Phase field modeling of the ring-banded spherulites of crystalline polymers: The role of thermal diffusion*

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The ring-banded spherulite is a special morphology of polymer crystals and has attracted considerable attention over recent decades. In this study, a new phase field model with polymer characteristics is established to investigate the emergence and formation mechanism of the ring-banded spherulites of crystalline polymers. The model consists of a non-conserved phase field representing the phase transition and a temperature field describing the diffusion of the released latent heat. The corresponding model parameters can be obtained from experimentally accessible material parameters. Two-dimensional calculations are carried out for the ring-banded spherulitic growth of polyethylene film under a series of crystallization temperatures. The results of these calculations demonstrate that the formation of ring-banded spherulites can be triggered by the self-generated thermal field. Moreover, some temperature-dependent characteristics of the ring-banded spherulites observed in experiments are reproduced by simulations, which may help to study the effects of crystallization temperature on the ring-banded structures.

Keywords: ring-banded spherulite, phase field model, thermal diffusion, crystalline polymers

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1. Introduction

The ring-banded spherulite is one of the special morphologies of crystalline polymers. It has a periodic structure of concentric rings or bands attributable to lamellar twisting or discontinuous lamellar stacking in radial directions.[1] This structure was first observed by Keller[2] with the polarized light microscope in 1955 during the crystallization of polyethylene. So far, the ring-banded spherulites have been observed during the crystallizations of many polymers under certain conditions, such as polyethylene, polyvinylidene fluoride, polyester, and polyamide.

At present, the ring-banded spherulites have attracted considerable attention for their beautiful outward appearances, mysterious internal structures, and potential application values. The phenomenal characteristics of ring-banded spherulites have been known from experimental studies,[3–9] but the specific formation mechanisms of such intricate structures remain poorly understood.[3,10,11] A potential way to assist the experimental studies in finding out further mechanisms of such structures is through mathematical modeling. As the microscopic simulation of polymer crystallization is still impractical, the coarse grained models, which are semi-empirical models based on physical laws or experimental results, have gained more attention from researchers. The most prevalent conception among the coarse grained models is the phase field theory.

The phase field theory describes interfacial problems based on the Allen–Cahn equation or (and) the Cahn–Hilliard equation.[12] The Allen-Cahn equation is a non-conserved phase field equation often used to describe phase transitions, and the Cahn–Hilliard equation is a conserved phase field equation often used to describe phase separations. The two equations were originally developed from the time-dependent Ginzburg–Landau (TDGL) equation. In the phase field models for crystallization, a non-conserved crystal order parameter ψ is defined to indicate whether the material is solid or liquid. The evolution of ψ is governed by an Allen–Cahn equation coupled to either a temperature field for pure substances or a concentration field for blends. The phase field models have been successfully applied to understand the dendritic growth of metals.[13,14] And more recently, they have been applied to polymer systems for modeling more complex crystal morphologies.[15–24]

For the ring-banded spherulites of crystalline polymer blends, simulation work has been done based on the phase field models. Kyu *et al.*[16] revealed that the target and spiral growth patterns in ring-banded spherulites of crystalline polymer blends can be predicted from a phase field model, which is established by coupling a non-conserved crystal order parameter and a conserved compositional order parameter. Subsequently, Xu *et al.*[17] modified the model of Kyu *et al.* to investigate the phenomenon of ring-band breakup in spherulites of poly(vinylidene fluoride) and poly(ethylene-co-vinyl acetate) blends. The above two studies concern the poly-

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mer blends, for which the phase separation is prominent during the crystallization. So, a concentration field is involved to describe the competition between the phase separation and crystallization. However, there are still many polymers, which are not blended with other polymers, exhibiting ring-banded spherulites in their crystallizations. For these polymers, the equation pertaining to concentration is unnecessary because the phase separation during crystallization can be ignored. This leaves only the equation about the non-conserved crystal order parameter remaining. Therefore, in this case, the phase field model proposed by Kyu *et al*. is incapable of modeling the ring-banded spherulites of these polymers. And as far as we know, other existing phase field models for polymer crystallization are also incapable of doing this.

The primary objective of the present paper is to establish a new phase field model to model the ring-banded spherulites of crystalline polymers (single component), and further to elucidate the formation mechanism of these ring bands. From the simulation studies of Kyu *et al*.[16,17] as well as some theoretical predictions,[25] the formation mechanism of the ring-banded spherulites of crystalline polymer blends may be the competition between lamellar growth and melt diffusion. However, for crystalline polymers, the formation mechanism may be the competition between lamellar growth and thermal diffusion.[25] Therefore, the phase field model for crystalline polymers should include a temperature field rather than a concentration field.

Xu *et al*.[18,19] have proposed a phase field model for crystalline polymers, which couples a non-conserved phase field with a temperature field and has the advantage of obtaining its model parameters from experimentally accessible material parameters. It has been demonstrated that the model is capable of modeling the faceted, dendritic and lamellar branching spherulites of crystalline polymers. But through large amounts of simulations, we found that this model cannot simulate the ring-banded spherulites. In order to model the ring-banded spherulites of crystalline polymers, a new phase field model is established in this paper by modifying the model of Xu *et al*.[18,19] Compared with the original model, the thermodynamic driving force part of the free energy is intensified. After the modification, the new model is endowed with the ability to reproduce the ring-banded spherulites of crystalline polymers. The simulation results obtained by the new model at different crystallization temperatures are qualitatively in accordance with the experimental observations. Therefore, the new model can be used to determine the effects of the crystallization temperature on the ring-banded structures. On the whole, the present paper demonstrates the formation of ring-banded spherulites can be triggered by thermal diffusion.

The remainder of this paper is organized as follows. In Section 2, a new phase field model is established for modeling the ring-banded spherulites of crystalline polymers. And then, in Section 3, the proposed model is used to simulate the ring-banded spherulites of polyethylene film. Finally, some brief conclusions are drawn in Section 4.

2. Theoretical model

The phase field model used in this work is based on the Ginzburg–Laudau theory. The classical model for the solidification of a pure substance includes a phase field and a self-generated temperature field.[26] At present, this kind of model has been successfully used to reveal the mechanisms of the faceted, dendritic, and lamellar branching growth of polymer spherulites under quiescent conditions.[18,19] However, for another growth pattern, that is the ring-banded growth of polymer spherulites, the existing phase field model is incapable of reproducing it. In this section, a new phase field model is established to model the ring-banded spherulites of crystalline polymers. The detailed descriptions of the model are as follows.

2.1. Free energy of the system

In the phase field modeling for the solidification of a pure substance, we proceed by writing the Ginzburg–Laudau free energy of the system $F(\psi,T)$ in terms of a combination of a local free energy density $f_{\text{local}}(\psi,T)$ and a nonlocal free energy density $f_{\text{grad}}(\psi)$ involving a non-conserved crystal order parameter ψ as

$$F(\psi,T)=\int[f_{\text{local}}(\psi,T)+f_{\text{grad}}(\psi)]\,\mathrm{d}\Omega, \tag{1}$$

where T is the temperature and Ω is the region occupied by the system. The crystal order parameter ψ is defined as the ratio of lamellar thickness over optimum lamellar thickness, and its value indicates whether the substance is liquid or solid. The evolution of ψ represents the crystal growth during solidification.

It is generally known that the polymer crystals are inherently imperfect due to the complex long-chain structures. This is one of the main distinguishing characteristics between polymer and other crystalline materials. In order to account for the various metastable states of polymer crystals, Harrowell and Oxtoby[27] have given a local free energy density in form of an asymmetric double well as follows:

$$f_{\text{local}}(\psi,T)=W\int_0^{\psi}\phi(\phi-\zeta_0)[\phi-\zeta(T)]\,\mathrm{d}\phi, \tag{2}$$

where W is a dimensionless coefficient describing the height of energy barrier for surface nucleation, ζ_0 is the corresponding value of ψ at the supercooling-dependent stable solidification potential, and $\zeta(T)$ is the unstable energy barrier.

Specifically, the value of ψ is usually between 0 and 1, where 0 represents the amorphous state and 1 the crystalline

state at equilibrium. Because the true thermodynamic equilibrium is rarely realized in polymer crystallization, the polymer crystals are inherently imperfect containing sizable defects or amorphous materials. For this reason, when the polymer is at its stable solidification state, the crystal order parameter ψ would be less than 1. Because the degree of the imperfection usually depends on supercooling or melting temperature, the value of ψ at the stable solidification potential may be simply estimated as $\zeta_0=T_m/T_m^0$,[18] where T_m and T_m^0 are respectively the experimental melting temperature and equilibrium melting temperature. In particular, T_m is dependent on the crystallization temperature T_c (the initial temperature), since the crystallinity, crystalline morphology, and imperfection of the polymer crystals would be strongly dependent on supercooling.[28]

It should be noted that ζ_0 is not the commonly known crystallinity of polymer sample, but the local crystallinity of the single crystal. Indeed, the local crystallinity of the single crystal would be higher than the crystallinity of the spherulite due to its greater crystal perfection, and further the crystallinity of the spherulite would be higher than the overall crystallinity of the polymer sample in experiments.[29]

The unstable energy barrier $\zeta(T)$ is a monotonic increasing function of temperature T with $\zeta=\zeta_0/2$ at the melting temperature T_m. It has the most significant influence on the simulation results. The configuration of the $f_{local}(\psi,T)$ curve can be varied by ζ. When $T<T_m$ ($\zeta<\zeta_0/2$), the melt state is metastable and $f_{local}(\psi,T)$ has a global minimum at $\psi=\zeta_0$. In this case, the crystalline state is the stable phase as it has the lowest free energy. On the other hand, when $T>T_m$ ($\zeta>\zeta_0/2$), the crystalline state becomes metastable as the global minimum of $f_{local}(\psi,T)$ is at ψ=0, which corresponds to a stable liquid phase.

Note that the expression of $f_{local}(\psi,T)$ given in Eq. (2) is different from the one used in common phase field models,[30] where $f_{local}(\psi,T)$ consists of two parts, which are a double well potential part corresponding to the energy barrier and a supercooling-dependent interpolating part corresponding to the driving force. By contrast, the current expression has a coupled double well form, where the unstable energy barrier ζ is responsible for the competition between the driving force and energy barrier. By using the expression of ζ given in Ref. [18], we failed to predict the ring-banded structures of polymer spherulites. And there is no previously published literature concerning the simulation of ring-banded spherulites for pure substance by the phase field models. In order to model the ring-banded spherulites for crystalline polymers, we attempt to modify the expression of ζ. Considering the fact that polymer crystallization is very sensitive to the change of temperature, we infer that the diving force part in ζ is underestimated for the growth of the ring-banded spherulites. So a modified ζ reflecting steeper temperature dependence of polymer crystallization is given as

$$\zeta=\hat{\zeta}+\beta(T), \tag{3}$$

where $\beta(T)$ is the added thermodynamic driving force and

$$\hat{\zeta}=\frac{4\zeta_0\hat{\psi}-3\hat{\psi}^2}{6\zeta_0-4\hat{\psi}} \tag{4}$$

is the original expression given in Refs. [18] and [19] with

$$\hat{\psi}=\frac{T_m^0-T_m}{T_m^0-T}\zeta_0. \tag{5}$$

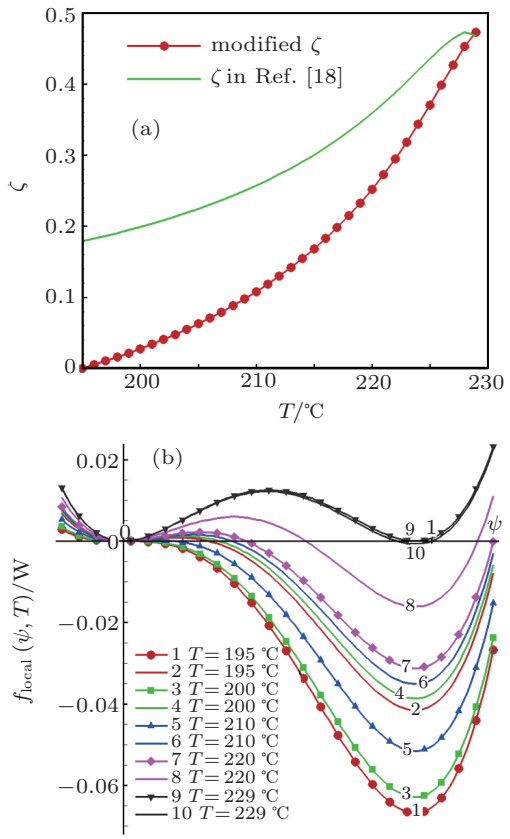


Fig. 1. (color online) Comparisons of the modified ζ and the corresponding local free energy density with those used in Ref. [18] (curves 2, 4, 6, 8, 10). The equilibrium melting point, melting temperature, and crystallization temperature used are from Ref. [18], which are $T_m^0=242$ °C, $T_m=229$ °C, and $T_c=195$ °C, respectively. (a) Unstable energy barrier ζ; (b) local free energy density.

In practice, the added driving force $\beta(T)$ should be a monotonic function of temperature (or supercooling). One of the simplest formulations[30,31] which meet the requirement is

$$\beta(T)=a\frac{T-T_m}{T_m}, \tag{6}$$

where a is a dimensionless parameter dependent on the crystallization temperature T_c. In order to determine a for a specific T_c, a value of ζ at a certain temperature $T\neq T_m$ should be known. Generally, the temperature near the growing interface is greater than T_c, and the value of ζ at T_c has no direct influence on the growth of the crystal. Based on this, we may

assume $\zeta = 0$ at T_c. From this assumption, by inserting $T = T_c$ into Eq. (3) we get

$$a = \hat{\zeta}\frac{T_m}{T_m - T_c}, \tag{7}$$

and hence

$$\beta(T) = \hat{\zeta}\frac{T - T_m}{T_m - T_c}, \tag{8}$$

$$\zeta = \hat{\zeta}\cdot\frac{T - T_c}{T_m - T_c}. \tag{9}$$

Figure 1 shows the unstable energy barrier ζ and the local free energy density $f_{local}(\psi, T)$ given in this work and Ref. [18]. As can be seen, the modified ζ and the corresponding $f_{local}(\psi, T)$ have stronger temperature dependence. By employing the modified ζ we have obtained a series of ring-banded morphologies in the simulations of polymer crystallizations (see Section 3). This in turn indicates that the ring-banded spherulites are more sensitive to temperature variations than the faceted, dendritic, and lamellar branching spherulites.

In addition, the nonlocal free energy density can be written in form of the gradient of crystal order parameter describing the symmetric or asymmetric growth process as follows:

$$f_{grad}(\psi) = \frac{1}{2}\kappa_0^2(\nabla\psi)^2, \tag{10}$$

where κ_0 is the coefficient of interface gradient. Because the ring-banded morphologies are homogenous, the anisotropy of the surface energy is not involved.

2.2. Phase field model

According to the Ginzburg–Laudau theory, the temporal evolution of the crystal order parameter can be governed by the following non-conserved phase field equation:

$$\frac{\partial\psi(\boldsymbol{x},t)}{\partial t} = -\Gamma\frac{\delta F(\psi,T)}{\delta\psi(\boldsymbol{x},t)}, \tag{11}$$

where Γ is the rotational mobility of the system which is inversely proportional to the viscosity of the melt, $\boldsymbol{x}$ is the spatial coordinates within Ω and t is the time.

By substituting Eqs. (1), (2), (9), and (10) into Eq. (11), we obtain

$$\frac{\partial\psi(\boldsymbol{x},t)}{\partial t} = -\Gamma\left(W\psi(\psi-\zeta)(\psi-\zeta_0) - \kappa_0^2\nabla\cdot(\nabla\psi)\right). \tag{12}$$

Before use, the model parameters W and κ_0 should be determined. In practice, the two parameters may be calculated through experimentally measurable quantities by[18]

$$W = 6\frac{\Delta H}{RT\zeta_0^3}\left(\frac{T_m - T}{T_m^0}\right)\left(\frac{\zeta_0}{2} - \hat{\zeta}\right)^{-1}, \tag{13}$$

$$\kappa_0 = 6\frac{\sigma}{nRT}\left(\frac{2}{W}\right)^{1/2}, \tag{14}$$

where ΔH is the latent heat, R is the gas constant, σ is the surface free energy per unit area, and n is the amount of substance of polymer monomers per unit volume. Although the formulas for W and κ_0 are temperature-dependent, it is not essential to change their values during the solidification. In reality, it is hard to accurately estimate the two parameters during the solidification, because not only the temperature but also the latent heat ΔH and surface free energy σ may change during the solidification. Thus, equations (13) and (14) are used only to supply estimations for the two parameters from experimentally measurable quantities. For isothermal crystallization, the two parameters are calculated by directly inserting the initial temperature T_c into the formulas and remain unchanged during the solidification. That is to say, we regard W and κ_0 as a function of T_c instead of T for isothermal crystallizations.

Another important factor in polymer crystallization is the temperature field created by the liberation of latent heat. The latent heat could exert an appreciable effect on the growth of crystal interface. To determine the temperature at the growing crystal fronts, a heat conduction equation may be deduced from the conservation law of enthalpy taking the form of

$$\frac{\partial T}{\partial t} = \alpha\nabla^2 T + K\frac{\partial\psi}{\partial t}, \tag{15}$$

where $\alpha = k_T/(\rho C_p)$ and $K = \Delta H/C_p$ with ρ, C_p, and k_T being the density, specific heat capacity, and thermal conductivity respectively.

In order to write the phase field equation (12) and heat conduction equation (15) in dimensionless form, we introduce the parameters of the characteristic length for single crystals d and the mass diffusivity D. Then, the temporal and spatial variables are rescaled to $\tau = Dt/d^2$, $\tilde{x} = x/d$, $\tilde{y} = y/d$, and the temperature is rescaled to $U = (T - T_c)/(T_m - T_c)$ with T_c being the experimental temperature of crystallization. The mobility Γ may be estimated from d and D as $\Gamma = D/d^2$. With these dimensionless variables, the final governing equations can be rewritten in the following dimensionless form:

$$\frac{\partial\psi}{\partial\tau} = -\left(W\psi(\psi - \zeta(U))(\psi - \zeta_0) - \tilde{\kappa}_0^2\tilde{\nabla}\cdot\left(\tilde{\nabla}\psi\right)\right), \tag{16}$$

$$\frac{\partial U}{\partial\tau} = \tilde{\alpha}\tilde{\nabla}^2 U + \tilde{K}\frac{\partial\psi}{\partial\tau}, \tag{17}$$

where

$$\tilde{\nabla} = \left(\frac{\partial}{\partial\tilde{x}}, \frac{\partial}{\partial\tilde{y}}\right), \quad \tilde{\kappa}_0^2 = \frac{\kappa_0^2}{d^2}, \quad \tilde{\alpha} = \frac{\alpha}{D}, \quad \tilde{K} = \frac{K}{T_m - T_c}.$$

In this study, equations (16) and (17) are solved numerically in two dimensions over rectangular domains Ω by using a central finite difference method for spatial discretization and an explicit forward difference for temporal discretization. The homogeneous Neumann boundary conditions $\partial\psi/\partial\tau = 0$ and $\partial U/\partial\tau = 0$ are imposed on the domain boundaries $\partial\Omega$. Initially, several points are placed in the domain to serve as seeds for initializing solidification. Initial value of ψ is prescribed

as ζ_0 at seeds and 0 elsewhere, and initial value of U is prescribed as 0 throughout the entire domain, that is, the initial temperature for the crystallization is T_c.

In reality, the heat diffusion is much faster than the mass diffusion. Therefore, when α is the thermal diffusivity and D the mass diffusivity, the ratio α/D would be several orders of magnitude greater than 1. But this will bring tremendous computation cost to the simulation of the phase field model, because the temporal step size $\Delta\tau$ would be very small to ensure numerical stability of the heat conduction equation. For the simulations in this paper, if a physical value of the ratio α/D is used, then these already huge calculations would take about 10^4 times longer. Therefore, because a personal computer is used in simulations, we are constrained to take a greater mass diffusivity D. In order to reduce the computation cost in phase field modeling, similar approaches were also used by many other researchers. For instance, Warren *et al*. in their work increased the interface thickness[32] and Gránásy *et al*. increased the interface thickness as well as the diffusion coefficient.[15] The experience of us and these researchers implies that the structures obtained by these approaches are not qualitatively correct, but also have predictive power. Since we seek here a qualitative understanding, the mass diffusivity D will be properly increased in this study.

3. Results and discussion

It has been found that the ring-banded spherulites of polyethylene film can be observed when the samples are crystallized at 80 °C and above, and the spacing between the rings becomes increasing narrower at lower crystallization temperatures, until they could not be resolved any longer.[1,2,33,34] These findings present challenge to us in testing the ability of our phase field model for ring-banded spherulites. In this section, we attempt to reproduce these findings related to polyethylene by the proposed model, and further try to predict more features of the ring-banded spherulites and reveal the possible mechanisms behind them.

3.1. Parameters

The model parameters in our phase field model can be calculated by using experimentally accessible physical parameters, so a set of material parameters of polyethylene from references is used in our simulations. These parameters are $T_m^0 = 146$ °C, $T_c = 90$ °C, $T_m = 130.9$ °C, $\rho = 980$ kg/m^3, $\Delta H = 3.73$ kJ/mol (of CH_2 units),[35] $C_p = 34.3$ J/(mol·K) (of CH_2 units), $k_T = 0.52$ J/(m·s·K),[36] $\sigma = 0.031$ J/m^2,[37] $D = 1\times10^{-7}$ cm^2/s,[36] and $d = 1\times10^{-9}$ m (unit cell dimension of crystallized melt).[36] According to these data, a set of model parameters are calculated and specified in Table 1. Remember that $\tilde{\alpha}$ is calculated by properly increasing D. In practice, T_m may be supercooling-dependent. However, its value is often not determined experimentally for each crystallization temperature. In this work, T_m is estimated from T_c and T_m^0 in accordance with the Hoffman–Week approach.[28,38] This may allow obtaining sets of model parameters associated with other experimental temperatures.

Table 1. Model parameters calculated from experimentally determined material parameters of polyethylene.

Symbol	Data set	Symbol	Data set
ζ_0	0.896	$\tilde{\kappa}_0^2$	0.449
$\hat{\zeta}$	0.157	$\tilde{\alpha}$	0.217
W	3.477	$\tilde{K}$	2.661

In the simulations, grid sizes of 256×256 and 512×512 are employed for single crystal and multiple crystals, respectively. The dimensionless temporal step size and spatial step size are fixed as $\Delta\tau$=0.1 and $\Delta\tilde{x} = \Delta\tilde{y} = 1.0$.

3.2. Single crystals

The single crystals are the most studied case in polymer crystallization. In this case, because the crystal has no neighborhoods (competitors), its growth will not be constrained by space. Figure 2 shows the simulated growth of a regular ring-banded spherulite of polyethylene crystallized at a temperature of 90 °C. It is obvious that the bands are self-similar and uniformly distributed. The new band is usually born before the previous one completing its growth. And as the elapse of time, the band located in the center of the spherulite, which has been transformed into a circle, becomes smaller and smaller. This phenomenon corresponds to the melting of the crystal in physics. So, one reasonable prediction is that the crystallized structure can be remelted during the crystallization due to the increase of temperature.

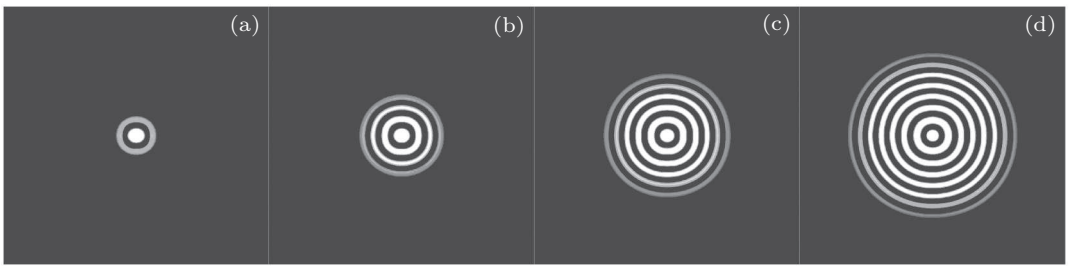


Fig. 2. The simulated spatiotemporal growth of ring-banded single crystal of polyethylene film at a crystallization temperature of 90 °C in the crystal order parameter field. (a) $\tau = 100$; (b) $\tau = 200$; (c) $\tau = 300$; (d) $\tau = 400$.

Figure 3 shows the variation of the spherulite radius over time during the crystal growth. As seen, the radial growth rate fluctuates periodically with banding. But the average radial growth rate in each period is nearly constant, which results in a uniform increase of the band number. Without considering the fluctuates, the prediction will be consistent with the theory given by Lauritzen and Hoffman,[39] who indicated that the radial growth rate of polymer spherulites is a function of crystallization temperature and when a constant crystallization temperature is specified the radial growth rate will be constant.

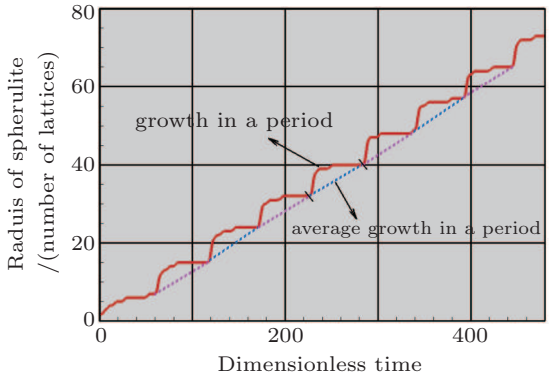


Fig. 3. (color online) The variation of the spherulite radius over time during the crystal growth.

As is well known, the crystalline morphology of polymers is influenced and controlled by many factors, such as thermal history, concentration diffusion, chain conformation, thickness of polymer film, etc. However, for the crystallization of a given polymer sample under quiescent and isothermal conditions, the crystallization temperature becomes a deciding factor of the crystalline morphology. Therefore, testing the temperature dependence of the proposed model is essential. As has been revealed by Ren *et al.*,[40] the ring-banded spherulites can be observed not at any crystallization temperature but only at the temperature located in a certain range. To investigate whether the proposed phase field model can represent the effects of temperature on the ring-banded spherulites, a wide range of crystallization temperature is used in simulations. Figure 4 shows the morphologies of the simulated crystals under a series of crystallization temperatures. The results demonstrate that the crystalline morphology indeed has great dependence on the crystallization temperature. When the sample is crystallized at the temperatures between 85 °C and 100 °C, the simulated ring bands are regular. But when the crystallization temperature reduces to 80 °C, some imperfections begin to appear in the center of the ring-banded spherulites.[41] And as the crystallization temperature is further decreased, the imperfections turn out to be more serious so that it is hard to clearly distinguish each band from the irregular ring-banded spherulites.[3] This predication shows good agreement with the experimental observations of Keller.[2] Furthermore, when the sample is crystallized at the temperatures greater than 100 °C, the ring-banded structures begin to disappear. At this stage, the simulated spherulites are neither ring-banded nor lamellar branching. As can be seen, the crystal obtained at the crystallization temperature of 105 °C is of the spherical shape without exhibiting any internal textures.[18] In summary, the above results together indicate that the ring-banded spherulites of polyethylene may be observed experimentally at a temperature range from 80 °C to 100 °C. This is qualitatively in accordance with the experimental findings revealed by Ren *et al.*,[40] that is, the ring-banded spherulites for a given polymer can only be observed in a certain temperature range.

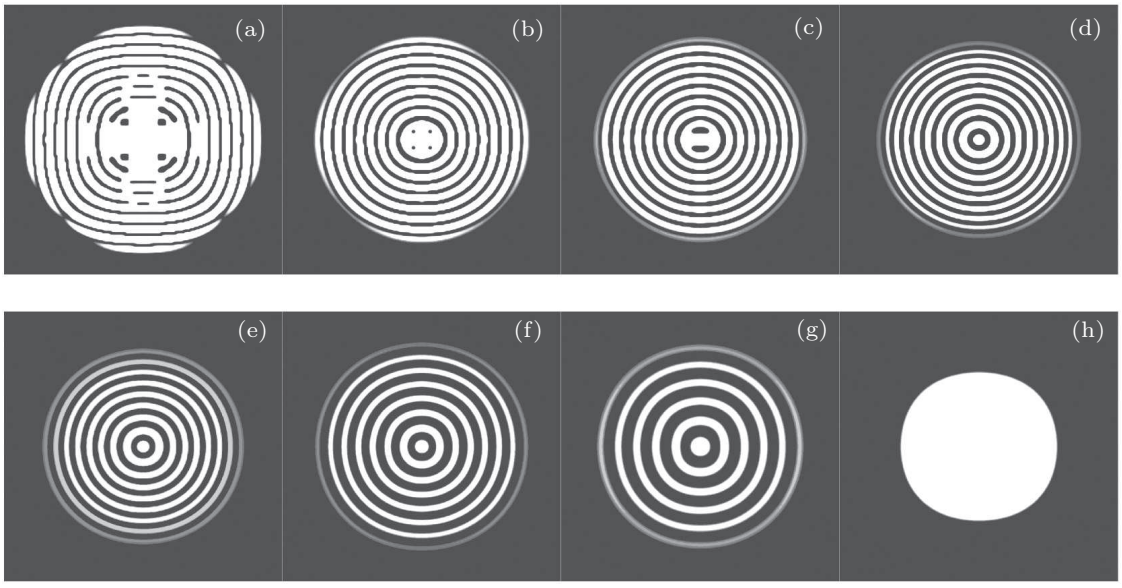


Fig. 4. The simulated morphologies of the ring-banded single crystals of polyethylene film under different crystallization temperatures. (a) $T_c = 70$ °C, $\tau = 260$; (b) $T_c = 75$ °C, $\tau = 280$; (c) $T_c = 80$ °C, $\tau = 320$; (d) $T_c = 85$ °C, $\tau = 380$; (e) $T_c = 90$ °C, $\tau = 440$; (f) $T_c = 95$ °C, $\tau = 600$; (g) $T_c = 100$ °C, $\tau = 740$; (h) $T_c = 105$ °C, $\tau = 21000$.

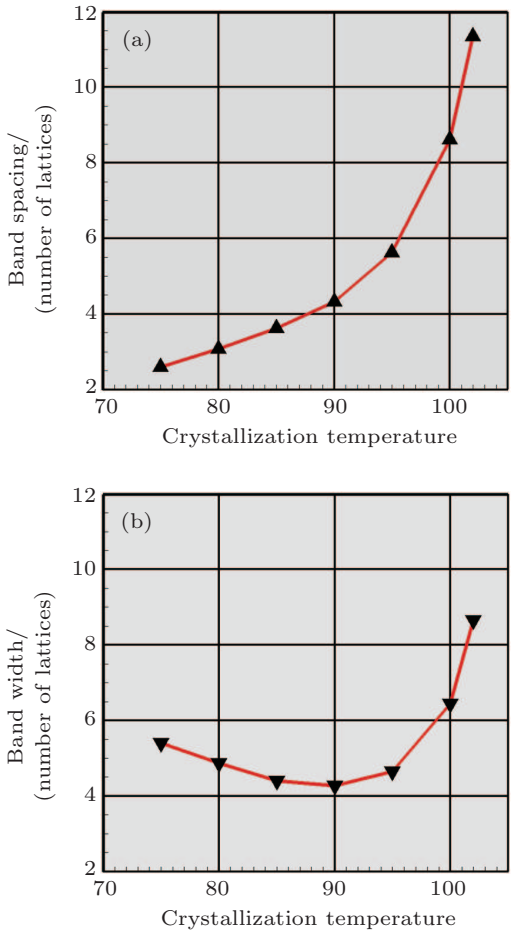


Fig. 5. (color online) Plots of band spacing and band width of the ring-banded spherulites about the crystallization temperature: (a) band spacing; (b) band width.

Except for the formation and regularity of the ring-banded spherulites, the crystallization temperature still influences the band width and band spacing of the ring-banded spherulites in morphology. Experimental studies of both Keller[2] and Ren *et al.*[40] pointed out that the band spacing of the ring-banded spherulites decreases with decreasing the crystallization temperature. This phenomenon can be clearly observed from Fig. 4. Therefore, the proposed phase field model may provide a quantitative approach to study the relationship between the band spacing and crystallization temperature. Figure 5(a) shows the plot of the band spacing against the crystallization temperature. This figure demonstrates a sharp decrease of the band spacing with decreasing the crystallization temperature. Furthermore, the band width of the ring-banded spherulites seems still to be varying with the crystallization temperature from Fig. 4. For clarity, figure 5(b) shows the quantitative relationship between the band width and crystallization temperature. It is obvious that the band width first decreases and then increases with increasing the crystallization temperature. When combined with Fig. 5(a), we find that there is a turning point at which the band width and band spacing are equal. For the polyethylene studied in this work, the turning point is approximately at 90 °C. So far, the influence of the crystallization temperature on the band width has not yet been reported by other researchers. Therefore, the proposed phase field model may have the ability to reveal new features of the ring-banded spherulites.

In reality, the crystallization temperature influences not only the crystalline morphology but also the crystallization kinetics. In this work, the kinetics mainly means the average radial growth rate of the spherulites. It is generally appreciated that the spherulites formed under a deeper supercooling usually grow faster than that formed under a shallower supercooling. From Fig. 4, we can found that the simulated ring-banded spherulites possess this feature. To make a quantitative study, figure 6 shows a plot of the average radial growth rate versus the crystallization temperature. As we can see, the average radial growth rate of the ring-banded spherulites dramatically decreases as the crystallization temperature increases. Besides, it is worthwhile to note that there is a temperature, above which the average radial growth rate of the spherulites reduces sharply. For the current study, this temperature is about 100 °C, which means that the crystallization procedure of the polyethylene will become very difficult when the crystallization temperature is greater than 100 °C. This prediction is again qualitatively in accordance with the experimental results of the previous researchers.[2,42]

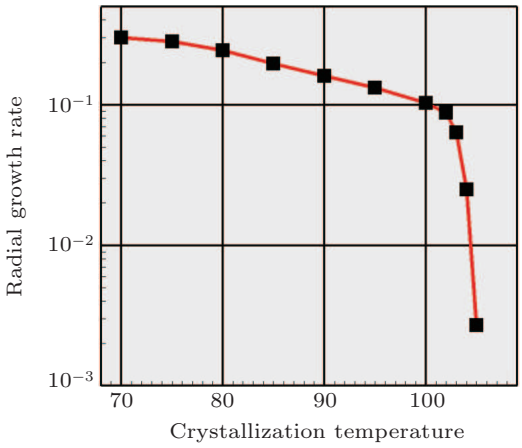


Fig. 6. (color online) Relationship between average radial growth rate of the spherulites and crystallization temperature.

3.3. Multiple crystals

Multiple nuclei are usually formed in a confined space at the nucleating stage during polymer crystallization. In this case, the crystals cannot grow freely but compete with others for space to grow big. Eventually, the neighboring crystals impinge on each other and grain boundaries appear between them. In simulations, nine crystal nuclei are randomly generated in the computational domain. Figures 7–9 show the simulation results obtained at crystallization temperatures of 80 °C, 90 °C, and 100 °C respectively. As seen, grain boundaries

appear between the neighboring ring-banded spherulites, and consequently the impinged spherulites transform into polyhedron in shape. The ring bands of each spherulite near the interface are broken by grain boundaries. Moreover, the simulation results reveal that the appearances of grain boundaries are dependent on the crystallization temperature. For the results shown in Figs. 7–9, three different types of grain boundaries are observed.

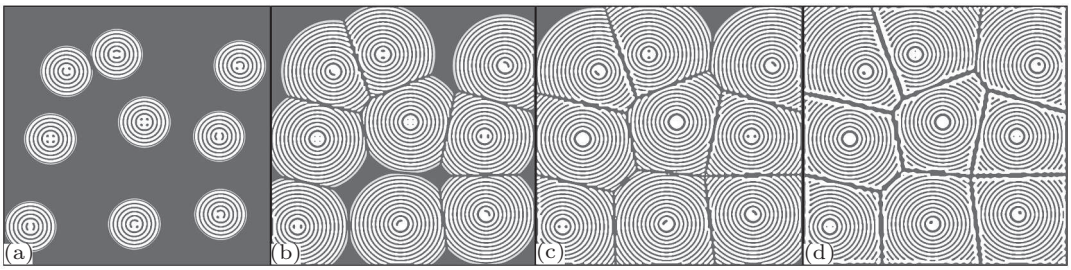


Fig. 7. The simulated spatiotemporal growth of ring-banded multiple crystals of polyethylene film at a crystallization temperature of 80 °C. (a) $\tau = 200$; (b) $\tau = 400$; (c) $\tau = 500$; (d) $\tau = 700$.

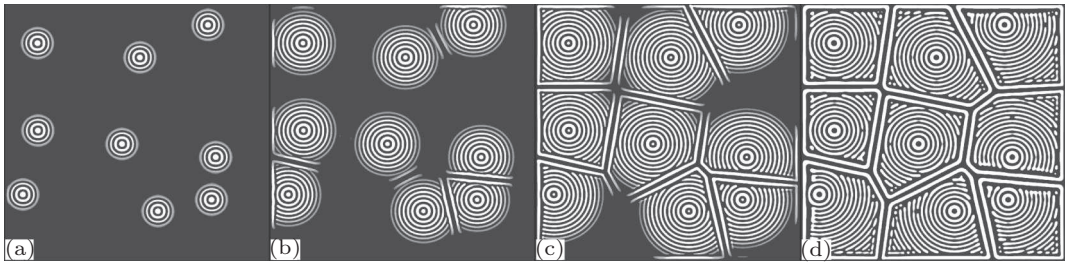


Fig. 8. The simulated spatiotemporal growth of ring-banded multiple crystals of polyethylene film at a crystallization temperature of 90 °C. (a) $\tau = 200$; (b) $\tau = 400$; (c) $\tau = 600$; (d) $\tau = 1000$.

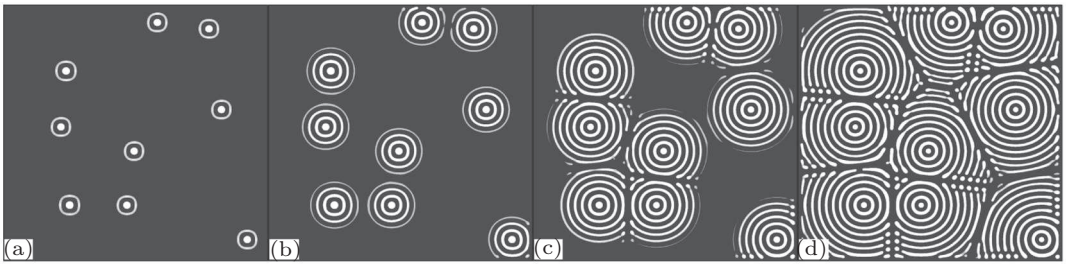


Fig. 9. The simulated spatiotemporal growth of ring-banded multiple crystals of polyethylene film at a crystallization temperature of 100 °C. (a) $\tau = 300$; (b) $\tau = 500$; (c) $\tau = 800$; (d) $\tau = 1200$.

3.4. Influence of noises

As demonstrated by Kobayashi,[26] small noises added on the interface may show great influence on crystalline morphology. In this subsection, we consider the fluctuation of metastable states by introducing a random noise to the unstable energy barrier ζ, which can be expressed as

$$\zeta = \zeta(1.0 + \delta), \tag{18}$$

where δ represents a small noise which is assumed uniformly distributed between $-A/2$ and $A/2$. Here A is the amplitude of the noise. After adding the noise term, the simulations might become somewhat more realistic and we can examine the stability of the interfaces of ring-banded spherulites against the noise.

First, let us study the influences of noises on the morphologies of single ring-banded spherulites. The simulation results at time $\tau = 480$ under a crystallization temperature of 90 °C with noises of different strength are shown in Fig. 10. As can be seen, the amplitudes of the noises show strong influence on the morphologies of single ring-banded spherulites. Once a noise is introduced, the ring-banded structures become irregular and the degree of irregularity increases with increasing the amplitude of the noise. When the noise is big enough, the breakup of ring-banded structures[17] takes place. Generally, the bigger noise causes more serious breakup. Therefore, the "noise" in reality may be one of the potential causes for the emergence of irregular ring-banded structures and the breakup of these structures.

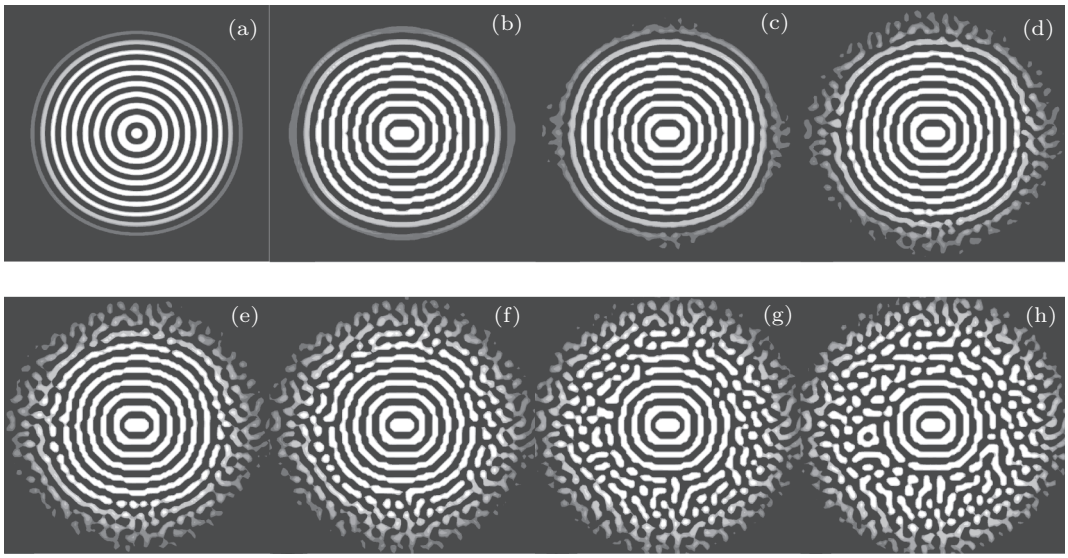


Fig. 10. Influence of the noises on the morphologies of single ring-banded spherulites of polyethylene film at a crystallization temperature of 90 °C at time $\tau = 480$. (a) $A = 0.0$; (b) $A = 0.001$; (c) $A = 0.002$; (d) $A = 0.005$; (e) $A = 0.01$; (f) $A = 0.02$; (g) $A = 0.05$; (h) $A = 0.1$.

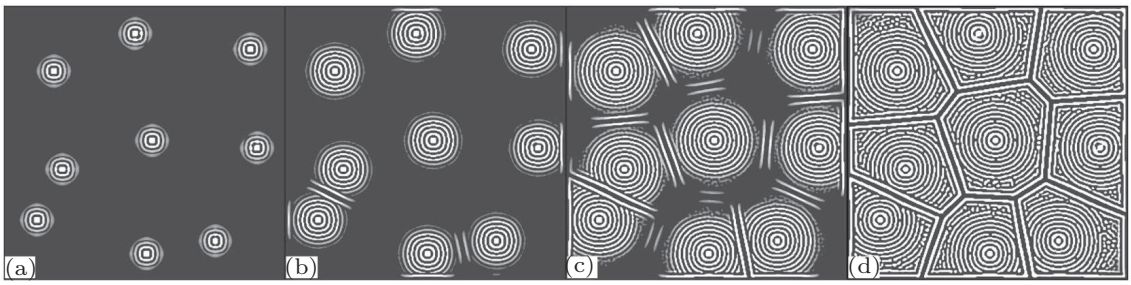


Fig. 11. The simulated spatiotemporal growth of ring-banded multiple crystals of polyethylene film at a crystallization temperature of 90 °C with a noise amplitude $A = 0.001$. (a) $\tau = 200$; (b) $\tau = 400$; (c) $\tau = 600$; (d) $\tau = 800$.

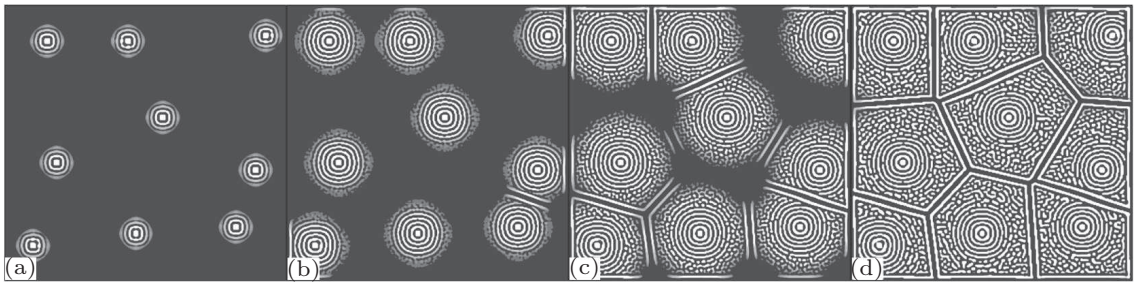


Fig. 12. The simulated spatiotemporal growth of ring-banded multiple crystals of polyethylene film at a crystallization temperature of 90 °C with a noise amplitude $A = 0.01$. (a) $\tau = 200$; (b) $\tau = 400$; (c) $\tau = 600$; (d) $\tau = 800$.

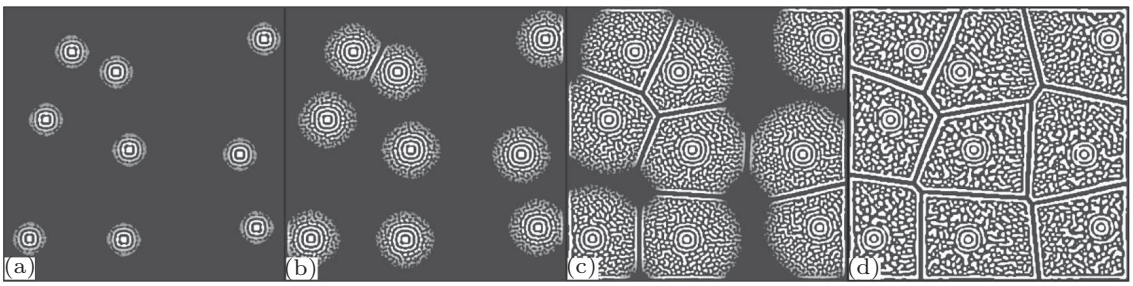


Fig. 13. The simulated spatiotemporal growth of ring-banded multiple crystals of polyethylene film at a crystallization temperature of 90 °C with a noise amplitude $A = 0.1$. (a) $\tau = 200$; (b) $\tau = 400$; (c) $\tau = 600$; (d) $\tau = 800$.

The influences of noises on the morphologies of multiple ring-banded spherulites are also studied. Figures 11–13 show the simulated spatiotemporal growth of ring-banded multiple crystals of polyethylene at a crystallization temperature of 90 °C with noises of amplitudes $A = 0.001$, $A = 0.01$, and $A = 0.1$, respectively. As seen, the noises have strong effect on the morphologies of multiple ring-banded spherulites, but seemingly have no effect on the grain boundaries.

4. Conclusions

In this paper, we have presented a new phase field model to investigate the emergence and formation mechanism of the ring-banded spherulites of crystalline polymers. It demonstrates that the ring-banded spherulites of crystalline polymers can be modeled by the phase field model consisting of a non-conserved phase field and a temperature field. The model calculations and predications for the crystallizations of polyethylene film at a series of crystallization temperatures show good agreement with the experimental observations. It predicts that the ring-banded spherulites for a given polymer can be observed only in a certain temperature range, and the average radial growth rate decreases as the crystallization temperature increases. An interesting feature is that the core of the spherulite becomes smaller as time elapses, which may indicate that the crystallized structure can be remelted during the crystallization due to the accumulation of heat. Moreover, the important finding which is the band spacing of ring-banded spherulites decreases as the crystallization temperature increases can be confirmed in our simulations. Of particular importance, it reveals a new feature of ring-banded spherulites that is the band width first decreases and then increases with increasing the crystallization temperature. The simulations of multiple crystals show that the appearances of grain boundaries are temperature-dependent. Besides, the predicted effects of noise on the morphologies of ring-banded spherulites indicate that "noise" in reality may be one of the potential causes for the emergence of irregular ring-banded structures and breakup of these structures. On the whole, the present paper provides a theoretical evidence for the experimental predication that the thermal diffusion is responsible for the formation of the ring-banded spherulites.[25]

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