A slip-link model with 3D network structure

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A slip-link model with 3D network structure

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In this study, a multi-body slip-link model in 3D space described by total free energy of system is proposed. Though a 3D slip-link simulation based on Brownian dynamics [1] has presented good agreements with rheological properties of various systems, thermodynamical expression has been incomplete. As a promising approach, Schiebers' description [2, 3] based on chain energy is modified for multi-body motion in 3D space.

A chain is composed of $Z$ strands and each strand has $N_i$ Kuhn steps with length of $b$. End-to-end vector of the strand is $Q_i$ which connects consecutive slip-links as $Q_i \equiv R_i - R_{i-1}$. The free energy of a chain is expressed as

$$F = \sum_{i=2}^{Z-1} F_S (Q_i, N_i) + F_E (N_1) + F_E (N_Z),$$

(1)

where $F_S$ and $F_E$ are free energies of an entangled strand [2]. Kuhn steps transfer through the slip-link by chemical potential differences and Brownian force obeying

$$N_i(t + \Delta t) \cong N_i(t) + \frac{\Delta t}{k_B T \tau_K} \{ \mu_{i-1}(t) - 2\mu_i(t) + \mu_{i+1}(t) \} + \sqrt{\frac{2}{\tau_K} (\Delta W_i - \Delta W_{i-1})}.$$  

(2)

where $\tau_K$ is relaxation time of a Kuhn step, $\mu_i \equiv (\partial F/\partial N_i)$ is chemical potential of strand $i$ and $\Delta W_i$ is Wiener increment with zero mean and variance $\Delta t$. Entanglements are created or destructed only chain end by reptation. In monitoring $N_i$ at end strand, when $N_i$ becomes less than given minimum, an entanglement is destructed. On the contrary, $N_i$ becomes more than

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given maximum, an entanglement with any surrounding strand within $a_0 = N_e b^2$ is created. $N_e$ is the average number of $N_i$. The number window of $N_i$ is given by

$$0.5N_e < N_i < 1.5N_e.$$  \hskip 1em (3)

Dynamical equation of $R_i$ is written as

$$R_i(t + \Delta t) \equiv R_i(t) + \kappa R_i(t) \Delta t - \frac{N_e b^2}{12k_B T \xi \tau_e} \left[ \left( \frac{\partial F^\alpha}{\partial R_i} \right) + \left( \frac{\partial F^\beta}{\partial R_i} \right) \right] \Delta t + \sqrt{\frac{N_e b^2}{6 \xi \tau_e}} \Delta W_i,$$  \hskip 1em (4)

where $\tau_e = N_e^2 \tau_K$, $\xi$ is time ratio of $\tau_e$ and constraint release time and $\alpha$ and $\beta$ indicate test chain and another chain sharing the entanglement locating at $R_i$.

It has been confirmed that distribution of $N$ (Fig. 1) is consistent with the theoretical prediction [4]. Tests for other quantities and chain dynamics shall be discussed elsewhere.

![Figure 1: The simulated distribution (open triangle: ensemble average, closed square: time average) of number of Kuhn steps in a strand compared with the theoretical prediction (line) [4]](image)

References


