Conformation and dynamics of a self-avoiding active flexible polymer

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We investigate conformations and dynamics of a polymer considering its monomers to be active Brownian particles. This active polymer shows very intriguing physical behavior which is absent in an active Rouse chain. The chain initially shrinks with active force, which starts swelling on further increase in force. The shrinkage followed by swelling is attributed purely to excluded-volume interactions among the monomers. In the swelling regime, chain shows a cross-over from the self-avoiding behavior to Rouse-behavior with scaling exponent \( \nu_a \approx 1/2 \) for end-to-end distance. The non-monotonicity in the structure is analysed through various physical quantities specifically, radial distribution function of monomers, scattering time, as well as various energy calculations. The chain relaxes faster than the Rouse chain in the intermediate force regime, with a cross-over in variation of relaxation time at large active force as given by a power-law \( \tau_r \sim Pe^{-4/3} \) (\( Pe \) is Péclet number).

Introduction— A collection of freely moving active Brownian particles has drawn immense research activities in past few years in view of interdisciplinary applications [1][6]. These individual agents ballistically propel themselves by conversion of chemical energy into mechanical energy, thus their motion can be controlled in experiments in a desired manner consequently they display rich collective dynamics [7][13]. A collection of such active particles connected via linear chain exhibits numerous interesting features [14][24], which is often absent in passive systems. For example, an active chain exhibits shrinkage and swelling [24][31], spontaneous oscillations [32][31], enhanced diffusion [24][28], etc. The collective dynamics of such systems display various emergent structures, understanding them is a fundamental quest from biophysics point of view as it poses a great challenge [35][13].

With the help of minimal models, behavior of an active flexible chain or rigid filaments has been investigated [24][28][34][31][44][64]. An accessible analytically tractable model for the polymer is Rouse model and inclusion of the activity in this model is studied in literature [26][30][54][55]. An active Rouse chain shows swelling with a power law scaling relation on active force with exponent 1/3. Analytical calculations suggest that a flexible polymer always swells, whereas a semi-flexible chain shrinks at smaller force and in the asymptotic limit it swells akin to an active Rouse chain with same exponent [27][28][66]. The swelling of chain, relaxation, and its centre-of-mass diffusion can be strongly influenced by the solvent properties and viscoelastic behavior of the medium [67][68]. The competition between elastic and self-avoiding forces causes shrinkage to passive chain in an active bath in two-spatial dimensions (2D) [58]. On the other hand a self-avoiding active chain in 2D shrinks, which is followed by swelling at larger active strength [59]. How does excluded-volume interactions influence the structure of a chain in 3D, its relaxation, and scaling exponents are important questions and have not been addressed very well in the previous studies.

The present work elucidates the role of excluded volume together with the activity on the relaxation and structure of the chain. In our simulations, we found that the end-to-end distance (\( R_e \)) and radius of gyration (\( R_g \)) of the chain shrinks in the intermediate range of active force (\( Pe \)) in absence of hydrodynamics. In a recent study, it has been shown that the effect of hydrodynamics brings a similar behavior [50]. We analyse here the shrinkage of chain through relaxation time, mean collision of monomers, radial distribution function, softness of the potential, and elastic and repulsive energies. The scaling exponent of the chain in stretching regime follows a power-law on active force as, \( R_e \approx Pe^{1/3} \) and further with variation on the chain length as \( R_e \approx N^{\nu_{ax}} \), where \( \nu_{ax} \approx 1/2 \) in the stretching regime.

Model— A flexible chain is composed of linear sequence of \( N \) Brownian particles, the consecutive monomers in the chain are connected by harmonic potential \( \Phi_h = \frac{k_s}{2} \sum_{i=1}^{N-1} (r_i - x_i - l_0)^2 \), where \( r_i, l_0 \), and \( k_s \) denote position of \( i^{th} \) monomer, average equilibrium bond length and spring constant, respectively. The excluded-volume potential restricts overlapping of beads in a polymer, and it is implemented here as standard repulsive part of Lennard-Jones interactions for shorter distance, i.e., \( R_{ij} < 2^{1/6} \sigma \),

\[
\Phi_{LJ} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \epsilon \left( \frac{\sigma}{R_{ij}} \right)^{12} - \left( \frac{\sigma}{R_{ij}} \right)^{6} + \epsilon,
\]

and for \( R_{ij} \geq 2^{1/6} \sigma \), \( u_{ij} = 0 \), where \( R_{ij} = r_j - r_i \), \( \epsilon \) is interaction energy and \( \sigma \) is the diameter of the monomer. The total LJ energy can be expressed as, \( \Phi_{LJ} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} u_{ij} \). The prime in second summation excludes the LJ interaction between consecutive...
bonded neighbors.

The equation of motion of an active Brownian bead of the polymer chain in an overdamped limit is,

\[
\gamma \frac{d\mathbf{r}_i}{dt} = -\nabla_i \Phi + \mathbf{F}_i^a + F_a \hat{u}_i,
\]  

(2)

where \(\gamma\) is the friction coefficient, \(\mathbf{F}_i^a\) is the thermal noise with zero mean, and \(F_a\) is the strength of self-propulsion force exerted on \(i^{th}\) bead along \(\hat{u}_i\) direction. The viscous drag and the thermal noise obey fluctuation-dissipation relation, \(\langle \mathbf{F}_i^a(t) \mathbf{F}_j^a(t') \rangle = 6k_BT\gamma \delta_{ij} \delta(t - t')\). The long-range hydrodynamic interactions are neglected here.

Active Brownian beads are modelled as polar molecules, their orientations \(\hat{u}_i\) are described by the rotational counter-part of the Langevin equation,

\[
\gamma_r \frac{d\hat{u}_i}{dt} = \zeta_i \times \hat{u}_i. 
\]  

(3)

Here \(\zeta_i\) is a random torque with zero-mean and variance \(\zeta(t) \otimes \zeta(t') = (2k_BT)^2 \delta(t - t')/D_r\), and \(\gamma_r\) is the rotational friction coefficient given as \(\gamma_r = k_BT/D_r\). The rotational diffusion is expressed in terms of translational diffusion \((D_m)\) as, \(D_r = 3D_m/l_0^2\). The strength of active force is presented here as a ratio of active force with thermal force given as, \(Pe = (F_a l_0)/(k_BT)\), with Péclet number \(Pe\) as a dimensionless quantity. A schematics of polymer chain is displayed in Fig. 1 where arrow shows the direction of active force on a monomer.

All the physical parameters presented in this article are scaled in units of the bond length \(l_0\), diffusion coefficient of a monomer \(D_m\), and thermal energy \(k_BT\). Simulations are performed in cubic periodic boxes in three spatial dimensions, polymer length is varied in the range of \(N = 50\) to \(300\). Other parameters are chosen as, \(k_s\) in range of \(10^3\) to \(10^4\) in units of \(k_BT/l_0^2\), \(\epsilon/k_BT = 1\), and time is in units of \(\tau = l_0^2/D_m\). For higher \(Pe\), larger values of \(k_s\) is chosen to avoid stretching of bonds. The monomer size \(\sigma\) is varied in the range of \(\sigma/l_0 = 0.2\) to 1.0 and \(Pe\) is varied in the range of 0 to 1000. We use Euler integration technique to solve Eq. 2 and 3 with time step \(\Delta t\) in the range of \(10^{-3}\tau\) to \(10^{-5}\tau\) to ensure stable simulation results. In order to obtain better statistics, each data point is averaged over 20 independent simulations.

**Structural Properties**— There is vast literature on the equilibrium behavior of a polymer chain \([69, 77]\) followed by extension to an active chain \([24, 60, 78]\). We present effective active noise on the structure of a self-avoiding chain in form of radius-of-gyration, end-to-end distance and its distribution, pair-correlation function, and scaling exponents.

The quantification of structural change is analysed in terms of end-to-end distance \(R_e\) and radius of gyration \(R_g\) as,

\[
R_e^2 = \left( \langle r_1 - r_N \rangle^2 \right); \quad R_g^2 = \frac{1}{N} \left( \sum_{i=1}^{N} (r_i - R_{cm})^2 \right), \quad (4)
\]

where \(R_{cm}\) is the centre-of-mass of the chain and angular bracket indicates ensemble average. The computed \(R_e\) is displayed in Fig. 2-a, which reflects a significant shrinkage of polymer with \(Pe\) in the range of \(Pe < 50\) for \(N > 50\). The initial shrinkage of chain is followed by stretching in the range of \(Pe > 50\) as Fig. 2-a illustrates. The swelling behavior of \(R_e\) appears quite alike to Rouse chain. The normalized end-to-end distance for various chain lengths follows the same trend with relatively higher compression for large chain lengths. In the stretching regime, \(R_e\) follows a power-law variation on Péclet number given by \(R_e^2 \sim Pe^{2/3}\) with an exponent \(2/3\) identical to Rouse chain \([27, 55, 58]\).

Now, we turn our attention to scaling exponents \(\nu_a\) of the chain in various regimes. The inset of Fig. 2-a compares various plots of \(R_e\) as a function of chain length at \(Pe = 0, 15, 70, 150,\) and 200. These curves indicate variation of the scaling exponents \(\nu_a\) with \(Pe\). It clearly suggest that for \(1 < Pe < 50\), the exponent is slightly smaller than \(3/5\), for comparison a solid line is drawn in inset of Fig. 2-a at \(\nu_a = 3/5\). A dashed line illustrates the variation of \(R_e \sim N^{\nu_a}\) with \(\nu_a = 1\pm 0.05\). For \(Pe > 100\), the exponent \(\nu_a\) of chain approaches Rouse regime \(\nu_a = 1/2\). To summarize the results in compression regime (triangle and diamond), we found that \(\nu_a\) is smaller than \(3/5\) and slightly larger than \(1/2\).

The shrinkage of active chain is visible in terms of probability distribution of \(R_e\). Figure 2-b reflects shift in the location of peak with propulsion strength \(Pe\) at a fixed chain length \(N = 200\). The peak shifts weakly towards left for the smaller values of \(Pe\) with shape almost identical to passive polymer. The initial shift of peak towards small \(R_e\) changes its coarse of variation with shifting towards right for large \(Pe\). The change in distribution is consistent with the non-monotonicity in the structure. The end-to-end distance and probability distribution confirms the compression in the intermediate regime, i.e., \(1 < Pe < 50\).

In order to bridge the gap between monotonic swelling
FIG. 2. a) Relative variation of mean square end-to-end distance ($R_e^2/R_{e,0}^2$) of the chain as a function of $Pe$ for various lengths. Solid line shows a power law variation $Pe^{2/3}$. The inset shows $R_e$ with $N$ at $Pe = 0, 15, 70, 150$ and $200$, at $\sigma = 1$. The solid and dashed lines are showing power law variation at exponents $\nu_a = 3/5$ and $1/2$, respectively. b) The distribution of end-to-end distance at $N = 200$ and $\sigma = 1$. c) Relative variation of end-to-end distance ($R_e^2/R_{e,0}^2$) of an active chain with $N = 200$ as a function of $Pe$ for various monomer diameters $\sigma = 0.2, 0.5, 0.75$ and $1.0$, and Rouse chain (bullet).
creasing activity in the range $0 < Pe < 50$. Further, they start dispersing far from each other on higher strength of $Pe$ as already pointed out in terms of radial distribution. With higher strength ($Pe$), collision becomes frequent as expected from the kinetic theory $t_c \sim \frac{1}{v_r}$, $v_r$ read as average relative speed of monomers. The onset of increase of $t_c$ appears nearly at same $Pe$ as onset of $R_c$ and $R_g$

(see Fig. SI-1-a in supplementary text). With increase in active fluctuations, the polymer gets stretched thus the frequency of collision goes down hence $t_c$ (collision time) goes up as Fig. 5a reflects. The effect of monomer size on scattering time indicates variation in active polymer’s conformation from self-avoiding to ideal behavior. A smaller monomer has larger collision time as it exhibits smaller scattering cross-section ($b = \pi \sigma^2$), which is reflected in Fig. 5a. It’s noteworthy that the relative variation in $t_c/t_0$ for small $\sigma = 0.5$ has strikingly significant variation, importantly in the intermediate regime of $Pe$ as inset of Fig. 5a reflects. The depth in $t_c/t_0$ ($10 < Pe < 50$) becomes shallow with $\sigma$, which diminishes in the asymptotic limit of $\sigma \to 0$.

To enlighten the difference in relaxation behavior of a Rouse and a self-avoiding active chain, we compute the end-to-end correlation of polymer. The end-to-end correlation follows an exponential decay (in longer time $\gamma r \tau_t >> 1$), $< R_e(0).R_e(t) > \approx \exp(-t/\tau_r)$, with $\tau_r$ as the longest relaxation time of polymer. The estimated relaxation time $\tau_r/\tau_r^0$ from the correlation is displayed in Fig. 5b. It presents relative variation of $\tau_r$ with respect to that of passive chain $\tau_r^0$ for various monomer diameters, along with Rouse chain. In the limit of smaller monomer size, we achieve relaxation behavior of Rouse chain with pronounced variation in $\tau_r$. The relaxation behavior indicates a power-law variation given as, $\tau_r \approx Pe^{-\beta_a}$, for Rouse chain $\beta_a \approx 4/3$. The self-avoiding chain exhibits very intriguing feature with a sharp variation $\tau_r$ in the limit $Pe < 100$. The scaling exponent is found to be $\beta_a \approx 5/3$, see solid line in Fig. 5b. A cross over from the sharp relative variation ($\beta_a \approx 5/3$ for $Pe < 100$) to the exponent $\beta_a = 4/3$ is observed in the limit of $Pe > 100$. More importantly the variation in relaxation with $Pe$ becomes faster in compression regime. The larger relative change in the relaxation time in the presence of hydrodynamics than the Rouse chain is also reported in Ref. [66], where it was shown that the competition between active force and variation in $\tau_r$ controls the structure leading to compression of chain. The relatively faster variation of $\tau_r$ obtained in our simulations for self-avoiding chain resembles results of Ref. [66]. A smooth variation in $\tau_r$ from the self-avoiding chain to Rouse chain is obtained by variation in monomer size as Fig. 5b illustrates in various plots.

In this section, diffusion of active chain is presented through mean squared displacement (MSD) of the centre-of-mass (COM) of chain. The long time MSD of the COM is expressed as, $< R_{cm}(t)^2 >= < (r_{cm}(t) - r_{cm}(0))^2 >$. The MSD shows ballistic motion $< R_{cm}^2(t) > \sim t^2$ in the short time and diffusive regime $< R_{cm}^2(t) > = 6Dt$ in the long time limit. Inset of Fig. 5 displays MSD of the chain at various $Pe = 0, 5, 10, 30$ and $50$, it clearly indicates enhanced diffusion with $Pe$. This can be understood in terms of drag of monomers through active forces in random directions, which causes faster movement relative to the passive monomers resulting in enhanced MSD of the chain with $Pe$. The diffusive regime of the MSD
gives self-diffusion coefficient, as Fig. 5 displays normalized effective diffusion coefficient $D/D_0$. The effective diffusivity increases quadratically as, $D \sim Pe^2$. Moreover as expected, $D$ is independent of the chain length when scaled by diffusion coefficient of passive chain ($D_0$, at $Pe = 0$), thus we can express, $D = D_0(1 + aPe^2)$, where $a \approx 0.06$ is a constant. The effective diffusion can be used to define the effective temperature of the chain as $T_{eff} = 1 + aPe^2$. In particular cases, this expression is argued to be identical to a passive system with temperature equivalent to $T_{eff} \approx 79 \approx 81$. However, mapping of effective temperature of active polymer to temperature would not be sufficient for all physical behaviors.

The segmental MSD of the chain reveals internal dynamics specifically sub-diffusive behavior in the intermediate time limit ($10^{-1}$ to $10^2$). The cross-over from sub-diffusive to diffusive survives relatively at longer time for larger chain lengths in a broad window of $Pe$ (see ESI SI-2 a and b). This enlightens the internal dynamical picture of chain in the discussed parameter space.

Discussion and Summary—In summary, we have unveiled the effect of excluded-volume interactions on the structural properties and internal dynamics of an active polymer in 3D. A polymer shrinks in the presence of activity, which is followed by swelling. A pronounced non-monotonic behavior in $R_e$ is depicted in a broad range of activity strength for larger chain lengths. This compression is more pronounced in 2D [5]. We have shown that in limit of $Pe < 50$, the compression is primarily a consequence of interaction of monomers from its neighbors, which brings an increase in local density. This increase can be understood in terms of rotational diffusion which requires $1/D$ time to change monomers orientation to escape from the local environment. The radial distribution function substantiates the effect of softness and increase in local density. The softness of repulsive potential exhibits a weak contribution in the structure at large active forces. A systematic study on the softness of the potential due to activity is taken into account here by varying $\epsilon$ over a range of $10$ to $10^{-3}$. Larger epsilon corresponds to stiffer potential, which exhibits very nominal change in the values with preserving the qualitative behavior. On the other hand relatively softer potentials lead to a significant change in $R_e^2$ with activity (see Fig-SI 3). We have also tested our results for a different potential which looks similar in nature to LJ potential but more steeper. This potential also exhibits a non-monotonic behavior in structure.

Fast random motion of monomers results into stretching of the chain for large $Pe > 50$, thereby increase in the elastic energy. Interestingly, the power law scaling exponent of self-avoiding chain ($R_e \approx N^{\nu_a} \nu_a$) becomes smaller in this regime and approaches to Rouse limit ($\nu_a = 1/2$), despite stretching of polymer due to activity. In addition, the longest relaxation decreases with power law as $\tau_r \approx Pe^{-\nu_a}$, for Rouse and self-avoiding chains in the large $Pe$ limit with exponent $\beta_0 \approx 4/3$. The relaxation behavior of self-avoiding chain’s exhibits a crossover from the exponent $\beta_0 \approx 5/3$ to $4/3$ with $Pe$. In conclusion, the role of self-avoidance has been explored in a systematic way by varying monomer’s diameter that bridges the gap between an excluded volume chain and a Rouse chain, consequently it connects variation of numerous physical properties such as $R_e$, $\tau_r$, and scattering time smoothly from one to another limit. The effect of excluded volume is substantial in flexible limit, which slowly diminishes with semi-flexibility of the chain [8]. A theoretical approach for the radius of gyration and relaxation time of the excluded volume chain would be essential for the complete understanding of system. In addition a detailed study on the softness of potential and effect of rotational diffusion on the structure of an active chain would be further interesting to investigate.

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SUPPLEMENTARY TEXT

The Fig. SI-1(a) displays the radius of gyration of chain w.r.t. $Pe$. It shows a non-monotonic behavior for various chain lengths.

The effect of activity on the interaction of the chain is also illustrated in terms of variation in elastic and excluded volume energy contributions. The elastic energy per monomer is defined here as $\phi_h = \Phi_h / N$ and excluded-volume energy as $\phi_{LJ} = \Phi_{LJ} / N$. Figure SI-1(b) displays both energies as a function of $Pe$ for various chain lengths. The elastic energy is nearly unperturbed for $Pe < 10$, it grows further rapidly with $Pe$ in the range of $Pe > 10$ as inset of Fig. SI-1(b) illustrates. In the higher $Pe$ regime, monomers are randomly moving with relatively larger speed, which causes local stretching on the chain thereby elastic energy grows. The contribution of the excluded-volume energy is displayed in Fig. SI-1(b). As expected, $\phi_{LJ}$ exhibits sharp increase followed by a slump in the energy in the limit of $Pe > 100$. The
The MSD of a monomer in chain is displayed ($N = 50$ and 200) in Fig. SI-2(a) and (b). As evident from the figure, the MSD of a monomer of a passive chain undergoes diffusive, sub-diffusive followed by a long-time diffusive behavior. In the intermediate time $10^{-1}$ to $10^{2}$, the MSD exhibits sub-diffusive motion with exponent $t^\alpha$, $\alpha \approx 2/3$. At moderate strength of $Pe$, a super-diffusive motion at shorter times, and sub-diffusive at relatively longer times is shown in the plot. The time window of the sub-diffusive regime narrows with $Pe$, and it almost disappears for shorter chain for $Pe = 50$ and 100. However, the sub-

diffusion for relatively longer chain, i.e., $N = 200$, persist in the active regime of $Pe < 100$ and it disappears beyond $Pe > 100$. Thus for longer active chain, motion of monomers are influenced by other monomers for much longer time.

A systematic study of end-to-end distance of the active chain due to softness of potential is taken into account here by varying $\epsilon$ over a range of $10$ to $10^{-3}$. Here larger epsilon corresponds to relatively steeper potential. Figure SI-3 compares results of various $\epsilon$, it exhibits very nominal change in the values of $R_e^2$ for $\epsilon = 1$ and 10. However for the $\epsilon < 1$, the potentials becomes softer thus the relative compression of the chain decreases. In the limit of $\epsilon \to 0$ the results will approach to the Rouse behaviour.