

Entanglement on Nucleation Barrier of Polymer Crystal

Fan Peng, Cui Nie, Ting-Yu Xu, Jun-Fang Sheng*, Wei Chen, Wan-Cheng Yu, and Liang-Bin Li*

National Synchrotron Radiation Laboratory, Anhui Provincial Engineering Laboratory of Advanced Functional Polymer Film, CAS Key Laboratory of Soft Matter Chemistry, University of Science and Technology of China, Hefei 230026, China

 Electronic Supplementary Information

Abstract We propose a theoretical approach to quantitatively account for the role of entanglement in the nucleation of polymer melts, which is the unique feature of polymer differentiated from small molecules. By performing molecular dynamics simulations, we obtain the nucleation barriers of polymer systems with different entanglement densities, which exhibits an opposite trend compared to the prediction of the classic nucleation theory (CNT). To amend the deficiency of the CNT in polymer crystallization, we introduce the entanglement free energy to reflect the role of entanglement in polymer nucleation. Specifically, the polymer nucleation not only involves free energies of monomers inside and on the surface of a nucleus as considered in the CNT, but also affects the entanglement network around the nucleus. Our theoretical approach provides a reasonable interpretation for the unsolved nucleation phenomena of polymers in simulations and experiments.

Keywords Nucleation; Entanglement; Molecular simulation

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INTRODUCTION

The connectivity of polymer chains is the unique feature that distinguishes polymers from small molecules,^[1–5] which is manifested as entanglement in bulk or concentrated solution. Entanglement is considered as a rheological concept well formulated by the tube model.^[6–9] However, how the entanglement affects phase transitions, like polymer crystallization, has not been well understood yet.^[10–16] Compared to small molecules, homogeneous nucleation of polymer crystal usually requires a large undercooling,^[17] implying that entanglement inhibits the nucleation. The nucleation of polymeric systems with high entanglement density like polycarbonate (PC) is completely suppressed under conventional conditions.^[18,19] It is not clear whether this nucleation inhibition mainly stems from the entanglement-enhanced nucleation barrier or constrained chain dynamics. Therefore, the understanding of the role of entanglement in nucleation is critical for developing polymer crystallization theory, which is a longstanding challenge in polymer physics.

For decades, how the entanglement affects polymer crystallization has attracted great attention. Previous experiments revealed that the nucleation rate decreases with increasing the entanglement density.^[16,20] Yamazaki *et al.* proposed an empirical relation between the nucleation rate J and

the entanglement density ν_e as $J \sim \exp(-k\nu_e)$.^[21] Computer simulations demonstrated that the distribution of thickness of lamellar crystal statistically follows the local entanglement length.^[22,23] Yet, no quantitatively thermodynamic analysis of the entanglement on nucleation has been reported. Classic nucleation theory (CNT) regards the nucleation of polymers as the behavior of independent monomers, and subsequent modifications only consider the chain connectivity in amorphous structure on the fold surface of nucleus.^[24] Although the concept of reptation has been introduced into polymer crystallization model,^[1,25] we still lack a nucleation theory incorporating the unique connectivity of polymer chain explicitly.

In this work, we performed large-scale molecular dynamics (MD) simulations to study the role of entanglement in nucleation. Two methods are employed to obtain the nucleation barriers of systems with different entanglement densities, *i.e.*, sampling nucleation events from the MD simulations directly, and theoretical calculation according to the CNT. Regrettably, the nucleation barriers obtained by these two methods show opposite trends with increasing the entanglement density. We ascribed this contradiction to the absence of the entanglement effect in the CNT. To amend this defect of the CNT, we introduce the entanglement free energy:

$$G_z = U_z - TS_z \quad (1)$$

where U_z and S_z are the entanglement energy and entropy, respectively. By incorporating the effect of G_z into the CNT, we propose a new theoretical approach for the nucleation of polymers, which is in a good agreement with the nucleation barriers obtained through sampling events in MD simulations.

* Corresponding authors, E-mail: jfsheng@ustc.edu.cn (J.F.S.)

E-mail: lbli@ustc.edu.cn (L.B.L.)

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METHODOLOGY

Model and Simulations

All simulations are performed using the open-source code LAMMPS.^[26] As we focus on the generic behavior of entangled polymeric systems rather than microscopic properties, the widely used coarse-grained polyvinyl alcohol (CG-PVA) model with a fast crystallization rate is chosen to study polymer crystallization.^[27] Parameters of the CG-PVA model in reduced units originate from experimental data. Namely, the Boltzmann constant k_B , the mass of a monomer m , the length σ , and the time τ are reduced to 1. The bond length is $b_0 = 0.5\sigma$. The reduced temperature $T=1$ corresponds to a real temperature 550 K, $\sigma=1$ corresponds to 0.52 nm, and $\tau=1$ is about 3.5 ps. The bond interaction is approximated by a harmonic potential:

$$U_{\text{bond}}(r) = \frac{1}{2}k_{\text{bond}}(r - b_0)^2 \quad (2)$$

where $k_{\text{bond}} = 2704 k_B T / \sigma^2$. The angular interaction is represented by a tabulated potential, and the non-bonded interaction is given by Lennard-Jones 9-6 potential:

$$U_{\text{nonb}}(r) = \varepsilon \left[\left(\frac{\sigma_0}{r} \right)^9 - \left(\frac{\sigma_0}{r} \right)^6 \right] \quad (3)$$

where $\sigma_0 = 0.89\sigma$, and $\varepsilon = 1.511k_B T$. The potential is truncated and shifted to 0 at the minimum of $r_c = 1.02\sigma$, which makes the non-bonded potential purely repulsive. The pressure $P=8$ is adopted to compensate for the attractive interaction, through which the crystallization is accelerated.

By using the CG-PVA model, a series of polymer melts with different entanglement densities are generated. Firstly, simulation boxes with different initial side lengths L_0 (see Table S1 in the electronic supplementary information, ESI) are created. Then, 200 single equilibrated chains with 1000 monomers ($N=1000$) are randomly placed into a simulation box. This step

is referred to the *place* shown in Fig. 1. In this way, a non-equilibrium polymer system with an initial entanglement density is prepared. The initial entanglement density relies on the magnitude of L_0 . After the *place*, the simulation box is gradually compressed to a final side length $L = ca. 45$ in a time duration of 2000τ , during which the pressure of the polymer system is adjusted to $P=8$. However, during the compression, there would be some unreasonably local conformations in the polymer system. To eliminate these unreasonably local conformations, chains are relaxed for 500τ with both their ends being fixed, which assures that no obvious disentanglement occurs in the system during the relaxation. With the above procedures being completed, polymer systems with different entanglement densities are obtained. Note that for the largest simulation box with an initial side length $L_0=600$, as the space is large enough for the placement of chains, chains are regularly arrayed in the box, and keep wholly separated and thus unentangled. Naturally, the entanglement density in this case is the lowest for the cases studied in this work. More details about the entire modeling process are given in S1 of ESI. The relationship between the density of the initial system before compression (ρ_{place}) and the entanglement length in melt systems ($\langle N_{e0} \rangle$) is plotted in Fig. 1. The Z1-code is used to identify the primitive path of chains, and measure the entanglement length of melts (N_e) in the early stage of nucleation.^[28–31] The average entanglement length $\langle N_{e0} \rangle$ of prepared polymer systems ($t=0\tau$) ranges from 267 to 17. $\langle N_{e0} \rangle$ of the equilibrium melt is about 16.4.^[32]

Next, all melt systems are quenched to $T=0.77$ (423.5 K) for isothermal crystallization, during which the time step is chosen as 0.01 (~35 fs), and the periodic boundary conditions are applied on all three axes. The crystallization proceeds in the NPT ensemble with the pressure $P=8$ (1 atm), where the

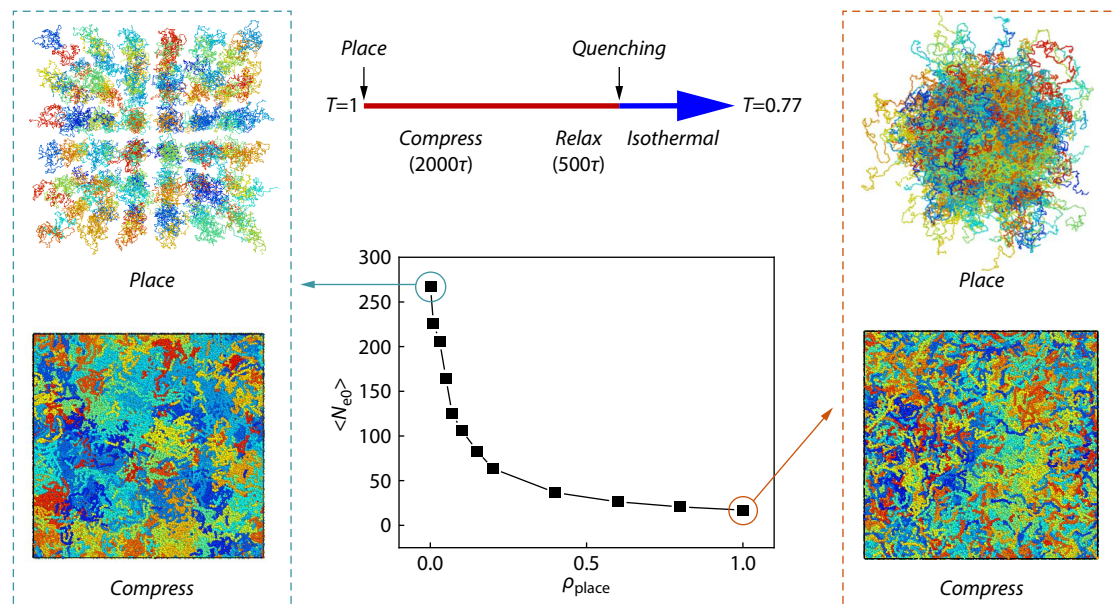


Fig. 1 Schematic diagram of the modeling process, and snapshots of polymer systems with $\langle N_{e0} \rangle = 267$ and $\langle N_{e0} \rangle = 17$. Here, “place” means that randomly picking 200 points inside the simulation box first, and then laying the pre-prepared equilibrated chains with their center of mass on these picked points. Especially, for the largest simulation box $L_0=600$, 200 points are no longer randomly picked but regularly arrayed.

pressure and temperature are controlled by the Nosé-Hoover barostat and thermostat with a damp time of 1000 and 100 MD time steps, respectively. The centrosymmetry parameter (P_{cs})^[33] and the length of successive trans-trans monomers (L_{tt})^[34] are used to identify the crystalline monomers. The nucleation criterion, i.e., $P_{cs} < 1$ and $L_{tt} \geq 8$ is determined according to the distribution analyses of P_{cs} and L_{tt} , which is included in S2 and Fig. S2 in ESI.

It should be noticed that systems with $\langle N_{e0} \rangle = 6 \sim 15$ are also built. However, the nucleation of these systems is extremely difficult and takes a long incubation period. In addition, disentanglement takes place during the incubation, leading to a significant deviation of the entanglement densities from the initial set values when the nucleation occurs. Therefore, these systems are not included in the current work.

Analysis of the Nucleation Free Energy Barrier

The nucleation barrier was obtained by using the mean first-passage time (MFPT) method proposed by Wedekind *et al.*^[35] The MFPT method provides a simple and efficient strategy to analyze MD trajectories of activated processes. By using the MFPT method, the information of the nucleation process can be directly extracted from the trajectories of MD simulations, including the nucleation free energy barrier and the critical nucleus size. However, the huge difference between the time scales of nucleation and growth would affect the analysis results. To overcome this problem, Nicholson *et al.* introduced an analysis method based on the MFPT, and applied it to the simulation of nucleation in *n*-eicosane successfully.^[35,36] This modified MFPT method allows us to extract valuable nucleation kinetic parameters from the simulation data of the nucleation process. The detailed fitting process can be found in S4 of ESI. Then, we can attempt to understand the evolution trend of the nucleation barrier with the entanglement density in the framework of the CNT.

The CNT is a simple and flexible framework to describe nucleation phenomena. Based on the CNT, the nucleation free

energy barrier of a cylindrical nucleus is given as:^[37,38]

$$\Delta G_{\text{CNT}}^* = 2\sigma_l \sigma_f / \varepsilon^2 \quad (4)$$

where σ_l and σ_f are the lateral and fold surface free energy per monomer, respectively, ε is the bulk free energy of the formation of a nucleus per monomer:

$$\varepsilon = \Delta H_i - T(\Delta S_{\text{con},i} + \Delta S_{\text{atom}}) \quad (5)$$

where ΔH_i represents the enthalpy change of a monomer, $\Delta S_{\text{con},i}$ and ΔS_{atom} are the local conformational entropy and atomic entropy changes of a monomer during the nucleation, respectively. Here we are interested in the variation trend of ΔG^* with $\langle N_{e0} \rangle$ rather than the absolute value of ΔG^* . Thus, based on the simulation results, the variation trends of each term in the right side of Eq. (4) with $\langle N_{e0} \rangle$ are evaluated independently in the following sections. (See S5–S7 in ESI for the calculation details)

RESULTS AND THEORY

Simulation Results

The polymer melts with different initial entanglement densities show significantly different nucleation behaviors. Figs. 2(a) and 2(b) present snapshots of the nucleus formation and early growth of the systems with $\langle N_{e0} \rangle = 267$ and $\langle N_{e0} \rangle = 17$, respectively. Nucleation of the former system occurs rapidly involving just a few polymer chains. In contrast, nucleation of the latter system takes a long incubation time involving multiple polymer chains. It is found that the higher entanglement density is, the slower nucleation rate becomes, which is consistent with previous experimental and simulation results.^[21,39,40]

The effect of entanglement on the nucleation kinetics is evaluated by calculating the mean square displacement (MSD) of monomers and the center of mass of a chain. The expressions for the MSD of monomers and the center of mass of a chain are $g_1(t) = \langle [r_i(t) - r_i(0)]^2 \rangle$, and $g_3(t) = \langle [r_{\text{cm}}(t) -$

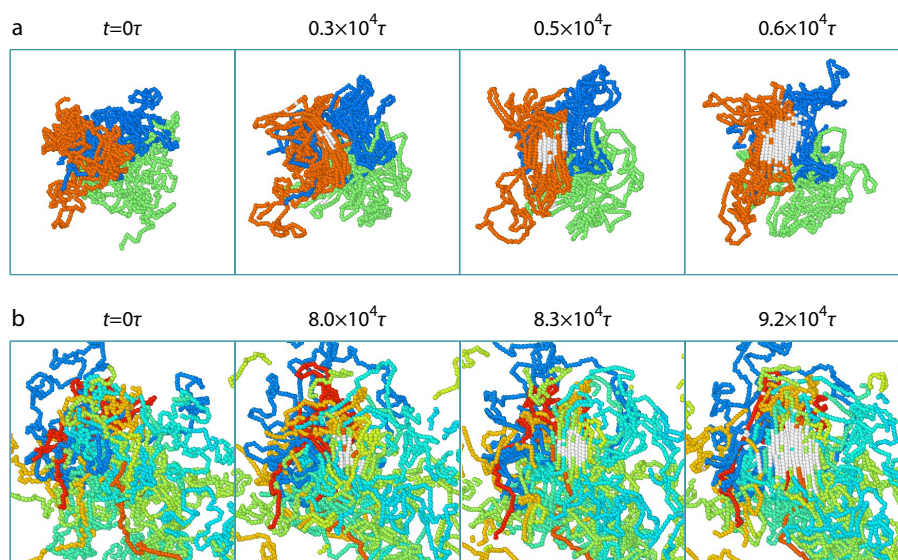


Fig. 2 Snapshots of the formation and growth of the primary nucleus in systems with (a) $\langle N_{e0} \rangle = 267$, and (b) $\langle N_{e0} \rangle = 17$. Only chains involved in the formation of a nucleus are drawn here. Segments in the amorphous part and the nucleus are marked in different colors and white, respectively.

$r_{\text{cm}}(0)]^2$), respectively. Here, r_i and r_{cm} are the coordinates of the i^{th} monomer and the center of mass of a chain, respectively. Fig. 3(a) presents the variations of g_1 and g_3 with time for all the samples examined in the study. The curves of $g_1(t)$ for all systems overlap almost completely, suggesting that the movement of monomers is not sensitive to the entanglement density. $g_3(t)$ characterizes the movement of a polymer chain, and is found to be independent of the entanglement density at short time scales, while becomes diverging at long time scales. Namely, the diffusion of a polymer chain at the nucleus interface during crystal growth is restricted by the entanglement. In brief, although the diffusion of a polymer chain scale is indeed influenced by the entanglement, its effect on the diffusion of monomers is quite limited. Considering the nucleation is a behavior occurring at the monomeric scale, the diffusion at the polymer chain scale should not be responsible for the significantly different nucleation rates of systems with different entanglement densities.

To determine whether the long nucleation incubation period is related to the disentanglement process, the evolution of $\langle N_e \rangle$ for the system with $\langle N_{e0} \rangle = 17$ during the nucleation is measured. First, the spatial positions of critical nuclei are determined. The three-dimensional region surrounded by the boundary of each nucleus is defined as the convex hull. The value of the entanglement length N_e is assigned to each monomer in the corresponding entangled segment. The obtained ensemble average entanglement lengths $\langle N_e \rangle$ in the whole system, the amorphous region, and the convex hulls are shown in Fig. 3(b). In this system, most nuclei reach the critical nucleus size and start to grow at $12 \times 10^5 \tau - 15 \times 10^5 \tau$. As can be seen, $\langle N_e \rangle$ in the convex hulls keeps almost constant, indicating that no obvious disentanglement occurs during the nucleation. It is generally considered that the nucleation rate is determined together by the activation energy for the transport process at the interface between the melt and the nucleus surface (ΔE) and the nucleation barrier (ΔG^*), i.e.,

$J = J_0 \exp \left[-\frac{\Delta E}{RT} - \frac{\Delta G^*}{RT} \right]$.^[41] The above calculations demonstrate clearly that the effect of the entanglement density on the nucleation rate mainly stems from changing ΔG^* rather

than ΔE .

By applying the modified mean first-passage time (MFPT) method^[35] (See S4, Fig. S3, and Table S2 in ESI for calculation details) to 50 MD trajectories of each polymer system, we can obtain the nucleation free energy barrier (ΔG^*) and critical nucleus size (n^*), and plot them in Figs. 4(a) and 4(b). With the increase of $\langle N_{e0} \rangle$, both ΔG^* and n^* decrease, and the down-trends slow down as $\langle N_{e0} \rangle > 64$. ΔG^* and n^* show an approximately linear relationship, which is in agreement with the CNT if the bulk free energy density ε for different systems is the same. As shown in Fig. S4 in ESI, an almost linear relationship between ΔG^* and $1/\langle N_{e0} \rangle$ (number density of entanglement) is found, which is consistent with the previous experimental study.^[21] It is noteworthy that the nucleation barrier is close to or even less than $1k_B T$ when the entanglement length is large, which means that nucleation can occur spontaneously due to thermal fluctuation. One possible explanation is that these less entangled systems have higher initial free energy, which can be reduced by crystallization and structural entanglement, in which thermal fluctuations as a means of screening pathway. The whole crystallization process is similar to spinodal decomposition. However, spinodal decomposition has no obvious interface between the two phases, and the crystallization process is generally considered a nucleation-growth mode. In this case of crystallization from system far from equilibrium, more evidence is needed to discuss whether nucleation-growth or spinodal decomposition crystallization.

According to Eq. (4), to verify whether the CNT can account for the nucleation barrier presented in Fig. 4(a), we need to figure out how the lateral surface free energy per monomer σ_l , the fold surface free energy per monomer σ_f , and the bulk free energy of the formation of a nucleus per monomer ε vary with the entanglement length $\langle N_{e0} \rangle$. Our first concern here is ε . Specifically, the enthalpy changes per monomer $\Delta H_i = H/N_c$ keeps constant for polymer systems with different $\langle N_{e0} \rangle$, and is estimated to be $-0.77k_B T$, where ΔH is the total enthalpy loss, and N_c is the number of monomers in the nucleus. The conformational entropy change ΔS_{con} is calculated from the end-to-end distance distribution of the chains^[42] (see S5 and Fig. S5 in ESI for the calculation details). As shown in Fig. 5(a),

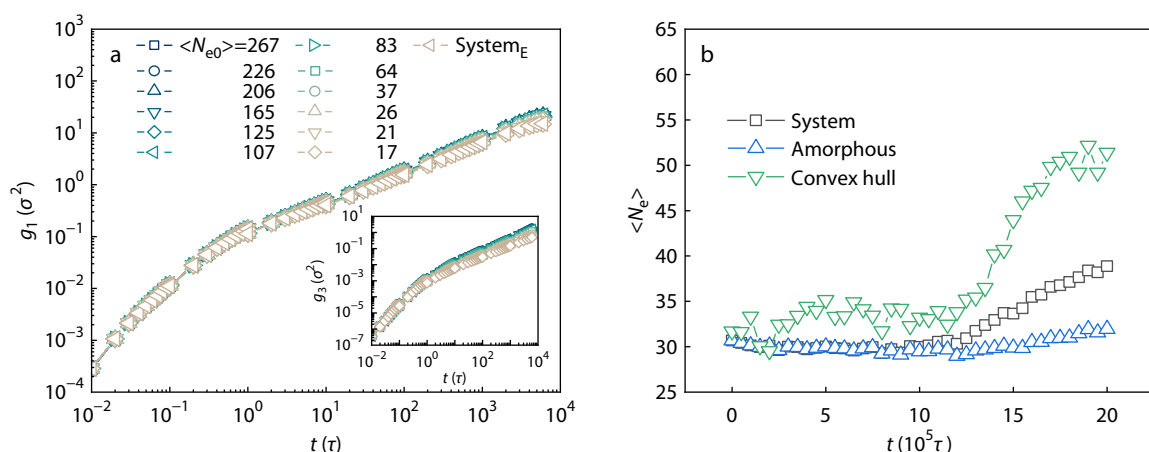


Fig. 3 (a) The MSD of monomers (g_1) for all polymer melt systems. The inset is the MSD of the center of mass of polymer chains (g_3) for all systems. (b) The change of average entanglement length in the whole system, the amorphous region, and the convex hulls during the crystallization process.

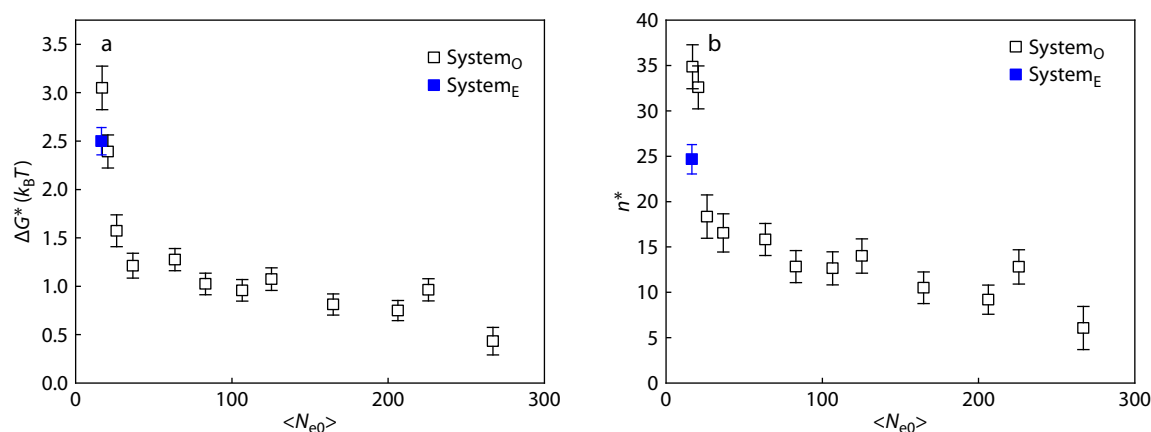


Fig. 4 (a) The nucleation free energy barrier ΔG^* , and (b) the critical nucleus size n^* as a function of the entanglement length $\langle N_{e0} \rangle$. The solid blue and open-black symbols represent the systems in and out of equilibrium, respectively.

ΔS_{con} decreases slightly due to the relaxation of the systems and the increased chain stiffness caused by quenching. $\Delta S_{\text{con},i} = \Delta S_{\text{con}}/N_t$ with N_t being the total number of monomers 2×10^5 is rather small and thus can be negligible during the nucleation. The atomic entropy S_{atom} describes the periodic symmetry property of the system, and can be used to characterize the configurational entropy of a nucleus. Based on the quadratic term in the expansion of the excess entropy of liquid, the configurational entropic difference ΔS_{atom} of a monomer between the target system and the ideal gas can be calculated.^[43–45] Fig. 5(b) suggests that ΔS_{atom} hardly changes with the entanglement density. It should be pointed out that the obtained data is a relative value owing to the used Dirac broadening function and local averaging (see S6 and Fig. S6 in ESI for details). Furthermore, a prefactor β_1 is required for numerical corrections. Hereto, we can conclude that ϵ does not vary with the entanglement density, and thus is not responsible for the decreasing ΔG^* with the increase of $\langle N_{e0} \rangle$.

As to the lateral surface free energy σ_l , it is mainly determined by the interaction potential difference between a nucleus and its surrounding amorphous. Thus, σ_l should be dependent on the lattice structure and the amorphous density, and is irrelevant to the entangled state of the polymer systems. In other words, σ_l can be considered as a constant independent of $\langle N_{e0} \rangle$. σ_f is determined by the entropy loss in the amorphous region during the nucleation rather than by the potential difference.^[24] After extracting nuclei from the polymer systems, the free energy of the amorphous structures (tails/loops/ties) on the fold surface is calculated according to the theory of Muthukumar^[46] (see S7 in ESI for details). Fig. 5(c) shows the distributions of the free energy of amorphous structures ($G_{\text{tails,loops,ties}}$). The free energy of loops G_{loops} is higher than those of tails G_{tails} and ties G_{ties} , which can be attributed to the lower conformational entropy of loops. Fig. S7 (in ESI) shows that the formation of loops prevails over that of tails and ties, giving rise to an increase of σ_f with the increasing $\langle N_{e0} \rangle$ shown in Fig. 5(d). The above analyses show clearly that in the framework of the CNT, the nucleation free energy barrier rises as the entanglement length increases. Obviously, this prediction does not agree with our simulation results. Actually, the failure of the CNT in describing the nucleation of

polymer systems is not surprising since it does not take into account the unique connectivity of polymer chains, and the accompanying effects such as the entanglement.

Entanglement Free Energy Theory

During the nucleation, the freedom of an amorphous segment gets reduced due to its transformation into a crystal stem. Considering that the constraint imposed by the crystal stem is similar to the entanglement, the crystal stem can be regarded as an additional entanglement point.^[47] The entanglement state of the amorphous segments is changed by the formation of crystal stems, which might play an important role in the nucleation and cause a variation of the nucleation barrier with the entanglement density. To capture the underlying physics of the nucleation in polymeric systems, we propose a theoretical approach in which an entanglement free energy (G_z) is introduced to quantify the effect of entanglement on nucleation. G_z originates from the redistribution of the entanglement length caused by the slip of entanglement points, and can be expressed as $G_z = U_z - TS_z$. Here, the entanglement energy (U_z) describes the repulsive interactions between entanglement points, and the entanglement entropy (S_z) reflects the entanglement density and its spatial distribution, which compensates the attractive interactions between two adjacent entanglement points.

The slip-link model predicts that systems with entanglement densities below and above the equilibrium value have the same free energy.^[47–50] Clearly, it cannot explain the increased nucleation barrier as the entanglement density rises. Inspired by the slip-link model and also the local-knots model,^[51,52] we use the harmonic oscillator model to describe the motion of entanglement points. In the harmonic oscillator model, adjacent entanglement points in a polymer chain are considered to interact repulsively, and the repulsive strength is determined by the distance between the adjacent entanglement points (entanglement length N_e). Under the thermal fluctuations, entanglement points keep sliding along the chain, and the global entanglement network changes dynamically. Note that this change induced by thermal fluctuations is slight when the observation period is short or the entanglement state is stable. In these cases, an entanglement point just oscillates nearby its original position. Similar to the slip-link model, a polymer chain can be considered as a series

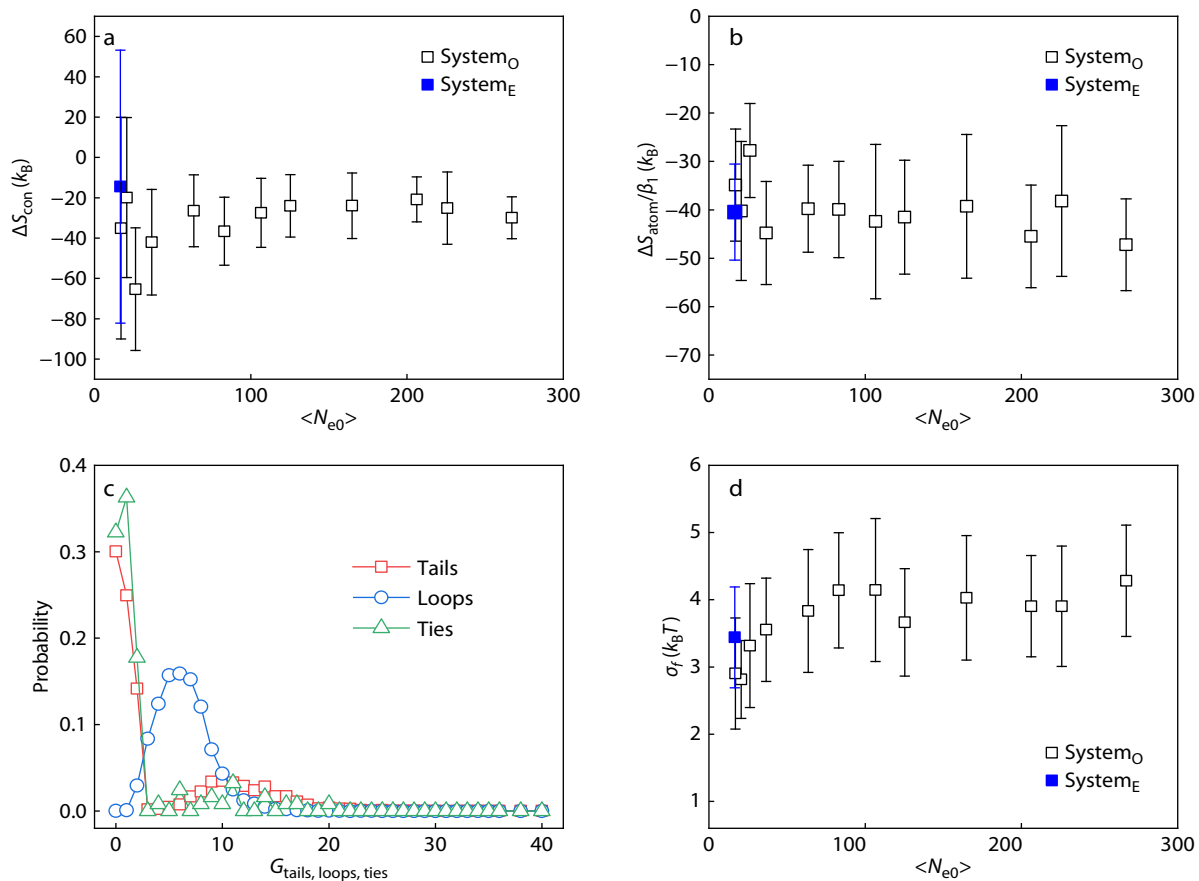


Fig. 5 Variations of (a) the conformational entropy of polymer chains, and (b) the atomic entropy of polymer systems with different entanglement densities during nucleation. (c) The distributions of the free energy of the amorphous structures (tails, loops, and ties). (d) The fold surface free energy density of a nucleus as a function of the entanglement length. All data points are obtained by averaging the calculation results of 10 MD trajectories of each system.

of untangled segments connected by small springs (*i.e.*, entanglement points).

Let's suppose that the entanglement points are uniformly distributed in a polymer chain, and each entanglement point can be treated as an independent harmonic oscillator to describe its local slip. Then, the one-dimensional motion of an entanglement point is controlled by a harmonic potential:

$$U_z = \frac{1}{2} k_s \Delta x^2 \quad (6)$$

where U_z is the entanglement energy, which is the energy of each entanglement point. Δx is the slip distance of an entanglement point under thermal fluctuations, which is in the units of a coarse-grained bead. $\Delta x = N_e$ in the limit case that two adjacent entanglement points overlap. Polymer chains with N monomers in each chain are involved in the entanglement overlapping, during which the freedom of monomers decreases. We take monomer number N as the scale parameter and the energy penalty for the overlapping is assumed to be $\gamma N k_B T$ with γ being a constant. Here, $N k_B T$ can be considered as the reduced unit. Then, the stiffness coefficient of the oscillator can be deduced as $k_s = 2\gamma N k_B T / N_e^2$. Obviously, k_s is a variable relying on the chain length N and the entanglement length N_e . Thus, we have:

$$U_z = \frac{1}{2} k_s \Delta x^2 \xrightarrow{\beta_2 = \gamma \Delta x^2} \beta_2 N k_B T / N_e^2 \quad (7)$$

where $\beta_2 = \gamma \Delta x^2$ is the prefactor. During the nucleation, the entanglement network is considered to be stable, and its evolution occurs at a small spatial scale. It implies that the value of Δx is small and keeps nearly constant. Then, β_2 can be approximately treated as a constant for polymer systems with different N_e . Most importantly, Eq. (7) predicts the relationship between the entanglement energy and the entanglement length, *i.e.*, $U_z \sim 1/N_e^2$. A higher U_z with smaller N_e implies that a more untangled state is preferred (N_e increases). Note that a dramatic variation in U_z does not originate from the vibration of the harmonic oscillator itself (Δx), but a sharp change in N_e induced by the formation of crystal stem.

The change of the entanglement state of the amorphous segments in nucleation is accompanied by a variation in U_z . However, the crystal stem is considered to be fixed ($\Delta x = 0$), and does not contribute to the variation in U_z . The formation of a crystal stem also keeps the adjacent entanglement points away. Namely, the constraints brought by the crystal stem do not affect the original entanglement network, but can restrict its evolution. The stem acts like a molecular chain end, cutting off the original untangled segment, and the breakpoint itself does not contribute any free energy. Consider the case where a crystal stem forms at the midpoint of the amorphous segment of the length N_e during the time interval $[t_1, t_2]$. As a result, two new amorphous segments of the length $N_e/2$

form. Since the nucleation takes place at the time scale much smaller than the reptation time, the assumption that $\Delta x=1$ during the nucleation process is reasonable. Therefore, the entanglement energy change due to the formation of a crystal stem can be given as:

$$\Delta U_z = U_{z,t_2} - U_{z,t_1} = \beta_2 6 N k_B T / N_e^2 \quad (8)$$

where, $U_{z,t_1} = \beta_2 2 N k_B T / N_e^2$ is the entanglement energy of the amorphous segments between two adjacent entanglement points at the time t_1 with $N_e(t=t_1) = N_e$. When a crystal stem at the time t_2 , $U_{z,t_2} = \beta_2 8 N k_B T / N_e^2$ with $N_e(t=t_2) = N_e/2$.

Next, let's turn our attention to the entanglement entropy S_z . The concept of S_z comes from the excess entropy. By expanding the configurational entropy of simple liquids with the many-body correlation function, the second term only involving the correlation function is usually called the two-body excess entropy, which makes a nearly 90% contribution to the configurational entropy.^[43,53] Polymer chains are divided into multiple untangled segments by the entanglement points. The length of these untangled segments is the entanglement length N_e . The distribution of N_e is ever-changing due to the slip of entanglement points. Essentially, N_e is a reflection of the interaction between two adjacent entanglement points, i.e., a special two-body interaction. This two-body interaction can be well described by the excess entropy, and the magnitude of excess entropy is a function of the number of entanglement points.

The original excess entropy is the configurational entropy, which incorporates the interactions between any two particles in the system. Considering our focus here is to describe the two-body interactions between entanglement points, the probability density of the entanglement length N_e rather than the radial distribution of entanglement points in the expression of the original excess entropy ($f(r)$ in Eq. S8.1 in ESI) is used to calculate S_z . For the sake of simplicity, the calculations are carried out in the spherical coordinate system, which is referred to as the Z-space in this work. As shown in Fig. 6, an untangled segment of the length N_e between two adjacent entanglement points along a chain in the real space is projected as a point with a distance $r = N_e$ from the origin in the Z-space. Here, the angular coordinates of the points are ignored. The N_e calculated by the Z1 code is taken as an integer value, so r in the Z-space takes discrete values like 1, 2, ..., N . In this way, the probability density function of N_e in the real space is converted into that of the distance r in the Z-space, $g(r)$.

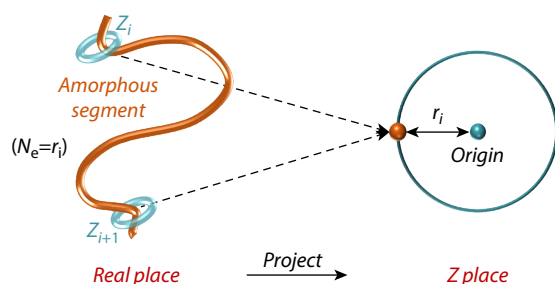


Fig. 6 Schematic illustration of the projection of two adjacent entanglement points in the real space into the Z-space. N_e is the entanglement length between two adjacent entanglement points.

For an ideally untangled system consisting of N_{chain} chains of the length N , $r = N$. That is, there are N_{chain} points with $r = N$ in the Z-space. Thus, we should have $g_0(r=N) = 1$. $g(r)$ would be different for a given entangled system. Then, S_z is defined as the entropic difference of points in the Z-space projected by the given entangled systems and the ideally untangled system (see S8 in ESI for the detailed derivation process):

$$S_z = \beta_3 k_B \int_1^N [g(r) \ln g(r) - g_0(r) \ln g_0(r) - g(r) + g_0(r)] r^2 dr \quad (9)$$

where r is the distance of a point from the origin in the Z-space, and β_3 is a constant dependent on the system size and chain length. Since the density of points in the Z-space is independent of the shell volume, the probability density function rather than the radial distribution function is used here. In this way, the normalization of the integral volume is not necessary. Moreover, an additional point is added to each r in the Z-space to fill the singularity in the integral function. The influence of the additional points is negligible for sufficiently long segments as the probability density function of the additional points $g(r) = 1/N$ is small.

Evolutions of S_z of systems at the beginning and the ending of nucleation with the entanglement density are plotted in Fig. 7(a). $S_z=0$ for untangled systems, and $S_z>0$ for entangled systems. Again, consider the case where a portion of an amorphous segment of the length N_e turns into a crystal

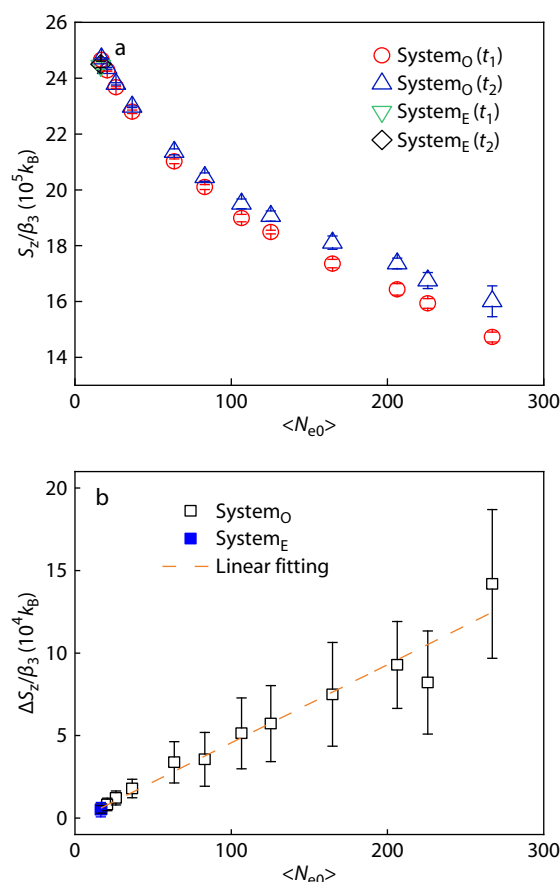


Fig. 7 (a) S_z of the whole systems at the beginning and the ending of nucleation. (b) The variations in S_z of the whole system during the nucleation with the entanglement density.

stem during the time interval $[t_1, t_2]$. Then, the variation of S_z of this segment due to the formation of the crystal stem is:

$$\Delta S_z = \beta_3 k_B \int_1^{N_e} (g_{t_2}(r) \ln g_{t_2}(r) - g_{t_1}(r) \ln g_{t_1}(r) - g_{t_2}(r) + g_{t_1}(r)) r^2 dr \quad (10)$$

where $g_{t_1}(r)$ and $g_{t_2}(r)$ are the probability density functions of points in the Z -space at $t = t_1$ and t_2 , respectively. Generally, the length of a crystal stem in the primary nucleus is much smaller than N_e . Assuming that the nucleation occurs at the midpoint of the segment and the crystal stem is treated as an additional entanglement point, the segment can be divided into two subsegments of the length $ca. N_e/2$ at the time t_2 . In the Z -space, there is a point at $r = N_e$ and two points at $r = N_e/2$. A virtual point is added at each r in $r = [1, N_e]$ to compensate singularities. Then, the total number of points in the Z -space at $t = t_1$ and $t = t_2$ is $N_e + 1$ and $N_e + 2$, respectively. Therefore, the probability density function in Z -space can be given as:

$$g_{t_1}(r) = \begin{cases} \frac{2}{N_e + 1}, & r = N_e \\ \frac{1}{N_e + 1}, & r \neq N_e \end{cases} \quad (11)$$

$$g_{t_2}(r) = \begin{cases} \frac{3}{N_e + 2}, & r = N_e/2 \\ \frac{1}{N_e + 2}, & r \neq N_e/2 \end{cases} \quad (12)$$

where, r ranges from 1 to N . For a sufficiently long amorphous segment with $N_e \gg 1$, the denominators in Eqs. (11) and (12) can be approximated as N_e . Substituting Eq. (11) and Eq. (12) into Eq. (10), we get:

$$\Delta S_z = \beta_3 k_B N_e \left[\frac{1}{2} (\ln N_e + 1) + \frac{3}{4} \ln 3 - 2 \ln 2 \right] \approx \beta_3 k_B N_e \left(\frac{1}{2} \ln N_e - 0.0623 \right) \quad (13)$$

The detailed derivation of Eq. (13) can be found in S9 in ESI. Eq. (13) suggests that the entanglement entropy gained from the formation of a crystal stem is approximately proportional to N_e , which is consistent with our simulation results shown in Fig. 7(b).

Combining Eq. (8) and Eq. (13), we obtain the change in the entanglement free energy change during nucleation:

$$\Delta G_z = \mu (\Delta U_z - T \Delta S_z) \approx \mu k_B T \left[\beta_2 \frac{6N}{N_e^2} - \beta_3 N_e \left(\frac{1}{2} \ln N_e - 0.0623 \right) \right] \quad (14)$$

where μ is the number of crystal stems inside a nucleus. Then, the total change in the free energy for the formation of a nucleus with μ stems of the length l_s is given as:

$$\Delta G = \Delta G_{\text{CNT}} + \Delta G_z = -\mu l_s \varepsilon + \sqrt{\mu} l_s \sigma_1 + 2\mu \sigma_f + \Delta G_z \quad (15)$$

Minimizing ΔG with respect to μ and l_s , the free energy barrier for the nucleation is:

$$\Delta G^* = 2\sigma_f^2 \Lambda / \varepsilon^2 \quad (16)$$

where

$$\Lambda = \sigma_f + \frac{1}{2} k_B T \left[\beta_2 \frac{6N}{N_e^2} - \beta_3 N_e \left(\frac{1}{2} \ln N_e - 0.0623 \right) \right] \quad (17)$$

Note that the nucleation barrier given by Eq. (16) has the same mathematical form as that given by the CNT (Eq. 4). Λ consists of two parts, σ_f in Eq. (17) inherits from the CNT. The second term is the correction contributing from the entangle-

ment free energy, characterizing the disturbance on the entanglement network around the nucleus by the nucleation. Since the entanglement state of each system when nucleation occurs is similar to the initial entanglement, the entanglement length N_e is approximate to its initial value $\langle N_{e0} \rangle$. With the already obtained σ_f (Fig. 5d), ε and $N_e \approx \langle N_{e0} \rangle$, the validity of Eq. (16) can be verified. As shown in Fig. 8(a), the fitted values of ΔG^* agree well with these obtained by the MFPT method (Fig. 4a). The used parameters in the fittings are $\beta_1 = 4.28 \times 10^{-4}$, $\beta_2 = 0.356$ and $\beta_3 = 0.0027$, respectively. β_1 is the prefactor of atomic entropy in the bulk free energy term ε . Note that the difference in the magnitude of β_2 and β_3 is due to the magnitudes of $6N/N_e^2$ and $N_e \left(\frac{1}{2} \ln N_e - 0.0623 \right)$ are 1 and 100, respectively. The energy and the entropy contributions are of the same order. Based on the fitting parameters, as N_e increases, $\beta_2 \frac{6N}{N_e^2} - \beta_3 N_e \left(\frac{1}{2} \ln N_e - 0.0623 \right)$ gradually decreases from positive to negative.

The ratio of the entanglement induced nucleation free energy barrier to the total one, $\Delta G_z^* / \Delta G^*$ can quantify the effect of the entanglement on the nucleation. The prediction of Eq. (17) reverts to CNT when $\Delta G_z^* / \Delta G^*$ approaches 0. This means that the prediction of CNT may fit well with experimental observation at medium entanglement densities, where $\Delta G_z^* = 0$ means the contributions from its energy and entropy terms are canceled by each other. As shown in Fig. 8(b), $\Delta G_z^* / \Delta G^* \approx 0.5$ for the equilibrium system, revealing that the entanglement makes a considerable impact on the nucleation. $\Delta G_z^* / \Delta G^*$ increases rapidly when $\langle N_{e0} \rangle$ is smaller than the equilibrium value ($ca. 17$). This implies that the increased nucleation barrier is mainly caused by the denser entanglement. Indeed, our simulations show that the nucleation hardly takes place for systems with $\langle N_{e0} \rangle = 6-15$. For systems with $\langle N_{e0} \rangle$ being larger than the equilibrium value, $\Delta G_z^* / \Delta G^*$ decreases gradually with the increasing $\langle N_{e0} \rangle$ due to the significantly increased entanglement entropy ΔS_z . For systems with low entanglement densities, the formation of crystal stems increases constraints and drives the entanglement density close to the equilibrium value, which contributes a negative ΔG_z^* and consequently reduces the nucleation barrier predicted by the CNT.

The introduction of the entanglement free energy G_z not only establishes a quantitative model to explain the entanglement effect in polymer crystallization experiments, but also provides a solution for the discrepancies in polymer crystallization. The difficulty in crystallization of highly entangled polymers like PC,^[18,19] the enhanced nucleation in cyclic polymers^[54,55] and disentangled systems with reduced entanglement density^[56-58] can be quantitatively correlated with G_z via N_e . The discrepancies in the memory effect of crystallization^[22,23,59-62] and flow-induced crystallization of polymer^[63-70] might also be solved with G_z , where no theoretical consensus has been reached yet. In both cases, crystallization is accompanied by a higher initial G_z and a greater increase in S_z , which makes the nucleation barrier lower than that of the equilibrium melt. In addition, the different interceptions of the polymer crystallization and melting lines measured in experiment^[71] may be partly caused by the dif-

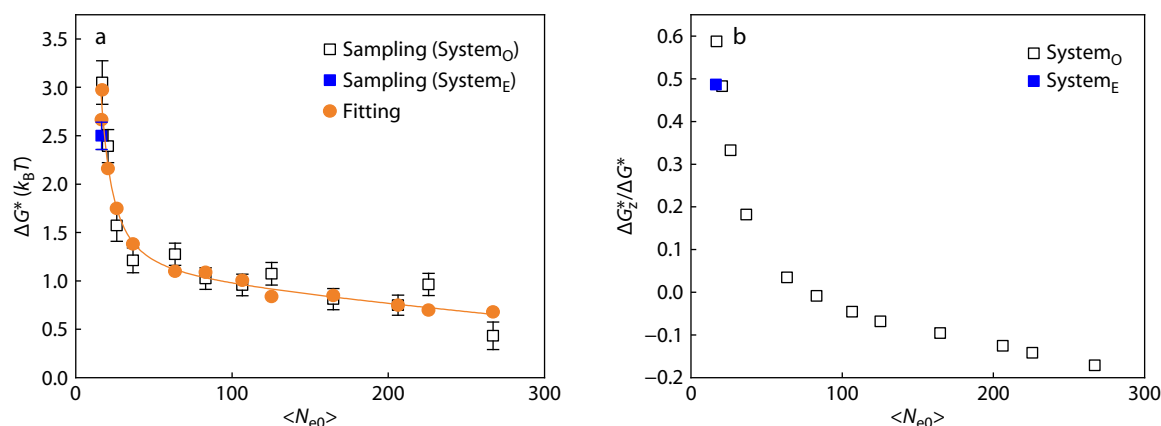


Fig. 8 (a) Comparison of the nucleation free energy barriers calculated by sampling (open black squares) and fitted with Eq. (16) (orange circles). (b) The ratio of the entanglement induced nucleation free energy barrier to the total one, $\Delta G_z^*/\Delta G^*$ as a function of the entanglement length.

ferent evolutionary pathways of the entanglement topology network during crystallization and melting, which makes the entanglement free energy change asymmetrical. Experimental and simulation efforts are encouraged to verify the quantitative correlation between entanglement and observations in polymer crystallization.

The entanglement free energy theory gives the theoretical expressions for entanglement in crystallization, which supplements the effect of the entanglement network in nucleation and diverts our attention from the chain conformation effect to the free energy of the entanglement network. Based on the entanglement free energy theory, the entanglement network has an intrinsic free energy G_z independent of polymer conformation and structural configuration. The nucleation process brings additional topological entanglement points for the original entanglement network, which modifies G_z that lives in the entanglement network. Therefore, during the nucleation process, not only the free energy of monomers inside a crystal nucleus is changed, but also the free energy of the neighboring entanglement network around the crystal nucleus is affected. Considering the chain connectivity, nucleation is no longer a local behavior among monomers, but a collaborative behavior between the nucleus and the entanglement network.

The concept of entanglement free energy proposed in this work builds a bridge between the entanglement network and the nucleation behavior of non-equilibrium entangled polymer systems. There are still several aspects to be improved in the future: (1) Strictly, $U_z \sim 1/N_e^2$ is still a phenomenological theory. An analytical solution from the strict initio derivation at the molecular scale will be a serious challenge. (2) An improved expression for the entanglement entropy. The method to measure the two-body interactions between entanglement points remains to be perfected. One possible way is to calculate the entropy by counting the probability of microscopic entanglement states directly. (3) Verification of the entanglement free energy theory by experiments. Although the predictions by our theoretical approach can fit the simulation results well, a direct experimental evidence for the verification of our new theoretical approach is still necessary.

CONCLUSIONS

In conclusion, we have performed a series of MD simulations of polymer melts with different entanglement densities, and obtained the nucleation free energy barrier by using the modified MFPT method. A monotonic increase of the nucleation free energy barrier with the increasing entanglement density is observed, which is opposite to the prediction of the CNT. Then, we propose a new theoretical approach to take into account the unique chain connectivity of polymers. Specifically, we introduce the entanglement free energy to reflect the role of entanglement in polymer nucleation. It is suggested that polymer nucleation not only involves free energies of monomers inside and on the surface of a nucleus as considered in the CNT, but also affects the entanglement network around the nucleus. The calculated values of the nucleation free energy barrier based on our theoretical approach are in good agreement with those obtained from the simulations. Our study here provides new insights on how the intrinsic entanglement in polymer melts affects the nucleation behavior.

NOTES

The authors declare no competing financial interest.



Electronic Supplementary Information

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