

MOLECULAR RHEOLOGY OF UNENTANGLED POLYMER MELTS IN NANOCHANNELS

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By
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MOLECULAR RHEOLOGY OF UNENTANGLED POLYMER
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We certify that we have read this thesis and that in our opinion it is fully adequate,
in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

MOLECULAR RHEOLOGY OF UNENTANGLED POLYMER MELTS IN NANOCANNELS

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M.S. in Mechanical Engineering

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We investigate the rheological properties of non-Newtonian melts of short polymer chains at the molecular level, with a focus on nanoscale confinement. Using a combination of all-atom molecular dynamics (MD) and coarse-grained simulations, we examine the behavior of oligomer melts with various topologies under non-equilibrium conditions. Our findings reveal significant deviations in the microscopic stress tensor under steady-state shear compared to predictions from continuum models, highlighting the limitations of the Oldroyd-B and generalized Phan-Thien–Tanner (gPTT) models in capturing nanoscale phenomena. We demonstrate that these deviations result in excess viscoelastic stress, which diminishes with decreasing confinement and vanishes in bulk systems. This excess stress is linked to the spatial orientation of carbon-carbon bonds near surfaces, where adsorbed chains form effective polymer brush-like layers. Additionally, we explore the effects of chain rigidity, surface-oligomer attraction, and molecular variables on rheological responses, providing a comprehensive understanding of the interplay between molecular-scale phenomena and macroscopic behavior in confined polymeric systems.

Keywords: Polymeric fluids, viscoelasticity, shear-thinning, rheology, molecular dynamics, coarse-grained models, statistical mechanics, thin films.

ÖZET

DOLANIK OLMAYAN POLİMER ERİYİKLERİNİN NANO-KANALLAR İÇERİSİNDEKİ MOLEKÜLER REOLOJİSİ

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Newton tipi davranış göstermeyen kısa zincirli polimer eriyiklerin reolojik özelliklerini nano ölçekli kısıtlanmaya odaklanarak moleküler düzeyde araştırıyoruz. Tüm-atom moleküler dinamik (MD) ve kaba-taneli simülasyonlar kullanarak çeşitli topolojilere sahip oligomer eriyiklerinin dengede olmayan koşullar altında davranışını inceliyoruz. Bulgularımız Oldroyd-B ve genelleştirilmiş Phan-Thien-Tanner (gPTT) modellerinin nano ölçekteki olayları yakalamadaki sınırlamalarını vurgulayarak sürekli modellerden elde edilen tahminlere kıyasla sabit durumunda mikroskobik gerilme tensöründe önemli sapmalar olduğunu ortaya koymaktadır. Bu sapmaların azalan kısıtlanma ile azalan ve yığın sistemlerde kaybolan aşırı viskoelastik gerilimle sonuçlandığını gösteriyoruz. Bu aşırı gerilme, adsorbe edilmiş zincirlerin polimer fırçalarına benzeyen katmanlar oluşturduğu yüzeylerin yakınındaki karbon-karbon bağlarının uzaysal yönelimine bağlıdır. Ek olarak, zincir sertliği, yüzey-oligomer çekimi ve moleküler değişkenlerin reolojik tepkiler üzerindeki etkilerini araştırarak, moleküler ölçekli gözlemler ile kısıtlanmış polimerik sistemlerdeki makroskopik davranışlar arasındaki etkileşimin kapsamlı bir şekilde anlaşılmasını sağlıyoruz.

Anahtar sözcükler: Polimerik akışkanlar, viskoelastisite, kayma incelmesi, reoloji, moleküler dinamik, kaba-taneli modeller, istatistiksel mekanik, ince filmler.

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Chapter 1

Introduction

Science is the most real guide for civilisation, for life, for success in the world. To search for a guide other than science is absurdity, ignorance and heresy.

- Mustafa Kemal Atatürk

1.1 Background and Motivation

Nanoscale confinement of polymeric liquids is often encountered in applications such as ultra-thin fluid film lubrication and nano-manufacturing [1, 2]. As the confinement of a solvent-free polymeric liquid (i.e., melt) approaches the dimensions of the constituting chains (e.g., the radius of gyration R_G), effects that are otherwise not visible in bulk can influence the rheological properties of the liquid [3, 4, 5]. For instance, as $h/R_G \rightarrow 1$, polymer chains can adjust their configuration to the confinement by forming well-defined and discrete molecular layers, altering the shear response of the melt in comparison to bulk [6, 7, 8, 9, 10, 11]. Further, confining surfaces can directly interact and induce non-negligible forces as the surfaces approach each other [12, 13]. Additionally, the molecular variables of continuing chains, such as polymerization degree, topology, and composition,

can affect chain dynamics substantially compared to bulk [14]. Thus, describing the rheological properties of melts at nanoscale confinement requires methods to account for phenomena arising from finite-system dimensions.

While continuum models, such as the Oldroyd-B and generalized Phan-Thien–Tanner (gPTT) models, rely on constitutive equations to establish a relationship between deformation and the stress tensor by introducing response functions (i.e., moduli [15]), they fall short of capturing the rheological response as one of the dimensions of the system becomes comparable to molecular dimensions, R_G [16, 17, 18, 19, 20, 21, 22]. Furthermore, a microscopic definition of the stress tensor can describe the viscoelastic response of melts if all the forces and coordinates of constituting atoms are available [3, 23], for instance, from molecular simulations. Nevertheless, such an approach can be computationally expensive as the system dimensions become larger or when longer sampling times are needed. Alternatively, leveraging the contributions of continuum and molecular models, the complex rheological response of polymer/oligomer melts across different length scales can be captured [24, 25, 26, 27, 28].

In this work, we attempt to bridge molecular-scale phenomena and macroscopic behavior of strongly-confined (i.e., nanoscale) oligomer melts with different topologies (i.e., monodisperse linear or star chains) under non-equilibrium conditions. Using all-atom molecular dynamics (MD) and coarse-grained simulations, we demonstrate that the microscopic stress tensor under steady-state shear deviates significantly from what the continuum model of a simple generalized Newtonian fluid (GNF) would predict despite the minimal impact of entanglement on the system. Our calculations show that these deviations lead to excess viscoelastic stress, which decreases as the confinement decreases ($h \gg R_G$) and eventually vanishes for bulk systems for a wide range of molecular conditions (e.g., chain topology and rigidity), confinement levels, and surface-oligomer attraction strengths. We further relate the excess stress with the spatial orientation of the carbon-carbon bonds of the chains near the surface. Unexpectedly, chains adsorbed on the surface lead to an effective polymer brush-like layer, further decreasing the shear response [29, 30]. The work is further extended using the

coarse-grained approach, which allows us to explore the effects of various polymerization degrees and different aspects of molecular behavior (e.g., tumbling) of the chains. This model provides additional connections into how varying the polymerization degree influences the stress response and how the tumbling of chains under shear and confinement can affect the rheological properties. The insights gained from this work can be useful in developing more effective lubricants, as well as new continuum approaches for capturing the neglected molecular behavior under nanoconfinement.

1.2 Scope and Organization of the Thesis

This thesis covers both theoretical and numerical studies of the rheology of non-Newtonian polymeric fluids at the molecular level. The goal is to understand the mechanisms behind the observed behavior of these fluids through molecular dynamics simulations.

The organization of the thesis is as follows:

Chapter 2 reviews the basic concepts of rheology, explaining the difference between Newtonian and non-Newtonian behavior. It discusses viscoelasticity and the limitations of traditional continuum approaches, such as the Oldroyd-B and generalized Phan-Thien–Tanner models.

Chapter 3 structures the theoretical framework behind our simulations by revisiting important principles of statistical mechanics and polymer physics. It covers both equilibrium and non-equilibrium statistical mechanics and discusses their relevance to polymer physics. The chapter also introduces the theory behind molecular dynamics, compares atomistic and coarse-grained modeling approaches, and outlines the simulation methods and validation techniques used in this study.

Chapter 4 presents the numerical simulations and results. It includes discussions on the (atomistic) DREIDING and OPLS force fields and the (coarse-grained) Kremer-Grest model, providing details on the simulations, characteristic relaxation times, stress tensors, and velocity profiles. The chapter also covers the role of surface attraction and the viscoelastic response of polymeric fluids over different scales (detailed and realistic to coarse-grained and generic), complemented by the analysis of tumbling behavior in the coarse-grained model.

Chapter 5 concludes the thesis, summarizing the main findings and suggesting areas for future research. It emphasizes the importance of understanding polymer rheology at the molecular level and highlights areas where further study could be beneficial.

Overall, the thesis aims to connect macroscopic observations (in particular, viscosity and viscoelastic stress response) with molecular-level observations (in particular, bond orientation and tumbling) when continuum models become insufficient, providing a framework for future studies in this field. Some of the key findings of this study have been published in Ref. [31], as we believe the insights gained from this work can be useful in the development of more effective lubricants, as well as new continuum approaches for capturing the neglected molecular behavior under nanoconfinement.

Chapter 2

Rheology of Polymeric Fluids

Panta rhei. (Everything flows.)

- Heraclitus of Ephesus

The motion of a fluid is fundamentally described by the principles of continuum mechanics, which assumes that fluid properties are continuously distributed. Although the continuum approach is historically well-developed and valid over a range of length/time scales [32], as dimensions approach the size of constituting molecules¹, these assumptions start to fail and the underlying physics may require a molecular-level understanding. As we aim to establish molecular-level insight, our first goal will be to comprehend what the continuum models predict and where they fall short, and we will later dive into the molecular models.

In this chapter, we will explore several aspects of polymeric fluid rheology, starting from the principles of Newtonian and non-Newtonian fluid dynamics in Sec. 2.1, followed by the viscoelasticity in Sec. 2.2. Lastly, we will highlight the limitations of continuum models at molecular scales to rationalize the necessity of molecular dynamics simulations in Sec. 2.3.

¹This is an example where the length scale of interest becomes comparable to the correlation length, that is, the size of the molecules, to be discussed thoroughly in Sec. 3.1.1.

2.1 Newtonian and Non-Newtonian Behavior

At the macroscopic level, Euler's law of mechanics governs the behavior of fluid elements by examining the balance of forces. A key concept is the stress vector, representing internal forces per unit area within the fluid. The stress vector $\mathbf{s}_{\mathbf{n}}(\mathbf{x}, t)$ acting on a surface with normal vector $\mathbf{n}(\mathbf{x}, t)$ relates to the stress tensor $\boldsymbol{\sigma}$ through the Cauchy stress relation [33]:

$$\mathbf{s}_{\mathbf{n}}(\mathbf{x}, t) = \boldsymbol{\sigma}(\mathbf{x}, t) \cdot \mathbf{n}(\mathbf{x}, t). \quad (2.1)$$

The stress tensor $\boldsymbol{\sigma}$ is a second-order tensor, which, by definition, captures the internal force distribution in the fluid. The fundamental equation governed by the conservation of linear momentum for an incompressible fluid (i.e., $\nabla \cdot \mathbf{u} = 0$, a consequence of the conservation of mass) is expressed as:

$$\rho \frac{D\mathbf{u}}{Dt} = \nabla \cdot \boldsymbol{\sigma} + \rho \mathbf{b}, \quad (2.2)$$

where ρ is the fluid density, $\mathbf{u}$ is the velocity field, and $\mathbf{b}$ represents body force per mass unit. The material derivative $\frac{D}{Dt}$ accounts for the rate of change of a quantity (e.g., the velocity field $\mathbf{u}$) for a moving fluid element with the definition:

$$\frac{D\mathbf{u}}{Dt} = \frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}. \quad (2.3)$$

Another important property of the stress tensor $\boldsymbol{\sigma}$ is its symmetry, $\boldsymbol{\sigma} = \boldsymbol{\sigma}^T$, which is the consequence of the conservation of angular momentum. This symmetry implies that shear stresses on orthogonal planes are equal (e.g., $\sigma_{xy} = \sigma_{yx}$), reflecting internal force equilibrium.

As the equations governing the fluid motion will be identical, the primary distinction between how Newtonian and non-Newtonian fluids behave lies in how the stress tensor $\boldsymbol{\sigma}$ is related with the deformation, more specifically with the rate of deformation.

In order to derive an explicit form for the stress tensor, we write the components σ_{ij} as:

$$\sigma_{ij} = -p\delta_{ij} + \tau_{ij}, \quad (2.4)$$

where p is the pressure, δ_{ij} is the Kronecker delta, and τ_{ij} represents the *extra-stress* tensor. The pressure p can be obtained by summing the normal components of the stress tensor:

$$p = -\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}). \quad (2.5)$$

The extra-stress tensor generally accounts for various complex behaviors not adequately captured by Newtonian fluid assumptions. The extra-stress tensor emerges when the fluid is subjected to deformation, meaning that the stress tensor reduces to the negative of the pressure *at rest* (i.e., $\sigma_{ij} = -p\delta_{ij}$ at rest) [32, 33].

For Newtonian fluids, the *extra-stress* tensor, which accounts for the additional stress contributions beyond hydrostatic pressure, is simply the *deviatoric* stress tensor. This *assumption* for Newtonian fluids relates the deviatoric stress tensor to the rate of strain tensor by a direct proportionality. The strain rate tensor measures the deformation rate and is defined as²:

$$\gamma_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right). \quad (2.6)$$

Thus, the constitutive equation relating the deviatoric stress tensor in a Newtonian fluid to the strain rate tensor is given by:

$$\tau_{ij} = 2\eta\dot{\gamma}_{ij}, \quad (2.7)$$

where η represents the dynamic viscosity. This relationship highlights the linear viscous behavior of Newtonian fluids, where the stress is purely dependent on the instantaneous deformation rate.

Now, substituting the deviatoric stress tensor (2.7) back into the expression for the stress tensor (2.4) gives us the Newtonian stress tensor:

$$\sigma_{ij} = -p\delta_{ij} + 2\eta\dot{\gamma}_{ij}. \quad (2.8)$$

²The ' $\frac{1}{2}$ ' factor in front of the partial derivatives in (2.6) gives the average deformation. Another notation that can be found in the literature does not include the ' $\frac{1}{2}$ ' factor and only sums the partial derivatives. Instead, the '2' factor in (2.7) is dropped, eventually leading to the identical formulation.

If we insert the definition of the material derivative (2.3) and the Newtonian stress tensor (2.8), into the momentum equation (2.2), we obtain the Navier-Stokes equation for an incompressible Newtonian fluid:

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \eta \nabla^2 \mathbf{u} + \rho \mathbf{b}. \quad (2.9)$$

Before introducing the non-Newtonian features of the fluids by relaxing the Newtonian assumptions, we first consider the steady, simple shear flow, which is the primary focus of this study:

$$\mathbf{u} = (u_x, u_y, u_z) = (\dot{\gamma}_{xy}y, 0, 0). \quad (2.10)$$

This leads to the Newtonian stress tensor (2.8) to reduce into:

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} = \begin{pmatrix} -p & 2\eta\dot{\gamma}_{xy} & 0 \\ 2\eta\dot{\gamma}_{xy} & -p & 0 \\ 0 & 0 & -p \end{pmatrix}. \quad (2.11)$$

This stress tensor can be inserted into the Navier-Stokes momentum equation (2.9), while considering the Couette flow driving the flow due to the relative motion of the two parallel plates (i.e., no pressure gradient, $\nabla p = 0$), without any body force effects (i.e., $\mathbf{b} = 0$), and at steady state (i.e., $\partial \mathbf{u} / \partial t = 0$). With these conditions, the momentum equation reduces to:

$$\rho (\mathbf{u} \cdot \nabla \mathbf{u}) = \eta \nabla^2 \mathbf{u}. \quad (2.12)$$

Since the flow is only present in $-x$ direction and its magnitude only varies with y , the convective term $(\mathbf{u} \cdot \nabla \mathbf{u})$ simplifies to zero:

$$\mathbf{u} \cdot \nabla \mathbf{u} = u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} + u_z \frac{\partial u_x}{\partial z} = 0, \quad (2.13)$$

due to $u_x = u_x(y)$. As a consequence, $\partial u_x / \partial x = 0$, $\partial u_x / \partial y = du_x / dy$, and $u_y = u_z = 0$.

Eventually, the momentum equation (2.12) reduces to:

$$0 = \eta \frac{d^2 u_x}{dy^2}. \quad (2.14)$$

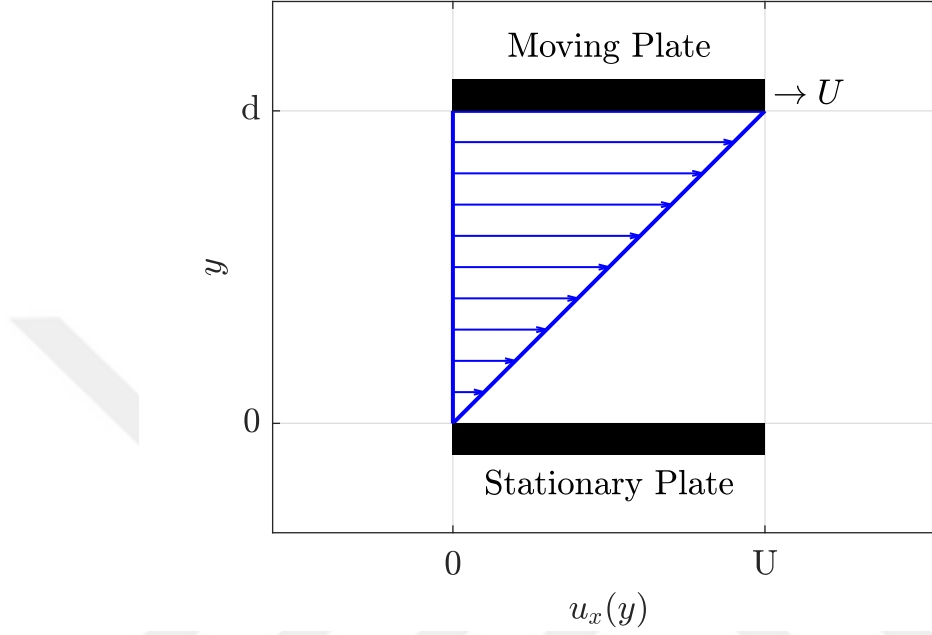


Figure 2.1: Couette flow between parallel plates. The lower plate is stationary while the upper plate moves at velocity U , creating a linear velocity profile $u_x(y)$ in the fluid between the plates (shown in blue). The distance between the plates, also called the film thickness, is d .

To obtain the velocity profile $u_x(y)$, we integrate the equation twice:

$$\frac{d^2 u_x}{dy^2} = 0 \implies \frac{du_x}{dy} = C_1 \implies u_x(y) = C_1 y + C_2. \quad (2.15)$$

As we introduce the *no-slip* boundary conditions, at $y = 0$: $u_x(0) = 0 \implies C_2 = 0$ and at $y = d$: $u_x(d) = U \implies C_1 d = U \implies C_1 = \frac{U}{d}$, where d is the width of the channel, we obtain the velocity profile for Couette flow:

$$u_x(y) = \frac{U}{d} y. \quad (2.16)$$

This linear profile shows that the velocity varies linearly from 0 at the stationary plate to U at the moving plate, as depicted in Fig. 2.1.

Now, we can start incorporating non-Newtonian features into the Newtonian model by relaxing the constant viscosity assumption, leading to the generalized Newtonian fluid (GNF) model. For many non-Newtonian fluids, the viscosity is a function of shear rate, $\eta(\dot{\gamma})$, and after modifying the Newtonian stress tensor

(2.11) accordingly, the stress tensor of the GNF model becomes [33]:

$$\boldsymbol{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{pmatrix} = \begin{pmatrix} -p & 2\eta(\dot{\gamma})\dot{\gamma} & 0 \\ 2\eta(\dot{\gamma})\dot{\gamma} & -p & 0 \\ 0 & 0 & -p \end{pmatrix}, \quad (2.17)$$

where $\dot{\gamma} = \dot{\gamma}_{xy}$ and $\eta(\dot{\gamma})$ captures the shear rate dependency of the viscosity.

If the viscosity experiences a decrease with the increasing shear rate, this behavior is known as *shear-thinning* (pseudo-plastic) and is observed in many non-Newtonian fluids consisting of polymers. In shear-thinning fluids, the particles or molecular chains are initially entangled and randomly distributed, creating a relatively high viscosity at low shear rates. As the shear rate increases, the flow aligns the particles or molecular chains in the direction of the applied shear, reducing the internal resistance to flow and eventually decreasing the viscosity [32].

In contrast, the viscosity can also increase with increasing shear rate, and this behavior is known as *shear-thickening* (dilatant), commonly observed in suspensions of solid particles. In shear-thickening fluids, the particles are found in an ordered phase that keeps them well separated from each other, resulting in relatively low viscosity when left unperturbed. However, this ordered structure becomes disrupted at higher shear rates, bringing some particles into direct contact. These contacts result in higher friction forces between the particles and cause the overall viscosity of the fluid to increase. The comparison of the viscosity behavior between Newtonian and non-Newtonian fluids (shear-thinning and shear-thickening) can be depicted in Fig. 2.2 [32].

Additionally, some fluids exhibit time-dependent viscosity behaviors such as thixotropy (where viscosity decreases over time under a constant shear rate) and rheopexy (where viscosity increases over time under a constant shear rate) [33]. However, the time-dependent viscosity response is not in the context of this study, but rather this study focuses on shear-dependent features, especially given by the shear-thinning behavior of the viscosity for polymers in their molten state.

Given that, one of the common ways to describe the shear-thinning behavior

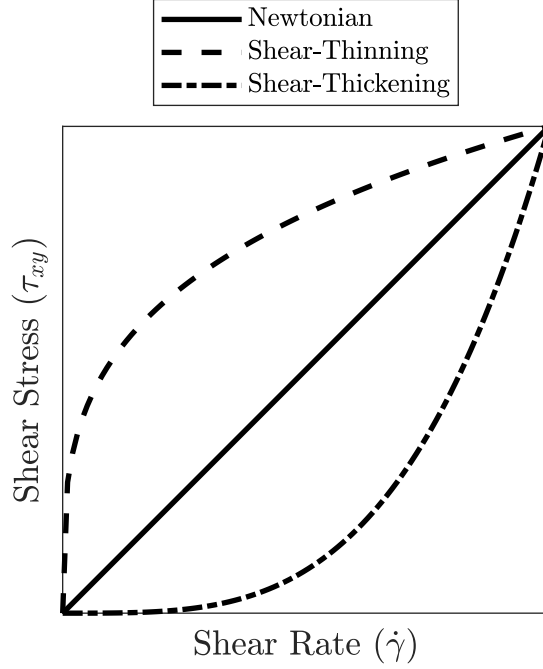


Figure 2.2: Viscosity dependence: Newtonian and non-Newtonian. The graph illustrates the relationship between shear stress (τ_{xy}) and shear rate ($\dot{\gamma}$) for Newtonian, and non-Newtonian (shear-thinning, and shear-thickening) fluids, demonstrating how viscosity changes with shear rate.

is the Carreau-Yasuda model, which provides a smooth transition between the zero-shear viscosity η_0 and the infinite-shear viscosity η_∞ [32, 33]:

$$\eta(\dot{\gamma}) = \eta_\infty + (\eta_0 - \eta_\infty) [1 + (\lambda \dot{\gamma})^a]^{\frac{n-1}{a}}, \quad (2.18)$$

where η_0 is the zero-shear viscosity, η_∞ is the infinite-shear viscosity, λ is a time constant, a and n are dimensionless parameters that control the shape of the viscosity curve. This model captures the transition from Newtonian behavior at low shear rates to shear-thinning behavior at higher shear rates. The general behavior of the Carreau-Yasuda model with first (i.e., zero-shear viscosity) and second (i.e., infinite-shear viscosity) Newtonian plateau is depicted in Fig. 2.3. The zero-shear and infinite-shear viscosity are also known as the first and second Newtonian plateau, respectively.

Beyond these generalized Newtonian models, viscoelastic fluids exhibit both viscous and elastic characteristics. These fluids require more complex constitutive

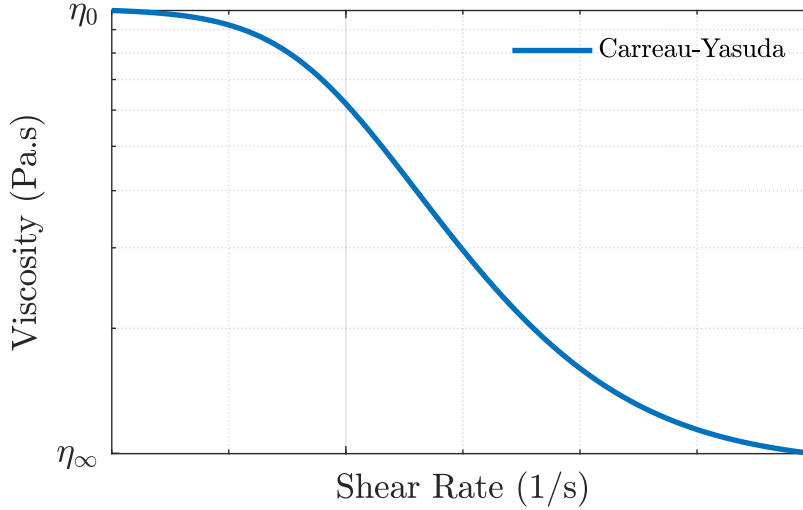


Figure 2.3: Carreau-Yasuda model for shear-thinning fluids. The graph illustrates the relationship between viscosity (Pa.s) and shear rate (1/s) on a logarithmic scale, showing the characteristic decrease in viscosity from the first Newtonian plateau, η_0 , at low shear rates to the second Newtonian plateau, η_∞ , at high shear rates.

models to describe their behavior accurately since they include memory effects and normal stress differences that are observed in experiments. This discussion acts as an introduction to our exploration of viscoelasticity, a field that involves complex responses arising from the concurrent presence of viscous and elastic properties.

2.2 Viscoelasticity

Viscoelasticity describes materials that exhibit both viscous and elastic characteristics simultaneously when undergoing deformation. Consequently, these materials can store and dissipate energy³, making it significant in many complex fluids such as polymers, biological tissues, and suspensions.

One of the fundamental models to describe viscoelastic behavior is the Maxwell

³This dissipation is not necessarily isotropic, influenced by factors like molecular orientation, structural properties of materials (e.g., composites, suspensions), or phase transformations.

model, which combines a viscous damper and an elastic spring in series (as illustrated in Fig. 2.4). The constitutive equation for the Maxwell model is [32]:

$$\sigma + \lambda \dot{\sigma} = \eta \dot{\gamma}, \quad (2.19)$$

where σ is the stress, γ is the strain, η is the viscosity, and $\lambda = \frac{\eta}{E}$ is the relaxation time, and E is the elastic modulus. The relaxation time λ characterizes the rate at which the material relaxes stress under constant strain. For times smaller than λ , the material behaves elastically, while for times much longer than λ , it behaves viscously.

Another viscoelastic model is called the Kelvin-Voigt model, which consists of a viscous damper and an elastic spring in parallel (as illustrated in Fig. 2.5). This model describes creep behavior, where strain increases over time under constant stress. The constitutive equation for the Kelvin-Voigt model is [32]:

$$\sigma = E\gamma + \eta \dot{\gamma}, \quad (2.20)$$

where $\eta \frac{d\gamma}{dt}$ represents the viscous response, and $E\gamma$ represents the elastic response. The retardation time, defined as $\tau_r = \frac{\eta}{E}$, indicates how quickly the material responds to applied stress. Despite having the same formula, the difference between relaxation and retardation time comes from which response is being considered, either the stress response to the given elongation (relaxation time) or the elongation response to the given stress (retardation time).

We can obtain a more complicated model by combining the features of both Maxwell and Kelvin-Voigt models, the so-called linear viscoelastic model (as illustrated in Fig. 2.6). This model consists of a Maxwell element where the dashpot is replaced with a Kelvin-Voigt element (spring and dashpot in parallel). The constitutive equation reads [34]:

$$\sigma + \frac{\eta}{E_1 + E_2} \dot{\sigma} = \frac{E_1 E_2}{E_1 + E_2} \gamma + \frac{E_1 \eta}{E_1 + E_2} \dot{\gamma}, \quad (2.21)$$

with the relaxation time $\lambda = \frac{\eta}{E_1}$ and the retardation time $\tau_r = \frac{\eta}{E_2}$.

Now, we can consider a scenario that is the main focus of this thesis, that is, the deformation under constant strain rate ($\dot{\gamma} = \dot{\gamma}_0$). We will evaluate the

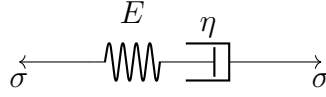


Figure 2.4: Maxwell model. A series combination of a spring (elastic element) and a dashpot (viscous element). The total strain is the sum of the strains in the spring and the dashpot.

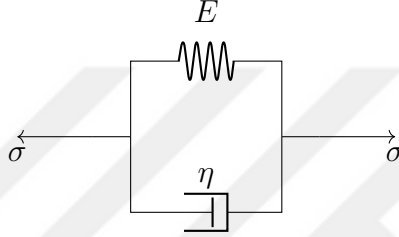


Figure 2.5: Kelvin-Voigt model. A parallel combination of a spring (elastic element) and a dashpot (viscous element). The total stress is the sum of the stresses in the spring and the dashpot.

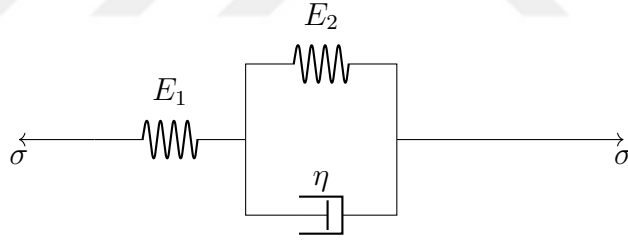


Figure 2.6: Linear viscoelastic model. A possible linear imposition of Maxwell and Kelvin-Voigt models, a combination of a spring in series with a parallel arrangement of another spring and a dashpot. It captures both the instantaneous elastic response and the delayed viscoelastic response.

predictions of Maxwell, Kelvin-Voigt, and linear viscoelastic models as we obtain their solutions for the case as mentioned earlier.

For Maxwell model, we recall the equation (2.19), and replace $\dot{\gamma}$ with a constant $\dot{\gamma}_0$. The integration with respect to t yields:

$$\sigma(t) = C_1 \exp(-t/\lambda) + \eta \dot{\gamma}_0. \quad (2.22)$$

We refer to the initial condition to determine the integration constant C_1 , assuming no initial stress $\sigma(t = 0) = 0$. With this, the solution becomes:

$$\sigma(t) = \eta \dot{\gamma}_0 (1 - \exp(-t/\lambda)). \quad (2.23)$$

Here, we note that the Maxwell model reaches a plateau of $\eta\dot{\gamma}$ with $t \rightarrow \infty$ and yields a steady stress response.

For Kelvin-Voigt model, we recall the equation (2.20), and similarly replace $\dot{\gamma}$ with a constant $\dot{\gamma}_0$. Moreover, we rewrite the strain term as $\gamma = \dot{\gamma}_0 t$. With these changes, we simply arrive at the solution:

$$\sigma(t) = \dot{\gamma}_0(E_2 t + \eta). \quad (2.24)$$

In contrast to the Maxwell model, the Kelvin-Voigt model predicts constantly increasing stress with time.

Lastly, we recall the equation (2.21) for the linear viscoelastic model and perform the changes that we made for Maxwell and Kelvin-Voigt models. After some algebraic manipulations, the solution leads to:

$$\sigma(t) = \dot{\gamma}_0 \left[\frac{\eta E_1^2}{(E_1 + E_2)^2} (1 - \exp(-(E_1 + E_2)t/\eta)) + \frac{E_1 E_2}{E_1 + E_2} t \right]. \quad (2.25)$$

which includes an exponential term similar to Maxwell solution and a term that linearly increases with time similar to Kelvin-Voigt solution.

We can visualize the solutions in Fig. 2.2, where a constant strain rate of $\dot{\gamma}_0$ is applied after an initial delay. While the Maxwell solution gradually increases and eventually reaches $\eta\dot{\gamma}_0$, the Kelvin-Voigt solution starts with a sudden jump to $\eta\dot{\gamma}_0$ followed by a linear increase with a slope of $\dot{\gamma}E_2$. Finally, the linear viscoelastic model shows the characteristic features of both Maxwell and Kelvin-Voigt models, as the stress shows a gradual increase (i.e., the Maxwell model), and a unbounded increase with time (i.e., the Kelvin-Voigt model).

As it can be noted, these models provide a simplified and one-dimensional stress response and only act as a beginning point for our goal of understanding the viscoelastic response of polymeric liquids. Further generalizations and superimpositions of Maxwell and Kelvin-Voigt models also will not account for the nonlinear viscoelastic responses often faced in three-dimensional cases (i.e., real-life scenarios).

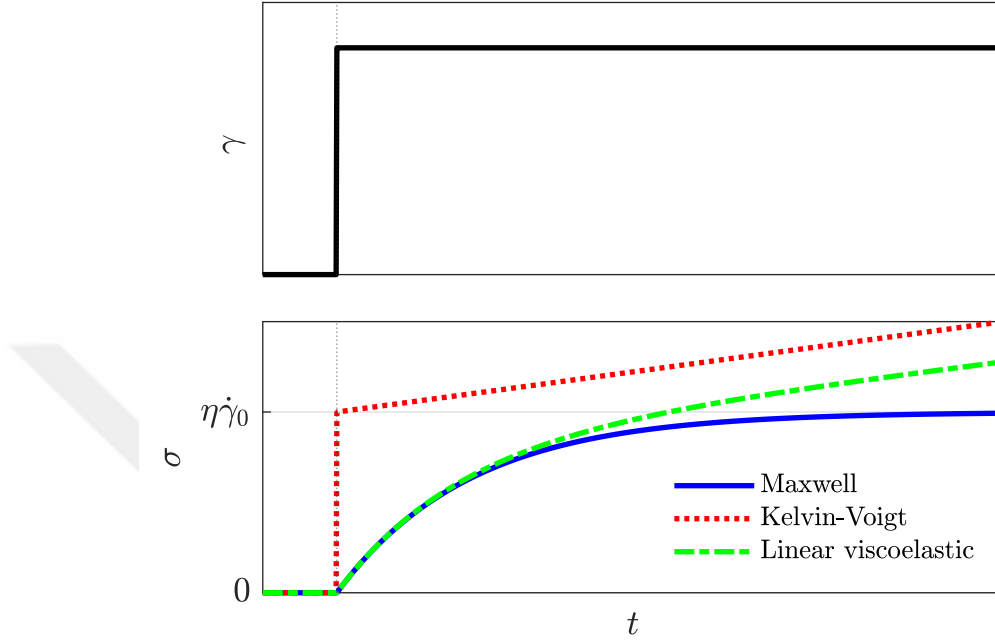


Figure 2.7: Constant strain rate solutions for different viscoelastic models. The upper plot shows the applied constant strain rate $\dot{\gamma}$. The lower plot depicts the resulting stress σ over time t for the Maxwell model (blue solid line), Kelvin-Voigt model (red dotted line), and a linear viscoelastic model (green dashed line). The Maxwell model shows a linear increase in stress, the Kelvin-Voigt model shows an immediate stress response followed by a linear increase, and the linear viscoelastic model demonstrates an intermediate behavior.

A key concept that differentiates the viscoelastic fluids from linear viscoelasticity models (e.g., Maxwell, Kelvin-Voigt, linear viscoelastic and possible superimpositions) is the existence of non-zero normal stress differences, denoted as N_1 and N_2 . These stress differences arise from the anisotropic nature of stress distribution in viscoelastic materials and are defined as⁴ [32, 35]:

$$N_1 = \sigma_{xx} - \sigma_{yy}, \quad (2.26)$$

$$N_2 = \sigma_{yy} - \sigma_{zz}. \quad (2.27)$$

The normal stress differences are critical for characterizing non-Newtonian behavior and are responsible for phenomena such as the rod climbing effect [32]. Based on the available experimental evidence, non-zero normal stress differences are

⁴ N_1 and N_2 are also called viscometric functions.

associated with viscoelastic fluids whereas the normal stress differences become zero for Newtonian or generalized Newtonian fluids⁵ [33].

There exists plenty of continuum models that aim to explain the nonlinear stress response, such as Oldroyd, Giesekus, Phan-Thien–Tanner (PTT), together CONNFFESSIT⁶ approach that provides the much needed constitutive equation from molecular simulations [28, 33]. Moreover, since the viscoelastic fluids (materials, in general) exhibit memory effects, meaning that their current stress state depends on the history of deformation, these models often include integral formulations or differential equations with memory kernels, with the aim of capturing the ability of energy storage/dissipation. Although these models provide good predictions for the fluids within the continuum limit under specific cases (e.g., dilute solutions, suspensions, or melts), they fall apart in predicting the flow characteristics when the system dimensions (i.e., the film thickness) start to be comparable to the size of the molecules. The next section is devoted to the shortcomings of several continuum models (in particular, Oldroyd-B and generalized PTT), which are commonly used in the rheological modeling of viscoelastic fluids, that are analyzed in the context of their normal stress difference predictions.

2.3 Shortcomings of Continuum Models

The continuum models usually predict positive N_1 and zero or negative N_2 , telling us there exists a non-negligible amount of tension along the streamlines (i.e., the shear direction) due to viscoelasticity [36]. This prediction inherently leads to a microscopic expectation that the polymers are stretched along the shear direction and the anisotropy in stress distribution is a product of this peculiar molecular orientation [32]. Except for specifically-oriented microstructures (e.g., liquid crystalline phases), the experiments almost always predict $N_1 > 0$ and $N_2 \leq 0$, where

⁵As we recall the Newtonian stress tensor (2.11) and GNF stress tensor (2.17), we note the diagonal components of the stress tensors are equal, $\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$, and do not show anisotropy [33].

⁶This is an abbreviation for "Calculation of Non-Newtonian Flow: Finite Elements and Stochastic Simulation Technique."

$|N_2|$ is smaller than $|N_1|$ and N_2 often neglected due of this [37, 38]. However, the assumptions on molecular orientation (and the consequent stress response of the fluid) that work respectively well for the systems that are bulky or within the continuum limit may become too naive to predict the complexities arising in nanoconfined systems. As the molecular orientation and the corresponding stress tensor will be highly affected by the film thickness, molecular size, and surface effects, the aforementioned continuum models will not be sufficient as they lack any underlying theory or parameterization in that regard.

Here, we will focus on Oldroyd-B and generalized Phan-Thien-Tanner (gPTT) models to show why they will be insufficient for our problem of interest. Still, the shortcomings of the continuum models are not limited to these models, but instead we decide to focus on these two commonly used models. Experimental results for different fluid systems and asymptotic predictions for other viscoelastic models are thoroughly reviewed in Ref. [36].

2.3.1 Oldroyd-B model

The Oldroyd-B model extends the Maxwell model to account for both viscous and elastic effects in a more generalized way. It is particularly effective in describing the flow of *dilute polymer solutions*. The constitutive equation for the Oldroyd-B model is [19, 39]:

$$\boldsymbol{\sigma} + \lambda \left(\frac{D\boldsymbol{\sigma}}{Dt} - \boldsymbol{\sigma} \cdot \nabla \mathbf{u} - \nabla \mathbf{u}^T \cdot \boldsymbol{\sigma} \right) = \eta (\nabla \mathbf{u} + \nabla \mathbf{u}^T), \quad (2.28)$$

where $\boldsymbol{\sigma}$ is the stress tensor, λ is the relaxation time, η is the (solvent) viscosity, and $\mathbf{u}$ is the velocity field. This model incorporates both the convective effects and the viscoelastic stress relaxation, providing a more comprehensive description of fluid behavior with respect to linear viscoelastic models. We further add the divergence of stress tensor ($\nabla \cdot \boldsymbol{\sigma}$) to the Navier-Stokes momentum equation (2.9), replacing the body force.

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla p + \eta \nabla^2 \mathbf{u} + \nabla \cdot \boldsymbol{\sigma}. \quad (2.29)$$

2.3.1.1 Perturbation Method and Approximate Solutions

Since the governing equations (2.28 and 2.29) are nonlinear, we may refer to a perturbative approach to obtain the approximate solutions. Noting that the Oldroyd-B model presumes $\sigma_{zz} = 0$ for a shearing applied in the $-xy$ plane, we first write the mass/momentum conservation and Oldroyd-B constitutive equations in Cartesian coordinates, respectively [39]:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(u_x \rho)}{\partial x} + \frac{\partial(u_y \rho)}{\partial y} = 0, \quad (2.30a)$$

$$\frac{\partial p}{\partial x} = \beta \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial \sigma_{xy}}{\partial y} + \frac{\partial \sigma_{xx}}{\partial x}, \quad (2.30b)$$

$$\frac{\partial p}{\partial y} = 0, \quad (2.30c)$$

$$\sigma_{xx} + De \left(-2\sigma_{xy} \frac{\partial u_x}{\partial y} - 2\sigma_{xx} \frac{\partial u_x}{\partial x} \right) = 0, \quad (2.30d)$$

$$\sigma_{xy} + De \left(-\sigma_{yy} \frac{\partial u_x}{\partial y} - \sigma_{xx} \frac{\partial u_y}{\partial x} \right) = (1 - \beta) \frac{\partial u_x}{\partial y}, \quad (2.30e)$$

$$\sigma_{yy} + De \left(-2\sigma_{xy} \frac{\partial u_y}{\partial x} - 2\sigma_{yy} \frac{\partial u_y}{\partial y} \right) = 2(1 - \beta) \frac{\partial u_y}{\partial y}, \quad (2.30f)$$

where the symbols have the following meanings: ρ is the density, u_x and u_y are the velocity components in the x and y directions, respectively, p is the pressure, σ_{ij} are the components of the stress tensor, β is a dimensionless parameter related to the fluid viscosity, and $De = \tau_R/\tau_F$ is the Deborah number, representing the ratio of the characteristic time of the fluid's relaxation (τ_R) to the characteristic time of the flow (τ_F).

To proceed with a perturbative approach for $De \ll 1$, we introduce small perturbations around the base flow. Assuming that the base state is at rest and the perturbations are small, we write:

$$u_x = u_x^{(0)} + De u_x^{(1)} + De^2 u_x^{(2)} + \dots, \quad (2.31a)$$

$$u_y = u_y^{(0)} + De u_y^{(1)} + De^2 u_y^{(2)} + \dots, \quad (2.31b)$$

$$p = p^{(0)} + De p^{(1)} + De^2 p^{(2)} + \dots, \quad (2.31c)$$

$$\sigma_{ij} = \sigma_{ij}^{(0)} + De \sigma_{ij}^{(1)} + De^2 \sigma_{ij}^{(2)} + \dots, \quad (2.31d)$$

where De is a small parameter representing the magnitude of the perturbation; in a molecular simulation setting, we may be interested in cases where the molecular relaxation is comparable but shorter than the timescale of the simulation, such that the steady-state stress response will be reached. With this, we assume that the second-order perturbations in De are negligible and limit the perturbations up to the first order.

Substituting these expansions into the governing equations and collecting terms of the same order of De , we obtain a set of equations that can be solved sequentially [39]. At the zeroth order (base state), we have:

$$\frac{\partial \rho^{(0)}}{\partial t} + \frac{\partial(u_x^{(0)} \rho^{(0)})}{\partial x} + \frac{\partial(u_y^{(0)} \rho^{(0)})}{\partial y} = 0, \quad (2.32a)$$

$$\frac{\partial p^{(0)}}{\partial x} = \beta \frac{\partial^2 u_x^{(0)}}{\partial y^2} + \frac{\partial \sigma_{xy}^{(0)}}{\partial y} + \frac{\partial \sigma_{xx}^{(0)}}{\partial x}, \quad (2.32b)$$

$$\frac{\partial p^{(0)}}{\partial y} = 0, \quad (2.32c)$$

$$\sigma_{xx}^{(0)} = 0, \quad (2.32d)$$

$$\sigma_{xy}^{(0)} = (1 - \beta) \frac{\partial u_x^{(0)}}{\partial y}, \quad (2.32e)$$

$$\sigma_{yy}^{(0)} = 2(1 - \beta) \frac{\partial u_y^{(0)}}{\partial y}. \quad (2.32f)$$

At the first order in De , we have:

$$\frac{\partial \rho^{(1)}}{\partial t} + \frac{\partial(u_x^{(1)} \rho^{(0)} + u_x^{(0)} \rho^{(1)})}{\partial x} + \frac{\partial(u_y^{(1)} \rho^{(0)} + u_y^{(0)} \rho^{(1)})}{\partial y} = 0, \quad (2.33a)$$

$$\frac{\partial p^{(1)}}{\partial x} = \beta \frac{\partial^2 u_x^{(1)}}{\partial y^2} + \frac{\partial \sigma_{xy}^{(1)}}{\partial y} + \frac{\partial \sigma_{xx}^{(1)}}{\partial x}, \quad (2.33b)$$

$$\frac{\partial p^{(1)}}{\partial y} = 0, \quad (2.33c)$$

$$\sigma_{xx}^{(1)} - 2\sigma_{xy}^{(0)} \frac{\partial u_x^{(0)}}{\partial y} - 2\sigma_{xx}^{(0)} \frac{\partial u_x^{(0)}}{\partial x} = 0, \quad (2.33d)$$

$$\sigma_{xy}^{(1)} - \sigma_{yy}^{(0)} \frac{\partial u_x^{(0)}}{\partial y} - \sigma_{xx}^{(0)} \frac{\partial u_y^{(0)}}{\partial x} = (1 - \beta) \frac{\partial u_x^{(1)}}{\partial y}, \quad (2.33e)$$

$$\sigma_{yy}^{(1)} - 2\sigma_{xy}^{(0)} \frac{\partial u_y^{(0)}}{\partial x} - 2\sigma_{yy}^{(0)} \frac{\partial u_y^{(0)}}{\partial y} = 2(1 - \beta) \frac{\partial u_y^{(1)}}{\partial y}. \quad (2.33f)$$

By considering the steady-state response and eliminating the time derivatives, the equations in the first order can be written as:

$$0 = \beta \frac{\partial^2 u_x^{(0)}}{\partial y^2} + \frac{\partial \sigma_{xy}^{(0)}}{\partial y} + \frac{\partial \sigma_{xx}^{(0)}}{\partial x}, \quad (2.34a)$$

$$0 = \sigma_{xx}^{(0)}, \quad (2.34b)$$

$$\sigma_{xy}^{(0)} = (1 - \beta) \frac{\partial u_x^{(0)}}{\partial y}, \quad (2.34c)$$

$$\sigma_{yy}^{(0)} = 2(1 - \beta) \frac{\partial u_y^{(0)}}{\partial y}, \quad (2.34d)$$

$$0 = \beta \frac{\partial^2 u_x^{(1)}}{\partial y^2} + \frac{\partial \sigma_{xy}^{(1)}}{\partial y} + \frac{\partial \sigma_{xx}^{(1)}}{\partial x}, \quad (2.34e)$$

$$\sigma_{xx}^{(1)} = 2(1 - \beta) \left(\frac{\partial u_x^{(0)}}{\partial y} \right)^2, \quad (2.34f)$$

$$\sigma_{xy}^{(1)} = -(1 - \beta) \frac{\partial u_x^{(0)}}{\partial y}, \quad (2.34g)$$

$$\sigma_{yy}^{(1)} = 2(1 - \beta) \left(\frac{\partial u_y^{(0)}}{\partial y} \right)^2. \quad (2.34h)$$

2.3.1.2 Normal Stress Differences

We first note that the parameter β , which represents the ratio of the solvent viscosity to the total viscosity, becomes zero for polymer melts, as the melts are typically regarded as purely elastic with negligible solvent contribution. Moreover, we focus on a shear flow characterized by a constant shear rate $\dot{\gamma}$ in the $-xy$ direction. Recalling the velocity field for our shear flow:

$$u_x = \dot{\gamma}y, \quad (2.35a)$$

$$u_y = 0. \quad (2.35b)$$

With $\beta = 0$ and substituting the shear flow velocity field into the steady-state equations derived earlier, we obtain the shear stress:

$$\sigma_{xy} = (1 - \beta) \frac{\partial u_x}{\partial y} = \dot{\gamma}. \quad (2.36)$$

For the normal stress components, we first determine the values at each order for each component and use the perturbation equation (2.31d) to obtain the final forms:

$$\sigma_{xx}^{(0)} = 0, \quad \sigma_{xx}^{(1)} = 2\dot{\gamma}^2, \quad \sigma_{xx} = 2De\dot{\gamma}^2 \quad (2.37a)$$

$$\sigma_{yy}^{(0)} = 0, \quad \sigma_{yy}^{(1)} = 0, \quad \sigma_{yy} = 0 \quad (2.37b)$$

$$\sigma_{zz} = 0 \text{ (by definition)}, \quad (2.37c)$$

At last, we find the normal stress differences:

$$N_1 = \sigma_{xx} - \sigma_{yy} = 2De\dot{\gamma}^2, \quad (2.38a)$$

$$N_2 = \sigma_{yy} - \sigma_{zz} = 0, \quad (2.38b)$$

and verify that the Oldroyd-B model naively predicts $N_1 \geq 0$ and $N_2 = 0$, regardless of the complexities that may arise due to molecular configuration and confinement effects.

2.3.2 Generalized Phan-Thien—Tanner model (gPTT)

Based on the Lodge-Yamamoto network theory [32], Phan-Thien and Tanner have developed a constitutive equation, PTT model, for incompressible polymeric fluids [40], which has the form:

$$Y(\theta, \sigma_{kk}) \boldsymbol{\sigma} + \lambda \overset{\circ}{\boldsymbol{\sigma}} = 2\eta_p \mathbf{D}, \quad (2.39)$$

where $\mathbf{D}$ is the rate of deformation tensor, $\boldsymbol{\sigma}$ is the stress tensor, λ is a relaxation time, η_p is the constant polymeric viscosity, σ_{kk} is the trace of the stress tensor, $Y(\sigma_{kk})$ corresponds to the rate of destruction of junctions and the behavior of complex materials at some temperature θ , and $\overset{\circ}{\boldsymbol{\sigma}}$ represents the Gordon-Schowalter derivative of the stress tensor $\boldsymbol{\sigma}$.

The Gordon-Schowalter derivative is a mathematical operator, often used in viscoelastic fluid mechanics, to describe fractional differentiation and has the following definition:

$$\overset{\circ}{\sigma} = \frac{\partial \sigma}{\partial t} + (\mathbf{u} \cdot \nabla) \sigma - (\nabla \mathbf{u})^T \cdot \sigma - \sigma \cdot (\nabla \mathbf{u}) + \xi(\sigma \cdot \mathbf{D} + \mathbf{D} \cdot \sigma), \quad (2.40)$$

where $\mathbf{u}$ is the velocity vector, $\nabla \mathbf{u}$ is the velocity gradient, and the parameter $\xi (0 \leq \xi \leq 1)$ accounts for the slip between the molecular network and the continuous medium.

The network destruction function, $Y(\theta, \sigma_{kk})$, considers the formation and destruction of junctions, intersection points of network strands, as the viscoelastic fluid deforms where the deformation is not necessarily isothermal. Following Phan-Thien's work [41], $Y(\sigma_{kk})$ can be decomposed to two parts, $Y(\theta, \sigma_{kk}) = \phi(\theta) K(\sigma_{kk})$. Under isothermal conditions⁷ ($\theta = \theta_r$), θ_r being the reference temperature of the polymeric fluid, $Y(\theta, \sigma_{kk})$ no longer depends on temperature and simplifies to $Y(\theta, \sigma_{kk}) = K(\sigma_{kk})$ as $\phi(\theta) = 1$.

For $K(\sigma_{kk})$, gPTT model [42] suggests the following form by introducing two fitting parameters, α and β ($\alpha, \beta \in \mathbb{R}^+ \mid \alpha, \beta > 0$):

$$Y(\theta, \sigma_{kk}) = \phi(\theta) K(\sigma_{kk}) = \phi(\theta) \Gamma(\beta) E_{\alpha, \beta} \left(\frac{\varepsilon \lambda}{\eta_p} \sigma_{kk} \right), \quad (2.41)$$

where ε represents the extensibility parameter, $\Gamma(\beta)$ is the Gamma function ensuring $K(0) = 1$ for all choices of β , and $E_{\alpha, \beta}$ is the Mittag-Leffler function.

Noting that, with $\alpha = \beta = 1$, we obtain $\Gamma(\beta = 1) = 1$ and $E_{\alpha=1, \beta=1}(z) = e^z$, in which the generalized PTT equation (2.41) reduces to simplified PTT model [32]:

$$K(\sigma_{kk}) = \exp \left(\frac{\varepsilon \lambda}{\eta_p} \right). \quad (2.42)$$

⁷We will also consider isothermal shear flow, maintained by thermostats, under various conditions in molecular simulations.

2.3.2.1 Analytical Solution for Couette Flow

We now consider the (weak) Couette flow, assuming the microstructure of the polymeric fluid does not deform drastically, and deformation is obtained by pure shear flow aligned with the x-direction. Denoting the strain rate with $\dot{\gamma}$, we can expand the constitutive equation (2.39), and obtain the following set of equations [43]:

$$K(\sigma_{kk}) \sigma_{xx} = \lambda (2 - \xi) \dot{\gamma} \sigma_{xy}, \quad (2.43a)$$

$$K(\sigma_{kk}) \sigma_{yy} = -\lambda \xi \dot{\gamma} \sigma_{xy}, \quad (2.43b)$$

$$K(\sigma_{kk}) \sigma_{xy} = \eta \dot{\gamma} + \lambda \left(1 - \frac{\xi}{2}\right) \dot{\gamma} \sigma_{yy} - \frac{\lambda \xi}{2} \dot{\gamma} \sigma_{xx}, \quad (2.43c)$$

where we also have $\sigma_{zz} = 0$, and therefore the second normal stress difference reduces to $N_2 = \sigma_{yy}$, by definition.

Dividing equation (2.43a) by (2.43b) yields a relationship between the normal stress components:

$$\sigma_{yy} = -\frac{\xi}{2 - \xi} \sigma_{xx}. \quad (2.44)$$

We may further arrive at the following equation after some algebraic manipulations:

$$K^2(\sigma_{kk}) \sigma_{xx} = \lambda \eta (2 - \xi) \dot{\gamma}^2 + \lambda^2 (\xi^2 - 2\xi) \dot{\gamma}^2 \sigma_{xx}, \quad (2.45)$$

noting that $K^2(\sigma_{kk})$ is the parameter creating the non-linearity in the given equation.

To obtain the analytical solution, we first recall the Mittag-Leffler function [44]:

$$E_{\alpha, \beta}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(\beta + \alpha k)}. \quad (2.46)$$

By setting $\beta = 1$, we not only get rid of the Gamma function in front of the Mittag-Leffler function since $\Gamma(1) = 1$ (see the most general form of the gPTT equation (2.41)), but also become able to consider some of the following known expressions different α values [44]:

$$E_{1,1}(z) = e^z, \quad (2.47a)$$

$$E_{2,1}(z) = \cosh(\sqrt{z}), \quad (2.47b)$$

$$E_{3,1}(z) = \frac{1}{2} \left[e^{z^{1/3}} + 2e^{-(1/2)z^{1/3}} \cos \left(\frac{\sqrt{3}}{2} z^{1/3} \right) \right]. \quad (2.47c)$$

Writing the quadratic $K(z)$ as $K^2(z) = E_{\alpha,1}^2(z)$ for $\beta = 1$, making $E^2(z)$ the quadratic $E(z)$, we can perform quadratic approximation using Taylor series, which results in:

$$E_{1,1}^2(z) \approx 1 + 2z + 2z^2, \quad (2.48a)$$

$$E_{2,1}^2(z) \approx 1 + z + \frac{1}{3}z^2, \quad (2.48b)$$

$$E_{3,1}^2(z) \approx \frac{9}{2} + \frac{3}{2}z + \frac{11}{80}z^2. \quad (2.48c)$$

Here, we also note that the common practice of using the linearized Mittag-Leffler function results in quadratic expressions different from the ones shown above ($E_{1,1}(z) = \exp(z) \approx 1 + z$ and hence $[E_{1,1}(z)]^2 \approx (1 + z)^2$).

Evaluation of the network destruction and hence the determination of σ_{xx} is now only depends on the trace of the stress tensor, which is $\sigma_{kk} = \sigma_{xx} + \sigma_{yy} + \sigma_{zz} = \sigma_{xx} + \sigma_{yy}$. Together with the equation (2.44), the trace can be written as:

$$\sigma_{kk} = \text{Tr}(\boldsymbol{\sigma}) = \left(1 - \frac{\xi}{2 - \xi} \right) \sigma_{xx}. \quad (2.49)$$

We arrive to the following expression for σ_{xx} after inserting the equations (2.41) and (2.49) into (2.45), in which σ_{xx} is defined in terms of the material parameters ($\lambda, \xi, \eta, \alpha$) and the strain rate ($\dot{\gamma}$):

$$E_{\alpha,1}^2 \left(\frac{\varepsilon \lambda}{\eta_p} \left(\frac{2 - 2\xi}{2 - \xi} \right) \sigma_{xx} \right) \sigma_{xx} = \lambda \eta (2 - \xi) \dot{\gamma}^2 + \lambda^2 (\xi^2 - 2\xi) \dot{\gamma}^2 \sigma_{xx}. \quad (2.50)$$

Here, the Mittag-Leffler function must be evaluated according to (2.46). By taking the approximate forms of functions given in (2.48a-c), we can arrive at a cubic equation to be solved for σ_{xx} analytically.

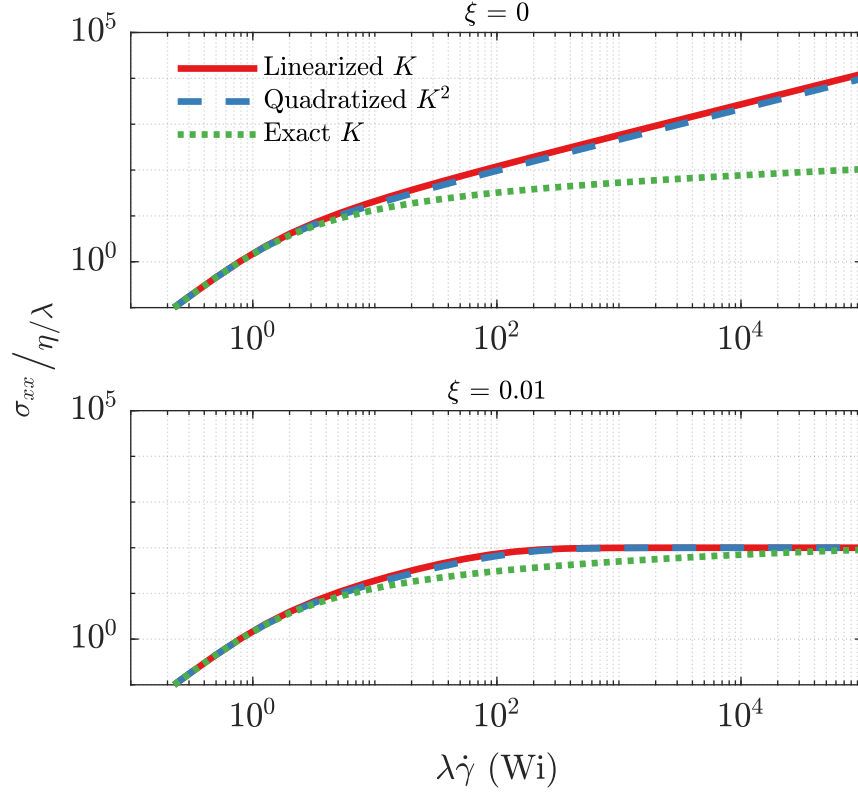


Figure 2.8: Effect of using approximate forms of the network destruction function compared to the exact form, including power series. The graph illustrates the increase in deviation from the exact K when linearization is performed, where quadratic approximation yields slight improvement.

2.3.2.2 Further Generalizations and Numerical Solutions of Semi-analytical Formulation

We write the semi-analytical formulation by reverting the prior approximations and relaxing the limitation on α and β (where we had only considered $\alpha = 1, 2, 3$ and $\beta = 1$):

$$\Gamma(\beta) E_{\alpha,\beta}^2 \left(\frac{\varepsilon\lambda}{\eta_p} \left(\frac{2-2\xi}{2-\xi} \right) \sigma_{xx} \right) \sigma_{xx} = \lambda\eta (2-\xi) \dot{\gamma}^2 + \lambda^2 (\xi^2 - 2\xi) \dot{\gamma}^2 \sigma_{xx}. \quad (2.51)$$

This expression can be solved numerically for $\sigma_{xx}/\eta/\lambda$ by defining the material-specific parameters α , β , ε , and ξ . The physical meaning of these parameters can be deduced from Fig. 2.9.

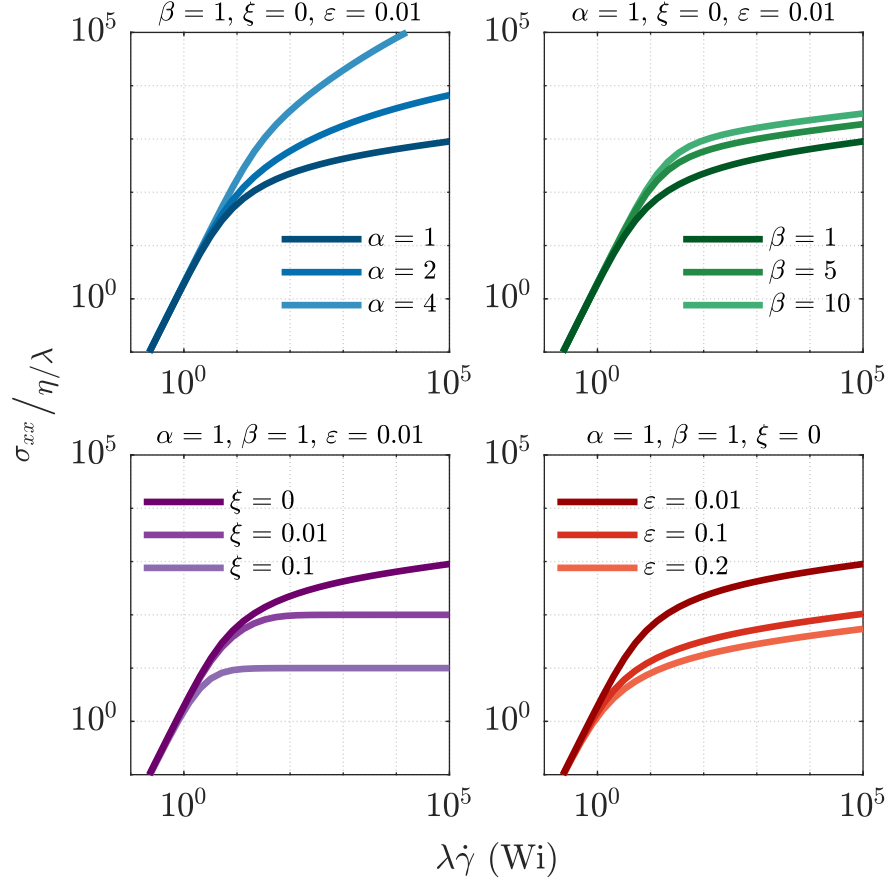


Figure 2.9: Effect of three fitting parameters α , β , ϵ , and slip parameter ξ on the normalized stress component $\frac{\sigma_{xx}}{\eta/\lambda}$ as a function of the Weissenberg number $\lambda \dot{\gamma}$ (Wi) in the gPTT model. The plots show: (a) Variation with α for fixed $\beta = 1$, $\xi = 0$, and $\epsilon = 0.01$. (b) Variation with β for fixed $\alpha = 1$, $\xi = 0$, and $\epsilon = 0.01$. (c) Variation with ξ for fixed $\alpha = 1$, $\beta = 1$, and $\epsilon = 0.01$. (d) Variation with ϵ for fixed $\alpha = 1$, $\beta = 1$, and $\xi = 0$.

Regarding α , we observe that it controls the initial stiffness and the rate at which the stress increases with Wi. The parameter β influences the asymptotic value of the stress, reflecting its effect on the long-term behavior of the material. The slip parameter ξ affects the transition behavior, modulating the stress response during the deformation process, where $\xi = 0$ leads to a strictly increasing σ_{xx} . Finally, ϵ adjusts the overall magnitude of the stress response, indicating its scaling effect on the stress response.

2.3.2.3 Normal Stress Differences

Now, we turn our focus to the normal stress difference predictions of the gPTT model. We have previously shown in (2.42) that N_1 and N_2 are related to each other by a factor including the slip parameter, ξ . The relation does not necessarily enforce the signs of N_1 and N_2 and opens a door for the existence of $N_2 > 0$ in the case of $N_1 < 0$. We further note that $N_2 \neq 0$ only occurs in the presence of a slip (i.e., $\xi \neq 0$). While being against the commonly adapted no-slip condition in the continuum regime, the slip between the molecular network and the continuous medium is necessary for N_2 to develop in the context of the gPTT model.

However, we observe that (2.50) always yields $N_1 \geq 0$ for any parameterization (of α , β , ϵ , ξ) although it is not apparent at first glance due to its nonlinear formulation. One idea can be further modifying the slip parameter to account for the deviation between the strain rate applied to the system and the effective strain rate of the polymeric fluid, where the polymeric fluid can no longer follow the continuous medium precisely and moves with a lower speed. This decrease can be related to the slip length [45]. To consider this behavior in the gPTT model, we can define the slip parameter (ξ) as a function of Wi , in particular, $\dot{\gamma}$. Knowing that $0 \leq \xi \leq 1$, we search for an appropriate function bounded between 0 and 1, such as the logistic function having the specialized form:

$$\xi(Wi) = A_{\max} + \frac{A_{\min} - A_{\max}}{1 + \exp(-B \cdot \log_{10}(Wi - Wi_{\text{crit}}))} \quad (2.52)$$

where $A_{\max}$ and $A_{\min}$ denote the left and right asymptotes, B is the growth rate of the logistic function resulting in a sharper decay with the increase, and Wi_{crit} is the critical Wi at the middle point corresponding to the decay in the logistic function.

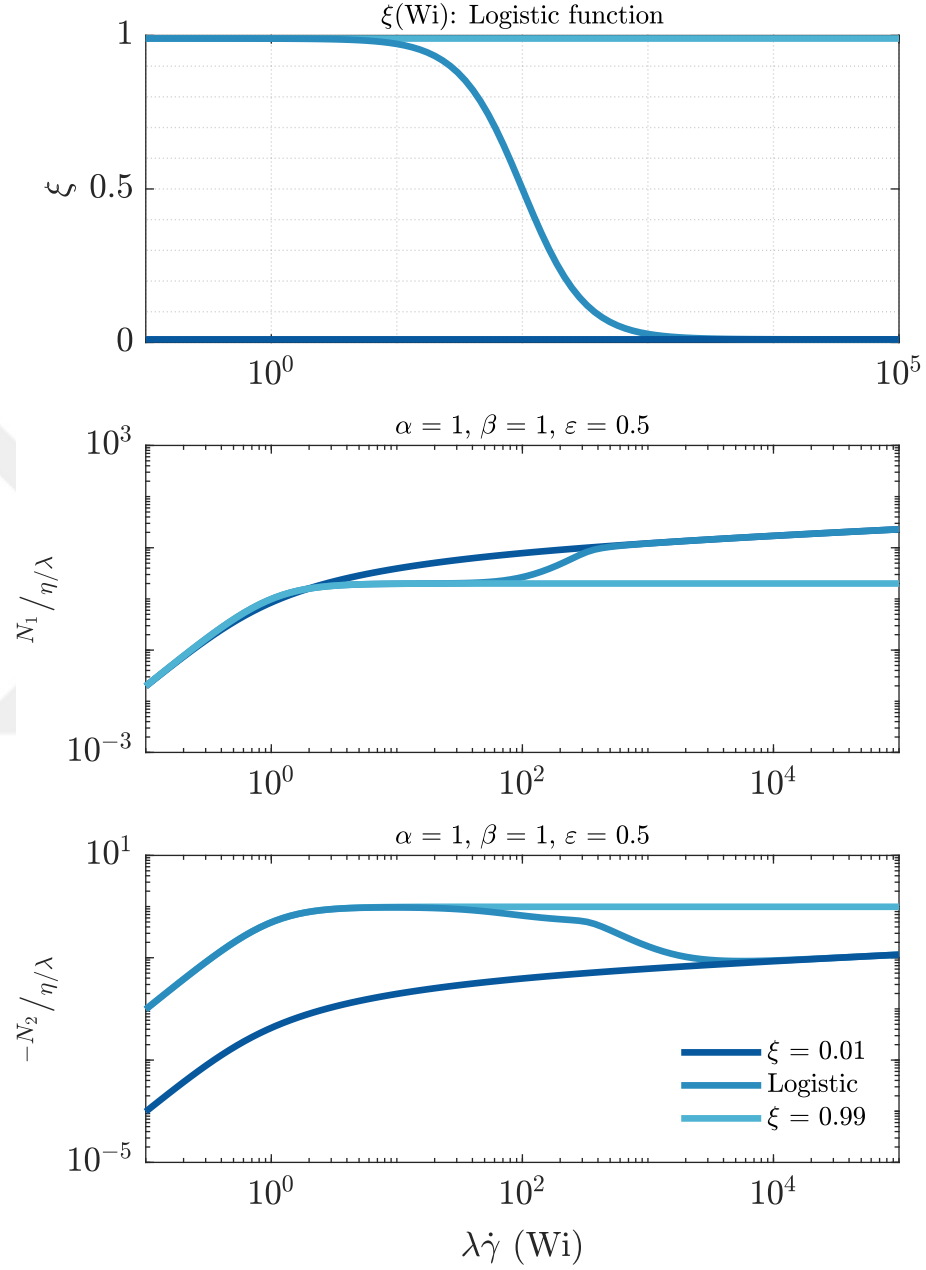


Figure 2.10: Viscosity behavior of polymer melts with varying chain lengths ($N = 10, 20, 40, 80, 160$). Top: Viscosity (η) versus shear rate ($1/\tau$), demonstrating shear-thinning. Middle: Viscosity (η) as a function of film thickness (σ), showing confinement effects. Bottom: Viscosity (η) against surface attraction strength (ε), illustrating the non-monotonic relationship between viscosity and surface interaction.

We observe that the gPTT model introduces a non-decreasing $N_1 \geq 0$, and hence a $N_2 \leq 0$ even if ξ becomes a function of Wi . It is important to emphasize that this constraint on the signs of N_1 and N_2 is a fundamental limitation of the gPTT model. Regardless of the choice of parameters $(\alpha, \beta, \epsilon, \xi)$ or any functional form of $\xi(Wi)$, the model cannot predict negative N_1 or positive N_2 under any circumstances. This limitation stems from the model's underlying assumptions and mathematical structure.

Although the gPTT model aims to incorporate molecular effects and its increased number of fitting parameters enables modeling a wider range of fluids, it has clear shortcomings, such as the impossibility of predicting negative N_1 and positive N_2 . This limitation restricts the applicability of this model in describing certain complex fluids or flow regimes, especially under nanoscale confinement. The constraints of the gPTT model, and continuum models in general (e.g., Oldroyd-B), highlight the necessity of approaches that can capture the full spectrum of rheological behaviors in complex fluids at the molecular level, such as molecular dynamics simulations that can capture emergent behaviors that are beyond the reach of continuum models. The following chapter presents the theoretical basis behind molecular simulations and polymers.

Chapter 3

Theory and Numerics

“Exactly!” said Deep Thought. “So once you do know what the question actually is, you’ll know what the answer means.”

- Douglas Adams, *The Hitchhiker’s Guide to the Galaxy*

Numerical simulations offer a detailed approach to studying the microscopic behavior of polymeric systems, extending our understanding beyond what is achievable solely through continuum mechanics. These simulations (e.g., molecular dynamics, Monte Carlo methods) are established based on the principles of statistical mechanics, where we seek to understand the macroscopic behavior of the system after tracking the movement and trajectory of all particles [46, 47, 48]. To obtain the connection between how each particle is affected individually and how the system behaves overall, we refer to statistical mechanics, as it provides a theoretical framework to describe the behavior of a large number of particles based on statistical laws and probabilities to predict the macroscopic behavior of the system.

In this chapter, we will examine the theoretical foundations and practical applications of numerical simulations (in particular, molecular dynamics) in fluids consisting of polymer chains. We begin by revisiting key concepts in statistical

mechanics (equilibrium in Sec. 3.1.1 and non-equilibrium in Sec. 3.1.2) and polymer physics (in Sec. 3.1.3), which form the basis for understanding the dynamics of polymeric systems. This will be followed by an in-depth discussion of molecular dynamics theory (in Sec. 3.2), including the fundamental equations and algorithms used to model molecular interactions and predict system behavior. The chapter will also cover the specific methodologies employed in our simulations (in Sec. 3.3), detailing the procedure that we follow for our simulations, together with validation techniques used to ensure the accuracy and reliability of our results. Through these simulations, we aim to explore how we can surpass the limitations of continuum models that will highlight the necessity of molecular-level analysis in capturing the complex dynamics of polymeric fluids and show the stages that will be followed throughout our analyses, which are given in Chapter 4.

3.1 Revisiting Statistical Mechanics and Polymer Physics

Polymeric systems are characterized by their complex behaviors, which are often not fully predictable by continuum models (as we demonstrated in before in Sec. 2.3 for normal stress difference predictions). In the context of molecular simulations, the polymer chains are modeled in a discrete way, and unlike continuum models, this modeling can yield better predictions of macroscopic observables (e.g., viscosity, stress response) if the theoretical model captures the polymer characteristics properly. Moreover, molecular-level modeling can help to look into the microscopic foundations of such macroscopic response since we now have the ability to see the dynamics of individual molecules, thanks to the molecular-level resolution of these simulations.

3.1.1 Equilibrium Statistical Mechanics

In the context of polymeric fluids, equilibrium statistical mechanics provides the theoretical framework to describe how polymer chains interact, equilibrate, and exhibit collective phenomena such as phase transitions and structural transformations under *thermal equilibrium*. This approach allows us to transition from the dynamics of individual chains to an overall understanding of the system behavior based on fundamental principles, including time and ensemble averaging and correlation functions. By applying these principles, we can predict and explain various phenomena in polymeric systems, such as the elasticity of rubber or the phase transition behavior of polymeric systems. In this study, we focus on the applications of statistical mechanics to unentangled polymer¹ melts.

For any system to be studied, we can start with one of the fundamental concepts in statistical mechanics, the partition function, which encapsulates all possible microstates² of the system. For a system with discrete energy levels, the partition function Z is given by [46, 47]:

$$Z = \sum_i e^{-E_i/k_B T}, \quad (3.1)$$

where E_i is the energy of the corresponding microstate i , k_B is Boltzmann's constant, and T is temperature. The partition function can be considered an ultimate function containing all the thermodynamic information about the system. The probability of finding the system in a particular microstate then becomes:

$$P_i = \frac{1}{Z} e^{-E_i/k_B T}, \quad (3.2)$$

where we use the partition function Z as a normalization factor in the denominator. These probabilities form the basis for calculating ensemble averages of various thermodynamic quantities, connecting microscopic properties to macroscopic observables. For instance, these probabilities can be used to calculate the average energy, entropy, or specific heat of a (e.g., polymeric) system [46].

¹Since we will deal with short chains to minimize the entanglement effects, we may prefer to call the constituting molecules *oligomers* instead of *polymers*.

²A microstate represents a specific configuration of all particles in the system.

Another important concept in statistical mechanics is the principle of equal *a priori* probabilities (i.e., the *first* fundamental postulate of statistical mechanics), which states that for an isolated system in equilibrium, all accessible microstates are equally probable. This principle is not obvious and cannot be derived from more fundamental principles, but it forms the foundation of statistical mechanics [49]. This postulate is universally applicable to all thermodynamics ensembles.

For this reason, before we consider the implications of *a priori* probabilities, we shall first define the thermodynamic ensembles:

- Microcanonical ensemble (NVE): The system is isolated with fixed energy, volume, and number of particles.
- Canonical ensemble (NVT): The system is in thermal equilibrium with a heat bath at constant temperature.
- Grand canonical ensemble (μ VT): The system is allowed to exchange both energy and particles with a reservoir.
- Isothermal-isobaric ensemble (NPT): The system is at constant temperature and pressure, allowing volume fluctuations.

The choice of ensemble depends on the specific problem and the constraints of the system under study. For instance, when we are to study the behavior of a polymer melt under constant pressure (and temperature), we use the NPT ensemble; or under constant density (and temperature), we use the NVT ensemble. In our MD simulations, we refer to a variety of ensembles during different stages of simulations (e.g., creation of unentangled melt of many chains starting from a single chain data, equilibrium of melt, confining, and shearing).

To understand how the principle of *a priori* probabilities applies across different ensembles, we may consider the following implications [47]:

- In the microcanonical ensemble (NVE), where the system has fixed energy,

volume, and number of particles, the principle directly implies that all microstates with the given energy are equally probable. This scenario might apply to an isolated polymeric system, such as a single polymer chain placed in a vacuum environment and has a fixed energy, or a melt of many chains together with a thermostat regulating the temperature while keeping the energy constant under equilibrium conditions (e.g., diffusion). This leads to the microcanonical probability distribution:

$$p_i = \frac{1}{\Omega(E)}, \quad (3.3)$$

where $\Omega(E)$ is the number of microstate with energy E . We note every microstate is equally probably in this ensemble.

- In the canonical ensemble (NVT), where the system is in thermal equilibrium with a heat bath, the principle is applied to the combined system of the system of interest plus the heat bath. This scenario is more common in real-world polymeric systems, where the polymer is in contact with its environment. This leads to the derivation of the Boltzmann distribution:

$$p_i = \frac{1}{Z} e^{-E_i/k_B T}, \quad (3.4)$$

where Z is the partition function. Here, we note that observing a low-energy (energetically-favored) state is more probable than a high-energy state. For instance, in a system with short-range pair interactions (with both attractive and repulsive components), particles are more likely to be found at the equilibrium separation rather than in such cases where particles are either too close or too far apart from each other.

- In the grand canonical ensemble (μ VT), where the system can exchange both energy and particles with a reservoir, the principle leads to the grand canonical distribution:

$$p_i = \frac{1}{\Xi} e^{-(E_i - \mu N_i)/k_B T}, \quad (3.5)$$

where Ξ is the grand partition function and μ is the chemical potential. This ensemble is particularly useful for studying open systems with variable numbers of particles, such as polymer solutions where chains can enter or leave the system.

- In the isothermal-isobaric ensemble (NPT), the system is maintained at constant temperature and pressure while allowing volume fluctuations. This ensemble is particularly relevant for studying polymer melts and other condensed phase systems under realistic conditions. The probability distribution for this ensemble is given by:

$$p_i = \frac{1}{\Delta} e^{-(E_i + PV_i)/k_B T}, \quad (3.6)$$

where Δ is the isothermal-isobaric partition function, P is the pressure, and V_i is the volume of the system in microstate i . This ensemble is especially useful for simulating systems where volume changes are important, such as phase transitions or systems under external pressure. The NPT ensemble is often preferred in polymer simulations because it allows for natural density fluctuations and can capture phenomena like thermal expansion. For instance, when studying the behavior of a polymer melt under typical processing conditions, where both temperature and pressure are controlled, the NPT ensemble may provide a more realistic representation [46, 47].

Another concept in statistical mechanics is the *equipartition theorem*, which relates temperature to the kinetic energy of the system [46, 47]. For a classical system (with d dimensions) in equilibrium, this theorem states:

$$E_{\text{kinetic}} \equiv \frac{dN}{2} k_B T = \frac{1}{2} \sum_{i=1}^N m_i \mathbf{c}_i \cdot \mathbf{c}_i, \quad (3.7)$$

where N represents the total number of atoms in the system, c_i is fluctuation velocity of particles, which is the difference the actual velocity of the particle and the average (streaming) velocity of the system, k_B is the Boltzmann constant, which is a fundamental physical constant that relates temperature to energy, T is the kinetic temperature of the system, and E_{kinetic} is the total fluctuation kinetic energy.

Assuming all particles have the same mass, the average speed of particles can be derived from this relation as $\langle |\mathbf{c}| \rangle = \sqrt{dk_B T/m}$. In practice, the speed of particles is not constant but varies and shows a distribution. For three-dimensional systems, if equipartition holds, the distribution then follows the Maxwell-Boltzmann

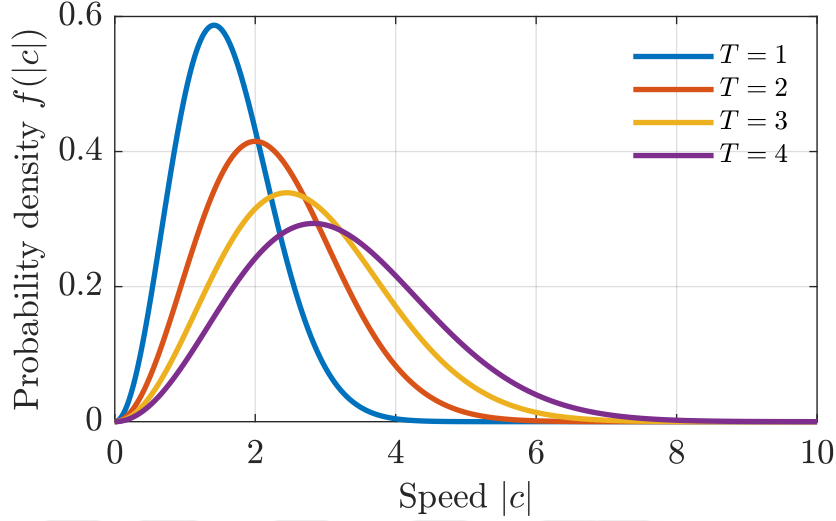


Figure 3.1: Maxwell-Boltzmann probability density distributions for different temperatures T . The curves show how the probability of finding a particle with speed $|c|$ changes as temperature increases from $T = 1$ to $T = 4$, demonstrating the widening of the distribution and shift of the peak towards higher speeds at higher temperatures.

relation:

$$f(|\mathbf{c}|) = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_B T} \right)^{3/2} |\mathbf{c}|^2 \exp \left(-\frac{m|\mathbf{c}|^2}{2k_B T} \right). \quad (3.8)$$

This distribution describes the probability of finding a particle with a particular speed in the system at equilibrium, as shown in Fig. 3.1.

Near equilibrium, the equipartition theorem is (approximately) satisfied, allowing us to use of kinetic temperature. However, we note that for non-equilibrium systems or with significant quantum effects, the thermodynamic definition of temperature, $(\delta S / \delta E)_V = 1/T$, may be more appropriate since this definition is more general and applies to all systems³. For polymer simulations, while the equipartition theorem generally applies to translational degrees of freedom, care must be taken when considering internal degrees of freedom, especially at low

³In equilibrium systems where classical mechanics apply, these two definitions of temperature converge. However, in non-equilibrium cases or systems where quantum effects are non-negligible, the definitions differ, and the thermodynamic temperature becomes the proper definition. In computer simulations, the kinetic temperature is often used due to its computational simplicity.

temperatures where quantum effects may become significant⁴ [46, 47].

A fundamental postulate in statistical mechanics is the principle of equal *a priori* probabilities, which states that for an isolated system in equilibrium, all accessible microstates are equally probable. To prove this principle, we can use the method of Lagrange multipliers to maximize the entropy subject to the constraint of constant energy [51]. The entropy S is given by Boltzmann's formula:

$$S = k_B \ln \Omega, \quad (3.9)$$

where Ω is the number of microstates. We want to maximize S subject to the constraints:

$$\sum_i p_i = 1 \quad \text{and} \quad \sum_i p_i E_i = E, \quad (3.10)$$

where p_i is the probability of microstate i . Using Lagrange multipliers α and β , we form the function f :

$$f = -k_B \sum_i p_i \ln p_i - \alpha (\sum_i p_i - 1) - \beta (\sum_i p_i E_i - E). \quad (3.11)$$

Differentiating f with respect to p_i and setting to zero yields:

$$\frac{\partial f}{\partial p_i} = -k_B (\ln p_i + 1) - \alpha - \beta E_i = 0. \quad (3.12)$$

Now we solve for p_i :

$$p_i = e^{-(\alpha/k_B + 1)} e^{-\beta E_i/k_B}. \quad (3.13)$$

For an isolated system with fixed energy, all microstates have the same energy E , so $e^{-\beta E_i/k_B}$ is a constant. The normalization condition $\sum_i p_i = 1$ then implies that all p_i are equal:

$$p_i = \frac{1}{\Omega} \quad (3.14)$$

⁴We can compare quantum fluctuations to thermal fluctuations using Planck's formula for quantum energy and aforementioned formula for thermal energy, $\hbar\nu_Q = \hbar/\tau_Q \sim k_B T$. Here, $\hbar$ is Planck's constant, ν_Q and τ_Q are quantum fluctuation frequency and timescale, k_B is Boltzmann's constant, and T is temperature. Noting the typical molecular vibration spectrum for alkanes, that is $\nu = 800\text{-}1300 \text{ cm}^{-1} \sim 10^{13} \text{ Hz}$ for C-C stretching [50], the temperature that will result in comparable quantum effects would be around 100 K. Therefore, at room temperature ($T = 300 \text{ K}$) we expect to have clear dominance of thermal fluctuations and justify our classical mechanistic approach.

This derivation confirms the fundamental postulate of equal a priori probabilities for isolated systems, showing that all accessible microstates are indeed equally probable.

We can continue with another important concept in statistical mechanics, that is the *ergodic hypothesis* (i.e., the *second* fundamental postulate of statistical mechanics), which tells us that the time average of a system's property is equal to its ensemble average [49]:

$$\langle A \rangle_{\text{time}} = \langle A \rangle_{\text{ensemble}}. \quad (3.15)$$

This hypothesis plays a key role for us to connect time-averaged experimental measurements with ensemble-averaged theoretical predictions and, therefore, make sense of molecular dynamics simulations as the macroscopically long (order of seconds) simulations are unreachable (and unrealistic⁵) in MD. In the context of polymer physics, this means that observing a single polymer chain for a long time is equivalent to observing many polymer chains at once, provided the system is *ergodic* [48, 51].

Another concept that we may note is the *fluctuation-dissipation theorem*, which relates the linear response of a system to an external perturbation to its equilibrium fluctuations [52]:

$$\chi''(\omega) = \frac{\omega}{2k_B T} \int_{-\infty}^{\infty} \langle A(0)A(t) \rangle e^{-i\omega t} dt, \quad (3.16)$$

where $\chi''(\omega)$ is the imaginary part of the susceptibility⁶, representing the response of a system to an external force at frequency ω , and $\langle A(0)A(t) \rangle$ is the autocorrelation function, describing the system's natural fluctuations over time. The right side of the equation involves the Fourier transform of this autocorrelation

⁵We define chaotic systems by their sensitivity to initial conditions. Small discrepancies arising from computational limitations or approximations lead to exponential divergence of trajectories. This results in complete decorrelation between a *true* trajectory of the system and our simulated one, even with minor variations in parameters like time steps.

⁶The susceptibility $\chi(\omega)$ is a complex quantity that describes the response of a system to an external perturbation. It can be expressed as $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$, where $\chi'(\omega)$ is the real part representing the in-phase response, and $\chi''(\omega)$ is the imaginary part representing the out-of-phase response. The imaginary part $\chi''(\omega)$ is specifically related to energy dissipation in the system, which is why it appears in the fluctuation-dissipation theorem.

function. In the context of polymer physics, this theorem connects the mechanical response of polymers to their thermal fluctuations (e.g., it allows us to relate the random Brownian motion of polymer chains to macroscopic properties such as viscosity). This connection between microscopic fluctuations and macroscopic behavior provides a way to understand and model complex polymeric systems, especially when we are interested in their response to external forces (or deformations).

The concepts of *correlation length* and *correlation time* are essential for understanding the spatial and temporal scales of fluctuations in polymeric systems. The correlation length, ξ , measures the distance, and the correlation time, τ , measures the time over which fluctuations in a physical property are correlated. For a simple isotropic system, the spatial correlation function $G(r)$ or the temporal correlation function $C(t)$ often decays exponentially [46, 47, 48]:

$$G(r) = G_0 \exp(-r/\xi) \quad \text{or} \quad C(t) = C_0 \exp(-t/\tau), \quad (3.17)$$

where G_0 is the correlation at $r = 0$ and r is the distance, and C_0 is the correlation at $t = 0$ and t is the time, as depicted in Fig. 3.2.

Near a critical point, the correlation length typically diverges following a power law [53]:

$$\xi \propto |T - T_c|^{-\nu}, \quad (3.18)$$

where T_c is the critical temperature, and ν is a critical exponent⁷. Similarly, the correlation time, τ , characterizes the time scale over which fluctuations persist. The temporal correlation function $C(t)$ for a given property $A(t)$ can be expressed as [46, 47, 48]:

$$C(t) = \langle A(0)A(t) \rangle - \langle A \rangle^2. \quad (3.19)$$

Diffusion processes in polymeric systems are often characterized by the mean square displacement (MSD):

$$\langle r^2(t) \rangle = 6Dt, \quad (3.20)$$

⁷Under isothermal conditions, our study will only consider molecular size as a rescaling factor to describe the severity of nanoconfinement.

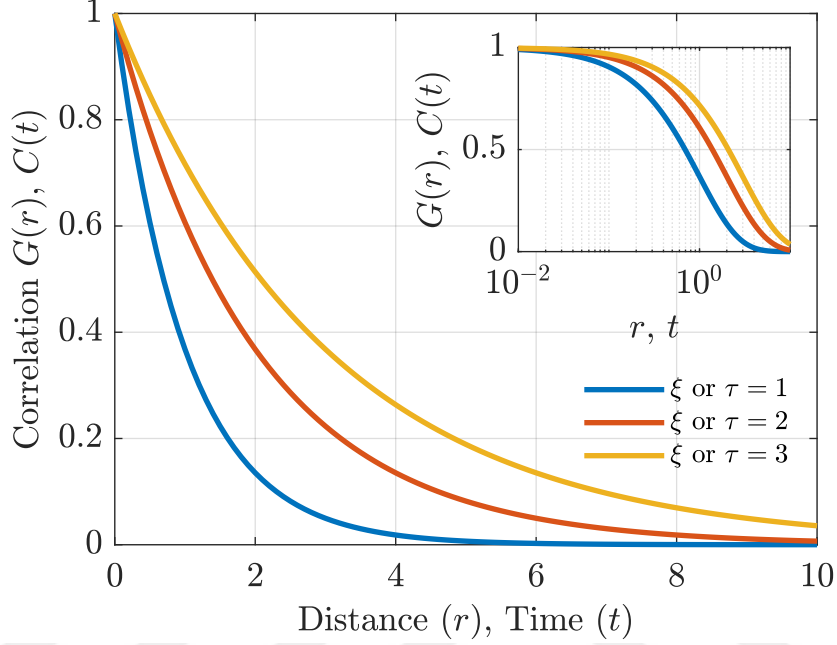


Figure 3.2: Correlation functions $G(r)$ and $G(t)$ plotted against distance (r) and time (t) for different values of correlation length ξ or correlation time τ . The main plot shows the decay of correlation over larger scales, while the inset provides a logarithmic view of the same data, highlighting the behavior at smaller scales. As ξ or τ increases from 1 to 3, the correlation persists over greater distances and longer times, respectively.

where r is the displacement vector (usually of the midpoint atom or the center of mass of the molecule), t is time, and D is the diffusion coefficient. This relation holds for normal diffusion, but polymeric systems can exhibit anomalous diffusion, where the MSD follows a power law:

$$\langle r^2(t) \rangle \propto t^\alpha, \quad (3.21)$$

with $\alpha \neq 1$. The sub-diffusive ($\alpha < 1$), diffusive ($\alpha = 1$) and super-diffusive ($\alpha > 1$) behavior of MSD is depicted in Fig. 3.3.

Relaxation times in polymeric systems can vary widely depending on the property and scale considered (e.g., unentangled or entangled, segment of a chain or whole chain). The Rouse relaxation time, τ_R , for a polymer chain characterizes the longest mode of motion in the Rouse model for polymer dynamics [54]. We will elaborate on the Rouse dynamics, the relaxation time, and why it will be

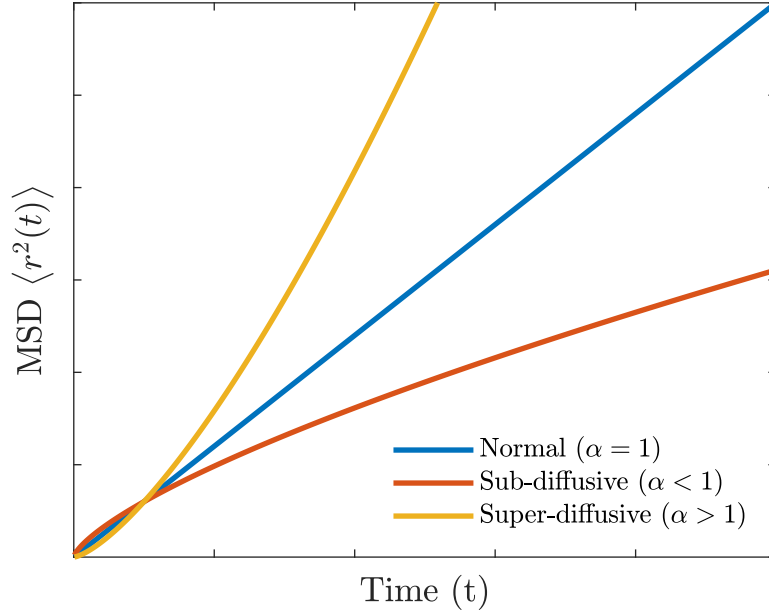


Figure 3.3: Mean square displacement (MSD) as a function of time for different diffusion regimes. The plot compares normal diffusion ($\alpha = 1$), sub-diffusive ($\alpha < 1$), and super-diffusive ($\alpha > 1$) processes. The slope of each line represents the rate of particle displacement (i.e., the diffusion coefficient), with steeper slopes indicating faster diffusion. Normal diffusion shows a linear relationship, while sub-diffusive and super-diffusive processes exhibit slower and faster rates of displacement, respectively. A polymer chain can exhibit multiple diffusion regimes over different timescales, typically transitioning from sub-diffusive behavior at short times due to local constraints (e.g., relaxation of each polymer segment), to normal diffusion at intermediate times, and potentially super-diffusive motion at longer timescales depending on the environment (e.g., entanglement effects).

important in our study in Section 3.1.3.

These equilibrium concepts, while important, are not enough to fully capture the behavior of polymers in many practical scenarios. In realistic cases, polymeric fluids often operate far from equilibrium, necessitating us to extend the current equilibrium statistical mechanical approaches [55]. In the following section, we aim to explore non-equilibrium statistical mechanics together with its application to polymeric fluids under external forces.

3.1.2 Non-equilibrium Statistical Mechanics

While equilibrium statistical mechanics provides a powerful framework for understanding many aspects of polymeric systems, many phenomena in polymer physics occur far from equilibrium. Non-equilibrium statistical mechanics extends our understanding to systems subjected to external forces, flows, or rapid changes in thermodynamic variables. Therefore, it becomes particularly important for polymeric systems, where materials are often subjected to complex flows and deformations.

In this study, we mainly focus on systems that are subjected to a shear rate, either by modifying the equations accordingly or by adding confining walls that are moving with constant velocity. The presence of shear can dramatically alter the conformation and dynamics of polymer chains, leading to phenomena such as shear-thinning or shear-thickening in polymer solutions and melts. The effect of shear on polymer conformation can be characterized by the Weissenberg number [33],

$$Wi = \dot{\gamma}\lambda, \quad (3.22)$$

where λ is a characteristic relaxation time⁸ of the polymer. When $Wi > 1$, the polymer chains start to become significantly deformed due to the flow. In other words, Wi gives us the balance between elastic and viscous effects as the elastic effects become more dominant with increasing Wi .

⁸We will have $\lambda = \tau_R$ as long as the Rouse model is applicable.

To describe the dynamics of polymers under non-equilibrium conditions, we often use stochastic methods, such as the Langevin equation [55]:

$$m \frac{d^2 \mathbf{r}}{dt^2} = -\zeta \frac{d\mathbf{r}}{dt} - \nabla U(\mathbf{r}) + \mathbf{F}(t), \quad (3.23)$$

where m is the mass, ζ is the friction coefficient, $U(\mathbf{r})$ is the potential energy, and $\mathbf{F}(t)$ is a random force representing thermal fluctuations. This equation balances inertial forces, frictional forces, potential forces, and random thermal forces acting on a polymer segment. The magnitude of $\mathbf{F}(t)$ is proportional to $\sqrt{k_B T / \zeta}$, as a consequence of the equipartition theorem.

The corresponding Fokker-Planck equation describes the time evolution of the probability distribution function $P(\mathbf{r}, t)$ [55]:

$$\frac{\partial P}{\partial t} = -\nabla \cdot \mathbf{J}, \quad (3.24)$$

where $\mathbf{J}$ is the probability current:

$$\mathbf{J} = -\frac{1}{\zeta} (k_B T \nabla P + P \nabla U). \quad (3.25)$$

The Fokker-Planck equation can be used as a tool for analyzing the statistical properties of polymeric systems out of equilibrium, and For polymers in flow fields, it can be modified to include the effects of the flow:

$$\frac{\partial P}{\partial t} + \nabla \cdot (\mathbf{v} P) = -\nabla \cdot \mathbf{J}. \quad (3.26)$$

This equation is commonly used in the theories of polymeric flow, including the Doi-Edwards theory for entangled polymers [54, 55]. Recent developments in nonequilibrium statistical mechanics have led to important results like the Jarzynski equality [56]:

$$\langle e^{-\beta W} \rangle = e^{-\beta \Delta F}, \quad (3.27)$$

where W is the work done on the system, ΔF is the free energy difference between the initial and final states, and $\beta = 1/(k_B T)$. This equality relates non-equilibrium work to equilibrium free energy differences, providing a way for studying thermodynamic systems driven out of equilibrium, such as during the stretching of a single polymer chain, which we discuss at the end of the following section.

3.1.3 Polymer Physics

Polymer physics focuses on the unique behaviors arising from the chain-like structure of polymers. This field combines concepts from statistical mechanics, soft matter physics, and materials science to describe the complex behavior of these macromolecules. Several models have been developed to describe polymer dynamics in different environments. The choice of model depends on factors such as polymer concentration, molecular weight, and the presence of entanglements.

The Rouse model describes the dynamics of *unentangled* polymer melts or concentrated solutions, and therefore it is proper for our studies. It represents a polymer as a series of beads connected by springs, neglecting hydrodynamic interactions and excluded volume effects [54, 57]. The equation of motion for the n^{th} bead is:

$$\zeta \frac{d\mathbf{r}_n}{dt} = k(\mathbf{r}_{n+1} + \mathbf{r}_{n-1} - 2\mathbf{r}_n) + \mathbf{f}_n(t), \quad (3.28)$$

where $\mathbf{r}_n$ is the position vector of the n^{th} bead, ζ is the friction coefficient, k is the spring constant, and $\mathbf{f}_n(t)$ is a random force representing thermal fluctuations. This equation balances the frictional force, the spring forces from (only) the neighboring beads, and the random thermal force.

Based on the Rouse model, there exists a characteristic timescale associated with the chains, so-called the Rouse relaxation time (τ_R), characterizing the longest relaxation mode, which is given by [54, 58]:

$$\tau_R = \frac{\zeta N^2 b^2}{3\pi^2 k_B T}, \quad (3.29)$$

where ζ is the friction coefficient, N is the number of monomers, and b is the Kuhn length⁹. This relaxation time will play an important role in our understanding of the viscoelastic properties of polymer melts, as it will be used in the dimensionless number Wi in the shear simulations.

⁹The characteristic polymer segment length is often called Kuhn length, which increases when the chain becomes more rigid. In a simulation, we can be calculated from time and ensemble-averaged end-to-end distance, $\langle r_{ee}^2 \rangle = Nb^2$, as long as the chains behave ideally (e.g., in melt state).

For polymers in dilute solutions, where hydrodynamic interactions become important, the Zimm model becomes more appropriate, as the equation of motion in the Zimm model includes a hydrodynamic interaction tensor $\mathbf{H}_{nm}$ [54]:

$$\frac{d\mathbf{r}_n}{dt} = \sum_m \mathbf{H}_{nm} \cdot \mathbf{F}_m + \mathbf{v}_n, \quad (3.30)$$

where $\mathbf{F}_m$ is the force on bead m and $\mathbf{v}_n$ is the velocity of the solvent at the position of bead n . The Zimm model predicts different scaling laws¹⁰ for polymer properties compared to the Rouse model, which we do not go into detail since the focus of this study is on unentangled melts where the Rouse model is applicable.

In polymer melts, the concept of the ideal chain becomes relevant. Unlike in dilute solutions, excluded volume interactions are screened in melts, leading to Gaussian statistics for chain conformations, although deviations are observed when the entanglement effects are dominant [60]. This screening occurs because the polymer is surrounded by other polymer chains, effectively neutralizing the excluded volume effect. So, the mean square end-to-end distance in a melt is given by:

$$\langle r_{ee}^2 \rangle = Nb^2, \quad (3.31)$$

where N is the number of Kuhn segments and b is the Kuhn length. This relationship is characteristic of a *random walk* and forms the basis for most of the theories that model polymer melts. The distribution function for the end-to-end vector $\mathbf{r}$ in an ideal chain is given by the Gaussian distribution:

$$P(\mathbf{r}) = \left(\frac{3}{2\pi Nb^2} \right)^{3/2} \exp \left(-\frac{3r^2}{2Nb^2} \right). \quad (3.32)$$

For long chains in melts, which is not the focus of this study, entanglement effects become important. The tube model, proposed by de Gennes, describes the motion of an entangled chain as being confined to a tube-like region formed by surrounding chains [54]. This confinement significantly alters the dynamics of the polymer. The characteristic time for a chain to escape its original tube, known as the reptation time, is given by:

$$\tau_d \approx \frac{N^3 b^4}{N_e k_B T}, \quad (3.33)$$

¹⁰For a detailed discussion in scaling laws, the reader may refer to [59].

where N_e is the number of monomers between entanglements. This reptation time is much longer than the Rouse time for long chains, explaining the high viscosity of melts of long chains. The tube model leads to unique predictions for the stress relaxation modulus $G(t)$ in entangled polymer melts:

$$G(t) \approx G_N^0 \begin{cases} (t/\tau_e)^{-1/2} & \text{for } \tau_e < t < \tau_R \\ (t/\tau_d)^{-1/2} & \text{for } \tau_R < t < \tau_d \end{cases} \quad (3.34)$$

where G_N^0 is the plateau modulus, τ_e is the entanglement time, and τ_R is the Rouse time. This prediction of a power-law stress relaxation is an important achievement of the tube model as it has been experimentally confirmed [54].

Turning our focus back to melts, we can derive the *entropic elasticity* of an ideal chain, as the configuration of a polymer chain in a melt is a random walk that maximizes configurational entropy [54, 57]. For a single polymer chain, we can express the entropy S in terms of the end-to-end distance r and the number of segments N , using the probability distribution function we introduced earlier, the Gaussian distribution (3.32):

$$S(r, N) = -\frac{3}{2}k_B \frac{r^2}{Nb^2} + S(0, N) \quad (3.35)$$

where $S(0, N)$ is a constant and independent of r , highlighting the dependence of entropy on the extension of a chain. The Helmholtz free energy F of the chain can then be defined as:

$$F(r, N) = U(r, N) - TS(r, N) \quad (3.36)$$

As we have an ideal polymer chain, the monomers have no interaction energy, leading to $U(r, N)$ being independent of r . This leads to a simplification for the expression of the Helmholtz free energy:

$$F(r, N) = \frac{3}{2}k_B T \frac{r^2}{Nb^2} + F(0, N) \quad (3.37)$$

where $F(0, N)$ is the free energy of the chain with both ends located in the same place, yielding r to be a parameter that can capture the extension of a chain purely. The force required to extend the chain is given by the derivative of the Helmholtz free energy with respect to the end-to-end vector, $\mathbf{r}$:

$$\mathbf{f} = \frac{\partial F(r, N)}{\partial \mathbf{r}} = \frac{3k_B T}{Nb^2} \mathbf{r} \quad (3.38)$$

This linear force-extension relationship, analogous to Hooke’s law, demonstrates the entropic nature of polymer elasticity, where the spring constant can be expressed as $k = 3k_B T / (Nb^2)$.

Although there are many models that exist and predict the dynamics of specific polymeric systems, the aforementioned models and concepts can form the basis that we need to understand the complex behaviors of many polymeric systems in various environments (from dilute solutions to melts) and under both equilibrium and non-equilibrium conditions. These models are successful in predicting and explaining phenomena such as the elasticity of rubbers, the high viscosity of polymer melts, and the unique phase behavior of block copolymers; however, they are not yet adequate to fully explain more complex systems, such as associating polymers, polyelectrolytes, and active polymer networks [54, 57].

3.2 Molecular Dynamics Theory

Molecular dynamics (MD) simulations are a set of powerful computational methods used to study the behavior of molecular systems, including polymers, by simulating their motion over time. The foundation of MD lies in classical mechanics, where atoms and molecules are treated as classical particles, obeying Newton’s laws of motion [47, 46, 48].

At the core of MD simulations are the interatomic potentials (also known as force fields), which describe the interactions between particles. One of the most commonly used potentials is the (12-6)¹¹ Lennard-Jones (LJ) potential [46]:

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (3.39)$$

where ϵ is the depth of the potential well, σ is the distance at which the potential is zero, and r is the distance between particles. The r^{-12} term describes the

¹¹These numbers represent the powers that are used in the Lennard-Jones model, where there exist other Lennard-Jones potentials with different power laws that are suitable for different systems.

strong repulsion at short distances due to overlapping electron orbitals, while the r^{-6} term represents the attractive van der Waals forces. The force acting on a particle is derived from the potential by taking its negative gradient:

$$\mathbf{F} = -\nabla V. \quad (3.40)$$

For the LJ potential, this leads to:

$$\mathbf{F}_{LJ}(r) = 24\epsilon \left[2 \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \frac{\mathbf{r}}{r^2}. \quad (3.41)$$

In addition to the LJ potential, MD simulations of polymers often include bonded interactions such as bond stretching, angle bending, and torsional terms [46]. For example, a simple harmonic bond potential¹² might be used:

$$V_{bond}(r) = \frac{1}{2}k(r - r_0)^2, \quad (3.42)$$

where k is the spring constant and r_0 is the equilibrium bond length. To integrate the equations of motion and update particle positions and velocities, the velocity Verlet algorithm is commonly used due to its simplicity and preferable energy conservation properties. The algorithm consists of the following steps [46]:

1. Update positions:

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2$$

2. Calculate forces and accelerations at the new positions:

$$\mathbf{a}(t + \Delta t) = \mathbf{F}(t + \Delta t)/m$$

3. Update velocities:

$$\mathbf{v}(t + \Delta t) = \mathbf{v}(t) + \frac{1}{2}[\mathbf{a}(t) + \mathbf{a}(t + \Delta t)]\Delta t$$

Here, $\mathbf{r}$, $\mathbf{v}$, and $\mathbf{a}$ are the position, velocity, and acceleration vectors respectively, m is the particle mass, and Δt is the time step. To improve computational

¹²The DREIDING force-field that we use for atomistic simulations also defines a harmonic bond potential [61]. For coarse-grained cases such as the Kremer-Grest model, FENE bonds are defined instead of a simple harmonic bond potential, but with a similar purpose of defining the interaction between consecutive beads [62, 63].

efficiency, MD simulations often use neighbor lists. Instead of calculating interactions between all pairs of particles at each time step, a list of nearby particles is maintained and updated periodically. This technique significantly reduces the computational cost, especially for large systems, at the expense of accuracy [46, 48].

Just like for any physical domain to be studied computationally, the boundary conditions also play an important role in MD simulations. Periodic boundary conditions (PBC) are commonly used to mimic bulk systems by replicating the simulation box in all directions [46]. This approach eliminates surface effects and allows for the simulation of a relatively small number of particles to represent a much larger system, often referred to as the *bulk* state. However, care must be taken to ensure that the box size is large enough to prevent artificial correlations due to periodicity, so-called finite size effects¹³[47]. For simulations of interfaces or confined systems, other boundary conditions may be more appropriate. For instance, reflective walls can be used to simulate confined polymers, or a combination of PBC in some directions and fixed boundaries in others can be employed for slab geometries. As we will explain later in the simulation details, our simulations where we introduce nanoconfinement to the polymeric fluid will consist of slabs that limit the periodicity to two dimensions.

In molecular dynamics simulations, maintaining the desired temperature for NVT or NPT ensembles is achieved through thermostatting algorithms. These methods modify particle velocities to control the system temperature. We may mention some of the common approaches, as follows [47]:

- Berendsen thermostat: This method rescales velocities to achieve the desired temperature. While simple and efficient, it fails to produce the canonical ensemble fully correct.
- Nosé-Hoover thermostat: This approach introduces an additional degree of

¹³To ensure the simulation box is large enough, we perform the simulations with various box sizes, track corresponding variables and see how they change with the box size. In practice, we should consider the box size when the changes are negligible and if the time/ensemble averages are performed properly. This approach is analogous to the grid independence study in finite element simulations

freedom representing a heat bath, producing the correct canonical ensemble (potential issues might arise in ergodicity assumption for small systems).

- Langevin thermostat (or dynamics): This method adds friction and random forces to mimic the effect of solvent collisions, providing both correct temperature control and ergodicity.

Similarly, pressure control can be implemented using barostats, which adjust the simulation box size to maintain a constant pressure. The Berendsen barostat and the Parrinello-Rahman barostat are some of the common methods for controlling the pressure in MD simulations [47].

The scale of MD simulations depends on the level of detail and the computational resources available. Depending on both the requirements and the availability of resources, atomistic or coarse-grained simulations may be used, where we compare the basics of these approaches in the following part.

3.2.1 Coarse-grained vs. Atomistic Modeling

In polymer simulations, two main approaches are used: atomistic and coarse-grained (CG) modeling. Atomistic modeling provides a high level of detail by representing every atom in the system explicitly. This approach is computationally intensive but can accurately capture specific chemical interactions and conformational changes. The time step in atomistic simulations is typically on the order of femtoseconds (10^{-15} seconds) to resolve fast vibrations, for timescales of nanoseconds to microseconds [64].

Coarse-grained modeling, on the other hand, groups multiple atoms into single interaction sites, reducing the number of degrees of freedom and allowing for larger time steps and longer simulation times to be used. In the context of polymeric systems, a common CG model is the bead-spring model, where each bead represents several monomers. The interactions between beads are typically described by simplified potentials that capture the essential physics of the

system, but the simplifications might cause such phenomena that are observable at the molecular-level resolution to be overlooked. In return, CG models can handle much larger systems (in terms of the number of atoms modeled) for longer timescales (microseconds to milliseconds), which can be useful for studying large-scale (i.e., number of particles) or long-scale (i.e., length of the simulation) polymer behavior which are inaccessible or not feasible with atomistic simulations [64].

The choice between atomistic and CG modeling depends on the system size, time scales of interest, and the level of detail required. Often, a multi-scale approach is used, where CG simulations inform larger-scale behavior, and atomistic simulations provide detailed insights into specific interactions. Compared to continuum approaches which enable modeling at significantly larger scales (e.g., CFD simulations of climate/weather modeling or aerospace industry), the number of particles that MD simulations are able to model *currently* is orders of magnitudes smaller than the Avogadro number, $N_A = 6.022 \times 10^{23}$. Further improvements in computational methods and computing hardware can help MD simulations become feasible for systems with larger complexity levels.

3.3 Simulation Methodology and Validation

Molecular dynamics (MD) simulations provide a valuable tool for examining the behavior of complex polymeric systems at the molecular level. All MD simulations were performed using LAMMPS MD package [65]. Our investigation encompasses both atomistic (all-atom) and coarse-grained models, where the core of our study focuses on the rheology of unentangled melts under nanoconfinement.

For atomistic simulations, the melt consists of $C_{25}H_{52}$ molecules, and the confining surfaces are hematite $\alpha - Fe_2O_3$ layers, with the aim of modeling hydrodynamic lubrication, having practical importance [66, 67, 68]. Hence, atomistic systems comprise two distinct molecular architectures: linear pentacosane and

star-shaped 9-octylheptadecane, with the identical molecular formula. This selection enables us to study the impact of molecular topology on rheological properties, together with the chain rigidity. We use mainly the DREIDING force field for atomistic simulations, later supplemented with the OPLS (Optimized Potentials for Liquid Simulations) force field for the verification of selected results [61, 69].

For coarse-grained simulations, the melts similarly consist of short alkane oligomers, but a range of the polymerization degrees is rather considered, noting that each bead is used to model more than one carbon atom. This also helps to see to what extent the atomistic results of short molecules will be applicable if they show the same qualitative trend with coarse-grained results. The surfaces are also modeled in a more straightforward fashion compared to the hematite walls of atomistic simulations. Kremer-Grest model is used for the coarse-graining [63, 70, 71].

Our simulation procedure for both atomistic and coarse-grained models, excluding intermediate simulations for preparation of simulation boxes for relevant cases, can be shown as follows:

1. (DREIDING) Diffusion simulations of unentangled melts at equilibrium, with fully-periodic boundary conditions: to calculate the relaxation time, which is the Rouse time of our unentangled melts and to be used while defining Wi , for each polymer topology and chain stiffness.
2. (DREIDING) Shear simulations of unentangled melts of linear and star-shaped polymers in bulk and under various nanoconfinement levels: to calculate the rheological properties including viscosity and stress response over a range of Wi , which to be compared with existing literature to validate the simulation methodology, and also to be linked with molecular-level observations.
3. (OPLS) Shear simulations of unentangled melts of only linear chains under single nanoconfinement level: to calculate the rheological properties including viscosity and stress response over a range of Wi , which to be compared

with the DREIDING force field.

4. (Kremer-Grest) Shear simulations of unentangled melts of only linear polymers with varying polymerization degree in bulk and under various nanoconfinement levels: to calculate the rheological properties including viscosity and stress response over a range of Wi , which to be compared with atomistic results and also linked with molecular-level observations.

The simulation methodologies outlined above provide a framework for investigating the rheological properties of unentangled oligomer melts under various conditions. The use of both atomistic and coarse-grained models allows us to study phenomena across different lengths and time scales, while the application of multiple force fields becomes useful in result validation.

With the simulation methodology and theoretical background established, we present our findings on the influence of molecular topology, chain stiffness, and nanoconfinement on the rheological properties of unentangled oligomer melts in the following chapter. We compare our findings from atomistic and coarse-grained models with theoretical expectations, validate our results against experimental literature, and analyze the molecular mechanisms underlying the observed macroscopic behaviors.

Chapter 4

Molecular Simulations, Results and Discussion

I have estimated how many letters there are in the Encyclopaedia, and I have assumed that each of my 24 million books is as big as an Encyclopaedia volume, and have calculated, then, how many bits of information there are. For each bit I allow 100 atoms. And it turns out that all of the information that man has carefully accumulated in all the books in the world can be written in this form in a cube of material one two-hundredth of an inch wide – which is the barest piece of dust that can be made out by the human eye. So there is plenty of room at the bottom!

- Richard P. Feynman, *Plenty of Room at the Bottom*

In this chapter, we first consider the atomistic model with the DREIDING force field, where we perform our main analyses regarding viscoelasticity and its microscopic reasoning in Sec. 4.1. Later, in Sec. 4.2, we perform a similar analysis using another atomistic force field, OPLS, which particularly provides a more detailed scheme for long-range interactions and verifies if our core findings

are coherent within different atomistic force fields. Then, in Sec. 4.3, we extend our analysis also to a coarse-grained model, Kremer-Grest, and similarly check the applicability of our atomistic findings into coarse-grained cases. Ultimately, we compare our atomistic and coarse-grained models in Sec. 4.4.

4.1 DREIDING Force Field

We first explain, in Sec. 4.1.1, the configuration for our MD simulations with the DREIDING force field. Afterward, we determine the relaxation time of the oligomer chains in Sec. 4.1.2, the stress response in Sec. 4.1.3, and flow characteristics in Sec. 4.1.4. Here, we calculate the shear-thinning viscosity and the normal stress differences to capture the viscoelastic response. Lastly, in Sec. 4.1.5, we aim to relate the macroscopic observations to the molecular-level quantities, such as the radius of gyration and bond orientation.

4.1.1 Simulation Details

This part includes two types of simulations: (i) diffusion to determine the relaxation times and (ii) shear to determine the viscoelastic response. For both types, the interactions between all atoms are modeled by the standard 12/6 Lennard-Jones potential using the DREIDING-AA (all-atom, i.e., including explicit hydrogens, and dihedral interactions) potential [61, 72], with the cutoff radius of $r_c = 9.85 \text{ \AA}$ and the time-integration is performed for the time step of $\tau = 1 \text{ fs}$. The hematite walls are generated with Ref. [73, 74], and the interaction energy and local-global cutoff values of all pairs of atoms/ions are obtained from Ref. [75]. The force field selection was based on its advantageous simplicity, particularly in altering chain rigidity for constructing toy models, and its computational efficiency, notably in simulations involving large values of h [76, 77]. The visualizations of the simulation boxes (e.g., snapshots) are obtained using OVITO [78].

The simulation box for the most confined case¹ contains $N_{\text{chain}} = 128$ (increasing proportionally with h for the larger domains) charge-neutral linear (pentacosane) or star (branched 3-arm, 9-octylheptadecane) $\text{C}_{25}\text{H}_{52}$ alkanes, being molecules of real practical interest in tribological contacts [66], equilibrated at constant temperature ($T = 372$ K) and constant pressure ($p = 1$ atm) [66]. We control the chain rigidity through an angle potential penalizing chain bending [79, 80] as $U_{\text{angle}}(\theta) = k_{\theta}(\theta - \theta_0)^2$, where θ is the angle between triplets of atoms in a chain, $\theta_0 = 109.47^\circ$ is the equilibrium value of the angle [72, 81], and $k_{\theta} \equiv \epsilon = 50$ kcal/mol is the potential strength [61].

To further reveal the physical mechanisms that we observe in our simulations, we obtain toy models by varying the bending potential strength [80], k_{θ} , and obtain chains with slower or faster relaxation dynamics [62], which in turn can modify the contribution of the elastic forces without altering the chemical details [79].

For the diffusion simulations, each domain contains $N = 216$ charge-neutral linear or star $\text{C}_{25}\text{H}_{52}$ oligomers equilibrated at $T = 372$ K at the *equilibrium* pressure at $p = 1$ atm, being analogous to a system studied by [66]. The resultant (unaltered, $k_{\theta} = \epsilon$) melt density of $\rho = 0.63$ g/cm³ is expected as DREIDING potential is known to underestimate the density of the polymeric liquids while giving accurate viscosity estimations [82]. We later change the chain rigidity (i.e., $k_{\theta} = 0.1\epsilon, 10\epsilon$) to obtain altered models and re-equilibrate the systems while keeping the density constant (i.e., NVT dynamics). Preserving the density does not guarantee that hydrostatic pressures are identical between the systems; the hydrostatic pressures are also prone to variations in the confinement level, chain topology, and rigidity. However, since we are mainly interested in acquiring identical geometric confinements and densities for all of our melt systems, we disregard the variations in hydrostatic pressure between the systems [83], but instead track the change in the flow-dependent (i.e., dynamic) components of the stress tensor. This helps us to construct N_1 , N_2 , $\boldsymbol{\sigma}^{(\text{VE})}$ independently of the

¹The most confined case has the film thickness of $h = 2.79$ nm, which is < 5 times the characteristic size of the molecules. The less confined case has a film thickness of $h = 22.28$ nm, which is > 30 times the characteristic size of the molecules.

hydrostatic pressure to study the rheological response.

To determine the relaxation times, we track the mean-square end-to-end vectors for $t = 10^8\tau$ under NVE dynamics regulated at $T = 372$ K using the Langevin thermostat² with a damping coefficient of 100τ [68, 82, 85, 86]. We later fit the correlation function following $\langle \mathbf{r}_{ee}(t) \cdot \mathbf{r}_{ee}(0) \rangle / \langle \mathbf{r}_{ee}(0) \cdot \mathbf{r}_{ee}(0) \rangle = A \exp(-t/\lambda)$, with constant A (≈ 1 for each fit).

For the shear simulations, the domains contain varying N oligomer chains, depending on the box size or confinement level, while keeping the density N/V constant for the volume V . For the bulk system, we start with our pre-equilibrated systems (that we used for diffusion simulations) and we run shear simulations by deforming the cubic simulation box ($h = 5.82$ nm, resulting in $p = 1$ atm for unaltered star chains). To have the analogous shear rate representation between bulk and confined shear simulations, we used *engineering strain rate* in our bulk simulations during the deformation of the simulation box. The deformation occurs under constant volume and temperature by solving SLLOD equations of motion coupled with Lees-Edwards periodic boundary conditions at $T = 372$ K with a damping coefficient of 100τ . For the confined melts, we introduce hematite walls (initially away from the melt to avoid artificial, metastable configurations) to our monodisperse (unaltered) oligomer melts whose motion is governed by NVE dynamics regulated at $T = 372$ K using the Langevin thermostat. To obtain $p \sim \mathcal{O}(1 \text{ atm})$, we systematically and slowly decrease (or increase, if the pressure exceeds the limits) the film thickness by moving the walls and tracking the time-averaged pressure exerted on the (top and bottom) hematite surfaces, in accordance with Ref. [86]. As we obtain the film thickness corresponding to our prescribed pressure levels, we alter the chain rigidity values and equilibrate (both unaltered and altered) systems for $t = 20 - 40$ ns under no shear, again with NVE dynamics regulated with the Langevin thermostat at 372 K. We later run shear simulations under NVE dynamics at $T = 372$ K using the Langevin thermostat ($N_{\text{chain}} = 216$ for box dimensions: $6.35 \text{ nm} \times 5.57 \text{ nm} \times 6.97 \text{ nm}$) with a damping

²The Langevin thermostat within NVE dynamics was chosen over the Nosé-Hoover thermostat in NVT to better simulate the stochastic thermal forces during diffusion processes while preserving energy conservation. This approach mitigates the risk of non-ergodic behavior in polymer systems, as discussed in [84].

coefficient of 10τ , which is achieved by moving the top and bottom surfaces at constant velocity in the x -direction [87].

While investigating the confinement effect on N_1 and N_2 , we change the number of oligomer chains, N , accordingly (i.e., $N = 216, h = 5.57$ nm). The thermostat is only applied to the non-sheared directions to preserve the increase in velocity due to shear correctly. The fixed and rigid wall configuration consists of five hematite ($\alpha - \text{Fe}_2\text{O}_3$) layers on the top and bottom surfaces [68], which results in a wall thickness of 1.31 nm to ensure a negligible wall deformation compared to thin and deformable walls. Unlike soft walls with variable film thickness, rigid walls are known to experience higher load variations, making them a better choice for observing the magnified confinement effects [11].

A Couette flow is simulated for $10^6 - 2 \times 10^7\tau$, ensuring that a typical chain passes through the periodic boundaries at least three times, eliminating the transient response. The damping coefficients are selected to ensure the temperature remains $\sim 372 \pm 0.1$ K throughout the simulations. Note that the volume of the bulk and confined systems differ due to wall interactions; hence, $p = 1$ atm is preserved for unaltered star oligomers while determining the volume of both linear and star oligomer systems. This enables us to validate some of the results for star oligomers with [66].

The set of parameters defining the surface attraction energy is modified in Sec. 4.1.6. The energy values for the modified sets ($0.1\varepsilon_0$, $0.5\varepsilon_0$, $2\varepsilon_0$, $4\varepsilon_0$), together with the default values (ε_0), from the DREIDING potential [61], are shown in Table 4.1.

4.1.2 Relaxation Time

As we discussed in Sec. 3.1.3, the relaxation time of a polymer chain, λ , can be related to the timescale, in which its deformed state returns to its undeformed configuration. Thus, the competition between λ and the shear time scale can be used to define the deviations from equilibrium [29, 30], requiring us to estimate

Table 4.1: Sets of parameters for modified surface attractions, i.e. the interatomic energy values non-bonding atom interactions between C-Fe, H-Fe, C-O, and H-O. The energy values are given in kcal/mol. For the equilibrium distance σ , the default values from the DREIDING potential are used. For the cut-off distance r_c , the previously defined $r_c = 9.85 \text{ \AA}$ is used for all the cases.

$\varepsilon_{\text{surf}}$	C-Fe	H-Fe	C-O	H-O
$0.1\varepsilon_0$	0.09514	0.038036	0.0282638	0.01129956
$0.5\varepsilon_0$	0.4757	0.19018	0.141319	0.0564978
ε_0	0.9514	0.38036	0.282638	0.1129956
$2\varepsilon_0$	1.9028	0.76072	0.565276	0.2259912
$4\varepsilon_0$	3.8056	1.52144	1.130552	0.4519824

λ . For this reason, we refer to the time autocorrelation function (TACF) for the Rouse model, which is valid for oligomer melt, and use the chain end-to-end vector $\mathbf{r}_{\text{ee}}$

$$\frac{\langle \mathbf{r}_{\text{ee}}(t) \cdot \mathbf{r}_{\text{ee}}(0) \rangle}{\langle \mathbf{r}_{\text{ee}}(0) \cdot \mathbf{r}_{\text{ee}}(0) \rangle} = \sum_{p=1,3,\dots} \frac{8}{p^2 \pi^2} \exp\left(-\frac{tp^2}{\tau_1}\right), \quad (4.1)$$

where $\langle \mathbf{r}_{\text{ee}}(0) \cdot \mathbf{r}_{\text{ee}}(0) \rangle$ is the equilibrium mean-square end-to-end distance of chains, τ_p is the spectrum of the relaxation times for the corresponding mode p (thus, τ_1 is the relaxation of the mode $p = 1$). A visual definition of $\mathbf{r}_{\text{ee}}$ ³ is given in the inset of Fig. 4.1(a). The relaxation dynamics are dominated by the slowest mode ($p = 1$) [62, 88], allowing us to use $\lambda \approx \tau_1$. Note that the definition of $\mathbf{r}_{\text{ee}}$ is not straightforward for branched polymers owing to the presence of more than two free ends. In the context of dilute solutions, the relationship between λ_{star} and λ_{linear} , as established by the Zimm’s approach [89], relies on the Rouse behavior of free-draining polymers, expressed as $\bar{\lambda} = \lambda_{\text{star}}/\lambda_{\text{linear}} = 4/f^2$ where f represents the number of branches for the star polymers. Instead, λ_{star} is related to λ_{linear} by Zimm’s approach to Rouse behavior of free-draining polymers (e.g., polymer chains in unentangled polymer melt), with the relation [89] $\lambda_{\text{star}}/\lambda_{\text{linear}} = 4/f^2$ where in our case $f = 3$ is the number of branches of the star oligomers [90]. Yet, the applicability of this relation may undergo notable shifts when moving from the context of dilute solutions to that of melts, owing to potential alterations in the chain dynamics.

³We prefer using explicitly $\mathbf{r}_{\text{ee}}$ for the end-to-end distance instead of $\mathbf{r}$ to avoid confusion.

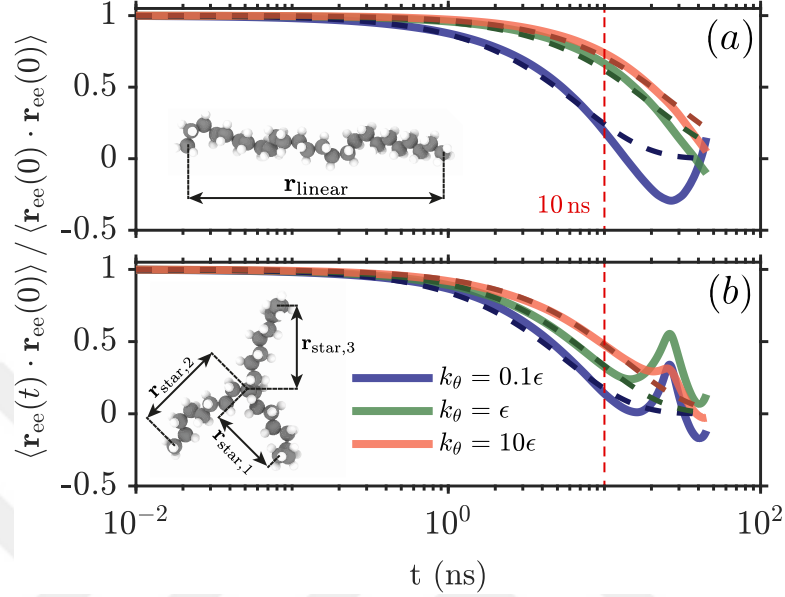


Figure 4.1: Calculation of the relaxation times of the linear and star oligomers for varying chain rigidity. Normalized time-autocorrelation function vs. time for linear (a) and star oligomers (b). The dashed lines denote the exponential fit associated with TACF.

In light of using end-to-end correlation, we introduce a modified $\mathbf{r}_{ee}$ definition for star oligomers, assuming independent arm relaxation. This method involves tracing end-to-end (for linear) and the branching point to the corner (for star) vectors over time, as illustrated in Fig. 4.1(b) (inset).

To obtain the relaxation time λ for linear and star oligomer chains, we calculate the equilibrium (i.e., no shear) TACF for the chains by using our simulation trajectories and fit them with an exponential decay function $\langle \mathbf{r}_{ee}(t) \cdot \mathbf{r}_{ee}(0) \rangle / \langle \mathbf{r}_{ee}(0) \cdot \mathbf{r}_{ee}(0) \rangle \propto \exp(-t/\lambda)$ (Fig. 4.1). In addition, we modify the default chain-rigidity parameter (i.e., $k_\theta = \epsilon$) to obtain less and more rigid chains and their corresponding relaxation times (See Table 4.2).

The initial decay of the TACF is described well by the exponential decay at timescales $t \lesssim 10$ ns. Despite this, for $t > 10$ ns, we observe deviations from the Rouse model, as reported previously for shorter chains (i.e., $C_{25}H_{52}$) [60, 88, 91]. Since the thermostats are known to affect the translational and orientational dynamics (in subnanosecond timescales [92], for water models [93, 94], and polymer

Table 4.2: Relaxation time (λ) and average end-to-end distance ($\langle r_{ee}^2 \rangle^{0.5}$) values of linear and star melts with different chain rigidities, calculated using trajectory data from diffusion simulations.

	Rigidity	λ (ns)	$\langle r_{ee}^2 \rangle^{0.5}$ (Å)
Linear	0.1 ϵ	7.1	16.7
	ϵ	20.8	27.9
	10 ϵ	29.1	30.0
Star	0.1 ϵ	5.7	8.3
	ϵ	9.1	9.2
	10 ϵ	13.5	9.7

models [95, 96]), we may connect these deviations to the choice of the Langevin thermostat. Nevertheless, since we use equilibrium simulation solely to obtain a rescaling factor for the time axis (i.e., chain relaxation time), based on previous studies with similar lubricants [68, 82, 85, 86], we decide to use the Langevin thermostat for both equilibrium and non-equilibrium simulations for consistency. Note that only the initial decay of TACF (up to $t \simeq 10$ ns) is used to obtain the relaxation time due to deviations from the Rouse behavior, as previously reported for the dynamic structure factor [60]. However, viscoelastic hydrodynamics in melts can also cause such anomalies in chain dynamics due to concentration fluctuations [97].

On longer timescales ($t > 10$ ns), deviations from the Rouse model, particularly concerning our expected exponential decay, are present and linked to the impact of *faster* ($p > 1$) modes. As p increases, the relaxation of the associated subchain contracts gradually, causing deviations from the Rouse model since the Gaussian approximation becomes less accurate in describing the conformational statistics of these contracting subchains [60, 88, 91]. Notably, these deviations are more significant in shorter polymer chains, such as $C_{25}H_{52}$ [91]. For this reason, we consider the initial decay of TACF where the Gaussian approximation stays valid while performing the Rouse analysis.

Together with the values of calculated relaxation times (λ), we report the averaged end-to-end distance ($\langle r_{ee}^2 \rangle^{0.5}$) that we obtain from our diffusion simulations in Table. 4.2. Note the tabulated end-to-end distances correspond to time and ensemble averages of r_{linear} for linear chains (end-to-end distance, depicted in the inset of Fig. 4.1(a)), and $r_{\text{star}} = \frac{1}{3} (r_{\text{star},1} + r_{\text{star},2} + r_{\text{star},3})$ for star chains (branching point-to-corner distance, depicted in the inset of Fig. 4.1(b)). Hence, these definitions yield $r_{ee,\text{linear}}$ to include 24 C-C bonds, whereas $r_{ee,\text{linear}}$ includes 8 C-C bonds. When we compare linear and star topologies, we observe that the ratio of 3 ($r_{ee,\text{linear}}/r_{ee,\text{star}}$) is present for the unaltered (1ϵ) model and also for the rigid model (10ϵ) up to some extent. We observe larger deviations in the flexible model (0.1ϵ), possibly due to effective torsional motion being different for the studied topologies. The shorter arm lengths of the star chains may contribute to these deviations compared with the longer counterparts in linear chains.

If we turn back to the relation between relaxation times of linear and star oligomer again, we exploit $\bar{\lambda}_{\text{Zimm}} = (\lambda_{\text{star}}/\lambda_{\text{linear}})_{\text{Zimm}} \approx 0.44$ [89]. On the other hand, our analysis with a modified definition of r_{ee} for star oligomers yields $\bar{\lambda}_{0.1\epsilon} \approx 0.80$, $\bar{\lambda}_{\epsilon} \approx 0.43$, and $\bar{\lambda}_{10\epsilon} \approx 0.46$. For the default chain (i.e., unaltered, $k_{\theta} = \epsilon$), our results agree well with the Zimm relation for the Rouse motion and deviate as the chain becomes artificially more rigid or, especially, more flexible.

As the chain flexibility increases (i.e., $k_{\theta} \rightarrow 0$), the chain needs less time to recover, asymptotically leading to $\lambda \rightarrow \lambda_0$, and λ_0 is the relaxation time of the corresponding ideal (freely-jointed) chain, neglecting dihedral effects. This relation between λ and chain rigidity (i.e., $\lambda^{(10\epsilon)} > \lambda^{(\epsilon)} > \lambda^{(0.1\epsilon)}$) is qualitatively consistent with the previous results [62], and so is the relation between λ and the polymer topology (i.e., $\lambda_{\text{linear}} > \lambda_{\text{star}}$) [98]. Additionally, this change in chain flexibility and stretching results in a corresponding change in the end-to-end distance, illustrating a similar qualitative trend: $r_{ee}^{(10\epsilon)} > r_{ee}^{(\epsilon)} > r_{ee}^{(0.1\epsilon)}$. Overall, our analyses lead to the chain relaxation times that will be used to define the non-equilibrium states of the force-driven systems in the following sections.

4.1.3 Stress Tensor

Next, we compare the steady-state rheology of the oligomer melts confined by two fixed and rigid hematite, $\alpha\text{-Fe}_2\text{O}_3$ layers to their bulk state under planar Couette flow to explore the confinement effects. We chose hematite walls since they have practical significance in combination with short alkanes $\text{C}_{25}\text{H}_{52}$ in tribological applications [66, 82]. We run shear simulations of (i) the bulk melts by deforming the simulation box (Fig. 4.2(a), inset) and (ii) the confined melts by moving the top and bottom surfaces at constant velocity in the $\pm x$ -directions (Fig. 4.2(b), inset). We set and fix the confinement level (i.e., the distance between two layers) to $h = 5.57$ nm (for $N = 216$ chains) to ensure that the *average* pressure ($\bar{p} = \frac{1}{3}(p_{xx} + p_{yy} + p_{zz})$) of the unaltered confined system at equilibrium is the same as the unaltered bulk (i.e., $\bar{p} = 1$ atm). Thus, any change in the (microscopic) stress tensor purely represents the flow characteristics.

From the simulation trajectories, the microscopic stress tensor $\boldsymbol{\sigma}$ can be calculated using the virial theorem [3, 99, 100]. Consequently, the ensemble-averaged total stress tensor, composed of the kinetic and virial contributions, is prone to thermal fluctuations [101]. Therefore, we compute the total stress tensor of the melt in bulk and confined configurations and consider the time-averaged steady-state stress response to eliminate thermal fluctuations. We define the macroscopic equivalent formulation [32]

$$\boldsymbol{\sigma} \equiv \underbrace{-\bar{p}\mathbf{I} + 2\eta(\dot{\boldsymbol{\gamma}})\dot{\boldsymbol{\gamma}}}_{\text{GNF}} + \boldsymbol{\sigma}^{(\text{VE})}, \quad (4.2)$$

where $\bar{p}$ is the mechanical pressure of the melt, $\bar{p} = -\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, $\dot{\boldsymbol{\gamma}}$ is the strain rate tensor with the only nonzero components, namely the shear rate, $\dot{\gamma} = \dot{\gamma}_{xy} = \dot{\gamma}_{yx}$, and the extra-stress component for the viscoelastic effects $\boldsymbol{\sigma}^{(\text{VE})}$. As $\boldsymbol{\sigma}^{(\text{VE})} \rightarrow 0$, equation (4.2) reduces to the GNF stress tensor, which introduces the shear-dependency to the Newtonian viscosity η_0 [32, 102, 103, 104].

4.1.3.1 Viscosity

To characterize the shear-dependent viscosity of our melts, we calculate the normalized viscosity, η/η_0 , where the shear viscosity is defined as $\eta \equiv \sigma_{xy}/\dot{\gamma}$, and the Newtonian plateau viscosity (of bulk) is η_0 [105]. The observed behavior of viscosity for bulk and confinement shows the shear-thinning behavior (for linear: Fig. 4.2(a), for star: Fig. 4.2(b)) in accordance with the prior findings (e.g., for similar alkanes [106, 107, 108, 109] and 9-octylheptadecane [66]). In Fig. 4.2, three regions are labeled to indicate the various shear responses; I, II, and III indicate the 1st Newtonian plateau, the shear-thinning regime, and the 2nd Newtonian plateau for bulk polymers, respectively.

The linear chains in bulk tend to form crystalline structures at the first Newtonian plateau for our default chain (i.e., unaltered, $k_\theta = \epsilon$) as well as for the stiff-toy model (i.e., $k_\theta = 10\epsilon$). This leads to a higher viscosity than the Newtonian plateau viscosity [22, 110] for these cases, independent of the size of our simulation boxes. The flow-induced crystallization and the resultant shear-thickening vanish as the shear rate increases [111, 112, 113]. Notably, we do not observe crystallization for the strongly flexible toy model (i.e., $k_\theta = 0.1\epsilon$). On the other hand, the viscosity values of (unaltered) star chains in bulk agree well with Ref. [66] while not showing crystallization for any rigidity level.

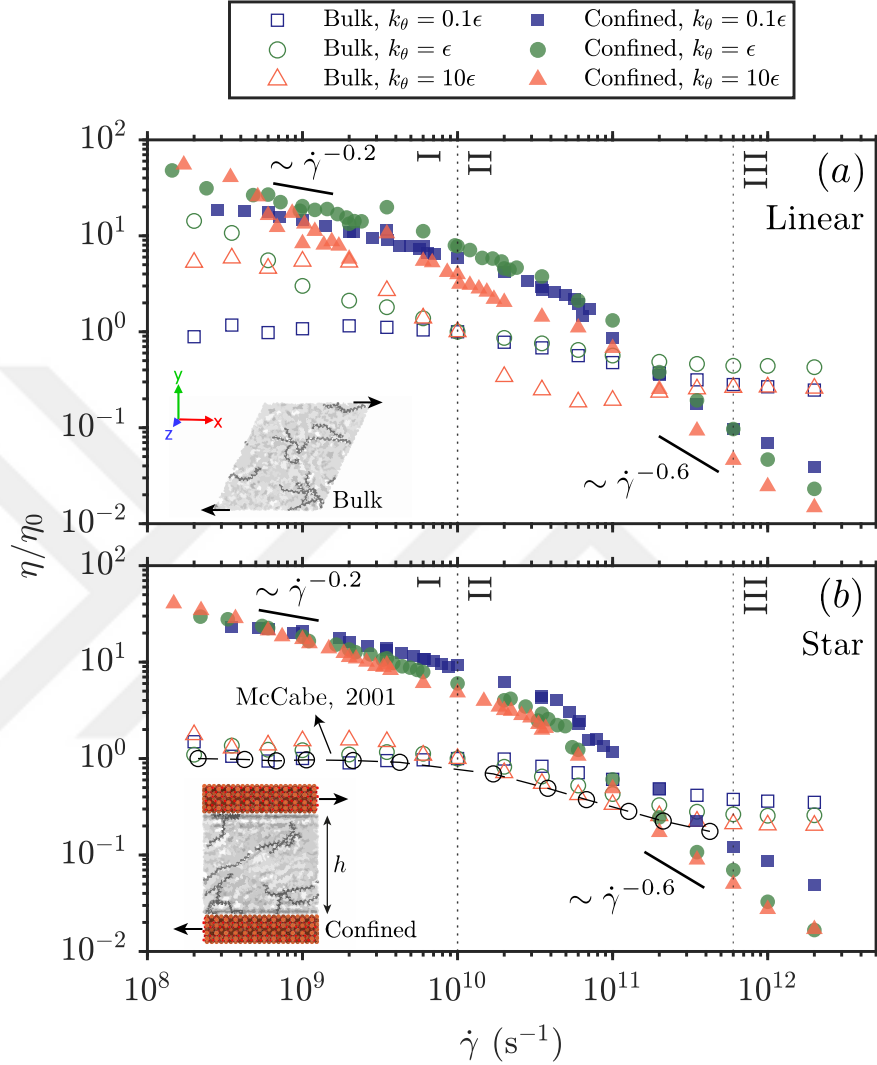


Figure 4.2: Viscosity normalized with respect to the Newtonian plateau viscosity of bulk state for bulk (empty markers) and the confined (filled markers) configurations for the linear (a) and the star chains (b). The black circles denote the viscosity values obtained from Ref. [66] for unaltered star chains ($k_\theta = \epsilon$). Error bars are of the size of markers.

Flow-induced crystallization of polymeric systems is a key factor in adjusting material properties and improving processing efficiency [114]. Keeping the computational expense of MD simulations in mind, our observations on at which conditions crystallization emerge for different topologies and chain rigidity might serve as a step to further incorporate atomistic variables (e.g., chain rigidity) into

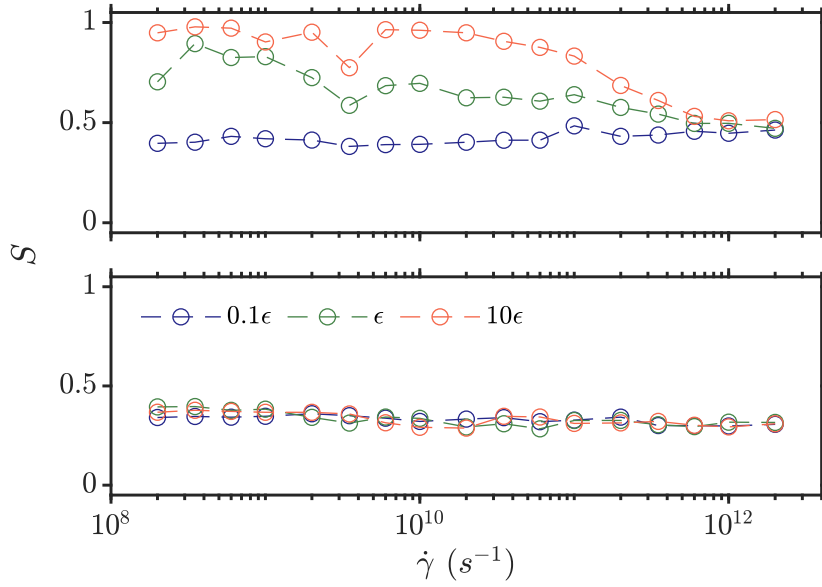


Figure 4.3: Nematic order parameter S in bulk systems to characterize flow-induced crystallization. The nematic order of linear chains becomes more apparent as the chain rigidity increases (top). The nematic order of star chains does not show significant change with chain rigidity (bottom).

coarse-grained simulations (e.g., chain stretching in the Graham and Olmsted model) [114, 115].

To characterize the flow-induced crystallization in bulk simulations, we consider the segments connecting midpoints of C-C bonds, define the average orientation of a molecule (i.e., director), and then compute the angle in between, giving us the nematic order parameter $S = \langle 3 \cos \theta - 1 \rangle / 2$, where $\langle \rangle$ denotes the time and ensemble averages. For a perfectly aligned system, $S = 1$, and for no alignment, $S = 0$. The usage of midpoints instead of atom coordinates helps us correctly characterize the high level of order in peculiar orientations (e.g., the perfectly aligned zigzag chain gives $S = 1$ if bond midpoints are used or gives $S < 1$ if atom coordinates are used, further diminishing as the dihedral angles decrease). In Fig. 4.3, we demonstrate the level of flow-induced crystallization of linear and star melts in bulk based on the nematic order metric. These results are in agreement with our observation (in Fig. 4.2) that the anomalous behavior in viscosity is present for linear chains (for $k_\theta = \epsilon, 10\epsilon$). We note that the crystallization increases with the chain rigidity for linear chains and is not present

for the highly flexible linear chains (i.e., $k_\theta = 0.1\epsilon$) or star chains with the same molecular weight (or polymerization degree).

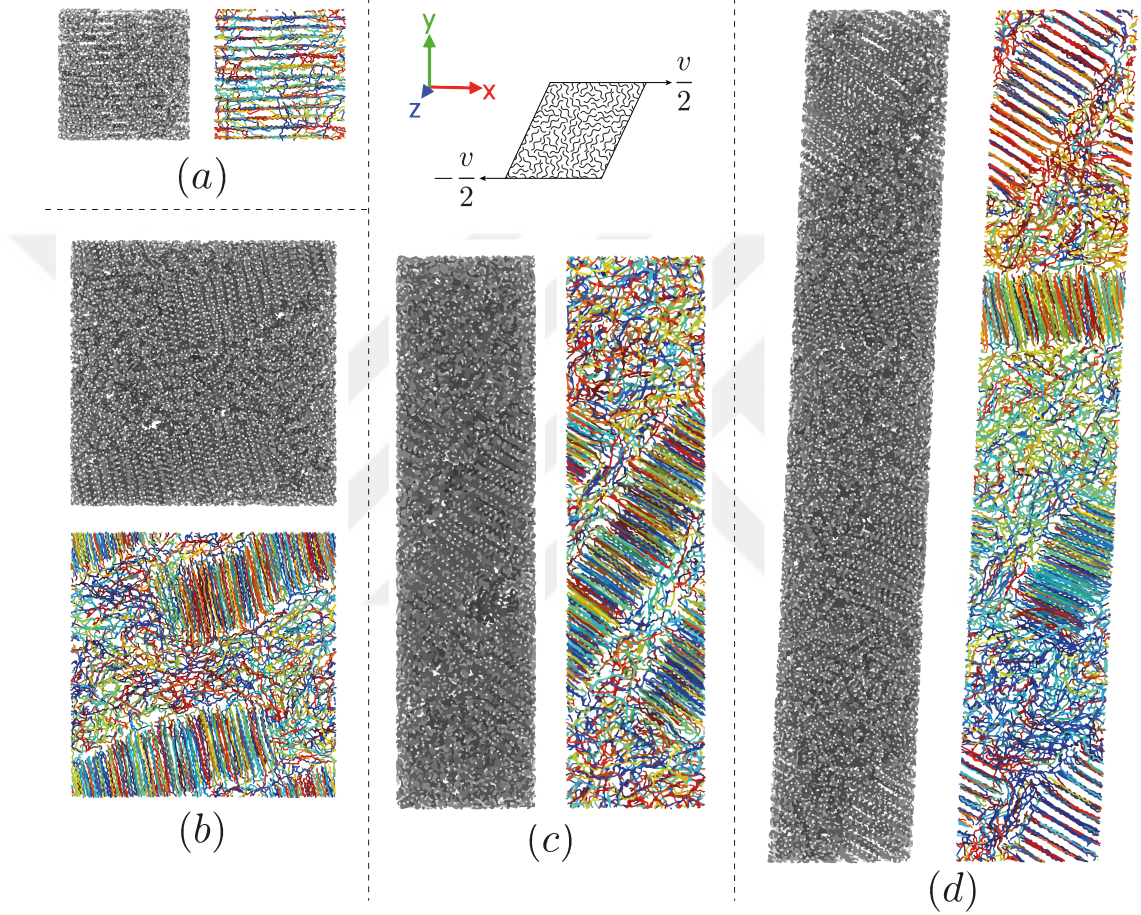


Figure 4.4: The snapshots of the crystalline structure formation of unaltered linear oligomer melt ($k_\theta = \epsilon$) under shear for different simulation box sizes. For each simulation box size, molecular and bond configurations are illustrated separately, where the coloring of the bonds is random. The corresponding simulation box sizes are (a) $(h, h, h; N_{\text{chain}} = 216)$, (b) $(2h, 2h, h; N_{\text{chain}} = 864)$, (c) $(h, 4h, h; N_{\text{chain}} = 864)$, and (d) $(h, 6h, h; N_{\text{chain}} = 1296)$ where $h \approx 5.82$ nm.

We further aim to verify that the emergence of crystalline structures is not a numerical artefact of finite-size effect by conducting the complementary simulations for the simulation box with dimensions (h, h, h) at $Wi = 12.5$. In Fig. 4.4, we demonstrate the crystallization for the simulation box sizes (a)

($h, h, h; N_{\text{chain}} = 216$), (b) ($2h, 2h, h; N_{\text{chain}} = 864$), (c) ($h, 4h, h; N_{\text{chain}} = 864$), and (d) ($h, 6h, h; N_{\text{chain}} = 1296$) where $h \approx 5.82$ nm to retain the identical density of $\rho = 0.63$ g/cm³. We note that, under identical settings, star oligomer melts do not exhibit crystallization. The crystalline structures yield a shear-thickening effect for the linear chains with rigidities ($k_\theta = \epsilon, 10\epsilon$).

Turning our focus back to the confined geometry, the viscosity of both polymer topologies is higher than their bulk states and decreases with the shear rate (Fig. 4.2) [99]. This decrease appears to follow (except linear chains with $k_\theta = 10\epsilon$) the slope $\eta \sim \dot{\gamma}^{-0.2}$ until shear bands start to develop in region II. In the transition regime, the Couette velocity profile starts to become centrally localized in the middle of the channel, disrupting the smoothness of the velocity profile [116, 117, 118]. With increasing shear rate, a discontinuity in the velocity profile develops, resulting in a plug slip behavior, and the decrease in viscosity follows the slope $\eta \sim \dot{\gamma}^{-0.6}$ (further discussed in Sec. 4.1.4 for the velocity profiles of the confined star oligomer melts, while the linear oligomer melts show qualitatively the same behavior). As the flexibility of the chains increases, the shear-thinning behavior becomes stronger. Notably, if we replace our chains with monomers (i.e., no chains) and run separate simulations, no additional resistance due to the confinement appears, which highlights the role of chain connectivity. Moreover, when there are no bonds, crystallization does not occur, and then the excess viscosity of the linear chains, with respect to star chains in bulk, also disappears (see Fig. 4.5).

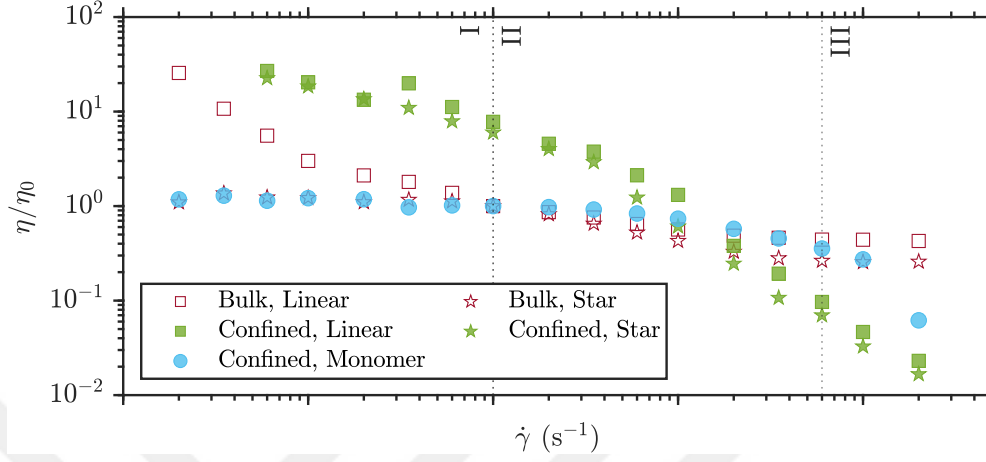


Figure 4.5: The normalized viscosity of monomers under confinement, obtained by breaking all the carbon-carbon bonds of the linear polymer melt, together with linear and star polymer melts in bulk and under confinement. Linear and star polymers have the unaltered configuration ($k_\theta = \epsilon$), whereas k_θ does not apply for the monomers. Error bars are of the size of markers.

4.1.3.2 Viscoelasticity and Normal Stress Differences

To quantify the viscoelastic contributions to the total rheological response, we turn our attention back to the stress tensor $\boldsymbol{\sigma}$ (4.2) and focus on the viscoelastic part of the stress tensor, $\boldsymbol{\sigma}^{(\text{VE})}$. According to Larson [35], viscoelasticity originates from unequal normal stress components, characterized by normal stress differences, with notable exceptions of the suspensions of non-Brownian non-spherical particles and porous polymer gels [36, 119, 120, 121]. Hence, the viscoelastic stress is given to be a function of the normal stress differences, $\boldsymbol{\sigma}^{(\text{VE})}(N_1, N_2)$ [32]. For concentrated polymeric liquids, the first and second normal stress differences ($N_1 = \sigma_{xx} - \sigma_{yy}$ and $N_2 = \sigma_{yy} - \sigma_{zz}$) arise due to the interactions between the chains trapped near the surfaces and the micro-structure dynamics, respectively [122]. Normal stress differences govern the viscoelasticity in the scope of polymer/oligomer melts. Conversely, observing shear-thinning viscosity behavior does not necessarily imply the fluid is viscoelastic and requires non-zero normal stress differences to exist [35, 36] (Fig. 4.6).

In Fig. 4.6, we explore the normal stress differences and the viscoelastic stress component as a function of the Weissenberg number ($Wi = \dot{\gamma}\lambda$). The Weissenberg number essentially characterizes the degree of non-linearity in the deformation behavior of viscoelastic materials. When $Wi \ll 1$, the fluid is known to exhibit characteristics similar to a Newtonian fluid. However, the fluid displays viscoelastic effects for $Wi \geq O(1)$ as normal forces become more dominant than shear forces, causing the polymers to stretch and store elastic energy [26].

With this in mind, we would theoretically expect that $N_1 = N_2 = \sigma_{yy}^{(VE)} = 0$ for $Wi = 0$, since the system is in equilibrium with no presence of external forces. Contrarily, in Fig. 4.6, we report an unexpected behavior for the normal stress differences at $Wi = 0$; $N_1 < 0$ and $N_2 > 0$ accompanying the viscoelasticity-induced tension ($\sigma_{yy}^{(VE)} = \sigma_{yy} + \bar{p}$ where $\bar{p} = -\frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$) for $0 \leq Wi < 50$ [35]. This unexpected behavior for the normal stress differences, with $N_1 < 0$ and $N_2 > 0$, complements findings from previous studies that highlighted similar features in nematic solutions of rod-like polymers (e.g., liquid crystalline [37, 38] or sulphuric acid solutions [123]) under shear flow, which were explained by the suppression of tumbling [124] (i.e., *arrested* tumbling [125]) motion of chains. Our observation of $N_1 < 0$ extends this discussion to short alkanes strongly confined within iron-oxide surfaces. Furthermore, introducing *artificially* less and more flexible chains by altering the chain rigidity enables us to reconsider the limitation of rodlike polymers.

We further determine that positive $\sigma_{yy}^{(VE)}$, present at $Wi = 0$, is followed by a constant plateau until $Wi \sim 10$ and, afterward, by a decrease at higher shear rates as shown in Fig. 4.6(e-f). The normal stress component is calculated for each atom and shown in Fig. 4.6(g-h), demonstrating stress localization near the surface. Notice that even at equilibrium (i.e., $Wi = 0$), nonzero viscoelastic stress emerges due to the stretched configurations of the free chains (as well as near-surface chains), possibly leading to an anisotropy in the stress response in the presence of strong confinement.

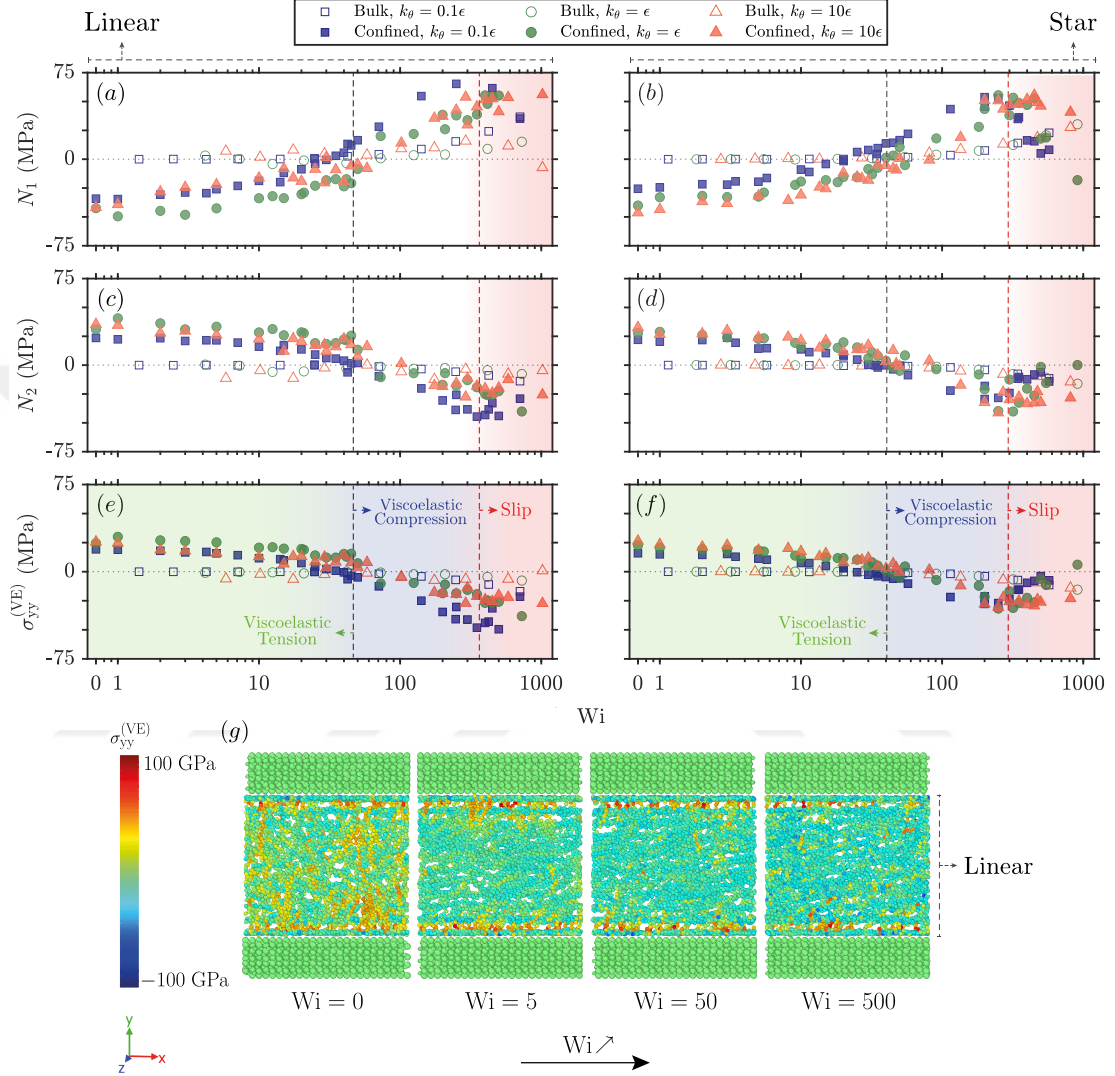


Figure 4.6: Normal stress differences N_1 , N_2 and viscoelastic stress component opposing the streamwise direction $\sigma_{yy}^{(VE)}$. N_1 for linear (a) and star (b) chains. N_2 for linear (c) and star (d) chains. $\sigma_{yy}^{(VE)}$ for linear (e) and star (f) chains, highlighting the regions of viscoelastic tension and compression applied to the confining surfaces. Local distribution of $\sigma_{yy}^{(VE)}$ for the unaltered ($k_\theta = \epsilon$) linear chains (g), illustrating both equilibrium ($Wi = 0$) and non-equilibrium ($Wi = 5, 50, 500$) states. The localization of tension in the near-surface chains and compression in free chains develop with increasing Wi . Error bars are of the size of markers (a-f); the snapshots of the simulation boxes are taken at an arbitrary time step in the steady state (g).

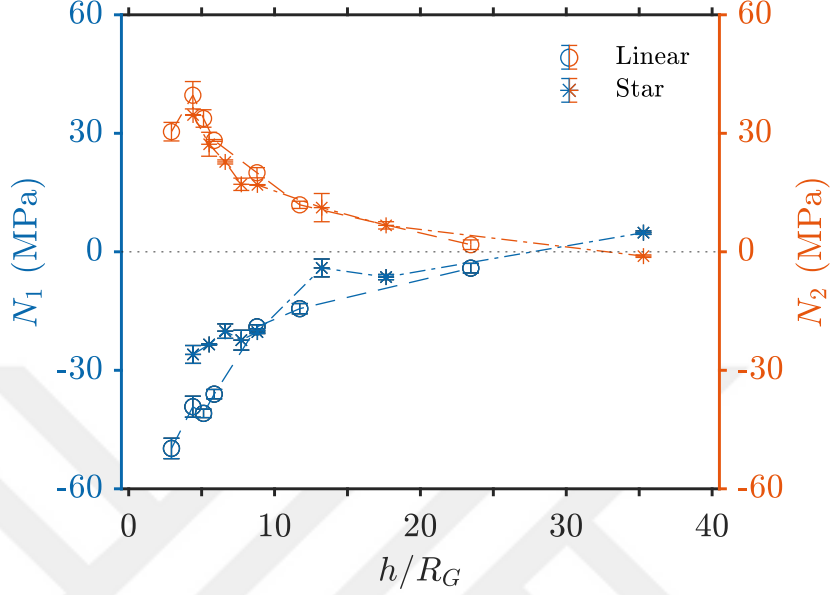


Figure 4.7: Sign-reversion of the normal stress differences with increasing film thickness for unaltered oligomer melts ($k_\theta = \epsilon$). N_1 and N_2 for the ratio of film thickness h to the radius of gyration R_G at $Wi = 10$.

Until $Wi \sim 40$, the surfaces are pushed apart from each other by the melt. As the initial (i.e., $Wi = 0$) viscoelastic stress (tension) governed by the chains away from the surfaces (i.e., the free chains in the bulky region) becomes more localized to the interfacial region. As Wi further increases, both the normal stress differences change sign, $N_1 > 0$ and $N_2 < 0$, also yielding $\sigma_{yy}^{(VE)} < 0$ (i.e., viscoelastic compression). Within the range of Wi values, similar behavior is present for both linear and star polymer topologies.

On the other hand, for bulk systems, we observe an order of magnitude decrease in N_1 , N_2 , and $\sigma_{yy}^{(VE)}$, as well as positive N_1 (negative N_2) increasing (decreasing) with Wi . Such behavior of N_1 and N_2 was observed previously for ring polymers with relatively small polymerization degrees [126] (e.g., C_{30}). The observed difference between confined and bulk systems suggests that the storage of the elastic energy depends on the restriction of movement of chains once confined. For very high Wi , we observe plug slip behavior as the smoothness of the velocity profile is disturbed (see Sec. 4.1.4 for the velocity profiles of the star oligomer melts).

In Fig. 4.7, we investigate the normal stress differences as a function of the film

thickness h . To explore the change in N_1 and N_2 as a function of h , we change the film thickness while keeping Wi and the density constant (i.e., for each film thickness h , N/h is preserved by varying N). In this way, we show how the normal stress differences increase in magnitude as the film thickness decreases. As h increases, ideally approaching the bulk system, the normal stress differences decrease substantially in magnitude and even change sign while retaining the same ratio N_1/N_2 , resulting in the well-known behavior of polymeric liquids with $N_1 > 0$ and $N_2 < 0$ [21, 24, 35, 36, 98, 127, 128]. Regarding the non-monotonic behavior of N_2 for the linear chains occurring for the most extreme confinement level, we suspect that fewer chains will be present between the layers as the confinement increases, eventually interrupting the load-carrying phenomena.

In the context of numerical studies with short alkanes under confinement, such as ours, prior findings mostly emphasized ultra-thin films modulated by a constant pressure [67, 86]. This type of modulation assigns a normal force to the confining walls. It makes them move accordingly in the vertical direction to achieve the desired pressure levels instead of preserving the constant film thickness. Prior studies further covered atomistically-flat [98, 129] and less energetic surfaces (e.g., mica [130, 131] or gold [132, 133, 134], not causing *arrested* tumbling), or surfaces covered with surfactant molecules [68, 135]. Also, considering the experimental side, as achieving smaller film thickness at atmospheric pressure becomes harder to achieve, we believe that these details might hint at the rationale behind negative N_1 (positive N_2) observations [5, 21, 136]. As the normal stress differences, and hence the viscoelastic stress component, become smaller for larger h , constitutive models, such as GNF, show less deviation from the real microscopic behavior as shown in Fig. 4.6(a-f).

4.1.4 Velocity Profiles and Slip

In the confined systems, the discontinuity in the velocity profile develops as the shear rate increases, and the plug slip occurs as the velocity profile for extreme shear rates. The resultant slip prevents the emergence of the 2nd Newtonian

plateau of shear-thinning viscosity for the confined systems (see Fig. 4.2) since the discrepancy between the externally applied shear rate and the effective shear rate of the system grows. Also, the slip between molecular layers corresponds to where the viscoelastic compression is halted (see Fig. 4.6(e-f)),

In Fig. 4.8, we consider a range of shear rates: $\dot{\gamma} = 6 \times 10^8 \text{ s}^{-1}$ (a), $\dot{\gamma} = 6 \times 10^9 \text{ s}^{-1}$ (b), $\dot{\gamma} = 6 \times 10^{10} \text{ s}^{-1}$ (c), $\dot{\gamma} = 6 \times 10^{11} \text{ s}^{-1}$ (d), and $\dot{\gamma} = 6 \times 10^{12} \text{ s}^{-1}$ (e), as a function of the normalized vertical component $\bar{y}$ with respect to the film thickness h . The corresponding Weissenberg numbers are (a) $Wi = 5.46$, (b) $Wi = 54.6$, (c) $Wi = 546$, (d) $Wi = 5460$, and (e) $Wi = 54600$, where $h = 5.57 \text{ nm}$. The smoothness of the velocity profiles becomes disturbed in Fig. 4.8(d), and the discontinuity is visible in Fig. 4.8(d).

Similarly, for star oligomer melts, when we alter the surface attraction energies (Fig. 4.9): $\varepsilon_{\text{surf}} = 0.1\varepsilon_0$ (a), $\varepsilon_{\text{surf}} = 0.5\varepsilon_0$ (b), $\varepsilon_{\text{surf}} = \varepsilon_0$ (c), $\varepsilon_{\text{surf}} = 2\varepsilon_0$ (d), and $\varepsilon_{\text{surf}} = 4\varepsilon_0$ (e), as a function of the normalized vertical component $\bar{y}$ with respect to the film thickness h . We discover different velocity profiles emerging, transitioning from wall slip (a) to Couette profile (b-d) to shear-banding (e) at constant Wi ($Wi = 10$). The shear banding regime, yielding the development of discrete blocks of chains and weakening the interconnectivity, is suspected of causing the decrease in the sign-reversed normal stress differences of the star chains. The shear bands are also present for linear chains; however, since the length of the linear chains is larger than star chains ($r_{\text{ee,linear}} > 2r_{\text{ce,star}}$), the increase in the magnitude of the sign-reversed normal stress difference is slowed down with $\varepsilon_{\text{surf}}$. Therefore, the linear oligomer chains are also expected to exhibit a decrease in the sign-reversed normal stress differences but with a delay due to chain lengths.

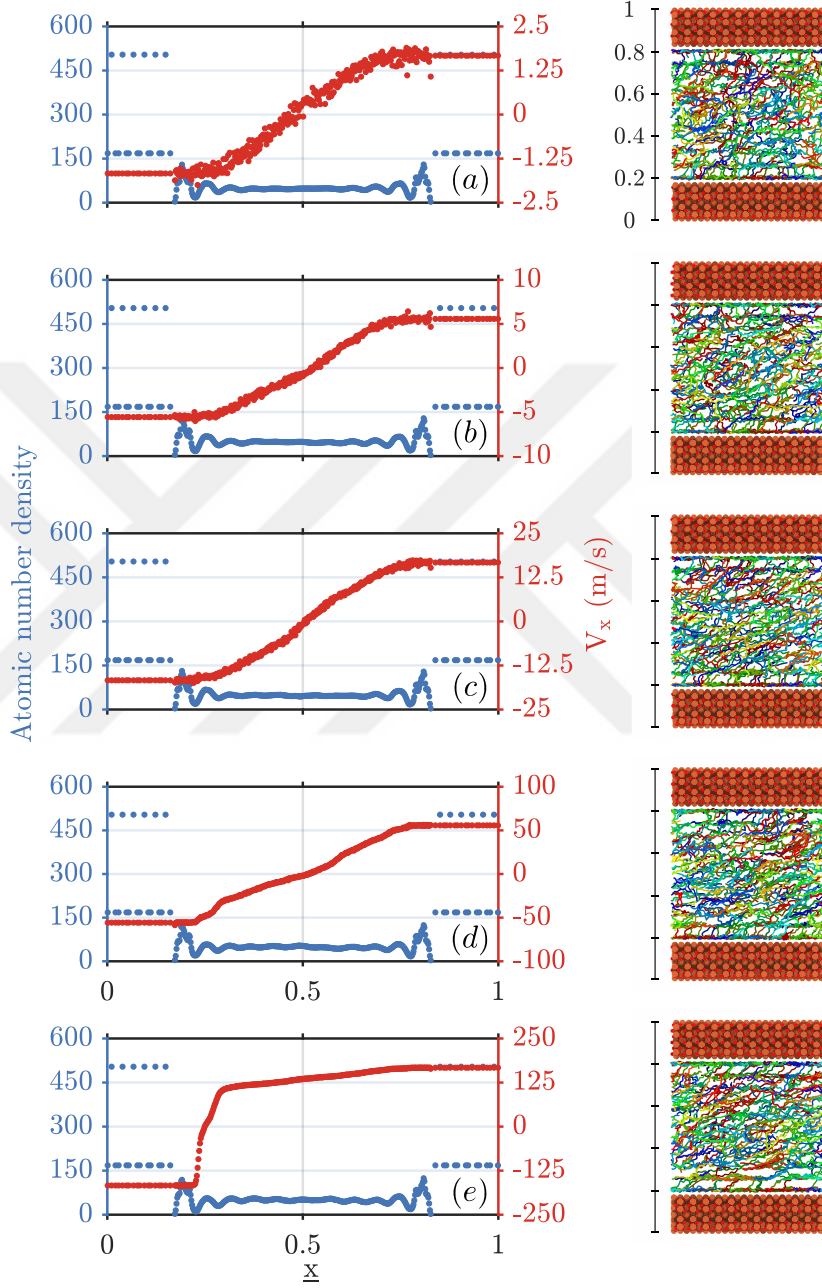


Figure 4.8: The steady-state spatial configuration and the velocity distribution within the shear of confined star oligomer melts at increasing shear rate. The snapshots of the simulation box given on the right illustrate the carbon-carbon bond configuration of the system, where the coloring of the bonds is random. The corresponding shear rates are $\dot{\gamma} = 6 \times 10^8 \text{ s}^{-1}$ (a), $\dot{\gamma} = 6 \times 10^9 \text{ s}^{-1}$ (b), $\dot{\gamma} = 6 \times 10^{10} \text{ s}^{-1}$ (c), $\dot{\gamma} = 6 \times 10^{11} \text{ s}^{-1}$ (d), and $\dot{\gamma} = 6 \times 10^{12} \text{ s}^{-1}$ (e).

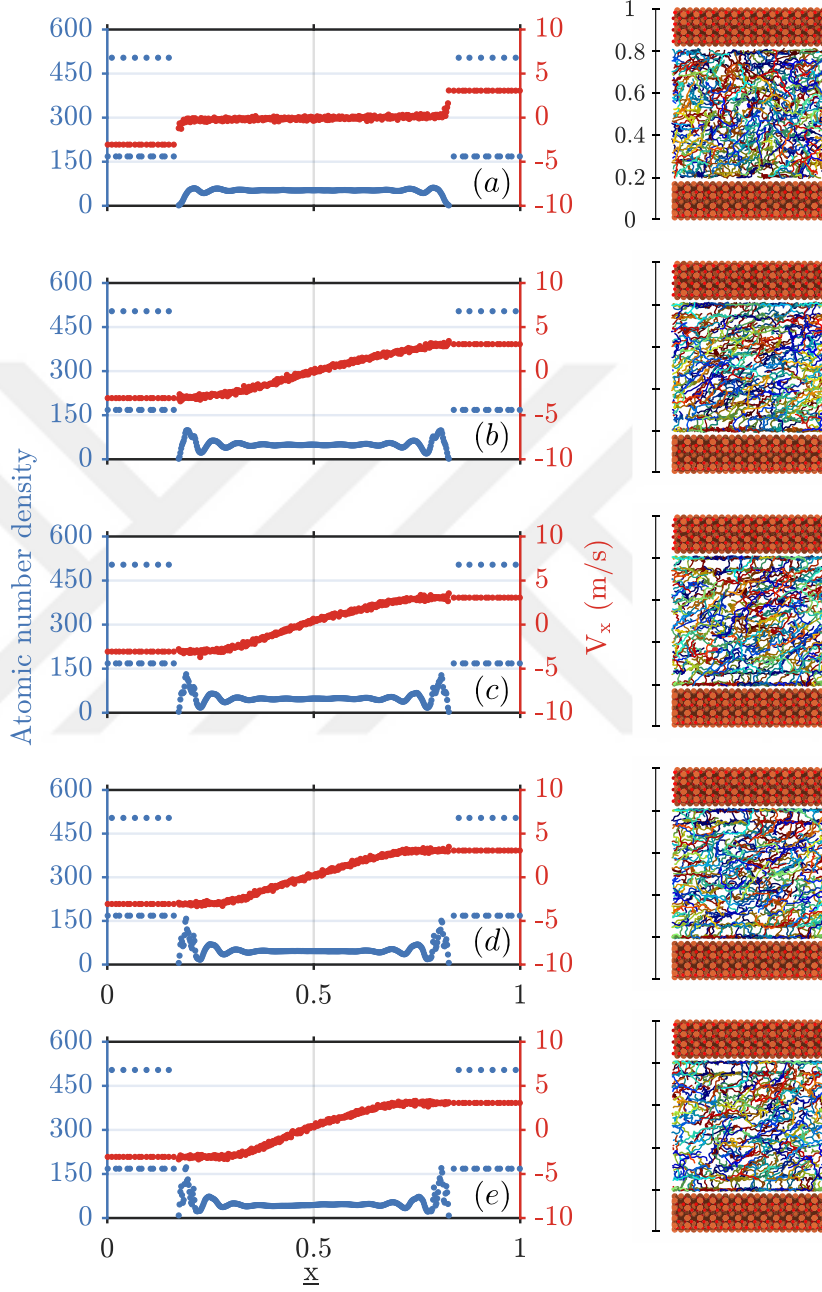


Figure 4.9: The steady-state spatial configuration and the velocity distribution within the shear of confined star oligomer melts at constant Wi and varying surface attraction. The snapshots of the simulation box given on the right illustrate the carbon-carbon bond configuration of the system, where the coloring of the bonds is random. The corresponding surface attraction energies are $\varepsilon_{\text{surf}} = 0.1\varepsilon_0$ (a), $\varepsilon_{\text{surf}} = 0.5\varepsilon_0$ (b), $\varepsilon_{\text{surf}} = \varepsilon_0$ (c), $\varepsilon_{\text{surf}} = 2\varepsilon_0$ (d), and $\varepsilon_{\text{surf}} = 4\varepsilon_0$ (e).

4.1.5 Microscopic Reasoning

Next, we aim to find molecular-scale phenomena leading to the observed macroscopic responses in our simulations (i.e., viscosity, normal stress differences, viscoelastic contributions to stress response). For this purpose, we first calculate the (near/away dynamics of) radius of gyration of chains in and then the bond-orientation tensor. In the end, we use the bond-orientation tensor to uncover the effect of the surface affinity on the conformation of the chains.

4.1.5.1 Local Radius of Gyration

The time-averaged radius of gyration of chains in bulk and confined oligomer melts $R_{G,\text{bulk}}$ and $R_{G,\text{confined}}$, do not show a significant dependency on $\dot{\gamma}$ (see Table 4.3 for averages). R_G shows a slight tendency to increase with the chain rigidity, particularly for linear chains.

Table 4.3: Radius of gyration R_G of linear and star melts with different chain rigidities, and in bulk or under confinement ($h = 5.57$ nm), averaged across the shear rate spectrum.

	Rigidity	$R_{G,\text{bulk}}$ (Å)	$R_{G,\text{confined}}$ (Å)
Linear	0.1ϵ	10.06	9.34
	ϵ	9.94	9.50
	10ϵ	10.26	9.52
Star	0.1ϵ	6.97	6.32
	ϵ	7.00	6.31
	10ϵ	7.05	6.36

In Fig. 4.10, we calculate x - and y -components of R_G for chains near and away from the surface at a given time. The steady-state response of the radius of gyration captures the shear-thinning behavior of confined melts as the x -component of R_G increases and represents the stretching of chains in the flow direction, while the y -component of R_G decreases, indicating the contraction

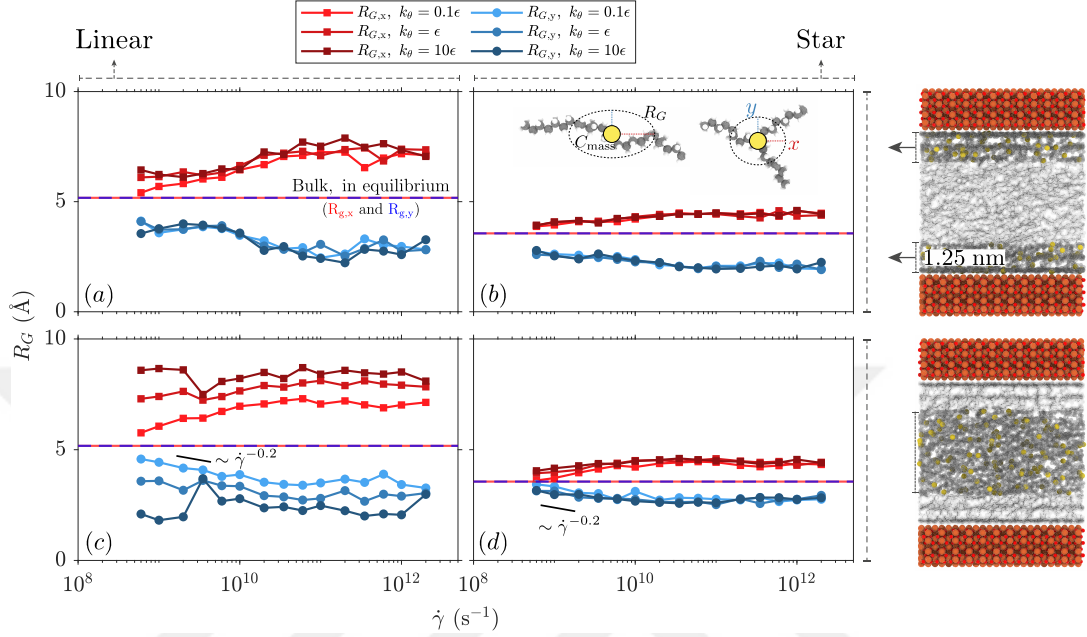


Figure 4.10: Steady-state radii of gyration (R_G) calculated near/away from the surface for confined linear and star oligomer melts at $h = 5.57$ nm. The x – and y –components of the radius of gyration are given near the surface for linear (a) and star (b) chains; away from the surface for linear (c) and star (d) chains. The snapshots depict the regions where the components of the radii of gyrations are calculated based on the positions of the center of mass of each chain, whose approximate positions are shown in yellow for a single time step.

of chains in the direction perpendicular to the flow. However, we further observe that the decrease of the y –component of R_G ($R_{G,y}$) with increasing $\dot{\gamma}$ is weaker for the molecules near the surfaces. For the chains away from the surface, the decrease in $R_{G,y}$ of star chains (as well as the strongly flexible linear chains, $k_\theta = 0.1\epsilon$, also showing no crystallization) can be described by a slope of $\sim \dot{\gamma}^{-0.2}$ at low shear rates (i.e., $\dot{\gamma} \lesssim 10^{10} \text{ s}^{-1}$). Nevertheless, the qualitatively similar behavior of the chains near or away from the surface does not hint at any mechanism for the observed stress response in the confined melt.

4.1.5.2 Bond-orientation Tensor

Despite there is not a qualitative difference in the characteristic sizes of the chains near and away from the surface, a visual inspection of our simulation trajectories

reveals that the chains near the surface are more aligned against the flow direction to some extent (Fig. 4.11). This *viscoelastic* layer resembles a polymer brush with surface-grafted chains [29] and has also been observed in previous studies (e.g., experimental and numerical characterization of polymer adsorption [134, 137, 138, 139] and surface-absorbed polymeric surfactant films [68, 140]). Thus, we turn our attention to the alignment of the bonds constituting the chains [11, 129, 141, 142, 143]. For this purpose, we define a bond-orientation tensor, where the orientation of each bond is calculated and time-averaged via the following expression [144, 145]

$$Q_{\alpha\beta} = \frac{1}{N_{\text{chain}}} \sum_{N_{\text{chain}}} \frac{1}{N-1} \sum_{j=1}^{N-1} \frac{b_{j\alpha} b_{j\beta}}{\|b\|^2}, \quad (4.3)$$

where N_{chain} is the number of chains, N is the number of carbon atoms in a chain, b_j for $1 \leq j \leq N-1$ is the bond vector between consecutive carbon atoms in the same chain, and $\|b\|$ is the Euclidean length of the bond. In equation (4.3), Q_{yy} component represents the alignment of bonds perpendicular to the surface (i.e., normal to the shear/flow direction), where $\text{Tr}(\mathbf{Q}) = 1$ holds over the entire system. To characterize the spatial variation in $Q_{yy}(y)$, we consider $Q_{yy}(y) = \int_0^h q_{yy}(y) dy$ with the discretization $Q_{yy} \approx \sum_0^h q_{yy}(y) \Delta y$, where $\Delta y \approx 0.5 \text{ \AA}$ and $\text{Tr}(\mathbf{q}) = 1$ also holds for each discrete region (i.e, each Δy).

In accordance with the discretization, we calculate the *local* bond orientation q_{yy} across the nanoscale confinement in Figs. 4.11 and 4.12. In these figures, the representative snapshots color-code the strength of bond orientation such that the bonds aligned perpendicular to the flow are shown in red, and those aligned horizontally are given in blue. If there is no confinement (i.e., in bulk), $Q_{yy}(y)$ reduces to its average value $\bar{Q}_{yy}$, as the spatial variation in y -direction (or any direction) is indifferent. For the confined system, a visual inspection reveals strongly absorbed oligomer layers localized near the surfaces (Figs. 4.6(g) and 4.12) and notably, the adsorbed chains do not exchange with the free chains throughout our simulations (see the movie in the Supplemental Material).

In Fig. 4.12, we plot the spatial variation of $Q_{yy}(y)$ for various h (a) and Wi (b) cases to capture the viscoelastic contributions to the stress. In Fig. 4.12(a),

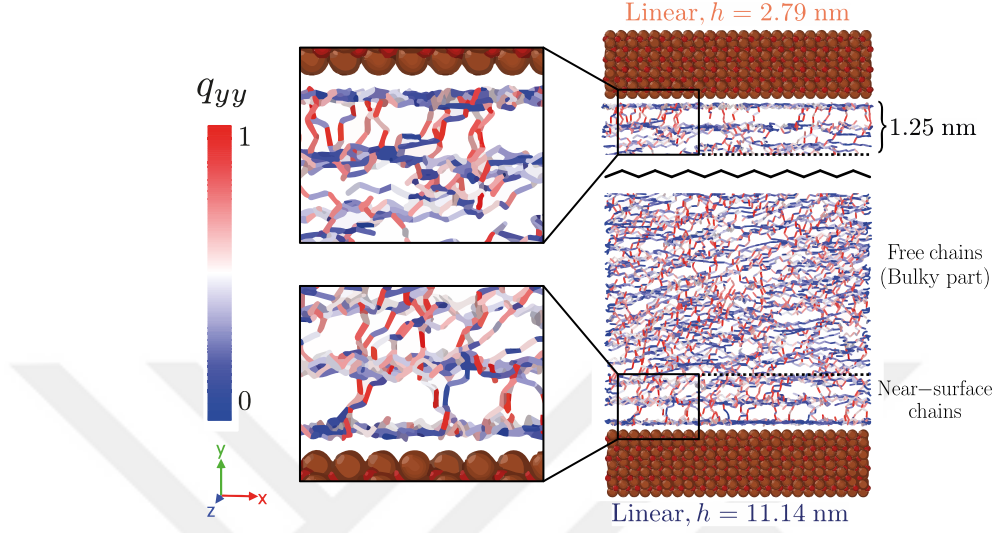


Figure 4.11: Visualization of the spatial resolution of the local bond orientation, q_{yy} , for $h = 2.79$ nm and $h = 11.14$ nm, color-coding the bonds opposing the flow direction (red) and aligned with the flow direction (blue). Simulations are of unaltered oligomer melts ($k_\theta = \epsilon$).

as the surfaces are separated further by increasing the film thickness, h , the bonds, overall, become more aligned with the flow in the x -direction across the confinement, albeit with preserved near-surface peaks of q_{yy} . As the film thickness decreases and the chains aligned with the flow (i.e., x -direction) contribute less to the overall conformation of the melt (e.g., Q_{yy}), the domination of the near-surface peaks of q_{yy} becomes more apparent in the normal stress differences, hinting at the enhancement in the sign-reversed response (as shown in Fig. 4.7).

In Fig. 4.12(b), at relatively fast shear rates (e.g., $Wi > 50$), the bonds become more aligned in the flow direction. The change in the alignment of the bonds (and so the chains) occurs not only for the free chains in the middle of the channel (i.e., the bulky part) but also for the surface-adsorbed chains. This leads to a decrease in both the near-surface peak and the overall behavior of q_{yy} (resulting in smaller Q_{yy}). In contrast, at lower shear rates (e.g., $Wi < 50$), the chains have more time to reorient to their entropically favored states. The change in the strength (and variation) bond alignment across the channel controls the magnitude of additional viscoelastic stress acting on the surfaces (as observed in Figs. 4.6(e-g)) [146, 147, 148].

The surface-normal conformation of the chains at lower Wi appears to modify the anisotropy of the stress response (i.e., $N_1 < 0, N_2 > 0$ instead of $N_1 > 0, N_2 < 0$) due to respective increase in the wall-normal stress component magnitudes. As a consequence, the elastic force stored within the chains may be redirected towards the walls, significantly amplifying the load-carrying capacity of the melt. This leads to an order-of-magnitude disparity when compared to the bulk ($\sigma_{yy}^{(VE)} \sim 25$ MPa vs. $p \sim 0.1$ MPa, Fig. 4.6(e,f)). Importantly, the thickness of the oligomer-adsorbed layer is independent of h ; thus, this layer's contribution to the overall viscoelastic response decreases as $h/R_G \rightarrow \infty$.

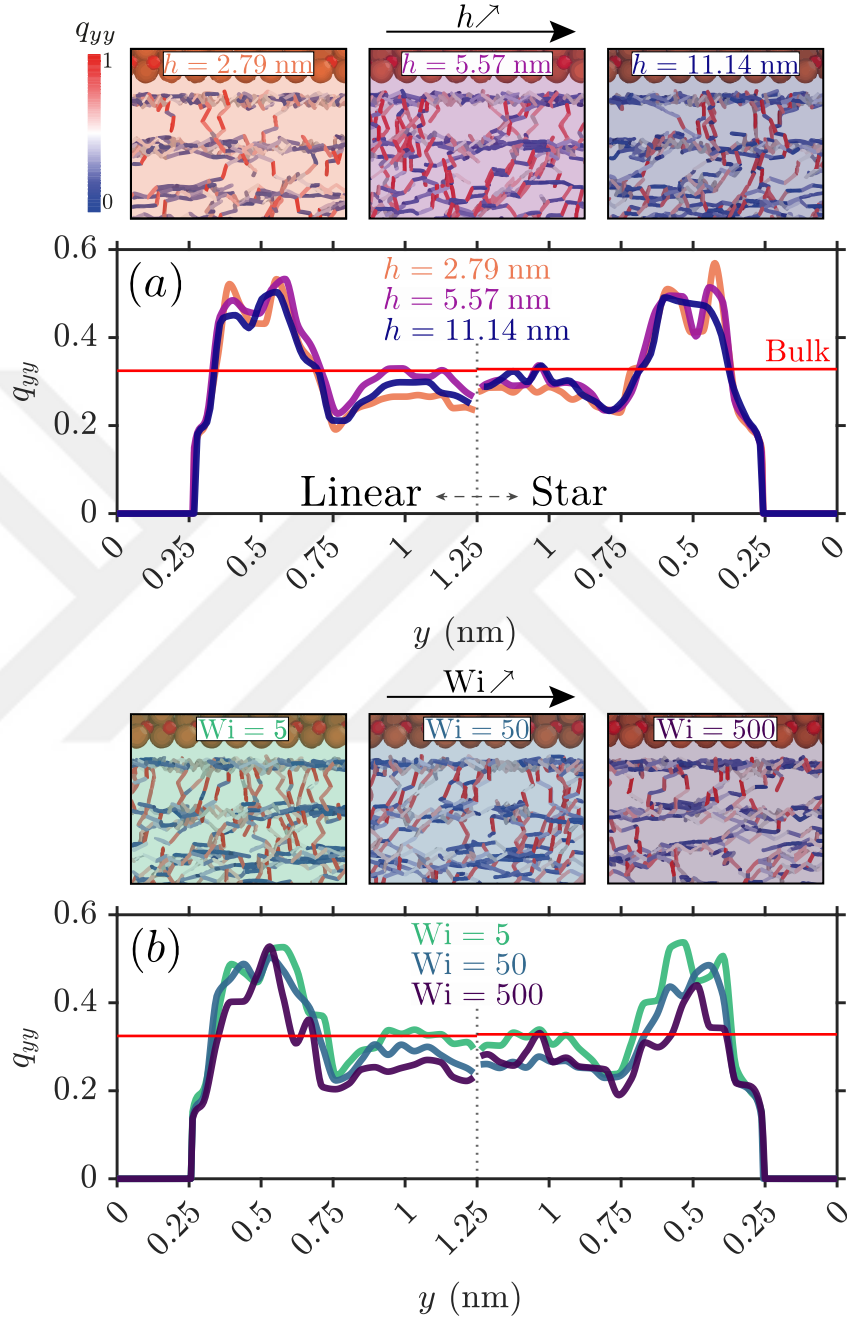


Figure 4.12: Local bond orientation, q_{yy} , (a) for different h at $Wi = 10$, and (b) for different Wi at $h = 5.57$ nm for linear (left) and star chains (right). The snapshots in (a-b) depict the near-surface bond alignment of the curves at a single time step. Simulations are of unaltered oligomer melts ($k_\theta = \epsilon$).

4.1.6 Role of Surface Attraction

The brush-like layer we observe in our simulations is due to the attractive nature of the wall surface. Next, we further investigate different surface attraction conditions that can affect the conformation of the near-surface chains. In Fig. 4.13, we artificially tune the strength of the attractive potential between the constituent atoms of the surfaces and the oligomer chains, $\varepsilon_{\text{surf}}$, to achieve surfaces with weaker (i.e., $\varepsilon_{\text{surf}} = 0.1\varepsilon_0, 0.5\varepsilon_0$) and stronger attraction (i.e., $\varepsilon_{\text{surf}} = 2\varepsilon_0, 4\varepsilon_0$). Note that ε_0 is the default value of the surface attraction strength [61] (see Table 4.1 for the sets of parameters used for modified surface attractions).

In Fig. 4.13(a), we show the normal stress differences as a function of the surface attraction strength $\varepsilon_{\text{surf}}$. As the surfaces become less attractive, normal stress differences vanish regardless of the surface separation. With decreasing surface attraction, we also observe a decrease in the number of vertically aligned (i.e., along the y -direction) bonds near the surfaces (Fig. 4.13(b)).

For weak surface-polymer attraction (i.e., $\varepsilon_{\text{surf}} < \varepsilon_0$), the chains near the surfaces are more aligned (q_{xx} increases while q_{yy} decreases) with the flow (i.e., x -direction), decreasing the near-surface peak of q_{yy} , resulting in a decline of the viscoelastic effects characterized by the normal stress differences (Fig. 4.13(a)). Conversely, an increase in $\varepsilon_{\text{surf}}$ leads to an increase in the near-surface peak of q_{yy} , and consequently, the anisotropy of the stress response and sign-reversal of the normal stress differences.

Both observations are coherent with our explanation of the mechanism behind the excess viscoelastic stress that is possibly controlled by the strength of the bond alignment (y -component) and its variation across the channel, in the case of oligomer melts. The number of chains that can be adsorbed into the surfaces is physically limited and eventually saturate with increasing surface attraction. This also creates a saturation in the viscoelasticity-induced effect observed in N_1 and N_2 for both star and linear oligomer chains. Notably, the topology of star chains allows multiple branches to be adsorbed into the surface and reduces the direct physical couplings between neighboring free chains. Consequently, the

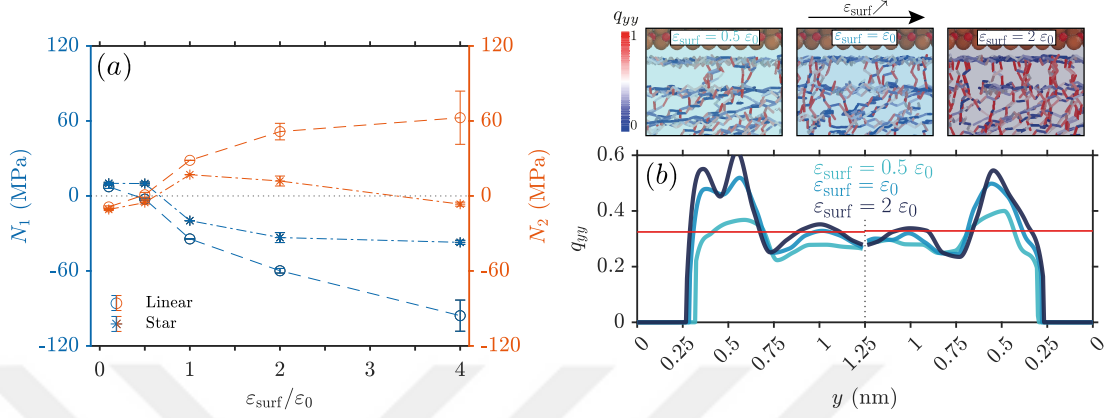


Figure 4.13: (a) Sign-reversion of the normal stress differences with increasing surface attraction. N_1 and N_2 for different surface attraction parameter sets ϵ_{surf} at $Wi = 10$ and $h = 5.57$ nm. (b) Local bond orientation, q_{yy} , for different ϵ_{surf} for linear (left) and star chains (right). The snapshots in (b) depict the near-surface bond alignment of the curves at a single time step. Simulations are of unaltered oligomer melts ($k_\theta = \epsilon$).

further increase in surface attraction leads to (i) disconnectivity between the molecular layers, (ii) nonuniformity in the density profile, and (iii) the emergence of vacancies along the channel. On the other hand, the linear chains preserve their inter-layer connectivity even for the highly attractive surface (i.e., $\epsilon_{\text{surf}} = 4\epsilon$), due to their relatively longer chain size and two terminal atoms, showing them to be less prone to saturation. Remarkably, inter-layer connectivity of oligomer chains (in addition to heterogeneity) may play an important role in governing the stress response at extreme confinements and become the driving factor of the sign-reversed normal stress differences and viscoelastic tension.

4.2 OPLS Force Field

The OPLS force field, known for its accuracy in liquid simulations [69, 82, 143, 149], allows for validation and extension of our findings, in particular for the positive-to-negative (negative-to-positive) transition of the first normal stress difference with increasing surface attraction.

4.2.1 Simulation Details

Here, we mainly replicate the scenario where we studied using the DREIDING force field consisting of unaltered linear chains sheared at $Wi = 10 - 50$ under a confinement level of $h = 5.57$ nm. The simulations are configured according to Ref. [73], conducted with the same thermostat settings ($T = 372$ K) and with the identical duration with the DREIDING model. Instead, the interatomic interactions are initialized in more detail: the terminal and the intermediate carbon atoms are treated differently within a chain, and long-range interactions are included with partial charges of atoms while ensuring the neutral structure of the melt and surfaces. For the long-range interactions, we use the Coulomb potential with the cut-off distance of $\sigma_{\text{long}} = 10\text{\AA}$ and particle-particle particle-mesh solver for K-Space with the accuracy of 10^{-5} . Due to the highly atom-specific parameterization of the OPLS model, we do not prefer tabulating the data (for charges and interaction parameters). Still, instead, we provide the default surface attraction energy associated with the surface atoms, $\varepsilon_{\text{surf}} = 0.04336$ eV⁴, and the cut-off distance of $\sigma_{\text{cut}} = 3\text{\AA}$. Further details about the corresponding parameterization are achievable from Ref. [73].

4.2.2 Role of Surface Attraction

While considering a short range of Wi and fixing the confinement level, we span a range of surface attraction energies, from $\varepsilon_{\text{surf}} = 0.25 - 4\varepsilon$ where ε corresponds to the unaltered attraction energy of the hematite surfaces. Note that the altered surface attraction energies other than $\varepsilon_{\text{surf}} = 1\varepsilon$ are only toy models and provide insights about the transition phenomena we observed with the DREIDING force field while not corresponding to a practical case of interest.

After equilibrium and before shear, we similarly observe the brush-like layer of chains due to attractive wall surfaces. In Fig. 4.14, we control the strength

⁴This corresponds to 1 kcal/mol, where the harmonic averaging is used for interatomic attraction energies, to be compared with the DREIDING force field.

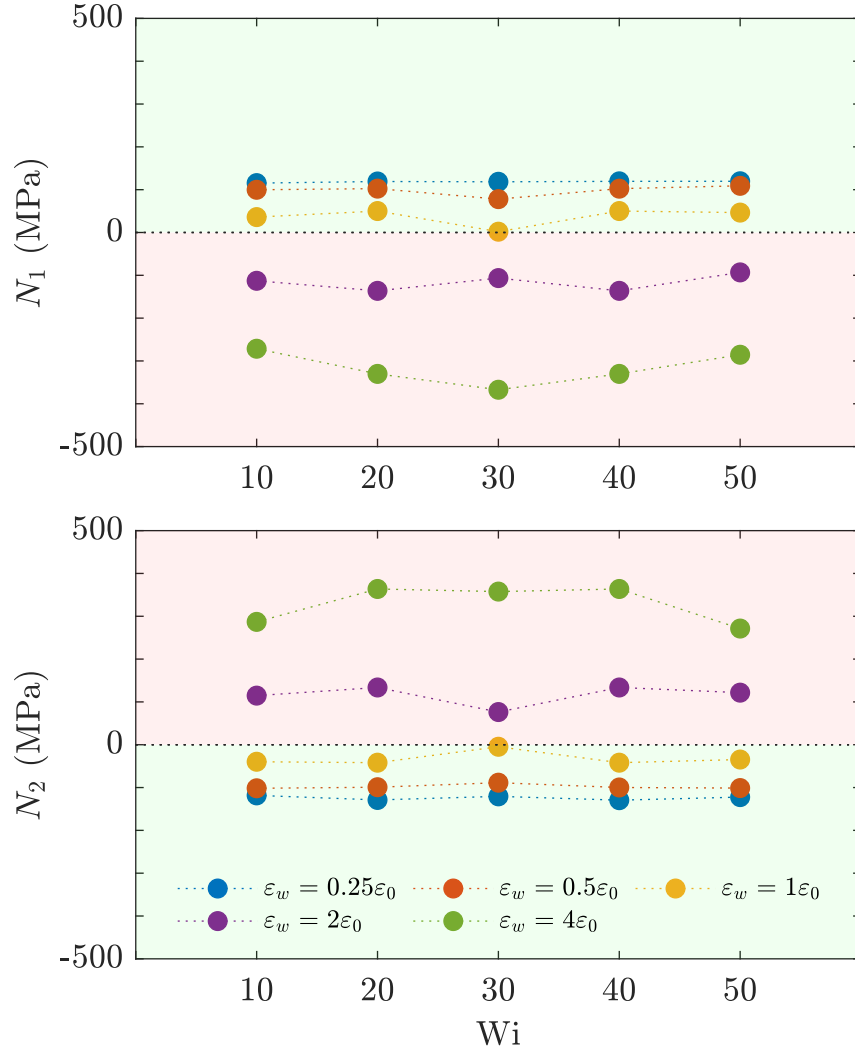


Figure 4.14: N_1 and N_2 for different surface attraction parameter sets (ϵ_{surf} , briefly denoted with ϵ_w in the legend) Green shaded areas indicate the theoretical expectation of $N_1 > 0$ and $N_2 < 0$, while red shaded areas highlight observations from this study that deviate from the theoretical prediction. Error bars are of the size of markers.

of the attractive potential between the constituent atoms of the surfaces and the oligomer chains artificially, $\varepsilon_{\text{surf}}$, to further achieve surfaces with various attraction energies (i.e., $\varepsilon_{\text{surf}} = 0.25\varepsilon_0, 0.5\varepsilon_0, 2\varepsilon_0, 4\varepsilon_0$).

In Fig. 4.13, we show the normal stress differences as a function of the surface attraction strength $\varepsilon_{\text{surf}}$. As the surfaces become more attractive, normal stress differences become more significant and coherent with the DREIDING case, while the magnitude of the normal stress differences exceeds 100 MPa (in comparison with 4.13(a)). A visual inspection also yields an observation of an increase in the number of vertically aligned (i.e., along the y -direction) bonds near the surfaces with increasing surface-polymer attraction. Notably, we do not observe the positive-to-negative (negative-to-positive) transition of N_1 (N_2) within the studies Wi interval, unlike the DREIDING counterpart (see Fig. 4.6(a,c)).

4.3 Kremer-Grest Model

We employ the Kremer-Grest (KG) bead-spring model to investigate the rheological properties of confined and bulk polymer melts under shear. This coarse-grained representation captures the essential physics of polymeric systems while allowing for the simulation of larger systems and longer time scales compared to atomistic models. In this section, we cover the simulation methodology, including the model parameters, system setup, and shearing protocols for both confined and bulk systems.

4.3.1 Simulation Details

The KG model represents each Kuhn segment⁵ of a polymer chain as a bead, with interactions governed by carefully chosen potentials. The simulations are conducted in a unitless setting, also known as LJ units in LAMMPS, without loss of generality. Non-bonded interactions between beads are described by the

⁵See Section 3.1.3 for the definition of Kuhn size.

truncated and shifted Lennard-Jones (LJ) potential 3.39 [47]:

$$U_{\text{LJ}}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + C, & r \leq r_c \\ 0, & r > r_c \end{cases} \quad (4.4)$$

where ϵ is the depth of the potential well, σ is the bead diameter, r is the inter-bead distance, and $r_c = 2.5\sigma$ is the cutoff radius. The constant C ensures continuity⁶ of the potential at $r = r_c$. Bonded interactions are modeled using the finitely extensible nonlinear elastic (FENE) potential [46]:

$$U_{\text{FENE}}(r) = -\frac{1}{2}kR_0^2 \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right] \quad (4.5)$$

with spring constant $k = 30\epsilon/\sigma^2$ and maximum extension $R_0 = 1.5\sigma$. This combination of LJ and FENE potentials does not let chains pass through one another, thereby preventing unphysical bond crossing and chain breaking, ensuring the topological integrity of the polymer chains.

As we use reduced LJ units throughout our simulations, we have ϵ , σ , and the bead mass m set to unity. The integration time step is $\Delta t = 0.002\tau$, where $\tau = \sigma\sqrt{m/\epsilon}$ is the LJ time unit. All simulations are performed at a constant temperature of $T = 1.0\epsilon/k_B$, where k_B is the Boltzmann constant, maintained using a Langevin thermostat with a damping parameter of $100\Delta t$ [63, 70].

To investigate the effects of chain length and confinement on polymer melt behavior, we systematically vary two key parameters: the chain length N and the confinement levels H . We consider chain lengths of $N = 10, 20, 40, 80$, and 160 beads per chain, spanning from oligomers to moderately long polymers. For confined systems, the confinement widths range from strongly confined to nearly bulk-like conditions: $H = 5\sigma, 6\sigma, 7\sigma, 8\sigma, 9\sigma, 10\sigma, 20\sigma$. The number of chains in each simulation is adjusted to maintain a constant monomer density of $\rho = 0.85\sigma^{-3}$, which is commonly used for polymer melts in the KG model [70].

⁶Without this shift, there would be a discontinuity in the potential energy at r_c , which could lead to numerical instabilities in molecular dynamics simulations. The constant C in the truncated and shifted Lennard-Jones potential is given by $C = -4\epsilon \left[\left(\frac{\sigma}{r_c} \right)^{12} - \left(\frac{\sigma}{r_c} \right)^6 \right]$, where r_c is the cutoff distance. For our cutoff $r_c = 2.5\sigma$, this constant becomes $C \approx 0.0163\epsilon$. We further note that while this modification affects the total potential energy of the system, it has no effect on force calculations.

In confined systems, smooth walls are introduced in the z -direction. Wall-bead interactions are described by the standard 12-6 Lennard-Jones potential, similar to the bead-bead interactions but with a different interaction strength:

$$U_{\text{wall}}(z) = 4\epsilon_w \left[\left(\frac{\sigma}{z} \right)^{12} - \left(\frac{\sigma}{z} \right)^6 \right] \quad (4.6)$$

where z is the distance between the bead and the wall, and ϵ_w is the wall attraction strength. We explore a range of wall attractions: $\epsilon_w = 0.4\epsilon, 0.65\epsilon, 1.0\epsilon, 1.6\epsilon, 2.5\epsilon, 4.0\epsilon$, allowing us to control surface-chain and chain-chain interactions, spanning from weakly to strongly attractive surfaces. This potential is also truncated and shifted at a cutoff distance, typically $r_c = 2.5\sigma$, consistent with the bead-bead interactions.

Our equilibration protocol consists of several stages designed to ensure proper relaxation of the polymer melt structure. We begin with an initial chain placement at low density, followed by a soft repulsion phase to remove overlaps. We then gradually introduce full LJ interactions and compress the system to the target density. For confined systems, we introduce the walls and adjust the film thickness to achieve the desired confinement. A final equilibration at constant volume and temperature is performed for both confined and bulk systems. The duration of these equilibration runs is tailored to the chain length and confinement conditions, typically ranging from 10^6 to 10^7 time steps, to ensure adequate relaxation of chain conformations.

For shearing confined systems, we employ a moving wall protocol, in the same way as the atomistic models. The top and bottom walls are moved in opposite directions along the x -axis with constant velocities, creating a linear velocity profile across the film thickness. The wall velocities are set to achieve the desired shear rate $\dot{\gamma}$, which is varied over several orders of magnitude, typically from $10^{-5}\tau^{-1}$ to $10^{-1}\tau^{-1}$. This approach allows us to directly simulate the effect of wall-induced shear on the confined polymer melt.

For the bulk system, we apply steady shear using the SLLOD equations of motion coupled with Lees-Edwards periodic boundary conditions in accordance with the DREIDING counterpart. Simulating the shear flow in a bulk polymer

melt without the presence of physical walls enables us to obtain a reference state for comparison with the confined systems.

Temperature control during shear is maintained using a Langevin thermostat applied only in the non-flow directions to avoid artifacts in the velocity profile. Shear simulations for both confined and bulk systems are run for a total strain of $\gamma = 100$, ensuring that the system reaches a steady state [63], then followed by a data gathering run with identical shear settings for $\tau_{\text{sim}} = 2 \times 10^7 \tau$.

Throughout our simulations, we collect comprehensive data on stress tensor components, chain conformations, and bead positions. These data form the basis for our subsequent analyses of the stress tensor, the role of surface attraction, and tumbling dynamics, which will be discussed in detail in the following sections. By systematically varying chain length, confinement width, wall attraction strength, and shear rate, we aim to develop a comprehensive understanding of confined and bulk polymer melt rheology across a wide range of conditions, identifying scaling relationships, universal behaviors, and novel phenomena arising from the connection between molecular structure, confinement, and flow.

4.3.2 Stress Tensor

Influenced by our previous analysis with the DREIDING force field, we investigate the viscoelastic behavior and normal stress differences for the Kremer-Grest (KG) model as well. Here, we present our results for viscosity in Sec. 4.3.2.1 and viscoelastic response in Sec. 4.3.2.2, which are later complemented with the analysis of tumbling behavior in Sec. 4.3.3. Our analyses, including viscosity, first and second normal stress differences, viscoelastic load in the y -direction, and tumbling, are made on shear rate, film thickness, and surface attraction⁷ for varying polymerization degrees.

⁷Here, we combine the surface attraction into the same picture with shear rate and film thickness in the context of the viscoelastic response.

4.3.2.1 Viscosity

To characterize the shear-dependent viscosity of our polymer melts, we calculate the viscosity η as a function of shear rate $\dot{\gamma}$, where $\eta \equiv \sigma_{xy}/\dot{\gamma}$. The observed behavior of viscosity for both bulk and confined systems exhibits shear-thinning characteristics, consistent with previous studies on various polymer systems [54]. In the bulk state, we observe a clear shear-thinning behavior for all chain lengths ($N = 10$ to 160). As the shear rate increases, the viscosity decreases, following a power-law relationship $\eta \sim \dot{\gamma}^{-\alpha}$, where α is observed to depend on the chain length. Longer chains ($N = 80, 160$) show a more enhanced shear-thinning effect compared to shorter chains ($N = 10, 20$), which can be attributed to the increased chain entanglement (and corresponding disentanglement under shear).

Under confinement, the viscosity shows a significant increase compared to the bulk state for all chain lengths. This enhancement in viscosity is more visible for stronger confinements (smaller film thicknesses). For instance, even at a film thickness of $h \sim 40\sigma$, the viscosity is notably higher than in the bulk, and it further increases as the film thickness decreases to $h \sim 10\sigma$. This behavior can be attributed to the layering of polymer chains near the walls and the restricted chain mobility in confined spaces [150]. The effect of confinement on viscosity is also chain-length dependent. Longer chains ($N = 80, 160$) show a more significant increase in viscosity under confinement compared to shorter chains ($N = 10, 20$). This trend is likely due to the greater impact of confinement on the conformational freedom of longer chains, leading to more pronounced viscosity enhancement.

Interestingly, the relationship between viscosity and surface attraction strength ($\varepsilon_{\text{wall}}$) reveals a non-monotonic behavior. As the surface attraction increases from 0.5ε to 4ε , we initially observe a slight increase in viscosity, followed by a decrease for stronger attractions. This non-monotonic trend is most evident for intermediate chain lengths ($N = 20, 40, 80$). The initial increase in viscosity with surface attraction can be attributed to stronger adsorption of polymer segments to the wall, reducing chain mobility. However, at very high surface attractions, the formation of a strongly adsorbed layer may lead to slip effects, potentially

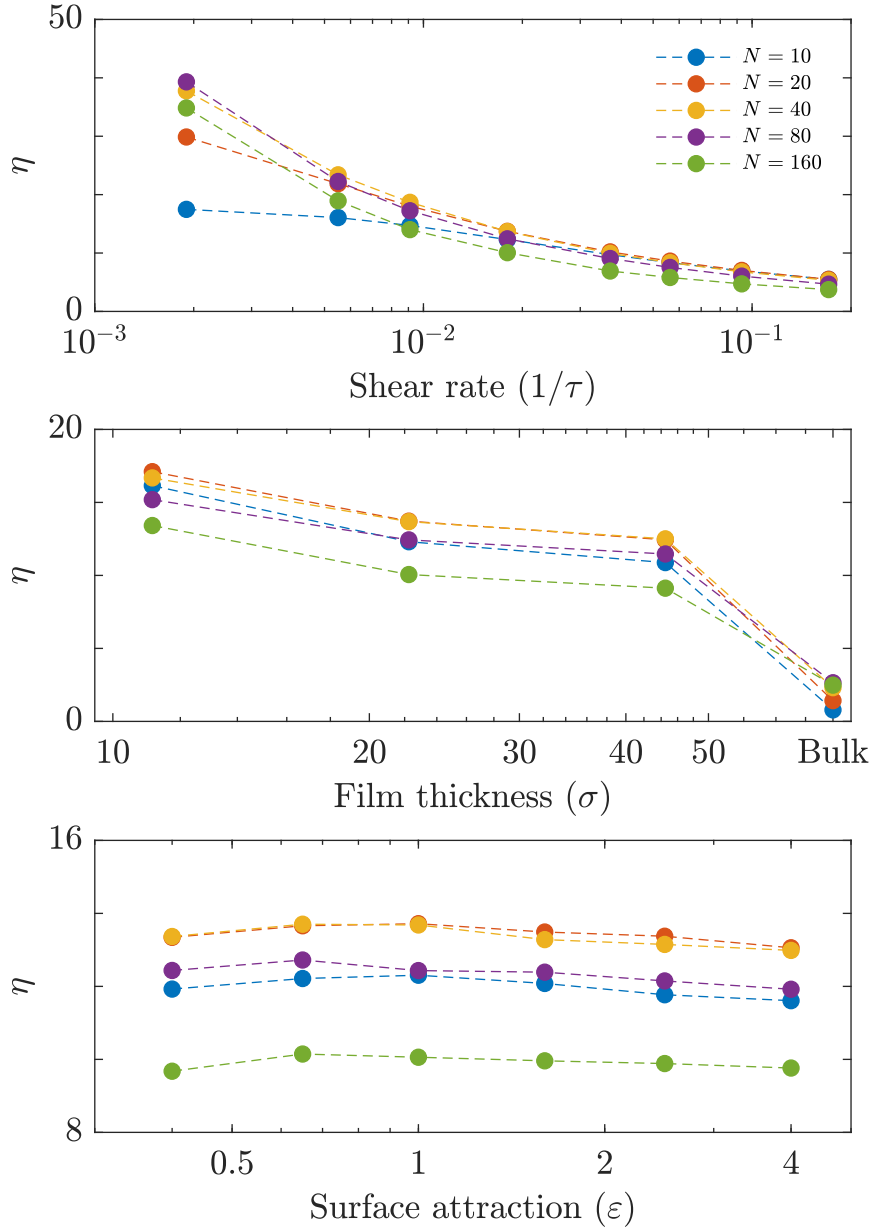


Figure 4.15: Viscosity (η) behavior for the KG model as functions of shear rate (left column; with $\varepsilon_{\text{surf}} = 1\varepsilon$, $h = 22.23\sigma$), film thickness (middle column; with $\varepsilon_{\text{surf}} = 1\varepsilon$, $\dot{\gamma} = 0.018\tau^{-1}$), and surface attraction (right column; with $h = 22.23\sigma$, $\dot{\gamma} = 0.018\tau^{-1}$), illustrating the non-monotonic relationship between viscosity and surface interaction.. Different colors represent various chain lengths as indicated in the legend.

explaining the subsequent decrease in viscosity. The shear-thinning behavior persists under confinement and varying surface attractions, but the onset and degree of shear-thinning are influenced by these factors. Generally, we observe more confined systems and those with moderate surface attractions to exhibit shear-thinning at lower shear rates compared to bulk or weakly attractive systems.

4.3.2.2 Viscoelasticity and Normal Stress Differences

Figure 4.16 demonstrates the viscoelastic behavior and normal stress differences for confined polymer melts under shear using the Kremer-Grest (KG) model. Just like the DREIDING case, we analyze the first normal stress difference (N_1), second normal stress difference (N_2), and viscoelastic stress component opposing the streamwise direction ($\sigma_{yy}^{(VE)}$) as functions of shear rate, film thickness, and surface attraction.

The first column of Fig. 4.16 illustrates the shear rate dependence. For low shear rates, N_1 remains relatively constant and positive for all chain lengths. As the shear rate increases, this increase in N_1 becomes sharper, particularly for longer chains (e.g., $N = 160$). For longer chains, this behavior differs from the DREIDING model, where N_1 was initially negative, which is only the case for $N = 10$. On the other hand, N_2 exhibits non-monotonic behavior, starting positive at low shear rates, then decreasing and becoming negative at higher shear rates. Together with $\sigma_{yy}^{(VE)}$, which follows a similar trend to N_2 , transitioning from positive to negative values with increasing shear rate, these behavior is in alignment with our observations from the DREIDING model.

The effect of film thickness is shown in the second column. As the film thickness increases towards bulk, N_1 decreases significantly, eventually becoming negative. This trend also aligns with the observations for the DREIDING model, suggesting a consistent confinement effect across different modeling schemes (i.e., atomistic and coarse-grained). N_2 initially decreases in magnitude with increasing film thickness, and then changes sign with a slight increase in bulk. For shorter chains ($N = 10, 20$) $\sigma_{yy}^{(VE)}$ show a positive-to-negative transition as the film

thickness increases, followed by a sharp decrease for bulk. Here, we note that the viscoelastic tension is only present if the chains are short, which verifies why we have observed such phenomena with $C_{25}H_{52}$ oligomers in the DREIDING model.

The third column presents the influence of surface attraction. We observe that N_1 decreases with surface attraction until the surface attraction becomes too severe, which is also coherent with our observation in the DREIDING model (see Fig. 4.13). On the other hand, N_2 shows a significant increase, becoming strongly positive at higher surface attractions, again followed by a small decrease for $\varepsilon_{\text{surf}} = 4\varepsilon$. More importantly, $\sigma_{yy}^{(\text{VE})}$ transitions from negative to positive values as surface attraction increases for most of the chain lengths (except $N = 160$), meaning that the transition between viscoelastic tension and compression can be modulated with surface attraction and the polymerization degree only leads to a shift in this response.

4.3.3 Tumbling

To analyze the tumbling dynamics of polymer chains, we implement two complementary algorithms, given in Appendix B. The first algorithm 1, based on the method described by Dalal *et al.* [151], focuses on shear-induced tumbling. Figures 4.17 and 4.18 illustrate the concept of shear-induced tumbling in the shear plane.

Figure 4.17 shows how a polymer chain is divided into different orientation zones as it undergoes shear-induced tumbling. The shear direction is indicated, and the chain's rotation through these zones constitutes a tumbling event.

Figure 4.18 demonstrates the various stages of a shear-induced tumbling event, illustrating how the chain's orientation changes over time in the shear plane.

While these figures focus on shear-induced tumbling in one plane, our second algorithm (2) takes a more comprehensive approach. This method enables us to capture all tumbling events, including those induced by thermal motion and

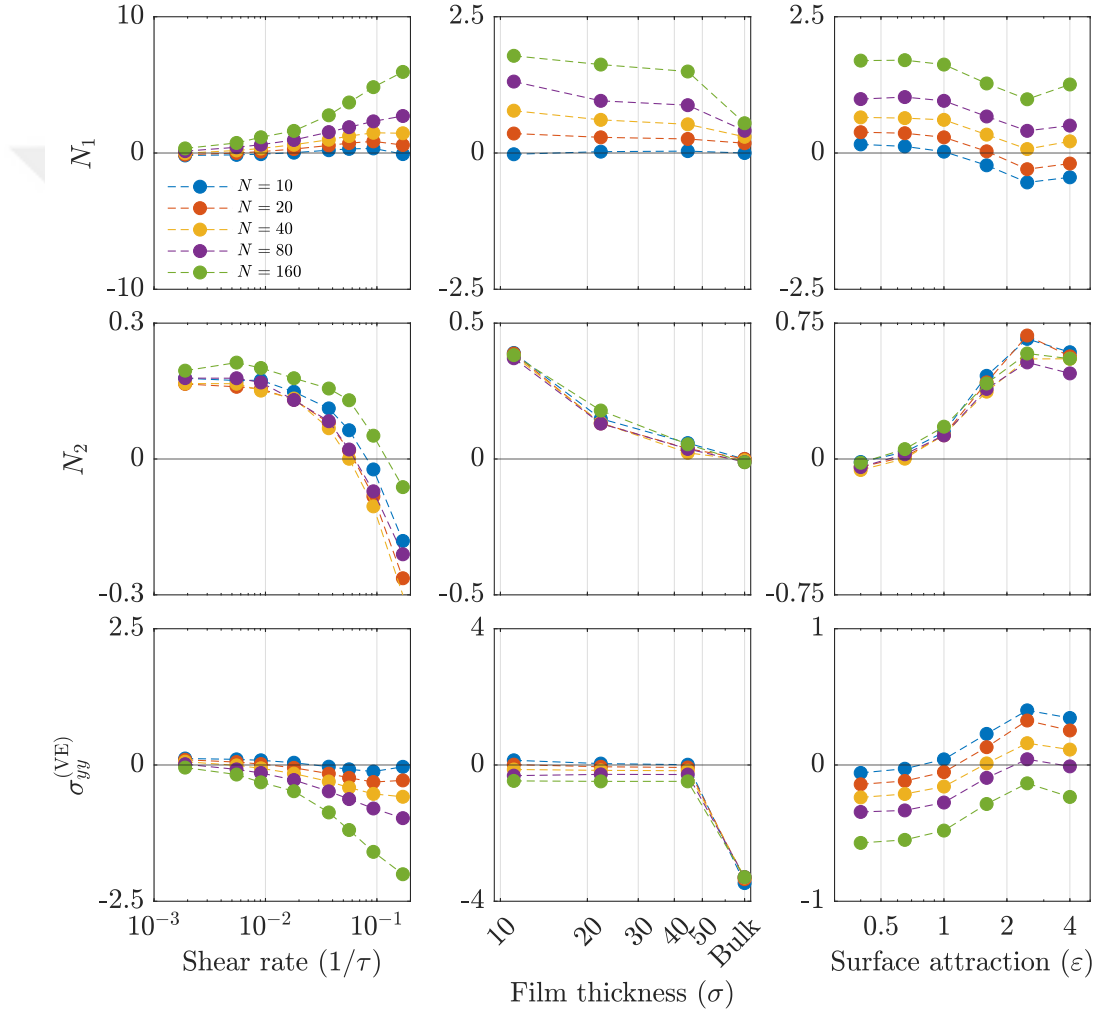


Figure 4.16: Normal stress differences (N_1 , N_2) and viscoelastic stress component $\sigma_{yy}^{(\text{VE})}$ for the KG model as functions of shear rate (left column; with $\varepsilon_{\text{surf}} = 1\varepsilon$, $h = 22.23\sigma$), film thickness (middle column; with $\varepsilon_{\text{surf}} = 1\varepsilon$, $\dot{\gamma} = 0.018\tau^{-1}$), and surface attraction (right column; with $h = 22.23\sigma$, $\dot{\gamma} = 0.018\tau^{-1}$). Different colors represent various chain lengths as indicated in the legend.

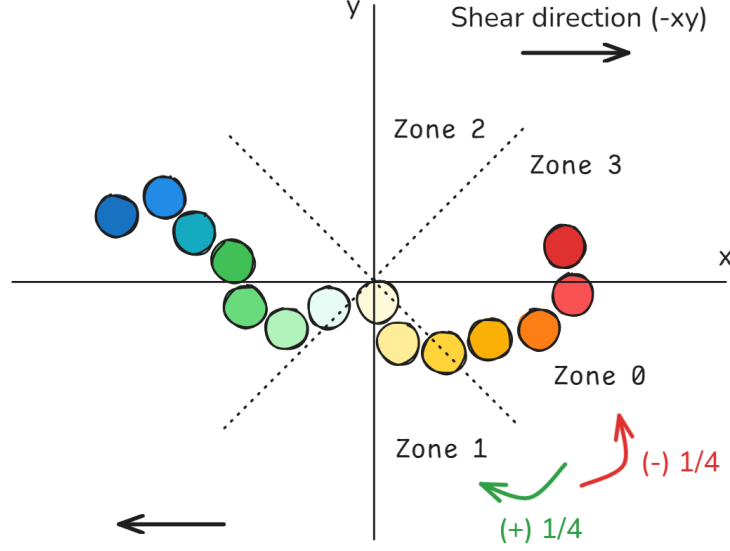


Figure 4.17: Illustration of shear-induced tumbling of a polymer chain. The chain rotates as it experiences shear flow, with different zones indicating its orientation relative to the flow direction.

tumbling in reverse directions, across each plane (xy , yz , and xz).

Using these algorithms, we analyze the tumbling dynamics across our range of chain lengths ($N = 10, 20, 40, 80, 160$), confinement widths ($h = 11.1\sigma$ to 44.5σ , also in bulk), wall attraction strengths ($\varepsilon_w = 0.4\varepsilon, 0.65\varepsilon, 1.0\varepsilon, 1.6\varepsilon, 2.5\varepsilon, 4.0\varepsilon$), and shear rates ($10^{-3}\tau^{-1}$ to $10^{-1}\tau^{-1}$). This comprehensive analysis allows us to investigate how confinement and surface interactions affect the tumbling behavior of polymer chains under shear and to compare these results with the bulk system behavior.

Figure 4.19 shows the relationship between the tumbling frequency⁸ and shear rate for various chain lengths. We observe that the tumbling frequency increases

⁸Instead of explicitly denoting the tumbling frequency, we multiply this number with the simulation duration of the data gathering run (τ_{sim}). While this change actually result in the number of tumbling events, which is plotted in the following figures for different polymerization degrees, we recall that τ_{sim} is constant and equal to each other for all simulations. For this reason, we refer to it as the tumbling frequency behavior instead of tumbling count, as by it, we provide more information at once.

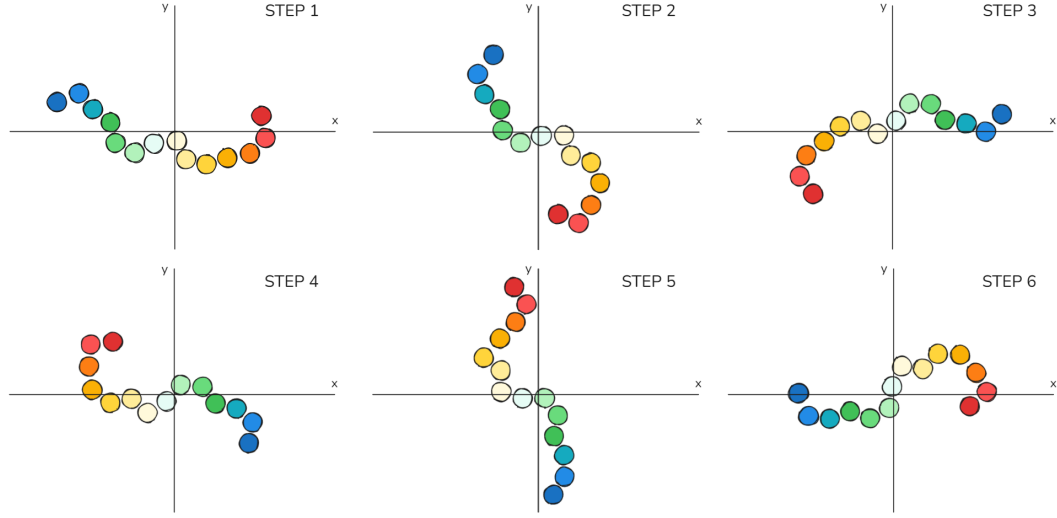


Figure 4.18: Steps of a shear-induced tumbling event. Each step represents a different orientation of the polymer chain during the tumbling process in the shear plane.

with the shear rate for all chain lengths, following a power law with an exponent of approximately $2/3$, which is in accordance with the findings of Chen *et al.* [152]. In general, this relationship holds across the entire range of shear rates studied, from $10^{-3}\tau^{-1}$ to $10^{-1}\tau^{-1}$, while some minor deviations start to be observable for long chains at lower shear rates. Longer chains exhibit lower tumbling frequencies compared to shorter chains at the same shear rate, which can be possibly attributed to their increased resistance to rotation due to higher moments of inertia.

Figure 4.20 presents the cumulative tumbling frequencies for different planes (xy , xz , and yz) as a function of polymerization degree (N) for three confinement scenarios: $h = 11.1\sigma$, $h = 44.5\sigma$, and bulk. The graph illustrates how confinement affects tumbling behavior across different planes. In all cases, the tumbling frequency decreases with increasing chain length. However, the relative contributions of tumbling in different planes vary with confinement. In the most confined system ($h = 11.1\sigma$), tumbling in the yz plane (represented by the green area) dominates, followed by xy (blue area) and xz (yellow area). As confinement is relaxed (h increases), the difference in tumbling frequencies between planes becomes less pronounced, indicating a more isotropic tumbling behavior

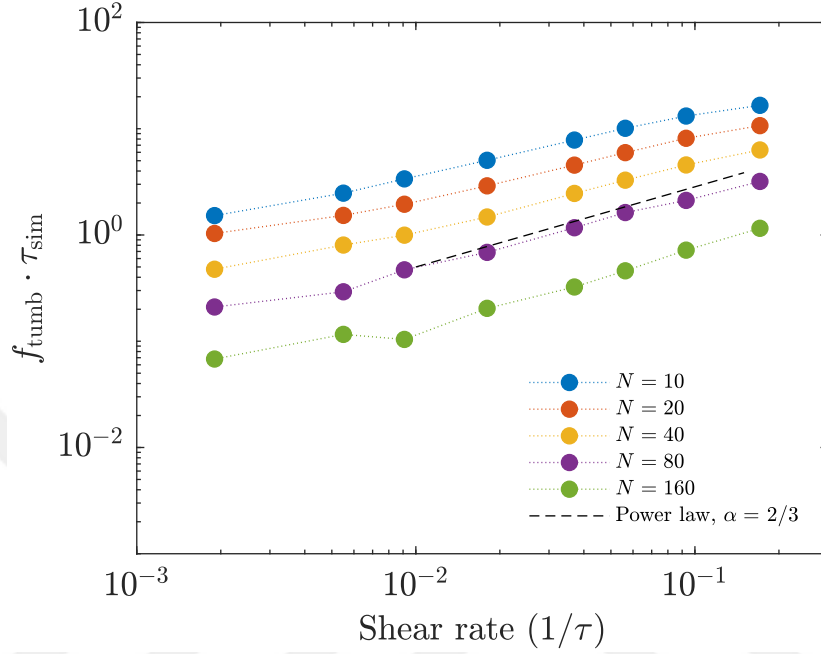


Figure 4.19: Tumbling frequency ($f_{\text{tumb}} \cdot \tau_{\text{sim}}$) as a function of shear rate (τ^{-1}) for polymer chains of different lengths (N). The dashed line represents a power law with exponent $\alpha = 2/3$, in agreement with Chen *et al.* [152]. τ_{sim} is the total simulation duration for the data gathering section.

in bulky systems. The shear-induced tumbling, on the other hand, is observed to be mostly influenced by the existence of confining walls.

Figure 4.21 demonstrates the effect of surface attraction on tumbling frequencies for different chain lengths ($N = 10, 40$, and 160) and planes. The x-axis represents the surface attraction strength (ε), ranging from 0.5 to 4 . For shorter chains ($N = 10$), surface attraction has minimal impact on tumbling frequencies across all planes, including shear-induced motions. As chain length increases, we observe a slight increase in tumbling frequencies with increasing surface attraction, particularly for $N = 160$. This effect is most pronounced in the yz -plane (green area), suggesting that stronger surface interactions may promote tumbling events perpendicular to the confining walls. The shear-induced tumbling

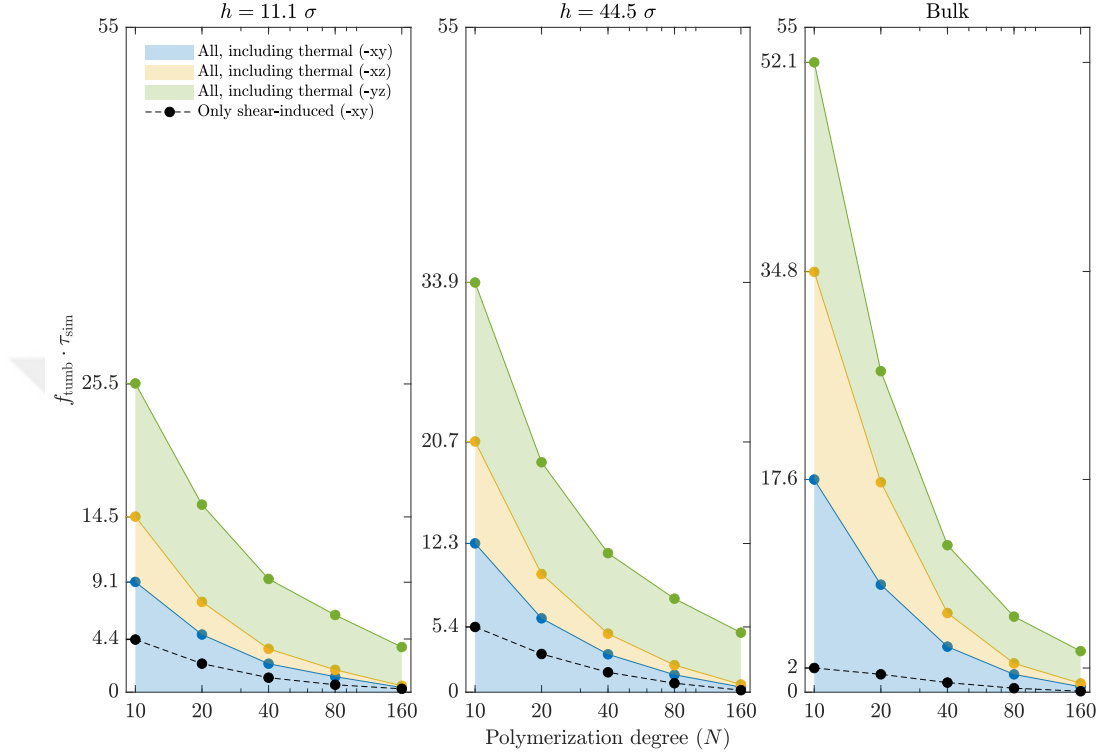


Figure 4.20: Cumulative tumbling frequencies ($f_{\text{tumb}} \cdot \tau_{\text{sim}}$) for different planes (xy , xz , and yz) as a function of polymerization degree (N) for three confinement scenarios: $h = 11.1\sigma$, $h = 44.5\sigma$, and bulk. The shaded areas represent the cumulative contributions from each plane, with xy (blue), xz (yellow), and yz (green). The dashed line shows the shear-induced tumbling frequency in the xz plane. τ_{sim} is the total simulation duration for the data gathering section.

The all-plane tumbling frequency data provides insights into the three-dimensional motion of the chains, allowing us to distinguish between shear-induced and thermal motion-induced tumbling events. This, along with the shear-induced tumbling frequencies, stress tensor components, and chain conformations, offers a potential relationship between molecular-level chain motion and macroscopic rheological properties in both confined and bulk polymer melts, as well as the impact of thermal fluctuations on chain dynamics.

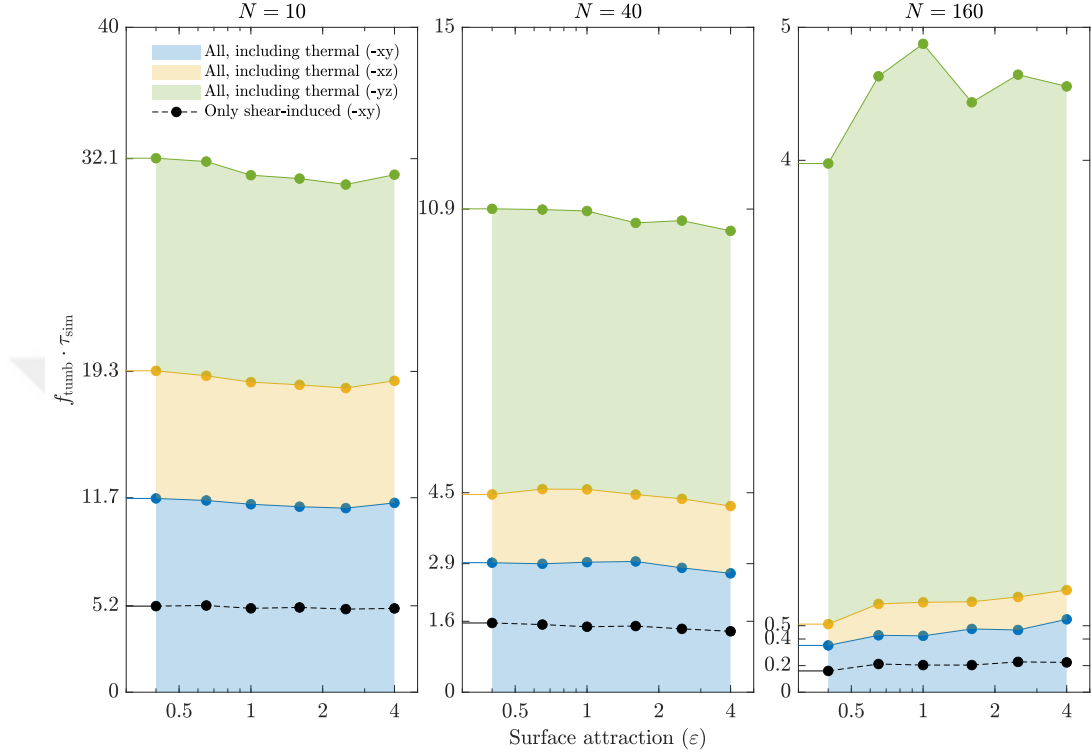


Figure 4.21: Effect of surface attraction (ε) on tumbling frequencies ($f_{\text{tumb}} \cdot \tau_{\text{sim}}$) for different chain lengths ($N = 10, 40$, and 160) and planes. The shaded areas represent the cumulative contributions from each plane, with xy (blue), xz (yellow), and yz (green). The dashed line shows the shear-induced tumbling frequency in the xy -plane. τ_{sim} is the total simulation duration for the data gathering section.

4.4 Viscoelastic Response over Scales

With these results, we basically reveal specific relationships between chain length, confinement, and surface interactions in determining the viscoelastic properties of oligomer melts. The sign changes in normal stress differences and viscoelastic stress component indicate a significant⁹ shift in the stress response mechanism as confinement increases or surface attraction strengthens. For instance, the transition of N_1 from positive to negative values with increasing film thickness suggests a reversal in the direction of chain stretching under confinement. Similarly, the

⁹This is unreported in the literature until our study, up to our knowledge.

strong positive N_2 values at high surface attractions point to enhanced chain-surface interactions that alter the stress distribution within the confined melt. While our OPLS simulations verify this observation showing that they are not numerical artefact of our DREIDING simulations, our findings in coarse-grained simulations provide further insights into the relationship between the molecular behavior (e.g., tumbling) of polymer chains under confinement and the rheological response, which, in general, appears to be coherent with our observations for both of these atomistic models.

Chapter 5

Conclusions and Future Work

There's a point, around the age of twenty, when you have to choose whether to be like everybody else the rest of your life, or to make a virtue of your peculiarities.

- Ursula K. Le Guin, *The Dispossessed: An Ambiguous Utopia*

To summarize, our all-atom simulations, using both the DREIDING and OPLS force fields, and coarse-grained simulations, using the Kremer-Grest model, demonstrated unexpected, sign-reversed normal stress differences, namely N_1 and N_2 , together with the emergence of a viscoelastic tension and compression as the confinement dimension approached that of the confined oligomer chains. We observed a peculiar orientation of the near-surface chains, suggesting that the chains near the surface are responsible for the elastic force exerted on the surface walls. This effect decayed as the chains became more aligned with the flow at higher shear rates (i.e., $Wi \gg 1$) or if the surface affinity toward chains decreased. With our simulations with the DREIDING force field, we noted that an excess tension emerged within this viscoelastic layer, in which the chains were vertically aligned, which increased the load-carrying capacity of the confined melt, regardless of the degree of chain rigidity. Instead, we revealed the dependence of the relaxation

time on the chain rigidity. With the OPLS force field, we verified that these surface attraction dominated effects in the rheological response with more detailed surface and chain models.

As our atomistic study was limited to the melts of (low molecular weight) linear and star¹ oligomer chains confined with rigid iron-oxide walls, the expectation was that the effects should have been apparent for any surface that can adsorb chains (with similar molecular weight and functionality) strongly enough [140, 149, 153, 154, 155, 156, 157]. Our results from coarse-grained simulations not only verified this expectation but also showed the decay of this effect for longer chain lengths and offered a possible connection between the rheological properties and the tumbling of the chains. While we employed commonly used the DREIDING [76, 77, 158, 159, 160, 161, 162, 163, 164] and OPLS [69, 82, 143, 149] force fields, other atomistic interaction sets, and thermostat algorithms, can provide more realistic descriptions of chain flexibility and modify (i) the molecular concentrations, (ii) the chain conformation, and (iii) both the stress and velocity profiles. On the other hand, the use of other coarse-graining methods, in addition to commonly used Kremer-Grest [62, 63, 70, 71, 79, 80, 85, 88, 165, 166, 167] model, or use of Kremer-Grest model for various systems under different confinement scenarios can lead to better generalization of our results. In principle, we expect $N_1 < 0$ and $N_2 > 0$ (together with $\sigma_{yy}^{(VE)} > 0$) to be apparent even in the any type of coarse-grained simulations of similar oligomer chains (e.g., short alkanes) since effects we observe are dependent on the chain-surface attraction strength (Fig. 4.13) [82, 168, 169], not the strength of the bending potential (Fig. 4.6). Whether our results can be observable in polymeric fluids consisting of longer chains, with more complex polymer topologies, under higher pressures or different surface roughness conditions [134, 166, 170] could be the subject of future studies.

¹Only for the DREIDING model.

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Appendix A

Effect of Cut-off Radius on Bond-orientation Tensor

Figure A.1 demonstrates the effect of different cut-off radii on the bond-orientation tensor (q_{yy}). The study primarily used $r_c = 9.85\text{\AA}$, while $r_c = 20\text{\AA}$ showed no significant change in the results. This observation supports the use of the smaller cut-off radius ($r_c = 9.85\text{\AA}$) for computational efficiency without compromising the accuracy of our analysis.

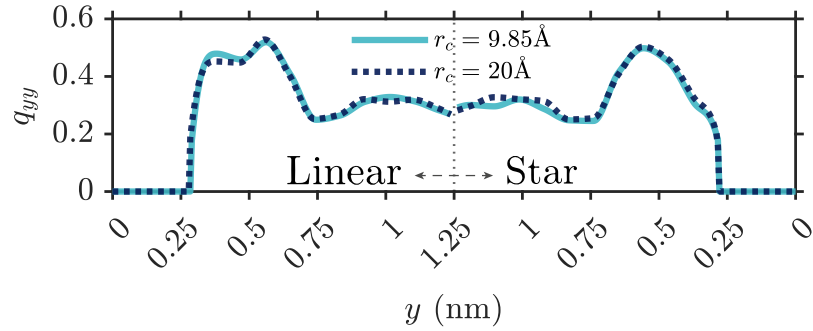


Figure A.1: Comparison of bond-orientation tensor component q_{yy} for cut-off radii $r_c = 9.85\text{\AA}$ and $r_c = 20\text{\AA}$. Parameters: surface interaction strength $\varepsilon_{\text{surf}} = \varepsilon_0$, Weissenberg number $Wi = 10$, and film thickness $h = 5.57\text{ nm}$.

Appendix B

Pseudocodes for Tumbling Frequency Calculation

Algorithm 1 Shear-Induced Tumbling Frequency Calculation

- 1: Calculate time-averaged positive (θ_{pos}) and negative (θ_{neg}) orientation angles in xy-plane
 - 2: Define zones: 0: $[0, \theta_{\text{neg}})$, 1: $[\theta_{\text{neg}}, \pi/2)$, 2: $[\pi/2, \theta_{\text{pos}})$, 3: $[\theta_{\text{pos}}, 0)$
 - 3: Initialize tumble count = 0
 - 4: **for** each time step **do**
 - 5: **for** each molecule **do**
 - 6: **if** clockwise zone crossing **then**
 - 7: tumble_{per-molecule} count + = 0.25
 - 8: **else if** counterclockwise zone crossing **then**
 - 9: tumble_{per-molecule} count - = 0.25
 - 10: **end if**
 - 11: **end for**
 - 12: **end for**
 - 13: tumble_{all} count = ensemble average of tumble_{per-molecule}
 - 14: shear-induced tumbling frequency (f_{tumble}) = tumble_{all} count / total simulation duration
-

Algorithm 2 All-Plane Tumbling Frequency Calculation

```
1: Initialize tumble counts: countxy = countyz = countxz = 0
2: for each time step do
3:   for each molecule do
4:     for each plane (xy, yz, xz) do
5:       Calculate angle  $\theta$  of end-to-end vector projection in plane
6:       if  $\theta$  crosses 0 or  $\pm\pi$  then
7:         Increment corresponding plane's tumbleper-molecule count
8:       end if
9:     end for
10:   end for
11: end for
12: Calculate tumbling frequencies for each plane:
13:   tumbleall count = ensemble average of tumbleper-molecule
14:   frequency ( $f_{\text{tumble}}$ ) = tumbleall count / total simulation duration
15:  $f_{\text{tumble,xy}} = \text{tumble}_{\text{all,xy}} \text{ count} / \text{total simulation time}$ 
16:  $f_{\text{tumble,yz}} = \text{tumble}_{\text{all,yz}} \text{ count} / \text{total simulation time}$ 
17:  $f_{\text{tumble,xz}} = \text{tumble}_{\text{all,xz}} \text{ count} / \text{total simulation time}$ 
```
