

Kinetics of polymer tumbling in shear flow: A coarse-grained descriptionSadhana Singh,^{1,*} R. K. Singh,^{2,†} Dibyendu Das,^{2,‡} and Sanjay Kumar^{1,§}¹*Department of Physics, Banaras Hindu University, Varanasi, Uttar Pradesh 221005, India*²*Department of Physics, Indian Institute of Technology, Bombay, Powai, Mumbai 400076, India*

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We study the classic problem of dynamical evolution of a polymer in a shear flow. Interestingly, the polymer goes through several distinctly identifiable conformations during its passage from coiled to stretched states back and forth. We identify these conformations assumed by the polymer while tumbling and study the kinetics of the process in terms of the residence and recurrence times of individual conformations. The distribution of residence times exhibits exponentially decaying tails which helps us build an effective Markovian picture of the truly non-Markovian problem. We present the explicit \mathbb{W} matrix for the coarse-grained evolution via a master equation and study its elements as a function of the Weissenberg number. We show that the timescales of decay of the autocorrelation function for the full Langevin dynamics compare quite well with the approximate results from the master equation approach.

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Introduction. Conformational changes in polymers in shear flows is a classic problem in polymer physics and has been studied extensively [1,2] with applications ranging from materials science to mechanical engineering, biology, and medicine [3–7]. Large fluctuations in chain extensions in such flows show that the polymers continually tumble from one end to the other, characteristic of the underlying dynamics of polymer in shear flow [8]. The typical time of tumbling varies sublinearly with the flow rate [9–17].

Under a shear flow a tumbling polymer [18] exhibits a nonequilibrium steady state [19,20] in which the probability of the two major states (stretched and coiled) as well as intermediate conformations [21] becomes time invariant. A complete description however has to go beyond and look at both residence times of intermediate states and transition rates among them. For example, Venkataramani and co-workers [21] discuss the various conformations taken by a polymer tumbling in shear flow at a coarse-grained level. However, their description is limited to classify different conformations and their relative occurrences. We take the study further by classifying the all major intermediate conformations and providing transition rates at which the polymer jumps from one conformation to another.

In this Rapid Communication, we approach the classic problem of a polymer tumbling in a shear flow in terms of the residence and recurrence time statistics of individual conformations. Using the results of our detailed microscopic simulations, we develop an effective theoretical “Markovian picture” for a truly non-Markovian problem [22,23]. We find that at this coarse-grained level, the Markovian approximation captures the underlying dynamics to a very good extent.

Langevin dynamics simulation. The polymer consists of N beads with interbead interaction given by the repulsive part of the Lennard-Jones (LJ) potential $V_{LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. The bonded beads experience finite extensible non-linear potential (FENE) $V_{FENE} = -(kR_0^2/2)\ln[1 - (r/R_0)^2]$. The symbols denote: r , separation between monomers; ϵ , strength of interaction; σ , diameter of monomer; R_0 , maximum extension of the bond; and k , the stiffness constant. The i th bead (of unit mass) in shear flow follows the Langevin equation [24–27]:

$$\ddot{\mathbf{r}}_i(t) = \mathbf{F}_i^c(t) - \Gamma[\dot{\mathbf{r}}_i(t) - \dot{\gamma}y_i\hat{\mathbf{i}}] + \dot{\gamma}y_i\hat{\mathbf{i}} + \mathbf{R}_i(t), \quad (1)$$

where $\mathbf{F}_i^c(t) = -\vec{\nabla}(V_{LJ} + V_{FENE})$ and the second and third terms are the contribution from the flow. The shear rate $\dot{\gamma}$ defines the flow profile $V_x(y) = \dot{\gamma}y$ and the Weissenberg number (Wi) $Wi = \dot{\gamma}\tau_0$, whereas τ_0 is the relaxation time of the autocorrelation of end-to-end distance at zero shear rate. The last term in Eq. (1) is Gaussian white noise with correlations [28]: $\langle \mathbf{R}_i(t)\mathbf{R}_j^T(t') \rangle = 2k_B T \Gamma \delta_{ij} \delta(t - t') \mathbf{I}_3$. We solve Eq. (1) using a fifth-order predictor corrector method [29] with a time step of $\Delta t = 0.006$ for a system of $N = 50$ monomers. We measure energy in units of ϵ and distance in units of σ . In addition, we choose $\epsilon = 1$, $\sigma = 1$, $R_0 = 1.5\sigma$, $k = 30\epsilon/\sigma^2$ [30], $k_B T = 1.2\epsilon$, and $\Gamma = 7.5$ in our simulations [27].

Classification of conformations. In order to develop a coarse-grained description of the polymer kinetics, we group different microscopic conformations along the lines of Refs. [1,19–21]. Sample conformations belonging to nine groups of “coarse-grained states” are depicted in Fig. 1(a). Let us define the x -directional extension $X = [\max\{x_1, \dots, x_N\} - \min\{x_1, \dots, x_N\}]$ of the chain in units of equilibrium bond length a and the contour length C_L of the polymer chain. The extension X varies as a function of time (see the Supplemental Material [31]).

We define c states to have small fractional extension $X/C_L (<0.3)$ and s states to have large $X/C_L (>0.6)$. As

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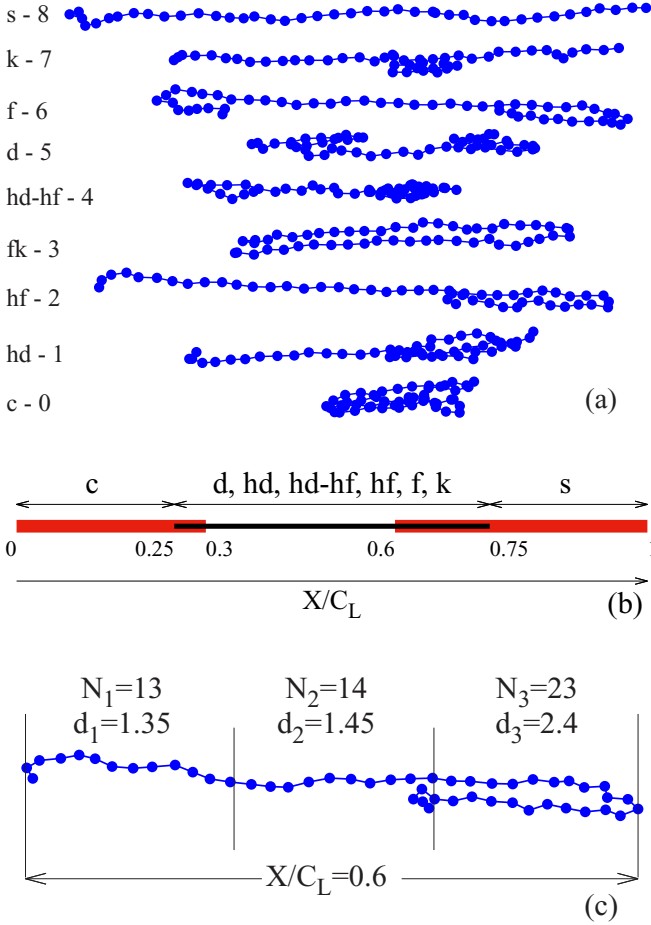


FIG. 1. (a) Sample conformations in coarse-grained states i during tumbling: coiled (c), half-dumbbell (hd), half-folded (hf), forked (fk), half-dumbbell-half-folded (hd-hf), dumbbell (d), folded (f), kink (k), and stretched (s). The corresponding values of $n_i \in \{0, \dots, 8\}$ are shown alongside (see the text). (b) The range of values of X/C_L of the nine states are shown. (c) A hf conformation is shown as an example with its X/C_L , d_1 , d_2 , and d_3 and N_1 , N_2 , and N_3 values.

shown in Fig. 1(b), other states (d, hd, hd-hf, hf, f, and k) have intermediate values of X/C_L in the range of (0.25, 0.75). As there are some overlapping regions, it is evident that finer criteria and more detailed quantities need to be considered, beyond merely X , to define these states precisely. For this purpose we imagine every conformation to have three equal segments of length $X_s = X/3$. We further consider three segment densities $d_1 = N_1/X_s$, $d_2 = N_2/X_s$, and $d_3 = N_3/X_s$, where N_1 , N_2 , and N_3 , respectively, are the number of monomers in each segment. We show a hf conformation in Fig. 1(c) which has a larger d_3 than d_1 and d_2 [as expected from Fig. 1(a)]. Similarly, a dumbbell should have larger d_1 and d_3 than d_2 [from Fig. 1(a)]. The precise ranges of (d_1 , d_2 , and d_3) used to distinguish the six groups of conformations are shown in Table I. Finally, the U-shaped forked conformations [see Fig. 1(a)] are classified by checking that the x -extensions X_1 and X_2 of the two halves of the chain are each $>0.35C_L$.

Conformations occurring during a transition over a small but finite time-interval Δt between two coarse-grained states are often ambiguous. We assign the ones over the interval

TABLE I. Classification of the six intermediate conformations according to the segment densities d_1 , d_2 , and d_3 of the three constituent parts of the polymer.

	d	f	hd-hf	hd	hf	k
d_1	≥ 3	(1.8, 3)	(1.8, 3)	≤ 1.8	≤ 1.8	< 2
d_2	≤ 1.8	< 2	< 2	≤ 3	< 2.5	≥ 3
d_3	≥ 3	(1.8, 3)	≤ 3	≥ 3	(1.8, 3)	< 2

$[0, \Delta t/2]$ to the initial state and the ones over times $\in (\Delta t/2, \Delta t]$ to the final state.

Results. To quantify the effect of the shear flow, we show in Fig. 2 the likelihood of individual coarse-grained states i at different Wi 's. The label i represents different coarse-grained states of the polymer tumbling in shear flow, viz. c, hd, hf, fk, hd-hf, d, f, k, and s, defined in the above section. Some conformations which have coil formation in all or some part of the chain viz. coil, half-dumbbell, dumbbell, etc., become unlikely conformations with increasing Wi . On the other hand, some other conformations, such as half-folded, folded, fork, stretch, etc., become more likely with increasing flow rate Wi . This is because at higher Wi 's the drag force to stretch the chain is dominant over the entropic force responsible to coil the chain. Hence, the tendency of stretching is higher at high values of the Wi . A central aim would be to study the nature of transitions between the different states i .

One of the ways in which the dynamical properties of a polymer tumbling can be addressed is using the autocorrelation $C(\tau)$ as a function of the Wi (see Fig. 3). It is defined as

$$C(\tau) = \frac{\langle n_i(t)n_i(t+\tau) \rangle - \langle n_i(t) \rangle \langle n_i(t+\tau) \rangle}{\sigma_{n_i(t)}\sigma_{n_i(t+\tau)}}, \quad (2)$$

where $\sigma_{n_i(t)}$ is the standard deviation of the stochastic variable $n_i(t)$ which takes the following values: $n_i \in \{0, \dots, 8\}$. Explicitly: $n_c = 0$, $n_{hd} = 1$, $n_{hf} = 2$, $n_{fk} = 3$, $n_d = 4$, $n_{hd-hf} = 5$, $n_f = 6$, $n_k = 7$, $n_s = 8$ [see Fig. 1(a) for i and n_i values]. $\langle \dots \rangle$ denotes a time average over the states. The autocorrelation exhibits an oscillatory behavior giving a characteristic timescale related to the cyclic conformational changes. Following Ref. [22], we fit the autocorrelation as $C(\tau) = \exp(-\tau/\tau_c) \cos(\omega_d \tau + \psi)$, wherein τ_c is the relaxation time, $\omega_0^2 = \omega_d^2 + \tau_c^{-2}$ is the natural frequency

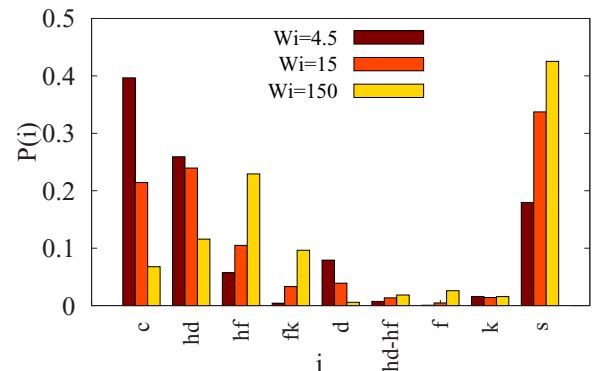


FIG. 2. Probability of different conformations with varying Wi .

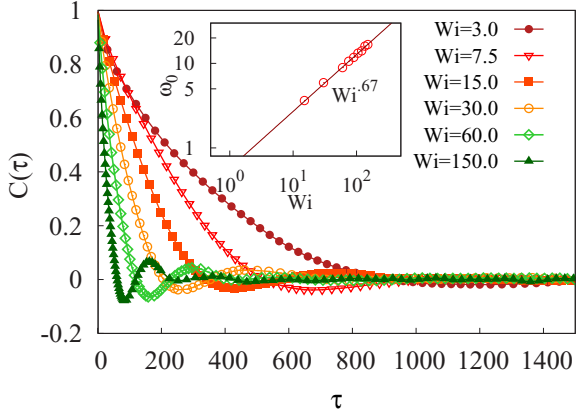


FIG. 3. Variation of autocorrelation $C(\tau)$ with lag τ for different Wi's. The inset (log-log scale) shows that $\omega_0 \sim Wi^{0.67}$.

of the oscillation, and ψ is the initial phase. As seen from the inset of Fig. 3, ω_0 varies sublinearly with the Wi with an exponent ≈ 0.67 . This is identical to the characteristic frequency of a polymer tumbling in shear flow [9,10,22]. This confirms that our classification of these coarse-grained conformations is consistent with the tumbling dynamics of the chain studied in earlier literature.

We now address the question of the transitions which take the polymer from one conformation to another during the tumbling process. We study these transitions in terms of residence and recurrence times of individual conformations. The residence time τ_{res} of a given conformation i is the time t spent by the polymer in that conformation before it jumps to any other conformation. Figure 4(a) shows the residence time probability $P(\tau_{\text{res}} \geq t)$ for the stretched state for different Wi's. The linear decay of $P(\tau_{\text{res}} \geq t)$ on a log-linear plot

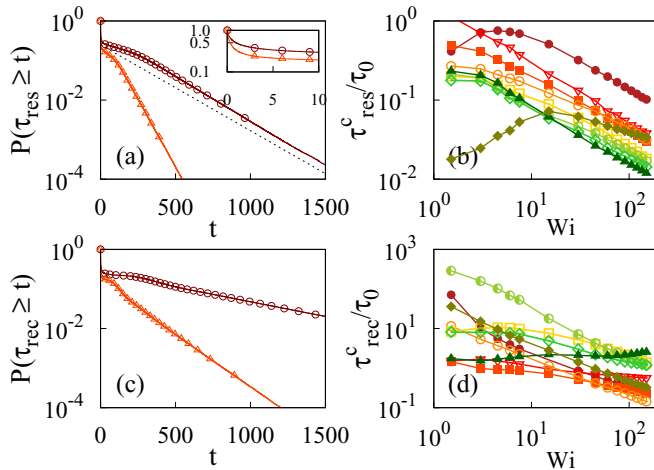


FIG. 4. (a) Distribution of residence times τ_{res} , $Wi = 15$ (\circ) and $Wi = 75$ (Δ) and (b) the algebraic decay of the characteristic residence time τ_{res}^c with the Wi. The inset in (a) shows the nonexponential behavior at short times, and the dashed line is a fit used to estimate the characteristic time of decay. The corresponding quantities for the recurrence time τ_{rec} are shown in parts (c) and (d). The symbols represent the corresponding conformations: ∇ , c; \blacksquare , hd; \circ , hf; \blacklozenge , fk; \diamond , hd-hf; \blacktriangle , d; \bullet , f; \square , k; \bullet , s.

implies that $P(\tau_{\text{res}} \geq t) \sim \exp(-t/\tau_{\text{res}}^c)$ with the inset in (a) showing the nonexponential character at short times. Other conformations show similar behavior, and from Fig. 4(b) we find that the characteristic time of residence is $\tau_{\text{res}}^c \sim Wi^{-0.68 \pm 0.08}$ for almost all the conformations.

In contrast to the residence time, the recurrence time τ_{rec} denotes the time intervals in which the system leaving a state i returns back to it. The recurrence time of a given conformation is related to the first-passage time to that conformation which has been used previously in Ref. [32] to provide typical times of the tumbling process. As observed from Fig. 4(c), the distributions of recurrence times $P(\tau_{\text{rec}} \geq t)$ for the stretched conformation are nonexponential at short times and become exponential at long times. The characteristic recurrence times of individual conformation τ_{rec}^c , however, do not exhibit similar behavior with the Weissenberg number. For example, the recurrence time of the coiled conformation decreases very slowly with the Wi, and the dumbbell becomes less recurrent with increasing Wi. This is because of the dominant nature of the drag force to stretch the polymer as compared to the entropic force tending to coil it. This is also the reason for increasing recurrence times of the dumbbell with the Wi as it becomes less feasible to maintain higher densities symmetrically at both ends of the chain at higher shear rates. Even though the characteristic recurrence times τ_{rec}^c show variability among the conformations, $\tau_{\text{rec}}^c \sim Wi^{-0.73 \pm 0.01}$ for the stretched state provides a measure of the timescale of the tumbling process as it becomes more likely with increasing Wi.

The observation of residence times vs Wi are similar to relaxation times from $C(\tau)$. Recurrence times vs Wi are more nontrivial, and that shows that first-passage properties can be quite distinct from transport properties. The whole story of recurrence is actually a step-by-step buildup of many intermediate transitions among coarse-grained states. This motivates us to now focus on the properties of transition. We hypothesize that an effective kinetic description does not require the inherent details of the model, and we may use the statistics of residence times and a knowledge of the transition probability to provide a coarse-grained description of the phenomenon. As we will see in the next section, this approach makes the problem effectively Markovian which may be addressed employing the master equation formalism.

Markovian description. The exponentially decaying tails of the residence distributions imply that the original non-Markovian problem can be reduced to an approximate Markovian limit. To achieve this, we employ the master equation formalism [33,34] for the stochastic process in which the polymer makes the transition from one conformation to another. This coarse-grained description would assume that the time taken by the polymer to jump from one conformation to another is instantaneous, and the residence time within a state is exponentially distributed with its characteristic time (calculated from Langevin dynamics simulations). Such a coarse-grained description uses minimal information from the underlying model of polymer tumbling and hence is expected to capture the essence of it.

To proceed with our goal, define the transition rate for a jump from state i to j ,

$$\omega_{ij} = p(j|i)/\tau_{\text{res}}^c, \quad (3)$$

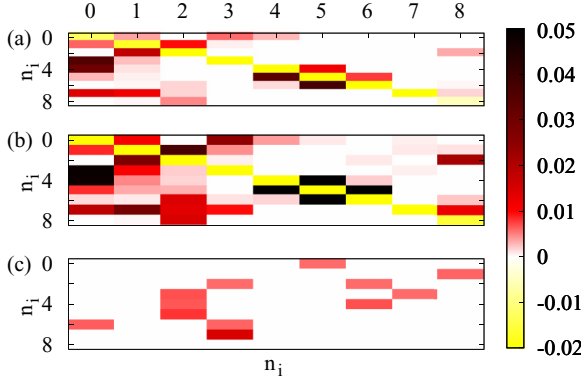


FIG. 5. Color map of the \mathbb{W} matrix for (a) $Wi = 15$ and (b) $Wi = 75$. With increasing Wi the jump rates increase, e.g., \mathbb{W}_{56} is higher for $Wi = 75$ as compared to that of $Wi = 15$. The diagonal elements of the \mathbb{W} matrix are negative. (c) The colored boxes indicate the matrix elements of \mathbb{W} for $Wi = 75$ which are zero for $Wi = 15$. The elements \mathbb{W}_{ij} are shifted for the purpose of visibility.

where $p(j|i)$ is the probability of a jump from i to j and τ_{res}^c is the characteristic time of residence in state i , defined in terms of its distribution $P(\tau_{\text{res}} \geq t) \sim \exp(-t/\tau_{\text{res}}^c)$ at long times. The jump probability $p(j|i)$ is calculated by dividing the number of jumps from a given i to a given j by the total number of jumps which occur from state i . The calculation is performed using a time series generated from the Langevin equation, long enough to realize all the conformations during the tumbling process. The probability of a given jump from i to j , however, is dependent on the Wi . This is because an increment in the Wi makes the polymer tumbling more frequent thus increasing $p(j|i)$. In addition, we have seen from Fig. 4(c) that the characteristic time of residence τ_{res}^c has a tendency to decrease with increasing Wi . This implies that the transition rate ω_{ij} , which is the ratio of $p(j|i)$ to τ_{res}^c , will increase with increasing Wi for arbitrary conformations i and j . The transition rates ω_{ij} are, however, constant in time, and this implies that the master equation,

$$\dot{\mathbf{p}} = \mathbf{p}\mathbb{W} \quad (4)$$

can be solved exactly in terms of the spectrum of the \mathbb{W} matrix, defined as $\mathbb{W}_{ij} = \omega_{ij}$ for $i \neq j$ and $\mathbb{W}_{ii} = -\sum_j \omega_{ij}$ otherwise.

The structure of the \mathbb{W} matrix becomes clear from Fig. 5, which shows the color map of the elements \mathbb{W}_{ij} for (a) low $Wi = 15$ and (b) high $Wi = 75$ shear rates. If we look at a coil-to-stretch transition, then we find that a direct jump is highly unlikely as $\mathbb{W}_{08} = 0$ [white color in Figs. 5(a) and 5(b)]. However, there exists a path $c \xrightarrow{\mathbb{W}_{01}} hd \xrightarrow{\mathbb{W}_{12}} hf \xrightarrow{\mathbb{W}_{28}} s$ [cf. Fig. 1(a)] which becomes more probable for higher Wi [compare the colors in (a) and (b)]. In addition, the increased shear rate also reduces the number of steps from four to three: $c \xrightarrow{\mathbb{W}_{01}} hd \xrightarrow{\mathbb{W}_{18}} s$; note $\mathbb{W}_{18} = 0$ for $Wi = 15$ and $\mathbb{W}_{18} > 0$ for $Wi = 75$. This implies that, in addition to increasing transition rates, new transition paths are also created with increasing Wi . The \mathbb{W} -matrix formalism also captures the increase in tumbling events (i.e., from stretched to coiled) with increasing shear rates. This becomes evident by the emergence of new

transitions paths $s \xrightarrow{\mathbb{W}_{82}} hf \xrightarrow{\mathbb{W}_{23}} fk \xrightarrow{\mathbb{W}_{30}} c$ and $s \xrightarrow{\mathbb{W}_{82}} hf \xrightarrow{\mathbb{W}_{26}} f \xrightarrow{\mathbb{W}_{60}} c$ for $Wi = 75$ in addition to $s \xrightarrow{\mathbb{W}_{82}} hf \xrightarrow{\mathbb{W}_{21}} hd \xrightarrow{\mathbb{W}_{10}} c$, which is also present for $Wi = 15$.

In Fig. 5(c), we show the emergence of new transitions for higher Wi —the terms of the \mathbb{W} matrix which are zero for $Wi = 15$ and nonzero for $Wi = 75$ are shown in colors. This implies that new paths involving new intermediate states emerge in the tumbling process. Particularly interesting are the nontrivial transitions, such as $f \xrightarrow{\mathbb{W}_{63}} fk$ and $k \xrightarrow{\mathbb{W}_{73}} fk$, which now take place in a single step. The difference in our coarse-grained approach is that it can capture the existence of such intermediate steps in the process of macroscopic tumbling from the stretched to the coiled state, which are far from obvious.

The master equation (4) admits a unique stationary distribution \mathbf{p}_{st} in accordance with the Perron-Frobenius theorem [35,36] defined as $0 = \mathbf{p}_{\text{st}}\mathbb{W}$. This defines the steady-state autocorrelation,

$$C(\tau) = \frac{1}{\sigma_{\text{st}}} \sum_{i,j} (n_i - \langle n_i \rangle_{\text{st}})(n_j - \langle n_i \rangle_{\text{st}})(e^{\mathbb{W}\tau})_{ji} p_{\text{st}}(j), \quad (5)$$

where $\langle n_i \rangle_{\text{st}} = \sum_i n_i p_{\text{st}}(i)$ and $\sigma_{\text{st}}^2 = \langle n_i^2 \rangle_{\text{st}} - \langle n_i \rangle_{\text{st}}^2$ are the steady-state mean and variance, respectively. The experimentally relevant quantity $C(\tau)$ can be calculated exactly using $[\exp(\mathbb{W}\tau)]_{ji}$. From Figs. 6(a)–6(c) we find that the

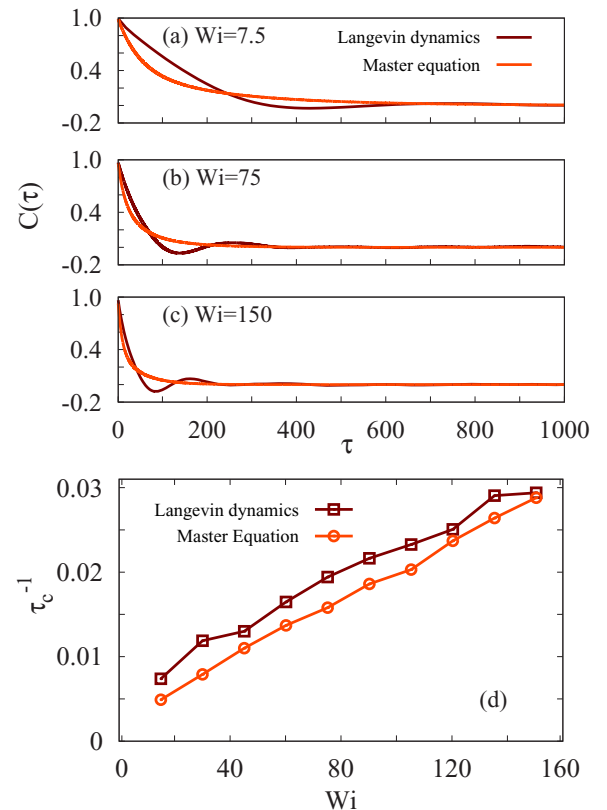


FIG. 6. Autocorrelation $C(\tau)$ for the time series of states from the Langevin dynamics simulations and master equation for (a) $Wi = 15$, (b) $Wi = 75$, and (c) $Wi = 150$. It is evident that the two autocorrelations decay at nearly the same timescale [see (d)].

autocorrelation $C(\tau)$ decreases exponentially with lag τ for the effective (Markovian) and full (non-Markovian) problem. The exponential decay of the autocorrelation implies that a relaxation time τ_c can be defined as $C(\tau) \sim \exp(-\tau/\tau_c)$ for its decay. We find from Fig. 6(d) that these relaxation times show a similar behavior with the Wi for the two approaches. The proximity of the two curves implies that the coarse-grained picture of the tumbling process captures the generic properties of the processes to a very good extent.

It is also noted from Figs. 6(a)–6(c) that the Markovian description does not capture the oscillatory behavior of the autocorrelation $C(\tau)$, which is present in the original problem. The reason for the difference is attributed to the approximation that the residence times of the states are exponentially distributed in the master equation formalism is only partly true as far as the original dynamics is concerned [37].

Discussion. Although polymer tumbling in shear flow is an old classic problem which has received wide attention in the literature, a kinetic description in terms of residence times and transitions from one conformation to another is still missing. We propose a coarse-grained approach to study the problem using the information about the residence times of individual conformations and jump probability from one conformation to another. The distributions of residence times exhibit exponentially decaying tails which helps us build an effective

Markovian picture of the truly non-Markovian problem. In the Markovian picture, the problem is solved using the master equation formalism. The structure of the \mathbb{W} matrix reveals a robust sequence of transitions between different conformations i taken by the polymer while tumbling in the flow. With increasing Wi new paths are realized, and rates of existing jumps tend to increase. The coarse-grained description provides us with insights about the intermediate steps which arise during the process of macroscopic tumbling. At this coarse-grained level, the autocorrelation between different conformations is calculated exactly, and we show that its relaxation time compares quite well with that estimated using Langevin dynamics simulations of the original non-Markovian problem. The two approaches predict almost identical dependence of the relaxation times on the Weissenberg number. This implies that the Markovian approach, despite being a coarse-grained representation of the full non-Markovian problem, captures the kinetics of the tumbling process to a very good extent. We hope that the ideas presented here will be useful in addressing similar problems in polymer kinetics under different flow fields from this perspective.

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