

Three-dimensional Numerical Simulation of Viscoelastic Phase Separation under Shear: the Roles of Bulk and Shear Relaxation Moduli^{*}

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Abstract The morphological, dynamic and rheological characteristics in the viscoelastic phase separation (VPS) of sheared polymer solutions are investigated by three-dimensional (3D) numerical simulations of viscoelastic model. The simulations are accelerated by graphic process unit (GPU) to break through the limitation of computation power. Firstly, the morphological and dynamic characteristics of VPS under shear are presented by comparing with those in classic phase separation (CPS). The results show that the phase inversion and phase shrink take place in VPS under shear. Then, the roles of bulk and shear relaxation moduli in VPS are investigated in details. The bulk relaxation modulus slows down the phase separation process under shear, but not affects the dynamic path of VPS. The dynamic path can be divided into three stages: freezing stage, growth stage and stable stage. The second overshoot phenomenon in the shear stress is observed, and explained by the breakdown and reform of string structures. The shear modulus affects morphology evolution in the late stage of VPS under shear.

Keywords: Viscoelastic model; Phase separation; Polymer solution; Shear.

INTRODUCTION

Phase separation in complex fluids such as polymers, surfactants, colloids, and biological materials involves very rich and general phenomena and therefore has been the subject of intense experimental, theoretical and numerical studies in recent years^[1, 2]. Understanding the phase separation mechanisms and controlling the morphological evolution are crucial to designing various functional materials with novel mechanical, optical, electrical and transport properties^[2–4]. The kinetics of phase separation in alloys and simple fluids, can be well described by the classical solid (model B) and fluid (model H) models, respectively. Tanaka *et al.*^[2, 5–8], Doi and Onuki^[9] have recently found a novel type of phase separation behavior, named as viscoelastic phase separation (VPS), beyond the classical phase separation (CPS) process. In contrast to the common sense of classical phase separation, in many real phase-separating mixtures, such as polymer blends and polymer solutions, the system components often exhibit a dynamic asymmetry, which arises from a large difference in molecular weight or glass-transition temperature. Dynamic asymmetry can strongly influence the pathway of a phase transition and produce unusual intermediate morphologies. For example, by deep-quenching a polymer solution into the spinodal region, Tanaka^[2, 10] found that, in addition to the initial diffusive and final hydrodynamic stages in the classical phase separation process, there is an intermediate viscoelastic stage within which the domain structure is dominated by the elastic force balance rather than by the interfacial tension and even the minority phase

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transiently forms a continuous sponge-like structure.

Apparently, the process of viscoelastic phase separation involves the coupling of viscoelastic effects to the composition and velocity fields and is thus beyond the classical phase separation models. By accounting for a crucial role of bulk modulus during the viscoelastic phase separation process, Tanaka and Araki^[2, 5, 6] developed a universal kinetic phase-field model, known as the viscoelastic model^[10, 11], within which dynamic asymmetry is measured by the ratios of moduli and relaxation times of the individual components in a polymer mixture. Indeed, this model can reproduce the experimentally observed kinetics and morphologies of phase-separating polymer systems with different viscoelastic properties, such as the phase inversion and volume shrinking of polymer-rich phase in polymer solutions^[2].

The effects of shear flow on morphology and kinetics of polymer systems has long been the interests from both fundamental and industrial viewpoints^[12]. Application of shear flow to polymer blends sometimes causes shear-induced mixing or demixing. Rheological effects of polymer solutions under shear are also very complex. For example, large stress fluctuations^[13] and a second overshoot in the shear stress^[14] are observed after the application of shear. Numerical simulation becomes an essential method to capture insights into the complex shear effects on polymer blends^[15, 16]. Without viscoelasticity, a number of simulations have been performed to investigate the phase separation of sheared simple fluids^[17–20]. For example, Buxton and Balazs^[20] studied the mechanical properties of phase separated morphologies by a model that considers elastic properties only and cannot describe the viscoelastic response. However, numerical simulations have still been rare for sheared viscoelastic fluids^[15, 16]. In a previous work Dwivedi *et al.*^[15] studied the roles of bulk modulus in 2D viscoelastic phase separation under shear. Nonetheless, the shear effect on the morphologies, rheology and dynamics in the late stage of VPS, especially in 3D case, is still poorly understood.

Furthermore, limited by computer power of CPU, previous simulations for sheared viscoelastic simulation are performed on 2D boxes, and VPS under shear in 3D have not been explored yet. Although the general features of the kinetics of phase separation including the crossover scaling and a self-similar behavior are applicable in both 3D and 2D, details like the value of the growth exponent in the crossover scaling functions as well as the lifetime of transiently formed bicontinuous network-like structure^[2] are expected to depend on dimension. To overwhelm the limitation in computational power, herein a graphic process unit (GPU)-accelerated package Gym_VE, which has been developed in our previous work^[21], is used to simulate the 3D VPS in polymer blends under shear. We focus on the morphological, dynamic and rheological characteristics. This paper is organized as follows. First, after the model of viscoelastic phase separation, the details to implement the shear are presented. Next, the morphologies and dynamics characteristics of VPS under shear are presented by comparing with that in CPS. Then, the roles of bulk and shear relaxation moduli in VPS are investigated in details. Finally, a summary of the paper is given.

THEORY AND IMPLEMENTATION

Theory of Viscoelastic Model

The kinetics of viscoelastic phase separation can be described by the so-called viscoelastic model^[2, 5, 6, 11], which involves the coupling of viscoelastic effects to the composition and velocity fields in a dynamic asymmetry system, *i.e.* polymer solution^[22, 23]. For polymer solutions, let $\phi(\mathbf{r}, t)$ be the volume fraction of polymers at position $\mathbf{r}$ and time t , while $\mathbf{v}_p(\mathbf{r}, t)$ and $\mathbf{v}_s(\mathbf{r}, t)$ be the velocity fields of polymer and solvent, respectively. To simplify, in the following they are abbreviated as the spatial and temporal dependent implicit variables ϕ , $\mathbf{v}_p$ and $\mathbf{v}_s$. Therefore, the appropriate kinetic equations of the viscoelastic phase separation in polymer solutions can be written as follows:

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot (\phi \mathbf{v}) - \nabla \cdot [\phi(1-\phi)(\mathbf{v}_p - \mathbf{v}_s)] \quad (1)$$

$$\mathbf{v}_p - \mathbf{v}_s = -\frac{1-\phi}{\zeta} [\nabla \cdot \mathbf{\Pi} - \nabla \cdot \boldsymbol{\sigma}] \quad (2)$$

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla \cdot \mathbf{\Pi} + \nabla \cdot \boldsymbol{\sigma} + \nabla p + \eta_s \nabla^2 \mathbf{v} \quad (3)$$

where the averaged volume velocity of mixture is defined as $\mathbf{v} = \phi \mathbf{v}_p + (1-\phi) \mathbf{v}_s$. p is the pressure field and is determined to satisfy the incompressible condition $\nabla \cdot \mathbf{v} = 0$. ζ is the friction coefficient and η_s is the solvent viscosity. $\mathbf{\Pi}$ is the thermodynamic osmotic pressure tensor and related to the mixing free energy F_{mix} as:

$$\nabla \cdot \mathbf{\Pi} = \phi \nabla \frac{\delta F_{\text{mix}}}{\delta \phi} = \phi \nabla \left(\frac{\delta f_{\text{FH}}}{\delta \phi} - C \nabla^2 \phi \right) \quad (4)$$

Here C is the interfacial tension coefficient and f_{FH} is the Flory-Huggins free energy function, defined as $f_{\text{FH}} = k_B T [(1/N_A) \phi \ln \phi + (1-\phi) \ln(1-\phi) + \chi \phi(1-\phi)]$, where N_A is the polymerization degree of polymers, χ is the Flory-Huggins interaction parameter, k_B is Boltzmann's constant, and T is the temperature of system. $\boldsymbol{\sigma}$ is the viscoelastic stress tensor of polymer solutions and is often calculated by considering the solvent to be a classical fluid^[7, 10, 11]. In this spirit, the solvent contribution to $\boldsymbol{\sigma}$ is ignored and $\boldsymbol{\sigma}$ only contains the contribution from polymers. Therefore $\boldsymbol{\sigma}$ is given by the constitutive equation of polymers:

$$\sigma_{ij} = \int_{-\infty}^t dt' \left\{ G(t-t') \left(\frac{\partial v_p^j}{\partial x_i} + \frac{\partial v_p^i}{\partial x_j} - \frac{2}{d} (\nabla \cdot \mathbf{v}_p) \delta_{ij} \right) + K(t-t') [\nabla \cdot \mathbf{v}_p(t')] \delta_{ij} \right\} \quad (5)$$

where d is the spatial dimensionality, and $G(t)$ and $K(t)$ are material functions containing information on all the spatiotemporal history, which are often called as the shear relaxation modulus and bulk relaxation modulus, respectively. In our simulation, the Maxwell-type relaxation equations are assumed for both $G(t)$ and $K(t)$ for simplicity,

$$G(t) = M_s \exp(-t / \tau_s), K(t) = M_b \exp(-t / \tau_b) \quad (6)$$

Here, M_s and M_b are the relaxation moduli of the shear and bulk stresses, respectively. τ_s and τ_b are the relaxation time of the shear and bulk stresses, respectively. Also, they are the functions of polymer volume fraction ϕ : $M_s = M_s^0 \phi^2$, $M_b = M_b^0 \theta(\phi - \phi_0)$, $\tau_s = \tau_s^0 \phi^2$ and $\tau_b = \tau_b^0 \phi^2$, where ϕ_0 is the average volume fraction of polymer. $\theta(\phi - \phi_0)$ is a step function which is equal to 1.0 when $\phi > \phi_0$ while to zero when $\phi < \phi_0$. Under these assumptions on G and K , the stress tensor in equation (5) is discretely calculated as follows

$$\boldsymbol{\sigma}_s(\mathbf{r}, t + \Delta t) = \boldsymbol{\sigma}_s(\mathbf{r}, t) \exp(-\frac{\Delta t}{\tau_s}) + \left[-\mathbf{v}_p \cdot \nabla \boldsymbol{\sigma}_s + \boldsymbol{\sigma}_s \cdot \nabla \mathbf{v}_p + (\nabla \mathbf{v}_p)^T \cdot \boldsymbol{\sigma}_s + G_s \left(\nabla \mathbf{v}_p + (\nabla \mathbf{v}_p)^T \right) \right] \Delta t \quad (7)$$

$$\sigma_b(\mathbf{r}, t + \Delta t) = \sigma_b(\mathbf{r}, t) \cdot \exp(-\frac{\Delta t}{\tau_b}) + \left[-\mathbf{v}_p \cdot \nabla \sigma_b + G_b \nabla \cdot \mathbf{v}_p \right] \Delta t \quad (8)$$

Δt is the time step size. $\boldsymbol{\sigma}_b = \sigma_b \mathbf{I}$. Finally, the total stress of polymer can be expressed as $\boldsymbol{\sigma} = \boldsymbol{\sigma}_s + \boldsymbol{\sigma}_b$.

It should be noted that the viscoelastic model is an universal kinetic phase-field model for the dynamic asymmetry mixtures and can be deduced to various phase separation models. For example, with an assumption of total stress $\boldsymbol{\sigma} = 0$, the viscoelastic model is reduced to model H, which is a powerful tool to study the aggregation and gel formation in colloidal suspensions with hydrodynamic interactions^[24-26]. In the following, the Model H will be applied to simulate the CPS case.

Implementation of Shear

As the fast Fourier transformation (FFT) is used in the computation of Eq. (2), the periodic boundary conditions should be maintained even when shear field is applied. In previous work, a scheme, which realized the periodic boundary conditions under shear by transforming coordinates^[27], was successfully applied to simulations with constant mobility in the kinetic equation for model H^[28], but led to numerical instabilities for simulations with the order-parameter-dependent mobility in the kinetic equation for viscoelastic model discussed in the present work. This method leads to numerical instability and heterogeneities at long times for high shear rates^[15]. Thus, for the sake of computational simplicity, we use a simple shear profile in this work:

$$\mathbf{v}_{\text{shear}} = \dot{\gamma} |y - y_0| \mathbf{i} \quad (9)$$

Here, $y_0 = \frac{Ly}{2}$, the applied velocity along x direction and symmetric about $y = y_0$. $\dot{\gamma}$ is the shear rate. Therefore, the average velocity field of mixture is $\mathbf{v} = \mathbf{v}_{\text{in}} + \mathbf{v}_{\text{shear}}$, where $\mathbf{v}_{\text{in}}$ is inner velocity. This allows periodic boundary conditions to be used during the application of shear. The effects of using such a profile are negligible in the long-time limit as the asymptotic morphologies are not influenced by the shear profile^[15].

Above all, the kinetic equations of the viscoelastic phase separation under shear in polymer solutions can be rewritten as follows:

$$\begin{cases} \frac{\partial \phi}{\partial t} = -\nabla \cdot (\phi \mathbf{v}) - \nabla \cdot [\phi(1-\phi)(\mathbf{v}_p - \mathbf{v}_s)] \\ \mathbf{v}_p - \mathbf{v}_s = -\frac{1-\phi}{\zeta} [\nabla \cdot \mathbf{\Pi} - \nabla \cdot \boldsymbol{\sigma}] \\ \rho \frac{\partial \mathbf{v}_{\text{in}}}{\partial t} = -\nabla \cdot \mathbf{\Pi} + \nabla \cdot \boldsymbol{\sigma} + \nabla p + \eta_s \nabla^2 \mathbf{v} \end{cases} \quad (10)$$

NUMERRICAL RESULTS AND DISCUSSION

In our simulation, the kinetic equations (10) are discretized on a $128 \times 128 \times 128$ box with periodic boundary conditions. The typical polymer solution is set as follows: The initial volume fraction distribution of polymer is $\phi_{\text{ini}} \in N(\bar{\phi}, \sigma^2)$, where $\bar{\phi} = 0.28$ is the average volume fraction of polymer and the Gaussian noise intensity is $\sigma^2 = 0.001$. Other parameter settings are listed in Table 1. Note that, following the previous studies^[5, 6, 10, 11, 18, 29–32] on viscoelastic model, the dimensionless parameters are used for the convenience in computations and applications of results to different systems.

Table 1. Simulation parameters

System parameters						Parameters for polymer relaxation moduli			
C	ζ	η_s	N_A	$k_B T$	Δt	M_s^0	τ_s^0	M_b^0	τ_b^0
1	0.1	0.1	1	1.3	0.02	0.2	10	5	10

Viscoelastic Phase Separation under Shear

In the static case, due to the coupling between the stress and diffusion, both the morphologies and kinetics in VPS are very different from those in CPS, which have been carefully investigated^[6, 11]. However, in the sheared case, the morphology and kinetics differences between the VPS and CPS are rarely studied, especially in 3D. In this section, the viscoelastic effect on the morphologies and kinetics of phase separation are studied in details in 3D. For the VPS, the parameters for the system and polymer relaxation moduli are set as Table 1. For the CPS, the system parameter is the same as Table 1, but all parameters for polymer relaxation moduli are zero.

Figure 1 presents the pattern evolution of these two types of phase separation process under shear rate $\dot{\gamma} = 0.02$. Figure 1(a) shows the pattern evolution in the CPS case. The polymer-rich droplets appear at $t = 100$ and then the droplets grow larger at $t = 200$. Due to the shear, the structure of droplet becomes ellipsoid. The ellipsoid

structures further grow (see $t = 400$), and then connect together (see $t = 800$). At end of our simulation (see $t = 2000$), the polymer-rich phase shows string-like structure. Figure 1(b) presents the pattern evolution in the VPS case. Coupling with viscoelastic effect, the pattern evolutions become different from those in CPS case. First, the phase separation is delayed by viscoelastic effect at beginning of the phase separation, the elongated droplet morphologies appear at $t = 500$. Secondly, the elongated and dispersive droplets appeared at $t = 500$, are consist of solvent-rich phase. Then these droplets grow and connect to each other. Thus, bicontinuous string-like structures form at $t = 700$. This structure can only be observed clearly in 3D simulation. The solvent-rich string structures further grow, which suppress the polymer-rich phase to break down and become dispersive strings at $t = 1000$. Therefore, the phase inverse takes place in VPS under shear, which is not observed in CPS case. Similar to the VPS in the static case, the reason of phase inversion under shear can be attributed to the existence of bulk relaxation modulus in VPS^[5]. At the end of our simulation ($t = 3000$), the larger elongated polymer-rich droplets structures are observed in the VPS.

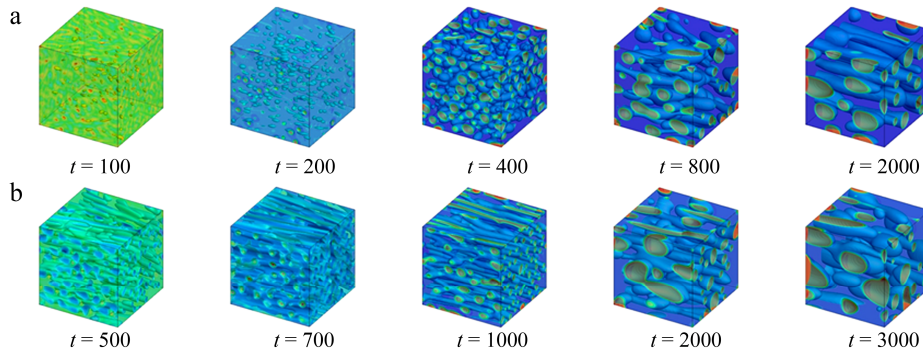


Fig. 1 The pattern evolutions in two phase separation processes under shear rate $\dot{\gamma} = 0.02$ for (a) CPS (Model H), and (b) VPS (viscoelastic model) Blue and red describe the solvent-rich phase and polymer-rich phase respectively.

Figure 2 shows the characters wave number $\langle k \rangle$ that is in inverse proportion to the size of domain R in CPS and VPS, respectively. The definition of $\langle k \rangle$ is introduced in details by Araki *et al.*^[6]. For the CPS case, after a freezing period ($t = 0-200$), the radius of domain of case (a) increases very fast and the growth index is -1.1 . Then the size of domain in $x-y$ plan become stable when $t > 800$, implying the stable string structure. The fluctuation of $\langle k \rangle$ at late stage of phase separation ($t > 800$) comes from the periodic morphology change along the shear direction, also observed by Onuki *et al.*^[16]. The average wave number at stable structure ($t > 800$) is $k_p \approx 2.7 \left(\frac{2\pi}{L} \right)$, thus the stable domains size is $R = \frac{2\pi}{k_p} \approx 47.4$. In the VPS case, it is found that the phase separation speed is slower than that in the CPS case when $400 < t < 2000$, because the viscoelastic stress that is coupled to diffusion slows down the phase separation speed. The turning point at $t = 900$ implies the phase inversion in phase separation process. Then the domain size grow faster with the index of -1.3 . After $t > 2500$ the phase domain size in $x-y$ plan seems to become stable and $k_p \approx 2.3$. The stable domain size in the VPS is $R = \frac{2\pi}{k_p} \approx 55.6$, which is larger than that in the CPS.

Figure 3 displays the structure factor S in three plans ($kx-ky$, $kx-kz$, $ky-kz$) of corresponding CPS and VPS patterns in Fig. 1 at $t = 2000$. For both CPS and VPS cases, the structure factors at $kx-ky$ and $kx-kz$ plans show marked anisotropy in the shapes of domains parallel to shear direction. The isotropy of structure factors S in $ky-kz$ plan implies that the domains are isotropic in the plan perpendicular to shear.

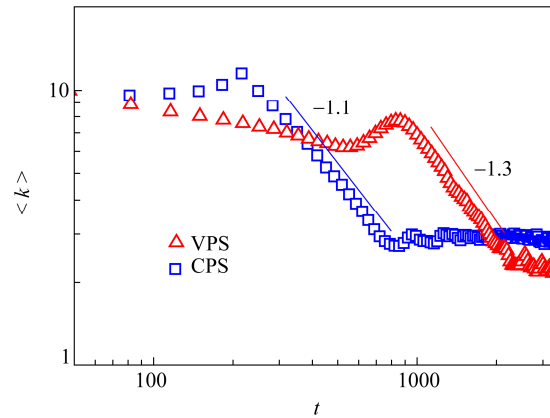


Fig. 2 The evolutions of characters wave numbers in the CPS and VPS under shear

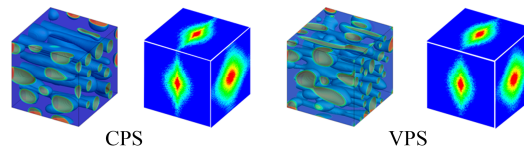


Fig. 3 The structure factors at k_x-k_y , k_x-k_z and k_y-k_z planes for corresponding stable CPS and VPS patterns at $t = 2000$ in Fig. 1

The average polymer fraction evolutions in polymer-rich phase and solvent rich phase are presented in Fig. 4(a). For both VPS and CPS cases, the polymer fractions evolution in two phase can be divided into three stages. Stage I: Frozen in the beginning of phase separation. As the stress is coupled to diffusion in the VPS, the phase separation is suppressed in the beginning, the frozen period in VPS is obviously longer than that in CPS. Stage II: Dramatical increase at intermediate stage of phase separation. The phase separation in this period is quick. Stage III: Relatively stable in the late stage of phase separation. In simulation, the relative stable average fraction of polymer shows 0.8 and 0.12 respectively in two phases. However, in theory, the equilibrium fraction of polymer in polymer-rich and solvent-rich phases is 0.9 and 0.1, respectively. The existence of phase interface, where the fraction of polymer transition between two phases, causes the average fraction of polymer in simulation to deviate from the equilibrium fraction in theory.

Figure 4(b) shows the evolution of polymer-rich phase volume fraction ϕ_p in the VPS and CPS under shear. ϕ_p is the fraction of lattices with $\phi > 0.27$. In the VPS case, the volume fraction of polymer-rich phase decreases, which indicates the volume shrinking behavior. However, for the CPS case, the volume fraction of polymer-rich phase is nearly unchanged, and phase separates without volume shrinking behavior.

Figure 5 shows the temporal changes in the average magnitudes of the three types of forces in the VPS and CPS: the thermodynamic force $\mathbf{F}_\phi = -\nabla \cdot \mathbf{\Pi}$, the bulk mechanical force $\mathbf{F}_b = -\nabla \cdot \mathbf{\sigma}_b$, and the shear mechanical force $\mathbf{F}_s = -\nabla \cdot \mathbf{\sigma}_s$ in each grid. In the CPS case, the peak of $|\mathbf{F}_\phi|$ appears at $t = 250$. This is because the stress is ignored in the CPS, $|\mathbf{F}_s| = |\mathbf{F}_b| = 0$. In the VPS case, the peaks of $|\mathbf{F}_\phi|$ and $|\mathbf{F}_s|$ appear at the same time of $t = 800$, since both of them are directly related to the velocity field $|\nabla \cdot \mathbf{v}_p|$. They cancel each other and the phase separation rate is delayed compare with the CPS in early stage of phase separation. The peak of $|\mathbf{F}_s|$ appears at $t = 1000$, which retards about $\Delta t \sim 200$ compare with that of $|\mathbf{F}_\phi|$ and $|\mathbf{F}_b|$. This is because $|\mathbf{F}_s|$ is directly related to un-diagonal part of stress tensor $\mathbf{\Pi}$. Compare with that in static case, the shear mechanic force is directly coupled to the shear velocity field, therefore $|\mathbf{F}_s|$ decays very slowly and almost keeps in a stable value at late stage of phase separation.

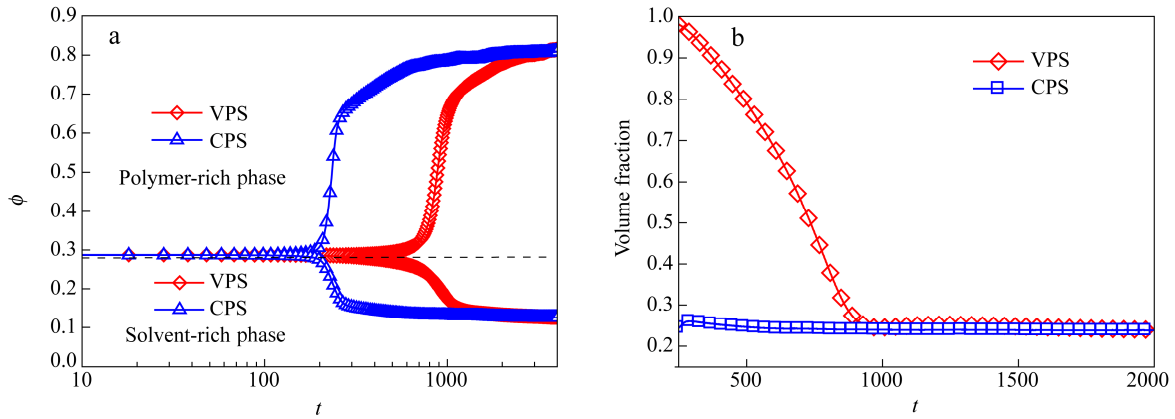


Fig. 4 (a) The time evolution of the average fraction of polymer in polymer rich phase and solvent rich phase for two cases in Fig. 1 (The short dash dot line is the initial fraction of polymer); (b) Temporal change in the volume fraction of the polymer-rich phase for two cases in Fig. 1

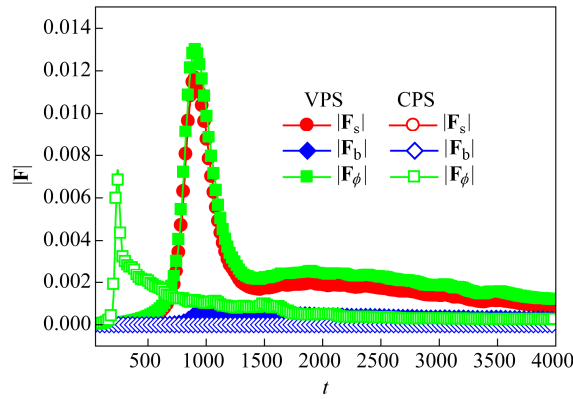


Fig. 5 Temporal changes in the average magnitudes of the three types of forces: the thermodynamic force, the bulk mechanical force and the shear mechanical force

Roles of Bulk and Shear Relaxation Moduli

As shown in the previous section, the viscoelastic properties would affect the phase separation under shear both in the morphologies and dynamics. The viscoelastic stresses in VPS can be divided into the bulk stress and shear stress. In previous works, for static case, Tanaka *et al.* have investigated the roles of bulk and shear moduli in 2D and 3D VPS, respectively^[5, 6, 11]. Dwivedi *et al.* studied the roles of bulk modulus in 2D VPS under shear^[15]. However, the roles of bulk and shear moduli in 3D VPS under shear have not been explored yet, which will be explored in details.

The role of bulk modulus

Figure 6 demonstrates the phase separation process at shear rate $\dot{\gamma} = 0.02$ for various bulk moduli and relaxation time: (a) $M_b^0 = 1$, $\tau_b^0 = 10$, (b) $M_b^0 = 3$, $\tau_b^0 = 10$, (c) $M_b^0 = 5$, $\tau_b^0 = 10$, and (d) $M_b^0 = 5$, $\tau_b^0 = 5$. The phase morphology evolutions are similar in these cases. At the beginning of phase separation, the solvent-rich phase forms the disperse ellipse structures in polymer-rich matrix phase. Then, the disperse solvent-rich phases grow and connect to each other, and form the bicontinuous structures. The solvent-rich phase further grows, and the polymer rich phase depresses to form the string structures. However, the polymer-rich strings are not stable, they break down and coalesce to form large elongated structure. This implies that the bulk relaxation moduli may not affect the morphology evolution pathway in the VPS under shear. However, the phase separation speed in VPS is delayed with M_b^0 and τ_b^0 increasing.

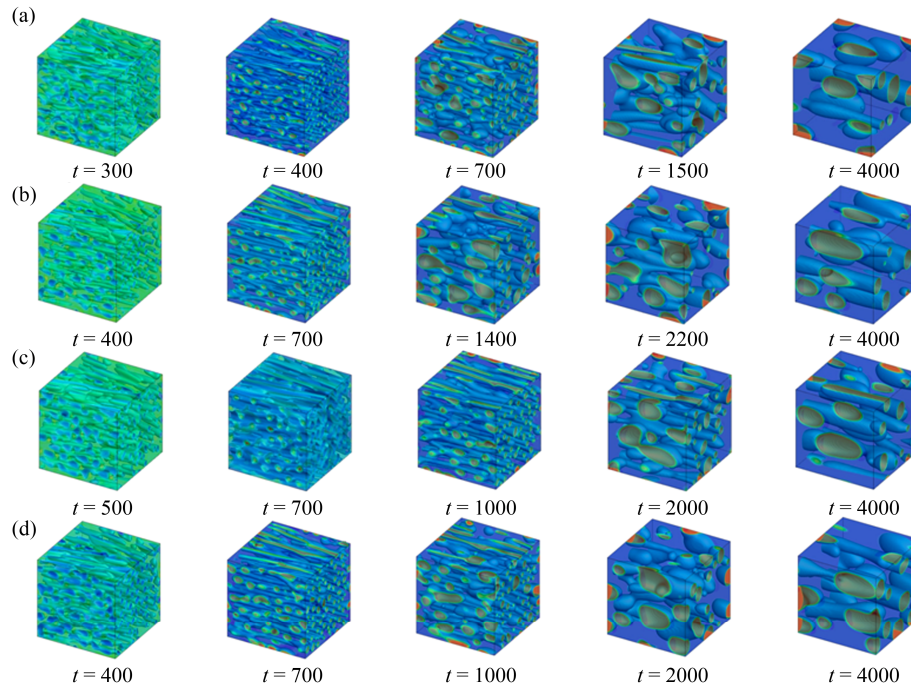


Fig. 6 Phase separation processes at shear rate $\dot{\gamma} = 0.02$ for various bulk modulus and relaxation time setting: (a) $M_b^0 = 1$, $\tau_b^0 = 10$, (b) $M_b^0 = 3$, $\tau_b^0 = 10$, (c) $M_b^0 = 5$, $\tau_b^0 = 10$, and (d) $M_b^0 = 5$, $\tau_b^0 = 5$. Blue and red describe the solvent-rich phase and polymer-rich phase, respectively.

The evolutions of characters wave numbers and the corresponding polymer fraction evolution in two phases are presented Figs. 7(a) and 7(b), respectively. The bulk modulus delays the phase separation as observed in the previous section. However, the evolution pathways of characters wave numbers and the corresponding polymer fraction evolution are similar for various bulk moduli, and can be divided into three stages. Stage I, in the beginning of the phase separation the systems are frozen, thus the domain grows very slowly. The corresponding polymer fraction evolution in two phase is nearly equal to the initial fraction (see Fig. 7b). At the end of stage I the ellipse solvent-rich phase droplets appear. Stage II: The ellipse solvent-rich phase droplets grow and connect each other. The continuous polymer-rich phase is suppressed and breaks down, thus the phase inversion was observed. Because of the character structures change in the phase inversion, the characters wave numbers show a peak in Fig. 7(a). The time of the phase inversion take place increase with M_b^0 and τ_b^0 . The polymer fractions in two phase change very fast when phase inversion takes place (see Fig. 7b). The domain size increases quickly after phase inversion. The domain growth indexes are all about -1 under various M_b^0 and τ_b^0 , which indicates that the phase domain growth mechanics should be similar. Stage III: $\langle k \rangle$ becomes relatively stable which implies that the phase structures are parallel to shear direction, and form stable phase structures under shear as shown in Fig. 6 at $t = 4000$. The stable domain size is decreased with the bulk modulus. The corresponding average polymer fractions in two phases reach equilibrium.

Figure 8 gives the temporal changes in the average magnitudes of the bulk mechanical force $|\mathbf{F}_b|$ and the shear mechanical force $|\mathbf{F}_s|$. Because the bulk stress should delay the phase separation and is coupled to thermodynamic diffusion, both the time and value of $|\mathbf{F}_b|$ peaks increase with bulk modulus as shown in Fig. 8. However, the peak value of shear mechanical force $|\mathbf{F}_s|$ decreases with bulk relaxation modulus and time. This is because the velocity in the VPS is depressed by bulk modulus, which causes the decrease of shear modulus. In the late stage of phase separation, bulk mechanical force $|\mathbf{F}_b|$ relaxes to near 0. The shear mechanical force $|\mathbf{F}_s|$ relaxes very slowly. Because the shear force is decided by the shear velocity.

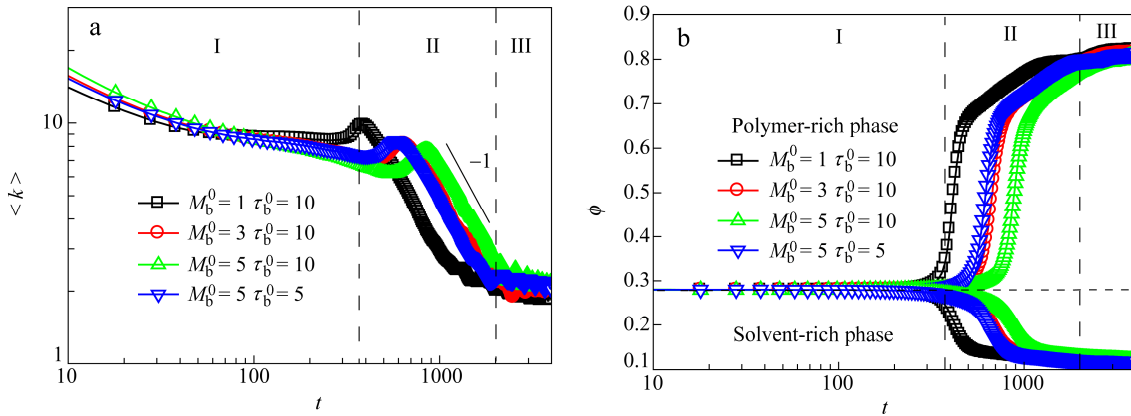


Fig. 7 (a) The evolutions of characters wave numbers, and (b) the corresponding polymer fractions evolution in two phases

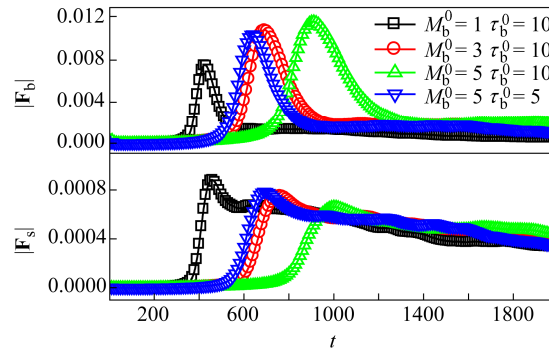


Fig. 8 Temporal changes in the average magnitudes of the bulk mechanical force and the shear mechanical force

The rheological character of VPS under shear is very important to the process of polymer blends. Here, the shear stress in VPS under shear is studied. In theory, the total shear stress $\sigma_{s\text{-total}}$ can be divided into two parts: the bulk contribution $\sigma_{s\text{-bulk}} = \sigma_s$ and the interface contribution $\sigma_{s\text{-interface}} = -\left\langle C \frac{\partial \phi}{\partial x} \frac{\partial \phi}{\partial y} \right\rangle$. Thus $\sigma_{s\text{-total}} = \sigma_s + \sigma_{s\text{-bulk}}$. Figure 9(a) shows the total shear stress evolution in the VPS. The total shear stress increases dramatically when phase separation takes place. Then, the second overshoot phenomenon is observed in the shear stress in the late stage of phase separation. The amplitude of vibration is decreasing with bulk relaxation modulus. Figure 9(b) presents the shear stress contribution from interface, and contribution from bulk, respectively. It is found that the contribution from bulk is stronger than that from interface. The contribution from bulk increases rapidly with the phase separation beginning, and maintains in a stable value in the late stage of phase separation. The bulk modulus nearly can not affect the bulk shear stress very much in the late stage of phase separation. Thus, the second overshoot in the late stage of total shear stress is caused by the interface contribution. The mechanics of second overshoot take place in the late stage of phase separation is shown in Fig. 9(c). The interface contribution rises at the beginning of phase separation for the phase interface appears as shown in Fig. 9(c) I. When the angle between the domains and shear directions approaches 45 degrees (see Fig. 9(c) II), the shear stress reaches peaks. Then due to the formation of the small string structure which becomes aligned along the shear direction, the interface contribution becomes smaller. When the string is parallel to the shear direction, the interface contribution becomes the smallest (see Fig. 9(c) III). However, because of the higher interface energy, the small string structure under shear is not stable, which would break down and coalesced into larger droplets (see Fig. 9(c) IV). Thus the interface contribution rises again and reaches a peak when the angle between the orientations of coalesced droplets and shear direction approaching 45° (see Fig. 9(c) V). The

amplitude of second overshoot is decreasing with bulk relaxation modulus since the domains with weak bulk modulus are easier to elongate and break down under shear. Then, the droplets are continually elongated and become aligned along the shear direction. Therefore, the interface contribution becomes decayed again until the elongated droplets formed. At last, the larger ellipsoid structure is formed, which is parallel to shear and stable under shear (see Fig. 9(c) VI), and the interface contribution becomes smaller and stable.

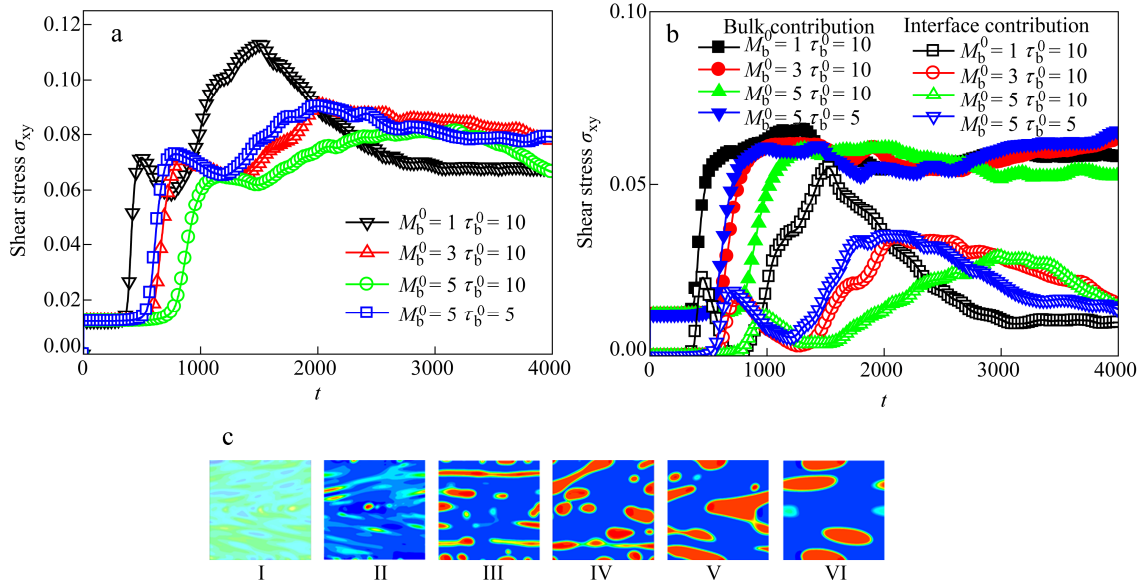


Fig. 9 The shear stress in the viscoelastic phase separation: (a) total shear stress, (b) shear stress contribution from interface, and contribution from bulk, (c) the corresponding patterns of x-y plan with the interface contribution evolution

Roles of shear relaxation modulus

To investigate the shear modulus effect on the morphologies, dynamics and rheological response of the VPS under shear, various shear moduli are simulated. Figure 10 presents patterns of the viscoelastic phase separation at $t = 4000$ for systems with different shear relaxation moduli and relaxation time.

The pattern evolutions are similar when $t < 2000$, similar to that in Fig. 1(b). After $t > 2000$, the surface of domain is coarser with the larger shear modulus, because the shear modulus suppresses the structures relaxation^[5, 31], and is helpful to maintain the irregular structures at late stage of phase separation. The domain character wave number with various shear moduli is shown in Fig. 11. When $t < 2000$, the domain growth dynamics is similar. However, for the suppression of the domain breakdown by the shear modulus, domain size increases with shear modulus in the late stage of phase separation ($t > 2000$).

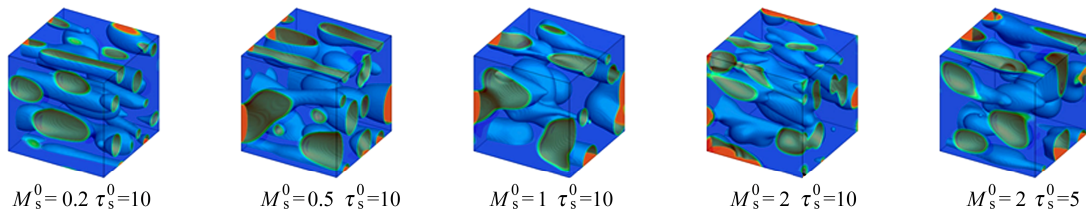


Fig. 10 Patterns of the viscoelastic phase separation at $t = 4000$ for systems with different shear relaxation moduli and relaxation time

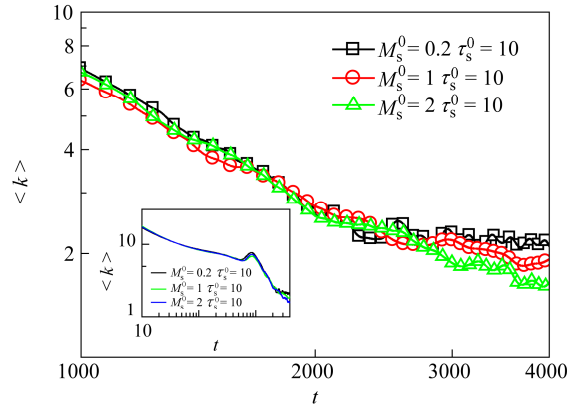


Fig. 11 The evolutions of characters wave numbers at late stage of VPS under shear (The insert shows the phase separation in all simulation time.)

Figure 12 shows the shear stress in the VPS with various shear moduli, total shear stresses, and shear stress contributions from interface and bulk. The total shear stress increases remarkably when phase separation begins. Then, the shear stress maintains in a stable value in the small shear modulus (*e.g.* $M_s^0 = 0.2$ $\tau_s^0 = 10$), while keeps increasing in the relative larger shear modulus (*e.g.* $M_s^0 = 2$ $\tau_s^0 = 10$). The increase of shear stress in the relative larger shear modulus (*e.g.* $M_s^0 = 2$ $\tau_s^0 = 10$) is mainly from the contribution of bulk, which is caused by the enhanced response of coarse interface under shear. The fluctuation of the interface contribution can be explained by the breakdown and reform phase structures as in the previous section.

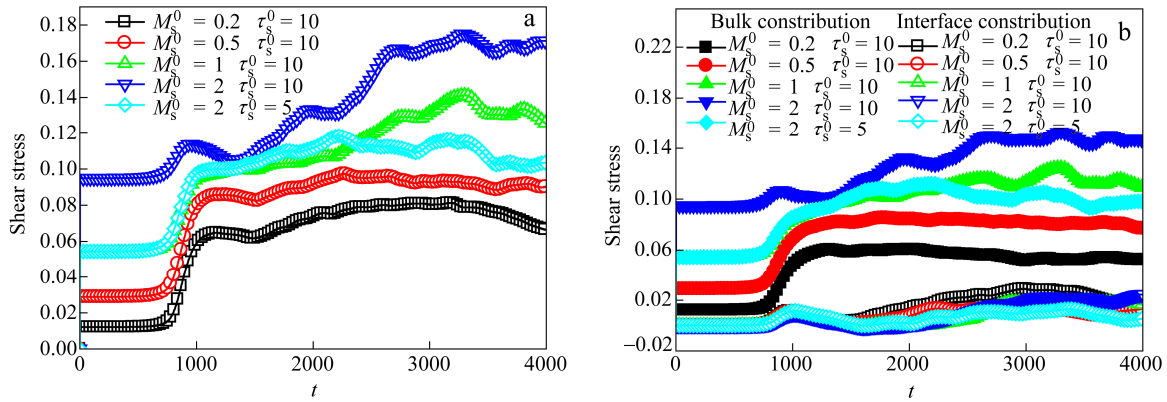


Fig. 12 The shear stress in the viscoelastic phase separation: (a) total shear stress, (b) shear stress contributions from interface and from bulk

CONCLUSIONS

In this work, we present a GPU-accelerated three-dimensional simulation to investigate the morphological, dynamic and rheological properties of VPS under shear. First, the morphologies and dynamics characters of VPS under shear are presented by comparing with those in CPS. The results show that the phase inversion and phase shrink take place in VPS under shear. Then, the roles of bulk and shear relaxation moduli in viscoelastic phase separation are investigated in details. The bulk relaxation modulus delays the phase separation process, but not affects the dynamic path of VPS. The dynamic path can be divided into three stages: freezing, growth and stable stages. The second overshoot phenomenon in the shear stress is caused by the breakdown and reform of string structures. The shear modulus affects the morphology evolution in the late stage of VPS under shear. The shear modulus will be helpful to form larger domains in the late stage of phase separation.

REFERENCES

- 1 Onuki, A., "Phase transition dynamics", Cambridge University Press, New York, 2002
- 2 Tanaka, H. and Araki, T., Chem. Eng. Sci., 2006, 61(7): 2108
- 3 Yu, W., Li, R.M. and Zho, C.X., Polymer, 2011, 52(12): 2693
- 4 Yu, W., Zhou, W. and Zhou, C.X., Polymer, 2010, 51(9): 2091
- 5 Tanaka, H. and Araki, T., Phys. Rev. Lett., 1997, 78(26): 4966
- 6 Araki, T. and Tanaka, H., Macromolecules, 2001, 34(6): 1953
- 7 Tanaka, H., Phys. Rev. Lett., 1993, 71(19): 3158
- 8 Tanaka, H., Phys. Rev. Lett., 1996, 76(5): 787
- 9 Doi, M. and Onuki, A., J. Phys. II, 1992, 2(8): 1631
- 10 Tanaka, H., J. Phys. Condes. Matter, 2000, 12(15): R207
- 11 Tanaka, H., Phys. Rev. E, 1997, 56(4): 4451
- 12 Zou, F.S., Dong, X., Liu, W., Yang, J., Lin, D.M., Liang, A.M., Li, W. and Han, C.C., Macromolecules, 2012, 45(3): 1692
- 13 Lodge, A.S., Polymer, 1961, 2(2): 195
- 14 Kume, T., Hattori, T. and Hashimoto, T., Macromolecules, 1997, 30(3): 427
- 15 Dwivedi, V., Ahluwalia, R., Lookman, T. and Saxena, A., Phys. Rev. E, 2004, 70(1): 011506
- 16 Imaeda, T., Furukawa, A. and Onuki, A., Phys. Rev. E, 2004, 70(5): 051503
- 17 Zhang, Z.L., Zhang, H.D. and Yang, Y.L., J. Chem. Phys., 2000, 113(18): 8348
- 18 Zhang, Z.L., Zhang, H.D., Yang, Y.L., Vinckier, I. and Laun, H.M., Macromolecules, 2001, 34(5): 1416
- 19 Zhang, Z.L., Zhang, H.D. and Yang, Y.L., J. Chem. Phys., 2001, 115(16): 7783
- 20 Buxton, G.A. and Balazs, A.C., Interf. Sci., 2003, 11(2): 175
- 21 Yang, K., Su, J. and Guo, H., J. Comput. Chem., 2012, 33(18): 1564
- 22 Brochard, F., J. De Phys., 1983, 44(1): 39
- 23 Brochard, F. and Degennes, P.G., Macromolecules, 1977, 10(5): 1157
- 24 Tanaka, H. and Araki, T., Phys. Rev. Lett., 2000, 85(6): 1338
- 25 Whitmer, J.K. and Luijten, E., J. Phys. Chem. B, 2011, 115(22): 7294
- 26 Cao, X.J., Cummins, H.Z. and Morris, J.F., J. Collid Interf. Sci., 2012, 368: 86
- 27 Onuki, A., J. Phys. Soc. Jpn., 1997, 66(6): 1836
- 28 Kobayashi, H. and Yamamoto, R., J. Chem. Phys., 2011, 134(6): 064110
- 29 Cao, Y., Zhang, H.D., Xiong, Z. and Yang, Y.L., Macromol. Theory Simul., 2001, 10(4): 314
- 30 Huo, Y.L., Zhang, H.D. and Yang, Y.L., Macromolecules, 2003, 36(14): 5383
- 31 Zhang, J.N., Zhang, Z.L., Zhang, H.D. and Yang, Y.L., Phys. Rev. E, 2001, 64(5): 051510
- 32 Zhou, D., Zhang, P.W. and E, W.N., Phys. Rev. E, 2006, 73(6): 061801