Electronic Supplementary Material (ESI) for Soft Matter.

Supplemental Material for 'Universal trend of the non-exponential Rouse mode relaxation in polymer systems: A theoretical interpretation based on a generalized Langevin equation'

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I. DEDUCTION OF THE FORMULA $\Gamma^{nRR}_{p\to 1}(t) = C\left[\frac{\tau^{(n-1)RR}_{p=1}}{t}\right]^{(3/4)^n}$ WITH $C \approx 7.8\pi^{(11/4)}AS(0)\sigma^{-5}N^{-3/2}$ AND $n \in [1,2,3]$ (EQ. 6 OF THE MANUSCRIPT)

The starting point is the Eq. 5 of the manuscript but for the so-called static limit, i. e., when $S(\bar{k},t) \sim S(0)$.

$$\Gamma_{p\to 1}(t) = 6A\sigma^{-5}S(0)\int_0^1 d\bar{k}\bar{k}^2 \exp\left[-\frac{\bar{k}^2}{6\sigma^2}\langle r^2(t)\rangle_Q\right] \tag{1}$$

(see the manuscript for the definition of the different parameters involved).

According to the general procedure for the n-Renormalization Rouse Model (n-RRM) described in the manuscript, $\langle r^2(t)\rangle_Q$ in Eq. 1 has to be replaced by the actual mean squared displacement (msd) for a polymer segment obtained in the $(n-1)$-RRM step. Then, for n=1, $\langle r^2(t)\rangle_Q$ has to be replaced by the actual msd corresponding to the zero-order RRM, i. e., to the Rouse model. This can be written as (see, e. g., Ref. [1] in the manuscript)

$$\langle r^2(t)\rangle = \frac{2N\sigma^2}{\pi^{3/2}}\left(\frac{t}{\tau^0_{p=1}}\right)^{1/2}.$$

Now, taking into account Eq. 1, $\Gamma^{1RR}_{p\to 1}(t)$ can be expressed as

$$\Gamma^{1RR}_{p\to 1}(t) = 6A\sigma^{-5}S(0)\int_0^1 d\bar{k}\bar{k}^2 \exp\left[-\bar{k}^2\left(\frac{t}{t_0}\right)^{1/2}\right]$$

with $t_0 = 9\pi^3\tau^0_{p=1}N^{-2}$.

Extending the upper limit of integration to ∞ for mathematical convenience we can solve the integral analytically. We obtain

$$\Gamma^{1RR}_{p\to 1}(t) \simeq \frac{3}{2}\sqrt{\pi}A\sigma^{-5}S(0)\left(\frac{t_0}{t}\right)^{3/4}$$

which can be expressed as

$$\Gamma^{1RR}_{p\to 1}(t) \simeq C\left(\frac{\tau^0_{p=1}}{t}\right)^{3/4} \tag{2}$$

with $C = (3/2)9^{3/4}\pi^{11/4}A\sigma^{-5}S(0)N^{-3/2}$.

As it is mentioned in the text of the manuscript, the solution of Eq. 2 of the manuscript, with this memory function, gives a stretched exponential function for $\Phi_{p=1}(t)$,

$$\Phi^{1RR}_{p=1}(t) = \exp\left[-\left(\frac{t}{\tau^{1RR}_{p=1}}\right)^{\beta_{1RR}}\right] \text{ with } \beta_{1RR} = \frac{3}{4}.$$

In such conditions, the corresponding msd, $\langle r^2_{1RR}(t)\rangle$, can be expressed as (see Ref. [17] in the manuscript):

$$\langle r^2_{1RR}(t)\rangle = \frac{2N\sigma^2}{\pi^{3/2}}\left(\frac{t}{\tau^{1RR}_{p=1}}\right)^{\beta_{1RR}/2}.$$

Now, replacing $\langle r^2(t)\rangle_Q$ in Eq. 1 by $\langle r^2_{1RR}(t)\rangle$ we would obtain $\Gamma^{2RR}_{p\to1}(t)$. Doing similar calculations that those described above for the case of $\Gamma^{1RR}_{p\to1}(t)$, we obtain

$$\Gamma^{2RR}_{p\to1}(t) \simeq C\left(\frac{\tau^{1RR}_{p=1}}{t}\right)^{9/16} \tag{3}$$

$$\Phi^{2RR}_{p=1}(t) = \exp\left[-\left(\frac{t}{\tau^{2RR}_{p=1}}\right)^{\beta_{2RR}}\right] \text{ with } \beta_{2RR} = \frac{9}{16} \tag{4}$$

$$\langle r^2_{2RR}(t)\rangle = \frac{2N\sigma^2}{\pi^{3/2}}\left(\frac{t}{\tau^{2RR}_{p=1}}\right)^{9/32}. \tag{5}$$

Repeating again the same procedure for $\Gamma^{3RR}_{p\to1}(t)$ we obtain

$$\Gamma^{3RR}_{p\to1}(t) \simeq C\left(\frac{\tau^{2RR}_{p=1}}{t}\right)^{27/64}. \tag{6}$$

Equations 2, 3 and 6 can be written in a general form as:

$$\Gamma^{nRR}_{p\to1}(t) \simeq C\left(\frac{\tau^{(n-1)RR}_{p=1}}{t}\right)^{(3/4)^n} \quad n \in [1,2,3] \tag{7}$$

II. EXPRESSING $\tau^{2RR}_{p=1}$ IN TERMS OF $\tau^{0}_{p=1}$

As it is described in the manuscript, $\Gamma^{s}_{p\to1}(t) \equiv \Gamma^{3RR}_{p\to1}(t)$ depends on $\tau^{2RR}_{p=1}$, i. e., the characteristic time of the $\Phi_{p\to1}(t)$ function obtained by solving Eq. 2 of the manuscript with the memory function corresponding to the n=2 renormalization Rouse model: $\Gamma^{2RR}_{p\to1}(t)$. In the following we will show how $\tau^{2RR}_{p=1}$ can be expressed in terms of $\tau^{0}_{p=1}$.

For convenience we will start expressing $\tau^{1RR}_{p=1}$ in terms of $\tau^{0}_{p=1}$. $\tau^{1RR}_{p=1}$ is the characteristic time of $\Phi^{1RR}_{p=1}(t)$, which is obtained by solving Eq. 2 of the manuscript with $\Gamma^{1RR}_{p\to1}(t) = C\left(\frac{\tau^{0}_{p=1}}{t}\right)^{3/4}$. As it is explained in the manuscript $\xi^{1RR}(t)$ in Eq. 2 of the manuscript is defined as $\xi^{1RR}(t) = \int_0^t dt'\Gamma^{1RR}_{p\to1}(t')$. Then it can be calculated as

$$\xi^{1RR}(t) = 4C(\tau^{0}_{p=1})^{3/4}t^{1/4}. \tag{8}$$

According to Eq. 2 in the manuscript for $t \;>>\; t_c$ (being t_c defined by the condition $\xi(t_c) \;\sim\; \xi_0$), $\Phi^{1RR}_{p=1}(t)$ can be written now as

$$\Phi^{1RR}_{p=1}(t) \simeq \exp\left[-\frac{\xi_0}{\tau^0_{p=1}}\int_0^t \frac{dt'}{\xi^{1RR}(t')}\right].$$

Taking into account the expression of $\xi^{1RR}(t)$ given above (Eq. 8), then

$$\Phi^{1RR}_{p=1}(t) = \exp\left[-\left(\frac{t}{\tau^{1RR}_{p=1}}\right)^{3/4}\right] \text{ with } \tau^{1RR}_{p=1} = \tau^0_{p=1}\left(\frac{3C\tau^0_{p=1}}{\xi_0}\right)^{4/3}.$$

Now, taking into account (see the manuscript) that:

$$\frac{\tau^0_{p=1}}{\xi_0} = \frac{\sigma^2 N^2}{3\pi^2 k_B T};$$

$$C = \frac{3}{2}9^{3/4}\pi^{11/4}AS(0)\sigma^{-5}N^{-3/2};$$

$$A = k_B T\rho_m d^6 g^2(d)$$

and

$$\psi = 6\rho_m d^6\sigma^{-3}g^2(d)S(0),$$

then $\frac{C\tau^0_{p=1}}{\xi_0}$ becomes

$$\frac{C\tau^0_{p=1}}{\xi_0} = \frac{9^{3/4}\pi^{3/4}N^{1/2}\Psi}{12}$$

and

$$\tau^{1RR}_{p=1} = \tau^0_{p=1}a$$

where, as it is mentioned in the text of the manuscript, $a = \left(\frac{9^{3/4}\pi^{3/4}N^{1/2}\Psi}{4}\right)^{4/3}$.

Now we can follow the same procedure for $\tau^{2RR}_{p=1}$. In that case,

$$\xi^{2RR}(t) = \int_0^t dt'\Gamma^{2RR}_{p\to 1}(t) = \frac{16}{7}C(\tau^{1RR}_{p=1})^{9/16}t^{7/16}$$

and then,

$$\Phi^{2RR}_{p=1}(t) = \exp\left[-\left(\frac{t}{\tau^{2RR}_{p=1}}\right)^{9/16}\right]$$

with

$$\tau^{2RR}_{p=1} = \tau^{1RR}_{p=1}\left(\frac{9C\tau^0_{p=1}}{7\xi_0}\right)^{16/9} = \left(\frac{3}{7}\right)^{16/9}\tau^{1RR}_{p=1}a^{4/3}.$$

Now taking into account that $\tau^{1RR}_{p=1} = \tau^0_{p=1}a$ (see above) then we finally obtain:

$$\tau^{2RR}_{p=1} = \tau^0_{p=1}\left(\frac{3}{7}\right)^{16/9}a^{7/3}.$$

III. CHECKING THE VALIDITY OF THE PSEUDO-MARKOV APPROXIMATION

The pseudo-Markov approximation used in this work can be expressed as:

$$\int_0^t dt' \Gamma_{p\to 1}(t-t') \frac{dC_{p\to 1}(t')}{dt'} \approx \frac{dC_{p\to 1}(t)}{dt} \int_0^t dt' \Gamma_{p\to 1}(t') \ . \tag{9}$$

The two terms of this equation can be calculated by taking into account the $\Gamma_{p\to 1}(t)$ function given by Eq. 7 of the manuscript

$$\Gamma_{p\to 1}(t) \simeq b \left(\frac{\tau_s^0}{t}\right)^{27/64} \exp\left[-\left(\frac{t}{2\tau_\alpha}\right)^{0.5}\right]$$

with particular values of τ_s^0 and τ_α and the corresponding stretched exponential functions

$$\Phi_{p\to 1}(t) = \frac{C_{p\to 1}(t)}{C_{p\to 1}(0)} = \exp\left[-\left(\frac{t}{\tau_{p=1}}\right)^{\beta}\right] .$$

In fact, as in the calculations described in the text of the manuscript we have used a fixed value of τ_s^0 and b, in order to check Eq. 9 we have considered a 'normalized' memory function $\tilde{\Gamma}_{p\to 1}(t)$ defined as

$$\tilde{\Gamma}_{p\to 1}(t) = \frac{\Gamma_{p\to 1}(t)}{b(\tau_s^0)^{27/64}}$$

together with $\Phi_{p\to 1}(t)$.

The results obtained for a representative case ($\beta = 0.7$; $\tau_{p=1} = 5950$ ns) which corresponds to $\tau_\alpha = 300$ ns, are shown below in Fig. 1. In this plot both, the 'convolution' term (left side of Eq. 9) and the 'pseudo-Markov' term (left side of Eq. 9) are represented (with changed sign) as a function of time. As can be seen, the agreement between them is rather good, giving consistency to the approach used in this work.

On the other hand, concerning the validity of the pseudo-Markov approximation in general, we can also compare the results obtained by Schweizer (Ref. 7 in the manuscript) by means of the pseudo-Markov approximation and those of Fatkullin (Ref. 14 in the manuscript). They both apply the GLE formalism to the same problem and in the framework of the first renormalization procedure (see the text of the manuscript). In that similar framework, Schweizer obtained for the mean squared displacement of a polymer segment of a tagged chain $\langle r^2(t)\rangle \propto t^{3/8}$ while Fatkullin reported $\langle r^2(t)\rangle \propto t^{2/5}$. As for a stretched exponential function for $C_p(t)$, $\langle r^2(t)\rangle \propto t^{\beta/2}$ (see section I of this Supplemental Material and

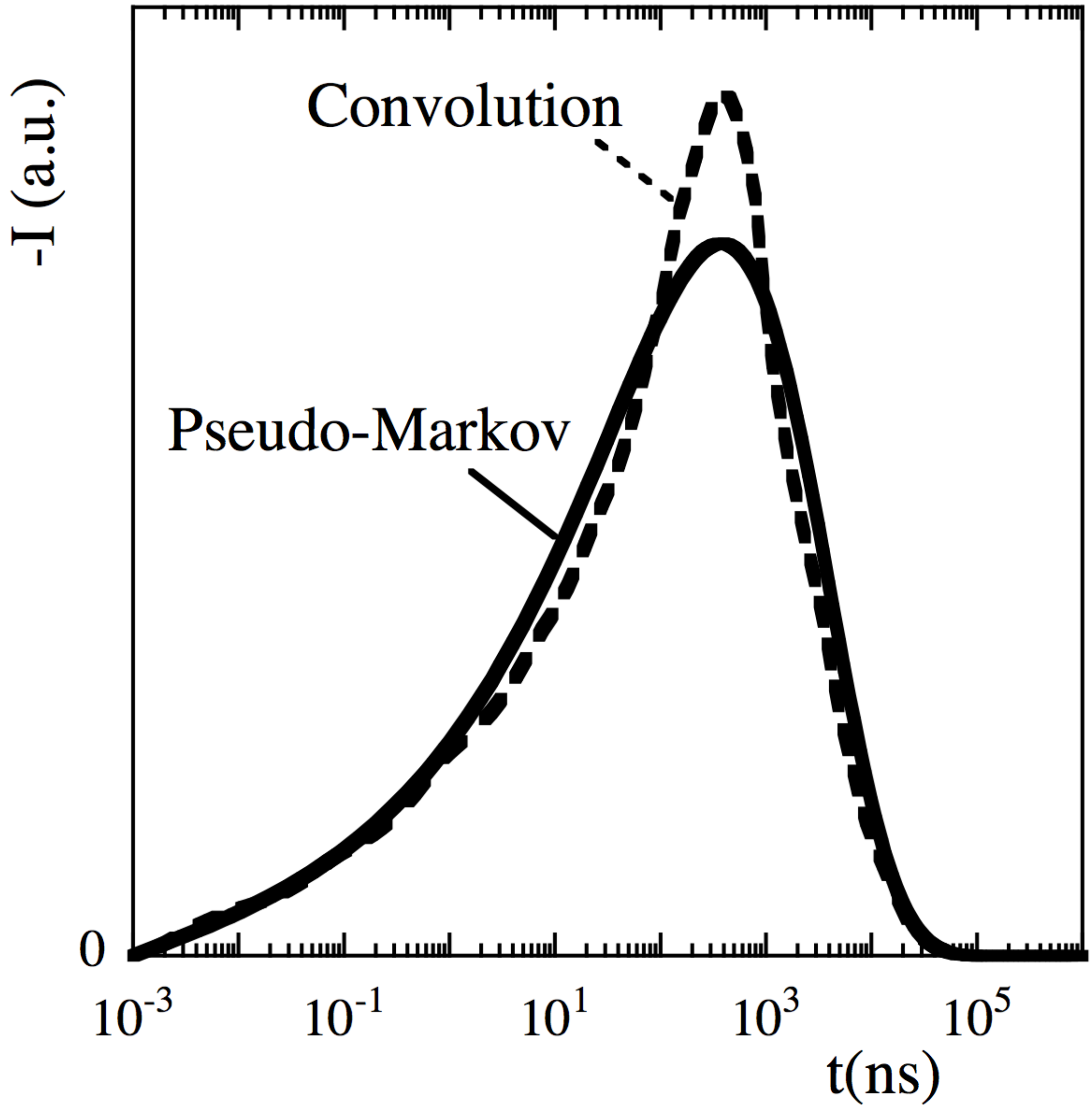

FIG. 1:

Ref. 8 of the manuscript), these results imply that the β value obtained in the framework of the pseudo-Markov approximation for this case would be $\beta = 0.75$ (this is by the way the value reported by Schweizer in Ref. 7) while the value obtained by solving numerically the GLE would be $\beta = 0.8$. This could be taken as an estimation of the error in β by using the pseudo-Markov approximation, at least in the framework used by Schweizer and Fatkullin.