Intramolecular reaction of a polymer : Renormalization group approach

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This paper is aimed to make a thorough review of renormalization group approach for the intramolecular reaction of a polymer. Using renormalization group approach, the long time limit reaction rate is analytically obtained for the various polymer models and cases of reaction groups. In addition, the Langevin-dynamics simulation shows agreement with the RG result, demonstrating potency of the RG analysis on polymer motion.

I. INTRODUCTION :

An intramolecular reaction of a polymer can occur only if the reactive groups, distantly located along the polymer chain, are brought to a close contact in space. The theoretical investigation of intramolecular reaction in polymers has great importance because it appears in a wide range of natural phenomena, such as protein foldings [1], polymerizations [2], and DNA[3]. Furthermore, the theory accompanied by photophysical experimental measurement can provide the probe of the internal dynamics of a polymer module.

The first theoretical approach to understand intramolecular reaction of a polymer was presented by Wilemski and Fixman [4] using the closure approximation. The extension was made for considering the dependency of capture radius was made by Doi [5]. Later, Friedman and O'Shaughnessy presented the renormalization group(RG) methods and sugegsted various novel features [6-8].

In this paper, we focus on reviewing the basic workflow of renormalization group approach for intramolecular polymer. In aligning to the historical order, We begin with renormalization group of polymer cyclization, the case that reactive groups are attached at the both ends of polymer. Next, we extend RG analysis on more general cases of intramolecular reactions depending on the location of reactive groups along with a polymer. Finally, we perform the Lagevin-dynamics simulation and compare with RG approach, showing high agreement between RG approach and simulation.

II. THEORIES FOR POLYMER CYCLIZATION

A. Problem definition

To begin, we start with deriving the theories for polymer cyclization, which refers to the reaction between two reactive groups placed at both ends of a polymer to form a ring structure as in Figure 1. Consider an experiment that a dilute polymer solution is suddenly activated to be reactive so that the cyclization reaction starts to occur since *t=0*. The experimentally measurable quantity is reaction rate as function of time *k(t)*, which is defined as the decay rate of *A(t)*, the fraction of uncyclized polymers after time t.

$$k(t) \equiv -\frac{dA(t)}{dt}. \tag{1}$$

The asymptotic long time behavior should be exponential decay, since the relative distribution of polymer conformation will reach to the new equilibrium. Once t is sufficiently larger than the polymer relaxation time τ, the decay rate converges to the constant level, k_∞.

$$A(t) \sim exp(-k_\infty t), t >> \tau. \tag{2}$$

k_∞ is often what measured from the experiment, and it is important since it provides understanding of the polymer through matching with theoetical analysis.

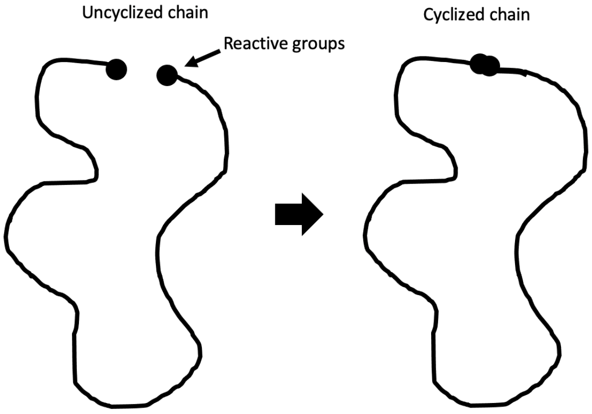

FIG. 1. Illustration of polymer cyclization. Cyclization reaction can occur only if the both reactive end groups are juxtaposed in space.

B. Wilemski-Fixmann approximation

The first analytic theory for polymer cyclization is suggested by Wilemski and Fixmann in 1973[4]. In this section, we derive the formulation of Wilemski-Fixmann(WF) approximation. Consider the polymer chain consists of N monomers in d dimensions. When the two reactive groups get close enough, the irreversible reaction can happen. Under the presence of cyclization reaction, the probabiltiy of $P(c,t)$ of a polymer configuration c of unreacted chains is described by the following Fokker-Planck equation modified by the reaction term:

$$\delta P/\delta t = FP + u_0 \delta(c(N_0) - c(0)))P. \tag{3}$$

F is an diffusion operator which incorporates effect of hydrodynamic interactions. u_0 is the bare reaction rate with minus sign.

$P_{eq}(c)$ denotes the probability of configuration c in equilibrium without the presence of cyclization reaction. By integrating the equation (3) over all possible configuration space, one can obtain the decay of $A(t)$:

$$\frac{dA}{dt} = u_0 \int dc\, \delta(c(0) - c(N_0))P(c,t'). \tag{4}$$

Here, WF approximation adopt <closure approximation> that cyclization reaction make no change on probability distribution of configuration, (i.e $P(c) \simeq \mathrm{P}_{eq}(c)$). Under the closure approximation, the decay rate simply becomes :

- *Wilemski-Fixmann(WF) approximation*

$$[\tfrac{dA}{dt}]_{WF} = u_0 \int dc\, \delta(c(0) - c(N_0))\, P_{eq}(c). \tag{5}$$

WF approximation generally works well only with small u_0 because the probability density distribution stays in approximately equilibrium.

C. Renormalization group argument

The following analytic approach is the renormalization group arguments by Friedman and O'Shaughnessy(FO) in 1991[6][7][8]. The recent studies employing Langevin dynamics simulation imply that the scaling argument successfully predicts the early time and long time power exponent of reaction rate[9]. In this section, we summarized the main argument of FO's work and some of the important consequences. Back to the equation (3), substituting diffusion operator with green's function $G(c', c, t)$, which refers to evolution from configuration c' to c in time t, we can derive:

$$\begin{aligned} P(c,t) &= P_{eq}(c) \\ &+ u_0 \textstyle\int_0^t dt' \int dc'\, G(c', c, t-t')\delta(c'(0) - c'(N_0)) \\ &P(c', t'). \end{aligned} \tag{6}$$

Setting equilibrium distribution for the unperturbed solution, solving the perturbation of P to the second power of u_0, we find:

$$\frac{dA}{dt} = u_0 < \delta(R) > + {u_0}^2 \int_0^t dt' < \delta(R_0)\delta(R_{t'}) > . \tag{7}$$

$< * >$ indicates an average over the equilibrium distribution $P_{eq}(c)$. The first term is first-order reaction term which corresponds to WF approximation, while the second term is time integral of "return probability" that initially co-localized chain ends are co-localized again in time t. To calculate the above terms explicitly, we need to clarify the diffusion operator and the subsequent Edwards Hamiltonian in equation (3)

$$\begin{aligned} F = \textstyle\int_0^N d\tau \int_0^N d\tau' \sum_{\alpha,\beta} \frac{\delta}{\delta c_\alpha(\tau)} \{ \frac{\delta_{\alpha\beta}}{\zeta_0} \delta(\tau - \tau') \quad (8) \\ + T_{\alpha\beta}(c(\tau) - c(\tau'))\}\{\frac{\delta}{\delta c_\beta(\tau')} + \frac{\delta H}{\delta c_\beta(\tau')}\} \\ T_{\alpha\beta} = 2\pi^{-d} \textstyle\int d^d k \frac{1}{\nu k^2}\{\delta_\alpha \beta - \frac{k_\alpha k_\beta}{k^2}\} e^{ik*x} \quad (9) \\ H = 1/2 \textstyle\int_0^N d\tau [c(\dot{\tau})] + \quad (10) \\ \tilde{e_0}/2 \textstyle\int_0^N d\tau \int_0^N d\tau' \delta(c(\tau) - c(\tau')). \end{aligned}$$

ζ_0 are bare friction constant, and $\tilde{e_0}$ is excluded-volume coupling constant. The important argument of FO's work is that $u_0\tilde{e_0}$ are natural coupling constant, which becomes dimensionless when $d = 4$. To expansion around $d = 4$, we define $\epsilon = 4 - d$. In terms of the dimensionless coupling constants $w_0 \equiv \mathrm{u}_0\ L^{\epsilon/2}\zeta_0$, $e_0 \equiv L^{\epsilon/2}$, and L is a phenomenological length scale. Inserting equations (8)(9)(10) to the equation (7) results in the following scaling relation (detailed derviation is refered to Appendix B of [8]):

$$\begin{aligned} -k(t){N_0}^2 &= A(w_0/\zeta_0)(N_0/L)^{\epsilon/2} \\ &+ B/\epsilon(w_0^2/\zeta_0)(N_0/L)^{\epsilon}(t/\tau_R)^{\epsilon/4} \\ &+ (D/\epsilon + E) * (w_0 e_0/\zeta_0)(N_0/L)^{\epsilon}. \end{aligned} \tag{11}$$

where A, B, D are

$$A = (2\pi)^{\epsilon/2-2} \tag{12}$$

$$B = 4^{5\epsilon/4-4}\pi^{\epsilon/4-3} \tag{13}$$

$$D = 6(2\pi)^{\epsilon-4}. \tag{14}$$

Now we apply the renormalizaation to this equation based on the formalism by Oono [10], which basically change the length scale of the polymer without altering the full hamiltonian. As the simplest example of polymer model, we performed the renormalization of a rouse chain, which has zero excluded volume effect. In such case, the Oono's renormalization formulation is:

$$\begin{gathered}(An\ example\ of\ Oono\text{'}s\ renormalization\ of\ polymer: \\ rouse\ chain) \\ c \to C^{1/2} c \\ N \to CN \\ D \to C^{\epsilon/2} D\ . \end{gathered} \tag{15}$$

where D is diffusion coefficient. Then, the bare series of cyclization coupling constant w according to the equation (11) is $w_0 = w - w^2/64\pi\epsilon$. The fixed point of w emerges at $w^* = 0$ or $w^* = -64\pi\epsilon$. For $d > 4$, $w^* = 0$ becomes stable. For $d < 4$, $w^* = -64\pi\epsilon$ becomes stable. In realistic case of $d = 2, 3$, the resulting renormalized series for the reaction rate k_∞ to $O(\epsilon)$:

$$\begin{gathered} k_\infty = \frac{16\epsilon}{pi\zeta N^2} \\ (Rouse) \end{gathered} \tag{16}$$

FO's work performed the renormalization group approach also for variations of polymer models. The renromalized series for the reaction rate for the case of (rouse+ excluded) and Zimm model:

$$\begin{gathered} k_\infty = \frac{8\epsilon}{pi\zeta N^2} \\ (Rouse + Excludedvolume) \end{gathered} \tag{17}$$

$$\begin{gathered} k_\infty = \frac{12\epsilon}{pi^3\nu\zeta N^{d/2}} \frac{1}{128\pi/w + ln(L/N)} \\ (Zimm) \end{gathered} \tag{18}$$

III. INTRAMOLECULAR REACTION

A. Problem definition

In thier following literature [7], FO applied the renormalization group argument on various cases of intramolecular reaction. Based on the location of groups along the polymer, we consider three cases as Figure 2.

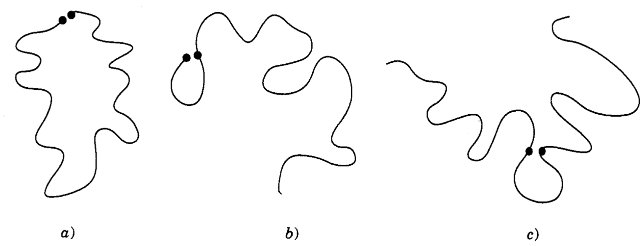

FIG. 2. An illustration of three instances of interanal reaction. a) case 1, both are end groups (cyclization) b) case 2, one are end group and the other is internal group c) case 3, both are internal groups.

Case 1 is when both are end groups, which is same as the cyclization problem. Case 2 is when one is end group and the other is internal group, while case 3 is when both are internal group. To distinguish with the total polymer length N, we denote the length of chain segment between two groups by s. Through renormalization argument same as in section II-C, we get the following relations

$$\begin{gathered} k_\infty \tau_s = Y(\tfrac{16\epsilon}{\pi^3}) \\ (case1 : cyclization) \end{gathered} \tag{19}$$

$$\begin{gathered} k_\infty \tau_s = Y(\tfrac{9\epsilon}{\pi^3})(1 - const * Y\epsilon(\alpha/s)^4 + ...) \\ (case2) \end{gathered} \tag{20}$$

$$\begin{gathered} k_\infty \tau_s = Y(\tfrac{4\epsilon}{\pi^3})(1 + Y(4\epsilon/\pi^2)ln(\alpha/s) + ...) \\ (case3) \end{gathered} \tag{21}$$

where Y and X are,

$$X \equiv (\tfrac{s}{L})^{\epsilon/2} \frac{w}{w - w^*} \tag{22}$$

$$Y \equiv \frac{X}{1+X} \tag{23}$$

For sufficiently large s (Y goes to 1), $k_\infty \tau_s$ are constant in every cases, with the values:

$$(case1 : cyclization)\ :\ k_\infty \tau_s \simeq 0.71 \tag{24}$$

$$(case2)\ :\ k_\infty \tau_s \simeq 0.46 \tag{25}$$

$$(case3)\ :\ k_\infty \tau_s \simeq 0.27 \tag{26}$$

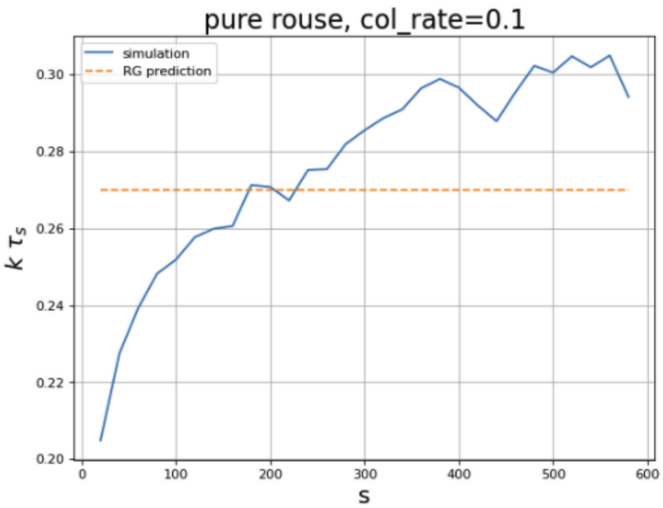

FIG. 3. the $k_\infty \tau_s$ value for case 3 calculated from the MD simulation result coincides well with the RG prediction by Wilemski-Fixmann. Here, the pure rouse polymer chain was simulated for MD timestep $\sim 10^9$ in OpenMM formalism. The intramolecular contact reaction rate was analyzed with varying from $s = 20$ to $s = 600$ monomers.

B. Simple simulation and comparing with FO's renormalization

In this subsection, we perform simple Lagevin-dynamics simulation of intramolecular polymer reaction and compared with the renormalization group result. We exploit the polymer simulation library "Polychrom"[11] that is based on OpenMM[12].

The procedure of simulation starts with assigning the every monomer's positions in $d = 3$. As time proceeds, the monomer locations are updated with the Langevin dynamics simulation method. The time points when intramolecular contact occurs are collected by iterations of simulation starting from initial equilibrium conditions. Figure 3 shows intramolecular reaction rate for case 3 obtained from the simulation is in well coincidence with the renormalization group prediction($k_\infty \tau_s \simeq 0.27$).

IV. CONCLUSION

The intramolecular reaction of a polymer is of great interest to analytical studies in relevance to various chemical and biological systems. Renormalization group approach by Friedman, B., and O'Shaughnes suggests universal realtions in intramolecular polymer reaction, including the long-time limit reaction rate scaling. In addition to it, our Langevin-dynamics simulation results coincide well with the RG prediction of reaction rate on the rouse chain of two internal reactive groups. Since the chemical and biological polymer in a natural system is far more complicated than the polymer model, advanced statistical theory with additional interaction terms and conditions is a possible topic for future study.

V. ACKNOWLEDGEMENTS

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