# Nonequilibrium structural and dynamic behaviors of polar active polymer controlled by head activity

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Thermodynamic behavior of polymer chains out of equilibrium is a fundamental problem in both polymer physics and biological physics. By using molecular dynamics simulation, we discover a nonequilibrium mechanism that controls the conformation and dynamics of polar active polymer; i.e., head activity commands the overall chain activity, resulting in a re-entrant swelling of active chains and a nonmonotonic variation of the Flory exponent  $\nu$ . These intriguing phenomena are the result of two competing nonequilibrium effects arising from the head-controlled railway motion of the chain, i.e., dynamic chain rigidity and the curling of chain conformation characterized by the negative bond vector correlation. Moreover, we identify several generic dynamic features of polar active polymers, i.e., *linear* decay of the end-to-end vector correlation function, polymer-size-dependent crossover from ballistic to diffusive dynamics, and diffusion coefficients sensitive to head activity. A simple dynamics theory is proposed to faithfully explain these interesting dynamic phenomena.

These sensitive structural and dynamical responses of active polymer to its head activity provide us a practical

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way to control active agents with applications in biomedical engineering.

# I. INTRODUCTION

The scaling theory of polymer introduced by De Gennes [1] lays the foundation of polymer physics [2,3]. One of its prediction is the universal scaling behavior of a polymer's size, or radius of gyration  $R_g$ , on the monomer number N, i.e.,  $R_g \sim N^{\nu}$ , with  $\nu$  being the well-known Flory exponent [4]. For thermally equilibrated polymer chains, there are three distinct scaling regimes, i.e., polymer in good solvent ( $\nu = 0.588$ ), theta solvent ( $\nu = 1/2$ ), and bad solvent ( $\nu = 1/3$ ). Nevertheless, how the introduction of nonequilibrium effects modifies these classical predictions is an open question relevant to some key biological processes. For example, biopolymers like DNA chromatin in nuclei and actin filaments in cellular cytoskeletons are subjected to propelling forces from either DNA helicases or motor proteins [5–9], metabolic enzymes can form filamentous membraneless organelles termed cytoophidia that are efficiently transported through threedimensional (3D) complex cellular structures with the help of actin filaments [10,11], and polymerlike worms exhibit distinct conformational and dynamic properties with or without driving activity [12–14]. These active polymers exhibit complicated self-organized structures and anomalous dynamics that challenge classical polymer physics theory [15–22]. On the other side, many artificial active polymers have also been realized, like motility assays of actin filaments [23,24], active colloidal polymers [25–30], and actuated mechanical chains and ribbons [31–34], which show potential application value in drug-delivery and soft-body robots. Thus, a deep understanding of the nonequilibrium behaviors of active polymers is of great significance for both biological physics and biomedical engineering [35].

Active polymers are generally categorized into polar and nonpolar. For polar active polymers like actin filaments, active forces are along the backbone of the polymer, and thus the total active force has a preferred direction [36-45]. This is different from the nonpolar active polymers like active Brownian chains, where the active forces on monomers are uncorrelated [46,46–48]. The mobility of the head of polar active polymers can significantly influence the structural and dynamic behaviors of the entire chain. For example, Bourdieu et al. observed that in motility assays the actin filaments rotate like spirals or undulate like flagella when the head movement is frustrated [49]. Subsequently, many efforts have been made to elucidate the effects of head mobility on the conformation and dynamics of polar active polymers [50–52]. Most recently, Patil et al. revealed that the changes in head chirality of the California blackworm are responsible for the rapid alternation of their self-assembly state [53]. Moreover, Krishnamurthy and Prakash developed an active filament model with programmable head activity to investigate the physical

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FIG. 1. (a) Schematic representation of the polar active polymer, where red arrows represent the active force on backbone monomers and blue arrows with gradient color denote the tunable active force on the head monomer. (b) The probability distribution of the radius of gyration  $P(R_g)$  for polymers with different head activity strengths  $\kappa$ , where the insets show corresponding chain configurations.

mechanisms underlying the predation behavior of *Lacrymaria olor* [54]. Nevertheless, a more general mechanism of head-activity-induced conformation and dynamics transition of the polar active polymer remains unknown [55,56].

In this study, we systemically study the structures and dynamics of polar active polymers with controllable head activity. We find that the head activity plays a commanding role in overall chain activity, resulting in the re-entrant swelling of active polymers and the nonmonotonic variation of the Flory exponent  $\nu$ , as well as head-activity-controlled polymer dynamics. These intriguing behaviors result from the competition between two nonequilibrium effects (i.e., dynamic chain rigidity and the curling of chain configurations) arising from the head-controlled railway motion of active polymers. Moreover, we also identify several generic dynamic features of polar active polymers, such as *linear* rather than exponential decay of the end-to-end vector correlation function, polymer-size-dependent crossover from ballistic to diffusive dynamics, and head-activity-controlled diffusion coefficients. These dynamic phenomena are satisfactorily explained by a dynamic theory based on the railway motion.

## **II. MODEL AND SIMULATIONS**

As shown in Fig. 1(a), we model the active polymer as a bead-spring chain of N monomers with bond length b. To ensure conformation stability under self-driving conditions, a modified Kremer-Grest model was used, where the excluded volume interactions are modeled by a WCA-like potential:

$$V_{mm}(r) = \begin{cases} 4\varepsilon \left[ \left(\frac{\sigma}{r}\right)^{44} - \left(\frac{\sigma}{r}\right)^{22} \right] + \varepsilon, & r < 2^{1/22}\sigma, \\ 0, & r \geqslant 2^{1/22}\sigma, \end{cases}$$
(1)

with  $\sigma$  and  $\varepsilon$  setting the units of length and energy, and r as the distance between two monomers. Neighboring beads are connected by the finitely extensible nonlinear elastic potential:

$$V_b(r) = \begin{cases} -150\varepsilon \left(\frac{R_m}{\sigma}\right)^2 \ln\left[1 - \left(\frac{r}{R_m}\right)^2\right], & r < R_m, \\ \infty, & r \ge R_m, \end{cases}$$
(2)

with  $R_m = 1.05\sigma$ . Such a pair of steep potentials severely limits the fluctuations in bond length and can avoid chain crossing in extremely contracted or extended conformations. Based on Ref. [55], we assume that the active force on the backbone monomer *i* has a constant magnitude  $F_{act}$  and its direction polarizes to the head monomer (*i* = 1) along the local tangent determined by the nearest two monomers, i.e.,

$$\mathbf{F}_{\text{act},i} = F_{\text{act}} \mathbf{e}_{i-1,i+1}, \quad i = 2, 3, \dots, N-1,$$
 (3)

with  $\mathbf{e}_{i,j} = (\mathbf{r}_i - \mathbf{r}_j)/|\mathbf{r}_i - \mathbf{r}_j|$ . The active force on the tail monomer (i = N) is set as  $\mathbf{F}_{\text{act},N} = F_{\text{act}}\mathbf{r}_{N-1,N}/|\mathbf{r}_{N-1,N}|$ , while the active force on the head monomer is controlled by the dimensionless head activity strength  $\kappa$ ,

$$\mathbf{F}_{\text{act},1} = \kappa F_{\text{act}} \mathbf{r}_{1,2} / |\mathbf{r}_{1,2}|.$$
(4)

 $\kappa$  can also be understood as the ratio between the head and the backbone activities. Standard Langevin dynamics is used to simulate the active polymer in free three-dimensional (3D) space:

$$m\frac{d^{2}\mathbf{r}}{dt^{2}} = -\gamma \frac{d\mathbf{r}}{dt} + \mathbf{F}_{C}(\mathbf{r}) + \mathbf{F}_{act} + \mathbf{F}_{R},$$
 (5)

with *m* and  $\gamma$  being the mass scale and the friction constant [36,38,40,57]. **F**<sub>C</sub> represents the conservative force arising from excluded volume interactions, Eq. (1), and bonding interactions, Eq. (2). **F**<sub>act</sub> is the active force applied on the beads. **F**<sub>R</sub> denotes the thermal noise with a magnitude of  $\sqrt{m\gamma k_B T}$ , where  $k_B$  and T are the Boltzmann constant and the temperature, respectively. The effects of inertia on the conformation and dynamics of polar active polymers were recently studied in detail by Fazelzadeh *et al.* [58]. Our results reveal that Langevin dynamics ( $\gamma = 1m/\tau_B$ , with  $\tau_B = \sqrt{m\sigma^2/\varepsilon}$  being the timescale of the Brownian motion of the monomer) yields essentially the same conclusions as overdamped Langevin dynamics ( $\gamma = 100m/\tau_B$ , Supplemental Fig. S1 [59]) regarding the head effect, while the computational cost of the former is over 2 orders of magnitude lower than that of the latter. The



FIG. 2. (a) Average radius of gyration  $\langle R_g \rangle$  as a function of activity Pe under different head activity strengths  $\kappa$ , where the gray dashed line represents the radius of gyration of passive polymers  $\langle R_{g,p} \rangle$ . (b) The Flory exponent  $\nu$  as a function of Pe. (c) The bond-vector correlation function  $C_b(n)$  for the passive polymer and active polymers under different  $\kappa$  values. (d) The persistence length  $L_p$  and (e) the negative correlation strength *h* obtained from  $C_b(n)$  as functions of Pe under different  $\kappa$  values.

Péclet number

$$Pe \equiv F_{act}b/(k_BT) \tag{6}$$

is introduced to quantify the overall activity of the polymer, where  $b \simeq \sigma$  is the equilibrated bond length. Without losing generality, we set  $F_{act}b = \varepsilon$  as the energy unit of the system, and adjust the Péclet number by changing the thermal energy  $k_BT$  [36,60]. The typical speed of active monomers is  $v_0 = F_{act}/\gamma$ , with  $\gamma$  being the friction coefficient, and the unit time of the system is chosen as  $\tau_0 = b/v_0$ . The velocity Verlet algorithm with a time step of  $\Delta t = 0.001\tau_0$  is used to integrate the equations of polymer motions. At least 160 separate simulations with sufficient time (at least  $20N\tau_0$ ) are performed for each parameter sequence. The control parameters of N, Pe, and  $\kappa$  are scanned in the range of  $40 \leq N \leq 2000, 0 \leq \text{Pe} \leq 500, \text{ and } 0 \leq \kappa \leq 1$ , respectively. All simulations are performed by a custom modified version of LAMMPS, and all visualizations are produced by OVITO.

### **III. RESULTS AND DISCUSSION**

#### A. Conformation of polar active polymers

To study the conformation of polymers, we calculate the gyration radius  $R_g$ ,

$$R_g = \frac{1}{N} \sqrt{\sum_{i=1}^{N} \sum_{j=i}^{N} \langle (\mathbf{r}_i - \mathbf{r}_j)^2 \rangle},$$
(7)

where *N* is the number of monomers, and  $\mathbf{r}_{i,j}$  denotes the position of the monomers. Figure 1(b) shows the probability

distribution of the radius of gyration  $P(R_g)$  for active polymers with various head activity under fixed Pe and N, where  $P(R_g)$ for passive polymers is also shown for comparison. In the absence of head activity ( $\kappa = 0$ ), we find strong activity-induced collapse of the polymer chain, consistent with previous studies [55,56]. However, with increasing head activity, the active polymer gradually swells and becomes even more expanded than the passive polymer.

In Fig. 2(a), we plot the average radius of gyration  $\langle R_g \rangle$ as a function of Pe under different  $\kappa$  values, where  $\langle R_{q,p} \rangle$  for passive polymers is drawn as a dashed line for comparison. For small head activity  $\kappa < 0.5$ , we find that  $\langle R_g \rangle$  shows a monotonic decrease with increasing Pe. Nevertheless, for large head activity, an unusual nonmonotonic behavior of  $\langle R_g \rangle$  is observed with a first-stage shrinkage when Pe  $\lesssim 10$ and late-stage expansion at large Pe. Additionally, the Flory exponent v is obtained through plotting  $\langle R_g \rangle$  as a function of N (see Supplemental Fig. S2 for more data [59]). In Fig. 2(b), we show  $\nu$  as a function of Pe under different  $\kappa$  values where the reference values of the random-walk chain ( $\nu = 0.5$ ) and the self-avoiding walk chain ( $\nu = 0.588$ ) are drawn as dashed lines. We find that under large head activity, v also exhibits a nonmonotonic variation with increasing Pe, which indicates a fundamental change of the fractal dimension of polymer configurations by head activity.

To explore these phenomena deeper, we calculate the bond-vector correlation function:

$$C_b(n) = \left\langle \frac{\mathbf{b}_i \cdot \mathbf{b}_{i+n}}{\mathbf{b}_i^2} \right\rangle,\tag{8}$$

where  $\mathbf{b}_i = \mathbf{e}_{i,i+1}$ . For typical semiflexible polymers,  $C_b(n)$ decays exponentially. The characteristic correlation length  $n^*$ at which  $C_b(n^*)$  decays to  $e^{-1}$  defines the persistence length  $L_p = n^* b$ . In Fig. 2(c), we plot  $C_b(n)$  for the passive polymer and active polymers with different  $\kappa$  values under fixed Pe. We find that compared with the passive polymer,  $C_b(n)$  for active polymers with small  $\kappa$  show a longer  $L_p$ , but with an anomalous negative correlation at intermediate length scale. This negative correlation indicates that the conformation of the active polymer has a strong inward curling tendency which is associated with the collapsed configuration. Nevertheless, this negative correlation is absent for passive polymers in bad solvent (Supplemental Fig. S3 [59]), which suggests a fundamental difference between these two systems, despite their apparent similarity. As  $\kappa$  grows, the persistence length increases significantly, with the negative correlation strength h decreasing rapidly to zero. Here, h is defined as the area ratio between negative and positive regions in correlation function. A large h signifies a more pronounced curling of the polymer chain. Thus, active polymers with large head activity exhibit conformational characteristics similar to those of semiflexible polymers. This emerging "dynamic rigidity" is a pure nonequilibrium effect, since the chain still remains mechanically flexible but exhibits apparently rigid configurations owing to the propelling force. Unlike semiflexible passive chains, this dynamic rigidity alone cannot predict the conformation of polymers. For example, Fig. 2(a) shows that even  $L_p$  is much larger than that of reference passive polymer;  $R_g$  is still smaller than  $R_{g,p}$  due to a large negative correlation in  $C_b(n)$ .

We summarize the behaviors of the persistence length  $L_p$ and h in Figs. 2(d) and 2(e), respectively. It can be observed that with increasing Pe,  $L_p$  remains at a low value and even decreases for polymers with small  $\kappa$ . In contrast, it rises significantly for polymers with large  $\kappa$ . Meanwhile, h increases monotonically at small  $\kappa$  but exhibits a strong nonmonotonic behavior at large  $\kappa$ . Therefore, the activity of a single head monomer determines the direction of the overall active forces acting on the chain: for small head activity, the total active driving is "inward", corresponding to a large h (small  $L_p$ ) and a collapsed state, while for large head activity, the total active force is "outward", corresponding to a large  $L_p$  (small h) and an expanded state.

#### B. Head-controlled railway motion

The above anomalous conformational behaviors have a deep connection with the dynamic motion of active polymers. Since the active propelling forces are along the chain's contour, the active polymer adopts *active reptation* motion, which is also referred to as "railway motion" because its behavior closely resembles that of a train moving along a railway [39] (see Supplemental Movies S1–S5 [59]). To quantify such motion, we define a correlation function of the head-tail position:

$$\Delta r_{\rm ht}^2(\Delta t) = \langle [\mathbf{r}_1(t) - \mathbf{r}_N(t + \Delta t)]^2 \rangle, \qquad (9)$$

where the angle brackets represent the time and ensemble average. For perfect railway motion,  $\Delta r_{ht}^2$  decays to zero at time  $\tau_{ht} \simeq Nb/v_0 = N\tau_0$  and bounces back, which is the time for the tail to reach the original position of the head. For pure diffusive dynamics,  $\Delta r_{\rm ht}^2$  will fluctuate around the polymer's mean squared end-to-end distance  $R_e^2 \equiv \langle (\mathbf{r}_N - \mathbf{r}_1)^2 \rangle$  with the diffusion of monomers and increase slightly with the diffusion of the polymer's center of mass. In Fig. 3(a), we plot  $\Delta r_{\rm ht}^2$  for passive polymers and active polymers with different  $\kappa$  values under fixed Pe, where we find for passive polymers  $\Delta r_{\rm ht}^2$  is nearly a flat line around  $R_e^2$ , indicating that the short time diffusion of the polymer's center of mass is negligible compared with  $R_e^2$ . For active polymers,  $\Delta r_{\rm ht}^2$  shows pronounced dips at the same  $\tau_{ht}$  independent of head activity. To quantify the deviation from the perfect railway motion, we further extract the minimal values of the correlation function of the head-tail position,  $\Delta r_{ht_min}^2 = \min[\Delta r_{ht}^2(\Delta t)]$ , and plot them as a function of Pe in Fig. 3(b). We find that  $\Delta r_{ht_min}^2$  decreases with increasing Pe and  $\kappa$ , which indicates that polymers with a higher head activity show relatively stronger railway motion.

For a perfect railway motion chain, the direction of the head monomer is the only degree of freedom that determines the chain conformation. This direction can be represented by the bond angle  $\theta$  between the first three monomers. In Fig. 3(c), we give the angle distribution  $P(\theta)$  for active polymers with different  $\kappa$  values along with the passive polymer under varying polymer lengths. We find that for the active polymer without head activity, the peak of  $P(\theta)$  locates at a small value around  $0.5\pi$ , indicating the averaged bent configuration of the polymer head. With increasing  $\kappa$ , the polymer head takes a more straight configuration. These results are independent of the polymer's length. Simple mechanical analyses in the inset of Fig. 3(c) and in the Appendix show that, when the propulsion force of the head monomer is smaller than that of the second monomer, the pushing force from the back will induce the bending of the polymer head (i.e., a smaller  $\theta$ ). One the contrary, when the propulsion force of the head monomer is large enough, the head monomer will pull the first three monomers straight (i.e., a larger  $\theta$ ). For railway motion chains,  $P(\theta)$  determines the bond angle distribution of the whole chain. Thus, an increasing average  $\theta$  corresponds to an increasing persistence length  $L_p$  and a decreasing curling degree h of polymer. In Fig. 3(d), we summarized the average value of  $\theta$ , which qualitatively agrees with the behavior of  $L_p$ and h in Figs. 2(d) and 2(e).

#### C. Dynamics of polar active polymers

To further explore the impacts of head activity on the dynamics of polar active polymers, we calculate the end-to-end vector correlation function,

$$C_{\rm ee}(t) = \frac{\mathbf{R}_{\mathbf{e}}(t_0) \cdot \mathbf{R}_{\mathbf{e}}(t_0 + t)}{\mathbf{R}_{\mathbf{e}}(t_0)^2},$$
(10)

and compare  $C_{ee}(t)$  of polymers with different head activity  $\kappa$  and polymer length N in Fig. 4(a). A surprising finding is that all  $C_{ee}(t)$  exhibit *linear* decay rather than exponential decay as for the passive polymer (Supplemental Fig. S4) [59,61,62]. Moreover, we find that  $C_{ee}(t)$  is insensitive to the head activity  $\kappa$  and the overall activity Pe but only depends on the chain length N. In Fig. 4(c), we plot the characteristic decay time  $\tau_{tr}$  of  $C_{ee}(t)$  [for active polymers  $C_{ee}(\tau_{tr}) = 0$ , while for passive polymers  $C_{ee}(\tau_{tr}) = 1/e$ ] as a function of



FIG. 3. (a) The correlation function of the head-tail position  $\Delta r_{ht}^2(\Delta t)$  for polymers with different head activity values, where the colored regions represent the error ranges. (b) The minimum value of  $\Delta r_{ht}^2$  as a function of Pe. (c) The probability distribution of the first angle  $P(\theta)$  normalized by  $\sin \theta/2$ , where the black dashed line represents  $P(\theta)/(\sin \theta/2) = 1$ . Insets: Schematic representation of the first angle  $\theta$  and a simple mechanical analysis. (d) Averaged  $\theta$  as a function of activity Pe, where the gray dashed line represents the averaged  $\theta$  of passive polymers.

*N*, we find all data from the active polymer falling around the line of  $\tau = N\tau_0$ . This behavior is also distinct from that of the passive polymer for which  $\tau_{tr} \propto N^2$ .

Such anomalous dynamics can be explained theoretically based on the railway motion of polymer chains. As shown in Fig. 4(b), assuming the initial ( $t_0 = 0$ ) and final configurations of the polymer on the same "railway" have an overlap part with end-to-end vector  $\mathbf{R}_2$ , we have  $\mathbf{R}_e(0) = \mathbf{R}_1 + \mathbf{R}_2$  and  $\mathbf{R}_e(t) = \mathbf{R}_2 + \mathbf{R}_3$ , where  $\mathbf{R}_1$  and  $\mathbf{R}_3$  are end-to-end vectors of the two nonoverlapped parts. Since the shape of the railway



FIG. 4. (a) The correlation function of end-to-end vector  $C_{ee}$  decays linearly with time. (b) A schematic representation of the railway motion. (c) The relaxation time of the end-to-end vector correlation function  $\tau_{tr}$  and the critical dynamic transition time  $\tau_R$  as functions of chain length. The solid line is a guide for the eyes and the dashed line represents  $\tau = N\tau_0$ .



FIG. 5. (a) The mean squared displacement of the polymer's center of mass MSD(t), where solid lines are linear fitting at different dynamic regimes and dashed lines indicate the critical MSD\* and  $\tau_R$ . (b) MSD\* and  $R_e^2$  as functions of chain length N. (c) The diffusion coefficient D and  $R_e^2/6N\tau_0$  as functions of  $\kappa$  under different polymer lengths.

closely resembles that of a three-dimensional self-avoiding random walk, the correlations among  $\mathbf{R}_1$ ,  $\mathbf{R}_2$ , and  $\mathbf{R}_3$  can be neglected, i.e.,  $\langle \mathbf{R}_i \cdot \mathbf{R}_j \rangle \simeq 0$  for  $i \neq j$ . Combining the nearly linear dependence of  $\mathbf{R}_e^2$  on N shown in Fig. 5(b), one can get

$$C_{\rm ee}(t) \simeq \frac{\mathbf{R}_2^2}{\mathbf{R}_{\rm e}(0)^2} \sim \frac{N - \frac{v_0 t}{b}}{N} = 1 - \frac{t}{N\tau_0}, \quad t < N\tau_0, \quad (11)$$

which suggests  $\tau_{tr} = N\tau_0$ . Note that this result is independent of the shape of the railway controlled by the head activity.

The railway motion also results in interesting polymer diffusion dynamics. Starting from the railway motion hypothesis in Fig. 4(b), one can get the expression of the center of mass of the polymer as

$$\mathbf{r}_{\rm cm}(0) = \frac{1}{N} \sum_{i=1}^{N} \mathbf{r}_i, \quad \mathbf{r}_{\rm cm}(t) = \frac{1}{N} \sum_{i=t}^{N+t} \mathbf{r}_i.$$
(12)

Here,  $\mathbf{r}_i$  is the local "trail" vector in the sequence of i = 1, 2, ..., N. When  $t < N\tau_0$ , the displacement of the center of mass could be rewritten as

$$\Delta \mathbf{r}_{\rm cm}(t) = \mathbf{r}_{\rm cm}(t) - \mathbf{r}_{\rm cm}(0) = \frac{1}{N} \sum_{i=1}^{I} (\mathbf{r}_{N+i} - \mathbf{r}_i).$$
(13)

Using an approximation of  $\mathbf{r}_{N+i} - \mathbf{r}_i \approx \mathbf{R}_{\mathbf{e}}(i)$  and considering continuous motion, we get

$$\Delta \mathbf{r}_{\rm cm}(t) \simeq \frac{1}{N} \sum_{i=1}^{t} \mathbf{R}_{\mathbf{e}}(i) = \frac{1}{N\tau_0} \int_0^t \mathbf{R}_{\mathbf{e}}(t_1) dt_1.$$
(14)

Thus, the mean square displacement (MSD) of the polymer's center of mass has the formation of

$$MSD(t) \equiv \Delta \mathbf{r}_{cm}^{2}(t)$$
$$\simeq \frac{1}{N^{2}\tau_{0}^{2}} \int_{0}^{t} \int_{0}^{t} \mathbf{R}_{\mathbf{e}}(t_{1}) \mathbf{R}_{\mathbf{e}}(t_{2}) dt_{1} dt_{2}.$$
(15)

Based on the linear decay of  $C_{ee}$  [Eq. (11)], the only contribution of the above integration is when  $|t_2 - t_1| \leq N\tau_0$ . Thus, we have

$$MSD(t) \simeq \frac{1}{N^{2}\tau_{0}^{2}} \int_{0}^{t} \int_{\max(t_{1}-N\tau_{0},t)}^{\min(t_{1}+N\tau_{0},t)} \mathbf{R}_{\mathbf{e}}^{2}(t_{1})C_{\mathrm{ee}}(|t_{2}-t_{1}|)dt_{1}dt_{2}$$
$$= \frac{2}{N^{2}\tau_{0}^{2}} \int_{0}^{t} \int_{t_{1}}^{\min(t_{1}+N\tau_{0},t)} \mathbf{R}_{\mathbf{e}}^{2}(t_{1})C_{\mathrm{ee}}(t_{2}-t_{1})dt_{1}dt_{2}, \quad (16)$$

where the last step is based on the symmetry of the integration. In the long-time limit  $t \gg N\tau_0$ , the main contribution of the above integration comes from the case of  $\min(t_1 + N\tau_0, t) = t_1 + N\tau_0$ . Thus,

$$MSD(t) \simeq \frac{2}{N^{2}\tau_{0}^{2}} \int_{0}^{t} \int_{t_{1}}^{t_{1}+N\tau_{0}} \mathbf{R}_{\mathbf{e}}^{2}(t_{1}) \left(1 - \frac{t_{2} - t_{1}}{N\tau_{0}}\right) dt_{1} dt_{2}$$
$$= \frac{2}{N^{2}\tau_{0}^{2}} \int_{0}^{t} \mathbf{R}_{\mathbf{e}}^{2}(t_{1}) \frac{N\tau_{0}}{2} dt_{1} \simeq \frac{R_{e}^{2}}{N\tau_{0}} t, \quad t \gg N\tau_{0},$$
(17)

where the last step is based on the approximation  $\mathbf{R}_{e}^{2}(t_{1}) \simeq R_{e}^{2}$  since  $\mathbf{R}_{e}^{2}(t_{1})$  is randomly fluctuated around the averaged mean-squared end-to-end distance  $R_{e}^{2}$ . In the short-time limit  $t \ll N\tau_{0}$ , we have

$$MSD(t) \simeq \frac{2}{N^{2}\tau_{0}^{2}} \int_{0}^{t} \int_{t_{1}}^{t} \mathbf{R}_{\mathbf{e}}^{2}(t_{1}) \left(1 - \frac{t_{2} - t_{1}}{N\tau_{0}}\right) dt_{1} dt_{2}$$
$$= \frac{2}{N^{2}\tau_{0}^{2}} \int_{0}^{t} \int_{0}^{t_{1}} \mathbf{R}_{\mathbf{e}}^{2}(t_{1}) \left(1 - \frac{t_{1} - t_{2}}{N\tau_{0}}\right) dt_{1} dt_{2}$$
$$\simeq \frac{2R_{e}^{2}}{N^{2}\tau_{0}^{2}} \left(\frac{t^{2}}{2} - \frac{t^{3}}{6N\tau_{0}}\right), \quad t \ll N\tau_{0}.$$
(18)

In summary, we have

$$\operatorname{MSD}(t) \simeq \begin{cases} \frac{R_e^2}{N^2 \tau_0^2} t^2, & t \ll N \tau_0, \\ \frac{R_e^2}{N \tau_0} t, & t \gg N \tau_0. \end{cases}$$
(19)

Equation (19) predicts a ballistic dynamics regime (MSD ~  $t^2$ ) and a diffusion dynamics regime (MSD ~ t) separated by the characteristic time  $\tau_R = N\tau_0$  and the characteristic MSD<sup>\*</sup>( $\tau_R$ )  $\simeq R_e^2$ . In Fig. 5(a) and Supplemental Fig. S5, we plot the MSD(t) for active polymers with different  $\kappa$  values, where the reference MSD(t) of the passive polymer is shown in gray. We find that the simulation results agree well with our theoretical prediction. Especially, MSD<sup>\*</sup>( $\tau_R$ ) matches with  $R_e^2$ excellently when varying the head activity and the polymer length [see Fig. 5(b)]. Furthermore, based on the Stokes-Einstein relation MSD = 6Dt and Eq. (19), we can obtain the diffusion coefficient

$$D = \frac{R_e^2}{6N\tau_0}.$$
 (20)

Since  $R_e^2 \sim N$ , the diffusion coefficient is independent of the chain length, which is in contrast with the behavior of the classical Rouse chain  $D \sim \frac{1}{N}$  [63] and consistent with previous work [55]. These predictions are also confirmed by the simulation results shown in Fig. 5(c) and Supplemental Fig. S6, at which D is independent of N and matches with  $R_e^2/6N\tau_0$  very well under different  $\kappa$  values. Moreover, from Fig. 5(c), one can see that the conformation and the dynamics are coupled: the diffusion coefficient of an extended active polymer with large head activity can be an order of magnitude larger than the collapsed active polymer with small head activity. Finally, we emphasize another scaling relation in Eq. (20),  $D \sim \tau_0^{-1}$ . Since  $\tau_0$  is defined as  $\tau_0 = b/v_0$ , with  $v_0 = F_{act}/\gamma$ , we have  $D \sim F_{act}$ , which provides a connection between the dynamics and the activity force. This correlation has been a subject of continuous debate and contention in the literature [37,55,64]. The dynamic theory developed here is based on railway motion, hence it is valid for all polar active polymers exhibiting railway motion, regardless of the model (Supplemental Fig. S7 [59]). This provides us an efficient way to control the conformation and dynamics of active polymers, which may have application values in drug delivery and biomedical engineering [57,65,66]. We also notice that recently Philipps et al. conducted an analytical study on polar active polymers, which reports dynamic equations similar to Eq. (20) [67].

#### **IV. CONCLUSION**

In conclusion, we find a general nonequilibrium mechanism that head activity commands the overall active forces on the polar active polymer performing railway motion, which leads to unusual conformational and dynamic behaviors of the polymer chain. We demonstrate that the low head activity favors a bent head configuration, which causes a pronounced curling and collapsing conformation of the polymer chain, while the high head activity helps the polymer straighten its head, resulting in an emerging "dynamic rigidity" and more extended chain conformations. The competition between the two nontrivial nonequilibrium effects leads to the re-entrant swelling of polar active polymers and nonmonotonic variation of the Flory exponent  $\nu$ . We also find many interesting dynamic features for polar active polymers, such as a linear decay of the end-to-end vector correlation function  $C_{ee}$ , a polymer-size-dependent crossover from ballistics to diffusion dynamics, as well as a length-independent diffusion coefficient controlled by the head activity. All these features are explained well by our dynamic theory. Our findings are not only meaningful for understanding the conformational and dynamic behaviors of complicated active polymer aggregations but are also suggestive for designing efficient polymer-based drug delivery systems. In this work, the hydrodynamic interactions (HIs) are not considered because the unique railway motion pattern of polar active polymers allows them to exhibit a qualitatively similar behavior regardless of the presence or absence of HIs [68,69]. Nevertheless, how this effect modifies the results of this work needs further investigation.

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FIG. 6. A stability analysis based on polymer configuration with infinitesimal curvature. (a) The stable state in which polymers have perfect circular motion with constant curvature. The velocity of each monomer is along with the contour direction. (b) The polar active polymer with head velocity  $\mathbf{v}_1$  aligned with the bond vector  $\mathbf{r}_{1,2}$ , which generates a velocity component perpendicular to the polymer contour and changes the curvature. (c, d) The distributions of relative velocities compared with the reference state when  $\kappa$  deviates from 1. When  $\kappa < 1$ , the relative velocity of the first monomer is backward and the perpendicular component is inward, which increases the head curvature leading to the curling of the polymer configuration. When  $\kappa > 1$ , the relative velocity of the first monomer is forward and the perpendicular component is outward, which decreases the head curvature.

## APPENDIX: STABILITY ANALYSIS OF POLYMER CONTOUR

A simple stability analysis can help us understand the determining factors of polymer collapse or expansion. As shown in Fig. 6(a), when the velocities of all monomers, including the first one, are aligned with their contour direction  $\mathbf{e}_{i-1,i+1}$ (blue vectors), the polymer is in a steady state with constant local curvature represented by the dashed line. This state with infinitesimal head curvature is the reference state for our stability analysis. For our polar active polymer model, the head velocity  $\mathbf{v}_1$  [green arrow in Fig. 6(b)] is aligned with the bond vector  $\mathbf{r}_{1,2}$ . Comparing with the reference state, there is an additional relative velocity component perpendicular to the contour direction for polymers with  $\kappa = 1$ . This reduces the head curvature as shown by the red arrow in Fig. 6(b). Moreover, the additional change of the head curvature also comes from the deviation of  $\kappa$  from 1, which leads to the

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bond stress/tension between the first and second monomers. As shown in Fig. 6(c), when  $\kappa < 1$ , the first monomer is decelerated compared with the reference state; this results in the backward relative velocity  $\Delta \mathbf{v}_1$  of the first monomer compared with the reference state. This relative velocity generates inward motions of the first monomer [i.e.,  $\Delta \mathbf{v}_{1,\perp}$  in Fig. 6(c)] and reduces the head curvature of the polymer. Therefore, under  $\kappa < 1$  (especially for passive head monomers,  $\kappa = 0$ ), the straight or expanded polymer conformation is unstable since any fluctuation of curvature will be amplified and lead to the curling of the polymer configuration. On the contrary, when  $\kappa > 1$  [Fig. 6(d)], the direction of  $\Delta \mathbf{v}_1$  is reversed, which reduces the head curvature by the generation of outward motions of the first monomer, i.e.,  $\Delta \mathbf{v}_{1,\perp}$  in Fig. 6(d). Thus, the straight conformation is a stable state and the polymer will stay in an extended state. These effects will be transmitted along the contour to the remaining monomers  $(2, 3, 4, \ldots)$ .

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