Flow-induced crystallization of a polyethylene liquid above the melting temperature and its nonequilibrium phase diagram

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Manufacturing of plastics is typically performed via flow processing of a polymer melt. Semicrystalline polymers, such as polyethylene (PE), play a critical role in the global plastics markets, but fundamental understanding of how process flow conditions affect their properties is lacking. Nonequilibrium molecular dynamics of a PE liquid above its melting point revealed reversible transitions from coiled, biphasic, stretched, pretransitional, and crystalline phases with applied stress in elongational flow. A nonequilibrium phase diagram was developed for the thermodynamic state space.

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I. INTRODUCTION

Of the 350 million tons of plastics produced worldwide during 2018, approximately one third were polyethylenes [1]. Global revenues derived from plastics surpass half a trillion US dollars each year, with \$150 billion due to polyethylene alone. These industries produce a huge variety of consumer goods ranging from simple household items to state-of-the-art electronic components, including many high-performance composites used in applications of critical national need.

Polyethylene (PE) is a semicrystalline material possessing a microstructure containing both crystalline and amorphous regions. This combination gives rise to the polymer's high strength and flexibility, which to a great extent can be tuned using the PE's degree of crystallinity as a parameter. The crystalline microdomains are formed by chain folding, wherein the long macromolecules fold back on themselves repeatedly, arranging into stacked structures called lamellae [2]. These high-strength lamellar domains are surrounded by amorphous regions of entangled polymer chains that provide flexibility and thermal/electrical resistance to the semicrystalline material.

Polyethylenes generally have normal melting points that vary greatly from low- to high-density materials (0.88–0.96 g/cm³), typically ranging from 383–423 K for common varieties with a heat of fusion (ΔH_f) of approximately 290 J/g [3–5]. Many studies point to single crystals grown from quiescent melts that possess orthorhombic or hexagonal lattices (both possessing a definite triple point with the melt phase)

[6,7], whereas crystals formed under mechanical stress tend to pack into a monoclinic structure [8–11].

Most polymeric materials are processed in the liquid state. The intricate nonlinear coupling between fluid motion and microstructural evolution greatly complicates the fabrication of polymeric materials, and the ability to induce the desired microstructure through manipulation of the flow field is to a great extent responsible for many useful products made of polymers. Indeed, most semicrystalline fiber materials are formed via crystallization under coupled flow and thermal transport processes. Consequently, the study of flow-induced crystallization (FIC) has been a rich subject of research over the past 50 years. FIC can be applied to form semicrystalline polymers into continuous fibers and plastic sheets with microstructures that are highly dependent on the nature and strength of the applied flow field.

Early pioneers of FIC, including Keller [12–14], Schultz [15], McHugh [16–18], and others [19–22], discovered that a wide array of semicrystalline morphologies could be generated under flow, such as the famous “shish-kebab” fibrillar structure of transverse lamellae growing from a central axial fibril [23–25], at temperatures several decades above the quiescent melting point [18,19]. Recent work by Wang *et al.* [7] has demonstrated that reversible nonequilibrium phase diagrams of FIC, in this case composed of distinct thermodynamic phases associated with the PE melt, orthorhombic and hexagonal crystalline phases, and noncrystalline preordered states, can be constructed in stress-temperature space. Such nonequilibrium phase diagrams have the potential to open up flow-induced tuning of crystallinity parameters to allow a much greater degree of control of product morphology than has previously been attainable.

A number of theories have been developed over the past 30 years aimed at understanding the essential physics of flow-induced crystallization, in terms of both morphology and kinetics; e.g., see Refs. [26–32]. Graham has recently reviewed some of the pertinent literature [33]. Although substantial progress has already been made at understanding the

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intimate coupling between flow history and morphology on the macroscopic and mesoscopic levels, what is currently missing is an atomic-scale understanding of the morphology and kinetics of the crystallization phenomenon and the effects of flow upon it; in particular, the experimental observation of what induces crystallization of these materials at temperatures far above the melting point and a viable theoretical means of constructing nonequilibrium phase diagrams.

Within the past 15 years, researchers have begun to use nonequilibrium molecular dynamics (NEMD) and nonequilibrium Monte Carlo (NEMC) to probe flow-induced crystallization phenomena at the atomic level using realistic potential models to describe the energetics of interactions between neighboring particles. Generally, Monte Carlo methods do not capture crystallization kinetics, and crystallization from a quiescent melt, regardless of temperature, is too slow to analyze using molecular dynamics (MD); however, the crystallization process is sped up dramatically through strong orientation and stretching [34–36], such as occurs under an elongational flow at high field strength. Such a speedup can occur because the highly stretched and oriented chains can more easily pack into a crystal lattice via energetically favorable side-to-side interactions [37] rather than undergo the kinetically slow chain-folding mechanisms to obtain a similar packing. Nevertheless, even at equilibrium, crystal nucleation events can be captured and analyzed via MD, which can shed light on similar nucleation kinetics induced under flow. Indeed, the majority of this work involves realistic atomistic and united-atoms models of PE [33,36–46], which are known to be quite accurate for both the liquid and solid phases due to the simplicity of the interatomic forces. Notable of the NEMD and NEMC studies of FIC are those of Baig and Edwards [40,41,47] and Rutledge and co-workers [36,39,44–46]. These works illustrated important crystal properties and nucleation mechanisms of PE morphologies under shear and extensional flows; however, all of these simulations of FIC were performed on relatively low molar mass PEs with few entanglements under quiescent conditions, and each ranged from 15%–35% undercooling; i.e., *below* the crystalline melting point.

II. METHODOLOGY

Our purpose here is to examine via virtual experimentation an entangled PE melt far *above* its quiescent melting point exposed to a strong elongational flow capable of producing nonequilibrium thermodynamic configurational states [48,49]. This is a similar endeavor to the experimental study of Wang *et al.* [7] to map out a nonequilibrium thermodynamic phase diagram for PEs. Such a suite of NEMD simulations would ultimately allow for the sampling of thermodynamic state points within temperature-stress parameter space, although herein we limit the analysis to a single temperature within the liquid phase under quiescent conditions (450 K). The simulated fluid is a monodisperse, linear polyethylene $C_{1000}H_{2002}$ melt under planar extensional flow (PEF) at elongation rates expressed in terms of the Deborah number $De \equiv \dot{\epsilon}\tau_R$ (where $\tau_R = 137$ ns is the Rouse relaxation time of the liquid [50] and $\dot{\epsilon}$ is the applied strain rate), in the range of $0 \leq De \leq 60$. NEMD simulations were performed in the

NVT statistical ensemble at 450 K and the experimental density of 0.766 g/cm^3 using the Siepmann-Karaboni-Smit (SKS) united-atom potential model [51], which has been used by many research groups to study the quiescent and nonequilibrium structure and dynamics via MD and MC of liquid and solid phase alkanes and PEs (e.g., [38,52–56]). NEMD simulations were performed using the p- $SLLOD$ equations of motion with a Nosé-Hoover thermostat [57–61] implemented within the large-scale atomic/molecular massively parallel simulator (LAMMPS) computing environment developed at Sandia National Laboratory (see [62]). The NEMD equations were integrated using the reversible-reference system propagator algorithm, r-RESPA, with two different time steps: for the small simulation cell in cases where $De > 0.5$, the long time step was 2.35 fs, which was used for the slowly varying nonbonded LJ interactions, and the short time step was 0.47 fs (one-fifth of the long time step) for the fast varying forces including bond-bending, bond-stretching, and bond-torsional interactions. For the large simulation cell and the small simulation cell where $De < 0.5$, the long time step was 4.70 fs and the small time step was 1.176 fs. The relaxation time of the thermostat was set equal to 100 times the long time step for all simulations. PEF simulations were started from an equilibrated configuration at $De = 0$ for a specific $De (\neq 0)$ and run until all statistical indicators revealed that a steady-state condition had been attained; generally, this steady state required less than 10 Hencky strain units to achieve. The topological analysis was performed using the Z1 code developed by Kröger [63], which reduces atomistic configurations to a primitive path network in which the chains are not allowed to cross through each other as the algorithm simultaneously minimizes the contour length of each polymer molecule [64].

A detailed description of the NEMD simulation methodology used in this study can be found in preceding work, including the SKS potential parameters employed as the united-atom potential model of PE [50,65,66] (also see the Supplemental Material of Ref. [49] for a complete description). The only differences herein from the preceding work lie in the size of the simulation cells, parameter values (such as De , T , etc.), time duration, and the statistical ensemble (NVT or NpT). Startup and steady-state PEF simulations were run in the NVT ensemble due to the necessity of using the Kraynik-Reinelt boundary condition [67]. NVT simulations were also used for flow cessation experiments, except when computing the crystal density, potential energy, stress, and/or structure factor and during temperature quenching, in which case the simulation was switched to NpT (at $p = 1$ atm and the T of interest) at the moment of flow cessation and/or quenching. Note that the velocity gradient for planar elongational flow (PEF) takes the form

$$\nabla \mathbf{u} = \begin{pmatrix} \dot{\epsilon} & 0 & 0 \\ 0 & -\dot{\epsilon} & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (1)$$

Equilibrium NpT simulations were also performed at a constant pressure of 1 atm and various temperatures ranging from 350–450 K. These were performed to examine the crystalline properties and quenching of the simulated systems upon cessation of flow. Note that performing steady-state PEF

TABLE I. The simulation cell dimensions: L_x , L_y , and L_z are cell length in the x , y , and z directions, respectively, in angstroms. For the NpT simulations, the box dimensions refer to the initial time instant.

Simulation	L_x	L_y	L_z	Number of particles
$0.06 \leq \text{De} \leq 30$	254	254	84.5	180 000
De = 60	508	508	84.5	720 000
All NpT				

simulations of sufficient time duration in the NpT ensemble is not possible due to the necessity of imposing the Kraynik-Reinelt boundary condition upon the simulation cell. Table I lists the simulations cell sizes and the number of particles for all NVT and NpT simulations performed in this study.

III. RESULTS AND DISCUSSION

From the quiescent MD simulations of the entangled $\text{C}_{1000}\text{H}_{2002}$ melt [50], the disengagement time τ_d was determined as 5270 ns, the number of entanglements per chain) Z (via the Z1 code [63]) was 12.9, and the fully *trans* conformation chain end-to-end distance was 1290.2 Å. Toda [68] measured a melting point (T_m) of 398–403 K for quiescently grown single crystals of a linear PE with molar mass 13 600 g/mol, which is fairly close to the $\text{C}_{1000}\text{H}_{2002}$ ($M_w = 14\,002$ g/mol) linear PE examined herein. Although it has thus far been impossible to determine a precise T_m range for quiescent PE systems via MD, the accrued evidence to date suggests that a viable range would be 385–400 K [37,41,44,45,69]. Hence, the simulated melt temperature (450 K) used in this study is likely greater than 50 K above the values of T_m as determined via experiment and equilibrium MD.

In prior work [48,49], it was demonstrated that the $\text{C}_{1000}\text{H}_{2002}$ melt used in this study exhibited a coil-stretch transition and a configurational microphase separation at low and intermediate deformation rates in PEF up to $\text{De} = 1.5$. At $\text{De} = 3.0$, the fluid exhibited only a highly stretched melt configuration. Here, we examine high De (>10) to determine the liquid's properties at high deformation rates where FIC phases might appear. To quantify FIC, a segmental order tensor is defined as $\mathbf{Q} \equiv \langle \mathbf{t}_i \mathbf{t}_i \rangle - \frac{1}{3} \mathbf{I}$, where $\mathbf{t}_i$ is a unit vector connecting monomers along the chain backbone separated by a single monomeric unit, $\langle \dots \rangle$ denotes an ensemble average over all unit vectors, and $\mathbf{I}$ is the unit dyadic. A scalar order parameter is defined as $q \equiv \frac{3}{2} \lambda$, where λ is the eigenvalue of $\mathbf{Q}$ with the largest absolute value. Note that $q = 0$ for a random (isotropic) system and $q = 1$ for fully aligned chains occupying all *trans* bond configurations. As a general rule of thumb, $q > 0.75$ for a semicrystalline material, $0.65 > q > 0.75$ for an ordered pretransitional liquid state, $0.25 > q > 0.65$ for a stretched liquid, and $q < 0.15$ for a coiled liquid.

Figure 1(a) shows a plot of the order parameter q , mean fractional chain extension x ($\equiv \langle R^2 \rangle^{1/2} / |\mathbf{R}|_{\text{max}}$, where $\mathbf{R}$ is the chain end-to-end vector and the denominator represents the chain length in the fully *trans* configuration; $|\mathbf{R}|_{\text{max}} = 1290$ Å), and the ensemble-averaged SKS potential energy ($\langle E \rangle$) of the $\text{C}_{1000}\text{H}_{2002}$ melt undergoing startup of PEF from

the quiescent liquid state as a function of Hencky strain ($\epsilon_H = \dot{\epsilon} t$, a dimensionless time or strain measurement) at 450 K and $\text{De} = 60$. Mean fractional extension increases rapidly upon inception of flow, approaching a steady-state value of about 0.9, indicating that most chains are almost fully extended. Similarly, the order parameter shows a rapid increase, ultimately approaching a steady-state plateau value of 0.8, which we would nominally consider to be a highly ordered semicrystalline state. On the other hand, the potential energy experiences a commensurate decrease in value, indicating that the molecules are assuming more energetically attractive positions once they become highly extended and oriented along the flow direction [37]. These molecules, once almost fully stretched and aligned along the direction (x) of flow, evidently experience a dramatic energetic reduction by packing into a crystalline lattice structure (as described below) over a timescale of 10 Hencky strain units (corresponding to ≈ 23 ns). Figure 1(a) also reveals that the local segmental ordering (q) occurs relatively quickly (saturating at ≈ 5 Hencky strain units), whereas the potential energy ($\langle E \rangle$) and the overall chain extension (x) are significantly slower (≈ 10 strain units). Taking the difference in enthalpy $\Delta H = H(\text{De} = 60) - H(\text{De} = 0) = \Delta \langle E_{\text{total}} \rangle + \Delta(PV)$, where $\langle E_{\text{total}} \rangle$ is the average potential and kinetic energies, ΔH is calculated to be 283.5 J/g, which is close to the experimental heat of fusion of PE of 290 J/g [3–5].

The pair correlation function $g(r)$ can be calculated from the simulation and the static structure factor $S(k)$, where k is the wave number, can be determined via numerical integration of $g(r)$ as

$$S(k) = 1 + \frac{4\pi\rho_0}{k} \int r[g(r) - 1] \sin(kr) dr, \quad (2)$$

where ρ_0 is the particle-number density ($32.94/\text{nm}^3$ for the quiescent liquid at 450 K; however, ρ_0 changes for semicrystalline states). $S(k)$ can thus be directly compared between simulation and scattering/diffraction experiments [71].

Figure 1(b) presents the structure factors for the simulated $\text{C}_{1000}\text{H}_{2002}$ system and an experimental *n*-alkane (eicosane; $\text{C}_{20}\text{H}_{42}$). $S(k)$ is presented for $\text{C}_{1000}\text{H}_{2002}$ at 450 K under quiescent conditions ($\text{De} = 0$) and at steady state (at $\text{De} = 60$), whereas for eicosane, x-ray diffraction data are shown for a liquid at 315 K [70] and at 298 K for a quiescently grown crystal [37]. Comparing $S(k)$ for the $\text{C}_{1000}\text{H}_{2002}$ melt at $\text{De} = 0$ and 450 K with the experimental structure factor of liquid $\text{C}_{20}\text{H}_{42}$ at 315 K, it is evident that the two curves essentially overlap over the entire range of wave numbers. This is not surprising given the identical atomistic architecture of the two liquids and the fact that their densities are similar at the examined state points (i.e., 0.766 g/cm^3 for PE and 0.81 g/cm^3 for eicosane). This provides evidence of the accuracy of the SKS model for quantifying the physiochemical properties of alkanes and PEs. Both structure factors display the signature characteristics of liquid alkane systems, as described elsewhere [38,70]. Of much more interest, however, are the $S(k)$ profiles for the simulated PE melt at $\text{De} = 60$ and the experimental data of the eicosane crystal. Specifically, the simulated PE at $\text{De} = 60$ shows distinct Bragg peaks at low wave numbers which correspond closely to similar peaks of the experimental eicosane crystal. Keep in mind that the

FIG. 1. (a) Fractional extension (x), order parameter (q), and potential energy ($\langle E \rangle$) of the PE melt versus Hencky strain ϵ_H under startup of PEF at $De = 60$ and 450 K. (b) Structure factor $S(k)$ and intermolecular pair correlation function $g_{\text{inter}}(r)$ (inset) for the simulated PE liquid at equilibrium and under steady-state flow conditions at $De = 60$, along with corresponding x-ray diffraction data of a liquid n -alkane (eicosane at 315 K; $C_{20}H_{42}$) [70] and the quiescently crystallized eicosane crystal analyzed at 298 K [38]. (c) Steady-state snapshot of the entire simulation cell. (d) An 11.8-Å-thick random slab of material viewed down the direction of flow (x axis). (e) Monoclinic crystal lattice structure and the corresponding total pair correlation function for a random 3-Å-thick slab of the simulation cell.

eicosane chains are too short to chain fold when forming a crystal, and hence they fully extend during crystallization and form into triclinic lattices, which have been indexed to lattice dimensions $a = 4.322$ Å, $b = 4.799$ Å, and $c = 27.43$ Å (chain axis) [37], where the c dimension is on the order of the fully extended chain length of 24.5 Å. Consequently, it is clear that the simulated PE has developed a significant degree of long-range crystalline order under high De PEF.

To observe the structure embedded within the $S(k)$ profiles, it is more straightforward to consider the intermolecular contribution to the pair correlation functions $g_{\text{inter}}(r)$, as shown in the inset of Fig. 1(b). Here, $g_{\text{inter}}(r)$ is shown for the simulated PE at both $De = 0$ and $De = 60$. The pair correlation function for the liquid at $De = 0$ displays only a short, broad peak corresponding to the nearest-neighbor shell, and a much smaller and broader peak corresponding to the more disarrayed second-nearest-neighbor shell; this is typical of a disordered liquid. For the $De = 60$ system, however, it is evident that the constituents of the nearest-neighbor shells are arrayed over much larger distances, even beyond

the fourth-nearest-neighbor shell; this is indicative of a much longer-range crystalline (as opposed to liquid) structure.

Figure 1(c) displays a snapshot of the simulation cell for steady-state conditions at $De = 60$, with different colors associated with random individual chains. As evident, the vast majority of chains are almost fully extended, not folded into lamellar structures as occurs under quiescent crystallization of PE. These extended chains are mostly oriented in the flow (x) direction, as can be viewed in Fig. 1(d) for a random 11.8-Å slab of the y - z plane of the simulation cell. In this snapshot, each atom of a PE chain lying within the slab is projected onto a single plane, such that stacked atoms depict chains that are fully aligned in the x direction. Clearly visible within this slab is a semicrystalline material that is predominantly possessing a monoclinic lattice structure with small domains of orthorhombic and hexagonal lattices, all interspersed with small regions of amorphous chains. This fact is consistent with experimental studies that have shown that PE crystallized under mechanical stress tends to pack into monoclinic structures with lattice parameters $a = 8.09$ Å,

FIG. 2. (a) Order parameter q and potential energy $\langle E \rangle$ of the PE melt versus time after cessation of PEF of $De = 60$ at 450 K and with simultaneous quenching by lowering the temperature to 420 and 415 K. (b) The intermolecular pair correlation function g_{inter} at the final t value for all three temperatures.

$b = 2.53$ Å (chain axis), and $c = 4.79$ Å, with a calculated density of 0.997 g/cm³ [10]. (Note that this density was calculated based on the density of the monoclinic ideal crystal; the actual density of the semicrystalline material would be significantly lower.) As shown in Fig. 1(e), the simulated system displays monoclinic lattice indices of roughly $a = 8.7$ Å, $b = 2.6$ Å (chain axis), and $c = 4.5$ Å, with a calculated density of 0.919 g/cm³. Given all of the above observations, the conclusion seems self-evident that a definite semicrystalline state has been formed under high deformation rate PEF at 450 K, roughly 50 K above the quiescent melting point, which is very similar to experimental PE crystals grown under similar highly stressed conditions near the quiescent melting point [10].

A reasonable question to ask is as follows: What happens to the semicrystalline phase formed under PEF after the flow is turned off? This question is addressed with reference to Fig. 2(a), in which $t = 0$ corresponds to the instant of flow cessation in the steady-state PEF at $De = 60$ shown in Fig. 1. If the temperature is maintained at 450 K, both q and $\langle E \rangle$ quickly return to their quiescent melt values, i.e., the crystalline phase formed under flow immediately begins to melt, indicating a completely reversible phase change. Note that $\langle E \rangle$ decays much faster than q ; the large change in energy at small times is indicative of the phase change from the

semicrystalline state to the highly ordered liquid state (≈ 5 ns) whereas the long time decay of q (≈ 50 ns) is mostly due to the reduction in order of the liquid state back to the disordered melt condition. The behavior is similar at 420 K, although the melting process is much slower (approximately 75 ns based on the $\langle E \rangle$); however, if the temperature is lowered sufficiently (to 415 K) at the instant of flow cessation, the crystalline phase formed under flow remains stable indefinitely; q remains practically constant and $\langle E \rangle$ decreases rather than increases (because $\langle E \rangle$ is a decreasing function of T). Hence, the crystalline phase exhibits a distinct melting point (somewhere between 420 and 415 K), which is still significantly higher than the nominal melting point of a quiescently grown crystal (385–400 K). To underscore this point, the intermolecular pair correlation function is shown in Fig. 2(b) for the three T values from Fig. 2(a), where g_{inter} was calculated at the final value of t shown in Fig. 2(a). Note that data at the higher two temperatures are practically identical to those of the quiescent melt [see Fig. 1(b)], whereas those at 415 K display the long-range order noted in Fig. 1(b).

These observations, taken together, provide strong evidence of the stability of the crystalline phase formed under PEF at $De = 60$ for thermally quenched systems; however, they also highlight the reversibility of the phase change at temperatures far above the melting point. As an interesting aside, these results also indicate that an irreversible phase change can be induced from a quiescent melt to a semicrystalline solid phase at sufficiently high De at a constant temperature of 415 K. Furthermore, there is also an evident hysteresis in the temperature profile since stable liquid and semicrystalline phases can both be induced by PEF: at $T = 415$ K and $De = 0$, an isotropic melt is present, whereas by quenching the crystalline phase formed under PEF at $De = 60$ and $T = 450$ K and then turning off the flow ($De = 0$) and simultaneously quenching to $T = 415$ K, a semicrystalline phase is observed.

Steady-state PEF simulations were performed over a wide range of $De \in [0, 60]$ at 450 K, as discussed previously [48,49]. Figure 3 displays the probability distribution functions (PDFs) of the order parameter at selected values of De for steady-state PEF at 450 K. At very low flow rates, the distribution is unimodal with a single peak at a low value of q , representing a coiled liquid state (C). For intermediate values of q , the PDFs become bimodal, with separate peaks corresponding to distinct states composed of highly elongated or tightly coiled chains. This biphasic region (B) consists of two distinct phases, one composed of elliptical domains of coiled molecules surrounded by thin sheets of highly stretched molecules [49]. At higher values of De , the distribution becomes unimodal again as only a liquid phase composed of stretched chains (S) manifests. As De becomes very high ($De = 30$), however, there are actually two steady-state phases, a metastable pretransitional liquid phase (P) and a globally stable semicrystalline solid phase (M). At extremely high De , only the semicrystalline solid phase is observed, exhibiting a unimodal PDF with a narrow peak at a very high value of q . This provides a strong indication of a bifurcating flow diagram for steady-state PEF at high De , as discussed below.

Figure 4(a) presents q and $\langle E \rangle$ as functions of De . Values of the order parameter at each De were taken from the local

FIG. 3. Order-parameter probability distribution functions for steady-state PEF at 450 K and various values of De . The label C denotes a distribution corresponding to a coiled state, B denotes the biphasic state, S denotes a stretched liquid phase, P denotes a pretransitional liquid state, and M denotes a predominantly monoclinic semicrystalline phase.

maxima of the probability distribution functions of q , as shown in Fig. 3. The order parameter displays an S-shaped profile, which is characteristic of a biphasic system at intermediate De . At low De , the macromolecules comprising the melt begin to stretch and orient relative to the direction of flow; however, these molecular chains remain close to the quiescent coiled configurations (C). As De increases, a two-phase system (C and S) develops as chains randomly form domains of coiled configurations surrounded by thin sheets of highly stretched molecules [49]. This biphasic behavior is captured in the probability distribution function of q , as shown in Fig. 3. (As demonstrated previously [48], there also exist metastable states of purely stretched chains that can be accessed via small incremental changes in De from above the upper critical value of the biphasic region; note the red symbols within the C and S region of Fig. 4(a) which overlap the biphasic data points (also see [72]). At high De , the coiled state disappears and only highly stretched chains are evident (S), which eventually form into a monoclinic semicrystalline phase at very high De , as shown in Fig. 1.

The potential energy $\langle E \rangle$ decreases very slowly at low and intermediate De , followed by a rapid decrease after a critical value ($De \approx 30$) is attained. This point demarcates the transition from an ordered, pretransitional liquid state to a semicrystalline solid phase, which occurs concomitantly with an enthalpy of fusion that is captured by the step change in $\langle E \rangle$. An interesting observation from the simulations is that most of the steady-state systems at all De are reversible, although it is possible to achieve a hysteresis in the flow response within certain regions of De space, as discussed above and in Ref. [48]. However, evidently the flow profile bifurcates above the stretched region into a stable semicrystalline solid branch (M) and a metastable stretched pretransitional liquid branch (P). Along the metastable pretransitional liquid branch, steady-state PEF will ultimately induce a random nucleation event that precipitates a rapid crystallization to the

FIG. 4. (a) Order parameter (triangles) and potential energy (circles) as functions of De for steady-state PEF of the PE melt at 450 K. Note that there are two data points located at each value $De = 0.6$ and 1.5 which overlap with each other. These appear as red symbols within the C and S region of the plot. (b) Nonequilibrium phase diagram expressed in q - σ space. C represents the coiled liquid phase, S is the stretched liquid phase, P is the pretransitional liquid state, and M is the predominantly monoclinic semicrystalline solid phase. Note that in both plots, dashed lines represent metastable states whereas solid lines represent stable states, and the lowest data point in each panel is for the quiescent system at $De = 0$, as assigned to $De = 0.01$ (a) and $\sigma = 1.0$ MPa (b) so that they possess finite values on a logarithmic scale. Red symbols in both panels denote data points associated with metastable branches.

M phase; see Figs. 5 and 6 below. At $De = 60$, there does not appear to be a pretransitional liquid state; rather, it appears that both the pretransitional liquid and semicrystalline solid branches converge near this De , thus manifesting a “critical point” where the stretched liquid phase and the semicrystalline phase become indistinguishable from each other, with equivalent values of density and energy (see [73]).

It is apparent from Fig. 4(a) that a nonequilibrium phase diagram can be constructed for the PE melt undergoing PEF at 450 K, as presented in Fig. 4(b). In this panel, q is plotted versus the applied stress $\sigma \equiv \sigma_{xx} - \sigma_{yy}$, revealing a complicated phase diagram. At low values of applied stress, the melt exists solely in a coiled configuration liquid state (C). A two-phase region exists at intermediate σ , with both coiled and stretched phases coexisting with each other (C

FIG. 5. (a) Mean fractional extension x , order parameter q , and mean potential energy $\langle E \rangle$ versus time starting from an arbitrary time instant in PEF of the $\text{C}_{1000}\text{H}_{2002}$ melt at $\text{De} = 30$. (b) The intermolecular contribution to the pair correlation function g_{inter} for the pretransitional liquid and semicrystalline solid phases. (c) The static structure factor of the pretransitional liquid and semicrystalline phases, as computed from $g(r)$ via Eq. (2).

and S ; see [74]). Also shown in the C and S region are two data points (red triangles) associated with purely stretched metastable liquid states, which can be accessed only by decreasing stress gradually from a higher value outside of the biphasic region. As σ increases beyond the two-phase region, the stretched liquid state (S) is followed by a metastable highly stretched pretransitional liquid state (P), which ultimately experiences a phase change to a stable semicrystalline (primarily

FIG. 6. Plots of order parameter (a) and potential energy (b) versus time after application of a change in flow rate from steady-state conditions between various De , as indicated in the panel legends.

monoclinic, M) solid phase at very high σ that occurs with an associated enthalpy of fusion, as evident from Fig. 4(a).

Figure 5(a) plots mean fractional extension x , order parameter q , and mean potential energy $\langle E \rangle$ versus time starting from an arbitrary time instant of steady-state PEF of the $\text{C}_{1000}\text{H}_{2002}$ melt at $\text{De} = 30$ and 450 K. This simulation was performed by instantaneously raising the flow rate to $\text{De} = 30$ from the quiescent melt. [Note: the initial value of time ($t = 0$) of the plot in Fig. 5(a) does not correspond to the instant when De was raised, but rather to an arbitrarily chosen instant of the steady-state flow at $\text{De} = 30$.] Initially, the liquid phase exists for an indefinite period of time, as indicated by relatively low values of the fractional extension and order parameter and high values of the potential energy; however, at some particular instant in time, a phase transition to a solid state is induced by some sudden random nucleation event. At this time, both x and q exhibit a rapid increase, whereas $\langle E \rangle$ decreases almost instantaneously. At the same time, the density increases from the quiescent melt value of 0.766 g/cm³ to about 0.83 g/cm³, indicating a phase transition to a rather amorphous semicrystalline solid phase with a low degree of crystallinity. This phase change, once nucleated, occurs over a timescale of approximately 5 ns. Furthermore, g_{inter} is quite different for the two phases, as shown in Fig. 5(b). The solid phase possesses

much narrower and higher peaks, which are shifted to lower r values than those of the liquid phase. Furthermore, these peaks persist to much higher r values than those of the liquid state, which indicates a packing of the highly stretch chains into a definite crystalline lattice structure, on the average. This statement is confirmed by Fig. 5(c), which displays the static structure factor of both physical states. The pretransitional liquid exhibits the qualitative features of a stretched liquid [38], whereas that of the semicrystalline solid resembles that of the eicosane crystal sample displayed in Fig. 1(b).

It is evident that two phases, liquid and solid, can both be present under steady-state PEF at $De = 30$, depending on the flow history, with the solid phase corresponding to a globally stable state and the liquid phase corresponding to a metastable state. As evident from Fig. 5(a), the metastable liquid phase will generally experience a random nucleation event at some point in time causing a rapid phase transition to the stable solid phase. We could not run the simulation indefinitely, so it is unknown if the reverse phase transformation is possible by continuing steady-state PEF at $De = 30$, but we find this possibility to be highly unlikely. Through additional simulations, we were able to hypothesize a steady-state flow stability curve, as described above [see Fig. 4(a)].

The various phases of the diagrams presented in Fig. 4 are generally reversible with respect to changes in steady-state flow rate (i.e., changes in De). At high values of De , there exists a flow-rate region in which the system will exist in either a pretransitional stretched liquid state or a semicrystalline solid state. Within this region (see Fig. 4), the pretransitional state appears to be metastable, whereas the semicrystalline state appears to be globally stable. Therefore, the pretransitional state can only be accessed via increasing the strain rate (De) from a lower value of De , not by decreasing from a higher value of De . This behavior is exhibited in Fig. 6, where plots of q and $\langle E \rangle$ are shown versus t after a change in the applied steady-state flow rate. For reduction in strain rate of a semicrystalline phase undergoing steady-state PEF at $De = 60$ and 450 K to $De = 15$, the semicrystalline solid phase rapidly melts over 3–4 ns to the stretched liquid state, indicating a reversible phase transition between these two states. For a reduction of strain rate from $De = 60$ to 30, however, there is no change of phase: the semicrystalline solid changes into the semicrystalline solid phase at $De = 30$, not the pretransitional liquid phase at $De = 30$. Hence, it is possible that there exists

a hysteresis effect in the steady-state flow profile of Fig. 4(a). When the pretransitional liquid state undergoing steady-state PEF at $De = 30$ is subjected to an increase in strain rate to $De = 45$, there is a rapid initial transformation (< 1 ns) to the steady-state pretransitional liquid state at the new De number, followed shortly thereafter by a random nucleation event which leads to the (slower) transition (≈ 5 ns) to the semicrystalline phase at the same value of De ($= 45$).

IV. CONCLUSION

The nonequilibrium phase diagram of Fig. 4(b) is very similar to the experimental deductions of Wang *et al.* [7]. Similar to equilibrium thermodynamic phase diagrams, the state changes are primarily reversible in $(T-q-\sigma)$ space; however, metastable “overstressed” and “understressed” states also appear in particular circumstances analogously to supercooled vapor and superheated liquid states on a typical $p-V-T$ diagram. Such a nonequilibrium phase diagram is of great practical interest since it allows in principle for an *a priori* determination of optimal processing conditions for achieving a desired level of crystallinity (as quantified via q). Molecular simulations can provide a useful tool for the development of these nonequilibrium phase diagrams, provided accurate potential models exist for quantifying the atomic-level energetic interactions between architectural units of the polymer macromolecules. Although not pursued here in depth, molecular simulation also offers insight into the nucleation and kinetics of phase changes and the stresses necessary to generate them. New methods to quantify FIC nucleation and kinetics are currently under development [44–46], offering promising pathways for improving our understanding and modeling of these important phenomena in the near future.

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- [74] In the biphasic region, there might be significant error in the value of the nominal stress due to the finite size of the simulation cell. As shown in previous work [48,49], the biphasic state is constantly undergoing transitions of a small number of individual chains between the coiled and stretched configuration states, which implies on short timescales a fluctuation in the system stress which, for sufficiently large simulation cells (or over sufficiently long times), would average out to a steady-state (similar to the equilibrium state of a liquid-vapor system) situation in which configuration shifts between states occurred at equivalent rates.