

Ph.D. Synopsis of
Theoretical investigations of looping of a long chain
polymer molecule in dilute solution

A THESIS

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1. Introduction

One can view the few biological events as the process of interconnection amongst disparate segments. The rates of such biological events and how one can predict the system's behavior from interactions between several parameters governing the process remains a broad interest topic. The process can be determined by several methodologies consisting of theory, computational modeling, experimental validation of the theoretical model, and then employing the newly collected data to refine the theory or model. Despite a growing body of research over the area, accurate prediction and a general insight into the kinetics and dynamics of bio-molecular structures remains a significant challenge. Thus there is always a need for improved discussion over such events. Furthermore, dealing theoretically with the detailed dynamics exact analytically is beyond the scope. The biological systems are dynamic and consist of a considerable number of degrees of freedom; thus, solving for the equation of individual monomers' motions is almost impossible because of the presence of many monomers and a large number of solvent molecules. Thus theoreticians frame analytical models by reducing the high dimensional dynamics to effective one-dimensional dynamics using appropriate reaction coordinate. Thus, using this reductionist paradigm and probability theory, one can view the dynamical phenomenon in the simplest form. The reaction coordinate is taken to be the change in the molecular configuration as a function of end-to-end distance. The statistical description of such processes explains different experimental observable like the rate of the reaction, the survival probability, the mean-first passage time of the system , *etc.*

Polymer end-to-end looping studies experimentally can help probe the internal dynamics of polymer chains in solution. The *looping* and *unlooping* phenomena of long-chain polymers are systemically studied for understanding the initial events of several bio-molecular phenomena such as the folding and unfolding of proteins [1], the kinetics of gene regulation [2], regulation of transcription in both prokaryotes and eukaryotes , *etc.* There are extensive experimental (such as the fluorescence resonance energy transfer studies, femtosecond spectroscopy) and theoretical [1, 3, 4, 5, 6, 7, 8, 9] studies devoted to understanding the kinetics and dynamics of such reactions [6, 10, 11, 12]. In general, the looping reactions can be broadly categorized under the diffusion influenced reaction formalism. A Smoluchowski-like equation is used to model the relative motion between two ends of the polymer. Recent theoretical studies of chemical reaction dynamics focusing on similar problems [13, 14, 15, 16] have used a simple stochastic description of the dynamics of end-to-end distance as a result of interaction between the polymer and the surrounding solvent molecules. Since the polymer is immersed in a solvent, it is impossible to provide a complete description of the dynamics that include all of the polymer's solvent molecules. Thus one relies on a random walk description of the phenomena [13]. Despite discretizing the monomer's motion from the highly coupled solvent forces, one represents the motion as an effect from the random (Brownian) motion of molecular conformations immersed in dilute solution. The end-to-end looping reaction is modeled by adding a sink term to the corresponding continuum equation for end-to-end distribution. [17]. In this representation, one solves the corresponding equation to derive the analytical expression of probability distribution $P(x, t)$ or its Laplace domain counterpart $\tilde{P}(x, s)$, which can be used to find the analytical expression of different rate constants.

2. Motivation & Objectives

The corresponding equation solution is possible only in the time domain if one uses a point sink of infinite strength and the sink is placed at the minimum of the potential [13]. This sink's presence ensures unit looping or unlooping probability at the particular distance between two ends of the polymer - which is not realistic. In the presence of solvent molecules looping or un-looping may or may not happen even if the end-to-end distance comes to a particular value. Therefore we use a Dirac delta function of arbitrary strength and place the sink in an arbitrary location for modeling polymer looping or unlooping process. It should be noted that the location of the sink function can be used to model the finite value of the end-to-end bond length of the looped polymer. The point-sink model is not very realistic. Both looping and unlooping processes are expected to happen over a finite distance; therefore, adding a sink of finite width is more realistic. Therefore we have used a sink function of a rectangular shape as well as Gaussian and exponential. The corresponding Smoluchowski-like equation with a general sink function is given below

$$\frac{\partial}{\partial t}P(x, t) = LP(x, t) - S(x)P(x, t) \quad (1)$$

where, L is the Smoluchowski operator expressed in the following form,

$$L = \left(\frac{4Nb^2}{\tau_r} \frac{\partial^2}{\partial x^2} + \frac{2}{\tau_r} \frac{\partial}{\partial x} x \right) \quad (2)$$

x represents the end-to-end distance of the monomer, N represents the total number of monomers in the polymer, b represents the Kuhn Length. Understandably, this equation (single state model) can model both looping and unlooping process separately, but the process has to be irreversible. For modeling reversible process, one has to use a two-state model with a coupling term as shown below

$$\begin{aligned} \frac{\partial}{\partial t}P_1(x, t) &= L_1P_1(x, t) - S(x)P_2(x, t) \\ \frac{\partial}{\partial t}P_2(x, t) &= L_2P_2(x, t) - S(x)P_1(x, t) \end{aligned} \quad (3)$$

where

$$L_i = \left(\frac{4Nb^2}{\tau_r^i} \frac{\partial^2}{\partial x^2} + \frac{2}{\tau_r^i} \frac{\partial}{\partial x} x \right) \quad (4)$$

In the above, two equations represent two states; one is for the open and the other for the closed one. If the sink function is assumed to be represented by a Dirac delta function of arbitrary strength, we can find an analytical solution in the time domain. For the sink function of finite width, we can find an analytical solution in the Laplace domain. It is interesting to note that one can derive analytical expressions of rate constants from the Laplace domain solution.

3. Description of the Research Work

In the following we divide the whole research works in the following subsections

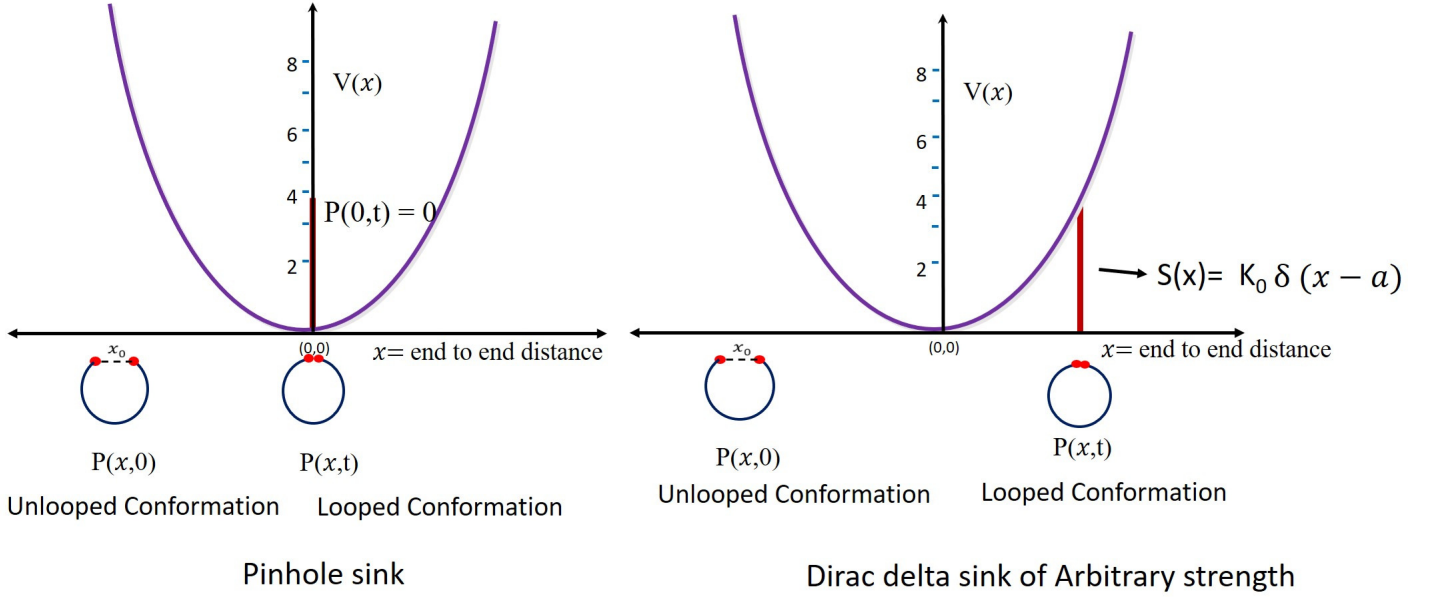


Figure 1: Schematic diagram of various models useful in modeling the polymer looping reaction. (a) The situation when the end-to-end distance is zero at the minimum. When the end-to-ends meet, the reaction takes place with a probability 1, if we add a pinhole sink at the minimum. (b) Situation where the sink function is represented by $S(x) = k_0\delta(x - a)$. The non-zero value of "a" accounts for the finite value of end-to-end bond length.

3.1. On the development of a single state diffusion-reaction model with a point sink

The individual monomers are considered to perform the random walk. As a result of this random walk - end-to-end distance also does random walk, and a Smoluchowski-like equation can model the dynamics of end-to-end distance for harmonic potential. The end-to-end looping process is ensured by adding a Dirac delta function sink of arbitrary strength in that equation. The strength of the sink or the reaction window refers to the extent of the looping reaction's possibility. The earlier model used the Dirac delta sink of infinite strength. Thus any exact result regarding the finite strength of the sink is of great importance. For the first time, this has been done in any analytical model for polymer looping problems to the best of our knowledge. Furthermore, we consider the case of a delocalized sink and calculate the rate constant in the presence of such a sink function. We consider a generalization of the diffusion-reaction approach for understanding the end-to-end looping process in detail using the following equation framework.

$$\tau_R \frac{\partial}{\partial t} P(x, t) = \left(4Nb^2 \frac{\partial^2}{\partial x^2} + 2 \frac{\partial}{\partial x} x - k_s - S(x) \right) P(x, t), \quad (5)$$

where $S(x) = k_0\delta(x - x_c)$. In the model, the effect of all other chemical reactions (involving at least one-end of the polymer) apart from the end-to-end loop formation are incorporated through the $k_s P(x, t)$ term. The term N refers to the total number of segments in the polymer chain, b is the Kuhn Length, and τ_r is the relaxation time that denotes the polymer's time to go from one conformation to another.

An explicit solution of the above equation in the Laplace domain with a Dirac delta function sink can be obtained using the Green's function technique. If the chain with the end-to-distance x_0 at time $t = 0$ has the end-to-end distance x at time t , then the probability of finding the particle at x in Laplace domain s is given by the $G(x, s|x_0)$

and $P_0(x_0)$ is the initial distribution of the end-to-end distances. The above term $G(x, s|x_0)$ is the Greens function that describes the probability density of finding both ends at a certain value of end-to-end distance x with its initial end-to-end distance located at x_0 . The Laplace transform of the reactive Green's function is expressed in terms of Green's function for diffusion in the absence of sink (reaction). The result of the equation in terms of $G(x, s|x_0)$ can be expressed as [17, 18].

$$\tilde{P}(x, s) = \int_{-\infty}^{\infty} dx_0 G(x, s + \frac{k_s}{\tau_R}|x_0) P(x_0, 0), \quad (6)$$

The Figure 1 represents the simple schematic diagram of the problem. The experimental observable quantity, the time-dependent reactant survival probability $P(t)$, which gives the probability of unlooped polymers is obtained from $P(x, t)$ by averaging over the entire reaction coordinate x i.e., $P(t) = \int_{-\infty}^{\infty} dx P(x, t)$. Two different rate constants are generally used, one is the time average rate constant k_I and another is long time rate constant k_L expressed by $k_I = \frac{1}{P(s=0)}$, $k_L = -$ pole of $Q(s)$, survival probability near $s = 0$ for negative s value, respectively, where $Q(s) = \int_{-\infty}^{\infty} dx Q(x, s)$. The mean looping time of a polymer is given by the inverse of the average rate constant. The obtained solution match with the numerical results and also with the available solutions under the pinhole sink limit. [19, 20].

3.2. *On the development of a single state diffusion-reaction model with a sink term for semi-flexible polymers*

Unfortunately, the bio-polymers like DNA, protein, actin, and microtubules have enough internal stiffness to be successfully modeled as flexible chains. Thus this section deals with the distribution of semi-flexible polymers in solution. This study has developed a fractional diffusion model [21] to understand the end-to-end looping process. The model begins with the discrete time-fractional derivative form, where $\frac{\partial^\beta}{\partial t^\beta}$ is the fractional integral of order β and is a parameter that may take non-integral values greater than zero. A generalized equation in the continuum limit in the form

$$\frac{\partial^\beta P(x, t)}{\partial t^\beta} = \left(A \frac{\partial^2}{\partial x^2} + B \frac{\partial}{\partial x} x + \frac{t^{-\beta} \delta(x)}{\tau_R \Gamma(1 - \beta)} \right) P(x, t), \quad (7)$$

which is without a sink term. In this section, we see how the parameter β influences looping dynamics. We find the explicit analytical formula of $P(x, t)$. The obtained solution match with the results given by Kenkre [19] for the particular case of the value of $\beta = 1$ when the above equation gives the solution for flexible polymer case.

3.3. *On the development of two state diffusion-reaction model with a coupling term*

In this part, we study the dynamics of reversible polymer looping or un-looping reactions. This new framework [22] interpolates the kinetics of looping as a function of the end-to-end distance between an open state, and a closed state represented *via* coupled Smoluchowski-like equations for a single particle diffusing under two different harmonic potentials. Fig. 2 represents a simplified schematic illustration of the problem. The interconversion of open and closed configurations can be understood using a physical function representing the coupling between both potentials. The coupling function is assumed to be represented by a Dirac delta function and takes care of the transition from the open configuration to closed and *vice versa*. This method has been extended to deal with

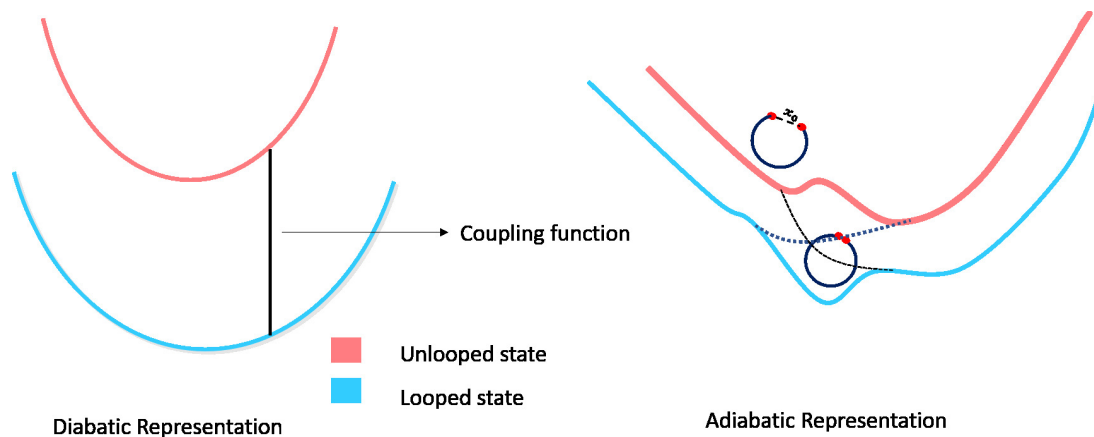


Figure 2: Schematic of harmonic potential with delocalised coupling

Figure 3: (a) Schematic Diabatic representation of two-state model. (b) Schematic Adiabatic representation of two state model. One of the potentials in the adiabatic representation can be used in single state state problem. It is interesting to note that coupling function in two state problem is actually the effective sink function in the single state problem.

delocalized coupling case [23]. The proposed model can be applied for modeling tethering in chromosomes, Bicoid development, enzyme kinetics , *etc.*.

3.4. On the development of a time domain analytical method for Dirac delta sink

Diffusion is a process that happens in real-time. Therefore it is always interesting to have the solution in the time domain. The advantage of the time-domain solution is that one can easily fit time-domain experimental data to get different parameters used in the diffusion-reaction model. This thesis reports the first exact time-domain analytical solution for the polymer looping problem [24]. In a different context, the same equation's solution has been approached in the time domain for the case of Dirac delta function sink of infinite strength, placed at the origin of the harmonic potential [25], which is a particular case of our model. We first solve the flat potential problem case in the time domain, and then we used a transformation formula to transform the solution to that for the harmonic potential case. A particular case of our solution is the one given by [13, 26]. We have extended our method to deal with the Dirac delta function sink with time-dependent strength, and this result is used to fit real experimental data, which were otherwise not possible to fit.

3.5. Analytical solution beyond point sink model

As the point-sink model is not very realistic, we use a sink function of finite width in this subsection and solve the corresponding Smoluchowski equation in the Laplace domain. We have derived an analytical expression of rate constants for the looping/unlooping process from the solution. We have used the following sink functions for our calculations , *e.g.*, rectangular sink, gaussian sink, and exponential sink. We have analyzed the effect of the sink function's width and the effect of the shape of the sink function on the rate constants. It is well understood that one has to use sink functions of a different shape to explain different experimental data.

4. Conclusions

The thesis can be broadly divided into four parts. In the first part, we conclude that the rate constants for irreversible looping processes are proportional to the square root of the polymer's length in one dimension. We also find the variation in relaxation times with two different rate constants. In the second part, we look into the reversible two-state phenomenon. And in the third part, we conclude by giving the time-domain solution to the problem. In the third part, we provide an exact analytical solution in the case of time-dependent sink functions. We show some experimental data, which can fit with the result from our current model only. In the fourth part, we go beyond the point sink model, e.g., rectangular, exponential, and gaussian sink, and find an analytical solution in the time domain. Finally, we want to mention that all our proposed models are important additions to this field. The same model can also be used to understand the un-looping process [27]. Also, similar model can be easily be recognized in areas other than polymer looping problems in solution, well-known examples of this include electron-transfer reactions [28, 29], ligand-receptor binding kinetics [30], bimolecular recombination reactions [26], enzyme kinetics studies [31] and other processes probed by single-molecule spectroscopy [32], femtosecond spectroscopy [33] *etc.*

This research's crucial future direction is to understand the dynamics of contact formation between different parts of a long chain molecule. One can perform Brownian dynamics simulation studies of single polymer chains' looping to see how the sink function's shape decides the looping dynamics.

5. Summary

This thesis deals with developing various analytical models for looping/unlooping for a long polymer chain having reactive ends. We start with a single Smoluchowski equation having a reactive term and then move to coupled Smoluchowski equations. We start with the model developed by Szabo *et al.*, and used a more realistic architecture of reactive sink. This model is used elsewhere by Sebastian [34]. This model's exact solution is available in the Laplace domain, which can use used to find different rate constants' analytical expressions. Here we provide an alternative but straightforward method to get the results by Sebastian [34]. This method can be extended to deal with the case of a delocalized sink , *e.g.*, [14]. We have proposed an analytical method for obtaining a time-domain solution for this model. Our method is then generalized to get an analytical solution in the Dirac delta function sink of time-dependent sink strength. This model's result is used to fit the specific experimental data, which looked impossible to fit using any other model. The exact analytical solution is derived for the case of sink functions with finite width, , *e.g.*, rectangular sink, exponential sink, and gaussian sink. These solutions are used to derive an analytical expression for rate constants. Effect of the width of the sink function and shape of the sink function on different rate constants are analyzed. We also proposed a new analytically solvable model for the looping process in a semi-flexible polymer system. We have proposed a two-state model to understand the reversible looping process. All these models mentioned above can be used to understand the reverse process , *i.e.*, *un-looping*.

6. Outline of the thesis

The thesis entitled "Theoretical investigations of looping of a long chain polymer molecule in dilute solution" is a report of the work I have done over the last five years to investigate polymer looping or unlooping process theoretically. This thesis consists of four main chapters (**Chapters 2-4**), along with an introductory chapter (**Chapter 1**), and a chapter (**Chapter 6**) describing the overall conclusion and future scope.

A brief description associated with each chapter of the thesis is provided below. **Chapter 1** provides the literature review of rate theories required for investigating the polymer looping process, a brief description of the experimental and the existing theoretical methods, some measurement parameters like length of the chain that are related to the experimental and the computational study along with the motivation and objective of this thesis. In **Chapter 2**, we propose an analytical irreversible polymer looping model, which is mathematically represented with the help of a Smoluchowski-like equation with a reactive sink term arbitrary strength and arbitrary location [17, 18, 35]. This equation's solution is expressed in terms of the Laplace Transform of the Green's function for the end-to-end motion of the polymer in the absence of the sink. We derive two different rate constants, the long-term rate constant and the time average rate constant. We provide solutions for generalized delocalized sink case [36]. We use models for both flexible and semi-flexible polymers. In **Chapter 3**, we give an explicit solution of the two-state model. We describe the reversible looping formulation and give a coupled partial differential equation-based model for reversible looping of long-chain polymer in solution [22]. We provide solutions for delocalized coupling cases as well [27]. We use models for both flexible and semi-flexible polymers. The **chapter 4** provides an analytical solution for both reversible and irreversible looping problems in the time domain. The model where the strength of the Dirac delta function is time-dependent is also solved exactly analytically. In **Chapter 5**, we go beyond the point sink model and solve the cases where the sink function has a finite width, *i.e.*, rectangular function, exponential function, and Gaussian function. The **Chapter 6** summarizes the main contribution of the research work and the scopes for future research.

Furthermore, we provide areas in which the proposed solutions can be applied along-with providing an improvement over the existing methods. This thesis's analytical models are useful to study a variety of dynamical processes and several diffusion-controlled reactions. Such a model can be used to study electron transfer reactions in polar solvents, barrierless electronic relaxation in solutions, multi-channel and electrochemical electron transfer reactions.

LIST OF PUBLICATIONS

List of published papers

1. **M. Ganguly** and A. Chakraborty, Understanding looping kinetics of a long polymer molecule in solution. Exact solution for delta function sink model, *Physica A*, 484, 163 (2017).
2. **M. Ganguly** and A. Chakraborty, Exploring the role of relaxation time, bond length and the length of the polymer chain in the end-to-end looping kinetics of a long polymer chain in solution. An exact analytical model, *Chem. Phys. Lett.* 733, 136673 (2019).
3. **M. Ganguly** and A. Chakraborty, Understanding the reversible looping kinetics of a long chain polymer molecule in solution with Dirac Delta coupling. An exact analytical perspective, *Physica A*, 536, 122509 (2019)
4. **M. Ganguly** and A. Chakraborty, The two-state reversible kinetics of a long polymer molecule in solution with a delocalized coupling term. An exact analytical model, *Phys. Scri.*, 95, 115006 (2020)
5. **M. Ganguly** and A. Chakraborty, Opening of a weak link of a closed looped polymer immersed in solution. Analytical modelling using a delta function sink, *Phys. Scri.*, 96, 015003 (2020)
6. **M. Ganguly** and A. Chakraborty, Interpreting the looping rates of a polymer molecule in solution: Exact solution using a simple analytical method, *Chem. Phys. Lett.* 749, 137370 (2020).

List of papers under revision

1. **M. Ganguly** and A. Chakraborty, Deciphering the end-to-end looping kinetics of polymer molecule in solution in presence of a delocalised sink model, *Physica A* (2021).

List of papers under review

1. **M. Ganguly** and A. Chakraborty, Diffusion-reaction approach to polymer cyclization in solution: Exact time domain solution for Dirac delta function sink model, *Chem. Phys.* 2020.
2. **M. Ganguly** and A. Chakraborty, Self-organized criticality for the phenomenon of polymer looping in solution, *Mol. Phys.* 2020.
3. **M. Ganguly** and A. Chakraborty, Effect of different architecture of sink function beyond Dirac delta sink model in looping kinetics of a long polymer molecule in solution, *Mol. Phys.* 2020.

List of papers submitted

4. **M. Ganguly** and A. Chakraborty, Dynamical disorder in looping of polymer in solution: An exact analytical solution, *Chem. Phys.* 2020.
5. **M. Ganguly** and A. Chakraborty, Diffusion-reaction approach for understanding the dynamics of looping of a long chain polymer molecule in solution : Time domain solution for pinhole sink, *Mol. Phys.* 2021.
6. **M. Ganguly** and A. Chakraborty, Analytical expression for end-to-end-auto correlation function of a long chain polymer molecule in solution, *Chem. Phys. Lett.* 2021.
7. **M. Ganguly** and A. Chakraborty, Dynamics of end-to-end distribution of a semiflexible polymer. An exact analytical model, *Journal of Phys. A* 2021.

List of papers in preparation

1. **M. Ganguly** and A. Chakraborty, End-to-end looping : Comparison of existing analytical model (under preparation) 2021.
2. **M. Ganguly** and A. Chakraborty, Understanding the dynamics of unlooping of a long chain polymer molecule in solution using a simple analytically solvable model (under preparation) 2021
3. **M. Ganguly** and A. Chakraborty, Reversible unlooping or looping of a long polymer chain in solution: An alternative method for finding exact solution in Laplace domain (under preparation) 2021

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