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Memory effect and fluctuating anomalous dynamics of a tagged monomer

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We analyze the anomalous dynamics of a tagged monomer under external navigation. The memory effect causing the anomaly is elucidated, which depends on the magnitude of the force. In particular, the nonlinear and nonequilibrium memory effect under strong force is characterized by the force-dependent self-affine process for the tension transmission along the connectivity. Utilizing such knowledge, a generalized Langevin equation approach is proposed to quantify the fluctuating dynamics of driven anomalous walkers.

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The connectivity and resultant large internal degrees of freedom are intrinsic characteristics of polymers, which have a number of consequences on their dynamical properties. A nontrivial example is already found in the motion of a tagged monomer. It has been long known that, unlike an unconnected simple particle, the diffusion of the tagged monomer is anomalous; its mean square displacement scales as $t^{2\alpha}$ with $2\alpha < 1$ up to a terminal time $\tau_{\rm eq}$ [1,2]. Recently, Panja has suggested a generalized Langevin equation (GLE) approach to the problem, where the memory kernel, derived from the stress relaxation after step strain, and the colored noise are related via the fluctuation-dissipation theorem (FDT) [3].

From a broader perspective, the motion of a tagged monomer is regarded as belonging to a class of stochastic processes in which the anomaly originates from the memory built by the superposition of modes with widely separated time scales [4,5]. Such a situation naturally arises in the connected systems; yet another important example can be found in the fluctuation of equilibrium and growing interfaces [6,7], where the term "monomer" may be used to designate one part of the spatially extended system. In this paper, we wish to address the fluctuating dynamical response of a tagged monomer, i.e., a fundamental question one encounters when trying to escort such an anomalous walker.

To reveal the underlying physics causing the memory effect, we look at the evolution of the tension front, i.e., how the force guiding a tagged monomer is transmitted through the connectivity. For weak enough forces, the linear response theory provides a general answer. However, much less is known about the motion of the tagged monomer guided by stronger forces. Here, more dramatic dynamics, including intense morphological evolution and fluctuating nonequilibrium behaviors, are expected, where nonlinear effects inherent to polymers may set in. Elucidating the memory effect in such situations is required in various sectors of polymer and nanobiological sciences, hence it is regarded as an important challenge. As we shall see, the onset of the strong driving is identified as a qualitative change in the dynamical scaling governing the force transmission.

We start with a microscopic model of polymers and derive a GLE for a tagged monomer. Apart from being a slight generalization of the Rouse model result in Ref. [3], this exercise discloses the limit of the equilibrium approach and at the same time provides a hint to broaden the use of the GLE beyond the ordinary linear response regime.

Consider the motion of a tagged monomer in a polymer chain (with N monomers of size a). Its mathematical description depends on the time resolution of the observation. To see the point, let us define the characteristic times $\tau_0 \simeq \gamma a^2/k_BT$ and $\tau_{\rm eq} \simeq \tau_0(R_{\rm eq}/a)^z \simeq \tau_0 N^{\nu z}$, where γ and k_BT are the friction coefficient of individual monomers and the thermal energy, respectively, and $R_{\rm eq} \simeq aN^\nu$ is the equilibrium coil size. While the first is the microscopic (the monomer scale) time, the second is the terminal (longest relaxation) time of the system, where ν and z are as usual the static (Flory) and dynamical critical indices, respectively [8]. In the standard approach, the microscopic state of the polymer is specified by the position vectors of beads $\{\vec{x}_n(t)\}$ $(n = 0 \sim N)$ and their dynamics is governed by a coupled Langevin equation for all of them. The use of white noise there is based on the separation of the time scale; while we are interested in phenomena coarser than the time resolution τ_0, solvent degrees freedom relax to equilibrium on a much faster time scale.

Now let us tag a monomer at the chain end and follow its trajectory $\vec{x}(t) = \vec{x}_0(t)$. To obtain a closed equation for the tagged monomer only, we need to eliminate all the other monomers' degrees of freedom. This makes the stochastic motion of the tagged monomer a non-Markovian process. The Markovian description is recovered only in a time resolution coarser than $\tau_{\rm eq}$. Therefore, for long polymers ($N \gg 1$), there is an abundant time window for the anomalous dynamics, which is described by the following equation

$$\vec{v}(t) = \int_{-\infty}^{t} ds\, \mu_m(t-s)\vec{f}(s) + \vec{\eta}(t), \tag{1}$$

where $\vec{v}(t) = d\vec{x}(t)/dt$, $\mu_m(t)$ is a mobility kernel, and $\vec{f}(t)$ is an external force acting on the tagged monomer. The random force $\vec{\eta}(t)$ satisfies $\langle\overline{\eta_\alpha(t)}\rangle = 0$ and its autocorrelation is related to the kernel via FDT $\langle\overline{\eta_\alpha(t)\eta_\beta(s)}\rangle = k_BT\mu_m(t-s)\delta_{\alpha\beta}$, where the averaging operations, denoted by $\langle\cdots\rangle$ and $\overline{\cdots}$, are taken over the stochastic noise realizations and the initial configurations of the polymer at $t = -\infty$, respectively.

To derive Eq. (1) from a microscopic polymer model, we adopt the "creep" protocol in which one monitors the time course of the velocity $\vec{v}(t)$ of the tagged monomer

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upon switching on the force at $t = 0$, i.e., $\vec{f}(t) = 2\vec{f}\delta(n)u(t)$, where $u(t) = 1$ for $t > 0$ and $u(t) = 0$ for $t < 0$. Assuming that the chain conformation is not severely distorted during the operation process, the long-range excluded-volume (EV) and hydrodynamic interactions (HIs) are taken into account through the preaveraging approximation with the equilibrium monomer distribution [9]. By introducing the normal coordinate $\vec{X}_p(t) = N^{-1}\int_0^N dn \cos(pn\pi/N)\vec{x}_n(t)$ for $p = 0,1,\ldots$, the equation of motion in the normal coordinate space reads

$$\gamma_p \frac{\partial \vec{X}_p}{\partial t} = -k_p \vec{X}_p + \vec{g}_p + \vec{f}_p \quad (p = 0, 1, \ldots), \tag{2}$$

with the friction and spring constants $\gamma_p \simeq \gamma N^{\nu(z-2)}/(p^{\nu(z-2)-1} + \delta_{p0})$ and $k_p \simeq k_B T p^{1+2\nu}/a^2 N^{2\nu}$. The random force $\vec{g}_{p\alpha}(t)$ satisfies $\langle g_{p\alpha}(t)\rangle = 0$ and $\langle g_{p\alpha}(t) g_{q\beta}(t')\rangle = 2\gamma_p k_B T \delta_{pq}\delta_{\alpha\beta}\delta(t-t')$ [10]. The external force $\vec{f}$ acting on the end monomer is distributed in the normal coordinate space according to $\vec{f}_p(t) = 2/(1+\delta_{p0})u(t)\vec{f}$ [9,11].

For $p \geqslant 1$ and $t > 0$, Eq. (2) is solved as

$$\vec{X}_p(t) = \frac{2\vec{f}}{k_p} + \left(\vec{X}_p(0) - \frac{2\vec{f}}{k_p}\right)\exp\left(-\frac{k_p}{\gamma_p}t\right) + \gamma_p^{-1}\int_0^t \exp\left(-\frac{k_p}{\gamma_p}(t-t')\right)\vec{g}_p(t')dt'. \tag{3}$$

Upon time derivative and returning to the real coordinate, one can identify the elements in Eq. (1) as

$$\mu_m(t) = -\frac{2}{\gamma\tau_0 N^{2\nu(z-1)}}\sum_{p=1} p^{2\nu(z-1)-1} e^{(-t/\tau_{\rm eq})p^{\nu z}}, \tag{4}$$

$$\eta(t) = -2\sum_{p=1}\frac{p^{\nu z}}{\gamma_p \tau_{\rm eq}}\int_0^t e^{\{(t-t')/\tau_{\rm eq}\}p^{\nu z}}\vec{g}_p(t')dt' - 2\sum_{p=1}\frac{p^{\nu z}}{\tau_{\rm eq}}\vec{X}_p(0)e^{-(t/\tau_{\rm eq})p^{\nu z}} + 2\sum_{p=1}\frac{1}{\gamma_p}\vec{g}_p(t). \tag{5}$$

By invoking the initial equilibrium distribution $\overline{X_{p\alpha}(-\infty)} = \overline{X_{p\alpha}(0)} = 0$ and $\overline{X_{p\alpha}(0)X_{q\beta}(0)} = (k_B T/k_p)\delta_{pq}\delta_{\alpha\beta}$ [9], the desired FDT relation follows, which ensures the thermalization of the tagged monomer's degrees of freedom. Replacing the summation in Eq. (4) by the integral, we obtain the power-low memory kernel

$$\mu_m(t) \simeq -\frac{1}{\gamma\tau_0}\left(\frac{t}{\tau_0}\right)^{2(z^{-1}-1)}, \tag{6}$$

where the negative sign indicates the anticorrelation of the temporal noise $\eta(t)$. Together with Eq. (1), the anomalous exponent is identified as $\alpha = 1/z$. In the presence of the guiding force, one finds the average drift

$$\frac{\langle\overline{\Delta\vec{x}(t)}\rangle}{a} \simeq \left(\frac{\vec{f}a}{k_B T}\right)\left(\frac{t}{\tau_0}\right)^{2\alpha} \tag{7}$$

and the fluctuation around it

$$\frac{\langle\overline{[\delta\Delta\vec{x}(t)]^2}\rangle}{a^2} \simeq \left(\frac{t}{\tau_0}\right)^{2\alpha}, \tag{8}$$

where $\Delta\vec{x}(t) = \vec{x}(t) - \vec{x}(0)$ and $\delta\Delta\vec{x}(t) = \Delta\vec{x}(t) - \langle\overline{\Delta\vec{x}(t)}\rangle$. Such an anomalous dynamics persists up to the terminal time $\tau_{\rm eq}$, after which the normal drift and diffusion around it follow with the average velocity $\langle\overline{\vec{v}(t)}\rangle \simeq \vec{f}_{\rm ex}/\gamma N^{\nu(z-2)}$ and the diffusion coefficient $\simeq k_B T/\gamma N^{\nu(z-2)}$, respectively.

What about the tension transmission? At $t < \tau_{\rm eq}$, only some of the monomers $M(t) < N$ close to the guided monomer are under the influence of the force, while other $N - M(t)$ monomers in the rear are still beyond the tension front. The force balance equation $\gamma M(t)^{\nu(z-2)}\langle\overline{v(t)}\rangle \simeq f$ leads to the evolution of the tension front in the internal coordinate as $M(t) \simeq (t/\tau_0)^{1/\nu z}$. The corresponding physical distance coincides with the diffusion length of the tagged monomer

$$R(t) \simeq a(t/\tau_0)^{\alpha} \simeq \sqrt{\langle\overline{[\delta\Delta\vec{x}(t)]^2}\rangle}. \tag{9}$$

The following two points should be noted: (i) Eq. (9) can be cast into the so-called Family-Vicsek scaling form $R(t) \sim R_{\rm eq}\mathcal{F}_{\rm eq}(t/\tau_{\rm eq})$ with a scaling function $\mathcal{F}_{\rm eq}(u) \sim u^{\alpha}$ for $u \ll 1$ [12]. Thus it naturally follows from the hypothesis that the tension propagation is a self-affine process along with the relations $R_{\rm eq} \simeq aN^{\nu}$ and $\tau_{\rm eq} \simeq \tau_0 N^{\nu z}$. (ii) In a Rouse model ($\nu = 1/2$, $z = 4$), the tension is diffusively transmitted along the internal coordinate. The EV [$z = (2\nu+1)/\nu$ with $\nu > 1/2$] or HI ($z = 3$) alters it in opposite ways, making it a subdiffusive or superdiffusive process, respectively.

So far, our derivation of the memory kernel relies on the assumption that the chain conformation is described by the equilibrium monomer distribution during the whole process. This, however, breaks down when the guiding force exceeds the threshold $f > f^* \simeq k_B T/R_{\rm eq}$, making the preaveraging scheme unavailable and thus the microscopic derivation of the GLE for the motion of a tagged monomer elusive. However, a close inspection of the above derivation indicates that it is the local equilibration of the tagged monomer's degrees of freedom, but not the global equilibration of the system, that, combined with its linear response property, is essential for the GLE formalism.

For $f > f^*$, one may generalize the anomalous drift and diffusion relations (7) and (8) as

$$\frac{\langle\overline{\Delta x(t)}\rangle}{a} \simeq \left(\frac{fa}{k_B T}\right)^{\beta_1}\left(\frac{t}{\tau_0}\right)^{2\alpha_1}, \tag{10}$$

$$\frac{\langle\overline{[\delta\Delta x(t)]^2}\rangle}{a^2} \simeq \left(\frac{fa}{k_B T}\right)^{\beta_2}\left(\frac{t}{\tau_0}\right)^{2\alpha_2}, \tag{11}$$

with the possible nonlinear effect through the exponents β_i ($i = 1,2$). To derive these anomalous exponents α_i and β_i in terms of the memory effect, one needs to analyze the dynamical behaviors of the whole chain. Note first that the chain initially at rest cannot follow the tagged monomer while keeping its equilibrium conformation, thus entailing the strong deformation [11,13,14]. To get the onset of this nonequilibrium dynamics, let us assume that M_f monomers initially follow the driving force $\vec{f}$ by keeping the equilibrium size $R_f \simeq aM_f^{\nu}$ with the average velocity $\vec{v}_f \simeq \vec{f}/\gamma M_f^{\nu(z-2)}$. For the argument to be consistent, the shear rate in the spatial domain of size R_f should be smaller than the relevant relaxation rate. We thus find $\tau_0 M_f^{\nu z} v_f/R_f \simeq 1 \Leftrightarrow R_f \simeq k_B T/f$. For $R_f < R_{\rm eq} \Leftrightarrow f > f^* \simeq k_B T/R_{\rm eq}$, the equilibrium treatment is valid only up to the time

$$\tau_{0f} \simeq \tau_0 M_f^{\nu z} \simeq \tau_0 (fa/k_B T)^{-z}. \tag{12}$$

From then on, the progressive conformational deformation process sets in toward the global steady state, which is characterized by the longitudinal length $R_{ss} \sim N f^{(1-\nu)/\nu}$ and the velocity $v_{ss} \sim f^{z-2}/R_{ss}$ [11,15].

At time $t > \tau_{0f}$, $M(t)$ ($>M_f$) anterior monomers constitute the responding domain assuming an instantaneous steady-state conformation with longitudinal length $R(t)$ and the moving velocity $v(t) \simeq dR(t)/dt$. The growth of $M(t)$ with time is identified as the evolution of the tension front, which in turn operates as a memory effect for the motion of the tagged monomer. The above view of the growing moving domain provides the following construction of the dynamical scaling, for which one may apply the steady-state friction and extensional laws to the moving domain:

$$\frac{R(t)}{a}\frac{v(t)\tau_0}{a} \simeq \left(\frac{fa}{k_BT}\right)^{z-2}, \qquad \frac{R(t)}{a} \simeq M(t)\left(\frac{fa}{k_BT}\right)^{(1-\nu)/\nu}. \tag{13}$$

This leads us to identify the exponents $\alpha_1 = 1/4$ and $\beta_1 = (z-2)/2$ with the "force-dependent" self-affine growth law for the tension front

$$R(t) \simeq a\left(\frac{fa}{k_BT}\right)^{(z-2)/2}\left(\frac{t}{\tau_0}\right)^{1/2} \tag{14}$$

and the terminal time

$$\tau_{ss} \simeq \left(\frac{fa}{k_BT}\right)^{(2/\nu)-z} N^2 \tag{15}$$

at which the tension reaches the rear end and thus the polymer attains the global steady-state conformation in compliance with the guiding force. At $t > \tau_{ss}$, the drift becomes normal with $d\langle\overline{\Delta x(t)}\rangle/dt = v_{ss}$. Equations (14) and (15) together with the steady-state extension R_{ss} given below Eq. (12) constitute the Family-Vicsek scaling [12] $\langle\overline{\Delta x(t)}\rangle \sim R(t) \sim R_{ss}\mathcal{F}(t/\tau_{ss})$ with a scaling function $\mathcal{F}(u) \sim u^{1/2}$ for $u \ll 1$ to characterize the self-affinity of the nonequilibrium tension transmission process.

To derive the diffusion exponents α_2 and β_2 one notes that the frictional response is generally nonlinear, i.e., $\beta_1 \neq 1$. We thus extend Eq. (1) as

$$\delta_\epsilon \vec{v}(t;\vec{f}) = \epsilon \int_{-\infty}^{t} ds\, \mu_m(t-s;f)\vec{f}(s) + \vec{\eta}(t;f), \tag{16}$$

where $\delta_\epsilon \vec{v}(t;\vec{f}) = \vec{v}(t;\vec{f}(1+\epsilon)) - \vec{v}(t;\vec{f})$ and $\epsilon\vec{f}$ (with $\epsilon \ll 1$) is an additional small force to probe the linear response property of the driven tagged monomer around its dynamical average state. The nonlinear mobility kernel $\mu_m(t;f)$ now depends on the guiding force, which can be obtained as

$$\mu_m(t;f) \simeq -\frac{1}{\gamma\tau_0}\left(\frac{fa}{k_BT}\right)^{\beta_1-1}\left(\frac{t}{\tau_0}\right)^{2(\alpha_1-1)}. \tag{17}$$

Despite the nonequilibrium conformation of the entire polymer, the local relaxation of the tagged monomer is achieved on much faster time scale. This fact is in fact implicit in the above derivation of the memory kernel in conformity with the growing steady-state domain. This indicates that the FDT relating the noise intensity to the mobility is still valid to ensure the local relaxation of the tagged monomer's degrees of freedom to the instantaneous steady-state within our time resolution. Therefore, we have $\langle\eta_\alpha(t;f)\eta_\beta(s;f)\rangle = k_BT\mu_m(t-s;f)\delta_{\alpha\beta}$ and hence the GLE formalism to describe the fluctuation of the tagged monomer around the average dynamics, leading to the identifications $\alpha_2 = \alpha_1$ and $\beta_2 = \beta_1 - 1$.

We now discuss the preceding results: (i) First, let us check the dynamical crossover and associated time scales emerging from the present theory. Upon comparing the drift [Eqs. (7) and (10)] with the diffusion [Eqs. (8) and (11)], we again find the characteristic time τ_{0f} [Eq. (12)], which separates the diffusion dominating equilibrium dynamics $\sqrt{\langle\overline{[\delta\Delta x(t)]^2}\rangle} \simeq R(t) > \langle\overline{\Delta x(t)}\rangle$ at $t < \tau_{0f}$ and the drift dominating nonequilibrium dynamics $\langle\overline{\Delta x(t)}\rangle \simeq R(t) > \sqrt{\langle\overline{[\delta\Delta x(t)]^2}\rangle}$ at $t > \tau_{0f}$. In approaching the weak force limit $f \to f^*$, two characteristic time scales converge to the equilibrium terminal time, i.e., τ_{0f}, $\tau_{ss} \to \tau_{\rm eq} \simeq \tau_0(R_{\rm eq}/a)^z$, ensuring the correct crossover to the near-equilibrium regime discussed earlier. (ii) A Rouse model is special in that the superficial response behaviors remain the same across $f = f^*$, i.e., $\alpha = \alpha_1 = \alpha_2 = 1/4$, $\beta_1 = 1$, and $\beta_2 = 0$. The reason of course lies in the strict linearity of the Rouse model. However, a qualitative change in the underlying physics shows up, as evidenced by the crossover from diffusive to driven tension transmissions. The latter is accompanied by the progressive morphological evolution, signaling the nonequilibrium dynamics. The same remark applies also to the fluctuation of interfaces. (iii) For long chains ($N \gg 1$) driven by moderate forces $f^* \ll f \ll k_BT/a$, there is a wide time window $\tau_0 < t < \tau_{0f} < \tau_{ss}$ during which the fluctuations play a major role.

To summarize, we have clarified a link between equilibrium and nonequilibrium memory effects causing anomalous dynamics in a class of stochastic processes. The physical origin of the memory is the self-affine tension transmission process through the connectivity. While in near equilibrium the growth of the tension front is controlled by the dynamic exponent z, its scaling behavior qualitatively changes in the nonequilibrium regime. In polymers, this entails the nonlinear force dependence in the growth law due to the EV and/or HIs. The GLE approach is proposed to be useful to describe the fluctuating dynamics of such strongly driven anomalous walkers. We hope that the present study will stimulate a range of related fields by providing a fresh viewpoint from which to analyze nonequilibrium memory effects. For instance, its application to various dynamical processes, e.g., the surface growth [6,7], the zipping of two strands [16], and the polymer detachment from absorbing surfaces [17], is an interesting challenge, where the role of fluctuations is expected to be important if driven by moderate forces. Among others, the polymer translocation across a pore would be a good candidate, which is currently a subject of interdisciplinary research. Indeed, the fluctuation effect in the driven translocation is one of the latest topics under debate [18–21].

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