Electronic Supplementary Information for

Mesoscale modeling of phase transition dynamics of thermoresponsive polymers

Zhen Li,[a] Yu-Hang Tang,[a] Xuejin Li,[a] and George Em Karniadakis*[a]

1 Energy-conserving DPD formulation

The energy-conserving dissipative particle dynamics (eDPD) method is an extension of the classic DPD method. It was developed by introducing the internal energy as an additional property to the DPD system for consideration of the energy equation [1]. Similarly to the classic DPD method, an eDPD system consists of many coarse-grained particles. Each of them represents a group of actual molecules rather than a single atom/molecule directly. The time evolution of an eDPD particle i with unit mass is governed by the conservation of momentum and energy, which is described by the following set of equations [2]

$$\frac{\mathrm{d}\mathbf{r}_i}{\mathrm{d}t} = \mathbf{v}_i \ , \tag{1}$$

$$\frac{\mathrm{d}\mathbf{v}_i}{\mathrm{d}t} = \mathbf{F}_i = \sum_{j\neq i}(\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R) \ , \tag{2}$$

$$C_v\frac{\mathrm{d}T_i}{\mathrm{d}t} = Q_i = \sum_{j\neq i}(Q_{ij}^C + Q_{ij}^V + Q_{ij}^R) \ , \tag{3}$$

where t, $\mathbf{r}_i$, $\mathbf{v}_i$ and $\mathbf{F}_i$ denote time, and position, velocity, force vectors, respectively. C_v is the thermal capacity of eDPD particles, T_i the temperature and Q_i the net heat flux of particle i. The summations are carried out over all other particles within a cutoff radius r_c. Specifically, the three components of $\mathbf{F}_i$ including the conservative force $\mathbf{F}_{ij}^C$, dissipative force $\mathbf{F}_{ij}^D$ and random force $\mathbf{F}_{ij}^R$ are expressed as

$$\mathbf{F}_{ij}^C = a_{ij}(T)\omega_C(r_{ij})\mathbf{e}_{ij} \ , \tag{4}$$

$$\mathbf{F}_{ij}^D = -\gamma_{ij}\omega_D(r_{ij})(\mathbf{v}_{ij}\cdot\mathbf{e}_{ij})\mathbf{e}_{ij} \ , \tag{5}$$

$$\mathbf{F}_{ij}^R = \sigma_{ij}\omega_R(r_{ij})\xi_{ij}\Delta t^{-1/2}\mathbf{e}_{ij} \ , \tag{6}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between particles i and j, $\mathbf{e}_{ij} = \mathbf{r}_{ij}/r_{ij}$ the unit vector from particle j to i, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ the velocity difference and Δt the time step for time integration. Also, $a_{ij}(T)$ is the

---

[a] *Division of Applied Mathematics, Brown University, Providence, RI 02912, U.S.A.*

* *E-mail: George_Karniadakis@brown.edu*

temperature-dependent repulsive force parameters, γ_{ij} the dissipative coefficient and σ_{ij} the strength of random force. Moreover, the heat flux between particles includes the collisional heat flux Q_{ij}^{C}, viscous heat flux Q_{ij}^{V} and random heat flux Q_{ij}^{R}, which are given by [2]

$$Q_{ij}^{C} = k_{ij}\omega_{CT}(r_{ij})\left(\frac{1}{T_i} - \frac{1}{T_j}\right) , \tag{7}$$

$$Q_{ij}^{V} = \frac{1}{2C_v}\left\{\omega_D(r_{ij})\left[\gamma_{ij}(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})^2 - \frac{\sigma_{ij}^2}{m}\right] - \sigma_{ij}\omega_R(r_{ij})(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})\xi_{ij}\right\} , \tag{8}$$

$$Q_{ij}^{R} = \beta_{ij}\omega_{RT}(r_{ij})\Delta t^{-1/2}\zeta_{ij} . \tag{9}$$

where $k_{ij} = C_v^2\kappa(T_i + T_j)^2/4k_B$ and β_{ij} determine the strength of the collisional and random heat fluxes. $\omega_C(r)$, $\omega_D(r)$, $\omega_R(r)$, $\omega_{CT}(r)$ and $\omega_{RT}(r)$ are the weight functions of $\mathbf{F}^C$, $\mathbf{F}^D$, $\mathbf{F}^R$, Q_{ij}^C and Q_{ij}^R, respectively. They are often given by $\omega(r) = (1 - r/r_c)^{\Lambda}$ in which Λ is the exponent of these weight functions, i.e., $\Lambda = 1$ for $\omega_C(r)$ and $\Lambda = 2$ for $\omega_D(r)$. Also, ξ_{ij} and ζ_{ij} are symmetric Gaussian random variables with zero mean and unit variance. To satisfy the fluctuation-dissipation theorem, the dissipative and random forces are coupled via $\sigma_{ij}^2 = 4\gamma_{ij}k_BT_iT_j/(T_i + T_j)$ and $\omega_D(r) = \omega_R^2(r)$, and the collisional and random heat fluxes are coupled via $\beta_{ij}^2 = 2k_Bk_{ij}$ and $\omega_{CT}(r) = \omega_{RT}^2(r)$. Interested readers should refer to Refs. [1, 2] for further details of the eDPD framework.

2 Modeling of thermoresponsive polymer

In the eDPD method, the bead-spring representation of polymer chains is employed to model polymers in complex fluids. Different spring models can be used for describing the spring interactions between connected DPD particles. Examples include the Hookean spring, the finitely extensible nonlinear elastic (FENE) spring and the wormlike chain (WLC) [3]. In this study, we consider linear polymer chains with Hookean springs. The elastic spring force is expressed as

$$\mathbf{F}_{ij}^{S} = k_s(1 - r_{ij}/r_s)\mathbf{e}_{ij} , \tag{10}$$

where $k_s = 200$ is the spring constant, and the equilibrium bond length between two consecutive particles is set to $r_s = 0.4r_c$. Cross-links are also modeled as Hookean springs with $k_s = 200$ and $r_s = 0.4r_c$. As shown in Fig. S1, many linear polymer chains are cross-linked to generate a microgel bead, and each chain is made up of 50 eDPD particles. The cross-links with a density of approximately 3% of total bonds are randomly distributed in the microgel bead. Fig. S1 shows a microgel bead consisting of four linear polymer chains bonded by cross-links. In the simulations, we consider different size of microgels, which consist of 100, 200, 500 and 1000 cross-linked polymer chains, respectively.

The potential between thermoresponsive polymer (TRP) and solvent is sensitive to the temperature, and the polymer-solvent interaction parameter χ is a function of temperature [4]. In the DPD method, the Flory-Huggins χ-parameter is linear with respect to the excess repulsion Δa given by $\chi \approx 0.487\Delta a/k_BT$ [5] when the number density is set to $\rho = 4$. Here, the excess repulsion is defined by $\Delta a = a_{sp} - a_{ss}$ where s represents solvent and p stands for polymer. To model the thermally induced phase transition of TRP, we define the excess repulsion Δa as a function of temperature to consider the temperature-dependence of the Flory-Huggins χ-parameter.

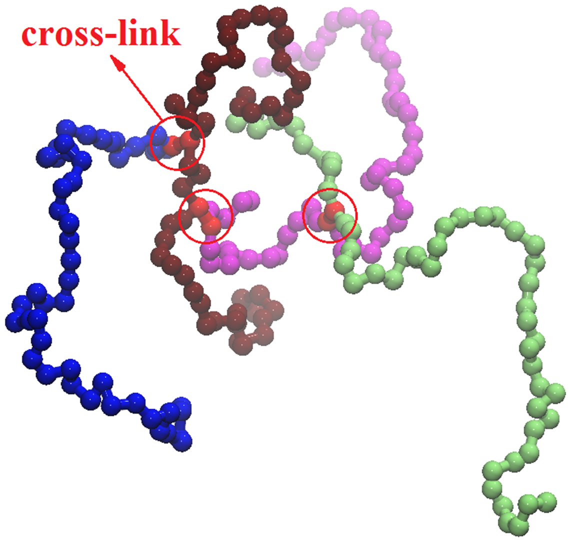

Figure S1: Coarse-grained eDPD model of cross-linked polymer chains. Cross-links are marked with circles. Each chain consists of 50 connected eDPD particles through Hookean spring. As an example, only four linear polymer chains are presented.

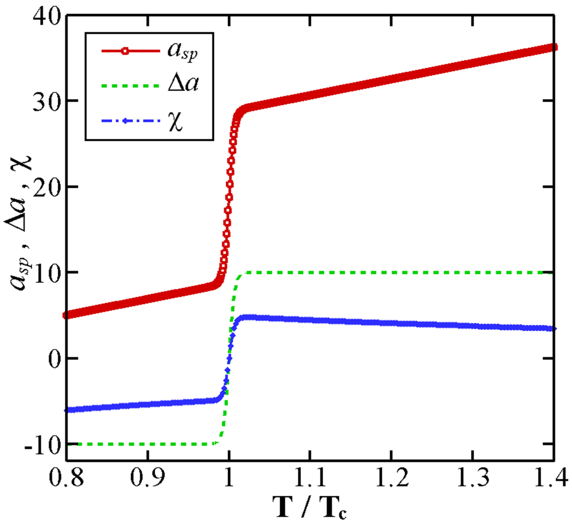

Figure S2: Temperature-dependence of conservative force between polymer and solvent particles a_{sp}, the excess repulsion Δa and corresponding Flory-Huggins χ-parameter. The polymer is hydrophilic for at low temperatures ($T < T_c$) and hydrophobic at high temperatures ($T > T_c$).

For the conservative force, between particles of same type the repulsion parameters are taken as $a_{ss}(T) = a_{pp}(T) = 75k_BT/\rho = 18.75k_BT$, and the cross terms are given as

$$a_{sp}(T) = \frac{75k_BT}{\rho} + A_0 + \frac{\Delta A}{1.0 + exp(-\tau \cdot (T - T_c))} \, , \tag{11}$$

which contains a sharp change by ΔA at $T = T_c$, and the sharpness is determined by the parameter τ. In the simulations, we use $A_0 = -10$, $\Delta A = 20$ and $\tau = 300$ so that the polymer is hydrophilic ($\chi < 0$) at low temperatures ($T < T_c$) and hydrophobic ($\chi > 0$) at high temperatures ($T > T_c$), as shown in Fig. S2.

The parameters involved in Eqs. (1)-(9) are listed in Table 1. Since the conservative force can be written as the negative gradient of potential energy, when the conservative force between particles is given by $\mathbf{F}^C_{ij}(r_{ij}) = a_{ij}(T)(1 - r_{ij}/r_c)\mathbf{e}_{ij}$, the corresponding potential is $U_{ij}(r_{ij}) = \frac{1}{2}a_{ij}(T)r_c(1 - r_{ij}/r_c)^2$. As the temperature of the eDPD system increases, the pair potential between particles changes with temperature because of the variation of repulsive coefficient a_{ij}. To satisfy the conservation of energy, the change of potential energy is considered to be balanced by a change of internal energy. Specifically, the total energy for each pair is considered invariable and its variation is zero upon time integration, i.e., $\Delta E_{ij} = \Delta U_{ij} + \Delta e_i - Q_i + \Delta e_j - Q_j = 0$, where $\Delta e_i = C_v\Delta T_i$ and $\Delta e_j = C_v\Delta T_j$ are the changes of internal energy of particles i and j, and Q_i and Q_j represent their net heat fluxes.

Table 1 Parameters for simulations of thermally induced phase transition of TRP. The symbol s represents solvent and p stands for polymer.

Name	Symbol	Value
Number density	ρ	4
Cutoff radius	r_c	1.0
Critical temperature	T_c	1.0
Temperature of system	k_BT	$0.8T_c$-$1.4T_c$
Time step	Δt	0.01
Repulsive coefficient	a_{ss}, a_{pp}	$75k_BT/\rho$
	a_{sp}	$75k_BT/\rho - 10 + 20/\{1.0 + exp[-300(T - T_c)]\}$
Dissipative coefficient	γ_{ij}	4.5
Strength of random force	σ_{ij}	$\sigma_{ij}^2 = 4\gamma_{ij}k_BT_iT_j/(T_i + T_j)$
Thermal capacity	C_v	1.0×10^3
Heat friction coefficient	κ	1.0×10^{-3}
Weight functions	$\omega(r)$	$\omega_C(r) = \omega_R(r) = \omega_{RT}(r) = 1 - r/r_c$, $\omega_D(r) = \omega_{CT}(r) = (1 - r/r_c)^2$

3 Simulation setup

In the present study, the eDPD systems consist of half a million particles, and the simulations are performed using a GPU-accelerated DPD ${}_{USER}\mathtt{MESO}$ package [6]. A modified velocity-Verlet algorithm [5] is employed for the numerical integration of the eDPD equations with time step $\Delta t = 0.01$.

In practice, four eDPD systems involving different size of microgels are constructed in a computational domain of $50r_c \times 50r_c \times 50r_c$. Periodic boundary conditions are applied for all boundaries. The particle number density is set to $\rho = 4$ and the total number of particles used in the simulations is 500 000. We consider the microgels consisting of 100, 200, 500 and 1000 cross-linked polymer chains with 50 eDPD particles per chain, which correspond to polymer concentration of 1 wt%, 2 wt%, 5 wt% and 10 wt%, respectively. Here, the mass of polymer particle is equal to the mass of solvent particle.

The particle systems of a microgel bead surrounded by solvent particles are initialized with random configurations at a low temperature $T_0 = 0.8T_c$. To obtain the thermal equilibrium state, we run the eDPD simulations at $T_0 = 0.8T_c$ for at least twice the relaxation time t_{relax} of the microgels. The relaxation time t_{relax} is obtained by computing their gyration radius R_g and fitting the time evolution of R_g with an exponential function $exp(-t/t_{\text{relax}})$. For instance, Fig. S3 shows the time evolution of R_g for a microgel bead (5 wt%) at low temperature $T = 0.8T_c$. The computed R_g is fitted by $R_g(t) = 16.31 - 3.54 \cdot exp(-t/272.01)$, which indicates $t_{\text{relax}} = 272.01$. Therefore, a pre-run simulation for 600 time units ($> 2t_{\text{relax}}$) is carried out for obtaining the thermal equilibrium state. Then, similarly to the differential scanning calorimetry (DSC) experiments, the temperature of the eDPD system is increased linearly from $T_0 = 0.8T_c$ to $T_1 = 1.4T_c$ within 1500 time units.

For linearly heating up the eDPD system, each eDPD particle is coupled with a thermal background of desired temperature $T^B(t)$. Therefore, an eDPD particle i with temperature $T_i(t)$ can obtain a heat flux $Q_i^S(t)$ from the thermal background dependent on the temperature difference $\Delta T = T^B(t) - T_i(t)$,

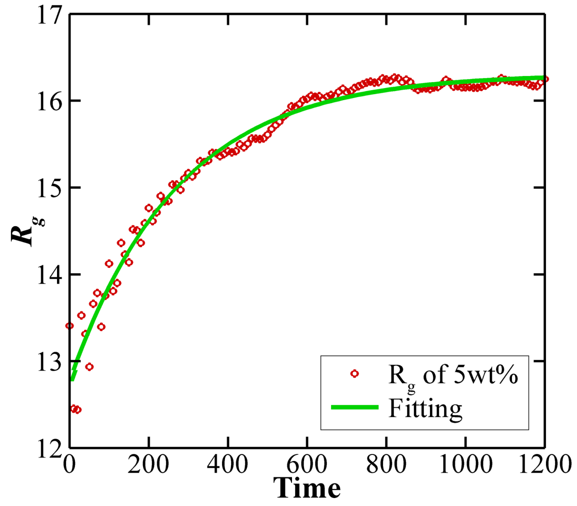

Figure S3: Time evolution of the gyration radius R_g of a microgel bead (5 wt%) at low temperature $T = 0.8T_c$. The gyration radius obtained from the eDPD simulation is fitted by $R_g(t) = 16.31 - 3.54 \cdot exp(-t/272.01)$, which indicates that the relaxation time is $t_{\text{relax}} = 272.01$.

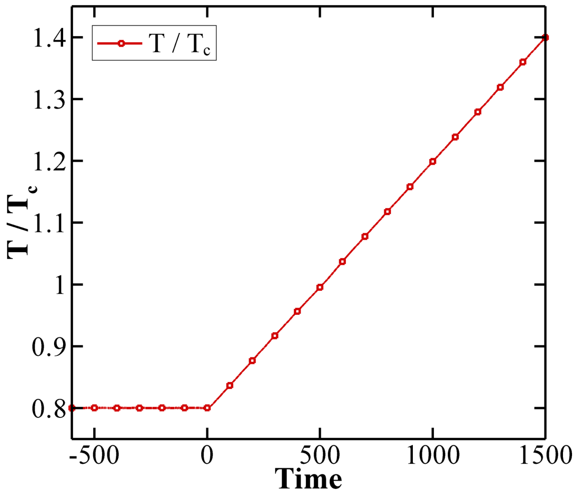

Figure S4: Temperature evolution of the eDPD systems during the simulations. A heating process is performed after the pre-run simulation. The curve reveals that the temperature is increased linearly with time during heating from $T = 0.8T_c$ to $T = 1.4T_c$.

which is given by

$$Q_i^S(t) = \lambda \cdot C_v \cdot \Delta T = \lambda \cdot C_v \cdot \left(T^B(t) - T_i(t)\right) , \tag{12}$$

where λ is a relaxation factor and we set $\lambda = 0.1$ in the simulations. Then, the total heat flow (endothermic energy) of the eDPD system can be computed by a summation of Q_i^S over all the particles. The temperature evolution of the eDPD systems during the simulations is illustrated in Fig. S4, which reveals that the temperature is increased linearly with time during heating from $T = 0.8T_c$ to $T = 1.4T_c$.

4 Size of microgel beads

In the present work, "small" and "large" microgel beads are defined with respect to the size of cooperative unit in eDPD systems. Let n be the number of cooperative unit in a thermally induced phase transition. When a microgel bead has only one cooperative unit, i.e., $n \leq 1$, the microgel bead undergoes a transition as a whole ("all-or-none" transition), which is denoted by "small", while "large" microgel bead represents a microgel bead that has two or more cooperative units.

In experiments, it is well-known that the number of cooperative units in hydrogels or macromolecules is proportional to the molecular weight. The number of cooperative units can be computed by the ratio of the enthalpy change of transition ΔH and the effective (van't Hoff) enthalpy ΔH^{eff}, i.e., $n = \Delta H/\Delta H^{\text{eff}}$, where $\Delta H = MQ_{tr}$ and $\Delta H^{\text{eff}} = 4RT_p^2 C_p(T_p)/Q_{tr}$. Here, M is the molecular weight, Q_{tr} is the heat of transition (the area under the heat absorption peak). More detailed description of the cooperative units ("domains") can be found in Tiktopolo et al.'s paper [7].

Based on the heating curves in our simulations, for the microgel bead of 1 wt$\%$, the enthalpies are $\Delta H = 9.84 \times 10^4$ and $\Delta H^{\text{eff}} = 2.30 \times 10^5$, and hence the number of cooperative unit ("domain") is

$n = 0.43 < 1$, which indicates that the microgel bead of of 1 wt% has only one single cooperative unit undergoing "all-or-none" transition. Therefore, it is denoted by "small" microgel bead in the manuscript. Similarly, we have $n = 3.60$ for the microgel bead of 5 wt% and $n = 7.69$ for the microgel bead of 10 wt%. This means that they have multiple cooperative units and they are denoted by "large" microgel beads.

5 Discussion on the shift of endothermic peaks

The endothermic peaks of LCST-type TRPs shift slightly to lower temperatures when the concentration increases, as has been observed in many experiments [7, 8]. Usually, the magnitude of the peak shift is small. For example, Kunugi et al. [8] quantified the endothermic peak shifts using polymers (PNVIBA and PNIPAM) at various concentrations. Their experimental data showed that the endothermic peak widths are larger than 10°C while the peak temperatures shift by approximately 1°C.

In our mesoscopic modeling, the peak widths are affected by the variation of temperature on polymer particles. In particular, the distribution of internal energy in an eDPD system depends on the heat capacity C_v of each eDPD particle,

$$P(k_BT) = \frac{1}{\sqrt{2\pi/C_v}} e^{-\frac{1}{2}C_v(k_BT - k_BT_0)^2} \tag{13}$$

which indicates that the mean temperature of eDPD particles is T_0 and the variance is the reciprocal of thermal capacity $1/C_v$.

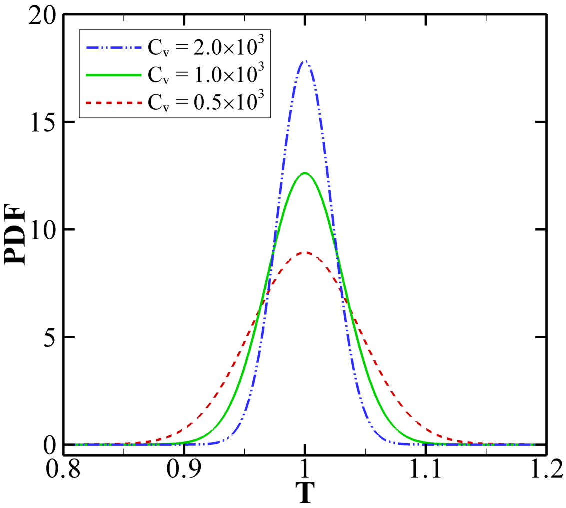

Figure S5: Probability distribution functions (PDF) of temperature in eDPD systems at $T_0 = 1.0$ with various thermal capacities, $C_v = 0.5 \times 10^3$, 1.0×10^3 and 2.0×10^3.

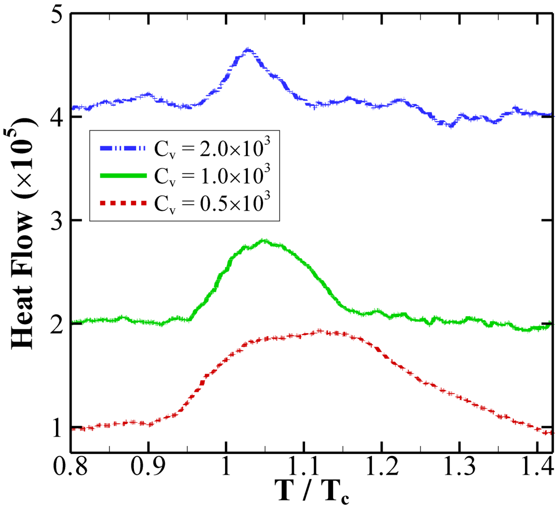

Figure S6: Thermogram analog to differential scanning calorimetry (DSC) heating curve with a fixed scanning rate ($4.0 \times 10^{-4} T_c$ per time unit) at a concentration of 5 wt%. Each eDPD system has 5.0×10^5 particles.

Figure S5 shows the probability distribution functions (PDF) of temperature in eDPD systems with $C_v = 0.5 \times 10^3$, 1.0×10^3 and 2.0×10^3. Larger fluctuations in temperature will result in wider endothermic peaks. Since the variance is $1/C_v$, increasing C_v will decrease the variation of temperature and will diminish the distribution of temperature, which yields a narrower endothermic peak, as shown in Fig. S6.

The thermal capacity of eDPD particle C_v is proportional to the size of particle, i.e., $C_v = C_v^* {L^*}^3/\rho k_B^*$ in which C_v^* is the volumetric heat capacity of polymers or fluids, L^* the length scale, k_B^* the Boltzmann constant and ρ the number density of eDPD particles. Therefore, eDPD systems having larger length scales should have narrower endothermic peak when the heterogeneities of polymers are not considered.

6 Video Clips

1. Video clip S1 illustrates the dynamic behavior of a small microgel bead (1 wt%) in the coil-to-globule phase transition during heating from $T = 0.8T_c$ to $T = 1.4T_c$. The phase transition of the small microgel bead is a relatively simple "all-or-none" process.
2. Video clip S2 illustrates the dynamic behavior of a large microgel bead (5 wt%) in the coil-to-globule phase transition during heating from $T = 0.8T_c$ to $T = 1.4T_c$. The dynamic details confirm that the large microgel bead has many "independent domains" that start their self-aggregation processes simultaneously.

References

[1] Español, P. Dissipative particle dynamics with energy conservation. *Europhys. Lett.* 1997, 40(6): 631-636.

[2] Li, Z., Tang, Y.-H., Lei, H., Caswell, B. and Karniadakis, G. E. Energy-conserving dissipative particle dynamics with temperature-dependent properties. *J. Comput. Phys.* 2014, 265:113-127.

[3] Symeonidis, V., Karniadakis, G. E. and Caswell, B. Dissipative Particle Dynamics Simulations of Polymer Chains: Scaling Laws and Shearing Response Compared to DNA Experiments. *Phys. Rev. Lett.* 2005, 95(7): 076001.

[4] Wu, J. Z., Huang, G. and Hu, Z. B. Interparticle potential and the phase behavior of temperature-sensitive microgel dispersions. *Macromolecules.* 2003, 36(2): 440-448.

[5] Groot, R. D. and Warren, P. B. Dissipative particle dynamics: Bridging the gap between atomistic and mesoscopic simulation. *J. Chem. Phys.* 1997, 107(11): 4423-4435.

[6] Tang, Y.-H. and Karniadakis, G. E. Accelerating dissipative particle dynamics simulations on GPUs: Algorithms, numerics and applications. *Comput. Phys. Commun.* 2014, 185(11): 2809-2822.

[7] Tiktopulo, E. I., Uversky, V. N., Lushchik, V. B., Klenin, S. I., Bychkova, V. E. and Ptitsyn, O. B. "Domain" Coil-Globule Transition in Homopolymers. *Macromolecules.* 1995, 28(22): 7519-7524.

[8] Kunugi, S., Tada, T., Tanaka, N., Yamamoto, K. and Akashi, M. Microcalorimetric study of aqueous solution of a thermoresponsive polymer, poly(N-vinylisobutyramide) (PNVIBA). *Polym. J.* 2002, 34(5): 383-388.