

NUCLEATION IN POLYMER CRYSTALLIZATION

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Acknowledgments

References

I. INTRODUCTION

When a metastable liquid of small molecules undergoes a phase transition into a crystal, the mechanism of this ordering process [1] is recognized to be nucleation and growth. As sketched in Figure 1.1(a), nuclei of crystalline phase with linear dimension larger than a critical value r_c are formed by thermal fluctuations that then offer surfaces for further growth into full-fledged crystalline phase. The rate of nucleation of viable nuclei and the system-dependent value of r_c are determined by the extent of metastability [1].

Now, what happens to the nucleation and growth process if the small molecules are tethered together to form polymer chains, as sketched in Figure 1.1(b)? Clearly the ability of different portions of a long polymer chain to participate in different initial nuclei inevitably prohibits a polymer melt from forming a perfect polymer crystal. This results in a semicrystalline state. Starting from the original declaration [2] by Storks in 1938 that chains must fold back and forth in the formation of crystals, there has been a cultivation of rich phenomenology [3–9].

The modern availability of sensitive experimental techniques using synchrotron radiation and atomic force microscopy, and fast computers for molecular modeling, has spurred recent intense interest in following the mechanism of polymer crystallization. In spite of the heroic efforts by the

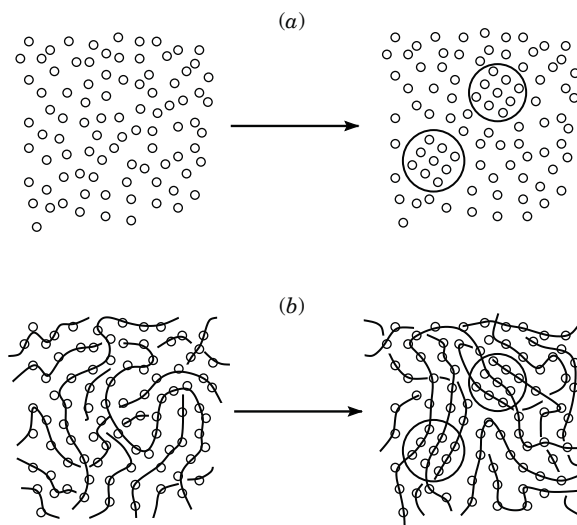


Figure 1.1. Effect of chain connectivity on nucleation.

polymer community since the early 1940s, the fundamental mechanism of polymer crystallization is still not understood. From a conceptual point of view, polymer crystallization requires an understanding of the free-energy landscape with many metastable states frustrated by entropic barriers separating them.

Among the numerous challenges faced in understanding polymer crystallization, the present review focuses only on the following issues, which are directly pertinent to the phenomenon of nucleation in polymer crystals.

A. Spontaneous Selection of Lamellar Thickness

Independent of crystallization conditions, whether from solutions or melt, the polymer molecules crystallize into thin lamellae. The lamellar thickness is about 10 nm, about two orders of magnitude smaller than values allowed by existing equilibrium considerations. This is in contrast to the case of crystallized short alkanes, where the lamellar thickness is proportional to the length of the molecules. Clearly the chains in the case of polymers should fold back and forth in the lamellae to support the experimentally observed lamellar thickness. It is believed in the literature [3–9] that the lamellar thickness is kinetically selected and that if enough time is permissible, the lamella would thicken to extended chain crystal dimension. What determines the spontaneous selection of lamellar thickness?

B. Nucleation in the Very Early Stage

There is considerable experimental evidence [9–15] for density fluctuations at very early times of crystallization before the full crystallographic features can be detected. What are the molecular origins of structural development in the primordial stage of polymer crystallization?

C. Kinetics at Growth Front

The problem of how a sufficiently large lamella grows further has attracted most of the theoretical effort [16–22] in the past and a vast amount of experimental data is available. In the analytically tractable model [4,8,16] of Lauritzen and Hoffman (LH) and further generalizations [17,19], the growth occurs via crossing another nucleation barrier associated with the formation of one stem of the polymer (of contour length comparable to lamellar thickness) followed by an essentially downhill process of lateral spreading by other stems. What are the molecular details of the barrier for the attachment of a stem at the growth front and what constitutes the stems?

D. Flow Effects

When polymers are crystallized under flow (stirring, extensional, etc.), the ubiquitous morphology [23] is the “shish-kebab” structure, consisting of central core (shish) surrounded by lamellae (kebabs) attached along the shish. What is the underlying mechanism behind the formation of “shish-kebab” structure?

Before addressing these fundamental questions, we present a brief review on phenomenology, classical thermodynamics, and kinetic models of polymer crystallization. Advances made recently (as of 2003) using molecular modeling are reviewed next.

II. PHENOMENOLOGY

Polymer crystals exhibit a myriad of morphologies with rich hierarchies of molecular organization, in distinct contrast to nonpolymeric systems. The chain connectivity plays a dramatic role in controlling the ordering process and the resulting semicrystalline morphologies, and has historically led to the emergence of the polymer age. Heroic efforts by the polymer community with exquisite structural elucidations since the early 1940s have resulted in rich phenomenology. Here we present only the very basic facts which are pertinent to the concept of nucleation.

A. Lamellae

When polyethylene is crystallized from its solutions in *p*-xylene at suitable temperatures (around 70°C), single crystals of polyethylene are formed as

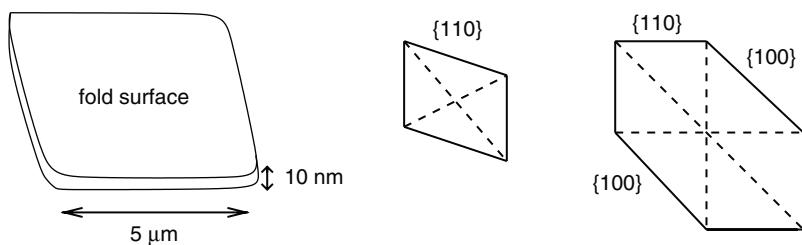


Figure 1.2. Sketch of a lamella and growth sectors.

lamellae. These are roughly 10-nm-thick platelets with regular facets, as sketched in Figure 1.2. As more molecules accumulate at the growth front, the lateral dimensions increase, by keeping the lamellar thickness (L) at 10–20 nm. Further, the small spontaneously selected lamellar thickness is essentially independent of molecular weight, for medium and high molecular weights.

The small ratio of lamellar thickness to the contour length of a polymer molecule clearly implies that chains must fold back and forth into stems with chain direction essentially perpendicular to the lamellar surface, as originally declared by Storks. The large surfaces of the lamellae containing the chain folds are called *fold surfaces*, and the thin surfaces are called *lateral surfaces*.

Crystallographic investigations showed that the polyethylene lamellae have growth sectors with orthorhombic crystal symmetry. For example, in the case of lamellae crystallized from 0.01% polyethylene in *p*-xylene at 70°C, there are four growth sectors, each with $\{110\}$ planes [Fig. 1.2(b)]. If crystallization is carried out at higher temperatures, new growth sectors with $\{100\}$ planes form. Different growth sectors have different thermal stability and growth rates. Further careful examination revealed that, for polyethylene lamellae, the chain axis is tilted at about 30° with respect to layer normal. This chain tilt results in a pyramid shape for the single-crystal lamella.

If crystallization is carried out from concentrated solutions, multilamellar aggregates are formed. In particular, melt crystallization of polyethylene gives bunched-up lamellae with an overall spherical symmetry. The space between the lamellae contains uncrystallized amorphous polymer. These objects are called *spherulites*, and their radii grow linearly with time, in spite of their intricate morphological features [9]. Another remarkable feature of spherulites formed by linear polyethylene is that they are gigantically chiral, although the molecules are achiral.

B. Lamellar Thickness

The initial lamellar thickness (L) depends on the degree of supercooling ΔT ($= T_m^0 - T_c$, where T_m^0 is the equilibrium melting temperature and T_c is the

crystallization temperature) according to [24]

$$L = \frac{C_1}{\Delta T} + C_2 \quad (1.1)$$

where C_1 and C_2 are system-dependent constants.

When the lamellae are annealed at a given temperature, they thicken with time. The thickening is usually continuous and L increases logarithmically with time. However, there are several examples, where the lamellar thickness increases in a stepwise manner. For example, the initial lamella may contain chains each with four folds (five stems). As thickening process continues, the lamellar thickness jumps discontinuously to three folds, and so on. This phenomenon is referred to as *quantized thickening* [25].

C. Crystallization Kinetics

As an example, we consider crystallization of polyethylene from a melt. As mentioned above, crystallization proceeds with the initial formation of isolated spherulites, which then grow until their mutual impingement with further slow crystallization. Time (t)-dependent measurements [26] of the density of the crystallizing melt at different temperatures are given in Figure 1.3 as a plot of degree of crystallinity versus logarithm of time.

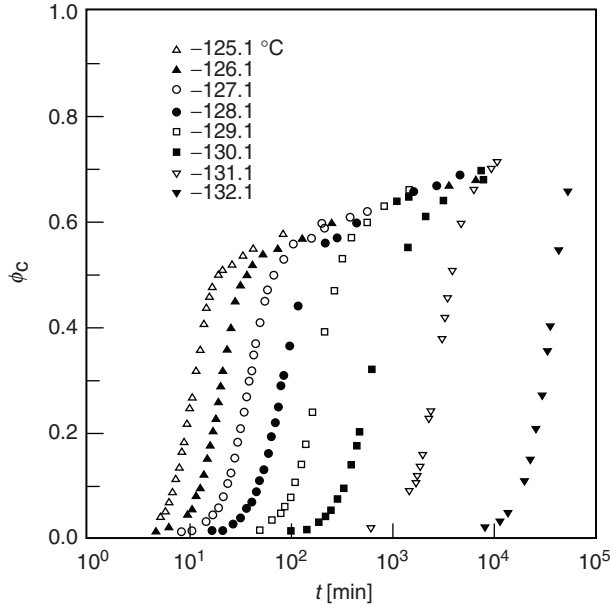


Figure 1.3. Degree of crystallinity ϕ_c versus time for linear polyethylene (molecular weight = 284,000) [26].

A decrease in the crystallization temperature results in a rapid increase in crystallization rate. All curves have similar sigmoidal shape. There is an initial induction time required for the formation of spherulitic nuclei, followed by a period of accelerated crystallization during which spherulites grow in radius. When the spherulites begin to touch each other, crystallization rates slow down again. Eventually, same degree of crystallinity is achieved, essentially independent of crystallization temperature. Complete crystallinity is almost never achieved, and the final degree of crystallinity is molecular-weight-dependent.

During the growth stage of spherulites, radial growth rate is a constant. This growth rate constant depends on temperature nonmonotonically, as illustrated in Figure 1.4 for spherulites of isotactic polystyrene [27]. As the supercooling is increased, growth rate increases first and then decreases after reaching a

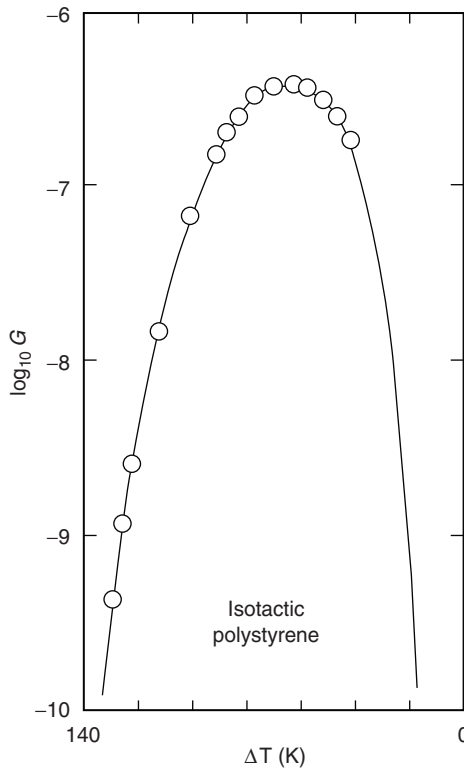


Figure 1.4. Dependence of spherulitic growth rate (cm/s) on supercooling (ΔT) for isotactic polystyrene [27].

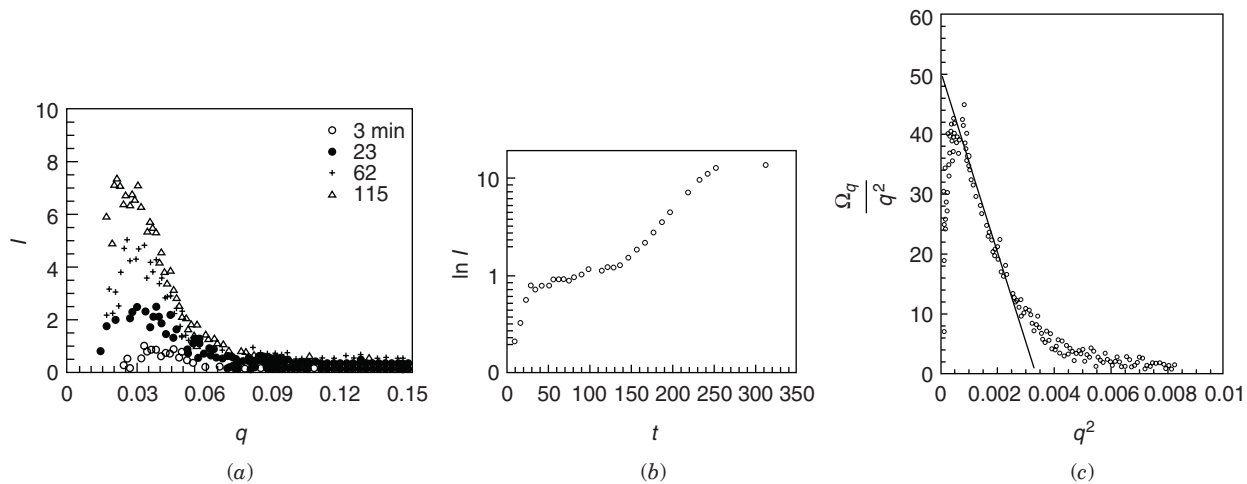


Figure 1.5. (a) Wavevector dependence of scattering intensity [10] at different times; (b) time dependence of integrated intensity [10]; (c) wavevector dependence of Ω_q/q^2 [14].

maximum value. As we will see below, the increase in rate with supercooling is due to nucleation processes and the decrease in rate with supercooling (i.e., decrease in temperature) is due to slowing down of diffusion of polymer chains.

At very early times of crystallization, there is considerable experimental evidence [9–15] for density fluctuations before the full crystallographic features can be detected. The major evidence is the appearance of a peak (at $q_{\max}$) in intensity, $I(q, t)$, of the small-angle X-ray scattering versus scattering wavevector $\mathbf{q}$ at an early time t , before any signal in the wide-angle X-ray scattering, for a wide variety of polymers. In the early stage, the integrated intensity grows exponentially with time, and $q_{\max}$ is proportional to $(\Delta T)^{1/2}$ (where ΔT is the supercooling). The rate (Ω_q) of growth of $I(q, t)$ divided by q^2 decreases linearly with q^2 for intermediate values of q , as shown in Figure 1.5.

These observations are analogous to those of phase-separating mixtures by spinodal decomposition mechanism, leading several researchers to invoke the idea that the early stage of polymer crystallization is spinodal decomposition.

D. Effect of Flow

In general, if the chains are oriented by external forces, the melting temperature is increased [28]. Further, it has been known for a long time that complex, “row-nucleated” structures occur if polymer solutions or melts are crystallized in the presence of flow [29,30]. These so-called shish-kebabs (sketched in Fig. 1.6), consist of a central fiber core, *shish*, surrounded by lamellar crystalline structures, *kebabs*, periodically attached along the shish.

The fiberlike crystalline structures (shish) are highly stable to the point that they can be superheated [31]. Therefore, it is believed that the core of the shish is formed by crystallization of completely stretched polymer chains. The kebabs are believed to be folded-chain lamellar structures. The direction of growth of the kebabs is normal to the shish. The chain alignment in the kebabs is believed to be parallel to the shish. Similar structures are obtained by crystallization in polymer melt films exposed to orientational deformation [32,33]. These “two-dimensional” shish-kebabs also consist of a central fiber, shish, and periodically attached “linear” kebabs, with growth direction normal to the shish.

III. THERMODYNAMICS

A. Melting Temperature and Supercooling

Consider a polymeric liquid where each polymer chain contains N repeat units. The chemical potential per repeat unit μ_u^0 in the liquid phase is

$$\mu_u^0 = h^l - Ts^l \quad (1.2)$$

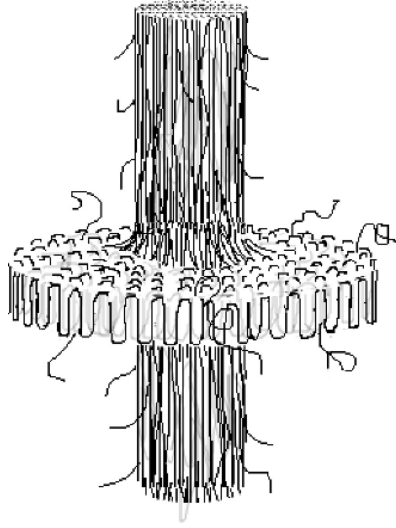


Figure 1.6. Sketch of shish-kebab morphology.

where h^l and s^l respectively are the corresponding enthalpy and entropy per repeat unit at the temperature T . Analogously, the chemical potential per repeat unit in the crystalline phase is

$$\mu_u^c = h^c - Ts^c \quad (1.3)$$

In writing these equations, effects of chain ends are not explicitly taken into account. At the equilibrium melting temperature T_m^0 , we obtain

$$\mu_u^c = \mu_u^0 \quad (1.4)$$

which results in

$$T_m^0 = \frac{\Delta h}{\Delta s} \quad (1.5)$$

Here, $\Delta h (\equiv h^l - h^c)$ is the latent heat of fusion and $\Delta s (\equiv s^l - s^c)$ is the entropy of fusion, both per repeat unit.

This simple result for the equilibrium melting temperature offers a guidance in the chemical design of elastomers (low T_m^0) and engineering plastics (high T_m^0). For example, if the chain backbone is more flexible, then the change in

entropy associated with the transformation of more flexible conformations to rigid chain conformations in the crystal is large and consequently leads to lower values of T_m^0 . Another example is polymer crystallization under elongational flows. In the presence of such flows, the polymer chains are already stretched (with lower conformational entropy) so that Δs accompanying crystallization is small. This is directly responsible for higher T_m^0 . Consequently, the crystallization temperature of a polymeric liquid in elongational flows is higher than that in the quiescent state. For temperatures greater than T_m^0 , μ_u^0 is lower than μ_u^c and the liquid phase is the stable phase. For $T < T_m^0$, the crystalline phase is more stable and the thermodynamic force for its formation is $\mu_u^0 - \mu_u^c$, given by

$$\mu_u^c - \mu_u^0 = -(\Delta h - T\Delta s) \quad (1.6)$$

Substituting Δs from Eq. (1.5), we obtain

$$\begin{aligned} \mu_u^c - \mu_u^0 &= -\Delta h \left(1 - \frac{T}{T_m^0} \right) \\ &= -\Delta h \frac{\Delta T}{T_m^0} \end{aligned} \quad (1.7)$$

where $\Delta T (\equiv T_m^0 - T)$, is the supercooling. Therefore, the free energy of the crystalline phase is increasingly lowered as the supercooling increases (i.e., as T decreases). We define the “gain in free energy” associated with the formation of the crystalline phase as

$$\begin{aligned} \mu_u^c - \mu_u^0 &= -\Delta\mu \\ \Delta\mu &= \Delta h \frac{\Delta T}{T_m^0} \end{aligned} \quad (1.8)$$

B. Depression of Melting Point

When a polymeric liquid contains a noncrystallizable component such as another polymer or impurity, the equilibrium melting temperature T_m is substantially different from T_m^0 and can be readily expected from thermodynamic arguments. As a specific example, consider a blend of n_1 chains of N_1 segments and n_2 chains of N_2 segments. According to the classical Flory–Huggins theory [34], the free energy of mixing is given by

$$\frac{\Delta G}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_1 N_1 \phi_2 \quad (1.9)$$

where χ is the chemical mismatch parameter, R is the gas constant, and

$$\begin{aligned}\phi_1 &= \frac{n_1 N_1}{n_1 N_1 + n_2 N_2} \\ \phi_2 &= \frac{n_2 N_2}{n_1 N_1 + n_2 N_2}\end{aligned}\tag{1.10}$$

For simplicity, we have taken the volume of each segment to be the same for both types of polymers, so that ϕ_1 and ϕ_2 are volume fractions. The case of polymer solutions is the special case of $N_1 = 1$. It follows from Eq. (1.9) that the chemical potential of the second component (assumed to be crystallizable) is given by

$$\frac{\mu_2 - \mu_2^0}{RT} = \left(\frac{\partial(\Delta G/RT)}{\partial n_2} \right)_{n_1, T} = \ln \phi_2 + \left(1 - \frac{N_2}{N_1} \right) (1 - \phi_2) + \chi N_2 (1 - \phi_2)^2\tag{1.11}$$

where μ_2^0 is the chemical potential per chain in the pure liquid state. The chemical potential per mole of repeat units of the crystallizable polymer in the liquid phase of the blend is

$$\mu_u^l - \mu_u^0 = \frac{\mu_2}{N_2(v_1/v_u)} = RT \left(\frac{v_u}{v_1} \right) \left[\frac{\ln \phi_2}{N_2} + \left(\frac{1}{N_2} - \frac{1}{N_1} \right) (1 - \phi_2) + \chi (1 - \phi_2)^2 \right]\tag{1.12}$$

Here, v_u and v_1 are the molar volumes of the repeating unit and a segment of the noncrystallizable first component, respectively. At the melting temperature T_m of the second polymer component in the blend

$$\mu_u^c = \mu_u^l\tag{1.13}$$

Note that at T_m^0 , $\mu_u^c = \mu_u^0$. Subtracting μ_u^0 from both sides of this equation and substituting the results of Eqs. (1.8) and (1.12) at T_m , we get

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta h} \frac{v_u}{v_1} \left[\frac{1}{N_2} \ln \phi_2 + \left(\frac{1}{N_2} - \frac{1}{N_1} \right) (1 - \phi_2) + \chi (1 - \phi_2)^2 \right]\tag{1.14}$$

In the case of polymer solutions, $N_1 = 1$ and $N_2 \gg 1$, we obtain

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta h} \frac{v_u}{v_1} (\phi_1 - \chi \phi_1^2)\tag{1.15}$$

For ideal solutions ($\chi = 0$), the melting temperature of the crystallizable polymer from solutions follows as

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta h} \frac{v_u}{v_1} \phi_1 \quad (1.16)$$

where ϕ_1 is the volume fraction of the solvent. Therefore the melting temperature is depressed by the presence of the diluent. Equation (1.15) has been used in earlier studies to determine the χ parameter and the equilibrium melting temperature T_m^0 .

In the case of blends, $N_1 \gg 1$ and $N_2 \gg 1$, Eq. (1.14) gives

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta h} \frac{v_u}{v_1} \chi \phi_1^2 \quad (1.17)$$

For homogeneous blends, $\chi < 0$ and consequently the presence of another noncrystallizable polymer depresses the melting point of a polymer.

Equation (1.14) is of general utility, where the first component can be any impurity instead of a solvent. As an example, even for the case of a pure polymer, the chain ends do not readily get incorporated into the crystal structure. Therefore the chain ends can be treated as impurities. Taking $\phi_1 = 2/N$ and v_1 to be the molar volume of the end group, the melting temperature increases with the molecular weight of the polymer according to

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta h} \frac{v_u}{v_1} \frac{2}{N} \quad (1.18)$$

in qualitative agreement with experimental observations [35]. Similarly, if the polymer chain contains branch points, then T_m is lowered in qualitative agreement with Eq. (1.16), where ϕ_1 is the volume fraction of the branch points. Another example is the class of copolymers consisting of crystallizable and noncrystallizable monomers. In this context, Eq. (1.16) leads to

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta h} \ln p \quad (1.19)$$

where p , called the *sequence propagation probability*, is the probability that a crystallizable unit is succeeded by another such unit. For random copolymers, $p = x_2$, where x_2 is the mole fraction of crystallizing unit. For blocky copolymers, $p > x_2$, and for alternating copolymers, $p < x_2$. The predictions of Eq. (1.19) on the sequence-dependence of T_m for copolymers have been remarkably successful [35].

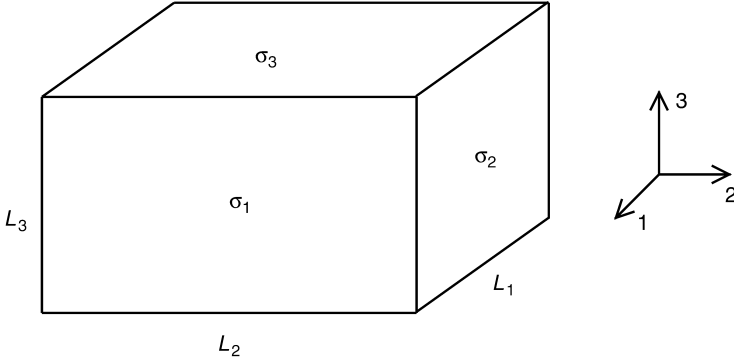


Figure 1.7. Sketch of a finite crystal.

C. Equilibrium Crystal Shape

Consider a finite crystal of thickness L_i along the i th axis, as sketched in Figure 1.7. Let σ_i be the surface free energy per unit area of surfaces perpendicular to the i th axis.

The free energy of formation of this crystal from the pure melt is

$$\Delta G = -V\Delta\mu + 2\sigma_1 L_2 L_3 + 2\sigma_2 L_3 L_1 + 2\sigma_3 L_1 L_2 \quad (1.20)$$

where $V(= L_1 L_2 L_3)$ is the volume of the crystal and $\Delta\mu$ is now per unit volume. We wish to minimize ΔG to determine the equilibrium shape. Because of the volume constraint, L_3 can be eliminated and then ΔG minimized with respect to L_1 and L_2 . Eliminating $L_3(= V/L_1 L_2)$, Eq. (1.20) gives

$$\Delta G = -V\Delta\mu + \frac{2\sigma_1 V}{L_1} + \frac{2\sigma_2 V}{L_2} + 2\sigma_3 L_1 L_2 \quad (1.21)$$

Minimizing ΔG with respect to L_1 and L_2 for fixed V gives

$$\begin{aligned} \frac{\partial \Delta G}{\partial L_1} &= -\frac{2\sigma_1 V}{L_1^2} + 2\sigma_3 L_2 = 0 \\ \frac{\partial \Delta G}{\partial L_2} &= -\frac{2\sigma_2 V}{L_2^2} + 2\sigma_3 L_1 = 0 \end{aligned} \quad (1.22)$$

which simplifies to

$$\frac{\sigma_1}{L_1} = \frac{\sigma_2}{L_2} \quad (1.23)$$

By repeating the above procedure, but now eliminating L_2 instead of L_3 , we obtain $\frac{\sigma_1}{L_1} = \frac{\sigma_3}{L_3}$. Therefore, based on only thermodynamic arguments, the dimensions of an equilibrium crystal in different orthogonal directions are proportional to the surface free energies of the perpendicular surfaces:

$$\frac{L_1}{\sigma_1} = \frac{L_2}{\sigma_2} = \frac{L_3}{\sigma_3} \quad (1.24)$$

For the specific case of a lamella (with thickness $L = L_3$, and lateral dimension $L_1 = L_2$)

$$\frac{L}{L_1} = \frac{\sigma_3}{\sigma_1} = \frac{\sigma_f}{\sigma_l} \quad (1.25)$$

The estimated value of the free energy of the fold surface ($\sigma_3 \equiv \sigma_f$) is 90 mJ/m^2 for polyethylene, whereas that of the lateral surface ($\sigma_1 \equiv \sigma_l$) is 15 mJ/m^2 . Therefore we expect the lamellar thickness to be 6 times larger than the lateral dimension, specifically, a cylinder shape, instead of a disklike shape. This is in stark contrast to the facts described in Section II. The thermodynamic estimate of lamellar thickness is about two orders of magnitude larger than the observed values for polyethylene and other polymers. In view of this discrepancy, we are led to the conclusion that lamellae are not in equilibrium.

D. Dependence of T_m on Lamellar Thickness (Gibbs–Thompson Equation)

The free energy of a lamella, where the fold surface area $A (= L_1 L_2)$ is taken to be much larger than lateral surface area ($L_3 L_1 + L_2 L_3$), follows from Eq. (1.20) as

$$\Delta G = -AL\Delta\mu + 2A\sigma_f \quad (1.26)$$

where L is the lamellar thickness (L_3) and σ_f is fold surface free energy. Substituting Eq. (1.8) for $\Delta\mu$, we obtain

$$\Delta G = -AL\Delta h \frac{\Delta T}{T_m^0} + 2A\sigma_f \quad (1.27)$$

where Δh is expressed per unit volume. At the melting temperature (T_m) of a lamella of thickness L , ΔG of Eq. (1.27) is zero, yielding

$$T_m = T_m^0 \left(1 - \frac{2\sigma_f}{L\Delta h} \right) \quad (1.28)$$

Therefore a plot of T_m versus $1/L$ is expected to be linear with the intercept and slope given by T_m^0 and $-2\sigma_f T_m^0/\Delta h$, respectively. This allows us to obtain the equilibrium melting temperature (T_m^0) for infinitely large lamellar thickness by extrapolation, and the fold surface free energy.

E. Minimum Lamellar Thickness

Let T_c be the crystallization temperature and $\Delta T \equiv T_m^0 - T_c$ be the supercooling. For the lamellar shape, and $\Delta T > 0$, it follows from Eq. (1.26) that $\Delta G < 0$ if

$$L > \frac{2\sigma_f}{\Delta\mu} \quad (1.29)$$

The lower limit of this inequality is the minimum possible lamellar thickness L_0 :

$$L_0 = \frac{2\sigma_f}{\Delta\mu} \quad (1.30)$$

For $L > L_0$, ΔG is negative and the most stable lamella is with infinite thickness. Thus, according to the argument presented above, we expect the formation of a “virgin lamella” with an initial thickness L_0 for a given supercooling, and then the lamella to thicken with time. Therefore, for a given supercooling, L is given by

$$L = L_0 + \delta L \quad (1.31)$$

where δL is $L - L_0$. Substituting Eq. (1.8) for $\Delta\mu$ in Eq. (1.30), we get

$$L_0 = \frac{2\sigma_f T_m^0}{\Delta h \Delta T} \quad (1.32)$$

Thus, the initial lamellar thickness is inversely proportional to supercooling. Combining Eqs. (1.31) and (1.32), the dependence of lamellar thickness on the crystallization temperature T_c is given by

$$\begin{aligned} L &= \frac{2\sigma_f T_m^0}{\Delta h (T_m^0 - T_c)} + \delta L \\ &= \frac{c}{\Delta T} + \delta L \end{aligned} \quad (1.33)$$

This form is often observed experimentally.

F. Thickening (Hoffman–Weeks Plot)

If $\delta L/L_0$ is small, as observed experimentally, perhaps due to very slow kinetics of chain rearrangements, then the relationship between L_0 and T_c is the same as the Gibbs–Thompson equation:

$$T_c = T_m^0 \left(1 - \frac{2\sigma_f}{L\Delta h} \right) \quad (1.34)$$

This implies that for a given lamellar thickness, the melting temperature and the crystallization temperature should be the same. In practice, this is not observed.

We now consider the role of lamellar thickening on the relation between T_c and T_m . At T_c , the initial thickness of the virgin lamella is given by Eq. (1.32) as

$$L_0 = \frac{2\sigma T_m^0}{\Delta h(T_m^0 - T_c)} \quad (1.35)$$

After certain duration of time, let the lamella have thickened by a factor of β so that $L = L_0\beta$. According to the Gibbs–Thompson equation, Eq. (1.28), the melting temperature of the thickened lamella is

$$T_m = T_m^0 \left(1 - \frac{2\sigma}{\Delta h L_0 \beta} \right) \quad (1.36)$$

Substituting Eq. (1.35) in Eq. (1.36) for L_0 , we obtain

$$T_m = \frac{1}{\beta} T_c + \left(1 - \frac{1}{\beta} \right) T_m^0 \quad (1.37)$$

A plot (called the *Hoffman–Weeks plot* [36]) of T_m versus T_c is linear for a constant thickening factor, and the extrapolated intersection of T_m with T_c is taken to be the equilibrium melting temperature T_m^0 . While this procedure has been improved [37], the whole concept is also contested [38].

IV. NUCLEATION

When a liquid is quenched to a temperature below its melting temperature, small nuclei of different sizes and shapes are initially born as a result of fluctuations in the density of the liquid. These nuclei are stabilized by lowering of the free energy associated with the formation of the more stable crystalline phase, but destabilized by the increase in free energy associated with the creation of interfaces. As is well known, sub-critical-size nuclei dissolve back

into the liquid phase. Those nuclei larger than the critical nucleus grow and eventually complete the phase transition. In this section, we give a brief review of the classical approach without any discussion of the topological connectivity of the polymer. The polymer specificity will be discussed in Section V. Although the nuclei can have irregular shapes in the initial stages of crystallization, we restrict ourselves to spherical and cylindrical nuclei.

A. Spherical Nucleus

For a spherical nucleus of radius r , the free energy of formation of a crystal from the liquid phase, follows analogous to Eq. (1.20) as

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta\mu + 4\pi r^2 \sigma \quad (1.38)$$

where σ is the interfacial tension at the spherical surface of the nucleus. $\Delta\mu$ is expressed per unit volume as given by Eq. (1.8)

$$\Delta\mu = \Delta h \frac{\Delta T}{T_m^0} \quad (1.39)$$

and is positive for $\Delta T = T_m^0 - T > 0$. A sketch of ΔG versus r is given in Figure 1.8.

The critical radius r_c is obtained from

$$\left(\frac{\partial \Delta G}{\partial r} \right)_{r=r_c} = 0 \quad (1.40)$$

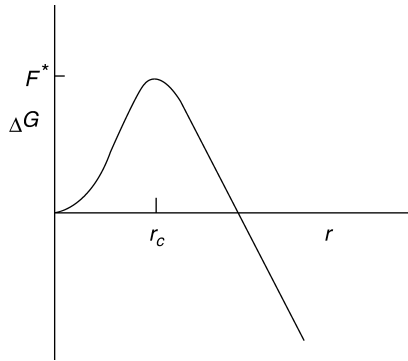


Figure 1.8. Nucleation barrier.

to be

$$r_c = \frac{2\sigma}{\Delta\mu} = \frac{2\sigma T_m^0}{\Delta h \Delta T} \quad (1.41)$$

The critical radius diverges inversely with supercooling. Substitution of this result for r_c into Eq. (1.38) leads to the free energy of formation of critical spherical nucleus as

$$F^* = \frac{16\pi}{3} \frac{\sigma^3}{(\Delta\mu)^2} = \frac{16\pi}{3} \frac{\sigma^3 (T_m^0)^2}{(\Delta h)^2 (\Delta T)^2} \quad (1.42)$$

diverging as $(\Delta T)^{-2}$ with the supercooling. The global free energy minimum corresponds to the infinitely large sphere of the crystalline phase.

B. Cylindrical Nucleus

Consider the cylinder sketched in Figure 1.9 with radius R and length L , where σ_f and σ_l are the fold and lateral surface free energies per unit area.

The free energy of formation of this nucleus is

$$\Delta G = -\pi R^2 L \Delta\mu + 2\pi R L \sigma_l + 2\pi R^2 \sigma_f \quad (1.43)$$

Defining R and L in units of the typical length l of a repeat unit

$$\begin{aligned} \pi R^2 &\equiv \mu l^2 \\ L &\equiv m l \end{aligned} \quad (1.44)$$

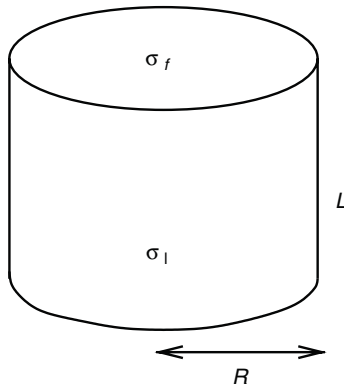


Figure 1.9. Cylindrical nucleus.

ΔG follows as

$$\Delta G = -\mu m \epsilon + m \sqrt{\mu} \sigma'_l + 2\mu \sigma'_f \quad (1.45)$$

where

$$\begin{aligned} \epsilon &= l^3 \Delta \mu = \frac{l^3 \Delta h \Delta T}{T_m^0} \\ \sigma'_l &= 2\sqrt{\pi} l^2 \sigma_l \end{aligned} \quad (1.46)$$

and

$$\sigma'_f = l^2 \sigma_f$$

Minimizing ΔG with respect to m and μ , $\frac{\partial \Delta G}{\partial m} = 0 = \frac{\partial \Delta G}{\partial \mu}$, gives the dimensions of the critical nucleus as

$$\begin{aligned} m_c &= \frac{4\sigma'_f}{\epsilon} = \frac{4\sigma_f T_m^0}{l \Delta h \Delta T} \\ \mu_c &= \left(\frac{\sigma'_l}{\epsilon} \right)^2 = \frac{4\pi \sigma_l^2 (T_m^0)^2}{l^2 (\Delta h)^2 (\Delta T)^2} \end{aligned} \quad (1.47)$$

The free energy of formation (F^*) of the critical nucleus is

$$F^* = \frac{\epsilon m_c \mu_c}{2} = \frac{8\pi \sigma_f \sigma_l^2 (T_m^0)^2}{(\Delta h)^2 (\Delta T)^2} \quad (1.48)$$

Defining $\bar{m} = m/m_c$, $\bar{\mu} = \mu/\mu_c$ and $\overline{\Delta G} = \Delta G/F^*$, the free energy of formation of the cylindrical nucleus is given by

$$\overline{\Delta G} = -2\bar{\mu}\bar{m} + 2\bar{m}\sqrt{\bar{\mu}} + \sqrt{\bar{\mu}} \quad (1.49)$$

The dependence of $\overline{\Delta G}$ on $\bar{m}$ (proportional to lamellar length) and $\bar{\mu}$ (proportional to lateral dimension) is given in Figure 1.10 as a contour plot.

The critical nucleus corresponds to $\bar{\mu} = 1 = \bar{m}$, and the global free-energy minimum corresponds to infinitely large dimensions of the cylinder in both length and radius.

Independent of the anisotropy of the shape of the crystal, it is to be recognized that the free-energy barrier required for the formation of the critical nucleus is inversely proportional to the square of supercooling

$$F^* \sim \frac{1}{(\Delta T)^2} \quad (1.50)$$

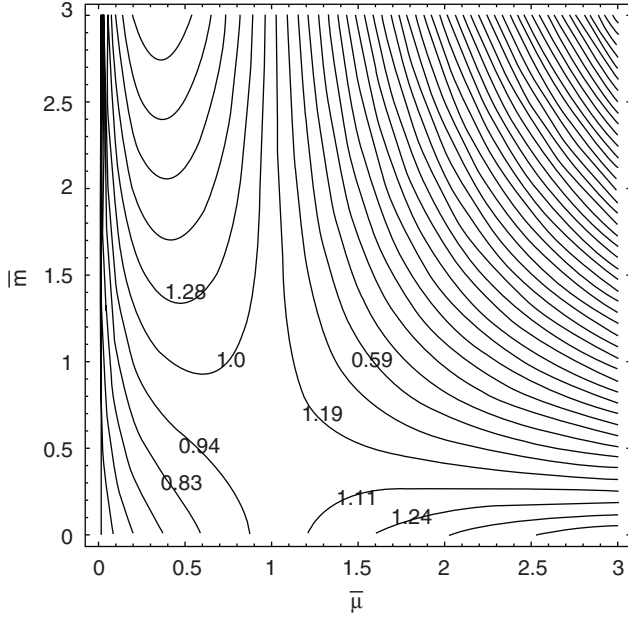


Figure 1.10. Free-energy landscape for a cylindrical nucleus.

where the prefactor depends on the geometry of the nucleus. In view of this general feature, we consider only the spherical nucleus in the following consideration of distribution of nuclei of different sizes and the rate of their formation.

C. Equilibrium Distribution of Nuclei

Expanding the free energy of formation of a spherical nucleus of radius r [given by Eq. (1.38)] around that (F^*) for a critical nucleus, we get

$$\Delta G = F^* + \frac{1}{2} \frac{\partial^2 \Delta G}{\partial r^2} \bigg|_{r=r_c} (r - r_c)^2 + \dots \quad (1.51)$$

where the coefficient of the quadratic term follows from Eq. (1.38) as

$$\frac{1}{2} \frac{\partial^2 \Delta G}{\partial r^2} \bigg|_{r=r_c} = -4\pi(r_c \Delta \mu - \sigma) \quad (1.52)$$

Replacing $\Delta\mu$ by $2\sigma/r_c$, due to Eq. (1.41), in Eqs. (1.51) and (1.52), we obtain

$$\Delta G = \frac{4}{3}\pi\sigma r_c^2 - 4\pi\sigma(r - r_c)^2 + \dots \quad (1.53)$$

The number of nuclei of radius r (close to r_c) in equilibrium is given by the Boltzmann distribution

$$n_0(r) = \mathcal{N}e^{-(\Delta G/kT)} = \mathcal{N}e^{-(4\pi/3kT)\sigma r_c^2 + (4\pi\sigma/kT)(r-r_c)^2} \quad (1.54)$$

where k is the Boltzmann constant, $\mathcal{N}$ is the normalization factor, and ΔG is r -dependent as given by Eq. (1.38). As a specific example, the number of critical nuclei is given by

$$n_0(r_c) = \mathcal{N}e^{-(16\pi/3)(\sigma^3/kT)\{(T_m^0)^2/[(\Delta h)^2(\Delta T)^2]\}} \quad (1.55)$$

and is strongly dependent on the supercooling. It also follows from Eqs. (1.53) and (1.54) that the mean-square fluctuation of the radius of the nucleus around r_c is inversely proportional to σ :

$$\langle (r - r_c)^2 \rangle \sim \frac{kT}{\sigma} \quad (1.56)$$

D. Nucleation Rate

In this section we give a brief summary of the classical Becker–Döring theory of nucleation [39] and then implement the results for the polymer crystallization. Let a crystalline nucleus of radius r contain N repeat units such that

$$\frac{4}{3}\pi r^3 = Nl^3 \quad (1.57)$$

In terms of N , ΔG of Eqs. (1.38) and (1.46) yield

$$F_N \equiv \Delta G = -N\epsilon + 3^{2/3}(4\pi)^{1/3}\sigma l^2 N^{2/3} \quad (1.58)$$

so that the critical number of repeat units for the formation of crystalline phase is

$$N_c = \frac{4\pi}{3} \left(\frac{2\sigma l^2}{\epsilon} \right)^3 = \frac{4}{3}\pi \left(\frac{r_c}{l} \right)^3 \quad (1.59)$$

Let the average number of nuclei of size N at time t be $n_N(t)$. We assume that the nuclei change their sizes only by the evaporation–condensation mechanism,

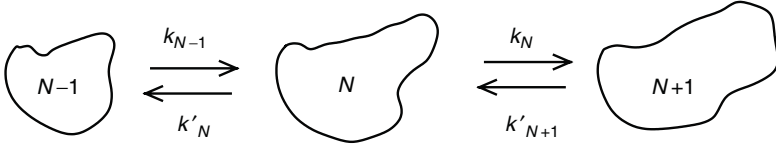


Figure 1.11. Elementary steps of growth of nuclei.

that is, in an elementary process only one repeat unit is either added or removed. This is sketched in Figure 1.11.

Let k_N represent the rate at which one repeat unit is added to a nucleus of size N . Let k'_N represent the rate at which one repeat unit is removed from a nucleus of size N . The rate of change of the number of nuclei of size N is dictated by four elementary steps (where $N - 1$ becomes N , N shrinks to $N - 1$, N is depleted to become $N + 1$, and $N + 1$ loses one repeat unit to become N) as given by

$$\begin{aligned} \frac{\partial n_N(t)}{\partial t} &= k_{N-1}n_{N-1} - k'_N n_N - k_N n_N + k'_{N+1}n_{N+1} \\ &= J_{N-1} - J_N \end{aligned} \quad (1.60)$$

where

$$J_N = k_N n_N(t) - k'_{N+1} n_{N+1} \quad (1.61)$$

is the rate per volume at which nuclei grow from size N to $N + 1$.

The rate constants k_N and k'_N are phenomenological constants. If we assume that there is a local equilibrium between nuclei of different sizes, k_N and k'_N are related by the “detailed balance,” that is, the ratio of the forward rate to the reverse rate is the equilibrium constant given by the exponential of the negative change in the free energy in units of kT :

$$\frac{k_N}{k'_{N+1}} = e^{-[(F_{N+1} - F_N)/kT]} \quad (1.62)$$

Substituting the expression for k'_{N+1} from Eq. (1.62) into Eq. (1.61), J_N is given by

$$J_N = k_N n_N(t) - k_N e^{(F_{N+1} - F_N)/kT} n_{N+1}(t) \quad (1.63)$$

Since N is usually very large, it can be taken as a continuous variable. Writing F_{N+1} as $F_N + \frac{\partial F_N}{\partial N} + \dots$, and n_{N+1} as $n_N + \frac{\partial n_N}{\partial N} + \dots$ and expanding the

exponential, J_N follows as

$$\begin{aligned}
 J_N &= k_N n_N(t) - k_N \left[1 + \frac{1}{kT} (F_{N+1} - F_N) + \dots \right] n_{N+1}(t) \\
 &= -k_N (n_{N+1}(t) - n_N(t)) - \frac{k_N}{kT} (F_{N+1} - F_N) n_{N+1}(t) \\
 &= -k_N \frac{\partial n_N}{\partial N} - \frac{k_N}{kT} \frac{\partial F_N}{\partial N} n_N(t) + \dots
 \end{aligned} \tag{1.64}$$

Within the same continuous notation for N , Eqs. (1.60) and (1.64) yield

$$\begin{aligned}
 \frac{\partial n_N(t)}{\partial t} &= -\frac{\partial J_N}{\partial N} \\
 &= \frac{\partial}{\partial N} \left[\frac{k_N}{kT} \frac{\partial F_N}{\partial N} n_N(t) + k_N \frac{\partial n_N(t)}{\partial N} \right]
 \end{aligned} \tag{1.65}$$

This equation is the familiar Fokker–Planck equation for the time evolution of the distribution function for the number density of the nuclei with different sizes N .

In equilibrium, the flux in the “size space” J_N is zero (i.e., the square-bracket term in Eq. (1.65) vanishes). The solution of this condition is given by Eqs. (1.54) and (1.65) as

$$n_N^0 = \mathcal{N} e^{-(F_N/kT)} \tag{1.66}$$

In the steady state, the flux J_N is a constant, J , independent of N . Rearranging Eq. (1.63), we obtain

$$J_N = k_N e^{-\frac{F_N}{kT}} \left[\frac{n_N(t)}{e^{-(F_N/kT)}} - \frac{n_{N+1}(t)}{e^{-(F_{N+1}/kT)}} \right] \tag{1.67}$$

Using the result for the equilibrium distribution [Eq. (1.66)], we get

$$\frac{J_N}{k_N n_N^0} = \frac{n_N(t)}{n_N^0} - \frac{n_{N+1}(t)}{n_{N+1}^0} \tag{1.68}$$

Summing this equation over N from 1 to a large number, say, Λ , we get in the steady state ($J_N = J$)

$$J \sum_{N=1}^{\Lambda} \frac{1}{k_N n_N^0} = \frac{n_1(t)}{n_1^0} - \frac{n_{\Lambda+1}(t)}{n_{\Lambda+1}^0} \tag{1.69}$$

If we take the steady-state distribution function $n_N(t)$ to be close to n_1^0 for $N \rightarrow 1$ and to be zero for $N \rightarrow \infty$, the right-hand side of Eq. (1.69) is unity so that the flux in the steady state, called the *nucleation rate*, is given by

$$J = \frac{1}{\sum_{N=1}^{\Lambda} \left(\frac{1}{k_N n_N^0} \right)} \cong \mathcal{N} \left[\int_0^{\infty} dN \frac{1}{k_N} e^{F_N/kT} \right]^{-1} \quad (1.70)$$

Substituting the result of Eq. (1.54) for $n_0(r)$, we get

$$J = \mathcal{N} e^{-(4\pi\sigma/3kT)r_c^2} \left[\int_0^{\infty} dr \frac{e^{-(4\pi\sigma/kT)(r-r_c)^2}}{k(r)} \right]^{-1} \quad (1.71)$$

Since the integrand of the integral inside the square brackets is sharply peaked around r_c , the integral can be performed by the “saddle point approximation,” and the result is

$$\begin{aligned} J &= \mathcal{N} e^{-(4\pi\sigma/3kT)r_c^2} \left(\frac{4\sigma}{kT} \right)^{1/2} k(r_c) \\ &= 2k(r_c) \left(\frac{\sigma}{kT} \right)^{1/2} n_0(r_c) \\ &\equiv J_0 e^{-(4\pi/3)(\sigma/kT)r_c^2} \\ &= J_0 \exp \left\{ -\frac{16\pi\sigma^3}{3kT} \frac{(T_m^0)^2}{(\Delta h)^2 (\Delta T)^2} \right\} \\ &= J_0 \exp \frac{-F^*}{kT} \end{aligned} \quad (1.72)$$

J_0 is called the *nucleation rate prefactor*.

In general, the rate at which critical nuclei are formed, called the *homogeneous nucleation rate*, is given by the form

$$J = Ck(r_c) \left(-\frac{\Delta G''(r_c)}{kT} \right)^{1/2} e^{-F^*/kT} \quad (1.73)$$

as a product of three factors where C is a prefactor reflecting the geometry of nucleus. $k(r_c)$ is the frequency of arrival of repeat units to the critical nucleus, F^* is the nucleation barrier associated with the formation of critical nucleus, and $\Delta G''(r_c)$ is the curvature of ΔG around r_c . As discussed in Section IV.B, $F^* \sim (\Delta T)^{-2}$. The nucleation rate is very low for weak supercooling, and it

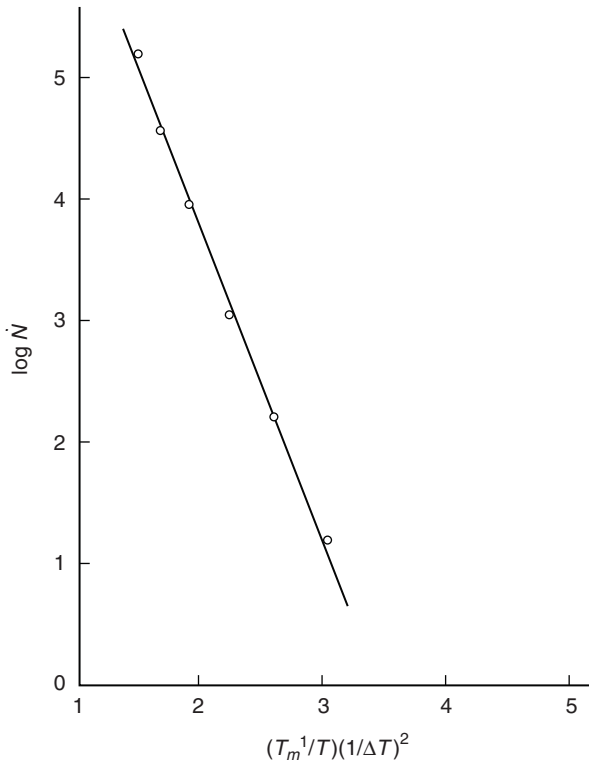


Figure 1.12. Dependence of nucleation rate on supercooling.

increases exponentially with an increase in the extent of supercooling. Therefore, a plot of $\log J$ versus $(T_m^0)^2/T(\Delta T)^2$ should be linear, in agreement with experimental data [28,40] on poly(decamethylene sebacate) as shown in Figure 1.12.

It is remarkable that the predictions of classical nucleation theory without any consideration of polymer connectivity are borne out in experiments. At higher supercooling, deviations are expected because of temperature dependence of the nucleation rate prefactor.

V. GROWTH, SECONDARY NUCLEATION, AND LAURITZEN-HOFFMAN THEORY

We now consider the growth of an already formed crystal at a given supercooling. The attachment of polymer molecules at the growth front is a very complex

process involving polymer diffusion, entanglement effects, competitive adsorption/desorption at the growth front, and other factors. The simplest approach to treat these features is to invoke a nucleation barrier for attachment of every polymer molecule at the growth front. Thus lamellar growth is assumed to occur by a nucleation process, called *secondary nucleation*. This is the basic premise of the very successful theory [4,5,16] of Lauritzen and Hoffman (LH). Although there have been several generalizations of the LH theory, we outline only the basic assumptions of the nucleation theory of LH.

A. Model

The basic model of LH theory is sketched in Figure 1.13, where polymer molecules are assumed to attach at the growth front in terms of stems, each of length comparable to the lamellar thickness L .

For each polymer molecule, the first step is to place its first stem at the growth surface, whose lateral dimension is taken as L_p . This step is assumed to be associated with a nucleation. After this step, the secondary nucleus spreads out laterally with the rate g . The thickness of the stem is a along the lateral direction and b along the growth direction with growth rate G .

Consider the attachment of the first stem, the free-energy change accompanying this step is

$$\Delta G_1 = -abL \Delta\mu + 2bL\sigma_l \quad (1.74)$$

Two new lateral surfaces, each of area bL , are created in this step. Since the first stem does not generate any chain folds on the fold surfaces, the free-energy cost

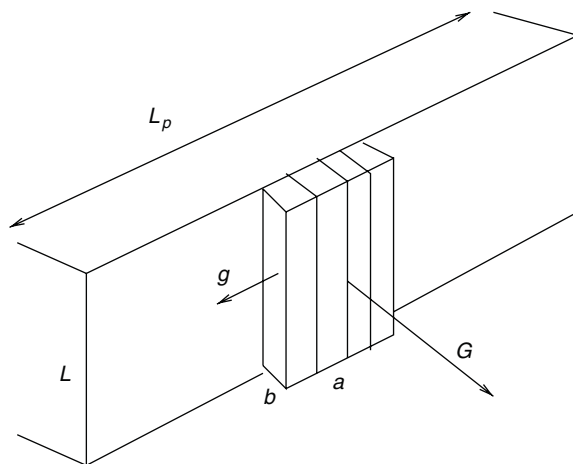


Figure 1.13. Model of growth front.

associated with fold surface areas ($2ab$) is ignored for the first stem. The initial and final states of this step are assumed to be separated by a free-energy barrier, which is taken to be the lateral surface free energy ($2bL\sigma_l$) reduced by an arbitrary fraction of the free energy of crystallization ($abL\Delta\mu$)

$$\Delta G_1^* = -\psi abL \Delta\mu + 2bL\sigma_l \quad (1.75)$$

for the forward process. For the reverse process the barrier is $(1 - \psi)abL \Delta\mu$. ψ is called an “apportioning” parameter. The free-energy change associated with the second stem (i.e., first fold) is

$$\Delta G_2 = -abL \Delta\mu + 2ab\sigma_f \quad (1.76)$$

The initial and final stages of the deposition of the second stem are assumed to be separated by a barrier

$$\Delta G_2^* = -\psi abL \Delta\mu + 2ab\sigma_f \quad (1.77)$$

in the forward direction. We have assumed the apportioning parameter to be the same for both steps, for convenience. The barrier for the reverse direction of the second step is $(1 - \psi)abL \Delta\mu$. The free-energy changes associated with the lateral attachment of subsequent stems are the same as for the second stem. The free-energy landscape of the process is illustrated in Figure 1.14.

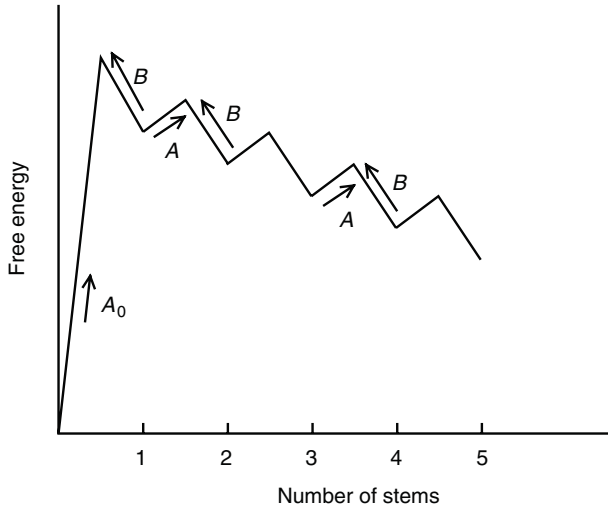


Figure 1.14. Free-energy landscape of the Lauritzen-Hoffman model.

In drawing the cartoon of Figure 1.14, we have assumed that $2\sigma_L/a > \Delta\mu$, $2\sigma_f/\Delta\mu < L$, and $0 < \psi < 1$. It is to be noted that the case of $\psi = 1$ corresponds to no barriers and that of $\psi = 0$ to the maximum barriers.

The rate of deposition of the first stem is proportional to $\exp(-\Delta G_1^*/kT)$ and is defined through

$$A_0 = \beta \exp \left[-\frac{2bL\sigma_l - \psi abL \Delta\mu}{kT} \right] \quad (1.78)$$

where β accounts for the approach rate of polymer segments at the growth front. The most familiar form of β is the same as that for low-molecular-weight supercooled liquids

$$\beta = CTe^{-[U^*/k(T-T_0)]} \quad (1.79)$$

where C is a constant prefactor, U^* is the free-energy barrier for local dynamics of repeat units, and T_0 is the temperature at which diffusion of polymer chains is essentially stopped. Other phenomenological expressions for β can be written, reflecting the dynamics of supercooled polymer melts. This, in itself, is not well understood, and it is presently sufficient to be content with Eq. (1.79).

The rate of removal of the first stem is given by

$$B = \beta \exp \left[-\frac{(1-\psi)abL \Delta\mu}{kT} \right] \quad (1.80)$$

For the particular choice of the apportioning used in the definition of barriers, B is the rate of removal of any stem (either the first or any of the subsequent stems). The rate of deposition of the second or any of the subsequent stems is given by

$$A = \beta \exp \left[-\frac{2ab\sigma_f - \psi abL \Delta\mu}{kT} \right] \quad (1.81)$$

B. Steady State

In the steady state, the flux of stems is a constant (S) and is given by the balance equation

$$S = v_0 A_0 - v_1 B = v_1 A - v_2 B = v_2 A - v_3 B = \dots \quad (1.82)$$

where v_i is the number density of systems with i stems in the growth layer. From the equality between S and the third term ($v_1 A - v_2 B$), we obtain

$$v_1 = \frac{1}{A} (S + v_2 B) \quad (1.83)$$

Substituting this result in the first identity of Eq. (1.82), we obtain

$$S\left(1 + \frac{B}{A}\right) = v_0 A_0 - \frac{B^2}{A} v_2 \quad (1.84)$$

Now eliminating v_2 in terms of S and v_3 (using the fourth term) and repeating this iteratively, we obtain

$$S\left(1 + \frac{B}{A} + \frac{B^2}{A^2} + \cdots\right) = v_0 A_0 \quad (1.85)$$

so that the steady-state flux is given by

$$S = v_0 A_0 \left(1 - \frac{B}{A}\right) \quad (1.86)$$

Substituting the expressions for A_0 , A and B from Eqs. (1.78)–(1.81), we obtain the steady-state flux of stems as an explicit function of the lamellar thickness (L)

$$S(L) = v_0 \beta \exp\left(-\frac{2bL\sigma_l - \psi abL \Delta\mu}{kT}\right) \left[1 - \exp\left(\frac{2ab\sigma_f - abL \Delta\mu}{kT}\right)\right] \quad (1.87)$$

where $S(L)$ is the nucleation rate for noninteracting nuclei and for the lamellar thickness L at a given supercooling. It is also the probability distribution for a crystal to have thickness L . The total flux S_T , in a collection of crystals, is calculated by summing $S(L)$ over all possible values of L . It is to be noted that the square bracket term becomes negative (i.e., the flux is unphysically negative) if $L < 2\sigma_f/\Delta\mu$ ($\equiv L_0$, obtained from the thermodynamic considerations of Section III.E). Therefore S_T follows as

$$S_T = \sum_{L_0}^{\infty} S(L) \cong \frac{1}{l_u} \int_{2\sigma_f/\Delta\mu}^{\infty} dL S(L) \quad (1.88)$$

where l_u is the length of the monomer repeat unit. Substituting Eq. (1.87) for $S(L)$ into the above equation, we get

$$S_T = \frac{\beta v_0 P}{l_u} \exp\left[\frac{2ab\psi\sigma_f}{kT} - \frac{4b\sigma_l\sigma_f}{kT \Delta\mu}\right] \quad (1.89)$$

with

$$P = kT \left[\frac{1}{(2b\sigma_l - ab\psi \Delta\mu)} - \frac{1}{(2b\sigma_l + (1 - \psi)ab \Delta\mu)} \right] \quad (1.90)$$

The lateral spreading rate g is given by

$$g = a(A - B) \quad (1.91)$$

Substituting A and B from Eqs. (1.80) and (1.81), g becomes

$$g = a\beta Q \exp \left[-\frac{2ab\sigma_f(1-\psi)}{kT} \right] \quad (1.92)$$

with

$$Q = \exp \left[\frac{\psi ab \Delta\mu(L - \frac{2\sigma_f}{\Delta\mu})}{kT} \right] \left\{ 1 - \exp \left[-\frac{ab \Delta\mu(L - \frac{2\sigma_f}{\Delta\mu})}{kT} \right] \right\} \quad (1.93)$$

Using the expressions for $S(L)$, S_T , and g , average lamellar thickness and growth rates can be calculated. For small values of $\Delta\mu$, P and Q approach approximately l_u and unity, respectively. It is therefore obvious from Eqs. (1.89) and (1.92) that S_T is a strongly increasing function of $\Delta\mu$, whereas g is negligibly dependent on temperature. Thus as the supercooling increases, S_T/g increases, with significant consequences discussed in the next section.

The thermodynamic arguments of Section III show that the minimum lamellar thickness L_0 is $2\sigma_f/\Delta\mu$. The average lamellar thickness L^* follows from Eq. (1.87) as its first moment

$$\begin{aligned} L^* &= \frac{\int_{L_0}^{\infty} dL L S(L)}{\int_{L_0}^{\infty} dL S(L)} \\ &= L_0 + \frac{kT}{2b\sigma_l} \frac{\left[2 + (1 - 2\psi) \frac{a\Delta\mu}{2\sigma_l} \right]}{\left[1 - \frac{a\psi\Delta\mu}{2\sigma_l} \right] \left[1 + \frac{a(1-\psi)\Delta\mu}{2\sigma_l} \right]} \\ &= L_0 + \delta L \end{aligned} \quad (1.94)$$

where $L_0 = 2\sigma_f/\Delta\mu$ and δL is independent of σ_f but depends on T , $\Delta\mu$, a , b , ψ , and σ_l .

One of the successes of the LH theory is its ability to provide an explicit result for the lamellar thickness, based on kinetic considerations of secondary nucleation. In the LH theory, δL is a natural result of the steady state and not due to any subsequent thickening. The form of Eq. (1.94) is exactly the same as Eq. (1.1), observed experimentally. However, one of the serious difficulties posed by Eq. (1.94) is that it predicts a divergence in δL at

$$\frac{2\sigma_l}{a} = \psi \Delta\mu \quad (1.95)$$

Since $\Delta\mu$ is proportional to the supercooling, the LH theory predicts that as the crystallization temperature is lowered to a value when Eq. (1.95) is satisfied, the lamellar thickness would diverge. This is referred to as the “ δL catastrophe.” By taking reasonable experimental values for the various parameters and assuming $\psi = 1$ (no barriers for attachment of each stem), the necessary supercooling for the appearance of this catastrophe is 55 K for polyethylene. This is not observed experimentally. To fix this discrepancy, ψ is taken to be zero so that

$$\delta L = \frac{kT}{2b\sigma_l} \frac{\left(\frac{4\sigma_l}{a} + \Delta\mu\right)}{\left(\frac{2\sigma_l}{a} + \Delta\mu\right)} \quad (1.96)$$

However, this choice of ψ implies that surfaces of stems need to be formed first before any gain in the bulk free energy of the stems.

In general, in the LH model, there are two key processes: nucleation of the first stem (with a rate i per unit substrate length per unit time), and the lateral growth rate (g) for the deposition of second and subsequent stems. Depending on the relative magnitudes of i and g , three regimes can be identified. Let the dark areas in Figure 1.15 represent the growth front and each square correspond to the cross section of a stem. In regime I [Fig. 1.15(b)] secondary nucleation controls the linear growth rate $G(g \gg i)$. In regime III [Fig. 1.15(d)], prolific multiple nucleation controls G .

Sanchez and DiMarzio identified [41] a crossover regime II [Fig. 1.15(c)], where g is more rapid than in I and less than in III. On the basis of the LH model, crystallization kinetics in these three regimes are obtained as follows.

C. Regime I

In this regime, the lateral growth rate (g) is significantly greater than the secondary nucleation rate (i), so that the latter is rate-determining for the growth rate (G). For $g \gg i$, the whole substrate is covered by stems as soon as the first stem is nucleated. Thus, monolayers are added one by one. If L_p is the substrate

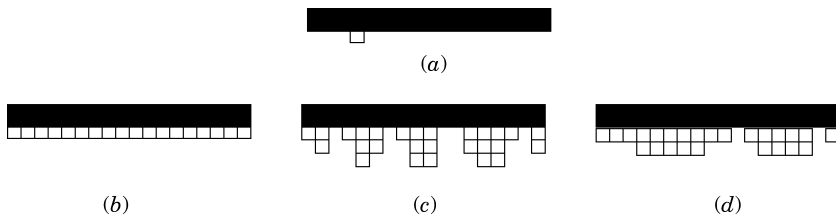


Figure 1.15. Lauritzen–Hoffman model.

length, iL_p is the rate of formation of secondary nuclei on the substrate. In regime I, each secondary nucleation leads to the formation of a monolayer of thickness b . Therefore, the linear growth rate G_I in regime I is given by

$$G_I = biL_p \quad (1.97)$$

The nucleation rate i is the total flux S_T per available sites (v_0). Substituting Eq. (1.89), for S_T , we get

$$G_I = \frac{b\beta L_p}{l_u} P \exp \left[\frac{2ab\psi\sigma_f}{kT} - \frac{4b\sigma_l\sigma_f}{kT\Delta\mu} \right] \quad (1.98)$$

For small values of supercooling, P is comparable to l_u . Substituting the expression for β from Eq. (1.79), G_I becomes

$$G_I = G_{I,0} e^{-[U^*/k(T-T_0)]} e^{-(4b\sigma_l\sigma_f/kT\Delta\mu)} \quad (1.99)$$

where the prefactor is

$$G_{I,0} = CbL_p T \exp \left(\frac{2ab\psi\sigma_f}{kT} \right) \quad (1.100)$$

Substituting the expression for $\Delta\mu$ in term of the supercooling, we obtain

$$\begin{aligned} G_I &= G_{I,0} \exp \left[-\frac{U^*}{k(T-T_0)} - \frac{4b\sigma_l\sigma_f T_m^0}{kT\Delta h(T_m^0 - T)} \right] \\ &\equiv G_{I,0} G_{I,D} G_{I,n} \end{aligned} \quad (1.101)$$

where the nucleation part ($G_{I,n}$) of the growth rate is given by

$$G_{I,n} \equiv e^{-(K_g/T\Delta T)} \quad (1.102)$$

with

$$K_g \equiv \frac{4b\sigma_l\sigma_f T_m^0}{k\Delta h} \quad (1.103)$$

The expression for G_I nicely shows its nonmonotonic dependence on the crystallization temperature. Close to the equilibrium melting temperature, the growth is nucleation-dominated and is given essentially by $G_{I,n}$. For temperatures far below T_m^0 , but closer to T_0 , the $G_{I,D}$ term dominates and the growth rate precipitously decreases with supercooling.

D. Regime II

If the lateral growth rate g is comparable or smaller than the nucleation rate i , then further layers are deposited before the first layer is fully formed [as sketched in Fig. 1.15(c)]. Under these circumstances (regime II), the linear growth rate is given by

$$G_{II} = b\sqrt{ig} \quad (1.104)$$

where $i = S_T/v_0$ and g are given in Eqs. (1.89) and (1.92). The above result emerges from the following scaling argument [41] of Sanchez and Dimarzio. Let an isolated stem undergo nucleation at time $t = 0$. As time progresses, the layer grows laterally in two opposite directions so that $2gt$ is the length of the substrate covered by the new monolayer at time t . While this patch of the monolayer tends to grow laterally, it also offers sites for nucleation of another layer. The rate at which new nuclei form on this patch is $2gti$. The total number of nuclei formed during a time τ is

$$\int_0^\tau 2gti \, dt = gi\tau^2 \quad (1.105)$$

assuming that g and i are independent of time. Therefore, the average time $\langle\tau\rangle$ required for the formation of a new nucleus on the growing patch is

$$\langle\tau\rangle \sim \frac{1}{\sqrt{gi}} \quad (1.106)$$

The rate at which new layers are formed is $b/\langle\tau\rangle$ so that

$$G_{II} = b\sqrt{ig} \quad (1.107)$$

Substituting the results of Eqs. (1.89) and (1.92) into the above equation, we get

$$\begin{aligned} G_{II} &= G_{II}^0 e^{-[U^*/k(T-T_0)]} e^{-(2b\sigma_f\sigma_f/kT \Delta\mu)} \\ &= G_{II}^0 G_{I,D} \sqrt{G_{I,n}} \end{aligned} \quad (1.108)$$

where

$$G_{II}^0 = CbT \exp \left[\frac{(2\psi - 1)ab\sigma_f}{kT} \right] \quad (1.109)$$

In writing this result, we have approximated Q of Eq. (1.93) to be unity, valid for low supercoolings.

The nucleation part of the linear growth rate is

$$G_{II,n} = \sqrt{G_{I,n}} = e^{-(K'_g/T \Delta T)} \quad (1.110)$$

where K'_g is half of K_g :

$$K'_g = \frac{2b\sigma_l\sigma_f T_m^0}{k \Delta h} \quad (1.111)$$

E. Regime III

In this regime the multiple nucleation of stems is so prolific [Fig. 1.15(d)] that the lateral spreading rate is irrelevant, $i \gg g$. Now the growth rate is exactly of the same form as in regime I

$$\begin{aligned} G_{III} &= biL_p \\ &= G_{III}^0 e^{-[U^*/k(T-T_0)] - (K_g/T \Delta T)} \end{aligned} \quad (1.112)$$

with

$$\begin{aligned} G_{III}^0 &= CTbL_p \exp\left(\frac{2ab\sigma_f\psi}{kT}\right) \\ K_g &= \frac{4b\sigma_l\sigma_f T_m^0}{k \Delta h} \end{aligned} \quad (1.113)$$

Equations (1.101), (1.108), and (1.112) suggest that three regimes would be manifest in a plot of $(\log G) + U^*/k(T - T_0)$ versus $1/T \Delta T$, as sketched in Figure 1.16.

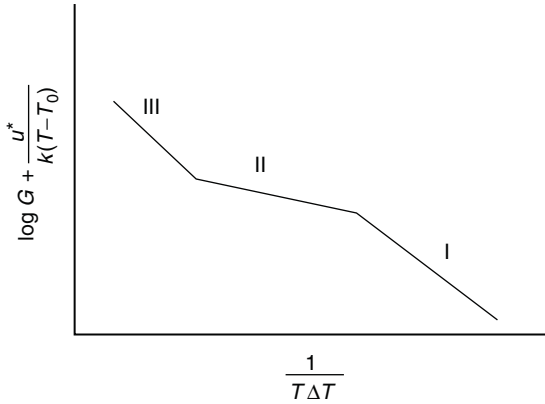


Figure 1.16. Three regimes in the LH model.

The slope of the line in regime II is predicted to be exactly half of that for regimes I and III. There is considerable experimental evidence [7] for the existence of regimes I and II and for the result, $K_g = 2K'_g$.

F. Extensions and Criticisms

The major extensions of the LH model are the following. For details, the original references should be consulted.

1. The deposition of each stem of m repeat units can be treated [8,41] as a set of m equilibria. While this generalization appears to account for more local details, the general conclusions are the same as in the LH theory. In realistic situations, we expect nonsequential deposition of repeat units into various stems. These partially formed stems will then sort out through entropic barriers to attain the lamellar thickness. We return to this issue in Section VII.

2. The kinetic factor β in Eq. (1.79) should reflect the contour length of the polymer (instead of only the monomer friction), as the polymer chains must diffuse from an entangled melt or a concentrated solution to a growth front. Based on the reptation model of polymer dynamics, an expression for β has been derived. According to this argument [22], the linear growth rate in melts is inversely proportional to the average molecular weight of the polymer, independent of the regime.

3. The LH theory has been extended [22] to account for the curvature of the growth front by incorporating the consequences of lattice strain behind the growth front.

4. When a melt of broad polydispersity in molecular weight is crystallized, lower molecular weights are rejected from growing crystals, although the temperature is below their respective melting points. This molecular fractionation has been explained [42] by the LH model, by adopting to individual molecules. This is termed *molecular nucleation*. Considering the free energy of formation of a molecular crystallite consisting of stems and surfaces (lateral and fold), the critical size of the crystalline nucleus is calculated in terms of supercooling and contour length. Nuclei smaller than the critical size will dissolve back. This leads to a critical molecular weight (below which chains do not crystallize) as an increasing function of the crystallization temperature, in good agreement with experimental data.

5. In the LH model, the stems are deposited such that the lamellar thickness is uniform throughout the growth. This restriction is partially removed by allowing the stems to diffuse by one repeat unit in the direction of layer normal, accompanied by a penalty in free energy. This model [43] is referred to as the “sliding diffusion model” and averts the “ δL catastrophe.”

6. In the case of crystallization of small molecules, there exists a critical temperature called the “roughening temperature [8]” T_R . For $T > T_R$, the crystalline surfaces are microscopically rough and macroscopically rounded. For $T < T_R$, the crystals are faceted. At temperatures higher than T_R , the free-energy barriers for fluctuations of density of molecules are weak, and the growth rate is proportional to the supercooling. Observation [8] of such a dependence of G for polyethylene oxide at weak supercoolings prompted Sadler to dispute the claim that nucleation is always the rate-determining factor in kinetic theories of polymer crystallization. On the other hand, for polyethylene samples, $\log G$ is proportional to $1/T\Delta T$. To explain these observations, Sadler and Gilmer proposed a model [21] for polymer crystallization by generalizing the surface roughening model for small molecules. This model is implemented by Monte Carlo simulations where repeat units at the growth front are allowed to rearrange with certain prescribed probabilities. Although the simulation results are in qualitative agreement with experimental observations, analytical expressions are not available.

7. There are many serious criticisms of the LH theory at all levels of the model and agreements with experiments. The review by Armitstead and Goldbeck-Wood [8] gives a fair and comprehensive review of this criticism. We mention only the most serious discrepancy. The value of the substrate length L_p fitted as a parameter to agree with kinetics data is unrealistically different from the experimental value measured directly by Point and collaborators [20]. They suggested that the change in K_g across the regimes I–II transition may arise from temperature dependence of interfacial energies, transport coefficients and molecular segregation, instead of validity of the LH theory.

VI. SPINODAL MODE IN POLYMER CRYSTALLIZATION

As discussed in Section II, measured excess scattering intensity, after a melt is cooled below its melting point, increases exponentially with time at all scattering wavevectors and the inverse of $q_{\max}$ (at which intensity is a maximum) diverges as $(\Delta T)^{-1/2}$. These observations are similar to those observed in mixtures undergoing phase separation by the spinodal decomposition mechanism [39], as described below. This similarity has led to the proposal of spinodal decomposition, instead of nucleation, as the primary mechanism of the very early stages of polymer crystallization. There has been extensive interest in establishing an understanding of nucleation versus spinodal decomposition in polymer crystallization. In view of this, we give below the salient features of the spinodal decomposition mechanism.

As a specific example, consider a blend (discussed in Section III.B) of n_1 chains of N_1 segments and n_2 chains of N_2 segments. The free-energy density

of mixing for this blend is obtained by dividing ΔG of Eq. (1.9) by $(n_1 N_1 + n_2 N_2)$

$$\frac{F}{kT} = \frac{\phi}{N_1} \ln \phi + \frac{(1-\phi)}{N_2} \ln(1-\phi) + \chi \phi(1-\phi) \quad (1.114)$$

where $\phi \equiv \phi_1$ and $\phi_2 = (1-\phi)$. Typically, χ is inversely proportional to T . Using the standard procedures to calculate the critical point for liquid–liquid demixing, Eq. (1.114) yields the critical point to be

$$\phi_c = \frac{\sqrt{N_2}}{\sqrt{N_1} + \sqrt{N_2}} \quad \chi_c = \frac{(\sqrt{N_1} + \sqrt{N_2})^2}{2N_1 N_2} \quad (1.115)$$

Defining an order parameter $\tilde{\phi}$ to be $\phi - \phi_c$, and expanding F as a Taylor series in $\tilde{\phi}$, we get

$$\frac{F}{kT} = \frac{F_0}{kT} + \frac{A}{2} \tilde{\phi}^2 + \frac{B}{4} \tilde{\phi}^4 + \dots \quad (1.116)$$

where

$$A = \left[\frac{1}{N_1 \phi_c} + \frac{1}{N_2 (1 - \phi_c)} \right] \frac{T - T_c}{T_c} \equiv -a_0 \Delta T \quad (1.117)$$

$$B = \frac{1}{3} \left[\frac{1}{N_1 \phi_c^3} + \frac{1}{N_2 (1 - \phi_c)^3} \right]$$

where $\Delta T = T_c - T > 0$ is now the quench depth for phase separation. In obtaining the expression for A , χ is assumed to be strictly proportional to $1/T$. F_0 is independent of $\tilde{\phi}$.

When fluctuations are present, the system is inhomogeneous in space and $\tilde{\phi}(\mathbf{r})$ is a function of the spatial coordinate $\mathbf{r}$. Also any local gradients $\nabla \tilde{\phi}(\mathbf{r})$ cost in free energy. Now, the change in free energy to excite a fluctuation $\psi = \tilde{\phi} - \tilde{\phi}_0$ (where $\tilde{\phi}_0$ is the equilibrium value) is given by the Landau–Ginzburg form

$$\frac{\Delta F}{kT} = \int \frac{d^3 r}{V} \left\{ \frac{A}{2} \psi^2 + \dots + \frac{\kappa}{2} (\nabla \psi)^2 + \dots \right\} \quad (1.118)$$

where κ is a positive quantity proportional to interfacial tension and V is the volume of the system. Decomposition of ψ in terms of its Fourier components gives

$$\frac{\Delta F}{kT} = \frac{1}{2} \sum_q (A + \kappa q^2) \psi_q^2 \quad (1.119)$$

The time evolution of the fluctuation $\psi(\mathbf{r})$ obeys the conservation law

$$\frac{\partial \psi(\mathbf{r}, t)}{\partial t} = \nabla \cdot \left(\Lambda_0 \nabla \frac{\delta \Delta F / kT}{\delta \psi} \right) \quad (1.120)$$

so that

$$\frac{\partial \psi_q(t)}{\partial t} = -\Lambda_0 q^2 (A + \kappa q^2) \psi_q(t) \quad (1.121)$$

where Λ_0 is the Onsager coefficient reflecting the relative diffusivity of polymer chains, and nonlinear terms of ψ in Eq. (1.118) are ignored. The scattered intensity $I(q, t)$ is proportional to $\langle \psi_q^2(t) \rangle$ and follows from Eq. (1.121) as

$$I(q, t) = I(q, 0) e^{2\Omega_q t} \quad (1.122)$$

where

$$\Omega_q = -\Lambda_0 q^2 (A + \kappa q^2) \quad (1.123)$$

Writing A in terms of the quench depth ΔT , given by Eq. (1.117), we get

$$\Omega_q = \Lambda_0 q^2 (a_0 \Delta T - \kappa q^2) \quad (1.124)$$

This result is sketched in Figure 1.17(a) for $\Delta T > 0$. For scattering wavevectors less than $q_0 = \left(\frac{a_0 \Delta T}{\kappa} \right)^{1/2}$ scattered intensity grows exponentially with time and the maximum growth occurs at $q = q_{\max} = \left(\frac{a_0 \Delta T}{2\kappa} \right)^{1/2}$. The same

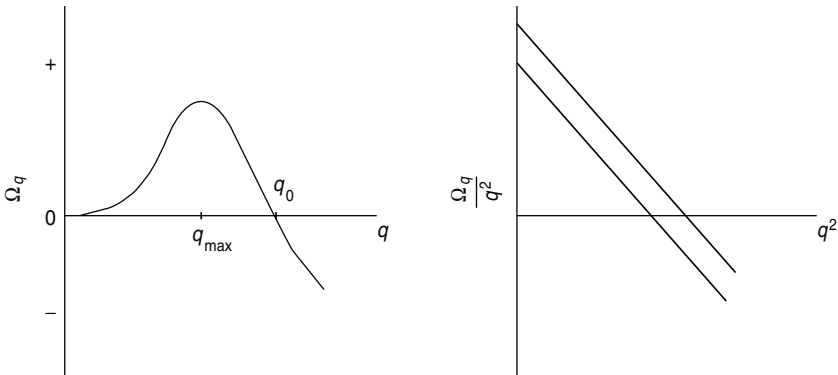


Figure 1.17. Predictions of spinodal decomposition mechanism.

result can be more conveniently written as

$$\frac{\Omega_q}{q^2} = \Lambda_0 a_0 \Delta T - \Lambda \kappa q^2 \quad (1.125)$$

which is sketched in Figure 1.17(b).

The intercept of the $(\Omega_q/q^2)/q^2$ plot is proportional to ΔT and the slope is independent of ΔT . Further, there is a cutoff wavevector q_0 delineating growing modes and decaying modes and q_0 is proportional to $\sqrt{\Delta T}$. Therefore, if spinodal decomposition occurs, all of the following features must be simultaneously observed:

1. Scattered intensity grows exponentially with time for $q < q_0$.
2. $q_{\max}$ is proportional to $(\Delta T)^{1/2}$.
3. The ordinate intercept of $\Omega_q/q^2 - q^2$ plot is proportional to ΔT .
4. The slope of $\Omega_q/q^2 - q^2$ plot is independent of ΔT .
5. The abscissa intercept of $\Omega_q/q^2 - q^2$ plot is proportional to ΔT .

If any of these features is not observed in the early stages of crystallization, the spinodal decomposition mechanism commonly encountered in phase-separating mixtures cannot be associated with polymer crystallization.

VII. RECENT ADVANCES

Availability of sensitive synchrotron radiation and atomic force microscopy (AFM) techniques have spurred recent (as of 2003) advances in following the mechanism of polymer crystallization in its early stages. Stimulated by the results of these investigations, complementary molecular modeling [44–59] of crystallization has been extensively carried out using molecular dynamics, Langevin dynamics, and Monte Carlo methods. All of these simulation methods provide converging viewpoint regarding the nature of initial stages of polymer crystallization. We review only the Langevin dynamics methodology.

Among the numerous challenges faced in understanding the formation and evolution of hierarchical structures in polymer crystallization, we restrict ourselves to explain the essential basic features of folded lamellae. Specifically, we consider (1) molecular origin of enhanced scattered intensity before any crystallographic features are apparent, (2) spontaneous selection of small lamellar thickness, (3) molecular details of growth front, and (4) formation of shish-kebab structures in the presence of a flow.

A. Molecular Modeling

In the Langevin dynamics simulations, the polymer crystallization is modeled by following the competition between the attraction among nonbonded

monomers and the torsional energies along the chain backbone. The simulation model attempts to incorporate just enough detail to observe chain folding without impeding the efficiency of the simulation. As a result, the united-atom model for polyethylene is chosen for a polymer chain, in which each methylene unit is treated as a bead in a bead-spring model of N beads. The motion of each bead is given by the Langevin equation consisting of inertial term, force field, frictional drag, and noise. The force fields include chain connectivity, bond angle, torsion angle, and nonbonded bead-bead interactions (Lennard-Jones of strength ϵ_0 and range σ_0). The force field parameters and details are given in Refs. 49, 57, and 58. The Langevin dynamics method simulates the effect of solvent through the noise, which is prescribed in accordance with the fluctuation-dissipation theorem. All simulation results given below are in reduced units (united-atom mass m of 1, equilibrium bond length ℓ_0 of 1, and Lennard-Jones ϵ_0 of 1). The reduced temperature T^* is equal to kT/ϵ_0 (with kT the Boltzmann constant times the absolute temperature), the reduced free energy is F/ϵ_0 and the reduced time is $t\sqrt{\epsilon_0/m\sigma_0^2}$. The protocol of a typical simulation is as follows. The first step is the determination of the melting temperature T_m^* for the model chains (for chosen values of N and force field parameters). An initially created random configuration is equilibrated at $T^* = 15.0$. The chain is then quenched to $T^* = 9.0$ and crystallization is allowed to take place. Once a single chain-folded structure is obtained, several runs are performed at heating rates ranging from 0.0001 to 0.002 $T^*/$ time units. Discontinuities are observed in the slopes of both the total potential energy and global orientational order parameter at the onset and ending of melting. The equilibrium melting temperature is estimated by extrapolation of the observed melting temperatures to zero heating rate. This temperature is approximately $T^* = 11.0 \pm 0.2$. After T_m^* is determined, a collection of chains (or an individual chain) is quenched to a prescribed T^* below T_m^* and the chain configurations are followed. Attempts were made to include all hydrogen atoms explicitly in the simulations. This computationally demanding explicit-atom model shows (Fig. 1.18) that the crystal symmetry is orthorhombic, in agreement with the well-known experimental result for polyethylene single crystals, instead of the hexagonal symmetry seen in united-atom model simulations.

However, the essential mechanisms of lamellar formation and growth are found to be the same in both the united-atom and explicit-atom models. Only the united-atom model simulation results are therefore discussed below.

B. Nucleation in the Very Early Stage

We first summarize the salient features of the Langevin dynamics simulation results from the literature, and then we give a theoretical analysis.

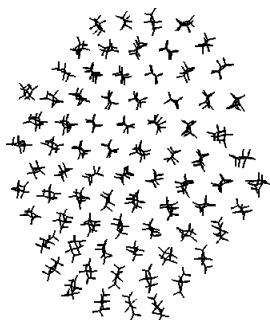


Figure 1.18. Explicit-atom model simulation.

1. Simulations

As reported in Refs. 49 and 57, Figure 1.19 shows a typical sequence of images depicting nucleation of a lamella by a single chain of $N = 700$ beads. The chain is quenched to $T^* = 9.0$ after equilibration at $T^* = 12.0$. Another example of $N = 2000$ (quenched to $T^* = 9.0$ from 20.0) is given in Figure 1.20. The timesteps shown in the sequence are selected from representative configurations during the course of crystallization.

As seen in these figures, several “baby nuclei” are formed, connected by the same single chain. The strands connecting these baby nuclei are flexible with

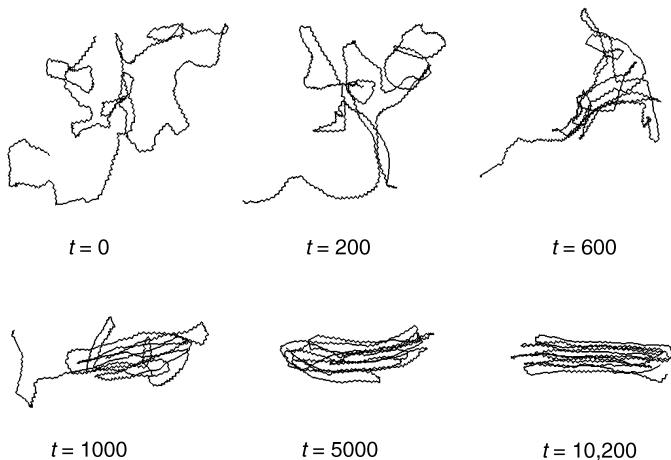


Figure 1.19. Snapshots of nucleation by a single chain ($N = 700$) [49].

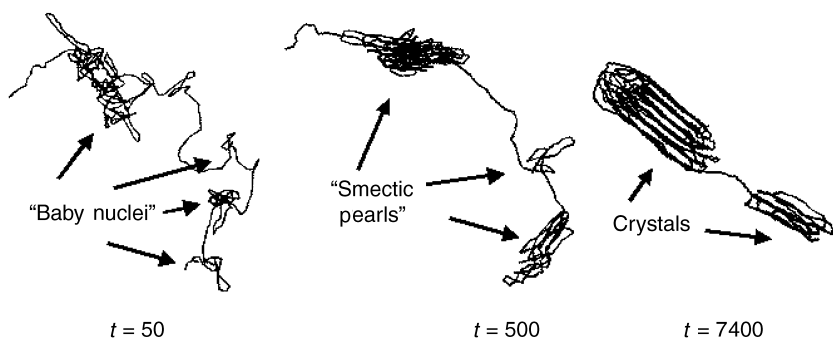


Figure 1.20. Growth of smectic pearls by reeling in the connector ($N = 2000$).

considerable configurational entropy. As time progresses, the monomers in the flexible strands are reeled into the baby nuclei while the orientational order in each nuclei increases, making them “smectic pearls.” Simultaneously, the competition between nuclei for further growth dissolves some nuclei. Eventually, folded-chain structure emerges. Thus, the description is essentially the same as nucleation and growth encountered in small molecular systems, except that the polymer now is long enough to participate in several nuclei. Immediately after the quench ($t < 500$ in Fig. 1.20), we observe that the average distance between baby nuclei does not change with time. But the number of monomers in the connectors is reduced, accompanied by an increase in segmental orientation inside the nuclei as time increases.

To quantify this result, the structure factor $S(\mathbf{q}, t)$ at time t and the initial structure factor $S(\mathbf{q}, 0)$ were computed. As seen in experiments, a scattering peak at $\mathbf{q}_{\max}$ was observed. In these simulations, $\mathbf{q}_{\max}$ was found to correspond to the spacing between baby nuclei and the peak position is essentially independent of time in the very early stages.

Figure 1.21 contains a plot of Ω_q/q^2 versus q^2 , where Ω_q is the rate of growth of monomer density fluctuations with wave vector $\mathbf{q}$. According to the linearized theory of spinodal decomposition for mixtures (Section VI), $S(\mathbf{q}, t) \propto \exp(2\Omega_q t)$, where $\Omega_q \propto q^2(1 - \kappa q^2)$, where κ is a positive constant. Therefore, a plot of Ω_q/q^2 versus q^2 must be linear with a negative slope if spinodal decomposition is present. Some experimentalists have used this criterion to claim that spinodal decomposition is the mechanism of polymer crystallization at the early stage. As in experiments, we also observe that Ω_q/q^2 versus q^2 is linear with a negative slope. However, this is not evidence for spinodal decomposition because this behavior is observed for only intermediate

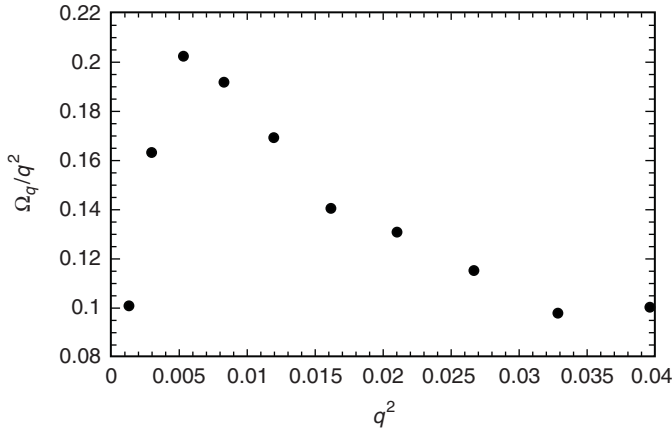


Figure 1.21. Dependence of growth rate of density fluctuations on the square of the wave-vector [57].

values of $\mathbf{q}$. Our results show that for small $\mathbf{q}$, $\Omega_q \propto q^4$, in agreement with experiments but in disagreement with the predictions of spinodal decomposition.

To get more insight into the further growth of smectic pearls, typical configurations at various times are presented in Figure 1.22 ($t = 500, 1550, 7400, 10,300, 12,850, 13,350$).

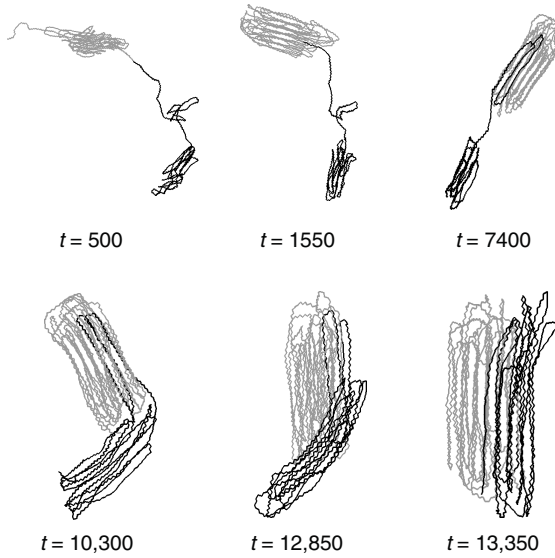


Figure 1.22. Merger of smectic pearls [57].

For the sake of clarity, we have used two shades for the polymer, although the chain is a homopolymer. As pointed out already, monomers in the connectors are transferred into the growing nuclei in the very early stage.

This process continues until the connector is essentially stretched out while keeping the average internuclei distance the same. Then, the connector is pulled into the nuclei to varying degrees until the nuclei impinge against each other. This is followed by a cooperative reorganization by which nuclei merge to form a single lamella. The mechanism of the merger is not by sequentially placing stems, but by a highly cooperative process involving all stems of the lamella.

2. Theory

We now present the simplest analytical model [60] for the origin of $q_{\max}$, the mechanism of growth of smectic pearls, and growth of density fluctuations in the very early stages of nucleation of lamella.

a. Origin of $q_{\max}$. To address why a certain average distance is maintained between two smectic pearls at very early times, let us consider a model chain of N beads with only two smectic pearls (containing N_1 and N_2 beads) connected by a strand of m ($= N - N_1 - N_2$) beads (Fig. 1.23).

Let the end-to-end distance of the strand be λ , which is comparable to the average distance between the smectic pearls. Let the average energy of a bead in either of the smectic pearls be ϵ .

The free energy F_0 of this configuration is given by

$$\frac{F_0}{k_B T} = -(N - m)\epsilon + \frac{3}{2} \frac{\lambda^2}{m l^2} \quad (1.126)$$

where the second term on the right-hand side is the entropic part from the strand (assuming Gaussian chain statistics and l as the Kuhn length, a multiple of l_0). Minimization of F_0 with respect to m gives the optimum value of m ($= m^*$) for the configuration of Figure 1.23:

$$m^* = \sqrt{\frac{3}{2\epsilon}} \left(\frac{\lambda}{l} \right) \quad (1.127)$$

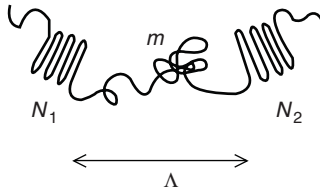


Figure 1.23. Model to consider connector entropy.

Since λ is roughly proportional to $\sqrt{m^*}$ according to the Gaussian statistics valid approximately before the quench, we expect

$$\frac{\lambda}{l} \sim \sqrt{m^*} \sim \frac{1}{\sqrt{\epsilon}} \quad (1.128)$$

Thus the initial selection of average distance between the smectic pearls is determined by ϵ (and consequently quench depth).

b. Kinetics of Growth of Smectic Pearls. Although arguments based on equilibrium are used above to estimate $q_{\max}$, the conformation discussed above is not in equilibrium and it evolves further by reeling in the connector. To address how this process takes place, let us consider the time-dependent probability $W_m(t)$ of finding m beads in the connector at time t . Let k_1 be the rate constant for one bead to detach from either of the smectic pearls, and k'_1 be the rate constant for one bead to attach to either of the smectic pearls. Using detailed balance to express k'_1 in terms of k_1 and letting m be a continuous variable, a mapping [60] with the standard arguments of the classical nucleation theory gives the Fokker–Planck equation

$$\frac{\partial W_m(t)}{\partial t} = k_1 \left[\frac{\partial}{\partial m} \frac{\partial (F_0/kT)}{\partial m} + \frac{\partial^2}{\partial m^2} \right] W_m(t) \quad (1.129)$$

where F_0 is given in Eq. (1.126). The prediction of Eq. (1.129) (solid curve) is compared with simulation data in Figure 1.24.

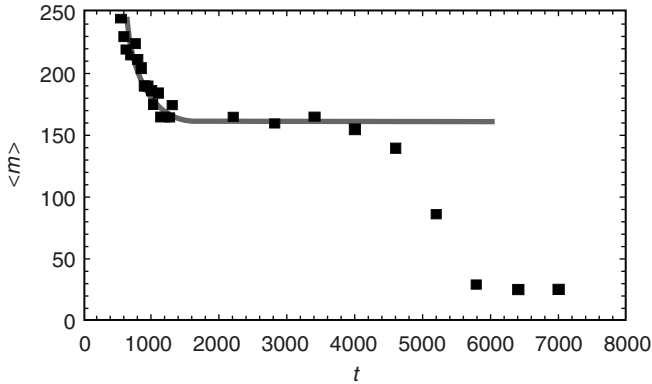


Figure 1.24. Time-dependence of average number of monomers $\langle m \rangle$ in the connector between smectic pearls. The simulation data (filled square) are from 8 simulations corresponding to the conditions of Figures 1.20 and 1.22; the solid line is calculated from Eq. (1.129).

In the comparison, λ is taken as an input from the simulations, ϵ is a parameter and the reduced time is $k_1 t$. The agreement is good, providing qualitative support to the present theoretical model, in the initial stages. For reduced times greater than 4000, the mechanism is not reeling in, and consequently, simulation data deviate from the solid curve.

c. Growth of Density Fluctuations. We now generalize the model of Figure 1.23 to account [56,60] for the wavevector dependence. There are three contributions to the free energy, F : (1) density difference ψ between the baby nuclei and the amorphous background giving free-energy contribution that is proportional to $-\Delta T \psi^2$ ($\Delta T \equiv T_m^0 - T$); (2) interfacial free energy given by the square gradient of ψ , proportional to $q^2 \psi_q^2$ (where q is the scattering wavevector); and (3) monomer–monomer correlation arising from the chain connectivity of the connector participating in multiple nuclei, leading to a free-energy contribution that is proportional to $q^{-2} \psi_q^2$ (as in the Debye structure factor for length scales shorter than R_g). Therefore the free energy of a system with baby nuclei connected by strands is

$$F \sim \sum_{\mathbf{q}} \left(-\Delta T + q^2 + \frac{1}{q^2} \right) \psi_{\mathbf{q}}^2 \quad (1.130)$$

where all the prefactors are left out. At this juncture of the early stage of nucleation and growth, ψ evolves with time, in accordance with the relaxation of chemical potential gradients

$$\frac{\partial \psi(r, t)}{\partial t} \simeq -\nabla \cdot \left(-\nabla \frac{\partial F}{\partial \psi} \right) \quad (1.131)$$

so that

$$\frac{\partial \psi_q(t)}{\partial t} = -q^2 \left(-\Delta T + q^2 + \frac{1}{q^2} \right) \psi_q(t) \quad (1.132)$$

Therefore, we expect the scattered intensity $I(\mathbf{q}, t)$, proportional to $\langle \psi_{\mathbf{q}}^2(t) \rangle$ to be exponential in time, $I(\mathbf{q}, t) \sim \exp(2\Omega_{\mathbf{q}} t)$, with the rate $\Omega_{\mathbf{q}} = q^2(\Delta T - q^2 - \frac{1}{q^2})$ with both lower and upper cutoffs in $\mathbf{q}$. If these arguments are valid, $\Omega_{\mathbf{q}}/q^2$ should rise sharply with q^2 , reach a maximum, and then decrease at higher $\mathbf{q}$ values. These predictions are fully consistent with the experimental [10] and simulation [57] observations on $I(\mathbf{q}, t)$ and $\Omega_{\mathbf{q}}$. If the mechanism is simply a spinodal decomposition into two liquid phases, then $\Omega_{\mathbf{q}}/q^2$ should show a monotonic linear decrease from a finite positive value at $\mathbf{q} \rightarrow 0$ with a slope independent of quench depth, which is not experimentally observed during

polymer crystallization. Thus, the mechanism of polymer crystallization even in the very early stage is nucleation and growth with an additional contribution arising from chain connectivity. When the original baby nuclei have grown into lamellae comparable to or larger in size than R_g , their further growth is dictated essentially by the nature of the growth front.

C. Spontaneous Selection of Lamellar Thickness

1. Simulations

Many simulations of n chains, each with N beads, such that $nN \leq 15,000$ and the volume fraction of the polymer $\phi \leq 0.5$, have been performed at different quench depths. The key observations are summarized below.

a. Quantization of Lamellar Thickness. The initial lamella formed as described in Section II, is typically thin and small. However, over a period of time, it thickens.

The lamellar thickening proceeds through many metastable states, each metastable state corresponding to a particular number of folds per chain, as illustrated in Figure 1.25. This quantization of number of folds has been observed in experiments [25], as already mentioned. The process by which a state with p folds changes into a state with $p + 1$ folds is highly cooperative. The

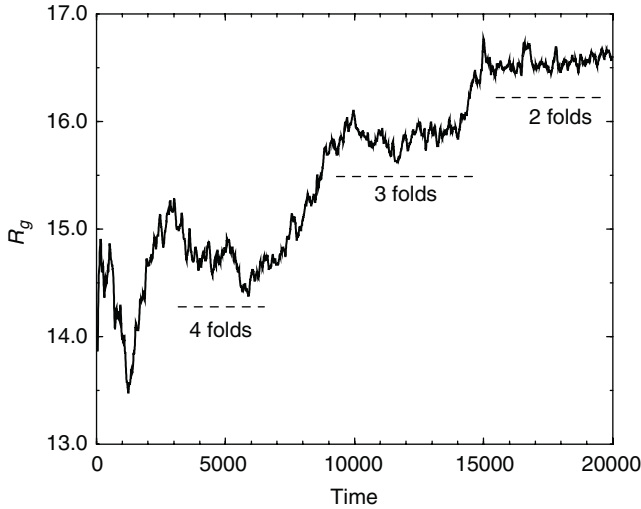


Figure 1.25. Quantized lamellar thickening, where R_g is the radius of gyration of the lamella [49].

precursor ‘lives’ in a quiescent state for a substantial time and “suddenly” it converts into the next state. By a succession of such processes, crystals thicken. If the simulation is run for a reasonably long time, the lamella settles down to the “equilibrium” number of folds per chain.

b. Lamellar Thickness and Quench Depth. The lamellar thickness L , after the thickening is apparently complete, is found in the simulations to obey the law

$$L = \frac{C_1}{\Delta T^*} + C_2 \quad (1.133)$$

where C_1 and C_2 are constants; for details, see Ref. 49. This relation was already observed experimentally [24]. Although the kinetic theory of Lauritzen and Hoffman predicts the same law as Eq. (1.133), it predicts a divergence in L at lower undercoolings. The simulations do not show any evidence for such a catastrophe.

c. Free-Energy Landscape. In an effort to quantify the free energies of different quantized states and free-energy barriers separating these states, the free-energy landscape has been calculated as a function of a measure, L , of lamellar thickness of single chains at a given quench depth and utilizing a histogram technique [58]. For example, the estimated free energy $F(L)$ for $N = 200$ at a quench depth of approximately 2.0 is given in Figure 1.26(a) exhibiting several wells. Each well corresponds to a different number of stems in the lamella. For example, six, five, and four stem structures are observed for chains composed of 200 united atoms. Increasing the number of united atoms results in the addition of more wells. For example, the free-energy profile [Fig. 1.26(b)] for $N = 300$ displays additional wells. As N increases, the chains increase the number of stems in the crystal to accommodate the optimum crystal thickness.

The minimum in $F(L)$ is observed to be near $L/\ell_0 \simeq 9$ for all chain lengths examined. It is to be noted that this minimum is the global minimum and the barrier between this state and other thicker lamellae increases prohibitively as the thickness increases. These simulations strongly suggest that a lamellar thickness that is much smaller than the extended chain thickness is actually an equilibrium result.

2. Theory

Motivated by simulation results, we now consider a theoretical model [60] that allows an exact calculation of the equilibrium lamellar thickness. Consider a nucleus sketched in Figure 1.27, of thickness $L = ml$ and radius R . For each of the n chains, let there be μ stems (and $\mu - 1$ loops and two chain tails), each of length L .

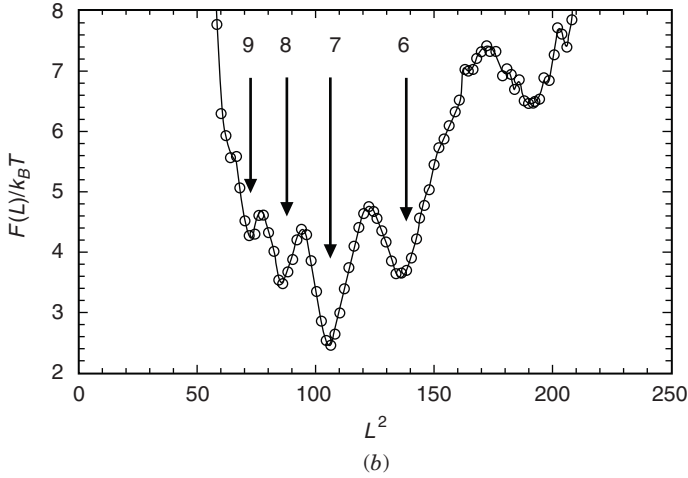
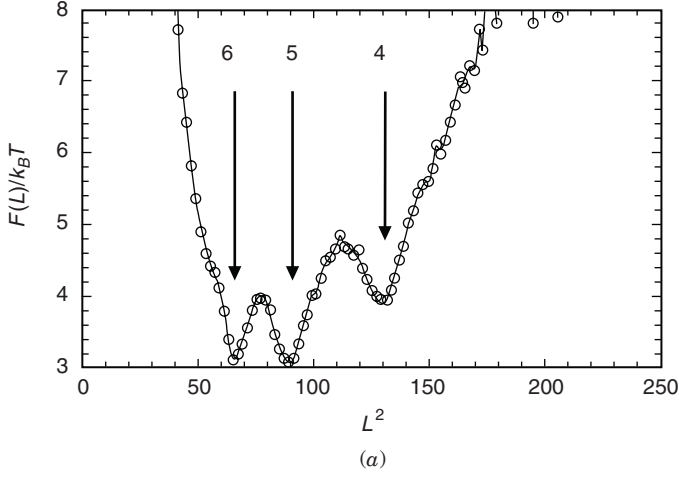


Figure 1.26. Free-energy landscape for (a) $N = 200$ and (b) $N = 300$.

Let $\epsilon > 0$ be the energy gain per segment in the nucleus (in units of kT) and σ' be the lateral surface free energy per unit area. The free energy $F_{m,\mu}$ per chain in the nucleus of Figure 1.27 is given by

$$\frac{F_{m,\mu}}{kT} = -\mu m \epsilon + \sigma \sqrt{\mu m} - \ln Z_{m,\mu} \quad (1.134)$$

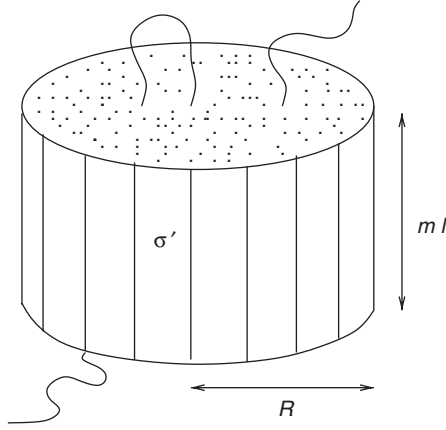


Figure 1.27. Role of loop entropy on the fold surface free energy.

where $\sigma = 2\sqrt{\pi}\sigma' l^2$. The third term on the right-hand side is due to the entropy associated with different ways of realizing loops and tails on the two fold surfaces. The partition sum of a loop of p monomers in semiinfinite space with ends at R_{11} and X_{11} (both located on the fold surface) is given by

$$g_{\text{loop}}(p) = 2 \left(\frac{3}{2\pi p l^2} \right)^{3/2} \exp \left[-\frac{3(\mathbf{R}_{11} - \mathbf{X}_{11})^2}{2p l^2} \right] [1 - \sqrt{\pi} \Gamma e^{\Gamma^2} \text{erfc}(\Gamma)] \quad (1.135)$$

with $\Gamma = c\sqrt{6p}$ and c is the strength of the interaction pseudopotential at the fold surface. For a tail of p segments in semiinfinite space, the partition sum is

$$g_{\text{tail}}(p) = e^{\Gamma^2} \text{erfc}(\Gamma) \quad (1.136)$$

Since the contour lengths of loops and tails are quite short ($c\sqrt{p}$ is small), as evident in the simulations, g_{loop} and g_{tail} approach the limits

$$g_{\text{loop}}(p) \rightarrow 2 \left(\frac{3}{2\pi p l^2} \right)^{3/2} \exp \left[-\frac{3(\mathbf{R}_{11} - \mathbf{X}_{11})^2}{2p l^2} \right]$$

and

$$g_{\text{tail}}(p) \rightarrow 1 \quad (1.137)$$

By following the field-theoretic technology of Ref. 61 and choosing a cutoff of l_c for $(R_{11} - X_{11})$, the partition sum $Z_{m,\mu}$ for distributing $(N - m\mu)$ segments

among $(\mu - 1)$ loops and 2 tails without breaking the chain connectivity is given by

$$Z_{m,\mu} = 4 \left(\frac{1}{\nu b_0} \right)^{\mu-1} (N - \mu m) \left[\left(\frac{z^2}{2} + \frac{1}{4} \right) \text{erfc}(z) - \frac{z}{2\sqrt{\pi}} e^{-z^2} \right] \quad (1.138)$$

where

$$z = \frac{(\mu - 1)b_0}{2\sqrt{N - \mu m}} \quad (1.139)$$

with $b_0 = \sqrt{6}l_c/l$ and $\nu = \pi l^3/3\sqrt{6}$.

Substitution of Eq. (1.138) into Eq. (1.134) gives the free-energy landscape in terms of the lamellar thickness ($\sim m$) and width ($\sim \mu$) per chain for a given choice of ϵ , σ , and l_c . The remarkable consequence of the entropic part of $F_{m,\mu}$ is that $F_{m,\mu}$ has a global minimum for a finite value of m .

This is illustrated in Figure 1.28, where $F_{m,\mu}/k_B T$ is plotted against m and μ for a representative set of $\epsilon = 1$, $\sigma = 5$, $N = 1000$, $l_c/l = \sqrt{32/3}$, $\nu/l^3 = \pi/3\sqrt{6}$. For the case of Figure 1.28, the global minimum (the ground state) is at $m^* = 14.26$ and $\mu^* = 45.3$. This result is to be contrasted with the standard model of Figure 1.9, where the fold surfaces are simply treated as

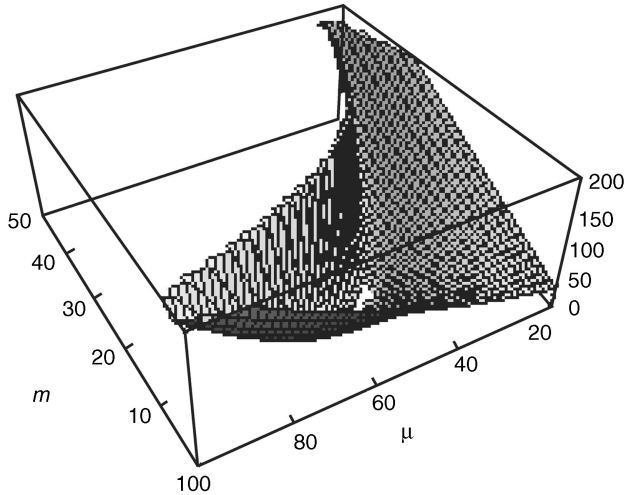


Figure 1.28. Chain entropy leads to thermodynamic stabilization of finite lamellar thickness.

planar interfaces with fold surface free energy σ_f per unit area. In the latter case, the free energy of the nucleus is given by

$$\frac{\Delta F}{k_B T} = -\mu m \epsilon + \sigma \sqrt{\mu} m + 2\mu \sigma_f \quad (1.140)$$

In terms of the critical nucleus ($m_c = 4\sigma_f/\epsilon$, $\mu_c = (\sigma/\epsilon)^2$, $\Delta F_c/k_B T = \epsilon \mu_c m_c/2$), ΔF becomes

$$\overline{\Delta F} = -2\bar{\mu}\bar{m} + 2\bar{m}\sqrt{\bar{\mu}} + \sqrt{\bar{\mu}} \quad (1.141)$$

where $\bar{m} = m/m_c$, $\bar{\mu} = \mu/\mu_c$ and $\overline{\Delta F} = \Delta F/\Delta F_c$. The free-energy landscape of Eq. (1.141) is given in Figure 1.10, and the lamella grows into infinitely large dimensions in all directions. In contrast, the exactly solved model of Figure 1.27 and Eqs. (1.126)–(1.139) show that finite lamellar thickness (much smaller than the extended chain value) is actually the equilibrium description.

D. Kinetics at Growth Front

Very long simulations have been carried out with as many as 15,000 united atoms with the following protocol. First, a single-chain crystal is placed at the origin. Next, a self-avoiding random chain is placed at a random location on a sphere whose radius is 1.5 times the radius of gyration of the crystal. The new system is equilibrated with the Langevin dynamics algorithm for 5000 time units. If the chain fails to add any segments to the crystal by the end of the addition period, the run is rejected and the crystal's coordinates are reset to their values at the beginning of the period. A new attempt to add a chain is then made. If the chain adds to the crystal, the process is repeated by moving the crystal to the origin and adding a new self-avoiding random chain to the simulation. Figure 1.29 illustrates the addition of the 40th chain to a 39 chain crystal for $k_B T/\epsilon = 9.0$.

The crystal reels in the chain one segment at a time, and then crystallographically attaches each to the growth face. This process continues until the entire chain is incorporated into the crystal. Once adsorbed, the chain continues to rearrange until its fold length is commensurate with that of the growth face. The rate-limiting step for the addition of the chain to the crystal is the diffusive contact with the surface. Once a few segments have come into contact with the crystal, the chain rapidly adds to the growth front. The numerical estimate of the free energy $F[s]$ as a function of the number of segments added to the crystal is given in Figure 1.30.

The addition of a new chain at the growth front is not hindered by a barrier, in contradiction with the underlying assumptions of the LH theory. Simultaneous to the addition of new chains at the growth front, chains inside

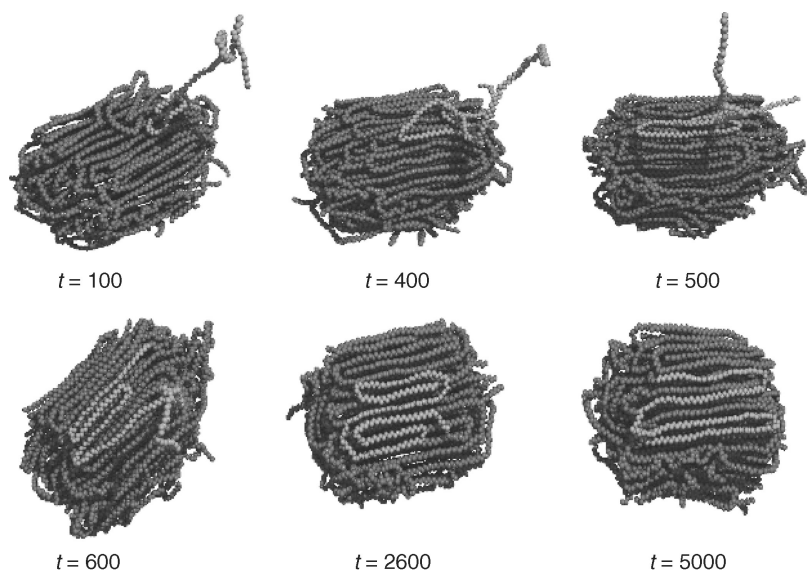


Figure 1.29. Adsorption of a new chain at the growth front [58].

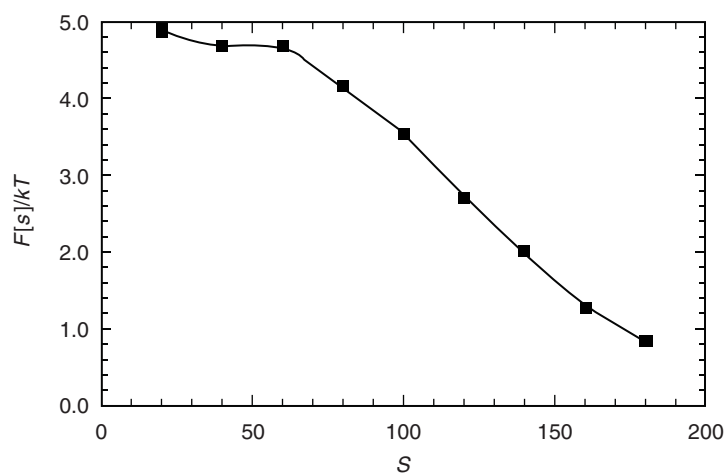


Figure 1.30. Absence of free-energy barrier for attachment of a new chain at the growth front [58].

the lamella move cooperatively. The center of mass of the lamella diffuses in space while the lamella thickens by a process of internal rearrangements; for details, see Ref. 58. The mean squared displacement of a labeled monomer varies with the elapsed time t with an effective power law of $t^{0.74}$ by shuffling back and forth between the lamellar and amorphous regions.

If the growth front is frozen, the crystallization at the growth front depends crucially on the commensurability between the thickness of the growth front and the length of crystallizing chains. For details, see Ref. 49. A collection of polydisperse chains gets effectively fractionated at the growth front.

E. Crystallization in an Elongational Flow

In the Langevin dynamics simulations [62], there is an additional force $\hat{S}\mathbf{r}_i$ acting on i th bead, where $\mathbf{r}_i$ is its position and

$$\hat{S} = \dot{\epsilon} \begin{pmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (1.142)$$

with the parameter $\dot{\epsilon}$ setting the flow rate. As expected, the chains undergo coil-stretch transition in the presence of flow and the melting temperature is elevated. For example, at the reduced temperature of 11.0 (which is the extrapolated melting temperature in reduced units for the united-atom model described above in the quiescent state) folded chains are readily formed in the presence of flow.

Several simulation runs were performed for a wide range of flow rates for chains of $N = 180$ beads. To ensure that the system is in the state of lowest free energy and to avoid the chain being in a metastable state, two initial conformations of the chain were chosen. One initial conformation is a random chain equilibrated at the given temperature without any flow. The second initial conformation is a fully extended chain obtained by equilibrating it at extremely high flow rate ($\dot{\epsilon} = 4.0$). Data were collected after the two chains with different initial conformation are in the same state, either coil or stretched polymer. The stagnation point at $\mathbf{r} = 0$ is unstable. In order to avoid the chain to be drifted away from the coordinate origin, the center of the mass of the polymer is fixed at $\mathbf{r} = 0$.

Figure 1.31 shows the square of the radius of gyration of the chain as a function of the flow rate $\dot{\epsilon}$ at relatively low temperature ($T = 9.0$).

A discontinuous coil-stretch transition is evident at $\dot{\epsilon}_c = 0.000725$. The transition point $\dot{\epsilon}_c$ was found by using two different initial conformations as described above. For values lower than $\dot{\epsilon}_c$, the random chain will eventually coil and form a folded-chain crystalline structure and stay in that conformation until the end of the run for relatively long run times. On the other hand, a prestretched chain would fluctuate and eventually form a crystallized folded chain that is

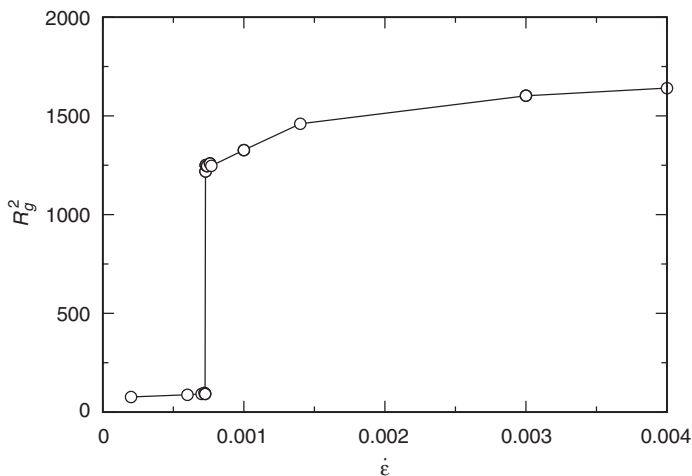


Figure 1.31. Radius of gyration squared as a function of flow rate for a chain of $N = 180$ and $T = 9.0$.

stable. Similarly, for flow rates higher than $\dot{\epsilon}_c$, a prestretched chain will never coil and a random chain will eventually stretch.

At a higher temperature $T = 11.0$, for flow rates near the transition rate $\dot{\epsilon}_c$, the free-energy barrier between the coiled and stretched conformation is much lower than for $T = 9.0$. The chain can therefore explore the phase space and jump back and forth from the coiled to the stretched states. Similar behavior has already been observed in Refs. 63 and 64. Figure 1.32 illustrates this feature.

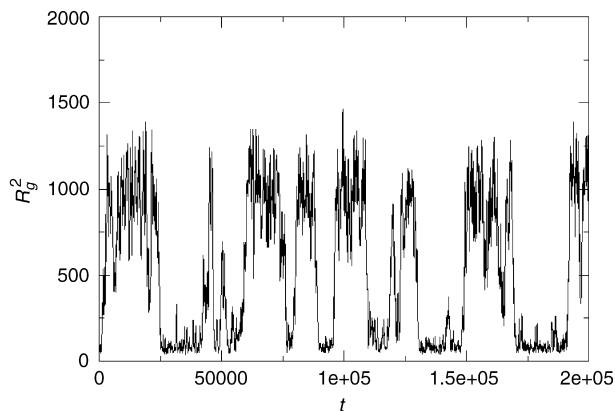


Figure 1.32. Radius of gyration squared as a function of time for $N = 180$, $T = 11.0$, and $\dot{\epsilon} = 0.00075$.

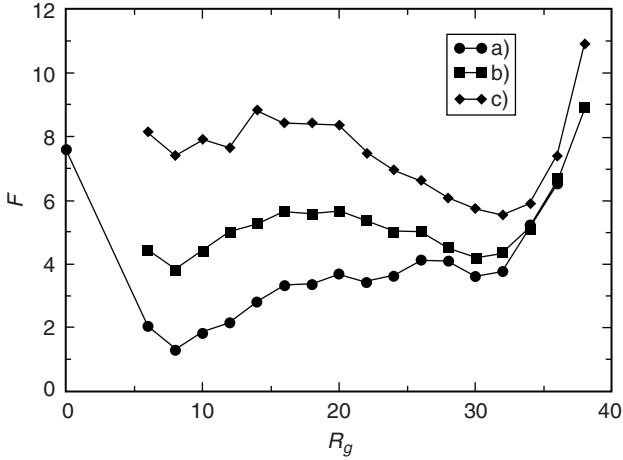


Figure 1.33. The free energy F versus R_g ($N = 180$); (a) $\dot{\epsilon} = 0.0006$; (b) $\dot{\epsilon} = 0.00075$; (c) $\dot{\epsilon} = 0.0009$.

From Figure 1.32, the free energy can be calculated according to

$$F(R_g) = -kT \ln \left(\frac{\tau(R_g)}{\tau_{\text{tot}}} \right) \quad (1.143)$$

where $\tau(R_g)$ is the time the system spends in states with a radius of gyration between R_g and $R_g + \Delta R_g$ and τ_{tot} is the total time. ΔR_g is chosen to be $2r_0$. Figure 1.33 shows the free energy of the chain at $T = 11.0$ for flow rates: (1) below, (2) very close to the transition, and (3) above the transition. It is clear that at the transition the stretched and the folded state coexist.

Making the flow rate higher or lower will change from stable to metastable the folded or the stretched state, respectively. The effects of hysteresis associated with this first-order discontinuous transition play an important role in the formation of composite crystalline structures.

When simulations were performed with many chains of uniform length, some chains were stretched out and aggregated among themselves to form the shish, whereas other chains formed folded structures that in turn attached to the shish, initiating the formation of kebabs. This is attributed to the coexisting populations of stretched and coiled states. This feature is much more pronounced if the chains have different lengths. For a given flow rate, the longer chain is predominantly in the stretched state and the shorter chain is

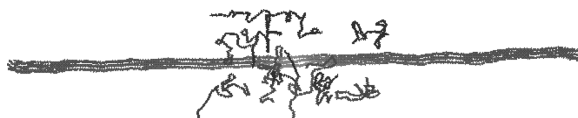


Figure 1.34. An example of initial position of chains for the kebab formation simulation.

predominantly in the coiled state. Now the shish is formed by the crystallization of stretched chains and the kebabs are mostly from the shorter chains.

To follow the crystallization of kebabs around a shish, the dynamics of 10 short chains ($N = 180$) near a preformed shish (from seven chains of length $N = 500$) were followed at $T = 9.0$, by fixing the center of mass of the shish. The initial position of the short free chains was chosen at random in a cylinder around the shish, with radius $30r_0$ and height of $60r_0$. Each run started with different initial conditions. Figure 1.34 shows one such initial state.

The flow rate is then maintained at $\dot{\epsilon} = 0.0001$ (lower than $\dot{\epsilon}_c$ corresponding to $N = 180$), and the short chains are allowed to assemble on the shish.

Figure 1.35 illustrates nine examples of the structures obtained in these simulations. It is clear that the chains group into crystallized kebabs on the shish surface. There are only very few areas where the chains are partially or completely stretched under the influence of the shish template. The dominant mode of crystal nucleation on the shish is growth of folded chains grouped into lamellar nuclei. Also, some of the chains do not join the central structure but drift away from it leaving a large gap on the shish between them. These simulations show clearly that the presence of ordered template (the shish) influences the nucleation of lamellae and formation of kebabs. Some of the chains, when in contact with the shish, will stretch almost completely. However, these highly stretched chains are not dominant compared to the highly folded bundles that form crystalline kebabs around the shish. Also, none of the

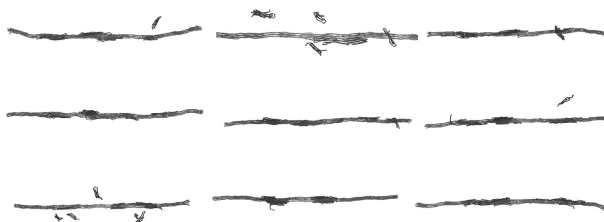


Figure 1.35. Nine examples of freely formed kebabs.

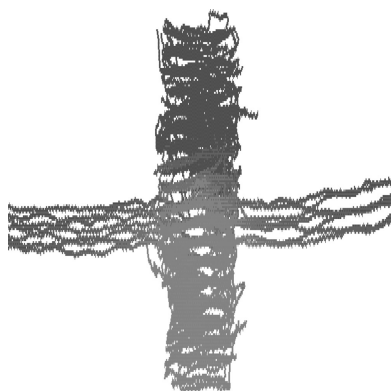


Figure 1.36. A stable shish (7 chains) and kebab (44 chains).

highly stretched chains formed a structure with part of it stretched and attached to the shish and part of it in folded crystalline lamella. The formation of kebab in these simulations is clearly growth of lamellae, nucleated on the shish.

Next, in order to study the stability of the kebab the flow rate was set at $\dot{\epsilon} = 0.001$ and four, initially equilibrated (i.e., in a precrystallized conformation), short chains were added per $t = 2000$ with initial position of $20r_0$ length units away from the stagnation point in the x and y directions. They form a kebab around the shish that was preformed. This procedure was repeated up to 44 short chains in the kebab as shown in Figure 1.36.

The kebab is stable even though $\dot{\epsilon}$ is larger than $\dot{\epsilon}_c$ for a single short chain. The kebab has uniform thickness and does not seem to resemble the flow contour. It must be stressed that the thickness of the kebab formed this way is determined independent of the presence of the shish. The short chains are precrystallized before they are incorporated in the kebab. The kebab formed this way is influenced very little by the shish, except for the fact that it was nucleated on it. The presence of already formed kebab clearly modifies the flow, a feature that is not present in these simulations. The flow, however, is modified in a way that it must be zero in the already formed shish and kebab. This will result in greater stability of the structures that are observed and therefore only emphasize the results in this section. Finally, when the rate of addition of the chains was lowered to one per $t = 5000$, most of the short chains stretched completely as shown on Figure 1.37.

Thus kinetics of the process clearly plays an important role in the kebab formation.

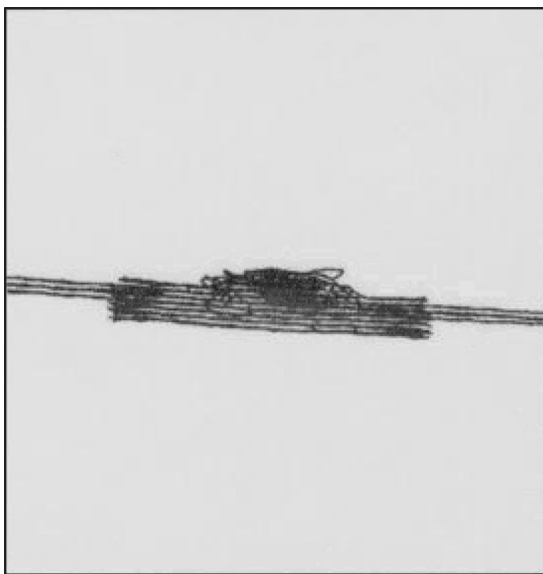


Figure 1.37. An example of completely stretched kebab grown with very slow rate.

VIII. CONCLUSIONS

The main results derived from Langevin dynamics simulations and theoretical considerations are as follows.

A. Initial Crystals

The mechanism of polymer crystallization at very early stages is nucleation and growth, although the computed scattering intensity can be superficially fitted, as in the synchrotron measurements of crystallizing polymers, to a spinodal decomposition description at intermediate wavevectors. The key feature that distinguishes polymers from small molecules at early stages of crystallization is that in the case of polymers, a single chain can participate in several nuclei. This is responsible for the spontaneous selection of a particular scattering wavevector at which the scattered intensity is a maximum.

B. Spontaneous Selection of Finite Lamellar Thickness

Historically, it had been believed that the finite lamellar thickness observed in experiments is completely due to kinetic control and that, if sufficient time is granted for the lamellae, the thickness would progressively grow to the extended chain value. The exact enumeration calculations and an exactly solvable model

discussed above show that this longstanding view might not be correct in general. The equilibrium thickness can be finite and much smaller than the extended-chain value. Before attaining the equilibrium thickness, the crystal evolves through several metastable “quantized” states with smaller lamellar thickness.

C. Kinetics at Growth Front

The growth at the crystalline interface is chain adsorption followed by crystallographic registry. This step is not hindered by a barrier. The newly added, folded chains undergo a rearrangement on the growth front to form stems that are commensurate with the crystal thickness at the growth front. Meanwhile, all chains in the growing lamella undergo significant dynamics, such that the center of mass of a labeled chain can be significantly displaced. These results challenge the conventional Lauritzen–Hoffman theory and its generalizations. More systematic modeling work is necessary to monitor the onset of entropic barriers at the growth front when many polymer chains are adsorbing at the growth front.

D. Molecular Origins of Shish-Kebab Morphology

Emergence of shish-kebabs in polymer crystallization under extensional flow is intimately related to the discontinuous coil–stretch transition of isolated chains. The computed free-energy landscape shows that there are in general two populations of stretched and coiled conformations at a given flow rate, even for monodisperse chains. While the stretched chains crystallize into shish, the coiled chains first form single-chain lamellae and then adsorb to the shish constituting the kebabs. Any local inhomogeneity in polymer concentration dramatically alters the population of stretched and coiled conformations, thus significantly influencing the onset of shish-kebab morphology. The propensity of kebabs is reduced by lowering the rate of crystallization and/or increasing the flow rate.

Although these results illustrate the inadequacies of the underlying assumptions of the classical theories, alternate analytically tractable theories accounting for newly discovered features have not yet emerged. The primary focus of this review is isolated lamellae. We have not discussed the fundamental issues behind the formation of hierarchy of morphological features starting from packing of monomers in unit cells at atomic length scales to packing of spherulites at macroscopic length scales. Specifically, how do lamellae branch out and form spherulites? What is the structure of the core of a spherulite, and why does the spherulite grow radially and linearly with time? Under what conditions are spherulites unstable? Why do the lamellae inside spherulites helically twist, although the lamellae are made up of achiral molecules? These are only a few of the intriguing puzzles in polymer crystallization.

Acknowledgments

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