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Approximations of the discrete slip-link model and their effect on nonlinear rheology predictions

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Synopsis

The discrete slip-link model (DSM) was developed to describe the dynamics of flexible polymer melts. The model is able to predict linear viscoelasticity of monodisperse linear, polydisperse linear, and branched systems. The model also shows good agreement with dielectric relaxation experiments, except for the single data set available for bidisperse linear systems with a small volume fraction of long chains. In this work, both shear and elongational flow predictions obtained using the DSM without parameter adjustment are shown. Model predictions for shear flow agree very well with experimental results. The DSM is able to capture the transient response as well as the steady-state viscosity. However, for elongational flow, agreement is unsatisfactory at large strains. The DSM captures the onset of strain hardening, but after a Hencky strain between 2 and 3, it predicts transient strain softening, whereas experiments show only monotonic growth. We explore a number of assumptions and approximations of the model and their effect on flow predictions. The approximations are related to the neglect of these phenomena, which are expected to be more sensitive in elongational flow: finite extensibility, convective constraint

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release, and deformation of dangling ends. We indeed find that shear flow predictions are insensitive to these approximations, but elongational flow is affected. However, none of these effects is able to bring prediction in line with experiments. We conclude that the currently accepted view of entanglement dynamics is incomplete. © 2013 The Society of Rheology. [http://dx.doi.org/10.1122/1.4788909]

I. INTRODUCTION

Entangled polymer melts and solutions have been the subject of study for more than 40 years [Berry and Fox (1968)]. Linear monodisperse systems, because of their relative simplicity, have attracted the most attention. It is believed that many relaxation (rheological, dielectrical, and optical) properties of these systems are determined by the dynamics of entanglements (which are topological constraints that chains exert on one another). The specific properties of linear melts and solutions generally scale with the average number of entanglements, i.e., the ratio of the molecular weight of the polymer chain to the average molecular weight between entanglements, and are independent of chain chemistry. The two most common nonlinear rheology experiments are shear flow and elongational flow. Because it is generally easier to maintain a homogeneous deformation for shear flow, there are more experimental data sets available, including most recently those by Auhl et al. (2008), Collis et al. (2005), Schweizer et al. (2004), Graham et al. (2003), and Pattamaprom and Larson (2001). These experiments show consistent results, and consequently the qualitative and quantitative behavior of melts and solutions in shear flow is well known. As the strain rate increases, the transient shear viscosity shows strain softening before reaching a steady state, which at high rates is preceded by an undershoot in viscosity. Even higher rates show decaying oscillations around the steady state. Elongational flow, on the other hand, is believed to produce qualitatively different behavior, although there are far fewer measurements of monodisperse linear systems in elongation. Bach et al. (2003) measured the elongational viscosity of melts, while Bhattacharjee et al. (2002) did the same for solutions. Elongational flow features transient strain hardening, which is not seen in shear flow. Also, no undershoots or oscillations before reaching steady-state have been seen for the transient elongational viscosity. Both groups saw that the steady-state elongational viscosity of solutions and melts decreases with increasing elongation rate for rates smaller than the inverse Rouse time, $\tau_R$. However, Bhattacharjee et al. (2002) saw an upturn in the steady-state viscosity of solutions at rates higher than $\tau_R^{-1}$, whereas Bach et al. (2003) did not.

In Auhl et al. (2008), Collis et al. (2005), Graham et al. (2003), Pattamaprom and Larson (2001), Schweizer et al. (2004), and Bhattacharjee et al. (2002), “tube” models were applied to predict linear rheology and flow experiments qualitatively. Tube models can predict linear rheology and flow experiments separately, but not simultaneously, because they typically do not have the same mathematical structure for equilibrium and flow calculations. Describing shear and elongational flow at the same time has not been accomplished by tube models, since they use a number of additional concepts (usually introducing adjustable parameters) to help improve their agreement with experiments. Auhl et al. (2008) applied the GLaMM model [Graham et al. (2003)] to their shear data. GLaMM is able to predict transient shear viscosity, but it shows unrealistic infinite viscosity in the case of elongational flow [Graham et al. (2003)]. Bhattacharjee et al. (2002) applied the Mead-Larson-Doi (MLD) “tube” model by Mead et al. (1998) to reproduce their experimental data for solutions. MLD shows smaller steady state viscosity than experimental data. Wagner et al. (2005) used a modified Doi–Edwards model to fit the
transient melt viscosity measured by Bach et al. (2003). While the model captures both strain hardening and steady-state viscosity, the effect of additional physics and adjustable parameters on shear predictions is unknown.

Multichain primitive chain network (PCN) simulations were performed by Yaoita et al. (2011) and Kushwaha and Shaqfeh (2011). However, later works point to problems with PCN implementations of detailed balance [Uneyama and Masubuchi (2011)] and osmotic force [Okuda et al. (2012)]. Also Kushwaha and Shaqfeh (2011) reported that constant constraint renewal/release frequency is a bad assumption in flow. According to them, constant constraint renewal/release result in oscillations around the steady-state viscosity value. While PCN qualitatively captures transient shear flow viscosity, it cannot predict elongational flow.

It is commonly believed that entanglement theory can in principle, at least qualitatively, predict shear flow as well as elongational flow simultaneously. Achieving the agreement may require adding physics and additional parameters to one of the existing models, trying to improve elongational flow predictions. On the other hand, it is possible that approximations in implementations of the original model could be the source of divergence from experimental data. Before exploring the effect of these approximations, it is unknown what kind of modification is required. We take the point of view that existing physics should first be tested unambiguously by removing assumptions and approximations from current state-of-the-art entanglement models, before adding new physical ideas to them. Therefore, in this paper we perform such a test on a single-chain mean-field entanglement model. Our starting point is the discrete slip-link model (DSM), which is able to predict linear viscoelasticity of monodisperse linear, polydisperse linear, and branched systems without any adjustment [Khaliullin (2010)]. The model also shows good agreement with dielectric relaxation experiments, except for a single data set of bidisperse linear systems with a small volume fraction of long chains [Pilyugina et al. (2012)]. We find that the DSM is capable of very good quantitative prediction of shear flow rheology, but is unable to predict either solution or melt elongational data. To examine the source of this discrepancy, we remove the few remaining approximations in the model. Namely, we consider finite extensibility, convective constraint release, and relaxation of dangling ends. While we find that elongational predictions are sensitive to each of these approximations, shear flow is not. Nonetheless, removal of all approximations is still not sufficient to predict either solution or melt elongational data. Therefore, we conclude that some physics is missing from current single-chain models. However, the DSM does reproduce the results of simultaneous stress and birefringence measurements during elongational flow by Luap et al. (2005).

II. DSM MODEL

The DSM is a single-chain mean-field mathematical model, which was first proposed by Schieber et al. (2003) and further developed by Khaliullin and Schieber (2009, 2010). In this model, the chain is represented as a random walk with constant step length $a_K$ (the Kuhn step). Entanglements are created and destroyed stochastically. As a result, the number of entanglements $Z(t) - 1$ on the chain fluctuates. The chain is coarse-grained to the entanglement level, which means that we integrate out information about individual Kuhn steps’ positions, and keep information only about the number of Kuhn steps in each strand between entanglements $N_i$, and the connector vector $Q_i$, where $i$ goes from 1 to $Z$ —the number of strands. The chain is subject to two dynamic processes: sliding dynamics (SD) and constraint dynamics (CD). SD corresponds to reallocation of Kuhn steps through entanglements with characteristic time $\tau_K$. SD can also create and destroy
entanglements at the ends of the chain. When the last Kuhn step of a dangling end goes through an entanglement, the entanglement is destroyed. The probability to create an entanglement at the end of the chain is connected with the destruction process through detailed balance. CD is the creation and destruction of entanglements due to SD of the surrounding chains. This process takes place along the entire length of the probe chain. We implement CD self-consistently with SD by introducing an entanglement lifetime distribution $p_{\text{CD}}(\tau_{i}^{\text{CD}})$. Upon creation, lifetimes are picked from the SD-consistent distribution $p_{\text{CD}}(\tau_{i}^{\text{CD}})$. Thus, the DSM has the set $\Omega$ of stochastic variables

$$\Omega = \{Z, \{N_i\}, \{Q_i\}, \{\tau_i^{\text{CD}}\}\}. \quad (1)$$

There are only three molecular-weight-independent parameters in the model: $M_K$, the molecular weight of a Kuhn step; $\beta$, which is related to the entanglement density; and $\tau_K$. $M_K$ is determined by chemistry and we do not treat it as an adjustable parameter, while $\beta$ and $\tau_K$ also depend on solvent concentration, and only $\tau_K$ is a function of temperature. These are fixed by comparison to $G^*$ data. Further details of the DSM can be found in the paper by Khaliullin and Schieber (2009). The stress tensor, which can be derived from thermodynamics [Schieber (2003); Steenbakkers and Schieber (2012)], is

$$\tau(t) = -n_c \left( \sum_{j=1}^{N} Q_j \left( \frac{\partial F_s(Q_j, N_j)}{\partial Q_j} \right)_{T,N_j} \right), \quad (2)$$

where $F_s(Q, N)$ is the Helmholtz free energy of a strand with $N$ Kuhn steps and end-to-end vector $Q$, $n_c$ is the number of polymer chains per unit volume, and $\langle\ldots\rangle$ is the ensemble average.

The equilibrium relaxation modulus can be calculated by using the Green–Kubo expression [Kubo (1957)]

$$G(t) = \frac{1}{n_c k_B T} \langle\tau_{xy}(0)\tau_{xy}(t)\rangle_{\text{eq}}, \quad (3)$$

Birefringence is calculated using the relation [Fuller (1995)]

$$n(t) = C \left( \sum_{j=1}^{N} \left[ 1 - \frac{3}{T(Q_j, N_j)} \frac{O_j}{O_j - 2 N_j} \right] \frac{O_j}{O_j - 2 N_j} \right), \quad (4)$$

where

$$T(Q_j, N_j) = \left( \frac{\partial F_s(Q_j, N_j)}{\partial Q_j} \right)_{T,N_j} \quad (5)$$

is the tension and $C$ is an adjusted constant coefficient.

### III. DSM ASSUMPTIONS AND APPROXIMATIONS

In the original implementation of the model, several approximations and assumptions were made to facilitate computation. While an approximation is purely mathematical, by assumptions we mean simplifying physical ideas, which cannot be proved, but whose effect can be investigated. These assumptions and approximations allow us to reduce the mathematical complexity and numerical cost of the model. While they are reasonable for
linear viscoelasticity, to which the DSM was first applied, when the DSM is applied to nonlinear flow, their validity might be questionable.

In the DSM, three assumptions and three approximations were made. We briefly introduce the assumptions, and then proceed to the approximations, each of which is discussed in detail in subsections below.

First, the DSM assumes that entanglements deform affinely. This is the simplest way to connect the macroscopic flow to the microscopic scale of the chain. This assumption might be relaxed by allowing the slip-links to fluctuate around affinely moving anchors [Likhtman (2005); Schieber and Horio (2010); Steenbakkers and Schieber (2012)]. Deriving a more-detailed description of entanglement motion is not a trivial task, which would likely require information from multichain models, and a more-detailed level of description.

Second, the DSM assumes a constant chain friction. This means that the sum of friction coefficients for all entanglements is proportional to the total number of Kuhn steps in the chain, $N_K$, and independent of the number of entanglements. This is done by making the friction coefficient, associated with the sliding of Kuhn steps through an entanglement, proportional to the number of Kuhn steps in the neighboring strands

$$
\tau_i = \frac{\tau_K k_B T}{a_K^2} \left\{ \begin{array}{ll}
N_1 + \frac{N_2}{2}, & i = 1 \\
\frac{N_i + N_{i+1}}{2}, & 1 < i < Z - 1 \\
\frac{N_{Z-1}}{2} + N_Z, & i = Z - 1.
\end{array} \right.
$$

Although the friction coefficient $\tau_i$ was not introduced in previous papers on the DSM, we point out that before we used a slightly less accurate expression. In Eq. (7) from Khaliullin and Schieber (2009), $\frac{2(\beta+1)}{\tau_K N_K N_{\text{ent}}}$ is in fact $\frac{b_T k_B T}{\tau_K}$. We implement constant chain friction more rigorously by modifying friction coefficients for the first and last entanglements. Also, we change the timescale of the model by a factor of $\beta + 1$. We previously found that constant chain friction leads to better shear flow predictions than does constant friction coefficient for all entanglements, as shown in Schieber et al. (2007). Constant chain friction is also in line with conventional thinking in tube models.

Third, we allow only binary entanglements in our model, i.e., entanglements involve only two chains. In a previous work, the effect of ternary entanglements [Pilyugina et al. (2012); Khaliullin and Schieber (2010)] was studied, and it was found that the addition of a fraction of ternary entanglements significantly reduces the quality of linear viscoelastic DSM predictions.

### A. Convective constraint release

The implementation of CD by Khaliullin and Schieber (2009) involves an entanglement lifetime distribution. Since their procedure to obtain this distribution is carried out in equilibrium, the result is not exact in flow.

For an ensemble of chains the rate of creation by SD and the rate of creation by CD should be the same, because when an entanglement is created on a dangling end of one chain by SD, it is also created on another chain by CD. The same argument holds for destruction by SD and CD. Therefore, there is an exact connection between entanglement lifetimes due to SD and CD. Although the DSM is a single-chain model, SD and CD can still be handled self-consistently.

To obtain entanglement creation and destruction rates that are self-consistent (at equilibrium), the following implementation of CD is used. First we make an equilibrium
dynamics calculation with just SD, following how long an entanglement lives by calculating time intervals between entanglement creation and destruction.

Because of fluctuations, this lifetime is part of a distribution. During this initial simulation, we follow the fraction \( f(t) \) of surviving entanglements with time from an arbitrarily chosen origin. If these entanglements were destroyed by a first-order decay (or reaction) rate instead of SD, then, in general, we would need a distribution of decay rates to obtain the same \( f(t) \)

\[
f(t) = \int_0^\infty \exp(-t/\tau_{\text{CD}})p_{\text{CD}}(\tau_{\text{CD}})d\tau_{\text{CD}}. \tag{7}
\]

We fit a Baumgaertel–Schausberger–Winter distribution for \( p_{\text{CD}}^{(1)}(\tau_{\text{CD}}) \) to the results from our simulation for \( f(t) \), where the superscript refers to an iteration number. With this distribution, we are now able to implement CD to a first approximation. Upon creation by SD, each entanglement is assigned a value for \( \tau_{\text{CD}} \) from the distribution \( p_{\text{CD}}^{(1)}(\tau_{\text{CD}}) \). From then on, the entanglement has a probability of being killed by CD with rate \( 1/\tau_{\text{CD}} \). If every entanglement were assigned the same value \( p_{\text{CD}}(\tau_{\text{CD}}) = \delta(\tau_{\text{CD}} - \tau) \), then we would observe \( f(t) = \exp(-t/\tau) \) from CD. However, since the value is chosen from a distribution, we then obtain a survival fraction obeying Eq. (7).

We can then simulate again with CD turned on. In other words, each chain in the ensemble obeys SD, but simultaneously entanglement \( i \) has a probability \( dt/\tau_{\text{CD}} \) of being killed by CD. We follow \( f(t) \) a second time to obtain \( p_{\text{CD}}^{(2)}(\tau_{\text{CD}}) \). After \( n \) iterations, we have \( p_{\text{CD}}^{(n)}(\tau_{\text{CD}}) \). The sequence \( \{p_{\text{CD}}^{(n)}(\tau_{\text{CD}})\} \) converges to \( p_{\text{CD}}(\tau_{\text{CD}}) \) with increasing \( n \). This convergence is quite fast: We typically find that a few (\( n = 1 \) or 2) iterations are enough.

Such a procedure is statistically equivalent at equilibrium to pairing entanglements randomly in an infinitely large ensemble of chains.

To get enough information for calculating \( p_{\text{CD}}(\tau_{\text{CD}}) \), we follow a single chain for a long time (hundreds of millions of \( \tau_k \)). That means that calculating \( p_{\text{CD}}(\tau_{\text{CD}}) \) is possible only if the system is in steady state. As an approximation, we use \( p_{\text{CD}}(\tau_{\text{CD}}) \), calculated at equilibrium as the entanglement lifetime distribution in transient flow predictions. Since flow accelerates the destruction of entanglements, the approximation cannot be exact. However, we previously showed [Schieber et al. (2007)] for the consistently unconstrained Brownian slip-link model that CCR was not important in shear flow. This approximation is examined here for the DSM.

To examine the importance of CCR, we avoid the use of the equilibrium distribution \( p_{\text{CD}}(\tau_{\text{CD}}) \) by pairing entanglements in the ensemble. CCR was originally introduced by Marrucci (1996) for the Doi–Edwards tube model; however, an adjustable parameter was used to fit flow predictions. In the slip-link model, it is possible to implement CCR without any additional parameters by using the Doi–Takimoto algorithm [Doi and Takimoto (2003); Hua and Schieber (1998)].

To implement CCR, we no longer assign a characteristic lifetime \( \tau_{\text{CD}} \) to each entanglement to determine its death by CD. Instead, whenever SD requires creation of a new entanglement at a chain end, another chain in the ensemble is chosen at random for creation of a new entanglement somewhere along its contour. These two entanglements are now paired “till death do they part”. In other words, whenever SD requires that either of the pair is destroyed, the other is destroyed as well, as a CD. At equilibrium, this commonly used algorithm [Doi and Takimoto (2003); Hua and Schieber (1998); Likhtman (2005)] is equivalent to our procedure above. However, during flow the two approaches give slightly different survival times of entanglements. The pairing algorithm preserves the self-consistency between CD and SD, even during flow, but breaks the independence between trajectories in the simulation.
For computational efficiency, we use an approximate time-evolution numerical algorithm. Namely, time-stepping is done for each chain independently, but we force all chains to synchronize every $\tau_K$. Thus, times of entanglement creation or destruction for the first and the second paired chains are accurate only up to $\tau_K$. This means that rates of creation and destruction by SD and CD are self-consistent in each time interval $\tau_K$. This should be an excellent approximation, since the timescale of importance in transient flow is on the order of millions of $\tau_K$.

B. Dangling end dynamics

In the DSM, it was assumed that the dynamics of a dangling end is very fast compared to other timescales of the model. As mentioned above, when coarse-graining the chain to the entanglement level, information about individual Kuhn steps’ positions is lost. Thus, we also lose information about the chain-end positions. When a new entanglement is created on a dangling end, detailed balance requires that its coordinates are picked from an isotropic distribution centered on the last entanglement position. The variance of this distribution depends on the number of Kuhn steps in the dangling end. Certainly, the isotropic distribution is a valid approximation in the absence of flow. However, during flow, a dangling end might orient and its average end-to-end vector would no longer be equal to $\mathbf{0}$. Here, we track the end of the chain and write a stochastic differential equation (SDE) for a connector vector between the last entanglement and a bead placed at the very end of the chain

$$dQ_1 = \kappa \cdot Q_1 dt - \frac{1}{\zeta_0} \frac{\partial F}{\partial Q_1} dt + \sqrt{\frac{2k_B T}{\zeta_0}} dW_0,$$

where $Q_1$ is the dangling end connector vector, $\zeta_0$ is the friction coefficient between the bead and the environment, and $W_0$ is a three-dimensional vector of independent Wiener processes. The SDE for the other dangling end is obtained by replacing $\{Q_1, \zeta_0, dW_0\}$ with $\{Q_Z, \zeta_Z, -dW_Z\}$.

Here we have not introduced any new parameters in the model. The friction coefficient on the bead is proportional to half the number of Kuhn steps in the dangling end. Keeping the total friction in the chain constant, with dangling end dynamics (DED), the friction coefficients become

$$\zeta_i = \frac{\tau_K k_B T}{d_K^2} \left\{ \begin{array}{ll} \frac{N_1}{2}, & i = 0 \\ \frac{N_i + N_{i+1}}{2}, & 0 < i < Z \\ \frac{N_Z}{2}, & i = Z. \end{array} \right.$$  

Due to the convective term in Eq. (8), the dangling end will orient and stretch in flow. The coordinates of the newly created entanglement are set equal to the coordinates of the bead, and thus the newly created strand is also oriented and stretched. Additionally, the dangling ends now contribute to the stress tensor equation (2) since they have free energy. The Helmholtz free energy for a dangling end is assumed to have exactly the same form as for all other strands. In flow, dangling ends with DED are on the same level of description as any inner strand. At the same time, in absence of flow, Eq. (8) gives us an average end-to-end vector of length zero, consistent with linear viscoelasticity dynamics.

With DED we need to rederive creation and destruction probabilities. SD destruction occurs when the last Kuhn step in the dangling end slides through the last entanglement. We
allow only one Kuhn step to slide at a time, thus SD destruction is possible only when the dangling end has one Kuhn step. Immediately following destruction, the tip of the chain has coordinates of the just-destroyed entanglement. With this physical picture and using friction coefficients from Eq. (9), we can write jump process probabilities for SD destruction

\[
W_{\text{d,d}}^{\text{SD}}(\Omega'|\Omega) = \delta_{Z',Z-1} \delta_{N_1',N_2+1} \delta_{N_1,1} \frac{1}{\zeta_1} \prod_{j=1}^{Z} \delta(\mathbf{Q}_{j-1}' - \mathbf{Q}_j) \prod_{j=2}^{Z} \delta_{N_{j-1}',N_{j}} \prod_{j=1}^{Z-1} \delta\left(\tau_{j+1}^{\text{CD}} - \tau_{j}^{\text{CD}}\right),
\]

(10)

\[
W_{\text{d,z}}^{\text{SD}}(\Omega'|\Omega) = \delta_{Z',Z-1} \delta_{N_2',N_2+1} \delta_{N_2,1} \frac{1}{\zeta_2} \prod_{j=1}^{Z-1} \delta(\mathbf{Q}_{j}' - \mathbf{Q}_j) \prod_{j=1}^{Z-2} \delta_{N_{j}',N_{j}} \prod_{j=1}^{Z-2} \delta\left(\tau_{j+1}^{\text{CD}} - \tau_{j}^{\text{CD}}\right).
\]

(11)

The above equations and detailed balance give us all details for SD creation: Upon SD creation we allow only one Kuhn step in the new dangling end; the connector vector of a newly created entangled strand (\(\mathbf{Q}'_s\) or \(\mathbf{Q}^{(r-1)}_s\)) is set equal to the old dangling end connector vector (\(\mathbf{Q}_1\) or \(\mathbf{Q}_Z\)). Thus, SD creation probabilities are

\[
W_{\text{c,1}}^{\text{SD}}(\Omega'|\Omega) = \delta_{Z',Z-1} \delta_{N_1',N_2+1} \delta_{N_1,1} H(N_1 - 2) \prod_{j=1}^{Z} \delta(\mathbf{Q}_{j+1}' - \mathbf{Q}_j) \prod_{j=2}^{Z} \delta_{N_{j+1}',N_{j}} \prod_{j=1}^{Z-1} \delta\left(\tau_{j+1}^{\text{CD}} - \tau_{j}^{\text{CD}}\right)
\times \frac{p^{\text{CD}}(\tau_{1}^{\text{CD}})}{\zeta_0 \beta} \exp\left[ - \frac{F_s(\mathbf{Q}_{1}', 1)}{k_B T} - \frac{F_s(\mathbf{Q}_{1}, N_1 - 1) - F_s(\mathbf{Q}_{1}, N_1)}{2k_B T}\right],
\]

(12)

\[
W_{\text{c,Z}}^{\text{SD}}(\Omega'|\Omega) = \delta_{Z',Z-1} \delta_{N_2',N_2+1} \delta_{N_2,1} H(N_Z - 2) \prod_{j=1}^{Z} \delta(\mathbf{Q}_{j}' - \mathbf{Q}_j) \prod_{j=1}^{Z-1} \delta_{N_{j}',N_{j}} \prod_{j=1}^{Z-1} \delta\left(\tau_{j+1}^{\text{CD}} - \tau_{j}^{\text{CD}}\right)
\times \frac{p^{\text{CD}}(\tau_{Z}^{\text{CD}})}{\zeta_2 \beta} \exp\left[ - \frac{F_s(\mathbf{Q}_{Z}', 1)}{k_B T} - \frac{F_s(\mathbf{Q}_{Z}, N_Z - 1) - F_s(\mathbf{Q}_{Z}, N_Z)}{2k_B T}\right].
\]

(13)

The new dangling end connector vector is picked from an isotropic distribution centered at the new entanglement with probability density given by

\[
p(\mathbf{Q}_1'|1) = \exp\left[ - \frac{F_s(\mathbf{Q}_{1}', 1)}{k_B T}\right],
\]

(14)

\[
p(\mathbf{Q}_Z'|1) = \exp\left[ - \frac{F_s(\mathbf{Q}_{Z}', 1)}{k_B T}\right].
\]

(15)

CD destruction probabilities are unchanged by DED, although we need to recalculate \(p^{\text{CD}}(\tau_{i}^{\text{CD}})\) to be consistent with SD.

\[
W_{\text{d,d}}^{\text{CD}}(\Omega'|\Omega) = \delta_{Z',Z-1} \prod_{j=1}^{i-1} \delta(\mathbf{Q}_j - \mathbf{Q}_j) \prod_{j=1}^{i-1} \delta_{N_{j}',N_{j}} \prod_{j=1}^{i-1} \delta\left(\tau_{j+1}^{\text{CD}} - \tau_{j}^{\text{CD}}\right) \prod_{j=i+2}^{Z} \delta(\mathbf{Q}_{j-1}' - \mathbf{Q}_j)
\times \frac{Z}{\zeta_1} \prod_{j=2}^{Z} \delta(\mathbf{Q}_{j}' - \mathbf{Q}_j) \prod_{j=1}^{Z-1} \delta\left(\tau_{j+1}^{\text{CD}} - \tau_{j}^{\text{CD}}\right)
\frac{1}{\tau_{ij}} \delta(\mathbf{Q}_i' - \mathbf{Q}_i + 1) \delta_{N_{i},N_{i+1},N_{i}'}.
\]

(16)

Detailed balance gives the CD creation probability
With dangling ends contributing to the chain free energy, Eq. (17) is valid for \( i = [1 : Z] \). The probabilities given above are used in equilibrium and flow.

### C. Finite extensibility

The derivation of the Helmholtz free energy, \( F_s(\mathbf{Q}, N) \) by [Khaliullin and Schieber (2011)] is repeated here. As mentioned before, we approximate each strand as a random walk. For a random walk of \( N \) steps of equal length \( a_k \), we can write the grand canonical partition function [Flory (1988); Treloar (1975)]

\[
\Delta(T, \mathbf{T}, N) = \left[ g(T) \frac{k_B T}{T a_k} \sinh \left( \frac{T a_k}{k_B T} \right) \right]^N
\]  

(18)

and the corresponding Gibbs free energy

\[
\frac{G(T, \mathbf{T}, N)}{N k_B T} = -\log \left[ g(T) \frac{k_B T}{T a_k} \sinh \left( \frac{T a_k}{k_B T} \right) \right],
\]

(19)

where \( g(T) \) is a function of temperature only and \( \mathbf{T} \) is the tension, defined in Eq. (5). The DSM requires the Helmholtz free energy of the strand as a function of its connector vector \( \mathbf{Q} \) and the number of Kuhn steps \( N \). This means that we need to switch to the canonical ensemble. For large \( N \), this can formally be done as follows: Take the derivative of the Gibbs free energy with respect to \( \mathbf{T} \),

\[
\left( \frac{\partial G}{\partial \mathbf{T}} \right)_{T, N} = -\mathbf{Q}(\mathbf{T}, N),
\]

invert it to get the tension as a function of \( \mathbf{Q} \), and then integrate the tension over \( d^3\mathbf{Q} \) to get the Helmholtz free energy, \( F_s(\mathbf{Q}, N) \). The normalized Helmholtz free energy is

\[
\frac{F_s(\mathbf{Q}, N)}{k_B T} = \frac{F_s(\mathbf{Q}, N)}{k_B T} + \log \int \exp \left( -\frac{F_s(\mathbf{Q}, N)}{k_B T} \right) d\mathbf{Q}.
\]

(20)

From Eqs. (19) and (20), we obtain

\[
\frac{Q(T, N)}{N a_k} = \coth \left( \frac{T a_k}{k_B T} \right) - \frac{k_B T}{T a_k} = \mathcal{L} \left( \frac{T a_k}{k_B T} \right),
\]

(21)

where \( \mathcal{L} \) is the Langevin function. Unfortunately, there is no analytical expression for its inverse.
Figure 1 shows the inverse Langevin function, the simplest (linear) Gaussian approximation, and a Padé approximation derived by Cohen (1991).

Using the Gaussian approximation results in the following form of the Helmholtz free energy:

\[
\frac{F_s^G(Q, N)}{k_B T} = \frac{3Q^2}{2Na_K^2} + \frac{3}{2} \log \left( \frac{2\pi N a_K^2}{3} \right),
\]

which we have used previously.

From the plot in Fig. 1, it is clear that the Gaussian approximation is accurate only at small stretch. The Cohen-Padé approximation, on the contrary, follows the inverse Langevin function very closely over the whole range. Also, it features finite extensibility (i.e., the tension diverges to infinity at a finite stretch). During equilibrium calculations, the Gaussian free energy is a good approximation. However, an examination of the strand stretch distribution in DSM elongational flow predictions (Fig. 15) using the Gaussian free energy [Eq. (22)] shows that a significant fraction (12%) of the strands stretch more than 0.4NaK, where the Gaussian approximation is inaccurate. There is even a small fraction (3%) of strands stretched beyond \( Q = Na_K \), which is physically impossible. Using a better approximation to the inverse Langevin function will change the shape of the strand stretch distribution.

We checked the effect of finite extensibility on DSM flow predictions by using the Cohen-Padé approximation

\[
\mathcal{L}^{-1}(\lambda) \approx \lambda \frac{3 - \lambda^2}{1 - \lambda^2}
\]

to obtain the Helmholtz free energy [Khaliullin and Schieber (2011)]

\[
\frac{F_s^C(Q, N)}{k_B T} = \frac{Q^2}{2Na_K^2} - N \log \left[ 1 - \left( \frac{Q}{Na_K} \right)^2 \right] + \log \left( \sqrt{\pi N} a_K \right)^3 \Gamma \left( \frac{N + 1}{2} \right) \Gamma \left( \frac{N + 5}{2} \right) \text{ hypergeom} \left( \frac{3}{2}, \frac{N + 5}{2}, 1 - \frac{N}{2} \right),
\]

FIG. 1. Approximations to the inverse Langevin function.
where $\Gamma(x)$ is the Gamma function and $\text{}_1F_1(a, b, z)$ is the confluent hypergeometric function [Abramowitz and Stegun (1964)]. We encountered several numerical complications while implementing this more complex free energy expression (24) in the DSM. These are explained in the Appendix.

IV. RESULTS

We apply the DSM to several entangled polymer melt, nonlinear rheology data sets; two sets of shear flow data: A polystyrene melt $200\,\text{kDa}$ investigated by Schweizer et al. (2004) and a polyisoprene melt investigated by Auhl et al. (2008); also two sets of elongational flow data of polystyrene melt $200\,\text{kDa}$: A set by Bach et al. (2003) and simultaneous stress and optical data by Luap et al. (2005). All DSM parameters were determined from $G^\ast$ fits, see Figs. 2 and 3.

A. Shear flow

The DSM predictions of transient shear viscosity with the same parameter values and approximations (no CCR, no DED, no finite extensibility) as were used for obtaining $G^\ast$
curves are shown in Figs. 4 and 5. We conclude that the DSM is able to capture the transient response as well as the steady-state viscosity over a wide range of shear rates. Neither CCR, DED, nor finite extensibility has a significant effect on shear flow predictions, Figs. 6 and 7. Figure 8 shows the role of disentanglement in transient flow predictions. A higher shear rate leads to a lower steady-state average number of entanglements. Interestingly, the peak in the transient viscosity (Fig. 5) corresponds roughly to the highest disentanglement rate (the inflection point in Fig. 8).

Auhl et al. (2008) compared GLaMM model predictions to their data (Fig. 5). The DSM does slightly better than GLaMM in predicting transient viscosity.

B. Elongational flow

Figure 9 shows the DSM prediction of the elongational flow experiments by Bach et al. (2003). The same parameter values and approximations (no CCR, no DED, no finite extensibility) were used as those for obtaining the polystyrene $G^*$ curve, Fig. 2, except for $\tau_K = 2.1 \times 10^{-3}$ s, which was found from fitting Bach’s $G^*$ data at the same temperature.

The DSM captures accurately the onset of strain hardening, but after a Hencky strain between 2 and 3, it predicts extreme strain softening, which is not present in the data.
FIG. 6. Effects of the DSM approximations on shear flow predictions: Polystyrene melt 200 kDa, 175 °C. Shown: Effect of convective constraint release (CCR), effect of DED, and effect of combined finite extensibility and DED (Cohen & DED).

FIG. 7. Effects of the DSM approximations on shear flow predictions: Polyisoprene melt 90 kDa, −35 °C. Shown: Effect of CCR, effect of DED, and effect of combined finite extensibility and DED (Cohen & DED).

FIG. 8. DSM shear flow prediction, transient $\langle Z \rangle$: Polyisoprene melt 90 kDa, −35 °C. Marked points correspond to peaks in transient viscosity.
The effect of CCR on the DSM elongational flow prediction is shown in Fig. 10. The DSM still follows the experimental curves up to a Hencky strain of 2, but the steady-state viscosity value is lower than without CCR, which is expected. The magnitude of the CCR effect (for example, the ratio of heights of the peaks in transient viscosity) increases with the elongation rate. Overall, we conclude that CCR is important for elongational flow predictions, but it does not explain the discrepancy between the DSM and the experiments, either qualitatively or quantitatively.

On the other hand, steady-state elongational viscosity increases with DED, see Fig. 11, although it is insignificant at low elongation rates. For the highest rate, steady-state viscosity increases 4 times and becomes close to the experimentally observed value. There are two contributions to the DED effect. First, the direct contribution from the dangling ends to the stress tensor—now all $Z$ strands contribute to the stress tensor. For higher rates, the magnitude of this effect is bigger than for lower rates. For the highest rate, severe disentanglement takes place ($Z = 4$, right side of Fig. 12) and this direct effect is therefore very significant.

Second, the dangling ends are stretched and oriented according to Eq. (8). Therefore, when a dangling end entangles, the orientation of the newly created entangled strand is picked from an anisotropic distribution, as explained above. This indirect effect increases with increasing elongation rate.

Since there is no significant effect for the lowest rate, DED does not explain the discrepancy between the DSM prediction and the experiment. It is important to mention that

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**Fig. 9.** DSM elongational flow prediction: Polystyrene melt 200 kDa, 130°C.

**Fig. 10.** Effect of CCR on DSM elongational flow prediction: Polystyrene melt 200 kDa, 130°C.
DED results in an upturn in the steady-state viscosity as a function of the elongation rate for the highest rate, Fig. 13. We use $R \equiv \frac{\tau_R}{\eta \zeta_{ij}}$ and $\tau_d = 1100s$ from fitting $p_{CD}$ to estimate that the highest rate has a Rouse Weissenberg number $Wi_R := \frac{\tau_R \dot{\gamma}}{C15} \approx 4.1$. Recall that the upturn in the steady-state was reported by Bhattacharjee et al. (2002) for solutions, but not by Bach et al. (2003) for melts.

Finally, finite extensibility results in a lower steady-state stress (Fig. 14). This might seem inconsistent with the nature of finite extensibility. Naïvely, one might expect higher stress with finite extensibility than from a Gaussian approximation since the tension in the chain diverges for a crucial strand length. However, although finite extensibility of a single strand becomes important at higher stretches ($Q/Na_K > 0.4$), it changes indirectly the shape of the whole stretch distribution, as seen in Fig. 15. Once again, the magnitude of the effect is in direct correspondence with the elongation rate. We conclude that finite extensibility is important for elongational flow predictions, but it is not the source of the deviation between the DSM and the experiments. Also the combined effect of DED and finite extensibility is only significant at high elongation rates (Fig. 14).

In Figs. 16 and 17, the DSM with DED and finite extensibility is compared to the experimental results of Luap et al. (2005). Transient elongational viscosity data are compared to DSM predictions in Fig. 16. The quality of DSM predictions is the same as for data by Bach et al. (2003); predictions capture strain hardening but show transient strain softening, whereas the data are monotonic. In Fig. 17, DSM predictions for birefringence versus stress, with DED and finite extensibility, are shown. The coefficient in Eq. (4) is

![FIG. 11. Effect of DED on DSM elongational flow prediction: Polystyrene melt 200kDa, 130 °C.](image)

![FIG. 12. Left: DSM shear flow prediction, transient (Z): Polystyrene melt 200kDa, 175 °C. Right: DSM elongational flow prediction, transient (Z): Polystyrene melt 200kDa, 130 °C.](image)

FIG. 14. Effect of finite extensibility on DSM elongational flow prediction: Polystyrene melt 200 kDa, 130 °C.

FIG. 15. Strand stretch distribution, DSM elongational flow prediction: Polystyrene melt 200 kDa, 130 °C, $\dot{\varepsilon} = 0.003 \text{s}^{-1}$, steady state, $\beta = 15.1$, $M_K = 727 \text{ Da}$, $\tau_K = 2.1 \times 10^{-3} \text{s}$. 
fitted to match the linear region. Although the DSM shows some deviation from transient viscosity data, it still captures the failure of the stress-optical rule.

V. CONCLUSIONS

We applied the DSM to shear and elongational flow, and checked the effect of three approximations on the resulting viscosity predictions: Neglecting convective constraint release, DED, and finite extensibility.

The DSM can predict the transient viscosity and steady-state viscosity of shear flow measurements without any adjustment to the two parameters fit to linear viscoelasticity. We found that DSM shear flow predictions are insensitive to the approximations made in the model.

The DSM is also able to predict the transient viscosity of elongational flow experiments up to a Hencky strain of 2–3 but shows significant deviation at larger strains. Independently removing approximations, we were not able to obtain full agreement with experiments. Except for the highest rate, we saw only quantitative changes, whereas experiments show a qualitatively different result. The effect of all studied modifications at the lower rates is insignificant. We also combined DED and finite extensibility, but the effects were not able to fix the discrepancy. We expect that combining them with CCR

FIG. 16. DSM elongational flow prediction: Polystyrene melt 200 kDa, 140°C, τk = 5.9 × 10^{-4}s.

FIG. 17. DSM stress-optical rule prediction: Polystyrene melt 200 kDa, 140°C. Straight (black) line is fit to linear region, color points are experimental data, color lines are DSM predictions with DED and Cohen-Padé free energy.
should result in a larger discrepancy with experiment, since CCR alone resulted in increased strain softening. We conclude that none of these approximations are the source of the deviation of the DSM from elongational experiments. While the improvements proposed here are important, it appears that some physics are missing from entanglement theories.

GLaMM model [Graham et al. (2003)] predictions also show strain hardening for elongational flow. However, for high elongational rates and high strains, GLaMM shows an infinite viscosity (from infinite extensibility), whereas experimental data shows a steady state.

The multichain slip-link PCN simulation predicts much higher steady-state viscosity than experiment, which is opposite to the DSM. Also Yaoita et al. (2011) showed a significant effect of finite extensibility for elongational flow, which again contradicts the result from this paper.

The right side of Fig. 12 shows that transient strain softening in DSM elongational flow predictions corresponds to significant disentanglement. The DSM diverges from experimental data as the number of entanglements drops. However, in the case of shear flow, disentanglement also occurs (left side of Fig. 12), and for some rates has a similar magnitude. For example, comparing the data for \( \dot{\gamma} = 0.003 \text{s}^{-1} \) on the right side to those for \( \dot{\gamma} = 10 \text{s}^{-1} \) on the left side, for the Polystyrene melt 200kDa, shows that both have steady-state \( (Z) \sim 13 \text{ down from (Z)}_{eq} = 18 \), but the transient prediction agrees well in shear flow, Fig. 4, whereas it does not in elongational flow, Fig. 11. Hence, it seems unlikely that disentanglement itself is the cause of the discrepancy—at least directly.

On the other hand, we showed the ability of the DSM with DED and finite extensibility to reproduce rheological and optical data simultaneously and predict the failure of the stress-optical rule in elongational flow when \( WiR > 5 \).

**APPENDIX: IMPLEMENTATION OF COHEN-PADÉ FREE ENERGY IN DSM**

Detailed balance for CD creation (Fig. 18) determines the distribution for the coordinates of a newly created entanglement

\[
p(Q'_i, N'_i; Q'_{i+1}, N'_{i+1}|Q_i, N_i) \sim \exp \left( -\frac{F_s(Q'_i, N'_i) + F_s(Q'_{i+1}, N'_{i+1}) - F_s(Q_i, N_i)}{k_B T} \right) \delta(Q'_i + Q'_{i+1} - Q_i)\delta(N'_i + N'_{i+1} - N_i),
\]

where \( i \) is the index of the strand where the entanglement is created, \( \{Q_i, N_i\} \) are the end-to-end vector and the number of Kuhn steps in the existing strand, \( \{Q'_i, N'_i\} \) and \( \{Q'_{i+1}, N'_{i+1}\} = \{Q_i - Q'_i, N_i - N'_i\} \) are the end-to-end vectors and the numbers of Kuhn

---

**FIG. 18.** Constraint dynamics creation. New entanglement splits strand \( \{Q_i, N_i\} \), into two strands \( \{Q'_i, N'_i\} \) and \( \{Q'_{i+1}, N'_{i+1}\} \).
steps of the two newly created strands. In the Gaussian case, Eq. (22), this expression results in a Gaussian distribution centered at $Q_i N_i$ with variance $\frac{3}{2} N (1 - \frac{N_i}{N})$. Thus, the distribution for the number of Kuhn steps in a newly created strand is

$$p_c^{CD}(N|Q_i, N_i) \sim \int p(Q, N|Q_i, N_i) dQ = \frac{1}{N_i}.$$  \hspace{1cm} (A2)

This expression yields the probability to create an entanglement anywhere on the strand that is just proportional to the number of Kuhn steps

$$w_c^{CD} = \frac{N - 1}{\beta} \int_0^\infty \frac{p_c^{CD}(\tau^{CD})}{\tau^{CD}} d\tau^{CD},$$ \hspace{1cm} (A3)

see details in Khaliullin and Schieber (2009).

However, if we use Eq. (24), the shape of the distribution for the coordinates of the new entanglement becomes much more complex. By taking into account the finite extensibility of the newly created strands, the domain of integration becomes the intersection of two spheres: One with radius $N'_{iK}$ centered on entanglement $i$, and the second with radius $N'_{i+1K}$ on entanglement $i + 1$. Depending on $\{N'_i, N'_{i+1}, N_i\}$ and the separation of the existing entanglements $Q_i$, the shape of the intersection can change from a sphere to a lens (Fig. 19). We found no way to calculate $p_c^{CD}(N|Q_i, N_i)$ analytically and calculating it numerically on the fly is very expensive. Examples of $p_c^{CD}$ as a function of one of the variables with the others kept constant are shown in Fig. 20 (points). The shapes of these functions are similar for different values of the fixed variables, so we are able to use several rational functions to approximate $p_c^{CD}(N|Q_i, N_i)$.

First, we approximate $p_c^{CD}$ as function of $N_i$ (Fig. 20, left) for a set of nine combinations of variable values $N = \{N_i/2, N_i/3, N_i/20\}$ and $Q_i = \{0, 0.3N_i a_K, 0.6N_i a_K\}$ as

$$p_c^{CD} \left( \left\{ \frac{N_i}{2}, \frac{N_i}{3}, \frac{N_i}{20} \right\} \right) \left\{ 0, 0.3N_i a_K, 0.6N_i a_K \right\} = \frac{aN_i^2 + bN_i + c}{N_i^2 + dN_i + e}. \hspace{1cm} (A4)$$

The choice of $N = \{N_i/2, N_i/3, N_i/20\}$ is dictated by the fact that $p_c^{CD}$ as a function of $N$ is symmetric, being nearly constant in the middle region, and changing significantly close to the borders (Fig. 20, right). Because $p_c^{CD}$ as a function of $Q_i$ is changing throughout the whole domain, the values $Q_i = \{0, 0.3N_i a_K, 0.6N_i a_K\}$ are spaced uniformly (Fig. 20, center). Thus, we precalculate nine sets of parameters $\{a, b, c, d, e\}$ and use them to calculate $p_c^{CD}$ on the fly. Using them, we have nine $p_c^{CD}$ values for given $N_i$.

FIG. 19. Cross-section of Cohen-Padé CD creation in plane of strand. Here $(N'_{i+1} = N_i - N'_i)$. The volume where the new entanglement can be created (the dark shaded region) depends on $(Q_i, N_i, N'_i)$. Possible shapes: lens—both existing entanglements can be inside or outside this volume, spheres—at least one of the existing entanglements is inside this volume.
Second, we approximate $p^{CD}_c$ as a function of $Q_i$ (Fig. 20, center) as

$$p^{CD}_c \left( \left\{ \frac{N_i}{2}, \frac{N_i}{5}, \frac{N_i}{20} \right\} \mid Q_i, N_i \right) = p^{CD}_c \left( \left\{ \frac{N_i}{2}, \frac{N_i}{5}, \frac{N_i}{20} \right\} \mid 0, N_i \right) \times \frac{(Q_i/N_i - 1)^2(1 + (2 + b_1)Q_i/N_i)}{1 + Q_i/N_i(b_1 + b_0Q_i/N_i)},$$

(A5)

which exploits the fact that \( \lim_{Q_i \to N_i} p^{CD}_c(Q_i, N_i) = 0 \) and \( \frac{\partial p^{CD}_c(Q_i, N_i)}{\partial Q_i} \bigg|_{Q_i=0} = 0 \). Also it goes through $p^{CD}_c \left( \left\{ \frac{N_i}{2}, \frac{N_i}{5}, \frac{N_i}{20} \right\} \mid 0, N_i \right)$, and $b_1$ and $b_0$ are calculated to match the values of $p^{CD}_c$ at $Q_i = 0.3N_ia_K$ and $Q_i = 0.6N_ia_K$. We use nine $p^{CD}_c$ values found previously and get three values for $N = \left\{ \frac{N_i}{2}, \frac{N_i}{5}, \frac{N_i}{20} \right\}$ for given $Q_i, N_i$.

Last, we approximate $p^{CD}_c$ as a function of $N$ (Fig. 20, right) as

$$p^{CD}_c(N|Q_i, N_i) = c \frac{ax^4 + bx^2}{x^2 + a + b - 1} + p^{CD}_c \left( \frac{N_i}{2} \mid Q_i, N_i \right).$$

(A6)

where $x = 2(N/N_i - 0.5)$, and \( \{a, b, c\} \) are found from $p^{CD}_c \left( \left\{ \frac{N_i}{2}, \frac{N_i}{5}, \frac{N_i}{20} \right\} \mid Q_i, N_i \right)$ and \( \lim_{N \to (N_i - N)} p^{CD}_c(N|Q_i, N_i) = 1 \). This expression is symmetric, i.e., invariant under change of variables $N \to (N_i - N)$. Using it, we get $p^{CD}_c$ given $N, Q_i, N_i$.

The rational function approximations to $p^{CD}_c$ are shown as lines in Fig. 20. We found that they allowed us to calculate the value of $p^{CD}_c(N|Q_i, N_i)$ fast and accurately.

Another problem that arose was anomalous stress from strands with only one Kuhn step. Consider the tension distribution for a strand with Cohen-Padé free energy

$$p(T|N) = T(Q, N)\exp \left( -\frac{F_s(Q, N)}{k_BT} \right) = C \left( 3 - \left( \frac{Q}{Na_K} \right)^2 \right) \frac{Q}{Na_K} \left( 1 - \left( \frac{Q}{Na_K} \right)^2 \right)^{N-1} \exp \left( -\frac{Q^2}{2Na_K^2} \right),$$

(A7)

where $C$ is a normalization constant. In Fig. 21, tension distributions for different numbers of Kuhn steps are shown. In the case of $N = 1$, the factor $\left( 1 - \left( \frac{Q}{Na_K} \right)^2 \right)^{N-1}$ becomes 1, which results in a finite probability of having infinite tension in the strand, when $Q = Na_K$. The problem is that the partition function (18) is not valid for a small number of Kuhn steps. Underhill and Doyle (2005) addressed many complications of the Cohen-Padé approximation for low $N$ as well as a way to overcome them. However, the values of $\beta$ for the systems in our study give very low fractions of strands with one Kuhn step,
even in equilibrium. Therefore, we assume that it is safe to exclude these strands from the stress tensor calculation. Using the expressions of Underhill and Doyle might change the results quantitatively, but not sufficient to bring prediction in line with experiments.

Combining DED and Cohen-Padé requires numerical solution of Eq. (8). We used a modified semi-implicit numerical algorithm from Sec. 4.3.2 of Öttinger (1996)

\[
Q(t_0 + \Delta t) = Q(t_0) + \left[ \kappa \cdot Q(t_0) - \frac{1}{\zeta} \left( 3 - \frac{(Q(t_0) + \Delta t)^2}{N\alpha K} \right) \right] \Delta t + \sqrt{\frac{2k_B T}{\zeta}} \Delta W_{t_0}, \tag{A8}
\]

\[
\left[ 1 + \frac{\Delta t}{2N\alpha K} \left( \frac{3 - \left( \frac{Q(t_0 + \Delta t)}{N\alpha K} \right)^2}{1 - \left( \frac{Q(t_0 + \Delta t)}{N\alpha K} \right)^2} \right) \right] Q(t_0 + \Delta t) = Q(t_0)
\]

\[
+ \frac{1}{2} \left[ \kappa \cdot Q(t_0 + \Delta t) + \kappa \cdot Q(t_0) - \frac{1}{\zeta} \left( 3 - \frac{(Q(t_0))^2}{N\alpha K} \right) \frac{Q(t_0)}{N\alpha K} \right] \Delta t + \sqrt{\frac{2k_B T}{\zeta}} \Delta W_{t_0}, \tag{A9}
\]

where \(\{Q, N, \zeta, W_0\}\) is \(\{Q_1, N_1, \zeta_0, W_0\}\) or \(\{Q_Z, N_Z, \zeta_Z, -W_Z\}\). However, in order to assure numerical stability using this algorithm we had to use much smaller (20 times smaller) time step size. This significantly increased computational cost.

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