Supplementary material for Dynamics of active Rouse chains

Dino Osmanović[1] and Yitzhak Rabin[1]

Department of Physics, and Institute of Nanotechnology and Advanced Materials,
Bar-Ilan University, Ramat Gan 52900, Israel

(Dated: 5 January 2017)

I. DERIVATION

For a generic noise:

$$\langle A_p(t) \rangle = 0 \tag{1.1}$$

$$\langle \widetilde{A}_p(t) \widetilde{A}_q(t') \rangle = B(t - t') I(p, q) \tag{1.2}$$

For a general form of the active noise the center of mass motion of the the polymer is given by the contribution of the zeroth Rouse mode,

$$\langle R_{CM}^2(t) \rangle = \langle (X_0(t) - X_0(0))^2 \rangle = \frac{6 k_b T}{N \gamma} t + \frac{1}{\gamma^2} I(0,0) \int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 B(t_1 - t_2) \tag{1.3}$$

where the first term is familiar from the standard Rouse model, and the second term is a correction due to the active kicks. Using the fact that the monomer position is given in terms of the Rouse modes by:

$$R_n(t) = X_0(t) + 2 \sum_{p=1}^{\infty} X_p(t) \cos\left(\frac{p \pi n}{N}\right) \tag{1.4}$$

then the diffusion of a labeled monomer is given by:

$$\begin{aligned} \langle (R_n(t) - R_n(0))^2 \rangle \equiv g_1^{(n)}(t) = {} & \langle R_{CM}^2(t) \rangle \\ & + 4 \sum_{p=1}^{\infty} \left(2 \langle X_0(t) X_p(t) \rangle - \langle X_0(0) X_p(t) \rangle - \langle X_0(t) X_p(0) \rangle \right) \cos\left(\frac{p \pi n}{N}\right) \\ & + 8 \sum_{p=1}^{\infty} \sum_{q=1}^{\infty} \left(\langle X_p(t) X_q(t) \rangle - \langle X_p(t) X_q(0) \rangle \right) \cos\left(\frac{p \pi n}{N}\right) \cos\left(\frac{q \pi n}{N}\right) \end{aligned} \tag{1.5}$$

All of these correlation functions between different modes can be written down:

$$\begin{aligned} & 2 \langle X_0(t) X_p(t) \rangle - \langle X_0(0) X_p(t) \rangle - \langle X_0(t) X_p(0) \rangle = \\ & + \frac{2}{\gamma^2} \int_{-\infty}^{t} dt_2 \int_{-\infty}^{t} dt_1 \mathrm{Exp}\left[-p^2 (t - t_1) / \tau_1\right] \left(\left\langle \widetilde{f}_p(t_1) \widetilde{f}_0(t_2) \right\rangle + \left\langle \widetilde{A}_p(t_1) \widetilde{A}_0(t_2) \right\rangle \right) \\ & - \frac{1}{\gamma^2} \int_{-\infty}^{0} dt_2 \int_{-\infty}^{t} dt_1 \mathrm{Exp}\left[-p^2 (t - t_1) / \tau_1\right] \left(\left\langle \widetilde{f}_p(t_1) \widetilde{f}_0(t_2) \right\rangle + \left\langle \widetilde{A}_p(t_1) \widetilde{A}_0(t_2) \right\rangle \right) \\ & - \frac{1}{\gamma^2} \int_{-\infty}^{t} dt_2 \int_{-\infty}^{0} dt_1 \mathrm{Exp}\left[p^2 t_1 / \tau_1\right] \left(\left\langle \widetilde{f}_p(t_1) \widetilde{f}_0(t_2) \right\rangle + \left\langle \widetilde{A}_p(t_1) \widetilde{A}_0(t_2) \right\rangle \right) \end{aligned} \tag{1.6}$$

However, the thermal modes are not coupled, therefore the only terms in this equation which are non-zero come from the contribution of the active modes:

$$
\begin{aligned}
&2\left\langle X_0(t)X_p(t)\right\rangle-\left\langle X_0(0)X_p(t)\right\rangle-\left\langle X_0(t)X_p(0)\right\rangle= \\
&+\frac{2}{\gamma^2}I(0,p)\int_{-\infty}^{t}dt_2\int_{-\infty}^{t}dt_1\mathrm{Exp}\left[-p^2\left(t-t_1\right)/\tau_1\right]B(t_1-t_2) \\
&-\frac{1}{\gamma^2}I(p,0)\int_{-\infty}^{0}dt_2\int_{-\infty}^{t}dt_1\mathrm{Exp}\left[-p^2\left(t-t_1\right)/\tau_1\right]B(t_1-t_2) \\
&-\frac{1}{\gamma^2}I(p,0)\int_{-\infty}^{t}dt_2\int_{-\infty}^{0}dt_1\mathrm{Exp}\left[p^2t_1/\tau_1\right]B(t_1-t_2),
\end{aligned}
\tag{1.7}
$$

and

$$
\begin{aligned}
&\left\langle X_p(t)X_q(t)\right\rangle-\left\langle X_p(t)X_q(0)\right\rangle= \\
&+\frac{1}{\gamma^2}\int_{-\infty}^{t}dt_2\int_{-\infty}^{t}dt_1\mathrm{Exp}\left[-p^2\left(t-t_1\right)/\tau_1\right]\mathrm{Exp}\left[-q^2\left(t-t_2\right)/\tau_1\right]\left(\left\langle\widetilde{f}_p\left(t_1\right)\widetilde{f}_q\left(t_2\right)\right\rangle+\left\langle\widetilde{A}_p\left(t_1\right)\widetilde{A}_q\left(t_2\right)\right\rangle\right) \\
&-\frac{1}{\gamma^2}\int_{-\infty}^{0}dt_2\int_{-\infty}^{t}dt_1\mathrm{Exp}\left[-p^2\left(t-t_1\right)/\tau_1\right]\mathrm{Exp}\left[-q^2\left(-t_2\right)/\tau_1\right]\left(\left\langle\widetilde{f}_p\left(t_1\right)\widetilde{f}_q\left(t_2\right)\right\rangle+\left\langle\widetilde{A}_p\left(t_1\right)\widetilde{A}_q\left(t_2\right)\right\rangle\right)
\end{aligned}
\tag{1.8}
$$

This is a combination of the standard Rouse term with the active correlations. After some calculation we are left with:

$$
\begin{aligned}
&\left\langle X_p(t)X_q(t)\right\rangle-\left\langle X_p(t)X_q(0)\right\rangle=\frac{3k_bT\tau_1\delta_{pq}}{2Np^2\gamma}\left(1-\exp\left(-\frac{p^2t}{\tau_1}\right)\right) \\
&+\frac{I(p,q)}{\gamma^2}\int_{-\infty}^{t}dt_2\int_{-\infty}^{t}dt_1\mathrm{Exp}\left[-p^2\left(t-t_1\right)/\tau_1\right]\mathrm{Exp}\left[-q^2\left(t-t_2\right)/\tau_1\right]B(t_1-t_2) \\
&-\frac{I(p,q)}{\gamma^2}\int_{-\infty}^{0}dt_2\int_{-\infty}^{t}dt_1\mathrm{Exp}\left[-p^2\left(t-t_1\right)/\tau_1\right]\mathrm{Exp}\left[-q^2\left(-t_2\right)/\tau_1\right]B(t_1-t_2)
\end{aligned}
\tag{1.9}
$$

Therefore, we can see that the active contribution of the mean squared displacement of a labeled monomer will be given by the product of a functional of the autocorrelation function of the noise and the function $I(p,q)$ which depends on the correlations along the chain. By changing the limits $a=t_1-t_2$ and $b=t_1+t_2$, one of the integrations can be performed, leaving the expression from the main text.

II. EXPONENTIAL CORRELATIONS IN TIME

A. Diffusion

In this section we describe in more detail the dynamics of Rouse chains where the active forces are exponentially correlated in time.

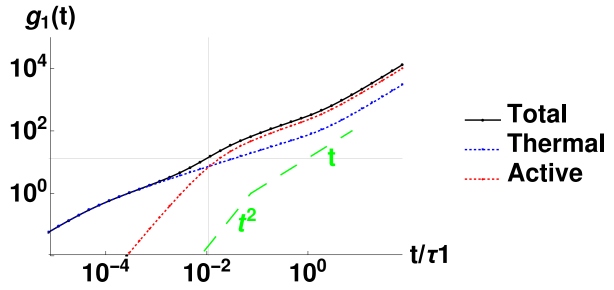

FIG. S1. The MSD (black) of a the middle monomer of a 200 monomer chain and the contributions of the active (red) and thermal (blue) parts to the MSD. The magnitude of the thermal and active forces is the same, the chain is 200 beads long and $\gamma = k = k_B T = 1$. The timescale of the active correlations is $\tau_A = 10$. At short times the thermal forces dominate, but there is a crossover to a regime where both active and thermal forces are important. Also plotted are examples of how different power laws scale (green).

Physically, we can get a better idea as to the processes which contribute to these exponents by looking at $g_1(t)$, and the contributions to it from the thermal and active parts. From fig. S1, it can be seen that at small times the main contribution to the MSD comes from the thermal forces, as the thermal forces scale as t and the active forces as t^2; for small times the behaviour will be diffusive and then switch to subdiffusive. However, the contribution of the active part to the MSD increases ballistically ($\approx t^2$), such that as t increases there is an increasing contribution of the active forces relative to the thermal forces. There is an effective crossover in the magnitude of the active and thermal parts at around $t \approx \tau_A^{1/\beta}$ where numerical estimates yield $\beta \approx 4$. Both the thermal and active forces are then counterbalanced by the effects of chain connectivity, reducing the exponents by which the MSD increases, but the timescale on which this happens is larger for the active forces than the thermal ones. This crossover then leads to a peak in $\alpha(t)$ seen in fig. 2 in the main text. At larger times ($> \tau_1$), both contributions increase linearly with time, leading to normal diffusion.

B. Natural Length Scale

For a system with exponential noise, there is an natural length scale to consider, which is the blob size where the relaxation time of that blob is equal to the correlation time of the active noise. With some calculation, it can be found to be:

$$l_A = \left(b\sqrt{\frac{3\pi^2 k_b T \tau_A}{\gamma}} \right)^{1/2} \tag{2.10}$$

Thus, for length scales shorter than this, the chain can relax before the active noise has diminished, and for length scales larger than this the relaxation time is larger than the active correlation time. When we look at the correlations of different modes of the polymer: $\langle X_p(t) X_p(0) \rangle$ where $X_p(t)$ corresponds to the motion of N/p segments, we are observing the correlation at length scales of $(Nb^2/p)^{1/2}$. This correlation can be further decomposed into thermal and active parts. The behaviour of the thermal part of the Rouse model is well known: $\langle X_p(t) X_p(0) \rangle_{\text{thermal}} \approx e^{-t/\tau_p}$ where τ_p is the well known relaxation time of each mode τ_1/p^2.

For the active modes, a similar expression can be derived, leaving:

$$\langle X_p(t) X_p(0) \rangle_{\text{active}} = \frac{3F}{N\gamma^2} \tau_p \tau_A \frac{\exp(-t/\tau_p) - \exp(-t/\tau_A)(\tau_A/\tau_p)}{(1 - \tau_A/\tau_p)(1 + \tau_A/\tau_p)} \tag{2.11}$$

We can rewrite this in terms of the variable $x = \tau_A/\tau_p$, leaving:

$$\langle X_p(t) X_p(0) \rangle_{\text{active}} = \frac{3F}{N\gamma^2} \tau_p^2 \exp(-t/\tau_p) \frac{x(1 - x \exp\left[(-t/\tau_p)(\frac{1}{x} - 1)\right])}{1 - x^2} \tag{2.12}$$

When plotted, it can be seen that in the limit that $x < 1$, corresponding to length scales which are larger than l_A, the active part of the mode correlation function has the same scaling as the thermal part $\langle X_p(t) X_p(0) \rangle_{\text{active}} \approx e^{-t/\tau_p}$. If the activity were to be renormalized by $(2\gamma k_b T)/(F\tau_A)$, the behaviour is the exactly the same. This accords with our intuition that as we coarse grain the system over larger length scales the subsequent polymer looks similar to the thermal one.

On the other hand when $x > 1$, i.e., for length scales shorter than l_A, the behaviour of the modes as a function of t is not qualitatively similar to the thermal case.

Such an anstatz also allows us to estimate when the active noise affects the MSD of the system, given by a sum of mode correlation functions $g_1(t) \approx \sum_p \langle X_p(t) X_p(0) \rangle$. We know when $\tau_p >> \tau_A$ the system looks like a normal Rouse chain. At large times the dynamics will look like thermal motion. Going back to our expression for the correlation function of the active modes, eq. 2.12, it can be shown that at large x there is no explicit time dependence. This means that when $\tau_p << \tau_A$ the thermal modes will again dominate and again there will be no difference from the normal Rouse chain. Therefore it is the crossover region, where one would expect there to be deviation from normal Rouse behaviour. This argument accords well with fig. 2 from the main text.

III. CORRELATIONS ALONG THE CHAIN

When we include the effect of correlations along the chain, most of the derivation remains the same, except that in this case the factors $I(p, q)$ have non-zero off diagonal elements. The subsequent plot of the exponent $\alpha(t)$ looks similar to that without correlations a long the chain, but now the exponents are slightly larger (see fig. S2) .

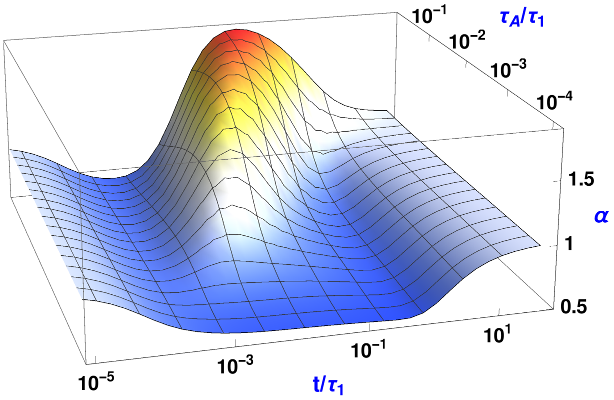

FIG. S2. The scaling exponent $\alpha(t)$ of the middle monomer of a chain of 200 monomers, as a function of both t and the correlation time t_A. The noise is also exponentially correlated along the chain with a correlation length of $\lambda = 10$. The effect of correlations along the chain increases the magnitude of the scaling exponent compared to cases without chain correlations.

Physically, when you add correlations along the chain to the active force, neighboring monomers are now being pushed in the same direction by the active forces, so the effect of elastic damping of the motion is lessened and the supperdiffusive exponent is larger.

IV. VELOCITY CORRELATION FUNCTION OF THE ROUSE MODEL

In the text it is mentioned that the velocity autocorrelation function of the Rouse model is:

$$R_v(t) = \begin{cases} 1 & t = 0 \\ 0 & t > 0 \end{cases} \tag{4.13}$$

where $R_v(t)$ is the correlation function. This appears to be at variance with the existing literature in which the subdiffusive behavior of monomers on intermediate time scales was shown to result from the presence of long time tails in the velocity autocorrelation function[1]. The apparent discrepancy can be traced back to the fact that the term correlation function is often used interchangeably to describe two related but actually distinct entities, which we will here refer to as the "normalized" and "unnormalized" correlation functions. For a stationary process of zero mean:

$$R_v^{(n)}(t) = \frac{\langle v(t)v(0)\rangle}{\sigma_v^2} \tag{4.14}$$

$$R_v^{(un)}(t) = \langle v(t)v(0)\rangle \tag{4.15}$$

where σ_v^2 is the variance of the process. At first sight it appears that the normalized correlation function is undefined as the variance of the velocity is infinite. However, as shown below, a proper evaluation of the overdamped limits of the Rouse model perfectly yields valid results for the normalized velocity correlation function.

In order to demonstrate the difference between these functions we use the equation for the time evolution of a Rouse mode, but where now we include an inertial term and take the overdamped limit $m \to 0$ later. The time evolution of a Rouse mode is given by the damped Harmonic oscillator equation:

$$m\frac{\partial^2 X(t)}{\partial t^2} = -\lambda\frac{\partial X(t)}{\partial t} - kX(t) + f(t) \tag{4.16}$$

The function f(t) is a random noise term with zero mean and variance:

$$\langle f(t)f(t')\rangle = 2\lambda k_b T\delta(t-t') \tag{4.17}$$

Subject to the initial conditions that $X(-\infty) = 0$ and $V(-\infty) = 0$ where $V(t) = \frac{\partial X(t)}{\partial t}$, this equation has the solution:

$$X(t) = \int_{-\infty}^{t} \frac{e^{-\frac{(t-t')\left(\sqrt{\lambda^2-4km}+\lambda\right)}{2m}}\left(e^{\frac{(t-t')\sqrt{\lambda^2-4km}}{m}} - 1\right)}{\sqrt{\lambda^2-4km}} f(t')\mathrm{d}t' \tag{4.18}$$

We can use this solution to craft the unnormalized velocity correlation function:

$$R_V^{(un)}(t) = \langle V(t)V(0)\rangle = \frac{k_b T e^{-\frac{\lambda t}{2m}}\left(\lambda\sqrt{\lambda^2-4km}\sinh\left(\frac{t\sqrt{\lambda^2-4km}}{2m}\right)+(4km-\lambda^2)\cosh\left(\frac{t\sqrt{\lambda^2-4km}}{2m}\right)\right)}{m\left(4km-\lambda^2\right)} \tag{4.19}$$

and the normalized correlation function, given by:

$$R_V^{(n)}(t) = \frac{\langle V(t)V(0)\rangle}{\langle V^2\rangle} = \frac{\langle V(t)V(0)\rangle}{k_bT/m} \tag{4.20}$$

For both of these functions, the limit $m \to 0$ can be readily evaluated, giving:

$$R_V^{(un)}(t) = \frac{k_bT}{\lambda}\delta(t) - \frac{kk_bT}{\lambda^2}\exp(-kt/\lambda) \tag{4.21}$$

$$R_V^{(n)}(t) = \begin{cases} 1 & t = 0 \\ 0 & t > 0 \end{cases} \tag{4.22}$$

For the normalized correlation function, the order of the limits is important, first the limit $t \to 0$ is taken, and then the limit $m \to 0$. Eq. 4.21 is consitent with known results for the Rouse model. In particular, the diffusion of a labelled particle is given by the integral over the unnormalized velocity autocorrelation function:

$$\langle(x(t)-x(0))^2\rangle = \int_0^t\int_0^t \mathrm{d}t_1\mathrm{d}t_2\langle v(t_1)v(t_2)\rangle \tag{4.23}$$

which leads to subdiffusion. However, this function is the sum of a distribution and a function and only makes physical sense as the kernel under some integral. The normalized correlation function is the correct experimental measure of velocity correlations (with a caveat that the velocity is measured over a time window, see next section)and is a well behaved function limited between 1 and -1 in general and 0 and 1 in this case.

When this logic is applied to systems which have an additional active contribution, the normalized velocity autocorrelation function looks as follows:

$$R_v^{(n)}(t) = \frac{\langle v_T(t)v_T(0)\rangle + \langle v_A(t)v_A(0)\rangle}{\langle(v_A+v_T)^2\rangle} \tag{4.24}$$

We break down the velocity into active and thermal parts as in our model the active and the thermal forces are uncorrelated. This allows us to expand out the denominator, leading to the following expression:

$$R_v^{(n)}(t) = \frac{\langle v_T(t)v_T(0)\rangle + \langle v_A(t)v_A(0)\rangle}{\langle v_A^2\rangle + \langle v_T^2\rangle} \tag{4.25}$$

This can be rearranged to give:

$$R_v^{(n)}(t) = \frac{\langle v_T(t) v_T(0)\rangle}{\langle v_T^2\rangle} \frac{1}{1+\langle v_A^2\rangle/\langle v_T^2\rangle} + \frac{\langle v_A(t) v_A(0)\rangle}{\langle v_A^2\rangle} \frac{1}{1+\langle v_T^2\rangle/\langle v_A^2\rangle} \tag{4.26}$$

which is the sum of the contributions of the thermal and the active normalized autocorrelation functions multiplied by some constants. As the system is no longer in thermal equilibrium the system does not obey equipartition, but as the thermal and active forces are uncorrelated and the active force is a stationary process, the total kinetic energy can be written as $\frac{1}{2}m\langle v^2\rangle = k_bT + E_A$ where E_A is some energy scale associated with the active force. We assume the magnitude of the applied active force does not depend on the mass on which it is being applied. Both the active and thermal velocity correlation functions then diverage as $1/m$, but their ratio is well defined.

An example of what would be measured in a simulation of the normalized velocity autocorrelation function is given in S3. A simple Langevin dynamics simulation was performed and the velocity autocorrelation function was measured.

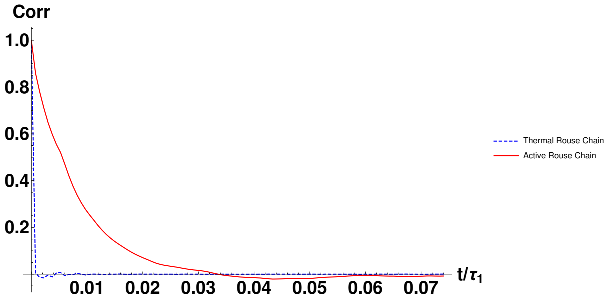

FIG. S3. The measured velocity autocorrelation function of polymers with and without active noise. The presence of active noise leads to a significant change in the velocity autocorrelation. Here $\gamma = k_bT = 1$ and $m = 0.01$. The activity is exponential with a magnitude of $F = 1$ and $\tau_A = 0.014\tau_1$

A. Experimental measurements of velocity correlation functions

When one considers experimental measures of the velocity correlation function, this has to be modified somewhat. It is difficult for an experiment to measure the instantenous velocity of a microscopic object. What is usually more accessible is the average velocity during a certain time interval T:

$$v_{\mathrm{av}}(t,T) = \frac{1}{T}\int_{t-T/2}^{t+T/2} v(t_1)\mathrm{d}t_1 \tag{4.27}$$

The unnormalized correlation function of this average velocity can then also be calculated, provided that the underlying unnormalized velocity correlation function is known.

$$\langle v_{\mathrm{av}}(t,T)v_{\mathrm{av}}(0,T)\rangle = \frac{1}{T^2}\int_{t-T/2}^{t+T/2}\mathrm{d}t_1\int_{-T/2}^{T/2}\mathrm{d}t_2\langle v(t_1)v(t_2)\rangle \tag{4.28}$$

Let us take the unnormalized velocity correlation function from the previous section (Eq. 4.21) as the example, rewriting it in terms of the correlation time $\tau = \lambda/k$ and setting the prefactor $k_bT/\lambda = 1$:

$$\langle v(t_1)v(t_2)\rangle = \delta(t_1 - t_2) - \frac{1}{\tau}\exp(-|t_1 - t_2|/\tau) \tag{4.29}$$

and calculate the normalized average velocity correlation function:

$$R_{v_{\mathrm{av}}}(t,T) = \frac{\langle v_{\mathrm{av}}(t,T)v_{\mathrm{av}}(0,T)\rangle}{\langle v_{\mathrm{av}}(0,T)^2\rangle} \tag{4.30}$$

Which is experimentally measurable. However this function is now dependent on the time resolution of the experiment, T. Thus, the important quantity becomes the ratio between the measurement time T and the relaxation time τ. When T/τ is sufficiently small, the results approach that of the bare normalized velocity correlation function. When this ratio is not sufficiently small, the exponential tail may be visible as can be seen from S4. Therefore in order to see activity clearly the velocity should be calculated with the maximum temporal resolution possible.

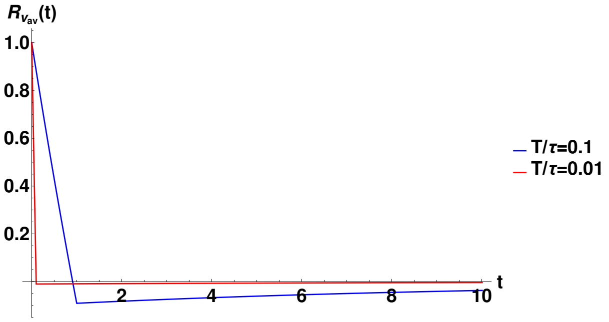

FIG. S4. The decay of the normalized average velocity correlation function depends on the size of the measurement window for $\tau = 10$ for the unnormalized velocity correlation in (Eq. 4.21). As the measurement window is reduced the expression approached the normalized correlation function of the instantaneous velocity. However, for larger windows the exponential tail can still be seen.

REFERENCES

[1] T. Saito and T. Sakaue, “Driven anomalous diffusion: An example from polymer stretching,” Physical Review E **92**, 012601 (2015).