Simulation of Peloids

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Cluster formation due to attractive potentials. The simulation was run in parallel on 32 processors and contained 10,560 colloidal particles. The solvent was represented by $1.3 \cdot 10^7$ fluid particles.
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Disclaimer

The contents of this thesis has been worked out within the project A1 of the research group “Peloide”, DFG-FOR 371 [107], of the German research foundation (DFG). Most results presented here have been published already in the following articles:


Hiermit versichere ich, dass ich diese Arbeit selbständig verfasst habe und nur die angegebenen Quellen und Hilfsmittel benutzt habe.

Kapitel 1

Zusammenfassung in deutscher Sprache

1.1 Fachlicher Hintergrund und Motivation


Ein Grund für das große Interesse an Kolloiden ist, dass sie überall in unserem alltäglichen Leben auftauchen. Dispersionsfarben, Böden, Kosmetikprodukte und ver-


Um diese Methode zu optimieren und um generell die Einflussgrößen, die die Homogenität und somit die Stabilität von keramischen Werkstücken bestimmen, zu erforschen, ist es von Nutzen, zunächst die gegenseitige Abhängigkeit der Partikelwechselwirkungen und der makroskopischen Eigenschaften der Suspension zu untersuchen.
Eine besondere Eigenschaft für das generelle Verständnis ist die Mikrostruktur, d. h. die Nahordnung, die die Teilchen innerhalb der Suspension während der Verarbeitung einnehmen. Ebenso von Bedeutung ist die Dynamik, mit der sich eine bestimmte Mikrostruktur unter gegebenen Bedingungen ausbildet, z. B. ob und wie schnell die Teilchen sich zu Clustern zusammenschließen. Weitere interessante Kenngrößen sind die Scherviskosität, sowie deren Abhängigkeit von der Scherrate oder der Teilchendichte, oder spezielle Eigenschaften der jeweiligen Mikrostruktur, z. B. die Clustergrößenverteilung für die Fälle, in denen Clusterbildung auftritt. Mit einem detaillierten Verständnis der Verbindung zwischen den Teilchenwechselwirkungen und der gebildeten Mikrostruktur, sowie deren Auswirkung auf die Eigenschaften der Suspension, ist es schließlich möglich, die Homogenität und die Stabilität eines herbestellten Werkstücks zu verbessern.

Der Schwerpunkt dieser Arbeit liegt auf einer Suspension von $\text{Al}_2\text{O}_3$-Teilchen, was ein weit verbreitetes Material in der Keramikindustrie [103, 114] ist. Das Material ist kommerziell in großen Mengen erhältlich. Es wird als Pulver mit verschiedenen Korngrößen und in verschiedenen Reinheitsstufen angeboten. Es kann auch als Modellsubstanz für bodenmechanische Versuche verwendet werden [116, 118], was den Schwerpunkt der Forschergruppe „DFG-FOR 371 – Peloide“ gebildet hat [107], innerhalb derer die vorliegende Arbeit entstanden ist.


Die Forschergruppe „Peloide“ wurde speziell gegründet, um die Zusammenhänge zwischen makroskopischen und mikroskopischen Eigenschaften, speziell von tonähnlichen Böden, zu untersuchen. Die Forschungen sollten zunächst auf einer abstrakten Ebene anhand einer Modellsubstanz wie $\text{Al}_2\text{O}_3$-Suspensionen für Schluff (tonartig) durchgeführt werden, und in einem zweiten Schritt mit Laponit für Tonböden. Die Verwendung von
Modellsubstanzen bietet den Vorteil, dass das System wohldefiniert ist, insbesondere im Hinblick auf Reinheit und Partikelgröße, was es einfacher macht, in einem weiteren Schritt ein bodenmechanisches Kontinuums-Modell zu entwickeln.

Im Gegensatz zu Ton, der aus dünnen Plättchen aufgebaut ist [148], können die Schluffteilchen in erster Näherung als kugelförmig angenommen werden, was das Problem wesentlich vereinfacht. Dennoch bleibt, aufgrund der Teilchengröße in Mikrometerbereich und darunter, ein Wechselspiel von Diffusion, elektrostatischer Abstoßung, Van-der-Waals-Anziehung und hydrodynamischer Wechselwirkung, was die Suspension nach wie vor zu einem sehr komplexen System macht. Computersimulationen sind hier ein mächtiges Werkzeug, um ein Verständnis für die Statik und Dynamik dieser komplexen Systeme zu entwickeln. Wir haben ein Simulationsprogramm entwickelt, das eine Brownsche Suspension von wechselwirkenden Teilchen modelliert [60]. Die zugrundeliegenden Konzepte werden im folgenden Abschnitt näher erläutert.

1.2 Konzept und Hintergrund


1.3 Simulationsmethode

Teilchen bei niedriger Ionenstärke und bei geringen Oberflächenladungen gültig. Es wurden erhebliche Anstrengungen unternommen, um zu erforschen, in welchen Fällen DLVO-Potentiale angenommen werden können, selbst wenn die Voraussetzungen für ihre Gültigkeit streng genommen nicht erfüllt sind [7, 11, 12, 92, 106, 142]. Es muss dann eine renormierte Ladung („effektive Ladung“ genannt) und in manchen Fällen eine andere Debye-Abschneidekante angenommen werden. Trotz allem, die tatsächliche Ladung auf dem Kolloideilchen und ihre Abhängigkeit von den Umgebungsbedingungen ist a priori nicht bekannt.


1.3 Simulationsmethode

Zuerst beschreiben wir die Molekulardynamik-Simulation, die die Bewegung der suspendierten Teilchen beschreibt. Verschiedene Kräfte unterschiedlichen physikalischen Ursprungs wirken auf die Teilchen, wobei wir die folgenden berücksichtigen: Effektive elektrostatische und Van-der-Waals-Wechselwirkung, bekannt als DLVO-Potentiale [30, 60, 68, 86, 90, 100, 123, 133, 152], transversale Reibungskräfte, eine Hertz'sche Kontaktkraft, Gravitation und eine Lubrikationskraft zur Korrektur der kurzreichweitigen Hydrodynamik.

Das elektrostatische Potential als erster Beitrag zu den DLVO-Potentialen, ist ein ex-
ponentiell abgeschirmtes Coulomb-Potential. Die Ladung der suspendierten Teilchen wird von den im Lösungsmittel gelösten Ionen (H$_3$O$^+$, OH$^-$ und die Ionen von ggf. zugegebenem Salz, z. B. NH$_4^+$ und Cl$^-$) in der sogenannten „Stern-Schicht“ abgeschirmt, was auf die folgende Form des Potentials führt:

$$V_{\text{Coul}}(r) = \pi \varepsilon_r \varepsilon_0 \left[ \frac{2 + 2R \kappa}{1 + 2R \kappa} \cdot \frac{4k_B T}{ze} \tanh \left( \frac{ze \zeta}{4k_B T} \right) \right]^2 \frac{(2R)^2}{r} \exp \left( -\kappa |r - 2R| \right), \quad (1.1)$$

wobei $R$ den Teilchenradius bezeichnet und $r$ den Abstand zwischen zwei Teilchenmitelpunkten. $e$ ist die Einheitsladung, $T$ die Temperatur, $k_B$ die Boltzmann Konstante und $z$ die Valenz der hinzugegebenen Ionen. Das „effektive Oberflächenpotential“ $\zeta$ ist hier gleichzusetzen mit dem Potential an der Grenzschicht, innerhalb derer Ionen fest gebunden sind und außerhalb derer sie frei beweglich sind. Es handelt sich um das $\zeta$-Potential, das aus der Beweglichkeit der Kolloidteilchen in einem angelegten Feld berechnet werden kann. Die Abhängigkeit dieses Potentials von $p$H-Wert und Ionenstärke $I$, die eine repräsentative Ionenkonzentration ausdrückt (siehe Eq. (3.1)), wird mit dem Ladungs-Regulierungs-Modell wiedergegeben. Die Ionenstärke ist darüber hinaus mit der inversen Debye-Abschirmlänge $\kappa$ verkümpft gemäß $\kappa^2 = 8\pi\ell_B I$, wobei $\ell_B = 7$ Å die Bjerrumlänge ist. $\varepsilon_0$ ist die Dielektrizitätskonstante von Vakuum und $\varepsilon_r = 81$ die relative Dielektrizität von Wasser.

Zusätzlich zur elektrostatischen Abstoßung enthalten die DLVO-Potentiale die Van-der-Waals-Anziehung, die über zwei kugelförmige Teilchen analytisch integriert werden kann, was auf den folgenden Ausdruck führt:

$$V_{\text{vdW}}(r) = -\frac{A_H}{12} \left[ \frac{4R^2}{r^2 - 4R^2} + \frac{4R^2}{r^2} + 2 \ln \left( \frac{r^2 - 4R^2}{r^2} \right) \right]. \quad (1.2)$$

$A_H$ ist die Hamaker Konstante, die die Polarisierbarkeit des Lösungsmittels enthält. Eq. (1.2) weist für kleine Teilchenabstände eine Singularität auf, die daher rührt, dass in der Herleitung große Abstände und lineare Polarisierbarkeit vorausgesetzt werden. Für die Simulation muss das Potentialminimum, das in der Realität existiert und endliche Tiefe besitzt, gesondert modelliert werden. Wir legen dessen Tiefe mit $10k_B T$ fest und modellieren es mit einer Parabel, die stetig und stetig differenziierbar in das DLVO-Potential übergeht.

Für kleinere Abstände, d. h. wenn sich die Teilchen überlappen, benötigt man eine Rücktreibende Kraft, für die wir eine Hertz’sche Kraft annehmen. Zusätzlich modelliert eine Dämpfungskraft Verluste im Partikelkontakt. Außerdem wird transversale Reibung proportional zu der wirkenden Normalkraft angesetzt.

Für Teilchen, die sich nicht berühren, wirkt des weiteren eine Lubrikationskraft, die entlang der Verbindung der beiden Teilchen gerichtet ist und proportional zur Relativgeschwindigkeit und zum Kehrwert der des Abstandes der Bewegung entgegenwirkt. Durch die Einführung von Abschneideradien können wir die Kraft in ihrer Stärke und Reichweite regulieren und die nötige Korrektur der Hydrodynamik für kleine Abstände gezielt einstellen (siehe Eq. (4.8) und den Text dazu). Diese Korrektur ist erforderlich, da die Simulation der Flüssigkeit prinzipiell in ihrer Auflösung beschränkt ist. Dies gilt für alle diskretisierten Flüssigkeits-Simulationsmethoden.
Zur Integration der Bewegungsgleichungen verwenden wir einen „Velocity-Verlet-Algorithmus“ [9, 137], wobei die Teilchenpositionen \( x_i \) und -geschwindigkeiten \( v_i \) des Teilchens \( i \) mit der Masse \( m \) gemäß den Gleichungen
\[
\begin{align*}
x_i(t + \delta t) &= x_i(t) + \delta t \frac{v_i(t)}{m}, \quad (1.3) \\
v_i(t + \delta t) &= v_i(t) + \delta t \frac{F_i(t)}{2m} + F_i(t + \delta t). \quad (1.4)
\end{align*}
\]
von einem zum nächsten Zeitschritt der Größe \( \delta t \) aktualisiert werden. Für die Behandlung der Teilchenrotationen verwenden wir einen einfachen Euler-Algorithmus für Quaternionen [9, 10], jedoch hat sich herausgestellt, dass die Teilchenrotationen in vielen Fällen vernachlässigt werden können, da die wesentlichen Wechselwirkungskräfte Zentralkräfte sind [58].

Zur Simulation des Lösungsmittels verwenden wir „Stochastic Rotation Dynamics“, eine Simulationsmethode, die von Malevanets und Kapral eingeführt wurde [95, 96]. Sie basiert auf sogenannten Flüssigkeitsteilchen und enthält bereits intrinsisch thermische Fluktuationen. Der Algorithmus setzt sich aus zwei Schritten zusammen, die abwechselnd ausgeführt werden: Einem Strömungs- und einem Kollisionsschritt. Im Strömungsschritt wird jedes Flüssigkeitsteilchen \( i \) entsprechend seiner Geschwindigkeit \( v_i(t) \) zur Zeit \( t \) geradlinig weiterbewegt:
\[
r_i(t + \tau) = r_i(t) + \tau \cdot v_i(t). \quad (1.5)
\]
Im Kollisionsschritt werden die Flüssigkeitsteilchen in kubische Zellen der Kantenlänge \( a \) einsortiert, innerhalb derer eine künstliche Wechselwirkung modelliert wird, die kollektiv auf alle Teilchen derselben Zelle gleichermaßen wirkt: In jeder Zelle \( j \) wird zunächst die mittlere Geschwindigkeit \( u_j(t') \) zur Zeit \( t' = t + \tau \) berechnet:
\[
u_j(t') = \frac{1}{N_j(t')} \sum_{i=1}^{N_j(t')} v_i(t), \quad (1.6)
\]
wobei \( N_j(t') \) die Zahl der Teilchen zur Zeit \( t' \) in Zelle \( j \) angibt. Damit werden nun die Geschwindigkeiten \( v_i(t + \tau) \) der einzelnen Teilchen \( i \) gemäß
\[
v_i(t + \tau) = u_j(t') + \Omega_j(t') \cdot [v_i(t) - u_j(t')]. \quad (1.7)
\]
neu festgesetzt. Dabei bezeichnet \( \Omega_j(t') \) eine Rotationsmatrix, die für jede Zelle und in jedem Zeitschritt zufällig gewählt wird. Es werden nur die Relativkomponenten \( [v_i(t) - u_j(t')] \) gedreht und die mittlere Geschwindigkeit \( u_j(t') \) in jeder Zelle bleibt erhalten. Die Operation ist Teilchenzahl-, Energie- und Impulserhaltend. Als Rotationsmatrizen verwenden wir die 6 möglichen Drehungen um \( \alpha = \pm 90^\circ \) um die Koordinatenachsen, da hierfür die Matrizen besonders einfach werden [144], jedoch gibt es vielfältige Möglichkeiten in der Auswahl der Matrizen. Über den verwendeten Rotationswinkel bzw. die Auswahl der Matrizen wird die Viskosität der Flüssigkeit in der Simulation beeinflusst [71, 72, 119]. Wir verwenden eine modifizierte Variante des ursprünglichen Algorithmus, bei dem die Zellen in jedem Schritt um einen Zufallsvektor verschoben werden,
wobei die Komponenten aus dem Intervall \([-a/2, a/2]\) gezogen werden. Dadurch werden Anomalien im Tieftemperaturlimit beseitigt und exakte Galileiinvarianz erreicht [71, 72].

Um die Kolloidteilchen in der Simulation an die Flüssigkeit anzukoppeln, wurden in der Literatur verschiedene Methoden, die sich in der Auflösung der Umströmung der Teilchen unterscheiden, vorgeschlagen [37, 60, 74, 105]. Der nötige Rechenaufwand hängt stark von der für die Flüssigkeitssimulation verwendeten Auflösung und von der Kopplungsmethode ab. Wir haben zwei verschiedene Kopplungsmethoden implementiert und verwenden je nach Fragestellung die eine oder die andere.


Wenn eine Auflösung der Umströmung der einzelnen Kolloidteilchen nicht erforderlich ist, koppeln wir, wie von Falck et al. [37] vorgeschlagen, die Kolloidteilchen als Punktteilchen an die Flüssigkeitssimulation: In den Kollisionsschritt des SRD-Algorithmus werden die Kolloidteilchen mit einbezogen und zur Berechnung der mittleren Geschwindigkeit in der jeweiligen Zelle die jeweilige Teilchenmasse als Gewichtungsfaktor verwendet. Dabei werden alle Flüssigkeitsteilchen, die sich in der selben Zelle wie ein Kolloidteilchen befinden, von dem Kolloidteilchen beeinflusst. Die Zellengröße kann daher als hydrodynamisch wirksames Teilchenvolumen angesehen werden und muss daher gleich groß wie das Kolloidteilchen gewählt werden, um eine konsistente Simulation der Kolloidteilchen und der Flüssigkeit zu gewährleisten. Mit dieser Kopplungsmethode wird die Hydrodynamik grüber aufgelöst, dafür ist der Rechenaufwand für die Flüssigkeitssimulation erheblich geringer. Trotzdem ist es damit möglich, für die Sedimentationsgeschwindigkeit in einer Suspension ein Potenzgesetz bezüglich der Teilchenbeladung zu reproduzieren, wie es experimentell von Richardson und Zaki gefunden wurde [115], (siehe Abschnitt 7.3).

1.4 Bestimmung der Simulationsparameter

Das Haupt-Ziel dieser Arbeit ist es, mit der Simulation so nahe wie möglich an den Experimenten zu sein und im Computer die gleiche Situation wie im real existierenden Experiment zu reproduzieren, um dann die Ergebnisse quantitativ vergleichen zu
können. Wir wollen nicht nur qualitativ die im Experiment ablaufenden Vorgänge beschreiben, sondern wir sind an einem quantitativen Vergleich der Resultate interessiert. Für ein derart komplexes System, in dem mehrere Effekte in einem Wechselspiel stehen, ist es unabdingbar, die Bedeutung aller Kräfte zu analysieren, um nicht Gefahr zu laufen, ein System mit einer vom Experiment abweichenden Dynamik zu simulieren. Dafür gehen zwei wesentliche Dinge in unsere Simulationen ein: Realistische Teilchen-Paarwechselwirkungen und sorgfältig gewählte Simulationsparameter. Die Wechselwirkungen sind DLVO-Potentiale und werden im Abschnitt 1.3 bzw. in Kapitel 4 diskutiert, jedoch ist das Oberflächenpotential der Teilchen, das in die Wechselwirkungspotentiale eingeht, von vorne herein nicht bekannt. Wie bereits erwähnt, verwenden wir ein Ladungs-Regulierungs-Modell (siehe Abschnitt 5.1), um die Ladung der Kolloidteilchen zu berechnen. Darüber hinaus analysieren wir sorgfältig die für die Dynamik der Suspension relevanten Zeitskalen. Dabei stellt sich heraus, dass die charakteristischen Zeiten der beteiligten Prozesse von wenigen Nanosekunden für den schnellen Impulstransport in der Flüssigkeit bis zu mehreren Sekunden für langsane Prozesse wie Sedimentation reichen. Die verschiedenen Zeitskalen überdecken etwa acht Größenordnungen, was mit Simulationen kaum abgedeckt werden kann.


1.5 Ergebnisse

Bevor wir das Simulationsprogramm anwenden, ist es sinnvoll, einige einfache Tests durchzuführen, um sicherzustellen, dass die Simulationsmethode tatsächlich auf unser System angewendet werden kann und der Programmcode fehlerfrei läuft. Die Tests müssen auf einfachen Problemen basieren, die sich analytisch, zumindest in guter Näherung, lösen lassen, so dass man die Simulationswerte mit der analytischen Lösung
Kapitel 1. Zusammenfassung in deutscher Sprache

vergleichen kann. Wir überprüfen, ob in der Simulation die Energie konstant bleibt bzw. die erzielte Temperatur tatsächlich der eingestellten entspricht. Wir kontrollieren die Korrektheit der Teilchenrotationen und ihre Bedeutung für die zu bestimmenden Größen. Wir werten die Viskosität in der Simulation aus und prüfen, ob sie dem vorab berechneten Wert entspricht. Wir verifizieren, dass die Abhängigkeit der Sedimentationsgeschwindigkeit von Teilchen in einer Suspension von der Teilchenbeladung einem Potenzgesetz entspricht, wie man es ausgehend von experimentellen Beobachtungen erwarten würde [115], siehe section 7.3. Alle Tests bestätigen, dass unser Simulationsansatz für die Suspensionen, die wir untersuchen wollen, geeignet ist.

Nachdem wir uns also davon überzeugt haben, dass wir uns auf die Simulationsergebnisse unseres Programms verlassen können, verwenden wir es, um die Al₂O₃-Suspensionen, die wir modellieren, zu studieren. Die Ergebnisse können in einem „Stabilitätsdiagramm“ zusammengefasst werden (Fig. 8.1), in dem die Suspensionen je nach pH-Wert und Ionenstärke nach verschiedenen „Mikrostrukturen“ klassifiziert sind. Es erleichtert einen Überblick über die Zusammenhänge zwischen verschiedenen Eigenschaften der Suspensionen und erlaubt es, Eigenschaften für einen bestimmten Zustand, charakterisiert durch pH-Wert und Ionenstärke, vorherzusagen. Das Stabilitätsdiagramm ist im Rahmen dieser Arbeit zum ersten Mal in Simulationen quantitativ reproduziert worden. Es stellt eines der wichtigsten Ergebnisse des Projektes dar, das im Rahmen der vorliegenden Arbeit bearbeitet wurde. Es hat sich herausgestellt, dass die mikroskopische Struktur innerhalb der Suspension sehr stark von den Bedingungen abhängt, für die die Simulation durchgeführt wird. Wir unterscheiden drei verschiedene Mikrostrukturen: Ein geclustertes Regime, eine stabilisierte Suspension und eine repulsive Struktur.

Um zu verstehen, wie sich die Eigenschaften der Suspension in Abhängigkeit von der Mikrostruktur verändern, führen wir Simulationen bei pH = 6 in der Nähe der Grenze zwischen geclustertem Regime und stabilisierter Suspension durch. Wir simulieren im Scherfluss bei unterschiedlicher Scherrate und untersuchen deren Einfluss auf die Viskosität und die Mikrostruktur. Wir studieren das Geschwindigkeitsprofil und die Scherviskosität in Abhängigkeit von den Teilchenpaarwechselwirkungen und der Scherrate. Wir finden durch Schichtenbildung auf mikroskopischer Skala induzierte Scherverdünnung im suspendierten Regime. Wenn ein geclustertes System gesichert wird, werden die Cluster durch den Scherfluss aufgebrochen, was zu einem ausgeprägteren Scherverdünnungsverhalten als im suspendierten Regime führt. In der Nähe der Grenze zwischen beiden Regimes können wir die von J. Reinshagen gemessene Scherviskosität in unserer Simulation reproduzieren [58], (siehe Fig. 8.7).

Tief im geclusterten Regime stellen wir fest, dass die Teilchen im System zu einem einzigen großen Cluster verkleben. Für groß genug gewählte Scherraten kann dieser Cluster wieder aufgebrochen werden, jedoch sind bei stark geclusterten Systemen und geringen Scherraten (was für die Bodenmechanik der interessanteste Fall wäre) starke Artefakte durch die begrenzte Systemgröße zu beobachten. Bis zu einem gewissen Grad können größere Simulationen diesem Problem Abhilfe schaffen, allerdings scheinen Ansätze basierend auf einer vergrößerten Beschreibungsebene die bessere Wahl zu sein, um diese Fragen anzugehen.

Wir untersuchen die mikroskopische Nahordnung der Teilchen mittels ihrer Paarkorre-
1.5 Ergebnisse

lationsfunktion. Im repulsiven Regime des Stabilitätsdiagramms können langreichweitige Korrelationen beobachtet werden, die im suspendierten Regime weniger ausgeprägt sind. Im Gegensatz dazu können im geclustersten Regime einzelne Spitzen jeweils bestimmten lokalen Anordnungen zugeordnet werden (siehe Fig. 8.9). Das Integral über den Beitrag der jeweils nächsten Nachbarn (nearest neighbor peak) kann als Maß für den Cluster-Bildungs-Prozess herangezogen werden. In Abhängigkeit von der Scherrate und vom pH-Wert unterscheiden sich die Beiträge hierzu, was die Anzahl der Partikelkontakte in den Clustern widerspiegelt (siehe Fig. 8.12).

Aufgrund der begrenzten Größe des Simulationsvolumens und technischen Details unserer Implementation der Randbedingungen kann die Korrelationsfunktion nur Informationen bis zu einer beschränkten Längenskala in der Größenordnung der halben Systemabmessung wiedergeben. Daher gehen wir über zu ihrer komplementären Größe, nämlich zum Strukturfaktor. Im Prinzip enthält er dieselbe Information, jedoch ist es uns in unserer Implementation mit Hilfe des Strukturfaktor möglich, Informationen über größere Längenskalen zu erhalten. Wir integrieren über den Anstieg bei kleinen k-Vektoren, der die Informationen über Inhomogenitäten auf großen Längenskalen enthält. Damit können wir den Cluster-Bildungs-Prozess auf der Skala der Systemgröße beobachten (siehe Fig. 8.20). Dieselben typischen Merkmale wie bei der Verwendung der Beiträge der jeweils nächsten Nachbarn in der Paarkorrelationsfunktion können hier ebenfalls beobachtet werden, obwohl wir in diesem Fall eine sehr viel größere Längenskala herausgreifen. Somit haben wir nachgewiesen, dass der Cluster-Bildungs-Prozess gewissermaßen auf allen Längenskalen gleich abläuft und das Ergebnis nicht von der Methode bzw. der Längenskala der Beobachtung abhängt [57].


Um die repulsive Struktur näher zu charakterisieren, untersuchen wir die Scherkraft, die erforderlich ist, um eine vorgegebene Scherrate zu erzielen. Sie nimmt im repulsiven Regime zu, was mit einer Zunahme der effektiven Viskosität einhergeht. Da jedoch das Geschwindigkeitsprofil in diesen Simulationen oft nichtlinear verläuft, wird die Viskosität in gewisser Weise ortsabhängig und verändert sich je nach lokal vorliegender Teilchenanordnung innerhalb des Scherprofils. Darüber hinaus werten wir im repulsiven Regime das mittlere Verschiebungsquadrat der Kolloidteilchen aus und finden darin ein Plateau für intermediäre Zeitskalen, vergleichbar mit den Beobachtungen, die von glasartigen Systemen her bekannt sind.


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Viele andere interessante Fragestellungen könnten mit unserer Simulation untersucht werden. Unseres Wissens haben wir den ersten parallelen Programmc ode entwickelt, der auf einer gekoppelten Molekular-dynamik und Stochastic Rotation Dynamics Simulation aufbaut. Ferner wird selten in dem Maße ein quantitativer Vergleich zu experimentellen Daten angestrebt, wie wir es versucht haben. Oft werden entweder vereinfachte Potentiale verwendet, oder die Flüssigkeit wird in der Simulation vernachlässigt, oder die Ladung der Teilchen wird willkürlich festgelegt. Unser Simulationsprogramm hat sehr wohl auch seine Beschränkungen, aber wir streben so konsequent wie möglich eine quantitative Vergleichbarkeit der Simulationsergebnisse mit der realen Suspension an. Die Simulation könnte auf andere Materialien erweitert werden, z. B. auf SiO\(_2\)-Teilchen, über die es be-


Zykliche Scherung könnte sehr einfach implementiert werden und man könnte versuchen, Resonanzsäulenexperimente zu simulieren, wie sie in Kapitel 3 beschrieben sind (siehe Fig. 3.7). Viskoelastische Effekte könnte man so untersuchen. In der Simulation hat man die Möglichkeit, den äußeren Druck zu erniedrigen, so dass man möglicherweise einen Übergang von viskoser Dämpfung zu frequenzunabhängiger Dämpfung finden kann. Dieser Übergang könnte vom $pH$-Wert bzw. von der Existenz von Makroporen abhängen. In der Simulation ist es überdies möglich, einzelne Kräfte an- und auszuschalten, z. B. die Dämpfung in den Partikelkontakten, um ihren Einfluss auf die Materialeigenschaften zu sehen.

Eine weitere interessante Sache wäre es, die Wechselwirkungen auf den anisotropen Fall zu erweitern, wie zum Beispiel die Potentiale, die für Laponit vorgeschlagen wurden [5]. Die anisotropen Teilchen könnten als Ellipsoide oder einfach als zylindrische Plättchen implementiert werden. Simulationen, die Laponit modellieren, könnten Aufschluss darüber geben, wie wichtig attraktive Wechselwirkungen, wie sie von Balluff und Mitarbeitern [91] gefunden wurden für Laponit sind. Wir erwarten, dass der Rechenaufwand größer ist als für die $\text{Al}_2\text{O}_3$-Suspensionen, da die Berechnungen für anisotrope Teilchen deutlich aufwändigere werden. Hinzu kommt, dass die Teilchengröße im Nanometerbereich liegt und daher der Bereich der Zeitskalen, die für die Dynamik relevant sind, im Vergleich zu den hier diskutierten Suspensionen größer ist. Sogenannter „Mexican Clay“, der in der Region um Mexico City auftritt, wäre eine Herausforderung für ähnliche Untersuchungen, wie sie in der vorliegenden Arbeit an Schluff durchgeführt wurden. Kompression und zyklische Scherversuche, sowie Sedimentation von anisotropen Teilchen stellen ebenfalls interessante Themen für Simulationen dar. Die Mikrostruktur in Tonen hängt auch von der relativen Orientierung der Teilchen ab und in


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die Bodenmechanik haben. Das generelle Bewusstsein, Simulationen und Experimente in Verbindung zu bringen und die jeweils gewonnenen Daten quantitativ zu vergleichen, könnte durch die vorliegende Arbeit geschärft worden sein.
Chapter 2

Introduction

Colloid science is a very fascinating research field, gaining more and more importance in the last years. It closely connects physics, chemistry, material science, biology, and several branches of engineering technology. Colloidal suspensions consist of small particles with sizes approximately in the range between nanometers and micrometers. They are suspended in a liquid solvent. Their properties can be tailored by many different techniques. Examples are choosing particles made of materials with the desired properties, manipulating their surface by coating them with polymers, adjusting their interactions, e.g., by adding nano particles or salt or acid to the solvent. Many interesting questions arise and colloid science has grown to a large field of research and a lot of effort is spent on the challenging tasks of this domain. A research network dedicated to dynamical arrest in colloidal systems is financed by the European union. The German research foundation (DFG) supports several large research projects in colloid science, e.g., the “SFB Transregio 6 – Physics of Colloidal Dispersions in External Fields”, a new program “Schwerpunktprogramm 1273 – Kolloidverfahrenstechnik” on the industrial processing of colloids, and the research group “DFG-FOR 371 – Peloide” which is the framework of the present work [107]. Various books have been published reviewing the topic of colloid science [66, 86, 94, 100, 123, 128, 133] governing many different aspects.

The reason for this large interest in colloid science is that colloidal suspensions are present everywhere in our daily life. Paintings, soils, cosmetic products, and different kinds of food are only some examples. Many technical processes, e.g., in ceramics industry, are based on colloidal suspensions. According to their importance a considerable amount of research has been invested to describe colloidal suspensions from a theoretical point of view and by simulations [53, 82–84, 109] as well as to understand the particle-particle interactions [7, 30, 35, 49, 150, 152], the phase behavior [23, 69, 89, 139], the relevant processes on the microscale and their influence on macroscopic parameters [36, 106, 156]. Colloidal suspensions are in fact complicated systems, since different time and length scales are involved. The particle sizes are on a mesoscopic length scale, i.e., much larger than single atoms, but still orders of magnitude smaller than sand grains for example. On the one hand effects typical for microscopic length scales, i.e., Brownian motion and diffusion, start to become important. On the other hand observations are easier than on the atomistic length scale. Depending on the particle sizes, materials, and concentrations, different interactions are of relevance and often several of them are in a subtle interplay: electrostatic repulsion, depletion forces, van der Waals attraction, hydrodynamic inter-
action, Brownian motion, and gravity are the most important influences. The properties of the suspension strongly depend on the balance of the microscopic forces between the particles. Especially the role of attractive interactions (depletion forces as well as van der Waals attraction) have drawn attention in recent years [23, 97, 111, 125, 139].

A detailed understanding of the relevant influences is needed, if one needs to optimize industrial processes involving colloids. Seals, artificial teeth, parts for bearings, heat insulation and chemical protection coatings are some examples for the appliance of ceramics. Especially for applications, where mechanical load is imposed on ceramics parts, it is important to produce strong and homogeneous workpieces. Different consolidation techniques have been developed to achieve dense and homogeneous workpieces [90], but with oxidic ceramics this is a difficult task. However, with respect to chemical features or heat insulation and conduction properties, these ceramics are very appealing. Therefore, it would be interesting, to learn about the reasons for the inhomogeneities and to develop and to optimize processes that shall reinforce the material. A method called “direct coagulation casting” was proposed by Graule et al. [46, 47] which takes advantage of the dependency of the inter-particle potentials on the $pH$-value.

To improve this technique, and in general to learn about the influences on the homogeneity and stability of ceramic workpieces, it helps to study the interdependence of particle interactions and macroscopic properties. A key feature for the general understanding is the microstructure, i.e., the local order of particles within the suspension during processing, and the dynamics a certain microstructure is formed under given conditions, e.g., if and how fast the particles eventually form clusters. Other important properties of interest are the shear viscosity, its dependence on the shear rate or the volume fraction, specific properties for each microstructure, e.g., the cluster size distribution for the cases, when particles form clusters. With a detailed knowledge of the connections between the interactions and the microscopic structure, and their influence on the properties of the suspension, one is able to improve the homogeneity and strength of the fabricated workpiece.

In this work we focus on a suspension of $\text{Al}_2\text{O}_3$ particles which is a widely used material in ceramics [103, 114]. The material is commercially available in large quantities. It is offered as powders with different particle sizes, and in different qualities as well. The material can be used as a model material for soil mechanics [116, 118] which was the main focus of the research group “DFG-FOR 371 – Peloide” representing the context of this thesis [107]. In conjunction with soil mechanics the $\text{Al}_2\text{O}_3$ suspension can be regarded as a model for silt. Sometimes the term “peloid” (Greek: clay-like) is used which indicates that attractive van der Waals interactions are relevant. In soil mechanics one is interested in the mechanical properties of the ground. Especially for soils consisting of microscopic particles, like clays and clay-like soils, the behavior is very complex. Important properties like the shear viscosity or compressibility depend on the microscopic forces between the individual particles. Using standard methods of soil mechanics, it is possible to measure the macroscopic properties of the soil, but a deeper understanding of the underlying microscopic connections is still missing. Although the properties are poorly understood, they are of great importance for civil engineering. If buildings are constructed, one needs to know how much load can be deposited on the soil, or how big the foundation has to be made for a given subsoil. Similar arguments apply to streets in the mountains, where the
traffic loads the ground cyclically. Another very important issue is the stability of slopes in the mountains. Landslides suddenly start, and often it is not clear what the reason for the sudden event is. Since the interactions between the individual particles depend on the pH-value, for example, it is of great importance, to investigate the stability of soils against this background.

The research project “Peloide” has been founded, to investigate the interrelations of macroscopic and microscopic properties, especially of clay-like soils. The investigations should be made first on an abstract level, using model materials like Al₂O₃ suspensions for silt (clay-like) and in a second step laponite for clay. Using model materials has the advantage that the system is well defined, especially with respect to purity and particle size making it easier to develop a model.

In contrast to clays consisting of thin platelets [148] our silt particles are in first approximation spherical particles. For real clays the situation is much more complicated. The particle shape and their orientation is of relevance [5, 32–34, 147]. This leads to a rich phase behavior, for which different approaches for the microstructure have been proposed and tested in simulations and experiments [81, 91, 101, 124, 127]. The correct surface charge distribution on the particles is not known, but models have been developed to obtain an approximation for the interaction potentials [5, 140].

For spherical silt particles the description is less complex. However, due to the particle size of micrometers and below, the interplay of diffusion, electrostatic repulsion, van der Waals attraction, and hydrodynamics still renders the suspension a very complex system. Computer simulations are a powerful tool which helps to understand the statics and dynamics of complex systems like the one we are considering. We have developed a simulation code that models a Brownian suspension of interacting particles [60]. The particles are simulated using Molecular Dynamics (MD). Molecular Dynamics originally was developed to simulate the motion of molecules, however, the method can be extended by including rotation of rigid bodies and various types of interaction forces, so that it can be extended to a more general simulation method to generally solve equations of motion of rigid bodies. In this broader context it is sometimes called “Discrete Element Method” (DEM). In addition, we include hydrodynamic interactions and Brownian motion, by coupling the MD simulation to a Stochastic Rotation Dynamics (SRD) simulation which we use to simulate the solvent. SRD is a mesoscopic simulation method which was first introduced by Malevanets and Kapral [95, 96]. Assuming the particles in the MD part of the simulation to be spherical is an approximation in our program, but it suggests an isotropic surface charge distribution. This makes the description of the electrostatic interactions much easier: one can assume isotropic interactions between the MD particles. The surface charge leads to an electrostatic potential which in the absence of other charges would decay with \( \frac{1}{r} \) with \( r \) being the distance of the center of the particle. However, equally charged (co-)ions in the solvent are repelled and oppositely charged (counter-)ions are attracted by the electrostatic potential of the colloidal particle. This charge separation in turn influences the potential and leads to an exponential screening of the electrostatic (Coulomb) potential. This screened Coulomb potential, combined with an attractive van der Waals potential constitutes the celebrated DLVO potential [30, 152], suggested by Derjaguin, Landau, Vervey and Overbeek in the 1940s. DLVO theory in its original derivation is only
valid for low volume fractions, i.e., large particle distances of colloidal particles carrying low charges, and low concentration of ions. Much effort has been spent to investigate in which cases DLVO potentials may be assumed even beyond the validity of DLVO theory [7, 11, 12, 92, 106, 142]. Then a renormalized charge (called “effective charge”) and sometimes a new Debye screening length has to be used. But still the bare charge of the particles and its dependence on the surrounding conditions in the solvent is not known a priori.

The procedure to cope with this task is briefly sketched in the following (a detailed discussion follows in chapter 4): first, a charge regulation model is derived which relates the microscopic particle-particle interactions to macroscopic parameters, i.e. pH-value and ionic strength $I$, which expresses a representative concentration of ions in the solution weighted by their valency (see Eq. (3.1)). Measurements provide data about the so called “ζ-potential” of the particles which is used to adjust the remaining model parameters like density of surface sites. Second, one has to adjust the hydrodynamic interactions in the simulation code. To do so a scaling scheme is used which optimizes the efficiency of the simulation code under the constraint, that certain characteristic dimensionless numbers, e.g., the Peclé number which expresses the importance of thermal motion for the dynamics of the system, may not change. Third, viscosity measurements provide rheological data for a comparable experimental system. By this comparison, the effect of the approximations introduced by the coarse graining of the hydrodynamics can be estimated and corrected by an additional lubrication force in the MD simulation. The parameters which control the strength of the lubrication force are adjusted so that the underestimation of short range hydrodynamic forces is compensated and simulation data fits best the experimental results [58]. Finally, one can change the “experimental conditions”, i.e., pH-value and ionic strength $I$, for the charge regulation model and simulate different cases. This can be seen as an extrapolation to different experimental conditions [57].

For the different simulations various quantities can be evaluated, such as the shear viscosity, the structure factor, or the diffusion coefficient. Their dependence on the pH-value or the ionic strength $I$ can be studied. The strength of computer simulations is that one can not only reproduce what can be measured experimentally, but also other quantities which are difficult to measure. The structure factor is a good example for that. It can in principle be extracted from scattering data. However, for Al$_2$O$_3$ the scattering intensity in small angle X-ray scattering (SAXS) experiments is very low, especially for the high particle volume fraction and particle size we are interested in. Therefore, our computer simulations help to obtain structure data of the microstructure of Al$_2$O$_3$-suspensions which are quasi inaccessible by experiments.

In the following chapter we describe the experiments which were performed within the framework of the research group in which this thesis has been worked out as well. We also report briefly on the most important results of the other groups, so make the context clear, in which the investigations were undertaken. Already by carrying out a very simple sedimentation experiment, some key properties of the Al$_2$O$_3$-suspensions can be seen. Depending on the pH-value the interactions between the suspended particles change from a repulsive regime towards strongly attractive forces. In the former case particles are stabilized in suspension and in the latter one they form clusters, “flocculate”, and sedi-
The porosity of sediments is an important quantity in soil mechanics. It is tested in compression and shear experiments under an imposed confining pressure. For strongly attractive interactions, the single particles strongly tend to form clusters between which larger spaces ("macro pores") are left in the sediment. With cyclic shear experiments the frequency dependence of damping terms is investigated to learn about the processes responsible for the damping. It is likely that particle contacts determine the properties of the compressed samples and viscous effects play a minor role. On the other hand, in steady shear experiments without an additional confining pressure, the effective viscosity of the suspension is measured. It depends on the particle-particle interactions. For a fixed pH-value it can be varied by adding salt from high to low and back to high viscosity. This reflects three different regimes for the interactions among the particles. First, electrostatic repulsion hinders the particles from freely moving in the suspension. If salt is added, the repulsion is screened, therefore the mobility of the particles increases and thus, the viscosity decreases. If even more salt is added, the electrostatic interaction is further screened and the van der Waals attraction is not compensated anymore. As a result, particles form clusters and the attractive interactions between the particles lead to an increase of the suspension's viscosity. Especially these rheometric measurements are used to calibrate our simulation parameters and to check the accuracy of our results. All experiments have been carried out by our collaborators within the research group “DFG-FOR 371 – Peloide” in Karlsruhe, Germany [107].

In chapter 4 we describe the simulation method we apply. Different approaches to simulate suspensions can be found in the literature and we discuss the advantages and disadvantages of most of the common methods with regard to our problem. After that, we describe the method we apply for our simulations. First we discuss the Molecular Dynamics (MD) simulation for the colloidal particles and the particle-particle interactions directly included in the MD simulation: electrostatic repulsion, van der Waals attraction, Hertzian contact forces, as well as gravity and a lubrication force which corrects the finite resolution of the fluid simulation. After that we describe the Stochastic Rotation Dynamics (SRD) which yields the long range hydrodynamic interactions and Brownian motion. In the literature, one can find different methods to couple the colloidal particles to the fluid simulation [37, 60, 74, 105] which differ in the accuracy to which the flow around the particles is resolved. The computational effort strongly depends on the resolution used for the coarse graining of the hydrodynamics, as well as on how the coupling is implemented. We have implemented two different coupling methods which we describe at the end of that chapter.

The main goal of this work is, to be as close as possible to the experiments and to reproduce the same situation as in a real setup on the computer to quantitatively compare the results. We not only want to qualitatively describe what happens in the experiment—we are interested in a quantitative comparison of experimental and simulation results. For such complex systems, where several influences are in interplay, it is important to carefully check the relevance of all forces, otherwise one would run the risk to simulate a system which obeys a different dynamics. Two ingredients of our simulations are of central importance: realistic particle-particle interactions and accurately chosen simulation parameters. The interactions are described by DLVO-like potentials, as discussed in
chapter 4. However, the surface potential of the particles, which enters into the interaction potentials, is not a priori known. As already mentioned, we use a charge regulation model to calculate the charge of the particles and which we describe in the beginning of chapter 5. After that we present a detailed analysis of the time scales involved in the dynamical behavior of our suspension. It turns out that the typical time scales of the processes involved range from several nano seconds for the fast processes like momentum transport in the fluid up to seconds for slow processes like sedimentation. The different time scales span about eight decades which is nearly impossible to be covered by computer simulations.

However, if one arrives to rescale all quantities in a way that on the one hand preserves the main physics and on the other hand moves the characteristic time scales of the system closer to each other, one can reduce the computational effort. The time scale analysis of chapter 5 delivers the basis for such a rescaling scheme we use and which we describe in chapter 6. In our simulations we use rescaled values for viscosity, temperature, gravity, and interaction potentials. This rescaling has to be done very carefully, especially it is important to keep the order of the time scales in order to recover the characteristic features of the dynamics of the suspension. Quantities, which in chapter 5 have turned out to be in a competition, have to be scaled by the same factor. If one effect strongly dominates another one, the ratio between two characteristic quantities is much larger than unity. We assume that the physics does not change essentially if we reduce such ratios, as long as we take care that they still are considerably larger than unity. Based on this assumption, we rescale the physical quantities in our simulation. This is shown for two cases, once for each of the two coupling methods, since they differ in the spacial resolution. The values measured in a simulation have to be rescaled accordingly to be comparable to the original system.

After having discussed the setup of the simulation parameters, we describe a thermostat which we have applied for our simulation. It is based on a Monte Carlo scheme and re-scales the velocities, so that the system adopts a predefined temperature, but in contrast to other much simpler approaches, it preserves the streaming velocity and only re-scales the relative velocities which are responsible for the thermal noise in the simulation. At the end of the chapter, we turn to the discussion of boundary conditions. In our simulations we use various different boundary conditions, but we discuss two points in detail: first we discuss how we have implemented shear and then how one can deal with gravity in combination with periodic boundaries, since both of these points bury some technical problems, closely related to suspensions of attractive particles.

After this more technical chapter we turn back to the original task of simulating suspensions. Before actually running simulations, one should carry out several basic tests to ensure that the simulation method works well and the code is correct. The tests should be very simple, so that one can analytically solve the problem and compare the analytical solution to the simulation result. In chapter 7 we report on these tests. We test if the total energy in the simulation is constant and if the temperature actually fits the value we have adjusted. We check if particle rotations work correctly and how important they are with respect to the quantities we plan to investigate. We evaluate the viscosity of the fluid in the simulation and compare it to the value we have adjusted. We also check if the dependency of the sedimentation velocity of particles on their volume fraction in the suspension is a power law, as one would expect from experimental experience. All the tests confirm that
our simulation approach works well for the suspensions we are interested in.

After we have convinced ourselves that we can trust the results of the program, we can use it to learn about the suspensions we model. The results are presented in chapter 8. First an overview over the results is given and a “stability diagram” is introduced which shows a classification of the suspensions in different “microstructures”, depending on the experimental conditions expressed by pH-value and ionic strength. We distinguish three different microstructures: A clustered regime, a stable suspension and a repulsive structure. A discussion about the quantities, we use for the classification follows. The velocity profile in the shear flow is linear for a suspension, and in the clustered regime a plateau is formed. The shear viscosity shows a minimum in the suspended case and increases, as one enters the clustered regime of the stability diagram or the repulsive structure. In the first case, attractive interactions among the particles contribute to the shear resistance, in the latter case, electrostatic repulsion is responsible for an increase of the measured shear force. The viscosity found in the simulation is compared to measurements and finite size effects of the simulation are discussed. The particle-particle pair correlation function and the structure factor are used to analyze the local order of the particles. Different characteristics of the pair correlation function are found in the three different regimes of the stability diagram. Sharp peaks occurring in the clustered regime can be assigned to distinct local particle configurations. We use the nearest neighbor peak as a measure for the strength clustering process and investigate the dependence on the shear rate and the pH-value. To see if the cluster formation process depends on the length scale one is observing, we do the same analysis using the low-k-peak of the structure factor which contains information about the length scale of the system size. In principle the structure factor and the pair correlation function are complementary quantities, but for numerical reasons the structure factor turned out to yield better results. To characterize the repulsive structure, we analyze the mean squared displacement of the particles which shows a plateau for intermediate time scales, similar to observations known from glassy systems. Some of the features found by analyzing the different quantities we have mentioned, can be recognized again in the total energy contained in a simulation of a sheared suspension and last but not least first results of a newly developed cluster counting algorithm and the cluster size distribution are discussed. The mean cluster size and the total number of clusters are analyzed with respect to their time dependence and both quantities can be fitted by a power-law which allows to scale the data on a master curve.

After all the results have been presented in the main chapter of the present thesis, they are reviewed in chapter 9. They are discussed with respect to their relevance for the experiments presented in chapter 3. The main focus of this reviewing chapter is not only to summarize the results of the simulation, but more to draw the connection to the experiments, since they are the starting point, where the open questions raise.

To close this thesis the whole work, including the theoretical preparations are summarized in chapter 10 and their relevance to colloid science is discussed. An outlook is given at the end of the chapter.

In the appendix we describe our newly developed cluster recognition algorithm and we describe how we have parallelized our code and present investigations of the scaling of the code on up to 32 processors.
Chapter 3

Experiments

3.1 Introduction

This thesis has been worked out in the framework of a project of the DFG research group “Peloide”. For our numerical work we need experimental data as input for the potentials and to compare the results to findings in a real system. The experiments were carried out by the members of the DFG research group “Peloide” [107] in Karlsruhe within other projects. Some other experiments in the research group help to understand the results or they show different aspects of the underlying relations. In the research group people coming from different subjects, mainly engineers, meet to investigate properties of clay-like soils under different perspectives.

Most of the experiments are performed with $\text{Al}_2\text{O}_3$ powders suspended in water as a model material for silt. This is a widely used material in ceramics industry, and it has been selected as a model material to investigate properties of soils, because it is cheaply available in large quantities with well defined quality standards. The suspensions are analyzed using typical testing machines of soil mechanics. The aim is to enlighten the connections between particle particle interactions on the microscopic scale and macroscopic properties, such as viscosity of a soil. The volume fraction $\Phi$ of the $\text{Al}_2\text{O}_3$ material in the suspension can be varied which changes its flow behavior. However, more important and less understood is how the interactions between the particles can be varied. This is possible by changing the pH-value and the ionic strength, i.e., the representative concentration of ions in solution weighted by their valency,

$$I = \frac{1}{2} \sum_i c_i z_i^2,$$

where $c_i$ denotes the concentration of species $i$ and $z_i$ its valency. For a salt consisting of two single charged ions, e.g., $\text{NH}_4\text{Cl}$ or $\text{NaCl}$, $I$ is equal to the concentration of the salt.

3.2 Sedimentation

The most simple experiment is a sedimentation experiment: The suspension is prepared and sedimentation takes place due to gravity. In Fig. 3.1, all vessels have been filled with a
Figure 3.1: Sedimentation of $\text{Al}_2\text{O}_3$ suspensions at different $\text{pH}$-values. For increasing $\text{pH}$-value cluster formation increases which is the reason for faster sedimentation. The height sediment at the bottom of the vessel increases between $\text{pH} = 6$ and $\text{pH} = 7$, since rearrangement of the single particles in the clusters becomes impossible. The sediment therefore contains macro-pores between the individual clusters. Source: Ref. [107]

suspension, where only the $\text{pH}$-value has been varied, whereas ionic strength and volume fraction have been adjusted equally in all vessels. Sedimentation experiments of these $\text{Al}_2\text{O}_3$ suspensions were performed for four months at room temperature, then the photograph was taken. At $\text{pH} = 4$ nearly all material is still in suspension which can be seen at the turbidity. The particles are stabilized by the high charge which they carry at low $\text{pH}$-values. At $\text{pH} \approx 5 - 6$ the turbidity disappears which can be explained as follows: the charge on the particles decreases for an increasing $\text{pH}$-value. This is caused by protons which are bound to surface sites depending on their concentration in the bulk. If their concentration is changed in the bulk, the balance is shifted and the amount of “charge determining ions”, i.e., protons bound to the particle surface changes as well (for a detailed description of the theoretical background see section 5.1). The van der Waals attraction is not (over-)compensated any more, so that cluster formation sets in. The clusters sediment faster due to their larger size, compared to a single particle (compare Eq. (5.8)). But still, the attraction between the individual particles is moderate, so that the clusters stay small and the particles can easily rearrange. Around $\text{pH} = 7$ in this experiment, the attraction becomes stronger, so that rearrangement of the particles is not possible anymore. Therefore, the clusters sediment down to the bottom of the vessel and are piled up there as they have formed. They can not compactify, since particle rearrangement is inhibited by the strong attraction between them. Macro pores between the individual clusters cause the sediment to be less dense and more brittle when dried. These general investigations of the material properties are useful to design technical processes for the ceramics industry. For example, the brittleness which occurs for large $\text{pH}$-values is undesirable in a technical application for ceramic processing. Therefore, one has to avoid conditions where cluster formation is too strong during processing. On the other hand, when a workpiece has its desired shape, a certain attraction of the particles in the so-called green body (i.e., the workpiece before sintering) is desired. A controlled change of the $\text{pH}$-value by en-
3.3 Scattering Experiments

In one of the projects laponite suspensions are investigated by static light scattering and small angle X-ray scattering by Ballauff and co-workers [91]. Laponite is an artificial clay consisting of platelets of approximately 25 nm in diameter and 1 nm thick which has been intensively studied during the last years [5, 32, 51, 52, 81, 91, 101, 124, 127, 140]. The scattering experiments [91] suggest that, in contrast to the assumptions of many preceding works, short range attraction plays a role for laponite at moderate volume fractions and at relatively low ionic strengths already. In Fig. 3.2 the agreement of the structure factor extracted from experimental data and obtained by calculations within the framework of the “polymer reference interaction site model” (PRISM) [20, 54] is shown. The effective interaction potential which enters the calculations is displayed in the inset. Calculations using a purely repulsive potential could not recover all the features of the structure factor. Either

Figure 3.2: Structure factors for laponite suspensions at various volume fractions, taken from Ref. [91]. The agreement of the measured data (symbols) and the calculation (lines) can only be achieved by use of the effective potential shown in the inset, being repulsive for large separations and attractive on short distances. Using a purely repulsive potential, either the maximum or the value of $S(q \rightarrow 0)$ do not match. Different curves correspond to different times which shows the dynamics.

zyme catalyzed reaction and its application for ceramic processing has been proposed by Graule et al. [46] utilizing the dependency of the interactions on the pH-value.

3.3 Scattering Experiments

In one of the projects laponite suspensions are investigated by static light scattering and small angle X-ray scattering by Ballauff and co-workers [91]. Laponite is an artificial clay consisting of platelets of approximately 25 nm in diameter and 1 nm thick which has been intensively studied during the last years [5, 32, 51, 52, 81, 91, 101, 124, 127, 140]. The scattering experiments [91] suggest that, in contrast to the assumptions of many preceding works, short range attraction plays a role for laponite at moderate volume fractions and at relatively low ionic strengths already. In Fig. 3.2 the agreement of the structure factor extracted from experimental data and obtained by calculations within the framework of the “polymer reference interaction site model” (PRISM) [20, 54] is shown. The effective interaction potential which enters the calculations is displayed in the inset. Calculations using a purely repulsive potential could not recover all the features of the structure factor. Either
the value in the limit of small \( q \) or the height of the maximum did not agree. Consistently with the picture of attracting van der Waals forces, an increase in time of the scattering intensity at low \( q \)-vectors (shown by the different curves) can be observed for ionic strengths \((I \geq 5 \text{ mmol/l})\) [91]. This can be interpreted as an onset of cluster formation. But, even if cluster formation is inhibited by a potential barrier at lower ionic strengths, the presence of an attractive effective potential separated from the repulsive part of the potential by a barrier of moderate strength might explain the difficulties encountered when performing mechanical tests performed with laponite suspension. Results depend on the history of the material, and, under compression, the material does not stop creeping during experimental time scales as shortly discussed in the following sections. Another practical problem is caused by the low viscosity of a laponite suspension: It easily escapes through thin slits of the apparatus. Therefore, most of the experiments in this chapter did not yield useful results when they were repeated with laponite suspensions instead of \( \text{Al}_2\text{O}_3 \) suspensions. Analogous studies, as extensive as with \( \text{Al}_2\text{O}_3 \) suspensions, could not be carried out with laponite. This would have been a good comparison to see the influence of the particle shape, since, according to Ref. [91], van der Waals attraction and electrostatic repulsion are in competition in both cases, for \( \text{Al}_2\text{O}_3 \) and for laponite suspensions.

### 3.4 Soil Mechanics

In soil mechanics the structure and mechanical properties of sediments are a central point of interest. An application of the experimental setups to \( \text{Al}_2\text{O}_3 \) suspensions and other model materials can be found by M. Kölzer [50]. In the following we shortly describe some of these typical setups and the most important findings of the research group concerning \( \text{Al}_2\text{O}_3 \) and laponite, since this is in context of the present work.

In an oedometer (Fig. 3.3) experiment the soil, i.e., the highly concentrated
Al$_2$O$_3$ suspension as a model material, is compressed slowly by a constant pressure (Strictly speaking one would have to call it “stress”, since “pressure” usually denotes the isotropic part of the stress tensor, i.e., the hydrostatic pressure. However, since in soil mechanics the term “confining pressure” is often used for an externally applied stress, which may be anisotropic, we use this term here as well.) The lateral expansion is avoided by enclosing the sample in a stiff ring. On top and at the bottom of the sample water can escape through a filter stone. This compression under prevention of lateral expansion and with water outlet, is a so-called consolidation process. It reaches a final state, which then can be further compressed, if the pressure is increased. Compressibility of heterogenous soils is characterized by compression curves obtained in oedometer experiments, where compression versus pressure is recorded.

A typical quantity in soil mechanics is the pore number

\[ e = \frac{\text{pore volume}}{\text{volume of solid fraction}} = \frac{1 - \Phi}{\Phi}. \quad (3.2) \]

For clarity the relation of pore number $e$ and volume fraction $\Phi$ is plotted in Fig. 3.4. A decreased pore number denotes a compressed sample with larger volume fraction $\Phi$, whereby $e = 1$ corresponds to $\Phi = 0.5$.

In Fig. 3.5 (experiments by M. Külzer) the pore number $e$ of different Al$_2$O$_3$ suspensions is plotted against the effective confining pressure, i.e., the total confining pressure reduced by the pressure of the pore water. One can see that the pore number initially depends on the sample preparation. Depending on how much the sample is stirred during preparation, different initial pore numbers can be achieved. By increasing the pressure, the pores collapse and the sample is compressed to a value which mainly depends on the $pH$-value. For $pH = 4$ (Fig. 3.5a)) this state is not yet achieved up to a reduced pressure of $p' = 1$ MPa. The final pore number for $pH = 9$ is still larger than for $pH = 4$. This can be explained...
Figure 3.5: Results of an oedometer experiment: Compression of Al$_2$O$_3$ suspensions at pH = 4 (a) and pH = 9 (b). Depending on the sample preparation different pore numbers $e$ can be achieved. Upon compression the particle network collapses between 1 and 10 kPa and the sample is compressed to a higher density which mainly depends on the pH-value and on the stress $\sigma'_{V}$, and not on the initial pore number. Note that for pH = 9 (b) much larger pore numbers can be achieved, i.e., less densely packed sediments. The experiments were performed by M. Külzer.
by so called macro pores, i.e., pores which are larger than the mean particle diameter. The macro pores are formed, because the particles attract each other so strongly, so that a rearrangement of the particles during cluster-cluster aggregation is hindered by the attractive inter-particle forces. The resulting structure shows larger pore numbers than the one for \( p\text{H} = 4 \). When the sample is compressed by loading it with an appropriate weight, most of these pores collapse between 1 and 10 kPa, as one can see in the steep drop in the oedometer curve. Only a few of them remain, so that the pore number in the case of \( p\text{H} = 9 \) does not reach values of \( e < 1 \) unless stresses of several hundreds of kPa are applied.

However, without further investigations of the micro structure and its dependence on the potentials and the conditions (like \( p\text{H} \)-value and ionic strength \( I \), etc.) this explanation remains only an unproven picture. The present work is a contribution to gain a better understanding of the relations between the potentials, the microstructure and the effect on macroscopic properties such as the compression curves of such a suspension with attractive interactions.

Similar to the oedometer experiment, shear resistance is characterized by confined shear experiments, e.g., using a setup as depicted in Fig. 3.6. Here, a fixed vertical pressure is imposed on the sample, and the sample is then sheared slowly, while it is confined in a geometry which conserves its cross section. Expansion is only possible against the resistance of the (vertical) confining pressure. Pore-water can enter or escape through filter stones in the bottom and the top of the sample. Shear force and expansion are recorded during the experiment.

Cyclic shear experiments are performed [116, 117] using a resonance column (RC) setup as sketched in Fig. 3.7. The sample is stabilized by enclosing it in a rubber membrane. The sample is excited acoustically to rotational oscillations. Using a mass in top and at the bottom of the sample, one can select special oscillation modes or adjust the ratio of the
wave length $\lambda$ to the sample length $l$, respectively. The response of the sample to excited oscillations is recorded and analyzed with respect to its amplitude and phase behavior depending on the excitation frequency and amplitude.

In Fig. 3.8 (taken from Ref. [118]) the normalized response amplitude in an experiment with $\text{Al}_2\text{O}_3$ is plotted. The sample was compressed (“consolidated”) vertically with 50 kPa before performing the RC experiment. During the experiment an isotropic pressure of 20 kPa was applied. Band width limited random noise was used for excitation and the resulting response amplitude was recorded over several eigenmodes of the sample. Two models for the response are fitted to the data: for both of them a Kelvin-Voigt element which is a Newtonian spring in parallel with a viscous damper, was assumed to be a good description of the system. One can write down a wave equation for a torsional wave on the cylinder

$$\frac{\partial^2 \vartheta}{\partial t^2} = \frac{G}{\rho} \frac{\partial^2 \vartheta}{\partial x^2}, \quad (3.3)$$

where $G$ is the shear modulus of the sample, $\rho$ is the density, $\vartheta$ the amplitude of the torsion, and $x$ the coordinate along the axis of the cylinder. The additional masses enter into the boundary conditions, under which Eq. (3.3) is solved.

Compared to a classical Kelvin-Voigt element, the shear modulus plays the role of a spring constant. It can be calculated from the wave length or the resonance frequencies, respectively. The two models for Fig. 3.8 differ only in the way, the damper of the Kelvin-Voigt element is modeled. The first model assumes that damping is frequency independent, i.e.,
3.4 Soil Mechanics

Figure 3.8: Cyclic shear experiment with Al$_2$O$_3$, taken from S. Richter [118]. The consolidated sample was excited with broad band noise, while response amplitude is recorded. The experimental setup is shown in Fig. 3.7. Two different theoretical models of an oscillating column with different assumptions for the kind of damping are fitted to the experimental data. The model with frequency independent damping fits the measured data much better than the one that includes viscous damping.

the damping constant $\mu$ is assumed to follow $\mu \sim 1/\omega$, or $\mu \omega/G = \text{const.}$, so that the frequency dependency cancels out, when a damping term $\mu \frac{\partial \vartheta}{\partial t}$ is included in Eq. (3.3) and a harmonic ansatz $\vartheta(x,t) = \vartheta_0 \exp[i(\omega t - kx)]$ is applied in. However, from the width of only one resonance peak, let us say the first one, one can calculate the damping constant $\mu$ for this specific resonance frequency. Then, assuming a $1/\omega$ dependency, one can calculate the complete resonance curve and compare it to the measurements.

The second model assumes that $\mu$ is constant which is the case for viscous damping. The damping term $\mu \frac{\partial \vartheta}{\partial t}$ then becomes frequency dependent and higher eigenmodes are damped more strongly than compared to the case of frequency independent damping. In Fig. 3.8 one can see that the curve for viscous damping with $\mu = \text{const.}$ does not fit well the measurement data. One can conclude that the damping in the sample is due to non-viscous losses, presumably originated in the particle contacts. This statement is emphasized by the finding that the resonance curves do not depend much on the $pH$-value, and therefore are not influenced by the surface charge of the particles, as explained in section 5.1. Additionally, this finding fits well to the oedometer experiments in Fig. 3.5, where for 20 kPa already most of the macro pores have collapsed, so that one can assume that the particle network, regardless by which kind of forces it was stabilized, could not resist anymore against the confining pressure and most of the particles are already in contact. Since similar curves are measured independent on the $pH$-value it is likely that the particles are in contact. According to the findings of Fig. 3.5 it would be interesting to perform RC experiments at lower confining pressures, where the particle network still
Figure 3.9: Cyclic shear experiment performed with a consolidated laponite sample, performed by S. Richter [118]. The sample was excited with broad band noise, while response amplitudes are recorded. A comparison to two damping models is shown again. For the laponite sample also the model assuming frequency independent damping fits better than the one assuming viscous damping. Only two eigenmodes can be recorded due to the limitations of the setup. Additionally, for large frequencies the signal is very noisy.

is intact. However the column would not be stable enough to perform RC experiments at such low pressures due to the low viscosity of uncompressed samples.

In Fig. 3.9 (taken from Ref. [118]) an RC experiment was performed with a coagulated sample of laponite. To cover several eigenmodes one would have to move to larger frequencies, but the values obtained in that region are not reliable enough due to large noise. The damping seems again to be frequency independent. However, to support this, one would need to check higher frequencies as well. At low frequencies one can extract the storage and loss modulus from the response to monochromatic excitation. However, due to inertia effects of the top plate of the apparatus, the frequency range is limited to values below 3 Hz. One finds a frequency dependence in this range which might be explained by a creep rate in the laponite sample being of the same order of the shear rate. In fact, one can observe that the material creeps over long observation times. The shear modulus as well as the sample height and the damping ratio constantly change their values with time. Therefore, one has not reached a steady state corresponding to a well defined confining pressure. This causes the results shown in Fig. 3.9 to some extend to be questionable.

Scanning electron micrography (SEM), Fig. 3.10, is not a typical experiment in soil mechanics, but one can gain an intuitive impression of the material. Especially one can see the small polydispersity and the shape of the particles actually present in the sample. However, systematic evaluations of the micrographs were not performed. It turned out that the local ordering of the particles inside a sample can differ from the one seen at the surface and processes like freezing the sample and cutting it into slices would destroy the
Figure 3.10: Scanning electron micrograph of Al$_2$O$_3$ particles, taken from Ref. [21]. One can see the arrangement of the slightly irregularly shaped particles. Cryo-scanning electron micrography (SEM) has been applied to an Al$_2$O$_3$-suspension.

structure as well. However, to use SEM with non-metallic materials one needs to vaporize the surface with a thin metallic layer, for which the sample has to be solid, i.e., frozen. A computer simulation is not subject to these problems. One can easily cut out slices of larger simulations, draw the particles smaller so that they do not touch each other and one can see better inside the system, or one can render three dimensional data and rotate the simulation volume in a video sequence to be able to see it from different angles. In addition, structure data, like correlation functions or the structure factor can easily be extracted from simulation data, as it will be shown for example in section 8.4.

### 3.5 Rheometry

We describe the rheometry experiment, performed by J. Reinshagen, in more detail, since these measurements give the basis for the adjustment of our simulation parameters [58]. The material used in the rheometry experiments has been characterized to ensure that the potentials we assume are consistent with the experimental conditions. The experiments are carried out with high purity (99.97 %) α-Al$_2$O$_3$ powder (RCHP DBM, Baikowski Malakoff Industries, Inc., USA). The mean particle diameter is 0.367 µm (Coulter LS Particle Size Analyzer) and the size distribution is narrow ($d_{10} = 0.176 \mu m$, $d_{90} = 0.664 \mu m$). The powder is suspended in bidistilled water (Merck, Germany). The suspension is then dispersed with alumina balls in a ceramic container for 24 h at a small rotational speed to keep the abrasion low. Subsequently, the suspension is degassed at 50 mbar under agitation. Then, in order to reduce the ionic strength to the desired degree, the suspension is...
is purified by the dialysis technique. In this way the majority of ions are removed and a background electrolyte of a very low salt concentration (0.5 mmol/l) is obtained for suspensions of high solids loading. Starting from this master suspension, suspensions with increased ionic strength are obtained by adding different amounts of dry ammonium chloride NH₄Cl (Merck, Germany). The pH-value of the suspensions is adjusted to pH = 6 with 0.1 and 1 mol/l hydrochloric acid HCl (Merck, Germany), if necessary. Thereby the ionic strength and pH-value are revised by use of a laboratory pH- and conductivity meter (inoLab pH/Cond Level 2, WTW GmbH, Germany). The electrophoretic mobility of dilute suspensions is measured with a Coulter Delsa 440 SX. Irreversible aggregation due to inhomogeneous salt concentration is not of importance here. If the ionic strength is strongly increased and after that, a second dialysis step is performed to remove the ions again, the original viscosity is restored.

The ion concentrations of selected ions are measured before and after dialysis using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Model JY 70 plus, France). The suspensions are characterized using a Viscolab LC10 rheometer (Viscolab LM rheometer with control unit Viscolab LC10, Physica, Germany) with a cup and bob or a double gap geometry. The measurements are either performed immediately after suspension preparation, or they are stored on a roller bank to avoid sedimentation. Sedimentation during the experiment can be excluded, since it takes much longer than the whole experiment, and the shear forces are much larger than gravity. Shear rate controlled experiments are performed at a constant temperature of 20°C. The suspensions are sheared at a constant shear rate of \( \dot{\gamma} = 300/s \) (\( Pe = 8.8 \), according to Eq. (3.4)) before starting the actual ramp measurement. In the experiments the shear rate is increased up to \( \dot{\gamma} = 4000/s \) (\( Pe = 117 \)) and decreased again to zero. For comparison to other experimental or theoretical data the Peclét number of the shear flow

\[
Pe = 6\pi\eta R^3 \dot{\gamma} / k_B T,
\]

is often useful. When the suspensions are pre-sheared an occurring discrepancy between the measured viscosity in the increasing ramp and the decreasing one can be minimized. For a detailed description of the experiments see Ref. [113, 114].

In Fig. 3.11 (taken from J. Reinshagen [114]), the measured shear viscosity of an Al₂O₃-suspension is plotted for different ionic strengths. The conductivities can be converted into values for the ionic strength as denoted in the figure caption (for details see Ref. [114]). For low ionic strength the suspension shows shear thinning. The shear thinning gets less pronounced if the ionic strength is increased, until nearly a Newtonian viscosity is reached. If the ionic strength is further increased, shear thinning occurs again. This can be explained by DLVO theory and by our simulations: For low ionic strengths, the particle-particle interactions are repulsive, leading to a high viscosity. If the electrostatic interactions are screened by added ions, the viscosity decreases. If the electrostatic interaction is screened even more, the van der Waals attraction becomes more dominant and clusters are formed in the suspension which again increases the viscosity. However, that these effects are less pronounced for high shear rates must be a dynamic effect which becomes clearer by our simulation results described in chapter 8.

The experiments raise questions which may be answered by computer simulations, but one
Figure 3.11: Measured shear viscosity for different ionic strengths. The conductivities correspond to ionic strengths \( I = 0.3, 0.7, 1.5, 3, 4, 10 \) (a) and 3, 4, 10, 25, 65 mmol/l (b). For low ionic strength shear thinning can be observed. The shear thinning gets less pronounced for increasing ionic strength, until nearly a Newtonian viscosity is reached. (a) If the ionic strength is further increased, the shear thinning is recovered. (b). Experiments by J. Reinshagen [114]
has to choose an appropriate method. In the following chapter we describe our simulation
method, a coupled Molecular Dynamics and Stochastic Rotation Dynamics simulation.
We give reasons why this is an appropriate choice and later, in chapter 5 we discuss how
the input parameters for the simulation have to be adjusted.
Chapter 4

Simulation Method

4.1 Introduction

Computer simulations in general are a large field and many different methods have been developed in the recent years. Depending on the system which one wants to simulate, an appropriate method has to be chosen. For that it helps to recall the properties of the suspension we want to simulate. First of all we have small particles of sub-micrometer size, so that Brownian motion is important. Then, the particles interact by van der Waals attraction and electrostatic repulsion. There are freely moving ions in solution, which screen the electrostatic repulsion. Full hydrodynamic interactions, short- and long range couplings have to be considered.

Let us first discuss the electrostatic interactions. The surface charge on the colloidal particles is regulated by so-called charge determining ions. With a given surface charge the electrostatic field around the colloidal particles can be calculated. The ions remaining in the bulk are then influenced by the electrostatic field of the charged colloids. Several approaches to treat these so-called micro-ions have been established in the literature: Explicit simulation of micro-ions [92], density functional theory [44, 149, 150], response theory [27–29, 49], Poisson-Boltzmann cell models [31, 138, 153], and full Poisson-Boltzmann theory [14, 35, 36, 48]. Since the electrostatics is explicitly calculated, these approaches require a large computational effort and are therefore suitable only for small numbers of colloidal particles. However, in many investigations, where detailed descriptions of the micro-ions are used, it turns out that the effective interaction between the colloidal particles can be described by DLVO-like potentials [30, 152], i.e., a van der Waals interaction integrated over two particles and electrostatic repulsion by an effective charge on the colloidal particle, which is exponentially screened. The exponential screening describes the influence of the micro ions in the bulk of the solvent. In many cases this is a good description, even if certain assumptions for DLVO theory are not fulfilled [7, 79, 106, 141, 142], namely monovalent micro-ions, large particle separations, low charge of the colloidal particles. Since DLVO potentials are relatively simple pair potentials, we use them in our simulation instead of performing intensive calculations for the exact electrostatic potential. The effective charge as input parameter for the potential is not a priori known. For that we use a charge regulation model which we describe below in section 5.1.
For the decision which simulation method to use, we are left with the importance of Brownian motion and hydrodynamic interactions. There are simulation methods which address hydrodynamics, but they do not include Brownian motion, and there are ones that include thermal noise, but hydrodynamics is reduced to a simplified description. Molecular Dynamics (MD) for the water molecules could describe all effects very accurately, but this would be much too computationally demanding. Brownian Dynamics (BD) \[67, 68\] simulations include Brownian motion, but hydrodynamics is reduced to a simple Stokes force. BD with full hydrodynamic interactions \[6, 108\] utilizes a mobility matrix which has to be inverted, which takes a large amount of computing time, growing with the number of embedded particles. The matrix is a \(N \times N\) matrix, where \(N\) is the number of particles. The effort of matrix inversion usually grows with \(N^3\). However, special algorithms have been developed to reduce the effort – however, linear growth with the particle number can not be reached. In pair drag simulations \[82\] the hydrodynamic interactions are simplified as well. Due to the simplicity of the BD and the pair drag methods, one can handle large particle numbers using one of these techniques. Stokesian Dynamics (SD) \[15, 16, 109\] and Accelerated Stokesian Dynamics (ASD) \[134, 135\], include multi particle hydrodynamic interactions, but the methods are very computing time intensive for large particle numbers. The same applies to Navier Stokes solvers, to which particles are coupled \[64, 75, 76, 129, 130, 154\]. It is mathematically a very complex problem, to solve the Navier Stokes equation for a geometry with moving boundaries. However, an elegant solution is to couple the colloidal particles with so-called point-like “tracers” to the fluid, which are connected by elastic springs to the colloidal particle. This method has been applied to non-spherical particles as well \[40, 41\]. However, for high particle concentrations problems of numerical stability occur. Lattice Boltzmann (LB) is a powerful method for fluid simulation, and it has been successfully applied to particle suspensions \[80, 83–85\]. LB intrinsically does not include thermal noise, however, there are several, recently developed approaches to implicitly introduce noise in the method as well \[4, 146\]. Historically, LB has been developed to overcome the disadvantages of a much simpler method, namely Lattice Gas (LG). LG uses fluid particles which are placed on a discrete lattice, and which move along the bonds of the lattice with a fixed velocity. The main problem of LG is that the macroscopic equations of motion are not Galilean invariant due to the underlying grid. In LB the description is based on Boltzmann distribution functions, which solves the problem of non Galilean invariance. Additionally, LB is much faster and, like LG, too, it is an algorithm which is easy to parallelize. Another method developed as an improvement of LG is Dissipative Particle Dynamics (DPD) \[13, 24, 38\]. DPD includes both, hydrodynamics and Brownian motion. The method is based on fluid particles which interact via relatively soft, conservative pair potentials, complemented by a dissipative and a random force. However, for the random force, Gaussian distributed random numbers are needed and the calculation of the pair interactions is computing time intensive, as well. Reviewing the different simulation methods and their drawbacks, one may ask oneself the question, what is needed for a simple simulation method to model a fluctuating solvent: It should include thermal noise intrinsically, the algorithm should be based on very simple steps and it should mimic the hydrodynamic interactions of a real fluid. Based on these ideas, Malevanets and Kapral \[95, 96\] have developed a new method, called Stochastic Rotation Dynamics (SRD) which in the last years has successfully been applied to poly-
4.2 Molecular Dynamics (MD): Simulation of the colloidal particles

In the MD part of our simulation we represent the colloidal particles by three dimensional spheres. Various forces of different physical background act between them. In our simulation we include the following ones: effective electrostatic interactions and van der Waals attraction, known as DLVO potentials [30, 152], a lubrication force, transversal friction forces, Hertzian contact forces, and gravity.

In order to correctly model the statics and dynamics when approaching stationary states, realistic particle-particle interaction potentials are needed. As discussed above and in the literature, the interaction between the colloidal particles is well described by DLVO theory [68, 86, 90, 100, 123, 133].

DLVO potentials are composed of two terms, the first one being an exponentially screened
Coulomb potential due to the surface charge of the suspended particles. The ions in the bulk (H$_3$O$^+$, OH$^-$, and added salt, e.g., NH$_4^+$ and Cl$^-$) are influenced by the charge on the particles. Counter-ions are attracted, equally charged ions are repealed. The electric double layer is formed, where close to the colloidal particle, in the so-called “Stern layer”, the counter-ions are permanently attached to the particle, whereas more afar from the surface, in the “diffuse layer”, they are mobile.

The resulting electrostatic potential writes,

$$V_{\text{Coul}}(r) = \pi \varepsilon_r \varepsilon_0 \left[ \frac{2 + 2 R \kappa}{1 + 2 R \kappa} \cdot \frac{4 k_B T}{z e} \tanh \left( \frac{z e \zeta}{4 k_B T} \right) \right]^{2} \frac{(2R)^2}{r} \exp(-\kappa[r - 2R]), \quad (4.1)$$

where $R$ denotes the particle radius and $r$ is the distance between the particle centers. $e$ is the elementary charge, $T$ the temperature, $k_B$ the Boltzmann constant, and $z$ is the valency of the ions of added salt. Within DLVO theory one assumes linear screening, mainly by one species of ions with valency $z$ (e.g. $z = +1$ for NH$_4^+$). The first fraction in Eq. (4.1) is a correction to the original DLVO potential, which takes the surface curvature of the spherical particles into account [12].

The effective surface potential $\zeta$ is the electrostatic potential at the border between the diffuse layer and the compact layer, it may therefore be identified with the $\zeta$-potential. It includes the effect of the bare charge of the colloidal particle itself, as well as the charge of the ions in the Stern layer, where the ions are bound permanently to the colloidal particle. In other words, DLVO theory uses a renormalized surface charge which we determine by the model described in section 5.1. Smoluchowski [136] related the $\zeta$-potential to the electrokinetic mobility of the particle as

$$\mu = \frac{\zeta \varepsilon_0 \varepsilon_r}{\eta}. \quad (4.2)$$

The $\zeta$ potential can be related to the pH-value of the solvent as will be shown in section 5.1.

$\kappa$ is the inverse Debye length defined by $\kappa^2 = 8\pi \ell_B I$, with the ionic strength $I$. The Bjerrum length

$$\ell_B := \frac{\beta e^2}{4 \pi \varepsilon_0 \varepsilon_r} \quad (4.3)$$

measures the distance at which the electrostatic interaction of two elementary charges amounts $\beta^{-1} = k_B T$. $\varepsilon_0$ is the permittivity of the vacuum, $\varepsilon_r$ the relative dielectric constant of the solvent (we use 81 for water, i.e., $\ell_B = 7 \text{ Å}$ for room temperature). In Fig. 4.1 the double layer and the location of the $\zeta$ potential are illustrated.

In addition to the electrostatic repulsion, the behavior of the colloidal suspension is determined by the attractive van der Waals interaction which can analytically be integrated over the two spheres. This leads to the second part of the DLVO potential,

$$V_{\text{vdW}}(r) = -\frac{A_H}{12} \left[ \frac{4R^2}{r^2 - 4R^2} + \frac{4R^2}{r^2} + 2 \ln \left( \frac{r^2 - 4R^2}{r^2} \right) \right]. \quad (4.4)$$
4.2 Molecular Dynamics (MD): Simulation of the colloidal particles

A_H is the Hamaker constant which involves the polarizability of the particles and of the solvent. The DLVO potentials show a primary minimum for small particle separations \( r \) and depending on the parameters \( \kappa \) and \( \zeta \) there may be a secondary minimum which is separated from the primary one by an energy barrier. Examples are plotted in Fig. 4.2 for four typical parameters with different height of the barrier and depth of the secondary minimum. The primary minimum has to be modeled separately, as we discuss in the following. For polydisperse systems, where particles with different radii \( R_1 \) and \( R_2 \) interact, Eq. (4.4) has to be generalized as follows [94]:

\[
V_{\text{VdW}}(r) = -\frac{A_H}{12} \left[ \frac{C_3}{C_1} + \frac{C_3}{C_2} + 2 \ln \left( \frac{C_1}{C_2} \right) \right]
\]

(4.5)

with

\[
C_1 = r^2 - (R_1 + R_2)(R_1 + R_2)
\]

\[
C_2 = r^2 - (R_1 - R_2)(R_1 - R_2)
\]

\[
C_3 = 4R_1R_2.
\]

The generalization of Eq. (4.1) is more obvious: we replace every occurrence of \( 2R \) by the sum of the two particle radii \( R_1 + R_2 \).

Since DLVO theory contains the assumption of linear polarizability, it holds only for large distances, i.e. the singularity of Eq. (4.4) for \( r = d \), when the two spheres touch, does not exist in reality. Nevertheless, there is an energy minimum about \( 30k_B T \) deep, so that particles which come that close would very rarely become free again. To obtain numerical stability in our simulation, we remove the singularity of the DLVO potentials and model the primary minimum by a parabolic potential, some \( k_B T \) deep (e.g. \( 10k_B T \)). The depth

Figure 4.1: Schematic picture of the double layer and the location of the \( \zeta \) potential at the border between compact (Stern) layer and diffuse layer. The illustration is taken from Ref. [21].
Figure 4.2: DLVO Potentials for Al$_2$O$_3$ spheres of $2R = 0.37 \, \mu$m diameter suspended in water, close to the isoelectric point and for moderate ionic strengths. For these conditions, the secondary minimum is several $k_B T$ deep and the barrier towards the primary minimum is relatively small, as well. The primary minimum at $r/2R = 2.0$ is not reproduced correctly by DLVO theory. It has to be modeled separately.

of the minimum in our model is much less than in reality, but nevertheless the barrier between the primary and secondary minimum prevents two particles from moving apart, so that particles once trapped in the primary minimum very rarely would escape again during the simulation time.

To avoid that the particles penetrate each other, one needs a repulsive force depending on their overlap. We are using a Hertz force described by the potential

$$V_{\text{Hertz}} = K(R_1 + R_2 - r)^{5/2} \quad \text{if} \quad r < R_1 + R_2, \quad (4.6)$$

where $K$ could be expressed by the elastic modulus of Al$_2$O$_3$. This would determine the simulation time step, but to keep computational effort relatively small, we determine the time step using the DLVO-potentials as described later on and then choose a value for $K$. Two aspects have to be considered: $K$ has to be large enough so that the particles do not penetrate each other by more than approximately 10% and it may not be too big, so that numerical errors are kept small. This is the case when the collision time, assuming the Hertz contact force being the only interaction, is resolved with about 20 time steps. Otherwise total energy and momentum are not conserved well in the collision.

The Hertz force also contains a damping term in normal direction,

$$F_{\text{Damp}} = -(v_{\text{rel}}, \hat{r})\hat{r} \beta_D \sqrt{R_1 + R_2 - r}, \quad (4.7)$$

with a damping constant $\beta_D$. For the transverse direction a viscous friction proportional to the relative velocity of the particle surfaces and proportional to the Hertz force is applied
in the particle contact. However, in suspensions the contact forces are of minor importance in unless strong confining pressure is applied. Many features of the system depend on the hydrodynamic interactions.

Long range hydrodynamic interaction is taken into account in a separate simulation for the fluid as described below in section 4.3. This can only reproduce interactions correctly down to a certain level. On shorter distances, a lubrication force has to be introduced explicitly in the Molecular Dynamics simulation as described in [129]. The most dominant mode, the so-called squeezing mode, is an additional force

\[ F_{\text{lub}} = -(v_{\text{rel}} \cdot \hat{r}) \frac{6\pi \eta r_{\text{red}}^2}{r - R_1 - R_2}, \]  

with \( r_{\text{red}} = \frac{R_1 R_2}{R_1 + R_2} \)  

between two spheres with radii \( R_1, R_2 \) and the relative velocity \( v_{\text{rel}} \). \( \eta \) is the dynamic viscosity of the fluid. \( F_{\text{lub}} \) diverges if particles touch each other. To ensure numerical stability of the simulation, one has to limit \( F_{\text{lub}} \). We choose a maximum force at a certain gap width \( r_{\text{sc}} \) and shift the force so that the maximum force cannot be exceeded: instead of calculating \( F_{\text{lub}}(r) \) we take the value for \( F_{\text{lub}}(r + r_{\text{sc}}) \). In addition, since the force decays for large particle distances, we can introduce a large cutoff radius \( r_{\text{lc}} \) for which we assume \( F_{\text{lub}}(r) \equiv 0 \) if \( r - R_1 - R_2 > r_{\text{lc}} \). As the intention of \( F_{\text{lub}} \) is to correct the finite resolution of the fluid simulation, \( r_{\text{sc}} \) and \( r_{\text{lc}} \) have to be adjusted in a way that the dynamic properties, i.e., the viscosity of a simulated particle suspension with weak DLVO interactions fits the measurements. This case, for which the parameters of the lubrication force are adjusted, has to be a suspension with a minimal viscosity, i.e., a suspension without cluster formation and for which there is no considerable contribution of the electrostatic repulsion to the overall viscosity. It turns out that \( r_{\text{sc}} = \frac{R}{30} \) and \( r_{\text{lc}} = 3R \) work best. Our approach for \( F_{\text{lub}} \) is similar to the one often used in lattice Boltzmann simulations [85]. There are different approaches, e.g., for Stokesian dynamics [16], where the force field is expanded to a multi pole series and the far field part is subtracted afterwards.

For the integration of the translational motion we utilize a velocity Verlet algorithm [9, 137] to update the velocity \( \mathbf{v}_i \) and position \( \mathbf{x}_i \) of particle \( i \) with mass \( m \) according to the equations

\[ \mathbf{x}_i(t + \delta t) = \mathbf{x}_i(t) + \delta t \mathbf{v}_i(t) + \frac{\delta t^2}{2} \frac{\mathbf{F}_i(t)}{m}, \] 
\[ \mathbf{v}_i(t + \delta t) = \mathbf{v}_i(t) + \delta t \frac{\mathbf{F}_i(t) + \mathbf{F}_i(t + \delta t)}{2m}. \]

For the rotation, a simple Euler algorithm is applied:

\[ \omega_i(t + \delta t) = \omega_i(t) + \delta t \mathbf{T}_i, \]
\[ \vartheta_i(t + \delta t) = \vartheta_i(t) + F(\vartheta_i, \omega_i, \delta t), \]

where \( \omega_i(t) \) is the angular velocity of particle \( i \) at time \( t \), \( \vartheta_i(t) \) is the torque exerted by non central forces on the particle \( i \), \( \vartheta_i(t) \) is the orientation of particle \( i \) at time \( t \), expressed
by a quaternion, and $F(\vartheta_i, \omega_i, \delta t)$ gives the evolution of $\vartheta_i$ of particle $i$ rotating with the angular velocity $\omega_i(t)$ during the time step $\delta t$.

The concept of quaternions \cite{9, 10} is often used to calculate rotational motions in simulations, because the Euler angles and rotation matrices can easily be derived from quaternions. Using Euler angles to describe the orientation would give rise to singularities for the two orientations with $\vartheta = \pm 90^\circ$. The numerical problems related to this fact and the relatively high computational effort of a matrix inversion can be avoided using quaternions.

### 4.3 Stochastic Rotation Dynamics (SRD): Simulation of the Fluid

In the introduction of this chapter, section 4.1, we have already discussed that there are many different approaches to simulate a fluid. Most of the methods introduce certain approximations to reduce the computational effort. They all have their strengths and drawbacks, and it depends on the system one is interested in, which method is best suitable in the particular case. We apply the Stochastic Rotation Dynamics method (SRD) introduced by Malevanets and Kapral \cite{95, 96}. The method is also known as “Real-coded Lattice Gas” \cite{74} or as “multi-particle-collision dynamics” (MPCD) \cite{120}. It is easy to implement, intrinsically contains fluctuations, and it is a robust algorithm which runs stable, even for large volume fractions of embedded colloidal particles. The method is based on so-called fluid particles with continuous positions and velocities. Each time step is composed of two simple steps: one streaming step and one interaction step. In the streaming step momentum is transported, and in the interaction step an exchange of momentum between different directions takes place. The interaction step is modeled by a simultaneous stochastic rotation of the relative velocities of several particles. The dynamics is explicitly constructed to conserve mass, momentum, and energy, and the collective rotation is the most simple artificial interaction consistent with these conservation laws. It has been shown that there is an $H$–theorem for the dynamics and that this procedure yields the correct hydrodynamic equations for an ideal gas down to a length scale of the order of the grid resolution of the method \cite{95}.

Let us discuss the algorithm in detail, now. In the streaming step the positions of the fluid particles are updated as in the Euler integration scheme known from Molecular Dynamics simulations,

$$r_i(t + \tau) = r_i(t) + \tau \mathbf{v}_i(t),$$

(4.14)

where $r_i(t)$ denotes the position of the particle $i$ at time $t$, $\mathbf{v}_i(t)$ its velocity at time $t$ and $\tau$ is the time step used for the SRD simulation.

After updating the positions of all fluid particles they interact collectively in an interaction step which is constructed to preserve momentum, energy and particle number. The fluid particles are sorted into cubic cells of a regular lattice and only the particles within the same cell interact among each other. Interaction means, momentum is exchanged among
the particles, but total energy and momentum have to be conserved. The artificial interaction is designed to obey these constraints and to be very simple, i.e., computationally cheap: each cell \( j \) is treated independently. First, the mean velocity of cell \( j \)

\[
u_j(t') = \frac{1}{N_j(t')} \sum_{i=1}^{N_j(t')} v_i(t)
\]  

(4.15)
is calculated, where \( u_j(t') \) denotes the mean velocity of cell \( j \) containing \( N_j(t') \) fluid particles at time \( t' = t + \tau \). Then, the velocities of each fluid particle in cell \( j \) are updated as

\[
v_i(t + \tau) = u_j(t') + \Omega_j(t') \cdot [v_i(t) - u_j(t')].
\]

(4.16)

\( \Omega_j(t') \) is a rotation matrix which is independently chosen at random for each time step and each cell. There is a great deal of freedom in how the rotation step is implemented [70, 95], since, by construction, the local momentum and kinetic energy are invariant. Different implementations of the rotation step, e.g., different rotation angles, influence the viscosity of the simulated fluid [71, 72, 119]. We use rotations about one of the coordinate axes by an angle \( \pm \alpha \), with \( \alpha \) fixed [144].

The coordinate axis as well as the sign of the rotation are chosen at random, resulting in 6 possible rotation matrices. Especially for \( \alpha = \pm 90^\circ \) one obtains the most simple rotation matrices one can imagine in 3D, since they only contain entries out of \( \{0, \pm 1\} \):

\[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & 1 \\
0 & 1 & 0
\end{pmatrix},
\begin{pmatrix}
0 & 1 & 0 \\
-1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix},
\begin{pmatrix}
0 & 0 & 1 \\
0 & 1 & 0 \\
-1 & 0 & 0
\end{pmatrix},
\begin{pmatrix}
1 & 0 & 0 \\
0 & 0 & -1 \\
0 & 1 & 0
\end{pmatrix},
\begin{pmatrix}
0 & -1 & 0 \\
1 & 0 & 0 \\
0 & 0 & 1
\end{pmatrix},
\begin{pmatrix}
0 & 0 & -1 \\
0 & 1 & 0 \\
1 & 0 & 0
\end{pmatrix}.
\]

(4.17)

In this special case the rotations reduce to a procedure of simply permuting the entries for coordinates and a change of sign. This has been suggested by M. Strauß [144]. In every time step for each cell one of these 6 possibilities is chosen with equal probability \( 1/6 \). However, any stochastic rotation matrix consistent with detailed balance can be used.

The mean velocity \( u_j(t) \) in the cell \( j \) can be seen as streaming velocity of the fluid at the position of the cell \( j \) at the time \( t \), whereas the difference \( [v_i(t) - u_j(t')] \) entering the interaction step can be interpreted as a contribution to the thermal fluctuations. Thus, to calculate the local temperature in the cell under consideration one has to sum over the squares of this expression.

In order to remove low temperature anomalies and to achieve exact Galilean-invariance, we use a modification of the original algorithm [70]: the grid of SRD cells is shifted by a random vector with components in the interval \([-\alpha/2, \alpha/2]\) before the collision step. The random vectors of consecutive iterations are uncorrelated. Ihle and Kroll have discussed [71, 72] why this simple procedure works and have shown that it leads to transport coefficients independent of an imposed homogeneous flow field. In Ref. [73] and Ref. [78] analytical calculations of the transport coefficients in this method are presented.
Finally, having an MD simulation for the colloidal particles and an SRD simulation for the fluid, a remaining task is to couple the two of them consistently. The fluid particles have to interact with the colloidal particles and transfer momentum from one to the other part of the whole simulation, while globally momentum conservation has to be fulfilled.

Three different methods to couple the SRD and the MD simulation have been introduced in the literature. Inoue et al. proposed a way to implement no-slip boundary conditions on the particle surface [74]. This is the most accurate one in resolving the local velocity field around the colloidal particles. Lubrication effects are reproduced well by this coupling method. Padding and Louis very recently came up with full slip boundaries, where the fluid particles interact via Lennard-Jones potentials with the colloidal particles [105]. Usually no slip boundaries are needed on the particle surface, but Padding and Louis show that it is possible to correct the effect of the different boundary condition by assuming a different hydrodynamic radius of the embedded particles. Finally, Falck et al. [37] have developed a “more coarse grained” method which resolves the velocity field only down to a length scale of the particle diameter. On the other hand the method becomes much faster because of the lower resolution.

We have implemented two coupling methods, one of them, which we call “coupling I”, is similar to the one proposed by Inoue et al., and the other one, “coupling II”, is the collective rotation of Falck et al.. Depending on what we plan to measure, we use either of them. With both coupling methods the long range hydrodynamic interactions are reproduced. In the following sections we describe both coupling methods.

4.4 Coupling I: Placing Fluid Particles Outside of Colloidal Particles

Following the ideas of Inoue et al. [74], this coupling method implements no-slip boundary conditions on the surface of the colloidal particles. In addition, it transfers of course momentum between colloidal and fluid particles, and it equilibrates the colloidal particles to the temperature of the fluid. In our implementation an additional thermostat is included in this coupling method. It works as follows: after each streaming step one checks for each fluid particle $i$, if its new position $r_i(t + \tau)$ is within a colloidal particle and if yes, one has to modify its position and velocity. Since total momentum has to be conserved, one has to make sure that the change of momentum of the fluid particle is transferred to the suspended colloidal particle. The calculations described in the following are done in a frame fixed on the colloid particle.

One can think of several different methods to assign a new position to the fluid particle, which have been shown to work properly:

1. place it on the shortest distance to the surface of the colloidal particle and move it with its new velocity half of a time step,

2. place it on the shortest distance to the surface and move it with its new velocity a fraction of a time step, which is randomly chosen,
3. calculate the point and the exact time when the fluid particle has entered into the
colloidal particle and move it back to there. Then choose a new velocity and move
the fluid particle with the new velocity for the remainder of the time step.

Just to place the fluid particle directly on the surface and move it again in the next time
step turned out to produce an increase of the fluid particle density around the colloidal
particle. Anomalies in the fluid temperature can also be found when the fluid particles are
placed directly on the colloid surface. Placing the fluid particles on the surface and moving
them with a whole time step or moving them back for one time step and forward again
with a new velocity leads to a decrease of the fluid particle density around the colloidal
particle.

However, the methods listed above turned out to work, where the third one is more accu-
rate than the first ones, but more computationally intensive as well. Finally, we have de-
cided to use the second one. To increase stability of the simulation, we use a thermostat in
the collision step and choose the new velocities according to a given distribution. The new
velocities should point from the colloid surface to the outer area. Since the interior of the
colloidal particle usually does not contain any fluid particles, no fluid particles can move
from inside to outside in the streaming step. But, in equilibrium the velocity distribution
of the fluid particles should be the same everywhere, even locally and in any testing vol-
ume. Especially this should be valid in the vicinity of a colloidal particle. Consequently,
the fluid particles reflected in the coupling step have to compensate the consequences of
the fact that in the streaming step no fluid particles can leave the interior of a colloidal par-
ticle (since there are no fluid particles). Therefore the velocity distribution for the newly
chosen fluid particle velocities has to be the same as if the space inside the suspended
particle was filled with fluid particles and these imaginary fluid particles were passing
through the colloid surface. Imagine, they have the same density and temperature as in
the remainder of the fluid bath. Then, one could evaluate the velocity distribution for the
reflected fluid particles by taking the velocity distribution of the imaginary fluid particles
passing through the colloid surface. But it is a non-trivial task to analytically calculate
this distribution for a spherical area. However, if the mean free path of the fluid particles
is small compared to the diameter of the colloidal particles, we can safely assume the col-
loid surface to be an infinitely extended plane separating the space into two regions [74].

Then, one finds the following distribution:

\[
p(v_n) \sim v_n \exp(-\beta v_n^2), \quad (4.18)
\]

\[
p(v_t) \sim \exp(-\beta v_t^2), \quad (4.19)
\]

with \( \beta = \frac{m_f}{2k_B T} \),

where \( v_n \) is the normal component and \( v_t \) is the tangential component of the fluid particle
velocity in the frame fixed to the surface of the colloidal particle. \( m_f \) is the mass of a
fluid particle. In chapter 5 we describe how \( m_f \) has to be chosen. \( T \) is the temperature to
which this thermostat is adjusted and the whole system will adopt this temperature after a
transient time. The tangential component can be obtained by computing \( \sqrt{x_1^2 + x_2^2} \) of two
independent and Gaussian distributed random variables.
Since the fluid particles of the SRD are artificial particles within the context of this mesoscopic simulation method, their mean free path and their momentum are different from the corresponding values for single solvent molecules. Because of this, there is a depletion force acting on colloidal particles which is much larger than in reality. Depletion forces are only relevant in systems with very big molecules, e.g., polymer solutions with added small particles or binary mixtures of particles with clearly separated diameters. There, each of the small particles carries a considerable momentum - which is also the case in the SRD simulations. Nevertheless, unrealistically high depletion forces can be suppressed by reflecting fluid particles many times: if after the collision step the fluid particle is placed in another colloidal particle, the collision step is repeated for that colloidal particle and so on, until the fluid particle reaches a position outside any colloidal particle or until a maximum number $N_{\text{max}}$ of collisions has been calculated through. We have measured the depletion force and found out that a limit of $N_{\text{max}} \sim 10$ is a good compromise between computational speed and accuracy. The depletion force does not decay substantially stronger if the limit is increased, but the computational effort still grows with $N_{\text{max}}$ (at most linearly), because some fluid particles are trapped in a small gap between two colloidal particles and jump from one to the other. This in fact would still decrease the depletion force, but in the mean time the calculation for the remaining system is interrupted until finally eventually one single fluid particle is reflected the very last time. It is obvious that this scenario can easily be truncated. The remaining depletion force can be neglected at least in the cases where other, stronger forces are present in the MD simulation, e.g., attractive van der Waals forces or repulsive electrostatic forces.

### 4.5 Coupling II: Rotating Velocities of the Colloidal Particles

A second possibility to couple the SRD and the MD simulation is to sort the colloidal particles into the SRD boxes and include their velocity in the rotation step [37, 155]. This can be used, when the resolution of the hydrodynamic flow field has not to be resolved exactly, i.e., for low volume fractions, or when particle rotations are negligible. The mean velocity in each cell has then to be weighted with the mass of the particle (because the mass of colloid particles differs at least by one order of magnitude from the one of the fluid particles and their inertia dominates the flow field next to it). The calculation of the mean velocity $u_j(t')$ in Eq. (4.16) is modified to

$$
\mathbf{u}_j(t') = \frac{1}{M_j(t')} \sum_{i=1}^{N_j(t')} \mathbf{v}_i(t) m_i,
$$

with

$$
M_j(t') = \sum_{i=1}^{N_j(t')} m_i,
$$

where we sum over all colloidal and fluid particles in the cell, so that $N_j(t')$ is the total number of both particles, fluid plus colloidal ones. $m_i$ is the mass of the particle—
colloidal or fluid particle—with index \(i\) and \(M_j(t')\) gives the total mass contained in cell \(j\) at time \(t' = t + \tau\).

The coupling acts on the center of mass of the colloidal particles and affects only the fluid particles within the same cell. This means, to affect the same area of the flow field like in reality, one has to choose the cells to be of the same size as the colloidal particles. Obviously, the mesh size is drastically larger than in the first coupling method and the flow field cannot be resolved in detail. The fact that colloidal particles push away the solvent as well as depletion and lubrication forces cannot be reproduced with this coupling, since the fluid particles are allowed to be inside the colloidal particles.

This coupling method does not enforce no-slip boundaries on the particle surface, as in coupling method I. However, as very recently discussed by Padding and Louis [105], purely radial interactions effectively introduce slip boundary conditions. But, considering the drag coefficient only a pre factor changes and this could be corrected by considering a different hydrodynamic radius. The hydrodynamic radius can be measured, if the Stokes velocity or the diffusion constant of a single particle is measured in a simulation.

To see the influence of the coupling method and of the hydrodynamic interactions in general, we have in some simulations varied the resolution of the SRD simulation, we have changed the density of the fluid, and we have removed the fluid completely. We have compared the two coupling methods, as well. In sedimentation simulations, with both coupling methods, we could find a power law dependence of the sedimentation velocity, as experimentally found by Richardson and Zaki [115], (see section 7.3). In simulations of shear flow, the achieved shear rate as well as the viscosity differed strongly, if the fluid was completely removed, whereas the difference between the two coupling methods was in the order of some per cent only. The change of the density of the fluid by a factor of two did not influence much the viscosity of the suspension. Therefore, we can say that we need hydrodynamics to some extent, but for many investigations, we may choose coupling method II with less computational effort.
Chapter 5

Physical Background

5.1 The Charge Regulation Model

The colloidal particles we use consist of polycrystalline Al₂O₃. When they are suspended in water, so-called charge determining ions are bound to distinct surface sites. These sites in general are irregularities of the electron density at the surface, as they occur due to defects in the crystal structure, e.g., at the grain interfaces. The adsorption of the ions determines the total surface charge, and therefore the surface potential of the colloidal particles which enters the DLVO potential.

The potential difference between surface and bulk in turn influences the process of ion adsorption. We model this charge regulation process with a so-called $2p\mathbf{K}$ charge regulation model. Within this model two parts are needed to describe the regulation process: the first part describes the relation between surface charge density and surface potential due to the electrolytic environment, whereas the second part quantifies the ion adsorption depending on the surface concentration of charge determining ions.

Concerning the first part, a relation between the surface charge density $\sigma$ and the surface potential $\zeta$ of a charged spherical colloidal particle of radius $R$ immersed in an electrolytic environment of relative dielectric constant $\varepsilon_r$ and ionic strength $I$ is given within Debye-Hückel theory $[25, 99]$ by

$$\zeta = \frac{R\sigma}{\varepsilon_0\varepsilon_r(1 + \kappa R)},$$

where $\varepsilon_0$ denotes the dielectric constant and $\kappa$ the inverse Debye screening length. In our model, the surface charge density $\sigma$ includes all ions which are permanently bound to the surface. This means that we consider the Stern layer as a part of the surface charge and thus, we can identify the effective surface potential in DLVO theory with the $\zeta$-potential. Outside the Stern layer, the exponentially screened Coulomb potential of the DLVO potentials has been shown to work accurately for large particle distances, i.e., if the Stern layers do not overlap. For small particle separations the potential differs from the exponentially screened shape. This difference can be corrected by assuming an effective surface charge which reproduces the correct far field $[7, 11, 142]$. However, the bare charge of the particles cannot be measured nowadays, because there is no technique to measure such small charges in situ. However, it is possible to determine the $\zeta$-potential indirectly by measuring the electrophoretic mobility of the particles. Taking the measured $\zeta$-potential and
using it as an effective surface potential is the most reasonable ansatz. Then, by definition, the ions of the Stern layer belong to the surface charge.

In the second part of our model, the adsorption of charge determining ions on the surface of the colloidal particle is described by assuming that the only mechanism of adsorption is that of protons (H\(^+\)) on surface sites (\(-S\)). It turned out that this assumption leads to reasonable results for surfaces made of Al\(_2\)O\(_3\). Adsorption is described by the two chemical reactions [18]

\[
\begin{align*}
-\text{S}^- + \text{H}^+ & \rightleftharpoons -\text{SH}, \\
-\text{SH} + \text{H}^+ & \rightleftharpoons -\text{SH}^2+,
\end{align*}
\]

(5.2) (5.3)

with the two reaction constants

\[
K_1 := \frac{[-\text{S}^-][\text{H}^+]}{[-\text{SH}]} \exp(-\beta e \zeta),
\]

(5.4)

\[
K_2 := \frac{[-\text{SH}][\text{H}^+]}{[-\text{SH}^2]} \exp(-\beta e \zeta).
\]

(5.5)

In terms of the surface site concentrations, the total number of surface sites per area and the surface charge density are given by

\[
N_S = [-\text{S}^-] + [-\text{SH}] + [-\text{SH}^2],
\]

and

\[
\sigma = -e[-\text{S}^-] + e[-\text{SH}^2],
\]

respectively. Defining

\[
pK_1 := -\log_{10}(K_1)
\]

and

\[
pK_2 := -\log_{10}(K_2)
\]

yields the point of zero charge \(pH_z\), i.e., the \(pH\) value of vanishing surface charge, as

\[
\Delta pK := pK_1 - pK_2
\]

The surface site density \(N_S\) and the difference \(\Delta pK\) are treated as adjustable parameters.

The above equations lead to the relation

\[
\frac{\sigma}{eN_S} = \frac{\delta \sinh(\psi_N - \beta e \zeta)}{1 + \delta \cosh(\psi_N - \beta e \zeta)}
\]

(5.6)

with the Nernst potential

\[
\psi_N := \ln(10)(pH_z - pH)
\]

and

\[
\delta := 2 \cdot 10^{-\frac{\Delta pK}{2}}.
\]

Equations (5.1) and (5.6) can be solved numerically for \(\zeta\) as a function of \(pH\) using an iteration scheme. For our system of Al\(_2\)O\(_3\) particles we find \(\Delta pK = 4.2\) and \(N_S = 0.22/\text{nm}^2\). With these values the measured \(\zeta\)-potential of 52 mV at \(pH = 6\), \(I = 10\ \text{mmol/l}\) and up to 110 mV at \(pH = 4\), \(I = 10\ \text{mmol/l}\) can be reproduced best. For the experimental determination of the \(\zeta\)-potential electrophoretic (Delsa 440SX, Beckman-Coulter GmbH, Germany) and electrokinetic measurements (AcustoSixer IIs, Colloidal Dynamics Ind., USA) were performed. To calculate the \(\zeta\)-potential Henry’s theory [86] was used. The result of one of the titrations is shown in Fig. 5.1, but the ionic strength was adjusted by use of KCl. The measured values slightly depend on the method and the solvent. For details see Ref. [21, 114].

Using the model described above, we can calculate the \(\zeta\)-potential for a given \(pH\)-value and ionic strength \(I\). In Fig. 5.2 we show the calculated \(\zeta\)-potentials for selected ionic strengths in the range, where measurements of the shear viscosity were performed. The shape of the plots reflects the fact, that a \(2pK\) charge regulation model was used, meaning that two reactions with different reaction constants were included in the model. This allows to obtain a second plateau for low \(pH\)-values.
5.2 Brownian suspensions: A Time Scale Analysis

In Brownian suspensions many different influences are in a subtle interplay. The size of the particles is on a length scale, where van der Waals attraction may become important. The electrostatic repulsion, discussed in the previous section, competes with the attraction. The combination of both interactions is known as DLVO potentials. These potentials exhibit, depending on the conditions, a minimum or a barrier of in the order of some $k_B T$, i.e., the DLVO forces compete with the thermal motion. Additionally, gravity and diffusion are in competition as well.

This situation renders the system very complicated. To cope with this, let us have a look at the time scales occurring in the system. Each process or force defines its own time scale, and they differ by several orders of magnitude. Therefore, brute force simulations of systems of an acceptable size are impossible to run with present computers. However, one can define dimensionless characteristic numbers, such as the Reynolds- or the Peclét number as the ratio of two time scales. If one can manage to adjust the simulation parameters such that all these characteristic numbers are the same as in the experiment, the simulations should, within the assumptions of the model, exactly reproduce the dynamical

---

Figure 5.1: Measured $\zeta$-potential for Al$_2$O$_3$ particles at $I = 10$ mmol/l, adjusted with KCl, then titrated starting at $pH = 3$. More accurate measurements yielded slightly different values, taken from Ref. [21]. The points are measured data, connected by straight lines. The position of the isoelectric point, i.e., the point of zero charge, slightly depends on the measuring technique.

One desires to perform simulations for the same conditions as measurement data has been recorded, to obtain information about the respective microstructure. For the $pH$-value the range from $pH = 4$ up to the isoelectric point at $pH = 8.7$ is interesting. Below $pH = 4$ the Al$_2$O$_3$-particles start to be dissolved. Beyond the isoelectric point, the $\zeta$-potential is symmetric, but it is more difficult to experimentally adjust high potentials.
behavior present in reality.

However, reproducing all dimensionless numbers exactly, would mean, to keep the ratios of the timescales as they are. To reduce the computational effort, one has to change the parameters in a way that brings the timescales closer together, but keeps their order. In terms of dimensionless numbers this means, e.g., in sedimentation processes, where the Reynolds number is much smaller than unity, to make it larger, but to take care that it is still kept smaller than unity. The behavior of the system is not changed substantially by this modification, in contrast to the computational effort which may be reduced dramatically.

For Brownian suspensions, however, one has to be careful not to change significant dimensionless numbers, i.e., ones that are close to unity, and not to change the order of the timescales involved. In the following, we accurately inspect all the processes and timescales occurring in a Brownian suspension. Then, we decide which of them can be modified and how the simulation parameters have to be adjusted to achieve a realistic simulation. The results of the following analysis are plotted in Fig. 5.3. The different characteristic times are plotted depending on the particle radius for the real suspension (a) and for the simulation (b), where the time scales were moved closer to each other by the scaling scheme presented in chapter 6. The dashed vertical line denotes the particle size of most of our simulations corresponding to the mean particle size of the material used for the experiments.

We start with the largest scales. After a transient time, an isolated spherical particle of radius $R$ sedimenting in a liquid reaches the so-called Stokes velocity,

$$
\nu_S = \frac{2}{9} \frac{R^2 g}{\nu} \left( \frac{\rho_m}{\rho_w} - 1 \right).
$$

(5.7)

$\nu$ is the kinematic viscosity, $g$ denotes gravity, $\rho_m$ is the mass density of the particle, $\rho_w$...
Figure 5.3: Time scales found in reality (a) and in the simulation (b), depending on the particle radius. By applying the scaling scheme presented in chapter 6 the characteristic times in the simulation are closer to each other, which reduces the computational effort. Note: the vertical axis is scaled differently in Fig. a) and b). The dashed vertical line denotes the particle size of the suspensions we are focusing on in the present work. For the definition of the different characteristic times see the details in the text.
the mass density of the solvent. This velocity is obtained from the force balance between buoyancy and weight of the particle, 

$$F_G = \frac{4}{3} \pi R^3 (\rho_m - \rho_w) g$$

and the drag-force in a viscous fluid, 

$$F_D = 6 \pi \nu \rho_w R v.$$ 

The time for a particle to move a distance of its diameter, \(2R\), is denoted by 

$$\tau_S = \frac{2R}{v_S} = \frac{9\nu}{R g \left(\frac{\rho_m}{\rho_w} - 1\right)}.$$ 

The drag-force \(F_D\) also defines the mobility \(\mu = v/F_D = 1/(6\pi \nu \rho_w R)\) of a spherical particle. By means of the Einstein-relation \(D = \mu k_B T\) we obtain the diffusion constant \(D\) for the particle,

$$D = \frac{k_B T}{6 \pi \nu \rho_w R}.$$ 

The mean squared displacement of a diffusing particle in each dimension \(i\) is given by 

$$\langle x_i^2(t) \rangle = 2D t,$$

hence, the time the particle needs to diffuse a distance of \(2R\) is of the order of 

$$\tau_D = \frac{2R^2}{D} = \frac{12\pi \nu \rho_w R^3}{k_B T},$$ 

which we call diffusion time.

The ratio \(\tau_D/\tau_S\) measures the importance of Brownian motion in the system and is called Péclet number, \(P\varepsilon = \tau_D/\tau_S\). Inserting the definitions for \(\tau_D\) and \(\tau_S\), one notices that \(P\varepsilon\) depends on the fourth power of the radius \(R\),

$$P\varepsilon = \frac{v_S R}{D} = \frac{F_G R}{k_B T} = \frac{4\pi g R^4 (\rho_m - \rho_w)}{3k_B T}.$$ 

Let us consider another time proportional to \(\tau_D\): we assume a regular three-dimensional, cubic array of spheres. To achieve a given volume fraction, they have to be separated by a gap 

$$d_G = R \left(\frac{3}{\sqrt{4\pi}} - 2\right).$$ 

The time one sphere diffuses the distance of a gap \(d_G\) is given by 

$$\tau_G = \tau_D d_G^2/4.$$ 

Another important time is the particle relaxation time which is the time it takes for a particle to react on an imposed force. Consider Newton’s equation, 

$$m \frac{\partial v}{\partial t} = -\xi v + F,$$

for a particle of mass \(m\) subjected to an external force \(F\), while a friction coefficient \(\xi\) describes damping effects. Expanding the velocity \(v\) around the stationary state, \(v = v_S + \delta v\), gives

$$\frac{\partial \delta v}{\partial t} = -\frac{\xi}{m} \delta v.$$
5.2 Brownian suspensions: A Time Scale Analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle radius $R$</td>
<td>$0.185 , \mu m$</td>
</tr>
<tr>
<td>Particle volume fraction $\Phi$</td>
<td>$25%$</td>
</tr>
<tr>
<td>Temperature $T$</td>
<td>$295 , K$</td>
</tr>
<tr>
<td>mass density of particle $\rho_m$</td>
<td>$3.9 \cdot 10^3 , \text{kg/m}^3$</td>
</tr>
<tr>
<td>mass density of water $\rho_w$</td>
<td>$1.0 \cdot 10^3 , \text{kg/m}^3$</td>
</tr>
<tr>
<td>Boltzmann constant $k_B$</td>
<td>$1.38 \cdot 10^{-23} , \text{J/K}$</td>
</tr>
<tr>
<td>kin. viscosity of water $\nu$</td>
<td>$10^{-6} , \text{m}^2/\text{s}$</td>
</tr>
<tr>
<td>gravity $g$</td>
<td>$9.81 , \text{m/s}^2$</td>
</tr>
<tr>
<td>Hamaker constant $A_H$ of $\text{Al}_2\text{O}_3$ in $\text{H}_2\text{O}$</td>
<td>$4.76 \cdot 10^{-20} , \text{J}$</td>
</tr>
<tr>
<td>width of the primary minimum $l$</td>
<td>$0.007 , \mu m$</td>
</tr>
</tbody>
</table>

Table 5.1: Parameters for the simulation

which leads to an exponential decay on a time scale $\tau_P = m/\xi$. Identifying the friction $\xi$ with $1/\mu$ and inserting the mass leads to

$$\tau_P = \frac{2}{9} \frac{R^2 \rho_m}{\nu \rho_w}. \tag{5.16}$$

Let us now turn to the time it takes for the fluid to transport momentum, by diffusion, on a distance of the particle diameter. This time scale $\tau_F$ follows from simply inserting the given parameters in the diffusion equation, $(2R)^2 = 2\nu\tau_F$, which leads to

$$\tau_F = \frac{2R^2}{\nu}. \tag{5.17}$$

The particle Reynolds number may be defined as the ratio of momentum transport by motion of the particles, e.g., by sedimentation, and the momentum transport in the fluid. Here we have

$$Re = \frac{\tau_F}{\tau_S} = \frac{R \nu_S}{\nu}. \tag{5.18}$$

Finally, we have to discuss another important short time scale due to a short range potential among the colloidal particles. This scale usually determines the maximum time step in the Molecular Dynamics algorithm. Guided by the analogy to a harmonic oscillator with frequency $\omega = \sqrt{k/m}$, we replace the spring constant $k$ with the second derivative of the inter-particle potential $\partial^2 V(R)/\partial R^2$ and use the period of this oscillation to define the interaction time scale

$$\tau_V = \frac{2\pi}{\omega} = 2\pi \sqrt{\frac{ml^2}{A_H}}, \tag{5.19}$$

where we approximate the derivative of the potential by means of the Hamaker-constant $A_H$ as a typical size of the potential and a typical distance $l$ such as the width of the primary potential minimum of the DLVO potentials. Comparison of $\tau_V$ and $\tau_P$ can answer the question, whether the oscillations of two particles around the primary or secondary
minimum are visible or whether the creeping or over-damped case is realized where friction is dominating over inertia. Analyzing a harmonic oscillator with damping constant $\xi$ one finds that creeping is established at

$$\tau_P \leq \frac{\tau_V}{4\pi}. \tag{5.20}$$

In using this relation a lubrication force described in Eq. (4.8) has to be taken into account. This force is proportional to the difference of normal velocities of two approaching particles and in this sense it can be seen as an additional contribution to the friction coefficient. It becomes huge at short inter-particle distances $d_G$. It not only prevents particles from oscillating in the primary minimum of the DLVO potentials, but the damping force is even that strong, that it has to be limited by the cutoff radius we introduced in Eq. (4.8).

To determine the time step in the MD simulation, one needs to consider the lubrication force in addition to the curvature of the inter-particle potentials.

The determination of parameters for a mesoscopic model to quantitatively compare with experiment is a non-trivial task. Typical values of the parameters in an experiment are listed in Tab. 5.1. For these values of the parameters in the experiment all the time scales defined in the previous section are calculated and listed in Tab. 5.2. Knowing the characteristic time scales, we can calculate the Peclét number $Pe = \tau_D/\tau_S = 0.034$. At first glance one might have the impression that this is far from a competition between diffusion and sedimentation, but, as we have seen in Eq. (5.12) the Peclét number strongly depends on the particle radius. To illustrate this, we have calculated the time scales for a particle radius to $R = 0.4 \mu m$ at the same conditions and shown the results in Tab. 5.2. Note that the time scales for the fluid properties also change, but only because the length scale to which we refer is the particle diameter which we have changed. The Peclét number for this case is $Pe = \tau_D/\tau_S = 0.7$ which tells us that sedimentation and diffusion indeed are in a competition for this system with only about twice the particle radius as the one mentioned before. Since in a real system particles are polydisperse—and in some of our simulations as well—we have to reproduce the Peclét number in our simulations.

Let us now turn to the particle Reynolds number for the case characterized in Tab. 5.1: $Re = \tau_F/\tau_S = 4.0 \cdot 10^{-8}$. This is much smaller than unity, i.e., it is a case far from a competition between momentum transport by the particles and by the fluid, or in other words, the viscous forces of the hydrodynamic interaction dominate the particle motion, as one would expect: turbulence does not play a role in micro fluidics[77].

For a sheared system the Reynolds number can be calculated in an analogous manner. Instead of the Stokes velocity one has to take the mean velocity of the particle in the shear flow. With a typical shear rate of, e.g., $\dot{\gamma} = 100/s$, in a system twelve particle diameters
Table 5.3: time scales for a system with particle radius $R = 0.4 \mu m$.

<table>
<thead>
<tr>
<th>$\tau_S$</th>
<th>$\tau_D$</th>
<th>$\tau_G$</th>
<th>$\tau_V$</th>
<th>$\tau_F$</th>
<th>$\tau_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.790 s</td>
<td>0.593 s</td>
<td>12.2 ms</td>
<td>0.58 $\mu$s</td>
<td>320 ns</td>
<td>138 ns</td>
</tr>
</tbody>
</table>

thick, the Reynolds number would be $Re = 2.0 \cdot 10^{-5}$ which is still much smaller than unity, in spite of the quite high shear rate.

The ratio of $\tau_V$ to $\tau_P$ is larger than $4\pi$, hence oscillations of particles in their short range potentials are over-damped, already without considering lubrication forces. We find $\tau_P \ll \tau_G$, since the particles are well relaxed before they hit each other due to Brownian motion. $\tau_F \ll \tau_D$, hence the transport of momentum through the fluid is much faster than if transported directly by the particle. These are the dynamical characteristics which have to be preserved by any parameter changes. In particular, the Péclet-number has to be kept constant. Of course, the static properties such as the ratio of kinetic energy $\sim k_B T$ to the potential energies, $\sim mgR$ and $\sim A_H$ have to be kept constant too.

However, using identical parameters as shown in Tab. 5.1 in an MD simulation would require of the order of $10 \tau_S/\tau_P \approx 6 \cdot 10^8$ iterations to see sufficient progress in the sedimentation process. This is an unacceptably high numerical effort which must be reduced without significantly changing the physics of this process.

In the next chapter we analyze how the simulation parameters have to be chosen to set up a simulation which meets all the conditions we have worked out in this section. First we refer to coupling method I, and after that, we show what has to be changed when using coupling method II.
Chapter 6

Simulation Setup

6.1 Determination of the parameters

6.1.1 Determination of the parameters for coupling I

In this chapter we describe, how we adjust the simulation parameters so that the dynamics of a given real system is reproduced in the simulation and the efficiency of the simulation method is optimized. We start by choosing reasonable parameters for the hydrodynamic part of the code, i.e., Stochastic Rotation Dynamics (SRD), since this is the most complex part of the task and can easily lead to very time-consuming and storage-intensive simulation setups, if not enough care is taken. Let us again consider a simulation of particles with a constant radius $R = 0.185 \mu m$. Let $a$ be the lattice constant of the SRD grid. By choosing $a = R/2$ a spherical particle covers about 34 boxes which is a sufficient resolution of the particle. We get $a = 92.5 \text{ nm}$.

We use an average number of $M = 2.5$ fluid particles per box. Too many fluid particles would increase the computational costs. If too few fluid particles are used (i.e. in average only one fluid particle per box or less) the fluid particles do not exchange momentum anymore among each other which means that hydrodynamics is not reproduced well any more by the method. The mean free path of the fluid particles would increase and the resolution of the flow field around the MD particles would become worse. For our choice of $M$ we obtain a mass

$$m_f = \rho_f a^3/M = 3.17 \cdot 10^{-19} \text{ kg},$$

which is 327 times smaller than the mass

$$m_{MD} = \frac{4}{3} \pi R^3 \rho_{MD} = 1.03 \cdot 10^{-16} \text{ kg},$$

of the colloidal particles. This clear separation of the masses should be fulfilled to obtain a realistic simulation.

Next, we choose the ratio of the mean free path

$$\lambda = \tau \sqrt{k_B T/m_f}$$

(6.3)
to the lattice constant $a$, $m_f$ is the mass of the fluid particle and $T$ the effective temperature of the fluid particles which can differ by several orders of magnitude from the real temperature of the experiment as will be explained later. In Ref. [70] it was discovered that a ratio $\lambda/a$ smaller than 0.5 leads to anomalies in the model which can be corrected by a random shift of the lattice prior to every rotation. Here, we set $\lambda = 0.5 a = R/2 = 92.5 \text{ nm}$ to obtain a sufficient resolution of the flow. Random shifts are not needed in this case.

The angle of rotation $\alpha$ is taken to be $90^\circ$ because this gives the most simple rotation matrix. The shear viscosity for $\alpha = 90^\circ$ is given by [73]

$$\nu = \frac{a^2}{18\delta t_{\text{SRD}}} \left( 1 - \frac{1 - e^{-M}}{M} \right) + \frac{k_B T \delta t_{\text{SRD}}}{4m_f} \frac{M + 2}{M - 1}. \quad (6.4)$$

For different rotation angles or different choices of the rotation matrices, the pre-factor of the two terms change [72, 144], which would provide an additional parameter one could tune when adjusting the simulation parameters. Inserting $M = 2.5$ and expressing temperature by means of $\lambda$ it follows for our choice of parameters that

$$\nu = 0.22 \frac{a^2}{\delta t_{\text{SRD}}}. \quad (6.5)$$

In order to reproduce the same diffusion coefficient as seen in experiments, $\delta t_{\text{SRD}}$ has to be determined by means of the Einstein relation,

$$D = k_B T \mu = \frac{k_B T}{6\pi \rho_w R}. \quad (6.6)$$

Setting $\rho_w = M m_f / a^3$, using $\nu$ from Eq. (6.5) and the relation and expressing $k_B T / m_f$ by means of $\lambda$ according to Eq. (6.3) one finds

$$\delta t_{\text{SRD}} = 0.024 a^3 / (D R). \quad (6.7)$$

Inserting the diffusion coefficient expected in reality from the Einstein relation,

$$D = \frac{k_B T}{6\pi \rho_w R} = 1.167 \cdot 10^{-12} \text{ m}^2/\text{s}, \quad (6.8)$$

we arrive at a time step

$$\delta t_{\text{SRD}} = 87 \mu\text{s} \quad (6.9)$$

for the SRD algorithm. This time step is of course too large to resolve the motion of colloidal particles due to inter-particle forces and friction. Hence, a two-step method is needed: the trajectory for the colloidal particles is integrated by another, smaller time step $\delta t_{\text{MD}}$. This also means that the extensive SRD-procedure is only applied every $\delta t_{\text{SRD}}/\delta t_{\text{MD}}$th iteration of the MD-algorithm, thus reducing the required computer power substantially. The kinematic viscosity in the simulation, which we can calculate now, is much smaller than in nature:

$$\nu_{\text{model}} = 2.18 \cdot 10^{-11} \text{ m}^2/\text{s}. \quad (6.10)$$
This gives us a scaling factor which will occur also in the temperature and with which we have to multiply the particle-particle potentials, as well. Such scaling procedures are commonly used in the field of computer simulations to map real quantities on the natural units of the respective simulation method in use. Here, the way parameters are derived implicitly means that we keep $\tau_S$ and $\tau_D$ as in reality. This corresponds to $\tau_S / 0.87 \mu s = 19540$ SRD-iterations until a colloidal particle has fallen down by one diameter $2R$.

Next, one has to check what happens to the particle relaxation time $\tau_P$. The requirement is that it should be much larger than the one given in Tab. 5.1 (in order to increase numerical efficiency) and on the other hand it should still be smaller than $\tau_G$ to ensure that particles can relax between consecutive collisions caused by thermal motion. Following Eq. (5.16), we obtain $\tau_P = 1.36 \text{ ms}$. This is an acceptable value: it is much larger than the value of $29 \text{ ns}$ one obtains, when inserting the viscosity of the real system in Eq. (5.16), and still smaller than $\tau_G = 3.14 \text{ ms}$. Although the two time scales have approached very much, this is still acceptable, since for lower volume fractions $\tau_G$ is larger, so that the order of the time scales is restored. Especially in the cases where cluster formation takes place, there are parts of the volume with even higher local volume fraction, namely the regions where the clusters are located. There the hydrodynamics is not important anymore, since the motion is mainly dominated by the DLVO interactions, and the cluster moves as a whole. Consequently it is not important to maintain the correct order of the characteristic times of the hydrodynamics inside a cluster. More important is the flow in the bulk, around the cluster, where the volume fraction must have decreased in average. In the bulk, where the motion of single particles is influenced by hydrodynamics, they still can relax before a collision with the next single particle or cluster.

Let us turn to the Reynolds number which compares momentum transport in the fluid versus direct transport of momentum by the motion of particles: during time $\tau_D$, momentum in the fluid is transported a distance $x^2 = 2 \nu \tau_D = 300a^2$, i.e., $x = 17.3a = 8.6R$. Hence, momentum transport in the fluid is still faster than by diffusive transport of particles. In a real system it is much faster, but the reduction to about one order of magnitude difference in the time scales is a result of our rescaling procedure and by doing so, we can reduce the computational effort. In terms of the Reynolds number we have $Re = 4 \cdot 10^{-8}$ for sedimentation of the real suspension and by the scaling procedure we have increased it to $1.8 \cdot 10^{-3}$ which is still much smaller than unity. A Reynolds number much smaller than unity denotes that viscous effects dominate and inertia effects can be neglected[43, 45]. Therefore one can assume that the system still behaves the same regarding the hydrodynamic interactions for the sedimentation process. For the example with shear flow the Reynolds numbers are larger, in the real suspension as well as in the simulation. Here we find $Re = 0.94$.

Since we use a resolution for the hydrodynamics which is not much smaller than the particle size, we can accept Reynolds numbers even of the order of one. However, if we need to be more precise in this point, we can change the ratio $\lambda/a$ in our derivation of the simulation parameters: using $\lambda/a = 0.05$ generates a Reynolds number of $Re = 0.34$. Obviously, the prize to pay is of course a larger computational effort. Decreasing the mean free path means decreasing the SRD time step ($\delta t_{\text{SRD}} = 5 \mu s$). The fluid particles then move a shorter distance between the collision steps which causes strong correlations...
between the fluid particles contained in the same cell. To avoid these artefacts of the SRD grid, one has to perform random shifts of the grid prior to each collision step [71, 72].

Let us return to the sedimentation problem. As mentioned above, the viscosity of the simulation is much smaller than in reality. As a consequence, since we want to reproduce the sedimentation time $\tau_S$, we have to rescale the gravitational constant $g$. We require that the Stokes velocity is the same as given in Tab. 5.1. Since thermal convection of the fluid is not important for our simulation, we can neglect gravity on the fluid particles. Therefore, there is no buoyancy force in the simulation. We can correct for that by assuming a smaller gravitational constant modified by the density ratio of colloidal material and fluid. We find the following relation,

$$ g_{\text{model}} = g_{\text{real}} \frac{\nu_{\text{model}}}{\nu_{\text{real}}} \left( 1 - \frac{\rho_w}{\rho_m} \right) 1.59 \cdot 10^{-4} \frac{m}{s^2}. \quad (6.11) $$

As mentioned above, not only the viscosity, but also the temperature in our simulation is different from the one in nature. The temperature is directly linked to the time step and to the mean free path $\lambda$. In fact, the mean free path in the SRD simulation is adjusted by initializing the fluid particles with a certain kinetic energy, i.e., by selecting the correct temperature for the simulation setup. Using Eq. (6.3) we find

$$ T_{\text{model}} = \left( \frac{\lambda}{a} \right)^2 \frac{m_f}{k_B} \frac{a^2}{(\delta t_{\text{SRD}})^2} = 6.44 \cdot 10^{-3} \text{K}, \quad (6.12) $$

which is by a factor $f = 45832$ less than in reality. It has to be the same factor as the viscosity is scaled, since in Eq. (6.6) the only scaled variables are $\nu$ and $T$. The same factor has to be used to scale the potentials as well, so that the ratio of $k_B T$ and the interaction potentials are conserved. Otherwise, the static properties of the system would not be reproduced correctly. One could say that, e.g., the Hamaker constant $A_H$ and the effective surface charge are scaled by this factor $f$. Since the surface charge of the particles is calculated within our simulation program using the charge regulation model described in section 5.1, we have no direct access to the charge, so that we just insert $f$ as an additional factor after the numerical calculation of the $\zeta$-potential. For our time scale analysis let us continue with a scaled Hamaker constant $A_H = 4.76 \cdot 10^{-20} \text{J} / f = 1.039 \cdot 10^{-24} \text{J}$. From Eq. (5.19) we get a scaled $\tau_V$ of 0.11 ms corresponding to $\tau_V / \tau_P = 0.081$ (which is smaller than $4\pi$, see Eq. (5.20)). The un-scaled value is 17.38 which is larger than $4\pi$, i.e., two particles interacting with the DLVO potentials, approaching each other in a fluid, are an over-damped system. From the time scale analysis we see that due to our scaling procedure the particles would be able to oscillate in the primary minimum of the DLVO potentials. However, the creeping case is restored by the lubrication force which we have included in the MD simulation and which grows for smaller gaps between the particles. The lubrication force determines the small iteration time step $\delta t_{\text{MD}}$ for the MD simulation. We chose $\delta t_{\text{MD}} = 1 \mu s$ which is about 100 times larger than it would be if all the original parameters would have been kept and the un-scaled $\tau_P$, being much smaller, would determine the time step.

Comparing to the SRD time step we see that every 87 small MD steps one SRD step is performed. We need 19585 SRD steps and $1.71 \cdot 10^6$ MD steps to see a colloidal particle sinking down by one diameter. The time scales in the simulation are summarized
6.1.2 Determination of the parameters for coupling II

Table 6.1: Time scales in the simulation using coupling method I.

<table>
<thead>
<tr>
<th>$\tau_S$</th>
<th>$\tau_D$</th>
<th>$\tau_G$</th>
<th>$\tau_V$</th>
<th>$\tau_F$</th>
<th>$\tau_P$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.710 s</td>
<td>0.586 s</td>
<td>4.58 ms</td>
<td>0.11 ms</td>
<td>3.13 ms</td>
<td>1.36 ms</td>
</tr>
</tbody>
</table>

Again in Tab. 6.1. The smaller ones are increased to reduce the computational effort. This is possible and the dynamics of the system is kept the same, as long as the order of the time scales is conserved, or other corrections, like including an extra lubrication force are included. The potentials of the Molecular Dynamics simulation have to be scaled accordingly, too. The values measured in a simulation as well have to be rescaled accordingly to be comparable to the original system.

6.1.2 Determination of the parameters for coupling II

To simulate the same system with coupling method II, we use the same particle radius $R = 0.185 \mu m$. The lattice constant has now to be chosen differently because the colloidal particles are coupled to the SRD-simulation as point masses. They influence the fluid in the same cell and therefore the size of the cell can be understood as the volume within which the SRD-simulation “feels” the colloidal particles. We choose the lattice constant in a way that the volume of the cell is equal to the volume of a colloidal particle: $a = 0.296 \mu m$. A smaller lattice constant in this context would model smaller colloidal particles in the context of the SRD-part of the simulation. The velocity field would be resolved better, but since coupling method II does not allow a resolution smaller than the colloidal particles, one cannot expect to gain any information from the fluid simulation on smaller length scales than the colloidal particle size. Any attempt to increase the resolution of the SRD simulation would only cause a larger computational effort.

Since we do not modify the Peclé number, we have to choose approximately the same number of fluid particles per colloidal particle. Since the box size has increased with respect to the coupling method I, we have to assume more particles per box now. We choose $M = 60$ (which would correspond to two particles per box in the coupling method I, but since the boxes are much larger now, we can slightly reduce the ratio of fluid particles per colloidal particle).

We choose $\lambda/a = 0.5$ and a rotation angle $\alpha = 90^\circ$ again to achieve very simple matrices. Following the same procedure as for coupling method I (Eq. (6.4)) we find a time step for the SRD of

$$\delta t_{\text{SRD}} = 0.22 \text{ ms}.$$  \hspace{1cm} (6.13)

According to Eq. (6.5) the viscosity in the simulation results to $\nu_{\text{model}} = 4.778 \cdot 10^{-11} \text{m}^2/\text{s}$. The gravitational constant therefore has to be re-scaled by a factor of 28149, and the temperature and the potentials have to be scaled by 20931, where we take care of the fact that we do not apply gravity to the fluid particles.

The resulting characteristic times are shown in Tab. 6.2. $\tau_S$ and $\tau_D$ are again kept as in reality. Now we need $\tau_S/0.22 \text{ ms} = 7773$ SRD-iterations until a colloidal particle has
Table 6.2: Time scales in the simulation using coupling method II.

\[
\begin{array}{ccccccc}
\tau_S & \tau_D & \tau_G & \tau_V & \tau_F & \tau_P \\
1.71 \text{s} & 58.6 \text{ms} & 4.58 \text{ms} & 0.11 \text{ms} & 1.43 \text{ms} & 0.62 \text{ms}
\end{array}
\]

fallen down by one diameter which is much faster than by using coupling method I. \(\tau_P\) is still smaller than \(\tau_G\), and \(\tau_V/\tau_P = 0.177\) is again smaller than \(4\pi\), which means that a lubrication force in the MD simulation is needed again. They have to be integrated in the MD simulation anyway, if coupling method II is used, since the MD particles are coupled to the SRD simulation as point particles, and therefore lubrication effects can not be resolved.

However, momentum is transported 1.3 times faster in the fluid as by the particles themselves. Therefore, for long range interactions coarse grained hydrodynamic effects can be reproduced. Again, to model these effects in a way that is comparable to reality, the Reynolds number has to be much smaller than unity. We find \(Re = 8.4 \cdot 10^{-4}\) for the sedimentation example and \(Re = 0.43\) for the example system with shear flow of \(\dot{\gamma} = 100/\text{s}\).

In the MD simulation we have to choose the same time step as we have to use with coupling method I, but since the SRD time step for coupling method II is larger than for coupling I, we need approximately fifty per cent less CPU time for the hydrodynamics. Even though it seems to be a too simplified approach, we can reproduce a volume fraction dependent sedimentation velocity as will be described in chapter 8.

### 6.2 Temperature and Thermostat

As mentioned in the context of Eq. (6.12) in section 6.1.1 the mean free path in the simulation is adjusted by the initial kinetic energy of the fluid particles. It is important that the temperature in the simulation is kept constant, since the viscosity, and therefore the diffusion coefficient, depend on the mean free path. However, since the MD simulation and the SRD part are coupled, there is an exchange of energy between the two parts of the simulation. In the MD simulation energy can be dissipated, e.g., by the lubrication force, but it can also be increased by external forces, e.g., by gravity in conjunction with periodic boundary conditions. This extra energy would slowly spread out on all degrees of freedom contained in the simulation, which means that the temperature of the system would increase.

Without external force and without dissipative forces, particularly without a lubrication force in the MD simulation the temperature is constant. This has been tested for both, colloidal and fluid particles in several simulation setups. But, for simulations with lubrication force, or with gravity or external shear force, we have to take care that the temperature is kept constant.

For that we utilize a thermostat that treats each SRD cell separately to adjust its local temperature. One may not disturb the flow field, i.e., one has to preserve the mean velocity \(\mathbf{u}\) in the cell. What may be changed is the difference of each particle velocity with
6.2 Temperature and Thermostat

the mean velocity. We have developed a modified version of the thermostat described in Ref. [9] [Chap. 7.4.1, “Stochastic methods” p.227 f.]. The thermostat, originally suggested by Heyes [63], chooses a random scaling factor which is then accepted or rejected according to a Monte Carlo scheme. The detailed balance is not fulfilled for the scheme the scaling factor is chosen in [9] which is the less important the closer to unity the scaling is. For our application it is more important, since we only scale the difference $v_i - u$ for each particle and therefore we have to use larger scaling factors to achieve an efficient impact of the thermostat.

In our implementation of the thermostat, we randomly choose an $\varepsilon$ in the interval $[0, \chi]$, where $\chi$ defines the maximum relative change of the velocities. This can be seen as the “strength” of the thermostat (a large $\chi$ leads to a fast relaxation of the system towards the temperature to which the thermostat drives it). Then, we choose a scaling factor $\zeta$ which is one of the values $1 + \varepsilon$ or $\frac{1}{1 + \varepsilon}$, each of them with the probability of $\frac{1}{2}$. With one of these values the velocity is scaled by the Monte Carlo acceptance rate according to

$$v_i^{\text{new}} = \zeta \cdot (v_i - u) + u. \quad (6.14)$$

To calculate the Monte Carlo acceptance rate, we need to calculate the local temperature in the SRD cell. Thereby it is important, to correctly count the degrees of freedom which are involved in thermal fluctuations. If we have $M$ particles in a cell, there are $3M$ degrees of freedom, but 3 of them are the 3 components of the mean velocity $u$ in the SRD cell. The thermal fluctuations that the thermostat scales are contained in the contribution $v_i - u$ which, if summarized over all particles, always results in a null vector. That means, we have $3(M - 1)$ degrees of freedom which contain the fluctuations that are scaled by the thermostat. The local temperature is therefore given by

$$T = \frac{1}{3(M - 1)k_B} \sum_{i=1}^{M} m_f (v_i - u)^2. \quad (6.15)$$

If $T^*$ denotes the temperature to which the thermostat will drive the system, the Monte Carlo acceptance rate is given by

$$\zeta^{(3(M - 1))} \exp\left(-(M - 1)(\zeta^2 - 1)T/T^*\right). \quad (6.16)$$

As usual in Monte Carlo simulations, if the acceptance rate is larger than one, the scaling expressed by Eq. (6.14) is done, otherwise it is performed only with the acceptance rate given by Eq. (6.16).

In contrast to the original version of the thermostat in Ref. [9], we only scale the relative velocities in each SRD cell and conserve the mean velocity $u$. As a consequence we have a reduced number of degrees of freedom. Additionally, our implementation respects the detailed balance which becomes important for large $\chi$ and small numbers of particles per cell. The original version of the thermostat shows deviations of the achieved temperature from $T^*$.

In most cases we use the a generalized version of the thermostat which not only acts on the fluid particles, but also on the colloidal particles. To calculate the mean velocity $u$ of each
cell the velocities are weighted with the mass of the fluid particle or colloidal particle, analogous to the weighting done in the SRD rotation step when coupling method II is applied (see section 4.5). In Eq. (6.15) the mass of the particles has to be inserted instead of \( m_f \) accordingly, and the sum includes also the colloidal particles.

### 6.3 Introducing Shear Flow

In many simulations, we apply shear flow and investigate, e.g., the dependence of the viscosity on the shear rate, or the resulting microstructure, cluster size etc. depending on the potentials and the shear rate. The shear viscosity \( \eta \) of a fluid is defined as

\[
F = \eta A \frac{v}{z},
\]

where \( F \) denotes the force, which is needed to shear a volume element with cross section \( A \) and thickness \( z \) with a velocity \( v \). For Newtonian shear flow, \( \eta \) is a constant and the velocity gradient in the volume is spatially constant. However, for the suspensions we are interested in, \( \eta \) becomes dependent on the shear rate \( \dot{\gamma} = \frac{v}{z} \) and on the position at which it is measured in the flow profile. In Ref. [60] we have described a simple method to introduce shear at the fluid boundary by adding a velocity offset to all fluid particles reflected at the shear plane. From a constant velocity offset \( \Delta v \) one can calculate the mean shear force

\[
F_S = \left\langle \sum_{i=1}^{L} m_i \Delta v_i(t) \frac{1}{\tau} \right\rangle,
\]

where \( L \) denotes the average number of fluid particles crossing through the shear plane in one time step and \( \left\langle \ldots \right\rangle \) stands for a time average. \( L \) can be expressed by the mean free path and the number density of fluid particles. This would be a force driven shear, where one has only indirect control on the shear rate \( \dot{\gamma} \) or the shear velocity \( v_S \) respectively. Therefore, a different method is needed to apply shear rate controlled shear flow: we modify the mean velocity \( u_j(t') \) in the cells close to the shear plane by changing the velocity of each fluid particle as well as the velocity of the colloidal particles contained in that specific cell by the difference \( v_S - u_j(t') \). By construction the mean velocity in these cells is equal to the shear velocity \( v_S \) after that step. At the wall itself we implement full slip boundary conditions for the fluid and for the colloidal particles. The boundary in the direction of the shear profile (direction of the velocity gradient) is chosen to be non-periodic. By doing so, we can also observe phenomena like wall-slip, non-linear velocity profiles or density profiles in our shear cell (see section 8.3). In the case of a non-linear velocity profile the viscosity is not well defined. We extract the central region of the profile where it is in first approximation linear and estimate there an averaged viscosity. This is the ratio of the velocity gradient and the shear force which can be calculated in analogy to Eq. (6.18) by carrying out the sum over all velocity changes made. The region where we estimate the velocity gradient is half the system size.

We have tested a number of boundary conditions and different ways to impose shear, but the method just described turned out to work best. No-slip boundaries at a top and bottom
plane seemed to work for high volume fractions and unless the potentials get attractive. As soon as (only slight!) cluster formation sets in the particles concentrate in the center of the system and lose contact to the sheared walls. Shearing only the fluid and not the colloidal particles could be done, but the resulting viscosity is much too small then. In fact, what one measures is the flow of the fluid streaming around the particles like a flow through a porous medium. The next point is how to determine the shear force and the velocity gradient we need for the calculation of the shear viscosity. The force is always related to any velocity changes made in the system and its calculation is straightforward in most cases.

The imposed velocity difference divided by the system size perpendicular to the shear plane would give an averaged gradient. For clustered systems not even the shape of a plot of the shear viscosity against the shear rate is comparable to the measurements. If the velocity gradient changes within the system (compare Fig. 8.5), we have to take care that we measure the viscosity in the bulk, i.e., that we take the velocity gradient there. If the particles form clusters, a the plot of the shear velocity shows a plateau in the central region of the simulation volume. At least if the particles are not too strongly clustered, the slope of the plateau can be taken as a “good” velocity gradient. We use this velocity gradient as achieved shear rate as mentioned above. With this scheme for strongly attractive forces the obtained viscosity \( \eta(\dot{\gamma}) \) for the simulation stays in the vicinity of the measured curve, whereas for the other methods the points of the simulation usually end up far off the measured curve.

Fully periodic boundary conditions for sheared systems, known as Lees Edwards conditions would be a good choice for stable suspensions. As soon as clusters are formed, the velocity profile becomes non linear, as discussed above. But, additionally the location of the cluster, i.e., the position of the plateau, is not fixed anymore to the center of the system which makes it more difficult to extract the correct velocity gradient. In addition, the shear force would be determined from the velocity changes of the particles passing around the periodic boundaries. If the cluster by chance stays in the center of the system, again only the fluid would be sheared and only indirectly, transmitted by the fluid, the force would be exerted on the particles, as if with closed boundaries only the walls would move and no sheared regions close to the wall were implemented. Together with the periodic boundaries this would lead to large fluctuations of the shear force, caused by the present position of the cluster. Furthermore, the boundary conditions would have to be consistent for the MD and for the SRD simulation. For the MD part it is important that the position, where a particle re-enters the system after passing around the periodic boundary, is shifted by \( 2t v_S \) with \( t \) being the continuously increasing simulation time and \( v_S \) the shear velocity. Additionally this shift has to be wrapped around the periodic boundaries in shear direction. If we do the same with the fluid particles the shift could be any value, not necessarily an integer multiple of the fluid box size. What we want to point out, without any further restrictions, the grid in the SRD rotation step would not anymore be regular in this plane which in addition is the plane where one measures the shear force. To overcome this problem, one can restrict the shear rate to values determined by the SRD grid size and the SRD time step, but the other difficulties mentioned before remain.
6.4 Boundary conditions

In section 6.3 we have already discussed how shear flow can be exposed to the simulation and how the boundary conditions have to be chosen for these simulations. Here we focus on sedimenting systems. First, we assume periodic boundary conditions in all three directions. Without external forces, i.e., with gravity switched off, momentum is conserved in the simulation. For simulations where gravity is irrelevant, this is the best choice since finite size effects are less pronounced when using periodic boundaries. If gravity is imposed on the colloidal particles in a system with periodic boundary conditions, this would accelerate the whole system. When the colloidal particles are wrapped around the periodic boundaries, they gain potential energy in the gravity field. This additional energy is constantly introduced to the simulation. In a real system there is friction at the walls and even more important, there is an equilibrium between hydrostatic pressure acting on the surface of a given volume and the gravity acting as a body force. In the simulation the hydrostatic pressure is missing due to the periodic boundaries. There are several possibilities to deal with this problem:

1. One can close the boundaries in the direction where gravity is applied. The particles can then sediment until they have reached the bottom of the simulation volume. Since the simulation volume is small compared to a real experiment, some collective hydrodynamic effects might not be seen during a simulation of that kind. For high volume fractions the particles do not reach a constant sedimentation velocity, because they already feel the influence of the particles below.

2. If one would like to simulate sedimentation without a bottom where the particles accumulate, one can keep the periodic boundaries in the direction of gravity and instead close the other boundaries in the horizontal directions. Additionally, no-slip boundary conditions have to be applied for the fluid. This can be achieved by a direct bounce back rule, i.e., fluid particles which in a streaming step leave the system in that direction are moved back to their original position and their velocity is multiplied by $-1$ to change its direction. The effect of these boundary conditions is that the fluid experiences a wall friction which compensates the gravity on the colloidal particles. However, due to the closed boundaries in the horizontal directions, the simulation could be compared to a sedimentation experiment preformed in a capillary. One disadvantage is that under these conditions, the sedimentation process is much slower than in the bulk of a larger system. Another disadvantage are ordering effects induced by the closed walls.

3. To avoid wall induced effects, one has to use periodic boundary conditions in all three directions. However, one has to compensate the force of gravity. Instead of a wall friction, one can apply this compensation force as a body force on the fluid, which one could see as a negative gravity applied to the fluid. Since the gravity on the colloidal particles and the compensating force on the fluid sum up to zero, the center of mass is not accelerated. Since fluid and colloidal particles move in opposite direction, due to the coupling, they experience a friction force and the energy induced by the combination of gravity and periodic boundaries is transformed
6.4 Boundary conditions

to heat. This means, the kinetic energy spreads over all degrees of freedom of the system. However, since there are much less fluid particles than molecules in a real system, the heat capacity is much smaller and the system heats up quickly. This is the point, where the thermostat described in section 6.2 is needed. Especially its property to preserve the mean velocity $u$ in each cell is important, so that the sedimentation process is not disturbed, whereas the thermal fluctuations are re-scaled to an adjusted temperature.

In general, simulations with periodic boundaries show less pronounced finite size effects, but they are more sensitive to stability problems like accumulated drifts etc. One example is a simulation of sedimentation using fully periodic boundaries and a compensating force on the fluid, together with attractive forces and a high volume fraction. It can happen that a system spanning cluster is formed, which is connected around the periodic boundaries. It may be oriented inclined with respect to the direction of gravity. Since fluid and cluster were moving in opposite direction, the cluster then deflects the fluid like a sail in the wind and accumulates a sidewards drift. Using a smaller volume fraction or a much larger system, so that the size of the clusters formed in the system is small compared to the system size, they would not accumulate a large drift. However, small drifts of the whole system can be removed every some hundreds of time steps without disturbing the simulation substantially.
Chapter 7

Tests of the Simulation Code

7.1 Conservation of energy, velocity distributions

The total energy is an observable which is easy to measure and which can help to detect bugs or numerical instabilities of the code. A first test is, to switch off all dissipative forces in a simulation, and the thermostat as well. Then, the total energy should be constant. If this is not fulfilled, there can either be a programming error in the code, or, if the drift is not dramatically large, it may be caused by numerical impreciseness. Decreasing the simulation time step usually helps to decrease the numerical errors, otherwise a different integration method may be required for the Molecular Dynamics simulation. We have checked the constancy of the total energy separately for the Molecular Dynamics simulation, for the simulation of the fluid, and for the coupled simulation.

If we use coupling method II for the total system, energy is conserved within numerical accuracy. With coupling method I (where a thermostat is already included in the coupling method) or if we switch on an additional thermostat energy will not exactly be conserved but the system will reach a stable, i.e., equilibrated state. In that sense, in thermal equilibrium the total energy (including the internal energy of the fluid) will, averaged in time, converge to a constant value. However, the total energy may fluctuate around its mean value in an isothermal simulation. Due to the first law of thermodynamics,

\[ TdS = dE + pdV - \mu dN, \]

(7.1)

for constant volume \((dV = 0)\) and constant number of particles \((dN = 0)\), the fluctuations of the energy \(dE\) are related only to the variation of the entropy \(dS\). The entropy on the other hand depends on the order or disorder of the system, i.e., on the positions of the microscopic particles in phase space. In contrast to a real gas, where one usually has of the order of \(10^{23}\) molecules, there are only of the order of \(10^6\) in a coarse grained simulation (SRD in our case). Therefore, the number of degrees of freedom is drastically reduced with respect to a real gas, and thus fluctuations are stronger than in the simulation. However, the fluctuations of thermal origin are in the order of less than 1\% and can be assumed to be constant. If the thermostat is used to absorb the energy introduced by shear forces or gravity, fluctuations might become larger, but still in the order of a few percent. Note that without a thermostat the energy is conserved exactly in a SRD simulation. Numerical errors of the total energy are in the sub parts per million range. In SRD-Simulations without any embedded particles, without shear forces or
Figure 7.1: Velocity distribution of fluid (a) and colloidal (b) particles in a simulation after thermalization. The particle density is 3900 $\text{kg/m}^3$, the scaled model temperature $T = 10.57\text{mK}$, the fluid particle mass $m_f = 1.0667 \cdot 10^{-18}\text{kg}$, and the MD particle radius $R = 0.25\text{\mu m}$. The theoretically predicted Gaussian curves are plotted with lines and the measured velocity distributions in each Cartesian direction with points.

7.2 Particle Rotations

We also check that our implementation of the Molecular Dynamics code is correct by simulating eight large particles with Hertz-repulsion and Coulomb friction in a closed box at a volume fraction of $\Phi \approx 20\%$. We check that the collisions are realistic, i.e., that the individual angular velocities for two particles interacting in a non-central collision...
7.3 Viscosity and Sedimentation

before and after they have touched are consistent.

However, for most cases particle rotations are of minor importance. In our simulations the DLVO potentials strongly determine the behavior of the system. With respect to the tangential friction there are two cases: either the electrostatic repulsion is strong and prevents the particles from touching, but if there is no particle contact, friction forces are not applied either. The other possibility is that the van der Waals force dominates and electrostatics is screened or the particles are uncharged (at the isoelectric point). Then, the particles form clusters, but then the behavior of the system is dominated by the motion of the whole clusters in the system, not by the motion of single particles with respect to each other. The situation may be different, if in addition to shear forces a confining pressure is applied, so that the importance of the particle contacts is enforced and the material shows a behavior more similar as to what is known from granular media [22, 61, 62, 93].

We have compared how important rotations are for our shear simulations. To do so, we have increased the spacial resolution of the fluid simulation, so that the flow field around the particles can be resolved better. We have used coupling method I and we have included tangential forces on the particles and allowed particle rotations. We have compared this to a simulation with less spacial resolution of the fluid simulation, using coupling II without particle rotations. The computational effort was considerably larger in the more exact case and one could expect that more effects on the length scale below the particle diameter could be covered. However, one could observe only a change of some percent in the viscosity and in the velocity profile. Therefore we conclude that for our simulations particle rotations can be neglected, unless a confining pressure is applied.

7.3 Viscosity and Sedimentation

The diffusion coefficient of suspended colloidal particles can be used to check the desired viscosity of the fluid. For the SRD simulation the viscosity can be adjusted using Eq. (6.4). However, Eq. (6.4) is an approximation [73] and one should test, if the viscosity achieved in the simulation in fact coincides with the value one intents to adjust. Using Eq. (5.9) we can calculate the kinematic viscosity $\nu$, once we have measured the diffusion constant $D$ for the colloidal particles, and compare it to the value we have used to determine the simulation parameters. However, Eq. (5.9) also holds exactly for an idealized system with infinite dilution, i.e., one particle in an infinitely large system. Therefore, both values, the theoretically calculated diffusion coefficient, as well as the adjusted viscosity are not exact, but they should at least be comparable. We achieve a deviation of less than 5 \% in a simulation of a diluted system at $\Phi = 4$ volume fraction. During the work of this thesis the precision could be improved in this point, by applying more detailed knowledge on how the simulation parameters have to be chosen. Especially for coupling II, when the colloidal particles are included in the SRD rotation step, the proper choice of the box size defines the precision of the simulation with respect to the viscosity of the fluid “felt” by the particle.

We are using two different methods, either the Green-Kubo-method or direct evaluation of the mean square displacement. The first is even very accurate, if only few particles
Figure 7.2: Evaluation of $D$ using the Green-Kubo method: the plot shows the sum $\sum_{j=1,n} g_{x,y,z}(j)$, the mean value of it between $J = 50$ and 200, and the estimated $D$ from Eq. (5.9). The data is obtained by a simulation with 20 colloidal particles, coupled to the fluid with coupling II.

are used, but consumes much computer time and memory because all particle velocities have to be stored for all time steps used in the calculation. That means, for higher volume fractions, it is more efficient to just sum up all the mean square displacements within a given period of time. To calculate $D$ using the Green-Kubo method one uses the following relation:

$$g_x(j) = \lim_{I \to \infty} \frac{1}{IM_{\text{Tot}}} \sum_{i=1}^{I} \sum_{n=1}^{M_{\text{Tot}}} v_{x,n}(i \delta t) v_{x,n}(i \delta t)$$

$$D_x = \delta t \left( \frac{1}{2} g_x(0) + \sum_{j=1}^{\infty} g_x(j) \right)$$

where $M_{\text{Tot}}$ is the total number of particles in the system, $I$ is the number of time steps used to calculate the contribution $g_x(j). v_{x,n}(i \delta t)$ denotes the $x$ component of the velocity of particle $n$ in the $i$-th time step of size $\delta t$. The sum in the expression for $D_x$ is in principle an infinite one, but since the contributions $g_x(j)$ decay with $j^{-3/2}$, one can truncate this sum after some tens of terms. $D_y$ and $D_z$ can be calculated accordingly, using terms $g_y(j)$ and $g_z(j)$ defined analogous to Eq. (7.2). In Fig. 7.2 we show the diffusion coefficient calculated for a three dimensional simulation with twenty particles, resulting in a volume fraction of 4 permil. The sum in Eq. (7.3) is truncated after $J$ terms and and the finite sum for each direction is used to calculate the diffusion coefficient. The relation $D(J)$ is plotted in Fig. 7.2 and one can see that after about 50 terms the value is rather constant. Instead of taking the limes of $I \to \infty$ in Eq. (7.2), we set $I = 200 - j$, so that only the data of the first 200 time steps is needed to evaluate $D(J)$. For $J \to 200$ the value of
Figure 7.3: Mean sedimentation velocity over porosity $(1 - \Phi)$ according to Eq. (7.5): Measured values and fitted curve in a log-log-plot. The Peclét number is $Pe = 0.34$, and the Reynolds number is $Re = 1.8 \cdot 10^{-2}$.

$D(J)$ does not change anymore in a systematic way. Since the number of terms for each contribution $g_x(j)$ decreases with increasing $j$, we calculate the average $\bar{D}(D(j))_{j=50...200}$ and compare this value to the theoretical calculation of $D$. This average can be seen as a smooth cutoff of the sum in Eq. (7.3). The fluctuations of $D(j)$ become smaller for longer simulation runs, but the mean value $\bar{D}$ does not change. It differs from the one calculated from Eq. (5.9) by only 4%.

For the mean squared displacement in one direction during a time interval $\Delta t$ we calculate

$$D_x = \frac{1}{2\Delta t M_{\text{Tot}}} \sum_{i=1}^{M_{\text{Tot}}} (x_i(t + \Delta t) - x_i(t))^2 \quad (7.4)$$

and $D_y$ and $D_z$ accordingly. For medium densities we have compared both methods and achieved the same results within error bars. Depending on the number of particles, we use one of both methods.

Another way to test the viscosity is to apply gravity and compare the achieved Stokes velocity of a particle. But, it should also be an isolated particle, or at least a low volume fraction, since according to Richardson and Zaki [115], the mean sedimentation velocity of particles suspended in a liquid depends on the volume fraction $\phi$ as:

$$v_s(\Phi) = v_\infty (1 - \Phi)^l, \quad (7.5)$$

with a typical exponent $l$ between $\approx 2.5$ and 4 depending on the boundary conditions. We test if this dependence of the sedimentation velocity on the volume fraction can be reproduced by our simulations. For periodic boundary conditions, different Peclét numbers of the order $Pe = 1$ and Reynolds numbers $Re \ll 1$ we have found an exponent of $\approx 3.5$
even if we use coupling method II, where only long range hydrodynamic interaction can be resolved. Padding and Louis also have found that the exponent $l$ depends very weakly on the Peclét number [104]. In Fig. 7.3 we show the normalized sedimentation velocity versus the porosity $(1 - \Phi)$. This plot is based on simulations using coupling method II, but we find comparable results when using coupling method I. On the first view there is no big difference apparent between the two coupling methods, at least, as long as, like in this test of our simulation code, no attractive forces are included.
Chapter 8

Results

8.1 Introduction

In this chapter we present the main results of this thesis. They have been published in Ref. [55–60]. A “stability diagram” for Al$_2$O$_3$ suspensions has been worked out step by step. In Ref. [60] the diagram consists of snapshots of the simulation and the axes are labeled by the inverse Debye screening length $\kappa$ and by the effective surface potential $\Psi_0$. The simulation parameters are determined using the procedure described in section 6.1.1 and 6.1.2. In Ref. [60] the connection to the $p$H-value and the ionic strength $I$ is drawn by including the charge regulation model (see section 5.1). Simulations are carried out for three example states and the viscosity is compared to experimental data. The remaining parameters are adjusted to optimize the matching of the viscosity curves with the experiment. In Ref. [57] the different “microstructures” of which the stability diagram is composed are characterized and a considerable region of the stability diagram is explored by simulations. The cluster formation is studied by means of the pair correlation function and the structure factor. Ref. [55, 56] are articles reviewing the topic in a broader context, together with other results obtained in Lattice Boltzmann (LB) simulations. In Ref. [59] a newly developed cluster counting algorithm (see chapter A.1) is presented together with a description of the parallelization (see chapter A.2). These preliminary results are also discussed at the end of the current chapter.

In this chapter the results are sorted thematically. First, we present the stability diagram and shortly describe how it is obtained from the simulation data. We shortly discuss the different microstructures. Then, we discuss the velocity profile in the shear flow and the resulting viscosity, depending on the particle-particle interactions. After that we have a look at the microscopic structure, using the pair correlation function. Certain peaks can be assigned to microscopic local structures. The integral over the nearest neighbor peak can be used as a measure for the clustering process. In the next section we use the structure factor to analyze the cluster formation process and again an integrated value, here the integral over the “low-k-peak”, is evaluated. This value takes into account the long range inhomogeneities of the simulation volume, and thus can be used to observe the cluster formation process on a large length scale. In principle the structure factor and the pair correlation function are complementary quantities and contain exactly the same information. However, due to the finite size of the simulation volume, the pair correlation function is cut off...
Figure 8.1: Schematic stability diagram for volume a fraction of $\Phi = 35\%$ in terms of the pH-value and the ionic strength involving three different microstructures: a clustering regime due to van der Waals attraction, stable suspensions where the charge of the colloidal particles prevents clustering, and a repulsive structure for further increased electrostatic repulsion. We discuss the states marked by capital letters in more detail in the text: state $A$ ($pH = 6$, $I = 3\, \text{mmol/l}$) in the suspended region, state $B$ ($pH = 6$, $I = 7\, \text{mmol/l}$) close to the border with slight cluster formation, and state $C$ ($pH = 6$, $I = 25\, \text{mmol/l}$) well in the clustered region. The borders are not sharp transitions, but notable in a change of the shear viscosity.

at length scale of about half the system size. However, this cutoff depends on the position of the particular position of the particles and depends on the type of boundary condition in the different directions. Using the structure factor to evaluate the structure on large length scales turns out to be more convenient. Therefore, we use the integrated nearest neighbor peak of the pair correlation function and the “low-k-peak” of the structure factor to observe the cluster formation process on two different length scales. Both integrated values turn out to show the same features, and therefore the clustering process in this sense is length scale independent. In the next section the density inhomogeneity of the system is investigated by means of the demixing parameter $\Psi$ proposed by Cates et al. [110]. After that, the mean squared displacement and an increase of the shear force with respect to the suspended microstructure is shortly discussed in order to characterize the “repulsive structure”. section 8.8 is dedicated to the total energy that is contained in a simulation of a sheared suspension and how the cluster formation can be seen there. Finally, first results obtained by a newly developed cluster recognition algorithm [59] are presented in the last section of this chapter.
8.2 Stability Diagram

The main objective of this work is to relate the microscopic structure to macroscopic quantities. The first step to do so is to relate particle-particle interactions to certain experimental conditions, i.e., to the pH-value and to the ionic strength $I$. Then, simulations can be performed using these potentials and different quantities can be analyzed. These quantities are the microscopic structure in terms of pair correlation functions or structure factors, viscosity, velocity profiles of the shear flow, mean cluster size, and many more. Having the simulation results one can try to classify different conditions and assign them to a few “phases” and draw a “phase diagram”. However, since we are not talking about equilibrium phases in the sense of thermodynamics with phase transitions and coexistence regions, the term “phase diagram” may be misleading and suggest prerequisites which in fact are not fulfilled for our simulations. Therefore, we rather speak about a “stability diagram” where different regions are depicted each corresponding to a certain “microstructure”. This is useful to be able to directly predict properties of a suspension from the conditions, i.e., from the pH-value and the ionic strength $I$. The stability diagram in Fig. 8.1 summarizes the results of this chapter in just one concise plot.

However, one has to keep in mind that such a summarized plot can only be a guide to roughly understand how things are related to each other in the suspension. One quantity we investigate, is the shear force which is needed to achieve a shear flow with a certain shear rate $\dot{\gamma}$. For a complex fluid, like a suspension with attractive particle-particle interactions, the shear force not only depends on the respective interactions, but also on the shear rate and the history of the suspension.

Nevertheless, the stability diagram is useful, since it gives a first idea of the properties of the suspension. Such a stability diagram has been proposed already by Graule et al. [46, 47] ten years ago, but at that time only at a descriptive level. We have quantitatively related the interaction potentials to the experimental conditions by a charge regulation model (see section 5.1) and we evaluate the data of our simulations carried out using these potentials.

As depicted in Fig. 8.1, depending on the pH-value and the ionic strength, one can obtain three different microstructures: A clustered region, a suspended region, and a repulsive structure. Close to the isoelectric point ($\text{pH} = 8.7$), the particles form clusters for all ionic strengths since they are not charged and therefore the van der Waals attraction is not compensated. At lower or higher pH-values, one can prepare a stable suspension for low ionic strengths because of the charge which is carried by the colloidal particles. At even more extreme pH-values, one can obtain a repulsive structure due to very strong electrostatic potentials (at low pH-values and low ionic strength, see Fig. 5.2). The repulsive structure is characterized by an increased shear viscosity, by the dominance of repulsive electrostatic interactions and by a diffusion dynamics of the colloidal particles which reminds of a glassy dynamics (see section 8.7). Even though it is not possible to explain all details of the different microstructures already here, it helps the reader to understand the following discussions about the different microstructures, and therefore we first discuss the general properties and later on address the more detailed questions raising in this context.

The qualitative stability diagram of Ref. [46] is similar to Fig. 8.1. The borders there are shifted, since they depend on the criterions one uses to categorize the suspensions in
Figure 8.2: Stability diagram (plotted for $\Phi = 35\%$ and without shear): depicting three regions: a clustered region (filled circles), a suspended regime (open squares), and a repulsive structure (filled squares). The borders are not sharp, but depend on the shear rate and on the volume fraction. Lines are guides to the eye.

different microstructures. If one evaluates for example the viscosity and characterizes the clustered region by a state with an increased viscosity, the location of the border between the suspended and the clustered region depends on the threshold value for which one defines that the viscosity has increased. Correspondingly, if one is less sensitive on the viscosity increase, one would still consider the system to be suspended if only weak cluster formation takes place.

We explore the technically most interesting left part of the stability diagram sketched in Fig. 8.1, and classify the microstructure for several points of the diagram. The section, where we have run simulations is shown in more detail in Fig. 8.2. We first give an outline of how we obtain Fig. 8.2, before we discuss the different quantities in detail in the following sections.

To decide if a state is in the suspended region or in the repulsive one of the stability diagram, we compare the mean squared displacement $\langle (x_i(t) - x_i(t - \delta t))^2 \rangle_{i,t}$ of colloidal particles. If we find a pronounced plateau there for intermediate time scales, we count the state among the repulsive regime. As a second criterion one can compare the pair correlation function. If there are long range correlations even though the system is not sheared, then the microstructure is the repulsive one. Finally, the shear force can also be used to define the border between the microstructures. For a given shear rate and a fixed volume fraction, the shear force depends on the particle interactions. If the shear force increases compared to a state well in the suspended regime, the motion of the particles is either blocked by the electrostatic interaction in the repulsive regime, or in the clustered regime the particles start to stick together due to van der Waals attraction. In Fig. 8.3 we have plotted the dependence of the shear force on the $pH$-value and the ionic strength $I$.
for a volume fraction $\Phi = 35\%$ and a shear rate $\dot{\gamma} = 100/s \ (Pe = 2.9, \text{ according to Eq. (3.4)})$. One can see the valley of the suspended regime and the increase of the shear force towards the repulsive and the clustered regime.

Without shear weak clustering can be observed in the suspended case as well, since in the DLVO potentials there is no barrier for the particles to enter the secondary minimum, but the clusters can be broken up again very easily. Thus, to decide, if a state belongs to the clustered or to the suspended regime, we first study snapshots of the system. If we see no clusters there, the clustered regime can be excluded. But, if we see clusters, we next check the density of the clusters and the time it takes to form them in a simulation. These quantities can be evaluated using the so-called “demixing parameter” $\Psi$, suggested by Cates et al. [110]. Both, the density and the time are indications for the stability of the clusters. If they grow slowly and their density is low, we count the state to the suspended regime.

After we have introduced the stability diagram, we discuss the properties of the different microstructures in the following in more detail. At some points of the discussion we focus on three states marked in Fig. 8.2 with capital letters: State $A \ (pH = 6, I = 3 \text{ mmol/l})$ is in the suspended region, state $B \ (pH = 6, I = 7 \text{ mmol/l})$ is a point close to the border but where already weak cluster formation occurs, and state $C \ (pH = 6, I = 25 \text{ mmol/l})$ is located well in the clustered region. We apply shear in our simulations and discuss the dynamic properties seen in the shear flow exemplarily for the states $A - C$. To apply shear, we set the velocity of colloidal and fluid particles close to the border to the shear velocity
as described in section 6.3. The shear force is calculated from the velocity changes needed to achieve the desired shear velocity.

Some typical examples for the different microstructures are shown in Fig. 8.4 a)–d). These examples are meant to be illustrative only and do not correspond exactly to the cases A–C in Fig. 8.1 denoted by uppercase letters. In the suspended case (a), the particles are mainly coupled by hydrodynamic interactions. One can find a linear velocity profile and a slight shear thinning. If one increases the shear rate \( \dot{\gamma} > 500/s \) \((\text{Pe} > 15)\), the particles arrange in layers. The same can be observed if the Debye-screening length of the electrostatic potential is increased (b), which means that the solvent contains less ions \((I < 0.3 \text{ mmol/l})\) to screen the particle charges. On the other hand, if one increases the salt concentration, electrostatic repulsion is screened even more and attractive van der Waals interaction becomes dominant \((I > 4 \text{ mmol/l})\). Then the particles start to form clusters (c), and viscosity rises. A special case, called “plug flow”, can be observed for high shear rates, where it is possible to tear the clusters apart and smaller parts of them follow with the flow of the solvent (d). This happens in our simulations for \( I = 25 \text{ mmol/l} \) (state C) at a shear rate of \( \dot{\gamma} > 500/s \) \((\text{Pe} > 15)\). However, as long as there are only one or two big clusters in the system, it is too small to expect quantitative agreement with experiments. These finite size effects are discussed later in this chapter. To calculate a viscosity, which is comparable to experimental values, we have to focus on states close to the border between suspended and clustered regime, e.g., state B \((I = 7 \text{ mmol/l})\), where the cluster formation has just started. Let us now discuss different properties of the suspension in more detail.

### 8.3 Shear Profile and Shear Viscosity

If shear is applied, in each of the three regimes a typical velocity profile of the shear flow occurs. For the suspended microstructure one finds a linear velocity profile (Fig. 8.5 a)) corresponding to nearly Newtonian flow. The particles are distributed homogeneously, thus the density profile is structureless (Fig. 8.6 a)). The motion of the particles is only weakly coupled by the hydrodynamic forces. At high enough shear rates \((\dot{\gamma} > 500/s, \text{Pe} > 15)\) the particles arrange in layers parallel to the shear plane, as can be seen in the density profile (Fig. 8.6 b)), too. This arrangement minimizes collisions between the particles. As a result, the shear viscosity descents as shown in Fig. 8.7 which we discuss in more detail below. Shear induced layer formation has been reported in the literature for different experiments [1–3, 19, 151] and Stokesian dynamics simulations [42, 109]. For low shear rates Brownian motion disturbs the layers or prevents their formation. As shown in Ref. [109], hydrodynamic forces can destroy them as well, if the shear rate is high enough. In our simulations we do not reach these conditions. In the simulations shear rates up to \(2000/s \) \((\text{Pe} = 59)\) can be realized before limitations of the simulation method influence the results. The increment of the shear angle in one SRD time step \( \gamma = \dot{\gamma} \tau_{\text{SRD}} \) amounts to about \(\pi/4\) then, i.e., the offset in \(x\)-direction between two neighboring layers of SRD cells in \(z\)-direction amounts to one cell per SRD time step.

Furthermore, the layer formation is influenced by the volume fraction and the interaction
8.3 Shear Profile and Shear Viscosity

Figure 8.4: Images of four different cases. For better visibility we have chosen smaller systems than we usually use for the calculation of the viscosity. The colors denote velocities: red particles are slow, yellow ones move fast. The potentials do not correspond exactly to the cases $A - C$ in Fig. 8.1, but they show qualitatively the differences between the different states: a) suspension like in state $A$, at low shear rates. b) layer formation which occurs in the suspension (state $A$) at high shear rates and in the repulsive regime already at moderate shear rates c) strong clustering, like in state $C$, so that the single cluster in the simulation is formed d) weak clustering close to the border like in state $B$, where the cluster can be broken into pieces which follow the flow of the fluid (plug flow).
Chapter 8. Results

Figure 8.5: Profiles of tangential velocity component ($v_x$) in normal direction ($z$): a) Linear profile in the suspended regime, state $A$ of Fig. 8.1 ($I = 3$ mmol/l) at $\dot{\gamma} = 500/s$ ($Pe = 15$)). b) Cluster formation in state $C$ ($I = 25$ mmol/l) at $\dot{\gamma} = 100/s$ ($Pe = 2.9$). In principle one could determine the viscosity of one single cluster from the central plateau, but this is not the viscosity found in experiments. There, one measures the viscosity of a paste consisting of many of these clusters. c) Same as case b) but with higher shear rate ($\dot{\gamma} = 500/s$, $Pe = 15$). Hydrodynamic forces are large enough to break the cluster into two pieces. The velocity axis is scaled with the shear velocity $v_S$ for better comparability.

Figure 8.6: Density profiles of colloidal particles in the shear flow under different conditions: a) suspended case: state $A$ in Fig. 8.1 ($I = 3$ mmol/l), at low shear rates ($\dot{\gamma} = 50/s$, $Pe = 1.5$). The density distribution is homogeneous. b) Shear induced layer formation: This is state $A$ as in graph a) of this figure, but for a high shear rate ($\dot{\gamma} = 1000/s$, $Pe = 29$). c) Strong attractive forces in state $C$ ($I = 25$ mmol/l): for low shear rates ($\dot{\gamma} = 50/s$, $Pe = 1.5$) only one central cluster is formed which is deformed slowly.
8.3 Shear Profile and Shear Viscosity

Figure 8.7: Comparison between simulation and experiment: viscosity in dependence of the shear rate. for the states $A$ ($I = 3 \text{ mmol/l}$) and $B$ ($I = 7 \text{ mmol/l}$) of Fig. 8.1. Note: shear thinning is more pronounced for the slightly attractive interactions in state $B$ than for the well suspended state $A$. Lines denote experimental data [114], points are results from our simulations.

...range of the electrostatic repulsion, or the ionic strength respectively: In the repulsive regime the layers are formed more clearly already at moderate shear rates. It can be excluded that the effect is purely a finite size effect, since for un-sheared suspensions no layers can be observed, at least some particle diameters away from the walls. In the repulsive regime the particles try to optimize their local structure, but a long range order as in the case of a sheared system cannot be seen.

Deep in the clustered regime it occurs that only one big cluster remains in the system, which then moves in the fluid as a whole. It is deformed, but since the inter-particle forces are stronger than the hydrodynamic forces, the cluster moves more like a solid body than like a fluid. The density profile (Fig. 8.6 c)) then increases in the central region and decays at the regions close to the border, since particles from there join the central cluster. When averaging the velocity profile in the shear flow, one finds a very small velocity gradient in the center of the shear cell and fast moving particles close to the wall, where the shear is imposed (Fig. 8.5 b)). The velocity profile is non-linear on the length scale of the simulations. In the experiment the physical dimensions are much larger and therefore the velocity profile can become approximately linear again if the system consists of many large clusters. However, due to the high computational effort it is impossible today to measure the shear viscosity for these strongly inhomogeneous systems. We scale our system by a factor of two in $x$ and $z$-direction (keeping the volume fraction $\Phi = 35\%$ constant), but we still observe one big cluster after some hundreds of SRD time steps, i.e., finite size effects are still present in our simulations. Therefore, we cannot expect quantitatively correct results deep in the clustered regime, however, close to the border for not
too small shear rates the results are in good agreement with experimental data. Close to the border towards the suspended region clusters can be broken up into small pieces by the hydrodynamic forces at least for high shear rates. In state $C$ of Fig. 8.1 this happens for the first time at $\dot{\gamma} = 500/\text{s}$ ($Pe = 15$), so that one can find two clusters in the system moving in opposite directions. The velocity profile of this case is shown in Fig. 8.5 c). For even higher shear rates or closer to the border, the clusters are broken into smaller pieces. Then, they move in the shear flow with an approximately linear velocity profile. Due to van der Waals attraction the system resists with stronger shear forces and the viscosity is higher than in the suspended case (Fig. 8.7).

We have studied by which factors the shear viscosity is most influenced and how the parameters have to be adjusted to achieve the best compliance with the experiments. Therefore, we have simulated systems with size and charge polydispersity in the order of magnitude corresponding to the experimental conditions. We have tested different sorts of boundary conditions, different ways to implement shear and different coupling methods between fluid and particles. In most of the tests the achieved shear viscosity in the simulation did not change notably. To our experience the way shear is imposed and the particle mean size have the largest influence on the result. We chose the particle diameter equal to the mean diameter of the powder in use for the experiments. Since polydispersity does not strongly affect the viscosity, we use monodisperse spheres in our simulations.

In Fig. 8.7 the simulation results are shown together with the experimental results, both for the two cases of a slightly clustered system in state $B$ ($I = 7 \text{ mmol/l}$) and a suspension (state $A$, $I = 3 \text{ mmol/l}$). The experimental results [114] have been obtained by J. Reinshagen, Institute for Ceramics in Mechanical Engineering of the University of Karlsruhe (collaboration within the research group, compare section 3.5). For the suspension (state $A$) the viscosity decreases with the shear rate (“shear thinning”). The experimental data and the simulation are consistent within the accuracy of our model. There are several reasons for which our model does not fit the measurements exactly: due to experimental difficulties the most insecure factor which enters into the comparison is the measurement of the $\zeta$-potential. Starting from this point we set up our charge regulation model to extrapolate to different salt concentrations, assuming two reactions being the only processes that determine the surface charge of the colloidal particles. Furthermore, we assume spherical particles, which is another simplification in our model. However, more complicated particle shapes would require a much larger computational effort. Then, the lubrication force as a correction for the finite resolution of the fluid method can only recover to a certain degree the hydrodynamics on smaller length scales than the cell size of the fluid simulation, e.g., we have not implemented other modes of lubrication than the “squeezing mode” (Eq. (4.8)). However, this is a small effect, which can be neglected.

Finally, one has to keep in mind that the viscosity of the suspension can be varied by more than one order of magnitude, e.g., by changing the ionic strength. In this context the deviations between simulation and experiment are small.

For the slightly clustered case (state $B$) an increase of the shear viscosity, compared to the suspended case, can be observed in the experiment as well as in the simulations. Shear thinning becomes more pronounced, because clusters are broken up, as mentioned above.
8.3 Shear Profile and Shear Viscosity

Figure 8.8: Discrepancy between simulated viscosity and measurement for states $A$ and $B$ of Fig. 8.1 for different system sizes at low shear rates. The plot shows squared relative differences against $z$-extension of the simulation volume. The lines are a guide to the eye.

However, the shear rate dependence is stronger in the simulations than in the experiment. This can be the first indication of finite size effects.

We study the dependence of the simulated shear viscosity in dependence of the system size. The effect is most important for low shear rates and thus we carry out several simulations for state $A$ at $\dot{\gamma} = 20/s$ ($Pe = 0.6$) and for state $B$ at $\dot{\gamma} = 50/s$ ($Pe = 1.4$) We choose these values because clustering is already too strong in state $B$ at $\dot{\gamma} = 20/s$ to reasonably determine a viscosity and the dependence on the system size becomes too small for $\dot{\gamma} = 50/s$ in state $A$. In Fig. 8.8 we plot the squared relative deviation between simulation and measurements against the system size. The deviation becomes smaller for larger system sizes, but in order to reach the same accuracy in state $B$ as in state $A$ one would have at least to double the system size in each dimension. It then takes approximately twice as long for the system to relax to a steady state, resulting in a factor of 16 in the computational effort. Each single point of Fig. 8.7 would need approximately 3000 CPU hours. We could do this for single simulations using the parallelized version of the simulation program, but not for complete viscosity curves, since this is too computationally demanding. For smaller shear rates or even deeper in the clustered regime of the stability diagram, e.g., in state $C$ ($I = 25\text{ mmol/l}$), the finite size effects become more pronounced—ending up in the extreme case of only one big cluster existing in the system. For simulations with good accuracy the effort again increases at least by the same factor.

Unfortunately, exactly this would be the most interesting case with respect to soil mechanics and to understand landslides, which was our one of our initial motivations. Anyhow, if we compare state $A$ and state $B$, shear thinning becomes stronger with increasing ionic strength. In the experiments the effect becomes much stronger for larger ionic strengths (up to $I = 65\text{ mmol/l}$), where the viscosity for low shear rates is increased by more than a
factor of ten. However, the fact that there is shear thinning and that it depends on the ionic strength is an interesting result, which comes out of our simulation as well as of the experiments. Note that we did not explicitly model an interaction designed to reproduce shear thinning. We only had to adjust the lubrication force in the Molecular Dynamics part of the simulation, which compensates the finite resolution of the SRD part of the simulation, to the measurements.

Another argument are the limitations of the DLVO theory. DLVO potentials are derived for dilute suspensions and hence large particle distances. This is not fulfilled in our case—and even less inside the clusters. Theoretical attempts that address the shortcomings of DLVO theory exist: explicit simulation of micro-ions [92], density functional theory [44, 149, 150], response theory [27–29, 49], Poisson Boltzmann cell models [31, 138, 153], and full Poisson Boltzmann theory [14, 35, 36, 48], but they have other disadvantages—most of them require a large computational effort. For Poisson Boltzmann cell models one assumes homogeneously distributed colloidal particles, so that each of them can be regarded as a representative single particle in a Wigner-Seitz cell. Additionally, depending on the level Poisson Boltzmann theory is included, a mysterious phase separation could be identified as an artefact of linearization [138]. Full Poisson Boltzmann theory would require the calculation of the local potential, not only as done in our charge regulation model in the beginning of the simulation, but for the whole simulation box and in each time step. This would in principle provide a better description of the real system, but the computational effort would be much larger rendering simulations of several thousands of particles impossible. The same argument applies to the approach of including the micro-ions explicitly in the simulation. One could obtain three (many) body interactions from full Poisson Boltzmann theory and try to include them as a lookup table in the simulation. However, one would have to decrease the system size to keep the computational effort affordable. For our simulations we need relatively simple pair potentials to keep the computational costs within a limit. Nevertheless, the overall behavior can be reproduced by the simulation on a semiquantitative level. The reason for that might be that in some of the above mentioned theoretical attempts (density functional theory and cell models) DLVO-like potentials are obtained with a renormalized charge and screening length. But, in our charge regulation model we do nothing else than adjusting a renormalized charge to the measurements of the \( \zeta \)-potential and for the clustered state the Debye screening length is dominated by the added salt. This may be a general explanation why DLVO potentials can often be used although the assumptions for DLVO theory are not fulfilled [7, 79, 106, 141, 142].

### 8.4 Pair correlation function

For a quantitative description of the microscopic structure we use the pair correlation function of the colloidal particles. The pair correlation function is defined as

\[
g(r) = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(r - r_{ij}) \right\rangle,
\]
Figure 8.9: Correlation function of Al\textsubscript{2}O\textsubscript{3} for pH = 6 and I = 8 mmol/l. The potential is attractive, thus peaks (labeled by letters) can be identified and assigned to distinct local configurations (see text).

Figure 8.10: Correlation function of Al\textsubscript{2}O\textsubscript{3} for pH = 7 and I = 0.5 mmol/l. The potential is mainly repulsive due to the low ionic strength. One can see oscillations caused by the excluded volume.
Figure 8.11: Scanning electron micrograph pictures of clusters occurring in a real experiment taken from [126]. The corresponding geometry is shown below: The particle centers are connected to the centers of their neighbor particles. All lines contribute to the nearest neighbor beak. The diagonals contribute to different peaks, e.g., the one of the second picture contributes to peak B in Fig. 8.9.
8.4 Pair correlation function

(see Ref. [9] p.55), where \( V \) is the volume, \( N \) the number of particles and \( r_{ij} \) the distance of the centers of two particles \( i \) and \( j \). The pair correlation function shows different features depending on the microstructure. It is most structured for the clustered microstructure with attractive potentials. Several sharp peaks can be observed and we assign them to distinct local orders of particles.

As shown in Fig. 8.9 for \( pH = 6 \) and \( I = 8 \text{mmol/l} \) the particles cluster due to their attractive potentials and form stable configurations. There is a sharp peak at exactly that distance \( \frac{r}{2R} = 1 \), where two particles touch each other in the very left part of the plot (P1). Then, for larger particle separation, the correlation function starts to grow and suddenly drops after a peak at \( \frac{r}{2R} = 2 \) (P4).This is the contribution of two particles touching the same third particle. The distance between them depends on the angle that they form with the particle in the middle, but, it is at most twice the diameter, when they are in a straight line, which explains the sudden drop of the correlation function. If several particles stick together, the straight line is stabilized. This explains to some extend the peak at the end of this area of the correlation function. Additionally, the probability distribution of the distance between first and third particle shows a maximum if the angle of the arrangement of the three particles is assumed to be uniformly distributed. This would be a purely geometrical argument. However, the underlying argument of uniformly distributed angles is not fulfilled if the particles attract each other, and then especially not for large volume fractions. So, using geometrical arguments, one can only predict that there should be a peak, but one cannot predict how pronounced it is. However, the number of neighboring particles stabilizing a certain configuration also depends on the exact shape of the potentials. However, both effects lead to a peak at \( \frac{r}{2R} = 2 \) in the correlation function.

Two more peaks can clearly be assigned to configurations: one of them is from two particles touching two other particles which themselves touch each other (P3). There again the case of all particles being in the same plane can be stabilized by other particles surrounding them. The particles under consideration are then separated by a distance of \( \frac{r}{2R} = \sqrt{3} \). But indeed, a bending of this configuration is still a degree of freedom which brings the two particles closer to each other. Thus, their contribution to the correlation function is shifted to smaller \( r \).

The fourth peak at \( \frac{r}{2R} = \frac{2}{3} \sqrt{6} \) reflects two particles, both touching three particles which themselves are touching each other and define a plane (P2). There is no freedom anymore for the two particles touching all the three of them at the same time. One can place one of them at one side of the plane and the other one at the other side. Therefore, the peak is sharp, but, since several particles are needed to build up this structure in exactly this manner, the intensity of the peak is rather small.

In Fig. 8.11 scanning electron micrograph images of real colloidal particles are shown. Especially in the first row, the second picture shows the configuration that produces peak (P2). Below, the corresponding polyhedra are drawn which are constructed by connecting the centers of neighboring particles with lines. All of these lines are contributions to the large and sharp nearest neighbor peak (P1).

When the potentials are mainly repulsive and the minimum caused by the van der Waals attraction is only a fraction of \( k_B T \), the spatial correlation function looks completely dif-
Figure 8.12: Dependence of the particle correlation function on the pH value, $I = 3 \text{ mmol/l}$, $\dot{\gamma} = 0/s$, $\Phi = 35\%$. The plots for four different pH-values are shifted against each other for better visibility. For pH = 4 the particles are not clustered. Hence, the structure at $\frac{r}{2R} = 2$ is less sharp than in the other three plots of the figure and the nearest neighbor peak (at $\frac{r}{2R} = 1$) is broad. For pH = 6.5 slight clustering starts, the structures become sharper. For pH = 7.7 strong cluster formation is reflected in very sharp structures. For pH = 8.5 electrostatic repulsion nearly disappears so that no barrier between primary and secondary minimum exists anymore. The particles cannot rearrange anymore during the clustering process, and therefore the structures at $\frac{r}{2R} = 2$ become less sharp again due to the disorder in the system.

Different, as depicted in Fig. 8.10: the peaks described in the previous paragraphs have disappeared here. The primary peak has moved to a slightly larger distance, since the repulsive potential hinders the particles from touching each other. This is a typical picture of $g(r)$ in the repulsive regime. The correlation function can vary between those extreme cases as shown in Fig. 8.12, note that the plots are shifted vertically in the plot for better visibility. Depending on the pH-value the behavior of the system changes from a slightly repulsive structure around pH = 4, $I = 3 \text{ mmol/l}$ to a stable suspension around pH = 6, $I = 3 \text{ mmol/l}$ towards a clustered region if the pH-value is increased, until the isoelectric point is reached at pH = 8.7, where clustering occurs in any case, independent of the ionic strength. Electrostatic repulsion prevents clustering (at pH = 4). There is no strong long range ordering in the system since the state is close to the border between suspended and repulsive region. The correlation function shows a maximum at a typical nearest neighbor distance slightly above $\frac{r}{2R} = 1$ with $d$ denoting the particle diameter, then in the layer of nearest neighbors small correlations can be found (at $\frac{r}{2R} = 2$). For larger distances the correlation function is rather constant.

When the pH-value is increased, the surface charge is lower, which at first causes the particles to approach each other more closely. The maximum of the correlation function
Figure 8.13: Correlation function, $\dot{\gamma} = 100/s$, $pH = 7$, $I = 3\, \text{mmol/l}$, $\Phi = 35\%$: one finds clustering in the primary and the secondary minimum. Note: the vertical axis is logarithmic, and a constant offset has been added before plotting. Thereby, the coincidence of the minima in the potential with the maxima in the correlation function becomes more apparent. The dotted lines denote the position of the base line before shifting.

is shifted to smaller distances (see Fig. 8.12). Then, van der Waals attraction becomes more important and clustering begins. One can see this in the correlation function where a sharp structure at particle distances between 1.5 and 2 particle diameters occurs. In a solid like cluster the position of the nearest neighbor is fixed more sharply than in the suspension, consequently the nearest neighbor peak becomes sharper, too, and its height is increased. Close to the isoelectric point ($pH = 8.7$) the barrier between primary and secondary minimum disappears. The particles, once clustered, cannot rearrange anymore, and therefore the correlations to the nearest neighbors become less sharp again (compare the cases of $pH = 8.7$ and $pH = 7.7$ in Fig. 8.12 at the positions denoted by the arrows).

Instead of varying the $pH$-value, one can also vary the ionic strength (not shown) to achieve similar effects. Increasing the ionic strength, experimentally speaking “adding salt” decreases the screening length $1/\kappa$ and, therefore, the attractive forces become more important: the particles start to form clusters. On the contrary, if the ionic strength is decreased—experimentally speaking a dialysis step is performed—the electrostatic repulsion prevents cluster formation and, for sufficiently strong repulsion, long range correlations occur starting at a certain volume fraction.

In Fig. 8.13 one can see clustering in the primary minimum of the potential as well as in the very shallow secondary minimum. The correlation function plotted there is evaluated after 1000 SRD time steps in a simulation for $pH = 7$ and $I = 3\, \text{mmol/l}$ at a volume fraction of $\Phi = 35\%$ sheared with $\dot{\gamma} = 100/s$. Note that the shear flow is not of essential importance here, but it supports the particles to overcome the potential barrier between the primary and the secondary minimum. The dotted lines in Fig. 8.13 denote the zero line.
Figure 8.14: Correlation function for $\dot{\gamma} = 500/\text{s}$, $p\text{H} = 6$, $I = 0.3\ \text{mmol/l}$, $\Phi = 32\%$: depending on the simulation time the peaks indicated by the arrows from below split into two (indicated by the arrows from above), and long range correlations occur (for $r/2R > 4$). This reflects the process of layer formation and appearing of a regular (hexagonal) order in the layers. From bottom to top several states for increasing time are shown. The plots are shifted vertically for better visibility.

A secondary minimum only exists if the screening length of the electrostatic repulsion is short enough, i.e., if the ionic strength is large enough. According to the depth of the potential, clustering in the primary minimum is associated with much stronger forces than in the secondary minimum.

The effects described up to here can be seen with or without shear qualitatively in an analogous manner. If the suspension is sheared clustering occurs at higher $p\text{H}$-values and the peaks found in the correlation function are slightly broadened, because the relative particle positions are less fixed. But a new feature appears, if a stable suspension at not too high volume fraction is sheared. Induced by the shear particles arrange themselves in layers. Regular nearest neighbor distances in the shear plane cause the correlation function to become more structured even for large distances (see Fig. 8.14). The long range structure of the pair correlation function appears after a transient time the particles need to arrange themselves in the layered structure. The plots in Fig. 8.14 correspond to the same simulation, but for increasing time from bottom to top. The arrows from the bottom indicate the position of the nearest neighbor peak and the next nearest neighbors (Since the particles do not touch each other, the peaks are located not exactly at $r/2R = 1, 2, 3, \ldots$). Within one layer which moves as a whole, a hexagonal particle order appears which can be seen in the occurrence of a peak at $r/2R = \sqrt{3}$ times the position of the nearest neighbor peak, i.e., the nearest neighbor peak splits, as indicated by the arrows from above. The same applies to the next nearest neighbor peak marked by the second set of arrows at $3 < r/2R < 4$.

Let us now focus on the nearest neighbor peaks and discuss their dependence on the
Figure 8.15: Nearest neighbor peak (primary and secondary minimum of the potential) of the correlation function $I = 3 \text{mmol/l}$, $\Phi = 35\%$: for low pH-values clustering is prevented by the electrostatic repulsion. For high pH-values the particles form clusters, which is reflected by an increased nearest neighbor peak. First, shear prevents clustering, then depending on the shear rate, cluster formation takes place. Low shear rates even support cluster formation at high pH-values.

pH-value. We integrate over the nearest neighbor peaks, both, the peaks of the primary and the secondary minimum, and plot the integral versus pH-value in Fig. 8.15. We choose $I = 3 \text{mmol/l}$ and $\Phi = 35\%$ and three different shear rates: $\dot{\gamma} = 0$, 100 and 500/s. We integrate the correlation function for $r < 1.215d$, where for all pH-values the potential in the secondary minimum has a value of $-\frac{1}{2}k_B T$. In other words, we capture the primary and the secondary minimum of the potential for this plot. For low pH-values clustering (in the secondary minimum) is only possible for low shear rates. For high shear rates, the hydrodynamic forces do not allow the formation of stable clusters. For rising pH-values the clustering increases, first for the un-sheared suspension, at higher pH-values for low shear rates ($\dot{\gamma} = 100/s$) and finally for high shear rates ($\dot{\gamma} = 500/s$). Remarkably, for $pH > 7.5$ the plot for $\dot{\gamma} = 100/s$ shows stronger cluster formation than the other ones. Particles are brought together by the shear flow, so that compared to the case of no shear, the clustering process is supported here. On the other hand, the shear stress may not be too strong, because otherwise the clustering process is limited by the shear flow again (for $\dot{\gamma} = 500/s$ the clustering is less pronounced than for $\dot{\gamma} = 100/s$).

Fig. 8.16 shows selected examples of correlation functions ionic strengths without imposed shear flow. The volume fraction is $\Phi = 14\%$. One can see that for suspended particles only the first peak can be found in the correlation function. The secondary minimum in the potential causes the particles to glue together for short times before they continue their diffusion process. With increasing ionic strength the secondary minimum approaches the particle surface, and therefore the main peak is shifted to smaller distances.
Figure 8.16: Correlation function $g(r)$ and its dependence on the ionic strength. The $\zeta$-potential $\zeta = 20$ mV and $\Phi = 0.14$ have been kept constant. For shorter Debye screening lengths the attractive force becomes stronger and leads to clustering, which is reflected in the appearance of peaks. The single plots have been shifted with respect to each other for better visibility.

At the same time it becomes deeper so that clusters are formed and more peaks occur. The peak at a distance of $\frac{r}{2R} = \sqrt{2}$ appears and disappears again, when the attraction becomes stronger since this is a meta stable configuration of particles forming an octahedron. It is the configuration depicted in the third image of Fig. 8.11.

### 8.5 Structure Factor

Closely related to the pair correlation function is another important quantity which we use as an analysis tool for the microstructure: the structure factor, defined by

$$S(k) = \frac{1}{N} \sum_{l,m=1}^{N} \exp(i \mathbf{k} \cdot \mathbf{r}_{lm}),$$

(8.2)

where $N$ is the number of particles, and $\mathbf{r}_{lm}$ is the vector from particle $l$ to particle $m$. $i$ denotes the imaginary unit here. The structure factor is defined in $k$-space and it is related to the pair correlation function in real space by a three dimensional Fourier transform:

$$S(k) - 1 = \int \, d\mathbf{r} \exp(i \mathbf{k} \cdot \mathbf{r}) \rho g(r),$$

(8.3)

with the density $\rho$.

In principle $g(r)$ and $S(k)$ are complementary quantities and the information contained in them is the same. However, due to a limited resolution and finite system size, it makes
8.5 Structure Factor

sense to use \(g(r)\) when one is interested in the local order and \(S(k)\) when looking at the length scale of the system size.

In scattering experiments the structure factor can in principle be extracted from the scattered intensity \(I'\) [87] which is proportional to the incident intensity \(I(k)\), to the volume fraction \(\Phi\), and to \(S(q)\), where \(q = k' - k\) is the so called scattering vector:

\[
I'(k') \sim I(k)S(q)P(q)\Phi. \tag{8.4}
\]

\(P(q)\) is the form factor which describes the influence of the particle shape. In diluted suspensions the form factor dominates the dependency \(I'(k')\), whereas in dense suspensions, where particles influence each other, the information about the local order is expressed by the additional structure factor \(S(q)\).

To obtain the structure factor, one first has to measure or to model the form factor and divide it out of the measurements. Unfortunately, scattering experiments of suspensions like the ones we focus on, face severe problems. The suspension is not transparent enough for light scattering and the particles are too large for X-ray scattering experiments. Additionally, separating the different influences to the scattering intensity poses difficulties. Especially in order to be able to divide out the form factor, excellent measurements of the scattering intensity would be necessary.

However, from our simulations we can extract the structure information directly. In this sense the structure factor can be seen as a tool for quantitative analysis of the simulated system without facing the problems which arise when analyzing experimental scattering data. For illustration we can qualitatively compare our simulations to experimental results for different materials or to different simulation results in the literature. Similar peaks of the structure factor are reported by many authors, e.g., in Ref. [17] for a 2D system of Lennard Jones disks, and in Ref. [26] for a 3D system at low volume fractions. This comparison, obviously, has illustrative character only, since the systems inspected by the other authors are completely different. Measured data for dense \(\text{Al}_2\text{O}_3\) suspensions does not exist because of the experimental difficulties mentioned above.

In simulations one can directly evaluate \(S(k)\) according to Eq. (8.2). A peak at a certain \(k\)-vector corresponds to a typical distance between two particle centers \(r_{ij} = \frac{2\pi}{k}\) occurring frequently in the system. One typical length for dense systems is about one particle diameter, the distance particle centers have to keep so that they do not overlap. The corresponding peak of the structure factor is the nearest neighbor peak at \(k = \frac{2\pi}{2R}\). In a single crystal the peak would be sharp, since the particle positions are well defined, whereas in our case of a suspension there is a certain disorder which broadens the peak. This peak directly corresponds to the nearest neighbor peak of \(g(r)\). However, we notice that to analyze the nearest neighbor peak of \(g(r)\) yields better results than \(S(k)\) due to numerical approximations when we calculate \(S(k)\).

Similar to the nearest neighbor peak another peak can be detected at twice the \(k\)-vector which corresponds to a distance of one particle radius. This does not necessarily mean that there are particles whose centers are only one particle radius apart. It only means that for a certain \(k\)-vector the addends in Eq. (8.2) do not cancel out each other. In fact, this peak can be seen in experiments with latex particles [122, 145], where the interactions can
Figure 8.17: Comparison with literature and experimental data: main figure: our simulation for $pH = 6, I = 15 \text{ mmol/l}, \Phi = 35\%$. The triangles are ultra small angle X-ray scattering data taken from Ref. [131], Fig. 7b). The sample is a depletion induced gel of silica colloidal particles of $R = 59 \pm 3 \text{ nm}$ in a polystyrene solution. The arrows mark the position of the nearest neighbor peak and the 2nd-order-peak respectively. The same arrows are shown again in the inset, where we have plotted structure factor data taken from the literature: the dashed line is a Newtonian simulation of a binary mixture of spheres interacting with square well potentials taken from Ref. [39], Fig. 9b). The circles are experimental data extracted from small angle neutron scattering (SANS) experiments (taken from Ref. [65], Fig. 2b)). The system is a three-component micro emulsion consisting of small water droplets (radius $R = 60 \text{ Å}$) coated with a layer of surfactant and suspended in oil. The volume fraction is $\Phi = 7.5\%$. The squares represent SANS data taken from Ref. [88], Fig. 4) for star-like block copolymer micelles.

be described by DLVO theory, too. As in our case, the particle suspensions are stabilized by a surface charge which can be screened by increasing the ionic strength of the solvent. The samples can be observed via light scattering.

For small $k$-vectors there is another peak, or in our case an increase of the structure factor towards low $k$-vectors. The length scale corresponds to the size of the whole system. If large clusters are formed, this can be seen in an increase of the low-$k$-peak, since the contributions on this length scale do not cancel out each other anymore. This can be used in experiments to detect clustering or gelation, provided that the resolution of the measuring device allows to detect the respective $k$-vectors. In Ref. [132] and [131] Shah et al. report on their observations of depletion driven gelation of a colloid polymer mixture using X-ray scattering. Their samples show a strong increase of the low-$k$-peak as soon as it undergoes the sol-gel transition.

Even though the mechanism for the attractive interaction is different from our system, the resulting structure is comparable to what we find. Fig. 8.17 illustrates the similarities of
the structure factor of one of our simulations \( (pH = 6, I = 15 \text{ mmol/l}, \Phi = 35\%, \dot{\gamma} = 100/s) \) with experimental data taken from Ref. [131]. The structure factor was extracted from ultra small angle X-ray scattering at silica colloidal particles of \( R = 59 \pm 3 \text{ nm} \) in a polystyrene solution. The measurements show a nearest neighbor peak at the same position (marked by the arrow) as our data, which is typical for dense solutions. The “lift-up” at low \( k \)-vectors as well can be seen in both, simulation and measurements. Of course, the agreement is not perfect, since we did not adjust our simulation parameters explicitly to this experimental situation. Fig. 8.17 is meant as an illustration only.

It is difficult to gain accurate structure factors on the whole range from low \( k \)-vectors corresponding to cluster sizes or even the size of the whole system up to higher order peaks. Therefore, we have collected two more examples for the measurement of structure factors in the inset of Fig. 8.17: The low-k-peak can be seen in small angle neutron scattering (SANS) data of a micro emulsion taken from Ref. [65]. Small water droplets (radius \( R = 60 \text{ Å} \) coated with a layer of surfactant were suspended in oil at a volume fraction of \( \Phi = 7.5\% \). The nearest neighbor peak and the 2\(^{nd}\)-order-peak can be seen in SANS data taken from Ref. [88] where structures formed by star-like block copolymer micelles were investigated. The shift to smaller \( k \)-vectors (compare the position of the peaks relative to the arrows) reflects the larger inter-particle distances caused by the polymers attached to the core. To finish with this illustration, the dashed line finally is data of a Newtonian simulation taken from Ref. [39]. In this case a binary mixture of spheres interacting with square well potentials has been investigated. All the previously discussed features are present in the structure factor of this simulation.

In Fig. 8.18 we have plotted several typical structure factors of our simulations. For these plots the \( pH \)-value is fixed to \( pH = 6 \). The cases a) and b) are sheared with \( \dot{\gamma} = 500/s \) at an ionic strength of \( I = 0.3 \text{ mmol/l} \). In case a) the volume fraction \( \Phi = 20\% \) is relatively low. Therefore, the particles can arrange themselves in layers parallel to the shear plane, which move relatively independently in the shear flow. They have a certain distance fixed in space and time. This can be seen in a sharp peak at a dimensionless \( k \)-vector of \( k = 5.2 \) which corresponds to a distance of 1.2 particle diameters. In fact, this is exactly the distance between two neighboring layers, as one can easily verify by counting the layers in a snapshot of the system (Fig. 8.19 a)). The particles in the layers do not have a fixed distance and therefore no pronounced 2\(^{nd}\)-order-peak can be observed.

For case b) the volume fraction is increased to \( \Phi = 35\% \). The particle layers are packed more densely and therefore the interactions between one layer and the neighboring one become relevant. Particles jump from one layer to the other, which disturbs the flow and therefore the distance between the layers is not fixed anymore. The sharp peak on the nearest neighbor peak disappears. Instead, in each layer a regular hexagonal order appears and therefore the 2\(^{nd}\)-order-peak is much more pronounced.

In case c) the ionic strength is increased to \( I = 25 \text{ mmol/l} \). The inter-particle potentials are attractive, hence cluster formation takes place. In this simulation we do not apply shear, therefore one finds only one big cluster in the system (compare Fig. 8.19 c)). In the cluster the particles are packed more densely and consistently the nearest neighbor peak in the structure factor is shifted to larger \( k \)-vectors. The volume fraction is \( \Phi = 40\% \) in this case.
Figure 8.18: Structure factor for some selected examples, with $pH = 6$ fixed for all plots: $\dot{\gamma} = 500/s$, $I = 0.3$ mmol/l: a) $\Phi = 20\%$ and b) $\Phi = 35\%$, $\dot{\gamma} = 0$, $I = 25$ mmol/l: c) $\Phi = 40\%$ and d) $\Phi = 10\%$. The plots are shifted vertically for better visibility. In case a) ten layers can be identified in the system, resulting in the strong peak close to 5. But, since the particles in the layers can still move freely, there is no $2^{nd}$-order-peak. In case b) layers are formed, but particles are moving from one layer to the other, disturbing the flow. As a result the nearest neighbor peak is much broader. Due to the structure in the layers, a $2^{nd}$-order-peak appears. In case c) the interaction is strongly attractive, hence the particles approach each other and the nearest neighbor peak is shifted to higher $k$-vectors. In case d) the volume fraction is much less. The slope of the low-$k$-peak is much flatter, which means that the cluster is fractal.
Figure 8.19: Images of the systems for Fig. 8.18 (The pH-value is kept constant at $p\text{H} = 6$ for all plots): for case a) and b) the system is sheared at a shear rate of $\dot{\gamma} = 500/s$ and the potentials are repulsive due to a low ionic strength of $I = 0.3\text{ mmol/l}$. in case a) with a volume fraction of $\Phi = 20\%$ one can see the layers resulting in the sharp peak in the structure factor. In case b) with increased volume fraction $\Phi = 35\%$ the layers are packed closer due to the higher volume fraction. Collisions between particles of neighboring layers happen more frequently. For case c) and d) the potentials are made attractive due to a high ionic strength of $I = 25\text{ mmol/l}$. The systems are not sheared ($\dot{\gamma} = 0$) In case c) at high volume fraction $\Phi = 40\%$ one big cluster is formed. The particles are packed densely. In case d) for a low volume fraction of $\Phi = 10\%$ the fractal nature of the system can be seen directly.
Figure 8.20: low-k-peak for different pH-values and different shear rates. The ionic strength \( I \) is kept constant at \( I = 3 \text{ mmol/l} \) and the volume fraction is always \( \Phi = 35 \% \). For \( \dot{\gamma} = 0 / \text{s} \) the particles tend to cluster in the secondary minimum of the potential. This clustering can easily be broken up, if shear is applied. If the pH-value is increased, shear cannot prevent cluster formation anymore. At low shear rates (\( \dot{\gamma} = 100 / \text{s} \)) clustering is even enhanced, since the particles are brought closer to each other by the shear flow.

In case d) the volume fraction is decreased to \( \Phi = 10 \% \). The particles still form clusters, but their mobility is not high enough to create one compact cluster. The system is rather fractal (see Fig. 8.19 d)). This can be seen in the structure factor as well: the slope of the low-k-peak is flatter in this case compared to the cases a)– c). A flatter slope of the low-k-peak is typical for structure factors of fractal objects. Lattuada et al. [87] have evaluated the fractal dimension of agglomerates of latex particles from the slope of the structure factor. McCarthy et al. [98] give an introduction to scattering intensities at fractal objects, without mentioning the structure factor, but their arguments refer to the contribution of the structure factor on the scattering intensity.

Let us now focus on the low-k-peak and its dependence on the pH-value. This corresponds to an analysis of the structure on the length scale of the system size. Numerically it is easier to integrate over the low-k-peak of the structure factor than extracting the same information from \( g(r) \). In Fig. 8.20 we have shown the dependence of the low-k-peak of the structure factor on the pH-value. Here we have integrated over dimensionless k-vectors smaller than three which means, we have captured structures larger than twice a particle diameter. If the value of the integral of the low-k-peak is large, this means that there is a large inhomogeneity in the system, which is a sign of a cluster formation process. Without shear, particles cluster in the secondary minimum for all pH-values. If the system is slightly sheared (\( \dot{\gamma} = 100 / \text{s} \)) clustering is suppressed for low pH-values. Starting at pH = 6 the cluster formation starts and is even supported by the shear flow for pH-values larger than 7.5. For large shear rates (\( \dot{\gamma} = 500 / \text{s} \)) the cluster formation is suppressed by the
shear flow. In Fig. 8.15 we show the same plots as in Fig. 8.20, but there we plot the nearest neighboring peak of $g(r)$ whereas in Fig. 8.20 we show the low-$k$-peak of $S(k)$. The two plots show strong similarities, although in Fig. 8.15 we observe the cluster formation process locally, i.e., on the length scale of the neighboring particles. In contrast to Fig. 8.15, we observe on the length scale of the system size when we examine the low-$k$-peak of the structure factor in Fig. 8.20. The strong similarities of both plots shows that the cluster formation process can be observed independently from the length scale at which one observes.

8.6 Density Inhomogeneity

Another way to observe the cluster formation process is provided by the “demixing parameter” defined in Ref. [110] as follows: the system is divided into $n^3$ cubes and the particle density $\rho_k$ is evaluated in each cube. Then the demixing parameter is the mean squared deviation of the density

$$\Psi_n = \sum_{k=0}^{n^3} (\rho_k - \bar{\rho})^2,$$

(8.5)

where $\bar{\rho}$ is the mean density. For our elongated system we modify this definition and use $2n$ cubes in $x$-direction, resulting in $2n^3$ cubes in total. The demixing parameter implicitly contains information about the density of the clusters. It is the density fluctuation of the whole system. If the clusters are more compact, voids have to appear and the demixing parameter increases, since the distribution of the local density is broadened thereby.

In Fig. 8.21 we have plotted the demixing parameter $\Psi_4$ versus time for three different shear rates and four different ionic strengths in each plot. The pH-value is kept constant at $pH = 6$ and the volume fraction at $\Phi = 35\%$. Without shear $\Psi_4$ is nearly constant. Even if a cluster is formed, it does not move, so that the average density in the boxes does not change much. For lower volume fractions the time dependence without shear is stronger. If shear is applied the clusters are deformed so that stronger inhomogeneities appear. Depending on the ionic strength the demixing parameter increases with cluster formation (high ionic strength) or still stays constant when the interactions are repulsive (low ionic strength). For $\dot{\gamma} = 100/s$ the strongest cluster formation is achieved for the highest ionic strength $I = 20 \text{ mmol/l}$. If the ionic strength is decreased, the clustering effect decreases as well, until it disappears completely at $I = 1 \text{ mmol/l}$, where the repulsive regime is reached. To see the shear rate dependence, compare the plots for $\dot{\gamma} = 100/s$ and 500/s. If the shear rate is increased, the cluster formation starts faster because the shear flow brings the particles faster in contact, but the resulting inhomogeneity of the final state is less than for lower shear rates. This effect can be seen in Fig. 8.15 and Fig. 8.20, too. There, also the intensity of the respective peaks for $\dot{\gamma} = 500/s$ is less than for $\dot{\gamma} = 100/s$. This shows again that large shear rates can inhibit cluster formation, whereas moderate shear rates can support the clustering process (the plots in Fig. 8.21 b) for $\dot{\gamma} = 100/s$ are steeper than the ones in Fig. 8.21 a) for $\dot{\gamma} = 0/s$.) In addition to the information already
Figure 8.21: Demixing parameter for constant $pH = 6$ and volume fraction $\Phi = 35\%$ for three different shear rates: $\dot{\gamma} = 0/s$ (top), $100/s$ (center) and $500/s$ (bottom). Without shear only very weak demixing takes place. For $\dot{\gamma} = 100/s$ the strongest demixing can be observed for the system with the highest ionic strength $I = 20\,\text{mmol/l}$. For lower ionic strengths the effect decreases until it disappears completely at $I = 1\,\text{mmol/l}$, where the repulsive regime is reached. If the shear rate is further increased ($\dot{\gamma} = 500/s$), the clusters are less stable so that the system becomes less inhomogeneous. For $I = 5\,\text{mmol/l}$ the demixing is even suppressed completely.
8.7 Repulsive Regime: Mobility and Mean Squared Displacement

To characterize the repulsive regime, we evaluate the mean squared displacement for the particles. In Fig. 8.22 we plot the mean squared displacement for different ionic strengths. The pH-value is kept constant at \( pH = 6 \) and the volume fraction is \( \Phi = 35 \% \) for this plot. Three different regimes can be identified. For very short times, the ballistic regime: particles move on short distances without a notable influence by their neighbors. The dis-
Figure 8.23: Viscosity versus volume fraction for the repulsive region ($p\text{H} = 6$ and $I = 0.3 \text{ mmol/l}$). The shear rate was $\dot{\gamma} = 100/\text{s}$ ($Pe = 2.9$). The points are simulation results, the line is a spline function meant as a guide to the eye.

...
By looking at the snapshots of the system, we find layers parallel to the shear plane in analogy to Fig. 8.6b. In contrast to the suspended regime, in the repulsive regime the layer structure is present—at least locally, but orientationally disordered—even if no shear is applied. If shear flow is present, the shear plane marks an orientation which the layer structure adopts. In some cases for very low ionic strengths one can observe shear bands so that the velocity gradient and thus the viscosity vary strongly in the system. Again, in the experiment, physical dimensions are much larger and on that length scale the velocity profile might be assumed to be linear when enough shear bands are in the system.

8.8 Total Energy

In our simulations we calculate and monitor the total energy, because it can be used as a tool to check if the response of the simulation to the variation of any parameter is consistent with the expectations, e.g., a decrease of the surface charge on the colloidal particles should cause the secondary minimum of the DLVO potential to become deeper and thus decrease the total energy—however, if the total energy increases, this can be an indication for numerical instabilities.

The total energy comprises the kinetic energy of both fluid and colloidal particles, including thermal motion on the microscopic level, as well as the potential energy due to Coulomb repulsion, van der Waals attraction, and Hertz contact forces. Our simulations are carried out at room temperature ($T = 295$ K) and constant volume fraction. Supposing a linear velocity profile, the kinetic energy increases quadratically with the shear rate $\dot{\gamma}$. This can be observed if the electrostatic repulsion is, on the one hand, strong enough to prevent cluster formation due to van der Waals attraction and, on the other hand, weak enough, so that the colloidal particles can move relatively freely without being restricted in their motion by repulsive interactions to their neighbors, i.e., in the suspended regime.

If the interactions are strongly repulsive, i.e., in the case of very low salt concentration, where the Debye-screening length is large, one can see an extra contribution of the electrostatic repulsion to the total energy. If the volume fraction is low, the particles can still find a configuration, in which the mean nearest neighbor distance is larger than the interaction range of the repulsion. But, if the volume fraction is increased, the particles have to be packed closer, which leads to a constant positive offset to the total energy. It only depends on the potentials and on the volume fraction, but not on the shear rate.

In a similar way as for repulsive interactions, one can understand the negative energy contribution in the case of high salt concentrations: the DLVO potentials contain a minimum where attractive van der Waals interaction is stronger than electrostatic repulsion. Then the particles form clusters and “try” to minimize their energy. In Fig. 8.24 for small shear rates the values for the energy in the clustered case of state $C$ of Fig. 8.1 ($I = 25$ mmol/l, pH = 6) is lower than for the suspended case of state $A$ ($I = 3$ mmol/l). We plot the total energy divided by the total number of all particles (fluid particles plus colloidal particles) in units of $k_B T$. For $\dot{\gamma} \rightarrow 0$ the energy per particle approaches $\frac{3}{2} k_B T$ as one would expect.
Figure 8.24: Total energy depending on the shear rate $\dot{\gamma}$ for the states $A$ ($I = 3 \text{ mmol/l}$) and $C$ ($I = 25 \text{ mmol/l}$) of Fig. 8.1. In state $A$ the system is a stable suspension, in state $C$ cluster formation reduces the total energy at low shear rates. At $\dot{\gamma} = 500/\text{s} (Pe = 15)$, the cluster can be broken up into two parts moving in opposite directions. The two solid bodies have a larger kinetic energy than the suspension with a linear velocity profile. This explains the crossover of the two plots. For even higher $\dot{\gamma}$, the clusters are broken up in more pieces leading ultimately to the same structure as for the suspended state $A$. The energy axis has been scaled by the total number of particles (fluid particles plus colloidal particles) and plotted in units of $k_B T$. The solid line is the analytical solution (Eq. (8.6)) for a linear velocity profile, the dashed lines are a guide to the eye.
in 3D. The solid line in Fig. 8.24 is the sum of $\frac{3}{2}k_B T$ per particle with the kinetic energy of a fluid with a linear velocity profile:

$$E_{\text{tot}} = \frac{3}{2}k_B T N_{\text{tot}} + \frac{1}{24} V \bar{\rho} \dot{\gamma}^2 L_z^2,$$  \hspace{1cm} (8.6)

where $N_{\text{tot}}$ is the total number of both, fluid and colloidal particles, $V$ denotes the volume of the simulated system, $\bar{\rho}$ the averaged mass density of the suspension, and $L_z$ is the extension in $z$-direction (perpendicular to the shear plane). State A coincides very well with this curve.

For state C the behavior is shear rate dependent: in contrast to the repulsive case, clusters can be broken up. This occurs at a shear rate $\dot{\gamma} = 500/s$ ($Pe = 15$) (see Fig. 8.24) where one obtains two clusters moving in opposite directions. Since in this case the resistance of the system decreases, the velocity of the two clusters becomes larger. Since both clusters are moved as a whole, their energy even becomes larger than in the suspended case. If one further increases the shear rate, no (big) clusters can form anymore and the energies for both salt concentrations are nearly the same and correspond to the kinetic energy of a suspension with a nearly linear velocity profile. For $\dot{\gamma} = 1000/s$ ($Pe = 29$) state C coincides with the analytic curve.

### 8.9 Cluster Recognition

We have developed and implemented a new cluster recognition algorithm (see chapter A.1, first published in Ref. [59]). In this section we report on the first results obtained with our new algorithm. We use it to extract the cluster size distribution from our simulations. Furthermore, the algorithm allows us to trace each particle and its assignment to the respective cluster in time. This provides the possibility to investigate in more detail how clusters are formed. One can track the history of each cluster and see, e.g., if they grow by collecting single particles or by aggregation of smaller clusters. We expect that the process involved in the growth of clusters depends on the volume fraction and on the interaction range. We notice that the rate of cluster growth is limited by finite size effects. This happens after a typical time, depending on the volume fraction, system size and the particle-particle interactions. However, one can analyze cluster growth before this limit is reached and even partly correct it for later times.

In Fig. 8.25 we show how the clusters are formed during a simulation. We show a cubic system with $V = (8.88 \mu m)^3$, where $\Phi = 5\%$ MD particles of diameter $2R = 0.37 \mu m$ are contained. The ionic strength is adjusted to $I = 7 \text{ mmol/l}$ and the pH-value is $pH = 6$. We shear the suspension with $\dot{\gamma} = 20/s$. In the single images the time evolution is shown with increasing time from a) to h). The particles are colored with respect to the cluster size, where rainbow colors from red to violet denote cluster sizes from the smallest to the largest one found currently in the system. The color scale is readjusted in each time step.

The strength of our algorithm is the possibility to track individual particles and their assignment to different clusters in time. Clusters grow and break into pieces and we can follow the trajectory of each particle in this scenario. This enables us to draw cluster
Figure 8.25: Snapshots of a simulation of a system with $8.88 \mu m$ extension in each dimension, filled with $\Phi = 5\%$ MD particles of diameter $2R = 0.37 \mu m$. The conditions are ionic strength $I = 7 \text{ mmol/l}$, $pH = 6$, under shear with $\dot{\gamma} = 20/s$. The time is increasing from a) to h). The colors denote the cluster size, using the rainbow colors from red to violet for increasing cluster size. The color scale is adjusted separately for each image. Note that we use periodic boundaries, so that the clusters are connected although it looks as if they were separated in different corners of the simulation volume.
Figure 8.26: Tree-like structure of the assignment of colloidal particles to individual clusters. This cluster tree corresponds to the simulation presented in Fig. 8.25. For better visibility, the time is given on a logarithmic scale. All particles start at the bottom of the plot and aggregate in individual clusters as shown by the merging lines. After two seconds, only a single large cluster is left in the system. The thick line denotes the path of a single particle in order to demonstrate the possibility to track which cluster this particle belongs to and how these clusters break up and re-merge.

Assignment trees like the one in Fig. 8.26. In contrast to conventional algorithms, where clusters cannot be followed in time, the clusters are sorted here on the $x$-axis and they keep their position. The lines are gained by plotting the assignment of the particles to the clusters. The distance between the lines is scaled with respect to the cluster sizes, i.e., if a cluster contains a fraction $p$ of all particles in the simulation, a fraction $p$ at time $t$ is reserved for this cluster on the $x$-axis and the line is plotted in the center of this region. As a consequence, for large $t$, when all particles belong to the same cluster, the line is drawn at 0.5. To see the structure clearly, the clusters additionally have to be sorted on the $x$ axis by going through the output of the cluster algorithm in reversed order with respect to the time $t$. This cluster tree is drawn for the same simulation as the snapshots in Fig. 8.25. The red line demonstrates that we can follow the trajectory of each particle in the scenario of cluster formation. Depending on the inter-particle forces, different structures can be identified, corresponding to different scenarios like breaking up of large clusters or unification of smaller ones. Here, we just demonstrate that the algorithm works. The next step would be to investigate how the structures seen in the cluster tree plots depend on the inter-particle forces determined by the pH-value and the ionic strength $I$. However, within this thesis, we focus on dense suspensions for which the cluster recognition algorithm is inappropriate, especially when all particles belong to only a single cluster after a short time.

In Fig. 8.27 we evaluate the cluster size distribution and its time evolution. The probability
Figure 8.27: Here the time dependence of the cluster size distribution is shown in a color plot. The colors denote the probability density to find a particle in a cluster of a certain size for different times. Dark colors denote a low probability and bright ones a high probability. One can see the time evolution from small clusters to larger ones, until individual clusters appear as spikes in the distribution, which move to larger cluster sizes, as they adsorb more and more particles.

The information contained in Fig. 8.27 can be further extracted by integrating in different ways over the size distribution. One possibility is to extract the mean cluster size for each time step. Alternatively one can evaluate the number of clusters for each time step. Both quantities can be plotted over the time which we do in Fig. 8.28 for different simulations. Both quantities, the mean cluster size (Fig. 8.28 a)) and the number of clusters in
Figure 8.28: The time dependence of the mean cluster size is plotted for different simulation parameters (a). Fig. b) depicts the time dependence of the number of clusters found in the system. Each curve is shifted vertically by a factor of two for better visibility. While the symbols correspond to simulation data, lines are given by a power law fit as given by Eq. (8.7).
the system (Fig. 8.28 b)) can be fitted by a power law of the form

\[ f(t) = A \cdot (t + B)^C, \]  

(8.7)

where \( A, B, C \) are fitting parameters. The lines in the figure correspond to the fit and the symbols to the simulation data.

The process of cluster formation can be divided into three regimes:

- an initial regime, in which the cluster growth has not yet fully started. This leads to a shift in time expressed by parameter \( B \) in Eq. (8.7). The shear flow has to be established and particles have to move some short distance to reach their nearest neighbors. In the cluster size distribution (Fig. 8.27) one can not yet distinguish individual clusters for \( t < 100 \text{ ms} \).

- the power law regime, i.e., the central region of Fig. 8.27

- a region, where Eq. (8.7) breaks down and cluster growth is limited by the system size.

One can fit the parameters of Eq. (8.7) in the region, where the equation holds, and then use them to scale the data onto a master curve. One has to shift the data by \( B \) in \( x \)-direction, scale the \( y \)-value by \( A \) and then raise the value to the power of \( 1/C \). If all values exactly fulfill the relation \( y = f(x) \), with \( f \) being the function defined in Eq. (8.7), after the scaling they should collapse onto the line \( y = x \). The result is shown in Fig. 8.29. One can see that the plots collapse for small values of \( x \), corresponding to small times \( t \). However, for large values the data do not collapse anymore on the line \( y = x \). Due to the finite size of the system, the mean cluster size is limited by the total number of particles in the system, and therefore has to reach a constant value. The number of clusters as well starts initially at the total number of particles and decreases (\( C \) is negative then) and finally reaches the value 1 which is a constant, too. The data of the whole cluster formation process therefore are scaled on a function \( h(x) \) which first grows with slope 1 starting from the origin and reaches a constant value, let us say \( e \). We try different functions \( h_i(x) \) that are suitable:

\[
\begin{align*}
  h_1(x) & = x \cdot \frac{1}{(x/e)^2 + 1} + (|e| - 1) \cdot \left[ 1 - \frac{1}{(x/e)^2 + 1} \right], \\
  h_2(x) & = e \tanh(x/e), \\
  h_3(x) & = e \text{erf}(x/e) = \frac{e}{2\pi} \int_0^{x/e} \exp(-t^2/2)dt.
\end{align*}
\]

(8.8)  

(8.9)  

(8.10)

We plot these functions in Fig. 8.30 for \( e = 5 \). They slightly differ in the way they bend from the growing regime to the constant regime. It turns out that \( h_1(x) \) works best for the number of clusters, and \( h_2(x) \) seems to be more accurate to describe the mean cluster size. However, the differences between different functions \( h_i(x) \) are marginal. They only seem to become relevant if one tries to fit Eq. (8.7) to the data suitably scaled by a factor...
Figure 8.29: Scaling plots of a) mean cluster size and b) total number of clusters in the system. Using the fit parameters $A$, $B$, and $C$ of Eq. (8.7), one can map the data of Fig. 8.28 onto the line $y = x$ for small times. For large times (large $x$-values in this plot) the effect of the limited size of the system remains, which reduces the $y$-values in this plot. This effect can be modeled by one of the functions $h_i(x)$ plotted in Fig. 8.30. For their definitions, see in the text.
Figure 8.30: Different functions $h_i(x)$ to model the limitation of cluster growth: At the beginning a continuous growth along $y = x$ is modeled, and finally a constant value $e = 5$ is asymptotically approached by all functions. The crossover differs slightly, depending on the respective function used. The definition of $h_1(x)$ is given in the text.

$h(x, e)/x$ on the whole range of $x$, with $e$ as an additional fit parameter in a multi-step fit algorithm. This has to be done very carefully and it turns out that one needs well adjusted starting parameters for the fit.

To arrive at a conclusion of this chapter, combining Eq. (8.7) and one of the functions $h_i(x)$, we find a description of the whole cluster formation process, where Eq. (8.7) describes the initial regime as well as the power law regime in one equation, and the function $h_i(x)$ describes the limitations of the finite system size for large times. It would be of great interest to investigate if the scaling behavior can generally be linked to the volume fraction $\Phi$, the ionic strength $I$, and the pH-value. However, for this a detailed investigation of the parameter space would be needed which then allows to look for generalized dependencies $A(I, pH, \Phi)$, $B(I, pH, \Phi)$, $C(I, pH, \Phi)$, but this requires a very large computational effort, since each single simulation of the plots in Fig. 8.28 is run for several days on 32 processors. The simulations contained 10560 colloidal particles and $1.3 \cdot 10^7$ fluid particles.
Chapter 9

Comparison with the Experiments

In this chapter we review our results in the context of the experiments described in chapter 3 performed by our collaborators within the DFG research group “Peloide”. The first contact our work has to the experiments is already the simulation setup. When choosing the simulation parameters, we closely collaborate with the experimentalists. We have chosen SRD as simulation method for the fluid, since it is possible to calculate the transport coefficients like shear viscosity of the simulated fluid [144] and to adjust all parameters corresponding to the real experimental system. Especially, we have found that it is of great importance to choose the same particle diameter as in the experiment, when studying the shear viscosity of the suspension. A small polydispersity of 10%, as in the powder used for the experiments, on the other hand turned out to have minor influence on the results. The DLVO potentials in the MD part of the simulation are chosen because they are the most accurate pair potentials of the electrostatic and van der Waals interactions available in the literature. Especially, their dependence on the ionic strength can be calculated straightforward, and for the particle charge and its dependence on the pH-value we have developed the charge regulation model presented in section 5.1. Approaches that include the micro-ions either explicitly or their local concentrations are more accurate, but a much larger computational effort is needed for them. The hydrodynamic interactions are fine-tuned against experimental data obtained from rheological experiments described in section 3.5.

Due to this effort spent to the simulation setup, several results can be compared even quantitatively. The stability diagram Fig. 8.2 is known from experiments [46], and to our knowledge we have reproduced it for the first time by simulations. The sedimentation experiments discussed in section 3.2 represent one cross-section of the stability diagram for constant ionic strength. One can clearly see how the microscopic interactions changing from mainly repulsive ones to strongly attractive ones determine the macroscopic properties. At low pH-values, where the ζ-potential is high and therefore electrostatic repulsion dominates in the DLVO potentials, particles do not form clusters and therefore sedimentation takes place extremely slowly and thus the suspension remains turbid even for months. At larger pH-values clusters are formed and the sedimentation velocity of the clusters as a whole is much larger than for single particles (compare Eq. (5.7)). Between pH ≈ 5 – 6 cluster formation sets in, which is in good accordance to our simulations for ionic strengths between I = 5 – 10 mmol/l. The increasing height of the sediment for large pH-values can be explained as follows: the colloidal particles can not rearrange...
themselves inside a cluster due to strong attractions. Once they are attached to another particle, this connection is fixed. This effect that clusters do not compactify if the attraction is strong enough can be observed using the demixing parameter discussed in section 8.6. In Fig. 8.21 a), where different simulations without shear are analyzed, one can see that for large ionic strengths, in this case $I = 20 \, \text{mmol/l}$, i.e., for strongly attractive forces, the demixing parameter stops to grow after 0.3 s. For low ionic strengths the demixing parameter further increases due to rearrangements of the particles already bound in clusters.

Scattering experiments could not be successfully performed for $\text{Al}_2\text{O}_3$ suspensions. Especially for dense suspensions it is difficult to obtain scattering data. We have discussed these problems in detail in section 8.5. However, since in shear experiments the experimentalists had to face severe problems when handling laponite, we focus on silt particles in this work. Nevertheless, to perform simulations of non-spherical particles including van der Waals attractions and to compare the findings to the experimental results reported by Ballauff et al. [91], would be a challenging task for future work. We come back to this topic in chapter 10.

With respect to soil mechanics we could not yet simulate exactly the experiments. However, the results concerning the microstructure we have obtained in our simulations, can be compared to the findings in soil mechanics. The different curves seen in the oedometer experiments in Fig. 3.5 correspond to differently prepared samples. Especially in Fig. 3.5 b) the pore number can be varied strongly, depending on how the particles form clusters. For $p\text{H} = 9$ they feel strongly attractive forces and cannot rearrange themselves as soon as they have been connected to a cluster. Therefore, if the sample is not compressed during the initial stage of the cluster formation process large voids (macro pores) can be created inside the sample, and thus the resulting pore number is large. However, by stirring the sample during preparation, clusters may be broken up, depending on the depth of the potential minimum, i.e., depending on the $p\text{H}$-value and on the ionic strength. The fact that it is possible to break up clusters by shear flow, can be seen in Fig. 8.15, which shows that the number of particle contacts in the clusters is reduced, if a high shear rate ($\dot{\gamma} = 500/\text{s}$) is applied, compared to the simulations for a low shear rate ($\dot{\gamma} = 100/\text{s}$). The figure also shows that shear flow enhances cluster formation, i.e., that stirring the sample not too strongly ($\dot{\gamma} = 100/\text{s}$), causes the particles to form more contacts than without externally introduced forces ($\dot{\gamma} = 0/\text{s}$). As a consequence the sample is packed more densely. In Fig. 3.5 it is shown that when the sample is compressed the “skeleton” formed by the particles collapses, and for large confining pressures the particles are packed more densely. However, the confining pressures at $p\text{H} = 9$ have to be very strong to reach a dense packing of the particles. In Fig. 3.5 b) the sample is still compressible at 500 kPa and in particular has not yet reached pore numbers as small as in the experiments at $p\text{H} = 4$ shown in Fig. 3.5 a). Finally, for the arguments in section 3.4 we already have speculated that the different behavior of the samples for $p\text{H} = 4$ and $p\text{H} = 9$ may be caused by different microscopic structures due to different inter-particle interactions. Our investigations confirm that the microstructure depends on the $p\text{H}$-value, and for moderate ionic strengths, let us assume $10 \, \text{mmol/l}$, the state at $p\text{H} = 4$ is in the suspended regime and for $p\text{H} = 9$ for all ionic strengths accessible in the experiment the state is in the clustered regime (compare Fig. 8.2). In that sense, our investigations of cluster formation depending
on the pH-value helps to understand why the plots in Fig. 3.5 a) and Fig. 3.5 b) differ that strongly. One important point in this discussion is, that one can relate the local order of the particles and the global structure of the sample. We have confirmed that one does not have to distinguish different length scales on this level by our finding that the clustering process does not depend on the length scale of observation (see the discussion in section 8.5).

Let us now turn to the cyclic shear experiments. It was found that the main features of the response of the sample in resonance column (RC) experiments is independent on the pH-value [118]. Following the arguments in section 3.4, where we discuss the type of damping in the sample, it is likely that the particles are in contact. Viscous damping could be related to a lubrication force, i.e., to short range hydrodynamic interactions across small gaps between the particles. According to our experience in the simulations these hydrodynamic interactions are very important for the description of the suspensions in steady shear flow. However, if particles are clustered, the hydrodynamics is less important than in the suspended regime. Since in the RC experiments the behavior is even independent on the pH-value, we would suppose that the particles are clustered in the primary minimum of the DLVO potentials. This implies that they in fact are in close contact and the damping force studied in Fig. 3.8 has to be assigned to damping in the particle contact, which we model by Eq. (4.7) within the MD simulation. If one actually performs simulations of cyclic shear flow, which is one of the possibilities to continue the work presented here, it would be interesting, if changing the damping constant in Eq. (4.7) has an effect on the measured response and if the hydrodynamic interactions can be switched off for this simulation. In the experiment, the solvent is needed, since the DLVO interactions, especially the value of the Hamaker constant, which determines the strength of the van der Waals attraction, depend on the presence of the water.

However, to confirm or to disprove that the hydrodynamic interactions do not influence the results of the RC experiments, it is of essential importance to correctly model them in the simulation. This task not only comprises the theoretical work needed to set up a realistic simulation, which we have presented in chapter 5. A careful checking of the influences of the finite system size and of the finite resolution of the fluid simulation are indispensable as well. Especially, a correct adjustment of the short range hydrodynamics by comparing the shear viscosity in the simulation with experimental data is an important milestone on the way to a reliable simulation. This work has been done in the context of section 8.3, where the data of the experiments described in section 3.5 was used. In Fig. 8.7 we have compared simulation results with experimental data for two different ionic strengths. Shear thinning can be found in the simulations as well as in the experiments and the values for the viscosity quantitatively agree. The viscosity for low shear rates increases with the ionic strength, whereas the shear thinning is more pronounced as well, so that for large shear rates dependence of the viscosity on the ionic strength is less pronounced. With our simulations we can explain that the origin of the shear thinning in the suspended regime is a layer formation of the particles induced by the shear flow. In the clustered regime additionally clusters have to be broken up. The remaining clusters are smaller for larger shear rates. This effect is reflected in an enhanced shear thinning of the sample. Close to the border between the clustered and the suspended regime in the stability diagram (Fig. 8.2) we can quantitatively reproduce the measurements. Deeper in
the clustered regime, at least general trends can be reproduced. There, the finite system size in the simulation affects the results more strongly. In section 8.3 we have discussed this comparison of constant shear flow in the experiment and in the simulations in more detail. The results presented there and in Ref. [58] are a pre-requisites for simulations of the more advanced experiments, involving additionally a confining pressure or cyclic shear flow. However, in future work, one can build on these results and go further steps in the quantitative comparison of simulations and experiments.
Chapter 10

Conclusion

This thesis is dedicated to investigations of various properties of peloids, i.e., clay-like soils. The particle size of these materials is typically in the sub-micrometer range. These materials show a complex mechanical behavior, additionally depending on the pH-value and salt concentration of the soil. To investigate these properties the research group “DFG-FOR 371 – Peloide” \cite{107} was founded by the German research foundation DFG. Researchers from different subjects including physics, ceramics science, soil mechanics, civil engineering, have joined to investigate peloids under different aspects, like the shear behavior under various conditions, microscopic structure and compressibility. To have a well-defined material to work on, Al\textsubscript{2}O\textsubscript{3}-suspensions have been chosen as a model material for silt and laponite as a model clay.

Within the present thesis we have first reported on the experimental results of our co-workers in the research group, in order to provide an insight to the background of this work. M. Külzer has investigated the consolidation of the model soils using standard soil mechanics experiments \cite{50}. He found that the pore number of Al\textsubscript{2}O\textsubscript{3}-suspensions strongly depends on the sample preparation and on the pH-value. For pH = 9 the pore number turned out to be large, i.e., so-called macro pores are enclosed in the sample. For pH = 4 on the other hand, the samples are much denser and more homogeneous. In both cases the samples can be compressed. At several kPa confining pressure the enclosed pores start to collapse. Periodic shear experiments were carried out by S. Richter \cite{116–118}. He has found that the damping in the consolidated Al\textsubscript{2}O\textsubscript{3}-samples as well as in the laponite samples is independent of the frequency, i.e., it is not viscous damping. The damping can have its origin in the particle contacts. Scanning electron microscopy has been applied at the institute for ceramics in mechanical engineering of the university of Karlsruhe. One can visualize the structure of the suspensions, however, it turned out, that the sample preparation process influences the structure so that information about the local order of the particles cannot be extracted from the images. However, rheological experiments performed by J. Reinshagen \cite{103, 113, 114} could be applied to calibrate the computer simulation developed within the framework of the present thesis \cite{58}.

We have described the simulation methods we use: a Molecular Dynamics (MD) simulation for the colloidal particles, coupled to a Stochastic Rotation Dynamics (SRD) simulation of the fluid. The simulation method addresses long range hydrodynamic interactions and intrinsically contains Brownian noise. All the other particle-particle interactions are incorporated directly in the MD simulation. We use DLVO-like poten-
tials [30, 60, 68, 123, 152] to describe the electrostatic interactions of the colloidal particles, as well as van der Waals attraction. Depending on the pH-value and the ionic strength of the solvent, different parameters have to be used for the DLVO-potentials. Measurements of the $\zeta$-potential of the suspended particles by R. Cruz [21, 114] were utilized as input for a charge regulation model incorporated in the simulation code [58]. This model was developed in collaboration with M. Bier and L. Harnau, MPI Stuttgart, and describes the adsorption and desorption of ions on the colloidal surface. They determine the surface charge of the colloidal particles which enters into the DLVO potentials.

Not only the particle-particle interactions, but also the input parameters for the simulation of the solvent have to be adjusted carefully. We have presented an analysis of the time scales involved in the dynamics. Several processes contribute to the dynamics of the system, and diffusion of particles and sedimentation are in competition with each other for the particle sizes of our material. However, exactly reproducing the properties like viscosity and temperature of the real suspension turned out to be extremely computationally demanding. Therefore, we have developed a scheme that allows to adjust the simulation parameters of the SRD simulation in a way that the main features of the dynamics of the real suspension are recovered exactly, and some approximations are made to reduce the computational effort [60]. Thereby the viscosity, temperature and forces on the colloidal particles are scaled, but the ratios between the respective forces which enter into the dynamics, are kept constant. It is possible to relate a simulation, which was set up using this scheme, to very distinct experimental conditions since all parameters (density, temperature, potentials...) are scaled in a well defined manner.

After having carefully tested our simulation code, we have applied it to study Al$_2$O$_3$-suspensions. We have carried out simulations for different experimental conditions, i.e., different pH-values and different ionic strengths. We have found that the microscopic structure strongly depends on the conditions for which the simulation was set up. We have classified the microstructures in three regimes: a clustered regime, a suspended one, and a repulsive structure. Based on the classification of the microstructures, we have drawn a stability diagram for the Al$_2$O$_3$-suspension. It provides an overview of how properties are related and allows to predict them for a given state. This stability diagram is reproduced quantitatively for the first time from simulations and is one of the most important results obtained within the project presented in the current thesis.

To understand how properties change from one microstructure to the other one, we have carried out simulations close to the transition between the clustered and the suspended regime at pH = 6. We have applied shear in our simulations and varied the shear rate to investigate its influence on the viscosity and the microstructure. We have inspected the velocity profile of the shear flow and the resulting viscosity, depending on the particle-particle interactions and the shear rate. We have found shear thinning due to a layer formation on the microscopic scale in the case of a suspension. If a clustered system is sheared, clusters are broken up into pieces by the imposed shear, which leads to a stronger shear thinning than in the suspended case. Close to the border we are able to reproduce the shear viscosity measured by J. Reinshagen in our simulations [58].

Deep in the clustered regime we have found that our particles form a single large big cluster in the system. For high enough shear rates we have found that the cluster can be
broken up. But for strongly clustered systems at low shear rate, which would be the most interesting case for soil mechanics, there are strong finite size effects. To a certain degree larger simulations can face this problem, but more coarse grained models may be more appropriate to tackle the questions occurring here.

We have analyzed the microscopic structure of how particles arrange locally, using the pair correlation function. In the repulsive region of the stability diagram long range correlations can be observed, whereas in the suspended state they are less pronounced. However, in the clustered regime, peaks can be assigned to particular microscopic local structures. The integral over the nearest neighbor peak can be used as a measure for the clustering process. Depending on the shear rate and the pH-value the contributions to this peak differ, which reflects the number of particle contacts in the clusters.

Due to the finite size of the simulation volume and technical details of our implementation of the borders, the correlation function can only provide information up to a limited length scale of about half the system size. Therefore we went on to the complementary quantity, namely the structure factor. In principle it contains the same information, but in our implementation we can access information about larger length scales by means of the structure factor. We have integrated over the “low-k-peak” of it, which contains information on the long range inhomogeneities of the whole simulation volume, and therefore can be used to observe the clustering process on a large length scale. The same features as in the investigations using the nearest neighbor peak of the correlation function could be observed, although the length scale of observation was larger in this case. Thus we have confirmed, that the clustering process in this sense does not depend on the length scale on which one observes it.

Regarding the effect of the hydrodynamic forces on the clustering process we have found that cluster formation is suppressed by the shear flow at low pH-values. For large pH-values low shear rates even support the clustering process. In contrast, for high shear rates, cluster formation is suppressed by the shear flow even at high pH-values. To complete the analysis, we have evaluated the so-called demixing parameter $\Psi$ proposed by Cates et al. [110]. The investigation of the demixing parameter confirms the previous results. For some of the features found in the simulations we could also detect hints in the dependency of the total energy on the shear rate. Our findings on the cluster formation process suggest that soft stirring can enhance the cluster formation when this material is handled in industrial processing.

To characterize the repulsive structure we have evaluated the shear force needed to obtain a given shear rate. It increases in the repulsive regime, meaning that the effective viscosity increases. However, since the velocity profile often is not linear in these simulations, the shear viscosity in a sense becomes dependent on the location in the shear flow and on the local structure there. We also have evaluated the mean squared displacement of the colloidal particles and have found a plateau, similar to observations known from glassy systems.

Finally, before reviewing the results against the background of the experiments, we shortly turned to simulations of dilute suspensions. In this excursus we have demonstrated that our parallel code and a newly developed cluster recognition algorithm are a very powerful
tool to investigate cluster formation processes and to gain statistics from systems with large cluster counts \[59\]. We have evaluated the cluster size distribution for four different simulations. The total number of clusters in the system and the mean cluster size could be extracted and we have found that the time dependence can be fitted by a power law for both of them. Three different regimes could be observed: an initial regime, a regime described by a power-law growth of the clusters, and a regime for which cluster growth is limited by the system size. The initial regime together with the power-law regime could be described by a power-law shifted in time, and functions to describe the finite size limitations are proposed. We have shown for the mean cluster size and for the total number of clusters that all simulation results can be scaled on a single master curve.

It would be of great interest to see if the fit parameters, e.g., the exponent of the power law can be related to the \( \text{pH} \)-value or ionic strength. Additionally, the cluster recognition algorithm allows to track the assignment of single particles to the clusters during time. Combining those two ingredients is promising to find new and interesting details of how clusters are formed. Especially for low volume fractions the fractal dimension could be evaluated, e.g., by means of the slope of the low-\( k \)-peak of the structure factor. Furthermore, for dilute suspensions it is more likely that experimental scattering data could be obtained.

Many more interesting questions could now be studied within our simulation framework. To our knowledge we developed the first parallel code based on a coupled Molecular Dynamics and Stochastic Rotation Dynamics simulation. Additionally, quantitative comparison to experimental data is rarely aspired to the extend we did. Often, either simpler potentials are chosen, or the simulation of the solvent is neglected, or an arbitrary charge of the particles is assumed. Our simulation code has its limitations as well, but it aims very consequently at a quantitative comparability of the simulation results to a real suspension. The simulations could be extended to different materials, e.g., SiO\textsubscript{2} particles for which a large amount of literature can be found already. Only a few measurements would be needed: particle sizes, a calibration curve for the \( \zeta \)-potential, the Hamaker constant of the material, the density of the material, and possibly data from rheological experiments.

Regarding soil mechanics it would be of interest to actually implement an oedometer test and shear under a confining pressure. Possibly, the computational effort increases, if the time step of the MD simulation has to be decreased for large confining pressures. It may be necessary to choose a larger interaction constant for the Hertzian particle contacts, if an exact modeling of the contacts gains in importance for these simulations. A promising approach in this context could be to revise the scaling scheme and to optimize it for the interactions. Sedimentation and diffusion are less important, if due to the confining pressure the particle contacts dominate the behavior of the sample. However, the occurrence of macro pores could be investigated and one could try to simulate the consolidation tests presented in chapter 3. An interesting question in this context is, if by a consolidation process with high enough load, independently of the \( \text{pH} \)-value, the same microscopic structure can be achieved. In other words: is there a regime at high pressures, at which the particle contacts fully determine the structure and DLVO potentials can be neglected? The answer to this question would be interesting especially for geologists.

Cyclic shear could be implemented very easily and one could try to simulate RC exper-
iments as well. Viscoelastic effects could be investigated. In the simulation one has the possibility to reduce the confining pressure, so that one might be able to see a transition from viscous damping to frequency independent damping. This transition might depend on the pH-value or on the presence of macro pores. In the simulation it is also possible to switch certain effects on and off, e.g., the damping in the particle contacts, to see their influence on the material properties.

Another interesting issue would be to extend the interactions on anisotropic ones, like the potentials that have been suggested for laponite [5]. The anisotropic particles could be implemented as ellipsoids or just as cylindrical platelets. Simulations modeling laponite could be used to address the question how important attractive interactions found by Ballauff and co-workers [91] are in these suspensions. We expect the computational effort to be larger than for the Al2O3-suspensions, since the calculations become more complicated for anisotropic particles. Additionally, the particles are nanometer sized and therefore the range of time scales involved in the dynamics even becomes larger than for the suspensions discussed in the present thesis. So-called “Mexican clay” found in the region around Mexico City would be a challenge to be investigated in a similar manner as the current project dealt with silt. Compression and cyclic shear experiments, as well as sedimentation of the anisotropic particles would be interesting issues for simulation, too. The microstructure also depends on the relative particle orientations, and a controversial discussion about it can be found in the literature [32, 81, 101, 124, 127]. Therefore it would be very interesting to investigate the influence of attractive components in the interaction potential on the microstructure.

Further on, one can use our program for completely different projects, independent of the original task to simulate peloids. In general, colloidal particles in external fields would be a large field with many open questions. Since the method contains hydrodynamic interactions as well as Brownian motion, interesting questions on diffusion in general, possibly in confined geometries or collective phenomena could be investigated. Questions related to biophysics could be studied, as well. One could connect several MD particles to simulate molecules or polymers. With suitable interactions amphiphiles and the formation of membranes built assembled by them could be simulated. Transport of substances in biological systems or the impact of defects in biological membranes on their stability are exciting topics to which one could apply our code.

Last but not least, it is easy to enhance the simulation code to a hybrid simulation which simulates a fluid close to a wall by MD and far away by SRD. We could model experiments known from micro fluidics [77], where a so-called wall slip is often detected. In these systems, the usual assumption of no-slip boundaries in hydrodynamics breaks down on the microscopic level. The first layers of molecules in a fluid are influenced by the presence of a wall. Depending on the properties of the fluid and the wall the viscosity appears to be reduced in these first layers, which leads to a modified velocity profile of the shear flow. Such wall slip in conjunction with shear flow could be studied in this context using our simulation code. Wall roughness could also be implemented and studied applying our algorithm, which is closely related to this topic.

To conclude, this thesis has helped to understand many details related to peloids in the special case of Al2O3-suspensions. The stability diagram, which experimentally was known,
has been confirmed by simulations. The different microstructures and the influence of shear flow have been studied. We have found shear thinning in the suspended regime and consistent with the experiments we have found that it becomes more pronounced in the clustered regime. General topics concerning simulation methods have been addressed, e.g., how to adjust the simulation parameters in an SRD simulation realistically, or how to implement shear with attractive particles. Further, a very versatile simulation code has been developed, which can be used to address various problems in physics of mesoscopic systems in the near future. On a long time perspective, an improved understanding of the inter-relation between microscopic interactions and macroscopic properties might have an impact on theories related to soft matter or soil mechanics as well as related topics. The general consciousness to connect simulations and experiments and to quantitatively compare the data might be improved by this work.
Appendix

A.1 Cluster recognition algorithm

We have implemented a cluster algorithm which not only examines a certain configuration at a fixed time, but also takes care of the time evolution of the clusters. We introduce a cutoff radius, below which we consider two particles to be connected. If they are separated by more than this, we consider these distinct particles as not directly connected. However, they might both be connected to a third particle. Therefore, we have to check all particle pairs if they are connected. If not, nothing more has to be done. Otherwise, the following cases have to be considered:

- both particles do not belong to any cluster. Then, a new cluster has to be created and both particles are assigned to the new cluster.

- one of the particles already belongs to a cluster. Then, the other particle is assigned to this cluster.

- both particles belong to different clusters. Then, the clusters are unified, i.e., all particles of the smaller cluster are assigned to the larger one.

- By the step just described, it may happen that for a particle pair to be checked later on, both particles already belong to the same cluster. Then of course, nothing has to be done.

This checking of particle pairs is optimized by a linked cell algorithm, so that only particle pairs of the same and of neighboring cells are checked.

In an additional step, the clusters have to be identified with the clusters already recognized in the previous time step. This assignment is performed after each check for the particle pairs and the clusters are assigned an identification number (“cluster id”). Each particle keeps the information to which cluster id it had been assigned in the previous time step. According to the information to which cluster id the particles had been assigned in the previous time step, the cluster id is assigned to the new cluster. Again, different cases have to be considered:
• both particles belonged to the same cluster, and therefore refer to the same cluster id. This id is assigned to the new cluster.

• if one of the particles belonged to no cluster in the previous time step, a new cluster has formed during the last time step and a new cluster id is given to the newly created cluster.

• if one of the particles belonged to a cluster, and the other one not, the new cluster keeps the cluster id which one of the particles brings with it.

• if the particles are assigned to different cluster id’s one has to decide, which cluster id has to be assigned to the new cluster. Here we take the id of the larger one of the previous step. The cluster recognition process would contain to some extend arbitrariness, if one used the size of the current clusters. Therefore, one has to compare the sizes of the clusters of the previous time step. If two clusters unify, during the cluster recognition one particle after another of the small cluster is assigned to the larger one. If by chance both clusters have had the same size, it makes no difference which one of them is kept. In this detail one could even extend the algorithm by deciding with respect to the age of the clusters. However, one would have to argue about what it means to include the cluster age at this point and for which cases it is important (e.g., it might become important when focusing on certain features in the case of only very weakly attractive particle forces).

Finally, one has to check if the cluster id’s still are unique. If several clusters are assigned to the same id the largest one keeps the id and the smaller ones are given new id’s. Again there is a case in which two clusters might be of the same size, and one could extend the algorithm in this point, too. However, we randomly chose one of them.

The strength of our algorithm is that we can follow the particles and their assignment to the different clusters during time. We see clusters growing and breaking into pieces and we can follow the trajectory of each particle in this scenario. This enables us to draw cluster assignment trees like the one in Fig. 8.26. Depending on the inter-particle forces, different structures can be identified, corresponding to different scenarios like breaking up of large clusters or unification of smaller ones. A further step can now be to study systematically the dependence of the structures seen in such cluster tree plots on the inter-particle forces, determined by the pH-value and the ionic strength $I$.

A.2 Parallelization

We have parallelized our simulation code with MPI. The parallelization of our code is based on domain decomposition, both for Molecular Dynamics and for Stochastic Rotation Dynamics. In the Molecular Dynamics code one needs the neighboring particles to be able to calculate the interactions. Since the interactions have a limited range, and a linked cell algorithm is used already to optimize the speed of the computation on a single processor, we use the linked cells in the parallel code as well. The particles in the cells that meet
Figure A.1: Computation speed depending on the system size: The unit cell is a cube with 2.22 μm extension in each dimension, filled with Φ = 35 % MD particles of diameter \( d = 0.37 \) μm. The systems in the simulations are scaled in each of the three dimensions by a factor of \( N \). The volume fraction Φ is kept constant. The speed is measured in SRD time steps divided by the CPU hours needed and multiplied by the simulation volume \( V \) which is measured in units of \( 1000(2R)^3 \). For details see in the text.

the border of the simulation space of each processor are transferred to the neighboring processors for the calculation of the forces. Then, the MD propagation step is performed and the particle positions are updated, whereby the particles crossing the border between two processors are transferred from one processor to the other one. This way of parallelizing an MD code is often used[112].

Since SRD is a rather new simulation method, only few codes have been written and parallelization is a rather new and challenging task. Since (in principle), fluid particles can travel arbitrary large distances in one time step, one has either to limit the distance they can move, or one needs all-to-all communication between CPUs. In the current version of our code we use all-to-all communication. In a first step all processors send their fluid particles to the other processors using MPI_Isend. Which particle has to be sent to which processor can be calculated locally according to the particles’ coordinates. All particles that have to be transmitted to the same processor, are sent within one single message. For large systems, where not all processors are neighbors of each other, the MPI-messages are often empty. To avoid that processors then still keep on waiting although no fluid particles have to be received, we send one zero value which denotes that no particles are contained in the message (This extra communication can be avoided, if the fluid particles are not allowed to travel to others than the neighboring processors.) We use the MPI_Probe(MPI_ANY_SOURCE, 0, MY_MPI_COMM_CART, &status)-statement. It returns in status information about the next message to receive. Because of the usage of MPI_ANY_SOURCE it is not a priori known, from which sender the
Figure A.2: Computation speed depending on the number of processors, where the full simulation volume is kept constant at $V = (8.88 \, \mu m)^3$. Each processor has to calculate a part of the simulation box. The computation speed decreases with the number of processors due to the communication overhead. For more than 32 CPUs the amount of communication is extremely high, so that for such large systems further optimizations are necessary.

message to receive had been sent. However, this information is necessary to receive the message with MPI_Recv. The sender is the first thing we can read from the returned status. Additionally, MPI_Get_count extracts the message size which allows us first to check if the receive buffer is large enough to receive the next message, and second we need the message size for the call of MPI_Recv as well. In a loop all messages are received, always the next one to arrive, so that waiting times are minimized. At the end of the communication a call of MPI_Waitall ensures that all messages are in place before freeing the send-buffers. This communication procedure should be faster than a call to MPI_Alltoall. Internally, the implementation might be similar, but to call MPI_Alltoall one globally needs to know the largest number of particles to be communicated in one message. Additionally, MPI_Alltoall uses one fixed message size for all messages which has to be the largest one involved in the communication step. However, as mentioned above, the communication may be optimized further by limiting the communication to the neighboring processes, since for reasonable simulation volumes on each processor and realistic mean free paths the fluid particles should not travel further than to the neighboring processor.

The fluid particles have to be communicated after the streaming step. Additionally, the grid for the rotation steps in the SRD algorithm is shifted in every time step to achieve Galilean invariance of the algorithm [71, 72]. Since the regions treated by each of the processors do not move, this would mean that the borders between the processors cross SRD cells which is undesirable. Therefore, we keep the position of the grid fixed and
Instead shift the fluid particle positions before sorting them into the cells and shift them back after the rotation step.

We test performance of our parallel simulation code with the IBM compiler for AIX on the p690 Regatta “jump” in Jülich (p690), using the g++ compiler on the HP XC6000 cluster of the computing center in Karlsruhe (g++), and using the Intel compiler on the same machine (icc). The choice of the compiler obviously strongly influences the speed of the generated code due to different internal optimization levels.

Our first test is the performance scaling depending on the system size using only a single processor (Fig. A.1). The basic system was a cube with 2.22 $\mu$m extension in each dimension, filled with $\Phi = 35\%$ MD particles of diameter $d = 0.37 \mu m$. The systems in the simulations are scaled in each of the three dimensions by a factor of $N = 1, 2, 3, 4, 5, 6, 8$, keeping the volume fraction constant. The speed is measured in SRD time steps divided by the CPU hours needed and multiplied by the simulation volume $V$. This test shows, if, independently on the parallelization, other dependencies of the size of each domain influence the speed. The cache size might have an influence on this measurement. One can see that the simulation speed decreases slightly with the size of the domains. Systems larger than $(8.88 \mu m)^3$ proceed too slowly on a single processor, although there still would be enough memory to run them. However, the computation would already take two weeks to see the system approaching a final state, in which, e.g., the clustering process has reached...
a limit.

In Fig. A.2 the computation speed depending on the number of processors is shown. For this plot we keep the complete simulation volume constant at $V = (8.88 \mu m)^3$. Each processor has to calculate a part of the cubic simulation box, where the shape depends on how the total volume is divided. Of course one tries to optimize the ratio between computation and communication and one tries to use cubic subsystems for each of the processors. In the case of eight processors we test different arrangements of the processors, i.e., different geometries of the simulation volume. The values are rather close to one another. This tells us that the geometry is less important than one might think. Most of the loss in computation speed seems to be caused by initialization of communication and by the check if communication is finished, i.e., independent of the amount of communication. Using one single CPU no communication is needed, therefore the computation speed is roughly twice as high as for the parallel simulations. This means that using two CPUs is not optimal for our code. For 16 or 32 CPUs the code is more efficient. The computation speed decreases with the number of processors due to the communication. For more than 32 CPUs the communication was extremely high, so that for such large systems further optimizations are necessary.

In Fig. A.3 the computation speed depending on the number of processors is plotted again, but here each processor has to calculate a cubic simulation box of $8.88 \mu m$ in each dimension. The complete simulation volume is scaled with the number of processors. The volume fraction is again kept constant at $\Phi = 35\%$. The computation speed is measured in SRD time steps divided by the computing time in CPU hours and multiplied by the total simulation volume. Thus, if no communication was needed, one would obtain a constant value for the speed. The decrease of speed with the number of processors is due to communication overhead. Again, if the program is run on one single CPU, no communication takes place and the speed is greater than one would expect by extrapolation of the other values, meaning that a considerable part of the communication overhead is independent of the amount of data communicated. Avoiding communication between processors, where no particles have to be transferred, is a possibility for further optimization of the code.
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Bibliography


[107] internet pages of the research group “DFG-FOR 371 – Peloide”, Karlsruhe, Germany, URL: http://www.rz.uni-karlsruhe.de/~gn43/DFG_FOR371-Peloide.html. → p. 5, 7, 9, 23, 24, 27, 31, 32, 34, 37, 38, 131


[126] internet pages of College of Engineering, University of California, Santa Barbara, URL: http://www.engineering.ucsb.edu/Announce/colloidal_clusters.html. → p. 100


