Fast and accurate closure approximations for bead-spring models of dilute polymer solutions

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Abstract

Dilute polymer solutions, besides being widely used in the chemical industry, are used to understand the physical processes that govern the dynamics of isolated macromolecules in solution. Several recent studies used Brownian dynamics simulations of mesoscale bead-spring chain models to demonstrate that the finite extensibility of polymer chains and the existence of fluctuating hydrodynamic interactions between different parts of the chains play a key role in determining the behaviour of polymer solutions in strong flows. Three closure approximations which incorporate these phenomena are presented which offer considerable gains in computational efficiency. The predictions of these approximate models are in good agreement with the results of simulations in strong extensional flows.

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Contents

1　Introduction

Dilute polymer solutions find extensive use in the characterization of polymer molecules, besides playing a vital role in the form of polymeric additives in many industrial processes. In addition, studying the behaviour of dilute polymer solutions in simple and complex flows also throws light on the dynamics of isolated macromolecules in solution. In recent years, significant advances in the understanding of polymer solutions have been made possible by representing polymer molecules by coarse grained models of spherical beads connected by flexible springs. While it is possible to use detailed computer simulations of such bead-spring models to predict properties of dilute polymer solutions, these are computationally very expensive. In addition, the nonlinear spring force laws used typically to model finitely extensible chains cause the stochastic differential equations underlying Brownian simulations of polymer chains to become stiff in situations where chains can be stretched close to their maximum allowed extension. On the other hand, it is difficult to obtain closed form analytical solutions of the model equations, as a result of the nonlinearities due to finite chain extensibility and intra-chain interactions. The aim of this work is to present three closure approximations that

appear to hold promise in predicting the behaviour of long polymer chains in strong flows, with reduced computational intensity.

2   Model equations

In theories of polymer molecules in solution, the solvent is often treated as a continuum, and for spatially homogeneous flows, the velocity field of this solvent continuum can be decomposed as $\boldsymbol{v} = \boldsymbol{v}_0 + \boldsymbol{\kappa} \cdot \boldsymbol{r}$, where $\boldsymbol{v}_0$ is the constant velocity of the reference frame, $\boldsymbol{\kappa}$ is the transpose of the position independent velocity gradient $\nabla \boldsymbol{v}$, and $\boldsymbol{r}$ is the position vector of any point with respect to the origin of the frame of reference.

The bead-spring model of a macromolecule is obtained by coarse grain-ing a long, linear, flexible polymer as a chain of N spherical beads, each of hydrodynamic radius a, connected by $N_{\mathrm{s}} = N - 1$ springs. The in-stantaneous configurational state of any bead-spring chain suspended in the continuum solvent is completely specified by the set of connector vectors $\{\boldsymbol{Q}_i \mid i = 1, \ldots, N_{\mathrm{s}}\}$ of the N_{s} springs. The time evolution of the probability distribution function for the configurational state of the bead-spring chain, ψ, is governed by the Fokker–Planck equation [2]

$$
\begin{aligned}
\frac{\partial \psi}{\partial t} =\ & -\sum_{i=1}^{N_{\mathrm{s}}} \frac{\partial}{\partial \boldsymbol{Q}_i} \cdot \left\{ \boldsymbol{\kappa} \cdot \boldsymbol{Q}_i - \frac{1}{\zeta} \sum_{j=1}^{N_{\mathrm{s}}} \widetilde{\boldsymbol{A}}_{ij} \cdot \frac{\partial \phi}{\partial \boldsymbol{Q}_j} \right\} \psi \\
& + \frac{k_{\mathrm{B}} T}{\zeta} \sum_{i,j=1}^{N_{\mathrm{s}}} \frac{\partial}{\partial \boldsymbol{Q}_i} \cdot \widetilde{\boldsymbol{A}}_{ij} \cdot \frac{\partial \psi}{\partial \boldsymbol{Q}_j} ,
\end{aligned}
\tag{1}
$$

where k_{B} is Boltzmann's constant and T is the absolute temperature of the solution. The parameter $\zeta = 6\pi a \eta_{\mathrm{s}}$ in this equation is the Stokes friction coefficient of each spherical bead in a Newtonian solvent of shear viscos-ity η_{s}. The effect of non-hydrodynamic conservative intramolecular forces

is accounted for through the total potential energy ϕ. The dimensionless diffusion tensors $\widetilde{\boldsymbol{A}}_{ij}$ accounting for hydrodynamic interactions between the beads are, in general, functions of the instantaneous chain configuration and are given by

$$\bar{\boldsymbol{A}}_{ij} = A_{ij}\boldsymbol{\delta} + \frac{2\,\zeta}{3\,(2\pi)^{3/2}\,\eta_{\mathrm{s}}}\left[\boldsymbol{\Omega}_{ij} + \boldsymbol{\Omega}_{i+1,j+1} - \boldsymbol{\Omega}_{i+1,j} - \boldsymbol{\Omega}_{i,j+1}\right], \qquad (2)$$

where $\boldsymbol{\delta}$ is the unit tensor, $A_{i,j} = [\delta_{ij} + \delta_{i+1,j+1} - \delta_{i+1,j} - \delta_{i,j+1}]$, and the tensors $\boldsymbol{\Omega}_{\nu\mu}$, $\nu, \mu = 1, \ldots, N$ are the hydrodynamic interaction tensors. The tensor $\boldsymbol{\Omega}_{\nu\mu} = \boldsymbol{\Omega}(\boldsymbol{r}_{\nu\mu})$ is a function of the relative displacement between the νth and μth beads, $\boldsymbol{r}_{\nu\mu} = \boldsymbol{r}_\nu - \boldsymbol{r}_\mu$, and relates the perturbation $\Delta\boldsymbol{v}_\nu$ in velocity field at $\boldsymbol{r}_\nu$ to a point hydrodynamic force $\boldsymbol{F}_\mu^h$ exerted on the solvent at $\boldsymbol{r}_\mu$ by the μth bead through $\Delta\boldsymbol{v}_\nu = \boldsymbol{\Omega}_{\nu\mu} \cdot \boldsymbol{F}_\mu^h$. In the development of closure approximations for chains with HI, it is especially advantageous to use the Oseen–Burgers definition of the HI tensor, which is derived as the Greens function of the linearized Navier–Stokes equation:

$$\boldsymbol{\Omega}_{\nu\mu} = \frac{1}{(2\pi)^3\eta_{\mathrm{s}}} \int d\boldsymbol{k}\, \frac{1}{k^2}\left(\boldsymbol{\delta} - \frac{\boldsymbol{k}\boldsymbol{k}}{k^2}\right) e^{i\boldsymbol{k}\cdot\boldsymbol{r}_{\nu\mu}}. \qquad (3)$$

In general, $\boldsymbol{F}_\nu^\phi$ is the sum of contributions due to the spring forces, and those due to excluded volume (EV) interactions. These EV interactions arise as a consequence of the fact that no two parts of a polymer chain can occupy the same position in space at the same time. Two segments far apart from each other along the chain tend to strongly repel each other when they approach closely. At a special value of the temperature, known as the "theta" temperature, excluded volume interactions are *effectively* absent for polymer solutions, and the total non-hydrodynamic intramolecular force on the νth bead is solely due to the tensions in the springs adjacent to the bead. For finitely extensible springs, the "spring" force $\boldsymbol{F}^{\mathrm{C}}$ represents the mean entropic resistance of a segment of the underlying chain to stretching. Although an exact expression relating this force to the corresponding connector vector $\boldsymbol{Q}$ can be derived using equilibrium statistical mechanics, it is convenient to

use the following FENE (or Warner) force law which is known to be a good approximation:

$$\boldsymbol{F}^{\mathrm{c}} = H\,\frac{1}{1 - \boldsymbol{Q}^2/Q_0^2} = H\xi(Q^2; Q_0)\,\boldsymbol{Q}\,. \tag{4}$$

where H is the spring constant. The function ξ is parameterized by Q_0, the maximum permissible length of the spring. When $Q \ll Q_0$, that is when springs are not significantly stretched relative to Q_0, the FENE expression above reduces to the linear Hookean relation where $\xi = 1$. The value of the spring constant H is fixed by matching the equilibrium mean square end-to-end distance $R_{\mathrm{s,eq}}^2$ of any single spring to the experimentally measured value for the underlying segment of the macromolecule. The length scale $\ell_{\mathrm{s}} = R_{\mathrm{s,eq}}/\sqrt{3}$ and the time scale $\lambda_{\mathrm{s}} = \eta_{\mathrm{s}}\,\ell_{\mathrm{s}}^3/k_{\mathrm{B}}T$ are used in this study to obtain dimensionless quantities, such as $b = Q_0^2/\ell_{\mathrm{s}}^2$.

Kramer's expression [2] connects the microscopic dynamics governed by the Fokker–Planck equation above and the polymer's contribution to the macroscopically observed stress tensor:

$$\boldsymbol{\tau}_{\mathrm{p}} = (N-1)\,n_{\mathrm{p}}k_{\mathrm{B}}T\,\boldsymbol{\delta} \;+\; n_{\mathrm{p}}\sum_{\nu=1}^{N}\langle \boldsymbol{R}_\nu \boldsymbol{F}_\nu^\phi\rangle\,, \tag{5}$$

where $\boldsymbol{\tau}_{\mathrm{p}} \equiv \boldsymbol{\tau} + \eta_{\mathrm{s}}(\boldsymbol{\kappa} + \boldsymbol{\kappa}^{\mathrm{T}})$ is the polymer contribution to the dynamic stress tensor $\boldsymbol{\tau}$, n_{p} is the number density of the polymer solution, and $\boldsymbol{R}_\nu$ is the position vector of the νth bead relative to the centre of mass of the chain. The angle brackets indicate averages over the distribution function ψ.

Here we test the predictions of closure approximations against exact results of Brownian dynamics simulations of the rheological behaviour of a polymer solution following the sudden imposition of a spatially homogeneous uniaxial elongational velocity gradient, for which [1]

$$\boldsymbol{\kappa} = \dot{\epsilon}\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{pmatrix}\,. \tag{6}$$

Although the strain rate $\dot{\epsilon}$ may in general be a function of time, we restrict our attention to flows with constant strain rate.

For the bead-spring chain model described above, the equation for the time evolution of the second moment $\langle \boldsymbol{Q}_i \boldsymbol{Q}_j \rangle$ of the probability density ψ is [7, 4]

$$\langle \boldsymbol{Q}_i \boldsymbol{Q}_j \rangle_{(1)} = -\frac{H}{\zeta} \sum_{m=1}^{N_{\mathrm{s}}} \langle \boldsymbol{Q}_i \boldsymbol{Q}_m \xi_m \cdot \widetilde{\boldsymbol{A}}_{mj} + \widetilde{\boldsymbol{A}}_{im} \cdot \xi_m \boldsymbol{Q}_m \boldsymbol{Q}_j \rangle + \frac{2k_{\mathrm{B}}T}{\zeta} \langle \widetilde{\boldsymbol{A}}_{ij} \rangle , \quad (7)$$

where the subscript "(1)" signifies the lower convected derivative operator $(\boldsymbol{x}_{(1)} = d\boldsymbol{x}/dt - \boldsymbol{\kappa} \cdot \boldsymbol{x} - \boldsymbol{x} \cdot \boldsymbol{\kappa})$ and $\xi_m = \xi(Q_m^2)$. As a consequence of the nonlinearities in the functions ξ and $\widetilde{\boldsymbol{A}}_{ij}$, the evolution equation above involves averages of complicated functions of the connector vectors on the right-hand side. These averages cannot be expressed as functions of the second moments alone, and hence require evolution equations of their own which will involve more complicated averages, and so on. In other words, the evolution equations for the second moments and for most other macroscopic averages including the polymer stress tensor $\boldsymbol{\tau}_{\mathrm{p}}$, are not closed with respect to the averages in question. The resolution of this problem calls for the use of approximations that will eventually lead to the expression of the complicated averages on the right-hand sides of the evolution equations in terms of the averages of interest.

Several closure approximations have been proposed for bead-spring models of dilute polymer solutions, the most prominent among these being classified into two broad categories.

2.1 Consistent averaging

In the first approach, the fluctuating nonlinearities in the Fokker–Planck equation for the configurational probability distribution are replaced with

their averages. Öttinger [6] showed that strain rate dependent material functions could be obtained by using "consistent averaging" instead of equilibrium averaging, wherein the diffusion tensors $\widetilde{\boldsymbol{A}}_{ij}$ are replaced by their *non-equilibrium* averages $\bar{\boldsymbol{A}}_{ij} = \langle \widetilde{\boldsymbol{A}}_{ij} \rangle$. With this approximation, the modified Fokker–Planck equation for chains with Hookean springs becomes linear with respect to the connector vectors $\boldsymbol{Q}_i$, and the approximate probability distribution ψ is a multivariate Gaussian. Hence the contracted probability distribution $P(\boldsymbol{r}_{\nu\mu})$ for the displacement $\boldsymbol{r}_{\nu\mu} = \boldsymbol{r}_\nu - \boldsymbol{r}_\mu$ between the νth and μth beads is also a Gaussian, and the average of the HI tensor $\boldsymbol{\Omega}(\boldsymbol{r}_{\nu\mu})$ evaluated with $P(\boldsymbol{r}_{\nu\mu})$ can be shown to be [6]

$$\langle \zeta \boldsymbol{\Omega}(\boldsymbol{r}_{\nu\mu}) \rangle = \frac{2\zeta}{3(2\pi)^{3/2}\eta_{\mathrm{s}}} \boldsymbol{H}(\boldsymbol{S}_{\nu\mu}) \,, \tag{8}$$

where $\boldsymbol{S}_{\nu\mu} = \langle \boldsymbol{r}_{\nu\mu}\boldsymbol{r}_{\nu\mu} \rangle$ is the variance of the distribution $P(\boldsymbol{r}_{\nu\mu})$ and $\boldsymbol{H}$ is the second rank tensorial function

$$\boldsymbol{H}(\boldsymbol{x}) = \frac{3}{2(2\pi)^{3/2}} \int d\boldsymbol{k} \, \frac{1}{k^2} \left(\boldsymbol{\delta} - \frac{\boldsymbol{k}\boldsymbol{k}}{k^2} \right) \exp(-\tfrac{1}{2}\,\boldsymbol{k}\boldsymbol{k} : \boldsymbol{x}) \,. \tag{9}$$

Therefore, the consistently averaged diffusion tensors $\bar{\boldsymbol{A}}_{ij}$ can be expressed in terms of the second moment tensors $\langle \boldsymbol{Q}_i\boldsymbol{Q}_j \rangle$ through the $\boldsymbol{H}$ functions. To handle the nonlinearity due to the FENE force law, Peterlin [9] approximated the fluctuating function $\xi(Q_m^2)$ with $\bar{\xi}_m = \xi(\langle Q_m^2 \rangle)$. This FENE-P approximation was later combined with consistently averaged HI [7, 12, 4], wherein the use of the functions to $\bar{\xi}_m$ along with the tensors $\bar{\boldsymbol{A}}_{ij}$ lead to an approximate ψ that is Gaussian and render Eq. (7) closed with respect to the second moments $\boldsymbol{\sigma}_{ij} = \langle \boldsymbol{Q}_i\boldsymbol{Q}_j \rangle$ of the approximate ψ:

$$\boldsymbol{\sigma}_{ij,\,(1)} = -\frac{H}{\zeta} \sum_{m=1}^{N_{\mathrm{s}}} \left[\boldsymbol{\sigma}_{im}\bar{\xi}_m \cdot \bar{\boldsymbol{A}}_{mj} + \bar{\boldsymbol{A}}_{mi}^{\mathrm{T}} \cdot \bar{\xi}_m \boldsymbol{\sigma}_{mj} \right] + \frac{2k_{\mathrm{B}}T}{\zeta} \bar{\boldsymbol{A}}_{ij} \,. \tag{10}$$

Using Eq. (5), the stress tensor in this approximation is expressed in terms of $\boldsymbol{\sigma}_{ij}$ as

$$\boldsymbol{\tau}_{\mathrm{p}} = (N-1)n_{\mathrm{p}}k_{\mathrm{B}}T - n_{\mathrm{p}} \sum_{i=1}^{N_{\mathrm{s}}} \bar{\xi}(\mathrm{Tr}\,\boldsymbol{\sigma}_{ii})\boldsymbol{\sigma}_{ii} \,, \tag{11}$$

and the time evolution of the stress can be obtained after integrating Eq. (10), the closed set of ordinary differential equations for the second moments $\boldsymbol{\sigma}_{ij}$. Predictions obtained with this approximation in steady shear flows are in qualitative agreement with Brownian dynamics simulations and experimental observations [4, 13].

2.2   Canonical distribution functions

Noting that the replacement of the diffusion tensors $\widetilde{\boldsymbol{A}}_{ij}$ with their averages $\bar{\boldsymbol{A}}_{ij}$ ignores the influence of fluctuations in HI, Öttinger [8] suggested the Gaussian Approximation for chains with Hookean springs, which accounts for fluctuations in HI. This approximation has recently been shown to be a special case of a more general approach using "canonical distribution functions" (CDF's) to developing closure approximations [3]. In this approach, the macroscopic behaviour of the dilute polymer solution is sought to be completely described in terms of a set of n macroscopic "state variables", which are in general linear functionals of the original distribution function. A typical choice for the state variables is the second and higher order moments of the original distribution function. A CDF which has n unknown parameters is then used to approximate the original distribution function. Equations relating the parameters in the CDF to the state variables are then obtained by formally requiring that the predictions of the state variables using the CDF be equal in value to those obtained with the original distribution. As a consequence of this, the original parameters in the CDF are expressed in terms of the state variables. Finally, the special properties of the CDF are exploited to simplify the complicated averages in the evolution equations for the state variables. The resulting evolution equations so obtained are closed with respect to the state variables. Further, any other macroscopic property (that is, an ensemble average) such as the stress tensor is a function entirely of the state variables, and can in principle be evaluated.

Choosing the N_s^2 second moments of the distribution as the state variables

and a Gaussian distribution as the CDF leads to the Gaussian Approxima-
tion of Öttinger. The advantage of using a Gaussian is that it permits the
application of the Wick's theorem to decompose the complicated averages
occurring in the equation for the second moment into functions of the second
moments, thus enabling closure. For instance, the average $\langle \boldsymbol{Q}_i \zeta \boldsymbol{\Omega}_{\nu\mu} \boldsymbol{Q}_j \rangle$ is
resolved as [8]

$$
\begin{aligned}
\langle \boldsymbol{Q}_i \zeta \boldsymbol{\Omega}_{\nu\mu} \boldsymbol{Q}_j \rangle &= \frac{2\zeta}{3(2\pi)^{3/2}\eta_\mathrm{s}} \langle \boldsymbol{Q}_i \boldsymbol{H}(\boldsymbol{S}_{\nu\mu}) \boldsymbol{Q}_i \rangle \\
&+ \frac{\zeta}{2(2\pi)^{3/2}\eta_\mathrm{s}} \langle \boldsymbol{Q}_i \boldsymbol{r}_{\nu\mu} \rangle \cdot \boldsymbol{K}(\boldsymbol{S}_{\nu\mu}) \cdot \langle \boldsymbol{r}_{\nu\mu} \boldsymbol{Q}_j \rangle,
\end{aligned}
\tag{12}
$$

where the fourth rank tensorial function

$$
\boldsymbol{K}(\boldsymbol{x}) = \frac{-2}{2\pi^{3/2}} \int d\boldsymbol{k} \frac{1}{k^2} \boldsymbol{k} \left(\boldsymbol{\delta} - \frac{\boldsymbol{k}\boldsymbol{k}}{k^2} \right) \boldsymbol{k} \exp(-\tfrac{1}{2}\boldsymbol{k}\boldsymbol{k} : \boldsymbol{x}).
\tag{13}
$$

The first term on the right-hand side of Eq. (12) above is due to averaged
HI, and is also present in the consistent averaging approximation. However,
the additional term containing the $\boldsymbol{K}$ function accounts for the influence of
the fluctuations in the HI tensor. The equation for the second moments of
the Gaussian distribution is

$$
\begin{aligned}
\boldsymbol{\sigma}_{ij,(1)} = &-\frac{H}{\zeta} \sum_{m=1}^{N_\mathrm{s}} \left[\boldsymbol{\sigma}_{im}\bar{\xi}_m \cdot (\bar{\boldsymbol{A}}_{mj} + \boldsymbol{\Delta}_{mj}) + (\bar{\boldsymbol{A}}_{mi} + \boldsymbol{\Delta}_{mi})^\mathrm{T} \cdot \bar{\xi}_m \boldsymbol{\sigma}_{mj} \right] \\
&+ \frac{2k_\mathrm{B}T}{\zeta} \bar{\boldsymbol{A}}_{ij},
\end{aligned}
\tag{14}
$$

in which the tensors

$$
\boldsymbol{\Delta}_{pq} = \sum_{r,s=1}^{N_\mathrm{s}} \boldsymbol{\Gamma}_{ps,rq} : \boldsymbol{\sigma}_{sr} \frac{\bar{\bar{\xi}}_r}{\bar{\bar{\xi}}_p}.
\tag{15}
$$

The fourth rank tensors $\boldsymbol{\Gamma}_{ps,rq}$ are linear combinations of the $\boldsymbol{K}$ tensors [11],
and thus the tensors $\boldsymbol{\Delta}_{pq}$ in Eq. (14) above account for the fluctuations in HI.

The predictions of properties in steady shear flows with the Gaussian Approximation for chains with Hookean springs and without EV interactions are in quantitative agreement with the results of Brownian dynamics simulations [13]. However, models with Hookean springs cannot be used in strong extensional flows as they extend indefinitely without approaching a steady state. Here we use chains with FENE-P springs instead and apply the Gaussian Approximation. Consequently, we are able to study the influence of fluctuations in HI on the behaviour of polymer solutions in strong extensional flows.

2.3   The two-fold normal approximation

Although both the consistent averaging and Gaussian approximations lead to considerable gains in computational efficiency, the CPU time required to attain steady state from an initial equilibrium state scales steeply as $N^{4.5}$ [11]. It is therefore desirable to look for additional approximations that improve efficiency. One such approximation is obtained by mapping the bead connector vectors $\boldsymbol{Q}_j$ to a new set of vectors $\boldsymbol{Q}_i'$ through the linear transformation $\boldsymbol{Q}_i' = \sum_{j=1}^{N_s} \Pi_{ji} \boldsymbol{Q}_j$, where Π_{ji} are the elements of the Zimm or Rouse orthogonal matrix. Next, the following diagonalization assumption is made:

$$\sum_{i,j=1}^{N_s} \Pi_{ip}\, \boldsymbol{\sigma}_{ij}\, \Pi_{jq} = \boldsymbol{\sigma}_p'\, \delta_{pq}\,. \tag{16}$$

This assumption reduces the number of equations to be solved from N_s^2 to N_s. The diagonalize and decouple approach was proposed originally by Magda et al. [5] and later used by Kisbaugh and McHugh [4] in the context of the consistent averaging approximation. Later, Prakash and Öttinger [11] used it with the Gaussian Approximation to explore the universal behaviour of long chains with Hookean springs in shear flows, and named the combined approximation as the "Two-Fold Normal" (TFN) approximation to reflect the fact that the approximation involves two separate assumptions of "normality"—a

normal distribution and a normal modes transformation. In all these studies, the additional diagonalize and decouple assumption does not lead to any significant loss in accuracy in the predictions of the rheological properties, when compared with the original approximation. We use the Zimm orthogonal matrix [11] and extend the approximation to chains with FENE-P springs to examine behaviour in strong extensional flows.

3   Results and conclusions

Figure 1 shows the predictions of the three approximations discussed in this article for the growth in the first normal stress difference $N_1 = -(\tau_{xx} - \tau_{yy})$ after a sudden imposition of a steady homogeneous uniaxial extensional flow with a dimensionless strain rate $\dot{\epsilon}^* = \dot{\epsilon}\lambda_s = 0.1$, and the decay in N_1 after cessation of the flow. Observe that the approximations perform reasonably well overall in comparison with the exact results of the full model with fluctuating FENE forces and HI obtained through Brownian dynamics simulations. The ordinary differential equations governing the time evolution of the second moments in each approximation were integrated to steady state using a variable order, variable step size method (the D02EJF routine in the NAG Fortran Library). The details of the Brownian dynamics simulation algorithm are given elsewhere [10]. In particular, the agreement is good during the initial growth, at the final steady state, and during stress relaxation. The deviations observed at the "knee" before attainment of steady state is a well known feature of the FENE-P approximation, and can be improved by using better approximations of the FENE force law.

Table 1 compares the CPU times required for Brownian dynamics simulations and the approximations to obtain predictions of comparable accuracy in strong extensional flows for long chains incorporating finite extensibility and fluctuating hydrodynamic interactions. The computational efficiency of the TFN approximation coupled with its accuracy make it a useful tool in ex-
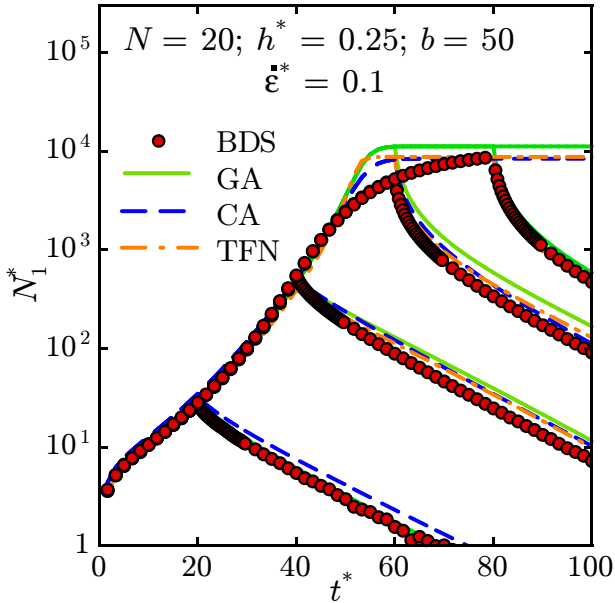
FIGURE 1: Comparison of predictions of the Gaussian (GA; green solid line), Consistent Averaging (CA; blue dash line), and Two-Fold Normal (TFN; orange dash-dot line) approximations with exact results of Brownian dynamics simulations (BDS; red circles) of bead-spring chains ($N = 20$) for the evolution of the dimensionless normal stress difference $N_1^* = -(\tau_{xx} - \tau_{yy})/(n_p k_B T)$ with respect to the dimensionless time $t^* = t/\lambda_s$. Data are shown for three different times of flow stoppage. The error bars in the simulations are smaller than the size of the symbols used.

Table 1: Comparison of cpu time required for Brownian dynamics simulations and the approximations, for chains with $N = 60$ and $N = 160$. The cpu time for the simulations is calculated for an ensemble of 10,000 chains, while the values for ca and ga for $N = 160$ have been estimated after fitting power laws through data for smaller N.

	CPU times (hrs.)			
N	BDS	CA	GA	TFN
60	220	10	51	0.9
160	10012	2073	3131	32

ploring the behaviour of dilute polymer solutions, particularly in simulations of complex flows.

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