Event-driven Brownian dynamics simulations of two-dimensional fluids far from equilibrium

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1. Introduction

The nature of the glass is a fascinating and intensely debated field in Statistical Physics and Materials Science. While a glass former structurally resembles a liquid, the slow dynamics and rigidity occurring at high densities basically renders it a solid. Under approach of the transition point of a melt, highly cooperative structural processes emerge and provoke a drastic increase in viscosity and relaxation times. In this context dense colloidal suspensions, solid particles suspended in a liquid, represent popular model systems to study highly viscous liquids and amorphous solids, lacking any long range order. The unique flow properties of such materials are astonishing and useful at the same time, as many everyday objects like ink, paint, cosmetics, but also peanut butter, milk and blood represent colloidal suspensions. Further dense dispersions are important for a wide range of other technological applications and industrial processes, such as liquid and mineral purification or oil recovery and processing [1, 2].

This work investigates a system made of hard disks that are suspended in a solvent and thus undergo Brownian motion. Certain binary mixtures of these disks represents a colloidal glass former in two dimensions. In the following we present a setup to study such materials close to their glass transition point by means of computer simulations. The present work focuses on two major objectives. On one hand, we contribute to the understanding of the dynamical slowing-down in quiescent glass-forming systems. Secondly, the interplay of glassy dynamics with external fields driving the system far from equilibrium promises insights to novel and intriguing phenomena. Complex structural and transport phenomena at the glass transition under far-from-equilibrium conditions are explored within several different setups. In this introductory chapter we present a brief overview over the basic concepts addressed in the following and give an outline of the topics covered in the upcoming chapters of this work.

1.1. Brownian motion and colloidal systems

The term colloidal suspension refers to multiphasic substances made of solid particles, roughly 10 nano- to 10 micrometers in size, suspended in a solvent. Thus colloids behave as “classical” particles, in a sense that quantum mechanical effects are largely negligible. On the other hand a colloidal particle is small enough to experience thermal fluctuations due to frequent, random collisions with surrounding solvent molecules. This erratic motion of particles immersed in a solvent was first reported by Robert Brown in [1],
1. Introduction

the early 19th century [3]. At the beginning of the last century Albert Einstein and Marian Smoluchowski were able to establish a theoretical framework for this Brownian motion [4]. By identifying the underlying stochastic Wiener process they derived the Einstein-Smoluchowski relation and quantified the mean squared displacements for diffusive Brownian motion. This relation sets a diffusive timescale $\tau_0$, which measures the average time a particle needs to travel its own radius and provides an estimate for the timescale on which correlation functions in dilute systems to decay. Under densification the dynamics change. For a hard body interparticle potential the only restriction placed upon the system is that particles are not allowed to overlap. Thus, as the system becomes denser, a particle is not able to move independently from its neighbors and only cooperative structural processes are feasible. By this, the dynamics is slowed down tremendously and a new structural relaxation timescale $\tau_\alpha \gg \tau_0$ is set.

Since several decades, colloids are used as model system for the study of glass transitions, although there are differences to their molecular counterparts. For example, the presence of a solvent leads to a diffusive rather than a ballistic short time motion and a coupling between the particles due to complex hydrodynamic effects. However, it is presumed that this differences do not influence the nature of the glass transition [5]. The benefits of examining colloidal suspensions on the other hand suggest itself: the spatial and temporal scales involved are accessible for a wide variety of experimental techniques. Particles can be manufactured comparably easy in various shapes and sizes and are trackable with sufficient accuracy by standard image processing techniques, such as video or confocal microscopy. Furthermore, compared to atomic glass formers, the energy densities in this soft matter systems are several decades smaller. Thus, colloidal suspensions exhibit a variety of excited states at moderate temperatures and thermal fluctuations are easily accessible. This unique possibility will be exploited in Chap. 7, where we give simulational and experimental evidence for long wavelength density fluctuations in colloidal suspensions in 2D. Such measurements are not feasible in atomic systems as e. g. graphene, where phonons suppress this process [6].

1.2. The glass transition

A dispersion of polydisperse colloidal hard spheres vitrifies upon densification without undergoing crystal nucleation. Adding colloids to the solution up to a finite concentration, the dispersion first becomes a viscoelastic liquid with (Newtonian) viscosity far exceeding the one of the pure solvent. Increasing the density beyond a critical value the liquid transforms into an amorphous solid. This crossing is accompanied by the emergence of mechanical rigidity to shear deformations on laboratory time scales. At the same time the structural relaxation time diverges due to the immense slowing down of the dynamics. The motion of a particle is strongly hindered by its impenetrable next neighbors. In sufficiently dense states such a cage of neighboring disks can only move collectively, resulting in a strong coupling of fluctuation
1.3. Couette and Poiseuille flow

A widely used and well studied method to melt amorphous solids is the imposition of shear flow \[14, 15, 16, 17\]. In this way rigid cages of neighbors can be broken, leading to a fluidization of the material. The resulting shear-induced decay is linked to a new, additional time scale \(\tau_\dot{\gamma}\) that is introduced to the system.

In the following we will investigate two different types of flow: Couette and Poiseuille flow. The former develops, when a viscous fluid is confined between two surfaces, where one of them is moving tangentially relative to the other. This gives rise to a (nearly) constant velocity gradient and thus spatially homogeneous shear flow. Studies using such setups contribute to the understanding of phenomena like shear thinning \[11\] and thickening \[18\], or are used in experiments to prepare or rejuvenate colloidal glasses \[19\]. Further the transient regimes of startup of flow \[16\] and relaxation from sheared states after flow cessation \[20\] reveal interesting features.

An alternative to imposing a spatially homogeneous and constant shear rate, is the introduction of a constant pressure gradient along a flat channel \[21, 22, 23\]. The interplay of glassy dynamics with external fields and rough solid walls evokes a spatially inhomogeneous Poiseuille flow, allowing for a study of local material properties and likewise inhomogeneous relaxation dynamics in the flowing suspension.

All flow regimes introduced are as well accessible by several extensions to a combination of an integration-through-transients (ITT) approach to nonlinear response with the mode-coupling
1. Introduction

theory of the glass transition (MCT) [24].

1.4. Simulation of glass former

Over the last decades computer simulations proofed to be a powerful tool to study the equilibrium and transport properties of N-body systems, whose dynamics are governed by the laws of classical mechanics [25, 26]. The colloidal Brownian disks investigated in the following are large enough to behave as hard objects and small enough to undergo thermal motion. The former requires employing a discontinuous step potential for the colloidal particles, the latter a coupling to a heat bath of solvent particles. Thus all particles have to move constantly due to thermal excitation, while neighboring disks are not allowed to interpenetrate. The algorithm employed and further developed in this thesis stems from a Monte-Carlo scheme [27] that constantly draws random displacements for all particles. If an assigned displacement would create overlap, it is rejected. This method is not suitable for the study of glassy systems, because the probability to create overlap increases drastically with increasing density. Among others De Michele improved this concept such that it produces physically correct results in line with Brownian N-particle dynamics at high densities [28, 29]. While the repeated drawing of random displacements remains, the rejection criterion is amended: potential overlaps are resolved by interpreting each displacement as a velocity. Therefore a performance of ballistic motion including elastic collisions between the particles is implementable. In this way overlap-free Brownian dynamics of quiescent and sheared hard disks in 2D can be modeled [11, 12, 13]. In this work we apply and further develop this method. In particular, we work out techniques to simulate larger systems, more elaborate setups and new regimes.

1.5. Outline of the chapters

Chapter 2 introduces the algorithm for event-driven Brownian dynamics simulations of hard disks and gives a short overview over the underlying theory of Brownian motion. Techniques to impose simple shear flow and to prepare dense systems are given.

Chapter 3 investigates quiescent and sheared Brownian mixtures to determine elastic shear moduli close to the glass transition. Results from three different methods are presented and compared to predictions of the mode-coupling theory. This elucidates the emergence of elasticity at the glass transition point. The results are published in [30].

Chapter 4 presents the strain correlation pattern in supercooled liquids and glasses for simulated and experimental data. Predictions from continuum mechanics in the solid and hydrodynamics in the viscous liquid are verified. The results are published in [31].
1.5. Outline of the chapters

Chapter 5 examines the relaxation of a glassy system from a non-equilibrium stationary state after the cessation of simple shear flow. The emergence of residual stresses and a localization length is discussed. Parts of the results are published in [32] and [33].

Chapter 6 develops a novel algorithm to investigate pressure-driven channel flow in rough channels. By that local dependencies of flow properties and structural quantities arise. Parts of the results are published in [33].

Chapter 7 demonstrates that amorphous solids in two dimensions are subject to Mermin-Wagner fluctuations. In this context simulational results are compared to findings from experiments on glasses and crystals in 2D and 3D. The results are published in [34].

Chapter 8 provides a summary of this thesis.
2. Simulation

Molecular Dynamics (MD) simulations are a widely used and an extremely helpful instrument to study the equilibrium and transport properties of multi-particle systems, as long as the dynamics follows the laws of classical mechanics [25, 26].

Let us first shortly visit a standard method for the modeling of such systems. It is rather straightforward: after preparation of a (virtual) sample of a material of interest, one evolves the system in time by integration of an appropriate equation of motion. This step involves calculating forces acting on all particles and a discretization of time. The microscopic inter-particle forces are known and can be approximated sufficiently well by employing a continuous potential, which allows for a fixed integration time step. Common examples for glass former on a molecular scale employ a Lennard-Jones potential and a certain mixing ratio of different particle types, like the Kob-Anderson [35] or Wahnstroem mixture [36].

However, in any model with a continuous potential, the particles will have a certain “softness”, since the particles are treated as point-particles and the inter-particle distance depends on the energy scale. For the purpose of this thesis we want to simulate true hard bodies. Therefore, we need to employ an algorithm, which guarantees overlap-free Brownian dynamics. This method is first briefly sketched here, before it is given in more detail in upcoming sections. We investigate the dynamics of a colloidal glass former in two dimensions, where particle diameters usually vary between $10^{-8}$m and $10^{-5}$m. Thus the particles are large enough to behave as hard objects and small enough to undergo thermal motion. The former requires an appropriate interparticle potential for the colloids: hard particles interact only via collisions, i.e. as long as they are not in contact, they do not influence each other. This can be modeled by a discontinuous step potential. Thermal motion on the other hand requires a coupling to a heat bath of solvent particles.

The challenge here, especially for very dense systems, is to prevent particle configurations in which particles overlap at any time. At the same time, the simulated system has to obey the physical laws. Furthermore, it has to reproduce the physical properties, which can be measured in experiments, as e. g. the radial distribution on the length scale of the mean particle distance. This is accomplished by an algorithm first introduced by De Michele [28, 29], who modified the method of discrete-event simulations in order to model Brownian dynamics. The key idea here is to turn away from fixed integration time steps towards proceeding in time collision by collision. For this a Monte-Carlo-like random sampling, combined with ballistic
2. Simulation

motion on short time scales, is implemented. After fixed times random moves are assigned
to all particles in the system, implementing a stochastic force which arises from interactions
with the solvent molecules. For the short time $\tau_b$ between two random moves, the assigned
displacements $u$ can then be interpreted as constant particle velocities $u/\tau_b$ (although they do
not represent the relevant particle velocity on Brownian time scales). This allows to perform
ballistic (Newtonian) dynamics between two random sampling steps. Due to the event-driven
algorithm, this evolution will be overlap-free. In this way a series of discrete events ensures
a rejection free simulation scheme. This comes at the expense of a higher complexity of
the algorithm and the data organization. The constant assignment of random velocities to
the colloidal particles follows a Maxwell-Boltzmann distribution. Besides Brownian random
motion, this ensures a constant temperature and removes additional energy due to external
fields from the system. Note however, that this algorithm does not account for hydrodynamic
interactions between colloidal particles. These contribution are negligible in studies of dense
systems close the glass transition [5].

In the following the Langevin description of a Brownian hard disk system is sketched.
Methods and technical details of the algorithm are described and it is shown that it solves the
Langevin equation of motion in the overdamped limit. In addition techniques to implement
external forces and boundaries to construct simple shear flow are introduced. Finally, the
preparation of systems with high density is demonstrated.

2.1. Langevin dynamics

The suitable equation of motion for this so-called free draining model of Brownian motion is
provided by the $N$-particle Langevin theory. We consider a system of $N$ particles in a solvent.
The coordinates of particle $i$ are given by $\mathbf{r}_i$. Instead of incorporating the interactions with
the solvent molecules explicitly, we can model their effect on the colloidal disks by a random
force $\mathbf{f}_r$ and a dissipative or friction force $\mathbf{f}_d$. The Langevin equation for the time evolution
of the $i$-th particle reads

$$m\frac{d\mathbf{r}_i}{dt} = \mathbf{f}_d^i + \mathbf{f}_p^i + \mathbf{f}_r^i + \mathbf{f}_{\text{ext}}^i,$$ (2.1)

where $\mathbf{f}_p^i$ denotes the potential or inter-particle forces and $\mathbf{f}_{\text{ext}}^i$ the external forces. The mass
$m$ is chosen to be equal for all particles. The change in particle velocity is given by a sum
of deterministic forces and a stochastic force, leading to a second order stochastic differential
equation. The dissipative force is given by $\mathbf{f}_d = -\xi (\dot{\mathbf{r}}_i - \mathbf{u})$ for a scalar friction coefficient $\xi$,
where $\dot{\mathbf{r}}_i - \mathbf{u}$ is the velocity relative to the local velocity field $\mathbf{u}$ of the surrounding solvent. For
the quiescent case $\mathbf{u}$ will vanish, for sheared systems or planar channel flow it has to be taken
into account. The random force that accounts for thermal collisions is solely characterized
by its vanishing mean value and delta-correlation

$$\langle f_i'(t) \rangle = 0 \quad (2.2)$$

$$\langle f_i'(t) f_j'(t') \rangle = G \delta_{ij} \delta(t - t') = 2k_B T \xi \delta_{ij} \delta(t - t') \quad (2.3)$$

with Boltzmann’s constant $k_B$, the temperature $T$ and the Kronecker delta $\delta_{ij}$. $\langle \cdot \rangle$ denotes the ensemble average. As an example of the fluctuation-dissipation theorem Eq. (2.3) connects the fluctuating thermal forces to the friction coefficient $\xi$, describing the dissipation of kinetic energy into heat [37].

### 2.1.1. Free draining particle

Let us first take a step back and study the random motion of a single particle immersed in a solvent in the absence of external forces, thus $\mathbf{f}_p = \mathbf{f}_{\text{ext}} = 0$. What follows is a sketch of the derivation of the according displacements by time discretization, a more detailed derivation is given in [38, 39]. From Eq. (2.1) one arrives at the following equation of motion

$$m \frac{d \dot{r}}{dt} = -\xi \dot{r} + \mathbf{f}_r, \quad (2.4)$$

where the general solution for the initial condition $\dot{r}(t = 0) = \dot{r}_0$ can be obtained by variation of constants and reads

$$\dot{r}(t) = \dot{r}_0 e^{-\frac{\xi}{m} t} + \frac{1}{m} \int_0^t dt' \mathbf{f}_r(t') e^{-\frac{\xi}{m} (t - t')} \quad (2.5)$$

After integration with respect to time one obtains an expression for the displacement at time $t$, where at $t = 0$ the particle started at $r(t = 0) = r_0$,

$$r(t) - r_0 = \int_0^t dt' \dot{r}_0 e^{-\frac{\xi}{m} t'} + \frac{1}{m} \int_0^t \int_0^{t''} dt' \mathbf{f}_r(t') e^{-\frac{\xi}{m} (t'' - t')} \quad (2.6)$$

$$= \frac{m}{\xi} \dot{r}_0 (1 - e^{-\frac{\xi}{m} t}) + \frac{1}{\xi} \int_0^t dt' \mathbf{f}_r(t') \left( 1 - e^{-\frac{\xi}{m} (t - t')} \right) \quad (2.7)$$

$$r(t) = r_0 + \frac{m}{\xi} \dot{r}_0 (1 - e^{-\frac{\xi}{m} t}) + \frac{1}{\xi} \sum_{i=0}^{M-1} \int_{i \tau_B}^{(i+1) \tau_B} dt' \mathbf{f}_r(t') \left( 1 - e^{-\frac{\xi}{m} (t - t')} \right) \quad (2.8)$$

In the last step the time interval $[0, t]$ is divided into $M$ small subintervals of equal length $\tau_B$ and the integral is split up into a sum of $M$ integrals. We demand $\tau_B$ to be large compared to the time scale of the fluctuations of the solvent inter-particle force $\tau_s$ and small compared to the friction time scale $m/\xi$, which is of the order of the Brownian relaxation time $\tau_0$. 

2. Simulation

For an experimental colloidal suspension with particle diameter \( \sim 1 \mu m \) typical values are \( \tau_s \approx 10^{-15} s \) and \( m/\xi \approx 10^0 s \) [40], where we demand \( \tau_s \ll \tau_B \ll m/\xi \). Hence we are able to approximate the exponential in the integrand as constant over a time interval of length \( \tau_B \),

\[
e^{-\frac{\xi}{m}(t-r_B)} \approx e^{-\frac{\xi}{m}(t-i \tau_B)},
\]

and move it outside the integral,

\[
\sum_{i=0}^{M-1} \int_{i \tau_B}^{(i+1) \tau_B} dt' f'(t') \left( 1 - e^{-\frac{\xi}{m}(t-t')} \right) = \sum_{i=0}^{M-1} \frac{1}{\tau_B} \int_{i \tau_B}^{(i+1) \tau_B} dt' f'(t'). \tag{2.9}
\]

From Eq. (2.2), (2.3) we know that the random force has a vanishing expectation value and is delta-correlated in time. As a consequence the central limit theorem can be applied, which states that a sum of \( n \) independent random variables with vanishing mean value tends toward a Gaussian distribution for large \( n \). Each of the integrals on the right hand side of Eq. (2.9) represents a sum of identically and independently distributed random variables and is therefore a Gaussian variable denoted by \( x_i^r \). Furthermore, the sum of this \( M \) independent Gaussian variables is equal to a Gaussian variable \( x_r^r \) itself [39] and we have

\[
x_r^r(t) = \frac{1}{\xi} \int_0^t dt' f_r(t') \left( 1 - e^{-\frac{\xi}{m}(t-t')} \right) \tag{2.10}
\]

\[
= \frac{1}{\xi} \sum_{i=0}^{M-1} \left( 1 - e^{-\frac{\xi}{m}(t-i \tau_B)} \right) x_r^r(i \tau_B) \tag{2.11}
\]

\[
= r(t) - r_0 - \frac{m}{\xi} \dot{r}_0(1 - e^{-\frac{\xi}{m} t}), \tag{2.12}
\]

with expectation value \( \langle r(t) \rangle = 0 \). An analogous calculation for the velocity \( \dot{r} \), starting with Eq. (2.5), yields

\[
x_r^{\dot{r}}(t) = \frac{1}{m} \int_0^t dt' f_r(t') e^{-\frac{\xi}{m}(t-t')} \tag{2.13}
\]

\[
= \frac{1}{m} \sum_{i=0}^{M-1} e^{-\frac{\xi}{m}(t-i \tau_B)} x_r^{\dot{r}}(i \tau_B) \tag{2.14}
\]

\[
= \dot{r}(t) - \dot{r}_0 e^{-\frac{\xi}{m} t}, \tag{2.15}
\]

The (conditional) probability distribution for a \( d \)-dimensional Gaussian variable is given by

\[
P(x^a, t|x_0^a, t = 0) = \frac{1}{(2\pi)^{d/2}(\det D)^{1/2}} \exp \left( -\frac{1}{2} x^a D^{-1} x^a \right), \tag{2.16}
\]
2.1. Langevin dynamics

with the covariance matrix $D = \langle x^a x^a \rangle$. Using Eq. (2.10) and (2.13) the second moments calculate to

$$\langle x^a x^b \rangle = \frac{m \xi}{\xi t} \left( \frac{\xi}{m} t - \frac{1}{2} \left( e^{-2 \frac{\xi}{m} t} - 1 \right) - 2 \left( 1 - e^{- \frac{\xi}{m} t} \right) \right)$$

(2.17)

$$\langle x^a \dot{x}^b \rangle = \frac{G}{2m \xi} \left( 1 - e^{-2 \frac{\xi}{m} t} \right) \rightarrow \frac{G}{2m \xi} \text{ for } \frac{m}{\xi} \rightarrow 0.$$

(2.18)

From here on we restrict our analysis to the limit of strong dissipation, $m/\xi \rightarrow 0$, also known as the overdamped limit, which assures that the timescale of friction and momentum relaxation is fast. Hence the second term of the right hand side of Eq. (2.15) is negligible compared to the stochastic component. We may use Eq. (2.18) and the equipartition theorem, connecting the kinetic energy to the temperature in the system, to verify

$$\langle \dot{x}(t) \dot{x}(t) \rangle = \frac{G}{2m \xi} = \frac{k_B T}{m} \frac{1}{2}.$$

(2.19)

$$\Leftrightarrow G = 2 \xi k_B T; \quad D = \frac{k_B T}{m} \mathbb{1}.$$

(2.20)

This justifies our choice of $G$ in the fluctuation-dissipation relation Eq. (2.3). Finally, the probability density function (pdf) for the velocity in $n_d = 2$ dimensions is given by

$$P(x^t, t|\dot{x}_0, t = 0) = \frac{m}{2\pi k_B T} \exp \left( -\frac{m}{2k_B T} \dot{x}^2 \right).$$

(2.21)

For this multivariate normal distribution we find $\langle \dot{x}(t) \rangle = 0$ for the average and the variance $\langle \dot{x}^2 \rangle = \sigma_x^2 + \sigma_y^2 = 2k_B T/m$ is connected to the temperature $T$. In the same manner we find for the mean squared displacement using Eq. (2.15)

$$\langle \Delta x^2(t) \rangle = \langle (r(t) - r(0))(r(t) - r(0)) \rangle$$

$$= \frac{m^2 \xi \dot{x}_0 \dot{r}_0}{\xi^2} \left( e^{- \frac{\xi}{m} t} - 1 \right)^2 + \frac{2m k_B T}{\xi^2} \left( \frac{\xi}{m} t - \frac{1}{2} \left( e^{- \frac{\xi}{m} t} - 1 \right) - 2 \left( 1 - e^{- \frac{\xi}{m} t} \right) \right)$$

(2.22)

$$\begin{cases} \frac{2k_B T}{\xi} \mathbb{1} t & \frac{m}{\xi} t \gg 1, \\ \dot{x}_0 \dot{r}_0 t^2 & \frac{m}{\xi} t \ll 1. \end{cases}$$

(2.23)

For times larger than the friction time scale $\frac{m}{\xi}$ we obtain the famous Einstein relation of diffusive Brownian motion with diffusion constant $D_0 = \frac{k_B T}{\xi}$, while the short time dynamics is purely ballistic.
2. Simulation

Figure 2.1.: Velocity profile (gray arrows) of a Couette flow with constant shear rate \( \dot{\gamma} = \partial_y u_x \) in a stationary state.

2.1.2. Shear flow

Simple shear flow is a common and simple setup for rheological experiments [14, 15, 16, 17]. By moving the confining walls, one can create a stationary velocity profile varying linearly in space. Fig. 2.1 shows the velocity profile \( u_\gamma \) of the solvent in the stationary state. With a velocity gradient matrix \( \Gamma_{\alpha\beta} = \partial v_\alpha / \partial r_\beta \) the velocity profile for simple shear flow in \( x \)-direction reads

\[
\begin{align*}
 u_\gamma(r) = \Gamma r = \dot{\gamma} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} r = \dot{\gamma} y \hat{x}, \quad (2.25)
\end{align*}
\]

with a constant scalar shear rate \( \dot{\gamma} = \partial u_x / \partial y \). In the Langevin description this non zero solvent velocity enters the frictional force, which is proportional to the relative velocity \( \dot{r}' = \dot{r} - u_\gamma(y) \),

\[
\begin{align*}
 f_d = -\xi (\dot{r} - u_\gamma(y)) = -\xi \dot{r}'. \quad (2.26)
\end{align*}
\]

By using \( \Gamma \Gamma = 0 \) one can reformulate the Langevin equations in terms of relative velocities

\[
\begin{align*}
 m \frac{d\dot{r}}{dt} &= -\xi (\dot{\Gamma} \dot{r} - \Gamma \dot{r}) + f', \quad (2.27) \\
m \frac{d\dot{r}'}{dt} &= m \frac{d\dot{r}}{dt} - m \frac{d\Gamma r}{dt} \\
&= -(\xi \hat{\Gamma} + m \Gamma) \dot{r}' + f'. \quad (2.29)
\end{align*}
\]
2.2. Algorithm for free draining or sheared particle

An modified version of the equipartition theorem connects the temperature to the second moment of the relative velocities in the stationary state [39],

\[ \langle \dot{v}'(t)\dot{v}'(t) \rangle = \frac{k_B T}{m}. \]  

(2.30)

Following a derivation analogous to the one in 2.1.1, again in the overdamped limit for Brownian dynamics, leads to a distribution of relative velocities [28, 41] and displacements over time

\[ P(x', t | \dot{r}_0', t = 0) = \frac{m}{2\pi k_B T} \exp \left( -\frac{m}{2k_B T} \dot{v}'^2 \right), \]  

(2.31)

\[ P(x', t | r_0 = 0, t = 0) = \frac{1}{4\pi D_0 t} \exp \left( -\frac{1}{4\pi D_0 t} \dot{v}'(t)^2 \right). \]  

(2.32)

For this approximation terms of order \( O(\dot{\gamma}t) \), leading to a non isotropic probability distribution of the relative displacements [39], are neglected. Thus in the following this approximation will only be employed in the context of small strains \( \dot{\gamma}t \ll 1 \). The resulting single particle motion is anisotropic as well and leads, again for \( t \gg \frac{m}{\dot{\gamma}} \), to superdiffusive Taylor dispersion in shear direction [42]

\[ \langle \Delta y(t)^2 \rangle = 2D_0 t, \]  

(2.33)

\[ \langle \Delta x(t)^2 \rangle = 2D_0 t + (y(0)\dot{\gamma}t)^2 + \frac{2}{3} D_0 \dot{\gamma}^2 t^3. \]  

(2.34)

The last term on the right hand side of Eq. 2.34 emerges from fluctuations of the position in shear gradient direction \((y)\) that constantly change the surrounding solvent velocity.

2.2. Algorithm for free draining or sheared particle

We will now introduce the tools to translate the findings of the previous section into an algorithm to simulate overdamped Langevin dynamics on the computer. Before tackling the problem of \( N \)-particle systems, let us first stick to the framework introduced in the last section: a single particle immersed in a solvent in the absence of external forces. To evolve the system we discretize time into intervals of length \( \tau_B \). At the end of each interval we assign new random velocities according to the pdf in Eq. (2.21). For a Brownian event taking place at time \( t \) we obtain particle velocities and displacements

\[ \dot{r}(t) = x' \]  

(2.35)

\[ r(t + \tau_B) = r(t) + \tau_B x'. \]  

(2.36)
2. Simulation

In case of simple shear flow the random velocities and displacements are drawn from the distribution Eq. (2.31), utilizing velocities relative to the convective flow,

\[ \dot{\mathbf{r}}(t) = \mathbf{x}^t + \dot{\gamma} y(t) \mathbf{\hat{x}} \]  \hspace{1cm} (2.37)

\[ \mathbf{r}(t + \tau_B) = \mathbf{r}(t) + \tau_B (\mathbf{x}^t + \dot{\gamma} y(t) \mathbf{\hat{x}}). \]  \hspace{1cm} (2.38)

After each time step the position is updated and the particle loses the memory of its former velocity as a new random velocity is assigned. The thermal energy \( k_B T \) determines the variance \( \langle \dot{\mathbf{r}}(t) \dot{\mathbf{r}}(t) \rangle = k_B T / m \). For our simulations we set \( k_B T \), mass \( m \) and the particle diameter \( d \) to unity.

Fig. 2.2 shows the mean squared displacement (MSD) \( \langle \Delta r^2(t) \rangle \) for a free single particle in \( n_d = 2 \) dimensions in absence of shear flow, \( \dot{\gamma} = 0 \). The expectation value is realized by an average over \( 10^4 \) independent trajectories.

For \( t < \tau_B \) the MSD follows the ballistic short time curve \( \sim 2 t^2 \). At larger times \( t > \tau_B \) diffusion kicks in and we obtain \( \langle \Delta r^2(t) \rangle = 4 D_0 t \), see Eq. (2.24).

The choice of \( \tau_B \) sets the friction coefficient and therefore the diffusion constant, as we can divide each particle trajectory \( \mathbf{r}(t) \) into \( n \) subintervals of straight linear motion, where \( t = n \tau_B \). By that we obtain

\[ \mathbf{r}(t) - \mathbf{r}(0) = \int_0^t dt' \dot{\mathbf{r}}(t') = \sum_{i=1}^n \tau_B \dot{\mathbf{r}}(i \tau_B), \]  \hspace{1cm} (2.39)

\[ \langle \Delta r^2(t) \rangle = \left( \left( \sum_{i=1}^n \tau_B \dot{\mathbf{r}}(i \tau_B) \right)^2 \right) = \tau_B^2 \sum_{i=1}^n \langle \dot{\mathbf{r}}(i \tau_B)^2 \rangle \]  \hspace{1cm} (2.40)

\[ = n \tau_B^2 \frac{n d k_B T}{m} = \frac{\tau_B n d k_B T}{m} t, \]  \hspace{1cm} (2.41)

where we again used the equipartition theorem Eq. (2.19). Comparison with Eq. (2.24) in the diffusive limit \( t \gg \frac{\tau_B}{\xi} \) now leads to

\[ \langle \Delta r^2(t) \rangle = 2 n_d D_0 t = \frac{2 n_d k_B T}{\xi} t \]  \hspace{1cm} (2.42)

\[ \Leftrightarrow D_0 = \frac{\tau_B k_B T}{2 m} = \frac{k_B T}{\xi}, \]  \hspace{1cm} (2.43)

\[ \Leftrightarrow \tau_B = \frac{2 m}{\xi}. \]  \hspace{1cm} (2.44)

The Brownian relaxation time \( \tau_0 \) is defined as the time it takes the MSD to reach twice the
2.3. Multiparticle systems

So far, our analysis was restricted to a single particle. If we demand our algorithm to solve the equation of motion Eq. (2.1) we have to introduce interparticle forces $f_{ij}$ that arise from a pair potential for impenetrable disks,

$$V(r_i(t), r_j(t)) = \begin{cases} \infty & |r_i(t) - r_j(t)| \leq \sigma_i + \sigma_j, \\ 0 & \text{else}. \end{cases}$$

(2.47)

This term describes the pair potential for two disks with radii $\sigma_i$ and $\sigma_j$. The discontinuous nature of this hard disk potential does not allow for time discretization and integration of the equation of motion in a standard molecular dynamics scheme.

By simply drawing displacements for each particle according to Eq. (2.36), it is inevitable to create configurations with overlapping particles, which are prohibited by the potential. Especially for systems with high densities the probability to run into conflicts is high. To
2. Simulation

satisfy the requirements of Eq. (2.47) one has to choose a protocol to predict and reject or modify particle displacements that would lead to interpenetration of the particles. The correction moves in this Monte Carlo random sampling scenarios do of course influence the dynamics and have to be chosen with great care. Simply ignoring the particle shifts violating the impenetrability condition [27] is highly unfavorable for dense systems, as a considerable fraction of moves is rejected. Therefore, the probability distribution function for the displacements is altered significantly leading to non diffusive displacements. It has been shown that only in the limit \( \tau_B \to 0 \) overdamped Langevin dynamics is obtained [43]. There are several other methods to correct the emerging overlap, for example by placing the particles at contact instead [43]. This alters the microscopic structure in an undesirable way, as the radial distribution function at contact is overestimated [44]. As a result, macroscopic quantities as e. g. the pressure are altered in a non physical manner. Another approach [44] is to check for particle overlaps after each time step of length \( \tau_B \). In case of positive feedback it is corrected by modifying the trajectories of the involved particles, as if they collided elastically in the past. The drawbacks here are that particles are able to tunnel through each other within a time span of length \( \tau_B \) and by that violate the impenetrability condition. Furthermore, there is no appropriate operation to handle second order overlaps after correcting the trajectories of two initially overlapping particles. This is quite probable in dense systems.

The algorithm employed in the scope of this work is based on De Michele’s algorithm [28]. As before, random displacements are drawn utilizing pseudo velocities according to Eq. (2.36) after fixed time steps. In the following, this is referred to as Brownian event. Between two of these events the system is evolved according to the laws of ballistic motion by performing event driven molecular dynamics. In this way the problem of emerging overlaps is circumvented by performing a cascade of elastic two body collision events at the exact time of collision. Thus, the time discretization is always fine enough to ensure non-overlapping configurations. Requiring the displacements to be small compared to the mean inter particle distance and the particle radius,

\[
4D_0 \tau_B \ll \sigma^2, (N/V)^{-1/2},
\]

the authors were able to show, that this protocol does not suffer from the complications arising from the mentioned existing algorithms for hard disk potentials. The correction moves are broken down into a time ordered series of events of which each one yields the correct 2-particle pdf. This was tested by comparing simulational results with the analytically exact solution of the Smoluchowski equation describing the time evolution of the pdf, which is known for \( N \leq 2 \) particles. Furthermore, results generated with this algorithm have been rationalized using ITT-MCT in numerous works [11, 12, 13].
2.4. Event driven Brownian Dynamics Simulation

To meet the requirements of ballistic motion between two Brownian events, the system has to be advanced in a series of discrete collision events. This involves the prediction and performance of collisions according to collision rules dictated by the conservation of momentum and energy. At time \( t \) a particle indexed by \( i \) is described by its position \( r_i(t) \), radius \( \sigma_i \), mass \( m_i \) and pseudo velocity \( \dot{r}_i(t) \) ("pseudo" because it does not represent the velocity on Brownian timescales \( t \gtrsim \tau_0 \)). Two particles \( i \) and \( j \) are at contact, if the absolute value of their separation \( \Delta r_{ij} \) is equal to the sum of their radii \( d_{ij} \)

\[
\Delta r_{ij}(t) = |r_i(t) - r_j(t)| = \sigma_i + \sigma_j = d_{ij}, \quad (2.48)
\]

Between two collisions each particle moves unaccelerated in a straight line with constant pseudo velocity \( \dot{r}_i(t) \) and the position at a time \( t + \tau \), for \( \tau > 0 \), is given by

\[
r_i(t + \tau) = r_i(t) + \tau \dot{r}_i(t). \quad (2.49)
\]

A crucial point is now to predict when two trajectories will intersect in the future. Two particles that are not at contact or overlapping at time \( t \) will collide if Eq. (2.48) has a solution \( t + \tau_{c,ij} > t \). Demanding \( |\Delta r_{ij}(t)| > d_{ij} \) a real, positive solution for \( \tau_{c,ij} \) exists if and only if

\[
\begin{align*}
   b_{ij}(t) &= \Delta r_{ij}(t) \Delta \dot{r}_{ij}(t) < 0, \\
   b_{ij}^2(t) - \Delta r_{ij}^2(t) \left( \Delta \dot{r}_{ij}^2(t) - d_{ij}^2 \right) &> 0, \\
   \tau_{c,ij} &= \frac{-b_{ij}(t) - \sqrt{b_{ij}^2(t) - \Delta r_{ij}^2(t) \left( \Delta \dot{r}_{ij}^2(t) - d_{ij}^2 \right)}}{\Delta \dot{r}_{ij}^2(t)}. \quad (2.50, 2.51, 2.52)
\end{align*}
\]

stating that the particles are approaching each other and their trajectories do intersect. In this case the collision time is given as

\[
\tau_{c,ij} = \frac{-b_{ij}(t) - \sqrt{b_{ij}^2(t) - \Delta r_{ij}^2(t) \left( \Delta \dot{r}_{ij}^2(t) - d_{ij}^2 \right)}}{\Delta \dot{r}_{ij}^2(t)}. \quad (2.52)
\]

Whenever an elastic collision occurs, the particle momenta are updated according to

\[
\begin{align*}
   \dot{r}_i^{\text{out}} &= \dot{r}_i^{\text{in}} - \frac{2b_{ij}}{d_{ij}^2 \left(1 + \frac{m_i}{m_j}\right)} \Delta r_{ij}, \quad (2.53) \\
   \dot{r}_j^{\text{out}} &= \dot{r}_j^{\text{in}} + \frac{2b_{ij}}{d_{ij}^2 \left(1 + \frac{m_j}{m_i}\right)} \Delta r_{ij}. \quad (2.54)
\end{align*}
\]

The process obeys the conservation of momentum and energy and is depicted in Fig. 2.3.

As a result, after setting an integer control variable \( n = 0 \), we proceed as follows:
2. Simulation

1. Draw random pseudo velocities for all particles according to Eq. (2.37), update time to \( t = n \tau_B \)

2. Predict each upcoming collision time (if existing) for all pairs of particles in the system according to Eq. (2.52)

3. Search for the first collision to happen after \( \tau_{\text{min}} = \min_{i \neq j} \tau_{c,ij} \).

4. If \( t + \tau_{\text{min}} \leq (n + 1) \tau_B \): update all particle trajectories to \( t = t + \tau_{\text{min}} \) according to Eq. (2.49), adjust the velocities of the colliding particles according to Eq. (2.53), (2.54) and proceed with Point 2.

   If \( t + \tau_{\text{min}} > (n + 1) \tau_B \): update all particle trajectories to \( t = (n + 1) \tau_B \) according to Eq. (2.49), set \( n = n + 1 \) and proceed with Point 1.

At this state, the introduced procedure is highly inefficient but illustrates the approach. In the upcoming sections several improvements, that enhance the efficiency, will be given.

Wrapping up, we sample Brownian diffusive dynamics by drawing random displacements every \( \tau_B \). Those moves stem from a random force (2.12) and represent the interaction with the solvent acting as a heat bath. These displacements over a time \( \tau_B \) define auxiliary velocities, that lose their magnitude and direction at each Brownian event. This pseudo-velocities allow for a ballistic treatment of the system between two Brownian events, breaking down the dynamics into a cascade of elastic two-body collisions. This procedure satisfies the requirements of the hard disk potential and the underlying N-body-Smoluchowski dynamics.

2.5. System properties and preparation

As already stated we want to study a colloidal suspension of hard disks close to its glass transition. Thus the system has to meet several requirements, such as reaching an amorphous, well-aged state and being able to approximate an arbitrary large or infinite system. Further,
2.5. System properties and preparation

the control parameters have to be chosen in a way that allows for thermal Brownian motion, as well as for slow relaxation dynamics in dense systems. In the following, the geometry, composition and control parameters are specified.

2.5.1. Simulation box

The particles are placed in a two dimensional, quadratic simulation box. The side length $L$ of the box is set by the relative area density or packing fraction $\phi$, the particle radii $\sigma_i$ and particle number $N$ via

$$\phi = \frac{\pi L^{-2} \sum_{i=1}^{N} \sigma_i^2}{\pi}.$$  \hfill (2.55)

Figure 2.4.: Simulation box (center) surrounded by its eight images. Particles interact across the boundaries of the boxes, particles leaving a box at one side simultaneously reenter at the opposite side.

The fact, that the number of particles and box size in simulations are finite, inevitably leads to the question on how to model the system boundaries. We aim on investigating a system that is large and not affected by e. g. rigid, reflecting walls or particle loss at the edge of the box. By employing periodic boundary conditions the system remains bounded but free of physical walls. As shown schematically in Fig. 2.4, we place 8 identical copies of the box around the original one. This means an object passing through one side of the simulation box re-enters at the opposite side at the same time with the same velocity. Further the particles in the box interact with copies of the particles of the adjacent images, disks collide with
2. Simulation

partners at the opposite boundary. The distance $\Delta r_{ij}$ from particle $i$ to particle $j$ is replaced by the minimum of distances between $i$ and all copies of $j$ in the image boxes

$$\Delta x_{ij} = \begin{cases} x_i - x_j & |x_i - x_j| \leq L/2 \\ x_i - x_j - \frac{x_i - x_j}{|x_i - x_j|} L & |x_i - x_j| > L/2 \end{cases}$$

(2.56)

$$\Delta y_{ij} = \begin{cases} y_i - y_j & |y_i - y_j| \leq L/2 \\ y_i - y_j - \frac{y_i - y_j}{|y_i - y_j|} L & |y_i - y_j| > L/2 \end{cases}$$

(2.57)

The use of periodicity limits the effective range of interactions to half the box size $L$, which in the following will lead to size related restrictions for e. g. spatial correlations of the density or strain in the system. Further, the finite system size will play a key role in the detection of long wavelength density fluctuations in Chap. 7. In case of shear the linear velocity profile is prescribed locally, we do not employ rigid, moving walls. The appropriate modification to Lees-Edwards boundary conditions in $y$-direction again provides the possibility to model an infinite bulk by simulating a relatively small sample $[45]$ . In doing so the rules for reinserting a particle into the box change. For disks leaving the box at the top or bottom the position in shear direction has to be corrected by taking into account the time dependent shear strain and the the local mean distance a particle traveled due to convective shear flow.

As sketched in Fig. 2.5 two neighboring boxes placed above each other move with a relative velocity $\dot{\gamma}L$ in $x$-direction.

Figure 2.5.: Simulation box of a sheared system (center) surrounded by its eight images. Two neighboring boxes placed above each other move with a relative velocity $\dot{\gamma}L$ in $x$-direction.
in the image box is \( \Delta x = \dot{\gamma} L t \). In such a case the coordinates change as

\[
\begin{align*}
\text{new}_{y} &= y \pm L, \\
\text{new}_{x} &= x \pm (\dot{\gamma} t \mod 1)L.
\end{align*}
\] (2.58) (2.59)

For the same reason the inter particle distance in \( x \)-direction reads

\[
\Delta x_{ij} = \begin{cases} 
  x_i - x_j & |x_i - x_j| \leq L/2 \\
  x_i - x_j - L \frac{x_i - x_j}{|x_i - x_j|} [1 + (\dot{\gamma} t \mod 1)] & |x_i - x_j| > L/2
\end{cases}.
\] (2.60)

Further only the particle velocities relative to the solvent flow are maintained in such a crossing event, therefore the difference in shear velocity at the two boarders has to be added or subtracted.

\[
\vec{v}_{\text{new}} = \vec{v}_{x,i} \pm \dot{\gamma} L.
\] (2.61)

The reinsertion rules for the remaining components of the velocity, position and relative distance are unaffected by the presence of shear flow. In fact the periodic boundary conditions in \( x \)-direction remain the same as in the quiescent case discussed above.

### 2.5.2. The bidisperse system

To obtain slow glassy dynamics the system needs to reach high packing fractions \( \phi \) before it arranges in a crystalline order. The key to evoke this behavior is a proper choice of size distribution and preparation of the suspension.

Monodisperse systems tend to pack hexagonally for packing fractions exceeding \( \phi \approx 0.69 \). A way to prevent the emergence of a crystalline state, and thus long range order, is the usage of polydisperse systems with certain particle size distributions [46]. For many experimental hard sphere like systems that experience glassy behavior the mixture is best described by continuous distributions of particle diameters [47, 48]. This is an efficient way to enhance glassy dynamics by shifting the glass transition to higher densities. At the same time the relaxation processes are slowed down, while freezing by crystallization is suppressed. For certain parameters a bidisperse mixture is sufficient to model glass-transition phenomena.

The mixing effects of such hard sphere systems have been studied intensely in the past [49, 50, 12] and will not be discussed in this work. We choose a binary system of hard disk with diameter ratio of \( d_s : d_b = 1 : 1.4 \), where the number of small and big particles in the system is identical, \( N_s/N_{\text{tot}} = 0.5 \). Fig. 2.6 shows a snapshot from a simulation of \( N = 16000 \) particles with packing fraction \( \phi = 0.81 \) and box length \( L = 151.5d_s \).

This composition has been tested in previous works [11, 12] and shows the desired slow glassy dynamics.
2. Simulation

Figure 2.6.: Snapshot of the quadratic simulation box for a binary system with large (small) particles in red (blue). The system contains \( N = 16000 \) particles at packing fraction \( \phi = 0.81 \).

2.5.3. System preparation

Several challenges arise in the preparation of configurations with amorphous structure at high packing fractions. Simply choosing random initial positions for the disks will inevitably result in particle overlaps prohibited by the hard disk potential for high densities. Another simple approach, placing the particles on a quadratic lattice limits the packing fraction to values \( \phi < \frac{\pi}{4} \approx 0.785 \), which is not sufficient to reach the critical density for the glass transition \( \phi^c = 0.7975 \). The determination of this value will be given later in Chap. 3.

A way to overcome this challenges is to concentrate a fluid-like suspension into a long-lived, amorphous state. We start at a packing fraction \( \phi \ll \frac{\pi}{4} \) and place all particles on a quadratic lattice. After that the system is evolved ballistically, using the described algorithm but omitting the repeated velocity reassignments (or Brownian steps). By that the system arrives at an amorphous state with relatively low packing fraction, corresponding to a fluid state. The idea now is to successively inflate each particle by increasing its radius until we...
2.5. System properties and preparation

Arrive at the desired composition with \( N_i (N - N_i) \) particles with radius \( \sigma_i \) (\( \sigma_j \)). After fixed time steps of length \( w \) we repeatedly stop the simulation for the time being. After each interruption each particle is enlarged to either its final radius or, if this would lead to overlap between neighboring disks, to 98% of the maximum radius possible. After that the system is again evolved in time. A sketch of several states of this procedure are shown in Fig. 2.7. Particles are swelled successively until each particle reaches the prescribed size and the desired packing fraction is achieved. The system is now in an amorphous configuration but still not in an equilibrium state. After this (unphysical) compression the systems show explicit aging dependence.

In a second step the system is equilibrated, again by undergoing purely ballistic dynamics. The process described before is a density quench to a glassy state, that by definition is non-ergodic as soon as \( \phi_c \) is exceeded. This is accompanied by a drastic slowing down of the dynamics, the structural relaxation is hindered by trapping particles in cages made up of their next neighbors. By switching from Brownian to Newtonian dynamics a structural decorrelation can be achieved nevertheless for the packing fractions employed in this work. In this way it is possible to prepare a system that is “well-aged” and shows no noticeable waiting time dependence.

Figure 2.8 shows coherent and incoherent density correlation functions of systems undergoing Newtonian dynamics that have been prepared using different swell rates \( w^{-1} \). The data for each swelling rate stem from an average over at least 50 runs from independent starting configurations. Deviations of single run curves from the averaged mean are negligible. The smaller we choose the time step \( w \) between two swelling events, the faster the structural relaxation takes place. The more “gentle” the quench, the more history dependence is seen in the dynamics after this quench. Thus, for the preparation of the initial configurations we choose \( w = 0.01 \). During the subsequent equilibration, we evolve the system until times are reached, that are larger than the relaxation time of the corresponding density correlation.
2. Simulation

![Graph](image)

Figure 2.8.: Incoherent density correlation function \( \Phi_s^q(t) = \langle \rho_s^q(t)^* \rho_s^q(0) \rangle \) (see Chap. 5 for the definition) during equilibration using Newtonian dynamics for a system with \( N = 4000 \) particles. Relaxation dynamics strongly depend on the swell rate \( w^{-1} \), that has been used previously to compress the system.

function. Further, we check for indications of crystallization in the system by determination of the director field. This is given by the bond direction of a particle \( i \) to its \( N_i \) nearest neighbors in \( n \)-folded space

\[
\langle \psi_n \rangle = \frac{1}{N} \sum_{i=1}^{N} \frac{1}{N_i} \sum_{j=1}^{N_i} e^{i n \theta_{ij}}
\]  

(2.62)

for \( n = 4, 5, \ldots, 8 \). Here \( \theta_{ij} \) denotes the angle of the bond direction between particle \( i \) and \( j \) and an arbitrary reference axis. The squared absolute value of this function gives an estimate for the orientational order in the system. For the mixture described above and for all packing fractions investigated in this work, this value does not exceed 0.42 for any of the systems, see Fig. 2.9. This is sufficiently far from crystallization. For comparison, a perfect hexagonal crystal in 2d would have \( \langle \psi_6(t)^* \psi_6(t) \rangle = 1 \). For more details and the analysis of the according correlation function see Chap. 7.
2.6. Technical details of the Algorithm

So far we developed the algorithm and its main ingredients and condensed it to a protocol of 4 steps in section 2.4. In the following the described procedure will be optimized by introduction of a sophisticated neighbor list and book keeping of the scheduled events. These techniques have been suggested and employed in a couple of similar works [51, 25, 29] and will be sketched briefly in the following.

2.6.1. Cell subdivision

In step 2 of the algorithm all upcoming collisions in the system have to be predicted repeatedly. The problem of checking for forthcoming intersections between the trajectories of all particle pairs has complexity $O(N^2)$ and is highly unfavorable for the system sizes in question. The interaction range of the hard disk potential is equal to the sum of the particle radii and therefore rather short. In high density systems it is highly unlikely that particles separated by distances higher than a couple of particle diameters will be at contact in the near future and a substantial amount of predicted events are obsolete. To avoid unnecessary work the simulation box is divided into a lattice of quadratic subcells. The length $l$ of the cell edges is just slightly longer than two times the maximum radius in the system $r_b$, as shown in Fig. 2.10. Each particle can be assigned to a single cell by the position of its center of mass, however the disc can still have overlap with up to 4 cells. Before leaving a cell a particle can only collide with particles in its own and in the 8 adjacent cells. With this modification the number of possible collision partners per particle is reduced to $\sim 10$, the complexity is now

Figure 2.9.: $\langle \psi_n \psi_n^* \rangle$ after the equilibration for systems with packing fractions $\phi$ close to the glass transition and $N = 16000$ particles.
2. Simulation

$O(N)$. In return a cell crossing event has to be scheduled for each particle, predicting when a particle will enter a new subcell. For this the wraparound required by the periodic boundary conditions has to be taken into account. Whenever a cell crossing happens the potential collision partners change and new collisions are predicted. Potential partners are taken from an updated neighbor list which is given by the particles in the same and all adjacent subcells. Another big advantage of this structure is the option to introduce local particle times. In the first version of the algorithm, whenever it proceeded from step 4 to step 2, the global time $t$ was updated and all collisions had to be scheduled. Now only the local particle time $t_i$ of all particles in the cells involved in the collision and its direct neighbors have to be updated. The events for those particles are rescheduled, the previously scheduled events involving all other particles remain unaffected, see [25] for further details.

2.6.2. Event book keeping

The simulation is propagated in time by physical events like collisions, cell crossings, velocity assignments or particle swellings. Additionally administrative tasks, like writing particle positions or conducted measurement to output or terminating the simulation, have to be specified. This results in an immense amount of events that have to be scheduled, stored, ordered in time and processed. A binary tree data structure is employed, an event calendar that is able to handle all this information with reasonable execution time and memory requirements [52, 25]. The tree is a generalization of a linked list, where each node represents
a scheduled event containing information about the time, event type and involved particles. For this one float variable for the time and two integer variables are sufficient. In case of a collision the integers identifies the particle numbers of the two involved disk, otherwise the event type and, if any, the number of the involved disk or directions. A node is linked to a parent node and can be linked to a right and left descendant node by pointers. Left-hand (right-hand) descendants are events that happen before (after) the event represented by the parent node. Starting from a root event the insertion of new events, deletion of events no longer required, the search for the event next in time as well as the initialization and deletion of the entire structure is straightforward. To minimize the size of the tree for each particle one circular list is utilized to store all events that involve this disk. Whenever a particle encounters a particle or cell collision the events on this list are (almost certainly) obsolete and are removed from the tree, rejuvenating it constantly. Hence the maximum number of pointers per node is seven (maximum 3 links for time ordering and maximum 4 links to events involving the same particles).

For Brownian dynamics particle velocities are reassigned constantly after fixed time steps of length $\tau_B$. At each of this Brownian events all collision and cell crossing events scheduled are obsolete and are erased. In fact all physical events that are scheduled at times after the next Brownian time step will never happen and may be rejected. In this way the tree is kept slim and its operation efficient. For Newtonian dynamics such an event horizon does not exist per se, in consequence the size of the event tree is far higher. Particularly, if the time span between the time of prediction and the actual time of a collision is large, it is very unlikely that this collision will be processed. The probability that earlier events interfere is very high. For this reason an artificial event horizon is introduced that constantly erases and rebuilds the event tree after fixed time steps $\tau_R$. This repeated reinitialization of the tree turned out to be more efficient than the rejuvenation of the tree taking improbable events far in the future into account. During test runs the highest gain in computational speed for a system with $\phi = 0.81$ and $N = 2000$ was found for $\tau_R = 10^{-2}$.

A further tweak to increase the numerical accuracy is the repeated rescaling of the time axis. By that a global and rescaled time is introduced, where the algorithm keeps track of both. The latter is set to zero at a so-called “rescaling events” every $10^6 \tau_B$. All upcoming events (of any type) are then scheduled in rescaled times. Due to the limited accuracy of the employed float variables, performing calculations with “small” rescaled times instead of “large” global times enhances the accuracy noticeably.
2. Simulation

2.6.3. Event types

In general we have 2 different classes of events: physical events, that process the microscopic particle dynamics, and administrative events, that manage the operational sequence and take care of the data storage.

1. Physical events

- **Brownian**, Information stored: event type and time,
  reassign velocities to all particles from a Gaussian random distribution using Eq. (2.36), erase and reinitialize the entire tree.

- **Collision**, Information stored: event type, two particle indices and time,
  elastic collision between two particles that is scheduled using Eq. (2.48).

- **Cell Crossing**, Information stored: event type, particle index, direction and time,
  one particle is transferred between two neighboring subcells.

- **Swelling**, Information stored: event type and time,
  inflating of all particles to a prescribed radius or a slightly smaller radius if this would lead to overlap.

2. Administrative events

- **Output**, Information stored: event type and time,
  write positional data or measurement results to file.

- **Time rescale**, Information stored: event type and time,
  rescale global and particle times by a constant time to sustain a sufficient numerical accuracy.

- **Quit**, Information stored: event type and time,
  terminate the simulation.

- **Rebuild**, Information stored: event type and time,
  erase and reinitialize the entire tree, only utilized for Newtonian dynamics.

2.7. Conclusions

In this chapter we presented a simulation method to model Brownian hard disks. We started with a description of the random motion of a colloidal particle immersed in a fluid in the framework of Langevin dynamics. This gave rise to a Monte-Carlo type sampling method. In a next step ballistic dynamics on short time scales was introduced to the algorithm. By that the requirement of overlap-free configurations at all times is fulfilled even at high densities. This construction is known to reproduce the statistics of hard disk systems correctly. In addition, we presented a method to implement simple shear flow.

We introduced the binary mixture of hard disks investigated in this work. Furthermore, we
2.7. Conclusions

showed how to set up and equilibrate these systems and used their director field to show that they are in an amorphous state. Technical details of the algorithm were given regarding boundary conditions and the prediction, book-keeping and processing of events. We developed new features, as e. g. rejuvenation-events, which rebuild the event-tree constantly, for systems undergoing Newtonian dynamics. The gained speed-up, combined with the employment of efficient swelling protocols, enables to prepare well-aged glassy systems containing several ten thousand particles.
3. Elastic shear moduli

In the previous chapter we introduced the simulation of a hard disk suspension, which can be used to model a colloidal glass-forming dispersion. Due to the wide range of technological applications, the rheology of such systems is of broad interest [2]. In particular, measurements of flow properties provide many informations about their viscoelastic behavior. Furthermore, such colloidal suspensions serve as model system for the analysis of the glass transition [5]. A dispersion of slightly polydisperse colloidal hard spheres vitrifies upon densification without undergoing crystal nucleation [46], and its rheology has been analyzed using concepts describing glassy arrest [53, 54]. Adding colloids to a solvent, the Newtonian viscosity of the mixture increases as compared to the pure solvent. At a critical value of concentration a crossover from the liquid into an amorphous solid occurs. This transition manifests itself by the emergence of mechanical rigidity to shear deformations on laboratory time scales. The arising macroscopic viscoelastic properties during this process are density-dependent and can be quantified in terms of the time-dependent shear modulus [2, 39]. At the colloidal glass transition the emergence of mechanical rigidity can be attributed to the (collective) excluded volume interactions [5]. Thus theoretical investigations and molecular dynamics simulations aiming for a microscopic understanding of shear stress correlations at the glass transition are suitable methods to investigate colloidal systems [55, 56, 57, 58, 59, 60, 61, 62, 63]. The rheology close to the glass transition of a binary mixture of Brownian hard disks moving in two dimensions as employed here was investigated in the past by several other works [11, 64, 13, 65]. In this chapter different strategies to determine the static shear modulus $G_\infty$ of a Brownian particle system close to its ideal MCT glass transition are presented. While parts of these methods were already suggested or tested in the works cited above, they are further developed, corrected and compared. Since MCT predicts the existence of a unique $G_\infty$, we will observe it and verify this claim employing the different measurement techniques. Furthermore, we aim to determine its dependence on the the packing fraction $\phi$, given by the fraction of the area filled by the disks and representing the only thermodynamic control parameter in our system. The shear modulus $G_\infty(\phi)$ close to the glass transition at $\phi_c$ is determined using three different simulation protocols.

- (I) The plateau values of the shear stress auto-correlation function,
- (II) the dispersion relations obtained from static displacement fluctuations,
- (III) the system’s linear response to strain deformations upon the start-up of simple
3. Elastic shear moduli

... shear flow are determined.

Comparing the mechanical properties seen via these three strategies provides insights into the vitrification process and the transition from viscous to emergent elastic response. The chapter is organized as follows: First the theoretical basis provided by MCT-ITT is recalled. It describes how to measure the static shear modulus $G_\infty$ in glass-forming systems of Brownian particles. This part was worked out by M. Fuchs and is taken from a publication worked out within this project [30]. This suggests three methods for computer simulations, which are described in Sect. 3.2. Simulations of shear-stress auto-correlation functions, transversal dispersion relations, and stress-strain relations in start-up shear flow are presented and studied in our two-dimensional binary mixture of hard disks. In Sect. 3.3, the different results for $G(t)$ and $G_\infty$ are discussed. Conclusions end the chapter.

3.1. Theory

The mode coupling theory (MCT) of the structural relaxation in liquids explains viscoelasticity in fluids and the emergence of elasticity at the glass transition [9]. It provides explicit results for the potential part of the time-dependent shear modulus $G(t)$ in fluids of hard spheres [66, 67, 50, 13], which have quantitatively been compared to colloid data [53, 47]. The theory has been generalized to the nonlinear rheological response for arbitrary homogeneous flow rates [68, 69], which also has been compared to rheology data from colloidal dispersions [47, 54, 17]. The central quantity of MCT capturing the shear elasticity is the static shear modulus $G_\infty$ [9], which e.g. determines the transverse sound velocity in molecular glasses. In overdamped systems, like colloidal dispersions or Brownian particle systems, it determines

- (i) the plateau at intermediate times of the shear stress correlation function in fluid states, or
- (ii) its long-time limit in (ideal) glass states.

In rheological experiments, it appears as a plateau in the linear storage modulus $G'(\omega)$ for low frequencies [54]. This plateau extends to arbitrarily low frequencies in ideal glass states (case (ii) above; but see Ref. [70] for deviations in nonideal glass states). For quiescent liquids, MCT predicts the existence of an ideal glass transition [9], which rationalizes many findings in colloidal dispersions [71, 5, 72, 73, 33]. It arises from a feedback mechanism in the coupling of local structural correlations (“cage effect”), and leads to transient particle localization and shear rigidity. The MCT for quiescent liquids has been generalized to homogeneously flowing systems considering colloidal glass former [68, 69]. Flow introduces the effect of the (affine) advection of long-wavelength fluctuations to short wavelengths. This causes a flow-induced breaking of cages and consequently a melting of glass. The history of the competition between
3.1. Theory

both dynamical mechanisms enters via integrating through the transients (ITT) even in cases where stationary states are considered. Predictions of ITT-MCT have been compared to experiments on model colloidal suspensions and found to provide a semi-quantitative description of many flow properties, including shear-thinning of the supercooled liquid and plastic flow or dynamic yielding of the glass \[54, 17, 72, 73, 33\]. Comparisons with computer simulations also verified many of the predictions \[74, 75, 76\], as well as did event driven simulations of the chosen Brownian particle mixture \[11, 12, 32, 31, 34\]. In the upcoming sections we will extend the tests of MCT-ITT by BD simulations by studying three different quantities simultaneously in order to test whether \(G_{\infty}\) is a well defined material parameter as predicted.

3.1.1. Stress response

The rheological response of a fluid of Brownian particles to homogeneous but otherwise arbitrary incompressible flows is given by a generalized Green-Kubo relation \[68, 69\]

\[
\sigma(t) = \frac{V}{k_B T} \int_{-\infty}^{t} dt_1 \left( \kappa(t_1) \cdot \hat{\sigma} e_{-1} \int_{t_1}^{t} ds \Omega(s) \hat{\sigma} \right)^{eq}. \tag{3.1}
\]

Here, \(\hat{\sigma}\) is the fluctuating stress tensor depending on the instantaneous particle positions and \(\sigma\) its macroscopic average. Brackets denote canonical averaging, and \(e_{-}\) the negatively time-ordered matrix exponential. \(V\) is the volume and \(k_B T\) thermal energy. The flow velocity gradient is denoted as \(\kappa(t) = (\nabla v)^T\). It is homogeneous and traceless, \(\kappa : 1 = 0\), in order to describe incompressible flow of the featureless background relative to which the particles perform random walks. The distribution function of the particles obeys Smoluchowski’s equation with the corresponding time evolution operator \(\Omega(t)\). Neglecting the flow-dependence of the time-evolution operator leads to the linear response result

\[
\sigma_{\text{lin resp}}(t) = \frac{2V}{k_B T} \int_{-\infty}^{t} dt_1 \left( \bar{\kappa}_{xy} G_{\|}^{\text{lin}}(t-t_1) \bar{\sigma}_{xy} \right)^{eq} \bar{\kappa}(t_1) \tag{3.2}
\]

Here, we used that only one response function, the time-dependent shear modulus \(G(t)\), appears for incompressible flow and that the microscopic stress tensor is symmetric \[77, 69\]. Thus, only the symmetrized velocity gradient \(\bar{\kappa} = (\kappa + \kappa^T)/2\) enters. Equation (3.2) defines the linear shear modulus \(G(t)\).

In the general flow case, not only the transversal (or shear) modulus appears but also the longitudinal one \[78, 65, 31\]:

\[
G(q, t) = \bar{q}q G_{\|}^q(t) + (1 - \bar{q}q) G_q(t). \tag{3.3}
\]

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3. Elastic shear moduli

Here, we stated the generalization of the stress memory kernel to finite wavevector \( q \) (with \( \hat{q} = q/q \) denoting its direction). We assume that the macroscopic shear modulus \( G(t) \) is obtained in the long wavelength limit, \( G(t) = \lim_{q \to 0} G_q(t) \); but see Ref. [79] for a discussion that this limit is actually non-analytic.

In the rheological investigations, we will consider the special case of simple shear flow in \( x \)-direction, varying linearly in \( y \)-direction: \( (\kappa_{\alpha\beta}(t) = \dot{\gamma}(t) \delta_{\alpha\beta}, \text{where } \dot{\gamma}(t) \text{ is the shear rate}) \). The shear stress at finite shear rates is then given by

\[
\sigma_{xy}(t) = \int_{-\infty}^{t} dt_1 \dot{\gamma}(t_1) G(t, t_1; [\dot{\gamma}]),
\]

which is used to define the nonlinear shear modulus, \( G(t, t_1; [\dot{\gamma}]) \). It is a functional of the velocity gradient tensor, and generalizes the linear modulus defined in Eq. (3.2) to finite shear rates.

3.1.2. Strain fluctuations

Displacement fluctuations at the glass transition have recently been of interest because they reveal intriguing far-field correlations [80]. These originate from force correlations in metastable solids and provide an alternative venue to access elastic correlations [65, 81]. In an idealized glass state, the long-time limit of the linear moduli is finite: \( G_\infty(q) = G(q, t \to \infty) \). Obtaining collective displacement fluctuations \( u_q(t) \) from integrating up velocity fluctuations, viz. solving \( \ddot{u}_q(t) = v_q(t) \), MCT predicts an equipartition theorem for static displacement correlations in glasses [65]:

\[
(\langle u_q^* u_q \rangle_{\text{glass}})^{-1} = \frac{q^2}{nk_B T} \left( G_\infty(q) + \frac{\dot{q} \hat{q}}{k_B T} \right) = \mathcal{D}(q),
\]

The equal time displacement variance, averaged over a restricted phase space associated with the glassy state, is determined by the tensor of elastic coefficients \( G_\infty(q) \). The long range of displacement correlations arises from the \( 1/q^2 \) variation in Eq. (3.5) for small \( q \). In Eq. (3.5), \( k_B T \) is the isothermal compressibility (of the underlying fluid state generalized to finite \( q \)) and \( \mathcal{D} \) stands for the dynamical matrix studied to obtain insight into the elastic spectrum of the system [81]. Its eigenvalues \( \lambda_{||}(q) \) and \( \lambda_{\perp}(q) \) represent the longitudinal and parallel dispersion relations and are related to the Lamé coefficients \( \mu \) and \( \lambda \) in the long wavelength limit [82]; see below.

3.1.3. MCT-ITT stability analysis of glassy structure

The theoretical results summarized in the previous two subsections contain various limits of a nonlinear, wavevector- and time-dependent shear memory kernel \( G(t, t_1, q; [\dot{\gamma}]) \). In the quiescent system, there holds \( G_q(t - t_1) = G(t, t_1, q; [\dot{\gamma} = 0]) \), and under steady homogeneous
3.2. Methods

flow, $G(t, t_1; \nu)$ = $G(t, t_1, q = 0; \nu)$. The crucial MCT-ITT prediction which we will test in the following is the nonlinear stability relation, first considered by Götze in 1985 for quiescent systems [83, 84], which has also been found to hold under steady homogeneous flow [85]. For states close to the glass transition at $\phi_c$, the decay of shear stress fluctuations at intermediate times is asymptotically given by

$$G(t, t_1, q; \nu) = G_c(\nu) + H(\nu) \frac{\gamma_0}{1 + a} + O(\nu^2).$$

The dominant term $G_c(\nu)$ is the frozen-in elasticity right at MCT’s glass transition point. It is seen at intermediate times in $G(t, \nu)$ for close by fluid states. It becomes the plateau shear modulus $G_c(0)$ at zero wavevector. The stability of the elastic structure is determined by the corrections to $G_c(\nu)$. $\Omega$ denotes a small scale and Eq. (3.6) holds for $\Omega \to 0$. The dominating correction contains the universal critical dynamics $G$ of MCT; the exponent $a$ is the critical exponent which takes the value $a = 0.32$ in a system of hard disks [86]. In quiescent glass states, viz. for $\dot{\gamma} = 0$ and $\phi > \phi_c$, elastic stresses are stored infinitely long, $G(t, \nu) \to \infty, x > 0, 0) \to \text{const.} > 0$. This predicts $G(t \to \infty) \to G_c(\phi) > G_c(\nu$ in glass. In fluid states, $\phi < \phi_c$, and under steady shear, $\dot{\gamma} > 0$, the correction initiates the decay of elastic stresses, $G(t, \nu) \to \infty, x < 0, y \neq 0) \to -\infty$. The final decay of the stress auto-correlation functions to zero is described by the $\alpha$-scaling law in quiescent fluids [9],

$$G(t) \to \tilde{G}(t, \dot{\gamma}) = G_c(1 - c t |\dot{\gamma}| + \ldots)$$

with constant $c > 0$ [85].

MCT-ITT thus predicts a well defined static shear modulus $G_c(\phi)$ close to the glass transition which can be observed by various rheological or other measurements. Testing this prediction using computer simulations, is the main aim of our work.

3.2. Methods

3.2.1. Simulational details

The Event driven algorithm for a 2D binary mixture of hard disks undergoing Brownian motion as introduced in Sect. 2 is employed. We use a quadratic simulation box with periodic boundary conditions (see Sect. 2.5.1) containing a 50:50 mixture of hard disks with diameters $d_s = 1$ and $d_b = 1.4$ (see Sect. 2.5.2). In a two-dimensional glass state finite size effects may appear [34, 87, 88], therefore the particle number $N$ was varied between $N = 1000$ and 32000. Apart from one exception for very high densities, the investigated functions show
3. Elastic shear moduli

no dependency on system size. This is discussed below and for the upcoming analysis a standard systems with $N = 1000$ disks were chosen. To avoid aging dependencies the system is driven into a well-aged state employing Newtonian dynamics for a time corresponding to $25 \times 10^3 \tau_0$ with $\tau_0 = d_s^2/D_0$ as defined in Eq. (2.45) being the Brownian diffusion time set by the diffusion constant. For details see Sect. 2.5.3. The mapping to the actual Brownian dynamics simulation (performed afterwards) is done by considering the final or $\alpha$-relaxation times. The shown data is based on at least 300 and up to 700 independent single runs for each packing fraction, shear rate or time interval, where the stress correlation functions were sampled for times up to $t = 5 \times 10^3 \tau_0$. The tested packing fractions, defined by the ratio of the area occupied by the disks to the total area, vary between $\phi = 0.77$ and $\phi = 0.81$. A fine grid with step width $\Delta \phi = 2.5 \times 10^{-3}$ is chosen in order to get an accurate estimate of the glass transition point which determined to $\phi_c \approx 0.7975$, see Chap. 3.

3.2.2. The stress tensor

A general macroscopic expression for the stress tensor originates from the continuity equation of momentum flux in the system [89, 25]

$$\sigma_{\alpha\beta} = \frac{1}{V} \left( \sum_i (v_i - u_i)_{\alpha}(v_i - u_i)_{\beta} + \sum_{ij} (f_{ij})_{\alpha}(r_{ij})_{\beta} \right), \quad (3.7)$$

where $u$ again denotes the coarse-grained local velocity and $f_{ij}$ the interparticle force associated with a pair potential, see Eq. (2.1). This expression represents the macroscopic stress, viz. a spatial average, which is legit for a spatially homogeneous structure. The first term on the right hand side represents the kinetic part, which is diagonal in the systems we investigate and linked to the thermal energy by the equipartition theorem Eq. (2.19). The thermostat introduced earlier in Sect.2.2 keeps this contribution constant and we will not pay particular attention to it in the following. The second term gives the potential part and contains the contributions of the particle interactions.

Technically the hard body potential is infinite at contact of the particles and zero otherwise. The interparticle force for a system with impulsive interaction is best described with the help of the Dirac delta function

$$f_{ij}(t) = \Delta p_{ij}\delta(t, \tau_c), \quad (3.8)$$

the force is only non-zero at time $\tau_c$ of a collision, with $\Delta p_{ij} = m_i \dot{r}_i - m_j \dot{r}_j$ the exchange of momentum between the partners $i$ and $j$ of an elastic collision, see Eq. (2.53), (2.54). This renders Eq. (3.7) in its current form unpractical. The appropriate modification is a
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reduction of the expression by its impulsive limit by integration over time leading to [90]

$$\sigma_{\alpha\beta} = \frac{1}{\Delta V} \sum_{\text{coll.}} \Delta p_{\alpha}(\tau_c) \Delta r_{\beta}(\tau_c),$$

(3.9)

where the sum runs over all binary collisions taking place in the volume $V$ within a short measurement period of length $\Delta t$. The relative distance between the two particle centers at collision is denoted as $\Delta r$, the momentum transfer as $\Delta p$. For reasonable results we demand the stress to be constant or vary slowly within the measurement interval.

3.2.3. Method I: Shear modulus from stress fluctuations

The first approach to quantify the rigidity goes back to a method to determine transport coefficients which is almost as old as MD simulations themselves. In 1970 Alder et al. [51] used the mean squared integrated stress $\langle (\int_0^t ds \sigma_{xy}(s))^2 \rangle$ to connect the low-shear viscosity $\eta(t)$ of a system to its equilibrium stress fluctuations

$$\eta(t) = \beta V \int_0^t dt' \langle \sigma_{xy}(t') \sigma_{xy}(0) \rangle,$$

(3.10)

where $\beta = 1/k_B T$ and $\langle \cdot \rangle$ denotes the average over simulation runs. An exact integral equation relates the transport coefficient $\eta(t)$ to the shear stress time auto correlation function $C_{\sigma\sigma}(t, t') = \langle \sigma_{xy}(t) \sigma_{xy}(t') \rangle$, where in the quiescent, stationary case $C_{\sigma\sigma}(t, t') = C_{\sigma\sigma}(t - t')$ holds. Hence, setting $t' = 0$, the long time shear modulus $G_\infty = \lim_{t \to \infty} G(t) = \lim_{t \to \infty} \beta V C_{\sigma\sigma}$ can be obtained by differentiation of the viscosity $\eta$ with respect to time $t$.

$$G(t) = \beta V \langle \sigma_{xy}(t) \sigma_{xy}(0) \rangle$$

(3.11)

$$= \frac{d}{dt} \eta(t)$$

(3.12)

$$= \beta V \frac{d}{dt} \int_0^t dt' \langle \sigma_{xy}(t') \sigma_{xy}(0) \rangle$$

(3.13)

$$= \frac{1}{2V k_B T} \frac{d^2}{dt^2} \left\langle \left( \sum_{\tau_c \in [0, t]} \Delta p_x(\tau_c) \Delta r_y(\tau_c) \right)^2 \right\rangle.$$  

(3.14)
3. Elastic shear moduli

\[
\eta(t) D_0 t = k_B T 
\]

where we used

\[
\frac{d}{dt} \left( \int_0^t dt' \sigma_{xy}(t') \right)^2 = 2 \int_0^t dt' \langle \sigma_{xy}(t') \sigma_{xy}(0) \rangle, \quad (3.15) 
\]

\[
\int_0^t dt' \sigma_{xy}(t') = \frac{1}{V} \sum_{\tau_c \in [0,t]} \Delta p_x(\tau_c) \Delta r_y(\tau_c). \quad (3.16) 
\]

With Eq. (3.14) the viscosity \( \eta(t) \) and the shear modulus \( G(t) \) are sampled by summing the oriented momentum transfer of all collisions within a time span \([0,t]\). The stress was sampled employing time intervals of exponentially growing length and the time derivatives were carried out numerically using difference quotients. An 11-point running average was performed on the resulting data. Figure 3.1 shows \( \eta(t) \) for several packing fractions \( \phi \) close to the glass transition at \( \phi_c \approx 0.7975 \). For packing fractions \( \phi \leq \phi_c \) a long time plateau \( \eta_{\infty} = \lim_{t \to \infty} \eta(t) \) indicated by dashed lines evolves.

![Figure 3.1: Shear viscosity \( \eta(t) \) for packing fractions close to the glass transition at \( \phi_c \approx 0.7975 \).](image)

For \( \phi \leq \phi_c \) a long time plateau \( \eta_{\infty} = \lim_{t \to \infty} \eta(t) \) indicates the viscous nature of the supercooled liquid. For values \( \phi \geq \phi_c \) the curves keep growing for long times. This indicates that the viscosity close to the glass transition diverges. With increasing packing fraction the stress relaxation is slowed down and the plateau is shifted to larger times. In line with this, Fig. 3.2 shows the two step relaxation process of \( G(t) \) in the liquid and the decay onto a long time plateau in the glass, which shows comparable features as simulation data from the literature [57, 60, 59, 91, 92, 93, 56]. For packing fractions \( \phi < \phi_c = 0.7975 \) the \( \alpha \)-relaxation with its characteristic decay time \( \tau_{\sigma}(\phi) \) is resolved. The timescale of the structural relaxation \( \tau_{\alpha} \) obtained from the incoherent density correlation function \( \Phi_{\eta} \) is presented later in Fig. 4.4 and shows the same density dependence.
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but is slightly larger than the stress relaxation time. The $\alpha$-relaxation superposition principle allows to shift the final relaxation of the time dependent shear modulus for all densities onto a master curve. See the open circles in Fig. 3.2 and upper x-axis; the shifted times $\tau_\sigma$ are given in the inset of Fig. 3.7 below. The scaling function is described by a stretched exponential

\[ G(t, \phi) = G_\infty^c \exp[-t_\phi^\beta], \]

a so-called Kohlrausch law, with rescaled time $t_\phi^\prime = t\tau_\sigma(\phi)/\tau_\sigma(\phi)$. We take the exponent $\beta = 0.6$ from a MCT calculation of hard disks [86] and fit the critical shear modulus, which gives $G_\infty^c = 54.4nk_B T$. The height of this intermediate plateau governs the elastic response to rapid shear deformations in supercooled liquids close to the glass transition point. The scaling breaks down for values $\phi \geq \phi_c$, viz. for densities in the glass, because the plateau value $G_\infty^c(\phi)$ grows larger than $G_\infty^c$ monotonically with $\phi - \phi_c$. While a fast-decay at $t \lesssim \tau_0$ is still observed, the final decay of the stress correlations shifts to the end of the simulation window when crossing the transition point. For an ideal glass transition as predicted by MCT [9], the plateau value $G_\infty^c$ holds out to infinite time for $\phi \geq \phi_c$, which is too large to be observed in experiments and simulations. Then, the stress relaxation simply occurs outside the observation time window. Also in our case, the observed plateau is not stable and a small decay can be observed, which can be approximated by $G(t) = G_\infty^c - c\sqrt{t}$.

Figure 3.2 shows that the MCT predictions concerning $G_\infty^c$ can be supported by the simulation data. Yet, using the superposition principle of the $\alpha$-process is crucial for determining an accurate estimate of the glass transition density because of the relaxation processes present in glass states but not contained in MCT. Also the limited time window accessible by simulations prevents fitting the plateau value $G_\infty^c$ without ambiguity in fluid states.
3. Elastic shear moduli

Figure 3.2.: Shear stress auto-correlation function $G(t)$ in equilibrium for different packing fractions $\phi$ in the supercooled liquid (left panel; $\phi < \phi_c$) and glass (right panel; $\phi > \phi_c$); from the $\alpha$-scaling we estimate $\phi_c \approx 0.7975$. Circles show the scaled stress correlation functions falling on a master curve that is described by a Kohlrausch law $G_\infty \exp\left(-\frac{(t\tau_\sigma(\phi_c))/\tau_\sigma(\phi)}{\tau_\sigma(\phi_c)}/\beta\right)$ for $G_\infty = 54.4 n k_B T$, $\tau_\sigma(0.7975) = 1554 \tau_0$ and $\beta = 0.60$ (black dashed line); see the upper x-axis for the rescaled times. In the glass a fit $G(t) = G_\infty - c\sqrt{t}$ is added (dashed lines).

3.2.4. Method II: Shear modulus from displacement fluctuations

In 2012 Klix et al. [65, 81] used the method presented in Sect. 3.1.2 to obtain microscopic expressions for the elastic shear and bulk modulus from the wave-vector dependent dispersion relations in amorphous solids. This approach is motivated by a technique to determine the dynamic matrix in a colloidal crystal in two dimensions by measurement of the spatial correlations via video microscopy [82]. Here the displacement field is defined via the centers of mass of the particle trajectories, which serve as the equivalents of lattice sites of a 3D crystal. A particle’s mean position $r_i$ is calculated by an average over a time $\Delta t$ where $\tau_0 \ll \Delta t < \tau_\alpha$, such that the glassy part of the dynamics of the suspension is evaluated. The displacement of particle $i$ is then defined as $u_i(t) = r_i(t) - \bar{r}_i$, with $r_i(t)$ its position at time $t$. The according collective displacement field is now, neglecting terms of order $O(\mathbf{qu}_i)$, approximated by

$$u_q(t) = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} e^{i\mathbf{q}\mathbf{r}_i} u_i(t), \quad (3.17)$$

where we require the expansion $e^{i\mathbf{q}\mathbf{r}_i} = e^{i\mathbf{q}\mathbf{r}} + O(\mathbf{qu}_i)$ to hold, which is true if the displacements are bounded within the measurement window. Under the assumption of a kinetic, ideal glass transition this leading order approximation can be justified within the framework of MCT, see [65, and references therein]. From the equation of motion for the displacement
3.2. Methods

Autocorrelation function in the overdamped limit one arrives at the equipartition theorem Eq. (3.5). From this the dispersion relations are obtained which in the limit for small wavevectors give the shear modulus $G_\infty = \mu$ and longitudinal modulus $G_\parallel = 2\mu + \lambda$, employing the familiar Lamé-notation. The elastic constants can be extracted from the longitudinal and transverse displacements $u^\parallel(q)$ and $u^\perp(q)$ in the small wavevector limit. Let us first look at an example, where we choose the wave vector parallel to the $x$-axis, $q = q\hat{x}$, such that the dynamical matrix $D$ is diagonal with the corresponding dispersion relations as only non-zero entries,

$$
\lim_{q \to 0} \frac{D(q)}{q^2 k_B T} = \lim_{q \to 0} \begin{pmatrix}
\frac{1}{q^2 u^\perp_1(q)} & 0 \\
0 & \frac{1}{q^2 u^\perp_\perp(q)}
\end{pmatrix} = \frac{1}{k_B T} \lim_{q \to 0} q^{-2} \lambda_\parallel(q) \begin{pmatrix}
0 & 0 \\
0 & q^{-2} \lambda_\perp(q)
\end{pmatrix} = \frac{1}{nk_B T} \begin{pmatrix}
2\mu + \lambda & 0 \\
0 & \mu
\end{pmatrix}.
$$

Figure 3.3 shows the components of the equal time quadratic displacement correlations $\langle u^*(q)u(q) \rangle$, where $q = q\hat{x}$, and the corresponding dispersion relations in the glass at $\phi = 0.81$. The off-diagonal elements $\langle u^*_x(q)u_y(q) \rangle = \langle u^*_y(q)u_x(q) \rangle$ fluctuate with negligible amplitude around zero, where the elastic spectrum is contained in the diagonal elements. Here a quadratic dependence on $q$ in the small wave vector limit of $\lambda_\perp(q)$ and $\lambda_\parallel(q)$ indicates the solidity of the glassy system. Therefore the elastic constants can be extracted from the longitudinal and transverse displacements $u^\parallel(q)$ and $u^\perp(q)$ by a quadratic fit for small

Figure 3.3.: Left panel: Components of $\langle u^*(q)u(q) \rangle$ for $\phi = 0.81 > \phi_c$, $\Delta t = 5.12\tau_0$ and $q = q\hat{x}$, the non-diagonal components are negligible compared to the diagonal ones, see Eq. (3.20); right panel: dispersion relations $\beta \lambda_\parallel(q)$ (blue) and $\beta \lambda_\perp(q)$ (orange), quadratic fit (dashed orange) in the small wave vector limit.
3. Elastic shear moduli

wavevectors to the dispersion relations. We use $qd_s \leq 0.6$ and that the system is 2D:

$$\langle u^*_{q\perp} u_{q\perp} \rangle^{-1}_{\text{glass}} = q^2 \frac{\mu}{nk_B T} = \frac{\lambda_{\perp}(q)}{k_B T},$$

(3.21)

$$\langle u^*_{q\parallel} u_{q\parallel} \rangle^{-1}_{\text{glass}} = q^2 \frac{2\mu + \lambda}{nk_B T} = \frac{\lambda_{\parallel}(q)}{k_B T}.$$  

(3.22)

As the displacement fluctuations are ergodic in this restricted phase space, $\langle \cdot \rangle_{\text{glass}}$ includes time averaging over a time interval of length $\Delta t < \tau$ using $10^4$ configurational snapshots. Further an average over simulation runs and, as the systems investigated are isotropic, over directions in reciprocal space are performed. For this Eq. (3.17) was evaluated on a quadratic grid in $q$-space with lattice constant $\Delta q d_s = 0.17$. Figure 3.4 shows the dispersion relations at two different packing fractions, one in the glass and one in the supercooled liquid. As predicted by Eq. (3.21) and (3.22) a quadratic dependence on $q$ in the small wave vector limit is found indicating the solidity of the system during the tested time interval. From the quadratic fits, an effective stiffness $G_{\text{samp}}(\Delta t)$ is obtained. Measured data are very sensitive to the length of the time interval $\Delta t$ over which positional data is collected [94]. While the precise functional form of the sampled stiffness $G_{\text{samp}}(\Delta t)$ cannot be related to the time-dependent shear modulus $G(\Delta t)$, we find that both track each other. For short times $\Delta t \approx \tau_0$ the initial decay caused by short time diffusion is sampled leading to high values of $G_{\text{samp}}(\Delta t)$ for the glassy and fluid systems. These values embody the stiffening that is also seen in $G(t)$ for short times, equivalently in the linear response moduli for high frequencies [95, 96]. In glass, for larger sampling intervals this value saturates at $\lim_{\Delta t \to \infty} G_{\text{samp}}(\Delta t) = G_{\infty}$, in agreement with Eq. (3.21). In fluid states, at larger times (or lower frequencies) comparable to the system’s $\alpha$-relaxation time $\tau_\alpha$ viscous flow due to the fluid structural rearrangements sets in. In this case the measurement time interval contains both short-time and long-time processes, but due to the equidistant sampling times of the configuration snapshots the latter dominate. Accordingly for densities below the critical value $\phi_c$ the dispersion relations flatten out and smaller and smaller $G_{\text{samp}}(\Delta t)$ are recorded for increasing $\Delta t$. This behavior allows for a rather strict distinction between glassy and fluid states. The values for the longitudinal moduli exceed the transversal ones clearly, it is $G_\parallel^{\infty} \approx 7G_\parallel$. In comparison to methods relying on the measurement of stresses and thus collision statistics, the dispersion relations determined by the displacement field profit from the good statistics from positional data. Consequently the noise level of the shown curves is very low and allows for an accurate determination of the moduli.
3.2. Methods

3.2.5. Method III: Shear modulus from stress-strain relations after startup shear

In the following we use a flow-protocol

\[
\dot{\gamma}(t) = \begin{cases} 
0 & t < 0 \\
\dot{\gamma} & t \geq 0
\end{cases}
\]  

(3.23)

to examine the effect of a shear rate on the shear stress in the system. At times \( t < 0 \) the system is in an unperturbed, well aged state with vanishing shear stress \( \langle \sigma_{xy}(t) \rangle = 0 \). From \( t = 0 \) on the system undergoes shear with a constant and spatially homogeneous shear rate \( \dot{\gamma} \) as described in Sect. 2. For \( t > 0 \) during start-up flow the transient stresses as function of the accumulated strain \( \gamma = \dot{\gamma} t \) are given by the constitutive equation

\[
\sigma(t) = \int_{-\infty}^{t} \dot{\gamma}(t') G(t', \dot{\gamma}(t)) dt'
\]

(3.24)

\[
= \int_{0}^{t} \dot{\gamma} G(t', \dot{\gamma}) dt'
\]

(3.25)

\[
= \frac{1}{\Delta t V} \sum_{\text{coll.}} \Delta p_x(\tau_c) \Delta r_y(\tau_c),
\]

(3.26)
3. Elastic shear moduli

Figure 3.5.: Stress-strain relation for the transient regime of startup of shear flow for the glass (upper panel, φ = 0.8075) and supercooled liquid (lower panel, φ = 0.7925) for varying shear rates \( \dot{\gamma} \) given in the legends. Dashed lines show the linear fits \( G_{\text{lin}}(1/\dot{\gamma})\gamma + C \) at the strain interval of elastic response at strain \( \dot{\gamma}t \approx 10^{-2} \). High (low) shear rates \( \dot{\gamma} \) correspond to short (long) times \( t \); see details in the main text. Again \( G_{\text{lin}}(1/\dot{\gamma}) \) asymptotically saturates in the glass, now for \( \dot{\gamma} \to 0 \), while it decays to zero in the fluid.

where again the sum runs over all collisions within a small time window \( \Delta t \) around \( t \) (see 3.2.2) and \( G(t, \dot{\gamma}) \) denotes the shear rate dependent stress kernel or stress correlation function of Eq. (3.4).

Figure 3.5 shows the transient stress \( \sigma_{xy} \) as function of the accumulated strain \( \dot{\gamma}t \) for a glassy system at packing fraction \( \phi = 0.8075 \) and a fluid one at \( \phi = 0.7925 \). In the initial response for strains \( \gamma \lesssim 0.02 \), the suspensions behave like a solid and the shear stress grows linearly with strain, just like Hooke's law describes the linear response of elastic bodies as \( \sigma_{xy} = G_{\text{lin}}\gamma \). Obviously this also holds in fluids for short times. Then the system transiently stores an increasing amount of elastic energy until it yields around the overshoot at \( \gamma \approx 0.07 \).

From there, the shear stress decreases monotonically to the steady stress level \( \sigma_{xy}^{\text{tot}} \) associated with a stationary state that is reached for \( \gamma \gtrsim 1 \); for comparable results see Refs. [16, 97, 98]. In the regime of elastic response we obtain \( G(t) \) from a linear fit \( f_{\dot{\gamma}}(\gamma) = G(t)\gamma + C \) to the stress data. Shear rates \( \dot{\gamma} \) corresponding to Peclet numbers \( \dot{\gamma}\tau_0 \in [4 \times 10^{-5}, 4 \times 10^{-1}] \) have been applied and \( C \) is negligible for \( \dot{\gamma}\tau_0 \) below \( 10^{-2} \). The stress vs accumulated strain curves depend rather weakly on the applied strain rates. The linear response regime and the stress overshoot region is shifted to smaller strain regions for lower shear rates. To fix the \( \dot{\gamma} \)-dependent interval of elastic response, we considered the time intervall \( [t_0, t_1] = [0.05t^*_s, 0.3t^*_s] \), where \( t^*_s \) denotes the time at the stress maximum. Accordingly for decreasing shear rate the value of \( t_1 \) increases nearly with \( 1/\dot{\gamma} \). Therefore we are able to sample \( G_{\text{lin}}(1/\dot{\gamma}) \) over 5
3.3. Results and discussion

decades by varying $\dot{\gamma}$ over 5 decades. For high $\dot{\gamma}$ the shear start-up interferes with the initial short-time motion resulting in high values. In the glass the values of the linear slopes saturate for decreasing shear rates, $G_{\text{lin}}(1/\dot{\gamma} \to \infty) \to G_{\infty}$, and yield the static shear modulus. The slow approach is in line with the very slow decay to the intermediate plateau seen in the time-dependent shear moduli. In the liquid for small shear rates corresponding to large times, the effective linear shear modulus $G_{\text{lin}}(1/\dot{\gamma})$ has almost completely decayed to zero. More precisely for $\dot{\gamma} \tau_0 \lesssim 10^{-4}$ the chosen time window exceeds the structural relaxation time and the response becomes viscous.

3.3. Results and discussion

The methods described above are capable of quantifying the level of rigidity in terms of the time dependent shear modulus $G(t)$ over five decades in time. Using identical initial positional configurations of the simulation runs, we are able to compare the findings of the different measurements unambiguously. Method III is based on the fact, that in the strain window of linear response the $\dot{\gamma}$-dependent shear modulus $G(t, \dot{\gamma})$ coincides with the shear modulus $G(t)$ at rest, see section 3.1.1. From Eq. (3.25), the nonlinear shear modulus is $G(t, \dot{\gamma}) = \dot{\gamma}^{-1} \partial_t \sigma_{xy}(t, \dot{\gamma})$. The derivative is numerically evaluated using a five point rule. Method I provides $G(t)$ directly, see Eq. 3.2. The two quantities are shown in Fig. 3.6 for packing fractions close to the glass transition point. Additionally, the estimates of $G_{\infty}(\phi)$ from the displacement fluctuations (Method II) for two different sampling windows $\Delta t$ are included as horizontal bars.

Figure 3.6 is the central result of our study. Both the quiescent and the sheared time-dependent modulus exhibit a fast short time relaxation, which is $\dot{\gamma}$-independent within the scatter of the data. For longer times, the linear time-dependent moduli exhibit the transient plateau given by $G_{\infty}(\phi)$ for time ranges limited by the $\alpha$-relaxation time $\tau$. The nonlinear moduli also relax onto the plateau $G_{\infty}(\phi)$, which is transient for the sheared system and corresponds to the linear growth of the shear stress during elastic response. After that $G(t, \dot{\gamma})$ decays on a time $\tau_{\gamma} \sim \dot{\gamma}^{-1}$ roughly proportional to the inverse shear rate. This shear rate dependence is equivalent to the observation of the peak position in the stress-strain relations that varies only slightly with $\dot{\gamma}$. Further this shear stress overshoot translates into an undershoot in the shear moduli. For large times the function vanishes as soon as a stationary state with a stress tensor that is constant in time is reached.

For densities $\phi \leq 0.805$ the quiescent modulus $G(t)$ can be reassembled by putting together the transient plateaus of the sheared modulus $G(t, \dot{\gamma})$ for the various shear rates. For densities not too high, a close agreement between the moduli from Methods I and III is found, both in the supercooled liquid as well as in the glass. The static moduli $G_{\infty}(\phi)$ from Method II are added in Fig. 3.6 using two different values $\Delta t$ of the sampling window. The values are indicated by vertical lines. As discussed, the estimated static moduli $G_{\infty}^{\text{method II}}(\phi)$ agree
3. Elastic shear moduli

Figure 3.6: Comparison between the estimates for the time-dependent shear modulus $G(t)$ for quiescent (black crosses) and sheared systems (colored symbols) for varying densities as labeled. The purple and orange dashed horizontal lines indicate the value for $G_{\infty}$ from displacement fluctuations determined for $\Delta t_1 = 22\tau_0$ and $\Delta t_1 = 203\tau_0$; these time intervals are marked by vertical dotted lines. In the glass for $\phi < 0.805$ the obtained plateau values are in very good agreement, while deep in the glass for $\phi \geq 0.805$ Method I overestimates $G(t)$ compared to Methods II and III.

if the time window $\Delta t$ is chosen such that the sampling is dominated by the elastic region, where $G(t) \approx G_{\infty}$. For low densities, choosing too large $\Delta t$ gives strongly differing estimates, because the displacement fluctuations are falsified by structural motion. For packing fraction above $\phi \geq 0.80$, the static moduli $G_{\infty}(\phi)$ from Methods II and III agree as expected from the assumptions entering both methods. Combining all three methods thus provides the static moduli for the complete range of densities around the glass transition value $\phi_c \approx 0.7975$, which was estimated from the $\alpha$-scaling property. This reinforces the validity of the applied methods and the underlying relations for the shear modulus predicted by MCT. The short time response for times $t < \tau_0$ cannot be determined reliably in our simulations, owing particularly to high noise levels because of short sampling times and high Péclet numbers.
(Method III) corresponding to strong external driving.

Figure 3.7.: Density dependence of the plateau shear modulus $G_\infty$ as worked out using the 3 methods: for two long times $t = 22\tau_0$ (purple) and $t = 203\tau_0$ (orange) (Method I), for the two largest measurement intervals of length $\Delta t = 22\tau_0$ (purple) and $\Delta t = 203\tau_0$ (orange) (Method II), and for the two corresponding smallest shear rates $\dot{\gamma}\tau_0 = 4 \times 10^{-4}$ (purple) and $\dot{\gamma}\tau_0 = 4 \times 10^{-5}$ (orange) (Method III). Also, the critical shear modulus $G_\infty^c$ from the $\alpha$-scaling in the fluid is included. The inset shows the divergence of the relaxation time $\tau$ with $\gamma = 2$. Predicted from theory [86], where the dashed line indicates a fit $y = 40.5(\phi^c - \phi)$ to the expected linear behavior.

For packing fractions $\phi \geq 0.805$, Method I overestimates the plateau value, predicted consistently by the other two methods (II and III), by up to 20%. This deviation was observed for several system sizes from $N = 500$ up to 64000 particles (not shown), where an additional spreading of the plateau values was found showing no clear trend in the size dependence. The other two methods found no dependence on the particle number $N$. Further in a careful analysis no signs of aging effects could be found and regarding the distribution of single runs no statistical outliers causing this behavior were detected. We therefore judge Method I to be untrustworthy for states deep in the glass. In [65], the same system was investigated by comparable simulations and different results were obtained for Method I. We found that the differences are based on inaccurate processing of the positional data in the simulations of Ref. [65], and judge our data to be correct.

Figure 3.7 shows the $\phi$-dependence of $G_\infty$ as obtained using all three Methods. A small step width of $\Delta\phi = 2.5 \times 10^{-3}$ allows to resolve the rapid but continuous increase of $G_\infty(\phi)$ in a narrow region around the glass transition. For all methods, data using the two very long measurement times $t$ (Method I), measurement intervals $\Delta t$ (Method II), or inverse shear rates $1/\dot{\gamma}$ (Method III), are shown with time spans considerably larger than $\tau_0$. For
3. Elastic shear moduli

packing fractions in the fluid the α-relaxation has already set in at the times employed and all methods obtain values smaller than the constant plateau modulus $G_{\infty}^c$ predicted by MCT. It can only reliably be determined from the α-scaling of the linear moduli for different $\phi$ (see upper panel in Fig. 3.2), or from the $\dot{\gamma}$-scaling of the nonlinear moduli visible in Fig. 3.6. The thus obtained estimates of the α-relaxation times $\tau$, which should algebraically diverge according to MCT, $\tau \sim (\phi_c - \phi)^{-\gamma}$ [9] with exponent $\gamma \approx 2.38$ for monodisperse hard disks [86], support the estimate of $\phi_c$; see the inset of Fig. 3.7. In the glass, the agreement between the values determined using the different methods is satisfactory except for the deviation of the plateau value in $G(t)$ (Method I) deep in the glass.

3.4. Conclusions

We presented simulational results on the sampling of the time dependent shear modulus of a two dimensional Brownian mixture of hard disks close to its glass transition. We showed that the shear modulus $G_{\infty}(\phi)$ as predicted by mode coupling theory is accessible from the plateau value of the stress correlation function, the suspension’s dispersion relations, and the linear stress-strain relations during startup of simple shear flow. Controlling the packing fraction we approached the glass transition from the fluid regime and determined a finite, constant shear modulus $G_{\infty}^c = G_{\infty}(\phi_c)$. Upon further densification in the glass this value grows representing a stiffening of the solid system. Verified by consistent results from all applied measurements we presented a procedure to unambiguously determine the glass transition point according to MCT which is in line with existing experimental works [99]. Deep in the glass we found deviations of $G_{\infty}$ obtained by sampling the stress auto correlation function from the values obtained by the two other methods. The plateau values of the stress correlation functions are above the values obtained from the response to external shear or from the dispersion relations. This discrepancy is presently not understood.
4. Strain patterns

In this chapter the strain-fields at the crossover from metastable glass states to supercooled liquids are investigated, an old [100] but nevertheless current research topic. This problem is sufficiently well understood for amorphous solids. However, as in Chapter 3 the crossover from elastic to emergent viscous response of the material reveals remarkable findings, which will be presented in the following.

Again, above the critical packing fraction of the glass transition colloidal suspensions behave like isotropic elastic solids. This fact gives rise to long-ranged and long-lived Eshelby-strain patterns familiar from classical continuum mechanics [101, 102]. A very similar concept, describing plastic deformations that are elastically coupled by strain fields, is also postulated by works on plasticity of solids with amorphous structure [103]. Eshelby-type strain fields, characterized by a hexadecupolar symmetry and a power-law decay in the far-field, are reported for a wide variety of similar systems. Among those are experiments on 3D colloidal glasses in quiescent state and under shear [104, 15], granular matter [105], 2D flowing emulsions [106] and 2D soft hexagonal crystals [107]. In simulations they are seen for several types of glass formers in 2D and 3D [15, 108, 109] and foams [110].

The project presented here was mainly motivated by findings of 2D Lennard-Jones simulations of sheared supercooled liquids presented by Anaël Lemaître [80, 58]. There the authors report the observation of this pattern, typical for elastic solids, in liquids for strains accumulated over times larger than the structural relaxation time. Since elastic stresses have already decayed in this time window, an interaction of strains over large distances in an underlying elastic structure is therefore implausible.

In the following, we present the emergence of this pattern in our BD simulation of quiescent colloidal suspensions while approaching the glass transition. In cooperation with Bernd Illing, Christian L. Klix and Peter Keim we were further able to provide the first experimental evidence of Eshelby-patterns in a 2D colloidal glass former in the supercooled state. A theory of generalized hydrodynamics suggests the existence of a viscosity-dependent temporal regime, where strain signatures are observed in the liquid. This can be confirmed in simulations.

This chapter is organized as follows. First, the experimental system is briefly introduced. Next, the strain tensor and its spatial autocorrelation, its determination in this context and its form for isotropic elastic solids is presented. After that, the same quantities are studied within generalized hydrodynamics for highly viscous fluids. This allows us to obtain
4. Strain patterns

predictions, which are then confirmed in simulations and experiments.

4.1. Strain tensor

In continuum mechanics, the strain tensor is a measure for the deformation of a solid body. If the displacements, on which this tensor is based, are small compared to any other relevant length scale in the system, it is sufficient to study the linearized strain tensor. The displacement of particle $i$ accumulated over a time interval $[t_1, t_2]$ is given by

$$u_i(t_1, t_2) = r_i(t_2) - r_i(t_1).$$ (4.1)

This differs from the definition used in section 3.2.4, where the displacement was defined as the deviation from a mean particle position. A displacement field $u(r, t_1, t_2)$ can be constructed from the displacements of all $N$ particles using an appropriate coarse-graining procedure similar to the one established in [111],

$$u(r, t_1, t_2) = \frac{1}{\rho(r, t_2)} \sum_{i=1}^{N} u_i(r_i, t_1, t_2) \phi_{\sigma, r_c}(|r - r_i(t_2)|),$$ (4.2)

with coarse-grained density $\rho(r, t) = \sum_{i=1}^{N} \phi_{\sigma, r_c}(|r - r_i(t)|)$ and a Gaussian coarse-graining function

$$\phi_{\sigma, r_c}(r) = \frac{1}{C(r_c, \sigma)} \begin{cases} \exp \left(-\frac{r^2}{2\sigma^2}\right) & \text{if } r < r_c, \\ 0 & \text{else}, \end{cases}$$ (4.3)

where in 2D the normalization constant reads $C(r_c, \sigma) = 2\pi\sigma^2 \left(1 - \exp(-r_c^2/2\sigma^2)\right)$. The standard deviation $\sigma = d_s$ and cutoff radius $r_c = 3d_s$ were chosen such that all 3 first order peaks of the radial distribution function of the binary system are taken into account, see Fig. 4.1. The linearized strain field at position $r$ in two dimensions is then given as the symmetrized displacement gradient

$$\varepsilon(r, t_1, t_2) = \frac{1}{2} \left( \nabla u(r, t_1, t_2) + \nabla u^\top(r, t_1, t_2) \right),$$ (4.4)

$$\varepsilon_{\alpha\beta}(r, t_1, t_2) = \frac{1}{2} \left( \frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha} \right).$$ (4.5)

An expansion taking into account second order terms $(\partial u_\gamma/\partial r_\alpha)(\partial u_\gamma/\partial r_\beta)$, where Einstein sum convention applies, was tested as well. It is found to slightly alter the values obtained for large absolute displacements accumulated in the long time diffusive regime for liquid states, which is irrelevant for the upcoming analysis. Therefore the key results described in the following are not affected, as shown (among further details on the calculation of the strain
4.1. Strain tensor

Figure 4.1.: Coarse-graining function $\phi^{\sigma, r_c}(r)$ (orange, multiplied by a factor $c = 62$) and radial distribution function $g(r)$ (blue), where the three first order peaks of the binary mixture are located at $\sigma_s + \sigma_s$, $\sigma_b + \sigma_s$ and $\sigma_b + \sigma_b$, with $\sigma_s = 0.5d_s$ ($\sigma_b = 0.7d_s$) the radius of the small (big) particles.

tensor) in A.2 in the appendix. An alternative way to determine the displacement field is to integrate a coarse-grained velocity field over time. This was not tested, since in [111] it is argued that Eq. (4.2) is the relevant displacement field for linear elasticity and the error in $u(r, t)$ made by this is nonlinear in strain and therefore negligible. A visualization of a typical strain field is given later in another context in Fig. 5.11. Following [80], the quantity investigated in the following is the transverse element of the average spatial autocorrelation of the strain field,

$$C_{xy}(r, t) = \langle \varepsilon_{xy}(r, t) \varepsilon_{xy}(0, 0) \rangle .$$

(4.6)

For the homogeneous systems tested here this quantity depends only on the relative distance $r = r_2 - r_1$. For an equilibrated liquid or well aged glass we may assume stationary conditions and a dependence on the time difference $t = t_2 - t_1$ only. This allows us to take spatial averages on a particle position based grid and time averages over multiple intervals of identical length, see A.2 for further details. Hence the transverse strain correlation function simplifies to

$$C_{xy}(r, t) = \langle \varepsilon_{xy}(r, t) \varepsilon_{xy}(0, t) \rangle ,$$

(4.7)

where in the case of simulations $\langle \rangle$ also includes an average over different runs.

First results on the dynamics of $C_{xy}(r, t)$ in solids date back to 1957, when J. D. Eshelby calculated the far-field caused by an elastic distortion of a solid around a homogeneous
deformation of a localized elliptical region [101], which in 2D reads

\[ C_{xy}(r, t) \rightarrow C^* (t) \frac{\cos (4\theta)}{4\pi nr^2} \text{ for } r \gg a, \]

where \( a = n^{-1/d} \) denotes the mean inter particle distance. We employ polar coordinates \( r = (r \cos \theta, r \sin \theta) \), where the angle \( \theta \) is measured relative to the cartesian \( x \)-axis. Note, that for the isotropic systems discussed here this choice of an preferred direction is completely arbitrary. In a \( d \)-dimensional system the pattern entails a spatial dependence characterized by a Green’s function \( \cos (4\theta)/4\pi nr^d \) with four-fold symmetry, a far-field power law decay \( \sim r^{-d} \) valid at distances \( r \) much larger than \( a \). Remarkably, the time-dependence affects only the amplitude function \( C_s(t) \) of this correlation. The fundamental equation of elastostatics predicts

\[ C^* (t \to \infty) = 2k_B T n \left( \frac{1}{G^\infty} - \frac{1}{G_{\perp}^\infty} \right), \]

where \( G^\infty \) and \( G_{\perp}^\infty \) denote the shear modulus and the transversal shear modulus, respectively, determined in Sect. 3.2.4. More recent works evaluate functions of the same type, to investigate plastic deformations, which are elastically coupled to strain fields. A detailed derivation of the dynamic elastic Green propagator in an elasto-plastic model for an infinite 2-dimensional system undergoing simple shear flow can be found in [112]. In [80] this function is derived using a fluctuation-response theorem for particle vibrations around so-called inherent states of the underlying elastic structure.

4.2. Strain pattern in hydrodynamics

To understand the emergence of this pattern in highly viscous supercooled fluids instead of solids, we turn to a microscopic hydrodynamic description of the problem. In this section the results are briefly sketched, for a full analysis see the original works [31, 65, 113]. The dynamics of a homogeneous system is captured by the wave-vector dependent transversal and longitudinal collective mean-squared displacements (CMSD)

\[ C^{\perp}(q, t) = \langle \Delta u_{3q}^\perp(t) \Delta u_{3q}^\perp(t) \rangle \]

\[ C^{||}(q, t) = \langle \Delta u_{q}^{\parallel}(t) \Delta u_{q}^{\parallel}(t) \rangle, \]

\[ C^{\parallel}(q, t) = \langle \Delta u_{q}^{\parallel}(t) \Delta u_{q}^{\parallel}(t) \rangle, \]
4.2. Strain pattern in hydrodynamics

where the relations

\[ \Delta u_q(t) = \int_0^t dt' v_q(t') \]  
\[ (4.12) \]

\[ C(q,t) = \langle \Delta u_q^*(t) \Delta u_q(t) \rangle = 2 \int_0^t dt' (t - t') \langle v_q(t) v_q(0) \rangle \]  
\[ (4.13) \]

between displacements and fluctuations of the velocity \( v_q \) are assumed to hold and the transversal (longitudinal) functions take into account only fluctuations perpendicular (parallel) to the wave vector \( q \). These quantities can be easily transferred into real space by an inverse Fourier transformation to obtain the transverse strain correlation function

\[ C_{xy}(r,t) = \mathcal{F}^{-1} \left[ \frac{q^2 x^2 + q^2 y^2}{4} C_\perp(q,t) + \left( C_\parallel(q,t) - C_\perp(q,t) \right) \frac{q^2 q_y^2}{q^2} q^2 \right] (r). \]  
\[ (4.14) \]

We can use known results \[78\] for the velocity correlation function to find equations of motion (EOM) for the strain correlation functions. In the overdamped and long wavelength limit, \( qa \ll 1 \), the transversal and longitudinal part are found to decouple. The EOM found in this generalized hydrodynamics (\( gH \)) framework are given by

\[ C_\perp^{gH}(q,t) + \frac{q^2}{\zeta_0 n} \int_0^t dt' G_\perp(t - t') C_\perp^{gH}(q,t') = 2D_0 t, \]  
\[ (4.15) \]

\[ C_\parallel^{gH}(q,t) + \frac{q^2}{\zeta_0 n} \int_0^t dt' \left( G_\parallel(t - t') + \frac{1}{\kappa_T^q} \right) C_\parallel^{gH}(q,t') = 2D_0 t, \]  
\[ (4.16) \]

with friction coefficient \( \zeta_0 = (\beta D_0)^{-1} \), isothermal compressibility \( \kappa_T^q \), transversal/longitudinal time dependent stress kernel \( G^{\perp/\parallel}(t) = \frac{n}{\kappa_T^q} (\sigma^{\perp/\parallel}(t)\sigma^{\perp/\parallel}) \). The prefactor \( q^2 \) stems from the momentum conservation that holds for interparticle interactions. As discussed in Chap. 3 stresses decay during the \( \alpha \)-relaxation process and add a timescale to the problem. For an amorphous solid the transversal shear modulus is constant \( G^{\perp}(t) = \mu \) (for times \( t > \tau_0 \)) while for viscous supercooled liquids at times exceeding the structural relaxation time \( \tau_\alpha \) a constant shear viscosity \( \eta = \int_0^\infty dt G^{\perp}(t) \) emerges, see Sect. 3.2.3 for details on the corresponding Green-Kubo relation. Furthermore, the two equations establish a length scale \( L = \sqrt{\eta/(n \zeta_0)} \gg a \) in liquid states. Only for values \( qL \gg 1 \gg qa \) the frictional term represented by the time integral in Eq. (4.15) hinders the diffusion at long times. The fact that displacements for highly viscous fluids do not grow diffusively ensures, that strain correlation functions in real space do not decay on local distances but the discussed hexadecupolar pattern with power-law decay in the far field forms. With the help of this two system parameters
4. Strain patterns

limiting solutions are possible. Demanding \( qa \ll 1 \) and \( nD_0 t \gg 1 \) leads to

\[
C_{\parallel gH}^{\perp}(q,t) = \left\{ \begin{array}{ll}
\frac{2k_B T n}{\eta q^2} & t \ll \tau_\alpha, \\
\frac{2k_B T n t}{\eta} & t \gg \tau_\alpha, qL \gg 1.
\end{array} \right.
\] (4.17)

For incompressible systems the longitudinal components vanish for vanishing \( \kappa_T^q \). Hence, this transversal solution suffices and Eq. (4.14) yields the Eshelby pattern (4.8) in real space, where

\[
C_{\parallel gH}^{\perp}(q,t) \rightarrow C^s(t) \quad \text{with} \quad C^s(t) \rightarrow \left\{ \begin{array}{ll}
\frac{2k_B T n}{\mu} & t \ll \tau_\alpha \\
\frac{2k_B T n t}{\eta} & t \gg \tau_\alpha,
\end{array} \right.
\] (4.18)

\[
C_{xy}(r,t) \rightarrow C^s(t) \cos(4\theta) \frac{1}{4\pi n r^2} \quad r \gg a,
\] (4.19)

As mentioned the \( q^{-2} \) divergence of the CMSD at low wave vectors is a direct consequence of Newton’s second law and furthermore effects the far field power-law decay with \( r^{-2} \) in real space. For the amplitude function \( C^s(t) \) two different regimes emerged. For times exceeding the relaxation time \( \tau_\alpha \) of the structural \( \alpha \)-decay the amplitude function \( C^s \) grows linearly with time. Further, it scales with the inverse shear viscosity \( \eta^{-1} \), a quantity that diverges at the glass transition. For \( t < \tau_\alpha \), the time regime of elastic response, \( C^s \) arrests on a constant level proportional to the inverse shear modulus \( \mu^{-1} \) and reproduces Eshelby’s solution for an elastic solid from continuum mechanics. Note, that \( \tau_\alpha \) diverges at the glass transition. The solution for isotropic compressible systems can be found in the supplemental material of [31].

The full analysis of the longitudinal CMSD shows that there is a small correction to the amplitude in the glass state

\[
C^s(t) \rightarrow \left\{ \begin{array}{ll}
\frac{2k_B T n}{\mu^\parallel} - \frac{1}{\mu^\parallel} & t \ll \tau_\alpha \\
\frac{2k_B T n t}{\eta} & t \gg \tau_\alpha,
\end{array} \right.
\] (4.20)

where \( \mu^\parallel \) denotes the longitudinal modulus \( G^\parallel(t \rightarrow \infty) + 1/\kappa_T^q \), which can be determined by a small wavevector fit to the longitudinal dispersion relation, see Eq. (3.22). In terms of the standard Lamé coefficients it is \( \mu^\parallel = 2\mu + \lambda \), where the analysis in section 3.2.4 revealed \( \mu^\parallel \approx 7\mu \) which is equivalent to a correction to the amplitude of about 14\%. The solution obtained for the amplitude function of a fluid Eq. (4.20) for \( t \ll \tau_\alpha \) is identical to Eshelby’s solution.

The derivation presented establishes, in which regime isotropic supercooled liquids exhibit the same strain as a solid: For sufficiently high viscosities \( \eta \) the solidity length \( L \sim \eta^{1/2} \) grows large enough to become relevant on experimental length scales. It has been shown, that on distances small against \( L \) and for times large compared to the Brownian relaxation time \( \tau_B \) Eshelby-type strain patterns emerge in supercooled liquids. At the glass transition point the result from classical continuum mechanics is obtained, whereby the two approaches
4.3. Experimental system

Experimentally, monolayers of binary mixtures of dipolar colloids were studied by Christian L. Klix in the group of Peter Keim. We will present the main features of this experiment. The technical details can be found in [114]. The possibility to follow single particle trajectories by video microscopy allows to take two dimensional suspensions as model systems for the exploration of the glass transition [115]. With such setups strain fields can be determined from particle trajectories in crystalline [82] as well as amorphous [65] solids. Furthermore, employing the methods presented in 3.2.4, the shear modulus $G_\infty$ and longitudinal modulus $G^\parallel_\infty$ could be measured [99]. Theoretical results for the glass transition for dipolar colloidal suspensions are provided by mode coupling theory (MCT) [116].

As for the simulations a binary mixture is employed to prevent the system from crystallization. Figure 4.2 shows a snapshot generated from measured positional data. The suspension is made up of species A (diameter $\sigma = 4.5 \mu m$) and B ($\sigma = 2.8 \mu m$) with a relative concentration...
4. Strain patterns

of \( x_B = N_B/(N_A + N_B) \approx 0.5 \) where \( N_A \) and \( N_B \) are the number of trackable particles of the two species in the field of view. In total, trajectories of \( N = N_A + N_B \approx 2300 \) colloidal particles (where the whole system consists of more than \( 10^5 \) particles) are recorded. All colloids are confined to two dimensions by sedimentation at a flat water-air interface, which is realized by a water droplet hanging by surface tension in a top-sealed cylindrical hole (6 mm in diameter) of a glass cuvette. In order to provide a stable flat interface the volume and thus the curvature of the droplet is actively regulated. Several computer controlled regulation loops guarantee sufficiently plane colloidal monolayers over a duration of several months with excellent long time stability.

Video microscopy enables to sample the full phase space information of the system at all relevant length and time scales. The superparamagnetic nature of the colloidal particles allows to control the ratio of repulsive potential energy to thermal energy \( \text{in situ} \) by an external magnetic field \( H \). This ratio represents the only control parameter in the experiments and is quantified by a dimensionless system parameter

\[
\Gamma = \frac{\mu_0 H^2 (\pi n)^{3/2}}{k_B T} \left( \xi \chi_B + (1 - \xi) \chi_A \right)^2,
\]

which effectively plays the role of an inverse temperature or, for fixed particle number and volume, acts as a dimensionless pressure. As before \( n = N/V \) denotes the particle density and is determined via a Voronoi tessellation, \( \xi = N_B/(N_A + N_B) \) is the relative particle concentration, \( \chi_{A,B} \) are the susceptibilities of species \( A \) and \( B \). From the discontinuity in the elastic moduli the critical value for the glass transition was found at \( \Gamma^c \approx 200 \) [99]. For the preparation the system was first equilibrated at high temperatures or low \( \Gamma \), respectively. In a second step it was cooled down stepwise. The actual sampling by video microscopy was carried out with a frame rate of \( \approx 0.5 \text{s}^{-1} \). Sampling times of \( t_{\text{fluid}} = 2 \times 10^4 \text{s} = 13/(nD_0) \) for the fluid and up to \( t_{\text{glass}} = 1.2 \times 10^5 \text{s} = 80/(nD_0) \) for the glassy system could be accomplished, which is sufficiently long to probe dynamics during the structural relaxation.

4.4. Simulational aspects

We perform simulations on the 2D binary mixture of hard disks undergoing Brownian motion employing the event-driven algorithm and mixture introduced in Sect. 2. In the following the far field of the spatial correlations of the strain tensor, Eq. (4.7), will be examined. This requires systems with box lengths \( b \gg a \), where \( a = n^{-1/2} \) denotes the mean inter particle distance. A system containing \( N = 10000 \) particles, which corresponds to a box length of \( b = 151.6d_s \) for \( \phi = 0.81 \), turned out to be sufficient to observe the power law behavior of \( C_{xy}(r,t) \). The usage of periodic boundary conditions in a quadratic simulation box limits the maximum distance where the correlation function can be sampled to \( r_{\text{max}} = b/2 \). Since the calculation of \( C_{xy}(r,t) \) is based on an average over particle pairs, the amount of data entering
the averaging process increases with the amount of particles $N$. Furthermore, an average over consecutive time intervals of length $t$ allows us to improve the statistics, especially for short time windows. For this purpose a particle position based polar coordinate system has been used. The details can be found in A.1 in the appendix. The packing fraction is varied between $\phi = 0.77$ and $\phi = 0.81$ to ensure states close to the mode-coupling glass transition point $\phi_c \approx 0.7975$. The shown strain correlation data is based on at least 150 independent single runs for each packing fraction.

4.5. Results and discussion

The far field of the transverse strain correlation function, as seen by continuum mechanics in an isotropic solid and hydrodynamic theory,

$$C_{xy}(r, t) \to C^s(t) \frac{\cos(4\theta)}{4\pi nr^2} \quad \text{for} \quad r \gg a,$$

is characterized by its angular dependence, a far field power law decay of the radial part and a time-dependent amplitude. The former enters via the $\cos(4\theta)$ term representing a 4-fold symmetry that can be seen in each of the lower insets of the panels of Fig. 4.3. It manifests itself in an alternation between each four lobes of minimal and maximal intensity. The $x$- and $y$-axes fall together with local maxima because of our choice of coordinates. Although the system is homogeneous and isotropic, we introduce a distinguished direction by the choice of coordinates, which enter the definition of the strain field Eq. (4.5). This symmetry is observable for states in the glass as well as in the supercooled liquid for both simulational and experimental data over a wide range of distances $r$ with $2a \lesssim r$. It can be found at all observable lengths in the systems, which are limited by $r \lesssim L/2 \approx 64a$ in the simulation and $r \lesssim 18a$ in experiments, given by the dimensions of the spatial window accessible by video microscopy. To focus on the power law the angular dependence is integrated out by projecting on the appropriate 2D spherical harmonic

$$C_{44}(r, t) = \frac{1}{\pi} \int_0^{2\pi} d\theta \cos(4\theta) C_{xy}(r, t) \to C^s(t)/(4\pi nr^2).$$

(4.23)

The main panels of Fig. 4.3 show the rescaled curves $C_{44}(r, t)/C^s(t)$. For all systems investigated the $r^{-2}$ power law is verified for times beyond short time dynamics where $nD_0t \gtrsim 1$. This result is in line with Eq. (4.23), because all curves collapse on $1/(4\pi nr^2)$ for distances $6a \lesssim r \lesssim L(\eta)$ in the far field. The upper panels show states in the glass at $\Gamma = 423$ and $\phi = 0.81$. Here the classical result from continuum mechanics with $C^s(t \to \infty) = 2k_BTn\left(1/G_\infty - 1/G_\parallel\right)$ is recovered. In the glass the elasticity results from a finite shear modulus $G_\infty$. Furthermore, the longitudinal modulus $G_\parallel$, measurable in a fluid, gives a (small) correction in $C_{xy}$. As before in Sect. 3, we observe a finite shear rigidity, the experi-
4. Strain patterns

Figure 4.3.: Experimental (left) and simulational (right) rescaled strain correlation data for a

- glass (upper panels; $\Gamma = 423$ and $\phi = 0.81$) and a supercooled fluid (lower panels; $\Gamma = 103$ and $\phi = 0.78$) state at different times. The spherical harmonic strain correlation functions $C^4(r, t) / C^4(t)$ are rescaled to overlap in the far-field power law decay. Main panels show the $r^{-k}$-power law decay (dashed black lines), with exponent $k = 2$ varying little with time (upper insets). The contourplots (lower insets) of the long-time limit of $C_{xy}(r, t) / C_{xy}(r = 0, t)$ illustrate the corresponding $\cos(4\theta)$-symmetry. The Eshelby-patterns are shown at $nD_0 t = 30.1$ and 256 (experiment and simulation for the glass) and $nD_0 t = 3.1$ and 247 (experiment and simulation for the fluid), respectively.

imenental and simulated colloidal monolayers are in a solid state at low temperatures $\Gamma > \Gamma^c$ or high packing fractions $\phi > \phi^c$, respectively.

The lower panels of Fig. 4.3 show results for fluid states at $\Gamma = 103 < \Gamma^c$ and $\phi = 0.78 < \phi^c$. The patterns persist in the supercooled liquid as well. At this temperature and density, respectively, considerably far from the transition point, the averaged strain fluctuations exhibit spatial correlations similar to the ones found in solids. In the simulations the spatial limitations predicted in Sect. 4.2 are verified. The power law is visible for distances $\tau$ that are small compared to the limiting length $L = \sqrt{\eta / (n\xi_0)}$ (vertical dashed line), where the viscosity $\eta$
is known from the stress correlation function $G(t)$, see Sect. 3.2.3, and $\zeta_0 = 1/(\beta D_0)$ is determined via the short time diffusion constant. In contrast, the features of Eq. (4.8) are observed even for times, which exceed the relaxation time $\tau_\alpha$ by far, as shown in the upper inset of the corresponding panels in Fig. 4.3. The $\alpha$-relaxation time $\tau_\alpha$ is determined from the decay of the incoherent density correlation function $\Phi_\mathbf{q}^\alpha(t)$ with wavelength of the average particle separation, see Fig. 4.4. The relaxation time $\tau_\alpha$ is also comparable to $\tau_\sigma$, which characterizes the decay of the shear stress auto-correlation function $G(t)$ analyzed in Sect. 3.2.3. At times that large, a fluid can not sustain elastic shear stresses. Lemaître and colleagues found that solid-like Eshelby strain fields survive in supercooled fluids even though density and stress correlations behave fluid-like. With our work we reproduced the findings for simulations of Brownian hard-disks and gave the first (at least to our knowledge) experimental verification for a 2D colloidal system. For our analysis we sampled the function

\[
\tilde{C}(r, t) = \frac{C_{xy}(r, t)}{C_{xy}(r = 0, t)},
\]

in real space and obtained the measured amplitude function $C^\alpha(t) \propto C_{xy}(r = 0, t)$ by fitting a $r^{-2}$ power law to the far field, for details see A.2 in the appendix. Amplitude functions are shown in Fig. 4.5, including additional data sets around the glass transition, which occurs at $\Gamma^c \approx 200$ and $\phi^c = 0.7975$, respectively. The measured data agree qualitatively with the

Figure 4.4.: Experimental (left) and simulational (right) incoherent density correlation data for different $\Gamma$ and $\phi$ (see legends) for wavevectors $qa = 7.3$ (experiment) and $qa = 7.4$ (simulation) (corresponding to the first peak of the structure factor $S(q)$). The dashed lines show stretched-exponential fits $\Phi_\mathbf{q}^\alpha(t) = A \exp\left(-t/\tau^\alpha\right)^\beta$ with $A = 0.80$, $\beta = 1.0$ (exp.) and $A = 0.58$, $\beta = 0.65$ (sim., $\phi < 0.8$). For the simulational data, the fitted $\tau_\alpha$ is marked by circles.
4. Strain patterns

behavior predicted in Sect. 4.2

\[ C^s(t) \rightarrow \begin{cases} 
\frac{2k_BTn}{\eta} \left( \frac{1}{\mu} - \frac{1}{\mu^\parallel} \right) & t \ll \tau_\alpha, \\
\frac{2k_BTn}{\eta} t & t \gg \tau. 
\end{cases} \]

While approaching the glass transition from the fluid, the structural relaxation time \( \tau_\alpha \) grows and the far-field amplitude \( C^s(t) \) arrests on a constant value for growing time windows. This corresponds to an elastic behavior of a solid. The plateau height in this intermediate time window matches the expected values, which were determined by the elastic moduli. For fluid states and large times \( C^s(t) \) increases linearly with time with an slope given by the inverse viscosity, which is equivalent to a slope proportional to the inverse final relaxation time \( \tau_\alpha \). The inset of Fig. 4.5 shows the amplitude rescaled with \( \tau_\alpha \) obtained from the density correlation function leading to a satisfactory collapse of the curves in the supercooled liquid.

In fact the collapse of the simulation data is far better if replotted versus \( nD_Lt \) (not shown), where \( D_L = \lim_{t \to \infty} \frac{\Delta r^2}{4t} \) is the long-time self-diffusion coefficient. The slightly different scaling behavior may indicate that strain fluctuations decouple from the structural relaxation. Such behavior if often seen for diffusive processes and is often taken as an indication for heterogeneous dynamics [117].

Figure 4.5.: Amplitude function \( C^s(t) \) of the far-field power-law decay of transversal strain correlations. It describes the strength of the algebraic \( 1/r^2 \) power-law decay with \( \cos(4\theta) \)-symmetry in \( C_{xy}(r,t) \), which holds for \( a \ll r \ll L \). The left panel gives data measured in the colloidal layers, the right panel gives corresponding data measured by BD simulations in a binary mixture of hard disks. Legends give the inverse temperatures \( \Gamma \) or the packing fractions \( \phi \) spanning from fluid to glass states. Circles mark the times, where Eshelby-strain patterns are shown in the inset of Fig. 4.3. Dashed lines give the elastic limits \( C^s(t \to \infty) = \frac{2k_BTn}{\eta} \left( 1/\mu - 1/\mu^\parallel \right) \) with moduli obtained from the dispersion relations following Ref. [65]. The insets show asymptotic collapse of the fluid curves when plotted versus rescaled time \( t/\tau_\alpha \) with the final relaxation times \( \tau_\alpha \) obtained from density correlation functions.
4.6. Conclusions

We detected Eshelby-type strain-correlation patterns in 2D colloidal suspensions in amorphous glass states as well as in supercooled liquid states. We used simulations and experiments to show, that the strain signatures are long-ranged and long-lived. For densities close to the glass transition, they follow a $r^{-2}$ scaling law valid in the far-field and exhibit a hexadecupolar $\cos(4\theta)$ symmetry. For large enough viscosities, the Eshelby-strain pattern is visible even on time scales longer than the structural relaxation time $\tau_\alpha$. This is remarkable, because in this limit the shear modulus has already relaxed to zero. The dynamics of the retarded averaged strain fluctuation functions can explain the emergence of this solid-like behavior: for highly viscous fluids a spatio-temporal window opens, where elastic correlations have already decayed to zero but correlated displacements diverge with length scale squared. This $q^{-2}$-dependence causes long-ranged strain fluctuations in real space and is a direct consequence of Newton’s laws of motion. For times larger than the Brownian relaxation time $\tau_0$, we were able to establish the viscosity dependent length scale $L(\eta)$, limiting this spatial window, in the simulations. At the crossover from a supercooled liquid to an amorphous solid the results from generalized hydrodynamics and Eshelby’s solution merge. Thus we presented an analysis of the far field, where on long times flow and elastic processes cause identical patterns. Nevertheless differences might be detectable at short scales. The theoretical analysis in Fourier-space is not limited to two dimensions, an analogous verification by simulation and experiment in three dimensions appears promising to rationalize data from colloidal glass formers in 3D. However, an observation of the far-field signatures in 3D requires large systems with high particle numbers.
5. Shear cessation

So far the equilibration process of the system after a density quench to packing fractions close to the glass transition, equilibrium dynamics and the imposition of simple shear flow was discussed. In the following we will go beyond this and examine the transient regime that follows a quench to a flowing nonequilibrium stationary state (NESS).

Amorphous solids are among the materials that display residual stresses after the relaxation from a flowing glassy state. Residual stresses develop if a system does not relax back to equilibrium after a interruption of the flow, but instead gets trapped in a nonergodic state. During a quench to a nonequilibrium state internal stresses build up and some part of them persists in the solid after the cessation of flow, emphasizing once more that glasses are not simply highly viscous fluids. The transient regime of relaxation from a NESS after cessation of simple shear flow displays various interesting characteristics that stem from a fight between past fluidization and ongoing solidification. Recently this has been analyzed for colloidal suspensions of nearly-hard-sphere particles employing macroscopic and microscopic experiment, computer simulation as well as mode-coupling theory of the glass transition (MCT) [20]. The occurrence of frozen in stresses that depend on the materials preparation history is neither new nor limited to amorphous or soft solids. Already in the 17th century Dutch Tears were known, small drops of ordinary window glass rapidly solidified in cold water [118, 119]. An emerging shield of compressive stresses on the surface of the head of the tadpole-shaped body results in a very high shock resistance, while the entire structure shatters upon minor damage done to the tails. A simple clipping of the tail releases the frozen-in residual stress network and renders the material instable [120]. An enhanced shock resistance is desirable in a wide range of applications, this is for example exploited in the manufacturing process of smart-cover glasses where chemical quenches are employed to create a network of residual stresses [121, 122, 123]. Furthermore, residual stresses play key rolls when it comes to the explanation of the material properties and impressive stability of railway rails [124, 125], the cytoskeleton of cells [126] or spider silk [127]. Experimentally residual stresses allow to fine tune material properties of polymer films [128] while for laponite gels the effect of past flow on the relaxation of stresses [129] and the linear viscoelastic moduli [130] are reported. Furthermore, flow at high shear rates is used in experiments to prepare or rejuvenate colloidal glasses, where pre-shear is found to speed up relaxation dynamics after the cessation of flow [19]. During this process a controlled history is needed for the preparation of well-defined samples, that allow for reproducible results. Therefore an understanding of the processes during relaxation.
5. Shear cessation

Figure 5.1.: Shear stress $\sigma_{xy}(t)$ (top) and shear rate $\dot{\gamma}(t)\tau_0$ at $\phi = 0.81$ for the different regimes discussed in the main text for $t_{on} = 0$ and $t_{off} = 2/\dot{\gamma}$. For negative times the system is in a well-aged equilibrated state (blue). For positive strains $\dot{\gamma}t < 1$ the intermediate regime of startup shear flow (orange) is shown with its characteristic overshoot for two different shear rates $\dot{\gamma}\tau_0 = 4 \times 10^{-3}, 4 \times 10^{-2}$ (dashed, solid lines). At strains $\gamma \gtrsim 1$ the system is in a stationary state (green) at constant stress until the cessation of flow at $\gamma = 2$. Although it is $\dot{\gamma} = 0$ during the relaxation (purple) the time axis is rescaled by the previous shear rate, which sets the time scale of the decay of stresses and structure.

from a stationary sheared state and their influence on the material properties is important. In this chapter we present a method to prepare our system of Brownian hard disks in two dimensions such that the dynamics after cessation of simple shear flow can be investigated and discussed. We examine the details of the macroscopic structural and elastic decay and connect our results to microscopic particle motion to characterize the remarkable mechanism present in this process.

5.1. Setup

Shear cessation experiments provide a clean setup to investigate residual stresses. For the realization we again consider our model system with hard-disk like interactions, at fixed temperature and packing fraction. We perform simulations utilizing the presented binary mixture of Brownian hard disks, where each curve is based on 360 to 600 independent runs of systems containing $N = 1000$ particles. Since the emergence of residual stresses requires non-ergodicity in the quiescent states we focus on packing fractions $\phi > \phi^c = 0.7975$ above
5.2. Results and discussion

the glass transition point. In Fig. 5.1 the flow protocol

$$\dot{\gamma}(t) = \begin{cases} 
0 & t < t_{\text{on}} \\
\dot{\gamma} & t_{\text{on}} \leq t \leq t_{\text{off}} \\
0 & t > t_{\text{off}}
\end{cases} \quad (5.1)$$

and the system’s stress response to shear during the different processes included in the preparation of the system are sketched, where we demand $t_{\text{off}} - t_{\text{on}} > 1/\dot{\gamma}$. Starting with a well-aged glassy state at $\phi = 0.81$ with vanishing shear stress $\sigma_{xy} = 0$, a switch-on of constant homogeneous shear with rate $\dot{\gamma}$ triggers a flow. As a result the previously solid suspension is shear melted and driven far from equilibrium, the stress response during the transient regime connected to the onset of simple shear flow has already been discussed in Sect. 3.2.5 and [16], for MD simulations of similar model glass formers see [131]. As soon as the accumulated strain $\dot{\gamma}(t - t_{\text{on}})$ exceeds 1 the dynamics becomes stationary [16, 97, 98] and a constant stress $\sigma_{xy}^{\text{stat}}(\dot{\gamma})$ emerges. Hence, a NESS is reached providing a well-defined starting point. In the following, the shear is set back to zero at $\gamma = 1$ to investigate the nonergodic transient regime of solidification afterwards. The fact that we employ the Gaussian thermostat introduced earlier leads to an abrupt stop of advective flow. Immediately after the cessation new displacements are drawn, thus the motion of the system’s center of gravity vanishes instantaneously and all memory of microscopic particle (pseudo-)velocities is discarded. The entire memory of the flow history is therefore contained in the structure, viz. particle configuration at the time of cessation. To capture the slow and rich dynamics during the relaxation from a fluidized state stresses are sampled according to Eq. (3.9) over time intervals of logarithmically growing length. Equally, positional data is stored after time steps of logarithmically growing length. In the following we limit discussion to a glass state at $\phi = 0.81$ and shear rates $\dot{\gamma} \tau_0 = 4 \times 10^{-n}$ for $n = 5, 4, 3, 2, 1, 0$.

5.2. Results and discussion

5.2.1. Stress relaxation, structural decay and localization length

Let us first discuss the relaxation of shear stresses implying the development of frozen-in stresses and its dependence on the intensity of past shear. The results for $\sigma(t)$ are shown in Fig. 5.2. In the region $-1 < \dot{\gamma} t < 0$, corresponding to startup shear, pronounced shear rate dependent stress overshoot phenomena are observed in the stress-strain curves $\sigma(\gamma)$. It will be argued later that this can be connected to the relaxation of the stress. For the highest shear rate applied, $\dot{\gamma} \tau_0 = 4$, qualitativ differences can be observed in comparison to the other curves (not shown). An additional undershoot after the stress overshoot followed by minor oscillations are indications for differences in the underlying dynamics of the severely sheared system. Therefore results from the analysis of this shear rate have to be interpreted with
5. Shear cessation

Figure 5.2.: Time-dependent shear stress $\sigma_{xy}(t)$ at packing fraction $\phi = 0.81$ for various shear rates as labeled. Steady shear with rate $\dot{\gamma}$ is switched on at $\dot{\gamma}t = -1$ and switched off after a strain $\gamma = 1$ is reached, corresponding to $t_{\text{on}} = -1/\dot{\gamma}$ and $t_{\text{off}} = 0$. The inset shows the flow curve of the system, crosses in both panels mark the stationary shear stress $\sigma^{\text{stat}}_{xy}(\dot{\gamma})$. The right panel shows only data measured after the interruption of flow at $t_{\text{off}} = 0$, where time is measured in $(\dot{\gamma}$-independent) units $nD_0$.

care, only generic features that are qualitatively identical to the ones for the lower shear rates will be shown and discussed. While the ED-BD algorithm remains well-defined and provides an overlap-free simulation scheme, see Sect. 2, it’s questionable whether its dynamics can still be approximated by the Smoluchowski equation for Brownian dynamics for shear rates larger than $\dot{\gamma}\tau_0 \approx 1$. The inset of Fig. 5.2 shows the flow curve, which can be approximated by a Herschel-Bulkley-type constitutive equation $\sigma_{xy}(\dot{\gamma})d^2_s/k_BT = 0.66 + 5.94(\dot{\gamma}\tau_0)^{1/2}$ [132], see also Fig. 6.7. The flow index $n = 1/2$ corresponds to a shear-thinning yield-stress material. Hence the steady-state shear stress $\sigma^{\text{stat}}_{xy}(\dot{\gamma})$, providing the initial value of the stress relaxation process, increases sublinearly with increasing shear. After the cessation only a part of this shear stress is able to relax. The right panel shows the same data where a logarithmic time axis is used, within this presentation it can be observed that the long time limit $\sigma_{\infty}(\dot{\gamma}) = \lim_{t \to \infty} \sigma_{xy}(\dot{\gamma})$ decreases with increasing $\dot{\gamma}$. This trend causes a crossing of $\sigma(t)$-versus-$t$ curves belonging to different $\dot{\gamma}$. Stronger shear causes higher steady-state stresses and a more severe fluidization of the glassy structure. Even after the cessation, this fluid-like structure remains and allows for particle rearrangements that initiate a fast and effective stress relaxation. This decrease of $\sigma_{\infty}$ with increasing pre-shear rate is observed in a wide range of experiments and simulations but is not an universal effect. Results from MD simulations on a binary Yukawa mixture with a dissipative-particle-dynamics thermostat and temperature as control variable show the same trend [20, 131, 133]. Furthermore, this behavior is found in experiments on hard-sphere-like suspensions of core-shell PS-PNIPAM particles and in experiments on hard-sphere suspensions of PMMA particles close to the glass transition.
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However, at packing fractions well above the glass transition these PMMA suspensions displayed a reverse trend, viz. residual stresses grow with increasing pre-shear rate. Furthermore, this setup is the only one that did not exhibit strong stress overshoots during the startup of shear flow. The Brownian hard disks discussed here as well as the other systems investigated in [20] show pronounced overshoot phenomena and a crossing of the stress curves during relaxation. The nonequilibrium transient dynamics in a colloidal glass former after the cessation of shear flow was also analyzed employing a schematic model of mode-coupling theory [32]. It was found that by introducing suitable empirical coupling constants to the memory kernel keeping track of the flow history the stress relaxation can be modified such that both trends described before can be obtained qualitatively.

The existence of finite residual stresses becomes apparent in a double-logarithmic representation of the stress divided by its initial value $\sigma_{xy}^{\text{stat}}$ as shown in Fig. 5.3. An additional rescaling of the time by the pre-shear rate $\dot{\gamma}$ leads to a shift of the stress curves onto a single master curve for low (pseudo) strains $\dot{\gamma} t \lesssim 0.1$. This demonstrates the apparent dependence on the flow history, the pre-shear rate determines the time scale of relaxation. The lower the pre-shear rates $\dot{\gamma}$, the earlier the rescaled time where the curve deviates from the master curve and starts to build up a finite long time plateau. This trend is apparent especially for low $\dot{\gamma}$, where the overall height of the rescaled plateau also increases with decreasing $\dot{\gamma}$. On the other hand, especially for larger shear rates fluctuations compromise the exploration of the long-time regime. Since here the initial part of the stress relaxation covers up to three orders of magnitude it reaches the noise limit of the statistical sampling. Yet the data are compatible with the emergence of a finite long-time plateau $\sigma_{xy}^\infty(\dot{\gamma}) = \lim_{t \to \infty} \sigma_{xy}(\dot{\gamma}; t) > 0$ as seen by MCT in the ideal glass [20, 32]. This limit represents a persistent residual stress, for shear rates $\dot{\gamma} \tau_0 \leq 4 \times 10^{-2}$ it is approximated by the time-averaged stress $\bar{\sigma}_{xy}$. The values were averaged over the interval $n D_0 t \in [6830, 17400]$ and are added in Fig. 5.3 as dashed lines. For the weakly pre-sheared systems $\bar{\sigma}_{xy}$ differs significantly from zero.

Furthermore, the local particle dynamics have been addressed in terms of the mean-squared displacements, as shown in the lower panels of Fig. 5.3. For this displacements of the larger particles in both $x$- and $y$-direction were averaged. For comparison the curves describing the quiescent dynamics and the sheared stationary state are shown as well. The former exhibits a short time diffusion followed by a long-time plateau linked to the permanent caging of the particles in a glass. For the latter this leads to a superdiffusive long-time limit due to shear advection, see Eq. (2.34) or [42]. A neglect of the contributions from shear advection leads to a long-time diffusive regime $\langle \Delta r^2 \rangle = 4Dt$ of the curves in the NESS. Unlike for the quiescent case the caging effect is non-permanent, where both curves exhibit the plateau at $\Delta r^2 \approx 0.02d_s^2$, a value linked to the Lindemann length scale $r_{\text{loc}}$ of localized in-cage dynamics [134]. For the simulations here we find $r_{\text{loc}}/d_s = \sqrt{\Delta r^2}/a \approx 12\%$, note that despite looking at the plateau values for big particles only we compare it to the mean particle distance $a = 1/\sqrt{n}$ of the binary mixture for this estimate. Furthermore, the height of the plateau is not universal
since it is altered by long wave length density fluctuations depending on the size of the system, see Chap. 7. In both panels the MSD after cessation for different pre-shear rates are shown. We measure the displacements starting at $t_w = 0$, which is the time where the shear flow is interrupted, and sample the quantity $\langle (\Delta r(t, t_w)^2) = (r(t) - r(t_w))(r(t) - r(t_w)) \rangle$. The curves describing the transient and quiescent dynamics are identical up to a time $\dot{\gamma} t \ll 1$, that depends on the intensity of the previous shear. Therefore the system maintains the memory of the past flow. After that the transient MSD increases and crosses over to a broad window of subdiffusive growth. The higher $\dot{\gamma}$ and the more the system has been fluidized in the past, the earlier deviations from quiescent behavior set in and the higher the MSD obtained in
that time window. Nevertheless, the data is compatible with the onset of a second, long-time plateau. This sets a length scale that does not depend on the previous shear rate. Again an additional rescaling of the time by the pre-shear rate $\dot{\gamma}$ is chosen to illustrate the existence of this limit value. A behavior contrary to the one of the stress curves before becomes evident: the curves are split up during short time dynamics but converge for growing times. Here the common master curve is reached at earlier strains $\dot{\gamma}t$ for lower pre-shear rates $\dot{\gamma}$. The subdiffusive grow of the MSD saturates at a plateau of height $\Delta r_b^2 \approx 0.75d_s^2$. This corresponds to particle movements of about 70%, much larger than Lindemann’s criterion for melting, but still small compared to a big particle diameter. This limit value constitutes a localization length. In a manner of speaking, it can be interpreted as a mean microscopic breaking distance of the single particles after the abrupt interruption of shear flow. Similar MSD are reported during aging after thermodynamic quenches for colloidal suspensions [135] and for computer simulations [136, 137]. The localization length in mean-squared displacements is also evident from the results on shear cessation in Ref. [20] from MD simulations and as measured for PMMA suspensions through confocal microscopy. Unlike here in this work an independence on the intensity of previous shear could not be resolved.

We now turn to an analysis of the structural decorrelation after flow interruption, which is closely related to the discussion of the MSD above. Therefore wave-vector-dependent density correlation functions were sampled for wave vectors $\mathbf{q}$ in four different directions: $\mathbf{q} \parallel \mathbf{e}_x$, parallel to the pre-shear direction; $\mathbf{q} \parallel \mathbf{e}_y$, in the pre-shear gradient direction; $\mathbf{q} \parallel (\mathbf{e}_x + \mathbf{e}_y)/\sqrt{2}$, in the elongational direction; and $\mathbf{q} \parallel (\mathbf{e}_x - \mathbf{e}_y)/\sqrt{2}$, in the compression direction of the pre-shear. Both the collective or coherent density correlation functions $\Phi^C_{\mathbf{q}}$ and tagged-particle or incoherent density correlation functions $\Phi^S_{\mathbf{q}}$ were obtained. Those quantities differ by their reliance on either the density fluctuations of all the particles, $\rho(\mathbf{q}) = \sum_{k=1}^{N} \exp[i\mathbf{q} \cdot \mathbf{r}_k]$, or on the single-particle density fluctuation $\rho^S(\mathbf{q}) = \exp[i\mathbf{q} \cdot \mathbf{r}_k]$, where a sample average over all particles $k$ is performed and $\mathbf{r}_k$ denotes the position of particle $k$. It is
\begin{align}
\Phi^S_{\mathbf{q}}(t + t_w, t_w) &= \langle \rho^S(\mathbf{q}, t + t_w)^\ast \rho^S(\mathbf{q}, t_w) \rangle, \quad (5.2) \\
\Phi^C_{\mathbf{q}}(t + t_w, t_w) &= \langle \rho(\mathbf{q}, t + t_w)^\ast \rho(\mathbf{q}, t_w) \rangle. \quad (5.3)
\end{align}

The dependence on the waiting time $t_w$ points out the transient nature of the cessation correlators. While the quiescent correlators shown in Fig. 4.4 are based on averages over the equilibrium distribution function this setup here evokes a waiting-time dependent nonequilibrium ensemble with particle trajectories influenced by the past shear rate. It is therefore assumed that the set of independent configurations used to start the single simulation runs is representative of the initial steady-state ensemble and they represent the nonequilibrium ensemble in question. The analysis here will focus on the incoherent correlation function, for simplicity we will stick to the wave-vector direction $\mathbf{q} \parallel \mathbf{e}_y$. A full theory of relaxation after
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Figure 5.4.: Upper Panels: Transient incoherent density correlation function $\Phi^S_{q}(t,t_w)$ for $t_w = 0$ at packing fraction $\phi = 0.81$ at wave-vector $q/d_s = 0.61\hat{e}_y$ (in pre-shear gradient direction) for various pre-shear rates as labeled. Stationary shear flow with rate $\dot{\gamma}$ is switched off at $t = 0$, the curves describing the non equilibrium stationary state NESS are shown as dashed lines, quiescent dynamics for a system that has not been pre-sheared are indicated by a red dotted line. The right panel shows the same data where time has been rescaled with pre-shear rate $\dot{\gamma}$, which sets the time of structural decorrelation after cessation. Lower Panels: Incoherent (left) and coherent (right) density correlation function $\Phi^S_{q}(t,t_w)$ and $\Phi^C_{q}(t,t_w)$, both for $t_w = 0$, for different orientations of the wave vector $q$ as explained in the main text.

cessation, such as an appropriately extended ITT-MCT [138, 20], will likely deal with the directional-dependent collective density correlations. For the cases studied here no qualitative difference between the different functions, Eq. (5.3) and (5.2), or directions of wave vectors is found. This is exemplified in Fig. 5.4, where a comparison of incoherent (or tagged-particle) and coherent (or collective) density correlation functions for the four different orientations of the wave vector are shown. For this a wave vector magnitude $qd_s \approx 6.10$, which is connected to the dynamics associated with fluctuations on the nearest-neighbor-cage length scale, was
chosen. The behavior at smaller wave vectors \( q \) linked to the dynamics at larger length scales was tested as well and exhibits comparable results that are not shown here. The tagged-particle correlators are shown in the left panels, where the lower panel displays an enlarged section and curves for all four principal directions associated with the pre-shear as explained above. Only during the \( \beta \)-decay and during the onset of the final \( \alpha \)-decay a weak anisotropy is detected. The height of the \( \beta \)-plateau is slightly raised for wave vectors \( \mathbf{q} \parallel \hat{e}_{x,y} = (\hat{e}_x + \hat{e}_y)/\sqrt{2} \) in elongational direction of the pre-shear and slightly lowered in compression direction of the pre-shear, viz. \( \mathbf{q} \parallel \hat{e}_{x,y} = (\hat{e}_x - \hat{e}_y)/\sqrt{2} \). For increasing times and by this decreasing values of \( \Phi_S^{\mathbf{q}}(t) \) the dependence on the orientation of \( \mathbf{q} \) becomes less pronounced and cannot be resolved for \( \Phi_S^{\mathbf{q}} \lesssim 0.6 \), in the selected enlarged area this can be seen for the largest shear rates. In the case of steady shear (representing the initial state here) a weak anisotropy of density correlation functions has already been reported for the present system \[11\]. Due to their collective nature the coherent correlation functions are subject to far larger fluctuations such that distinct differences induced by the wave-vector orientation are not resolved. Nevertheless for \( |\mathbf{q}| d_s \approx 6.10 \), no qualitative differences between the different types of correlation functions are visible, justifying the focus on incoherent correlators in the following. As visible in the top left panel of Fig. 5.4, the correlation functions for \( t_w = 0 \) (measurement starts at time of cessation of flow) deviate considerably from the quiescent non pre-sheared ones (red dotted line in the figure). This is true although they differ only by exchanging the equilibrium-ensemble average for the NESS one. The correlators for \( t_w = 0 \) also deviate significantly from the correlation functions measured in the stationary state (dashed lines). From these they differ, while taking the same distribution to average, by the fact that the particle trajectories are no longer subject to shear. While the initial \( \beta \)-decay is identical for all curves, only the initial decay of the transient correlation function from the plateau value \( f(q) \approx 0.8 \) is essentially the same as in the NESS. At larger times it becomes much slower and develops a tail with the indication of a second plateau \( f(q)' < 0.2 \) that is pre-shear rate dependent.

The decay of the steady-state correlation functions is expected to scale as \( 1/\dot{\gamma} \) for small shear rates. This is tested in the top right panel of Fig. 5.4, where these NESS correlation functions (dashed lines) are again shown as functions of the pseudo strain \( \dot{\gamma} t \). The scaling regime is difficult to access since it is reached only for the smallest shear rates investigated here, where a driving of the systems into a NESS and the actual conduct of the simulations is rather expensive in terms of computational time. For \( \dot{\gamma} \tau_0 = 4 \times 10^{-3}, 4 \times 10^{-4} \) and \( 4 \times 10^{-5} \) a clear-cut collapse for the steady-state correlation functions sets in. This master curve describes shear-induced relaxation of density fluctuations on a time scale \( \tau_\gamma \lesssim 0.1/\dot{\gamma} \). For shear rates \( \dot{\gamma} \tau_0 \geq 4 \times 10^{-2} \) deviations from the master curve become notable, although the corresponding bare Peclèt numbers may be small compared to unity.

The transient correlation functions \( \Phi_S^{\mathbf{q}}(t, t_w = 0) \) (solid lines in Fig. 5.4) evidence a slightly less pronounced approach to a scaling function. The slow decay that sets in after the deviation
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from the steady-state correlator becomes slower for lower pre-shear rate. Here a collapse on a single curve emerges only for the two lowest pre-shear rates \( \dot{\gamma} = \tau_0 4 \times 10^{-4} \text{ and } 4 \times 10^{-5} \) that as before in the NESS sets in for values \( \Phi_q^S \lesssim 0.6 \). In a (rescaled) time window \( 10^{-2} \lesssim \dot{\gamma}t \lesssim 1 \) the stress-relaxation curves for these two pre-shear rates exhibit approximate scaling as a function of \( \dot{\gamma}t \) as well. For higher pre-shear rates \( \dot{\gamma} \gtrsim 4 \times 10^{-2} \), where due to large fluctuations no finite residual stress could be resolved, the density correlators approach a single long-time curve at rescaled times \( \dot{\gamma}t \) growing with \( \dot{\gamma} \).

The non stationary nature of this relaxation process is reflected in the waiting-time dependence of \( \Phi_q^S(t+t_w, t_w) \). The evolution of the results with increasing \( t_w > 0 \) is shown in Fig. 5.5 and is qualitatively similar for all shear rates discussed here. Again the the pre-shear rate sets the relevant time scale of the initial steady-state relaxation as discussed above. Notable \( t_w \)-dependence of the correlation functions sets in only for \( \dot{\gamma}t_w \gtrsim 0.1 \), a value comparable with strains associated with cage yielding. Therefore in this aging regime the time scale of structural decay in NESS \( \tau_e \approx 0.1 \dot{\gamma}^{-1} \) has to be small compared to \( t_w \). Typical aging studies on glass-forming systems deal with similar yet different scenarios, which becomes clear when estimating the involved time scales. Most commonly they deal with the dynamics after a quench in some thermodynamic control variable, the obvious choice for glassy systems is a quench to low temperatures or high densities. With such a setup the system usually starts from an initial state showing fast relaxation dynamics on a time scale \( \tau_i \), which often is comparable to the microscopic relaxation time \( \tau_0 \). For the dynamics after flow cessation on the other hand the initial states are set by the shear rate and are subject to a rather slow relaxation, \( \tau_i = \tau_\dot{\gamma} \gg \tau_0 \). Therefore the regime \( t_w/\tau_i \ll 1 \), which is irrelevant in typical aging studies, is most revealing for the simulations here and extends to relatively long waiting times if measured in natural units \( t_w/\tau_0 \). Moreover it is, especially for lower shear-rates, rather expensive in terms of computational time to reach waiting times \( \dot{\gamma}t_w > 1 \).

For increasing \( t_w \) the decay of the transient correlator is shifted to larger times, a behavior qualitatively expected from the analogy with aging after temperature or density quenches. There the system ages towards a new equilibrium or (in the case of glassy dynamics) aged stationary state, where this final state usually shows a much slower structural decorrelation. For growing \( t_w \) the density correlations take longer to relax. For \( t \ll t_w \) the curves in many cases assimilate the equilibrium correlation function. In our case the correlators follow a transient plateau slightly lower than the one measured in equilibrium during this time span (open circles denote the point where \( t = t_w \)). As observed above for the \( t_w = 0 \) curves the indication of a second plateau remains for \( \dot{\gamma}t_w \gtrsim 0.1 \), at least for the shear rates where large enough waiting times are accessible. The amplitude of the second, slower part of the relaxation and of the indicated second plateau increases with increasing \( t_w \).

An aging scenario based on the theory of spin glasses has been established for similar systems
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Figure 5.5.: Waiting time-dependent transient incoherent density correlation function $\Phi^S_q(t,t_w)$ at packing fraction $\phi = 0.81$ and wave-vector $q/d_s = 0.61\hat{e}_y$ (in preshear gradient direction) for 4 different pre-shear rates as labeled. Stationary shear flow with rate $\dot{\gamma}$ is switched off at $t = 0$, the curves describing the non-equilibrium stationary state NESS are shown as dashed lines, quiescent dynamics for a system that has not been pre-sheared are indicated by a blue dashed-dotted line. Waiting times $\dot{\gamma}t$ between 0, corresponding to a measurement that starts at the time of cessation of shear flow, and 2 are shown. Colored open circles mark the point in time where $t = t_w$.

[139, 140, 141]. For large $t_w$ a scaling of the correlators with waiting time of the form

$$\Phi(t + t_w, t_w) \sim \Phi(h(t + t_w)/h(t_w))$$  \hspace{1cm} (5.4)

is observed up to a $t_w$-independent short-time part. The scaling function $h(t_w)$ follows a power law $h(t_w) \sim t_w^\mu$ for $t_w \to \infty$. Similar behavior was found in recent studies of density-quenched thermosensitive colloidal suspensions [142] and in simulations of polymer glasses [143]. However, our simulation data describing the relaxation after shear cessation is not compatible with a scaling of this form. Simulations of a binary Lennard-Jones glass
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The curve can be approximated by a Gaussian distribution within a time-dependent central interval \([-y_G, y_G]\), while the decline outside at fixed time \(t > t_w\) is best described by an exponential decay \(G_S(t, y) = \exp(-\frac{y - y_G(t)}{\xi(t)})\) (dashed lines indicate corresponding fits to the data).

The aging-induced decay found there differs significantly from the common stretched-exponential form that describes equilibrium-like structural relaxation and bears similarities to the curve shapes seen in Fig. 5.5. Furthermore, in 2000 Kob and Barrat presented simulations on binary Lennard-Jones system quenched to a low-temperature state deep in the glass [146]. The relaxation dynamics and aging characteristics exhibit noticeable similarities to the work presented here. Especially the emergence of an additional waiting-time dependent plateau \(f'(t_w) < f\) that increases with increasing \(t_w\) was observed as well. Indications of a second plateau in aging correlation functions can also be seen in recent simulations of a SiO\(_2\) model [136] and of polymers [147].

5.2.2. Dynamical heterogeneity and run-to-run fluctuations

So far the analysis focused on macroscopic and microscopic quantities that stem from spatial and ensemble averages quantifying the average dynamical behavior. A potential dynamical heterogeneity as seen for quenches to low temperatures [135, 146], where intriguing processes crucial for the evolution of relaxation occur that are limited to finite spatio-temporal windows, is invisible relying on the methods employed so far. A quantity sensitive to such processes is the probability distribution of single-particle displacements captured by the self-part of the
Van Hove function \[148\]

\[G^S(y, t, t_w) = \left\langle \frac{1}{N} \sum_{i=1}^{N} \delta[y - (y_i(t_w + t) - y_i(t_w))]) \right\rangle, \tag{5.5}\]

where the \(y\)-component of the displacements in direction of the pre-shear gradient is chosen and the upcoming analysis is restricted to vanishing waiting times \(t_w = 0\). The measured distributions are shown in Fig. 5.6 for two different shear rates \(\dot{\gamma} \tau_0 = 4 \times 10^{-1}\) and \(\dot{\gamma} \tau_0 = 4 \times 10^{-5}\) and displacements accumulated over several time intervals \([0, t]\). A purely diffusive behavior would result in a Gaussian distribution (in this linear-logarithmic presentation observable as an inverted parabola), where systems close to the glass transition are known to show somewhat broader spectra \[149\]. In line with this we observe, especially for lower pre-shear rates, a rather sharp crossover from a Gaussian form for small displacements to an exponentially decaying tail for large \(y\). This crossover is located at a time- and pre-shear rate-dependent displacement \(y_G\). Thus the particles are divided into two distinct groups, a small fraction of the particles is able to travel distances significantly larger than what is expected for a homogeneous, purely diffusive system. Such a division into fast and slow particles is well-established in the description of disordered glassy systems with heterogeneous dynamics \[150\]. The emergence of exponential tails has already been observed in simulations on binary Lennard-Jones mixtures in thermal equilibrium \[151\] and during relaxation dynamics after a thermal quench \[135\] and is in line with predictions made by the formalism of continuous time random walks (CTRW) \[152\]. In an experiment studying colloidal 2D systems non-Gaussian behavior of the self part of the van-Hove function turned out to be detectable only in local, cage-relative coordinates \[153\]. This was traced back to Mermin-Wagner fluctuations “smearing out” local events. Here such a local analysis is refrained, because in the following we argue that in this context the heterogeneities stem from collective instead of local structural rearrangements. Furthermore, the exponential tail of the form

\[G^S(t, y) = \exp\left(-\frac{y - y_G(t)}{\xi(t)}\right)\] \tag{5.6}

gives access to a time-dependent length scale \(\xi\) setting the rate of the decay. As shown in Fig. 5.6 according fits describe the form of the measured data well for all pre-shear rates and time intervals and allows for an accurate determination of the associated length scale. As shown in Fig. 5.7 the growth of \(\xi\) with time is reminiscent of the evolution of the MSD. The curves are identical up to a time \(\dot{\gamma} t \ll 1\) and split up in the following, where the time of deviation from the joint master curve occurs at earlier times for higher pre-shear rates \(\dot{\gamma}\). Other than for the MSD a convergence of all curves for times \(nD_0 t \gtrsim 10^3\) is observed, as before a transient and a second final plateau is indicated. The existence of surprisingly high displacements, exceeding the diameter of a particle after comparably short times, suggests that the relaxation process is accompanied by infrequent but rather severe structural rearrangements. The dynamics are
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characterized by a time-dependent length scale $\xi(t)$ determining the range of the according displacement and supporting the picture of a pre-shear rate independent localization length as presented during the discussion of the MSD.

At this point the question arises, whether these large displacements occur simultaneously. If yes, a larger number of particles within a certain neighborhood is rearranged collectively. Otherwise, if they appear one at a time, they are associated to jumps of single particles escaping their cage made up of next neighbors. This behavior is predicted for similar scenarios by hopping models or the formalism of CTRW [154, 155, 156]. To answer this we first revisit the density correlation function, this time analyzing the instantaneous single-run value before performing an average over all runs. With decreasing pre-shear rates a very rich structural relaxation sets in. Especially for the 3 smallest rates $\dot{\gamma}\tau_0 \leq 4 \times 10^{-3}$, where a finite residual stress plateau could be resolved, the run-to-run fluctuations are substantial. This is exemplified in Fig. 5.8, showing the decay of a single-run correlator that was pre-sheared with $\dot{\gamma}\tau_0 = 4 \times 10^{-5}$ and differs tremendously from the averaged curve discussed above. It follows the density correlation function describing the quiescent non-pre-sheared dynamics up to a time that corresponds to a (pseudo) strain $\dot{\gamma}t > 1$. From there it rapidly decays onto a second plateau $f \approx 0.2$. This sudden collapse within a time span significantly smaller than the one associated to the decay of the averaged transient correlator is linked to a structural rearrangement involving multiple particles. By that a large proportion of the frozen-in stresses is relaxed, as shown in the lower panel. The single-run macroscopic stress that stems from an spatial average over a single system realization remains on the NESS level until this collective motion triggers a sudden and rapid simultaneous structural and stress

Figure 5.7.: Length scale $\xi(t)$ extracted from fits $G^S(t, y) = \exp(-\frac{y-y_G(t)}{\xi(t)})$ (see also Fig. 5.6) to the self part of the Van Hove correlation function for different pre-shear rates $\dot{\gamma}$ as labeled.
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Figure 5.8.: Upper panel: single-run transient incoherent density correlation function \( \Phi_{S q}(t, t_w = 0) \) (orange) at packing fraction \( \phi = 0.81 \) and wave-vector \( q/d_s = 0.61\hat{e}_y \) (in pre-shear gradient direction) for \( \dot{\gamma} = 4 \times 10^{-5} \) compared to the averaged (solid blue), quiescent non pre-sheared (dashed-dotted blue) and NESS correlator (dashed blue). Lower panel: single-run stress relaxation of the same run as above (orange) compared to the average stress (blue).

relaxation. After an undershoot with an amplitude of \( \sim 25\% \) of the initial value the stress level fluctuates around zero. In contrast to the density correlator no second plateau could be resolved, where this might be owed to the fact that stresses are measured by summing up momentum transfers during particle collisions, see Eq. (3.9). Therefore the measured values are subject to major fluctuations in the analysis of a single sample. A structural decay combined with a stress relaxation does not suffice to eliminate the present memory effects. It does not drive the system into a well-aged state comparable to the one we started before applying constant shear. The secondary plateau obtained after a single drop is transient and not representative of the long-time behavior. Choosing a waiting time that excludes an event as described, the dynamics afterwards exhibits further memory effects and high run-to-run fluctuations (not shown). This behavior describes an avalanche incident, a class of events that undoubtedly has an impact on the averaged dynamics. To gain deeper insight into the involved processes driving this relaxation a classification of the runs has been developed. A
sudden drop is detected if there exists a time $t_s > \tau_0$ and a time window $[t_s, t_e]$ for $t_e = At_s$ and $A > 1$ such that

$$\Phi^S_q(t_e) < f\Phi^S_q(t_s). \tag{5.7}$$

As depicted in the upper left panel of Fig. 5.9, $\Phi^S_q(t_s)$ denotes the initial value given by the mean value of the function measured during an earlier interval $[t_s/A, t_s]$ and we demand $\Phi^S_q(t_s) > 0.5$. Since the events in question are found to last longer for growing $t_s$ they are
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described by a relative width of the time interval $A > 1$ limited by a maximum value $A_{\text{max}}$ and by a minimum relative amplitude drop $f > 0$. Using this definitions an extensive analysis of the relaxation data has been conducted. The amount of avalanche events increases with decreasing pre-shear rate (for fixed values of the dimensionless parameters $f$ and $A_{\text{max}}$), while the overall run-to-run fluctuations increase. As an example we show the results of a classification procedure for $\dot{\gamma} \tau_0 = 4 \times 10^{-5}$, $A_{\text{max}} = 1.4$ and $f = 0.5$ in Fig. 5.9. We detect 64 avalanche runs (8 exemplary single-run density correlation functions are shown in Fig. 5.10), where a total number of 364 runs were taken into account. A broad distribution of initial and final times illustrates that the sudden drops occur for $nD_0 t_s > 1$, while an increase of events is detected for times similar to the NESS relaxation time at $t_s \approx 1/\dot{\gamma}$. The initial values $\Phi^S_{q}(t_s)$ are limited by the plateau value of the curve describing the quiescent non-pre-sheared dynamics at $\Phi^S_{\text{math, Equ}} \approx 0.8$ and the prescribed minimum value $f = 0.5$. The evolution of the curves until this point varies strongly from run to run. Some follow the equilibrium plateau until the drop sets in, some decay in iterated smaller steps. It is remarkable, that the correlator during such a process never completely decays to zero, all avalanche drops terminate at values between 0.2 and $f/2 \approx 0.4$. The duration of this structural rearrangements $\Delta t = t_e - t_s$ increases with increasing initial time $t_s$ and is limited by $\Delta t < nD_0 A_{\text{max}} t_s$ due to the employed detection method. The distribution of the ratio between final and initial time $t_e/t_s$ on the other hand is apparently independent of the initial time and therefore a more meaningful quantity to characterize the timescale of an avalanche event.

It must be stated that this classification does not separate the runs into systems undergoing heterogeneous and homogeneous dynamics. An individual analysis of the scaling behavior or emergence of a second plateau as discussed above for both “classes” was not expedient. This is due to the fact that run-to-run fluctuations of non-avalanche runs are just as pronounced as for avalanche runs. As illustrated in Fig. 5.10 this procedure just filters the runs undergoing the most severe and rapid structural changes. Thereby they contribute slightly more to the exponential tails of the Van Hove functions associated to larger displacements (not shown). The dynamics of the remaining runs, some examples are shown in the right panel, are just as diverse and widely spread. They range from curves following the equilibrium plateau for all times to realizations where a structural decay faster than the average NESS decay is observed. The rich structural relaxation renders a meaningful description of the involved processes difficult. Such deviations from the average structural correlator are not present in the NESS or for quiescent non-pre-sheared systems. Surprisingly, the behavior of single-run correlators observed for low pre-shear rates is is to a great extend identical to the one reported for thermal quenches to temperatures well below the critical temperature of the glass transition [146, 135]. There an equally broad distribution of decay scenarios also led to a second plateau of the averaged density correlator but did not allow for a detailed characterization of the particle rearrangements

\footnote{Private communication with J. L. Barrat, Sept. 2014}.

There the runs exhibiting sudden and rapid
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Figure 5.10.: Examples of single-run transient incoherent density correlation functions $\Phi^S_q(t, t_w = 0)$ of avalanche (left) and non avalanche runs (right) at packing fraction $\phi = 0.81$ and wave-vector $q/d_s = 0.61\hat{e}_y$ for $\dot{\gamma} = 4 \times 10^{-5}$ for parameters $A_{\max} = 1.4$ and $f = 0.5$. For comparison the averaged (solid blue), quiescent non pre-sheared (dashed-dotted blue) and NESS correlator (dashed blue) are shown.

drops are linked to “earthquake-like” collective motion of many particles over a small average distance and are correlated to a significant release in local stresses after the quench.

To gain further insight we turn to a local analysis by studying displacement and strain maps for a time interval containing one of these events connected to severe structural rearrangements. Measurements of these quantities (neglecting their affine part) are commonly utilized to identify localized irreversible structural rearrangements, e.g. in experiments on sheared colloidal glasses in 3 dimensions [14] or atomistic computer simulations of amorphous sheared systems [157, 158, 159, 160]. We follow individual particle trajectories for the time of the simultaneous rapid decay of structure and relaxation of stress, starting in the highly stressed pre-sheared state. This provides insight into the spatial extent, the number of involved particles and nature of the reorganization process. We focus on a single event for a run at the lowest shear rate investigated $\dot{\gamma}_0 = 4 \times 10^{-5}$, where the avalanche was detected at $nD_0t_s = 45$ and lasts for $nD_0(t_e - t_s) \approx 7$. The according maps showing the local displacements $u_i = \mathbf{r}_i(t_e) - \mathbf{r}_i(t_s)$ and local strain $\varepsilon_{xy}(\mathbf{r}, t_s, t_e) = 1/2(\partial u_x/\partial r_y + \partial u_y/\partial r_x)$ are given in Fig. 5.11. For comparison the same quantities are also mapped for intervals of the same length intermediately before ($nD_0t \in [38, 45]$) and after ($nD_0t \in [45, 52]$) the avalanche event. For the latter the local variations in displacements and strain are comparably smooth, for both intervals the mean absolute displacement $\bar{u} = 1/N \sum_i |u_i| = 0.15d_s$ is significantly smaller than a particle diameter. Except for a few regions exhibiting vertices, where a single motionless particle is orbited by its nearest neighbors, the strain field varies between $-0.05 \leq \varepsilon_{xy} \leq 0.05$ and appears predominantly homogeneous. The positional data collected during the avalanche event results in slightly higher displacements with
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Figure 5.11.: Local map of particle displacements \( \mathbf{u}_i = \mathbf{r}_i(t_2) - \mathbf{r}_i(t_1) \) (top) and strain \( \varepsilon_{xy}(\mathbf{r}, t_1, t_2) \) (bottom) immediately before, during and immediately after a collective avalanche event at packing fraction \( \phi = 0.81 \) for a system made up of \( N = 1000 \) particles. Each map is based on a time window of length \( nD_0\Delta t = nD_0(t_e - t_s) = 7 \), where the avalanche event starts at \( nD_0t_s = 45.3 \).

\( \bar{u} = 1/N \sum |\mathbf{u}_i| = 0.27d_s \). Within a region close to the right border of the simulation box (and a small band at the opposite edge connected due to periodic boundary conditions) particles traveled larger distances up to \( |\mathbf{u}| \approx d_s \). Around 25% of the disks undergo a collective motion, rearrange the structure and by that relax the majority of the stresses built up during shear flow. This is impressively visualized by the local strains: regions of collective movement are strongly strained exhibiting values \(-0.2 \leq \varepsilon_{xy} \leq 0.2\) and a significantly higher spatial gradient as before. The remaining particles, making up around 75% of the entire system, are seemingly barely affected by this event. There the displacement and strain fields are reminiscent of the ones describing the dynamics just before and after the avalanche. Similar strain fields are reported for a sheared Lennard-Jones glass former in 2D [80], where the
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emergence of localized high strains are interpreted as an evidence of inelastic events, while
the weakly strained background is attributed to elastic fluctuations. In [135] it is found that
the magnitude of similar processes during the relaxation after a thermal quench to low $T$
depends on the system size $N$. Since driving larger systems into a stationary state at shear
rates that small demands extensive and long simulations a finite-size analysis has not been
carried out within the scope of this work.
Again it must be said that these values are not general for all avalanche events, as already
presented above the variety of relaxation scenarios is exceptionally rich. What can be stated
is that such events relax the structure and stresses by rearrangements involving at least 20%
of the particles. The involved disks move simultaneously and by a distance small compared
to the particle diameter $d_s$. Furthermore, the processes are accompanied by comparably high
strains in the affected regions.

5.3. Conclusions

We presented and discussed stress decays, microscopic dynamics and structural decorrelation
of a shear-melted glass after the cessation of steady shear flow. For weakly pre-sheared sam-
pies in the glass finite residual stresses remain, where the pre-shear rate sets the magnitude
and evolution from the stationary state to the non-equilibrium quiescent solid through long-
lived memory effects. The development of permanent stresses during relaxation from a highly
stressed state implies that the glass state can not solely be characterized by its thermodynamic
control variables. This signals the nonequilibrium nature of the amorphous solid that is being
produced. For identical control parameters but different preparation histories differences in
the structure and consequently in the emerging dynamics have been found. Furthermore, we
were able to identify a pre-shear rate independent localization length representing an upper
bound for the (averaged) distance particles are able to travel while moving subdiffusively
before an arrest sets in for large times. Our results are in line with similar findings from
previous experiments and 3D molecular-dynamics simulations [20] and qualitatively confirm
the picture provided by an ideal-glass model using schematic models of the mode-coupling
theory combined with the integration-through transients framework (ITT-MCT) [32]. Ana-
lyzing single-run dynamics we found a wide variety of relaxation scenarios, including spatially
inhomogeneous displacement and strain fields. For small pre-shear rates, exhibiting the high-
est residual stresses, sudden and rapid collective structural rearrangements were detected.
This avalanche events relax an substantial fraction of the stationary state stress within a
comparably short time window and are connected to simultaneous particle displacements
that are small compared to a particle diameter.
6. Channel flow

In the previous chapters, Brownian disks were studied at rest as well as under homogeneous simple shear flow. Although in these cases the results of each simulation run are subject to fluctuations, the spatially homogeneous nature of the system allows for building well-defined, system-wide spatial and time averages or correlations. In the following we will go beyond this and move to systems that are not only time-dependent, but in addition exhibit intriguing spatial dependencies. This chapter investigates the stationary flow dynamics of a colloidal glass former in a planar channel with rough walls driven by a pressure gradient. Pressure driven flow through a channel is also referred to as Poiseuille flow. The sole presence of rigid walls has an appreciable impact on the dynamics of supercooled liquids and amorphous solids [161, 162]. This is not surprising, since a confinement alters the localization in such systems, a process which is closely related to the yielding of next neighbor cages and thus the material’s flow properties. On top of that, the system is driven by an external stimulation. Already in the 1830s Jean Poiseuille presented results on flow of water through glass tubes and the influence of the pressure gradient, channel dimensions and Temperature [163]. He investigated the emerging laminar stationary flow of an incompressible Newtonian liquid through a channel in presence of a pressure drop. In the case of Non-Newtonian fluids as studied here, the interplay between the slow dynamics of colloidal suspensions and externally imposed flow can be investigated on a new playground. The setup gives rise to flow characteristics, such as shear rates and stresses, that heavily depend on the spatial position across the channel. In pressure-driven channel flows, Non-Newtonian fluids display blunted flow profiles that deviate from the parabolic velocity profile of a Newtonian fluid, as presented e. g. for monodisperse or multidisperse suspensions in 2D [164, 165], thin layers of emulsions in 3D [21] or numerical simulations on a binary Yukawa mixture in 3D [166]. Yield stress materials are known to exhibit a solid plug in the channel center where the material can resist the local shear stresses induced by the external driving [23, 167]. The surrounding regions however are subject to high shear stresses that suffice to fluidize the material close to the walls. Heterogeneous flow behavior is also reflected in experimentally determined diffusion constants of a hard-sphere suspension undergoing Poiseuille flow [22].

The upcoming chapter is organized as follows: First we present the algorithm employed. To carry out simulations the techniques used so far have to be extended to satisfy the balance equations of fluid dynamics, to construct the appropriate geometry and to measure certain quantities locally. Then the local flow properties in a stationary state are characterized. A
6. Channel flow

criterion, which is based on the suspension’s yield stress \cite{23} at densities beyond the glass transition point, is verified for a wide range of pressure gradients and channel widths. We then present results on the local microscopic particle movement and structural relaxation of the confined system in absence of external driving. We extend this analysis to a flowing suspension and investigate the density correlation functions and mean squared displacements as specified by the local shear rates. In addition, we justify our outcome for stationary flows by comparison to results from a hybrid Lattice Boltzmann-MCT model \cite{167, 168, 169}. Conclusions and an outlook close the chapter.

6.1. Simulational realization

6.1.1. Channel geometry

![Snapshot of a channel with width $w$, where larger (smaller) mobile particles are marked red (blue) and pinned ones gray. The pressure-drop along the channel induces a collective flow in $x$-direction, where periodic boundary conditions apply. Note, that this is a small sample with $N = 1000$ particles for the illustration of rough walls, while the actual system is shown in Fig. 6.2.](image)

There are several ways to introduce physical walls to the system. The easiest one to accomplish a channel geometry is to insert two flat reflecting walls parallel to the horizontal boundaries of the simulation box. This is not enough for our purpose because this approach lacks a friction component. We aim for a roughness, such that collisions with the wall slow down the dynamics and lead to vanishing advective flow at the (horizontal) boundaries, also
6.1. Simulational realization

Figure 6.2.: Snapshot of a channel with $N = 16000$ particles, width $w = 136.4d_s$ and length $l = 151.6d_s$. 

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6. Channel flow

referred to as no-slip condition. In experiments this is easily achieved by rough surfaces of the confining plates with height variations comparable to the particle diameters [22]. In simulations the same behavior can be realized by randomizing the momentum change during collisions between a particle and a flat wall leading to a desired corrugation effect [25]. However there is a second issue that comes with flat hard walls, namely the slight dilution of the suspension due to the hollow spaces between colloidal particles next to the wall. This certainly effects the physical properties at distances very close to the boundaries and adds further complexity on how to properly equilibrate the system in this region. We therefore choose to resolve the wall in more detail by simply pinning hard particles of the same sizes as the colloidal ones along the channel boundary as done in [161, 23]. By that we introduce roughness and friction at the wall and are able to reuse the well aged initial configurations created before, see Sect. 2.5.3. We start at \( t = 0 \) with a system that was equilibrated by undergoing Newtonian dynamics. All particles fulfilling

\[
y_i(0) - \sigma_i > \frac{L + w}{2} \quad \text{or} \quad y_i(0) + \sigma_i < \frac{L - w}{2}
\]

are pinned to their initial position, where \( \mathbf{r}_i(t) = (x_i(t), y_i(t)) \) and \( \sigma_i \) denote the position at time \( t \) and the radius of particle \( i \), \( L \) is the box length and \( w \) the width of the channel, where \( w < L \). As shown in Figs 6.1 and 6.2 for sample systems of different size this results in rough walls at the top and bottom. A permanent pinning of particles is equivalent to setting the mass of a disks to infinity or the short time diffusion constant to 0,

\[
D_i(y_i) = \begin{cases} 
0 & y_i(0) - \sigma_i > \frac{L + w}{2}, \\
0 & y_i(0) + \sigma_i < \frac{L - w}{2}, \\
D_0 & \text{else}.
\end{cases}
\]

With this construction disks are no longer able to pass through the top or bottom side while in \( x \)-direction periodic boundary conditions are maintained. In the quiescent confined system the particle mixture remains unchanged. Effects that cause a local demixing of the flowing suspension across the channel can be suppressed by limitation of the maximum pressure gradient applied, see B.2.

6.1.2. Collision treatment

The collision rules between mobile and pinned particles need to be adjusted to the scenario shown in Fig. 6.3. Simply looking at a confined system in absence of driving by the pressure gradient the prediction of collision times is not affected by this changes, Eq. (2.52) is still valid. The momentum transfer between the wall and a mobile particle, which is responsible for the emergence of the desired friction, has to be modified. The change in velocity experienced by a mobile particle \( j \) and a pinned particle \( i \) at contact is given by Eq. (2.53) and (2.54) in the
6.1. Simulational realization

Figure 6.3.: Pre-contact (left) and post-contact scenario (right) for a collision between two mobile particles (red and blue, top) and between a mobile and a pinned particle (blue and gray, bottom). Light red and light blue circles depict the positions at contact.

\[ \lim_{m_i \to \infty}, \]
\[ \vec{r}_{i_{out}}^i = \vec{r}_{i_{in}}^i = \vec{0}, \quad (6.2) \]
\[ \vec{r}_{j_{out}}^j = \vec{r}_{j_{in}}^j + \frac{2b_{ij}}{d_{ij}} \Delta \vec{r}_{ij}, \quad (6.3) \]

where \( b_{ij}(t) = \Delta \vec{r}_{ij}(t) \cdot \Delta \vec{f}_{ij}(t) \) and \( d_{ij} = \sigma_i + \sigma_j \). At contact the part of the momentum of the mobile particle parallel to the vector \( \Delta \vec{r}_{ij} \) connecting the centers of the colliding particles (direction of one of the gray dashed lines in Fig. 6.3) switches sign. As a consequence the initial total momentum is no longer conserved during a particle-wall collision. In this framework this is a necessary criterion for the advective flow to vanish in direct proximity to the boundaries.

As will be argued in the next subsection, the mobile particles inside the channel will be exposed to a constant body force and hence experience a uniform acceleration in \( x \)-direction. For this scenario the collision prediction rules have to be adjusted. As described in Sect. 2.4 two particles \( i \) and \( j \) are at contact at time \( t \) if the absolute value of their separation \( \Delta \vec{r}_{ij} \) is equal to the sum of their radii

\[ \Delta \vec{r}_{ij}(t) = |\vec{r}_i(t) - \vec{r}_j(t)| = \sigma_i + \sigma_j. \quad (6.4) \]

Unlike before each mobile particle is accelerated and follows a parabolic trajectory between
two collisions. The description of the path needs an initial position \( r_i(t) \), a pseudo velocity \( \dot{r}_i(t) \) and in addition an uniform acceleration \( \ddot{r} = F/m = (\ddot{x},0) \) that stems from a constant force \( F \) felt by each particle. If no collisions or Brownian events interfere within the time span \([t, t + \tau]\), the position of particle \( i \) at time \( t + \tau \) is given by

\[
    r_i(t + \tau) = r_i(t) + \tau \dot{r}_i(t) + \frac{\tau^2}{2} \ddot{r}.
\]  

(6.5)

To predict an upcoming intersection between trajectories of two particles Eq. (6.4) has to be solved for a time \( \tau_c \) in the future. In the case where both particles \( i \) and \( j \) are mobile the acceleration term is identical for both and does not affect the difference \( r_i(t) - r_j(t) \). The solution for the unaccelerated case Eq. (2.52) remains valid. The situation changes for a collision of a mobile particle \( i \) with a pinned particle \( j \), where the collision prediction using Eq. (6.4) and (6.5) reduces to a root finding problem of a quartic equation,

\[
    0 = (r_i(t + \tau_c) - r_j(t + \tau_c))^2 - (\sigma_i + \sigma_j)^2
    = \left( r_i(t) + \tau \dot{r}_i(t) + \frac{\tau^2}{2} \ddot{r} - r_j \right)^2 - (\sigma_i + \sigma_j)^2
\]  

(6.6)

Only real positive solutions for the collision time \( \tau_c \) are of interest. If several of these exist only the smallest value corresponding to the first collision to occur is relevant. A non existence of a real positive solution ensures that the two trajectories will not intersect. Eq. (6.7) can be solved exactly [170] for the collision time \( \tau_c \) which is not desirable in terms of efficiency and error susceptibility. Hence it is solved numerically using a balanced-QR reduction of the companion matrix, a root-finding method for general polynomial equations [171, 172] that is implemented in the GNU scientific library GSL. This of course adds further computational effort to the algorithm, since roots of a fourth order instead of a second order polynomial have to be calculated. Fortunately only in situations when one of the collision partner is pinned, which make around \( d_s/w \) percent of the total cases, this more expensive routine has to be employed. In addition the prediction of cell crossings is modified, the method of calculating the time when a particle hits a flat cell edge is updated. Unlike before roots of a second order instead of a first order polynomial have to be calculated for all mobile particles in the system, where here the method of finding exact solutions works reliably. Both implementations of the root-finding procedures were tested thoroughly. As before the accuracy of variables in time and space allows for a reliable overlap-free event driven hard disk simulation.

6.1.3. Flow and Thermostat

Compared to the shear rate driven Couette flow imposing a simple linear velocity field that is constant in time (see Chap. 2) the requirements here are more diverse and call for major amendments to the algorithm. The channel velocity field \( u(r, t) \) of a stationary state is not
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Figure 6.4.: The mobile particles (red and blue) experience an external force embodying the pressure gradient $\nabla p$, while the gray wall particles are pinned. This force drives a Poiseuille flow and can be realized either by a uniform acceleration or repeated velocity boosts.

known a priori but evolves from a transient regime with space- and time-dependent particle velocities driven by a constant pressure gradient. So the field is the result of the suspension’s complex response to spatially inhomogeneous stresses and shear rates. This renders the previous handling of velocity assignments Eq. (2.38) pointless here. Instead the realization of the pressure gradient is motivated by the Navier-Stokes equation for a continuum description of incompressible viscous fluids

$$\frac{\partial u}{\partial t} + (u \cdot \nabla)u - \nabla \sigma/\rho = -\nabla p/\rho + f^b, \quad (6.8)$$

where $\sigma$ denotes the stress tensor, $p$ the pressure, $\rho$ the mass density and $f^b$ an external body force density acting on the medium. The left hand side represents the time-dependent and convective components and the divergence of deviatoric stresses. The effect of $-\nabla p/\rho$ and $f^b$ on these terms is identical. Therefore it is legit to realize the pressure gradient by a body force. Actually, the derivation of of Eq. (6.8) is based on Newton’s second law, interpreting a force as the time derivative of a momentum density [78]. This becomes relevant for the interpretation of this continuum force density as an external force in the microscopic, particle based simulation. Consequently the acceleration experienced by a particle indexed by $i$ originates from a Newtonian interpretation as well,

$$f_{i}^{ext} = m_i \ddot{r}_i. \quad (6.9)$$
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Since the driving force is constant and points in flow direction it induces an uniform acceleration in $x$-direction experienced by all particles

$$f^\text{ext} = F \hat{x}, \quad (6.10)$$

$$\ddot{x} = \frac{F}{m_i}. \quad (6.11)$$

This is implemented into the event-driven ballistic part of the simulation, as described in Eq. (6.5). At this point, we deviate from a purely Langevin-type description, where in the overdamped limit an external force needs to balance the dissipative force $f^d = -\xi (\dot{r}_i - u(r_i))$, known as Stoke’s drag. This force is proportional to the particle velocity relative to the solvent velocity $\dot{r}_i - u(r_i)$ at that point, see Eq. (2.1) and (2.26), rather than to a uniform acceleration as in Eq. (6.9). This drag relation was used elsewhere for applying a strong external force to a single probe particle for micro rheology simulations [173], but proved to be unsuitable for the investigations done here.

Again we model the solvent friction by an implementation of random forces $f^\prime$ representing the effect of collisions between colloidal particles with their adjacent solvent molecules. As before this is done by redrawing the peculiar velocities $\dot{r}_i - u(r_i)$ from a Gaussian distribution during Brownian events after fixed time steps of length $\tau_B$. For this the advective flow part has to be separated from the velocity field at each of the events. It is reasonable to assume that at each point in the suspension the mean velocity of colloidal particles gives the local solvent velocity. We assume the average velocity field to be laminar (at least in a stationary state), viz. particles flow in $x$-direction in parallel layers, and invariant along the $x$-axis, $u(r) = u(y)$. At time $t^-$, immediately before a Brownian event is processed, the advective flow $u_x(t^-, y)$ is determined by dividing the $y$ range into bins of width $d_s$ and averaging over the velocities of all particles contained in a particular bin. The prescription for reassignments of particle velocities is then given by

$$\dot{r}_i(t^+, y_i) = \mathbf{x}^f + u_x(t^-, y_i)\hat{x}, \quad (6.12)$$

where $t^+$ denotes the time immediately after the event and $\mathbf{x}^f$ the Gaussian random variable defined in Eq. 2.21. As before the system is thermostated by a repeated adjustment of the distribution of peculiar velocities to a Gaussian distribution Eq. (2.21), for a detailed test of the method see B.1. The resulting superposition of diffusive motion and advective flow is known from experiments on channel flow of colloidal hard spheres [22]. In their work the analysis also requires a decomposition of the measured particle velocities into the two contributions. However, with this construction no straightforward way was found to establish a fluctuation-dissipation relation for the fluctuating thermal forces analogous to Eq. (2.3) that relates a friction coefficient $\xi$ to the short time diffusion constant $D_0$, Eq. (2.43). Nevertheless, the results presented below during the discussion of the MSD orthogonal to
6.2. Stationary flow

flow, suggest that these two parameters remain unchanged compared to the nonconfined quiescent systems investigated earlier.

In the constantly driven system the processing of collisions as described in 6.1.2 works reliably but finding the roots of a fourth order polynomial as in Eq. (6.7) reduces the speed compared to the method used before. Conversely, for Couette shear flow the velocity distribution is simply biased by a position dependent vector \( \gamma y \hat{x} \) to impose a linear profile which is known a priori, see Eq. (2.37). The same is done here in Eq. (6.12) for the time dependent advective part of the velocity profile \( u_x(t^-, y_i) \hat{x} \) that is given by the measured local particle movements. For small Brownian times \( \tau_B \) as used here, there is also the possibility to translate the constant body force into a velocity boost that is applied during thermostating events. Instead of a constant acceleration in the ballistic part of the algorithm, Eq. (6.5), the driving force is added to the frictional and advective components of the thermostat by shifting the drawn velocities by a constant \( \Delta v = F\tau_B/m \) in flow direction,

\[
\dot{r}_i(t^+, y_i) = \dot{r}_i(t^-, y_i) + u_x(t^-, y_i) \hat{x} + \frac{F\tau_B}{m} \hat{x}.
\]  

(6.13)

This simplifies the dynamics between two events, because we move back to particle trajectories that are chains of straight lines as in Chap. 2 and the straightforward collision rules worked out there apply again. In B.3 it is shown, that for the geometries and forces studied here the difference in the results for the two implementations of the body force is negligible. Therefore most of the data shown in the following is calculated using the more efficient realization relying on repeatedly applied velocity boosts, Eq. (6.13).

In summary a channel flow algorithm was developed for the simulation of a confined N-body system under a constant pressure gradient. It obeys the Navier-Stokes equation of momentum balance, which is rooted in a Newtonian interpretation of forces. This differs from the concept of drag forces experienced by particles moving through a liquid as used in the Langevin description of the previous chapters. A stochastic thermostat dissipates the heat by reassigning the peculiar velocities according to a prescribed distribution constantly. At the same time it simulates an interaction with the surrounding solvent incorporating frictional forces. Furthermore, the maintenance of the hyperactive thermostat used before allows for different implementations of an external body force.

6.2. Stationary flow

Having laid the foundations for the construction of a Brownian glass builder in a planar channel, we drive the system into a stationary flowing state. For this a sample is equilibrated, then all wall particles are frozen at the horizontal edges. After that the pressure gradient is immediately switched on as described in the previous subsections. The time span necessary to reach a stationary state is dictated by several criteria. We demand the velocity in \( x- \)
6. Channel flow

Figure 6.5.: Velocity profiles $v_x(y)$ for the flow in direction of the pressure gradient $\nabla p$ during start up (left) and in a stationary state for packing fraction $\phi = 0.81$, force $F = 0.25$ and channel width $w = 106d_s$. Note that the time axes in the two plots differ, $t$ was set to zero as soon as a stationary state was reached at $D_0t = 5 \times 10^4$.

direction, the local density, the concentrations of particle types and the shear stress profile to be stationary. This leads to a laminar flow with vanishing velocity in $y$-direction, which is also checked. For the forces and packing fractions shown a time $t = 10^6\tau_b = 5 \times 10^3\tau_0$ turned out to be sufficient. Note that this time does not exceed the inverse local shear rates $1/\dot{\gamma}(y)$ at all positions in the channel, indicating that a shear-induced relaxation time might not be reached everywhere. For simple shear flow memory effects are assumed to vanish within this time of structural relaxation. Nevertheless, after the chosen time interval no aging signatures could be measured, thus the flow is assumed to be in a stationary state. A limiting value for the force $F$ is given by the occurrence of a further process: for $F \geq 0.25k_BT/d_s^2$ a strong demixing of the particle types of different size is observed. This process enlarges the time window to arrive at a stationary flow significantly because a very slow particle motion orthogonal to the direction of flow sets in, for details see B.2. In Fig. 6.5 the velocity profile along the channel is shown for the intermediate regime of start up and for stationary flow. The data shown in the following is based on an average over at least 150 runs per force, channel width and packing fraction employing a quadratic simulation box containing $N = 16000$ particles (mobile and pinned) of the same composition as before. Further the quantities measured in stationary flow are averaged over $10^3$ configurational snapshots equally spaced in time or in case of stresses $10^3$ time intervals of length $10^3\tau_b = 5 \times 10^{-2}\tau_0$.

6.2.1. Yield stress analysis

For Newtonian fluids the emerging velocity profile across the channel is well described by the Hagen-Poiseuille equation [163], a parabolic profile derived from the Navier-Stokes momen-
6.2. Stationary flow

Figure 6.6.: Velocity $v_x$ (in direction of the force resp. $\nabla p$) as function of $y$ (perpendicular to the walls and flow) for varying forces $F$ and a fixed channel width $w = 106.1d_s$ (left) and vice versa for $F = 0.125k_BT/d_s$ (right) for $\phi = 0.81$. The dotted purple line shows a Hagen-Poiseuille velocity profile for a Newtonian liquid at $F = 0.1k_BT/d_s$. The profile of yield-stress fluids differs from this parabolic curve and shows a central flat region with vanishing shear rate. Beyond the solid-like part $\dot{\gamma}(y)$ becomes nonzero and reaches its maximum at the walls where the velocity vanishes.

The momentum equation (6.8). Demanding no-slip boundary conditions in 2 dimensions one finds

$$v_x(y) = \frac{y^2 - (w/2)^2}{2\eta} \frac{\partial p}{\partial x} = \frac{(w/2)^2 - y^2}{2\eta} nF,$$  \hspace{1cm} (6.14)

a velocity profile that is determined solely by a constant shear viscosity $\eta$, channel width $w$ and a pressure gradient $\nabla p$, which is equivalent to a body force density $nF$. For non-Newtonian fluids, characterized by a shear rate dependent viscosity $\eta(\dot{\gamma})$, the description gets more complex. This becomes evident from the simulated flow profiles for glassy states shown in Fig 6.6. Results are shown for packing fraction $\phi = 0.81$, a value well above the critical value $\phi_c = 0.7975$, corresponding to a state “deep in the glass”, that would solidify in a quiescent state. Data has been sampled for 5 different forces $F$ varying by more than a decade and 4 channel widths $w$ between $45.5d_s$ and $136d_s$, with $d_s$ the diameter of the small particles. For dense shear-thinning suspension as investigated here a central plug, a solid part at the center that moves uniformly at constant speed, develops. In contrast, regions undergoing high shear are localized in proximity to the walls. In this region Peclet numbers up to $\dot{\gamma} \tau_0 = 1$ are reached while the velocity decreases towards the boundary, where it vanishes. The strong dependence of the flow properties on the position inside the channel is accompanied by an increasing viscosity towards the center, causing a growth in viscous dissipation that blunts the flow profile stronger when compared to a Newtonian fluid. For comparison, a Newtonian parabolic velocity profile (dotted purple line, determined using Eq.
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Figure 6.7.: Left: Flow curve showing the stationary shear stress from Couette flow as function of the Peclet number for \( \phi = 0.81 \) (blue curve). This may be approximated by a Herschel-Bulkley-type constitutive equation \( \sigma_{xy}(\dot{\gamma}) \beta d_s^2 = 0.66 + 5.94(\dot{\gamma} \tau_0)^{1/2} \) [132] with a flow index \( n = 1/2 \) (orange dashed line) corresponding to a shear-thinning liquid. Right: local shear stress \( \sigma_{xy} \) as function of the local shear rate \( \dot{\gamma} \) (crosses) for Poiseuille flow. The flow curve for simple shear flow (black dashed line) is shown for comparison. Data points measured close to the walls for \( \delta y < 6d_s \) are displayed by circles, data points on the solid plug, where \( \dot{\gamma} \) fluctuates around zero, are not shown.

(6.14) is plotted for a force \( F = 0.1k_B T/d_s \). For this we used a constant viscosity, that coincides with the local viscosity measured close to the wall of the simulated system at same force. A \( w \)-dependent critical force has to be exceeded to initiate a flow. For \( w = 106.1d_s \), as shown here, values \( F \gtrsim 0.06k_B T/d_s \) are necessary. Only then the resistance caused by the presence of rough walls can be overcome and a surface rheology, different from that in the bulk, emerges. This frictional contribution at the edges of the channel also ensures no-slip boundary conditions. For the entire spectrum of forces and channel widths investigated we find \( v_x(\pm w/2) \approx 0 \). The absolute value of the shear rate close to the walls and the plateau height at the center region increases with the applied force \( F \) and channel width \( w \). On the other hand, the width of the plateau, where the shear rate vanishes, decreases with the applied body force and does not depend on the channel width. This can be understood by turning to a yield-stress analysis of the problem, as done in a couple of existing experimental and theoretical works, see e.g. [174, 175, 23, 176, 21]. The key idea here is to check whether the local stresses exceed the system’s yield stress or not. Only regions exposed to shear stress above this material constant can undergo shear flow, everywhere else the shear rate has to vanish. The local stresses across the channel are determined by the macroscopic momentum continuity equation Eq. (6.8), which in the stationary state, using \( u(y) = (u_x(y), 0) \) and
6.2. Stationary flow

\[ \sigma_{xy}(y) = \frac{-n F y}{d_s}, \]

or in components

\[ \partial_x \sigma_{xx} + \partial_y \sigma_{xy} = -n F \]  \hspace{1cm} (6.16)
\[ \partial_x \sigma_{yx} + \partial_y \sigma_{yy} = 0. \]  \hspace{1cm} (6.17)

Noticing that due to translational invariance the stress tensor components can not depend on \( x \) and considering the symmetry leads to a shear stress linear in \( y \) and a constant diagonal \( y \)-component

\[ \sigma_{xy}(y) = -n F y \]  \hspace{1cm} (6.18)
\[ \sigma_{yy} = \text{const.} \]  \hspace{1cm} (6.19)

As shown in Fig. 6.8 the above relation is verified quantitatively by the simulated data, the shear stress varies linearly across the channel and scales with the external force \( F \). Colloidal suspensions in a glass state show solid behavior and respond elastically to shear stresses up to the yield stress \( \sigma_{xy}^{\text{yield}} \), a material specific upper limit the system is able to withstand without deforming plastically. This onset of yielding depends on the experimental setup. Exposing the material to a constant shear rate reveals in the limit of small \( \dot{\gamma} \) the dynamic yield stress.
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\[ \sigma_{xy}^{\text{yield}} = \lim_{\dot{\gamma} \to 0} \sigma_{xy}(\dot{\gamma}), \]

while under constant external shear stress a flow is detected as soon as the static yield stress \( \sigma_{xy}^{s} \) is exceeded. For the tested system only the dynamic yield stress is known. The Couette flow simulations presented in 3.2.5 provide the flow curve and for a packing fraction \( \phi = 0.81 \) the limiting value is determined to \( \sigma_{xy}^{\text{yield}} = 0.66k_B T/d_x^2 \) as shown in Fig. 6.7. In the setup of a pressure-driven channel flow the existence of a yield stress behavior is responsible for the observed transition from a solid central part to a highly fluidized phase close to the walls. The spatial dependence of the stress divides the suspension into flowing regions, where this limit is exceeded, and weakly stressed solid-like regions. From Eq. (6.18) it follows that for

\[ y \in \left( -\frac{\sigma_{xy}^{\text{yield}}}{n F}, \frac{\sigma_{xy}^{\text{yield}}}{n F} \right) \]

the absolute value of \( \sigma_{xy}(y) \) is below the yield stress. Figure 6.9 shows the velocity profile compared to the shear rate and shear stress across the channel for different forces and densities. In the glass at \( \phi = 0.81 \), the boundaries of the region defined by Eq.6.20 are indicated by dotted lines and define the the solid-like plug. As predicted, this area is convected and not sheared: here the shear rate vanishes, thus the according velocity profile is flat. The width of this region is \( 2\sigma_{xy}^{\text{yield}}/(n F) \) and by this independent of the channel width \( w \), provided that the force is high enough to develop a blunted velocity profile. For narrow channels exceeding the dynamic yield stress locally turned out to be not sufficient. Some linear shear stress profiles are found where this condition is fulfilled, but the forces are too small to overcome the resistance imposed by the confinement by rough walls. If the regions, where stresses higher than \( \sigma_{xy}^{\text{yield}} \) are measured, are too narrow, high shear rates cannot be achieved and the blunted velocity profile is not able to develop. For example, for a non-zero velocity profile at \( \phi = 0.81 \) maximum shear rates \( |\dot{\gamma}| \tau_0 \gtrsim 10^{-1} \) in proximity of the walls are necessary.

For packing fractions below \( \phi^c \) no yield stress can be defined, it is \( \lim_{\dot{\gamma} \to 0} \sigma_{xy}(\dot{\gamma}) = 0 \). However an analogous analysis using the critical value \( \sigma_{xy}^{\text{yield}}(\phi^c) = 0.22k_B T/d_x^2 \) reveals the weakly sheared segment where \( \dot{\gamma}_0 \lesssim 10^{-3} \), see the lower panels of Fig. 6.9. Unlike in glassy systems the shear rate vanishes solely at the center at \( y = 0 \).

Furthermore, we observe that unlike \( \sigma_{xy}(y) \), the local shear rates \( \dot{\gamma}(y) \) across the channel for varying widths \( w \) do not collapse onto a single curve. This displays the non-trivial nature of the flow curves \( \sigma_{xy}(\dot{\gamma}) \) that is also shown in Fig. 6.9. The inhomogeneous flow created by the pressure gradient leads to a flow behavior that depends on the channel geometry and the applied pressure gradient and hence differs from the simple Herschel-Bulkley type found for planar Couette flow. The increase in shear stress with growing shear rate is weaker for lower forces, corresponding to a lower viscosity. This effects are also reported experimentally in the analysis of jammed states in thin layers of concentrated amorphous emulsions [21].

The diagonal components of the stress tensor are shown in Fig. 6.10. As stated by Eq.
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Figure 6.9: Yield stress analysis at $F = 0.0625 \frac{k_B T}{d_s}$ (left) and $F = 0.125 \frac{k_B T}{d_s}$ (right) for 4 different channel widths $w$ at $\phi = 0.81$ in the glass (top) and $\phi = 0.78$ in the supercooled liquid (bottom). The panels (from top to bottom) show the velocity $v_x$ in direction of $F$, Péclet number $\dot{\gamma}_T$ and shear stress $\sigma_{xy}$ as function of position $y$ across the channel. The horizontal dashed lines indicate the yield stress $\pm \sigma_{xy}^{\text{yield}}$, the horizontal dashed-dotted lines the points $y = \pm \sigma_{xy}^{\text{yield}}/(nF)$, where $|\sigma_{xy}^{\text{yield}}|$ is exceeded. In the liquid the critical yield stress at $\phi_c = 0.795$ is used.
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\[ (6.19) \]
\[ \sigma_{yy} \] is constant across the channel and only increases directly at the interface between flowing suspension and frozen wall particles. The \( x \)-component \( \sigma_{xx} \) on the other hand varies across the channel and hence indicates an anisotropic contribution to the pressure, where distinct differences for the behavior below and above the critical density for the glass transition occur. For \( \phi = 0.78 \) in the supercooled liquid the values measured for \( \sigma_{xx} \) in the fluidized region are larger than \( \sigma_{yy} \). This results in a positive normal stress difference \( N(y) = \sigma_{xx} - \sigma_{yy} \) and corresponds to a force towards the center felt by the colloids. As shown in the bottom panel of Fig. 6.10 this triggers particle migration towards the center that leads to non constant packing fractions across the channel in the stationary state. We observe a dilution at the walls and a local maximum at the center, a phenomenon that can also be seen under confocal microscopy [177]. Below the glass transition density \( N(y) \) reaches a local minimum at the center, which does not depend on force, but despite vanishing shear rate \( \dot{\gamma}(y = 0) = 0 \) is non-zero. The local pressure on the other hand, which in Fig. 6.10 has been shifted for clarity by the force-dependent value of the fluidized region, has its maximum at the concentrated center outbalancing the force directed inwards.

Deeper in the glass at \( \phi = 0.81 \) identical trends are found for the fluidized, highly sheared regions close to the walls. As before this yields positive normal stress differences and a particle accumulation in the center, rendering our system weakly compressible. For the solid-like plug the packing fraction is constant and hence exhibits a plateau, where the extension of this plateau is again prescribed by Eq. (6.20). The pressure profile across the channel in the plug differs considerably from the one measured for the supercooled liquid. Here the convected solid is found to respond elastically to the perturbation caused by the flowing boundaries. The deformations of this uniformly flowing solid caused by the body force and the flowing surroundings at the boundary result in an increase of \( \sigma_{xx} \) towards the center and a local maximum at \( y = 0 \). Again, values at the center increase with the applied body force, while at the same time the interface between fluid and solid regions is shifted towards smaller \( y \)-values, resulting in a sharper and more pronounced curve shape. Consequently, and contrary to the liquid case, the normal stress difference \( N(y) \) gets maximal while the local pressure \( p(y) \) is minimal at the channel center. This is remarkable, since this minimum in pressure coincides with a local maximum in density.
6.2. Stationary flow

Figure 6.10.: Diagonal stress tensor components $\sigma_{xx}$ (solid lines) and $\sigma_{yy}$ (dashed lines), normal stress difference $\sigma_{xx} - \sigma_{yy}$, pressure difference between fluid and solid region $\Delta p(y) = p(y) - p(w/2 - 10d_s)$ where $p = -1/2(\sigma_{xx} + \sigma_{yy})$ and local packing fraction $\phi(y)$ (from top to bottom) for varying forces as function of position $y$ across the channel in the liquid at $\phi = 0.78$ (left) and glass at $\phi = 0.81$ (right).
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6.2.2. Local structural decorrelation and microscopic dynamics

The presence of physical walls influences the dynamics of confined suspensions, the characteristic time- and length scales vary with the distance to the boundary. Such effects are rooted in the interplay of the immobility of the frozen wall particles with the cooperative nature of the mobile disks, which at high densities does not allow for particle motion independent of neighbors [161, 162, and references therein]. The influence of confinement on the structural relaxation dynamics and microscopic motion will be discussed in the following, first for non-sheared quiescent and after that for driven systems.

Confined quiescent system

As described in Sect. 6.1.1, walls are realized by freezing particles at the edges of a system that has been equilibrated previously. By doing so the static properties of the wall and in the bulk are identical. Thus, effects that stem from an interaction with a new type of surface structure that may trigger a change in the structure of the material in the vicinity of the wall are suppressed. Nevertheless, the immobility and by this the lack of density fluctuations of the frozen colloids hinders the in-cage and diffusion dynamics of the mobile particles nearby. An appropriate way to quantify this changes due to the confinement are the local wave-vector-dependent incoherent density correlation function and the local microscopic mean squared displacement (MSD). The former is defined as

$$\Phi_{q}^{S}(y,t) = \langle \rho_{q}^{s}(0)\rho_{q}^{s}(t) \rangle \delta(y_{i}(0) - y),$$

with local particle number density $n(y) = \sum_{i=1}^{N} \delta(y_{i} - y)$ and density $\rho_{q}^{s}(t) = e^{iqr_{s}(t)}$. The latter is given by

$$\langle \Delta r_{\alpha}^{2}(y,t) \rangle = \frac{1}{n(y)} \sum_{i=1}^{N} (r_{\alpha,i}(t) - r_{\alpha,i}(0))^2 \delta(y_{i}(0) - y),$$

where $\alpha = x,y$ specifies the Cartesian components. Introducing a $y$-dependence is a generalization of the conventional definitions. It allows for taking into account the spatial dependence for both quantities, while the translational invariance prohibits an $x$-dependence of this functions. A measurement of the dynamics parallel (perpendicular) to the wall is achieved by considering only displacements in $x$-direction ($y$-direction) for the MSD. In the same manner, the orientation of the wave vector $q$ is chosen in $x$-direction ($y$-direction) in the analysis of the density correlation function. The functions defined in Eq. (6.21) and (6.22) are calculated by dividing the channel into sub channels of width $\Delta y = d_{s}$. For the allocation initial $y$-positions at time $t = 0$ were used. As soon as the absolute displacements get large this
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Figure 6.11.: MSD $\Delta r^2 = \Delta x^2 + \Delta y^2$ across the channel as function of time $t$ and $y$-position in absence of external driving (top), $\Delta x^2$ (dashed lines) and $\Delta y^2$ (solid lines) at various distances to the wall $\delta y = w/2 - |y|$ (bottom) at the glass transition for a packing fraction $\phi = 0.795$ (right) and deeper in the glass for $\phi = 0.81$ (left). Solid gray lines indicate the bulk solution in absence of confinement and represent an upper bound that is approached by curves at the center of the channel. The inset of the lower right panel shows the same data over a smaller time window using a linear scale for the $y$-axis.

The definition has to be interpreted with caution. A particle that is assigned to a certain $y$-value might have spent most of the time interval $[0, t]$ at regions considerably far from its initial position. Especially for the pressure-driven systems, where the shear rate is known to vary strongly over short distances, the results using this spatial assignment can be misleading. Figure 6.11 shows the MSD of a quiescent system in a channel in absence of an external force compared to the bulk solution for a non-confined quiescent system.

In absence of physical walls the short time diffusive behavior causes a linear increase $\propto 2D_0 t$ for times between $\tau_b$ and $10^{-3}\tau_b$, see Eq. (2.43). This short time process lasts until potential forces, associated to the colloid-colloid interaction, dominate and the MSD arrives at an intermediate plateau. Here particles are trapped in a cage consisting of their neighbors.
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A Lindemann-type parameter of approximately 15%, defined as the ratio of the root of the plateau value and the nearest neighbor distance \( a = n^{-1/2} \) [134], identifies a length scale of in-cage motion. Note that due to long wave length density fluctuations this parameter is system size dependent in 2D, a more meaningful dynamic criterion will be defined in Chap. 7. For the system deep in the glass at \( \phi = 0.81 \) the particles are not able to escape this enclosure of nearby disks within the time window accessible by the simulations. Thus the structural relaxation is suppressed. For more liquid suspensions this cages can break after a certain time and long time diffusion accompanied by a structural relaxation sets in. Hence at \( \phi = 0.795 \) an intermediate plateau emerges with roughly the same Lindemann parameter. The onset of diffusive motion for times comparable to the structural relaxation time \( \tau_\alpha \) can be seen.

The presence of walls leads to significant deviations from the bulk curve, that serves as an upper bound for the local MSD. The short time diffusion up to \( D_0t = 10^{-3} \) remains unchanged. After a time that grows with the distance to the wall \( \delta y = w/2 - |y| \) the curves deviate from the bulk and saturate on a plateau. The height of this plateau is considerably smaller than the measure in the bulk and increases with \( \delta y \). The immobility and hence lack of density fluctuations of the nearby wall particles reduces the available cage space and decreases the Lindemann parameter by up to one decade. Note that the plateau measured directly at the boundary is roughly half as high as the cage-relative MSD quantifying local dynamics (see Sect. 7.5). Thus the presence of the wall not only inhibits Mermin-Wagner fluctuations but in addition results in a stronger localization of the particles nearby. This effect is more pronounced for the MSD perpendicular to the wall, the difference between \( \Delta x^2(t) \) and \( \Delta y^2(t) \) indicates the non-isotropic nature of the dynamics. For the densities and channel widths investigated, even at the center at maximal \( \delta y \), the impact of the walls is present. While the parallel component coincides with the bulk curve, the perpendicular component is still slightly smaller. Therefore the particles rearrange cooperatively over a length larger than \( w/2 \). The measured results are influenced by both the lower and upper wall at the same time and thus supposedly differ from the results one would obtain in presence of a single wall. Another effect of the confinement is the change in local time scales. While the \( \beta \)-relaxation on to the plateau takes less time than in the bulk the structural relaxation on the other hand is shifted to larger times or even completely suppressed, as seen for \( \delta y = 0 \) at \( \phi = 0.81 \). This is again in line with the findings of Chap. 7, the nearby wall is able to suppress Mermin-Wagner fluctuations and by that delay the relaxation.

As shown in Fig. 6.12 the same features are also observed from probing the local incoherent density correlation function Eq. (6.21). As already documented in Chap. 4 and 5 the bulk curve is described by a two step relaxation process: a short-time relaxation onto a long-time plateau in the glass or an intermediate plateau followed by a decay to zero during the \( \alpha \)-process for densities below the critical point. As already observed in the analysis of the MSD, the \( \beta \)-process is completed faster close to the wall and the time where deviations from
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Figure 6.12.: Incoherent density correlation function $\Phi^S_q(t)$ across the channel as function of time $t$ and $y$-position for a wave vector $\mathbf{q}$ in $y$-direction that corresponds to the first peak of the structure factor in absence of external driving (top), $\Phi^S_q(t)$ for $qd_s = 6.14\hat{x}$ (dashed lines) and $qd_s = 6.14\hat{y}$ (solid lines) at various distances to the wall $\delta y = w/2 - |y|$ (bottom) at the glass transition for a packing fraction $\phi = 0.795$ (right) and deeper in the glass for $\phi = 0.81$ (left). Solid gray lines indicate the bulk solution in absence of confinement and represent a lower bound that is approached by curves at the center of the channel.

the bulk curve occur decreases with the distance to the wall $\delta y$. The cage size characterized by a decreasing Lindemann parameter upon approaching the solid walls translates to an increasing plateau height in $\Phi^S(t)$ and higher ergodicity parameters $f = \lim_{t \to \infty} \Phi^S(t)$ in the glass. Additionally at the glass transition for $\phi = 0.795$ the $\alpha$-process is shifted to larger times for decreasing $\delta y$. For $\delta y \lesssim 5d_s$ the relaxation is suppressed completely as already seen in the long-time plateau of the MSD. The simultaneous change in plateau height and structural relaxation time renders an $\alpha$-scaling onto a single master curve impossible, as already found out in [161]. The anisotropy of the dynamics enters with the orientation of the wave vector $\mathbf{q}$, the motions parallel and perpendicular to the solid walls are probed by $\Phi^S_{q\hat{x}}(t)$ and $\Phi^S_{q\hat{y}}(t)$. As before the latter is suppressed stronger, which is evident through a stronger delay
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of the local α-decay and a higher non-ergodicity parameter \( f \). Again this holds even at the center at \( y = 0 \) or \( \delta y = w/2 \), where \( \Phi_{qy}^S(t) \) deviates from the curve in the bulk, which falls together with \( \Phi_{qx}^S(t) \). This is again a strong indicator that the local particle rearrangements are correlated over lengths that are comparable to at least half of the channel width \( w \). Again the non-ergodicity parameter of the conventional density correlator at the wall is higher than its cage-relative counterpart in the bulk, see Fig. 7.3. Thus the particle localization due to a nearby wall is significantly stronger than the localization in a local (and moving) cage of next neighbors.

**Flowing system, \( \nabla p > 0 \)**

Figure 6.13.: MSD \( \Delta y^2 \) across the channel as function of time \( t \) and \( y \)-position for \( F = 0.05 k_B T/d_s \) (top) in the glass at \( \phi = 0.81 \) (left) and at \( \phi = 0.795 \) close to the transition point (right); \( \Delta y^2 \) at various distances to the wall \( \delta y = w/2 - |y| \) (bottom) for forces \( Fd_s/k_B T = 0.05 \) (blue); 0.0625 (orange); 0.075 (yellow); 0.1 (purple). Gray lines indicate the curves in absence of external driving at \( F = 0 \) as shown in Fig. 6.11, the MSD remains unchanged for times where shear-induced relaxation is not dominant yet.
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So far we focused on the influence of the presence of the wall on the diffusion and structural relaxation. In the following the same analysis is extended to pressure-driven channel flow. Here not only the confinement but also the impact of the pressure gradient influences the dynamics. As seen before the combination of these two ingredients results in a complex and inhomogeneous flow. In Sect. 3 it was shown, that a homogeneous shear rate induces a structural relaxation time $\tau_{\alpha}$ that for weak shear is proportional to $\dot{\gamma}^{-1}$. Imposing a pressure gradient $\nabla p$ along the channel now gives rise to a local shear rate field $\dot{\gamma}(y)$, that enhances the structural relaxation and diffusion dynamics locally. Fig. 6.13 shows $\langle \Delta y^2(t,y) \rangle$ for systems in a stationary flowing state at different packing fractions for different external forces $F$ in the glass and close the transition point. The short time dynamics is identical as before in the non-driven case. It shows diffusive behavior until a transient plateau builds out, where the height of this plateau is not affected by the flow, but depends on the distance to the wall $\delta y$. This means the length scale for the displacement fluctuations inside the cage remains unchanged. Compared to the quiescent case, here shear flow enables particles to break and escape this construct of neighboring disks, that locks them up, at earlier times.

At a fixed position $\delta y > 0$ the curves leave the plateau at earlier times with increasing force and enter an intermediate phase of subdiffusive growth that transforms into a long time diffusive behavior. Colloids initially positioned in immediate proximity to the wall for $\delta y \approx 0$, where $\dot{\gamma}(y)$ varies strongly over distances comparable to a particle diameter $d_s$, are able to enter heavily sheared regions. This evokes intermediate superdiffusive growth that for long times also turns into diffusive behavior. For large displacements as found in this example the method and definition we apply here might be misleading, because the positional binning depends solely on the initial configuration, see Eq. (6.22). Particles are capable of traveling into regions where the shear flow differs considerably from the flow it experienced at $t = 0$.

Nevertheless, the measured displacements solely contribute to the local MSD at their initial $y$-position.

At a fixed force $F$ it is the local shear rate $\dot{\gamma}(y)$ that determines the length of the transient caging. At $\delta y = w/8$, a position sufficiently far both from the wall and the central solid plug, $\dot{\gamma}(y)$ is high. As a result the time interval of transient caging after the $\beta$-relaxation is short compared to e.g. the weakly sheared regions close to the channel center at $\delta y \approx w/2$. Additionally the long time diffusion constant $D_y$ grows with growing $\dot{\gamma}$, see also Fig. 6.15.

At $\delta y = w/2 - |y| = w/8$ in the highly fluidized domain, $\langle \Delta y^2(t) \rangle$ deviates from linear growth for large times. This is owed to the fact that the displacements in $y$-direction cannot grow arbitrarily large. The neighboring solid plug is barely penetrable and the dynamics is immediately slowed down significantly if a particle approaches the center. The solid wall in the opposite direction is of course completely impenetrable. In fact at some point for very large times the dynamics cannot be diffusive anymore and the MSD needs to saturate since the maximum distance a particle can travel is limited, $|\Delta y(t)| < w - \delta y(0) = w/2 + |y(0)|$. 

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Figure 6.14.: Top: Incoherent density correlation function $\Phi^S_q(t)$ across the channel as function of time $t$ and $y$-position for $F = 0.05 k_B T/d_s$ and a wave vector $qd_s = 6.14 \hat{y}$ that corresponds to the first peak of the structure factor in the glass at $\phi = 0.81$ (left) and at $\phi = 0.795$ close to the transition point (right). Bottom: $\Phi^S_q(t)$ for $qd_s = 6.14$ (solid lines) at various distances to the wall $\delta y = w/2 - |y|$. Dotted lines indicate the curves in absence of external driving. Deviations from this unperturbed behavior occur for times where shear-induced relaxation becomes dominant.

The picture provided by an analysis of the local incoherent density correlation function $\Phi^S_q(t, y)$, Fig. 6.14, is in line with the findings from the MSD. Again the height of the transient plateau after the $\beta$-relaxation is the same as for the unperturbed system at $F = 0$ and therefore given by the confinement. In the glass at $\phi = 0.81$ the curves for $F = 0.05 k_B T/d_s$ follow $\Phi^S_q(t, y, F = 0)$ for considerably longer times up to $10^2 \tau_0$ and a plateau is clearly visible. The time when the structural relaxation sets in and deviations from the unperturbed behavior occur is again connected to the local shear rate. In the highly sheared regions at $\delta y = w/8$ and $\delta y = w/4$ this decay sets in already at $t \approx \tau_0$. At $\delta y = 0$ at the wall or at $\delta y = w/2$ in the center of the channel the process sets in after considerably longer times. At $\phi = 0.795$, close to the critical packing fraction, and $F = 0.05 k_B T/d_s$ the structural relax-
Stationary flow happens significantly faster. In the heavily sheared region no clear distinction between the $\beta$- and $\alpha$-process is possible. The transient localization is suppressed and a decay to zero is completed at $t \approx \tau_0$. For densities below the glass transition a zero crossing of the shear rate is found at $\delta y = w/2$. Thus no solid plug is formed, even in the center the system is fluidized. While the structural relaxation time in this region is significantly faster than in the unperturbed system, the indicated plateau is slightly higher. Due to the particle migration in the flowing system discussed before the local packing fraction $\phi(y)$ in this region is enhanced. This hardens the suspension locally and therefore increases the value of the transient plateau.

The local relaxation time $\tau_\alpha(y, F)$ can be estimated by the time it takes the correlation function to decay to $1/e$ times its plateau value. Fig. 6.15 shows the relation between $\tau_\alpha(y, F)$ and the local shear rate $\dot{\gamma}(y, F)$ in the glass at $\phi = 0.81$. In the fluidized regions $\tau_\alpha$ and $\dot{\gamma}^{-1}$ increase simultaneously, the stronger the shear flow the faster the structural decorrelation. As seen for simple shear flow for $\dot{\gamma} < 10^{-2}$ the relation $\tau_\alpha \sim \dot{\gamma}^{-1}$ is a good approximation. In absence of confinement this leads to a scaling of the density correlation function with the inverse shear rate, here the presence of the walls varies the plateau height with the distance to the walls and renders an $\alpha$-scaling impossible. Shear rates inside the solid plug, whose dimensions are specified in Eq. (6.20), fluctuate around zero and are not shown. Furthermore, the local relation $\tau_\alpha(\dot{\gamma})$ depends on the applied force, for the lowest force $F = 0.0625k_B T/d_s$ the relaxation times are largest. Close to the walls the shear rates are high but the relaxation is slowed down by the proximity to frozen wall particles, leading to outliers at high $\dot{\gamma}$ for $\delta y < 6d_s$ (indicated by open circles).

The long time diffusion coefficient in direction perpendicular to the flow $D_y(y)$ is extracted from the MSD at positions where diffusive behavior occurred. This is the case for $\delta y \gtrsim 6d_s$. As discussed before, in direct proximity of the walls it is challenging to define and obtain local MSD because of the highly inhomogeneous flow in this region. The shear rate on the other hand can be determined reliably. The time interval needed to measure the velocity field and its gradient $\dot{\gamma}(y)$ is significantly shorter than the time intervals the displacements are accumulated over.

Again the combination of immobilization caused by the wall and mobilization due to the shear flow defines the diffusivity. The qualitative behavior is similar to the local shear rate in the fluidized regions. The point of maximal $D_y$ is shifted towards the channel center when compared to the point of maximum shear rate and minimal relaxation time. In the plug, where $\dot{\gamma}(y)$ vanishes, nevertheless diffusive behavior and a structural decorrelation are observed. This is in line with the observation that in the glass the local pressure is smaller in the plug. The static structure of the (advected) solid plug differs from that in a quiescent solid, the shear stress indicates a structural distortion. At the same time, the adjoining fluidized regions speed up the structural dynamics inside the plug.
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Figure 6.15.: Left: Absolute values of the inverse shear rate $1/|\dot{\gamma}_0|$ (top), structural relaxation time $\tau_\alpha$ (middle) and long time diffusion coefficient $D_y$ (bottom) across the channel for varying forces at $\phi = 0.81$. Dotted lines indicate the left border of the solid plug, see Eq. (6.20). $D_y$ is extracted from the MSD in direction perpendicular to the flow, points where $\delta y < 6d_s$ are neglected. Right: Local relaxation time $\tau_\alpha$ (top) and shear stress $\sigma_{xy}$ (bottom) as a function of the shear rate $\dot{\gamma}$ (crosses). The flow curve for simple shear flow (black dashed line) is shown for comparison. In both panels data points measured close to the walls for $\delta y < 6d_s$ are displayed by circles, data points on the solid plug where $\dot{\gamma}$ fluctuates around zero are not shown.
6.2.3. Comparison to LB-MCT and nonlinear Maxwell model

In 2015 Simon Papenkort and Thomas Voigtmann presented a hybrid-lattice Boltzmann-MCT (LB-MCT) algorithm for modeling the flow of shear-thinning glass-forming fluids [167, 168, 169]. This is accomplished by solving the Navier-Stokes equation by incorporating integral constitutive equations from first principles [178] for the local stresses. By this an extension to the schematic MCT model is realized that is able to describe inhomogeneous flows in complex geometries arising from a local approximation for the stresses and shear rates. This allowed for modeling pressure-driven channel flows of colloidal suspensions, as demonstrated before a scenario whose dynamics is strongly affected by inhomogeneous stresses and flow rates that dictate the driving towards a stationary velocity profile. In [167] the results for the stationary state are validated by the comparison to an extension of a nonlinear generalized Maxwell model (nlM) to arbitrary incompressible flow and its incorporation into the Navier-Stokes equations. In this context, the pressure-driven stationary Poiseuille flow of non-Newtonian fluids through channels in 2 dimensions is solved analytically capturing the non-linear mechanism of shear-thinning of glass-forming yield stress fluids. It is shown, that in the stationary state this rather simple model captures all characteristic features of the emerging flow profiles. This provides the opportunity for a comparison with the findings from Brownian dynamics simulations of this work. In the following the nlM is briefly sketched (for a full discussion see [167]) and it will be shown, that this analytical model describes the velocity profiles in a stationary state obtained from the Brownian simulations well. After that a comparison to the results from the more elaborate LB-MCT algorithm is carried out, again for the stationary state.

The nlM model is based on a generalized Green-Kubo relation for stresses $\Sigma$ derived in the microscopic ITT-MCT formalism [24]. Switching on a flow in an equilibrated system at $t = 0$ leads to

$$\Sigma(t) = \int_0^t [-\partial_t B(t, t')] G(t, t', [\kappa]) dt',$$

where the local deformation of the material between two points in time $t, t'$ is described by the Finger tensor $B(t, t')$ and $G(t, t', [\kappa])$ denotes the dynamical shear modulus, which is microscopically given by the stress autocorrelation function depending on the shear rate tensor $\kappa$, see Sect. 3.1. A White-Metzner-type relaxation [179] of the shear modulus

$$\partial_t G(t, t', [\kappa]) = -\frac{1}{\tau_M[\kappa]} G(t, t', [\kappa])$$

is employed, where the relaxation time $\tau_M$ is allowed to depend on the shear rate $\kappa$. Presuming now a stress-shear rate dependence that is required to be firstly local and secondly not time dependent, one arrives under appropriate assumption for the stress tensor in the
stationary state for laminar flow at constitutive equations

\[ \sigma^{ss} = \sum_{n \geq 1} G_\infty \tau_M^n \mathbf{d}^{(n)} \]  \hspace{1cm} (6.25)

\[ \mathbf{d}^{(n)} = \sum_{m=0}^{n} \binom{n}{m} \kappa^m \kappa^{Tn-m}, \]  \hspace{1cm} (6.26)

with \( G_\infty \) the low-frequency plateau modulus. This instantaneous constitutive equations relate the stress to the shear rate locally at the same time \( t \). A more sophisticated, non-instantaneous Maxwell model considering a dependence on the full flow history was developed as well but led to identical results in the stationary, flowing state as the instantaneous one discussed here \([168]\). The relaxation time \( \tau_M \) of the shear modulus is now modeled under the assumption of a dependence on the current local shear rate (analogous to the proceeding in homogeneous systems, e.g. \([85]\)) by

\[ \tau_M^{-1} = \tau^{-1} + \frac{\text{tr}(\mathbf{D}^2)^{1/2}}{2\gamma_c}. \]  \hspace{1cm} (6.27)

The dimensionless model parameter \( \gamma_c \) is set to the position of the stress overshoot for simple shear flow at \( \sim 10\% \), a strain amplitude corresponding to the shear-induced onset of yielding. The symmetrized shear rate tensor is denoted by \( \mathbf{D} \). For this relations to hold a shear-induced timescale which is large compared to the short time relaxation and small compared to the structural relaxation is required, \( \tau_0 \ll \dot{\gamma}^{-1} \ll \tau_o \) or \( \text{Pe}_0 \ll 1 \ll \text{Pe} \). For diverging relaxation times \( \tau_M \to \infty \), a behavior that is characteristic for the approach of the glass transition, this model entails a dynamical yield stress as already found in the simulations in Sect. 6.2.1.

To model a stationary state of pressure-driven channel flow of a non-Newtonian fluid the microscopic expression for the shear stress \( \sigma_{xy} \) Eq. (6.25) is combined with the shear stress derived from the macroscopic Navier-Stokes equation (6.18). This is legit for small Mach numbers, i.e. the motion of the colloids relative to the solvent is slow compared to the speed of sound in the solvent. Assuming laminar flow and incompressibility one arrives at a shear rate

\[ \partial_y v_y(y) \tau_0 = -\frac{w \partial_x p}{4G_\infty} + \frac{\gamma_c (1 + \theta)}{2\theta} - \sqrt{\left(\frac{w \partial_x p}{4G_\infty} - \frac{\gamma_c (1 + \theta)}{2\theta}\right)^2 + \frac{\gamma_c w \partial_y p}{2G_\infty \theta} y} \]  \hspace{1cm} (6.28)

with \( \partial_x p \) the \( x \)-component of the external pressure gradient and \( \theta = \eta/\eta_\infty \) the ratio of low-shear viscosity to Newtonian high-shear one at the critical density of the glass transition. The integration of this equation with respect to \( y \) demanding no-slip boundary conditions was calculated analytically and yields the desired velocity profile.

This provides a velocity profile that is determined solely by material constants accessible from equilibrium and simple shear flow simulations. Fig. 6.16 shows a comparison of simulated curves with the predictions from the nlM model. The pressure gradient entering Eq. (6.28) is
Figure 6.16.: Velocity profiles according to the nonlinear Maxwell model (blue curves) for a parameter set corresponding to the BD simulations of this work (gray curves). Results are shown for 4 different channel widths $w$ and forces $F = 0.05k_B T/d_s$ and $0.0625k_B T/d_s$.

given by the body force used in the simulations, $\partial_x p = nF$. The model parameter $\gamma_c = 0.07$ is known from simple shear flow simulations, just as the low- and high-shear viscosities stem from the according flow curves for the critical packing fraction $\phi = 0.795$ providing $\theta = 100$. Equilibrium simulations as described in Sect. 3.2.3 determine the critical plateau shear modulus $G_\infty = 54.4 nk_B T$. For the lowest forces investigated, $F = 0.05k_B T/d_s$ and $F = 0.0625k_B T/d_s$, the resulting shear rates fulfill the condition $Pe \ll 1$ everywhere across the channel. This corresponds to a shear-induced relaxation slow compared to the short-time diffusion and fast compared to the long-time structural dynamics. In this regime of low shear rates, which is required by the nlM model, the qualitative as well as the quantitative agreement with the BD simulation data is very good. The nlM model captures all features of the measured blunted profile. Only for the widest channel $w = 139d_s$ for $F = 0.0625k_B T/d_s$ the measured shear rates grow up to $Pe = 1$, as shown previously in Fig. 6.9, resulting in larger deviations. Analogously for a fixed channel width $w = 77.2d_s$ the agreement is good for forces up to $F = 0.075k_B T/d_s$ where bare Péclet numbers smaller than 1 are measured, see Fig. 6.17.

In the same works [167, 168, 169] a hybrid lattice Boltzmann method modeling non-Newtonian fluids was presented. The standard scheme of solving Navier-Stokes equations on a grid is extended by incorporating integral constitutive equations for the local stresses of the form given in Eq. (6.23). This allows for determining local stresses by solving schematic MCT equations, where the flow history enters from the shear rate tensor obtained from the LB simulation. The determined stresses are then passed back since they are required for the next collision step of the LB algorithm. With this method the analysis can be extended to non stationary flows as the transient startup and relaxation from stationary flow. The computations within this model are of course more elaborate and time consuming but provide
results that come closer to the findings of the BD simulations. Similar to the analysis in Sect. 6.2.1 the nM model finds regions of negligible shear rates \( \dot{\gamma} \sim \tau_0^{-1} \) at the channel center for stresses below the critical yield stress, which is indicated by dashed lines in Fig. 6.18. Only in this central region, that in the shown example makes up about 20% of the channel width, diagonal stresses are found to vary. As a result the normal stress difference \( N(y) \) builds out a parabolic minimum, while the pressure shows a parabolic maximum. The hybrid LB-MCT algorithm on the other hand finds variations over wider areas, even at regions that undergo heavy shear local variations of the diagonal components of the shear tensor are observed. This variations in the highly fluidized sections and a resulting weak increase in density at the central plug come closer to the findings of the BD simulations and are not seen by the nM. Also the qualitative agreement of the velocity and shear rate profile is improved by this more elaborate model. In comparison to the nM model the LB-MCT model predicts higher flow rates close to the wall, while the gradient close to the center is less steep. The shoulder in \( \dot{\gamma}(y) \) at \( y \approx 0.4 \) seen by the nM model is not present in the LB-MCT model and simulations.

The agreement with the simulations of this work validates the methods employed. In particular the constitutive equations incorporating the local stress-shear relations worked out within the nonlinear Maxwell model as well as in hybrid LB-MCT calculations are confirmed.
6.2. Stationary flow

Figure 6.18.: Comparison between hybrid-LB-MCT calculations (left, crosses), analytical results from the instantaneous nonlinear Maxwell model (solid lines, left) and Brownian dynamics simulations for 4 different channel widths $w$ at $F = 0.05k_B T/d_s$ and $\phi = 0.78$ in the supercooled fluid (right). The panels (from top to bottom) show the velocity $v_x$ in direction of $F$, Péclet number $\dot{\gamma} \tau_0$, shear stress $\sigma_{xy}$, normal stress difference $\sigma_{xx} - \sigma_{yy}$ and the pressure difference between fluid and solid region $\Delta p(y) = p(y) - \text{const}$, where $p = -1/2(\sigma_{xx} + \sigma_{yy})$. The horizontal dashed lines indicate the yield stress $\pm \sigma_{2y}^{\text{yield}}$ at the glass transition. Vertical dashed-dotted lines denote the points $y = \pm \sigma_{2y}^{\text{yield}}/(\alpha F)$, where $|\sigma_{xy}^{\text{yield}}|$ is exceeded.
6. Channel flow

6.3. Conclusions and outlook

We developed a novel method to simulate pressure-driven flow of a dense glass-forming suspension made up of Brownian hard disks through a rough channel in 2D. The algorithm represents a classical MD simulation with stochastic thermostat, that dissipates the heat by constant reassignment of peculiar velocities and incorporates random forces due to the solvent. Furthermore, a body force directed along the channel evokes a blunted velocity profile. This results in a linear shear stress profile as expected from the Navier-Stokes equation. At high packing fractions we observed the development of a central plug where the glassy material moves uniformly, while the shear is localized in narrow regions close to the walls. In this context we confirmed a criterion for plug formation based on the dynamic yield stress present in a glass, which is in line with existing simulations on glass former [23]. We generalized our analysis to sample micro- and macroscopic quantities locally. In this way it could be shown, that stationary inhomogeneous flow is accompanied by local variations of the shear-rate, pressure and density and strongly affects the structural dynamics. Normal stress and pressure profiles in yielding glassy states were found to differ strongly from the ones measured for viscous fluids. Surprisingly, in the glass a local minimum in pressure occurs in the solid central plug, although this region exhibits an increased local density. A detailed understanding of the underlying mechanisms leading to this observation remains to be developed. We further compared our results to hybrid-Lattice Boltzmann-Mode Coupling Theory calculations, which rationalize driven fluid states. By this we were able to confirm the constitutive equations incorporating local stress-shear relations used in the works of Papenkort and Voigtmann [167, 169, 168]. For the future an analysis of the transient regimes of startup of channel flow and relaxation after cessation of stationary channel flow, as in [168, 166], is practicable but lays beyond the scope of the present work. Further, existing theories were able to characterize how plastic activity spreads spatially during non-local elastic relaxations in soft glassy flows, giving rise to a characteristic “flow cooperativity” [21, 180]. In a more recent work this method was extended and intriguing local fluctuations of the shear rate were reported for simulated and experimental systems [181]. An analogous analysis with the data generated here could elucidate the mechanism in pressure-driven flow of Brownian hard disks.
7. Long wavelength density fluctuations

Recently the topic of phase transitions in two-dimensional systems got special attention and recognition because of the Nobel Prize in Physics 2016 awarded to David J. Thouless, F. Duncan M. Haldane and J. Michael Kosterlitz. Their theory of ordering and phase transitions in 2D [182, 183], together with works by B. Nelson [184] and A. Young[185], constitute a description of the melting process in 2D crystals within the KTHNY theory. By this, a phase transition fundamentally different from the one observed in 3D systems was established. The difference between those scenarios is closely related to a lack of broken symmetry associated with a transition in two dimensions, a direct consequence of Mermin-Wagner fluctuations. These thermal fluctuations in the form of long wavelength density modes, as acoustic phonons, rule out long-range positional order in dimensions \( d \leq 2 \) [186, 187]. Not only for crystals a reduction of dimensionality entails new physics, in 2015 Elijah Flenner and Grzegorz Szamel presented results from computer simulations reporting fundamental differences between the dynamics in 2D and 3D systems close to the glass transition and called for a re-examination of the present conception of the glass transition in 2D [188]. In this chapter we analyze data from our Brownian simulation in 2D and from experiments on 2D colloidal crystals and glass formers in 2D and 3D, where the experiments have been carried out by Bernd Illing, Herbert Kaiser, Christian L. Klix and Peter Keim at the University of Konstanz. Using concepts of crystallography we argue that Mermin-Wagner fluctuations are present in 2D amorphous solids as well and by that provide an additional relaxation channel on top of the structural relaxation already discussed in the previous chapters. This affects the structural and dynamical properties close to the glass transition substantially and accounts for observed finite size effects. Further, with the emerging fluctuations it is possible to explain most of the qualitative differences to glass formation in 3D observed in the simulations by Flenner and Szamel.

7.1. Dimensionality and phase transition

Let us first examine the scenario of melting of crystals, representing a structural phase transitions. Here the microscopic mechanisms that cause a breaking of symmetry in 3D differ from the ones observed in 2D. Most melting processes in 3D involve latent heat and can be classified as first-order transitions with two phases being in equilibrium at a certain critical value of a control variable, typically temperature or density. However, for the melting of crystals
7. Long wavelength density fluctuations

in 2D it takes two steps, the process involves an additional intermediate hexatic phase. This means that unlike in 3D, in 2D the breaking of translational and orientational symmetry do not appear simultaneously but at different (critical) values of the control variable. This process was predicted by the KTHNY-theory [182, 183, 184, 189, 185] and confirmed for a variety of systems, among them colloidal mono-layers as analyzed here [190, 191].

The question whether crystals characterized by long-range positional or magnetic order can exist in dimensions \(d \leq 2\) was raised long before Mermin-Wagner fluctuations were reported in the 1960s, the topic was debated heavily already more than 30 years earlier [192, 193, 194, 195]. At that time Sir Rudolf E. Peierls remarked that relative distance fluctuations \(\xi\) between neighboring particles in this low-dimensional systems should add up differently than in 3D [193]. In a 1D chain at finite temperature the fluctuations are statistically independent, for a chain counting \(N\) particles this results in fluctuations of the relative distance between the first and last particle scaling with \(\sqrt{N}\xi\). In 3D however, where a pair of particles is connected by more than a single path, the amplitude of fluctuations over large distances is bounded and of the order of \(\xi\). Obviously a divergence of fluctuations with growing system size \(N\) rules out long-range transitional order. This is as well the case for a 2D crystal, where at finite temperatures relative fluctuations grow logarithmically with the distance between the particles. Therefore translational correlation functions are required to decay algebraically while the fluctuations have no impact on the orientational order [186, 187, 193, 196, 197]. Further it is shown analytically that in 2D displacements from perfect lattice sites grow logarithmically with system size \(L\) [187, 196] Thus the effects are not only limited to structural quantities, they are also evident in the analysis of dynamic quantities like mean squared displacements or density correlation functions. This causes the MSD to diverge and a standard Lindemann criterion as in 3D can not be defined [134]. By an introduction of local coordinates [198, 199] this problem can be circumvented and the equivalent of a Lindemann criterion can be defined for 2D crystals. An analysis of displacements relative to the next neighbors leads to a reduced or local MSD, which stays finite in a 2D crystal but diverges in fluids [200].

A glass as an amorphous solid on the other hand lacks periodicity by definition, a phase transition into a glassy state is indicated by a drastic slow down of the dynamics accompanied by a divergence of the viscosity and the emergence of elastic rigidity. It is a considerably sharp kinetic crossover into a non-equilibrium state that does not reveal a structural relaxation (at least on accessible time ranges). Unlike for crystals the transition in 2D and 3D is often described within the same theoretical framework, assuming that the characteristics of the involved mechanisms are identical [201, 202, 203, 5], or as Peter Harrowell put it “in Flatland, glasses reproduce all the behaviour of their three-dimensional relatives” [204]. Recently large scale computer simulations revealed the opposite [188], namely a dependency on dimensionality because of the observation that translational motion proceeds differently in 2D and 3D systems. While in 3D a long time plateau evolves in the MSD, describing the trapping of
7.2. Colloidal systems

particles in a cage formed by nearest neighbors, this entire cage is apparently more mobile in 2D and capable of traveling distances higher as the mean particle distance. Therefore a transient localization is only weakly indicated while at the same time the structure of the local environment on a length scale of mean particle distances, as seen by the bond-orientational correlation function, is not affected. In other words, unlike as in 3D, the characteristic times of translational and orientational relaxation of the system seem to decouple. While the ratio of the two relaxation times is temperature independent in 3D, the translational correlation functions change on a faster time scale. The authors see this as a fundamental difference and demanded a re-examination of the present conception of the glass transition in 2D.

In order to resolve this disagreement one can revisit the discussion of long wavelength density fluctuations. The arguments given in [193] do not rest upon periodicity. Other 2D systems like quasi-crystals or amorphous structures are expected to be subject to this fluctuations as well, given that the variance of the nearest neighbor distance is low, a requirement that is usually met in glasses. It is therefore reasonable to assume that the impact on the dynamics is independent of periodicity [205] and that also amorphous solids are subject to Mermin-Wagner-like density fluctuations. As for crystalline systems this should affect the translational motion of the particles and by that cause translational correlation functions to decay algebraically and the MSD to diverge such that the standard Lindemann parameter fails. Turning to local coordinates in glassy systems introduces “a cage-relative” picture. The concept of an analysis of displacements relative to the ones of the surrounding particles (forming a cage) has been applied successfully to highlight dynamical heterogeneities in a 2D glass former [153, 206]. Recently Skanda Vivek et al. determined cage-relative intermediate scattering functions that are in line with the existence of the described fluctuations in amorphous systems [87, 207]. Further similar results from computer simulations are reported by Hayato Shiba et al. [88].

7.2. Colloidal systems

In the following some details of the experimental realization of the systems are presented, more detailed discussions can be found in the cited works, details on the 2D glass former were already given in Sect. 4.3. The 2D systems are well studied, with identical setups crystallization, defects [82, 191, 208, 209], and the glass transition [206, 65, 99] were examined. A colloidal mono-layer is realized in a hanging droplet geometry, where individual particles are sedimented to a flat water/air-interface. The diameter of the colloidal particles is in the range of microns, the particles undergo Brownian motion in two dimensions. The ratio of potential energy of the particles to the kinetic energy \( \Gamma = \frac{E_{\text{pot}}}{E_{\text{kin}}} \) serves as control parameter for the system, where the kinetic energy \( E_{\text{kin}} \sim T \) is due to thermal motion. It acts like an inverse temperature, thus an increasing \( \Gamma \) refers to a decreasing temperature and vice versa. Video microscopy and digital image analysis enables to follow the trajectories of
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few thousand particles, where the entire monolayer consists of a few hundred thousand of particles.

The 3D systems are made up of more than $10^9$ colloidal particles, in order to prevent sedimentation due to gravity they are dissolved in an organic solvent with identical mass-density. The particles are weakly charged and interact with a Coulomb-potential which is additionally screened by a small amount of counter-ions in the solvent. Particle tracking is realized employing confocal microscopy, providing three dimensional trajectories of several thousand particles.

For the simulations we employ the same mixtures as before consisting of $N = 16000$ particles. For the analysis of finite-size effects we further investigate smaller systems and vary the system size between $N = 1000$ and $N = 16000$. For each packing fraction and system size the data was averaged over at least 250 independent realizations.

7.3. Mean-squared displacements

In a first step the global and local fluctuations in 2D are compared. For the “global” part we revisit the conventional MSD, as investigated in the previous chapters, defined as

$$\langle \Delta r^2(t_1) \rangle = \left\langle \frac{1}{N} \sum_{j=1}^{N} \left( \mathbf{r}_j(t_1 + t_2) - \mathbf{r}_j(t_2) \right)^2 \right\rangle,$$

(7.1)

where the brackets denote an average over times $t_2$ for experimental and different runs for simulational data (here $t_2$ is set to 0). For the “local” part cage-relative mean squared displacements (CR-MSD)

$$\langle \Delta r^2(t_1, t_2) \rangle^{\text{CR}} = \left\langle \frac{1}{N} \sum_{j=1}^{N} \left( \mathbf{r}_j(t_1 + t_2) - \mathbf{r}_j(t_2) \right) - \frac{1}{N_j} \sum_{i=1}^{N_j} \left( \mathbf{r}_i(t_1 + t_2) - \mathbf{r}_i(t_2) \right) \right\rangle^2,$$

(7.2)

are determined. For this purpose, for each particle $j$ only the center of mass motion of the cage formed by the $N_j$ nearest neighbours is taken into account. The nearest neighbors in experimental systems have been identified by Voronoi-Tesselation, while in the simulations $N_j$ was set to 6 for all particles. In Fig. 7.1 the standard MSD (red curves) and the CR-MSD (blue curve) are shown as function of time for all investigated systems, namely glass formers in 2D (experiment and simulation) and 3D, and a crystalline experimental system in 2D. The top left panel shows results for a fluid system (triangles) and two crystalline samples (squares and circles) in 2D. As for the MSD describing glass curves discussed in the previous chapters a short time diffusive behavior is followed by a transient plateau and an increase for large times. However, for solid states this is not due to a structural relaxation, here Mermin-Wagner fluctuations of the density cause the mean squared displacement to diverge and by that the classical Lindemann criterion to fail. As expected, repeating the analysis
7.3. Mean-squared displacements

(a) Experiment: 2D crystal (top) and glass (bottom)

(b) Exp.: 3D glass (top); Sim.: 2D glass (bottom)

Figure 7.1.: (a): mean squared displacement (MSD, red) and cage-relative mean square displacements (CR-MSD, blue) of a defect free 2D crystal (top). Increasing the control parameter \( \Gamma \) triggers solidification (melting is at \( \Gamma^c = 60 \)). The divergence of the MSD is reminiscent of a curve describing a fluid but in the solid states caused by Mermin-Wagner fluctuations, because here the CR-MSD using local coordinates is bounded. In contrast, in a 2D glass (bottom) the onset of an \( \alpha \)-relaxation leads to an increase of the CR-MSD for large times, while the amplitude of the global fluctuation given by the MSD is significantly larger. The critical curve at glass transition at \( \Gamma_G \approx 200 \) is plotted transparent, fluid systems in 2D are labeled by triangles. (b): The findings are confirmed by simulations, the qualitative behavior is identical for the binary mixture of Brownian disks in 2D (bottom), where here a glass transition occurs at \( \phi^c = 0.7975 \). For the 3D experimental system (top) the difference in amplitude is significantly smaller, the time scales connected to the relaxation process are identical in both reference frames. For all amorphous systems states deep in the glass are labeled by diamonds, here an onset of the \( \alpha \)-process appears towards the end of the accessible time window.

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in a cage-relative reference frame, Eq. 7.2, alters the outcome considerably: fluid data still diverge (blue triangles) while the CR-MSD from solid samples are confined (blue squares and triangles). The dashed line shows the critical value given by the dynamic Lindemann criterion determined at $\Gamma^c$ [200, 210]. During the preparation of the sample grain boundaries emerge for finite cooling rates [211]. Since this might cause some plasticity all particles which have a non-crystalline environment for the time of investigation (more or less than six nearest neighbors) are excluded from the analysis.

The lower panels in Fig. 7.1 show the same analysis for glass forming systems, also in 2D. MSD (red) of fluid samples are labeled with triangles, squares label samples very close to the transition point and circles and diamonds represent amorphous solids, see [65, 99] for the experiments, Chapter 3 for the simulation or Chapter 4 for both. Here the CR-MSD (blue) reveals interesting differences to the conventional MSD. Again the amplitude of local displacements is reduced, but unlike in crystals even for the states deep in the glassy regime (blue diamond) the caging plateau is not stable, the MSD increase for large times. This method enables to suppress long wavelength phonons and isolate the structural $\alpha$-process, which is visible as (presumably) only remaining relaxation channel. The $\alpha$-process is linked to particles escaping their cage, an event detectable in glass but not in a crystal. Further it is remarkable, that in the 2D glass the upturn in CR-MSD is shifted to later times compared to the conventional MSD. This indicates that the impact of long wavelength density fluctuations is noticeable at times smaller than the structural relaxation time $\tau_\alpha$. This time shift is more pronounced in the experimental system, which may be linked to the nature of the interparticle interactions in the two systems. As pointed out in [196], a condition for the emergence of such fluctuations is a pair-potential that is analytical at the origin. Therefore the effect on hard body systems might be less pronounced, an observation in line with findings from an experiment using a hard sphere glass [87]. The upper right panel shows a 3D glass, a system where Mermin-Wagner fluctuations are not expected to occur. Hence the differences between the two quantities are less profound than in 2D, especially deep in the glass (diamonds), where no $\alpha$-relaxation is visible, they are negligible. Further no separation of time scales as before is visible. Thus an upturn of the MSD is solely caused by the structural relaxation. Insets in the single panels show typical snapshots of the 2D systems, the 3D system was visualized using measured structural data of the amorphous solid. A snapshot of the Brownian hard disks is shown in Fig. 2.6.

7.4. Density and orientational correlation functions

Again the function of choice to get insight into the structural decorrelation during the $\alpha$-process is the incoherent density correlation function or intermediate scattering function (as
7.4. Density and orientational correlation functions

Figure 7.2.: Incoherent density correlation function $\Phi_q(t)$ (red), cage-relative Incoherent density correlation function $\Phi_q^{CR}(t)$ (blue), both at a wavevector $q = 2\pi/a$, and bond order correlation function $G_6^b(t)$ (green) for various temperatures of a 2D crystal (upper left), a 2D glass (lower left), 3D glass (upper right) and a 2D glass from simulations (lower right). In the 2D crystal $\Phi_q^{CR}(t)$ and $G_6^b(t)$ reach a stable long-time plateau while $\Phi_q(t)$ decays due to Mermin-Wagner fluctuations. In the experimental and simulated 2D glass, a structural relaxation within the $\alpha$-process leads to a simultaneous decay of $\Phi_q^{CR}(t)$ and $G_6^b(t)$. In contrary $\Phi_q(t)$, being sensitive to Mermin-Wagner fluctuations as well as the $\alpha$-process, decays earlier. In the 3D glass, only an $\alpha$-process occurs and no separation in timescales is visible. The stiffest glasses (diamonds) do not decay within the accessible time window.
with the single-particle density fluctuation $\rho^S$, see also Eq. 5.2 (where here for readability we skip the label $S$ in the upper index). This corresponds to the Fourier transform of the displacements $u_j(t, t_2) = r_j(t + t_2) - r_j(t_2)$ at a wave vector $q = 2\pi/a$, where $a$ denotes the mean particle distance. This value corresponds to the first peak of structure factor $S(q)$. The brackets denote an average over orientations of the wave vector $q$ and as before times $t_2$ for experimental and different runs for simulative data (here $t_2$ is set to 0).

In analogy to the CR-MSD the cage relative incoherent density correlation function is based on displacements reduced by the center of mass motion of the nearest neighbors

$$
\Phi^\text{CR}_q(t) = \langle 1/N \sum_{j=1}^N e^{-i q \cdot (u_j(t, t_2) - u_j^{\text{cage}}(t, t_2))} \rangle, \tag{7.5}
$$

where again we sum over next neighbors of a particle indexed by $j$ to define

$$
u_j^{\text{cage}}(t, t_2) = 1/N_j \sum_{i=1}^{N_j} (r_i(t + t_2) - r_i(t_2)). \tag{7.6}
$$

The decay of orientational order is measured by the bond order correlation function $G^*_6(t)$ which correlates a local director field in time, in the crystal we investigate

$$G^*_6(t) = \langle \psi_6^*(t + t_2) \psi_6(t_2) \rangle \tag{7.7},$$

$$\psi_n = 1/N_i \sum_{i=1}^N e^{i n \theta_{ij}(t)}, \tag{7.8}
$$

the director field $\psi_6$ is given by the bond direction to the nearest neighbors in six-folded space, where $\theta_{ij}(t)$ denotes a time dependent angle of the direction of the bond connecting particles $i$ and $j$. For a 2D glass not all particles are six-folded, see Fig. 2.9, so all relevant director fields are summed up to

$$G^*_6(t) = \sum_{n=4}^8 \langle \psi_n^*(t + t_2) \psi_n(t_2) \rangle, \tag{7.9}
$$

where $G^*_6(t = 0) \lesssim 1$. In 3D an analogous director field is defined as a sum of spherical harmonics taking into account the additional azimuthal angle which is then correlated in time to obtain $G^*_6(t)$ [34].

In Fig. 7.2 this 3 correlation functions are shown for all 4 systems investigated. The
discussion of the density correlation functions and its dependence on the employed reference frame is analogous to what was found for the MSD. An increase in the MSD onto a plateau translates to a \( \beta \)-decay onto a plateau in density correlation functions, from there an upturn in MSD translates to a decay in density correlations and is linked to a relaxation. Thus the 2D crystal (upper left), experiencing Mermin-Wagner fluctuations but no structural \( \alpha \)-decay for the shown solid states, displays a decay in \( \Phi_q(t) \) (red). Again an analysis in local coordinates suppresses the long wavelength fluctuations such that \( \Phi_{q\text{CR}}(t) \) (blue) saturates on a stable long-time plateau higher than the one observed in \( \Phi_q(t) \). In the 2D crystal the modulus of rotational stiffness, called Frank’s constant, is infinite [189, 190], thus the orientational order measured by \( G^*_6(t) \) does not decay although translational order decays and the MSD diverges in this case. The lower panels show the same analysis for a 2D glass for experimental (left) and simulated data (right) for temperatures around the glass transition. For the two higher temperatures (lower \( \Gamma \)) the findings of Flenner and Szamel [188] are confirmed: at first sight translational and orientational motion seem to decouple. Density correlations decay at earlier times than orientational correlations. But this discrepancy can be resolved by turning to a cage-relative picture. Again \( \Phi_{q\text{CR}}(t) \) is higher than \( \Phi_q(t) \) but more interesting is the fact that \( \Phi_{q\text{CR}}(t) \) and \( G^*_6(t) \) decay simultaneously. Unlike \( \Phi_q(t) \) both quantities are not affected by long wavelength density fluctuations, so for both functions the characteristic time scale is solely set by the structural \( \alpha \)-relaxation. This is a clear indication that 2D glasses are subject to Mermin-Wagner fluctuations and cause the discussed time separation. Again this feature is less pronounced in the simulations employing hard-body pair potential. For the strongest glass labeled by diamonds the dynamic arrest is permanent since the structural relaxation is shifted to a time window not accessible by experiment and simulation, all correlation functions saturate on a stable plateau.

The upper right panel shows the 3D glass, where the relaxation is solely driven by structural rearrangements connected to an \( \alpha \)-process. Thus all correlation functions exhibit the expected two step decay, where the differences between \( \Phi_q(t) \) and \( \Phi_{q\text{CR}}(t) \) are small. The absence of Mermin-Wagner fluctuations ensures, that the time scales of the relaxation of translational and orientational motion are identical.

### 7.5. Finite size effects

So far we gave clear indications for the existence of Mermin-Wagner fluctuations in 2D glasses representing an additional relaxation channel on top of the \( \alpha \)-decay in amorphous solids. The latter depends strongly on the packing fraction or temperature but, being linked to a particle’s escape from its cage, is a local process and by that expected to not depend on system size. The amplitude of long wavelength density fluctuations on the other hand is expected to vary logarithmically with the box length of the investigated system [186, 187, 196]. No predictions exist whether system size also affects the time scale of the fluctuations. The size
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of the system is a parameter accessible only in the simulations where the particle number \( N \) and length of the quadratic box \( L \) can be controlled reliably. In contrary, the experiments are capable of monitoring only a small fraction of the total particles. The left panel of Fig. 7.3 shows the MSD and CR-MSD for a system deep in the glass at \( \phi = 0.81 \), where we vary the system size between \( N = 1000 \) and 16000. The conventional MSD reveals pronounced dependencies on \( N \), we observe two features: with growing particle number \( N \) the caging plateau increases while the time scale associated to the begin of a relaxation shifts to later times. Both observations can be traced back to Mermin-Wagner fluctuations, since the CR-MSD, sensitive to the \( \alpha \)-relaxation only, exhibits neither of the two. In local coordinates all curves collapse, the amplitude of thermal vibrations linked to the plateau height and structural relaxation time of the \( \alpha \)-decay \( \tau_\alpha \) show no strong dependencies on \( L \). The \((N\text{-dependent})\) height of the plateau is extracted by taking the amplitudes of the conventional MSD at the inflection point \( \langle \Delta r^2(\tau_i) \rangle \) indicated by open circles in Fig. 7.3. These points are determined by fitting a cubic polynomial to the data in the region of interest, where \( \tau_i \) is found to grow with system size. As shown in the inset the square root of the amplitude at the inflection point \( \sqrt{\langle \Delta r^2 (\tau_i) \rangle} \), representing a length scale connected to the transient plateau, grows linearly with the logarithm of the system size \( \log(L) \) (note the log-lin scale), where \( L \propto \sqrt{N} \), see Eq. 2.55. Again the findings observed in the analysis of MSD translate straightforwardly to the discussion of density correlations, which are shown in the right panel of Fig. 7.3. Both features seen before have as well an impact on the density correlation functions. During the \( \beta \)-process all curves \( \Phi_q(t) \) decay onto a plateau, where the height decreases with increasing system size. Further the plateau builds out at later times for growing \( N \), indicating the time shift also present in the MSD. In an analysis using local coordinates all curves \( \Phi^{\text{CR}}_q(t) \) collapse and saturate on a plateau higher than all plateaus of the conventional correlators, where the associated time-scale does not vary with system size. The observed logarithmic growth of the amplitude is again a clear indication for the existence of Mermin-Wagner fluctuations in 2D amorphous solids. This finding was recently (and independently) confirmed by simulations on soft sphere glasses in 2D [88], while to our knowledge this logarithmic growth has not yet been measured directly in 2D crystals.
7.6. Conclusions

In this chapter we presented a method to analyze the relaxation process of 2D colloidal glass former locally and gave arguments that Mermin-Wagner type density fluctuations, familiar from 2D crystals, are present in such systems. Colloidal glasses in 3D on the other hand are not affected by this collective motion. By this we contributed to the “reexamination of the glass transition in 2D” demanded in [188]. There fundamental differences between glassy dynamics in two and three dimensions and strong finite size effects in 2D were found using large scale simulations. We argued that the coexistence of Mermin-Wagner fluctuations and the α-process drive the relaxation in 2D. The impact on the localization in a 2D glass, as seen by density correlation functions and MSD, can be attributed to this long wavelength density fluctuations, since the observed features disappear in an analysis in a local reference frame: by this the separation of time scales of translational and orientational motion is resolved and a modified Lindemann-criterion can be established (using local frames), which is independent from the amplitude of the fluctuations, which is found to grow logarithmically with system size (in a global frame). Mermin-Wagner fluctuations exist on large scales but do not affect the local cage-escape mechanisms associated with the α-process. Therefore the underlying microscopic mechanism of the 2D glass transition is not necessarily different from its 3D counterpart, we motivated an additional process appearing only in 2D that is responsible for the discrepancies observed in the transient localization determined using global variables.

Figure 7.3.: Left: MSD and CR-MSD for the simulation data for various system sizes at \( \phi = 0.81 \) for \( N = 1000 \) up to 16000 particles, increasing opacity of the curves corresponds to increasing size. While the CR-MSD (blue) do not exhibit finite size effects, the conventional MSD (red) is strongly affected, gray circles mark the inflection points \( \tau \). The inset shows the amplitude of the fluctuations \( \sqrt{\langle \Delta r^2(\tau) \rangle} \) as function of the box length \( L \propto N \) in log-lin scale. A straight purple line stems from a linear fit of the from \( \sqrt{\langle \Delta r^2(\tau) \rangle} = \text{const.} \cdot \log(L) \), a clear hallmark of Mermin-Wagner fluctuations. Right: \( \Phi_q(t) \) (red) and \( \Phi^{CR}_q(t) \) (blue) at \( q = 2\pi/a \) for the same system.
In this thesis, the dynamics of a Brownian colloidal glass former in 2D was presented. We introduced various setups to study different regimes of such materials close to their glass transition point by means of computer simulations. We focused on two major topics. On the one hand, we investigated the emergence of mechanical rigidity during the dynamical slowing-down upon approach of the glass transition. Secondly, we presented several measurement protocols that employ external fields to drive the system far from equilibrium. The emerging nonlinear response phenomena triggered by disturbance provided insight into the underlying mechanism of complex transport and system properties.

We presented results on the sampling of the time dependent shear modulus in our system employing three different methods. We showed that the plateau shear modulus is not only accessible from the plateau value of the stress correlation function, but also from the suspension’s dispersion relations and the linear stress-strain relations during startup of simple shear flow. In line with predictions from MCT, we found a constant critical shear modulus approaching the glass transition from the fluid side. Upon further densification the glass moduli grow indicating further solidification. By that we were able to unambiguously determine the critical packing fraction associated to the glass transition point in our system. Further, we reported deviations from the expected behavior during the sampling of stress correlation functions deep in the glass.

We obtained Eshelby-type strain-correlation patterns in simulated and experimental 2D colloidal suspensions in amorphous glass states as well as in supercooled liquid states. In this way we verified existing simulational results, gave experimental proof of the existence of the patterns and were able to rationalize their presence in supercooled liquids by hydrodynamic theory. We showed under which circumstances highly viscous fluids exhibit a far field of strain correlations that is reminiscent of that in a solid. Particularly we were able to corroborate and explain the hotly debated presence of “elastic signatures” at times where elastic stresses have already decayed.

We investigated the relaxation process of a shear-melted glass after the cessation of steady shear flow. The evolution from the stationary state to the non-equilibrium quiescent solid was found to depend on long-lived memory effects. For identical control parameters but different preparation histories, differences in the structure and consequently in the emerging dynamics have been found. In line with existing works, we measured permanent residual stresses for weakly pre-sheared samples in the glass. Furthermore, we were able to identify a pre-shear
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rate independent localization length, significantly higher than the Lindemann parameter for the undisturbed quiescent systems. Our results qualitatively confirm the picture provided by ITT-MCT. Analyzing single-run dynamics, we found a wide variety of relaxation scenarios including spatially inhomogeneous displacement and strain fields and rapid collective structural rearrangements.

We developed a novel method to simulate pressure-driven flow of a dense glass-forming suspension made up of Brownian hard disks through a rough channel. This allowed us to explore inhomogeneous flow fields in the system. Therefore, we generalized our analysis to sample micro- and macroscopic quantities locally. At high packing fractions, we observed the development of a central plug where the glassy material moves uniformly, while the shear is localized to narrow regions close to the walls. In this context we confirmed a criterion for plug formation based on the dynamic yield stress present in a glass. In addition we found that stationary inhomogeneous flow is accompanied by local variations of the shear-rate, pressure, density and strongly affects the structural dynamics. Normal stress and pressure profiles in yielding glassy states were found to differ strongly from the ones measured for viscous fluids. Surprisingly, in the glass a local minimum in pressure occurs in the solid central plug, although this region exhibits an increased local density. Again, our results for flowing viscous liquids qualitatively confirm the picture provided by hybrid-Lattice Boltzmann-Mode Coupling Theory calculations.

Finally, we presented a method to locally analyze the relaxation process of 2D colloidal glass formers and gave arguments that Mermin-Wagner type density fluctuations are present in such systems. Colloidal glasses in 3D on the other hand are not affected by this collective motion. By this we contributed to the “reexamination of the glass transition in 2D” demanded by Szamel and Flenner, who reported fundamental differences between glassy dynamics in two and three dimensions. We argued that the coexistence of Mermin-Wagner fluctuations and the $\alpha$-process drive the relaxation in 2D. This long wavelength density fluctuations exist on large scales but do not affect the local cage-escape mechanisms associated with the $\alpha$-process. We showed, that the impact on the localization in a 2D glass, as seen by density correlation functions and MSD, can be attributed to this fluctuations. We gave proof, that an analysis in a local reference frame is able to resolve most of the observed differences: first, the separation of time scales of translational and orientational motion is resolved. Furthermore, a modified Lindemann-criterion was established (using local frames), which does not depend on the amplitude of the fluctuations. In a global reference frame, the amplitude grows logarithmically with system size, a hallmark of Mermin-Wagner fluctuations. Therefore the underlying microscopic mechanism of the 2D glass transition is not necessarily different from its 3D counterpart.
Zusammenfassung in deutscher Sprache


Darüber hinaus wurde ein Algorithmus entwickelt, um den Druckgradienten-getriebenen Fluss Brownscher harter Scheiben durch einen Kanal mit rauen Wänden zu realisieren. Die
8. Conclusions

dadurch entstehenden inhomogene Flüsse und Scherraten eröffneten neue Einblicke in die Dy-
namik fließender Systeme. Dispersionen mit Packungsdichten oberhalb des Glasübergangs
zeigen das Geschwindigkeitsprofil einer Pfropfenströmung. Ein Kriterium für die Entstehung
 dieses Zustands, basierend auf der Existenz einer Fließspannung der Suspension, konnte ver-
ifiziert werden. Im stationären Zustand wurden die bisherigen Analyseverfahren erweitert,
 um Spannungen, Dichten, Verschiebungsquadrature, Mischungskonzentrationen und Dichteko-
rrelatoren lokal zu bestimmen. Die gemessenen Resultate bestätigten Vorhersagen eines kom-
 binierten Lattice-Boltzmann-Modenkopplungs-Verfahren.

Schlussendlich konnten langwellige Dichtefluktuationen in zweidimensionalen Gläsern nach-
gewiesen werden. Hierfür wurde ein Vergleich von Simulationsergebnissen mit Daten aus
Experimenten an Gläsern in zwei und drei Dimensionen und einem Kristall in 2 Dimensionen
angestellt. Es konnte gezeigt werden, dass diese Mermin-Wagner-artigen Fluktuationen für
die meisten bekannten Unterschiede zwischen dem Glasübergang in zwei und dem in drei
Dimensionen verantwortlich gemacht werden können. Die Verwendung von lokalen, teilchen-
bezogenen Koordinaten ermöglichte das Aufstellen eines dynamischen Lindemannkriteriums
für kolloidale Gläser in 2d. Das zu erwartende logarithmische Anwachsen der Amplitude
der langwelligen Dichtefluktuationen mit der Systemgröße konnte in Simulationen bestätigt
werden. Die Mechanismen, die dem Glasübergang in 2D und 3D zugrunde liegen, müssen
derhalb nicht notwendigerweise unterschiedlich sein.
A. Calculational details

A.1. Dispersion relations

In 3.2.4 the dispersion relations $\lambda_s(q) = (u_s^2(q))^{-1}_{\text{glass}}$ are calculated.

The transverse dispersion relation $\lambda_\perp$. The projection of $u_q(t)$ on $\hat{q}_\perp = q^{-1}(-q_y, q_x)^T$, a normalized vector perpendicular to $q$, is given by

$$u_{q\perp}(t) = \langle u_q(t), \hat{q}_\perp \rangle$$

$$= \frac{1}{\sqrt{N}} \sum_{i=1}^{N} e^{iqr_i} \langle u_i(t), \hat{q}_\perp \rangle$$

$$= \frac{1}{\sqrt{N}} \sum_{i=1}^{N} e^{iqr_i} \frac{-q_y u_{ix}(t) + q_x u_{iy}(t)}{q}$$

$$= \frac{1}{\sqrt{N}} \sum_{i=1}^{N} (\cos(qr_i) + i \sin(qr_i)) \frac{-q_y u_{ix}(t) + q_x u_{iy}(t)}{q}.$$  

So the equal time correlation function reads

$$u_{q\perp}(t)u_{q\perp}(t) = \Re(u_{q\perp}(t))^2 + \Im(u_{q\perp}(t))^2$$

$$= \frac{1}{N} \left( \sum_{i=1}^{N} \cos(qr_i) u_{\perp i}(t) \right)^2 + \frac{1}{N} \left( \sum_{i=1}^{N} \sin(qr_i) u_{\perp i}(t) \right)^2,$$

and we arrive at

$$\lambda_\perp(q) = \frac{1}{\langle u_{q\perp}^2(q) \rangle_{\text{glass}}}.$$  

$\langle \cdot \rangle_{\text{glass}}$ includes time averaging over a time $\tau_0 < t < \tau_\alpha$, an average over at least 300 simulations runs per packing fraction and time was performed. Additionally, the isotropic nature of the system allowed for an average over directions in $q$-space. For this a quadratic grid in $q$-space with lattice constant $\Delta q d_s = 0.17$ was employed.
A. Calculational details

The longitudinal dispersion relation $\lambda_\parallel$ The projection of $u_q(t)$ on $\hat{q}_\parallel = q^{-1}(q_x, q_y)^T$, a normalized vector parallel to $q$, is done analogously

$$u_{q\parallel}(t) = \langle u_q(t), \hat{q}_\parallel \rangle,$$

(A.8)

$$u_{q\parallel}^*(t) u_{q\parallel}(t) = \frac{1}{N} \left( \sum_{i=1}^{N} \cos(q_r i) u_{i\parallel}(t) \right)^2 + \frac{1}{N} \left( \sum_{i=1}^{N} \sin(q_r i) u_{i\parallel}(t) \right)^2.$$  

(A.9)

A.2. Strain field

Coarse graining function The chosen coarse graining function reads

$$\phi(r, r_i, \sigma, r_c) = \frac{1}{C(r_c, \sigma)} \begin{cases} \exp \left( -\frac{|r - r_i|^2}{2\sigma^2} \right) & \text{if } |r - r_i| < r_c \\ 0 & \text{else}. \end{cases}$$\n
(A.11)

with normalization constant $C(r_c, \sigma) = 2\pi\sigma^2 \left( 1 - e^{-\frac{r_c^2}{2\sigma^2}} \right)$. It is

$$\partial_{r_x} \phi(r, r_i, \sigma, r_c) = \frac{(r_{ix} - r_x) e^{-\frac{(r_{ix} - r_x)^2 + (r_{iy} - r_y)^2}{2\sigma^2}}}{\sigma^2 C} = \frac{r_{ix} - r_x}{\sigma^2} \phi(r, r_i, \sigma, r_c)$$

$$\partial_{r_y} \phi(r, r_i, \sigma, r_c) = \frac{(r_{iy} - r_y) e^{-\frac{(r_{ix} - r_x)^2 + (r_{iy} - r_y)^2}{2\sigma^2}}}{\sigma^2 C} = \frac{r_{iy} - r_y}{\sigma^2} \phi(r, r_i, \sigma, r_c)$$

Displacement and strain field: The coarse grained displacement field at time $t$ is given by

$$u(r, t_1, t_2) = \frac{1}{\rho(r, t_2)} \sum_{i=1}^{N} u_i(r_i, t_1, t_2) \phi^{r_i r}(|r - r_i(t_2)|),$$

(A.12)

with the density

$$\rho(r, t) = \sum_{i=1}^{N} \phi^{r_i r}(r - r_i(t))$$

(A.13)

and the single particle displacement for the $i$th particle

$$u_i(t_1, t_2) = r_i(t_2) - r_i(t_1),$$

Note that we use the system configuration at time $t_2$ for coarse graining as in [111]. In [80] the configuration at time $t_1$ is employed. In the following we set $t_1 = 0$ and $t = t_2$. The
linearized strain field is defined as
\[
\epsilon_{\alpha\beta}(r, t) = \frac{1}{2} \left( \frac{\partial u_\alpha(r, t)}{\partial r_\beta} + \frac{\partial u_\beta(r, t)}{\partial r_\alpha} \right). \tag{A.14}
\]

Taking nonlinear contributions into account we have
\[
\epsilon^{\text{nonlin}}_{\alpha\beta}(r, t) = \frac{1}{2} \left( \frac{\partial u_\alpha(r, t)}{\partial r_\beta} + \frac{\partial u_\beta(r, t)}{\partial r_\alpha} + \frac{\partial u_\gamma(r, t)}{\partial r_\alpha} \frac{\partial u_\gamma(r, t)}{\partial r_\beta} \right), \tag{A.15}
\]
\[
= \frac{1}{2} \left( \frac{\partial u_\alpha(r, t)}{\partial r_\beta} + \frac{\partial u_\beta(r, t)}{\partial r_\alpha} + \frac{\partial u_x(r, t)}{\partial r_\alpha} \frac{\partial u_x(r, t)}{\partial r_\beta} + \frac{\partial u_y(r, t)}{\partial r_\alpha} \frac{\partial u_y(r, t)}{\partial r_\beta} \right), \tag{A.16}
\]

where the partial derivatives calculate to
\[
\frac{\partial u_\alpha(r, t)}{\partial r_\beta} = \frac{1}{\rho(r, t)} \sum_{i=1}^{N} u_{i\alpha}(r_i, t) \phi^{s, \sigma, \tau}(r - r_i(t)) \left( \frac{1}{\rho(r, t)} \sum_{i=1}^{N} u_{i\alpha}(r_i, t) \phi^{s, \sigma, \tau}(r - r_i(t)) \right) - \frac{1}{\rho^2(r, t)} \sum_{i=1}^{N} \frac{r_{i\beta}(t) - r_{i\beta}}{\sigma^2} \phi^{s, \sigma, \tau}(r - r_i(t)).
\]

The contribution of the second order terms in Eq. (A.16) are small and only observable in the long time diffusive regime in the fluid and does not affect the analysis presented in Sect. 4. The Eshelby pattern and power law decay discussed in the main text for the experiment in the glass and supercooled fluid does not change if the strain field is obtained with Eq. (A.16), see Fig. A.2. Fig. A.1 shows a comparison of the amplitude functions $C_s(t)$ obtained with a linearized strain field Eq. (A.14) and by taking nonlinear contributions into account, Eq. (A.16).
A. Calculational details

Figure A.1.: Amplitude function $C^s(t)$ of the far-field power-law decay of transversal strain correlations as discussed in Sect. 4.5. Dashed lines give the elastic limits $C^s(t \to \infty) = 2k_BT n(1/\mu - 1/\mu^\|)$ with moduli obtained from the dispersion relations. The dashed-dotted lines are obtained using Eq. (A.16) taking into account nonlinear contributions. The inset on the left shows asymptotic collapse of the fluid curves when plotted versus rescaled time $t/\tau_\alpha$ with the final relaxation times $\tau_\alpha$ obtained from density correlation functions.

Figure A.2.: Experimental rescaled strain correlation data obtained with Eq. (A.16) for a glass (left, $\Gamma = 423$) and a supercooled fluid (right; $\Gamma = 103$) state at different times. The spherical harmonic strain correlation functions $C^{xy}_{\ell}(r,t)/C^s(t)$ are rescaled to overlap in the far-field power law decay. Main panels show the $r^{-k}$-power law decay (dashed black lines), with exponent $k = 2$ varying little with time (upper insets). The contourplots (lower insets) of the long-time limit of $C^{xy}_{\ell}(r,t)/C^{xy}_{\ell}(r = 0,t)$ illustrate the corresponding $\cos(4\theta)$-symmetry; The Eshelby-patterns are shown at $nD_0t = 30.1$ and $nD_0t = 3.1$ for the glass and fluid, respectively.
A.3. Strain correlation

Employing the methods above one is able to define the coarse-grained displacement field and strain field. We choose to do so on a particle position based grid. The spatial correlation of this function is then calculated straightforward as

\[
C_{\alpha\beta}(r,t) = \langle \epsilon_{\alpha\beta}(r_0,t)\epsilon_{\alpha\beta}(r_0 + r,t) \rangle,
\]

(A.17)

where the average is performed over time intervals of length \(t\), particle position based lattice sites \(r_0\) and different runs (only for simulational data). Using both simulational and experimental data we sample the function

\[
\frac{C_{xy}(r,t)}{C_{xy}(r = 0,t)}.
\]

(A.18)

It is

\[
C_{xy}(r = 0,t) = \frac{1}{N_t} \sum_{k=1}^{N_t} \frac{1}{N} \sum_{i=1}^{N} \epsilon_{xy}(r_i,t_k)\epsilon_{xy}(r_i,t_k),
\]

(A.19)

where the average is taken over \(N\) particles. For simulational data \(N_t\) consecutive time intervals of equal length \(t\) are used with \(t_k\) denoting the time interval \([(k-1)t,kt]\). For the experimental data the \(N_t\) time intervals overlap to improve the statistics.

For the nominator in eq. A.18 the plane is divided into non overlapping subareas

\[
V_{ab} = [r_a,r_a + \Delta r] \times [\theta_b,\theta_b + \Delta \theta],
\]

where \(\Delta \theta\) and \(\Delta r\) are constant and \(r = r(\cos \theta, \sin \theta)\). Note that the area of this subarea grows with \(r\). With

\[
\chi_{ab}(r) = \begin{cases} 
1 & \text{for } r \in V_{ab} \\
0 & \text{else} 
\end{cases}
\]

(A.20)

the number of contributions per subarea is given by

\[
N_{ab} = \sum_{k=1}^{N_t} \sum_{i=1}^{N} \sum_{j=1}^{N} \chi_{ab}(r_i(kt) - r_j(kt)).
\]

(A.21)

Now the spatial correlation of the strain field is sampled as

\[
C_{xy}(r_a,\theta_b,t) = \frac{1}{N_{ab}} \sum_{k=1}^{N_t} \sum_{i=1}^{N} \sum_{j=1}^{N} \chi_{ab}(r_i(kt) - r_j(kt))\epsilon_{xy}(r_i,tk)\epsilon_{xy}(r_j,tk).
\]

(A.22)

The computational effort can be reduced by using \(C_{xy}(r_a,\theta_b,t) = C_{xy}(r_a,\theta_b + \pi,t)\).
A. Calculational details

A.4. Testing theory

For distances $r$ large compared to the mean particle distance $a$ we expect the power law

$$C_{xy}(r, t) \to \cos(4\theta) \frac{C^s(t)}{4\pi nr^2} \text{ for } 2\pi \sqrt{\zeta_0 \eta^{-1}} \gg r \gg a.$$  \hspace{1cm} (A.23)

to hold. The projection on $\cos(4\theta)$ is now defined as

$$C_{44}(r, t) = \frac{1}{\pi} \int_0^{2\pi} d\theta \cos(4\theta) C_{xy}(r, t) \to \frac{C^s(t)}{4\pi nr^2} \text{ for } 2\pi \sqrt{\zeta_0 \eta^{-1}} \gg r \gg a.$$  \hspace{1cm} (A.24)

Mode-coupling theory for the strain correlation functions in supercooled liquids finds

$$C^s(t) \to \begin{cases} 2k_B Tn \left( \frac{1}{c_\infty} - \frac{1}{c_\parallel} \right) & t \ll \tau, \\ \frac{2k_B Tn t}{\eta} & t \gg \tau. \end{cases}$$  \hspace{1cm} (A.25)

For our experimental and simulational data we sampled

$$\tilde{C}(r, t) = \frac{C_{xy}(r, t)}{C_{xy}(r = 0, t)};$$  \hspace{1cm} (A.26)

and therefore we have

$$\frac{1}{\pi} \int_0^{2\pi} d\theta \cos(4\theta) \tilde{C}(r, t) = \frac{C^s(t)}{C_{xy}(r = 0, t)} \frac{1}{4\pi nr^2} = b.$$  \hspace{1cm} (A.27)

We determine the parameter $b$ and test the equality

$$C^s(t) = bC_{xy}(r = 0, t) \to \begin{cases} 2k_B Tn \left( \frac{1}{c_\infty} - \frac{1}{c_\parallel} \right) & t \ll \tau, \\ \frac{2k_B Tn t}{\eta} & t \gg \tau. \end{cases}$$  \hspace{1cm} (A.28)

The parameter $b$ is determined from a least squares fit to the $1/r^2$-law for the long distance part of $C^4_2(r, t)$ at different times $t$. It was found that $b$ does not depend on time, but varies with packing fraction and temperature, respectively.
B. Testing the channel flow algorithm

In section 6.1 the methods for the realization of planar channel flow was introduced. In the following tests for the validity of the algorithm are shown.

B.1. Thermostat

\[ \text{Var}(v_i) = 2k_B T/m \]

During a time interval of length \( \tau_b \) the highly sheared regions close to the wall heat up. Therefore the distribution immediately before the next Brownian event is broadened leading to ratios smaller one. Directly at the wall for \( \delta y \approx 0 \) the system locally cools down.

The simulated suspension is exposed to a pressure gradient that is realized by an external body force. This leads to heat production by viscous dissipation inside the system, the occurring shear forces do work on adjacent layers which is transformed into heat. As a result, the width of the velocity distribution \( \langle (v - \langle v \rangle)^2 \rangle \), which defines the local temperature \( T \), broadens temporarily. The coupling to the solvent, serving as a heat bath, is now realized by the thermostat that constantly kicks in and readjusts the overall velocity distribution to a Gaussian of prescribed width \( \text{Var}(v_i) = 2k_B T/m \) as shown in sections 2.2 and 6.1.3.

In order to produce physically meaningful results the interference of the thermostat has to
B. Testing the channel flow algorithm

be gentle in a sense that the repeated adjustments to the velocity distribution are small. During a Brownian time step of length $\tau_b$ the Gaussian distribution of the initial velocities $v_i$ is altered, to quantify this we measure the variance of the final velocity distribution $v_f$ just before the next Brownian event. Fig. B.1 shows the ratio of the initial and final variance. For the forces chosen the deviations from the initial distribution grow with local shear rate but are sufficiently small. Close to the wall, where the shear rate and therefore also the heat production are maximal, the change in temperature that develops between two thermostatting events is below 0.15% for the glass and below 0.22% at the glass transition. Only in direct proximity of the wall for $\delta y \approx 0$ the particles are trapped in very small cages made up partly of neighboring wall particles which narrows the velocity distribution and by that cools down the system locally. This shows that only small adjustments to the velocity distributions are needed to keep the system at a constant temperature $T$.

B.2. Demixing phenomena

![Figure B.2: Local concentration of small particles $c_s$ for varying forces as function of position $y$ across the channel at $\phi = 0.81$ (left) and $\phi = 0.78$ (right). Black dashed lines indicate the average values $c_s = 0.5$.](image)

To prevent the system from crystallizing a binary mixture is used, see section 2.5.2. The influence of the inhomogeneous shear flow and stresses on the local concentration of particle types is shown in Fig. B.2. The concentration of small particles $c_s(y)$ is constant at the channel center, while a slight demixing during the startup of shear flow can be observed in the fluidized shear melted regions. In direct proximity of the wall for $\delta y \approx 0$ the amount of small particles is enhanced, due to their smaller diameter they are able to occupy the space of the small cavities offered by the rough wall. As a result, in the highly fluidized region undergoing shear flow next to the wall a depletion of small particles is observed. The concentration $c_s(y) = N_s(y)/N_b(y)$ drops by up to 5% in the glass and 8% in the supercooled...
B.3. Imposing flow

Forces up to $F = 0.375 k_B T / d_s$ have been tested (not shown), where the change in concentration went up to 15% introducing further complex phenomena to our measurements. Since this is not desirable for the simulations performed here we limited our investigations to systems exhibiting changes in local concentration smaller than 8%.

B.3. Imposing flow

Figure B.3.: Distribution of particle velocities in flow direction at the channel center ($y = 0$) immediately after a Brownian event, characterized by the expectation value $\langle v_x(t^+) \rangle = \langle v_x(t^-) \rangle + F_T / m$ (dashed lines) and the variance $\langle (v_x - \langle v_x \rangle)^2 \rangle = k_B T / m$. The inset underlines, that for flowing systems ($F > 0.05 k_B T / d_s$) the amplitudes of velocity changes $\Delta v_x = F_T / m$ due to the applied force are small compared to the mean velocity of the stationary state $\langle v_x \rangle$.

In section 6.1.3 two different possibilities to implement the body force driving the flow are presented. First this can be done by incorporating a constant acceleration on the particles in the Newtonian part of the algorithm between two Brownian events. Alternatively it can be done by translation of the force into discrete kicks in velocity $\Delta v_x = \Delta \dot{r}_x = F_T / m$, that are added to the particle velocities during a Brownian event. As shown in section 6.1.3 in the latter of the two methods the particle velocities are updated as

$$v_i(t^+, y_i) = x^v + u_x(t^-, y_i) \hat{x} + \frac{F_T}{m} \hat{x},$$

see Eq. (6.13). The velocities of all particles are increased by a constant value with every Brownian event and by that a certain amount of work is done. This process can be assumed to be stationary, if firstly the amount of energy added is dissipated during a Brownian time interval because of the friction generated by the rough walls. By this a constant velocity and stress profile can set in. Secondly, the change in velocity $\Delta v_x$ has to be small compared to the average velocity $\langle v_x \rangle$ and the standard deviation or width of the velocity distribution.
B. Testing the channel flow algorithm

\[ \sqrt{\langle (v - \langle v \rangle)^2 \rangle} = \sqrt{k_B T / m}. \]

Fig. B.3 shows the distributions immediately after the velocity reassignments, for the parameter chosen in this work the listed requirements are met, it is \( \Delta v_x \ll \langle v_x \rangle \ll \sqrt{\langle (v - \langle v \rangle)^2 \rangle} \). The system is assumed to be in a stationary flowing state. The version of the algorithm utilizing a permanent particle acceleration for the realization of the external force allows for a true stationary state. In Fig. B.4 the results for the two different implementations are compared, the stress and velocity profiles are nearly identical. Only for the highest force studied at \( F = 0.125k_B T / d_s \) small deviations for the amplitude of the diagonal stress components occur, which are considered negligible. Results for local density, concentration, structural relaxation and MSD are also in good agreement. The use of discrete velocity adjustments for the implementation of the external body force as shown in Eq. B.1, which is considerably faster, is therefore justified.
Figure B.4.: Velocity profile, shear rate, shear stress, normal stress difference and relative pressure across the channel for the algorithm with continuous acceleration, see Eq. (6.5), (dashed-dotted lines) and discrete adjustments to the particle velocities, see Eq. (6.13), (solid lines) at $\phi = 0.81$ and $F = 0.0625k_BT/d_s$ and $F = 0.125k_BT/d_s$. 
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