r}}\cdot\boldsymbol{\Pi}(\boldsymbol{r}) & \psi(\boldsymbol{r},\boldsymbol{Q}')\dfrac{\partial}{\partial\boldsymbol{r}}-\dfrac{\partial}{\partial\boldsymbol{r}}\cdot\psi(\boldsymbol{r},\boldsymbol{Q}')\boldsymbol{Q}'\dfrac{\partial}{\partial\boldsymbol{Q}'} \\ 0 & \dfrac{\partial}{\partial\boldsymbol{r}}\epsilon(\boldsymbol{r})+p(\boldsymbol{r})\dfrac{\partial}{\partial\boldsymbol{r}}+\boldsymbol{\Pi}(\boldsymbol{r})\cdot\dfrac{\partial}{\partial\boldsymbol{r}} & 0 & 0 \\ 0 & \dfrac{\partial}{\partial\boldsymbol{r}}\psi(\boldsymbol{r},\boldsymbol{Q})+\dfrac{\partial}{\partial\boldsymbol{Q}}\psi(\boldsymbol{r},\boldsymbol{Q})\boldsymbol{Q}\cdot\dfrac{\partial}{\partial\boldsymbol{r}} & 0 & 0 \end{pmatrix}. \tag{58}$$

The above procedure for incorporating entropic spring contributions seems to suggest that there exists an arbitrariness in the description of reversible polymer contributions to the stress tensor: Incorporation via energy or entropy seem to be equivalent. However, there is an important difference concerning the role of temperature for these two possibilities: $V^{(S)}(\boldsymbol{r},Q)$ is proportional to temperature, whereas $V(Q)$ is independent of temperature. Therefore, by regarding the temperature dependence of the model parameters, there should be a natural way for incorporating an effect either through energy or through entropy contributions. Not surprisingly, for entropic springs the temperature dependence of the spring constant is such that the incorporation through the total entropy is the obvious choice.

Sarti and Marrucci calculated the nonequilibrium free energy for the Rouse-Zimm model [21]. For an arbitrary temperature dependence of the Hookean spring constant they developed a procedure for separating energetic and entropic contributions to the spring potential. When assuming an additive superposition of energetic and entropic contributions, the parameter μ of Sarti and Marrucci [21] has the temperature dependence $\mu=\mu_0(1+T_0/T)$ and their separation procedure for Hookean springs is fully equivalent to the splitting into energy and entropy in Eqs. (48) and (49). The importance of separating energetic and entropic effects is obvious in the GENERIC approach.

C. Metric matrix

Our suggestion for the metric matrix is an extension of Eq. (38):

$$\boldsymbol{M}(\boldsymbol{r},\boldsymbol{Q},\boldsymbol{Q}')$$
$$=\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -\left(\frac{\partial}{\partial\boldsymbol{r}}\,\eta_s T\frac{\partial}{\partial\boldsymbol{r}}\right)^T-\boldsymbol{1}\frac{\partial}{\partial\boldsymbol{r}}\cdot\eta_s T\frac{\partial}{\partial\boldsymbol{r}} & \frac{\partial}{\partial\boldsymbol{r}}\cdot\eta_s T\dot{\boldsymbol{\gamma}} & 0 \\ 0 & -\eta_s T\dot{\boldsymbol{\gamma}}\cdot\,\frac{\partial}{\partial\boldsymbol{r}} & \frac{1}{2}\,\eta_s T\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}}-\frac{\partial}{\partial\boldsymbol{r}}\cdot\lambda T^2\,\frac{\partial}{\partial\boldsymbol{r}}+\frac{2T}{\zeta}\int\left(\frac{\partial V}{\partial\boldsymbol{Q}}\right)^2\psi(\boldsymbol{r},\boldsymbol{Q})d^3Q & -\frac{2T}{\zeta}\,\frac{\partial V}{\partial\boldsymbol{Q}'}\cdot\psi(\boldsymbol{r},\boldsymbol{Q}')\frac{\partial}{\partial\boldsymbol{Q}'} \\ 0 & 0 & \frac{\partial}{\partial\boldsymbol{Q}}\cdot\frac{2T}{\zeta}\,\frac{\partial V}{\partial\boldsymbol{Q}}\,\psi(\boldsymbol{r},\boldsymbol{Q}) & -\frac{\partial}{\partial\boldsymbol{Q}}\cdot\frac{2T}{\zeta}\,\psi(\boldsymbol{r},\boldsymbol{Q})\frac{\partial}{\partial\boldsymbol{Q}}\,\delta(\boldsymbol{Q}-\boldsymbol{Q}')-\frac{\partial}{\partial\boldsymbol{r}}\cdot\frac{T}{2\zeta}\,\psi(\boldsymbol{r},\boldsymbol{Q})\frac{\partial}{\partial\boldsymbol{r}}\,\delta(\boldsymbol{Q}-\boldsymbol{Q}') \end{pmatrix}, \tag{59}$$

where η_s is the solvent viscosity and $\hat{\kappa}=0$ has been assumed to simplify the notation; this assumption indirectly corresponds to the solvent incompressibility usually assumed in polymer kinetic theory. A more formal treatment of the incompressibility constraint would require the elimination of the density field and a modified definition of functional derivatives (see Sec. 5.4 of [9]). Starting from the solvent building block, the above form of M was obtained by first determining the lower right corner element (to obtain the usual diffusion behavior in the dumbbell configuration space) and then adding further terms such that the gradient of energy (50) lies in the null space of M and M is symmetric. The degeneracy requirement (3) introduces V into M, in the same way as the degeneracy requirement (2) introduces $V^{(S)}$ (via $\boldsymbol{\Pi}$) into L. Again, M turns out to be positive semidefinite. As an additional observation, we note that the gradients of the total mass of the solution and of the total polymer mass lie in the null spaces of both L and M.

D. Time-evolution equations

The above procedure of developing a nonisothermal kinetic theory model for dilute polymer solutions is typical of our approach to nonequilibrium systems. After determining the building blocks in the GENERIC (1) we can now write down explicitly all the time-evolution equations, so that we can carefully interpret the results:

$$\frac{\partial\rho}{\partial t}=-\frac{\partial}{\partial\boldsymbol{r}}\cdot(\boldsymbol{v}\rho), \tag{60}$$

$$\frac{\partial\boldsymbol{u}}{\partial t}=-\frac{\partial}{\partial\boldsymbol{r}}\cdot(\boldsymbol{v}\boldsymbol{u})-\frac{\partial}{\partial\boldsymbol{r}}\left(p+2k_{\mathrm{B}}T\int\psi d^3Q\right)+\frac{\partial}{\partial\boldsymbol{r}}\cdot\eta_s\dot{\boldsymbol{\gamma}}$$
$$+\frac{\partial}{\partial\boldsymbol{r}}\cdot\int\boldsymbol{Q}\left(\frac{\partial V}{\partial\boldsymbol{Q}}+\frac{\partial V^{(S)}}{\partial\boldsymbol{Q}}\right)\psi d^3Q, \tag{61}$$

$$\frac{\partial\epsilon}{\partial t}=-\frac{\partial}{\partial\boldsymbol{r}}\cdot(\boldsymbol{v}\epsilon)+\frac{\partial}{\partial\boldsymbol{r}}\cdot\lambda\,\frac{\partial T}{\partial\boldsymbol{r}}+\frac{1}{2}\,\eta_s\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}}-\frac{1}{2}(p\boldsymbol{1}+\boldsymbol{\Pi}):\dot{\boldsymbol{\gamma}}$$
$$+\frac{2}{\zeta}\int\frac{\partial V}{\partial\boldsymbol{Q}}\cdot\left(\frac{\partial V}{\partial\boldsymbol{Q}}+\frac{\partial V^{(S)}}{\partial\boldsymbol{Q}}\right)\psi d^3Q$$
$$-\frac{2k_{\mathrm{B}}T}{\zeta}\int\psi\frac{\partial}{\partial\boldsymbol{Q}}\cdot\frac{\partial V}{\partial\boldsymbol{Q}}d^3Q, \tag{62}$$

$$\frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial \boldsymbol{r}} \cdot (\boldsymbol{v}\psi) - \frac{\partial}{\partial \boldsymbol{Q}} \cdot \left\{ \left[\left(\frac{\partial}{\partial \boldsymbol{r}} \boldsymbol{v} \right)^T \cdot \boldsymbol{Q} - \frac{2}{\zeta} \left(\frac{\partial V}{\partial \boldsymbol{Q}} + \frac{\partial V^{(S)}}{\partial \boldsymbol{Q}} \right) \right] \psi \right\} + \frac{\partial}{\partial \boldsymbol{r}} \cdot \frac{k_{\mathrm{B}} T}{2\zeta} \frac{\partial \psi}{\partial \boldsymbol{r}} + \frac{\partial}{\partial \boldsymbol{Q}} \cdot \frac{2 k_{\mathrm{B}} T}{\zeta} \frac{\partial \psi}{\partial \boldsymbol{Q}}. \tag{63}$$

In spite of their very different roles in the GENERIC building blocks, the potentials $V(Q)$ and $V^{(S)}(\boldsymbol{r},Q)$ enter the momentum balance equation (61) and the diffusion equation (63) in exactly the same way. However, they enter the solvent internal energy equation (62) differently.

The equation of continuity (60) coincides with Eq. (14). In Eq. (61), the pressure is modified by the osmotic pressure; this modification would be irrelevant for an incompressible fluid. More important is the Kramers-type polymer contribution to the stress tensor in the last term, where energetic and entropic forces occur in exactly the same way. In the solvent internal energy equation (62), various polymer contributions occur in addition to the effect of the osmotic pressure tensor. Finally, Eq. (63) is the usual diffusion equation of polymer kinetic theory, where again energetic and entropic forces occur in exactly the same way. Only the local solvent temperature occurs in this equation for the configurational distribution function; effects of temperature variations on the polymer scale are not taken into account.

If, for example, in engineering problems, one prefers to work with the variables $(\rho,\boldsymbol{v},T,\psi)$ instead of $(\rho,\boldsymbol{u},\epsilon,\psi)$, then the transformation between $\boldsymbol{v}$ and $\boldsymbol{u}$ is given in Eq. (13). The definition (25) gives $T(\rho,\epsilon)$ and, by inversion, $\epsilon(\rho,T)$. This relationship allows us to eliminate ϵ in favor of T in all the equations (60)–(63). Obviously, the caloric equation of state or certain material properties (e.g., the heat capacity) implied by the fundamental relation $s=s(\rho,\epsilon)$ enter the time-evolution equation obtained in this manner for T.

The energy balance equation can be written in a more transparent form when the total (solvent plus polymer) internal energy density

$$\epsilon^{\mathrm{tot}}(\boldsymbol{r}) = \epsilon(\boldsymbol{r}) + \int V(Q)\, \psi(\boldsymbol{r},\boldsymbol{Q})\, d^3Q \tag{64}$$

is introduced:

$$\frac{\partial \epsilon^{\mathrm{tot}}}{\partial t} = -\frac{\partial}{\partial \boldsymbol{r}} \cdot (\boldsymbol{v}\epsilon^{\mathrm{tot}}) + \frac{\partial}{\partial \boldsymbol{r}} \cdot \lambda \frac{\partial T}{\partial \boldsymbol{r}} + \frac{\partial}{\partial \boldsymbol{r}} \cdot \frac{k_{\mathrm{B}} T}{2\zeta} \frac{\partial}{\partial \boldsymbol{r}} \int V \psi d^3Q + \frac{1}{2} \eta_s \dot{\boldsymbol{\gamma}} : \dot{\boldsymbol{\gamma}} - \frac{1}{2} \left(p\boldsymbol{1} + \boldsymbol{\Pi} - \int \boldsymbol{Q} \frac{\partial V}{\partial \boldsymbol{Q}} \psi d^3Q \right) : \dot{\boldsymbol{\gamma}}. \tag{65}$$

All the terms describing the exchange of energy between solvent and polymers are canceled in this balance equation. Particularly interesting in Eq. (65) is the third term on the right-hand side, which implies that nonuniformities in the spatial distribution of polymer internal energy (resulting from a nonuniform polymer concentration) are smoothed by a diffusion process, thereby increasing the total internal energy. There is no corresponding term for the entropic spring potential; in fact, this term is the only one in all the time-evolution equations that allows us to distinguish between energetic and entropic springs.

Once more, the reader should pause and realize that the form of these equations may not be surprising, but the occurrence of the Kramers expression for the stress tensor for both energetic and entropic springs in the momentum and energy balance equations is actually quite remarkable. This is not assumed in the formulation of the equations, but it follows from the GENERIC structure.

IV. KINETIC THEORY FOR THE POLYMER CONTRIBUTION TO HEAT TRANSPORT

In this section we illustrate how the GENERIC approach can be used as a guideline for constructing an extended polymer kinetic theory of dilute solutions. We here want to go beyond reformulating previously developed time-evolution equations and in fact we will obtain important physical insight into a problem recently investigated by other methods. Of course, we first need some feeling for the physics to be described and we can then fix the structure of the theory by using the GENERIC formalism.

The physical effect we want to incorporate here is the influence of polymer conformation on heat transport (see [22–24] for recent investigations on this problem; see also Sec. 9.1 of [9]). Our starting point is the dumbbell kinetic theory of Sec. III. Since internal polymer motions are expected to be relevant for the heat flux we use the following list of state variables: $\rho(\boldsymbol{r})$, $\boldsymbol{u}(\boldsymbol{r})$, $\epsilon(\boldsymbol{r})$, and $\psi(\boldsymbol{r},\boldsymbol{Q},\tilde{\boldsymbol{v}},\tilde{\boldsymbol{V}})$, where the additional arguments $\tilde{\boldsymbol{v}}$ and $\tilde{\boldsymbol{V}}$ of the distribution function ψ can be thought of as relative velocity variables corresponding to changes in $\boldsymbol{r}$ and $\boldsymbol{Q}$. Another approach to a similar problem can be found in [25].

A further motivation for the development of this section is the desire to better understand the difference between spring potentials of energetic and entropic origin. We have carefully distinguished between energetic and entropic effects in the GENERIC approach, but they turned out to be almost on exactly the same footing in the nonisothermal kinetic theory of Sec. III (the only exception being the energy transport associated with polymer diffusion). This situation might change if we consider a more detailed theory not only of the polymer contribution to the momentum flux but also of the heat flux contribution. The general thermodynamic principles incorporated into the GENERIC structure should be helpful in clarifying the situation.

When using the total mass of a dumbbell $(2m)$ and the reduced mass of the two-bead system $(m/2)$ in formulating kinetic-energy contributions associated with center-of-mass and relative motions, we arrive at the following expression for the total energy:

$$E=\int\left\{\frac{1}{2}\,\frac{\boldsymbol{u}(\boldsymbol{r})^2}{\rho(\boldsymbol{r})}+\epsilon(\boldsymbol{r})+\int\left[\frac{1}{2}\,m\left(2\,\tilde{\boldsymbol{v}}^2+\frac{1}{2}\,\tilde{\boldsymbol{V}}^2\right)+V(Q)\right]\psi(\boldsymbol{r},\boldsymbol{Q},\tilde{\boldsymbol{v}},\tilde{\boldsymbol{V}})d^3Q\,d^3\tilde{v}\,d^3\tilde{V}\right\}\,d^3r. \tag{66}$$

The importance of a mass parameter m is natural in heat phenomena; it might simply be the bead mass as suggested by the above arguments, but it could also be some effective mass incorporating additional effects of solvent hydrodynamics.

For the entropy, we only extend the list of arguments of the distribution function in the previously given expression (49),

$$S=\int\left\{s(\rho(\boldsymbol{r}),\epsilon(\boldsymbol{r}))-\int\,\psi(\boldsymbol{r},\boldsymbol{Q},\tilde{\boldsymbol{v}},\tilde{\boldsymbol{V}})\left[\frac{V^{(S)}(\boldsymbol{r},Q)}{T(\boldsymbol{r})}+k_{\mathrm{B}}\ln\psi(\boldsymbol{r},\boldsymbol{Q},\tilde{\boldsymbol{v}},\tilde{\boldsymbol{V}})\right]d^3Q\,d^3\tilde{v}\,d^3\tilde{V}\right\}d^3r. \tag{67}$$

From these expressions for E and S we obtain the following functional derivatives with respect to the state variables:

$$\frac{\delta E}{\delta x}=\begin{pmatrix}-\frac{1}{2}\boldsymbol{v}(\boldsymbol{r})^2\\ \boldsymbol{v}(\boldsymbol{r})\\ 1\\ \frac{1}{2}m\left(2\,\tilde{\boldsymbol{v}}^2+\frac{1}{2}\tilde{\boldsymbol{V}}^2\right)+V(Q)\end{pmatrix} \tag{68}$$

and

$$\frac{\delta S}{\delta x}=\begin{pmatrix}-\frac{\mu(\boldsymbol{r})}{T(\boldsymbol{r})}\\ \boldsymbol{0}\\ \frac{1}{T(\boldsymbol{r})}\\ -\frac{V^{(S)}(\boldsymbol{r},Q)}{T(\boldsymbol{r})}-k_{\mathrm{B}}\ln\psi(\boldsymbol{r},\boldsymbol{Q},\tilde{\boldsymbol{v}},\tilde{\boldsymbol{V}})-k_{\mathrm{B}}\end{pmatrix}. \tag{69}$$

For the extended theory, a multiplication with the matrix $\boldsymbol{L}=\boldsymbol{L}(\boldsymbol{r},\boldsymbol{Q},\tilde{\boldsymbol{v}},\tilde{\boldsymbol{V}},\boldsymbol{Q}',\tilde{\boldsymbol{v}}',\tilde{\boldsymbol{V}}')$ implies additional integrations with respect to $\boldsymbol{Q}'$, $\tilde{\boldsymbol{v}}'$, and $\tilde{\boldsymbol{V}}'$ (as before, we assume that an $\boldsymbol{r}'$ integration can be carried out due to the occurrence of an overall δ function). For the extended kinetic theory we modify the Poisson operator of Eq. (58) as

$$\boldsymbol{L}=-\begin{pmatrix}0 & \frac{\partial}{\partial\boldsymbol{r}}\,\rho(\boldsymbol{r}) & 0 & 0\\ \rho(\boldsymbol{r})\,\frac{\partial}{\partial\boldsymbol{r}} & \left[\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{u}(\boldsymbol{r})+\boldsymbol{u}(\boldsymbol{r})\,\frac{\partial}{\partial\boldsymbol{r}}\right]^T & \epsilon(\boldsymbol{r})\,\frac{\partial}{\partial\boldsymbol{r}}+\frac{\partial}{\partial\boldsymbol{r}}\,p(\boldsymbol{r})+\frac{\partial}{\partial\boldsymbol{r}}\cdot\boldsymbol{\Pi}(\boldsymbol{r}) & \psi'\,\frac{\partial}{\partial\boldsymbol{r}}-\frac{\partial}{\partial\boldsymbol{r}}\cdot\psi'\boldsymbol{Q}'\,\frac{\partial}{\partial\boldsymbol{Q}'}+\frac{\partial}{\partial\boldsymbol{r}}\cdot\psi'\left(\tilde{\boldsymbol{V}}'\,\frac{\partial}{\partial\tilde{\boldsymbol{V}}'}+\tilde{\boldsymbol{v}}'\,\frac{\partial}{\partial\tilde{\boldsymbol{v}}'}\right)^T-\frac{1}{4}\,\frac{\partial}{\partial\boldsymbol{r}}\,\frac{\partial}{\partial\boldsymbol{r}}:\psi'\,\frac{\partial}{\partial\tilde{\boldsymbol{v}}'}\boldsymbol{Q}'\,\tilde{\boldsymbol{V}}'\\ 0 & \frac{\partial}{\partial\boldsymbol{r}}\,\epsilon(\boldsymbol{r})+p(\boldsymbol{r})\,\frac{\partial}{\partial\boldsymbol{r}}+\boldsymbol{\Pi}(\boldsymbol{r})\cdot\,\frac{\partial}{\partial\boldsymbol{r}} & 0 & \frac{2}{m}\,V^{(S)}(\boldsymbol{r},Q')\frac{\partial}{\partial\boldsymbol{Q}'}\cdot\psi'\,\frac{\partial}{\partial\tilde{\boldsymbol{V}}'}+\frac{1}{2m}\,V^{(S)}(\boldsymbol{r},Q')\frac{\partial}{\partial\boldsymbol{r}}\cdot\psi'\,\frac{\partial}{\partial\tilde{\boldsymbol{v}}'}\\ 0 & \frac{\partial}{\partial\boldsymbol{r}}\,\psi+\frac{\partial}{\partial\boldsymbol{Q}}\,\psi\boldsymbol{Q}\cdot\,\frac{\partial}{\partial\boldsymbol{r}}-\left(\frac{\partial}{\partial\tilde{\boldsymbol{V}}}\tilde{\boldsymbol{V}}+\frac{\partial}{\partial\tilde{\boldsymbol{v}}}\tilde{\boldsymbol{v}}\right)^T\cdot\psi\,\frac{\partial}{\partial\boldsymbol{r}}-\frac{1}{4}\tilde{\boldsymbol{V}}\boldsymbol{Q}\frac{\partial}{\partial\tilde{\boldsymbol{v}}}:\psi\,\frac{\partial}{\partial\boldsymbol{r}}\,\frac{\partial}{\partial\boldsymbol{r}} & -\frac{2}{m}\,\frac{\partial}{\partial\tilde{\boldsymbol{V}}}\cdot\psi\,\frac{\partial}{\partial\boldsymbol{Q}}\,V^{(S)}(\boldsymbol{r},Q)-\frac{1}{2m}\,\frac{\partial}{\partial\tilde{\boldsymbol{v}}}\cdot\psi\,\frac{\partial}{\partial\boldsymbol{r}}\,V^{(S)}(\boldsymbol{r},Q) & \frac{2}{m}\left(\frac{\partial}{\partial\boldsymbol{Q}}\cdot\psi\,\frac{\partial}{\partial\tilde{\boldsymbol{V}}}-\frac{\partial}{\partial\tilde{\boldsymbol{V}}}\cdot\psi\,\frac{\partial}{\partial\boldsymbol{Q}}\right)\delta+\frac{1}{2m}\left(\frac{\partial}{\partial\boldsymbol{r}}\cdot\psi\frac{\partial}{\partial\tilde{\boldsymbol{v}}}-\frac{\partial}{\partial\tilde{\boldsymbol{v}}}\cdot\psi\,\frac{\partial}{\partial\boldsymbol{r}}\right)\delta\end{pmatrix}, \tag{70}$$

where $\psi=\psi(\boldsymbol{r},\boldsymbol{Q},\tilde{\boldsymbol{v}},\tilde{\boldsymbol{V}})$, $\psi'=\psi(\boldsymbol{r},\boldsymbol{Q}',\tilde{\boldsymbol{v}}',\tilde{\boldsymbol{V}}')$, $\delta=\delta(\boldsymbol{Q}-\boldsymbol{Q}')\,\delta(\tilde{\boldsymbol{v}}-\tilde{\boldsymbol{v}}')\,\delta(\tilde{\boldsymbol{V}}-\tilde{\boldsymbol{V}}')$, and

$$\boldsymbol{\Pi}(\boldsymbol{r})=-\int \psi(\boldsymbol{r},\boldsymbol{Q},\tilde{\boldsymbol{v}},\tilde{\boldsymbol{V}})\boldsymbol{Q}\frac{\partial V^{(S)}(\boldsymbol{r},\boldsymbol{Q})}{\partial \boldsymbol{Q}}\,d^3Q\,d^3\tilde{v}\,d^3\tilde{V}. \tag{71}$$

Notice that there is a new feature in Eq. (70) compared to all the previously specified Poisson operators: It contains nonzero entries outside the second row and column (associated with the momentum density or velocity field). The entry in the lower right corner is determined by the kinematic effects associated with the velocity terms in the last row of Eq. (68) (this term is closely related to the L operator for the Boltzmann equation, which also expresses the kinematics of a distribution function in phase space). The off-diagonal terms involving the entropic potential $V^{(S)}$ are naturally introduced such that the gradient (69) lies in the null space of the Poisson operator (that is, $V^{(S)}$ occurs in the Poisson operator for exactly the same reasons as the osmotic pressure tensor $\boldsymbol{\Pi}$). It is remarkable that in the more microscopic approach of this section both the energetic and the entropic spring potentials enter the diffusion equation through the reversible dynamics, whereas in the approach of Sec. III they occurred in the irreversible dynamics. The osmotic pressure tensor (71) does not contain the isotropic contribution of Eq. (55); in the more microscopic approach one obtains a more detailed expression for the kinetic contribution to the polymer stress tensor. Actually, this kinetic contribution results from the new terms in the last entry of the second row, which have to be introduced in order to satisfy the Jacobi identity.

Finally, we need to specify the metric matrix. We use the same shorthand notation as for the Poisson operator and write the metric matrix in the form

$$\boldsymbol{M}(\boldsymbol{r},\boldsymbol{Q},\tilde{\boldsymbol{v}},\tilde{\boldsymbol{V}},\boldsymbol{Q}',\tilde{\boldsymbol{v}}',\tilde{\boldsymbol{V}}')=\boldsymbol{M}_1+\boldsymbol{M}_2, \tag{72}$$

where

$$\boldsymbol{M}_1=\begin{pmatrix} 0 & 0 & 0 & 0\\ 0 & -\left(\frac{\partial}{\partial \boldsymbol{r}}\eta_s T\frac{\partial}{\partial \boldsymbol{r}}+\boldsymbol{1}\frac{\partial}{\partial \boldsymbol{r}}\cdot\eta_s T\frac{\partial}{\partial \boldsymbol{r}}\right)^T & \frac{\partial}{\partial \boldsymbol{r}}\cdot\eta_s T\dot{\boldsymbol{\gamma}} & 0\\ 0 & -\eta_s T\dot{\boldsymbol{\gamma}}\cdot\frac{\partial}{\partial \boldsymbol{r}} & \frac{1}{2}\eta_s T\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}}-\frac{\partial}{\partial \boldsymbol{r}}\cdot\lambda T^2\frac{\partial}{\partial \boldsymbol{r}} & 0\\ 0 & 0 & 0 & 0 \end{pmatrix} \tag{73}$$

contains the typical solvent building block of Eq. (38), simplified by assuming $\hat{\kappa}=0$ (indirectly corresponding to solvent incompressibility). For the extended kinetic theory, we postulate (and justify later)

$$\boldsymbol{M}_2=\begin{pmatrix} 0 & 0 & 0 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & \frac{2\zeta}{m}\int\tilde{T}\frac{1}{2}m\left(2\tilde{\boldsymbol{v}}^2+\frac{1}{2}\tilde{\boldsymbol{V}}^2\right)\psi\,d^3Q\,d^3\tilde{v}\,d^3\tilde{V}+\zeta\frac{\partial T}{\partial \boldsymbol{r}}\cdot\int\boldsymbol{Q}\tilde{\boldsymbol{v}}\cdot\tilde{\boldsymbol{V}}\psi\,d^3Q\,d^3\tilde{v}\,d^3\tilde{V} & -\frac{\zeta}{m}\psi'\tilde{T}'\left(\tilde{\boldsymbol{v}}'\cdot\frac{\partial}{\partial\tilde{\boldsymbol{v}}'}+\tilde{\boldsymbol{V}}'\cdot\frac{\partial}{\partial\tilde{\boldsymbol{V}}'}\right)-\frac{\zeta}{m}\psi'\boldsymbol{Q}'\cdot\frac{\partial T}{\partial \boldsymbol{r}}\left(\frac{1}{4}\tilde{\boldsymbol{V}}'\cdot\frac{\partial}{\partial\tilde{\boldsymbol{v}}'}+\tilde{\boldsymbol{v}}'\cdot\frac{\partial}{\partial\tilde{\boldsymbol{V}}'}\right)\\ 0 & 0 & \frac{\zeta}{m}\tilde{T}\left(\frac{\partial}{\partial\tilde{\boldsymbol{v}}}\cdot\tilde{\boldsymbol{v}}\psi+\frac{\partial}{\partial\tilde{\boldsymbol{V}}}\cdot\tilde{\boldsymbol{V}}\psi\right)+\frac{\zeta}{m}\boldsymbol{Q}\cdot\frac{\partial T}{\partial \boldsymbol{r}}\left(\frac{1}{4}\frac{\partial}{\partial\tilde{\boldsymbol{v}}}\cdot\tilde{\boldsymbol{V}}\psi+\frac{\partial}{\partial\tilde{\boldsymbol{V}}}\cdot\tilde{\boldsymbol{v}}\psi\right) & -\frac{\zeta}{2m^2}\tilde{T}\left(\frac{\partial}{\partial\tilde{\boldsymbol{v}}}\cdot\psi\frac{\partial}{\partial\tilde{\boldsymbol{v}}}+4\frac{\partial}{\partial\tilde{\boldsymbol{V}}}\cdot\psi\frac{\partial}{\partial\tilde{\boldsymbol{V}}}\right)\delta-\frac{\zeta}{2m^2}\boldsymbol{Q}\cdot\frac{\partial T}{\partial \boldsymbol{r}}\left(\frac{\partial}{\partial\tilde{\boldsymbol{v}}}\cdot\psi\frac{\partial}{\partial\tilde{\boldsymbol{V}}}+\frac{\partial}{\partial\tilde{\boldsymbol{V}}}\cdot\psi\frac{\partial}{\partial\tilde{\boldsymbol{v}}}\right)\delta \end{pmatrix}, \tag{74}$$

where

$$\tilde{T}=\tilde{T}(\boldsymbol{r},\boldsymbol{Q})=T(\boldsymbol{r})+\frac{1}{16T(\boldsymbol{r})}\left(\boldsymbol{Q}\cdot\frac{\partial T(\boldsymbol{r})}{\partial \boldsymbol{r}}\right)^2 \tag{75}$$

and $\tilde{T}'=\tilde{T}(\boldsymbol{r},\boldsymbol{Q}')$.

The contribution $\boldsymbol{M}_2$ is completely determined by the entry in the lower right corner (the other entries are once more determined by the symmetry of the metric matrix and the requirement that the gradient of the energy must lie in the null space of the metric matrix). In writing down the entry in the lower right corner of Eq. (74), we first of all wanted to reproduce the diffusion equation for isothermal flows. Then we introduced a coupling of internal and center-of-mass diffusive motions due to temperature gradients, where the temperature variation over polymer dimensions $\boldsymbol{Q}\cdot\partial T/\partial\boldsymbol{r}$ is the natural parameter to occur. Second-order effects in $\boldsymbol{Q}\cdot\partial T/\partial\boldsymbol{r}$ had to be included in order to ensure that $\boldsymbol{M}_2$ is positive semidefinite, and this is the reason for $\tilde{T}$ to occur in Eq. (74). In the more microscopic approach of this section, the potential V does not occur in the metric matrix. After incorporating only these simple physical ideas and accounting for all the properties of the GENERIC structure we arrive at the symmetric, positive-semidefinite metric matrix (74) and we thus obtain all the time-evolution equations for the state variables. In order to see the most interesting implications of the GENERIC approach, we consider the predicted diffusion and energy balance equations in more detail.

The explicit form of the diffusion equation is

$$\begin{aligned}\frac{\partial\psi}{\partial t}=&-\frac{\partial}{\partial\boldsymbol{r}}\cdot[(\boldsymbol{v}+\widetilde{\boldsymbol{v}})\psi]-\frac{\partial}{\partial\boldsymbol{Q}}\cdot\left\{\left[\left(\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}\right)^T\cdot\boldsymbol{Q}+\widetilde{\boldsymbol{V}}\right]\psi\right\}+\frac{\partial}{\partial\widetilde{\boldsymbol{v}}}\cdot\left\{\left[\left(\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}\right)\cdot\widetilde{\boldsymbol{v}}+\frac{1}{4}\boldsymbol{Q}\cdot\left(\frac{\partial}{\partial\boldsymbol{r}}\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}\right)\cdot\widetilde{\boldsymbol{V}}\right]\psi\right\}+\frac{\partial}{\partial\widetilde{\boldsymbol{V}}}\cdot\left[\left(\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v}\right)\cdot\widetilde{\boldsymbol{V}}\psi\right]\\&+\frac{\zeta}{m}\frac{\partial}{\partial\widetilde{\boldsymbol{v}}}\cdot\left\{\left[\frac{\widetilde{T}}{T}\widetilde{\boldsymbol{v}}+\underline{\frac{1}{4T}\left(\boldsymbol{Q}\cdot\frac{\partial T}{\partial\boldsymbol{r}}\right)\widetilde{\boldsymbol{V}}}\right]\psi\right\}+\frac{\zeta}{m}\frac{\partial}{\partial\widetilde{\boldsymbol{v}}}\cdot\left\{\left[\frac{1}{2\zeta}\frac{\partial V^{(S)}}{\partial\boldsymbol{r}}\right]\psi\right\}+\frac{\zeta}{m}\frac{\partial}{\partial\widetilde{\boldsymbol{V}}}\cdot\left\{\left[\frac{\widetilde{T}}{T}\widetilde{\boldsymbol{V}}+\underline{\frac{1}{T}\left(\boldsymbol{Q}\cdot\frac{\partial T}{\partial\boldsymbol{r}}\right)\widetilde{\boldsymbol{v}}}+\frac{2}{\zeta}\frac{\partial(V^{(S)}+V)}{\partial\boldsymbol{Q}}\right]\psi\right\}\\&+\frac{k_{\mathrm{B}}\widetilde{T}\zeta}{2m^2}\left(\frac{\partial}{\partial\widetilde{\boldsymbol{v}}}\cdot\frac{\partial}{\partial\widetilde{\boldsymbol{v}}}+4\frac{\partial}{\partial\widetilde{\boldsymbol{V}}}\cdot\frac{\partial}{\partial\widetilde{\boldsymbol{V}}}\right)\psi+\frac{k_{\mathrm{B}}\zeta}{m^2}\left(\boldsymbol{Q}\cdot\frac{\partial T}{\partial\boldsymbol{r}}\right)\frac{\partial}{\partial\widetilde{\boldsymbol{v}}}\cdot\frac{\partial}{\partial\widetilde{\boldsymbol{V}}}\psi.\end{aligned}\tag{76}$$

This diffusion equation is closely related to the stochastic differential equations assumed as a starting point in [24]. When we regard the second-order terms in temperature gradients as minor effects ($\widetilde{T}\approx T$), the most interesting differences compared to [24] are the underlined frictional couplings between center-of-mass and relative velocities for our dumbbell model, the additional kinetic effects in the third and fourth terms of Eq. (76), and an additional term due to the temperature dependence of the entropic spring force. All these new terms are required by the GENERIC structure.

The energy balance becomes most transparent when we introduce the total internal energy density

$$\epsilon^{\mathrm{tot}}(\boldsymbol{r})=\epsilon(\boldsymbol{r})+\int\left[\frac{1}{2}m\left(2\widetilde{\boldsymbol{v}}^2+\frac{1}{2}\widetilde{\boldsymbol{V}}^2\right)+V(Q)\right]\psi d^3Q\,d^3\widetilde{v}\,d^3\widetilde{V}.\tag{77}$$

The time-evolution equation for the total internal energy density can be written as

$$\begin{aligned}\frac{\partial\epsilon^{\mathrm{tot}}}{\partial t}=&-\frac{\partial}{\partial\boldsymbol{r}}\cdot(\boldsymbol{v}\epsilon^{\mathrm{tot}})+\frac{\partial}{\partial\boldsymbol{r}}\cdot\lambda\frac{\partial T}{\partial\boldsymbol{r}}+\frac{1}{2}\eta_s\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}}-\frac{1}{2}(p\mathbf{1}\\&+\boldsymbol{\Pi}^{(\mathrm{k})}):\dot{\boldsymbol{\gamma}}+\frac{1}{2}\int\boldsymbol{Q}\frac{\partial(V^{(S)}+V)}{\partial\boldsymbol{Q}}\psi d^3Q\,d^3\widetilde{v}\,d^3\widetilde{V}:\dot{\boldsymbol{\gamma}}\\&-\frac{\partial}{\partial\boldsymbol{r}}\cdot\int\widetilde{\boldsymbol{v}}\left[\frac{1}{2}m\left(2\widetilde{\boldsymbol{v}}^2+\frac{1}{2}\widetilde{\boldsymbol{V}}^2\right)+V^{(S)}+V\right]\\&\times\psi d^3Q\,d^3\widetilde{v}\,d^3\widetilde{V}\\&-\frac{1}{2}m\int\widetilde{\boldsymbol{V}}\widetilde{\boldsymbol{v}}\boldsymbol{Q}\psi d^3Q\,d^3\widetilde{v}\,d^3\widetilde{V}\,\vdots\frac{\partial}{\partial\boldsymbol{r}}\frac{\partial}{\partial\boldsymbol{r}}\boldsymbol{v},\end{aligned}\tag{78}$$

where

$$\boldsymbol{\Pi}^{(\mathrm{k})}=m\int\left(2\widetilde{\boldsymbol{v}}\widetilde{\boldsymbol{v}}+\frac{1}{2}\widetilde{\boldsymbol{V}}\widetilde{\boldsymbol{V}}\right)\psi d^3Q\,d^3\widetilde{v}\,d^3\widetilde{V}.\tag{79}$$

This result is very similar to Eq. (65). The penultimate term in Eq. (78) allows us to identify the polymer contribution to the heat flux vector,

$$\boldsymbol{q}_p=\int\widetilde{\boldsymbol{v}}\left[m\left(\widetilde{\boldsymbol{v}}^2+\frac{1}{4}\widetilde{\boldsymbol{V}}^2\right)+V^{(S)}+V\right]\psi d^3Q\,d^3\widetilde{v}\,d^3\widetilde{V}.\tag{80}$$

In exactly the same manner as the time evolution of the diffusion equation in configuration space determines the form of the polymer contribution to the stress tensor (Kramers expression), within the GENERIC structure, the diffusion equation in velocity space determines the form of the heat flux vector. Expression (80) is a natural and minor modification of Eq. (8.11) of [22] in the absence of intermolecular interactions. Although we carefully kept track of energetic and entropic spring potentials, these potentials of very different physical origins occur on exactly the same footing in the equation for the total energy density. It is only in one of the terms of the diffusion equation that an entropic and no energetic spring potential occurs. However, this is very important because the difference between entropic and energetic springs hence occurs indirectly in the momentum and energy balance equations (because the solution of the diffusion equation occurs in these balance equations). In the detailed discussion of the polymer contribution to the heat flux, the GENERIC approach allows us a very clear separation of energetic and entropic spring potentials in all the time-evolution equations. The crucial difference results from the temperature dependence of the parameters occurring in the respective potentials.

While, in the momentum balance, the term containing second-order derivatives with respect to $\boldsymbol{r}$ in the last entry of the second row of Eq. (70) could formally be incorporated into the stress tensor, this is not the case for the corresponding second-order derivative term in the balance equation for the total energy density [the last term in Eq. (78)]. In order to develop a more explicit theory of the heat flux vector, one would need to solve the diffusion equation (76) and to evaluate the integral in Eq. (80) (see, e.g., the procedure in [24]). Alternatively, one could try to pass from the equations of this section to a more coarse-grained description. The GENERIC approach has provided us not only a new starting point for such calculations but also important information concerning the role of potentials of energetic or entropic origins in heat transport. Again, the gradients of the total mass of the solution and of the total polymer mass lie in the null spaces of both L and M.

V. COMMENTS ON FURTHER EXAMPLES

A. Extended irreversible thermodynamics

In an attempt to reproduce the equations of extended irreversible thermodynamics (EIT) [26] within the GENERIC approach, we consider the nonisothermal kinetic theory of polymeric fluids of Sec. III in a more macroscopic formulation in which we use a conformation tensor instead of a configurational distribution function. While EIT is a phenomenological approach in which the stress tensor is among the independent state variables, we anticipate that the conformation tensor for a Hookean dumbbell model is closely related to the stress tensor. Once we have identified the structure of the conformation tensor kinetic theory, we can easily find the GENERIC formulation of EIT by transforming from the conformation tensor to the stress tensor.

We assume a constant polymer concentration throughout the polymer solution, that is,

$$n_p = \int \psi(\boldsymbol{r},\boldsymbol{Q})\, d^3Q \tag{81}$$

is assumed to be independent of $\boldsymbol{r}$. Otherwise, we would have to introduce the polymer number density as an additional field.

We define a conformation tensor field by

$$\boldsymbol{c}(\boldsymbol{r}) = \frac{1}{n_p}\int \boldsymbol{Q}\boldsymbol{Q}\psi(\boldsymbol{r},\boldsymbol{Q})\, d^3Q \tag{82}$$

and we then choose the following fields as independent state variables for a dilute solution with constant polymer concentration: the mass density $\rho(\boldsymbol{r})$ of solution, the momentum density $\boldsymbol{u}(\boldsymbol{r})$ of the solution, the solvent internal energy density $\epsilon(\boldsymbol{r})$, and the conformation tensor field $\boldsymbol{c}(\boldsymbol{r})$. As a word of warning, we would like to point out that only the second moment (82) of the distribution function is here kept as an independent state variable. Such a description can only be valid if all the higher moments either are functions of the second moment or possess a rapid time evolution. If one misses slow independent variables in the thermodynamic modeling of a system, such as a higher moment, then incorrect predictions must be expected from any kind of general thermodynamic formalism. This is the risk of assuming that a rather limited set of state variables is sufficient. As pointed out before, the choice of suitable state variables is a crucial step and there is no universal choice of state variables for complex fluids.

In this section, we consider only entropic and no energetic effects for the polymers, so that Eq. (48) reduces to the energy of hydrodynamics,

$$E = \int \left[\frac{1}{2}\,\frac{\boldsymbol{u}(\boldsymbol{r})^2}{\rho(\boldsymbol{r})} + \epsilon(\boldsymbol{r})\right] d^3r. \tag{83}$$

When we assume a quadratic entropic potential $V^{(S)}(\boldsymbol{r},Q)$ and a corresponding configurational distribution function of the Gaussian type [the Gaussian form of the distribution function actually follows from maximizing the entropy (49) under the constraints (81) and (82)], then the $\boldsymbol{Q}$ integration in Eq. (49) can be carried out and, after neglecting an additive constant, we obtain

$$S = \int s(\rho(\boldsymbol{r}),\epsilon(\boldsymbol{r}))\, d^3r + S_p, \tag{84}$$

where the polymer contribution to the entropy is [27]

$$S_p = \frac{1}{2} n_p k_{\mathrm{B}} \int \{\mathrm{tr}[\boldsymbol{1} - c\boldsymbol{c}(\boldsymbol{r})] + \ln[\det c\boldsymbol{c}(\boldsymbol{r})]\}\, d^3r. \tag{85}$$

The constant c is chosen such that $c\boldsymbol{c}(\boldsymbol{r}) = \boldsymbol{1}$ at equilibrium and we can then write

$$\frac{V^{(S)}(\boldsymbol{r},Q)}{T(\boldsymbol{r})} = \frac{1}{2} k_{\mathrm{B}} c \boldsymbol{Q}^2. \tag{86}$$

Note that

$$\frac{\delta S}{\delta \boldsymbol{c}(\boldsymbol{r})} = \frac{\delta S_p}{\delta \boldsymbol{c}(\boldsymbol{r})} = \frac{1}{2} n_p k_{\mathrm{B}} [\boldsymbol{c}(\boldsymbol{r})^{-1} - c\boldsymbol{1}]. \tag{87}$$

The Poisson operator for the conformation tensor theory is very similar to the one in Eq. (58). We only need to modify the last entry in the second column (the last entry in the second row is then fixed by the antisymmetry of L). In the more macroscopic theory based on a conformation tensor rather than on the configurational distribution function, the continuous label $\boldsymbol{Q}$ is replaced by the discrete tensor indices j,k. If the three components of the vector in the last entry in the second column of Eq. (58) are labeled by l, then these components should be replaced by

$$\frac{\partial c_{jk}}{\partial r_l} - \delta_{jl}\left(\boldsymbol{c}\cdot\frac{\partial}{\partial \boldsymbol{r}}\right)_k - \delta_{kl}\left(\boldsymbol{c}\cdot\frac{\partial}{\partial \boldsymbol{r}}\right)_j. \tag{88}$$

In the first term in expression (88), the spatial derivative acts only on the tensor $\boldsymbol{c}$ and, unlike in the other entries in the second column of Eq. (58), not on the components of the vector that is multiplied by L. This difference results from the fact that $\boldsymbol{c}$ is an *absolute* tensor field, whereas scalar and vector *density* fields occur in the other components.

The osmotic pressure tensor occurring in L should be chosen such that the gradient of the entropy lies in the null space of L. A possible choice is

$$\boldsymbol{\Pi} = T\left(2\boldsymbol{c}\cdot\frac{\delta S_p}{\delta \boldsymbol{c}} + S_p\boldsymbol{1}\right), \tag{89}$$

where a divergence-free term may be added to $\boldsymbol{\Pi}/T$. Since we determined S_p only up to an additive constant, we do not keep track of all the isotropic contributions to $\boldsymbol{\Pi}$ and we then obtain from Eqs. (87) and (89)

$$\boldsymbol{\Pi} = n_p k_{\mathrm{B}} T(\boldsymbol{1} - c\boldsymbol{c}). \tag{90}$$

Neglecting isotropic contributions once again, this result agrees with what one obtains by carrying out the integral in Eq. (55) with the Gaussian distribution maximizing the entropy.

For the metric matrix M we suggest the following modification of Eq. (38):

$$\boldsymbol{M}(\boldsymbol{r})=\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -\left(\frac{\partial}{\partial \boldsymbol{r}}\eta_s T\frac{\partial}{\partial \boldsymbol{r}}+\mathbf{1}\frac{\partial}{\partial \boldsymbol{r}}\cdot\eta_s T\frac{\partial}{\partial \boldsymbol{r}}\right)^T & \frac{\partial}{\partial \boldsymbol{r}}\cdot\eta_s T\dot{\boldsymbol{\gamma}} & 0 \\ 0 & -\eta_s T\dot{\boldsymbol{\gamma}}\cdot\frac{\partial}{\partial \boldsymbol{r}} & \frac{1}{2}\eta_s T\dot{\boldsymbol{\gamma}}:\dot{\boldsymbol{\gamma}}-\frac{\partial}{\partial \boldsymbol{r}}\cdot\lambda T^2\frac{\partial}{\partial \boldsymbol{r}} & 0 \\ 0 & 0 & 0 & \frac{2}{n_p k_{\mathrm{B}} c\lambda_H}\boldsymbol{c}\cdot \end{pmatrix}, \tag{91}$$

where λ_H is a time constant. For the lower right block, which transforms a tensor into another one, a simplified but obvious notation has been used (assuming that the tensor to be multiplied is symmetric and commutes with $\boldsymbol{c}$). Now the conformation tensor model is completely specified. It reproduces the so-called Maxwell expression for the stress tensor and hence the momentum balance equation corresponding to EIT:

$$\left(1+\lambda_H\frac{\mathcal{D}}{\mathcal{D}t}\right)\frac{\mathbf{\Pi}}{n_p k_{\mathrm{B}} T}=-\lambda_H\dot{\boldsymbol{\gamma}}, \tag{92}$$

where $\mathcal{D}/\mathcal{D}t$ is the convected time derivative (here of a contravariant tensor field; see, e.g., Appendix D.2 of [16] or pp. 106 and 107 of [17]).

In order to reproduce also the EIT expression for the heat flux vector, a larger set of variables would have to be considered.

Our expression (85) for the polymer contribution to the entropy does not coincide with the quadratic form usually assumed in EIT [see, e.g., Eq. (2.39) of [26]],

$$S_p=-\frac{1}{4}n_p k_{\mathrm{B}}\int[\mathbf{1}-c\boldsymbol{c}(\boldsymbol{r})]:[\mathbf{1}-c\boldsymbol{c}(\boldsymbol{r})]d^3r, \tag{93}$$

which may be obtained by expansion of the expression (85) around equilibrium. For the gradient of the total entropy (84) with the polymer contribution given in Eq. (93) to lie in the null space of the Poisson operator, the anisotropic osmotic pressure tensor must, however, be changed to

$$\mathbf{\Pi}=n_p k_{\mathrm{B}} T c\boldsymbol{c}\cdot(\mathbf{1}-c\boldsymbol{c}), \tag{94}$$

where the unusual form of the stress tensor should be noted. Only close to equilibrium this coincides with the familiar stress tensor expression $n_{\mathrm{p}}k_{\mathrm{B}}T(\mathbf{1}-c\boldsymbol{c})$. We hence believe that the entropy expression (85), or

$$S_p=\frac{1}{2}n_p k_{\mathrm{B}}\int\left[\mathrm{tr}\frac{\mathbf{\Pi}}{n_p k_{\mathrm{B}} T}+\ln\det\left(\mathbf{1}-\frac{\mathbf{\Pi}}{n_p k_{\mathrm{B}} T}\right)\right]d^3r, \tag{95}$$

is preferable in EIT.

B. Bracket formalism of Beris and Edwards

The structure of a large number of time-evolution equations for complex fluids has been analyzed by Beris and Edwards [9]. They developed a bracket formalism as a general framework for formulating all these time-evolution equations in a unified manner. The key idea is the construction of a nonlinear dissipation bracket by generalizing the original ideas of Kaufman [28], Morrison [29], and Grmela [30]. Beris and Edwards have not only considered many examples but also accounted for various basic principles, such as the first and second laws of thermodynamics, the Onsager-Casimir relations, the Curie principle, and the principle of material objectivity (or frame indifference). In view of the remarkable body of evidence they have collected for establishing and verifying the bracket formalism we want to show how their bracket formalism can be reproduced from the GENERIC approach. In short, it turns out that the GENERIC approach allows us a more general choice of variables while, at the same time, it has more predictive power and a more symmetric form than the bracket formalism of Beris and Edwards (see below). By establishing the relationship between the two formalisms we also gain additional insight into the typical structure of metric matrices (in particular, we learn how to incorporate material objectivity). Furthermore, since Beris and Edwards have shown that the celebrated theory known as *linear thermodynamics of irreversible processes* [31,32] is fully contained in their bracket formalism, it is here recognized also as a special case of the GENERIC approach (concerning the Onsager-Casimir reciprocity relations, the mutual degeneracy requirements of the GENERIC structure imply additional restrictions that, in the previous approaches, need to be introduced and justified separately). Since both the bracket formalism and the GENERIC approach employ the energy for generating the reversible dynamics, the Poisson bracket (4) must coincide with the one used by Beris and Edwards.

For formulating the irreversible dynamics in the bracket formalism, the total entropy density always needs to be in the list of state variables x. If one wants to use temperature instead of entropy density, this can be achieved by a subsequent Legendre transformation (see Sec. 9.1 of [9]). We assume that x is of the form (ω_i,s), where s is the total entropy density and all the other variables are labeled by i (as in hydrodynamics, this label i generally contains continuous position labels). When the label 0 is used, it corresponds to the variable $s=s(\boldsymbol{r})$.

We first consider the dissipation bracket formulated in Eqs. (7.1-19) and (7.1-24) of [9]. Since we are using the entropy S for generating the irreversible dynamics while Beris and Edwards are using the energy E, our dissipative bracket (5) does not coincide with the dissipation bracket of Beris and Edwards. Their linearized dissipation bracket has four contributions corresponding to the matrices A, B, C, and D in Eq. (7.1-24) in [9]. We first consider the A contribution and we give the corresponding metric matrix $M_A^{(E)}$ in the GENERIC (1). As before, the superscript (E) on the metric matrix indicates that the list of variables x contains the entropy density (so that the energy is the corresponding thermodynamic potential), as required when using the bracket formalism. The metric matrix

$$M_A^{(E)}=\begin{pmatrix} -TA_{ij} & A_{ij}\dfrac{\delta E}{\delta \omega_j} \\ \dfrac{\delta E}{\delta \omega_i}A_{ij} & -\dfrac{1}{T}\dfrac{\delta E}{\delta \omega_i}A_{ij}\dfrac{\delta E}{\delta \omega_j} \end{pmatrix} \tag{96}$$

reproduces the dissipative time evolution corresponding to the A contribution to the dissipation bracket. In this equation, the Einstein summation convention applies (the summation over labels i or j excludes 0). The symmetry of $M_A^{(E)}$ follows from the symmetry of A. Furthermore, $M_A^{(E)}$ is positive semidefinite if A is negative semidefinite. The matrix elements A_{i0} of Beris and Edwards need to be zero in order to satisfy the degeneracy condition

$$M_A^{(E)}\begin{pmatrix} \dfrac{\delta E}{\delta \omega_j} \\ T \end{pmatrix}=0. \tag{97}$$

In that sense, in the GENERIC formalism there exist additional restrictions on the metric matrix or the corresponding dissipation bracket. For the present choice of variables $x=(\omega_i,s)$, the dissipative contribution to the time evolution of x is simply given by the last column vector of the metric matrix. It is then straightforward to verify the equivalence of the resulting equations with those of the bracket formalism.

The B, C, and D contributions in Eq. (7.1-24) of [9] can be reformulated in a similar way. We next discuss the D contribution, which has the most complicated form and is the only one required in hydrodynamics. For $D_{ij}^{\alpha\beta}=D_{ji}^{\beta\alpha}$, the dissipation bracket is equivalently represented and a degeneracy condition analogous to Eq. (97) is satisfied by the symmetric matrix

$$M_D^{(E)}=\begin{pmatrix} \dfrac{\partial}{\partial r_\alpha}TD_{ij}^{\alpha\beta}\dfrac{\partial}{\partial r_\beta} & -\dfrac{\partial}{\partial r_\alpha}D_{ij}^{\alpha\beta}\left[\dfrac{\partial}{\partial r_\beta}\dfrac{\delta E}{\delta \omega_j}\right]+\dfrac{\partial}{\partial r_\alpha}T^2D_{i0}^{\alpha\beta}\dfrac{\partial}{\partial r_\beta}\dfrac{1}{T} \\ \left[\dfrac{\partial}{\partial r_\alpha}\dfrac{\delta E}{\delta \omega_i}\right]D_{ij}^{\alpha\beta}\dfrac{\partial}{\partial r_\beta}+\dfrac{1}{T}\dfrac{\partial}{\partial r_\alpha}T^2D_{0j}^{\alpha\beta}\dfrac{\partial}{\partial r_\beta} & -\dfrac{1}{T}\left[\dfrac{\partial}{\partial r_\alpha}\dfrac{\delta E}{\delta \omega_i}\right]D_{ij}^{\alpha\beta}\left[\dfrac{\partial}{\partial r_\beta}\dfrac{\delta E}{\delta \omega_j}\right]+\dfrac{1}{T}\dfrac{\partial}{\partial r_\alpha}T^3D_{00}^{\alpha\beta}\dfrac{\partial}{\partial r_\beta}\dfrac{1}{T}-\dfrac{1}{T^2}\left[\dfrac{\partial}{\partial r_\alpha}T^2D_{0j}^{\alpha\beta}\dfrac{\partial}{\partial r_\beta}\dfrac{\delta E}{\delta \omega_j}\right] \end{pmatrix}. \tag{98}$$

The spatial indices α and β are summed from 1 to 3 and derivatives in square brackets do not act on any terms outside the brackets. The matrix $M_D^{(E)}$ can be shown to be positive semidefinite if D is assumed to be negative semidefinite. For hydrodynamics, we have verified explicitly that the matrix (98) implied by the matrix D of Beris and Edwards, after transformation to the proper independent variables, coincides with the one in Eq. (38).

The B and C contributions in Eq. (7.1-24) of [9] need to be considered simultaneously because they can be formulated in the GENERIC form only if the matrices B and C are related. For $B_{ij}^{\alpha}=C_{ji}^{\alpha}$, $B_{i0}^{\alpha}=C_{0i}^{\alpha}$, and $C_{i0}^{\alpha}=C_{00}^{\alpha}=0$, the dissipation bracket is equivalent to the symmetric matrix

$$M_{BC}^{(E)}=\begin{pmatrix} -TB_{ij}^{\alpha}\dfrac{\partial}{\partial r_\alpha}+\dfrac{\partial}{\partial r_\alpha}TC_{ij}^{\alpha} & B_{ij}^{\alpha}\left[\dfrac{\partial}{\partial r_\alpha}\dfrac{\delta E}{\delta \omega_j}\right]-\dfrac{\partial}{\partial r_\alpha}C_{ij}^{\alpha}\dfrac{\delta E}{\delta \omega_j}-T^2B_{i0}^{\alpha}\dfrac{\partial}{\partial r_\alpha}\dfrac{1}{T} \\ \left[\dfrac{\partial}{\partial r_\alpha}\dfrac{\delta E}{\delta \omega_i}\right]C_{ij}^{\alpha}+\dfrac{\delta E}{\delta \omega_i}B_{ij}^{\alpha}\dfrac{\partial}{\partial r_\alpha}+\dfrac{1}{T}\dfrac{\partial}{\partial r_\alpha}T^2C_{0j}^{\alpha} & -\dfrac{2}{T}\dfrac{\delta E}{\delta \omega_i}B_{ij}^{\alpha}\left[\dfrac{\partial}{\partial r_\alpha}\dfrac{\delta E}{\delta \omega_j}\right]-\dfrac{1}{T^2}\left[\dfrac{\partial}{\partial r_\alpha}\left(T^2C_{0j}^{\alpha}\dfrac{\delta E}{\delta \omega_j}\right)\right] \end{pmatrix}. \tag{99}$$

Again, a degeneracy condition analogous to Eq. (97) is satisfied. The conditions on the matrices B and C imply Onsager symmetry [9], which is thus inherent to the GENERIC structure (in the bracket formalism, this symmetry is imposed *a posteriori*).

The various contributions to the dissipation bracket can be expressed in a more compact way by introducing the matrices

$$\Omega=\begin{pmatrix} \delta_{ij} & -\dfrac{1}{T}\dfrac{\delta E}{\delta \omega_i} \\ 0 & 0 \end{pmatrix} \tag{100}$$

and

$$\Omega^{\alpha}=\begin{pmatrix} \delta_{ij}\dfrac{\partial}{\partial r_\alpha} & -\dfrac{1}{T}\left[\dfrac{\partial}{\partial r_\alpha}\dfrac{\delta E}{\delta \omega_i}\right] \\ 0 & T\dfrac{\partial}{\partial r_\alpha}\dfrac{1}{T} \end{pmatrix}. \tag{101}$$

We then have the identity

$$\langle y, M^{(E)}z\rangle=-\int T\Xi(\Omega y,\Omega^{\alpha}y;\Omega z,\Omega^{\alpha}z)d^3r, \tag{102}$$

where Ξ is the dissipation function characterizing the dissipation bracket as introduced in Eq. (7.1-19) of [9]. We have explicitly verified this equivalence for bilinear functions Ξ. Since y and z are arbitrary, Eq. (102) defines the metric matrix. Its positive semidefiniteness generally follows from the negative-semidefinite character of the dissipation function Ξ. The discussion on p. 175 of [9] shows that the symmetry and degeneracy conditions for the metric matrix automatically imply the Onsager-Casimir reciprocity relations.

Beris and Edwards have introduced more general nonlinear dissipation functions Ξ. In order to illustrate how the more general situation can be handled within the GENERIC approach, we here consider the prototype of an example for which Beris and Edwards need a nonlinear dissipation function: a chemical reaction far from equilibrium (see Chap. 12 of [9] and [33,34]). For the sake of clarity we consider an explicit example of a chemical reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3. \tag{103}$$

Three species of particles are involved in this reaction (nitrogen, hydrogen, and ammonia) and the corresponding stoichiometric coefficients are $\nu_1 = -1$, $\nu_2 = -3$, and $\nu_3 = 2$. The mass of a particle of species i is denoted by m_i. For this three-component system, we use the following list of state variables: the mass densities $\rho_1(\boldsymbol{r})$, $\rho_2(\boldsymbol{r})$, and $\rho_3(\boldsymbol{r})$, the total momentum density $\boldsymbol{u}(\boldsymbol{r})$, and the total entropy density $s(\boldsymbol{r})$.

The energy and entropy are given by

$$E = \int \left[\frac{1}{2} \frac{\boldsymbol{u}(\boldsymbol{r})^2}{\rho_1(\boldsymbol{r}) + \rho_2(\boldsymbol{r}) + \rho_3(\boldsymbol{r})} + \epsilon(\rho_1(\boldsymbol{r}), \rho_2(\boldsymbol{r}), \rho_3(\boldsymbol{r}), s(\boldsymbol{r})) \right] d^3 r \tag{104}$$

and

$$S = \int s(\boldsymbol{r}) d^3 r. \tag{105}$$

We furthermore introduce the auxiliary quantities

$$\tilde{\mu}_j(\boldsymbol{r}) = \frac{m_j}{k_B T(\boldsymbol{r})} \frac{\delta E}{\delta \rho_j(\boldsymbol{r})} \quad (j = 1,2,3), \tag{106}$$

which are closely related to the chemical potentials of the different species [33],

$$\tilde{\mu}_j = \frac{m_j}{k_B T} \left(\mu_j - \frac{1}{2} \boldsymbol{v}^2 \right). \tag{107}$$

By taking functional derivatives with respect to the state variables we then obtain

$$\frac{\delta E}{\delta x} = \begin{pmatrix} \dfrac{k_B T}{m_1} \tilde{\mu}_1(\boldsymbol{r}) \\ \dfrac{k_B T}{m_2} \tilde{\mu}_2(\boldsymbol{r}) \\ \dfrac{k_B T}{m_3} \tilde{\mu}_3(\boldsymbol{r}) \\ \boldsymbol{v}(\boldsymbol{r}) \\ T(\boldsymbol{r}) \end{pmatrix}. \tag{108}$$

The time-evolution equations for the densities ρ_j due to the chemical reaction (103) are of the form (see, e.g., Sec. 17.B.2 of [4] or Sec. 12.4 of [9])

$$\frac{\partial \rho_j}{\partial t} = \frac{\nu_j m_j p}{k_B T} r(p,T) \left(e^{-\nu_1 \tilde{\mu}_1 - \nu_2 \tilde{\mu}_2} - e^{\nu_3 \tilde{\mu}_3} \right), \tag{109}$$

where the pressure p and the temperature T in the above equations are functions of ρ_1, ρ_2, ρ_3, and s,

$$p = \left(\sum_{j=1}^{3} \rho_j \frac{\partial}{\partial \rho_j} + s \frac{\partial}{\partial s} - 1 \right) \epsilon(\rho_1, \rho_2, \rho_3, s), \tag{110}$$

$$T = \frac{\partial \epsilon(\rho_1, \rho_2, \rho_3, s)}{\partial s}, \tag{111}$$

and $r(p,T)$ is a reciprocal time scale characterizing the reaction rate. Equilibrium states are characterized by the condition

$$\mathcal{A} = \nu_1 \tilde{\mu}_1 + \nu_2 \tilde{\mu}_2 + \nu_3 \tilde{\mu}_3 = 0. \tag{112}$$

The quantity $\mathcal{A}$ is closely related to the weighted combination of chemical potentials of the reaction partners, which is known as the affinity of the chemical reaction. By assuming an ideal concentration dependence of the chemical potentials one recovers the mass action law (see Sec. 3.E of [4]).

As mentioned above, we here consider only the contribution to $\partial \rho_j / \partial t$ resulting from chemical reactions. The other contributions are analogous to those previously discussed in the context of hydrodynamics. Chemical reactions are part of the irreversible dynamics. We suggest the following metric matrix for reproducing the time-evolution equations (109) for our three-component system:

$$\boldsymbol{M} = \begin{pmatrix} m_1^2 \nu_1^2 & m_1 m_2 \nu_1 \nu_2 & m_1 m_3 \nu_1 \nu_3 & 0 & -k_B m_1 \nu_1 \mathcal{A} \\ m_1 m_2 \nu_1 \nu_2 & m_2^2 \nu_2^2 & m_2 m_3 \nu_2 \nu_3 & 0 & -k_B m_2 \nu_2 \mathcal{A} \\ m_1 m_3 \nu_1 \nu_3 & m_2 m_3 \nu_2 \nu_3 & m_3^2 \nu_3^2 & 0 & -k_B m_3 \nu_3 \mathcal{A} \\ 0 & 0 & 0 & 0 & 0 \\ -k_B m_1 \nu_1 \mathcal{A} & -k_B m_2 \nu_2 \mathcal{A} & -k_B m_3 \nu_3 \mathcal{A} & 0 & k_B^2 \mathcal{A}^2 \end{pmatrix} \frac{p}{k_B^2 T} r(p,T) \frac{e^{\nu_3 \tilde{\mu}_3} - e^{-\nu_1 \tilde{\mu}_1 - \nu_2 \tilde{\mu}_2}}{\nu_1 \tilde{\mu}_1 + \nu_2 \tilde{\mu}_2 + \nu_3 \tilde{\mu}_3}. \tag{113}$$

This matrix $\boldsymbol{M}$ is symmetric and positive semidefinite and satisfies the degeneracy requirement (3). Not only the gradient of energy but also the gradient of the total mass $(1,1,1,0,0)$ lies in the null space of M (due to the conservation of mass $m_1\nu_1+m_2\nu_2+m_3\nu_3=0$). The time evolution of the entropy density due to chemical reactions, as implied by Eq. (109) and the GENERIC structure, is

$$\frac{\partial s}{\partial t}=\frac{\mathcal{A}p}{T}r(p,T)(e^{-\nu_1\tilde{\mu}_1-\nu_2\tilde{\mu}_2}-e^{\nu_3\tilde{\mu}_3}), \tag{114}$$

which coincides with Eq. (12.4-14) of [9]. Even when Beris and Edwards need a nonlinear dissipation function Ξ, we can reproduce their equations with the GENERIC (1). The more nonlinear appearance of the basic equations in the bracket formalism results from considering the explicit functional dependence of the dissipation bracket on $\delta E/\delta x$ and its gradients, whereas in the GENERIC framework only the overall x dependence of the building blocks is considered. This observation also shows why more nonlocal theories can be treated by the GENERIC but not by the bracket formalism.

In summary, we have shown how the general structure of the bracket formalism results from the GENERIC approach. The disadvantages of using the energy for generating the irreversible dynamics are that (i) the total entropy density needs to be in the list of variables and (ii) the dissipative bracket has a rather complicated form that cannot easily be interpreted in geometric terms. The greater flexibility in the choice of variables is a major advantage when one is interested in more microscopic levels of description. The GENERIC approach not only allows us such more general choices of variables but, in view of the great simplicity and geometric significance of the irreversible term, is better suited for deriving equations from more microscopic theories by coarse graining. Microscopic expressions for the GENERIC building blocks E, S, L, and M have been derived by projection operator techniques [35]. An important example for which neither the entropy density nor the temperature is in the list of variables is the Boltzmann equation (no local-equilibrium assumption can be made). While the formulation of the Boltzmann equation in the bracket formalism is therefore unclear, its GENERIC reformulation is possible due to the use of energy and entropy as two separate generators [1,36]. Furthermore, the requirement (3) imposes additional restrictions on the dissipation bracket, thus increasing the predictive power of the GENERIC formalism compared to the bracket formalism (the Onsager-Casimir reciprocal relations are automatically implemented).

C. Rigid dumbbells

In order to illustrate how constraints can be incorporated into our general framework we consider a dilute solution of rigid dumbbell molecules (see Chap. 14 of [16]). Our discussion is based on the nonisothermal kinetic theory of Hookean dumbbell molecules presented in Sec. III. For rigid dumbbells, the interaction potential in the total energy (48) and the entropic potential in the entropy (49) can be omitted. The further modifications can be described most efficiently in terms of the symmetric projection operator

$$\boldsymbol{P}(\boldsymbol{Q})=\boldsymbol{1}-\frac{\boldsymbol{Q}\boldsymbol{Q}}{Q^2}. \tag{115}$$

The crucial change in the Poisson operator (58) is the replacement of the last block in the second column by

$$\frac{\partial}{\partial \boldsymbol{r}}\psi(\boldsymbol{r},\boldsymbol{Q})+\frac{\partial}{\partial \boldsymbol{Q}}\cdot\psi(\boldsymbol{r},\boldsymbol{Q})\boldsymbol{P}(\boldsymbol{Q})\boldsymbol{Q}\cdot\frac{\partial}{\partial \boldsymbol{r}}, \tag{116}$$

with a corresponding change in the second row dictated by the antisymmetry requirement. In the group theoretical construction of the Poisson operator, the transverse projector $\boldsymbol{P}(\boldsymbol{Q})$ expresses the fact that the connector vector describing the rigid dumbbell can only be rotated by the action of space transformations.

For the gradient of the entropy to remain in the null space of the modified Poisson operator (58) one also needs to change the osmotic pressure tensor. The proper choice is

$$\begin{aligned}\boldsymbol{\Pi}(\boldsymbol{r})&=k_{\mathrm{B}}T(\boldsymbol{r})\int\psi(\boldsymbol{r},\boldsymbol{Q})\left\{\boldsymbol{1}+\frac{\partial}{\partial \boldsymbol{Q}}\cdot[\boldsymbol{P}(\boldsymbol{Q})\boldsymbol{Q}]\right\}d^3Q\\&=k_{\mathrm{B}}T(\boldsymbol{r})\int\left(2\boldsymbol{1}-3\frac{\boldsymbol{Q}\boldsymbol{Q}}{Q^2}\right)\psi(\boldsymbol{r},\boldsymbol{Q})d^3Q.\end{aligned} \tag{117}$$

Once more we see how powerful the requirement that the gradient of the entropy must lie in the null space of the Poisson operator is: It fixes the well-known anisotropic contribution to the stress tensor of rigid rods.

Finally, we need to give the proper modifications of the metric matrix (59). As mentioned before, we assume $V=0$, so that we actually start from a simplified version of Eq. (59). We discuss the modifications of the entry in the lower right corner and of the central block with entries proportional to $\eta_s T$ separately.

The entry in the lower right corner is replaced by

$$\begin{aligned}&-\frac{\partial}{\partial \boldsymbol{Q}}\cdot\frac{2T}{\zeta}\psi(\boldsymbol{r},\boldsymbol{Q})\boldsymbol{P}(\boldsymbol{Q})\cdot\frac{\partial}{\partial \boldsymbol{Q}}\delta(\boldsymbol{Q}-\boldsymbol{Q}')\\&\quad-\frac{\partial}{\partial \boldsymbol{r}}\cdot\frac{T}{2\zeta}\psi(\boldsymbol{r},\boldsymbol{Q})\boldsymbol{D}(\boldsymbol{Q})\cdot\frac{\partial}{\partial \boldsymbol{r}}\delta(\boldsymbol{Q}-\boldsymbol{Q}').\end{aligned} \tag{118}$$

The transverse projection operator between the $\boldsymbol{Q}$ derivatives again expresses the fact that the connector vector cannot change its length. Between the $\boldsymbol{r}$ derivatives we allow for a tensor $\boldsymbol{D}(\boldsymbol{Q})$ different from the unit tensor, that is, for configuration-dependent translational diffusivity. The tensor $\boldsymbol{D}(\boldsymbol{Q})$ must be positive semidefinite in order to ensure the same property for the metric matrix M.

While the diffusion equation obtained after the modification (118) has the well-known form for rigid rods (cf. Eq. (14.2-8) of [16]), a dissipative contribution to the stress tensor is still missing. This can be incorporated in a compact form after introducing the fourth-rank tensor

$$\boldsymbol{I}=\boldsymbol{I}(\boldsymbol{r})=\frac{\zeta T}{4}\int\frac{\boldsymbol{Q}\boldsymbol{Q}\boldsymbol{Q}\boldsymbol{Q}}{Q^2}\psi(\boldsymbol{r},\boldsymbol{Q})d^3Q \tag{119}$$

as an auxiliary variable. If one adds

$$\begin{pmatrix} -2\frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{I}\cdot\frac{\partial}{\partial \boldsymbol{r}} & \frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{I}:\dot{\boldsymbol{\gamma}} \\ -\dot{\boldsymbol{\gamma}}:\boldsymbol{I}\cdot\frac{\partial}{\partial \boldsymbol{r}} & \frac{1}{2}\dot{\boldsymbol{\gamma}}:\boldsymbol{I}:\dot{\boldsymbol{\gamma}} \end{pmatrix} \tag{120}$$

to the central block with entries proportional to $\eta_s T$ in the metric matrix (59), then the usual dissipative contribution to the stress tensor obtained in the kinetic theory of rigid rods is reproduced. Guided by the example of the Newtonian solvent contribution, this additional symmetric and positive-semidefinite block is constructed such that the gradient of the energy remains in the null space of the metric matrix. The additional dissipative stress tensor shows up in the expected manner in the energy balance equation.

D. Reptation models

Many models for concentrated polymer solutions and melts are based on the idea of reptation or anisotropic friction (see Chap. 19 of [16]; see also [37]). Reptation models can be described by a configurational distribution function $\psi(\boldsymbol{r},\boldsymbol{Q},\sigma)$, where $\boldsymbol{Q}$ is a unit vector and $\sigma\in[0,1]$ is a position label varying from 0 to 1 in going from one end of a polymer chain to the other. With the usual independent alignment approximation, the position label is not affected by space transformations so that the Poisson operator coincides with the one for rigid dumbbells [Eq. (58) with the modification (116)]. More sophisticated ideas about the chain retraction after deformation can be incorporated very elegantly through the action of space transformations on $\psi(\boldsymbol{r},\boldsymbol{Q},\sigma)$; the degeneracy requirement (2) then determines the corresponding modification of the stress tensor.

We again use the energy E of hydrodynamics [Eq. (19)], and for the entropy S we essentially use Eq. (49),

$$S=\int\left[s(\rho(\boldsymbol{r}),\epsilon(\boldsymbol{r}))-k_{\mathrm{B}}\int_0^1\int \psi(\boldsymbol{r},\boldsymbol{Q},\sigma)\times\ln\psi(\boldsymbol{r},\boldsymbol{Q},\sigma)d^3Q\,d\sigma\right]d^3r. \tag{121}$$

The osmotic pressure tensor turns out to be very similar to Eq. (117) for rigid dumbbells:

$$\boldsymbol{\Pi}(\boldsymbol{r})=k_{\mathrm{B}}T(\boldsymbol{r})\int_0^1\int\left(2\boldsymbol{1}-3\frac{\boldsymbol{QQ}}{Q^2}\right)\psi(\boldsymbol{r},\boldsymbol{Q},\sigma)d^3Q\,d\sigma. \tag{122}$$

It should be noticed that the normalization of ψ affects the entropy and the osmotic pressure tensor. It is natural to assume that $\int\int\int\psi d^3r\,d^3Q\,d\sigma$ is proportional to the total number of polymer molecules times the number of segments in each molecule. Further numerical factors included in the normalization of ψ, and hence further factors in the stress tensor, cannot be obtained from the GENERIC formalism.

The metric matrix $\boldsymbol{M}=\boldsymbol{M}(\boldsymbol{r},\boldsymbol{Q},\sigma)$ for reptation models has the form

$$\boldsymbol{M}=\begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -2\frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{I}\cdot\frac{\partial}{\partial \boldsymbol{r}} & \frac{\partial}{\partial \boldsymbol{r}}\cdot\boldsymbol{I}:\dot{\boldsymbol{\gamma}} & 0 \\ 0 & -\dot{\boldsymbol{\gamma}}:\boldsymbol{I}\cdot\frac{\partial}{\partial \boldsymbol{r}} & \frac{1}{2}\dot{\boldsymbol{\gamma}}:\boldsymbol{I}:\dot{\boldsymbol{\gamma}} & 0 \\ 0 & 0 & 0 & -\frac{\partial}{\partial\sigma}\frac{\psi}{\lambda k_{\mathrm{B}}}\frac{\partial}{\partial\sigma} \end{pmatrix}, \tag{123}$$

where λ is the reptation time scale (no integrations over $\boldsymbol{r}$, $\boldsymbol{Q}$, and σ are required). For the Doi-Edwards model, the osmotic pressure tensor (122) is the full stress tensor ($\boldsymbol{I}=\boldsymbol{0}$). In the Curtiss-Bird model, an additional dissipative contribution to the stress tensor occurs. This can be reproduced by choosing

$$\boldsymbol{I}=\frac{3}{2}\varepsilon\lambda k_{\mathrm{B}}T^2\int_0^1\int\sigma(1-\sigma)\frac{\boldsymbol{QQQQ}}{Q^4}\psi(\boldsymbol{r},\boldsymbol{Q},\sigma)d^3Q\,d\sigma \tag{124}$$

in Eq. (123), where ε is the link tension coefficient.

While the above equations show how the diffusion equation and the stress tensor of reptation models can be reproduced, they do not provide the boundary conditions for the configurational distribution function ψ at $\sigma=0$ and $\sigma=1$. These need to be specified separately. It might be possible to incorporate boundary conditions into the formalism by mimicking their effect through strongly repulsive and strongly randomizing dynamical terms.

Des Cloizeaux suggested a modification of the Doi-Edwards model, which he named ‘‘basic diffusion model’’ [38]. This modification can be incorporated into the GENERIC formalism by the replacements

$$\ln\psi(\boldsymbol{r},\boldsymbol{Q},\sigma)\rightarrow\ln[B(\sigma)\psi(\boldsymbol{r},\boldsymbol{Q},\sigma)] \tag{125}$$

in Eq. (121) and

$$\psi=\psi(\boldsymbol{r},\boldsymbol{Q},\sigma)\rightarrow B(\sigma)^2\psi(\boldsymbol{r},\boldsymbol{Q},\sigma) \tag{126}$$

in Eq. (123), where $B(\sigma)$ is a given function. The replacement (125) implies a modification of the equilibrium distribution function, which is no longer uniform in σ, whereas Eq. (126) can be interpreted as a modification of the diffusion along the chain contour. The important consequence of the GENERIC structure is that no additional modification of the pressure tensor (122) is required.

Polymer diffusion is not accounted for in the above theories of concentrated solutions and melts (there is no stochastic influence on the dynamics of $\boldsymbol{r}$). For polymer melts, the density $\rho(\boldsymbol{r})$ is proportional to $\int\int\psi d^3Q\,d\sigma$, so that ρ could be eliminated from the list of variables.

E. Hydrodynamic interaction

Incorporation of hydrodynamic interactions into the dumbbell kinetic theory of Sec. III requires only a modification of the metric matrix (59). In all places where ζ occurs in terms involving derivatives with respect to $\boldsymbol{Q}$, the following replacement should be made:

$$\frac{1}{\zeta} \rightarrow \frac{1}{\zeta}(\mathbf{1} - \zeta \boldsymbol{\Omega}), \tag{127}$$

where $\boldsymbol{\Omega}$ is the hydrodynamic interaction tensor (e.g., the Oseen-Burgers tensor), and the tensor introduced by the replacement (127) should be contracted with the $\boldsymbol{Q}$ derivatives. In the lower right corner of the metric matrix (59), where ζ occurs in combination with derivatives with respect to $\boldsymbol{r}$, we need the replacement

$$\frac{1}{\zeta} \rightarrow \frac{1}{\zeta}(\mathbf{1} + \zeta \boldsymbol{\Omega}). \tag{128}$$

With these minor modifications, hydrodynamic interaction is fully incorporated into the polymer kinetic theory of Sec. III and the usual diffusion equation is reproduced (see, e.g., Sec. 4.2.1 of [39] and, in particular, Exercise 4.18). Notice that while hydrodynamic interactions do affect the energy balance (62), they do not affect the momentum balance (61), that is, the polymer contribution to the stress tensor for a dilute solution remains unchanged.

While the incorporation of the hydrodynamic interaction effect is mathematically unproblematic, it can be used to discuss a subtle point about physical limitations. Hydrodynamic interactions are related to the solvent dynamics, which is part of the full time evolution of the system under consideration. More precisely, the solvent dynamics on the polymer length scale has already been taken into account by introducing hydrodynamic interaction tensors. Therefore, the momentum balance equation (61) should certainly be used on length scales much larger than the polymer size in order to avoid considering the same effect twice (probably even in an inconsistent manner). The mere fact that hydrodynamic interaction has been incorporated sets a limit for the length scale down to which the equations can be physically meaningful, and that should be kept in mind when discretizing the equations in numerical calculations. As long as no hydrodynamic interactions had been incorporated, the full set of equations could have been used for the solvent dynamics between the beads, that is, on much shorter length scales [40] (of course, boundary conditions for the solvent velocity on the beads would then be required).

VI. SUMMARY, CONCLUSIONS, AND OUTLOOK

We have shown in great detail how various time-evolution equations for nonequilibrium systems can be formulated in the GENERIC form (1). Important parts of the proposed GENERIC structure are the complementary degeneracy requirements (2) and (3) and the conditions (7)–(11). Equation (2) has, for example, important implications for the pressure (Gibbs-Duhem equation and osmotic pressure), for the form of the stress tensor (Kramers expression, effects of constraints and hydrodynamic interactions), and for the heat-flux vector. Equation (3), together with the symmetry of the metric matrix, implies that specifying a few elements of the metric matrix is sufficient for determining the entire matrix uniquely.

We have not only shown the way in which many different models can be expressed in the GENERIC form, but we have also demonstrated that previously proposed formalisms (linear thermodynamics of irreversible processes, extended irreversible thermodynamics, and the bracket formalism of Beris and Edwards) are contained in the GENERIC approach. The relationship between the matrix formalism of Jongschaap (see [41] and references therein) and the GENERIC approach has been elaborated recently [42]. In order to establish this relationship it was necessary to study systems consisting of open subsystems and their environments in some detail; as a result, one also finds the GENERIC approach to driven systems.

Concerning the four building blocks occurring in the GENERIC (1), the various equations presented in this paper should have made clear that the expressions for the total energy E and for the entropy S typically have forms expected from equilibrium thermodynamics. In all cases, the formulation of the Poisson operator L was unproblematic and it typically required only assumptions about the transformation behavior of the state variables under space transformations. The most difficult task is thus the determination of the metric matrix or friction matrix M. Its matrix elements contain parameters such as viscosities, thermal conductivities, friction or diffusion coefficients, hydrodynamic interaction tensors, or chemical reaction rates, that is, detailed material information related to nonequilibrium processes.

If the metric matrix cannot be determined empirically, one needs a framework for calculating it from more microscopic arguments. We need a recipe for determining M, of similar significance to the well-known rule that the thermodynamic potentials of equilibrium thermodynamics can be obtained by calculating partition functions. Such microscopic expressions for all the GENERIC building blocks have recently been obtained by the projection operator method [35]. Once we have formal expressions for the building blocks, we need numerical methods for actually evaluating them, at least approximately or with statistical error bars (like Monte Carlo methods for evaluating partition functions). In view of computer simulations, it is very desirable to generalize the GENERIC structure to time-discrete systems (see paper I). When fundamental thermodynamic principles are respected in numerical calculations then they might be much more stable and more meaningful.

Since jumping from one level of description to another one should be an integral part of the GENERIC approach, it is natural to ask whether one could start from such a detailed level of description that quantum-mechanical effects should be taken into account. The GENERIC formulation for quantum systems still remains to be worked out.

Throughout these papers, we have ignored integral models or constitutive equations with memory effects in which stresses are obtained from suitable functionals of strain history [43]. We believe that such models are less fundamental and that memory effects enter the description because some relevant slow variables have been ignored. Assuming the existence of variables that would eliminate all memory effects, one could try to develop a general theory of thermodynamically admissible integral models from the GENERIC framework presented here.

The discussion of this section shows that a number of questions concerning the GENERIC approach to nonequilibrium systems as developed in these papers remain open. While many of these questions are studied in various ongoing research projects, we hope that the GENERIC approach as presented here already provides a useful framework for learning more about previously considered nonequilibrium systems and for formulating the proper time-evolution equations for new problems.

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