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Kinetic mechanism of chain folding in polymer crystallization

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I develop a kinetic mechanism to explain chain folding in polymer crystallization which is based on the competition between the formation of stems, which is due to frequent occupations of trans states along the chains in the supercooled polymer melt, and the random coil structure of the polymer chains. Setting equal the average formation time of stems of length d_l with the Rouse time of a piece of polymer of the same arc length d_l yields a lower bound for the thickness of stems and bundles. The estimated lamellar thickness is inversely proportional to the supercooling. The present approach emphasizes the importance of repulsive interactions in polymer crystallization, which are expected to be responsible for the logarithmic lamellar thickening and the increase of lamellar thickness with pressure. An expression for the growth rate for formation and deposition of stems is derived by considering the growth as a dynamic multistage process.

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I. INTRODUCTION

The understanding of polymer crystallization and its theoretical description in the framework of polymer statistics remains a challenging problem since its discovery [1–3]. The classical theories of polymer crystallization [4–6] (see also [7–9] and citations therein) are based on the nucleation theories developed for low molecular weight systems. The lamellar thickness is identified *ad hoc* with the critical size of nuclei, and is not related with the key features of polymers in melts and solutions. Despite enormous interest in polymer crystallization over many decades, the molecular mechanism of polymer crystallization is not understood, and a polymer statistics related description is not available. A review of the research in the field of polymer crystallization in the 1980s can be found in [10]. Many important specific features of polymer crystallization were established in the recent research in the field, which includes experimental work [11–17], computer simulations [18–29], and theoretical studies [30–36] (and citations therein). The progress in the field of polymer crystallization in recent years is reviewed in [37–39].

A new view of polymer crystallization was developed by Strobl, Refs. [40] and [41], who started from the observation that the nucleation based theories are in disagreement with experiments [42–44]. The dependence of the crystallization temperature T on the inverse lamella thickness d_l^{-1} has a larger slope than that of the melting temperature, so that these curves intersect at some temperature (comparable with the temperature of zero growth T_{zg}), which implies that the polymer crystallization can develop only below T_{zg}. The picture proposed by Strobl is based on a multistage character of the crystallization process, and the existence of a mesomorphic layer as precursor to the crystalline phase without however specifying the statistical mechanical origin of his scenario.

The aim of this article is to develop a description of polymer crystallization on a more microscopic level relying on polymer specific properties, e.g., the coil structure of the polymers, and in terms of the relevant microscopic interactions between the monomers in the supercooled polymer melt. I develop a kinetic mechanism of chain folding in polymer crystallization which is based on the competition between the formation of stems and the random coil shape of polymer chains, and is based on the view that the driving force is due to the repulsions between fluctuational stems, which form below a characteristic temperature T_m^0 due to favored occupation of the trans states along chains, and orient in order to minimize the excluded volume. The importance of repulsive interactions in this approach is in accordance with the general evidence of the role of repulsive interactions in liquid-solid phase transformations. The dynamic interplay between forming stems and Rouse dynamics considered in the present approach is expected to manifest itself as specific fluctuations prior formation of polymer crystals, and might be responsible for the mesomorphic layer postulated by Strobl. The relevance of density and orientation fluctuations for polymer crystallization is not new and is the start point of the spinodal decomposition theories for the description of early stages of polymer crystallization in [32] and [31]. To cite [45], "These (*density and orientation*) fluctuations are caused by an increase in the average length of rigid trans segments along the polymer backbone during the induction period." However, the lamellae thickness in these approaches was not brought in connection with polymer properties.

The article is organized as follows. Section II introduces the basic ideas of the kinetic mechanism of chain folding. Section III introduces to the calculation of the growth rate. Section IV summarizes our conclusions.

II. KINETIC MECHANISM OF CHAIN FOLDING

Fluctuational occupations of the trans states in a supercooled polymer melt of interpenetrating chains result in formation of stems possessing a finite lifetime. The repulsion between the neighbor stems forces them to orient parallel to each other in order to minimize the excluded volume and results in formation of bundles. The increase of average occupation of trans states below a temperature T_m^0 increases the lifetime of stems, and enforces the effect of repulsions. The orientations of stems due to their mutual repulsions is similar to the mechanism of the isotropic-nematic transition in lyotropic liquid crystals, where according to Onsager [46] the minimization of the excluded volume is responsible for the transition. The difference between liquid crystals and polymers is that in the case of polymer crystallization the stems do not exist from the beginning, but emerge due to occupation of trans states, and orient and grow due to repulsive interactions between the stems. The present approach is in accordance with simulations in [23] and [24], where chain folding takes place in polymer crystallization by taking into account only repulsive intermolecular interactions. The intramolecular dihedral energies are associated with the differences between, e.g., gauche and trans states, and are responsible for the formation of stems.

The length scale of forming fluctuational stems, which are forced to orient due to mutual repulsive interactions, is determined by the competition between the growth of stems and their relaxation due to Rouse dynamics. For the average formation time of stems we adopt the following phenomenological expression:

$$\tau_s = \frac{d_l}{v_0 + c\Delta T}, \tag{1}$$

where $\Delta T = T_m^0 - T$ is the supercooling and v_0 and c are constants. The term in (1) which is proportional to ΔT means that nonzero supercooling is necessary for stem growth. The nonzero value of v_0 accounts for the effect of an orienting crystal surface on the formation of stems and bundles, and is thus legitimate for secondary crystallization and in heterogeneous nucleation at small supercooling, where the crystal growth begins at seeds. Equation (1) yields for the ratio $G_s = d_l/\tau_s$ the expression $G_s = v_0 + c\Delta T$ for the longitudinal growth rate of stems. A similar expression for the lateral growth rate for small supercooling is well known in the literature (see, for example, [36]). Because stems at the time scale τ_s are expected to form and decompose, the quantity G_s, which has the dimensionality of velocity rate, is a fluctuational quantity, so that the above estimate has to be understood as the typical value of G_s.

The Rouse time of a polymer with arc length d_l is given by

$$\tau_{\rm Rouse}(d_l) = \frac{\zeta d_l^2}{3\pi^2 k_B T_m^0}, \tag{2}$$

where ζ is the monomer friction coefficient ($\zeta \simeq 4.74 \times 10^{-13}$ Ns/m for polyethylene), and we have replaced T in (2) by T_m^0 ($\simeq$135 °C for polyethylene), which is legitimate for small supercooling. The quantity $k_B T_m^0/\zeta$ is the monomer diffusion coefficient. The balance between the stem growth and their spatial orientations, which is determined by the coil structure of the polymer, can be expressed as follows:

$$\tau_s \simeq \tau_{\rm Rouse}(d_l). \tag{3}$$

Resolving (3) with respect to d_l we obtain the characteristic length scale determined by the interplay between the stem growth and the random coil structure of polymer chains as

$$d_l \simeq \frac{3\pi^2 k_B T_m^0}{\zeta c\left(T_c^0 - T\right)}, \tag{4}$$

where $T_c^0 = T_m^0 + v_0/c$. Equation (4) gives an estimate of the lower bound of the lamellar thickness. The experimental lamellar thickness is always larger than that given by Eq. (4), because two subsequent stems along a polymer can fold or form one stem with some probabilities (see Fig. 1). Other processes, e.g., those responsible for lamellar thickening, also result in an increase of d_l. Resolving Eq. (4) with respect to T we arrive at the following relation between the crystallization temperature and the lamellar thickness:

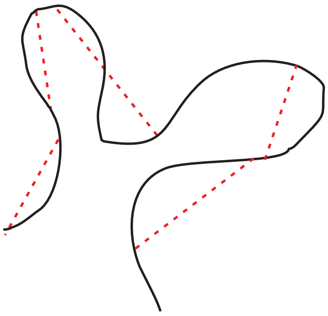

FIG. 1. (Color online) Visualization of fluctuating stems along the polymer coil. The two first and two last stems are likely to constitute longer stems, while the third stem (from the left) is likely to build a fold with the second stem.

$$T = T_c^0 - \frac{3\pi^2 k_B T_m^0}{c\zeta}\frac{1}{d_l}. \tag{5}$$

The $T - d_l^{-1}$ relation without replacing T in the expression of the Rouse time by T_m^0 reads $T = T_c^0/(1 + 3\pi^2 k_B/\zeta c d_l^{-1})$.

Let us compare the orientation of stems in polymer crystallization with the isotropic-nematic transition in lyotropic liquid crystals, where the transition is determined by the condition $\Delta S_{\rm or} + \Delta S_{\rm trans} = 0$, where $\Delta S_{\rm or} = k_B \ln(\Omega_n/\Omega_i) \simeq -k_B$ and $\Delta S_{\rm trans} = k_B n L^2 D$ (n is the density of rods, L is their length, and D is the transverse size) are the decrease of orientation entropy and the increase of the translational entropy, respectively. Because the forming stems in the polymer melt overlap, the above Onsager condition is fulfilled and the stems can directly orient due to repulsive interactions. The van der Waals interactions will be enhanced in bundles and contribute to their stabilization. The present kinetic mechanism of folding favors the switchboard fold surface, which is the consequence of the coil structure of polymers. The formation of stems and lamellae can be visually interpreted as space segregation of the trans and gauche states. It is intuitively expected that the repulsive forces promote a local disentanglement of interpenetrated chains, while the attractive van der Waals interactions favor an amorphous state, and are therefore expected to be only important for stabilization of the bundles and consequently of the lamellar structure. The van der Waals forces between polymer pieces outside the bundles and with the fold surface would result in their adsorption on the latter. Therefore, we expect that the (logarithmic) thickening of bundles and lamellae is also caused by repulsive interactions. The enthalpic contributions to the processes of polymer crystallization are due to (i) the energy difference between trans and gauche states and (ii) the difference of the contribution of van der Waals forces in the amorphous and the lamellar crystalline states.

The condition $T_c^0 > T_m^0$ is a consequence of the assumption $v_0 \neq 0$ in the ansatz in Eq. (1). The van der Waals attraction of formed stems to the surface is expected also to contribute to the nonzero value of v_0. The estimate of $\tau_{\rm Rouse}$ for $d_l = 15$ nm yields, for example, for polyethylene the value of order of

10^{-9} s. Setting τ_s given by Eq. (1) equal to $\tau_{\rm Rouse}$ expresses the interplay between the isotropic-nematic ordering of emerging stems and the coil structure of polymers. The qualitative picture is that the stems grow until the parts of a chain outside a bundle, which are also forced to form stems, will be located on the lateral side of the bundle, and will likely belong to the same bundle (see Fig. 1). Thus, the competition between the growth and orientation of stems and the coil structure of the polymer chains yields that the consecutive stems along the polymer fold and belong to the same bundle. Therefore, the longitudinal growth of the bundles is restricted by the coil structure of polymers, which applies in the Rouse theory on all scales. The slower (logarithmic) thickening of bundles can further occur. At larger supercooling, a smaller stem length will be selected as a result of this interplay. The kinetic mechanism of chain folding suggests that the lamellar thickness d_l follows the change of supercooling. The latter is in accordance with observations made long ago [47]. The chains in polymer melts are Gaussian coils irrespective of the presence of entanglements, so that according to the above picture we expect that entanglements weakly influence the condition (3). However, the influence of entanglements on the growth rate is more complex (see [9], Vol. II, Sec. 9.14, and [48]). The proposed folding mechanism is expected to apply for both primary and secondary crystallization processes. For primary crystallization, where the surface effect is marginal ($v_0 \simeq 0$), one can apply (5) with $T_c^0 = T_m^0$. We expect that the above folding mechanism applies for crystallization from polymer solution too, where the slow collapse due to van der Waals interactions occurs first, which is followed by the fast folding mechanism due to repulsion-orientation coupling after the repulsive interactions become significant as a result of increase of density. We also expect that the above folding mechanism based on trans and gauche conformation states is generic for polymers with more complicated local conformation states.

Equation (3) implies that the folding length d_l is selected in the fluctuational regime associated with the ("microscopic") time τ_s. Because the ansatz given by Eq. (3) is local, the lamellar thickness is expected, in contrast to the growth rate, to be robust with respect to changes of external parameters such as molecular weight, etc. This consequence of the ansatz in Eq. (3) is in accordance with experiments [9]. The lamella thickness d_l lies for melts or solutions in the range between 10 and 20 nm, and shows a weak dependence on the moderate increase of pressure [49], whereas the melting temperature significantly increases under pressure.

The influence of external pressure on polymer crystallization shows [see [50] and [9], Vol. II, Fig. 12.8 (spherulites)] that the melting temperature increases with pressure. The lamellar thickness increases smoothly for moderate pressures [50]. At large pressures the lamellar thickness increases considerably and can achieve a few microns, and approaches that of an extended crystal [16]. A hexagonal phase was observed for large pressure [51], which has at the coexistence curve a lower density than the orthorhombic phase ([52], p. 171). These observations emphasize the importance of the repulsive interactions in polymer crystallization. This is similar to the van der Waals gas where the increase of the pressure shifts the interplay between the repulsive and attractive interactions in favor of the former. The responsibility of the repulsive interactions for stability of the hexagonal phase in polymer crystals is similar to the formation of the triangular lattice of flux lines in type II superconductors, which has its origin in repulsive interactions between the flux lines [53]. The repulsive interactions in the spatially ordered stems in the lamellae facilitates the sliding diffusion, which is expected to be responsible for the increase of lamellae thickness at large pressures [16]. Thus, the increase of the lamellar thickness, the development of the hexagonal phase at high pressures are direct evidences of the importance of repulsive interactions for stem formation in polymer crystallization.

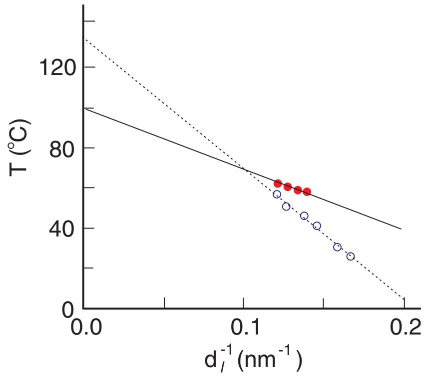

FIG. 2. (Color online) Open circles: experimental data for poly (ϵ -caprolactone) from [54]. Dashes: Our fit of the crystallization line. Filled circles and the continuous line: the melting line.

Since $T_c^0 > T_m^0$ and because of fact that crystallization can occur for $T_c(d_l) < T_m(d_l)$, the crystallization line, which is described by Eq. (5), has to cross the melting line, which is given by the Gibbs-Thomson relation

$$T = T_m^0 - \frac{2\sigma_e T_m^0}{\Delta h}\frac{1}{d_l}, \tag{6}$$

where Δh is the heat of fusion and σ_e is the surface tension of the fold surface.

Note that Eq. (5) with $T_c^0 > T_m^0$ is in accordance with Strobl's analysis of experimental data. The parameters in Eq. (5) can be estimated from the fit to the crystallization line using the experimental data from [54], which is shown in Fig. 2. The ratio v_0/c is equal to $T_c^0 - T_m^0$ and possesses for poly(ϵ -caprolactone), according to Fig. 2, the value 36 K. The slope of (5), which is obtained as $\partial T/\partial d_l^{-1} = -3\pi^2 k_B T_m^0/c\zeta$, possesses, according to Fig. 2, the value -650 K nm. Thus, Eq. (5) with constants $v_0\zeta$ and $c\zeta$ estimated for poly(ϵ-caprolactone) as $v_0\zeta \simeq 610\, k_B$ and $c\zeta \simeq 17\, k_B$ coincides with the crystallization line in Fig. 2 (Fig. 10 in [41], and Fig. 11 in [54]). It is likely that uncertainties of the experimental data are responsible for the not too excellent fit in Fig. 2.

III. GROWTH RATE

We now will consider the time evolution of formation and deposition of stems in the vicinity of the crystallization front. A self-consistent treatment of the mutual correlations of different stems enables one to consider a time-dependent growth rate of one stem $G(t)$. At the time $t = t_l$, when, on average, one stem attaches to the crystal surface, the quantity $G \equiv G(t = t_l)$ is the growth velocity given by the ratio of one attached stem per time t_l. The multistage character of the growth means that the growth occurs by sequences of processes, and implies that $G(t+\Delta t)$ depends on $G(t)$, which enables one to write down the following phenomenological differential master-type equation for $G(t)$ as a function of time:

$$\frac{dG}{dt} = -\gamma G t^{-\alpha}, \tag{7}$$

where $\alpha < 1$ ($\alpha = 1/2$ in the following) and γ is a constant. The factor $t^{-\alpha}$ in (7) takes into account the slow-down of the variation of G with time, which is expected to be due to the random character of the attachment process. The absence of a positive term on the right-hand side of (7) ensures that Eq. (7) does not possess a steady state solution. Note that master-type equations for crystal growth (see, e.g., [8]) describe many stems growth, and do possess a steady state solution. Equation (7) is similar to the multiplicative renormalization of quantities from microscopic to macroscopic scales in the theory of critical phenomena in the case when the coupling constant does not renormalize [55]. Because Eq. (7) is intended to describe the growth rate of one stem it should be integrated from $t = 0$ until the time $t = t_l$, which corresponds to formation and attachment time of one stem to the crystalline front. The integration of Eq. (7) from $t = 0$ until the time $t = t_l$ yields

$$G \equiv G(t_l) = G_0 \exp(-2\gamma\sqrt{t_l}). \tag{8}$$

For comparison, the growth rate for ballistic deposition is independent of t, while G for diffusion controlled deposition is proportional to $t^{-1/2}$. The above equation suggests that t_l is infinite at the onset of crystallization, where the growth rate is zero, i.e., $G(t_l \simeq \tau_s) = 0$ at $T = T_c^0$. Note that in contrast to (8) with $t_l \simeq \tau_s$ the expression for the longitudinal growth rate, which follows from Eq. (1), is given by $G_s = d_l/\tau_s = v_0 + c\Delta T$.

A naive identification of t_l with the time given by condition (3) yields

$$t_l \simeq \tau_s = \frac{d_l}{c\left(T_c^0 - T\right)} = \frac{3\pi^2 k_B T_m^0}{c^2\zeta}\left(T_c^0 - T\right)^{-2}. \tag{9}$$

However, as consequence of the intersection of the crystallization and melting lines given by Eqs. (5) and (6) shown in Fig. 2 the growth rate is nonzero only below the intersection temperature T_{is}. The latter is also in accordance with Strobl's analysis of experimental data [41], where the growth rate becomes zero at the temperature $T_{zg} < T_m^0$. Thus, to take this circumstance into account we adopt (9) with T_c^0 replaced by T_{zg} which yields the time t_g, which is larger than t_l. The difference between t_l and t_g can be understood as follows: While t_l ($\simeq \tau_s$) gives the selection rule for lamella thickness from the comparison of time scales of competing processes (i) stem formation and (ii) coil shape of polymers, and does not make a statement on the time course of the growth process, the time t_g is associated with the real time of formation and attachment of a stem at the crystal surface by taking into account the complicated dynamics, and is therefore much larger than t_l. Note that the orientation time of stems is not included in t_l, but in t_g. Inserting t_g for t_l in (8) we arrive at the following estimate of the growth rate:

$$G = \tilde{G}_0 \exp\left(-\frac{a}{T} - 2\gamma\sqrt{\frac{3\pi^2 k_B T_m^0}{c^2\zeta}}\,\frac{1}{T_{zg} - T}\right), \tag{10}$$

where $G_0 = \tilde{G}_0 \exp(-a/T)$ is introduced to take into account the increase of the relaxation time (viscosity) with decrease of temperature. It follows from Eq. (10) that G possesses a pronounced maximum as a function of $T \leqslant T_{zg}$. Note that in contrast to the Turnbull-Fisher expression [56] for G in nucleation theory, the above expression describes the attachment rate of one stem. To obtain the experimentally measured growth rate one should multiply (10) with the average number of stems formed per time and per volume. The quantity $(2\gamma/\sqrt{c})\sqrt{3\pi^2 k_B T_m^0/c\zeta} = 51\gamma/\sqrt{c}$ is equal to the characteristic temperature T_G appearing in the growth rate $u = u_0 \exp[-T_A^*/T - T_G/(T_{zg} - T)]$ given by Eq. (6) in [57]. The fit for poly(ϵ-caprolactone) yields $T_G = 397\,^\circ\mathrm{C}$, so that one obtains $\gamma/\sqrt{c} \simeq 7.8$.

Note that the existence of two separated time scales τ_s and t_g, which have a clear physical meaning in the present approach, is in accordance with the experimental finding that the growth rate depends exponentially on t_g and γ, which is expected to depend considerably on external parameters such as pressure, molecular weight, entanglements, etc. [9], while the lamellar thickness is determined by the "microscopic" time τ_s, which, as it follows from the definition, is less sensitive to the external parameters.

IV. CONCLUSIONS

To summarize, I developed a kinetic mechanism for polymer folding in polymer crystallization, which is based on the competition between the stem formation, which is the consequence of preferential occupations of trans states in the supercooled polymer melt, their orientation to minimize the excluded volume, and the coil shape of polymer chains. In contrast to the phenomenological nucleation based theories, where the size of critical nucleus is identified *ad hoc* with the lamellar thickness, our approach has the aim to understand the basic features of polymer crystallization in terms of microscopic interactions between the monomers in supercooled polymer melts, and the coil structure of polymers. The present approach suggests that the selection of lamella thickness in polymer crystallization is of kinetic origin, and is determined by the microscopic time scale τ_s. The (logarithmic) lamellar thickening as well as the increase of the lamellar thickness with pressure substantiate the importance of the repulsive interactions in polymer crystallization. The dynamic interplay between forming stems and Rouse dynamics considered in the present approach is expected to manifest itself as an ordered precursor prior formation of polymer crystals, and might be responsible for the mesomorphic layer postulated by Strobl.

Note that the present kinetic mechanism of chain folding is in accordance with results of very recent molecular dynamics simulation [58] on the time sequence of basic processes in formation of the crystalline order: "first the chain segments align, then they straighten, and finally the cluster become denser and local positional and orientational order are established." Further, the finding in [58] that entanglements affect not the nucleation but the growth process is also in accordance with the main conclusion of the present work that there are well separated time scales responsible for selection of the lamellar thickness and formation and attachment of stems, i.e., the crystal growth.

The growth rate for formation and deposition of one stem at the growing surface is derived from the differential master-type equation for the scale dependent attachment rate of one stem, which incorporates the multistage character of the secondary crystallization. The implementation of the picture of polymer folding in polymer crystallization proposed in this article in coarse grained analytic and numeric models will allow more quantitative predictions on polymer crystallization.

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