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Crystallization in ultra-thin polymer films Morphogenesis and thermodynamical aspects

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Abstract

We present a computer model for polymer crystallization in ultra-thin films where chains are considered as dynamical units. In our model chains can change their internal state of order by cooperative motions to improve thermodynamic stability. The interplay between reorganization, enthalpic interactions and the morphology of crystals enables us to explain many properties of growth, morphogenesis and melting of polymer lamellae. We emphasize the relation between the thermodynamic stability of non-equilibrium crystals and morphological features which are beyond the average thickness of the lamellae. In particular, we show that melting of polymers is preceded by reorganization processes and the stability of polymer crystals is not necessarily related to the structure formed at the crystallization point. The simulations allow for the determination of some non-equilibrium properties such as the internal energy and the non-equilibrium heat capacity. We show that multiple-peak melting endotherms result from morphological transformations. The results of our computer simulations are compared with AFM observations in ultra-thin polyethyleneoxide films.

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Keywords: Polymer crystallization; Computer simulation; Thin films; Meta-stability; Morphogenesis

1. Introduction: the non-equilibrium nature of polymer crystals

The outstanding feature of flexible polymers is their high conformational entropy which is the basis for the understanding of many universal features of polymeric systems and plays an important role for the understanding of material properties of soft-matter. A long chain molecule may be even considered as a small thermodynamic system where the entropy is related to the many conformational degrees of freedom (typically an exponential function of the chain length). During crystallization a great part of this conformational entropy has to be reduced and the resulting crystal has to obey strong constraints due the linear connectivity of crystallizing units. As discovered by Keller [1], Till [2] and Fischer [3] polymers crystallize in form of lamellae which are usually much thinner compared to the fully extended chains. Therefore, every chain has to transverse many times through the lamella thus leading to the picture of folded chain crystals, see left part of Fig. 1. The thickness of these crystalline lamellae is usually of the order of 10 nm while its lateral extension can be hundreds of μm. Since the surface free energy of the fold-surfaces (top and bottom surfaces of the lamella) is much higher that that of the lateral surfaces such a structure cannot be the equilibrium form of the polymer crystal [4,5]. A thicker lamella corresponds to a lower free energy and thus lamellae containing fully extended chains are thermodynamically optimal. In fact, for short *n*-alkanes [6] up to a length of about 150 CH_2-units and for polyethylene under high external pressure extended chain crystals can be observed. In the latter case this happens because of the high mobility in the hexagonal phase of polyethylene chains under high pressure/temperature conditions [7]. Thus the extended chain form is not obtained in equilibrium with the melt but due to a specific kinetic pathway from starting with an undercooled melt.

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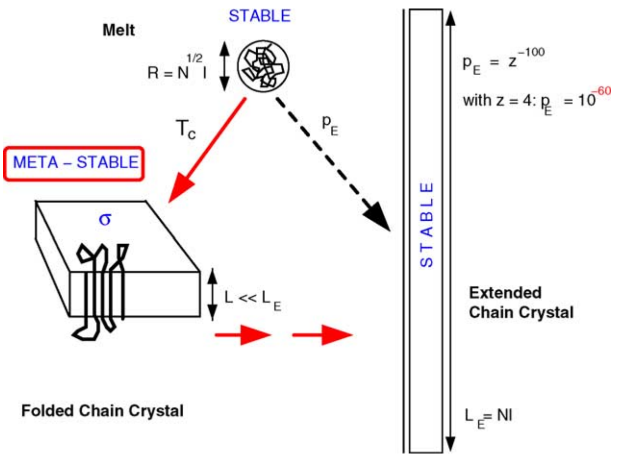

Fig. 1. Sketch of the different phases of a polymer chain. In the melt all possible chains conformations are realized which results in average in a random coil-like shape. In the hypothetical equilibrium state of the crystalline lamella only the stretched chain conformation is realized which corresponds to an enormous decrease of entropy per molecule. The meta-stable lamella is formed by partially stretched chains and at a substantial undercooling.

In order to understand the appearance of meta-stable folded-chain lamellae instead of extended chain lamellae we imagine a phase equilibrium between an extended chain crystal and the corresponding melt. At the hypothetical phase equilibrium detailed balance conditions have to be obeyed. Chains from the melt phase can join the crystal phase with the same rate as chains leave the crystal phase. Moreover, at the true phase coexistence no intermediate states will be favored such as partially folded states. In fact, such states have a lower melting temperature which destroys the reversibility. The situation is sketched in the right part of Fig. 1. The particular problem for chain molecules is now that all crystal units have to be arranged exactly in a straight array and cannot be attached at random points on the growth front. This corresponds to a huge entropy reduction per chain attachment. In the melt phase the chain attains a random coil conformation which corresponds to a typical spatial extension of $R = l\sqrt{N}$, where l denotes Kuhn's segment and N is the number of Kuhn segments in the chain. This corresponds to the state where all possible conformations of the chain can be obtained with equal probability. The number of these conformations can be expressed as

$$Z = z^N, \tag{1}$$

where z denotes the (effective) coordination number (number of orientational states) of each segment. The probability to realize the fully extended chain conformation is therefore given by $p_0 = 2/Z$. Assuming a chain of only 100 units and a coordination number of $z = 4$ we obtain the unphysical small number of about $p_0 = 10^{-60}$. By taking into account a molecular time scale of about $t_0 = 10^{-12}$ s we obtain for the average time of fluctuation from the melt state to the crystalline state: $t = 10^{48}$ s which corresponds to about 10^{40} years. This calculation example shows that detailed balance conditions (and hence a true phase coexistence) may be impossible.

However, if the system is substantially supercooled (up to hundred Kelvin and more) partially ordered chain conformations which can be reached rather easily from the disordered state at the growth front can be stable enough to allow for further growth. In this way only part of the entropy of the chain has to be reduced. The resulting lamellar is then much thinner compared to the extended chain crystal as sketched in the left part of Fig. 1 and will be denoted as folded chain crystals. Because of the excess surface tension of folded chain crystals they are only meta-stable. Spontaneous thickening processes which increase the degree of order of each chain yield to crystal forms of increasing thermal stability.

The problem emerges of how to characterize the meta-stable state of polymer lamellae. In thermodynamic equilibrium the temperature T is the only control parameter if the external pressure is not varied. Non-equilibrium states, however, require the introduction of additional variables in order to characterize them uniquely. These additional variables represent all information about the history of a non-equilibrium system necessary to reproduce a given state uniquely [8]. The traditional representation of the state of polymer lamellae is the diagram which is displayed in Fig. 2. Here, the averaged thickness of the lamella L is taken as the only relevant information about the state of the lamella. Note, that L cannot be adjusted externally *independent of temperature* but is just the consequence of a particular temperature protocol applied to the system.

The states in Fig. 2 have to be understood in the following way. First, a true equilibrium state in the disordered phase has to be prepared (liquid state at a temperature well

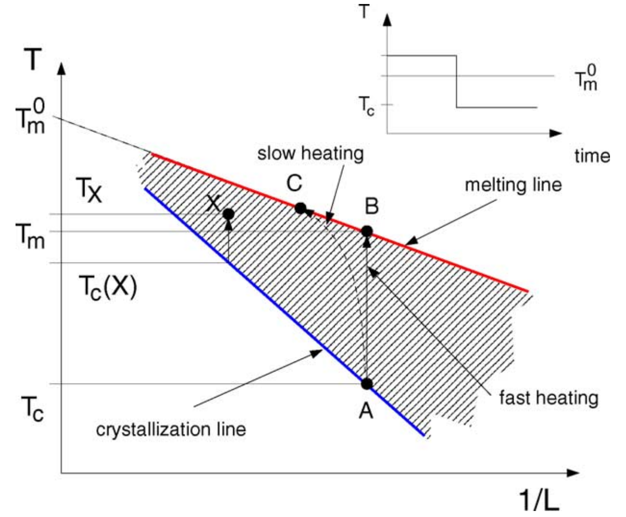

Fig. 2. Sketch of the standard non-equilibrium state diagram for lamellar crystals. States are characterized by the temperature T and the inverse average lamellar thickness $1/L$. Only the hatched region between the crystallization line and the melting line is physically accessible. The lamellar thickness represents the history of the polymer crystal.