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On Maxwell's Relations of Thermodynamics for Polymeric Liquids away from Equilibrium

Chunggi Baig,*[†] Vlasis G. Mavrantzas,*[†] and Hans Christian Öttinger[‡]

[†]*Department of Chemical Engineering, University of Patras & FORTH-ICE/HT, Patras, GR 26504, Greece, and* [‡]*Department of Materials, Polymer Physics, ETH Zürich, HCI H 543, CH-8093 Zürich, Switzerland*

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ABSTRACT: To describe complex systems deeply in the nonlinear regime, advanced formulations of nonequilibrium thermodynamics such as the extended irreversible thermodynamics (EIT), the matrix model, the generalized bracket formalism, and the GENERIC (= general equation for the nonequilibrium reversible−irreversible coupling) formalism consider generalized versions of thermodynamic potentials in terms of a few, well-defined position-dependent state variables (defining the system at a *coarse-grained* level). Straightforward statistical mechanics considerations then imply a set of equalities for its second derivatives with respect to the corresponding state variables, typically known as Maxwell's relations. We provide here direct numerical estimates of these relations from detailed atomistic Monte Carlo (MC) simulations of an unentangled polymeric melt coarse-grained to the level of the chain conformation tensor, under both weak and strong flows. We also report results for the nonequilbrium (i.e., relative to the quiescent fluid) internal energy, entropy, and free energy functions of the simulated melt, which indicate a strong coupling of the second derivatives of the corresponding thermodynamic potential at high flow fields.

1. Introduction

Since Onsager's pioneering work[1] on irreversible phenomena back in 1931, thermodynamics began to describe a wide variety of dissipative processes (e.g., diffusion, heat and electric conduction, viscous relaxation, chemical reactions, dielectric relaxation) and their coupling (leading, e.g., to electrokinetic, thermoelectric, thermokinetic, and other effects) by assuming a linear relationship between the generalized thermodynamic (or driving) forces and the resulting fluxes. Onsager's reciprocal relations, which were later generalized by Casimir,[2] were derived based on the classical principle of microscopic reversibility at equilibrium and the so-called regression hypothesis (namely that the dissipation mechanism accompanying natural fluctuations is the same both at equilibrium and under nonequilibrium conditions). Following Onsager's and Casimir's seminal contributions, intense research work in the ensuing years led to a number of elegant thermodynamic and statistical theories on the fundamental nature of irreversible processes,[3−9] which eventually culminated to what is known today as the theory of linear irreversible thermodynamics (LIT) for dissipative systems.[10] Founded on the local equilibrium assumption (which allows one to take full advantage of the rigor of the known fundamental laws of equilibrium thermodynamics), LIT has offered a unified description of many nonequilibrium processes (associated with the transport of conserved quantities such as mass, momentum and energy) in a systematic and compact way.[10,11]

Modern nonequilibrium thermodynamic formulations, on the other hand, such as the extended irreversible thermodynamics,[12] the generalized bracket formalism,[13−17] the matrix model,[18,19] and the GENERIC (general equation for the nonequilibrium reversible-irreversible coupling) approach[20−22] recover LIT as a special case. The starting point in these formalisms is to choose the set $\mathbf{x}$ of the proper state variables, a step of paramount importance requiring deep physical insight and experience. This happens because thermodynamics is generally concerned with the description of a system at a coarse-grained level where, by eliminating an enormous number of microscopic degrees of freedom associated with fast dynamics (*fast degrees of freedom*), the emphasis is placed on the evolution of a limited set of slowly evolving variables (*slow degrees of freedom*). This in turn implies the existence of an intermediate time scale τ separating fast and slow variables;[23] coarse-graining then means that it is only the latter that are kept in the list of state variables.[24] The next step is to identify generalizations of thermodynamic potentials as the primary source of complete thermodynamic information. In the generalized bracket formalism, this is the dissipative Hamiltonian H. In the GENERIC framework, it is the generators E (the energy) and S (the entropy) describing reversible and irreversible contributions, respectively. The third and final step is to obtain the transport equations by *postulating* a fundamental equation for the time evolution of the set $\mathbf{x}$ of nonequilibrium variables. In GENERIC, for example, such an equation reads:

$$\frac{\mathrm{d}\mathbf{x}}{\mathrm{d}t} = \mathbf{L}(\mathbf{x})\frac{\delta E(\mathbf{x})}{\delta \mathbf{x}} + \mathbf{M}(\mathbf{x})\frac{\delta S(\mathbf{x})}{\delta \mathbf{x}} \qquad (1)$$

and comes together with a number of important properties for the generators E and S and the matrices $\mathbf{L}$ and $\mathbf{M}$. For example, $\mathbf{L}$ is always antisymmetric while $\mathbf{M}$ is symmetric (expressing the Onsager−Casimir symmetry of LIT) and positive-semidefinite (this can be considered as a strong nonequilibrium generalization of the second law of thermodynamics). In fact, a strict separation of reversible and irreversible contributions in GENERIC is provided by the mutual degeneracy requirements

$$\mathbf{M}(\mathbf{x})\frac{\delta E(\mathbf{x})}{\delta \mathbf{x}} = 0, \quad \mathbf{L}(\mathbf{x})\frac{\delta S(\mathbf{x})}{\delta \mathbf{x}} = 0 \qquad (2)$$

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*Authors to whom correspondence should be addressed. E-mail: cbaig@iceht.forth.gr (C.B.); vlasis@chemeng.upatras.gr (V.M.). Telephone: +30-2610-997398. Fax: +30-2610-965223.

expressing the conservation of energy even in the presence of dissipation and the conservation of entropy for any reversible dynamics (entropy can only be produced by irreversible dynamics), respectively. As explained by Öttinger,[24] E and $\mathbf{L}$ can be obtained by straightforwardly averaging the microscopic energy and Poisson bracket of classical mechanics. S and $\mathbf{M}$, on the other hand, should account correctly for the increase in entropy and dissipation (or friction) associated with the elimination of fast degrees of freedom or the grouping of microstates to coarser states. To see this, let $\rho_{\mathbf{x}}(\mathbf{z})$ be the probability density to find a microstate $\mathbf{z}$ (in classical mechanics, this is defined by the positions and momenta of the atomistic units) for given values of the set of coarse-grained variables $\mathbf{x}$, and $\Pi(\mathbf{z})$ a mapping that assigns a coarse-grained state to any microstate $\mathbf{z}$. In any ensemble, the variables $\mathbf{x}$ are the averages of $\Pi(\mathbf{z})$ evaluated with the probability density $\rho_{\mathbf{x}}(\mathbf{z})$, i.e., $\mathbf{x} = \langle \Pi(\mathbf{z}) \rangle_{\mathbf{x}}$. Then, one can show using projection operation techniques[25,26] that the friction matrix $\mathbf{M}$ can be obtained by the following Green–Kubo equation:[27]

$$\mathbf{M}(\mathbf{x}) = \frac{1}{k_{\mathrm{B}}} \int_0^{\tau} \langle \dot{\Pi}^f(\mathbf{z}(t)) \dot{\Pi}^f(\mathbf{z}(0)) \rangle_{\mathrm{x}} \, \mathrm{d}t \tag{3}$$

Here, k_B is the Boltzmann constant and $\dot{\Pi}^f$ denotes the (fast) time derivative of Π. How to apply eq 3 in order to compute $\mathbf{M}$ from dynamic simulations (executed, however, only for a small fraction of the longest system time scale, as dictated by the upper limit of integration in eq 3, namely the intermediate time τ) has been discussed by Ilg et al.[28]

Each of the new nonequilibrium thermodynamics formulations has its advantages and disadvantages; however, all of them are very useful in our effort to *consistently* understand or describe irreversible processes far away from equilibrium. Furthermore, and despite key differences in their fundamental structure or starting point, they bear striking similarities to a degree that one can even prove equivalence of any such two formalisms in certain cases.[29−31] Regarding, in particular, the issue of the existence of thermodynamic potentials, we recall that from a statistical mechanics point of view these are well-defined at equilibrium. And they can be calculated via partition functions in terms of statistical weighting by sampling equilibrium configurations in a predefined statistical ensemble. All the information about a particular system at equilibrium is thus contained in a single thermodynamic potential whose form is limited only by convexity conditions. For example, for a system specified by the variables T, V, and N, namely temperature, volume and number of molecules, the Helmholtz free energy $A = A(T,V,N)$ is the proper thermodynamic potential to consider, from which (e.g.) all equations of state can be obtained by simple partial differentiations. Furthermore, the function $A = A(T,V,N)$ is obtainable from molecular simulations in the NVT ensemble through the canonical partition function. Beyond equilibrium, however, even the choice of variables can be bad. But one can still check (based on the corresponding Green–Kubo equation for the $\mathbf{M}$ matrix, eq 3 above) whether a separating time scale does exist in which case the choice of the variables should be a reasonable one. On the other hand, the consideration of additional structural variables in the set $\mathbf{x}$ implies that we should resort to an expanded ensemble, wherein the coarse-grained variables appear explicitly. Then, despite the elegance and rigor (expressed through a set of consistency conditions) of the nonequilibrium thermodynamics approach adopted, one is still faced with the question whether or not "well-defined thermodynamic potentials (such as the entropy and energy functions postulated in GENERIC or the extended Helmholtz free energy function assumed in the generalized bracket) really exist far beyond equilibrium"[32−34] and how these can be computed. We demonstrate here how, given a set of nonequilibrium variables for a model system (an unentangled polymer melt), one can actually carry out accurate calculations of such a nonequilibrium potential (in particular of the entropy) and of a few other thermodynamic functions in terms of the chosen coarse-grained variable(s) through detailed atomistic MC simulations in an expanded statistical ensemble.[35−38] We also provide a consistency check of our numerical method by directly demonstrating the validity of Maxwell's relations relating certain pairs of the second derivatives of the generalized potential with respect to the nonequilibrium variables.

2. Nonequilibrium System Studied and Simulation Methodology

As a test case, let us consider a polymeric melt containing short polyethylene (PE) chains under an arbitrary flow field with shear rates covering both the linear and the nonlinear regime. For such a system, Mavrantzas and Theodorou already back in 1998[35] showed how one can compute the Helmholtz free energy function in terms of its density ρ, temperature T, and a tensorial structural variable, namely the conformation tensor $\mathbf{c}$ defined as $3\langle \mathbf{RR} \rangle / \langle R^2 \rangle_{eq}$ where $\mathbf{R}$ is the chain end-to-end vector, by making use of the conjugate thermodynamic variables to ρ and $\mathbf{c}$: The first is a scalar quantity, the "pressure" P, and the second a tensorial quantity, the "orienting field" $\boldsymbol{\alpha}$ which is intimately related to the strain rate in a flow situation.[36] Building on these very first considerations, Baig and Mavrantzas[37,38] proposed recently a powerful MC methodology capable of sampling nonequilibrium states for short polymers with an overall conformation identical to that obtained from a direct nonequilibrium molecular dynamics simulation. The method was termed GENERIC MC, because it was founded on the GENERIC formalism of nonequilibrium thermodynamics. However, it is more general, since it makes no a priori assumption about the relationship between thermodynamic field(s) employed in the simulation and the corresponding state variable(s). It can be routinely reformulated in any other nonequilibrium thermodynamics framework, in which the complete coarse-grained information is assumed to be contained in the generalized thermodynamic potential. But we should keep in mind that any MC method, being intrinsically nondynamic in nature, provides results that strictly apply only to stationary systems (systems for which the free energy A is time-independent). Thus, although thermodynamic potentials exist regardless of time and the same happens with the Maxwell equations (they hold independently of whether the system undergoes a stationary or a time-dependent process), our GENERIC MC methodology can provide numerical evaluation for them for a given system only when this system undergoes a stationary process. To confirm Maxwell's equations under general time-dependent process, one should devise a different methodology (see, e.g., ref 28).

The generalized fundamental Gibbs equation for the system under consideration is written as

$$\mathrm{d}E = \sum_k \lambda_k dx_k \tag{4}$$

where λ_k represents the thermodynamic force field conjugate to the extensive state variable x_k. Considering points in the nonequilibrium phase space as well-defined thermodynamic states, the energy function E plays the role of a generalized thermodynamic potential [and, of course, other thermodynamic potentials can be obtained via appropriate Legendre transforms[39]] for the nonequilibrium system considered. In this case, one comes up also with a set of equalities of the form

$$\left(\frac{\partial \lambda_i}{\partial x_j} \right)_{\forall x_{k \neq j}} = \left(\frac{\partial \lambda_j}{\partial x_i} \right)_{\forall x_{k \neq i}} \tag{5}$$

which are the analogues of the well-known Maxwell relations of equilibrium thermodynamics for nonequilibrium systems. In eq 5, the subscript $\forall x_{k \neq j}$ denotes all state variables x_k except x_j. Alternatively (see, e.g., eq 6.17 or the solution to exercise 139 in ref 22), eq 5 can be derived starting from the probability density function $\rho \sim \exp(\Sigma_j \lambda_j \Pi_j)$ computing the average of Π_i and differentiating with respect to λ_j. Then one obtains that $(\partial\langle\Pi_i\rangle)/(\partial\lambda_j) = (\partial\langle\Pi_j\rangle)/(\partial\lambda_i) = \langle\Pi_i\Pi_j\rangle - \langle\Pi_i\rangle\langle\Pi_j\rangle$, physically representing the degree of mutual correlation of the different thermodynamic variables or the degree of fluctuations for the same variable. Clearly, if one works with a different thermodynamic potential, a different set of Maxwell relations will be derived. It is also understood that for a given system the λ_k's have a different meaning under equilibrium and nonequilibrium conditions, since under nonequilibrium conditions they are affected by the extra structural variables considered to account for deviations from equilibrium.

For the system at hand, an unentangled polymer melt whose internal microstructure is described by the conformation tensor **c**, the fundamental thermodynamic representation in terms of the energy E dictates that

$$dE = T\,dS - P\,dV + \mu\,dN_{ch} + k_B T \boldsymbol{\alpha} : d(N_{ch}\mathbf{c}) \qquad (6)$$

where N_{ch} denotes the number of chains, P the pressure, T the temperature, V the volume, S the entropy, and $\boldsymbol{\alpha}$ the conjugate thermodynamic field to tensor **c** accounting for flow effects. Given that E is a first-order homogeneous thermodynamic function with respect to S, V, and $N_{ch}\mathbf{c}$, eq 6 implies the following Euler equation

$$E = TS - PV + \mu N_{ch} + N_{ch} k_B T \boldsymbol{\alpha} : \mathbf{c} \qquad (7)$$

and thus, also the following generalized Gibbs−Duhem relationship:

$$-S\,dT + V\,dP - N_{ch}\,d\mu - N_{ch}\mathbf{c} : d(k_B T \boldsymbol{\alpha}) = 0 \qquad (8)$$

Other thermodynamic functions can be derived from these expressions through appropriate Legendre transforms, such as the extended (generalized) Helmholtz free energy A and the extended (generalized) Gibbs free energy G:[36,38]

$$dA(T, V, N_{ch}, N_{ch}\tilde{c}) = -S\,dT - P\,dV + \mu\,dN_{ch} + k_B T \boldsymbol{\alpha} : d(N_{ch}\mathbf{c}) \qquad (9)$$

and

$$dG(T, P, N_{ch}, \boldsymbol{\alpha}) = -S\,dT + V\,dP + \mu\,dN_{ch} - N_{ch}\mathbf{c} : d(k_B T \boldsymbol{\alpha}) \qquad (10)$$

respectively. For the purpose of confirming Maxwell's relations, it is more convenient to work with the thermodynamic potential $A' = A'(T,V,N_{ch},\boldsymbol{\alpha})$ defined as $A' = A' - N_{ch}k_B T \boldsymbol{\alpha}:\mathbf{c}$ so that:

$$dA'(T, V, N_{ch}, \boldsymbol{\alpha}) = -S\,dT - P\,dV + \mu\,dN_{ch} - N_{ch}\mathbf{c} : d(k_B T \boldsymbol{\alpha}) \qquad (11)$$

Equation 11 is the starting point for executing MC simulations in the expanded ensemble $\{N_{ch}NVT\boldsymbol{\mu}^*\boldsymbol{\alpha}\}$, in which the following variables are specified: The number of chains N_{ch}, the average number of atoms per chain N, the volume V, the temperature T, the spectrum of chain relative chemical potentials $\boldsymbol{\mu}^*$controlling the distribution of chain lengths in the system,[40] and the tensorial field $\boldsymbol{\alpha}$ accounting indirectly for flow effects. The spectrum $\boldsymbol{\mu}^*$ enters the analysis when one converts from a description in terms of a Helmholtz free energy representation to a representation in terms of the variables $\{N_{ch}NVT\boldsymbol{\mu}^*\boldsymbol{\alpha}\}$ for an m-component system,[40−42] in which case if k (k = 1, 21...m) denotes the kth component in the mixture (characterized by chain length N_k) and (i,j) is a selected arbitrary pair of reference species (of lengths N_i and N_j, respectively) for which $\mu_i^* = \mu_i^* = 0$ to maintain the total number of atoms and the total number of chains constant, then each of the $\mu_k^*, k = 1, 2, ..., m$ denotes the relative chemical potential of chains of species k (and thus of length N_k). The spectrum $\boldsymbol{\mu}^*$ should reproduce the desired distribution of chain lengths (e.g., Gaussian, uniform, most probable, Flory, etc.) in the course of the simulations and should be an input to the MC algorithm[40−42] (see ref 40 for the mathematical specification of $\boldsymbol{\mu}^*$ that generates the most widely employed chain length distributions). The field $\boldsymbol{\alpha}$, on the other hand, couples with the tensor **c** in the thermodynamic function and drives the system away from equilibrium, based on the following probability density function:

$$\rho^{N_{ch}NVT\boldsymbol{\mu}^*\boldsymbol{\alpha}}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n, V) \sim \exp[-\beta(U(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n, V) - \sum_{k=1}^{N_{ch}} \mu_k^* N_k - k_B T \boldsymbol{\alpha} : \sum_{k=1}^{N_{ch}} \mathbf{c}_k)] \qquad (12)$$

Consequently, in the proposed GENERIC MC simulations, system configurations are sampled according to the following modified Metropolis criterion:

$$p_{acc}^{N_{ch}NVT\boldsymbol{\mu}^*\boldsymbol{\alpha}} \sim \exp[-\beta(\Delta U - \sum_{k=1}^{N_{ch}} \mu_k^* \Delta N_k - k_B T \boldsymbol{\alpha} : \sum_{k=1}^{N_{ch}} \Delta\mathbf{c}_k)] \qquad (13)$$

where $\beta \equiv 1/k_B T$, n $(= N_{ch} \times N)$ denotes the total number of atoms in the system, $\{\mathbf{r}\} = \{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_n\}$ the space of their position vectors, U the potential energy of the system, μ_k^* the relative chemical potential of the k-mer long chain and $\mathbf{c}_k$ the conformation tensor of this chain. With appropriate input data for the set $\{N_{ch}NVT\boldsymbol{\mu}^*\boldsymbol{\alpha}\}$, eq 13 allows one to sample nonequilbrium steady states by assigning nonzero values to $\boldsymbol{\alpha}$.

All simulation results presented here have been obtained with a model linear PE melt containing 160 $C_{78}H_{158}$ chains in a rectangular box [enlarged in the stretching, x, direction to avoid undesirable system-size effects, especially at high flow fields] with dimensions x, y, and z equal to 130.5, 54, and 54 Å, respectively. The simulations were executed at temperature T = 450 K and density ρ = 0.7638 g/cm^3 starting from a fully pre-equilibrated initial configuration of the $C_{78}H_{158}$ melt, using the following form of $\boldsymbol{\alpha}$:

$$\boldsymbol{\alpha} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & 0 \\ \alpha_{xy} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (14)$$

How $\boldsymbol{\alpha}$ is related to the velocity gradient tensor $\dot{\gamma}$ in a real flow has been analyzed in detail in ref 38 where it is also explained that the above form, eq 14, represents a mixed flow comprising both pure stretching and rotational components. We chose it because it gives rise to more intriguing set of Maxwell's relations than that corresponding either to pure shear or to pure elongation. The tensor $\boldsymbol{\alpha}$ is also intimately related to the stress tensor $\boldsymbol{\sigma}$ developing in the system. In fact, if the stress is only elastic in nature, then the tensor $\boldsymbol{\alpha}$ imposed directly in the MC simulations and the tensor **c** that results from the simulations should satisfy a consistency relation which reflects the inherent symmetric nature of the stress tensor $\boldsymbol{\sigma}$. We refer the interested reader to ref 38 for more details.

The phase space explored in the present simulations corresponded to α_{xx} and α_{xy} values in the interval [0, 0.35] with a spacing equal to 0.05. As also explained in ref 38, for the $C_{78}H_{158}$

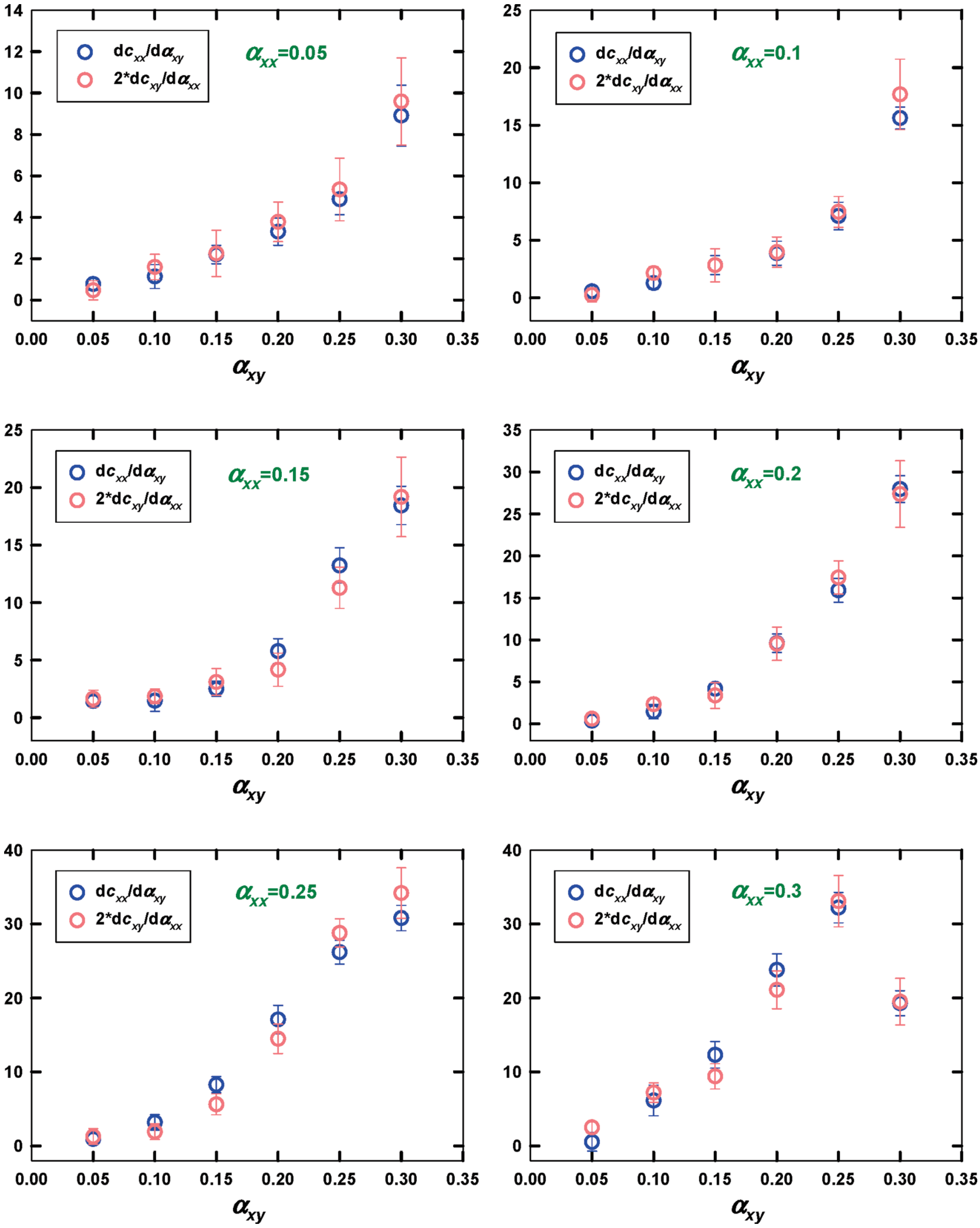

Figure 1. Comparison of the two thermodynamic derivatives ($\partial c_{xx}/\partial\alpha_{xy}$ and $\partial c_{xy}/\partial\alpha_{xx}$) in the entire range of values of the applied flow field $\boldsymbol{\alpha}$ investigated here.

PE melt considered here, this corresponds to Deborah numbers from 0.3 up to 1000, implying that our simulations spanned both the linear and the nonlinear regime. Of course, Deborah numbers equal to 1000 might be too large for a model based on a single mode (the chain end-to-end conformation tensor **c** here) to accurately describe its response to the applied flow but we included them in our study only in order to test the proposed numerical method in the highly nonlinear regime.

Substituting eq 14 for $\boldsymbol{\alpha}$ into eq 11 implies then the following Maxwell relation

$$\left(\frac{\partial c_{xx}}{\partial \alpha_{xy}}\right)_{T,\,V,\,N_{ch},\,\alpha_{xx}} = 2\left(\frac{\partial c_{xy}}{\partial \alpha_{xx}}\right)_{T,\,V,\,N_{ch},\,\alpha_{xy}} \qquad (15)$$

for the system at hand.

In the simulations, the well-known end-bridging MC algorithm$^{40-42}$ was employed, the most efficient MC method available today for the equilibration of the long-length scale characteristics of linear polymers irrespective of their length. The method is capable of generating disparate and practically uncorrelated polymer conformations with a probability prescribed by the acceptance criterion of eq 13. A small polydispersity was allowed in the simulations (in conjunction with the use of the end-bridging move) corresponding to a polydispersity index $I \approx 1.083$. In the simulations the following mix of MC moves was used: end-bridgings, 50%; reptations, 10%; end-mer rotations, 2%; flips, 6%; concerted rotations, 32%. A total of about 2 billion MC steps were seen to be enough for the full equilibration of the structural, volumetric and conformational properties of the simulated liquid at each state point.

3. Nonequilibrium Simulation Results

The simulation results for the two partial derivatives appearing in eq 15 are presented in Figure 1. We see that (a) the two derivatives are always positive and that (b) they increase monotonically and rather rapidly as the flow components are increased except for the very last (and highly nonlinear) point corresponding to $\alpha_{xx} = \alpha_{xy} = 0.3$. It is also surprising that $\partial c_{xx}/\partial\alpha_{xy}$ increases steeply with α_{xy} (at a fixed value of α_{xx}): given that α_{xy} is an off-diagonal component, it cannot cause any preferential deformation of the chain dimensions along the *x*- or *y*-directions by itself; clearly, this reflects the strong, highly nonlinear coupling of the α_{xx} and α_{xy} components. Regarding the maximum exhibited by the two derivatives for $\alpha_{xx} = 0.3$ (bottom right in Figure 1), this should be attributed to two effects: (a) the finite extensibility of the relatively short chains simulated here and (b) the nonzero value of the shear component α_{xy} which precludes chains from assuming fully stretched configurations along the *x*-direction. By far, however, the most important result of the simulations is that the two thermodynamic derivatives are practically identical to each other over the entire range of field values investigated. This can be seen more clearly in the 3-dimensional graphs reported in Figure 2; Maxwell's relations (eq 15) for the simulated system are numerically confirmed by our GENERIC MC simulations not only in the linear but also deeply in the nonlinear flow regime. The shapes of the resulting surfaces are convex upward and rather steep (except from the very last state point, corresponding to $\alpha_{xx} = \alpha_{xy} = 0.3$), also indicative of nonlinear effects.

In addition to directly evaluating the Maxwell equations, our GENERIC MC simulations have allowed us to calculate the nonequilibrium thermodynamic functions (energy, entropy and Helmholtz free energy; see eq 11) as a function of the imposed nonequilibrium field. Typical results for the system addressed here are reported in Figure 3 as 3-d plots and reveal that for small up to intermediate field values, the internal energy either remains unchanged or shows a small decrease but beyond a value of α_{xx} approximately equal to 0.15 and a value of α_{xy} approximately equal to 0.2 decreases abruptly (Figure 3A). A qualitatively similar behavior is observed for the entropy function S (Figure 3B), except for the highest fields where S is seen to drop rapidly (actually more rapidly than the energy). The decrease of S manifests the significant reduction in the number of allowed system configurations due to large chain stretching and orientation (accompanying the application of the flow). Finally, the sum of energy and entropy which defines the Helmholtz free energy of the system is seen to increase as the strength of the applied field is increased (Figure 3C), but rather smoothly, i.e., not as abruptly as is separately observed for the (decrease in) energy and entropy.

A few additional points are in order here:

(a) We evaluated numerically the Helmholtz free energy function at the various state points following different thermodynamic paths and we always obtained the same result.

(b) One can show analytically that expressions for the Helmholtz free energy function underlying the most widely used conformation-tensor viscoelastic models (e.g., the upper-convected Maxwell, the Giesekus, the finite-extensible nonlinear elastic, the Leonov, etc.) satisfy the Maxwell relations. In fact, the proof covers all models whose Helmholtz free energy is expressible in terms of the three invariants of the conformation tensor (i.e., tr($\mathbf{c}$), tr($\mathbf{c}\cdot\mathbf{c}$), and det($\mathbf{c}$), where "tr" and "det" denotes the trace and determinant, respectively). No such assumption was made in the present work: we addressed the problem to its full generality and showed that the Maxwell relations are a more general property. As a result, one can use Maxwell's relations in order to admit or not new rheological models built on the concept of the conformation tensor.

(c) Although only the *xx* and *yy* components of the tensor $\boldsymbol{\alpha}$ were taken to be nonzero (for simplicity), the general conclusions drawn from our computations are valid for any other type of flow.

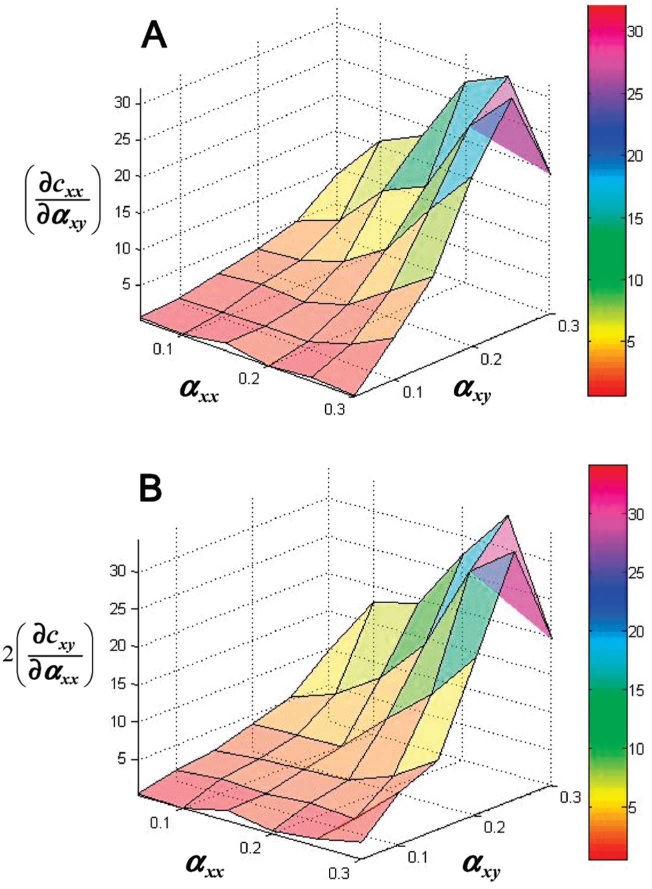

Figure 2. Three-dimensional representations of the thermodynamic derivatives (A) $\partial c_{xx}/\partial\alpha_{xy}$ and (B) $\partial c_{xy}/\partial\alpha_{xx}$), as a function of field strength.

By nature, polymer molecules possess an enormous number of configurational degrees of freedom at the atomistic level. Thus, entropic contributions should dominate their response to an externally applied flow field relative to energetic ones, especially for truly long molecules. We can therefore assume that the entropy function is separable into an equilibrium part S_0 (corresponding to $\boldsymbol{\alpha} = \mathbf{0}$ or, equivalently, to $\mathbf{c} = \mathbf{I}$) and a configurational part S_{config} accounting for flow effects; and thus to rewrite eq 6 as

$$\mathrm{d}E = T\,\mathrm{d}S_0 + T\,\mathrm{d}S_{config} - P\,\mathrm{d}V + \mu\,\mathrm{d}N_{ch} + k_{\mathrm{B}}T\alpha : \mathrm{d}(N_{ch}\mathbf{c}) \tag{16}$$

We can even go one step further and completely neglect the energy change during deformation; i.e., we can set $E = E_0$ in eq 16 or, equivalently, $E_{config} = 0$ (this is what is customarily assumed in typical viscoelastic models) at fixed values of temperature and density. Then eq 16 leads to

$$T\,\mathrm{d}S_{config} = -k_{\mathrm{B}}T\alpha : \mathrm{d}(N_{ch}\mathbf{c}) \tag{17}$$

implying that

$$S_{config} = -N_{ch}k_{\mathrm{B}}\alpha : \mathbf{c} \tag{18}$$

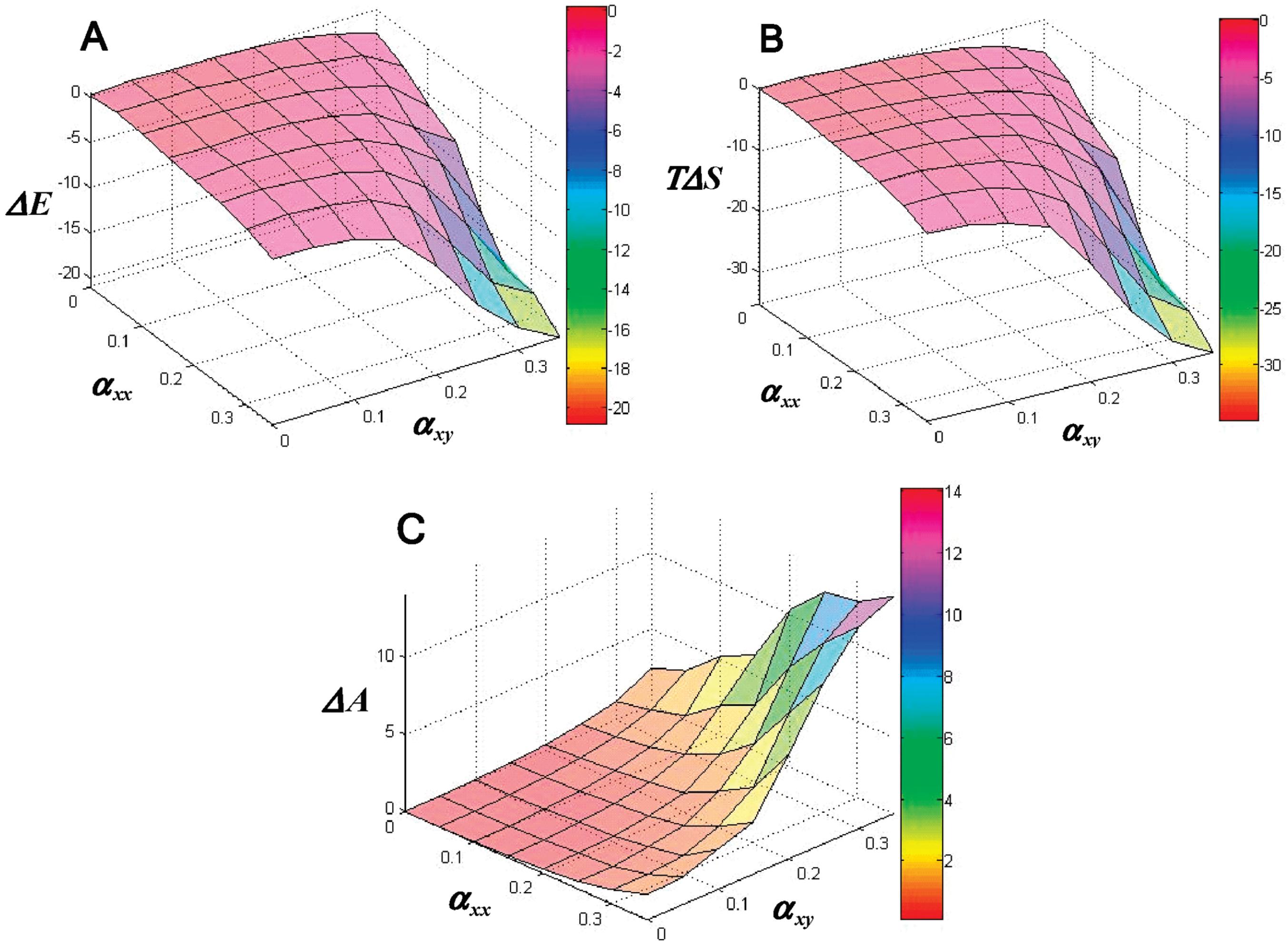

Figure 3. Three-dimensional plots of the fundamental nonequilibrium thermodynamic functions (relative to equilibrium) vs field strength: (A) the internal energy U, (B) the entropy multiplied by temperature TS, and (C) the Helmholtz free energy A.

This expression sheds some extra light on the principles underlying eqs 6 and 7, since it makes the connection with models (e.g., transient network models) based on the theory of purely entropic polymer elasticity. Conversely, one can arrive at eqs 6 and 7 starting from a proposition for the configuational entropy of the form of eq 18. In fact, GENERIC MC simulations of the type presented here can be used[35,43] to quantify the relative magnitude of enthalpic and entropic contributions to the Helmholtz free energy of deformation for short PE melts. For the system addressed here, a $C_{78}H_{158}$ PE melt, the results are shown in Figure 3 clearly demonstrating that energetic contributions to the free energy of deformation are as significant as entropic ones. In fact, by computing the changes in the different components of the total potential energy due to flow,[43] one can see that for the simulated system the ones that are mostly responsible for its decrease are the nonbonded intermolecular Lennard-Jones interactions (a direct consequence of the tendency of chains to orient with the flow, which enhances attractive lateral interactions) and the interactions associated with torsional angles (due to enhancement of *trans* conformational states, as chains tend to unravel and assume rather elongated shapes at high deformations).

4. Discussion and Outlook

We have shown how one can employ detailed atomistic MC simulations in an expanded ensemble to accurately calculate important thermodynamic functions (such as the entropy and its derivatives) for systems away from equilibrium and deeply in the nonlinear regime. We have also demonstrated the internal consistency of these calculations through a computation of the corresponding Maxwell equations for the nonequilibrium variables. In fact, in extended irreversible thermodynamics[12,30] where the thermodynamic fluxes are also taken as independent state variables in the extended Gibbs equation (eqs 4 and 5), the corresponding conjugate fields are usually assumed to be proportional to the thermodynamic fluxes (in order for the formalism to automatically satisfy the second law of thermodynamics); in this case, the Maxwell relations are automatically satisfied. In the present GENERIC MC methodology, however, based on the extended thermodynamic formulation prescribed by eqs 6−11, we have not made any such assumption about the relationship between forces and fluxes as a function of the field strength. This further indicates that thermodynamic integration works quite well in practice even in the highly nonlinear regime thereby allowing one to calculate the entropy and other thermodynamic functions for a nonequilibrium system. We also note that our GENERIC MC-based approach of estimating the entropy change accompanying the deformation of polymeric liquids, which relies on the judicious choice of a few state variables describing the conformation of polymer chains beyond equilibrium in an overall sense, is more advantageous over direct statistical methods[44,45] because of its simplicity and computational efficiency.

Our methodology for confirming Maxwell's equations and the results obtained here refer to the family of systems known as unentangled polymer melts. But the general principles carry on to other polymeric fluids as well. For example, our work is of relevance to entangled polymers where one can resort to a description either in terms of the conformation tensor for the entanglement strands in the topological network underlying their atomistic structure or in terms of the orientational distribution function $f(\mathbf{u},s)$ representing the probability that the tangent vector $\mathbf{u}$ at segment s along the reduced primitive path of a given chain is $\mathbf{u}$ within $d\mathbf{u}$ (inspired by Doi–Edwards' perspective). It is also applicable to block copolymers and self-assembled systems, as long as the selected structural variables are capable of describing morphology (e.g., lamellae, perforated layers, etc.) at the nanoscale. Guided by experimental observations and field theoretical approaches to the problem,[46] proper candidate variables here could be the volume fraction for each block component and a set of (scalar or tensorial) parameters capturing ordering (pattern formation) at long length scales.

In general, we could say that our results for the generalized Gibbs equation (eqs 4 and 5) *are of relevance to any system* (and not just to polymeric fluids) as long as a proper set of state variables has been chosen. In contrast, if an improper choice of structural variable(s) is made, the obtained numerical results may either be not useful or bear no meaning. To appreciate the value of the proper choice of state variables, we can consider an interesting problem often encountered in viscoelastic constitutive modeling when one attempts a jump in the system description from the level of the distribution function to the level of the tensor $\mathbf{c}$: closed-form nonequilibrium equations cannot be derived without additional "closure" approximations for polymers under nonequilibrium conditions.[47] Rigorously, the evolution equation for $\mathbf{c}$ in the case of nonlinear elastic models is obtained from the diffusion equation for the distribution function through some preaveraging procedure. The same (or a very similar) equation can practically be obtained by working directly at the level of $\mathbf{c}$ by assuming a particular functional form for the free energy in terms of this variable. The choice is dictated by the available closed-form evolution equation from kinetic theory. The present work justifies our search for a nonequilibrium thermodynamic potential function that can match the evolution equations as derived from the two descriptions. That is, it justifies the strategy to adopt certain closure approximations either at the beginning (nonequilibrium thermodynamics approach) or at the end (kinetic theory approach). Of course, one can even go one step further and ask if, based solely on principles of nonequilibrium thermodynamics, one could guess (somewhat) the exact form of this potential. Unfortunately, the answer is "no": although thermodynamics (especially the second law) puts certain restrictions on the allowed form of this potential, the admissible solutions are too many. The interested reader is referred to a recent work (ref 38) on this issue.

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