Supporting Information for "Molecular dynamics study of shear-induced lamellar alignment of ABA triblock copolymer thin films"

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1. The calculation of Flory-Huggins parameter χ from the energy constant ε_{AB} and Temperature T. ([J. Chem. Phys. 140, 054909 (2014)])

The value of the Flory-Huggins parameter χ can be derived from the equation 5-7 in [J. Chem. Phys. 140, 054909 (2014)]. This equation is only valid in a diblock copolymer melt system.

$$\chi = \frac{\alpha}{T} + \beta$$

$$\alpha(\varepsilon_{BB}, \varepsilon_{AB}) = 9.8\varepsilon_{BB} - 18.4\varepsilon_{AB} + 8.6$$

$$\beta(\varepsilon_{BB}, \varepsilon_{AB}) = -4.6\varepsilon_{BB} + 6.9\varepsilon_{AB} - 2.4$$

The energy constant ε_{AB}, ranging from 0.2ϵ to 0.85ϵ, at a temperature T of $2.0\epsilon/k_B$, corresponds to a Flory-Huggins parameter χ in the range of 1.740 to 0.245.

2. The simulation for observing order-disorder transition (ODT) point under shear condition

Order-disorder transition (ODT) analysis is conducted to observe the phase behavior of the copolymers near the transition point. Temperature T is fixed to $2.0\varepsilon/k_B$, and energy constant ε_{AB} is varied in the range less than 1.0. Fourier amplitude of the composition field $\psi(q)$ is applied to get accurate analysis of the order-disorder transition. The equation for the $\psi(q)$ is represented as follows:

$$\psi(q) = \frac{1}{NM}\sum_{j=1}^{MN} \varepsilon_j e^{iq \cdot r_j}$$

where ε_j is a prefactor of representing particle type ($\varepsilon_j = 1$ for type A and $\varepsilon_j = -1$ for type B), q is a wavevector, and r_j is a coordinate of the particle normalized by box size. $\psi(q)$ is coincidence with the signal intensity in the inverse Fourier space. Therefore, the argument wavevector q^* of max value of $\psi(q)$ indicates the direction and period of the lamellar unit. By using collective variable Ψ, the degree of order can be quantified.

$$\Psi = \left[\sum_q |\psi(q)|^n f(|q|)\right]^{1/n}$$

The more certain the periodicity and the degree of order, $\psi(q^*)$ has significantly high value compared to the other values of $\psi(q)$, which denotes that Ψ has high value.

In Figure S1, collective variables of triblock copolymers are calculated under different ε_{AB} and v_s conditions. When the ε_{AB} is in the range of 0.71~0.73, collective variables change significantly due to the variance of the degree of order. Therefore, this region can be considered as near ODT.

Additionally, from the transverse shear simulation (Case 2), ordered state and disordered state can be discriminated. Under the ordered condition (Figure S2(a)), transverse shear induces the reduction of collective variables in early stage, where the ordered part of the system is broken by the transverse shear. In sequence, the collective variable is recovered over the simulation time until reaching the value that similar to initial. The realignment of the lamellar system is occurred and the degree of order is recovered after the early stage. On the other hand, under the disordered condition (Figure S2(b)), collective variable shows fluctuation over all simulation time. As ordered part did not exist from the beginning, the transverse shear only causes the fluctuation by momentary change of the polymer matrix.

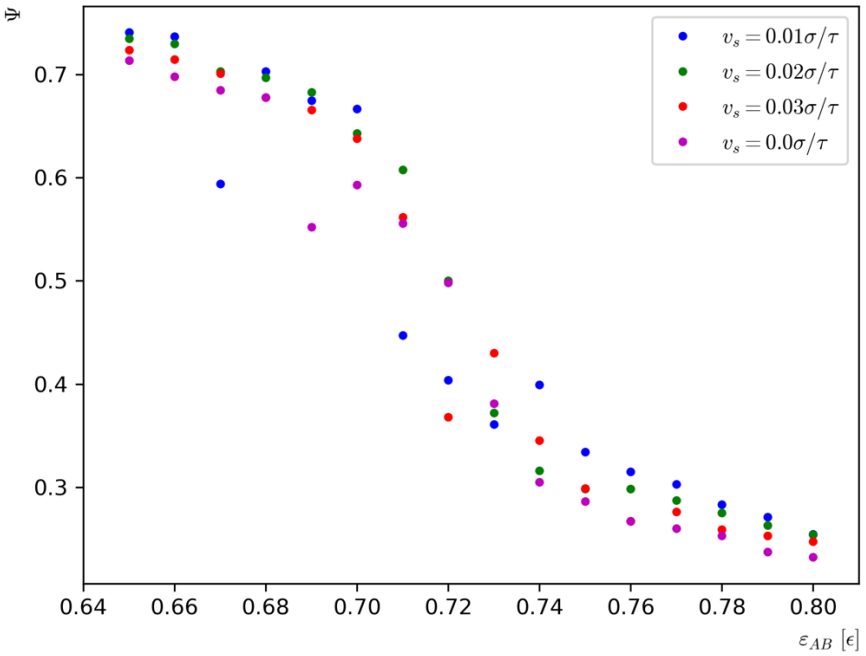

Figure S1. The collective variable Ψ of the triblock copolymer melt under shear. The range of ε_{AB} is set near the order-disorder transition point. Mean value of the collective variable is calculated after the simulation system reach steady-state.

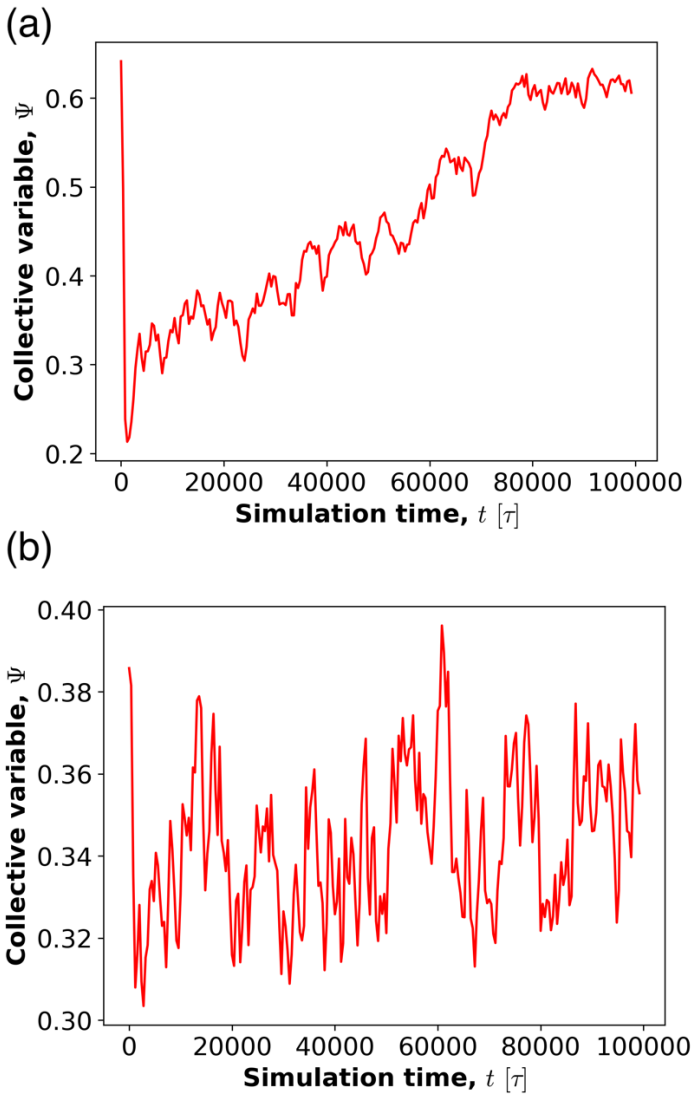

Figure S2. The change of collective variables of triblock copolymer as a function of time under transverse shear condition. (a) Ordered case, $\varepsilon_{AB} = 0.71\epsilon, v_s = 0.02\sigma/\tau$. (b) Disordered case, $\varepsilon_{AB} = 0.73\epsilon, v_s = 0.02\sigma/\tau$.

3. The visualization of polymer flow under shear

In transverse simulation, polymer flows are observed only in the realigned lamellar structure. Polymer chains does not display the specific flow when tilted structure is formed by weak wall velocity (Figure S3(a)). On the other hand, polymer chains are moved toward shear direction near wall surface when lamellar structure are realigned toward shear direction (Figure S3(b)).

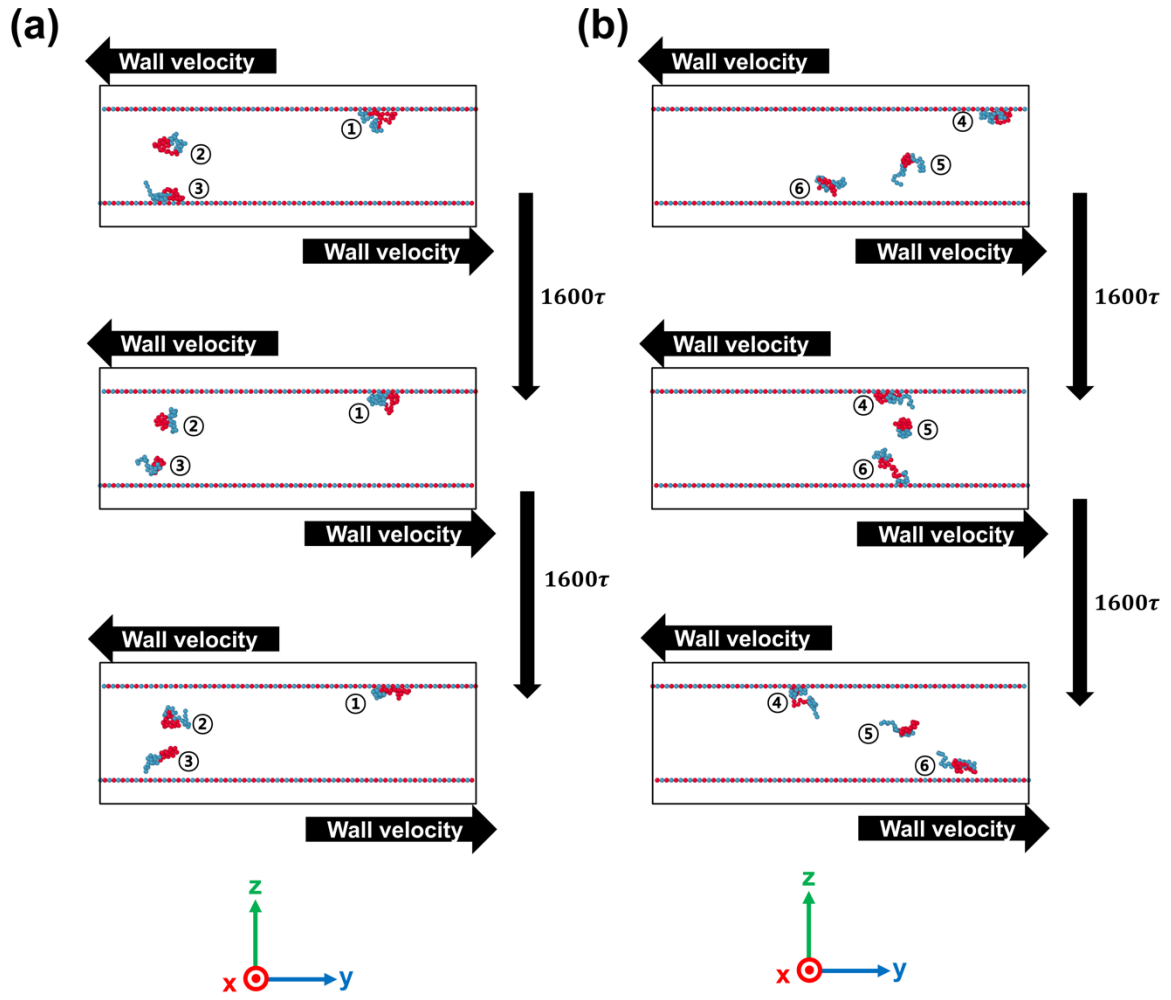

Figure S3. Snapshot of polymer chain every 1600τ in shear simulation. Same number refers to the same polymer chain. Lattice wall is visualized for checking the location of wall. (a) Polymer chains of tilted structure: $v_s = 0.01\sigma/\tau$, and $\varepsilon_{AB} = 0.4\epsilon$. (b) Polymer chains of realigned lamellar structure: $v_s = 0.04\sigma/\tau$, and $\varepsilon_{AB} = 0.4\epsilon$.

4. Force and energy calculation model using TSLJ potential and displacement of wall velocity.

In order to define force and energy calculation model, two assumptions are applied. First, two-dimensional space is assumed for simplification of model. Second, the particle neighboring the wall is located at the relaxed distance ($r = 2^{1/6}\sigma$) from the two wall particles before the displacement, where

the model neglects the fluctuation of particles. The displacement of the wall particle Δx in one timestep is calculated by below equation:

$$\Delta x = v_s \times \Delta t$$

The truncated and shifted Lennard-Jones (TSLJ) potential is used to calculate energy and the derivative of TSLJ is used for the force calculation. The distances between particle neighboring the wall and two wall particles (r_1, r_2) are represented as follows:

$$r_1 = 4\varepsilon\sqrt{2^{1/3} - 0.5^2 + (0.5 + x)^2} \quad (relatively\ far\ distance)$$

$$r_2 = 4\varepsilon\sqrt{2^{1/3} - 0.5^2 + (0.5 + x)^2} \quad (relatively\ close\ distance)$$

In order to separate force as *x* and *y* direction, the angle terms are calculated.

$$\theta_1 = arcsin(\frac{0.5 + x}{r_1})$$

$$\theta_2 = arcsin(\frac{0.5 - x}{r_2})$$

The force works on shear direction in all cases, which induces the polymer flow to the shear direction. Additionally, if polymer flows to the shear direction, the relative displacement of wall decreases, which causes the energy stabilization. Figure S4 displays the calculated energy and force in both low and high wall velocity.

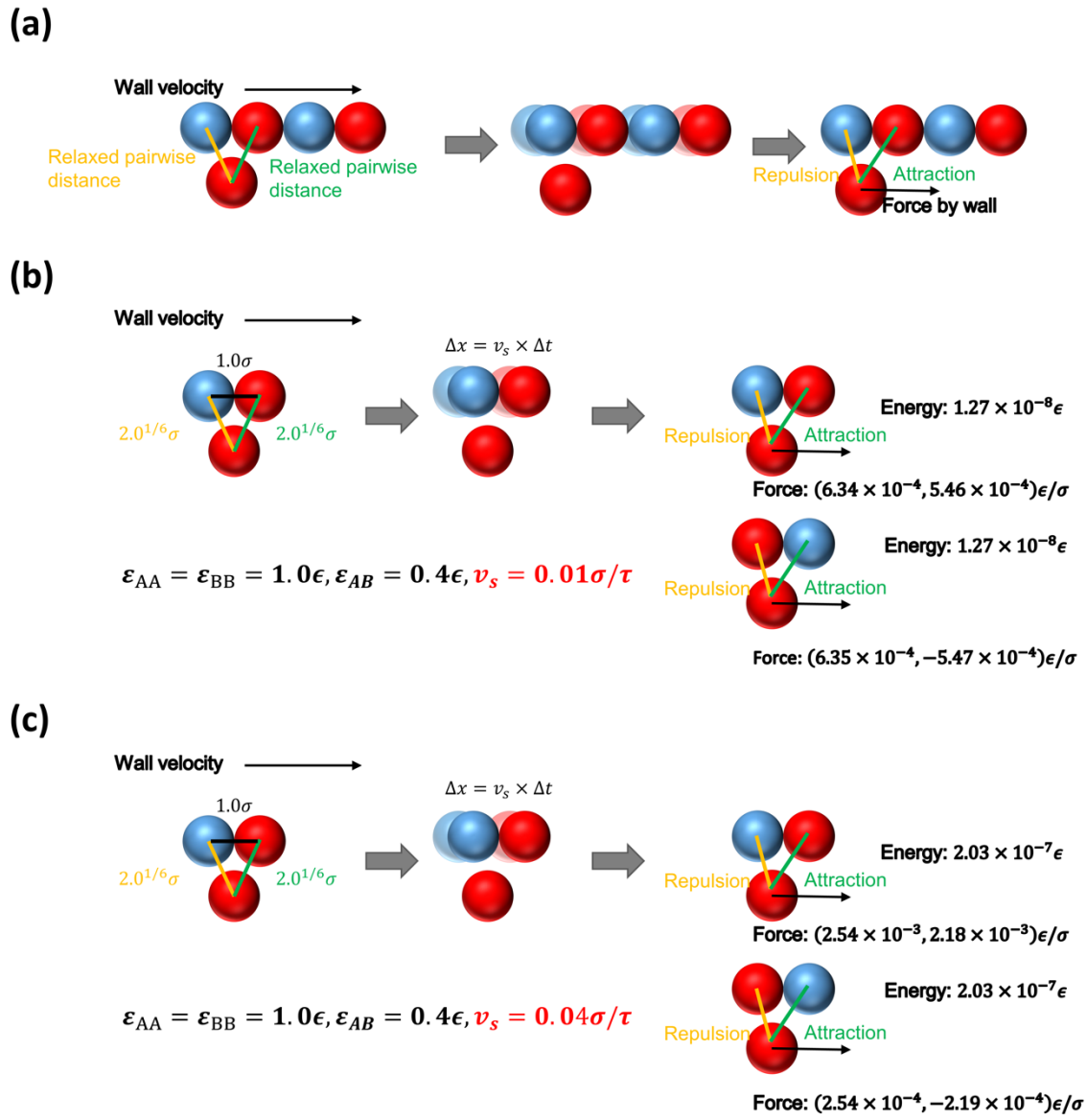

Figure S4. Overview of force and energy calculation model. Energies and forces are calculated by the truncated and shifted Lennard Jones (TSLJ) potential in two-dimensional space. Force is expressed as (x,y). (a) Schematic of particles near the wall. (b) Energy and force calculation under $\varepsilon_{AA} = \varepsilon_{BB} = 1.0\epsilon$, $\varepsilon_{AB} = 0.4\epsilon, v_s = 0.01\sigma/\tau$ condition. (c) Energy and force calculation under $\varepsilon_{AA} = \varepsilon_{BB} = 1.0\epsilon$, $\varepsilon_{AB} = 0.4\epsilon, v_s = 0.04\sigma/\tau$ condition.