# Exact sampling of polymer conformations using Brownian bridges

Cite as: J. Chem. Phys. **153**, 034901 (2020); https://doi.org/10.1063/5.0010368 Submitted: 09 April 2020 . Accepted: 22 June 2020 . Published Online: 15 July 2020

២ Shiyan Wang, ២ Doraiswami Ramkrishna, and ២ Vivek Narsimhan



### ARTICLES YOU MAY BE INTERESTED IN

Nonmonotonic adsorption behavior of semiflexible polymers The Journal of Chemical Physics **153**, 034902 (2020); https://doi.org/10.1063/5.0014209

The physics of active polymers and filaments The Journal of Chemical Physics **153**, 040901 (2020); https://doi.org/10.1063/5.0011466

Simulations of activities, solubilities, transport properties, and nucleation rates for aqueous electrolyte solutions

The Journal of Chemical Physics 153, 010903 (2020); https://doi.org/10.1063/5.0012102



Meet the Next Generation of Quantum Analyzers And Join the Launch Event on November 17th



**Register now** 

Zurich

nstruments

**153**, 034901

J. Chem. Phys. **153**, 034901 (2020); https://doi.org/10.1063/5.0010368 © 2020 Author(s).

## Exact sampling of polymer conformations using Brownian bridges

Cite as: J. Chem. Phys. 153, 034901 (2020); doi: 10.1063/5.0010368 Submitted: 9 April 2020 • Accepted: 22 June 2020 • Published Online: 15 July 2020





Shiyan Wang, ២ Doraiswami Ramkrishna, ២ and Vivek Narsimhan<sup>a)</sup> ២

#### **AFFILIATIONS**

Davidson School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, USA

a) Author to whom correspondence should be addressed: vnarsim@purdue.edu

#### ABSTRACT

The equilibrium conformation of a polymer molecule in an external field is often used in field theories to calculate macroscopic polymer properties of melts and solutions. We use a mathematical method called a Brownian bridge to exactly sample continuous polymer chains to end in a given state. We show that one can systematically develop such processes to sample specific polymer topologies, to confine polymers in a given geometry for its entire path, to efficiently generate high-probability conformations by excluding small Boltzmann weights, or to simulate rare events in a rugged energy landscape. This formalism can improve the polymer sampling efficiency significantly compared to traditional methods (e.g., Monte Carlo or Rosenbluth).

Published under license by AIP Publishing. https://doi.org/10.1063/5.0010368

#### I. INTRODUCTION

The simulation of a single polymer conformation in an external field is not only an excellent example of a molecular process but also has tremendous applications in materials science and biology, such as DNA separation by sedimentation or electrophoresis.<sup>1</sup> This problem is also fundamental in describing concentrated melts and solutions, where field theories can represent the many-body interactions as an effective (and sometimes fluctuating) field acting on a single polymer chain.<sup>2,3</sup> For example, field theories are often used to describe phase transitions in polymer solutions, blends, composites, and gels induced by mechanical, electromagnetic, or temperature perturbations.<sup>2,4–7</sup> To describe the statistical properties of a system in thermodynamic equilibrium, one calculates the partition function as follows:

$$Q = \int e^{-\beta U\{X\}} \delta P\{X\}, \qquad (1)$$

where **X** is the polymer conformation,  $\beta = 1/kT$  is the inverse temperature,  $U\{X\}$  is the potential energy, and  $P\{X\}$  is the probability measure of the conformation in the absence of the external field.

The calculation of a partition function is nontrivial in many situations when one wants to sample (i) polymer chains of a given topology, (ii) polymer chains in a complicated energy landscape, i.e., a landscape with metastable states separated by large free-energy barriers,<sup>8</sup> or (iii) rare conformational states in phase space. In these situations, people often resort to biased sampling techniques in order to efficiently generate conformations of interest. Classical approaches are Rosenbluth methods<sup>9</sup> (Rosenbulth-Rosenbluth, PERM, etc.) for self-avoiding polymers and importance/weighted sampling methods,<sup>10,11</sup> the latter of which represents that a large class of sampling algorithms are based on the Markov Chain Monte Carlo method<sup>10</sup> and umbrella sampling.<sup>12</sup> Suppose we let p(x) be a probability density for a random variable X and we aim to compute an expectation  $\mu_f = E_p[f(X)]$ . Importance sampling suggests a new probability measure  $\chi(x)$  such that one has  $\mu_f = E_{\chi}[w(X)f(X)]$ , where  $w(x) = \frac{p(x)}{\chi(x)}$ . However, a good choice of  $\chi(x)$  is often challenging and involves some intuition.<sup>11</sup>

In this paper, we will discuss an exact sampling technique, a concept known as a Brownian bridge. A bridge is a stochastic process with its start point and end point specified.<sup>13</sup> For polymer conformations, this idea can be used to sample polymer chains with its end topology known, or its final energy known.<sup>14</sup> The latter statement can be used to sample rare events (i.e., high energy conformation or low Boltzmann weights) or most probable configurations (low energy conformations or high Boltzmann weights). In this work, we generate bridges for polymers in an arbitrary external field and show that this can be done through the solution of a backward Fokker–Planck equation. We will show how one can systematically generate

bridges to sample specific polymer topologies, most probable configurations, and rare events. We will further show how we can extend this methodology to condition stochastic processes to lie in a region of phase space for its entire trajectory, not just its end points. The efficiency of our techniques will be compared to brute force and Metropolis Monte Carlo calculations. We note that the ideas discussed here have broad applicability in any process described by a Markov chain, and thus envision applications in physical chemistry beyond polymer physics, such as chemical kinetics and phase transitions.

#### **II. MODEL**

At large enough length scales and time scales, a polymer chain can be treated as a continuous filament that fluctuates randomly in solvent. In other words, the conformations can be treated using the language of random walks, i.e., stochastic differential equations (SDEs). A stochastic differential equation is a continuous random process with drift and diffusion,

$$dX = A(X,s)ds + M(X,s) \cdot d\mathcal{B}(s), \tag{2}$$

where X(s) represents the polymer conformation at arc-length s (0 < s < L). A is the drift, M is a diffusion matrix, and  $d\mathcal{B}$  is a Weiner process. There are many different models to describe polymer conformations depending on the level of detail needed.<sup>15,16</sup> For example, a flexible Gaussian chain in the absence of a field has X(s) = R(s), A = 0, and  $M = \sqrt{2\ell_p I}$ , where R(s) is the position of the polymer chain, I is the identity matrix, and  $\ell_p$  is the persistence length of the polymer. For a worm-like chain, one tracks the position and tangent along the polymer backbone (i.e.,  $X = \{R, u\}$ ). Here,  $\mathbf{A} = [\mathbf{u}, -\mathbf{u}/\ell_p]$  and  $\mathbf{M} = [0, 0; 0, \ell_p^{-1/2}(\mathbf{I} - \mathbf{u}\mathbf{u})]$ . We will choose to keep the SDE as general as possible and refer to specific models when studying examples later in the manuscript. In the presence of an external field U(X), there is an additional process one can use to describe the accumulated Boltzmann weight along the chain,  $dW = -\beta WUds$ . Note that this process resembles the Rosenbluth type method but neglecting self-avoidance, and we call this process as the brute force (naive sampling) approach. To calculate the partition function, one samples the augmented stochastic process  $\Omega(s) = \{X(s), W(s)\}$  and takes an ensemble average of the total Boltzmann weight:  $Q = \langle W_L \rangle$ , where  $W_L = W(L)$ .

To derive a bridge for the chain conformation and accumulated Boltzmann weight  $\Omega(s) = \{X(s), W(s)\}\)$ , we will use Bayes's theorem to determine the probability distribution with the start point and end point specified,

$$Br = \mathbb{P}\{\Omega(s)|\Omega_o, \Omega_L\} = \frac{\mathbb{P}\{\Omega_L|\Omega_o, \Omega(s)\} * \mathbb{P}\{\Omega(s)|\Omega_o\}}{\mathbb{P}\{\Omega_o|\Omega_L\}}, \quad (3)$$

where  $\Omega_o = \Omega(0)$  and  $\Omega_L = \Omega(L)$ . Note that  $q = \mathbb{P}\{\Omega_L | \Omega_o, \Omega(s)\}$  is the hitting probability [i.e., probability of reaching the end point  $\Omega_L$  given an intermediate point  $\Omega(s)$ ], while  $p = \mathbb{P}\{\Omega(s) | \Omega_o\}$  is the forward probability distribution [i.e., probability of reaching an intermediate point  $\Omega(s)$  given the start point  $\Omega_o$ ].

The forward probability,  $p(\mathbf{x}, w, s)$ , satisfies a Fokker–Planck equation,

$$\frac{\partial p}{\partial s} + \frac{\partial}{\partial x} \cdot (Ap) - \frac{\partial (w\beta U(x)p)}{\partial w} = \frac{1}{2} \frac{\partial^2}{\partial x \partial x} : (M \cdot M^T p), \quad (4)$$

with an initial condition  $p(\mathbf{x}, w, 0) = \delta(\mathbf{x} - \mathbf{x}_o)\delta(w - 1)$ , where  $\delta$  is the Dirac delta function. Note that the random variables are denoted as the capital letters (*W*, *X*), while the corresponding specific values take on the lower case letters (*w*, *x*).

The hitting probability  $q(\mathbf{x}, w, s)$  satisfies the backward Fokker–Planck equation,

$$\frac{\partial q}{\partial s} + \mathbf{A} \cdot \frac{\partial q}{\partial \mathbf{x}} - \beta U(\mathbf{x}) \frac{\partial q}{\partial (\ln w)} = -\frac{\mathbf{M} \cdot \mathbf{M}^T}{2} : \frac{\partial^2 q}{\partial \mathbf{x} \partial \mathbf{x}}, \quad (5)$$

Noting that the Brownian bridge satisfies  $Br \propto q * p$ , it is straightforward to show using Eqs. (4) and (5) that Br satisfies the same partial differential equation (PDE) as the forward probability density function in Eq. (4), but with an additional drift in terms of hitting probability q:  $u_{drift} = M \cdot M^T \cdot \frac{\partial}{\partial X}(\ln q)$  (see Appendix A). Therefore, the stochastic differential equation that samples the bridge is

$$d\mathbf{X}^{\mathrm{Br}} = d\mathbf{X} + \left(\mathbf{M} \cdot \mathbf{M}^{\mathrm{T}}\right) \cdot \frac{\partial}{\partial \mathbf{X}} (\ln q) ds.$$
 (6)

The additional drift term with  $\ln(q)$  resembles an entropic force associated with a canonical ensemble,<sup>17</sup> which is needed to bias the chain end in a proper configuration [see *q* at different *s* in Figs. 1(a) and 1(b)]. Therefore, the algorithm for sampling polymer conformations using a Brownian bridge is as follows:

**FIG.** 1. (a) Example of a Gaussian, 1D polymer X(s) (0 < s < L, monomer length ds) in a double-well potential  $U(X) = ((X^2 - 12X + 18)/9)^2$ . The Brownian bridge directs the polymer toward the end region  $\{X, W\} \in \Omega$ , where W is the Boltzmann weight. (b) Example of 13 Brownian bridge trajectories from part (a) starting at different positions and guided by the entropic force  $\nabla_X \ln(q)$  to region  $X_L = 5, W_L > 10^{-8}$ . Two instances of hitting probabilities q(X, W) are presented at s = 0.2 and s = 0.8.





- 1. Solve the hitting probability *q* from Eq. (5) by integrating backward from s = L to s = 0 with a specified end condition  $\Omega_L$ —i.e., q(s = L) = 1 if  $\{X(L), W(L)\} \in \Omega_L$  and q(s = L) = 0 if  $\{X(L), W(L)\} \notin \Omega_L$ ;
- 2. Once the hitting probability *q* is known, calculate the entropic force for any general potential *U*: i.e.,  $F = \frac{\partial}{\partial X} ln(q)$ ;
- 3. Sample the bridge using Eq. (6), which is guaranteed to condition the chains to end in a specified configuration;
- 4. Gather unbiased statistics in this modified ensemble.

#### **III. RESULTS AND DISCUSSIONS**

The first example we examine is a Gaussian polymer ring, where the start point and end point are the same at  $X_o = X_L$ . The entropic force to achieve this process is  $\nabla_X \ln(q) = -(X - X_o)/(L - s)$ . Figure 2 shows the generated probability density function (PDF) of an intermediate position on the chain using the Brownian bridge. These results are consistent with the predicted probability of a 3D polymer ring,<sup>18</sup>

$$PDF(s,\rho) = \frac{2}{s(L-s)} \frac{\rho^2}{\sqrt{2\pi s(L-s)}} \exp\left(-\frac{3\rho^2}{2s(L-s)}\right), \quad (7)$$

where  $\rho = |X - X_o|$ .

Furthermore, we can control the winding number (WN) of the 2D polymer ring, which is frequently observed in cell biology: the DNA helix enables transcription by winding/unwinding histone complexes.<sup>19</sup> Given the hitting probability  $q(\theta(s), r(s)) = p(r_L, \theta_L | r(s), \theta(s))$  for a planar diffusion process,<sup>20</sup> we condition the WN for a 2D polymer ring, where  $r_L$  and  $\theta_L$  are the end conditions for radius and polar angle (see Appendix B for SDEs in polar coordinates). Figures 3(a) and 3(b) show configurations of 2D rings wrapping around the center point for different winding numbers. Although not shown, one can also choose to control only the final angle  $\theta_L$  by using the hitting probability  $f(\theta_L | \theta(s)) = \int_0^\infty p(\theta_L, r_L | r(s), \theta(s)) \cdot r_L dr_L$ .

We will now consider a Gaussian chain in a quadratic potential  $[U(x) = x^2]$  and use a Brownian bridge to generate polymer



**FIG. 2.** The probability density function between two points on a 3D polymer ring (L = 1). Symbols = Brownian bridge simulation (ds = 0.001, sample size:  $n = 10^5$ ) and solid lines = analytical PDF [Eq. (7)].



**FIG. 3**. Control of the winding number for a 2D polymer ring (L = 1, ds = 0.001): (a) trajectories of the polar angle of a polymer as a function of the polymer contour length *s*; (b) trajectories of the radial distance of the polymer as a function of the polymer contour length for different winding numbers: (b-1)  $\theta_L/2\pi = 1$ , (b-2)  $\theta_L/2\pi = 2$ , and (b-3)  $\theta_L/2\pi = 4$ . Note that, for all polymer rings, the radial distance starts and ends at r = R (R = 1).

configurations efficiently, where both ends of the chain are fixed ( $X_0$  and  $X_L$ ) or only one end is fixed ( $X_0$ ). When two ends of a polymer are fixed, the end condition of the hitting probability becomes  $q(\mathbf{x}, w, L) = \delta(\mathbf{x} - \mathbf{x}_L)$ . In this case, the analytical formula of the hitting probability is known,  $q(\mathbf{x}, w, s) = \frac{1}{\sqrt{2\pi(L-s)}} \exp\left(-\frac{(\mathbf{x}-\mathbf{x}_L)^2}{2(L-s)}\right)$ . We should also note that when both ends of a polymer are clamped, there is an analytical formula for the associated partition function of a 1D polymer,

$$Q = E\left[\exp\left(-\int_{o}^{L}\beta U(X(s))ds\right)|X_{o}, X_{L}\right]$$
$$= \sqrt{C_{1}}\exp\left(-\frac{X_{o}^{2} + X_{L}^{2}}{2L}(C_{2} - 1) + \frac{X_{o}X_{L}}{L}(C_{1} - 1)\right), \quad (8)$$



**FIG. 4.** Comparison of partition function *Q* from analytical results to Brownian bridge simulations for a 1D Gaussian polymer in a quadratic potential  $[U(x) = x^2]$ : (a) both end points of the polymer are fixed ( $X_o = 0, L = 1, ds = 0.001$ , sample size:  $n = 10^4$ ); (b) one end point is fixed (L = 1, ds = 0.01, sample size:  $n = 10^3$ ) with a specified Boltzmann weight threshold  $W_L > \varepsilon$  for the Brownian bridge simulations.



**FIG. 5.** (a) Average squared radius of gyration  $\langle R_g^2 \rangle$  as a function of initial polymer position  $X_o$  for a Gaussian chain in a quadratic potential. BB = Brownian bridge (BB) and NS = naive sampling (NS). The end condition for the bridge is  $(X_L \in [-2, 2], W_L \in [10^{-10}, 1])$ . (b)  $\langle R_g^2 \rangle$  as a function of sample size *n* for sampling schemes BB and NS. The initial position is  $X_o = 4$ . (c) 1D histogram of total Boltzmann weight  $W_L$  and  $R_g^2 \cdot W_L$  for  $X_0 = 4$ . [(d)–(f)]: 2D histogram of  $\{R_g^2 \cdot W_L\}$  and  $\{W_L\}$  for  $X_0 = 4$ : (d) naive sampling with a sample size of  $n = 10^2$ ; (e) naive sampling with  $n = 10^4$ ; (f) Brownian bridge with  $n = 10^2$ .

where  $C_1 = \frac{\sqrt{2\beta L}}{\sinh(\sqrt{2\beta L})}$  and  $C_2 = \frac{\sqrt{2\beta L}}{\tanh(\sqrt{2\beta L})}$ . Figure 4(a) shows that the partition function *Q* decreases with large *X*<sub>L</sub>. Simulations from the bridge process are consistent with the analytical result, Eq. (8), which demonstrates that the bridge indeed samples the probability distribution properly.

In the next example, we start the 1D chain at  $X_o$  and let the other end be free, which is shown in Fig. 4(b). The corresponding partition function is again explicit,  $Q = \frac{1}{\sqrt{\cosh(\sqrt{2\beta}L)}} \times \exp\left(-\frac{X_o^2\sqrt{2\beta}}{2} \tanh\sqrt{2\beta}L\right)$ . We solve the hitting probability q(x, w, s) from the backward Fokker–Planck equation to constrain the total Boltzmann weight  $W_L$  of the chain (see Appendix C for the numerical method). Here, we demonstrate how well a bridge captures the polymer's free energy when we condition the chains to lie in regions of high total Boltzmann weight. By omitting highly improbable configurations (small Boltzmann weight), we expect the partition function to be essentially the theoretical value while having a more efficient simulation process. We solve the backward Fokker–Planck equation with the following boundary conditions,

$$q \to 0 \quad \text{when } |x| \to \infty,$$
 (9)

$$q \to 0 \quad \text{when } \ln(w) \to -\infty,$$
 (10)

$$\frac{\partial q}{\partial \ln(w)} = 0 \quad \text{when } \ln(w) = 0. \tag{11}$$

The end condition satisfies  $q(x, w, s = L) = H(w - \varepsilon)$ , where H(z) is the Heaviside step function [i.e., H(z) = 1 if z > 0; H(z) = 0 if z < 0]. We choose to condition the final Boltzmann weight to be  $W_L > \varepsilon$  ( $\varepsilon \ll 1$ ). In Fig. 4(b), we design the end condition by varying  $\varepsilon$  such that the bridge process does an excellent job capturing the partition function for the given range of  $X_o$ .

To examine the polymer properties in an external field, any macroscopic quantity F (e.g., radius of gyration) can be estimated by

$$\langle F \rangle = \frac{1}{Q} \int_{\{\mathbf{X}, W\} \in \Omega} W_L F(\{\mathbf{X}\}) \delta P = \frac{\langle W_L F(\{\mathbf{X}\}) \rangle}{Q}.$$
 (12)

Instead of sampling the entire phase space, we could sample the polymer conformations in high probability of phase space,  $\Omega_{\varepsilon} \equiv [\{X, W\} \in \Omega: W_L > \varepsilon]$  such that

$$\langle F \rangle \approx \frac{\sum_{k} F^{(k)} W_{L}^{(k)}}{\sum_{k} W_{L}^{(k)}}.$$
(13)

Here, we investigate the radius of gyration  $(R_g^2)$  for a 1D polymer in a quadratic field where only one end is constrained. Figure 5(a) shows that both naive sampling (without entropic force) and Brownian bridge could provide an equivalent ensemble of  $\langle R_g^2 \rangle$  except that the naive sampling has to conduct an excessive number of simulations. Figure 5(b) shows that when a polymer is far away from the minimum of the potential ( $X_o = 4$ ), the rate of convergence for  $\langle R_g^2 \rangle$  using the Brownian bridge is significantly faster than naive



**FIG. 6.** Comparison of the Brownian bridge to Monte Carlo and naive sampling methods: Gaussian 1D polymer in rugged potential. (a) Schematic of rugged potential  $U(x) = 2(\sin(x) + \cos(2x) + \sin(4x)) + 6.5$ . (b) Distribution of polymer end location  $X_L$  and final Boltzmann weight  $\ln(W_L)$  for the rare event sampling using various sampling approaches: Brownian bridge (BB), Monte Carlo (MC), and Naive Sampling (NS). The dashed square indicates the designated region for the Brownian bridge. (c) 1D histogram of polymer position  $X_L$  and Boltzmann weight  $W_L$  for methods NS ( $n = 10^3$ ), MC (n = 50), and BB (n = 50). (d) Polymer trajectories (n = 50,  $X_o = 0$ ) using the Brownian bridge where the black box at s = 1 indicates the end conditions [ $5 < X_L < 6$ ,  $-8 < \ln(W) < -5$ ]. (e) Hitting probabilities  $q(X, \ln(W))$  at s = 0 and s = L, with L = 1.

sampling. From Figs. 5(d) and 5(e), the inefficiency in naive sampling arises because this approach has to swipe all regions of phase space. Therefore, one has to resort to a high number of simulations to estimate macroscopic observables. On the other hand, the Brownian bridge enables efficient sampling by only targeting the highly probable regions. Based on Eq. (12), parameters of  $\{R_g^2 \cdot W_L\}$  and  $\{W_L\}$  are critical. One can hit the highly probable regions [Fig. 5(c)] in terms of both parameters using the Brownian bridge [Figs. 5(d)–5(f)] and thus reduce the required number of samples significantly.

The Brownian bridge also has its convenience for rare event sampling. The traditional biased sampling uses a custom probability distribution to enhance the acceptance probabilities in a hardly visited region. Here, we examine a 1D Gaussian polymer under a rugged potential [Fig. 6(a)], which is expressed as a specified Fourier series. In naive sampling, a sampling size of  $n = 10^3$  would not reach the phase space  $5 < X_L < 6$  and  $-8 < \ln(W_L) < -5$  when the start point is  $X_o = 0$ . These events are incredibly rare, occurring less than 0.001% of the time. The Metropolis Monte Carlo method uses the Boltzmann probability distribution to further enhance the acceptance [66% and n = 50, see Figs. 6(b) and 6(c)]. On the other hand, in Fig. 6(d), the Brownian bridge guarantees the rare event is always visited [see the end condition of q at s = 1 in Fig. 6(e)].

Finally, we note that the Brownian bridge formalism can be used to constrain a stochastic process to lie in a given region in phase space during its entire path, not just its end points. This idea



**FIG. 7.** Example of Brownian excursion (n = 10): (a) with Brownian bridge and (b) without Brownian bridge. The excursion constrains 2D Gaussian polymers in the domain {X, Y}  $\subset [0, 1] \times [0, 1]$  for the entire path 0 < s < 1 (domain shown as red).

is known as a Brownian excursion and is derived in Appendix D. Essentially, if one uses the backward Fokker–Planck equation to calculate a hitting probability q(x, w, s), but uses a vanishing Dirichlet boundary condition q = 0 on the boundary in which one constrains the polymer path, one can confine the polymer to be in a region with the correct conditional statistics. In Fig. 7, we show an example of using a Brownian excursion to confine a 2D polymer in a box for its entire path.

We conclude this section by discussing the advantages and disadvantages of the Brownian bridge method. As a statistically mechanically exact sampling method, it can sample a polymer chain for a given topology. To estimate a partition function for an ensemble, the Brownian bridge can improve the sampling speed by controlling the end point in the phase space [e.g., space (x) and Boltzmann weight w], which can be advantageous compared to other approaches based on the trial and error approaches (e.g., umbrella sampling,<sup>12</sup> metadynamics,<sup>21</sup> and transition path methods<sup>22</sup>). However, in order to better estimate the hitting probability q, one needs to solve a backward Fokker–Planck equation, which can be computationally demanding for high dimensional systems. Overcoming this issue will be a subject pursued in future studies.

#### **IV. CONCLUSIONS**

In this work, we have established a general framework for controlling stochastic processes using a Brownian bridge, where we in particular use this technique to control polymer conformations. The exact sampling from a Brownian bridge allows one to design (a) polymer topologies, (b) most probable configurations (for estimation of macroscopic properties), and (c) rare events by specifying the end condition. The methodology is further extended to condition a polymer to lie in a particular region of phase space for its entire path. We note that this general framework can be applied to any dynamical process described by a Markov chain and thus envision it having broad applicability in physical chemistry, such as chemical reactions,<sup>23</sup> phase transitions, quantum mechanics,<sup>24</sup> and signal processing.<sup>25</sup>

#### ACKNOWLEDGMENTS

This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by the National Science Foundation, Grant Nos. CTS190055 and CHE190089.

#### APPENDIX A: DERIVATION OF BROWNIAN BRIDGE

Since the Brownian bridge satisfies  $Br \propto q * p$ , we have  $Br(\mathbf{x}, w, s) = C * p * q$ , where *C* is a constant. We express  $\partial Br/\partial s$  as

$$\frac{\partial Br}{\partial s} = C \bigg( \frac{\partial p}{\partial s} q + \frac{\partial q}{\partial s} p \bigg). \tag{A1}$$

Using Eqs. (4) and (5), we write Eq. (A1) as

$$\frac{\partial Br}{\partial s} = C * q * \left( -\frac{\partial}{\partial x} \cdot (Ap) + \frac{\partial (w\beta U(\mathbf{x})p)}{\partial w} + \frac{1}{2} \frac{\partial^2}{\partial x \partial x} : (\mathbf{M} \cdot \mathbf{M}^T p) \right) 
+ C * p * \left( -\mathbf{A} \cdot \frac{\partial q}{\partial \mathbf{x}} + \beta U(\mathbf{x}) \frac{\partial q}{\partial (\ln w)} - \frac{\mathbf{M} \cdot \mathbf{M}^T}{2} : \frac{\partial^2 q}{\partial \mathbf{x} \partial \mathbf{x}} \right) 
= -\frac{\partial}{\partial \mathbf{x}} \cdot (Ap * C * q) + \frac{\partial (w\beta U(\mathbf{x})p * C * q)}{\partial w} 
+ \frac{1}{2} \frac{\partial^2}{\partial x \partial \mathbf{x}} : \left( \mathbf{M} \cdot \mathbf{M}^T p * C * q \right) - \frac{\partial}{\partial \mathbf{x}} \left( \mathbf{M} \cdot \mathbf{M}^T \cdot \frac{1}{q} \frac{\partial q}{\partial \mathbf{x}} q * C * p \right) 
= -\frac{\partial}{\partial \mathbf{x}} \cdot (ABr) + \frac{\partial (w\beta U(\mathbf{x})Br)}{\partial w} + \frac{1}{2} \frac{\partial^2}{\partial \mathbf{x} \partial \mathbf{x}} : \left( \mathbf{M} \cdot \mathbf{M}^T Br \right) 
- \frac{\partial}{\partial \mathbf{x}} \left( \mathbf{M} \cdot \mathbf{M}^T \cdot \frac{\partial \ln(q)}{\partial \mathbf{x}} Br \right).$$
(A2)

By reorganizing Eq. (A2), we have

$$\frac{\partial Br}{\partial s} + \frac{\partial}{\partial x} \cdot \left[ \left( \mathbf{A} + \mathbf{M} \cdot \mathbf{M}^T \cdot \frac{\partial \ln(q)}{\partial x} \right) Br \right] - \frac{\partial (w\beta U(\mathbf{x})Br)}{\partial w}$$
$$= \frac{1}{2} \frac{\partial^2}{\partial x \partial x} : \left( \mathbf{M} \cdot \mathbf{M}^T Br \right). \tag{A3}$$

By comparing to Eq. (4), the Brownian bridge *Br* satisfies the same partial differential equation as the forward probability density function with an additional drift in terms of hitting probability  $q: \mathbf{M} \cdot \mathbf{M}^T \cdot \frac{\partial}{\partial r}(\ln q)$ .

#### APPENDIX B: WINDING NUMBER: STOCHASTIC SIMULATION OF 2D FLEXIBLE POLYMER IN POLAR COORDINATE

#### 1. Itô formula for random walk

Let  $(\mathscr{B}_1, \mathscr{B}_2)$  be the two-dimensional Wiener process in Cartesian coordinates,

$$dx_1 = Md\mathscr{B}_1, \quad dx_2 = Md\mathscr{B}_2, \tag{B1}$$

where *M* is the diffusion coefficient. The relationships between polar and Cartesian coordinates are given below:

$$f_1: r = \sqrt{x_1^2 + x_2^2},$$
 (B2)

$$f_2: \theta = \arctan\left(\frac{x_2}{x_1}\right).$$
 (B3)

Therefore, the associated stochastic differential equations (SDEs) in the polar coordinate are

$$d\theta = \frac{\partial f_2}{\partial x_1} dx_1 + \frac{\partial f_2}{\partial x_2} dx_2 + \frac{1}{2} \frac{\partial^2 f_2}{\partial x_1^2} dx_1 dx_1 + \frac{1}{2} \frac{\partial^2 f_2}{\partial x_2^2} dx_2 dx_2 + O(ds^{3/2}).$$
(B5)

By neglecting higher order terms, we reach the SDE in the polar coordinate,

$$dr = \frac{M^2}{2r} + M\cos\theta d\mathcal{B}_1 + M\sin\theta d\mathcal{B}_2,$$
 (B6)

$$d\theta = -\frac{\sin\theta}{r}Md\mathscr{B}_1 + \frac{\cos\theta}{r}Md\mathscr{B}_2.$$
 (B7)

#### 2. Brownian bridge: hitting probability

For a 2D Brownian motion, the joint probability of  $\theta$  and r is  $^{20,26}$ 

$$p(r,\theta,t;\rho,\alpha) = \frac{1}{\pi t} \exp\left(-\frac{r^2 + \rho^2}{2t}\right) \int_0^\infty \cos(\nu(\theta - \alpha)) I_\nu\left(\frac{\rho r}{t}\right) d\nu,$$
(B8)

which is the solution of the corresponding Fokker-Planck equation,

$$\frac{\partial p}{\partial t} = \frac{1}{2} \left( \frac{\partial^2 p}{\partial r^2} + \frac{1}{r} \frac{\partial p}{\partial r} + \frac{1}{r^2} \frac{\partial^2 p}{\partial \theta^2} \right), \tag{B9}$$

$$p|_{t=0} = \delta(\theta - \alpha, r - \rho). \tag{B10}$$

Note that  $I_v$  is the modified Bessel function of the first kind. In this case, the hitting probability q of the backward Fokker–Planck equation should be

$$q(r,\theta,s;r_L,\theta_L) \propto \frac{1}{\pi(L-s)} \exp\left(-\frac{r^2 + r_L^2}{2(L-s)}\right) \\ \times \int_0^\infty \cos(\nu(\theta-\theta_L)) I_\nu\left(\frac{r_L r}{L-s}\right) d\nu, \tag{B11}$$

where  $q(r_L, \theta_L, L) = 1$ . By letting  $r_o = r_L$  and specifying  $\theta_L$ , we can design a polymer ring with a given winding number,  $WN = \theta_L/2\pi$ .

Figure 8 shows the hitting probability function for two different moments: (a) s = 0.2 and (b) s = 0.7. Note that the corresponding modeling parameters are the same as Fig. 3 of the manuscript. When  $|\theta/(2\pi)| \gg 1$ ,

$$\frac{d\ln(q)}{dr} < 0, \tag{B12}$$

which explains the reason why the radial distance r most likely first decreases during the polymer growth shown in Fig. 3(b) of the manuscript.

Once the hitting probability is known, the stochastic differential equations associated with the Brownian bridge are

$$dr^{Br} = dr + M^2 \frac{\partial \ln(q)}{\partial r} ds,$$
 (B13)



**FIG. 8**. Control of winding numbers for a 2D polymer ring (L = 1, ds = 0.001). The logarithmic hitting probability ln q is plotted as a function of r and  $\theta/(2\pi)$  at (a) s = 0.2 and (b) s = 0.7.

$$d\theta^{Br} = d\theta + \frac{M^2}{r} \frac{\partial \ln(q)}{\partial \theta} ds.$$
 (B14)

One can also choose to only control the winding number  $\theta_L$  by using the following hitting probability function,<sup>20</sup>

$$q^{\theta}(\theta, s, r; \theta_L) = \int_0^{\infty} q(r, \theta, s; r_L, \theta_L) r_L dr_L = \frac{r e^{\frac{\rho^2}{4(L-s)}}}{2\sqrt{2\pi(L-s)}}$$
$$\times \int_0^{\infty} \cos(\nu(\theta - \theta_L)) \left[ I_{\frac{\nu-1}{2}} \left( \frac{r^2}{4(L-s)} \right) + I_{\frac{\nu+1}{2}} \left( \frac{r^2}{4(L-s)} \right) \right] d\nu. \tag{B15}$$

#### APPENDIX C: NUMERICAL SIMULATION OF BACKWARD FOKKER-PLANCK EQUATION: PROPER GENERALIZED DECOMPOSITION

We choose the method of proper generalized decomposition (PGD) to solve the multidimensional backward Fokker–Planck equation: for the conventional finite difference method, the demand of memory is tremendous ( $n^N$ , n is the number of discretizations in each dimension, and N is the dimensions); however, for PGD, it is  $N \cdot n^2$ . We refer both Refs. 27 and 28 for the general framework of PGD. In the following, we demonstrate the procedure of using PGD to solve the backward Fokker–Planck equation.

Here, we write the backward Fokker-Planck equation as

$$\frac{\partial q}{\partial s} - U(x_k)\frac{\partial q}{\partial \xi} = -\frac{1}{2}\frac{\partial^2 q}{\partial x_k^2}, \quad k = 1, 2, \dots, N,$$
(C1)

where *N* indicates the dimensions of the space and  $\xi = \ln(w)$ . The above equation characterizes the probability *q* for a random walk in an external field *U*. For convenience, let s = L - t, and we solve the following equation forward in *t*,

$$\frac{\partial q}{\partial t} + U(x_k)\frac{\partial q}{\partial \xi} = \frac{1}{2}\frac{\partial^2 q}{\partial x_k^2}.$$
 (C2)

Based on the definition of PGD,<sup>27</sup> the hitting probability is regarded as

$$q(\xi, x_1, x_2, \dots, x_N; t) = \sum_{j=1}^m G_j(\xi) \prod_{k=1}^N F_{kj}(x_k),$$
(C3)

J. Chem. Phys. **153**, 034901 (2020); doi: 10.1063/5.0010368 Published under license by AIP Publishing ARTICLE

where *m* is the number of convergent series. For the *t*-derivative term, we use the backward Euler scheme,

$$\frac{q^{(i+1)}-q^{(i)}}{\Delta t}+U(x_k)\frac{\partial q^{(i+1)}}{\partial \xi}=\frac{1}{2}\frac{\partial^2 q^{(i+1)}}{\partial x_k^2},$$
(C4)

where  $\Delta t = \Delta s$  is the length of the polymer segment. In the initial value problems,  $q^{(i)}$  is always known, and we may regard it as the source function  $[f = q^{(i)}/\Delta t$ , also  $u = q^{(i+1)}]$  and write Eq. (C4) as

$$\frac{u}{\Delta t} + U(x_k)\frac{\partial u}{\partial \xi} - \frac{1}{2}\frac{\partial^2 u}{\partial x_k^2} = f.$$
 (C5)

For any *i*th step in terms of *t*, we solve for *u* from Eq. (C5).

#### 1. Weak formulation

To solve Eq. (C5), we utilize the weak formulation from the finite element approach, which is formulated as

$$\int_{\Omega} v \left( \frac{u}{\Delta t} + U(x_k) \frac{\partial u}{\partial \xi} - \frac{1}{2} \frac{\partial^2 u}{\partial x_k^2} \right) d\Omega = \int_{\Omega} f v d\Omega, \qquad (C6)$$

where the domain is  $\Omega = \{\xi, x_k\}$ . It would be straightforward to show that

$$\frac{1}{\Delta t} \int_{\Omega} v u d\Omega + \int_{\Omega} U(x_k) v \frac{\partial u}{\partial \xi} d\Omega + \frac{1}{2} \int_{\Omega} \frac{\partial v}{\partial x_k} \frac{\partial u}{\partial x_k} d\Omega = \int_{\Omega} f v d\Omega.$$
(C7)

Due to the convective character of Eq. (C7), one can add an artificial diffusion to allow larger  $\Delta t$ , and the modified equation is expressed as<sup>28</sup>

$$\frac{1}{\Delta t} \int_{\Omega} v u d\Omega + \int_{\Omega} U(x_k) v \frac{\partial u}{\partial \xi} d\Omega + \int_{\Omega} \frac{\beta U(x_k) h}{2} \frac{\partial v}{\partial x_k} \frac{\partial u}{\partial x_k} d\Omega + \frac{1}{2} \int_{\Omega} \frac{\partial v}{\partial x_k} \frac{\partial u}{\partial x_k} d\Omega = \int_{\Omega} f v d\Omega,$$
(C8)

where  $\beta = \operatorname{coth}(Pe) - 1/Pe$ , and *h* is the size of the discretization. The Peclet number is defined as  $Pe = U \cdot h$ . In our simulations, we choose Pe = 0.1.

#### 2. Numerical procedure

To solve Eq. (C7), we choose to proceed with 1D problem (N = 1). Our numerical procedure can be extended to the multidimensional problem. For the 1D problem, the approximation of *u* is now defined at iteration *n*,

$$u^{(n)}(\xi, x) = \sum_{j=1}^{n} F_j(x) G_j(\xi),$$
(C9)

and the enrichment step consists of looking for the function  $[R(\xi), S(x)]$  such that

$$u^{(n+1)}(\xi, x) = u^{(n)}(\xi, x) + R(x)S(\xi).$$
(C10)

Functions  $(F_{n+1}, G_{n+1})$  are obtained by normalizing the function (R, S). The iteration procedure stops when the solution converges to a small (R, S). In the following, we elaborate the steps of solving (R, S) using an enrichment procedure. We refer Ref. 27 for the detailed enrichment procedure.

#### APPENDIX D: BROWNIAN EXCURSION

An excursion is a process that is constrained to lie in a given region  $\Omega_s$  at all times and have its start and end points conditioned to lie in regions  $\Omega_o$  and  $\Omega_L$  that are subsets of  $\Omega_s$ . Note that if  $\Omega_L = \Omega_s$ , then there is no additional constraint on the end point.

Let us look at a random walk with drift A and diffusion M,

$$dX = Ads + M \cdot d\mathcal{B}. \tag{D1}$$

The forward probability p(x, s) for the random walk satisfies a Fokker–Planck equation,

$$\frac{\partial p}{\partial s} + \frac{\partial}{\partial x} \cdot (Ap) = \frac{1}{2} \frac{\partial^2}{\partial x \partial x} : (M \cdot M^T p), \quad (D2)$$

where the initial conditions and boundary conditions are the following if the process is to start in region  $\Omega_o$  and lie in region  $\Omega_s$  for all time,

$$p(\mathbf{x},0) = \mathbb{1}\{\mathbf{x}\in\Omega_o\}, \quad p(\mathbf{x}\in\partial\Omega_s,s) = 0.$$
(D3)

Note: in the above equation, the notation  $\partial \Omega_s$  represents the boundary of region  $\Omega_s$ .

The hitting probability  $q(\mathbf{x}, s)$  for this random walk satisfies a backward Fokker–Planck equation,

$$\frac{\partial q}{\partial s} + \mathbf{A} \cdot \frac{\partial q}{\partial \mathbf{x}} = -\frac{\mathbf{M} \cdot \mathbf{M}^{\mathrm{T}}}{2} : \frac{\partial^{2} q}{\partial \mathbf{x} \partial \mathbf{x}}, \tag{D4}$$

with the boundary condition  $q(\mathbf{x} \in \partial \Omega_s, s) = 0$  and the end condition  $q(\mathbf{x}, L) = \mathbb{I}\{\mathbf{x} \in \Omega_L\}.$ 

Similar to the derivation in the manuscript, the Bridge process  $Br^{Ex}$  for excursion that conditions both start and end points is

$$Br^{Ex}(\mathbf{x},s) \propto p \cdot q.$$
 (D5)

Thus, the process satisfies

$$\frac{\partial Br^{Ex}}{\partial s} + \frac{\partial}{\partial \mathbf{x}} \left( \left( \mathbf{A} + \mathbf{M} \cdot \mathbf{M} \frac{\partial \ln(q)}{\partial \mathbf{x}} \right) Br^{Ex} \right) = \frac{1}{2} \frac{\partial^2}{\partial \mathbf{x} \partial \mathbf{x}} : \left( \mathbf{M} \cdot \mathbf{M}^T B r^{Ex} \right),$$
(D6)

where the boundary condition is  $Br^{Ex}(\mathbf{x} \in \partial \Omega_s, s) = 0$ .

The only difference between the partial differential equation (PDE), Eq. (D6), and the Brownian bridge PDE is the inclusion of the boundary condition  $Br^{Ex}(\mathbf{x} \in \partial\Omega_s, s) = 0$ . However, the additional drift term  $\partial_X(\ln q)$  allows the process to automatically satisfy this boundary condition, since  $\partial_X(\ln q)$  will have an infinite magnitude as we approach the boundary  $\partial\Omega_s$  and point normal to the boundary (see Fig. 9). Thus, an unconstrained process that has the additional drift  $\mathbf{M} \cdot \mathbf{M} \frac{\partial \ln(q)}{\partial \mathbf{x}}$  will satisfy the PDE [Eq. (D6)], which allows us to write a modified stochastic differential equation (SDE) for the Brownian excursion as

$$d\mathbf{X}^{\mathrm{Br}^{\mathrm{Ex}}} = d\mathbf{X} + \left(\mathbf{M} \cdot \mathbf{M}^{\mathrm{T}}\right) \cdot \frac{\partial}{\partial \mathbf{X}} (\ln q) ds. \tag{D7}$$

#### Brownian excursion for 2D polymer

For a 2D flexible polymer A = 0, the corresponding Fokker–Planck equation is

$$\frac{\partial q}{\partial t} = \frac{1}{2} \left( \frac{\partial^2 q}{\partial x_1^2} + \frac{\partial^2 q}{\partial x_2^2} \right), \tag{D8}$$

J. Chem. Phys. **153**, 034901 (2020); doi: 10.1063/5.0010368 Published under license by AIP Publishing



**FIG. 9.** The entropic force (a) 
$$\frac{\partial \ln q}{\partial x}$$
 and  
(b)  $\frac{\partial \ln q}{\partial y}$  for a Gaussian chain confined  
to a rectangular box  $\Omega_s = x, y \in [0, 1]$   
 $\times [0, 1]$ . Plots are at  $s = 0.5$  with  $L = 1$ .

where t = L - s and  $\mathbf{M} = \delta$ . The excursion is defined as  $q(\mathbf{x} \in \partial \Omega_s, s) = 0$  and  $\Omega_s = \{x, y\} \subset [0, 1] \times [0, 1]$ . Using the separation of variables, we have the solution for q,

$$q(x, y, t) = \sum_{n,m=1}^{\infty} B_{nm} \sin((2n-1)\pi x) \sin((2m-1)\pi y)$$
$$\times e^{-\frac{1}{2}\left(\left((2n-1)\pi\right)^{2} + \left((2m-1)\pi\right)^{2}\right)t}.$$
(D9)

Here, we impose the initial condition as constant uniform probability  $q(\mathbf{x} \in \Omega_s, t = 0) = 1$ . Then, the corresponding coefficient is

$$B_{nm} = \frac{1}{(2n-1)(2m-1)}.$$
 (D10)

In Fig. 7(a), the Brownian bridge can exactly control the excursion. In addition, the corresponding entropic force is shown in Fig. 9.

#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### REFERENCES

<sup>1</sup>D. C. Schwartz and C. R. Cantor, "Separation of yeast chromosome-sized DNAs by pulsed field gradient gel electrophoresis," Cell **37**, 67–75 (1984).

<sup>2</sup>G. Fredrickson *et al.*, *The Equilibrium Theory of Inhomogeneous Polymers* (Oxford University Press on Demand, 2006), Vol. 134.

<sup>3</sup>S. W. Sides, B. J. Kim, E. J. Kramer, and G. H. Fredrickson, "Hybrid particle-field simulations of polymer nanocomposites," Phys. Rev. Lett. 96, 250601 (2006).

<sup>4</sup>S. A. Vshivkov, *Phase Transitions and Structure of Polymer Systems in External Fields* (Cambridge Scholars Publishing, 2019).

<sup>5</sup>A. Arora, J. Qin, D. C. Morse, K. T. Delaney, G. H. Fredrickson, F. S. Bates, and K. D. Dorfman, "Broadly accessible self-consistent field theory for block polymer materials discovery," Macromolecules 49, 4675–4690 (2016).

<sup>6</sup>R. R. Netz and M. Schick, "Polymer brushes: From self-consistent field theory to classical theory," Macromolecules **31**, 5105–5122 (1998).

<sup>7</sup>Q. Wang, T. Taniguchi, and G. H. Fredrickson, "Self-consistent field theory of polyelectrolyte systems," J. Phys. Chem. B 108, 6733–6744 (2004).

<sup>8</sup>V. Arkhipov, E. Emelianova, and H. Bässler, "Hot exciton dissociation in a conjugated polymer," Phys. Rev. Lett. **82**, 1321 (1999).

<sup>9</sup>D. Frenkel and B. Smit, Understanding Molecular Simulation: From Algorithms to Applications (Elsevier, 2001), Vol. 1.

<sup>10</sup>J. S. Liu, Monte Carlo Strategies in Scientific Computing (Springer Science & Business Media, 2008). <sup>11</sup>S. T. Tokdar and R. E. Kass, "Importance sampling: A review," WIREs Comput. Stat. 2, 54–60 (2010).

<sup>12</sup>J. Kästner, "Umbrella sampling," Wiley Interdiscip. Rev.: Comput. Mol. Sci. 1, 932–942 (2011).

<sup>13</sup>J. L. Doob, Classical Potential Theory and its Probabilistic Counterpart: Advanced Problems (Springer Science & Business Media, 2012), Vol. 262.

<sup>14</sup>S. Krishnaswami, D. Ramkrishna, and J. M. Caruthers, "Statistical-mechanically exact simulation of polymer conformation in an external field," J. Chem. Phys. 107, 5929–5944 (1997).

<sup>15</sup>E. F. Koslover and A. J. Spakowitz, "Systematic coarse-graining of microscale polymer models as effective elastic chains," Macromolecules **46**, 2003–2014 (2013).

<sup>16</sup>A. J. Spakowitz and Z.-G. Wang, "DNA packaging in bacteriophage: Is twist important?," Biophys. J. 88, 3912–3923 (2005).

<sup>17</sup>A. D. Wissner-Gross and C. E. Freer, "Causal entropic forces," Phys. Rev. Lett. 110, 168702 (2013).

<sup>18</sup>I. Teraoka, Polymer Solutions: An Introduction to Physical Properties (John Wiley & Sons, 2002).

<sup>19</sup>J. Murn and Y. Shi, "The winding path of protein methylation research: Milestones and new frontiers," Nat. Rev. Mol. Cell Biol. 18, 517 (2017).

<sup>20</sup>S. Brassesco and S. C. G. Pire, "On the density of the winding number of planar Brownian motion," J. Theor. Probab. 27, 899–914 (2014).

<sup>21</sup>C. Micheletti, A. Laio, and M. Parrinello, "Reconstructing the density of states by history-dependent metadynamics," Phys. Rev. Lett. **92**, 170601 (2004).

<sup>22</sup> P. G. Bolhuis, D. Chandler, C. Dellago, and P. L. Geissler, "Transition path sampling: Throwing ropes over rough mountain passes, in the dark," <u>Annu. Rev. Phys. Chem.</u> **53**, 291–318 (2002).

<sup>23</sup>N. G. Van Kampen, Stochastic Processes in Physics and Chemistry (Elsevier, 1992), Vol. 1.

<sup>24</sup> J. Goold, M. Huber, A. Riera, L. del Rio, and P. Skrzypczyk, "The role of quantum information in thermodynamics—A topical review," J. Phys. A: Math. Theor. 49, 143001 (2016).

<sup>25</sup>L. Hu and H. Zhu, "Bounded Brownian bridge model for UWB indoor multipath channel," in 2005 IEEE International Symposium on Microwave, Antenna, Propagation and EMC Technologies for Wireless Communications (IEEE, 2005), Vol. 2, pp. 1411–1414.

<sup>26</sup>S. Brassesco, "A note on planar Brownian motion," Ann. Probab. 20, 1498–1503 (1992).

<sup>27</sup>A. Ammar, B. Mokdad, F. Chinesta, and R. Keunings, "A new family of solvers for some classes of multidimensional partial differential equations encountered in kinetic theory modeling of complex fluids," J. Non-Newtonian Fluid Mech. **139**, 153–176 (2006).

<sup>28</sup>A. Ammar, B. Mokdad, F. Chinesta, and R. Keunings, "A new family of solvers for some classes of multidimensional partial differential equations encountered in kinetic theory modelling of complex fluids: Part II: Transient simulation using space-time separated representations," J. Non-Newtonian Fluid Mech. **144**, 98– 121 (2007).

J. Chem. Phys. **153**, 034901 (2020); doi: 10.1063/5.0010368 Published under license by AIP Publishing