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Atomistic Monte Carlo Simulations of Polymer Melt Elasticity: Their Nonequilibrium Thermodynamics GENERIC Formulation in a Generalized Canonical Ensemble

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ABSTRACT: A novel atomistic Monte Carlo (MC) methodology is presented for the simulation of systems with a complex internal microstructure away from equilibrium, directly from first principles. The methodology is based on the general equation for the nonequilibrium reversible−irreversible coupling (GENERIC) and proposes MC, and not molecular dynamics (MD), simulations in a generalized canonical ensemble. The new approach, also termed GENERIC MC, is hierarchical and starts with the definition or selection of the set of *state* variables describing the system at a coarse-grained level. To each state variable, a *field* or *conjugate* variable is introduced as a proper *Lagrange multiplier* when projecting atomistic coordinates onto the macroscopic state variables. Each conjugate variable is formally defined as the partial derivative of the system thermodynamic potential (the entropy) with respect to the corresponding coarse-grained state variable, keeping the rest of the state variables constant. The set of conjugate variables defines the extended canonical ensemble of the atomistic GENERIC MC simulation. By analyzing the structure of the canonical GENERIC equation for spatially homogeneous, time-independent flows, a kinematic interpretation is attributed to the conjugate variables of the structural state variables connecting them to the velocity gradient tensor. This sets the framework for performing realistic atomistic MC simulations, guided by the thermodynamically admissible macroscopic models derived from GENERIC, to calculate the free energy of the nonequilibrium system, without going through the full dynamical problem. The formulation is outlined here for three different viscoelastic fluid models: the single- and multiple-conformation tensor viscoelastic models for unentangled polymers and the pompon model for long-chain branched (LCB) molecules. Results are presented from detailed end-bridging, atomistic MC simulations with the new method for the elasticity of a linear C_{156} polyethylene (PE) melt, in a steady-state uniaxial elongational flow. In the simulations, a four-mode conformation tensor viscoelastic model was employed to project atomistic coordinates. The dependence of the melt free energy of elasticity on chain degree of deformation due to applied flow field is reported and compared against the predictions of simple analytic models, commonly used in polymer flow calculations, such as the Hookean dumbbell and the FENE-P. The latter, which accounts for the finite extensibility of the polymer, is seen to be more representative of the actual melt response than the former. It is also seen that, in the regime of small Deborah numbers studied, only the components of the first-mode conformation tensor deviate from their equilibrium values; higher-mode conformation tensors retain their equilibrium, spherical symmetry. This explains the success of the single conformation tensor FENE-P viscoelastic model in fitting rheological data.

1. Introduction

In a recent series of papers,[1−3] a general formalism for the description of nonequilibrium systems was developed by proposing a general equation for the nonequilibrium reversible−irreversible coupling through the use of two generator functionals, the entropy and the energy. In the proposed formalism, known by the acronym GENERIC, the time evolution of an isolated thermodynamic system is defined by the evolution equations of a prespecified set of independent state variables, appropriately chosen to provide a complete description of the given nonequilibrium system at a coarse-grained, macroscopic level. According to GENERIC, if **x** represents the set of state variables chosen to describe the system, its time evolution reads as follows:

$$\frac{d\mathbf{x}}{dt} = \mathbf{L}(\mathbf{x}) \cdot \frac{\delta E(\mathbf{x})}{\delta \mathbf{x}} + \mathbf{M}(\mathbf{x}) \cdot \frac{\delta S(\mathbf{x})}{\delta \mathbf{x}} \tag{1}$$

In eq 1, the functionals E and S represent the system total energy and total entropy, respectively, expressed in terms of the state variables **x**, while **L** and **M** are the reversible and dissipative matrices, respectively. Unless **x** contains all the particle momenta and positions, with such a formulation, we refer to as a *coarse-grained* description of the system of interest.

In the GENERIC framework, eq 1 is supplemented by the complementary degeneracy requirements that

$$\mathbf{L}(\mathbf{x}) \cdot \frac{\delta S(\mathbf{x})}{\delta \mathbf{x}} = 0 \tag{2}$$

and

$$\mathbf{M}(\mathbf{x}) \cdot \frac{\delta E(\mathbf{x})}{\delta \mathbf{x}} = 0 \tag{3}$$

The requirement that the gradient $\delta S(\mathbf{x})/\delta \mathbf{x}$ lies in the

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null space of **L** in eq 2 expresses the reversible nature of the **L** contribution to the system dynamics. The requirement that the gradient $\delta E(\mathbf{x})/\delta\mathbf{x}$ lies in the null space of **M** in eq 3 expresses the conservation of the total energy by the **M** contribution to the system dynamics. Furthermore, it is required that the matrix **L** is antisymmetric and satisfies the Jacobi identity, whereas **M** is symmetric and positive semidefinite. The two contributions to the time evolution of **x** generated by the energy E and entropy S in eq 1 are called the *reversible* and *irreversible* contributions to GENERIC, respectively.

With the above formulation, a large number of important examples of nonequilibrium systems have been expressed in the GENERIC framework by considering the compatibility between two levels of analysis, e.g., a molecular based on a mechanical model for the system and that of the present nonequilibrium thermodynamics-based coarse-grained description, and by studying a large number of specific examples: hydrodynamics, polymer kinetic theory (including hydrodynamic interaction, rigid constraints, reptation models, and polymer heat conductivity), and chemical reactions.

More recently, explicit expressions have been derived for the building blocks E, S, **L**, and **M** by a projection-operator technique from Hamilton's equations of motion.[4] Atomistic expressions for the building blocks E, S, **L**, and **M** for the most widely used state variables (mass density, momentum density, energy, and entropy), with emphasis in hydrodynamics, have also been derived on the basis of projection operator techniques.[5] Both of these derivations have been carried out in a generalized microcanonical ensemble.

Projection operator techniques have also been used to derive the two-generator (energy–entropy) formulation of GENERIC, starting not from the classical but from the *quantum* description of an isolated system at the microscopic level.[6] In the derivation, a generalized canonical ensemble is employed, thus opening up the way toward the generalized canonical ensemble reformulation of classical GENERIC, too; simultaneously, all usual disadvantages of the previously adopted microcanonical formalism, which rendered GENERIC almost inapplicable for practical calculations, are completely avoided.

It is this advancement, the generalized *canonical* ensemble formulation of GENERIC, that has driven the present work, with an eye on how to use it as a strict nonequilibrium thermodynamics tool for the design and implementation of MC (and not MD) algorithms for useful calculations in systems away from equilibrium. To this direction, the recent work of Mavrantzas and Theodorou,[7] on the atomistic simulation of the elasticity of an unentangled polyethylene (PE) melt, constitutes one of the very first examples where such actual calculations of the elastic properties of a macromolecular system were obtained, starting from first principles. The main output of the Mavrantzas–Theodorou[7] work was the calculation of the Helmholtz free energy of the system, and, therefore, the calculation of the entropy of orientation and/or deformation of the polymer melt when subjected to a given flow field. The work of Mavrantzas and Theodorou[7] was in fact inspired by the purely macroscopic one-generator (or generalized bracket) formalism for nonequilibrium systems of Beris and Edwards.[8] In the end of the present paper, the Mavrantzas–Theodorou work will be analyzed in the framework of canonical GENERIC. It will be seen that it constitutes a formal application of canonical GENERIC, where the coarse-graining includes mapping of the atomistic system onto a single-conformation tensor viscoelastic fluid model.

The paper is organized as follows: Section 2 completes the discussion on GENERIC by presenting how it is implemented for the modeling of a particular class of materials, namely polymer melts. Issues related to the choice of the proper state variables, their distinction between hydrodynamic and structural, and the definition of the formulas describing the system energy and entropy (as a function of the system state variables) are brought up and addressed here briefly. Section 3 presents a complete summary of canonical GENERIC. Section 4 discusses the form to which the relevant GENERIC time evolution equation is reduced for spatially homogeneous, time-independent flows. Section 5 gives a detailed description of the new (also termed GENERIC MC) methodology for the design of atomistic simulations to get at the elasticity of polymer melts, guided by the macroscopic models derived by GENERIC. In section 6, results are presented for the elasticity of unentangled PE melts obtained by implementing either a single- or a multiple-conformation tensor viscoelastic model. Section 7 follows with a discussion of the most important features of the present work and plans for immediate future work.

2. GENERIC Modeling of Melts

2.1. State Variables. In the description of any type of fluid flow, the hydrodynamic variables associated with the conserved quantities play an important role. By including the hydrodynamic variables in the list of independent state variables, appropriate, thermodynamically admissible balance equations can be formulated, which play a central role in any approach to nonequilibrium thermodynamics.[9] In applications of GENERIC to fluid flow problems, the following variables are usually chosen as the independent hydrodynamic variables: the polymer mass density $\rho(\mathbf{r})$, the momentum density $\mathbf{u}(\mathbf{r})$, and the internal energy density $\epsilon(\mathbf{r})$. The internal energy density $\epsilon(\mathbf{r})$ includes all interactions between atoms of all chains as well as the kinetic energies associated with their motions with respect to the local fluid velocity $\mathbf{v}(\mathbf{r})$ $(= \mathbf{u}(\mathbf{r})/\rho(\mathbf{r}))$.

To capture the effects of the complex structure of fluids such as polymers, in addition to the hydrodynamic variables, use is also made of a small number of carefully selected structural state variables. For the appropriate choice of the structural variables, good physical insight is needed. This usually requires that we be guided by the mechanical or continuum mechanics macroscopic models developed over the years to describe polymer dynamics. For unentangled polymer melts, for example, such a structural variable is the *conformation tensor* **c**[7,8] for the chain end-to-end vector, whereas quite often use is also made of multiple conformation tensors, describing the dynamics of internal segments further along the chain. For entangled polymer melts, the well-established reptation picture offers a very good description of their dynamics. The reptation model[10–12] is mathematically quantified by the use of the configurational distribution function, defining the probability of orientation for the unit vector at a given bead position along the chain contour. For highly entangled, long-chain branched (LCB) polymer melts, the pom-pom[13] and the more recent pompon models[14] offer a satisfactory description. According to the GENERIC version of the pompon model,[14] the structural state variables considered for LCB polymers are the tube conformation tensor $\mathbf{A}(\mathbf{r})$ and the tube length $\Lambda(\mathbf{r})$. The former is used to construct the (traceless) tube orientation tensor $\mathbf{S}(\mathbf{r}) = \mathbf{A}(\mathbf{r})/\mathrm{tr}\,\mathbf{A}(\mathbf{r})$ while the latter defines the backbone stretch ratio accounting also for the portion of the tube into which the pompon arms are dragged due to flow.

Choosing the state variables is equivalent to defining the level of description of the system analyzed. In the subsequent discussion, attention is paid to systems for which the vector $\mathbf{x}$ of state variables is of the form

$$\mathbf{x} = [\rho(\mathbf{r}), \mathbf{u}(\mathbf{r}), \epsilon(\mathbf{r}), \mathbf{X}(\mathbf{r})] = \{x_k\}, \quad k = 1, 2, ... \tag{4}$$

where $\mathbf{X}$ denotes the vector of the structural (not hydrodyamic) variables used and $k = 1, 2, ...$ runs over all state variables (hydrodynamic and structural).

2.2. Energy−Entropy. The energy of the system E is assumed to be of the simple form

$$E(\mathbf{x}) = \int\left[\frac{\mathbf{u}^2}{2\rho(\mathbf{r})} + \epsilon(\mathbf{r})\right] \mathrm{d}\mathbf{r} \tag{5}$$

where ϵ denotes the internal energy density of the system. The internal energy of the system, ϵ, is one of the primary state variables; thus, no dependence of ϵ on any of the structural state variable(s) $\mathbf{X}$ is allowed. If one wishes to describe energetic effects due, for example, to an externally applied field, an additional term, $e_\mathrm{m}(\mathbf{r},\rho,\mathbf{X})$, should be included in the above expression. However, in the present study, the analysis will be restricted to cases where the energy E of the system is given by the simple form of eq 5.

The entropy S of the system is associated with the very local arrangements and motions of atoms and with the *structural* state variables describing, for example, overall chain conformation, tube orientation, chain stretching, etc. No dependence of the entropy is assumed on the hydrodynamic momentum density state variable $\mathbf{u}$. In this framework, the expression for the entropy has the following form:

$$S(\mathbf{x}) = \int s(\rho(\mathbf{r}), \epsilon(\mathbf{r}), \mathbf{X}(\mathbf{r}))\, \mathrm{d}\mathbf{r} \tag{6}$$

This is a very general expression for $S(\mathbf{x})$, including among others the possibility of its splitting into a local and a nonlocal, configuration-dependent part, the local term defining the absolute temperature (see section 3). For more detailed expressions for the two generators E and S, the interested reader is referred to Chapters 4 and 5 of ref 15.

3. Formulation of GENERIC in a Generalized Canonical Ensemble: The Use of Conjugate Variables

The starting point in the generalized canonical GENERIC formulation is a coarse-graining or level-jumping procedure according to which the microscopic or atomistic variables $\mathbf{z}$ (atomic positions $\mathbf{r}_i$ and conjugate momenta $\mathbf{p}_i$, $i = 1, 2, ..., n$, where n is the total number of atomistic units in the system) are mapped or projected onto a list of slowly changing or slowly relaxing state variables, the set $\mathbf{x} = \{x_k\}$, $k = 1, 2, ...$ The coarse-grained or state variables are chosen in exactly the same way as within the context of the microcanonical ensemble. The projection is realized by the use of appropriately defined phase-space functions $\Pi_k(\mathbf{z})$, which we call the *observables* and whose averages yield the values of the coarse-grained state variables. Such an averaging requires the use of a system phase space probability density function. In *microcanonical* GENERIC, this is

$$\tilde{\rho}_{\mathbf{x}}(\mathbf{z}) = \exp\left(-\frac{S(\mathbf{x})}{k_\mathrm{B}}\right) \delta(\Pi(\mathbf{z}) - \mathbf{x}) \tag{7}$$

where the occurrence of the projection functions $\Pi(\mathbf{z})$ inside the delta function guarantees that, in the transformation from atomistic to coarse-grained quantities, the counting of states is restricted over atomistic configurations consistent with the values of the (macroscopic) coarse-grained state variables $\mathbf{x}$. Explicit expressions for the phase-space functions $\Pi(\mathbf{z})$ at the hydrodynamic level related to mass, momentum, and internal density fields are given by de Pablo and Öttinger.[5] A similar expression for the single-particle distribution function is also provided by Öttinger[16] when projecting from the full N-particle phase space to the level of atomistic, single-particle distribution functions in his GENERIC projection-operator derivation of Boltzmann's kinetic equation. Similar expressions will be reported in section 5 of this paper where coarse-grained variables, such as the conformation tensors and the stretching ratio of a polymer chain, will be defined in terms of atomistic coordinates.

In *canonical* GENERIC, the appropriate probability density function is defined by resorting to the corresponding two-generator GENERIC formalism for quantum systems.[6] Then, one finds that

$$\rho_{[\boldsymbol{\lambda}]}(\mathbf{z}) = \frac{1}{Z(\boldsymbol{\lambda})} \exp(-\sum_k \lambda_k \Pi_k(\mathbf{z})) \tag{8}$$

where the normalization constant $Z(\boldsymbol{\lambda})$ defines the generalized canonical partition function of the system:

$$Z(\boldsymbol{\lambda}) = \int \exp(-\sum_k \lambda_k \Pi_k(\mathbf{z}))\, \mathrm{d}\mathbf{z} \tag{9}$$

The subscript $\boldsymbol{\lambda}$ in $\rho_{[\boldsymbol{\lambda}]}$ is used to emphasize that, in the extended canonical ensemble, not the state variables x_k, $k = 1, 2, ...$, but rather their corresponding conjugate variables λ_k, $k = 1, 2, ...$, are considered to be the primary variables. These variables arise naturally as Lagrange multipliers associated with the constraint that the mean or average values of the *observables* should coincide with the values of the macroscopically measured state variables,

$$x_k = \int \rho_{[\boldsymbol{\lambda}]}(\mathbf{z}) \Pi_k(\mathbf{z})\, \mathrm{d}\mathbf{z} \tag{10}$$

The latter are obtained as ensemble averages over the configurations accumulated in the course of an atomistic simulation. This establishes a one-to-one correspondence between the nonequilibrium (hydrodynamic and structural) state variables x_k, $k = 1, 2, ...$, and their corresponding Lagrange multipliers or conjugate variables λ_k, $k = 1, 2, ...$:

$$\lambda_k \leftrightarrow x_k, \quad k = 1, 2, ... \tag{11}$$

Clearly, if the Lagrange multiplier of a state variable is assumed to be identically zero, then this Lagrange multiplier does not appear among the arguments of Z. The same holds also for the arguments of the probability density function $\rho_{[\lambda]}(\mathbf{z})$.

With the use of the phase-space probability density function $\rho_{[\lambda]}(\mathbf{z})$, the system total energy $E = E(\mathbf{x})$ and total entropy $S = S(\mathbf{x})$ are given by the ensemble averages of their corresponding density functions:

$$E(\mathbf{x}) = \langle E_0 \rangle = \int \rho_{[\lambda]}(\mathbf{z})\, E_0(\mathbf{z})\, \mathrm{d}\mathbf{z} \qquad (12)$$

where $E_0(\mathbf{z})$ denotes the microscopic Hamiltonian, and

$$S(\mathbf{x}) = -k_{\mathrm{B}} \int \rho_{[\lambda]}(\mathbf{z}) \ln(\rho_{[\lambda]}(\mathbf{z}))\, \mathrm{d}\mathbf{z} = k_{\mathrm{B}}(\ln Z(\lambda) + \sum_k \lambda_k x_k) \qquad (13)$$

respectively. In eq 13 and in the subsequent, by λ_k, $k = 1, 2, ...$, we will always mean the Lagrange multiplier corresponding to the state variable x_k, $k = 1, 2, ...$. Equation 13 is very important because it shows how one can attribute a strict thermodynamic meaning to the Lagrange multipliers λ_k, $k = 1, 2, ...$: By taking the Volterra derivatives of the entropy functional S with respect to the corresponding state variables x_k, $k = 1, 2, ...$, it is found that

$$\frac{\delta S(\mathbf{x})}{\delta x_k} = k_{\mathrm{B}} \lambda_k \qquad (14)$$

i.e., each $k_{\mathrm{B}}\lambda_k$, $k = 1, 2, ...$, is equal to the partial derivative of the entropy S with respect to the corresponding state variable x_k, $k = 1, 2, ...$.

The proper choice of the state variables, the definition of their conjugate fields through eq 14, and the definition of the probability density function of eq 8 are the essential ingredients of the new theory which will be used in the next sections to design a MC approach to map out the free energy of the nonequilibrium system, for set values of the field variables. We will term the new method *GENERIC MC*, since it is founded on the nonequilibrium thermodynamics framework of GENERIC. This ensures that the atomistic system is excited not arbitrarily but in a physically meaningful manner, i.e., in harmony with a thermodynamically admissible macroscopic model. It further allows extracting the two thermodynamic functions, the system energy E and entropy S, without explicitly considering the flow field in the simulation, that is, without addressing the full dynamical problem. As will be seen in the next sections, this is achieved by taking advantage of the role of symmetries of the underlying atomistic system on the structure of the density matrix of canonical GENERIC, which restricts the dependence of the probability density function on the momentum density variable. In particular, we will exploit the consequences of Galilean invariance and its relation to the local equilibrium assumption (see eq 27) to illustrate why we can ignore the flow field in the GENERIC MC simulation. Then, however, the question will remain how to connect certain field variables to the velocity gradient tensor in actual flow calculations used to bring the system away from equilibrium. We will address this issue in section 4 by investigating the form to which the GENERIC equation reduces for steady-state, homogeneous flows. There, it will be shown (see eq 37) that the Lagrange multiplier of the coarse-grained variable describing the internal conformation of the complex system in an overall sense is intimately related to the underlying velocity gradient tensor, which itself is not explicitly considered in the atomistic GENERIC MC simulation.

To complete the discussion on canonical GENERIC, we should also specify the two remaining building blocks, the matrices $\mathbf{L}$ and $\mathbf{M}$, appearing in eq 1, in terms of the probability density function $\rho_{[\lambda]}$. By following the projection operator techniques oulined in refs 4 and 6, one finds that

$$L_{jk} = \langle \{\Pi_j, \Pi_k\} \rangle_{[\lambda]} = \int \rho_{[\lambda]}(\mathbf{z}) \left(\frac{\partial \Pi_j(\mathbf{z})}{\partial \mathbf{z}} \cdot \mathbf{L}_0 \cdot \frac{\partial \Pi_k(\mathbf{z})}{\partial \mathbf{z}} \right) \mathrm{d}\mathbf{z} \qquad (15)$$

and

$$M_{jk} = \frac{1}{k_{\mathrm{B}}} \int_0^{\tau} \langle \{\Pi_j, E_0\} Q(\mathbf{x}) \mathrm{e}^{iL_0 Q(\mathbf{x}) t}\, Q(\mathbf{x}) \{\Pi_k, E_0\} \rangle_{[\lambda]}\, \mathrm{d}t \qquad (16)$$

where $\{\Pi, E_0\}$ denotes the Poisson bracket satisfying

$$\{\Pi, E_0\} = \dot{x}_0(\mathbf{z}) \qquad (17)$$

in the atomistic system. In eq 16, τ is the time scale over which fast degrees of freedom have been equilibrated but slow degrees of freedom still evolve. Also, $Q(\mathbf{x})$ is an operator whose action on a functional A is given by

$$Q(\mathbf{x})A = A - \langle A \rangle_{[\lambda]} + \frac{1}{k_{\mathrm{B}}} \sum_{j,k} \frac{\delta^2 S(\mathbf{x})}{\delta x_j\, \delta x_k} [\Pi_j - x_j] \langle [\Pi_k - x_k] A \rangle_{[\lambda]} \qquad (18)$$

The first two terms on the right of eq 18 are similar to those arising also in microcanonical GENERIC. The third term takes into account second-order effects due to fluctuations in the values of variables of the vector $\mathbf{x}$ for fixed values of their conjugate fields.

Equations 8–18 define GENERIC in a generalized canonical ensemble, with the four building blocks E, S, $\mathbf{L}$, and $\mathbf{M}$ conveying all the information necessary to fully describe the evolution of the nonequilibrium system.

3.1. A System at Equilibrium.

For a system at equilibrium, all we need to know in order to describe the system is its free energy. In terms of GENERIC, what we assume is that, for such a system, there exists no dependence of the entropy density s on any structural state variable, i.e.,

$$S(\mathbf{x}) = \int s(\rho(\mathbf{r}), \epsilon(\mathbf{r}))\, \mathrm{d}\mathbf{r} \qquad (19)$$

which allows defining the Lagrange multipliers by the known equations of equilibrium thermodynamics:

$$\frac{1}{T} = \frac{\partial s(\rho, \epsilon)}{\partial \epsilon} \qquad (20)$$

and

$$-\frac{\mu}{T} = \frac{\partial s(\rho,\epsilon)}{\partial \rho} \tag{21}$$

respectively. That is, the partial derivative of the entropy density s with respect to energy density ϵ defines the absolute temperature T of the system, whereas the partial derivative of s with respect to mass density ρ defines the chemical potential μ of the system. The latter is intimately related to the pressure P of the equilibrium system by the known formulas of equilibrium thermodynamics.

In a simulation, usually, the total number of atoms remains constant, and the density of the system is controlled by variations in volume V. In this case, eq 8 for the probability density function boils down to the corresponding canonical probability density function of equilibrium thermodynamics. The relevant thermodynamic free energy function is then the potential G/N_{ch} defined as

$$-\frac{1}{T}\frac{G(\boldsymbol{\lambda})}{N_{\mathrm{ch}}} \equiv s(\mathbf{x}) - \sum_k \lambda_k x_k \tag{22}$$

where N_{ch} is the number of chains in the system. This function defines the Legendre transform of the entropy with respect to energy and volume; therefore, it is the Gibbs free energy of equilibrium thermodynamics, exactly as required by the canonical ensemble. In the thermodynamic limit, therefore,

$$G(T,P,N_{\mathrm{ch}}) = -k_{\mathrm{B}}T \ln Z(T,P,N_{\mathrm{ch}}) \tag{23}$$

where $Z(T,P,N_{\mathrm{ch}})$ symbolizes the partition function of the system.

3.2. A System Away from Equilibrium. For a system away from equilibrium, what we would ideally like to know is the time evolution of all relevant system state variables. In terms of GENERIC, this is tantamount to knowing all four building blocks E, S, $\mathbf{L}$, and $\mathbf{M}$. Obtaining all of them in terms of atomistic quantities for any system is clearly too difficult. We are still far away from calculating all four functions directly from first principles. As a first step toward this direction, however, the present paper discusses two important advances: (a) how one can extract the first two of these four building blocks, the generators E and S, directly from first principles, without violating the laws of nonequilibrium thermodynamics, and (b) how one can get the stress tensor of the nonequilibrium system. How to obtain, also from first principles, the matrices $\mathbf{L}$ and $\mathbf{M}$ to complete the description of the nonequilibrium system, will be the subject of future efforts, and here we will only outline the first ideas behind these new works.

As mentioned in the previous paragraphs, for the proper description of the nonequilibrium system, new structural state variables are considered (in addition to the traditional ones of equilibrium thermodynamics) during the projection of atomistic to coarse-grained state variables. Through these, canonical GENERIC provides the framework for calculating the dependence of the system entropy or free energy (i.e., its elasticity) on the structural parameters. The starting point is eq 8, which allows considering as independent variables the set $\boldsymbol{\lambda}$ of the conjugate variables or Lagrange multipliers. Then, the methodology for calculating the elasticity of the polymer melt goes as follows: (i) Choose the state variables and express them in terms of atomistic coordinates. This is equivalent to mathematically defining the projection functions $\Pi_k(\mathbf{z})$. (ii) For each state variable, introduce the appropriate Lagrange multiplier (or conjugate variable). The values of the set $\boldsymbol{\lambda}$ of the Lagrange multipliers are the input data to the simulation. (iii) Attribute a physical meaning to the Lagrange multipliers or assign a kinematic interpretation to them, by investigating the GENERIC equation for steady-state, homogeneous flows. (iv) For the given set of Lagrange multipliers, perform detailed MC simulations to sample the phase space of atomistic coordinates under the macroscopic restrictions imposed by the Lagrange multipliers. (v) Calculate the values of the state variables as ensemble averages over the set of atomistic configurations sampled during the MC run. (vi) Calculate the entropy of the system by thermodynamic integration, using eq 14.

Using eq 14 to obtain the entropy of deformation of the system presents some mathematical difficulties, because the arguments that should be kept constant during the partial differentiation are the values of the rest of the state variables, except those whose Lagrange multipliers are used as input in the simulation. These, however, are not fixed during the simulation; they fluctuate continuously and can only be calculated at the very end of the simulation as proper configurational averages in the generalized canonical ensemble. The difficulty is overcome by considering not the entropy S as the proper thermodynamic potential in the simulation but the potential (or Massieu function) Φ, defined through

$$\Phi(\boldsymbol{\lambda}) \equiv S(\mathbf{x}) - \sum_k \lambda_k x_k \tag{24}$$

Equations 24 and 13 demonstrate that Φ satisfies the following fundamental relationship:

$$\Phi(\boldsymbol{\lambda}) = k_{\mathrm{B}} \ln Z(\boldsymbol{\lambda}) \tag{25}$$

i.e., it is the generalized thermodynamic function generated by the partition function Z in the phase space of the Lagrange multipliers. From the thermodynamics point of view, eq 24 defines Φ as the Legendre transform of the entropy S with respect to variables x_k, $k = 1, 2, ...$. According to the properties of the Legendre transform, the Lagrange multipliers satisfy also the equation conjugate to eq 14:

$$-\frac{\delta \Phi(\boldsymbol{\lambda})}{\delta \lambda_k} = k_{\mathrm{B}} x_k, \quad k = 1, 2, ... \tag{26}$$

Through this equation, the partial derivative with respect to a particular Lagrange multiplier λ_k, $k = 1, 2, ...$, can be calculated keeping constant the values of the rest of the Lagrange multiplier, which is very convenient, because it is the values of these multipliers (and not of the state variables) that are held fixed during the simulation. Thus, eq 26 allows us to calculate the entropy of the nonequilibrium system by employing the technique of thermodynamic integration: First, the value of the function Φ is calculated through the integral over the values of the state variable x_k, $k = 1, 2, ...$, accumulated at progressively larger values of the imposed Lagrange multiplier λ_k, $k = 1, 2, ...$. Then, the entropy of the system in the nonequilibrium state relative to its value in the field-free, equilibrium state is readily obtained by using eq 24 (see also sections 4 and 5).

The entire methodology is facilitated from the fact that the entropy of the system has been assumed *not* to depend on the momentum density state variable (see eq 6). That is, the Lagrange multiplier of the momentum density variable has been assumed to be identically zero. Such a relation, i.e., that

$$\left[\frac{\delta S(\rho,\epsilon,\mathbf{u})}{\delta \mathbf{u}}\right]_{\rho,\epsilon} = \mathbf{0} \tag{27}$$

has been discussed recently by Öttinger[17] on the basis of the Galilean invariance of the transformation from the atomistic to the coarse-grained level. Öttinger showed how to construct a generalized canonical ensemble possessing the proper symmetries, even for representations of the symmetry groups on the level of the coarse-grained state space which are nonlinear or which are not induced by atomistic symmetry transformations. For example, if one works with the mass, momentum, and internal energy densities as the proper state variables, the corresponding canonical ensemble cannot be normalized or symmetrized with respect to Galilean transformations; the problem is alleviated if the internal energy density is replaced by the total energy density. For this ensemble, Galilean invariance results into an expression for the entropy of the system which is a functional of the density and energy density but not of the momentum density.

The incorporation of Galilean invariance and its relation to the local equilibrium assumption is of fundamental importance in the present work, because it allows us to sample in the generalized canonical ensemble through the MC simulation by ignoring the flow field imposed externally. In such a case, however, the methodology does not provide any *direct* information about the connection of the Lagrange multipliers (or conjugate variables) to the system hydrodynamic variables. This is alleviated by examining the form to which GENERIC reduces under steady-state conditions. To identically satisfy the equation, one sees then that a relationship arises connecting the Lagrange multiplier for the structural variable to the velocity gradient tensor. This relation between Lagrange multipliers and velocity gradients depends on the macroscopic model underlying the mapping from the atomistic to the coarse-grained level. Thus, different forms of the Lagrange multipliers will be found for different types of flows; further, these forms will differ for different macroscopic models employed to excite the atomistic system.[18] Specific examples demonstrating these features of the new method are discussed in detail in the next section.

In general, it has to be realized that designing an atomistic MC methodology to simulate a system away from equilibrium requires that we resort to a nonequilibrium thermodynamics framework. This guarantees that the system is excited (a) in a physically meaningful way and (b) in harmony with a thermodynamically admissible model. Only then can one ascribe a correct kinematic interpretation to the parameters of the MC simulation and extract useful information for the response of the system structure to the flow-field. The next section presents the methodology for assigning a kinematic interpretation to the Lagrange multipliers of the structural variables by discussing the reduction of the GENERIC equation for homogeneous, time-independent flows.

4. Reduction of GENERIC for Homogeneous, Time-Independent Flows

For homogeneous, time-independent flows, the following assumptions apply: (i) no explicit dependence of the entropy density s on spatial location $\mathbf{r}$; (ii) no explicit dependence of the entropy density s on the momentum density field $\mathbf{u}$ (as mentioned above, this is not an assumption; it is a direct consequence of the requirement of Galilean invariance for the transformation from the space of atomistic to the space of the coarse-grained state variables); (iii) a direct dependence of the entropy density s on density ρ, local energy density ϵ, and the properly chosen coarse-grained state variables $\mathbf{X}$. With these assumptions, the evolution equations for the structural state variables can be analyzed in detail. First, it is observed that, under the above conditions, all Volterra derivatives $\delta S/\delta x_k$ boil down to partial derivatives of the entropy density s with respect to the corresponding state variable x_k:

$$\frac{\delta S(\mathbf{x})}{\delta x_k(\mathbf{r})} = \left[\frac{\partial s(\mathbf{x})}{\partial x_k}\right]_{x_k = x_k(\mathbf{r})} \tag{28}$$

The partial derivatives appearing on the right of eq 28 define the conjugate variables or Lagrange multipliers. So, at steady state, the GENERIC equation for the set of the structural state variables reads

$$0 = \mathbf{L}(\mathbf{x}) \cdot \frac{\delta E}{\delta \mathbf{x}} + \mathbf{M}(\mathbf{x}) \cdot k_{\mathrm{B}} \boldsymbol{\lambda} \tag{29}$$

Equation 29 is very important because, in principle, it can be solved for the Lagrange multipliers $\boldsymbol{\lambda}$. Usually, the positive-semidefinite, symmetric matrix $\mathbf{M}$ has a diagonally dominant structure with positive-definite blocks along the diagonal for each one of the state variables considered. Usually, these blocks are invertible, which allows us to solve eq 28 for $\boldsymbol{\lambda}$:

$$\boldsymbol{\lambda} = -\frac{1}{k_{\mathrm{B}}} \mathbf{M}^{-1} \cdot \mathbf{L} \cdot \frac{\delta E}{\delta \mathbf{x}} \tag{30}$$

To see the applicability of eq 30, we recall that, for the majority of models considered for flowing polymer systems, the matrix $\mathbf{L}$ has the following form:[2]

$$\mathbf{L} = -\begin{pmatrix} 0 & L_{12} & 0 & 0 \\ L_{21} & L_{22} & L_{23} & L_{24} \\ 0 & L_{32} & 0 & 0 \\ 0 & L_{42} & 0 & 0 \end{pmatrix} \tag{31}$$

where all L_{12}, L_{21}, L_{22}, L_{23}, L_{24}, L_{32}, and L_{42} depend on the momentum density and the structural state variables. For example, for all single-conformation tensor models,[2]

$$L_{12} = \nabla_{\epsilon}\rho$$

$$L_{21} = \rho\nabla_{\alpha}$$

$$L_{22} = \nabla_{\epsilon}u_{\alpha} + u_{\epsilon}\nabla_{\alpha}$$

$$L_{23} = \nabla_{\alpha}P + \epsilon\nabla_{\alpha} + 2T\nabla_{\beta}c_{\gamma\beta}\frac{\partial s}{c_{\alpha\gamma}}$$

$$L_{24} = -(\nabla_{\alpha}c_{\eta\zeta}) - \nabla_{\beta}c_{\beta\eta}I_{\alpha\zeta} - \nabla_{\beta}c_{\beta\zeta}I_{\alpha\eta}$$

$$L_{32} = P\nabla_{\epsilon} + \nabla_{\epsilon}\epsilon + 2Tc_{\gamma\beta}\frac{\partial s}{c_{\gamma\epsilon}}\nabla_{\beta}$$

$$L_{42} = (\nabla_{\epsilon}c_{\alpha\beta}) - c_{\alpha\gamma}\nabla_{\gamma}I_{\beta\epsilon} - c_{\beta\gamma}\nabla_{\gamma}I_{\alpha\epsilon} \tag{32}$$

where P denotes the isotropic pressure and $\mathbf{I}$ the unit tensor; also, the Einstein summation convention has been introduced in this and subsequent expressions. For these models, the $\mathbf{M}$ matrix has a symmetric blocklike form, as the one below corresponding to the upper-convected Maxwell model:

$$\mathbf{M} = \begin{pmatrix} - & - & - & 0 \\ - & - & - & 0 \\ - & - & - & 0 \\ 0 & 0 & 0 & M_{44} \end{pmatrix} \tag{33}$$

only the diagonal M_{44} block element of which expresses structural dissipative (relaxation) effects (with the rest of terms not shown in eq 33 accounting for the common bulk viscous solvent and heat conduction effects). Usually, the dissipative M_{44} term has the form

$$M_{44} = T\Lambda_{\alpha\beta\eta\zeta} \tag{34}$$

where the fourth-rank tensor $\mathbf{\Lambda}$ depends on the rheological model employed. With such a form for the matrix $\mathbf{M}$, in the matrix inversion equation, eq 30, only the M_{44} term of $\mathbf{M}$ contributes, coupled only with the L_{42} element of the Poisson matrix $\mathbf{L}$:

$$\mathbf{M}^{-1}\cdot\mathbf{L} = \begin{pmatrix} - & - & - & - \\ - & - & - & - \\ - & - & - & - \\ 0 & -M_{44}^{-1}L_{42} & 0 & 0 \end{pmatrix} \tag{35}$$

On the other hand,

$$\frac{\delta E}{\delta \mathbf{x}} = \begin{pmatrix} -{}^{1}/_{2}u_{\alpha}u_{\alpha} \\ u_{\epsilon} \\ 1 \\ \mathbf{0} \end{pmatrix} \tag{36}$$

Consequently, the matrix $\mathbf{M}^{-1}\cdot\mathbf{L}$ couples only with the second element of the vector $\delta E/\delta\mathbf{x}$, which is exactly the momentum density field $\mathbf{u}$, which was not considered as an argument in the definition of the entropy density function s in eq 6 above. Therefore, the field variable conjugate to the coarse-grained structural parameter $\mathbf{X}$ is given by

$$\lambda_{\mathbf{X}} = \frac{1}{k_B}M_{44}{}^{-1}L_{42}\mathbf{u} \tag{37}$$

Equation 37 presents the reduced form of canonical GENERIC for the structural state variable under conditions of homogeneous, steady-state flows. It is the most important equation of the present work because it helps assign the correct kinematic interpretation to the Lagrange multiplier of the coarse-grained state variable that was lost when we used the properties of the Galilean transformation to get rid of the momentum density field in the analysis. It also allows us to recognize that, depending on the model used, certain model parameters, which were used in the specification of the dissipative matrix $\mathbf{M}$ of the model, may enter into the analysis. A typical example is the parameter β of the Giesekus viscoelastic model; as will be shown in the next section, this enters directly into eq 37.

In fact, the matrix element M_{44} is in most cases inversely proportional to a system characteristic relaxation time λ_H. Equation 37, therefore, gives the Lagrange multiplier $\lambda_{\mathbf{X}}$ of the structural parameter $\mathbf{X}$ the meaning of a dimensionless strain-rate tensor. And this is the novel feature of the methodology, which emerges as an excellent complementary approach to the NEMD method for the simulation of nonequilibrium systems. For polymer melts, in particular, the new method, equipped with a set of novel MC moves[7,19] for the robust sampling of configuration space, for the first time opens up the way toward the direct atomistic simulation of their viscoelasticity and its dependence on chemical architecture (linear vs branched chains, unentangled vs entangled systems). However, one should mention that, in contrast to NEMD where a unique result is obtained for the relationship between polymer elasticity and strain-rate tensor, the corresponding relationship obtained by GENERIC MC is not unique and depends on the macroscopic model used as the guide in the design of the simulation. In this respect, NEMD may be useful to select the appropriate model. On the other hand, GENERIC MC does also rule out models based on the comparison between the stress−conformation tensor relationship obtained by the atomistic simulation and the one assumed by the macroscopic model. But if the comparison is to be made at the level of the rate-of-strain tensor, one should also extract the value of the characteristic relaxation time of the system, λ_H. This can be obtained only by direct molecular dynamics (MD) simulations through a normal model analysis. Alternatively, one can resort to a molecular theory, such as the Rouse or the reptation theory. Such a hierarchical modeling scheme was recently proposed by Harmandaris et al.[20,21] which extracts the spectrum of relaxation times for unentangled polymers, by executing MD simulations either on equilibrium or on oriented melts and mapping the system dynamics onto the Rouse model. In a more recent study,[22] the methodology has been extended to entangled PE melts.

Concrete kinematic expressions for the Lagrange multipliers of the various structural variables considered in the most widely used macroscopic models of polymer dynamics are presented in full detail in the next section. The section discusses also applications of the new theory to polymer systems which are macroscopically described by three different viscoelastic models: the single- and the multiple-conformation tensor models for unentangled polymers and the pompon model for long-chain branched (LCB) polymers.

5. Applications to Modeling the Elasticity of Polymer Melts

For all models considered in the following, the hydrodynamic state variables will always include: the mass density $\rho(\mathbf{r})$, the momentum density $\mathbf{u}(\mathbf{r})$, and the energy density $\epsilon(\mathbf{r})$. The mass density ρ can be used interchangeably with the system volume V,

$$\frac{V}{N_{\mathrm{ch}}} = \frac{1}{\rho}\frac{M}{N_{\mathrm{A}}} \tag{38}$$

where N_{ch} is the number of chains in volume V, M is their number-average molecular weight, and N_{A} denotes Avogadro's number.

The corresponding Lagrange multipliers or conjugate variables are equal to the scalar b (the generalized pressure) for the mass density, the zero vector $\mathbf{0}$ for the momentum density, and $1/T$ for the internal energy density, defined by the following equations:

$$\frac{b}{k_{\mathrm{B}}T} = \frac{1}{k_{\mathrm{B}}}\left[\frac{\partial s(\rho,\epsilon,\mathbf{c})}{\partial(V/N_{\mathrm{ch}})}\right]_{\epsilon,\mathbf{c}} = \frac{\rho^2}{k_{\mathrm{B}}}\left[\frac{\partial s(\rho,\epsilon,\mathbf{c})}{\partial\rho}\right]_{\epsilon,\mathbf{c}}\frac{N_{\mathrm{A}}}{M} \tag{39}$$

$$\frac{1}{k_{\mathrm{B}}T} = \frac{1}{k_{\mathrm{B}}}\left[\frac{\partial s(\rho,\epsilon,\mathbf{c})}{\partial\epsilon}\right]_{\rho,\mathbf{c}} \tag{40}$$

Where the various macroscopic models differ from each other is in the choice of the structural state variables. This is discussed in the next subsections.

5.1. A Single-Conformation Tensor Viscoelastic Model. For the single-conformation tensor models, such as the upper-convected Maxwell, the FENE-P, and the Giesekus models, the only structural state variable used is the conformation tensor $\mathbf{c}$. This is most naturally introduced as the reduced second moment tensor of the chain end-to-end vector, averaged over all chains in the system:

$$\mathbf{c} = 3\left\langle\frac{\mathbf{RR}}{\langle R^2\rangle_0}\right\rangle \tag{41}$$

In eq 41, $\mathbf{R}$ stands for the end-to-end vector of a macromolecule and $\langle R^2\rangle_0$ is the mean-squared magnitude of that vector in the unperturbed state. The outer average is taken over all chains in the system under study. In a quiescent (undeformed) equilibrium polyethylene melt, chain conformational statistics is isotropic; then, $\mathbf{c}$ reduces to the unit tensor $\mathbf{I}$. When the melt is subjected to deformation over time scales shorter than or comparable to the longest relaxation time of the chains, however, the chains will be oriented and $\mathbf{c}$ will depart from its equilibrium isotropic value. In such a case, the six independent components of $\mathbf{c}$ provide a measure of the extension and orientation of the chains along the three axes of the coordinate system.

The Lagrange multiplier of the conformation tensor is a tensorial quantity, the "orienting field" $\boldsymbol{\alpha}$, defined as

$$\boldsymbol{\alpha} = -\frac{1}{k_{\mathrm{B}}}\left[\frac{\partial s(\rho,\epsilon,\mathbf{c})}{\partial\mathbf{c}}\right]_{\rho,\epsilon} \tag{42}$$

Clearly, both tensors $\mathbf{c}$ and $\boldsymbol{\alpha}$ are symmetric.

For the single-conformation tensor models, therefore, the vectors of state and conjugate variables read

$$\mathbf{x} = \left[\frac{V}{N_{\mathrm{ch}}}, \mathbf{u}, \epsilon, \mathbf{c}\right] \tag{43}$$

and

$$\boldsymbol{\lambda} = \left[\frac{b}{k_{\mathrm{B}}T}, \mathbf{0}, \frac{1}{k_{\mathrm{B}}T}, -\boldsymbol{\alpha}\right] \tag{44}$$

A Legendre transformation of the entropy density function $s = s(V/N_{\mathrm{ch}},\epsilon,\mathbf{c})$ with respect to all variables V/N_{ch}, ϵ, and $\mathbf{c}$ defines a new thermodynamic function, the potential

$$\Phi = \Phi(b,T,\boldsymbol{\alpha}) = \frac{1}{T}\left(sT - b\frac{V}{N_{\mathrm{ch}}} - \epsilon + k_{\mathrm{B}}T\boldsymbol{\alpha}{:}\mathbf{c}\right) \tag{45}$$

that is

$$\Phi(b,T,\boldsymbol{\alpha}) = -\frac{1}{T}\left(\frac{A}{N_{\mathrm{ch}}} + \frac{b}{\rho}\frac{M}{N_{\mathrm{A}}} - k_{\mathrm{B}}T\boldsymbol{\alpha}{:}\mathbf{c}\right) \tag{46}$$

or, equivalently,

$$\Phi(b,T,\boldsymbol{\alpha}) = -\frac{1}{T}\frac{G}{N_{\mathrm{ch}}}(b,T,\boldsymbol{\alpha}) \tag{47}$$

where

$$\frac{A}{N_{\mathrm{ch}}} = -sT + \epsilon \tag{48}$$

has the meaning of a Helmholtz free energy function, and

$$\frac{G(b,T,\boldsymbol{\alpha})}{N_{\mathrm{ch}}} = \frac{A}{N_{\mathrm{ch}}} + \frac{b}{\rho}\frac{M}{N_{\mathrm{A}}} - k_{\mathrm{B}}T\boldsymbol{\alpha}{:}\mathbf{c} \tag{49}$$

the meaning of a generalized Gibbs free energy function, with $k_{\mathrm{B}}T\boldsymbol{\alpha}{:}\mathbf{c}$ accounting for the energy due to field $\boldsymbol{\alpha}$ (field energy). Furthermore, from the properties of the Legendre transformation

$$\mathbf{c} = -\frac{1}{k_{\mathrm{B}}T}\left[\frac{\partial}{\partial\boldsymbol{\alpha}}\frac{G}{N_{\mathrm{ch}}}(b,T,\boldsymbol{\alpha})\right]_{T,b} \tag{50}$$

If the relationship between $\mathbf{c}$ and $\boldsymbol{\alpha}$ is known, then, according to eq 50, the thermodynamic potential G of eq 49 relative to the equilibrium field-free state can be obtained by thermodynamic integration:

$$\frac{G}{N_{\mathrm{ch}}} - \frac{G_0}{N_{\mathrm{ch}}} \equiv \frac{G}{N_{\mathrm{ch}}}(b,T,\boldsymbol{\alpha}) - \frac{G}{N_{\mathrm{ch}}}(b,T,\mathbf{0}) = -k_{\mathrm{B}}T\left[\sum_{\gamma}\sum_{\delta}\int_0^{\alpha_{\gamma\delta}} c_{\gamma\delta}\,\mathrm{d}\alpha_{\gamma\delta}\right]_{T,b} \tag{51}$$

The Helmholtz free energy can also be obtained from eq 49 as

$$\frac{A}{N_{\mathrm{ch}}} - \frac{A_0}{N_{\mathrm{ch}}} \equiv \frac{A}{N_{\mathrm{ch}}}(T,\rho,\mathbf{c}) - \frac{A}{N_{\mathrm{ch}}}(T,\rho,\mathbf{I}) = \frac{G}{N_{\mathrm{ch}}} - \frac{G_0}{N_{\mathrm{ch}}} - b\frac{M}{N_{\mathrm{A}}}\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right) + k_{\mathrm{B}}T\boldsymbol{\alpha}{:}\mathbf{c} \tag{52}$$

with $\rho = \rho(T,b,\boldsymbol{\alpha})$, $\rho_0 = \rho(T,b,\mathbf{0})$, and $\mathbf{c} = \mathbf{c}(T,b,\boldsymbol{\alpha})$.

The probability density function in this $\{N_{\text{ch}}, b, T, \boldsymbol{\alpha}\}$-generalized statistical ensemble is

$$\rho[N_{\text{ch}},b,T,\boldsymbol{\alpha}](V,\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n) \propto \exp\left[-\frac{1}{k_{\text{B}}T}(\epsilon(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n) + bV - k_{\text{B}}T\sum_{i=1}^{N_{\text{ch}}}\boldsymbol{\alpha}:\mathbf{c}_i)\right] \quad (53)$$

where N_{ch} is the number of chains of length N in volume V, n $(= N_{\text{ch}} \times N)$ denotes the total number of mers in the same volume, and $\mathbf{c}_i$ denotes the instantaneous value of the conformation tensor of the ith chain. Given the relationship between the canonical partition function and the Helmholtz free energy, one then can readily show that in the thermodynamic limit

$$\Phi(b,T,\boldsymbol{\alpha}) = k_{\text{B}} \ln Z(b,T,\boldsymbol{\alpha}) \quad (54)$$

where $Z(b,T,\boldsymbol{\alpha})$ denotes the partition function, that is, the normalization constant of the probability density function of eq 53.

The stress tensor $\boldsymbol{\tau}$ in the system is determined by using that $\boldsymbol{\alpha}$ should be such that the gradient of the entropy lies in the null space of $\mathbf{L}$. If the form of eq 32 is chosen for $\mathbf{L}$, then one finds that

$$\boldsymbol{\tau} = -b\mathbf{I} - 2\frac{N_{\text{A}}}{M}\rho T\mathbf{c}\cdot\left[\frac{\partial s(\rho,\epsilon,\mathbf{c})}{\partial \mathbf{c}}\right]_{\rho,\epsilon} = -b\mathbf{I} + 2\frac{N_{\text{A}}}{M}\rho k_{\text{B}}T(\mathbf{c}\cdot\boldsymbol{\alpha}) \quad (55)$$

The analysis is completed by specifying the kinematic character of the conjugate variables b and $\boldsymbol{\alpha}$. The scalar b has the meaning of a generalized pressure, although in general, $-3b$ cannot be equated to the stress tensor, as clearly seen from eq 55. Only at equilibrium can b be identified with the pressure of the system. For a consistent methodology on how to connect b to the isotropic pressure of the system, see relevant discussion following eq 95 in section 6. The kinematic nature of the orienting field $\boldsymbol{\alpha}$ is more difficult to ascribe, because, as was discussed in the previous section, it depends on the viscoelastic model assumed. For the upper-convected-Maxwell (UCM) and FENE-P models, upon substituting

$$\Lambda_{\alpha\beta\gamma\epsilon} = \frac{1}{2\rho\lambda_{\text{H}}K}[c_{\alpha\gamma}I_{\beta\epsilon} + c_{\alpha\epsilon}I_{\beta\gamma} + c_{\beta\epsilon}I_{\alpha\gamma} + c_{\beta\gamma}I_{\alpha\epsilon}] \quad (56)$$

for the relaxation matrix $\boldsymbol{\Lambda}$ into eq 37, we obtain that

$$\boldsymbol{\alpha} = \frac{1}{2}\lambda_H\dot{\boldsymbol{\gamma}} \quad (57)$$

where $\dot{\boldsymbol{\gamma}}$ is the rate of strain tensor:

$$\dot{\boldsymbol{\gamma}} \equiv \frac{1}{2}[(\nabla\mathbf{v}) + (\nabla\mathbf{v})^T] \quad (58)$$

Therefore, the kinematic interpretation of the Lagrange multiplier $\boldsymbol{\alpha}$ for the UCM model is that of a dimensionless velocity gradient tensor; that is, the elements of $\boldsymbol{\alpha}$ are indicative of the Deborah number of the applied flow field.

For the Giesekus model, on the other hand, upon substituting

$$\Lambda_{\alpha\beta\gamma\epsilon} = \frac{1}{2\rho\lambda_H K}\left[(1-\beta)(c_{\alpha\gamma}I_{\beta\epsilon} + c_{\alpha\epsilon}I_{\beta\gamma} + c_{\beta\epsilon}I_{\alpha\gamma} + c_{\beta\gamma}I_{\alpha\epsilon}) + \frac{2\beta K}{k_{\text{B}}T}(c_{\alpha\gamma}c_{\beta\epsilon} + c_{\alpha\epsilon}c_{\beta\gamma})\right] \quad (59)$$

for the relaxation matrix Λ into eq 37, we obtain that

$$\boldsymbol{\alpha} = \frac{1}{2}\lambda_H[\mathbf{I} + \beta(\mathbf{c} - \mathbf{I})]^{-1}\cdot\dot{\boldsymbol{\gamma}} \quad (60)$$

where β is the Giesekus model parameter. The kinematic interpretation of the Lagrange multiplier $\boldsymbol{\alpha}$ for the Giesekus model, therefore, is not that of a dimensionless velocity gradient tensor, but of a *corrected* dimensionless velocity gradient tensor, the correction accounting for the effect of the anisotropic polymer melt conformation on friction coefficient due to orientation of the constituent chains.

The derivation of eqs 57 and 60 through the kinematic equation (37) presents some mathematical difficulties because of the presence of the component $M_{44}{}^{-1}$ which requires calculating the inverse $\mathbf{M}^{-1}$ of the matrix $\mathbf{M}$. Alternatively, these relations can be derived by starting with the GENERIC time evolution for the coarse-grained variable $\mathbf{c}$ itself. For all conformation tensor models considered in this work, this reads as follows:[1,2,15]

$$\frac{\partial c_{\alpha\beta}}{\partial t} = -u_\gamma\nabla_\gamma c_{\alpha\beta} + c_{\gamma\alpha}\nabla_\gamma u_\beta + c_{\gamma\beta}\nabla_\gamma u_\alpha + T\Lambda_{\alpha\beta\gamma\epsilon}\frac{\partial s}{\partial c_{\gamma\epsilon}} \quad (61)$$

where $\Lambda_{\alpha\beta\gamma\epsilon}$ is given by eq 56 for the UCM model and by eq 59 for the Giesekus model. By identifying the partial derivative $\partial s/\partial c_{\gamma\epsilon}$ with the component $-k_{\text{B}}\alpha_{\gamma\epsilon}$ of the corresponding Lagrange multiplier, one verifies easily that for a steady-state flow, the only form of $\boldsymbol{\alpha}$ that satisfies the GENERIC equation identically is eq 57 for the UCM model and eq 60 for the Giesekus model.

5.2. A Multiple-Conformation Tensor Viscoelastic Model. Higher-mode conformation tensor models constitute a generalization of the single-mode conformation tensor models discussed in the previous subsection. A typical example of this category of models is the Rouse or bead−spring chain model. In general, from an N-mer chain, $N(N-1)/2$ different conformation tensors $\boldsymbol{c}^{ij}$, i, $j = 1, 2, \ldots, N-1$, can be constructed, each one identified as a properly dimensionalized average dyadic $\langle\mathbf{Q}_i\mathbf{Q}_j\rangle$. Here, $\mathbf{Q}_i$ denotes the connector vector between mers $i+1$ and i along the chain,

$$\boldsymbol{Q}_i \equiv \mathbf{r}_{i+1} - \mathbf{r}_i \qquad i = 1, 2, \ldots, N-1 \quad (62)$$

with $\mathbf{r}_i$, $i = 1, 2, \ldots, N$, symbolizing the position vector of the ith mer.

From the point of view of applications, the analysis is greatly facilitated if one makes use of only the $N-1$ diagonal conformation tensors $\mathbf{c}_p$, $p = 1, 2, \ldots, N-1$, constructed from the corresponding normal coordinates $\mathbf{X}_p$, $p = 1, 2, \ldots, N-1$, through

$$\mathbf{c}_p = 3\left\langle\frac{\mathbf{X}_p\mathbf{X}_p}{\langle\mathbf{X}_p{}^2\rangle_0}\right\rangle \quad (63)$$

where

$$\mathbf{X}_p = \sum_{j=1}^{N-1} \Omega_{jp} \mathbf{Q}_j \tag{64}$$

$\langle \mathbf{X}_p{}^2 \rangle_0$ in the above is the mean-squared magnitude of $\mathbf{X}_p$ in the unperturbed state and $\boldsymbol{\Omega}$ the orthogonal matrix given by

$$\Omega_{jp} = \sqrt{\frac{2}{N}} \sin\left(\frac{jp\pi}{N}\right) \tag{65}$$

with $j = 1, 2, ..., N - 1$ and $p = 1, 2, ..., N - 1$.

To each one of the conformation tensors $\mathbf{c}_p$, a Lagrange multiplier $\boldsymbol{\alpha}_p$ is assigned according to

$$\boldsymbol{\alpha}_{\mathbf{p}} = -\frac{1}{k_B}\left[\frac{\partial s(\rho,\epsilon,\mathbf{c}_1,\mathbf{c}_2,...,\mathbf{c}_{N-1})}{\partial \mathbf{c}_p}\right]_{\rho,\epsilon} \tag{66}$$

For the multiple-conformation tensor models, therefore, the vectors of state and conjugate variables read

$$\mathbf{x} = \left[\frac{V}{N_{ch}}, \mathbf{u},\epsilon,\mathbf{c}_1,\mathbf{c}_2,...,\mathbf{c}_{N-1}\right] \tag{67}$$

and

$$\boldsymbol{\lambda} = \left[\frac{b}{k_B T}, \mathbf{0}, \frac{1}{k_B T}, -\boldsymbol{\alpha}_1, -\boldsymbol{\alpha}_2, ..., -\boldsymbol{\alpha}_{N-1}\right] \tag{68}$$

By performing a Legendre transformation of the entropy density function s with respect to all variables that s depends on, as was done in the previous subsection for the single conformation tensor viscoelastic model, one can show that the relevant thermodynamic potential is

$$\Phi(b,T,\boldsymbol{\alpha}_1,\boldsymbol{\alpha}_2,...,\boldsymbol{\alpha}_{N-1}) = -\frac{1}{T}\frac{G}{N_{ch}}(b,T,\boldsymbol{\alpha}_1,\boldsymbol{\alpha}_2,...,\boldsymbol{\alpha}_{N-1}) \tag{69}$$

where

$$\frac{G(b,T,\boldsymbol{\alpha}_1,\boldsymbol{\alpha}_2,...,\boldsymbol{\alpha}_{N-1})}{N_{ch}} = \frac{A}{N_{ch}} + \frac{b}{\rho}\frac{M}{N_A} - k_B T \sum_{p=1}^{N-1} \boldsymbol{\alpha}_p : \mathbf{c}_p \tag{70}$$

is the corresponding generalized Gibbs free energy function, with $k_B T \sum_{p=1}^{N-1} \boldsymbol{\alpha}_p : \mathbf{c}_p$ accounting for the energy due to fields $\boldsymbol{\alpha}_p$, $p = 1, 2, ..., N - 1$ (field energy). The probability density function in this $\{N_{ch}, b, T, \boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, ..., \boldsymbol{\alpha}_{N-1}\}$ generalized statistical ensemble is

$$\rho[N_{ch}, b, T, \boldsymbol{\alpha}_1, \boldsymbol{\alpha}_2, ..., \boldsymbol{\alpha}_{N-1}](V, \mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) \propto \exp\left[-\frac{1}{k_B T}(\epsilon(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n) + bV - k_B T \sum_{i=1}^{N_{ch}} \sum_{p=1}^{N-1} \boldsymbol{\alpha}_p : \mathbf{c}_p^i)\right] \tag{71}$$

where $\mathbf{c}_p^i$ denotes the pth mode conformation tensor of the ith chain.

The stress tensor $\boldsymbol{\tau}$ in the system is defined by using that $\boldsymbol{\tau}$ should be such that the gradient of the entropy lies in the null space of $\mathbf{L}$:

$$\boldsymbol{\tau} = -b\mathbf{I} - 2\frac{N_A}{M}\rho T \sum_{p=1}^{N-1} \mathbf{c}_p \cdot \left[\frac{\partial s(\rho,\epsilon,\mathbf{c}_1,\mathbf{c}_2,...,\mathbf{c}_{N-1})}{\partial \mathbf{c}_p}\right]_{\rho,\epsilon} = -b\mathbf{I} + 2\frac{N_A}{M}\rho k_B T (\sum_{p=1}^{N-1} \mathbf{c}_p \cdot \boldsymbol{\alpha}_p) \tag{72}$$

To ascribe a kinematic interpretation to the Lagrange multipliers, use is made of the fact that, similar to the single conformation tensor model, each one of the $\boldsymbol{\alpha}_p$, $p = 1, 2, ..., N - 1$, contributes to the matrix $\mathbf{M}$ a block diagonal element of the form of eq 33, with a characteristic time not λ_H but λ_p. Because of the use of the normal coordinates in constructing the state variables $\mathbf{c}_p$, $p = 1, 2, ...,$ in eq 63, the conformation tensors $\mathbf{c}_p$, $p = 1, 2, ...,$ contribute independently to the dissipation matrix. Each such contribution is defined in terms of a characteristic time given by the spectrum of relaxation times of the macroscopic Rouse model,

$$\lambda_p = \frac{\zeta/2H}{4\sin^2\left(\frac{p\pi}{2N}\right)} = \frac{\lambda_H}{2\sin^2\left(\frac{p\pi}{2N}\right)} \tag{73}$$

which for large chain lengths N can also be written as

$$\lambda_p \approx \lambda_1 / p^2 \tag{74}$$

where λ_1 is the longest characteristic time. Then, it is found that each one of the Lagrange multipliers is ascribed to the following kinematics:

$$\boldsymbol{\alpha}_p = \frac{1}{2}\lambda_p \dot{\boldsymbol{\gamma}} \tag{75}$$

which for large N can also be written as

$$\boldsymbol{\alpha}_p \approx \frac{\boldsymbol{\alpha}_1}{p^2} \tag{76}$$

Equations 75 and 76 show that the Lagrange multipliers $\boldsymbol{\alpha}_p$, $p = 1, 2, ..., N - 1$, employed to excite the atomistic system according to a higher-mode conformation tensor viscoelastic model should not be assigned arbitrarily; instead, their values should be chosen in accord with the spectrum of characteristic times of the macroscopic Rouse model. This is one of the most significant insights of the present work, because it demonstrates the power of the methodology. If a MC algorithm was to be designed to model the elasticity of an unentangled polymer melt through a multiple conformation tensor approach, then, perhaps, different Lagrange multipliers would have been chosen to drive each one of the conformation tensors employed in the coarse-graining procedure away from equilibrium. Guided by the canonical GENERIC formalism, however, the present analysis suggests that all these Lagrange multipliers must not be assigned independently, let alone arbitrarily: they should be consistent with formulas 73 and 75. From the physical point of view, the requirement that the fields $\boldsymbol{\alpha}_p$ should follow eq 75 reflects the fact that, for a given flow field, segments corresponding to smaller length scales along the chain deform less than segments corresponding to larger length scales.

Since the function Φ of eq 69 is the Legendre transformation of the entropy density function s, eq 66 leads directly to the following relationship:

$$\mathbf{c}_p = -\frac{1}{k_\mathrm{B}T}\left[\frac{\partial}{\partial\boldsymbol{\alpha}_p}\frac{G}{N_\mathrm{ch}}(b,T,\boldsymbol{\alpha}_\mathbf{p})\right]_{\mathrm{T},b}, \quad p = 1, 2, ..., N - 1 \tag{77}$$

These $N - 1$ independent equtions can be used to calculate the thermodynamic potential G of eq 70 relative to the equilibrium field free state through an equation completely analogous to eq 51 for the case of a single-conformation tensor:

$$\frac{G}{N_\mathrm{ch}} - \frac{G_0}{N_\mathrm{ch}} \equiv \frac{G}{N_\mathrm{ch}}(b,T,\boldsymbol{\alpha}) - \frac{G}{N_\mathrm{ch}}(b,T,\mathbf{0}) = -k_\mathrm{B}T\sum_{p=1}^{N\text{-}1}[\sum_{\gamma}\sum_{\delta}\int_0^{\alpha_{p,\gamma\delta}} c_{\mathrm{p},\gamma\delta}\,\mathrm{d}\alpha_{p,\gamma\delta}]_{T,b} \tag{78}$$

The Helmholtz free energy can also be obtained from eq 70 as

$$\frac{A}{N_\mathrm{ch}} - \frac{A_0}{N_\mathrm{ch}} \equiv \frac{A}{N_\mathrm{ch}}(T,\rho,\mathbf{c}) - \frac{A}{N_\mathrm{ch}}(T,\rho,\mathbf{I}) = \frac{G}{N_\mathrm{ch}} - \frac{G_0}{N_\mathrm{ch}} - b\,\frac{M}{N_\mathrm{A}}\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right) + k_\mathrm{B}T\sum_{p=1}^{N\text{-}1}\boldsymbol{\alpha}_p{:}\mathbf{c}_p \tag{79}$$

with $\rho = \rho(T,b,\boldsymbol{\alpha})$, $\rho_0 = \rho(T,b,\mathbf{0})$, and $\mathbf{c}_p = \mathbf{c}_p(T,b,\boldsymbol{\alpha}_p)$, $p = 1, 2, ..., N - 1$.

5.3. The Pompon Model for Long Chain Branched PE Melts. Guided by the tube model, McLeish and Larson[13] proposed the pom-pom model for multiply branched polymers, where the backbone of the molecules can reptate in the tubes formed by other backbones after sidearms have relaxed by deep retractions or breathing modes. More recently, the pom-pom model has been reformulated within the context of GENERIC, the modified model known as the pompon model.[14] The pompon model is built on two structural parameters: The first is the conformation tensor **A** defined by following the contour length of the backbone tube, and the second is a scalar quantity Λ describing the length of the tube divided by the backbone tube length at equilibrium. If q is the nunber of sidearms, then for $\Lambda \le q$, the variable Λ is equal to the dimensionless stretch factor of the pom-pom model, whereas for $\Lambda > q$, the variable Λ is equal to $\lambda + s_c/s_b$, where s_c/s_b is the ratio of the molecular weights per arm in the tube (at either tube end) and in the backbone. In the latter case, Λ accounts not only for the stretch factor of the backbone tube but also for the portion of the tube into which the pompon arms have been dragged. The conformation tensor **A** is used to define the tube orientation tensor **S** = **A**/tr**A**.

Assuming independent relaxation mechanisms for orientation and stretching, the relaxational contributions of the two structural variables are described by the following form of the matrix **M**:

$$\mathbf{M}(\mathbf{x}) = \begin{bmatrix} - & - & - & 0 & 0 \\ - & - & - & 0 & 0 \\ - & - & - & 0 & 0 \\ 0 & 0 & 0 & \mathbf{M}_\mathbf{A} & 0 \\ 0 & 0 & 0 & 0 & M_\Lambda \end{bmatrix} \tag{80}$$

where the fourth-rank tensor $\mathbf{M}_\mathbf{A}$ is positive-semidefinite and symmetric (in pairs of indices) and the scalar quantity M_Λ nonnegative. Öttinger[14] found that if the matrix $\mathbf{M}_\mathbf{A}$ is constructed as a bilinear contribution of the tensors **A** and (*tr***A**)**I**, with **I** denoting the unit tensor, i.e., if

$$(\mathbf{M}_\mathbf{A})_{ijkl} \propto \frac{1}{\tau_b}[a_1A_{ik}A_{jl} + a_2\mathrm{tr}(\mathbf{A})(\delta_{ik}A_{jl} + A_{ik}\delta_{jl} + \delta_{ij}A_{kl} + A_{ij}\delta_{kl}) + a_3\mathrm{tr}(\mathbf{A})^2(\delta_{ik}\delta_{jl} + \delta_{ij}\delta_{kl})] \tag{81}$$

with a_1, a_2, and a_3 being numerical constants and τ_b the characteristic time for the relaxation of the tube backbone, one obtains a closed time evolution equation directly for the orientation tensor **S**. In this case, the tube orientation order parameter **S** itself and not **A** can be used as the proper structural variable; this choice is made here.

To excite long-chain branched polymer molecules according to the present GENERIC MC methodology, two Lagrange multipiers should be assigned to the two structural variables **S** and Λ:

$$\boldsymbol{\alpha} = -\frac{1}{k_\mathrm{B}}\left[\frac{\partial s(\rho,\epsilon,\mathbf{S},\Lambda)}{\partial\mathbf{S}}\right]_{\rho,\epsilon,\Lambda} \tag{82}$$

and

$$a = -\frac{1}{k_\mathrm{B}}\left[\frac{\partial s(\rho,\epsilon,\mathbf{S},\Lambda)}{\partial\Lambda}\right]_{\rho,\epsilon,\mathbf{S}} \tag{83}$$

For the pompon model, therefore, of highly branched polymer melts, the vectors of the state and conjugate variables read

$$\mathbf{x} = \left[\frac{V}{N_\mathrm{ch}}, \mathbf{u}, \epsilon, \mathbf{S}, \Lambda\right] \tag{84}$$

and

$$\boldsymbol{\lambda} = \left[\frac{b}{k_\mathrm{B}T}, \mathbf{0}, \frac{1}{k_\mathrm{B}T}, -\boldsymbol{\alpha}, -a\right] \tag{85}$$

The probability density function in this $\{N_\mathrm{ch}, b, T, \boldsymbol{\alpha}, a\}$ generalized statistical ensemble is

$$\rho_{[N_\mathrm{ch},b,T,\boldsymbol{\alpha},a]}(V,\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_n) \propto \exp\left[-\frac{1}{k_\mathrm{B}T}(\epsilon(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_n) + bV - k_\mathrm{B}T\sum_{i=1}^{N_\mathrm{ch}}\boldsymbol{\alpha}{:}\mathbf{S}_i - k_\mathrm{B}T\sum_{i=1}^{N_\mathrm{ch}}a\Lambda_i)\right] \tag{86}$$

where $\mathbf{S}_i$ and Λ_i denote the instantaneous orientation tensor and stretch ratio, respectively, of the ith chain.

The stress tensor $\boldsymbol{\tau}$ in the system is defined by using that $\boldsymbol{\tau}$ should be such that the gradient of the entropy should belong to the null space of **L**:

$$\boldsymbol{\tau} = -b\mathbf{I} - 2Z_{\mathrm{e}}\frac{N_{\mathrm{A}}}{M}\rho T\mathbf{S}\cdot\left[\frac{\partial s(\rho,\epsilon,\mathbf{S},\Lambda)}{\partial \mathbf{S}}\right]_{\rho,\epsilon,\Lambda} - Z_{\mathrm{e}}\frac{N_{\mathrm{A}}}{M}\rho T\mathbf{S}\Lambda\left[\frac{\partial s(\rho,\epsilon,\mathbf{S},\Lambda)}{\partial \Lambda}\right]_{\rho,\epsilon,\mathbf{S}} = -b\mathbf{I} + 2Z_{\mathrm{e}}\frac{N_{\mathrm{A}}}{M}\rho k_{\mathrm{B}}T(\mathbf{S}\cdot\boldsymbol{\alpha}) + Z_{\mathrm{e}}\frac{N_{\mathrm{A}}}{M}\rho k_{\mathrm{B}}T\mathbf{S}(\Lambda a) \quad (87)$$

where Z_{e} denotes the number of entanglements per branched chain in the tube.

The analysis is completed by ascribing a kinematic interpretation to both $\boldsymbol{\alpha}$ and a. By choosing the matrix **M** to be of the form of eq 81 with $a_1 = 1$ and $a_2 = a_3 = 0$, it is found that

$$\boldsymbol{\alpha} = \frac{1}{2}\tau_b\dot{\boldsymbol{\gamma}} \quad (88)$$

and

$$a \propto \nabla\mathbf{u}:\mathbf{S} \quad (89)$$

Therefore, the Lagrange multiplier $\boldsymbol{\alpha}$ has the meaning of a dimensionless velocity gradient tensor, while in the scalar Lagrange multiplier a the velocity gradient tensor is contracted with the orientation tensor.

6. A Paradigm: Modeling the Elasticity of an Unentangled Polymer Melt

In this section, the framework developed in the previous sections for designing thermodynamically consistent atomistic MC simulation algorithms to calculate the elasticity of polymer melts is applied to the simplest case possible, that of a linear polyethylene (PE) melt in the unentangled regime.

6.1. Use of a Single-Conformation Tensor Model. It turns out that for an unentangled PE melt a simulation technique very close in spirit to the framework presented in this work has already been performed by Mavrantzas and Theodorou,[7] by employing the end-bridging Monte Carlo technique in the presence of an orienting tensorial field. The starting point in the Mavrantzas and Theodorou[7] approach is the postulate that an oriented or deformed polymer melt is governed by a Helmholtz energy function A/N_{ch} which has a direct dependence not only on temperature T and volume V but also on a structural parameter. Guided by the purely macroscopic generalized bracket formulation of transport phenomena,[8] this structural parameter was taken to be the conformation tensor, defined exactly as in eq 41. Accordingly,

$$\frac{A}{N_{\mathrm{ch}}} = \frac{A}{N_{\mathrm{ch}}}(\rho,T,\mathbf{c}) \quad (90)$$

Having postulated eq 90, the question that Mavrantzas and Theodorou addressed was how to obtain A/N_{ch} as a function of **c**. To this end, they found it convenient to work not with the variables ρ and **c** directly, but with the variables conjugate to them, playing the role of thermodynamic fields. The first is a scalar quantity, the field $b^{(MT)}$ playing the role of a generalized pressure, defined as

$$b^{(MT)} = -\frac{\partial}{(\partial V/N_{\mathrm{ch}})}\left[\frac{A}{N_{\mathrm{ch}}}(\rho,T,\mathbf{c})\right]_{T,\mathbf{c}} = \rho^2\left[\frac{\partial}{\partial\rho}\frac{A}{N_{\mathrm{ch}}}(\rho,T,\mathbf{c})\right]_{T,\mathbf{c}}\frac{N_{\mathrm{A}}}{M} \quad (91)$$

and the second is a tensorial quantity, the orienting field $\boldsymbol{\alpha}^{(MT)}$, defined as

$$\alpha_{\gamma\delta}^{(MT)} = \frac{1}{k_{\mathrm{B}}T}\left[\frac{\partial}{\partial c_{\gamma\delta}}\frac{A}{N_{\mathrm{ch}}}(\rho,T,\mathbf{c})\right]_{T,\rho} \quad (92)$$

where we have used the superscript (MT) to denote definitions according to the Mavrantzas–Theodorou approach as opposed to the definitions of the present work.

Mavrantzas and Theodorou[7] mapped out **c**, A, and τ for melts subjected to elongational flow by conducting Monte Carlo (MC) simulations for the case of a uniaxial extensional field of the form

$$\boldsymbol{\alpha}^{(MT)} = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (93)$$

only the xx component of which is nonzero. Apparently, such a form for $\boldsymbol{\alpha}$ generates the correct stress boundary conditions encountered locally in the steady-state fiber spinning process. Two linear PE melts, of mean chain lengths C_{24} and C_{78} and polydispersity index 1.08, were then studied first. In all simulations, efficient sampling of oriented melt configurations was made possible through the use of the very robust end-bridging MC algorithm.[19,23] Comparison of the melt response to that of isolated chains subjected to the same orienting field showed that, while at low fields the two responses are similar, at high fields more anisotropy develops in the melt due to favorable lateral interactions between the oriented chains. Mavrantzas and Theodorou[7] presented also comparisons against simple models used in flow calculations, which proved that FENE dumbbells and freely jointed chains are more representative of the actual melt response than Hookean dumbbells, because they account for the finite extensibility of the polymer. Further, by partitioning A into its energetic and entropic components, Mavrantzas and Theodorou[7] found that the melt response is purely entropic for long chains and low orienting fields, which leaves the intrinsic shape of chains (averaged in the coordinate frame of their principal axes) practically unaltered. A significant energetic contribution develops for small chains and high orienting fields, where the chain intrinsic shape becomes more elongated and attractive lateral interchain interactions are intensified.

To cast the work of Mavrantzas and Theodorou into the nonequilibrium thermodynamics framework developed in the present paper, it is observed that the Helmholtz free energy function $A(\rho,T,\mathbf{c})/N_{\mathrm{ch}}$ considered in their approach is the Legendre transform of the entropy density $s(\epsilon,\rho,\mathbf{c})$ considered in the present work as the proper generalized thermodynamic potential with respect to the energy density ϵ:

$$\frac{1}{T}\frac{A(\rho,T,\mathbf{c})}{N_{\mathrm{ch}}} = s(\epsilon,\rho,\mathbf{c}) - \frac{1}{T}\epsilon \tag{94}$$

Consequently, the conjugate field $\boldsymbol{\alpha}^{(MT)}$ considered by Mavrantzas–Theodorou is fully compatible with the definition of the Lagrange multiplier $\boldsymbol{\alpha}$ for a single-conformation tensor viscoelastic model, eq 42, introduced formally in the present study. However, the use in the simulations of a field $\boldsymbol{\alpha}$ of the form 93 gives rise to a highly compressible flow, regarding the rate of change of the mass density, as fluid is convected by the flow in the fluid domain. Indeed, although a field of the form of eq 93 does provide the correct stress conditions locally encountered in the uniaxial fiber spinning problem, it is seen to correspond to a velocity gradient tensor $\dot{\epsilon}$ that is not divergence free. When this field is introduced in the time evolution equation for the mass density ρ, aphysical fast changes of ρ along the x-direction of the flow are obtained. Identifying $\boldsymbol{\alpha}$ with the dimensionless velocity gradient tensor in the present work (see eq 57) implies that the *true* form of the field $\boldsymbol{\alpha}$ that corresponds to a general uniaxial elongational flow should be the following:

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & -\dfrac{\alpha_{xx}}{2} & 0 \\ 0 & 0 & -\dfrac{\alpha_{xx}}{2} \end{pmatrix} \tag{95}$$

In this case, b is not the isotropic pressure. For a known value of the ambient pressure, one needs to implement an iterative scheme in order to satisfy the correct boundary condition for the total stress: For a given value of the field α_{xx}, a value of the scalar quantity b is assumed. Then detailed atomistic MC simulations are executed and the conformation tensor c_{xx} is calculated as an ensemble average over all chains in the system and all system configurations, and eq 55 shoud be used to check whether the total normal stress equals the ambient pressure. If not, a new value is guessed for b and the procedure is iterated until eq 55 is satisfied, for the given value of the ambient (atmospheric) pressure.

In the next subsection, new results are presented for the elasticity of the C_{78} PE melt system originally studied by Mavrantzas and Theodorou with the form of $\boldsymbol{\alpha}$ given by eq 95 and not by eq 93. Further, a four-mode conformation tensor model is used as opposed to a single-mode viscoelastic model. Additional results where also the boundary condition for the stress is satisfied for an ambient pressure exactly equal to 1 atm will be presented in a forthcoming communication.

6.2. Use of a Multiple-Conformation Tensor Model. In this section results are presented for the elasticity of the C_{78} PE melt, first studied by Mavrantzas and Theodorou, by making use of a higher-mode conformation tensor model with four conformation tensors, $\mathbf{c}_p$, $p = 1, 2, 3, 4$, used as independent structural state variables. The work involves the following steps:

(i) Definition of the vector $\mathbf{x}$ of state variables. According to eq 67, this includes the molecular volume of the system V/N_{ch}, the internal energy density ϵ and the four conformation tensors $\mathbf{c}_1$, $\mathbf{c}_2$, $\mathbf{c}_3$, and $\mathbf{c}_4$, defined according to eq 63.

(ii) Definition of the vector $\boldsymbol{\lambda}$ of conjugate variables. According to eq 68, this includes the generalized pressure b, the inverse of he temperature $1/T$, and the four tensorial fields $\boldsymbol{\alpha}_1$, $\boldsymbol{\alpha}_2$, $\boldsymbol{\alpha}_3$, and $\boldsymbol{\alpha}_4$. Since the system is excited using Rouse as the thermodynamically admissible macroscopic model, only the first tensor of these, the field $\boldsymbol{\alpha}_1$, should be specified. The components of the rest of the orienting fields $\boldsymbol{\alpha}_2$, $\boldsymbol{\alpha}_3$, and $\boldsymbol{\alpha}_4$ are specified according to eq 76. To simulate the response of the system to a steady-state uniaxial elongational flow, $\boldsymbol{\alpha}_1$ is assumed to have the form of eq 98, with the values of the component $\alpha_{1,xx}$ ranging from 0.0 to 1.0.

(iii) Assignment of a physical meaning to each one of the Lagrange multipliers. As already mentioned above, b plays the role of a generalized pressure, T is the temperature, and each one of the four orienting fields $\boldsymbol{\alpha}_1$, $\boldsymbol{\alpha}_2$, $\boldsymbol{\alpha}_3$, and $\boldsymbol{\alpha}_4$ plays the role of a dimensionless rate-of-strain tensor, exciting chain segments of length on the order of N/p, where N is the molecular length of the melt and $p = 1, 2, 3, 4$.

(iv) Definition of the generalized canonical ensemble. This includes the vector $\boldsymbol{\lambda}$ of the Lagrange multipliers. However, all simulations were executed with the very powerful end-bridging MC (EBMC) method, which, as explained in detail in refs 23 and 19, induces polydispersity in the system. Thus, to control it, use is made in the simulations of a set of chain relative chemical potentials $\boldsymbol{\mu}^*$ for all chain species present except two which are taken as reference species.[23] The simulation is therefore realized in an extended generalized semigrand-canonical ensemble, in which, in addition to the Lagrange multipliers discussed in the present study, also the set of the relative chemical potentials $\boldsymbol{\mu}^*$ are considered as Lagrange multipliers. For the multiple-conformation tensor model employed here, the probability density function used to sample oriented or deformed PE melt configurations reads then as follows:

$$\rho_{[N_{\mathrm{ch}},n,b,\mathrm{T},\boldsymbol{\alpha}_1,\boldsymbol{\alpha}_2,\ldots,\boldsymbol{\alpha}_{N-1},\boldsymbol{\mu}^*]}(V, \mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n; \text{connectivity}) \propto \exp\left[-\frac{1}{k_{\mathrm{B}}T}\left(\epsilon(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{\mathrm{n}}; \text{connectivity}) + bV - k_{\mathrm{B}}T\sum_{i=1}^{N_{\mathrm{ch}}}\sum_{p}\boldsymbol{\alpha}_p{:}\mathbf{c}_p^i + \frac{1}{k_{\mathrm{B}}T}\sum_{\substack{k=1\\ k\neq l,j}}^{n}\mu_k^* N_k\right)\right] \tag{96}$$

whereas N_k stands for the number of chains of k-mers long present in the system at the given time instance, $\mathbf{c}_p^i$ denotes the pth mode conformarion tensor of the ith chain, and $k = l, j$ denotes the two reference chemical species with respect to which the rest of the chain relative chemical potentials $\boldsymbol{\mu}^*$ are defined.

(v) Calculation of the mean values of the state variables as ensemble averages over the set of atomistic configurations sampled during the end-bridging GENERIC MC simulations.

(vi) Calculation of the Gibbs free energy of the system through eq 78 using the technique of thermodynamic integration and of the Helmholtz free energy of the system through eq 79.

All simulations were performed in a cubic box containing 80 chains of mean molecular length C_{78} and polydispersity index I around 1.08 and characterized by periodic boundary conditions in all three directions. Simulations were executed for three different $\alpha_{1,xx}$

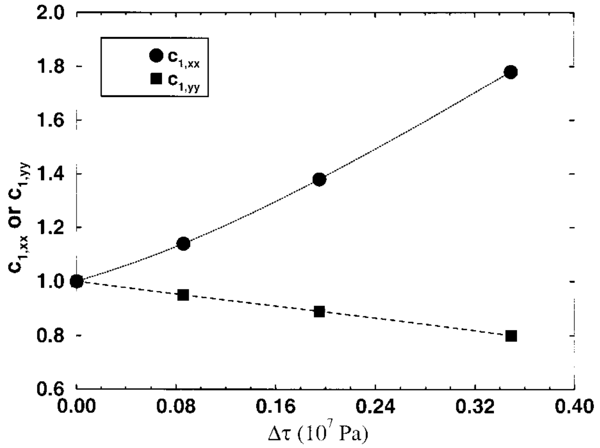

Figure 1. Diagonal components of the first mode conformation tensor $\mathbf{c}_1$ as functions of the first normal stress difference $\Delta\tau = \tau_{xx} - \tau_{yy}$, for the C_{78} system, obtained by using the multiple-conformation tensor approach with four modes and eq 95 for the Lagrange multipliers $\boldsymbol{\alpha}_p$, $p = 1, 2, 3, 4$ ($T = 450$ K, $b = 1$ atm). The statistical error in the results is approximately equal to the size of the symbols.

values: 0.10, 0.20, and 0.30, with the same molecular model as the one employed in the previous elasticity calculations.[7,24,25] In all simulations carried out, $b = 1$ atm and $T = 450$ K.

The use of a Lagrange multipler $\boldsymbol{\alpha}$ of the form of eq 95, as opposed to eq 93 used before, gives rise also to normal stresses τ_{yy} and τ_{zz} in y and z directions, respectively. Thus, in the presentation of the results, the first normal stress difference $\Delta\tau \equiv \tau_{xx} - \tau_{yy}$will be used as the proper independent variable.

Figure 1presents results for the dependence of the two diagonal components $c_{1,xx}$ and $c_{1,yy}$ of the first mode conformation tensor $\mathbf{c}_1$ as a function of $\Delta\tau$ with the multiple conformation tensor model employed here. Because of the cylindrical symmetry of the applied field, $c_{1,yy} = c_{1,zz}$, on the average. It is seen that as $\Delta\tau$ increases, $c_{1,xx}$ increases monotonically and nonlinearly, whereas $c_{1,yy}$ decreases, indicative of the ellipsoidal conformation assumed by the chains due to the applied elongational flow field. Overall, this picture is very similar to that observed by Mavrantzas–Theodorou in their original study of the elasticity of a polymer melt.

Collected results for the dependence of the *xx* and *yy* diagonal components of all four mode conformation tensors excited in the simulations of the present study relative to their equilibrium values are shown in Table 1. It is clear in the table that for the relatively short PE melt studied here (C_{78}) in the regime of small Deborah numbers (small field $\boldsymbol{\alpha}_p$, $p = 1, 2, 3, 4$, values applied), only the first-mode conformation tensor components deviate from their equilibrium ($\boldsymbol{\alpha}_p = \mathbf{0}$) values. The higher-mode conformation tensors $\mathbf{c}_p$, $p = 2, 3, 4$, retain their isotropic spherical symmetry, indicative of an equilibrium structure. This is an astonishing result which proves that the C_{78} PE melt can be modeled by employing only a single-conformation tensor viscoelastic model. This finding validates the approach of Mavrantzas and Theodorou, who modeled the elasticity of the C_{24} and C_{78} PE melts by neglecting contributions from higher than $p = 1$ modes. It should be expected though that, for stronger fields $\boldsymbol{\alpha}_p$ applied and/or longer PE melts such as the C_{156} and C_{200}, the picture will change and significant deviations should be expected also for the components of the conformation tensors $\mathbf{c}_p$ with $p > 1$.

Figure 2 presents results for the Helmholtz free energy of the deformed C_{78} PE melt relative to its equilibrium value, $\Delta A/N_{\mathrm{ch}}$, as a function of the first normal stress difference $\Delta\tau$ applied. Also shown in the figure are the results for $\Delta A/N_{\mathrm{ch}}$ obtained from the two analytical expressions generating the upper-convected Maxwell (UCM) and the FENE-P rheological models,[8,15]

$$\frac{A}{N_{\mathrm{ch}}}(T,\rho,\mathbf{c}) - \frac{A}{N_{\mathrm{ch}}}(T,\rho,\mathbf{I}) = \frac{1}{2}k_{\mathrm{B}}T[\mathrm{tr}(\mathbf{c}) - 3] - \frac{1}{2}k_{\mathrm{B}}T\ln[\det(\mathbf{c})] \quad (97)$$

and

$$\frac{A}{N_{\mathrm{ch}}}(T,\rho,\mathbf{c}) - \frac{A}{N_{\mathrm{ch}}}(T,\rho,\mathbf{I}) = -\frac{3}{2}k_{\mathrm{B}}T\,\bar{L}^2\ln\left[\frac{1 - \dfrac{\mathrm{tr}(\mathbf{c})}{3\bar{L}^2}}{1 - \dfrac{1}{\bar{L}^2}}\right] - \frac{1}{2}k_{\mathrm{B}}T\ln[\det(\mathbf{c})] \quad (98)$$

In eq 98, $\bar{L}$ is the maximum extension length L of the FENE dumbbell made dimensionless with the equilibrium mean-square chain end-to-end distance $\langle R_0{}^2\rangle$. L is identified here with the maximum contour length of the atomistically represented chain.[7] We refer to eqs 97 and 98 as simply the UCM and the FENE-P models, respectively. In calculating $\Delta A/N_{\mathrm{ch}}$ for the two models, we directly introduced in eqs 97 and 98 the values for the first mode conformation tensor $\mathbf{c}_1$ components calculated from the field-on MC atomistic simulations.

The figure shows that for small enough $\Delta\tau$ values applied, both analytical models offer a satisfactory description of the system nonequilibrium thermodynamics. For larger $\Delta\tau$ values applied, however, the analytical expression underlying the UCM model shows significant deviations from the simulation findings, which are seen to get enhanced with further increasing $\Delta\tau$. On the contrary, the expression behind the FENE-P model, which has explicitly built in chain finite extensibility effects through the parameter L, seems to follow the simulation results quite faithfully. This explains the success of this model in fitting rheological data over a wide variety of processing conditions and its popularity in the polymer rheology community. The reader should be reminded here that a similar comparison of the simulation findings against simple analytical models had also been made in the paper by Mavrantzas and Theodorou. However, the comparison there had been reported at the level of the conformation tensor $\mathbf{c}$ and its dependence on the applied field α_{xx}. This required starting with an expression for the probability distribution function for the chain end-to-end vector $\mathbf{R}$. Here the comparison is made at the level of the free energy density A/N_{ch} directly, whose derivatives with respect to the conformation tensor components enter directly in the constitutive equation of the corresponding rheological model, avoiding the need to resort to the corresponding probability distribution function for $\mathbf{R}$.

7. Discussion

We have presented the formulation of the general nonequilibrium equation for the reversible–irreversible

Table 1. ***xx* and *yy* Components of the Conformation Tensors α_p, $p = 1, 2, 3, 4$, Relative to Their Equilibrium Values, for the C_{78} Chain System, as Functions of the Orienting Field $\alpha_{1,xx}$[a]**

	$p = 1$		$p = 2$		$p = 3$		$p = 4$	
$\alpha_{1,xx}$	$c_{p,xx}/c_{p,xx,\mathrm{eq}}$	$c_{yy}/c_{p,yy,\mathrm{eq}}$	$c_{p,xx}/c_{p,xx,eq}$	$c_{yy}/c_{p,yy,\ \mathrm{eq}}$	$c_{p,xx}/c_{p,xx,\mathrm{eq}}$	$c_{yy}/c_{p,yy,\mathrm{eq}}$	$c_{p,xx}/c_{p,xx,\ \mathrm{eq}}$	$c_{yy}/c_{p,yy,\mathrm{eq}}$
0.00	0.98 ± 0.06	0.99 ± 0.06	1.01 ± 0.06	1.02 ± 0.06	1.03 ± 0.06	1.01 ± 0.06	0.99 ± 0.06	1.03 ± 0.06
0.10	1.18 ± 0.06	0.95 ± 0.06	1.02 ± 0.06	0.97 ± 0.06	0.98 ± 0.06	1.00 ± 0.06	0.99 ± 0.06	1.03 ± 0.06
0.20	1.46 ± 0.08	0.89 ± 0.06	1.03 ± 0.06	0.97 ± 0.06	0.99 ± 0.06	1.03 ± 0.06	1.02 ± 0.06	1.01 ± 0.06
0.30	1.79 ± 0.10	0.80 ± 0.05	0.97 ± 0.06	1.03 ± 0.06	0.98 ± 0.06	1.01 ± 0.06	1.03 ± 0.06	0.96 ± 0.06

[a] The simulations have been performed on bulk melts following the methodology outlined in the main text ($T = 450$ K and $b = 1$ atm).

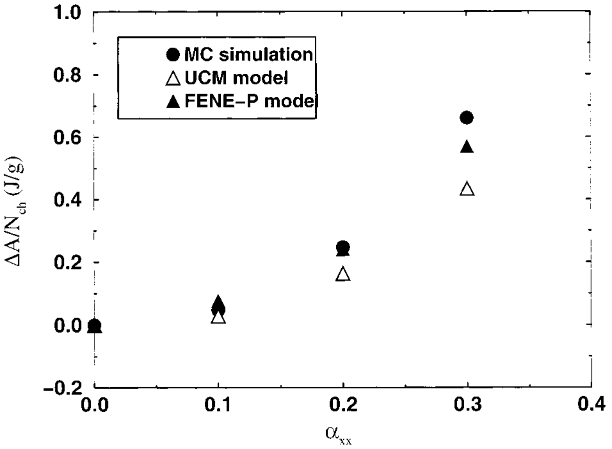

Figure 2. Change in the Helmholtz free energy $\Delta A/N_{\mathrm{ch}}$ of deformation (in units of J/g) relative to the equilibrium undeformed ($\alpha_{p,xx} = 0.0$) state for the C_{78} polymer melt as a function of the first normal stress difference $\Delta\tau$. Filled circles correspond to the results of the preesent study, by employing a multiple-conformation tensor model and eq 95 for the form of the Lagrange multpliers $\boldsymbol{\alpha}_p$. Open triangles correspond to the analytical expression, eq 97, underlying the rheological upper-convected Maxwell model, and filled triangles correspond to the analytical expression, eq 98, underlying the rheological FENE-P model ($T = 450$ K, $b = 1$ atm).

coupling (GENERIC) in a generalized canonical ensemble. The new formulation is based on the use of variables which are conjugate to the state variables of the macroscopic model and play the role of thermodynamic fields. This enables us to overcome the shortcomings of the original GENERIC formulation in a generalized microcanonical ensemble, which, for practical calculations, required the calculation of the system entropy. The new development has opened up the way toward interfacing thermodynamically founded, admissible macroscopic models, describing the dynamics of complex systems, with atomistic simulations, through the design of thermodynamically consistent, field-on Monte Carlo simulation algorithms for nonequilibrium systems. With the proper choice of the conjugate variables or fields, the new formulation, also termed GENERIC MC,[18] enables driving the atomistic system away from equilibrium in a physically meaningful way and in accord with the response of the corresponding macroscopic system to the applied flow field.

In the present work, particular emphasis was placed on the modeling of polymer melts. Three different macroscopic models were considered: the single- and multiple-conformation tensor models appropriate for the study of unentangled polymer melts and the pompon model for long-chain branched polymer molecules. For each one of these three macroscopic models, the relevant set of state and conjugate variables was defined and connected to quantities describing the system at the atomistic level. The methodology was presented for designing GENERIC MC algorithms aiming at the simulation of these systems under nonequilibrium conditions such as those encountered in polymer fluid flow operations. This was done by specifying the pertinent phase-space probability density functions needed to sample oriented or deformed melt configurations, representative of the actual system under prescribed rheological conditions. By inspecting the structure of the relevant GENERIC equation for spatially homogeneous, time-independent flows, a kinematic interpretation was assigned to the conjugate variables, establishing the connection with the velocity gradient tensor and, therefore, with the flow kinematics.

Results were presented from simulating the response of an unentangled PE melt subjected to a steady-state elongational flow field at low Deborah numbers, by mapping the atomistic model onto a multiple conformation tensor macroscopic model. This consitutes a generalization of the previous modeling work of Mavrantzas–Theodorou through a single-conformation tensor viscoelastic model.

Future plans will be directed toward three main directions:

(i) Modeling long-chain branched polymers by following the methodology outlined in section 5. Here, the emphasis will be placed on the so-called H-shaped molecules. The limiting step in the simulation of these molecules is the equilibration of the corresponding atomistic systems. The robust end-bridging Monte Carlo technique widely used for equilibrating linear PE melts of length up to C_{1000} mers long[25] is of no use here, since it does not preserve the architecture of the H-shaped molecule. To overcome this, a new Monte Carlo move is being formulated, the double bridging.[26] Through the formation of a double trimer bridging between four mers properly chosen along the backbones of a bridgeable pair of H-shaped molecules, the new move induces system equilibration without destroying the molecular architecture of the branched molecule, since no chain ends are involved in the move. In conjunction with the definition of the variables $\boldsymbol{\alpha}$ and a conjugate to the orientation tensor $\mathbf{S}$ and strech ratio Λ state variables, respectively, introduced in the present work, the new move will be used to calculate the free energy of the H-shaped branched molecules and to propose an improved constitutive equation for the pompon model.

(ii) Modeling nonequilibrium systems by exciting directly the system configurational distribution function and not its second moment (as is the case when working with conformation tensors). Indeed, a whole class of systems exist for which the appropriate state variable is not the conformation tensor or a set of conformation tensors but a distribution function. A typical system of this kind is the entangled polymer melts. On the basis of the well-established reptation picture for melts of linear polymer molecules,[10] the proper structural parameter to consider for these systems is the configurational distribution function $f(\mathbf{u},\sigma,\mathbf{r},t)$, expressing the distribution of the tangent unit vector **u** along the contour of the primitive path of a reptating chain at position σ, at a given position **r** and time t. For homogeneous, time-independent flows on which the present work is focused, the dependence of f on **r** and t is ommitted, and the distribution function is simply denoted as $f(\mathbf{u},\sigma)$. The orientation vector **u** is thought of as a property of *a smoothed chain* obtained by coarse-graining the original atomistic chain down to the entanglement length scale.[27] The parameter σ is normalized by the instantaneous total contour length so that the values $\sigma = 0$ and $\sigma = 1$ correspond to the chain ends, with the understanding that σ varies proportionally with the contour length. For the sake of simplicity, the use of additional, more refined parameters, such as an additional vector describing anisotropic tube cross-section effects can initially be neglected.[12] In the generalized canonical GENERIC formalism, the variable conjugate to the distribution function $f(\mathbf{u},\sigma)$ is a function $g(\mathbf{u},\sigma)$, defined by the partial derivative of the entropy density of the system s with respect to $f(\mathbf{u},\sigma)$:

$$g(\mathbf{u},\sigma) = -\frac{1}{k_B}\left[\frac{\partial s(\rho,\epsilon,f(\mathbf{u},\sigma),\lambda)}{\partial f(\mathbf{u},\sigma)}\right]_{\rho,\epsilon,\lambda} \tag{99}$$

How one can excite the distribution function $f(\mathbf{u},\sigma)$ by properly choosing the Lagrange multiplier function $g(\mathbf{u},\sigma)$ is not trivial at all and will be the subject of future work in the area.

(iii) Designing a methodology for calculating, in addition to energy E and entropy S, also the other two remaining blocks of GENERIC, the matrices **L** and **M**. The solution to this question is given by eqs 15 and 16, defining **L** and **M** as ensemble averages of the derivatives of projection functions with respect to atomistic coordinates in the canonical ensemble. Using these equations to get the components of the matrices **L** and **M** is not an easy task: They involve the derivatives of the projection functions with respect to atomistic coordinates whose calculation is a very formidable task. They also involve the second derivatives of the system entropy with respect to the state variables. To calculate them, on the basis of eq 27, we notice that all second derivatives involving the momentum density state variable are zero. As regards the rest of these derivatives, of interest are those with respect to the coarse-grained variable **X**. To evaluate them, one can split the Helmholtz energy function ΔA into its energetic and entropic parts (see ref 7 for details), fit the entropic part with a polynomial in the components of the variable **c** and extract the second derivative with respect to **c** analytically. The last derivative with respect to the density variable ρ can be calculated borrowing ideas from equilibrium thermodynamics. Work is currently in progress implementing these ideas for simpler systems, before extending the analysis to polymer melts. As mentioned, most of the efforts focus on the efficient calculation of the derivatives of the projection functions and on the use of the atomistic configurations sampled during the atomistic GENERIC MC runs to calculate the configurational averages appearing in eqs 15 and 16.

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