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Discussion

Reply: Discussion of problems of non-equilibrium thermodynamics of polymers

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We thank Prof. Wunderlich for his thoughtfull comments [1] to our contribution [2]. In the following we would like to address a few points raised by Prof. Wunderlich.

1. High conformational entropy

What distinguishes macromolecules from other systems and even justifies a unique branch of (theoretical) physics? We think that the universality of macromolecules, in particular the model of flexible chains as expressed in several mathematical formulations, is the origin of this physical understanding of polymer systems. The conformational entropy together with the definition of a universal "statistical" segment and a dimensionless universal chain length (in units of statistical segments) is unique to macromolecules and makes it possible to abstract from chemical details. Novel properties as diverse as rubber elasticity, the osmotic pressure in semi-dilute solutions or adsorption of macromolecules (to note only a few examples) originate in the interplay between conformational entropy and other interactions imposed on the monomeric units. Thus, it is fair to say that conformational entropy is the most characteristic feature of flexible molecules. When polymers crystallize conformational entropy (better to say conformational disorder) plays a new role. It is no more the simple equilibrium properties which are of importance here but the kinetic pathways between disordered and ordered states which dominate the crystallization processes. For instance, a polymer chain has not only to reduce its entropy during crystallization but also the succession of monomeric units along the chain has to be respected in order to obtain a stable crystal form. This influences the time needed for crystallization rather than the entropy of fusion (crystallization) as compared to low-molecular systems. The latter being controlled by many other properties of the system and can be widely different for various types of polymers. In this respect, conformational disorder plays a new, *kinetic* role in polymer crystallization. The mathematical tools which were developed for equilibrium properties of amorphous polymers provide rather limited possibilities to describe polymer crystallization.

2. Phase equilibrium for semicrystalline polymers

The state diagram sketched in Fig. 2 in our article corresponds to a non-equilibrium phase diagram where the inverse averaged lamellar thickness plays the role of a non-equilibrium variable in the sense of Bridgeman [3]. The main goal of our presentation was to emphasize the role of history (processes) which leads to a given state of a polymer crystal. In particular, the averaged lamellar thickness is a result of the preparation of the crystalline state (for instance given by the degree of under-cooling in a rapid quench). For a one-

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parameter set of processes (for instance characterized by the temperature of the quench) this leads to a well-defined curve in the non-equilibrium state diagram. The fact that polymer crystals are formed far from thermodynamic equilibrium is represented by a melting temperature which is higher than the crystallization temperature. This is a primary observation in polymer crystallization. We argue (in agreement with empirical observations) that the state of formation of a polymer crystal is not stable and is prone to reorganization such as spontaneous increase of the averaged lamellar thickness. Thus, different processes such as heating jumps followed by annealing processes lead to different traces in the state diagram. In general, annealing steps (thus slower heating) can be used to increase the observed melting temperature [4]. The representation of Fig. 2 is based on empirical arguments and we fully agree with Prof. Wunderlich that it has to be extended to more than one non-equilibrium parameter in order to characterize the non-equilibrium states of polymer crystals. In our manuscript, we have shown for crystallization in quasi-two-dimensional systems that indeed more than one length scale is necessary to characterize the crystalline state.

3. Shapes of equilibrium crystal

The Wulff construction is a splendid argument to demonstrate that folded chain crystals are not equilibrium states of polymers. Otherwise, the excess free energy of the fold-surface has to be orders of magnitude lower that that of the lateral surfaces to reflect the observed lamellar shape! On the other hand, the Wulff construction is based on two basic arguments: First, surface roughening is not an important contribution to the surface free energy excess and second, the formation of the thermodynamic optimal shape is not hindered by kinetics or defects such as chain ends in case of polymer crystals. As an example, extended chain crystals of short n-alkanes do not correspond to Wulff’s shape because an increase of the thickness is limited by the chain length and stacking of chains results in an additional interface free energy contribution. In case of annealing of polymer crystals close to the melting point, surface roughening will be important and rounded shapes can be expected as well. Examples for this state are given in our manuscript (droplet phase in Fig. 16 and the corresponding experimental result given in Fig. 19). On the other hand, our argument does not change if the spheres in the sketch are replaced by rounded blocks. The stability limit for melting of the reorganized crystal is given by the morphology (surface excess free energy) before melting.

4. Mechanisms of crystallization

The difference between internal an external degrees of freedom (in particular for polymer molecules) can be easily defined. External degrees of freedom correspond to unconfined motions such as center of mass diffusion while internal degrees of freedom are bounded. Note that in this definition also rotations would belong to internal degrees of freedom. This is reflected in the theory of polymer dynamics where the zero Rouse mode (in the Rouse model) corresponds to the translational motion and plays a special role in the treatment of chain dynamics. The special role of external degrees of freedom, i.e. translational motion is manifested in many practical situations. An example is the mixing entropy of polymers which is determined by external degrees of freedom only. Therefore, the interaction strength per chain between different monomeric units in a perfectly mixed blend is proportional to the degree of polymerization but the entropy loss due to demixing is independent of N which explains the strong incompatibility of most polymer blends. According to this definition a crystal has only three external degrees of freedom which correspond to its center of mass motion. All external degrees of freedom of the constituent molecules are thus transferred into internal degrees of freedom of the crystal, but are of course not lost.

5. Crystallization in ultra-thin films

Thin polymer films attract the polymer community since several years and various techniques for their preparation have been developed. A qualitative new situation is encountered when the film reduces to the size of a single molecule. This motivates the term “ultra-thin” in our definition. Here, molecules usually form large loops and penetrate each other. Adsorption on rough (not atomically flat) substrates leads to such states. Kinetic effects can lead to even thinner films, in particular if the molecules are strongly adsorbed to the substrate and adsorption can be regarded as a sequential process out of a dilute solution. A very special situation is epitaxial growth. In our case the substrate is atomically rough and the adsorption strength is moderate. Thus, we assume that loops are formed in the adsorbed layer. The perpendicular orientation of the stems is usually observed when the film is ultra-thin. Here, growth of crystals with stems parallel to the substrate would result in a high additional excess surface free energy. This is due to the very narrow width of the edge-on lamella where the growth in the direction perpendicular to the substrate is limited. In fact, such objects would correspond to quasi-1-dimensional threads rather than to lamellae. This geometric argument might exclude edge-on growth of polymer crystals from ultra-thin films. Note that edge-on growth can be preferred in thicker films because the alignment of chains might be facilitated in the niche formed by the edge-on crystal and the substrate.

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