Conformational changes of short, discrete Rouse chain during creep and recovery processes

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Abstract

For the Rouse chain composed of infinite number of beads (continuous limit), conformational changes during the creep and creep recovery processes was recently analyzed to reveal the interplay among all Rouse eigenmodes under the constant stress condition (Watanabe and Inoue, Rheol. Acta, 2004). For completeness of the analysis of the Rouse model, this paper analyzes the conformational changes of the discrete Rouse chain having a finite number of beads (N = 3 and 4). The analysis demonstrates that the chain of finite N exhibits the affine deformation on imposition/removal of the stress and this deformation gives the instantaneous component of the recoverable compliance, $J_R(t) = \frac{1}{N-1} k_B T$ with $\nu$ and $k_B$ being the number density and Boltzmann constant, respectively. (This component vanishes for $N \to \infty$.) For $N = 2$, it is known that the chain has only one internal eigenmode so that the affinely deformed conformation at the onset of the creep process does not change with time $t$ and $J_R(t)$ coincides with $J_R(0)$ at any $t$ (no transient increase of $J_R(t)$). However, for $N \geq 3$, the chain has $N-1$ eigenmodes ($N-1 \geq 2$), and this coincidence vanishes. For this case, the chain conformation changes with $t$ to the non-affine conformation under steady flow, and this change is governed by the interplay of the Rouse eigenmodes (under the constant stress condition). This conformational change gives the non-instantaneous increase of $J_R(t)$ with $t$, as also noted in the continuous limit ($N \to \infty$).

Keywords: discrete Rouse model, creep, creep recovery, eigenmodes, orientational anisotropy

1. Introduction

The Rouse model (bead-spring model without hydrodynamic interaction) is well established for non-entangled polymers and its viscoelastic behavior has been fully elucidated (Graessley, 1974; Ferry, 1980; Doi and Edwards, 1986; Pearson, 1987; Watanabe, 1999). However, the conformational change of the Rouse chain during the creep and recovery processes was not analyzed so far, and no analytical expression of the recoverable creep compliance $J_R(t)$ was reported (although results of numerical calculation of $J_R$ were available; Berry, 1987).

Recently, we made a molecular analysis for the Rouse model in the continuous limit where a chain was subdivided into an infinite number of beads connected with Gaussian springs (Watanabe and Inoue, 2004). The analysis revealed interplay of the Rouse eigenmodes during the creep and recovery processes under the controlled-stress condition. This interplay governs an evolution of the orientational anisotropy distribution along the chain backbone during these processes to determine the functional form of the recoverable compliance,

$$J_R(t) = \frac{1}{\nu k_B T} \sum_{p=1}^{4} \theta_p \left[ 1 - \exp \left( -\frac{t}{\lambda_p^\theta} \right) \right]$$

with $\lambda_p = \frac{\pi^2 \tau_1}{\theta_p^2}$ (in continuous limit) (1)

Here, $\nu$, $k_B$, $T$, $\tau_1$, and $\lambda_p$ are the chain number density, Boltzmann constant, absolute temperature, the longest viscoelastic relaxation time, and $p$-th retardation time, respectively: The numerical coefficient $\theta_p$ appearing in Eqn. (1) is determined by

$$\tan \theta_p = \theta_p \ (\pi < \theta_1 < \theta_2 < \theta_3 < \cdots)$$ (2)

$\theta_p$ approaches $(p+1)/2\pi$ for $p \to \infty$ and satisfies a summation rule, $\sum_{p=1}^{\infty} 1/\theta_p^2 = 1/10$.

The continuous Rouse model is applicable to a real chain in a time scale not very shorter than $\tau_1$ of this chain. However, this model has an infinite number of retardation modes and its $\lambda_p$ approaches zero with increasing mode index $p \to \infty$; see Eqns. (1) and (2). This feature is an arti-
fact of the continuous model using infinite number of the beads, and the fast dynamics of the real chain (having a finite number of modes with \( \lambda_\alpha > 0 \)) cannot be described by this model. A corresponding artifact is well known for the relaxation modulus \( G(t) \): The continuous model has an infinitely large instantaneous modulus \( G(0) \) while the real chain exhibits a finite value of \( G(0) \).

From this point of view, it is important to analyze the conformational changes of a discrete Rouse chain (having a finite number of retardation modes) during the creep/recovery processes. Specifically, it is of interest to examine how this chain having \( \lambda_\alpha > 0 \) abruptly changes its conformation on step-wise imposition/removal of the stress. However, to our knowledge, the conformation (orientational anisotropy) during these processes has not been analyzed for the discrete Rouse chain having a finite number (\( N \)) of the beads.

As the simplest but informative model cases, we have chosen discrete Rouse chains with \( N = 3 \) and 4 to analyze their orientational anisotropy and calculate \( J_\phi(t) \). The analysis revealed that the chain is affinely deformed on step-wise imposition/removal of the stress and this deformation determines the instantaneous component of the recoverable compliance, \( J_\phi(0) = 1/(N - 1)\nu k_B T \). (Thus, \( J_\phi(0) = 0 \) for \( N \to \infty \); see Eqn. (1).) Furthermore, the analysis indicated that the chain with \( N \geq 3 \) is deformed non-affinely in the steady flowing state and the time-dependent part of \( J_\phi(t) \) reflects a transient change from the initial, affine state to this non-affine steady state in the creep process. (For the chain with \( N = 2 \), the initial, affine deformation is preserved in the whole creep process and the time-dependent part of \( J_\phi(t) \) vanishes.) Details of these results are presented in this paper.

2. Theoretical framework (Ferry, 1980; Doi and Edwards, 1986; Watanabe, 1999)

2.1. Equation of motion

We consider a linear Rouse chain composed of \( N \) beads each having the friction coefficient \( \zeta \). The neighboring beads are connected by a Gaussian spring of the stiffness \( k_B T \alpha (n - 1) \nu \delta_{\alpha\beta} \delta(t - t') \), where \( \zeta \) and \( \alpha \) are the x- and y-component of the bond vector \( u_{\alpha}(n(t)) = r_{\alpha}(n(t)) \). The shear stress at the time \( t \), \( \sigma(t) \), is simply related to the total anisotropy,

\[
\sigma(t) = 3 \nu k_B T \sum_{n=1}^{N-1} S(n,t)
\]

(5)

(In general, Eqn. (5) is valid not only in the linear viscoelastic limit but also under large shear field.)

\( \sigma(t) \) is kept constant during the creep/recovery processes. Consequently, the flow velocity \( V(n,t) \) is determined by the Rouse chain itself in a way that the chain satisfies this constant stress condition and Eqn. (3) simultaneously. For the \( V(n,t) \) thus determined, we can solve Eqn. (3) to calculate \( u(n,t) \) and \( S(n,t) \). The calculation of \( u(n,t) \) can be conveniently achieved by using appropriate eigenvectors (normal coordinates), as explained below. The readers who are familiar with the Rouse analysis can skip the following section and directly proceed to section 4.1.

3. Results

3.1. Four-bead Rouse chain \( (N = 4) \)

For \( N = 4 \), the Rouse matrix is given by

\[
A = \begin{bmatrix}
-1 & 1 & 0 & 0 \\
1 & -2 & 1 & 0 \\
0 & 1 & -2 & 1 \\
0 & 0 & 1 & -1
\end{bmatrix}
\]

(6)

This \( A \) is associated with four (zero-th to third) Rouse eigenmodes, and the zero-th mode represents the diffusion of the center of mass of the chain. For the first to third internal eigenmodes \( (p = 1-3) \) related to the chain confor-
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A linear algebraic calculation gives the eigenvectors \( \xi \) (expressed as a linear combination of the bond vectors \( u(n,t) \)) and the eigenvalues \( \alpha \):

\[
p = 1: \quad \xi_1(t) = -u(1,t) - \sqrt{2}u(2,t)+u(3,t), \quad \alpha_1 = -(2-\sqrt{2}) \tag{7a}
\]

\[
p = 2: \quad \xi_2(t) = -u(1,t)+u(3,t), \quad \alpha_2 = -2 \tag{7b}
\]

\[
p = 3: \quad \xi_3(t) = -u(1,t)+\sqrt{2}u(2,t)-u(3,t), \quad \alpha_3 = -(2+\sqrt{2}) \tag{7c}
\]

(These \( \xi \) are not normalized.) The shear stress (Eqn. 5) is rewritten in terms of the \( x \)-and \( y \)-components of \( \xi \), \( X_p(t) \) and \( Y_p(t) \), as

\[
\sigma(t) = \frac{3v_kT}{4a^2} \left( X_p(t) Y_p(t) + 2X_p(t) Y_p(t) + (X_p(t) Y_p(t)) \right) \tag{8}
\]

Thus, the stress is completely determined by the shear components \( X_p(t) Y_p(t) \) of the orientational anisotropies of respective eigenmodes.

For \( X_p(t) \) and \( Y_p(t) \), Eqn. (3) is rewritten in a decoupled form

\[
dX_p(t) = -\frac{1}{2\tau_p} X_p(t)+\gamma Y_p(t)+\frac{1}{\zeta} f_{x,p}(t) \tag{9}
\]

\[
dY_p(t) = -\frac{1}{2\tau_p} Y_p(t)+\gamma X_p(t)+\frac{1}{\zeta} f_{y,p}(t) \tag{10}
\]

Here, \( \tau_p \) is the viscoelastic relaxation time for the first to third eigenmodes given by

\[
\tau_p = \frac{\zeta}{2k\alpha_p} = \frac{(2+\sqrt{2})\zeta}{4\kappa} \quad \text{(}p = 1\text{),} \quad \frac{(2-\sqrt{2})\zeta}{4\kappa} \quad \text{(}p = 2\text{),} \quad \frac{(2+\sqrt{2})\zeta}{4\kappa} \quad \text{(}p = 3\text{)} \tag{11}
\]

(The superscript \( \text{‘}4\text{’} \) specifies that \( \tau_p \) is the relaxation time of the four-bead Rouse chain.) \( f_{x,p} \) and \( f_{y,p} \), appearing in Eqns. (9) and (10), are the \( x \)- and \( y \)-components of linearly combined Brownian forces \( f_p(t) \),

\[
p = 1: \quad f_1(t) = F(1,t)+\sqrt{2}F(2,t)+\sqrt{2}F(3,t)+F(4,t) \tag{12a}
\]

\[
p = 2: \quad f_2(t) = F(1,t)-\sqrt{2}F(2,t)+F(3,t) \tag{12b}
\]

\[
p = 3: \quad f_3(t) = F(1,t)+\sqrt{2}F(2,t)+\sqrt{2}F(3,t)+F(4,t) \tag{12c}
\]

From Eqns. (4), (9), (10), and (12) together with appropriate initial conditions \( X_p(0) \) and \( Y_p(0) \), we calculated the orientation function \( S(n,t) \) and the recoverable compliance \( J_R(t) \). The results for the creep and creep recovery processes are summarized below.

3.1.1. Calculation for creep process

For the creep process, the initial values \( X_p(0) \) and \( Y_p(0) \) coincide with \( X_p^{eq} \) and \( Y_p^{eq} \) at equilibrium and are characterized by the second-moment averages,

\[
\langle \{X_p(t)\}^2 \rangle = \langle \{Y_p(t)\}^2 \rangle = \langle \{X_p(t)\} \rangle = \langle \{Y_p(t)\} \rangle = \frac{4a^2}{3} \tag{13a}
\]

\[
\langle \{X_2(t)\}^2 \rangle = \langle \{Y_2(t)\}^2 \rangle = \frac{2a^2}{3}, \quad \langle X_p(0) Y_p(0) \rangle = 0 \tag{13b}
\]

From Eqns. (4), (9), (10), and (12) together with this initial condition, we find

\[
\langle X_p(t) Y_p(t) \rangle = \langle \{Y_p(0)\} \rangle \delta_{p,p} \exp \left( \frac{t-\tau}{\tau_p} \right) \tag{14}
\]

Requiring the stress \( \sigma(t) \) to be always identical to \( \sigma_0 \) (applied stress) during the creep process, we find an integral equation determining the shear rate \( \gamma(t) \) (cf. Eqns. (8) and (14)):

\[
\sigma(t) = \frac{\sigma_0}{\tau_p} + \frac{\sigma_0}{3v_kT} \int_0^t d\tau' \gamma(t') \sum_{p=1}^3 \exp \left( \frac{t-\tau'}{\tau_p} \right) \tag{15}
\]

This equation can be solved with the Laplace transformation method (explained in Appendix A) to give

\[
\hat{\gamma}(t) = \frac{\sigma_0}{\tau_p} + \frac{\sigma_0}{3v_kT} \left[ \delta(t) + \frac{2(6+\sqrt{6})}{15\zeta} \exp \left( \frac{-t}{\lambda_1^{[4]}} \right) + \frac{2(6-\sqrt{6})}{15\zeta} \exp \left( \frac{-t}{\lambda_2^{[4]}} \right) \right] \tag{16}
\]

Here, \( \eta_0^{[4]} = 5v_kT \sum_{p=1}^3 \zeta_p \) is the zero-shear viscosity of the four-bead Rouse chain, and \( \lambda_1^{[4]} \) and \( \lambda_2^{[4]} \) are the first- and second retardation times given by

\[
\lambda_1^{[4]} = \frac{(6+\sqrt{6})\zeta}{20\kappa}, \quad \lambda_2^{[4]} = \frac{(6-\sqrt{6})\zeta}{20\kappa} \tag{17}
\]

The corresponding recoverable compliance \( J_R(t) = \gamma(t)/\sigma_0 - \eta_0^{[4]} \) is written as

\[
J_R(t) = \frac{1}{3v_kT} \left[ 1+\frac{2\sqrt{6}}{25} \exp \left( \frac{-t}{\lambda_1^{[4]}} \right) + \frac{7-2\sqrt{6}}{25} \exp \left( \frac{-t}{\lambda_2^{[4]}} \right) \right] \tag{18}
\]

The eigenmode anisotropies \( \langle X_p(t) Y_p(t) \rangle \) are calculated by substituting Eqn. (16) into Eqn. (14). These anisotropies, expressed in a form of the stress \( \sigma(t) \) sustained by the \( p \)-th eigenmode (cf. Eqn. (8)), are summarized as

\[
\sigma_1(t) = \frac{3v_kT}{4a^2} \langle X_p(0) Y_p(t) \rangle = \frac{2+\sqrt{2}}{5} \frac{(\sqrt{6}+1)(\sqrt{6}+3)}{30} \exp \left( \frac{-t}{\lambda_1^{[4]}} \right) \tag{19}
\]
Of course, a sum $\sigma_2(t) + \sigma_2(t) + \sigma_2(t)$ coincides with $\sigma_2$ at any $t$. The orientation function $S(n,t) = a^2\langle u_i(t)u_i(t)\rangle$ of the $n$-th bond vector is calculated from the eigenmode anisotropies $\langle X_i(t)Y_j(t)\rangle$ thus determined. The results are:

\[
S(1,t) = S(3,t)
\]
\[
= \frac{1}{16a^2}[(X_1(t)Y_1(t))^2 + (X_1(t)Y_2(t))^2 + (X_1(t)Y_3(t))^2]
\]
\[
S(2,t) = \frac{1}{8a^2}[(X_2(t)Y_1(t))^2 + (X_2(t)Y_2(t))^2 + (X_2(t)Y_3(t))^2]
\]
\[
= \frac{1}{45}(X_n(t)Y_1(t))^2 + (X_n(t)Y_2(t))^2 + (X_n(t)Y_3(t))^2)
\]

An effective shear strain for the $n$-th bond vector is given by $3S(n,t)$, as explained in Appendix B. This effective strain becomes a key in our later discussion of the chain conformation during the creep and recovery processes.

For the end-to-end vector $R(t) = \sum u(n,t)$, the orientation function is defined as $S_R(t) = \langle R(t)R(t)\rangle/\langle R(t)\rangle^2$ with $\langle R(t)\rangle^2 = (2a^2)$ being the mean-square end-to-end distance at equilibrium. As clear from this definition, $S_R(t)$ is contributed from the orientation of respective bond vectors $S(n,t) = a^2\langle u_i(t)u_i(t)\rangle$ and the cross-correlation function $S(n,n',t) = a^2\langle u_i(t)u_j(t)\rangle_{n,n'\neq t}$.

\[
S_R(t) = \sum S(n,t) + \sum S(n,n',t)
\]

Note that the bond vectors always have a statistical distribution in their orientation and $S(n,n',t)$ represents a tendency of $n$-th and $n'$-th bond vectors to be oriented in the same direction. $S(n,n',t)$ has a non-zero value when the distribution functions for the $n$-th and $n'$-th bond vectors are not independent with each other.

$S(n,t)$ appearing in Eqn. (21) is given by Eqns. (20a) and (20b), and $S(n,n',t)$ is calculated from the eigenmode anisotropies as

\[
S(1,2,t) = S(2,3,t) = \frac{1}{16a^2}[(X_1(t)Y_1(t))^2 + (X_1(t)Y_2(t))^2]
\]
\[
= \frac{1}{60a^2}[(X_1(t)Y_1(t))^2 + (X_1(t)Y_2(t))^2]
\]

From Eqns. (20)-(22), we obtain an explicit expression of $S_R(t)$:

\[
S_R(t) = \frac{1}{18a^2}[(X_1(t)Y_1(t))^2 + (X_1(t)Y_2(t))^2]
\]

It should be emphasized that the chain conformation is characterized not only with $S(n,t)$ but also with $S_R(n,r,t)$ and $S_R(t)$.

### 3.1.2 Calculation for creep recovery process

The eigenmode anisotropies in the creep process at $t \rightarrow \infty$ are given by (cf. Eqn. (19))

\[
\langle X_1(t)Y_1(t)\rangle_{\infty} = \frac{1}{15a^2}\langle Y_1(t)\rangle, \langle X_2(t)Y_2(t)\rangle_{\infty} = \frac{1}{15a^2}\langle Y_2(t)\rangle.
\]

\[
\langle X_3(t)Y_3(t)\rangle_{\infty} = \frac{1}{15a^2}\langle Y_3(t)\rangle.
\]

These $\langle X_i(t)Y_j(t)\rangle_{\infty}$ serve as the initial condition for the creep recovery from the steady flowing state.

From Eqns. (4), (9), (10), and (12) and this initial condition, we calculated the eigenmode anisotropies for the creep recovery process with a method similar to that utilized for the creep process. The stress $\sigma_{c}(t)$ sustained by the $p$-th eigenmode, the orientation functions $S(n,t)$ and $S_R(t)$, and the cross-correlation function $S(n,n',t)$ obtained from those anisotropies are summarized as

\[
[S(t)]_{\text{recovery}} = [S(t)]_{\text{creep}} - [S(t)]_{\text{creep}}
\]

\[
[S(n,t)]_{\text{recovery}} = [S(n,t)]_{\text{creep}} - [S(n,t)]_{\text{creep}}
\]

\[
[S(n,t)]_{\text{recovery}} = [S(n,t)]_{\text{creep}} - [S(n,t)]_{\text{creep}}
\]

\[
[S(n,n',t)]_{\text{recovery}} = [S(n,n',t)]_{\text{creep}} - [S(n,n',t)]_{\text{creep}}
\]

Here, the subscript 'creep' stands for the properties for the creep process specified by Eqns. (19), (20), (22), and (23).

The shear rate, that matches the eigenmode anisotropies to ensure the zero-stress condition during the creep recovery, is given by...
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\[ \langle J(t) \rangle_{\text{recovery}} = \frac{\sigma_0}{3v_k T} \left[ \delta(t) + \frac{2(6+\zeta)K}{15\zeta} \exp \left( -\frac{t}{3\zeta} \right) + \frac{2(6-\zeta)K}{15\zeta} \exp \left( -\frac{t}{3\zeta} \right) \right] \] (29)

3.2. Three-bead and Two-bead Rouse chains (N=3 and 2)

3.2.1. N=3

For the three-bead Rouse chain, we introduced eigen-vectors to solve the equation of motion (Eqn. (3)) and calculate the eigenmode anisotropies with a method similar to that explained for the four-bead chain. The calculation is much easier for the three-bead chain having only two internal eigenmodes related to the chain conformation.

For the creep process, the eigenmode anisotropies thus obtained were utilized to calculate the stress \( \sigma_p(t) \) sustained by the \( p \)-th eigenmode \((p = 1, 2)\), the orientation functions \( S(n,t) \) \((n = 1, 2)\) and \( S_0(t) \), and the cross-correlation function \( \tilde{S}_n(n,n',t) \):

\[ \sigma_p(t) = \frac{\sigma_0}{6v_k T} \left[ \frac{3}{4} \exp \left( -\frac{t}{\lambda_1^{[4]}} \right) \right] \quad \sigma_c(t) = \frac{\sigma_0}{6v_k T} \left[ \frac{3}{4} \exp \left( -\frac{t}{\lambda_1^{[4]}} \right) \right] \] (30)

\[ S(1,t) = S(2,t) = \frac{\sigma_0}{12v_k T} \left[ 3 \exp \left( -\frac{t}{\lambda_1^{[3]}} \right) \right] \] (31)

\[ S_{n}(1,2,t) = \tilde{S}_{1,2}(2,1,t) = \frac{\sigma_0}{12v_k T} \left[ 1 \exp \left( -\frac{t}{\lambda_1^{[4]}} \right) \right] \] (32)

The corresponding recoverable compliance is given by

\[ J_d(t) = \frac{1}{2v_k T} \left[ \frac{3}{4} \exp \left( -\frac{t}{\lambda_1^{[4]}} \right) \right] \] (33)

The three-bead Rouse chain has single retardation mode, and \( \lambda_1^{[3]} \) appearing in Eqns. (30)-(33) is the retardation time of this mode,

\[ \lambda_1^{[3]} = \frac{\zeta}{4\kappa} = \frac{\tau_1^{[3]}}{2} \] (34)

(This chain has two relaxation modes, and \( \tau_1^{[3]} \) appearing in Eqn. (34) is the longest relaxation time.)

Eqns. (25)-(28) hold also for the creep recovery of the three-bead Rouse chain. Thus, \( \sigma_p(t) \), \( S(n,t) \), \( S_0(t) \), and \( \tilde{S}_n(n,n',t) \) for the recovery process is obtained from those for the creep process (Eqns. (30)-(32)).

3.2.2. N=2

The two-bead Rouse chain exhibits the single Maxwell relaxation with the relaxation time \( \tau_1^{[3]} = \zeta/4\kappa \) and the instantaneous modulus \( G(0)=v_k T \). This chain is known to have only instantaneous component of the recoverable compliance:

\[ J_d(t) = \frac{1}{v_k T} \] (t-independent) (35)

The stress during the creep/recovery process is sustained by the single bond vector, and the end-to-end vector (\( \tau_0 \)-bond vector) has the \( t \)-independent orientation function,

\[ S_0(t) = \frac{\sigma_0}{3v_k T} = \frac{\sigma_0}{3G(0)} \] (for creep), 0 (for recovery) (36)

4. Discussion

4.1. Crossover from affine to non-affine conformation during creep/recovery process

4.1.1. N=4

For the four-bead Rouse chain, Fig. 1a shows plots of the

![Fig. 1. Creep behavior of four-bead Rouse chain. Fractional stress sustained by \( p \)-th eigenmode \( \tilde{S}_p(t) \) (part a), normalized orientation function of the bond vectors \( \tilde{S}_{n}(n,t) \) (part b), and normalized orientation function of the end-to-end vector \( \tilde{S}_E(t) \) (part c) are plotted against the normalized time \( \nu \tau_1^{[4]} \) (\( \tau_1^{[4]} \)-longest relaxation time of the four-bead chain).](image)
fractional stress sustained by the $p$-th eigenmode during the creep process, $\sigma_i(t) = \sigma_j(t)/\sigma_0$ (cf. Eqn. (19)), against the normalized time $t/\tau^{(\infty)}$, with $\tau^{(\infty)}$ being the longest relaxation time; Eqn. (11)). Figs. 1b and 1c show plots of the normalized orientation functions corresponding to the fractional stress, $S(t) = S(t)/\sigma_0$ and $\tilde{S}(t) = \tilde{S}(t)/\sigma_0$ (cf. Eqns. (20) and (23)) where $\gamma_n = \sigma_n / 3v_kT$ is the instantaneous strain of the four-bead Rouse chain (having the instantaneous modulus $G(0) = 3v_kT$) induced by the stress $\sigma_0$.

At the onset of creep ($t = 0$), $\tilde{S}(n,0) = 1/3$ is independent of $n$; see Fig. 1a. Furthermore, different bond vectors exhibit no cross-correlation at $t = 0$ (cf. Appendix B). Thus, the isotropic chain conformation at equilibrium ($t < 0$) is affinely deformed at $t = 0$ by the magnitude $\gamma_0 = 3\sigma_0/S(n,0) = \sigma_0/G(0)$. (Note that $3\sigma_0/S(n,0) = 3\gamma_0\tilde{S}(n,t)$ represents an effective strain for the $n$-th bond vector; cf. Appendix B.)

The end-to-end vector $R$ is also deformed by the magnitude $\gamma_0$ at $t = 0$, as confirmed a simple calculation: This deformation gives $R(0) = E(0)\gamma_0 R(n)$, where $R(n)$ is the end-to-end vector at equilibrium ($t < 0$) and $E(0)$ is the shear displacement tensor for the strain $\gamma_0$ (cf. Eqn. (B1) in Appendix B). For this $R(0)$, we find $\tilde{S}_R(0) = <\{E(0)\gamma_0 R(n)\},\{E(0)\gamma_0 R(n)\}>/3\alpha^n = (3\alpha^n)^{-1/3}$, which is in agreement with the $\tilde{S}_R(0)$ value given by Eqn. (23) and shown in Fig. 1c.

As seen in Fig. 1a, the stress is equally sustained by the three eigenmodes ($\sigma_i(t) = 1/3$) at the onset of creep where the equilibrium chain conformation is affinely deformed. For $t > 0$, the fractional stress for the lowest eigenmode $\sigma_i(t)$ increases with $t$ and those for the higher eigenmodes $\sigma_j(t)$ and $\sigma_k(t)$ decrease with $t$. Correspondingly, $\tilde{S}(1,t)$ increases while $\tilde{S}(2,t)$ and $\tilde{S}(3,t)$ decrease with $t$; see Fig. 1b. These changes of $\tilde{S}(n,t)$ indicate that the orientation at $t > 0$ is larger for the chain center than for the chain end and the chain conformation exhibits a crossover from the initial affine state to the steady non-affine state during the creep process. Specifically, the orientation of respective bond vectors ($n = 1$-3) in the steadily flowing state is quantified by an effective shear strain $\gamma_n(n) = S(n,\infty)$ (cf. Eqn. (20)),

$$
\gamma_n(1) = \gamma_n(3) = \frac{3\sigma_0}{10v_kT} = \frac{9}{10L}, \quad \gamma_n(2) = \frac{2\sigma_0}{5v_kT} = \frac{6}{5L}
$$

with $\sigma_0 = \sigma_0/G(0) = \sigma_0/3v_kT$.

The above crossover is associated with a growth of the cross-correlation of different bond vectors characterized by $S_n(n,t) > 0$ at $t > 0$; see Fig. (22)). Because of this cross-correlation, the orientation at $t > 0$ is larger for the end-to-end vector than for respective bond vectors ($\tilde{S}_n(t) > \tilde{S}(n,t)$); cf. Figs. 1b and 1c.

The crossover from the affine to non-affine state results from the interplay among the eigenmodes under the constant stress condition. Namely, the growth of the anisotropy of the lowest eigenmode ($\sim \sigma_1$) to its steady state value is achieved only at $t > \lambda_1^{(\infty)}$ (cf. Eqn. (19a)), and the higher eigenmodes compensate this retarded growth by first increasing their anisotropies ($\sim \sigma_2$, $\sigma_3$) above the steady state values and then exhibiting the decay to these values; see Fig. 1a. Similar interplay has been noted for the continuous Rouse chain with $N \rightarrow \infty$ (Watanabe and Inoue, 2004).

Now, we turn our attention to the conformational changes during the creep recovery from the steadily flowing state. For this recovery process, Figs. 2a-2c show plots of the fractional stress for the eigenmodes $\sigma_i(t)$ and the normalized orientation functions $S(n,t)$ and $\tilde{S}_n(t)$ against the
At the onset of recovery \( (t = 0) \), the chain has \( \hat{S}(1,0) = \hat{S}(3,0) = -1/30 \) and \( \hat{S}(2,0) = 1/15 \) (Fig. 2b). The effective strains of respective bond vectors obtained from these \( \hat{S}(n,0) \) values, \( \gamma_n = 3 \gamma_n \hat{S}(n,0) = -\gamma_n/10 \) (for \( n = 1, 3 \)) and \( \gamma_n/\hat{S} \) (for \( n = 2 \)), are smaller than the effective strain \( \gamma_n \) under steady flow (Eqn. (37)) and the decrease, \( \gamma_n - \gamma_n = -\gamma_n \), is the same for all bond vectors. This result indicates that the non-uniformly oriented chain conformation under steady flow is affinely deformed on removal of the stress at \( t = 0 \) by the magnitude \( -\gamma_n = -\sigma_n/G(0) \) (cf. Appendix B). The \( \hat{S}_e(0) \) value \( (=1/3) \) (Fig. 2b) indicates that the end-to-end vector having the orientation \( \hat{S}_e = 2/3 \) under steady flow (Fig. 1c) is also deformed by the magnitude \( -\gamma_n \) on removal of the stress.

The affine deformation of the non-uniformly oriented chain under steady flow leads to an instantaneous adjustment of the stresses sustained by respective eigenmodes thereby ensuring the zero-stress condition at \( t = 0 \) (\( \sum \sigma_n(0) / \gamma_n = 0 \); see Fig. 2a). In this state, the central bond vector is still oriented in the positive direction (flow direction during the creep) to have \( \hat{S}(2,0) > 0 \), while the end bond vectors are negatively oriented to compensate the positive orientation at the center \( \hat{S}(1,0) = \hat{S}(3,0) = -\hat{S}(2,0)/2 \); see Fig. 2b). The orientations of these bond vectors and end-to-end vector decay with \( \tau \) (Figs. 2b and 2c), and the stresses sustained by respective eigenmodes decay accordingly (Fig. 2a). During this decay process, the eigenmodes exhibit the interplay to tune the decay rates of their \( \sigma_n(t) \) and \( S(n,t) \) thereby satisfying the zero-stress condition. Similar interplay has been noted also for the continuous Rouse chain with \( N \rightarrow \infty \) (Watanabe and Inoue, 2004).

### 4.1.2. \( N=3 \) and 2

For the three-bead Rouse chain having the instantaneous modulus \( G(0) = 2 \lambda_0 T \), changes of \( \sigma_n(t)/\gamma_n \) (cf. Fig. 2a, \( S(1,0)/\gamma_1 \) with \( \gamma_1 = \sigma_1/G(0) \)), and \( \hat{S}_e(0) = \hat{S}_e(0)/\gamma_e \) during the creep and recovery processes are shown in Figs. 3 and 4, respectively. The \( \sigma_n(t) \), \( S(n,t) \), \( \hat{S}_e(t) \), specified by Eqns. (30) and (31) together with Eqns. (25)-(27), are plotted against the normalized time \( t/\tau _{1}^{[3]} \) (\( \tau _{1}^{[3]} \)=longest relaxation time of the three-bead chain).

Fig. 3. Creep behavior of three-bead Rouse chain. Fractional stress sustained by \( p \)-th eigenmode \( \sigma_n(t) \) (part a) and normalized orientation functions of the bond vectors and end-to-end vectors \( \hat{S}(n,t) \) and \( \hat{S}_e(t) \) (part b) are plotted against the normalized time \( t/\tau _{1}^{[3]} \) (\( \tau _{1}^{[3]} \)=longest relaxation time of the three-bead chain).

Concerning this change, we note that the orientation functions of the bond vectors \( \hat{S}(n,t) \) are independent of \( t \); see Fig. 3b. This result is a natural consequence of an equivalence of the two (all) bond vectors of the three-bead chain: These bond vectors have the same \( \hat{S}(n,t) \) at any \( t \) because of this equivalence, so that the initial orientation \( \hat{S}(n,0)=1/3 \) being in balance with the applied stress is preserved throughout the creep process. (For the four-bead chain, the center and end bond vectors are not equivalent and thus \( \hat{S}(n,t) \) exhibits the \( t \)-dependent changes; cf. Fig. 1b.)

Here, it should be emphasized that the \( t \)-independence of \( \hat{S}(n,t) \) of the three-bead chain does not mean an instantaneous achievement of the steady flow: The positive cross-correlation of the two bond vectors grows with \( t \) (see Eqn. (32)), meaning that a tendency of these vectors to be oriented in the same direction is enhanced with \( t \). This growth results in the increase of \( \hat{S}_e(t) \) of the end-to-end vector seen in Fig. 3b. The steady flow (under which the cross-correlation is fully developed) is achieved only at \( t > \lambda_1^{[3]} \). The corresponding steady conformation does not coincide with that obtained by affinely deforming the isotropic equi-
growth of the cross-correlation and changes of (t) affine deformation, as explained in Appendix B. The equilibrium conformation: No cross-correlation emerges on this.

Creep recovery behavior of three-bead Rouse chain. Frac-

tively. This decay is governed by the interplay of the eigen-

eqns. (32) and (28)) and (remaining after this affine deformation, decays with t (cf. Eqn. (98)). In the successive recovery process, the orientation of the two bond vectors exhibits no further change (S(0)=0 at t > 0) because of their equivalence explained above. However, their cross-correlation, remaining after this affine deformation, decays with t (cf. Eqns. (32) and (28)) and (t) and S R (t) decay accordingly. This decay is governed by the interplay of the eigen-

degs, as similar to the situation for the four-bead chain.

On removal of the stress, the three-bead chain exhibits

fication under steady flow to have S(0)=0 and S R (0)=1/6. In the successive recovery process, the orientation of the two bond vectors exhibits no further change (S(0)=0 at t > 0) because of their equivalence explained above. However, their cross-correlation, remaining after this affine deformation, decays with t (cf. Eqns. (32) and (28)) and (t) and S R (t) decay accordingly. This decay is governed by the interplay of the eigen-

degs, as similar to the situation for the four-bead chain.

The creep/recovery features of the three-bead and four-

bead chains demonstrate the importance of the interplay of the Rouse eigenmodes for the bead number N ≥ 3. However, the situation is different for N = 2.

No interplay among different eigenmodes exists for the
two-bead chain having only one internal eigenmode. For this reason, the chain exhibits the constant orientation S R (0)=σ/T G(0) throughout the creep process and this orien-
tation vanishes instantaneously on removal of the stress; see Eqn. (36). This result in turn demonstrates the impor-
tance of the interplay of the eigenmodes in the transient

4.2. Additional comments

The fundamental feature of the discrete Rouse chain with N = 3 and 4, the transient conformational changes during the creep/recovery processes governed by the interplay
among the eigenmodes, remains the same for the chains with larger N. Indeed, these changes have been confirmed for the continuous Rouse chain with N → ∞ (Watanabe and Inoue, 2004).

It should be also noted that each retardation mode of J R (t) (for N ≥ 3; Eqns. (1), (18), and (33)) is contributed from all Rouse eigenmodes (that are defined as the coor-
dinates obeying the decoupled equation of motion; cf. Eqn. (9) and (10)). This fact indicates that the functional form of the non-instantaneous part of J R (t) is determined by the interplay of the eigenmodes under the constant stress condition.

Finally, we focus on the instantaneous component of the recoverable compliance, J R (0)=1/G(0) with G(0) being the instantaneous modulus given by ν(T−1)κ T; cf. Eqns. (18), (33), and (35). This component, corresponding to the delta function terms appearing in Eqns. (16) and (29), reflects the affine deformation of the chain on imposition/removal of the stress. In relation to this point, we note that the continuous Rouse chain has an infinitely large G(0) and thus exhibits the affine deformation of infinitely small magnitude. This leads to J R (0)=0 for this chain (cf. Eqn. (1)).

5. Concluding remarks

For completeness of the analysis of the Rouse model, we have examined the conformational changes of the discrete Rouse chains (N=3 and 4) during the creep/recovery pro-
cess. These chains exhibit the affine deformation of the magnitude (G(0)=(N−1)κ T) on imposition/removal of the stress σ, and this deformation gives the instantaneous component of the recoverable compliance, J R (0)=1/G(0). Transient conformational changes occur after this affine deformation, and these changes are gov-

ermed by the interplay among the Rouse eigenmodes under the constant stress condition. The non-instantaneous (t-
dependent) part of J R (t) of the chains with N ≥ 3 reflects these conformational changes and is determined by the interplay among the eigenmodes.
Appendix A. Solution of Eqn. (15)

For the Laplace transformation of the shear rate, \( \Gamma'(s) = \int_0^\infty dt \gamma(t) \exp(-st) \), Eqn. (15) is rewritten as

\[
\frac{\sigma_0}{s} = v_k \beta \Gamma'(s) \sum_{\rho=1}^3 \frac{1}{s + 1/s_\rho^4}
\]

with \( \tau_p^{[4]} \) being given by Eqn. (11). After rearrangement of Eqn. (A1), we find

\[
\Gamma'(s) = \frac{\sigma_0}{3v_k T} \left[ 1 + \frac{12k}{5s} \right] \frac{2(6 + \sqrt{6})\zeta}{15s(1/\lambda_1^{[4]})} + \frac{2(6 - \sqrt{6})\zeta}{15s(1/\lambda_2^{[4]})}
\]

(A2)

Here, \( \lambda_1^{[4]} \) and \( \lambda_2^{[4]} \) are the first- and second retardation times given by

\[
\lambda_1^{[4]} = \frac{(6 + \sqrt{6})\zeta}{20k}, \quad \lambda_2^{[4]} = \frac{(6 - \sqrt{6})\zeta}{20k}
\]

(A3)

The Laplace inversion of Eqn. (A2) gives

\[
\gamma(t) = \frac{\sigma_0}{\eta_0^{[4]} + \frac{\sigma_0}{3v_k T}} \left[ \delta(t) + \frac{2(6 + \sqrt{6})\zeta}{15s} \exp \left( \frac{-t}{\lambda_1^{[4]}} \right) + \frac{2(6 - \sqrt{6})\zeta}{15s} \exp \left( \frac{-t}{\lambda_2^{[4]}} \right) \right]
\]

(A4)

Here, \( \eta_0^{[4]} = \frac{v_k T \sum_{\rho=1}^3 \tau_p^{[4]} - 5v_k T \zeta^2/4k} {3} \) is the zero-shear viscosity of the four-bead Rouse chain.

Appendix B. Effective strain for bond vector

For the Rouse chain during the creep and recovery processes in the linear viscoelastic limit, no correlation exists between \( z \)-component and \( x \) - and \( y \)-components of its bond vector \( u(n,t) \) at any time \( t \). For this case, the bond vector can be expressed as

\[
u(n,t) = E(\gamma(n)) u^\circ(n) \quad \text{with} \quad E(\gamma(n)) = \begin{bmatrix} 1 & \gamma(n) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}
\]

(B1)

Here, \( u^\circ(n) \) is a reference vector that is isotropically oriented and has the mean-square size \( \langle u^\circ(n) \rangle = a^2 \).

\( E(\gamma(n)) \) is a shear displacement tensor corresponding to an effective shear strain \( \gamma(n) \) defined for \( u(n,t) \). From Eqn. (B1), we find

\[
\langle u(n,t) u(n,t) \rangle = \langle [E(\gamma(n)) u^\circ(n)] \rangle, [E(\gamma(n)) u^\circ(n)] \rangle = \gamma(n) \langle u^\circ(n) \rangle^2 = a^2 \gamma(n)/3
\]

(B2)

Namely, the orientation function \( S(n,t) = a^2 \langle u(n,t) u(n,t) \rangle \) coincides with \( \gamma(n)/3 \).

If no cross-correlation exists between different bond vectors at a given time \( t \) (\( \langle u(n,t) u(n',t) \rangle = 0 \) for \( n \neq n' \)) and the effective strain is independent of \( n \) (\( \gamma(n) = \gamma \)), the reference vector \( u^\circ(n) \) coincides with the \( n \)-th bond vector \( u^\circ(n) \) at equilibrium. For this case, the chain conformation at the time \( t \) coincides with that obtained by affinely deforming the equilibrium conformation to a magnitude \( \gamma \). In presence of the cross-correlation (\( \langle u(n,t) u(n',t) \rangle \neq 0 \) for \( n \neq n' \)), this coincidence vanishes even if \( \gamma(n) = 3S(n,t) \) is independent of \( n \).

If \( \gamma(n) \) is dependent on \( n \), the chain is non-uniformly oriented along its backbone. After an affine deformation of this non-uniform conformation to a magnitude \( \gamma' \), the effective strain for the bond vector becomes \( \gamma(n) + \gamma' \). Namely, the affine deformation gives the same increment of the effective strain to all bond vectors irrespective of the orientation distribution along the chain backbone just before this deformation.

References


