ON THE MECHANICAL INTERACTIONS BETWEEN TiO$_2$ NANOPARTICLES

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DISSERTATION

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Preface

This dissertation describes the results obtained during my time as a PhD-student from January 2012 until November 2016 in the Hybrid Materials Interfaces group at the University of Bremen under the supervision of Prof. Dr. Lucio Colombi Ciacchi.

The results presented in chapters 4, 5 and 6 of this work contain exclusively my own research, apart from the following exceptions:

All experimental results contained in the thesis have been derived by Dr. Samir Salameh and have been published in parts in his doctoral thesis “Contact behaviour of metal oxide nanoparticle aggregates” under the supervision of Prof. Dr. Lutz Mädler, which was submitted in 2015 at the University of Bremen. [1]

The model generation of polydisperse nanoparticle films in chapter 6 was conducted by Valentin Baric under the supervision of Prof. Dr. Lutz Mädler at the University of Bremen.

The capillary simlations in chapter 4 were performed by Dr. Michael Dörmann under the supervision of Prof. Dr. Hans-Joachim Schmid at the University of Paderborn.

The simulation data in Figs. 6.5 and 6.6 in chapter 6 results from the supervision of a Bachelor’s thesis prepared by Tim Streckhardt with the title “Untersuchung des mechanischen Verhaltens von TiO_2 Nanopartikelfilmen bei unterschiedlichen Luftfeuchtigkeiten mithilfe der Diskrete Elemente Methode.”

Parts of this thesis have been published as follows:

Chapter 4


Chapter 5 and 6

A publication with the title: “A new contact model for the discrete element method simulation of TiO$_2$ nanoparticles in films under external load.” is currently in preparation.

Since the colloquium, the following changes to the document have been made:

- Insertion of permissions for images from other authors.
- Insertion of references for own images.
- Insertion of reference [4].
- Relocation of supporting videos to different web-address. Removal of AFM-TEM videos.
- Adjustment of symbols and equations to the mathematical standards.
- Correction of author name in reference [244].
Zusammenfassung


Um die Gegebenheiten in technisch relevanten Systemen sinnvoll wiederzugeben, werden dazu die Einflüsse von Luftfeuchtigkeit, Oberflächenrauheit, Form und Hydrophilizität auf die resultierenden Kräfte untersucht. Da die experimentelle Messung der molekularen Phänomene, die in dieser Größenordnung auftreten, schwierig bis unmöglich ist, stellt die atomistische molekulardynamische Simulation eine adäquate Methode dar, um eine hinreichende atomistische Auflösung bei gleichzeitig ausreichender Systemgröße und Simulationszeit zu ermöglichen. Die chemischen Eigenschaften der Partikeloberflächen werden dazu durch ein realistisches atomistisches Modell wiedergegeben, das außerhalb dieser Arbeit mithilfe quantenmechanischer Simulationen entwickelt wurde.

Die Untersuchung der Haftkräfte zwischen TiO$_2$ Nanopartikeln unterschiedlicher Größe, Rauheit und Hydrophilizität bei unterschiedlichen Luftfeuchtigkeiten zeigt, dass makroskopisch gültige Gleichungen zur Berechnung von interpartikulären Kräften auch auf die Wechselwirkungen im Nanometer Bereich angewandt werden können, wenn die Eigenschaften der oberflächenadsorbierten Wasserschicht berücksichtigt werden. Diese Wasserschicht erhöht zum einen den Partikelradius für die Berechnung von Kapillarkräften und führt außerdem durch die molekulare Strukturierung des Wassers innerhalb der Schicht zu alternierenden Solvataions-Kräften, die, abhängig von der lokalen Oberflächenstruktur, die wirkenden Kapillarkräfte...

Neben der Untersuchung der Haftkräfte zeigt sich weiterhin, dass die Roll- und Gleitreibungskräfte zwischen den Partikeln nicht mehr dem Coulombschen Reibungsgesetz folgen, sondern vielmehr ein nicht-lineares abwechselndes Haften und Gleiten zeigen und in ihrer Höhe von der Kontaktfläche zwischen den Partikeln abhängen. Ähnlich wie bei den Haftkräften, wird auch die Höhe und Form der Reibungskräfte maßgeblich durch die Eigenschaften der oberflächenadsorbierten Wasserschicht bestimmt und sind damit weitgehend unabhängig von makroskopischen Materialkennwerten.

Abstract

In this dissertation the mechanical interaction mechanisms between TiO$_2$ nanoparticles are investigated by using molecular dynamics (MD) simulations. From this investigation, comprehensive equations are derived for the calculation of interparticle forces under ambient conditions at the nanoscale and implemented into particle contact models, enabling the fast and accurate simulation of the mechanical behaviour of nanoparticle assemblies. The results of this work shall help to gain fundamental information about the mechanical interactions between nanoparticles in technical systems, thus supporting the design of new fabrication and handling methods for applications, such as sensorics, catalysis or filtration.

To respect the conditions in technically relevant systems, the influence of air humidity, surface roughness, shape and hydrophilicity on the resulting interparticle forces are investigated. As the measurement of the atomistic phenomena, which arise at this size scale, is difficult or impossible by experiments, all-atom molecular dynamics simulations represent a suitable method to enable a sufficiently high resolution together with a sufficiently large system size and simulation time. In these simulations, the chemical properties of the particle surfaces are based on a realistic atomistic material model which has been developed separately from this work by quantum mechanical simulations.

The investigation of the adhesion forces between nanoparticles with different size, roughness and hydrophilicity shows that macroscopically established equations for the calculation of interparticle forces can still be applied at the nanoscale if the properties of the surface adsorbed water layer are respected. This water layer on the one hand increases the particle radius for the determination of capillary forces, and on the other hand leads to alternating solvation forces between the particles through the molecular structuring of the water inside the layer. Depending on the local particle surface structure, these solvation forces can exceed the capillary forces between the particles significantly. Furthermore, the surface tension of the water layer increases notably at decreasing air humidity and particle size because of the
geometrical confinement of the layer below a thickness of about 1 nm. Due
to this particular dependence of the interparticle forces on the water layer,
the trend of these forces with varying humidity can be crucially influenced
by the tuning of surface roughness and hydrophilicity.

The further investigation of the tangential forces between the nanoparticles shows that the rolling and sliding friction forces do not obey Coulomb’s law of friction anymore, but rather show a non-linear stick-slip behaviour, with their strength depending on the contact area between the particles. Similar to the adhesion forces, also the strength and shape of the tangential forces are crucially determined by the properties of the surface adsorbed water layer and are largely independent of macroscopic material parameters.

The implementation of these insights into a contact model is used in discrete element method (DEM) simulations, enabling an extensive validation of the results to different size scales, ranging from atomistic simulations of single agglomerates up to atomic force microscopy (AFM) experiments on entire nanoparticle films. Furthermore, these simulations emphasize the influence of the mesoscopic structure of the nanoparticle films on their general mechanical properties. The developed contact model therefore represents a link between the chemical properties of the particle surfaces and the macroscopic mechanical properties of entire nanoparticle films, thus enabling a profound improvement of technically relevant applications in particle technology by respecting the realistic mechanical interactions between the single particles.
Chapter 1

Motivation

Nanotechnology is an upcoming field that promises huge efficiency enhancements as well as new possibilities for disciplines relevant to the society such as electronics, medicine, energy or mobility [5–9]. In the wide range of nanotechnology, nanoparticles represent a frequently used building block, which is easy to fabricate, tune and process, due to the characteristics of particulate systems [10]. The use of nanoparticles in technical applications provides a high surface to volume ratio, fast charge transfer pathways, high reactivities and peculiar optical properties [11,12]. However, to take advantage of these characteristics in ready-to-use devices, the selective and predictable manipulation of the mechanical properties of the particulate systems must be ensured. This context can perhaps be understood best in terms of the exemplary lamination of flame sprayed nanoparticles creating porous and mechanically stable particle films, which are intended for the use in a variety of applications such as gas sensing or catalysis (Fig. [11,13]. The dependence of the final film properties, such as the porosity, the pore size distribution, the percolation or the mechanical strength on the process parameters, such as lamination pressure, particle size distribution and surface modification, can so far be only achieved by extensive experimental testing, rather than predictive approaches. Thus, without an understanding of the mechanisms underlying these dependencies, the transfer of the technology to new applications is always connected to an expensive configuration procedure.

On the other hand, the lack of a comprehensive knowledge about the responses of organisms to the exposure with nanoparticles makes this material
Figure 1.1: Top: Schematic of a film lamination process to create porous and mechanically stable nanoparticle films on different substrates out of flame-sprayed nanoparticles for the use in gas sensing or catalysis applications. Bottom: Nanoparticle films before (left) and after (right) lamination. Reproduced from Ref. [13] with permission from The Royal Society of Chemistry.

a potential hazard to the ecosystem [14][15]. It is still unknown how much and where nanoparticles accumulate in the environment and which are the critical doses to certain organisms.

Therefore, controlling the agglomeration, dispersion and rheological behaviour of nanoparticles is key to technical applications such as catalysis, sensorics or hybrid materials synthesis [16][17]. Especially in large-scale industrial process units such as filtering, fluidization and transportation, the contact forces between individual nanoparticles directly influence the process safety as well as the process efficiency and thus, indirectly, the production costs. The particle based simulation of these processes can provide a variety of new insights concerning the macroscopic mechanical and rheological properties of the particle assemblies, the heat and mass transfer-rates between the particles and the accessibility of the particle surfaces [18]. At a larger particle size scale, this tool is already frequently applied as can be seen in
Fig. 1.2: Shear band analysis in a split-bottom ring shear cell from particle simulations using cohesive and non-cohesive mm-sized particles. Panels (a) and (b) show the shear band formation in terms of velocity for non-cohesive and strongly cohesive particles respectively (top and side view, blue to red particle color shows increasing tangential velocity). Panels (c) and (d) show the acting interparticle forces for weakly and strongly cohesive particles (blue color in the bottom part shows adhesive forces, while red color in the top part shows repulsive forces). Reproduced from Ref. [19] with permission from the American Physical Society.

Fig. 1.2 for the investigation of particle flow in a shear cell. It becomes directly obvious that the particle simulation provides precise information about the particle trajectory and the distribution and maximum values of interparticle forces in the process, thus enabling the approximation of the mixing and the residence time of the particles and of the stress acting on surface coatings. Furthermore, the influence of process parameters such as particle cohesion, device geometry and external forces and velocities on these characteristics can be analysed in a fast and efficient way.

Now, for a reliable simulation of the kinematics and dynamics in particulate systems, the thorough knowledge of the height and shape of the acting interparticle forces is inevitable. However, equal to other particle properties, also the nature of the mechanical interactions between the particles might change when entering the nanoscale [20–23]. It is questionable if common assumptions of continuum models, which are reasonable at the macroscopic scale, still hold at the nanoscale, where the size of the particles approaches the dimensions of single atoms. Especially geometrical assumptions typically used for macroscopic particles are expected not to be valid when the length scales of the interacting forces and the particle dimensions are in the same order of magnitude [24]. Furthermore it is widely accepted that,
Figure 1.3: Interparticle force model containing various kinds of different inter-particle forces. The overall force exerted by one particle on another one can contain a non-contact term $F_{nc}$ acting between the particle centers always when the particle distance is below a certain cutoff distance, of a normal contact term $F_n$ acting only when the particles are in contact and of a tangential term $F_t$ also acting only when the particles are in contact. The overall torque exerted by a particle on another one can contain for example the torque resulting from $F_t$ and a rolling friction torque $M_r$ also acting only when the particles are in contact.

especially for small particles, the interparticle forces do not simply depend on the particle size, but also on their surface properties such as roughness, hydrophilicity and shape \[25, 27\]. Due to their discrete size, we can expect the nanoparticles to interact via a variety of different forces as outlined in Fig. 1.3. These interactions may cover forces emerging from the direct contact of the particle surfaces, such as normal ($F_n$) or tangential ($F_t$) forces or rolling torques ($M_r$), or might be contact-independent ($F_{nc}$) due to capillary, Van der Waals, solvation or electrostatic effects.

We note that in technical applications, nanoparticle assemblies are often processed or employed under non-ideal conditions such as broad particle size distributions, particles exhibiting a surface roughness or the presence of a layer of adsorbed water molecules on the particles’ surfaces due to the contact with humid air. As mentioned above, these conditions are assumed to have a high impact on the forces between nanoparticles, owing to the altered proportion of the particle dimensions, which is already apparent for $\mu$m sized particles \[27, 28\]. The task of this work is to answer the question, how the mechanical interactions between nanoparticles under ambient conditions can be described by comprehensive force models that consider a variety of external and internal influences such as humidity, roughness,
hydrophilicity and particle size, and yield robust force predictions. For this purpose we choose TiO$_2$ nanoparticles in the rutile phase as our material of investigation, because oxide nanoparticles and especially TiO$_2$ nanoparticles are frequently used in technical applications due to their stability, optical and photocatalytic properties and low-cost production [5]. Furthermore, experimental TiO$_2$ nanoparticles with a high sphericity and a narrow particle size distribution can be produced via Flame Spray pyrolysis (FSP), which enables an experimental validation of our simulation results by using AFM force-spectroscopy and a combined AFM/TEM setup [2].

To realize an in depth analysis of the mechanisms occurring between TiO$_2$ nanoparticles and to account for the above mentioned effects, this study has been started in a former work with the investigation of the chemical interactions taking place on the particles surfaces at the quantum level [29–31]. In the present work, we use now this chemical information in all-atom molecular dynamics (MD) simulations, which enable the investigation of the interactions between entire nanoparticles under the consideration of a variety of environmental and material effects. The findings from these atomistic simulations are then further up-scaled to develop comprehensive interaction force models which can be implemented into simulations using the discrete element method (DEM), thus closing the gap to experimentally accessible mechanical information and providing a ready-to-use tool for the analysis of the above mentioned technical applications of nanoparticles.

This thesis is therefore structured as follows:

Chapter 2 gives an overview about the state-of-the-art of existing contact models between particles with a special emphasis put on their applicability to nanoparticle interactions. In chapter 3 the simulation methods which we use in this work, are described. In chapter 4 we investigate the non-contact adhesion forces between nanoparticles by considering different humidities, hydrophilicity and surface roughness. Chapter 5 then treats the contact forces, namely the normal repulsion forces, the tangential forces and the rolling torque, by considering different relative displacements and different loading states of the particle contacts. Furthermore, our findings from chapters 4 and 5 are transferred to a discrete element method contact model. In chapter 6 this contact model is validated extensively against both all-atom simulations and different experimental findings. Chapter 7 finally summarizes our findings from chapters 4 to 6, compares them to existing knowledge
from chapter 2 and puts them into the broader context of different materials and future applications.
Chapter 2

Existing contact models for interparticle forces

To describe the mechanical interactions between particles at different length scales and under different environmental conditions, a multitude of interparticle contact force models exist. These contact models are derived from diverse approaches and therefore express specific advantages, simplifications and limitations, suitable for different fields of application. In the following chapter, we will introduce those models, which are most relevant for nanoparticle interactions under ambient conditions, highlighting the respective applicability and shortcomings. The coordinates and variables in the equations are employed as defined in Fig. 2.1.

![Figure 2.1: Illustration of the coordinates and symbols used for the interparticle contact force models.](image_url)
2.1 Non-cohesive normal force models

The easiest way to describe the mechanical interactions between two spheres, which do not adhere to each other due to cohesion, is to apply a hard-sphere model [32]. In this model, the particles are assumed to be perfectly rigid and the lateral velocities of two particles after an instantaneous contact are a direct result of the velocities before the particle contact. This model enables an efficient computation of the sphere movement and can be applied to large spheres, where the deformations during the contact are negligible in relation to the particle size. However, the model does not consider any material dependencies during the contact, which becomes more important when the particle size decreases, and it cannot be applied to multi-contact problems, as the state during the contact is not defined.

This second shortcoming can be overcome by applying a Hookean spring model assuming a linear dependency of the repulsive normal force \( F_n \) on the normal penetration depth \( \delta_n \) between two particle surfaces:

\[
F_n = k_n \delta_n n ,
\]

with the spring stiffness \( k_n \) and the normalized vector between the surfaces \( n \). The linear spring model is now applicable to multi-contact and quasi-static problems, where the particle dynamics exhibit prolonged contact times, but still the assumption of a linear dependency of the normal force on the penetration depth between two three dimensional bodies is unphysical and limited to the case in which the contact deformation is small in relation to the particle size. Furthermore, the parametrization of the spring stiffness \( k_n \) is not directly linked to any material property but rather empirical.

The Hertz-Model [33], in contrast, considers the three dimensional stress and strain conditions inside the particles and allows that the contact zone deforms under load, which leads to a contact stiffening with increasing penetration depth:

\[
k_n = k_{n,0} \sqrt{R^* \delta_n} = \frac{4}{3} Y^* \sqrt{R^* \delta_n} .
\]

In this model the stiffness of the contact \( Y^* \) can be determined approximately from the Young’s Moduli \( Y \) and the poisson ratios \( \nu \) of the involved
particle materials by:

\[
\frac{1}{Y^*} = \frac{1 - \nu^2_i}{Y_i} + \frac{1 - \nu^2_j}{Y_j},
\]

(2.3)
while the combined radius \(R^*\) results from the Derjaguin approximation

\[
\frac{1}{R^*} = \frac{1}{R_i} + \frac{1}{R_j}.
\]

(2.4)

The consideration of the flattening of the particle surface under the application of an uniaxial normal force leads to a higher order dependence of the contact force on the penetration depth:

\[
F_n = k_{n,0} \sqrt{R^* \delta_n} \delta_n.
\]

(2.5)

This makes the model suitable to larger deformations and smaller particle sizes than the linear spring model. Still, the model does not consider anisotropic material behaviour nor does it account for a possible deviation from Hooke’s law of elasticity at small length scales, which makes the straight-forward application to nanoparticles questionable.

In addition to the reversible elastic spring forces acting between two particles, also a force hysteresis can arise from energy dissipation during the material deformation. A dissipative damping term \(F^d_n\) can therefore be defined as:

\[
F_n = F^k_n + F^d_n = F^k_n(k_n, \delta_n) + \gamma_n v_n,
\]

(2.6)
which depends on the normal damping coefficient \(\gamma_n\) and on the normal relative velocity \(v_n\) (cf. Fig. 2.2) [35]. For macroscopic particles, the damping coefficient is usually determined from the coefficient of restitution, which describes the ratio of the relative particle velocity before and after a contact and can be determined from experiments. However, due to this procedure, the damping coefficient is not only specific to the investigated material but also to other investigated particle properties such as the particle shape, surface modifications and roughness. Therefore, the experimental determination of the damping coefficient in the case of nanoparticles, where the surface properties play a dominating role and where the direct measurement of single particle velocities is technically not feasible at the current state, is basically impossible.
More sophisticated models exist to describe the contact forces between two particles in normal direction taking into account more complex visco-elastic behaviour or assuming elasto-plastic behaviour often in combination with interparticle adhesion. These models are not considered here but can be found in [36–42] and the references therein.

## 2.2 Cohesive normal force models

The models described above so far treat the particles as not being "cohesive", which means that they do not attract each other. However, a variety of physical characteristics results in attraction between surfaces and thus also between particles. As the particle size and with this the ratio between volume and surface area decreases, the influence of attractive forces over mass inertia increases. Especially under ambient conditions, where the investigated systems contain more phases than only the particles, cohesion becomes crucially important. Therefore, we will introduce some important interparticle adhesion force mechanisms and their respective modelling in the following section.

The model proposed by Johnson, Kendall and Roberts [43] (JKR) accounts for adhesion between two particles by considering the gain of surface energy when two particles come into contact.

\[
F_n = F_{n,Hertz} + F_{n,ad} = F_{n,Hertz} - a^2 \gamma n ,
\]  

(2.7)
with the surface energy $2\gamma$ of the two surfaces and the contact area $a^2$. This model results in an attractive force arising between two particles as soon as they come into contact and leads to an increased contact radius at a given normal force:

$$a^3 = \frac{R^*}{V^*} \left[ F_n + 6\gamma\pi R^* + \sqrt{12\gamma\pi R^* F_n + (6\gamma\pi R^*)^2} \right]. \quad (2.8)$$

The adhesion produces a pull-off force $F_{ad} = -3\pi R^*\gamma$, which has to be overcome to separate two particles and thus leads to “sticky” surfaces. Furthermore, it is assumed that the contact region deforms due to the modified stress conditions, which results in an attractive neck force for small negative particle overlaps at retraction. As the two particles will not merge into one continuous body under the usual load conditions but form an interface at the surface contact, the surface energy used for the cohesion model is rather the work of adhesion between the two bodies [44], which can be measured experimentally. This work of adhesion in turn depends again largely on the surface properties of the particles and on the surrounding conditions, which makes also this model difficult to parametrize at the nanoscale.

In contrast to the JKR model, Derjaguin, Muller and Toporov proposed
Figure 2.4: Illustration of the symbols used for the interparticle non contact force models.

a model (DMT), which exclusively accounts for the adhesive forces from long-range interactions adjacent to the contact zone, while the interactions inside the contact zone remain unchanged from the Hertz model [46]. This assumption leads to the following dependence of the contact radius on the applied normal force:

\[ a^3 = \frac{3R^*}{4Y^*} (F + 4\gamma \pi R^*) \]  

(2.9)

and to a pull-off force of \( F_{ad} = -4\pi R^*\gamma \). Differently from the JKR model, the DMT model does not produce a neck force at negative particle overlaps, as the interactions inside the contact zone are assumed to be equal to the Hertz model. the JKR and the DMT model represent the extreme cases of large, soft particles with high adhesion energies on the one hand and of small, stiff particles with small adhesion energies on the other hand, respectively. The transition between the two models has been described in the works of Tabor [44], and Dugdale and Maugis [45] (See Fig. 2.3). However, apart from the short attractive neck of the JKR model at retraction, both the JKR and the DMT model do not produce non-contact adhesion forces at negative particle overlaps \( \delta \), which are known to arise from long-range atomistic attraction and from capillary condensation and crucially change the force-displacement curves between two particles.

If two surfaces approach towards each other, the long-range Van der Waals (VdW) attraction between single atoms results in an overall adhesion between the surfaces, which can be described in the Hamaker approach by summation of the attractive intermolecular energies between all atoms contained in the two opposing bodies [47] This leads to the following dependence of the adhesion force \( F_{VdW} \) between two spherical particles on the
combined particle radius and the distance between the particles surfaces $D$ (see Fig. 2.4):}

$$F_{VdW} = -\frac{A_{ij} R^* n}{6D^2}, \quad (2.10)$$

with the Hamaker constant $A$, which is specific to the interactions between the two surface materials via a third transmitting material. This Hamaker constant results from the interaction constants $C$ of the interatomic VdW potentials and from the atom densities $\rho$ inside the two bodies by

$$A_{ij} = \pi^2 C \rho_1 \rho_2 \quad (2.11)$$

and has been determined both theoretically and experimentally for a multitude of material combinations $^{25,26}$. Due to their inverse 2nd order dependence on the surface distance $D$, the VdW forces calculated by the hamaker approach exhibit a singularity at surface contact and exceed the repulsive forces of the linear spring or the Hertz model at small distances. Therefore, the VdW forces in practice usually have to be truncated at a positive surface distance of e.g. 0.2-0.4 nm (representing molecular contact), when applied together with the above mentioned contact models of elasticity $^{48}$. Furthermore, the Hamaker constants are commonly derived for clean surfaces, while under ambient conditions again surface modifications or adsorbates have to be considered, which can crucially influence the VdW forces between spheres.

Electrostatic forces result from electrically charged surfaces and can be described by Coulomb’s law:

$$F_{El} = -\frac{q_i q_j}{4\pi \epsilon_0 \epsilon_r D^2} n, \quad (2.12)$$

with the particle charges $q$, the vacuum permittivity $\epsilon_0$ and the relative permittivity of the intermediate material $\epsilon_r$. The charging of particles can arise for suspended particles from surface ionization caused by the surrounding liquid medium $^{26}$ or for particles in gas from the attachment of surrounding ions, static electrification, thermoionic charging or radioactive decay $^{49}$. It has been shown though that electrostatic forces play a minor role for decreasing particle size and small particle distances $^{50,51}$.

If a condensable substance is added to the particulate system, for example water vapour under ambient conditions, this substance condenses on
the particle surfaces and inside narrow gaps between the particles due to
the material specific adsorption isotherm and leads to capillary forces be-
tween the particles [25,26,52,53]. The surface of this condensed phase in a
gap between two particles is bent, forming a meniscus, whose curvature $r_K$
(the Kelvin radius) depends on the the vapour partial pressure $P/P_0$ of the
condensing substance through the Kelvin equation by

$$r_K = \frac{\gamma L V_M}{RT \ln \left( \frac{P}{P_0} \right)},$$  \hspace{1cm} (2.13)

with the liquid/gas surface tension $\gamma_L$, the specific gas constant $R$, the
temperature $T$ and the liquid molar volume $V_M$. This curvature of the
liquid surface is linked to a pressure difference across the interface, the so-
called Laplace pressure $\Delta P$, which can be described by the Young-Laplace
equation

$$\Delta P = \frac{\gamma L}{r_K}.$$ \hspace{1cm} (2.14)

Together with the acting of the surface tension along the meniscus surface,
the Laplace pressure produces the capillary force $F_{Cap}$ between the two
surfaces, which can be calculated from the force equilibrium at the neck of
the connecting liquid meniscus:

$$F_{Cap} = (\Delta PA_m + 2\gamma L U_m) n,$$ \hspace{1cm} (2.15)

where $A_m$ and $U_m$ are the cross-section and the circumference of the menis-
cus neck. The Kelvin radius can be further divided into the curvature radius
$r_m$ and the cross-section radius $l_m$ (cf. Fig. 2.4) via

$$r_K = \left( \frac{1}{r_m} - \frac{1}{l_m} \right)^{-1}.$$ \hspace{1cm} (2.16)

It is widely accepted that capillary forces crucially influence the interparticle
adhesion under ambient conditions at the presence of air humidity [27,28,
52,56].

The exact calculation of the capillary forces between particles is far from
easy due to the nodoidal shape of the liquid meniscus. To facilitate the cal-
culation of the capillary forces, for example for the efficient use in particle
simulation methods, a variety of geometrical simplifications can be carried
2.2. COHESIVE NORMAL FORCE MODELS

out, which ease the determination of the meniscus shape. One of the most-
often used simplifications is the circular approximation, which assumes the
meniscus curvature parallel and perpendicular to its symmetry axis to be
circular. From this approximation, for two opposing perfectly smooth spher-
ical particles of equal radius and material the curvature radii $r_m$ and $l_m$ are
linked to the water/solid contact angle $\Theta$, the filling angle $\beta$, the particle
radius $R$ and the particle distance $D$ (cf Fig. 2.4) via

\[
    r_m = \frac{2R(1 - \cos(\beta)) + D}{2\cos(\Theta + \beta)}, \tag{2.17}
\]

and

\[
    l_m = R\sin(\beta) - r_m[1 - \sin(\Theta + \beta)]. \tag{2.18}
\]

With these constraints, the capillary force between the two particles at a
certain humidity and distance can be calculated by iterating over equa-
tions (2.13), (2.17) and (2.18) until the matching partial pressure is hit and
then inserting the final values into equations (2.14) and (2.15).

The capillary force as calculated from the circular approximation de-
pends sensitively on the interplay of several parameters, as can be observed
in Fig. 2.5. It becomes obvious that the force magnitude can change sig-
nificantly under the variation of the parameters contact angle, humidity,
liquid surface tension, particle size or particle distance. These all depend
sensitively on the surface configuration of the particles and can therefore
deviate largely between different systems and size scales. Special attention
should be put on the trend of the capillary force between two particles with
varying humidity, which depends crucially on the distance $D$ between the
two particle surfaces and can become either positive, constant or negative,
which will become important later in this work. Furthermore, the increase
of the liquid surface tension $\gamma_L$, for example due to the use of a different
condensable substance or due to the confinement of the liquid/vapour inter-
face, results in a significant increase of the capillary forces, which will also
become important later.

Under the assumption that $R > l_m > r_m, D$, the equations of the cir-
cular approximation can be further simplified to different expressions with
the meniscus volume as the independent variable instead of the meniscus curva-
ture $57, 61$. In the constant-volume approach this meniscus volume is
additionally assumed to be constant over the entire particle separation lead-
CHAPTER 2. EXISTING CONTACT MODELS

Figure 2.5: Variation of the capillary forces between nanoparticles in dependence on different parameters.

According to an analytical expression for the capillary force, if the liquid content inside a system is predistributed to the single menisci. Due to its low computational costs, this approach is frequently used for particle-based simulations such as DEM [61] together with the definition of a suitable rupture criterion for the liquid bridge [57, 62–64]. The agreement of these constant volume models with the true capillary forces is good for large particles in the μm range [61], but worsens with decreasing particle size, where the assumption $R >> l_m >> r_m$, $D$ does not hold anymore [24].

At the discrete molecular level, the adsorption of a liquid substance on the particle surfaces leads to a structuring of the liquid molecules adjacent to the solid surface [65–67]. The sharp transition between the liquid and the solid phase causes the liquid molecules to order geometrically at this boundary and to create a pronounced solvent density peak at the surface. Due to the intermolecular spacing inside the solvent, this peak is followed by a density minimum and again by a peak resulting in an oscillatory propagation of the density into the bulk liquid phase (See Fig. 2.6). The thermal fluctuations lead to a smearing of these density peaks and thus to a decrease
of the oscillation amplitude with increasing distance to the surface.

If the liquid is now confined between two solid surfaces, the two isolated liquid structures of both surfaces interfere with each other, building a combined solid/liquid/solid ordering. Depending on the distance between the two surfaces, this confined ordering leads to entropic favorable or unfavorable liquid conformations resulting in an oscillatory solvation pressure between the surfaces [26, 68, 69], which has been observed for instance by means of AFM force spectroscopy [70–72] or molecular dynamics simulations [73]. With increasing surface separation, the amplitude of this solvation pressure decreases, as the density profile relaxes towards the density profile of an isolated surface.

The specific shape of the confined density profile at a given surface separation $\rho_D(z)$ can be quantified in terms of a product (interference) of the solvent density profiles over isolated surfaces $\rho_\infty(z)$ when they come into close contact [74, 75]. Together with the solid-liquid interaction forces $f(z)$ (related to the degree of hydrophilicity, in the case of water) this confined profile can be directly used to calculate the solvation pressure $P(D)$ between two flat surfaces [74, 77]:

$$P(D) = \int_0^\infty \left[ \rho_D(z) - \rho_\infty(z) \right] f(z) \, dz,$$

(2.19)

The challenge of this approach is the precise determination of the solid-liquid
interactions at the molecular level and of the solvent density profile over the isolated surfaces, which can be difficult for other than model systems, as the surface composition and conformation is often not known and far from uniform in real systems. Kralchevsky and Denkov proposed a more simple and empirical approach, where the development of the solvation pressure with increasing surface separation is approximated by an exponentially decaying cosine function \[78,79\]:

\[
P(D) = -\rho_{\text{bulk}}k_BT \cos(2\pi D/\sigma)e^{-D/\sigma},
\]

with the bulk density of the liquid \(\rho_{\text{bulk}}\) and the intermolecular spacing of the solvent molecules \(\sigma\). While the intermolecular spacing \(\sigma\) needed for this approach can usually be easily determined experimentally for non-complex solvents, the equations are still developed for perfectly smooth surfaces, which often does not apply to real systems.

The restriction to smooth surfaces makes the solvation forces strongly sensitive and hard to predict for the case of surface roughness, as even a small disturbance of the liquid density profile counteracts the solvation forces by smearing out the density oscillations. This characteristic leads to the fact that solvation forces are mainly negligible for large interacting geometries, where the height deviations of the surface inside the contact zone are usually large multiples of the molecular diameters. However, when the size decreases, the contact areas become close to flat and the molecular nature of the solvent becomes perceptible, leading to significant contributions from the solvation between the surfaces. On the other hand, the impact of solvation forces on the interactions between technical nanoparticles is highly unclear, due to the influence of surface roughness, curvature, termination and irregular crystallinity [26].

2.3 Tangential force models

Tangential forces between particles arise from the friction between the surfaces during tangential movement. This friction has diverse origins, ranging from intersurface and asperity interlocking and junction adhesion to plastic deformation and depends highly on the specific conformation of the opposing surfaces [80,81]. The magnitude of the friction forces can be described
by a linear relation between the friction force \( F_t \) and the applied normal force \( F_n \) using an empirical friction coefficient \( \mu \), as it was first postulated by Amontons and later refined by Coulomb with the law of friction \[82\]:

\[
F_t \leq \mu F_n .
\] (2.21)

This relation can be applied to the tangential forces between particles, if the acting normal force is known from the applied normal force models \[83\]. To this aim, Hertz, Mindlin and Deresiewicz \[84\] proposed a model, which introduces a tangential overlap \( \delta_t \), being the equivalent to \( \delta_n \) for relative tangential displacement of the particle surfaces. This tangential overlap is initiated as soon as two particles come into contact, and leads to an elastic restoring force acting against the relative tangential particle movement. This restoring force can be seen as the static friction force, acting below the Coulomb criterion without irreversible relative displacement of the surfaces. As soon as the coulomb criterion is reached, the tangential overlap is truncated such that the restoring force stays constant at the coulomb criterion, which leads to an irreversible relative displacement and thus to energy dissipation between the surfaces. (cf. Fig. 2.2). Furthermore, an additional damping term can be applied to consider energy dissipation also during the elastic build up of the restoring force, similar to the damping force in the normal force models. The governing equations of the Hertz-Mindlin and Deresiewicz model are as follows:

\[
F_t = F_t^k(k_t, \delta_t) + F_t^d(\gamma_t, v_t) ,
\] (2.22)

\[
\delta_t = \begin{cases} 
\delta_t, & \text{if } F_t < F_{t,\text{max}} \\
\delta_t(F_{t,\text{max}}), & \text{otherwise ,}
\end{cases}
\] (2.23)

\[
F_t^{d} = \begin{cases} 
F_t^d, & \text{if } F_t < F_{t,\text{max}} \\
0, & \text{otherwise ,}
\end{cases}
\] (2.24)

with the tangential contact stiffness \( k_t \), the tangential damping coefficient \( \gamma_t \) and the threshold force \( F_{t,\text{max}} \) depending on the coefficient of friction \( \mu_t \) and on the applied normal force between the particles as stated in Coulomb’s
### LAW OF FRICTION

The tangential contact stiffness $k_t$ can be usually estimated from the normal contact stiffness $k_n$. The material and surface-specific empirical coefficients of friction $\mu_t$ and of tangential damping $\gamma_t$ have to be determined otherwise, which is especially difficult in the case of nanoparticles, due to the restrictions of experimental measurement possibilities [85].

To account for rolling friction forces between particles, the elastic-plastic spring-dashpot (EPSD) model proposed by Iwashita et al. [86] can be used, in which the rolling friction torque is calculated in an equivalent manner to the sliding tangential forces in the Hertz-Mindlin and Deresiewicz model with an angular overlap $\Delta\theta_r$ and a rolling coefficient of friction $\mu_r$ between the particles. A physically less realistic but more robust model is the constant directional torque (CDT) model proposed by Zhou et al. [87], which applies a constant rolling torque equal to the Coulomb criterion to the particles in opposite direction to the relative rolling movement $\omega_r$:

$$M_r = -\mu_r F_n R \frac{\omega_r}{\omega_r}$$  \hspace{1cm} (2.26)

As in the case of the sliding friction model, also the rolling friction models require the specification of friction and/or damping coefficients, which are even harder to determine experimentally for nanoparticles, due to the complex rolling movement. The torques arising from torsion between two
spheres can be calculated similarly \[^{[88]}\], but are not considered here.

If the particle size and with this also the contact area between the particles decreases, it could be necessary to consider atomistic models of friction. At this order of magnitude usually a pronounced stick-slip behaviour is observed during tangential movement, due to the atomistically inhomogeneous surface compositions, which result in a sawtooth-like shape of the tangential force-displacement curve \[^{[89-91]}\]. Furthermore, several authors argue that the linear relationship between the tangential friction force and the normal load, as postulated by Coulomb’s law of friction, does not hold at this size scale, but is rather replaced by the true linear relationship to the contact area:

\[
F_t \leq \tau A ,
\]  

with the contact stiffness \(\tau\). In macroscopic contacts the microscopic roughness of the surfaces leads to a real contact area that is usually significantly lower than the nominal contact area and increases linearly with the normal load \[^{[92]}\]. This in turn leads to the physically much less intuitive linear dependence of the tangential forces on the normal load in Coulomb’s law of friction \[^{[80]}\]. However, as soon as the real contact area is equal to the nominal area due to the decreasing size of the contact zone, it does not necessarily depend linearly on the normal load any more and the linear relationship of the friction force to the normal load cannot be applied but has to be replaced by the linear relationship to the contact area \[^{[93]}\].

### 2.4 Application to nanoparticulate systems

Determining the strength of the adhesion forces between nanoparticles and their dependence on the environment has been addressed by numerous experimental and theoretical studies until today \[^{[2, 24, 94-109]}\]. These forces can be reproduced by the JKR or the DMT model only in a few specific cases, such as for hydrophobic surfaces \[^{[105, 110]}\]. For sufficiently hydrophilic surfaces of particles in the micrometer-range or below, many studies detect a clear trend of the interparticle adhesion forces with humidity \[^{[100-103, 111-113]}\], which is not observable for less hydrophilic surfaces \[^{[98, 101, 114, 115]}\] and can be usually only explained by the acting of capillary forces. Furthermore, it has been shown that for particles at this size scale classical capillary effects are modulated crucially by both
the overall particle shape and the surface roughness \[97, 106, 107, 116–120\]. However, predictive models that account for controlled changes of the interparticle forces at the nanoscale are mostly limited to single contributions and are often applied to model systems with little transferability to real material/adsorbate combinations. In fact, a rationalization of the relative changes between dispersion, solvation and capillary interparticle forces across the transition between dry and wet conditions in a realistic system is often challenging and not intuitive \[95, 102, 121, 122\].

For particle sizes above 100 nm it is known that the capillary, Van der Waals and electrostatic forces typically scale linearly with the particle radius \[123, 124\]. The capillary forces dominate for particle sizes below 1 µm (cf. Fig. 2.8) and electrostatic forces can be neglected \[50, 125\]. However, it remains unclear whether the same linear-scaling law extends to particle sizes between 1 and 100 nm or if other molecular origins of interparticle forces, such as the solvation forces, have to be considered in this size range \[126–132\]. It is also unclear how these forces would behave under varying humidity conditions \[133, 134\]. In any case, the dimension of the water layer that adsorbs to the particle surface under ambient conditions \[135, 136\] approaches the same order of magnitude of the particle itself when the particle size decreases. By explicitly taking into account this surface adsorbed water layer, it has been recently shown that the continuum capillary theory may be also applied to rationalize the forces at nanocontacts in humid air \[96, 99, 137, 138\]. On the other hand, it is discussed controversially in the literature, whether general relations resulting from continuum considerations such as the Kelvin equation or the concept of a macroscopic contact angle can be applied at the nanoscale \[20, 23, 139\], and if the precision yielded by the circular approximation is sufficient \[24, 140–142\].

In matters of the tangential sliding forces, it has been found frequently that the mechanisms of friction at the nanoscale deviate largely from the macroscopic equations due to the influence of atomic roughness, microscopic contact area and confined water between the interfaces \[143, 149\]. Several authors find a typical stick-slip behaviour for the friction at nanocontacts \[150, 156\] as well as a significant deviation from the linear Coulomb’s law of friction \[157, 165\] and an influence of the sliding velocity on the height of the friction forces \[166, 168\]. These findings are however mostly restricted to sliding friction, while rolling friction is, due to its complex relative move-
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Figure 2.8: Dependence of different interparticle forces on the particle diameter.

The contribution $F(Cap.)$ water describes the capillary force calculated from the simplified equation $F_{Cap} = 4\pi R \gamma$ assuming a contact angle of $\Theta = 0^\circ$. The contribution $F(vdW) 4$ eV describes the Van der Waals force using a Hamaker constant $4\pi A/3 = 4$ eV, while the contribution $F(vdW) 4eV 1%$ def. considers an additional particle deformation of 1%. Reproduced from Ref. [50] with permission from The Electrochemical Society.

A possible tool for the simulation of particulate systems is the discrete element method (DEM), which was developed in 1979 by Cundall and Strack [35] and has since then been improved with more and more sophisticated models [36, 37, 43, 46, 84, 87, 169–172]. It has been frequently applied, yielding a high degree of precision and computational performance [18]. Nevertheless, the specific simulation of nanoparticulate systems until the current day has been approached only sporadically [48, 173–177] and with inadequate methodology due to the lack of knowledge about the mechanical properties of nanoparticles. A widely-used approach to determine the necessary contact models and the respective material parameters for the DEM simulations consists in adapting the models and parameters in the simulations to match macroscopic system properties between equivalent simulations and experi-
iments. However, this approach cannot be used for the determination of parameters at the nanoscale, as the resolution of the respective experiments is too small and, what is more crucial, the validity of the models themselves is questionable, as already mentioned above. It is therefore still unclear how to apply meaningful and transferable interaction models and how to choose the respective parameters at the nanoscale with physical correctness.

The scope of this work intends to close this gap by a thorough analysis of the physics behind nanoparticle adhesion and friction at the atomistic scale and by a verification of the applicability and validity of macroscopic force models to the nanoparticle interactions. The findings of this work should help to establish a detailed understanding of the interaction mechanisms between nanoparticles at ambient conditions. They shall yield a solid basis for the further investigation of TiO$_2$ nanoparticulate systems on the one hand, and for the development of further nanoscopic contact models considering different particle properties such as material, shape or surface termination on the other hand. To the best of our knowledge, this comprehensive bottom-up approach to develop a substantiated interparticle contact model for a technical particle system is novel to the literature.
Chapter 3

Methods

In order to investigate the mechanical interaction mechanisms between nanoparticles at the microscopic level, we choose all-atom molecular dynamics (MD) simulations as our main method. This method provides the advantage of yielding a detailed time-dependent atomistic view into the interactions between nanoparticles in contrast to other methods like Monte-Carlo simulations, where atomistic resolution is achieved but without time-dependence. MD methods complement continuum simulations and force-detecting experimental techniques, where the atomistic interaction mechanisms are below the resolution limit (Fig. 3.1). On the other hand, the simulation times and system sizes accessible in all-atom MD are sufficiently large to cover the time and size scales of the adhesion mechanisms between entire nanoparticles. This is not the case for more precise methods like quantum mechanical simulations, where the entire electronic state of the atoms is considered. In order to be able to validate our findings to experimental results, we use the mesoscopic discrete element method (DEM), which represents a special case of MD simulations. This method treats entire particles as single simulation entities, neglecting the underlying atomistic details, and thus enables the simulation of larger systems containing a high amount of nanoparticles for larger simulation times. Our methods therefore create a link from quantum mechanical simulations, which provide precise chemical information about the surfaces, to continuum simulations, which enable the consideration of entire technically relevant systems as becomes obvious from Fig. 3.1 The basics of these methods are described in the following chapter.
3.1 All-atom molecular dynamic simulations

Molecular dynamics simulations are commonly used to predict the time evolution of an atomistic system, which can then be used to extract conformational or thermodynamic information about that system. Examples of this are the conformational change of biomolecules after adsorption to a surface or the forces and energies acting between specific molecules. The principles of this technique are briefly described in the following sections and can be found in more detail for example in the works of Jensen [179] and Leach [180].

3.1.1 Equations of motion

In the simulation of an atomistic system usually all atoms are considered to be point masses. If the properties of the atoms remain unchanged, the state of a single atom $i$ in this system is thus defined by its position $\mathbf{r}_i$ and momentum $\mathbf{p}_i$ resulting in six degrees of freedom in a 3D cartesian coordinate system. Due to interatomic interactions such as bonds or electrostatic attraction/repulsion, the atoms in a system exert forces on each other which are specific to every atom pair. These interatomic forces lead to a movement of the atoms following Newton’s laws of motion as can be calculated.
by solving the differential equations from Newton’s second law:

\[ \frac{d^2 r_i}{dt^2} = \frac{F_i}{m_i}, \tag{3.1} \]

where the movement of an atom with the mass \( m_i \) depends on the overall force \( F_i \) exerted onto that atom and on its initial position and velocity. The solution of these equations of motion then leads to atom trajectories, which describe the changing state of the system during the whole timespan of the simulation.

### 3.1.2 Time integration

As the analytical solution of the differential equations of motion becomes complicated or impossible for more than two atoms in a system, the determination of the atom positions and velocities is discretised into single timesteps \( \Delta t \) during the simulation. The solution of the differential equations thus becomes possible by stepwise solving the equations of motion in a fixed system configuration at a specific timestep and subsequent interpolation of the positions and velocities to the next step. A frequently used algorithm to solve the equations of motion iteratively is the velocity-verlet algorithm [181]. In this approach it is assumed that the positions and velocities of the next timestep can be approximated by tailor expansions in time:

\[ r(t + \Delta t) = r(t) + \dot{r}(t) \Delta t + \ddot{r}(t) \frac{\Delta t^2}{2}, \tag{3.2} \]

\[ \dot{r}(t + \Delta t) = \dot{r}(t) + \frac{1}{2} [\ddot{r}(t) + \ddot{r}(t + \Delta t)] \Delta t, \tag{3.3} \]

From the known configuration at a certain time \( t \), the accelerations \( \ddot{r} \) of the atoms can be calculated knowing the force field \( F_i \) using Newton’s equation of motion (3.1), and with this the positions of the atoms in the next timestep \( t + \Delta t \) can be calculated via equation (3.2). From the atom positions in the next timestep, again the accelerations can be calculated, which are finally used to calculate the velocities in that timestep via equation (3.3). Because of its precision, speed and time reversibility, the velocity-verlet approach is preferred for the time integration in most molecular dynamic simulations. With an increasing timestep the errors in the tailor expansions grow, which leads to simulation instability above a certain critical timestep. This critical
timestep depends on the fastest motions in the system, which are usually the motions of the lightweighted hydrogen-atoms, and lies in the range of 0.2-1 femtoseconds for all-atom simulations containing hydrogen. By keeping the bonds and angles connected to hydrogen atoms fixed with a so called SHAKE algorithm \cite{182}, the critical timestep can be increased to around 2 femtoseconds and thus the simulation speed can be at least doubled.

In the above equations, the boundary conditions at the edges of the simulation system have to be explicitly defined. The possibility to mimic infinitely large systems is provided by the usage of periodic boundary conditions (PBC), where the simulation box is repeated infinitely in all directions. In practice this means that an atom that leaves the simulation box at the border enters again at the opposite side with the same displacement and velocity. This approach has the advantage of eliminating finite-size boundary effects by e.g. boundary walls which do not appear in macroscopic systems. Still the periodic images of the simulation cell can influence each other, necessitating the use of a sufficiently large box size.

### 3.1.3 Force fields

To determine the forces acting on all atoms in a system, the interaction forces between all single atom pairs $F_{ij}$ and also of certain manybody terms have to be known:

$$ F_i = \sum_j F_{ij} + \sum_{j,k} F_{ijk} + \sum_{j,k,l} F_{ijkl} + \ldots. $$

(3.4)

These interatomic forces are derived from the interatomic energies $E_{ij}$, $E_{ijk}$, ..., which in the case of all-atom simulations are defined by interatomic potentials, the so called force fields. The definition of the force fields is not trivial and varies largely between atom species, bonding neighbourhood and external conditions. Furthermore the definition of interaction potentials between entire atoms can only be seen as an approximation of the complex electronic processes underlying the attraction or repulsion between atoms. In all-atom simulations the interaction potentials are usually composed of an electrostatic, a Van der Waals (VdW), several bonding and eventually additional terms (See Fig. 3.2):

$$ E_{ij} = E_{ij,el} + E_{ij,VdW} + E_{ij,bonds} + \ldots, $$

(3.5)
3.1. ALL-ATOM MOLECULAR DYNAMIC SIMULATIONS

\[ E_{ij} = E_{ij,\text{angles}} + \ldots, \quad (3.6) \]

\[ E_{ijkl} = \ldots. \quad (3.7) \]

The electrostatic interactions can be calculated from Coulomb’s law by

\[ E_{ij,el} = \frac{q_i q_j}{4 \pi \epsilon_0 r_{ij}}, \quad (3.8) \]

with the point charges of the two atoms \( q_i \) and \( q_j \), the vacuum permitivity \( \epsilon_0 \) and the distance between the atoms \( r_{ij} \). The VdW interactions can be approximated for example by a Lennard-Jones (LJ) potential \[ 183 \]:

\[ E_{ij,VdW} = \epsilon_{ij} \left( \left( \frac{r_{m,ij}}{r_{ij}} \right)^{12} - 2 \left( \frac{r_{m,ij}}{r_{ij}} \right)^{6} \right), \quad (3.9) \]

with the depth of the potential minimum \( \epsilon_{ij} \) and the minimum energy distance \( r_{m,ij} \). In this equation the 12th order term mimics the steric Pauli repulsion between atoms at small distances, while the 6th order term represents the Van der Waals attraction at higher distances. Although the

**Figure 3.2:** Different types of interaction energies acting between atoms in all-atom simulations.
Lennard-Jones potential form is frequently used for atomic interactions due to its generality and efficiency, the interaction between atoms inside a crystal lattice can sometimes be better described by the more accurate Buckingham potential form \[184\], where the repulsive 12th order term is replaced by an exponential term:

\[
E_{ij,VdW} = \epsilon_{ij} \left[ \frac{6}{\alpha_{ij} - 6} \alpha_{ij} \left( 1 - \frac{r_{ij}}{r_{m,ij}} \right) - \frac{\alpha_{ij}}{\alpha_{ij} - 6} \left( \frac{r_{m,ij}}{r_{ij}} \right)^6 \right],
\]

(3.10)

with the additional fitting parameter \( \alpha \) (cf. left part of Fig 3.3). The bond and angle potential of covalently bound atoms inside molecules is only applied, where respective bonds are specified and is usually approximated by a quadratic spring term:

\[
E_{ij,bond} = \frac{k_{bond,ij}}{2} (r_{ij} - r_{m,ij})^2,
\]

(3.11)

\[
E_{ijk,angle} = \frac{k_{angle,ijk}}{2} (\theta_{ijk} - \theta_{m,ijk})^2,
\]

(3.12)

with the bond and angle stiffness \( k_{bond,ij} \) and \( k_{angle,ijk} \) and the angle \( \theta_{ijk} \) opening between the two atoms \( i \) and \( j \) bound to a third atom \( k \) (cf. right part of Fig. 3.3). For the higher order bonding potentials different potential forms have to be applied. All parameters used for the force-fields such as the partial charges of the atoms, the Van der Waals coefficients and the bonding coefficients have to be derived for every atom species individually by validation of simulation system properties with experimental values or with higher order atomistic simulations, such as quantum chemical simulations.

To reduce computational costs, usually a cutoff distance \( r_c \) is defined for the nonbonding electrostatic and VdW terms above which the interactions are neglected. The error of this simplification depends on the value of the cutoff distance and is usually small for the VdW interactions, where the energies scale with the atom distance to the power of six. For the electrostatic interactions however, where the interaction energy scales linearly with the atom distance, the cutoff error is significantly larger, which is often overcome by the use of long range solvers such as the ewald summation \[185\], evaluating the electrostatic energy above the cutoff-distance. These methods
3.1. **ALL-ATOM MOLECULAR DYNAMIC SIMULATIONS**

**Figure 3.3:** Left: Van der Waals interaction energies between two oxygen atoms as modeled in this work for two water molecules by a Lennard-Jones potential (red line) and for two TiO$_2$ rutile crystal oxygens by a Buckingham potential (blue line). Right: Bond interaction energies between the oxygen and the hydrogen atom of a water molecule as modeled in this work by a quadratic bond potential.

...calculate the electrostatic energy in a periodic system by introducing gaussian screening functions of the point charges and evaluating the near-field contribution inside these screening functions directly, while the far-field contributions between the screening functions are evaluated in the reciprocal space, providing an exact determination of the electrostatic energy...

...In order to realistically reproduce the interactions between the TiO$_2$ particles under ambient conditions, in this work we use the comprehensive all-atom model developed by Schneider et al. [29–31]. In this model the chemical composition of a TiO$_2$ rutile surface as well as the interacting force field between crystal atoms and between crystal atoms and biological molecules (including water) were derived from extensive quantum mechanical simulations. Beside the correct dissociation behaviour of water molecules at undercoordinated atoms of the crystal surface, the model also considers the variation of partial charges at the surface.

### 3.1.4 Ensembles

Due to the energy conservation in the equations of motion together with a fixed simulation box, an unconstrained molecular dynamic simulation produces an ensemble of constant particle number, constant volume and constant energy (NVE) also called a microcanonical ensemble. As the total energy is composed of the potential and the kinetic energy and the potential energy varies in the course of the simulation, a constant total energy...
leads to fluctuations in the kinetic energy and thus to fluctuations of the temperature by

\[ \langle E_{\text{kin}} \rangle = \frac{1}{2}(3N_{\text{atoms}} - N_{\text{constraints}})k_b T, \]  

(3.13)

with the triangular brackets denoting the ensemble average, \( k_b \) denoting the Boltzmann constant and \( T \) denoting the absolute temperature of the system.

To reach a canonical ensemble with constant number of atoms, constant volume and constant temperature (NVT), a variety of thermostats can be applied, which modify the atom motion such that a constant kinetic energy and thus a constant temperature is achieved. The most direct intervention is a simple rescaling of the velocities by the ratio of the target temperature to the actual temperature in the system:

\[ v_{\text{scaled}} = v_{\text{Newton}} \left( \frac{T_{\text{target}}}{T_{\text{actual}}} \right)^{1/2}, \]  

(3.14)

yielding a constant temperature over the entire simulation length. This approach however does not reproduce the correct dynamics of a canonical ensemble and is therefore seldomly used. A better way of controlling the temperature is modifying the equations of motion to couple the simulation system to a virtual heat bath, which exchanges energy with the atoms.

\[ \frac{d^2 \mathbf{r}}{dt^2} = \frac{F}{m} - \zeta \frac{d\mathbf{r}}{dt}, \]  

(3.15)

\[ \zeta = \frac{2\Delta E_{\text{kin}}}{Q}, \]  

(3.16)

with the eligible damping parameter \( Q \) \[186\]. The Nosé-Hoover thermostat \[186\] further introduces a time-dependent coupling of the heat bath to the atoms

\[ \frac{d\zeta}{dt} = \frac{2\Delta E_{\text{kin}}}{Q}, \]  

(3.17)

which exactly reproduces a canonical ensemble and is therefore preferred to control the temperature of many all-atom simulations. The canonical ensemble represents the simulation of a system at a constant Helmholtz free energy and compares therefore well to macroscopic conditions where the temperature of a system can normally be assumed to be constant. The above described thermostats can be equivalently applied to control the box
3.1. ALL-ATOM MOLECULAR DYNAMIC SIMULATIONS

size in an ensemble of constant atom number, constant pressure and constant temperature (NPT) thus simulating the system at constant Gibbs free energy.

3.1.5 Discrete Element Method simulations

A severe shortcoming of all-atom molecular dynamic simulations is the restricted size and time of the simulations due to the number of atoms and the height of the critical timestep. Even by using massive parallel computing, it is mostly not possible to exceed system sizes of several hundred nanometers and time spans of a few microseconds which represents a major problem when comparing simulation results to experimental observations. For the simulation of particulate systems, the coarse graining discrete element method first proposed by Cundall and Strack [35] addresses this problem by treating entire particles consisting of many atoms as one simulation entity. Depending on the size of the particles, this method reduces the number of elements in a simulation significantly by a factor of $10^4$ (small nanoparticles) to $10^{20}$ (millimeter sized particles) enabling an enormous increase of the system size to reach experimental orders of magnitude. Furthermore, the dynamics of the system containing elements with a higher mass allows for the choice of a much larger timestep leading to elongated simulation times also close to experimental conditions.

The discrete element method is a special case of molecular dynamics, where the particles are not any more considered to be point masses, but rather objects with a discrete size such as spheres, squares or more complex geometries. In practice, however, the use of other geometries than spheres is coupled to a significant increase of the computation complexity, which leads to crucially higher simulation times and is therefore seldomly applied. In fact, complex particle geometries are rather realized by the assembly of multiple smaller spheres.

The implementation of a finite particle size results in an addition of six rotationary degrees of freedom (three positions and three velocities) which have to be considered in the equations of motion:

$$\frac{d^2 r_i}{dt^2} = \frac{F_i}{m_i}, \quad (3.18)$$
with the rotational motion $\theta_{r,i}$, the overall torque $M_i$ acting on the particle and the moment of inertia of the particle $I_i$. These equations can still be solved by the methods described above like the velocity-verlet algorithm. Furthermore, the force fields developed for atomic interactions cannot be applied anymore but have to be replaced by contact models, which reproduce the correct forces and energies in normal direction as well as in tangential direction between the particles. The contact models are traditionally derived from macroscopic constitutive laws and validated by extensive comparison between theoretical and experimental results. Due to the sensitive dependence of the interaction forces on the surface conformation of a particle, the DEM contact models are not only specific to the single particle materials, but also to several other particle properties, which results in a multitude of different models and parameters developed for different applications.

As the kinetic energy of the atom motion is not computed in the DEM simulation scheme, the temperature of the system is not relevant and the simulations are therefore performed in the NVE ensemble. However, in contrast to the classical all-atom MD simulations, most of the contact models usually contain energy dissipating terms (see previous chapter), which leads to a decrease of the potential energy of a system in the course of a simulation towards its equilibrium state, if no new energy is added to the system.
Chapter 4

Adhesion forces under ambient conditions

In order to achieve a comprehensive view on the interparticle adhesion at the nanoscale under ambient conditions, we perform an extensive study of the water-mediated adhesion between TiO$_2$ nanoparticles using all-atom molecular dynamics modelling. This study covers the influence of particle size, humidity, roughness and surface hydrophilicity on the interparticle forces to account for the peculiarities of a polydisperse nanoparticulate system (Fig. 4.1) under ambient conditions. The description of the specific materials and methods used to generate particular results is placed into separate emphasized paragraphs close to their respective application in the text.

4.1 Forces between smooth particles at different water coverages

We first concentrate on pairs of fairly smooth, spherical 4 nm, 6 nm, 8 nm, 10 nm and 20 nm rutile particles, on the caps of two 50 nm particles and on a pair of an 8 nm particle and a 4 nm particle, all with different particle orientations facing each other (Fig. 4.2) to account for the statistical distribution of contact pairings occurring in a real system. This selection of particle sizes covers the whole size distribution of flame-made TiO$_2$ nanoparticle films and refines towards small particles, where we expect the peculiarities of nano-adhesion to be most significant. The particle models are created as follows:
Methods: Atomistic TiO$_2$ nanoparticle models are created by using the methods developed by Schneider et al. [29,30]. In this approach smooth nanoparticles with diameters between 4 nm and 20 nm are created by carving a sphere off a rutile single crystal respecting the TiO$_2$ stoichiometry. Rough particles including asperities are created by carving the union region of a large sphere together with smaller spheres placed on the particles surface such as to receive hemispheres or caps on the surface (see scheme Fig. 4.27). Furthermore a slab model with a size of approximately 16x14 nm is created by cleaving the infinite single crystal in the $<$213$>$ lattice direction, which forms a highly amorphous surface during annealing. This amorphous surface represents the majority of the particles surfaces best, rather than exhibiting a single crystal facet, which is found only seldomly on the particles. Subsequent charge rescaling and annealing of the crystal atoms of the different cutouts then leads to the TiO$_2$-surface model as described by Schneider et al. [29], which reasonably represents the surfaces of our experimental particles (cf. Fig. 4.1). The accessible titanium atoms with less than 5 oxygen neighbours are hydrated assuming dissociative water adsorption [30], leading to a coverage of approximately 3.0 nm$^{-2}$ terminal OH-groups for the slab and the smooth particles independent of the particle size. Due to a higher amount of undercoordinated titanium atoms at the asperities, the OH-group coverage is increased at
the rough particle models to between 4.3 nm$^{-2}$ and 5.4 nm$^{-2}$ depending on the specific shape. These different coverages of OH-groups, however, do not influence the interparticle forces, as the first water layer is very strongly bound to the surface anyway (see below).

To represent ambient conditions, the particles are then covered with different amounts of TIP3P [188] water molecules corresponding to a specific air humidity [135, 136]. For the sake of simplicity the water coverage of the particle models is always calculated from the nominal surface of the large sphere. This value deviates slightly from the true surface of the rough particle models but since the coverage is not a direct parameter in the equations used to predict the forces analytically, the resulting approximation for the case of rough particles is negligible for the purposes of this work.

Interparticle forces are calculated from keeping the crystal atom positions at a certain particle distance fixed and averaging the forces exerted on them during classical Molecular Dynamics (MD) simulation runs. These runs take 0.6 ns each after an equilibration of 0.4 ns and are performed in the NVT ensemble at 300 K, with a timestep of 2 fs, using the LAMMPS programme package [189]. The interactions between the oxide atoms of the particles are described by a Matsui/Akaogi force field, as described in Ref. [29]. The TIP3P [188] water molecules interact with the oxide atoms via the force field developed by Schneider et al. [30,31].

The exemplarily computed force-displacement (F-D) curves between two 4 nm particles whose surfaces are separated by a distance $d - 2R$ (see scheme in Fig. 4.2) at different water coverages are shown in Figs. 4.3 and 4.4. They display an oscillatory behaviour at short particle-particle distances, superimposed on a typical long-range capillary behaviour [2]. In agreement with common knowledge [24,56] (See also Fig. 2.5), the slope of the capillary contribution to the F-D curves decreases and the length of the capillary interaction increases with increasing water coverage. Obviously, the capillary contribution vanishes when the particles are immersed in bulk water or in the absence of adsorbed water. The F-D oscillations display nearly constant amplitudes at all water coverages (including in bulk liquid), and are only absent when no adsorbed water molecules are present on the surface, i.e. when the interparticle attraction force is only due to van-der-Waals interac-
COM1, COM2: particles’ centers of mass

R: particle radius
d: distance of particle centers
h: thickness of adsorbate layer

\( R_{\text{Cap}} \): capillary particle radius

\( R_{\text{Cap}} = R + h \)

D: effective particle-particle separation, \( D = d - 2R - 2h \)

\( \Theta \): particle/meniscus contact angle

\( \beta \): filling angle

\( r_m \): outer meniscus radius

\( l_m \): inner meniscus radius

r: radial direction from COM (origin at COM+R)

z: direction connecting COM1 and COM2 (origin at COM1)

Figure 4.2: Schematic illustration of the coordinates and symbols used in this work along with a cut through a representative atomistic model of two 4 nm TiO\(_2\) particles facing each other along the \( \langle 110 \rangle \) direction in the presence of an adsorbed water layer [3].

Furthermore it is also obvious that, while the capillary contribution is nearly identical for the different particle orientations, the shape of the force oscillations strongly depends on the particle orientation (See further force curves in the Appendix section A.1).

Proceeding to different particle sizes and size combinations as shown in Fig. 4.5, the resulting F-D curves reveal in all cases the same characteristic superposition of monotonous capillary and oscillatory solvation forces as for the 4 nm particles. However it is again visible that the intensity of the force oscillations depends strongly on the local contact geometry, which is much more dominant than the dependence on the particle size. For larger particles, the share of the force oscillations decreases although never entirely disappearing. The height of the capillary part changes, as expected, with rising particle size, while we note, that the range does not increase significantly [24] (cf. Fig. 2.5). This makes the capillary force contribution strongly sensitive to asperities especially at larger particle sizes, as we will see later.
Figure 4.3: Force-displacement curves calculated for 4 nm TiO$_2$ particles facing each other along the $\langle 110 \rangle$ direction (see Fig. 4.2) with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. [3]
Figure 4.4: Force-displacement curves calculated for 4 nm TiO$_2$ particles facing each other along the ⟨001⟩ direction (see Fig. 4.2) with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter 2R [3].
Figure 4.5: Top Left to bottom right: Representative force displacement curves of two 4 nm, 8 nm, 10 nm and 20 nm particles, of an 8 nm particle together with a 4 nm particle and of two caps cut from 50 nm particles covered with 16.2 water molecules per surface nm² and facing each other along the ⟨100⟩ direction. The insets display volumetric density isosurfaces of the crystal and water phase of the respective simulated particle models at a surface distance of approximately 1 nm [4].
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4.2 Solvation forces

The oscillatory behaviour of the force-distance curves at $d - 2R \lesssim 1$ nm commonly arises between interacting surfaces in an ordered molecular solvent [26,190]. The solvent structuring around a single TiO$_2$ nanoparticle in bulk water can be expressed in terms of the radial distribution function $g(r)$ and the radial-angular distribution function $g(r, \alpha)$ of the water O atoms in surface proximity. The distance $r$ is defined as the difference between the length of the radial position vector of each water oxygen atom from the center of mass (COM) of the particle and the length of the position vector of the nearest titanium atom of the particle surface (Fig. 4.2), whereas $\alpha$ is the angle between the water molecular dipole and the $r$ direction. The superimposed $g(r)$ and $g(r, \alpha)$ (Fig. 4.6) highlight a tightly bound first hydration layer (up to $r \sim 0.25$ nm) with the O atoms of all molecules pointing towards the surface, and a second hydration double layer ($r$ between 0.25 and 0.5 nm) including molecules with opposite orientations. Integration of $g(r)$ over the single density peaks reveal, on average, 5.2 molecules per nm$^2$ of particle surface in the first layer (which we will refer to as ‘chemisorbed’ water) and 12.2 molecules per nm$^2$ in the second layer (which includes ‘physisorbed’ water).
4.2. SOLVATION FORCES

In the case of particles in humid air separated by a distance \( d - 2R \), analogous structuring of the adsorbed water molecules in the interparticle region is quantified by means of the unidirectional distribution functions \( g_{d-2R}(z) \) and \( g_{d-2R}(z, \alpha) \), computed in a cylindrical volume with an arbitrarily small cross-section \( A \) around the \( z \) axis connecting the COM of the two particles. As shown in Fig. 4.7 for the \( \langle 110 \rangle \) orientation, at the separation corresponding to the first potential energy minimum around \( d - 2R = 0.33 \) nm (see the force curve in Fig. 4.3), a single water double-layer is present between the two particles. Increasing \( d - 2R \) leads first to stretching of this double-layer (attractive forces) up to an energy maximum at \( d - 2R = 0.41 \) nm and then to insertion of a new double layer, which is under compression (repulsive forces) up to the next potential energy minimum at \( d - 2R = 0.56 \) nm. The same applies for decreasing \( d - 2R \), where the influence of water structuring is superimposed to steric repulsion of the atoms. The reason for the dependency of the solvation forces on the local surface geometry becomes clear from Fig. 4.8, where the water structuring between two particles facing each other in the \( \langle 001 \rangle \) direction is much less pronounced than for the \( \langle 110 \rangle \) orientation, due to less faceting (See also section A.2 in the Appendix).

This qualitative description of the solvation contribution of the interparticle force can be put in more rigorous terms by noting that \( g_{d-2R}(z) \) corresponds to the product of the unidirectional distribution functions of the solvent around each single particle \( (d - 2R \rightarrow \infty) \) assuming a linear superposition of the potentials of mean force [74],

\[
g_{d-2R}(z) = g_\infty(z)g_\infty(d - 2R - z). \tag{4.1}
\]

This results in predicted \( g_{d-2R}(z) \) functions, which agree very well with the corresponding distribution functions calculated explicitly in the MD simulations, irrespective of the chosen water coverage and for all considered orientations as can be seen in Figs. 4.7 and 4.8 (black lines). Furthermore the solvation pressure \( p \) between the two particle surfaces can be obtained by integration of the particle-water force function \( f(z) \) weighted by the density excess in the interparticle region as already described in equation (2.19):

\[
p(d - 2R) = \int_0^\infty [g_{d-2R}(z) - g_\infty(z)] \rho_b f(z) \, dz, \tag{4.2}
\]
with \( \rho_b \) being the solvent bulk density.

Rather than computing different force-displacement curves for different mutual particle-particle orientations, we compute a single curve by using orientation-independent \( f(z) \) and \( g(z) \) functions, to obtain a universal force contribution. In particular, instead of averaging \( g(z) \) over only a few orientations, we directly use the radial distribution function \( g(r) \) (Fig. 4.6) for this purpose. The averaged particle-water force function \( f(z) \) is determined as follows.

**Methods:** For a local particle-water force function \( f_n(z) \) a single water molecule is first relaxed at the surface of a bare crystal and is then moved along the radial direction from the particle surface, while keeping the conformation fixed and recording the forces acting on the molecule. This procedure is repeated for all particle orientations con-
4.2. SOLVATION FORCES

Figure 4.8: Same as in Fig. 4.6 for $g(z)$ and $g(z, \alpha)$ between 4 nm particles in humid air facing each other along the ⟨001⟩ direction at a surface separation of $d - 2R = 0.72$ nm, 0.8 nm, 0.9 nm and 1.05 nm from top left to bottom right. As above, the red lines show the axial distribution function $g(z)$ and the underlying colour plot shows the axial-angular distribution function $g(z, \alpha)$, with red representing regions higher than in the bulk, on a logarithmic scale. The density values were obtained from averaging the water positions in a cylinder between the particles with a cross-sectional area of $A = \pi(0.7)^2$ nm$^2$. The black lines are theoretical predictions from Eq. (4.1) using the $g(z)$ in bulk water over an isolated particle in the same orientation.

Considered in the analysis of the solvation forces. The equilibrium point $z_{equ}$ of all local interaction force curves is then shifted along the z-axis to match the position of the first peak of the radial distribution function $z_{max}$. Finally, an orientation-independent interaction force function is calculated from averaging over all shifted local interaction force curves:

$$f(z) = \frac{1}{N} \sum_{n=1}^{N} f_n(z - z_{equ} + z_{max}),$$

(4.3)

with $N$ being the number of different orientations considered. To avoid an overestimation of small density changes at small particle distances, a force-cutoff of 50 nN is used, above which the interaction force function is kept constant.
CHAPTER 4. ADHESION FORCES

The resulting function $f(z)$ for TIP3P water over our TiO$_2$ particle model (Fig. 4.9) allows us to apply Eq. (4.2) in a general form and compare the predicted solvation-like contribution of the interparticle forces $F_{solv}(d - 2R) = p(d - 2R)A$ with the results of the explicit MD calculations. In doing this, the interaction cross-sectional area $A$ is treated as a free parameter, which we have fitted to achieve optimal agreement between the force intensity of the analytical curve and the values between our nanoparticles in bulk water calculated explicitly in MD simulations, as is shown in Fig. 4.10.

Figure 4.9: The particle-water interaction force profile $f(z)$ over the TiO$_2$ particle surface.

Figure 4.10: Left: Solvation forces between two 4 nm particles in bulk water calculated via Eq. (4.2) ($A = \pi(0.25)^2 \text{ nm}^2$) compared to the forces calculated explicitly along several mutual orientations (black symbols). The latter are shifted to match the position of the maximum attractive force at $d - 2R = 0.62$ nm and divided by the particle diameter $2R$. Right: The same as above for two 8 nm particles ($A = \pi(0.4)^2 \text{ nm}^2$) (See further particle sizes in section A.3 in the Appendix).
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The overall agreement between the predicted (blue line) and the explicitly calculated (black symbols) solvation forces is excellent both regarding the position and the intensity of the force oscillations, if an optimal value of the cross-section $A$ is chosen (here its diameter is 0.5 nm for 4 nm particles and 0.8 nm for 8 nm particles, which is considerably smaller than the diameter of the capillary meniscus). However, notable differences related to the specific interaction orientations are visible and point towards the important role played by the local surface structure in governing the interaction force. As one might intuitively expect, the flatter surfaces (e.g. $\langle 110 \rangle$) result in deeper attractive forces, while the more corrugated surfaces (e.g. $\langle 001 \rangle$) result in less pronounced oscillations than the ensemble average (predicted blue curve).

### 4.3 Capillary forces

For particles in humid air, i.e. with a limited amount of adsorbed water molecules, the solvation-like oscillatory force contribution described above is superimposed to a long-range contribution due to the formation of a capillary water neck (meniscus) between the particles (see Figs. 4.3 and 4.4). While the former contribution is insensitive to the variation of water coverage, except for the extreme case of completely dry particles, the latter is strongly humidity-dependent \cite{25, 56}. The reason for this is the explicit dependence of the meniscus’ geometry (expressed via the curvature radius $r_m$ and the cross-section radius $l_m$, see Fig. 4.2) on the water vapour partial pressure $P/P_0$ through the Kelvin equation (2.13)

$$
\frac{P}{P_0} = \exp \left[ -\frac{\gamma_L V_M}{RT} \left( \frac{1}{r_m} - \frac{1}{l_m} \right) \right],
$$

(4.4)

which was already described in chapter \ref{2}. As mentioned, for a given solid / solvent pair (i.e. given $\gamma_L$ and $\Theta$), the shape of the meniscus ($r_m$, $l_m$ and $\beta$) uniquely defines an attractive force between two particles, which can be calculated for two spheres of equal capillary radius $R_{Cap}$ (Fig. 4.2) within the limits of the circular approximation through

$$
F = \pi \gamma_L R_{Cap} \sin(\beta) \left[ 2 \sin(\Theta + \beta) + R_{Cap} \sin(\beta) \left( \frac{1}{r_m} - \frac{1}{l_m} \right) \right].
$$

(4.5)
When we apply the equations above to our system for a relative humidity, which corresponds to the respective water coverage (see below) using a contact angle $\Theta = 10^\circ$ (representative of highly hydrophilic TiO$_2$ particles, also see below), a surface tension $\gamma_L = 0.0523$ nN/nm (for bulk TIP3P water [191], which is known to differ from the experimental value of 0.072 nN/nm) and a nominal particle radius of $R_{Cap} = R = 2$ nm, we obtain force-displacement curves that miss by far the force values calculated in our MD simulations for all investigated water coverages and particle sizes (Figs. 4.11 and 4.12, green curve, labelled $F_{Cap,Conv}$). The reason for this striking discrepancy is the large influence of adsorbed water molecules forming an adsorbate layer with non-negligible thickness $h$ (about 0.5 nm).

In order to take this effect properly into account, we obtain directly all parameters necessary to compute the capillary force according to Eq. (4.5) via a geometrical analysis of our atomistic particle/water/particle models at each particle-particle separation distance in the MD trajectories.

**Methods:** To do so, we first perform a radial averaging of the water density around the $z$ coordinate connecting the COM of the two particles (taking into account all different mutual orientations) and plot the averaged iso-density lines at different fixed distances and coverages (Fig. 4.13, top panels). We then use the equimolar dividing surface between liquid and vapour (at the density value of 0.5 g/cm$^3$) to fit one circle to the region of the interconnecting meniscus and two circles to the regions of the surrounding particles in line with the analysis of Ko et al. [108] (Fig. 4.13, bottom panels).

This leads to variable values of $\beta$, $r_m$ and $l_m$, to nearly constant values of $R_{Cap}$ for all separation distances of a specific water coverage and particle size, and to a contact angle $\Theta \sim 0^\circ$ for all separation distances, water coverages and particle sizes, which is very reasonable given that the water molecules within the meniscus are in contact with the water molecules adsorbed on the particle surface.

We are now able to compute the capillary contribution to the interparticle force via Eq. (4.5). In doing so, the water surface tension $\gamma_L$ is treated as a free parameter and optimized to best-fit the results of the MD simulations in the long-range regions of the force-displacement curves for all considered mutual orientations between the particles (Figs. 4.11 and 4.12, red curve, labelled $F_{Cap,Geom}$) to account for the influence of the film thickness and...
Figure 4.11: Comparison between the F-D curves computed explicitly in MD simulations of various orientations of two 4 nm particles at a coverage of 5.2, 10.2, 16.2, 20.2, 25.2 and 30.2 water molecules per surface nm$^2$ from top left to bottom right respectively (black crosses, shifted as in Fig. 4.10) and the theoretically predicted capillary force contributions. The capillary contributions are calculated from the nominal particle geometries (green) and from geometrical fits of the MD trajectories without constraints on particle radius and humidity (red), with the circular approximation constraints (blue) and with the non-circular constraints (blue dashed). The magenta curve is the total sum of steric, dispersion, solvation and capillary force contributions [3, 4]. Please find the comparison for further particle sizes and water coverages in the Appendix section A.4.
Figure 4.12: Comparison between the F-D curves computed explicitly in MD simulations of various orientations of two 4 nm, 6 nm, 8 nm, 10 nm and 20 nm particles and of an 8 nm in contact with a 4 nm particle from top left to bottom right respectively covered with 16.2 water molecules per surface nm$^2$ (black crosses, shifted as in Fig. 4.10) and the theoretically predicted capillary force contributions. The capillary contributions are calculated from the nominal particle geometries (green) and from geometrical fits of the MD trajectories without constraints on particle radius and humidity (red), with the circular approximation contraints (blue) and with the non-circular constraints (blue dashed). The magenta curve is the total sum of steric, dispersion, solvation and capillary force contributions. 

\[ F_{\text{Total}} \]
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Figure 4.13: Analysis of the meniscus geometry between two 4 nm particles at a distance of $d - 2R = 0.6$ nm (left) and between an 8 and a 4 nm particle at a distance of $d - 2R = 0.65$ nm (right) each covered with 10.2 (top) and 25.2 (bottom) water molecules per surface nm$^2$. The respective upper part of the charts shows the iso-value lines of the radially-averaged water density around the two particles considering different mutual orientations, while in the lower part a geometrical fit of the meniscus geometry to the iso-density line at 0.5 g/cm$^3$ is displayed [3,4].

Applying the Kelvin equation (4.4) on our fitted capillary neck geometries together with the optimized $\gamma_L$ value of the respective coverage and particle size and averaging over all separation distances, connects the single coverages to a specific humidity, thus yielding water adsorption isotherms for every particle size (Fig. 4.14). These adsorption isotherms highly match the available experimental measurements on different TiO$_2$ surfaces [135,136] and also our own thermogravimetric measurements on the FSP produced nanoparticles, thus strongly confirming the choice of our particle model. The relation between the water coverage set in the simulations and the air humidity given by the Kelvin equation (2.13) matches very well experimentally measured adsorption isotherms on different TiO$_2$ surfaces (See Fig. 4.14).

As shown above, the capillary contribution calculated directly from the meniscus geometry agrees remarkably well with the results of the MD simulations. Fundamental for the obtained agreement is not only the contact angle $\Theta = 0^\circ$, but especially the value of the radius $R_{Cap}$, which is considerably larger than the nominal particle radius and now includes the adsorbed
Figure 4.14: Isotherm relating $P/P_0$ to the adsorbed water coverage, as obtained from our capillary force analysis (red squares and magenta and cyan triangles) in comparison with previous experiments [135,136] (black symbols) and an own TGA measurement (green circle) on FSP-produced particles. The error bars denote the standard deviation relative to all particle orientations and separations.

Water layer, consistently with previous works [95,96,112]. This implies negative values of the separation distance $D$ at the point of maximum attractive force between the particles (Fig. 4.15), which is approximately independent of the particle size and is an important factor influencing the humidity-dependency of the capillary force contribution as we will see later in this chapter.

We note that forcing the system to obey the circular approximation leads to very small variations of the fitted $R_{Cap}$ values and to slightly more evident variations of the humidity $P/P_0$, which we obtain from the Kelvin equation over the whole range of particle separations (see Appendix section A.4). Choosing the distance-averaged values of humidity, particle radius and surface tension together with a contact angle $\Theta = 0^\circ$ and solving iteratively Eqs. 2.13–2.18 leads to predicted F-D curves that deviate from the ones obtained through local geometrical fitting only at very high separation distances (Figs. 4.11 and 4.12 blue curve, labelled $F_{Cap,Mod}$). This deviation close to the rupture of the meniscus results mainly from the constant volume of the meniscus in the simulations and from the known shortcomings of the circular approximation [24,141] which naturally increase with increasing meniscus length and become obvious by inserting the same parameters into capillary simulations that calculate the capillary forces without a priori assumptions (Figs. 4.11 and 4.12 blue dashed curve). However, in the
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Figure 4.15: Predicted variations of the effective interparticle separation $D$ (continuous lines, filled symbols) and the adsorbed water layer thickness $h$ (dashed lines, empty symbols, see Fig. 4.2) with changing humidity $P/P_0$ (Fig. 4.14) and particle size calculated from the dimensions of the surface adsorbed water layer on the particles [4].

Coming back to the optimization of the surface tension, we note that the obtained values of $\gamma_L$ are close to the bulk water surface tension at high relative humidities, but increase significantly with decreasing humidity for all particle sizes (Fig. 4.17), which is in good agreement with the results from Benet et al. [192] and Werner et al. [193]. This is the combined result of the water confinement in thin liquid films on one side and of the small curvature radius of these films on the other side.

In order to decouple the two effects, we compute the surface tension of water layers adsorbed to a flat TiO$_2$ surface model (infinite curvature radius) presenting the same amount of water molecules per surface area as for the particle models both using the Kirkwood/Buff method and computing the energy needed to separate the two surfaces.

Methods: The interfacial tension $\gamma$ between two phases can be calcu-
lated from the method proposed by Kirkwood and Buff \cite{194,195} by computing the pressure gradient across the interface:

\[
\gamma = \int_{z_{lo}}^{z_{hi}} \left[ p_z(z) - \frac{1}{2} \left( p_x(z) + p_y(z) \right) \right] dz ,
\] (4.6)

with the variable \( z \) pointing in orthogonal direction to the surface plane and the integration boundaries \( z_{lo} \) and \( z_{hi} \) far enough away from the position of the interface. To calculate the liquid/vapour surface tension \( \gamma_L \) of water layers with different thicknesses adsorbed at our TiO\textsubscript{2} slab model, the pressure tensor acting on the water molecules is recorded every 0.002 ns in a 50 ns NVT simulation after a previous relaxation. The pressure gradient present at a specific height \( z \) is then computed by summing the pressure tensor of all atoms and snapshots in bins with a thickness of 0.1 Å along the \( z \) axis (see Appendix section A.5). As the system under investigation exhibits one solid/liquid and one liquid/gas interface, the influence of the solid/liquid interface on the pressure gradient has to be eliminated from the calculation. To this aim, the pressure gradient values at a sufficiently thick water layer below a \( z \) value of 1.65 nm, where the gradient starts to deviate significantly from the bulk value 0, are subtracted from the respective pressure gradient values of all other layers (see Appendix section A.5).

To assess the inaccuracy of this method at small layer thicknesses due to the variation of the pressure gradient at the solid/liquid interface, the surface tension of the water layers is alternatively computed from the work of adhesion between the two surfaces. In this approach, two slabs covered with the same amount of water are brought into contact and the work needed to separate the slabs is computed from integrating the force-displacement (F-D) curve recorded during the detachment of the slabs. The detachment F-D curve is computed from a steered MD simulation in the NVT ensemble with a timestep of 2 fs, during which one slab is displaced along the \( z \) axis at a speed of 0.5 m/s and the forces acting on both slabs are averaged over \( 10^4 \) steps. To eliminate the portion of the crystal forces, the forces between two slabs without water and OH-groups are subtracted from the respective force curves. As the water meniscus between the slabs is metastable close to the breaking distance, the forces between the slabs are additionally
4.3. CAPILLARY FORCES

![Figure 4.16: Work of adhesion needed to separate two surfaces from the integration of the detachment F-D curve as illustrated for a slab covered with 20 water molecules per surface nm$^2$. The dark grey area depicts the work considered for two approaching surfaces while the light grey area depicts the additional area considered for two detaching surfaces [4].](image)

calculated from quasi-static simulations with a duration of 3 ns as described above after placing two slabs at a specified distance. The detachment force curves are then truncated at the distance where no meniscus is formed during the quasi-static simulations thus providing a hysteresis between approaching and detaching surfaces (see Fig. 4.16).

To assess the inaccuracy of this method at small layer thicknesses due to the variation of the pressure gradient at the solid/liquid interface, the surface tension of the water layers is alternatively computed from the energy needed to separate two surfaces. In this approach, two slabs covered with the same amount of water are brought into contact and the energy needed to separate the slabs is computed from integrating the force-displacement (F-D) curve recorded during the detachment of the slabs. The detachment F-D curve is computed from a steered MD simulation in the NVT ensemble with a timestep of 2 fs, during which one slab is displaced along the z axis at a speed of 0.5 m/s and the forces acting on both slabs are averaged over $10^4$ steps. To eliminate the portion of the crystal forces, the forces between two slabs without water and OH-groups are subtracted from the respective force curves. As the water meniscus between the slabs is metastable close to the breaking distance, the forces between the slabs are additionally calculated from quasi-static simulations with a duration of 3 ns as described above after placing two slabs at a specified distance. The
detachment force curves are then truncated at the distance where no meniscus is formed during the quasistatic simulations thus providing a hysteresys between approaching and detaching surfaces (see Appendix section A.5). The values obtained via the Kirkwood/buff method (black solid line in Fig. 4.17) converge to the bulk surface tension at 100% relative humidity and match the computed values for the largest particle sizes (10 or 20 nm) in the region of high humidity. However, they diverge from them for humidities below 60% due to the strong variations of the solid/liquid interfacial pressure gradient at small liquid layer thicknesses (see Appendix section A.5). Instead, the values obtained from the work of adhesion (grey area in Fig. 4.17) do follow the model prediction for larger particles in the entire humidity range, although the uncertainty associated with the calculation increases with humidity. This is due to the increasing hysteresis encountered when thick water layers are put in contact or separated, which is caused by the decreasing probability to form water menisci between the layers at increasing surface separations (see Appendix section A.5). Overall, the data computed with the various methods allow us to conclude that only for particles smaller than about 10 nm does the small curvature radius of the liquid/vapour interface produce a significant increase of \( \gamma_L \). For small particles, however, this effect is very pronounced. Interestingly, for pairs of particles of different sizes (8 and 4 nm, in our case), the smaller particle seems to dominate, the computed values corresponding roughly to those of two equal 4 nm particles.

From a molecular point of view, the increase of surface tension in thin films arises from the limited mobility of the water molecules due to the film structuring. As a consequence, their rearrangement after separation of the liquid phase in two free surfaces is partly prevented, resulting in a higher net energy penalty associated with the surface creation than in the case of thick films \([192,196,197]\). The effect of curvature is less intuitive and is based on the inherent spacial separation between the Gibbs’ surface plane (i.e. the equimolar dividing surface between liquid and gas) and the surface plane of force equilibrium in the Laplace equation (the surface of tension). This separation is known as the Tolman length \([21,198]\) and is of the order of -0.05 nm for our water model \([199]\). For spherical droplets, the surface tension increases by an amount equal to twice the ratio between the
4.4. THE INFLUENCE OF HUMIDITY

Tolman length and the particle radius \( R \), which becomes appreciable at particle radii of the order of a few 1 nm. Alternatively, both effects can be readily rationalized if the surface tension is thought to originate from the presence of surface “capillary waves” \( \gamma_L \). In confined liquids, either because of very thin films or of small droplet radii, the long-range amplitudes of the capillary waves are suppressed, which leads to a free energy penalty and thus a surface tension increase.

The observed trend for water adsorbed on other materials than TiO\(_2\) is expected to differ only slightly, through the material-dependent water structuring at the solid/liquid interface. However, the dominant role is played by the liquid/vapour interface. For different liquid adsorbates, the trend will strongly depend on the value of the Tolman length, that can be either negative or positive, in which case a decrease of \( \gamma_L \) with decreasing particle radius could also be obtained.

4.4 The influence of humidity on the interparticle forces

Following our previous work \(^2\), we can safely assume that measured interparticle forces (e.g. by means of AFM force spectroscopy) are the maximum attractive forces corresponding to the minima of the F-D curves before the onset of steric repulsion, located at a separation \( d = 2R \sim 0.4 \text{ nm or } 0.6 \text{ nm} \), depending on the specific orientation (See Figs. 4.11 and 4.12). We call \( F_{\text{max}} \) the force at this point. To understand the behaviour of our experimental systems under ambient conditions in more detail, we now highlight the development of this \( F_{\text{max}} \) under varying humidity for selected particle combinations. Fig. 4.18 shows that the maximum adhesion forces exhibit a characteristic behaviour with a maximum at low air humidities and a subsequent decrease of the force with rising humidity for all particle sizes and combinations. This trend is differently pronounced for the different particle sizes but always observable and cannot be covered by the traditional capillary theory which disregards the influence of the surface adsorbed water layer.

In fact, having rationalized both the structural (solvation) and the capillary contributions to the interparticle forces, we are now able to understand how the latter varies with humidity (the former being, as stated above,
Figure 4.17: Development of the surface tension $\gamma_L$ with changing humidity and particle size calculated from the fitting of the capillary geometries to the MD forces between the particles (different symbols with solid lines as a guide to the eye). The error bars in y-direction denote the standard deviation relative to all particle orientations and separations, while the errorbars in x-direction are omitted to increase the clarity of the figure and can be adopted from Fig. 4.14. The surface tension for a flat surface representing an infinite particle radius is calculated from the Kirkwood-Buff method (KB, solid line) and from the work of adhesion (WA, the grey area highlights the hysteresis between approaching and retracting surfaces). The humidity values for the flat surface are adopted from the respective coverages of the 10 nm particles. The bulk surface tension of the used water model as calculated by the KB-method on a thick water slab is indicated by a horizontal black dashed line [4].

Figure 4.18: Variation of the maximum adhesion forces with humidity and in bulk water between representative orientations of differently sized nanoparticles [4].
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Roughly constant for all adsorbed water coverages. As a first observation, we note that a key parameter determining whether the capillary attraction either increases or decreases with humidity is the separation distance \( D \) between the particles at the point of maximum attractive force. This is visible when plotting force-humidity curves after solving analytically Eq. (2.13)–(2.18) at constant \( D \) and constant \( \gamma_L \) as was done in Fig. 4.29. For these parameters, which correspond to the classical picture of capillary theory where the adsorbate thickness can be neglected because of much larger particle radii, the attractive forces increase. For smaller \( D \) and variable \( \gamma_L \) values (Fig. 4.19 grey lines), which are a consequence of adsorbate layer thicknesses only about ten times smaller than the particle diameter, the forces decrease. However, it has to be taken into account that \( D \) is itself a function of humidity, and moves from positive values for completely dry particles to negative values for high water coverages (Fig. 4.15). It is therefore crucial to quantify the actual capillary contribution at the point of maximum attractive force for each different water coverage.

Regarding the explicitly calculated forces in MD simulations, the capillary contributions can be obtained by direct subtraction of the maximum attractive forces in bulk water, \( F_{\text{bulk}} \), from the corresponding \( F_{\text{max}} \) values.
for each considered particle orientation. The differences $F_{\text{max}} - F_{\text{bulk}}$ are plotted for different orientations of 4 nm particles as a function of humidity in Fig. 4.19 over the parametrized curves at constant $D$ and together with the theoretically predicted $F_{\text{Cap,Mod}}$ values at $\delta = 0.37$ nm and 0.62 nm, which are independent of the actual particle orientation. In the obtained plot, at humidities between 10 and 30 % the calculated forces initially increase. This is consistent with initially positive values of $D$ for very thin adsorbed water layers, which shift towards smaller and eventually negative values with increasing water adsorption, leading to a force increase (since the curves at constant $D$ shift to larger forces as $D$ decreases). The forces then decrease with a slope that does not depend on the orientation (apart from a slight scatter due to phase space sampling issues in the simulations). Indeed, at higher humidities the decrease of force dictated by negative $D$ values cannot be compensated by the force increase that results from thicker adsorbed layers. In summary, the analysis above suggests that the force dependency on humidity is strongly affected by the way the adsorbate layer thickness $h$ (on which both $\gamma_L$ and $D$ directly depend) varies for increasing $P/P_0$ values (see Fig. 4.15).

In order to frame our theoretical prediction in an experimental context, we have measured the interparticle forces within FSP-deposited TiO$_2$ films of nanoparticles with an average radius of 12 nm using our previously developed AFM force-spectroscopy technique [2].

TiO$_2$ nanoparticle aggregates are synthesized by Flame Spray Pyrolysis (FSP) and in-situ deposited on mica sheets (Science Service) as highly porous films based on our developed standard protocol [2]. The precursors are mixed with a molarity of 0.5 M. The precursor feed rate and the gas flow rates are adjusted to 5 ml/min and 5 l/min, respectively. Force measurements are performed on the nanoparticle films with an atomic force microscope (Nanowizard 3 from JPK Instruments) with Si$_3$N$_4$ cantilevers (DNP-S from Bruker Nano GmbH) using a force mapping over 10x10 $\mu$m$^2$ with 8x8 force measurements. The force mapping is performed using a fixed setpoint load of 2.5 nN and a retraction speed of 2 $\mu$m/s. The spring constant of each single cantilever (nominal stiffness 0.12 nN/nm) is determined using the thermal noise method [203]. The measurements are performed in an environmental cell (JPX) at specified humidities. The humidity in the
The influence of hydrophilicity on the inter-particle forces

The analysis above suggests that different trends should be observed for materials presenting different water affinities, depending on the way the adsorbate layer thickness (and thus $D$) varies for increasing $P/P_0$ values. To investigate this issue we have modified the parameters of our force field by downscaling the partial charges of the crystal atoms (Fig. 4.21) leading to a reduced hydrophilicity of the TiO$_2$ particles, and thus to an increased macroscopic water/TiO$_2$ contact angle, which we measure by using the method suggested by Werder et al. [204][206].
CHAPTER 4. ADHESION FORCES

Figure 4.20: Contact forces between FSP-produced TiO$_2$ nanoparticles measured by AFM force spectroscopy at different relative humidities (box plot showing median, quartiles, extremes and outliers of the force distributions) [3].

Methods: To calculate the contact angle between TIP3P water and our TiO$_2$ model, different amounts of water molecules are placed in a rectangular volume above our slab model and an NVT run at 300 K of 2 ns for the hydrophobic and 4.5 ns for the original hydrophilic model is performed to allow the water to spread over the slab (Fig. 4.22). After discarding the first 0.5 ns for the hydrophobic and 3 ns for the hydrophilic model for equilibration, the water density of the droplet is calculated in circular bins with a width of $\Delta r = 0.1$ nm and a height of $\Delta z = 0.1$ nm around the center of mass of the drop.

If the water density in the vapour-phase is assumed to be 0, the water density profile across the liquid/vapour-interface can be approx-
4.5. THE INFLUENCE OF HYDROPHILICITY

Figure 4.22: Formation of a water drop exhibiting a specific microscopic contact angle on the initial hydrophilic model (left) and on the model with reduced hydrophilicity (right). Top: Initial configuration. Bottom: Final configuration after 4.5 ns (left) and 2 ns (right) of an NVT simulation with the respective circular fit to the averaged liquid-vapour dividing surface.

Imitated by [200]:

\[
\rho(r) = \rho_l \left( 1 - \tanh \left( \frac{2(r-r_e)}{H} \right) \right). \tag{4.7}
\]

In this equation \(\rho_l\) stands for the water density in the bulk liquid-phase, \(r_e\) denotes the position of the equimolar dividing surface at \(\rho(r)/\rho_l = 0.5\) and \(H\) denotes the thickness of the liquid/air-interface. Fitting of equation 4.7 in radial direction to the averaged density values of the drop with \(r_e\) as a free parameter, thus provides \(z/r_e\)-values of the equimolar dividing surface of the drop. The microscopic contact angle for the specific drop size \(R_{\text{drop}}\) can then be evaluated by a circular fit to this dividing surface (see Fig. 4.22) and the macroscopic contact angle for an infinite drop size \(R_{\text{drop}} \rightarrow \infty\) can finally be derived from extrapolating the microscopic contact angles of multiple dropsizes.

The extrapolation to a macroscopic contact angle in Fig. 4.23 yields a macroscopic contact angle of \(\Theta_{\text{macr}} = 18.7^\circ\) for the original hydrophilic model. However, by looking at the drop formation in the hydrophilic case (Fig. 4.22 left), it becomes clear that complete wetting of the slab occurs and that the fitting of the contact angle is somewhat inappropriate. In fact, the contact angle of the hydrophilic model has to be approximated to lie rather between 0 and 10°. By downscaling the crystal charges, the macroscopic contact angle of the model increases to \(\Theta_{\text{macr}} = 43.4^\circ\), which is closer to the contact angle of water on TiO\(_2\) as measured in most experiments [207, 209].

For the case of the less hydrophilic model the interparticle forces are...
similarly dominated by a structural (solvation) contribution (Fig. 4.24 top right) and a capillary contribution (Fig. 4.24 bottom right), which we can quantify as performed above (See underlying force curves in the Appendix section A.6). In doing so, we find that in contrast to the macroscopic contact angle, the microscopic contact angle between the capillary meniscus and the adsorbed water layer that is used for the calculation of the capillary forces still remains at $\Theta = 0^\circ$. The reduced hydrophilicity leads to a considerable reduction of the oscillation amplitudes in the solvation forces [71] (Fig. 4.24 top left), and to a nearly constant adsorbed water coverage over a wide range of $P/P_0$ values (Fig. 4.24 bottom left). This results in negligible variations of $D$ with $P/P_0$ between 0 and 100% humidity and, indirectly, to maximum attractive forces that change only very sightly with humidity (Fig. 4.25), and only at humidity values that are hardly accessible by experiments (very close and above the condensation threshold) This would be consistent both with our experimental observation (Fig. 4.20) and certain literature results [96, 98, 101]. However, the theoretical force values calculated by our modified capillary theory deviate from the force values resulting from the atomistic simulations. This shows that our calculation modifications are not fully applicable to less hydrophilic surfaces, as the water does not build a uniform adsorption layer on the particle surfaces but rather adsorption islands. The non-uniform distribution of the adsorbed water in turn hampers the correct determination of the particle radius and thus also of the particle distance $D$ for the capillary calculations and results in an overestimation of the particle overlap. Beside this, we suggest that the disappearance of the humidity

Figure 4.23: Calculation of the macroscopic contact angle of TIP3P-water on the hydrophilic (red circles) and on the hydrophobic (blue squares) rutile model used in this work by the methods described in [206,210].
4.5. THE INFLUENCE OF HYDROPHILICITY

Figure 4.24: Capillary and solvation forces between hydrophobic particles: Top left: Water structuring as in Fig. 4.6 at the hydrophobic solid-liquid interface. Top right: Solvation forces between two hydrophobic 4 nm particles in bulk water ($A = \pi (0.25)^2 \text{ nm}^2$) compared to the forces calculated explicitly along several mutual orientations (black symbols, shifted on the x-axis as for hydrophilic particles) as in Fig. 4.10. Bottom left: Comparison between the water adsorption isotherms as in Fig. 4.14 on a hydrophilic (red squares) and a hydrophobic (blue circles) 4 nm particle surface. Bottom right: Comparison between the F-D curves computed explicitly in MD simulations of various orientations of two hydrophobic 4 nm particles at a coverage of 7.2 water molecules per surface nm$^2$ (black crosses, shifted on the x-axis as for hydrophilic particles) and the theoretically predicted capillary and solvation force contributions as in Fig. 4.11.

dependence of the forces results from the altered adsorption isotherm of the particles.

To account for the influence of hydrophilicity, we therefore measure experimentally the contact forces in a nanoparticle film with decreased contact angle due to UV-light irradiation [1].

Methods: The TiO$_2$ films are exposed to UV-light LEDs ($\lambda = 375$ nm; relative humidity $\sim 90\%$) for 2 h prior to the force measurements in order to increase the hydrophilicity of the surface by changing the contact angle of the TiO$_2$ from around 70$^\circ$ to around 10$^\circ$ according to Wang et al. [207]. The AFM measurements at different humidities
Performing the same experiments as above using the nanoparticle films exposed to UV light results in a clear and reversible increase of the interparticle adhesion forces from about 3 to about 4.5 nN after irradiation (Fig. 4.26 left). This finding is in very good agreement to the increase of the maximum values of the adhesion forces in the simulations for 4 nm particles at 80% humidity from about 1.6 nN (weakly hydrophilic) to about 2.4 nN (strongly hydrophilic), considering the deepest minima in the F-D curves at $\delta = 0.23$ nm and $\delta = 0.37$ nm in the two respective cases. Unexpectedly, however, the contact forces in the experiments do still not vary with humidity even after UV irradiation (Fig. 4.26 right), which is contrary to the predictions from our simulations. Furthermore, we note that only small differences in the water coverage are measured by the thermogravimetric analysis before and after irradiation [1] and that the adsorption isotherm of the less hydrophilic simulation model deviates largely from the experimental findings. This suggests that the experimentally obtained increase of the contact forces may be rather related to the change of the water structuring on the particle surfaces than to the altered water affinity.

From these insights we infer that apart from the differences of the contact angle, our original hydrophilic atomistic model represents the real be-
4.6. THE INFLUENCE OF ROUGHNESS

Figure 4.26: Contact forces between FSP-produced TiO$_2$ nanoparticles measured by AFM force spectroscopy after UV-irradiation (box plot showing median, quartiles, extremes and outliers of the force distributions). Left: Variation of the forces with different relative humidities. Right: Variation of the forces before and after UV-irradiation.

haviour of the TiO$_2$ particles as found in experiments. The reduction of the hydrophilicity via decrease of the charge values leads to an artificial material, which is not comparable to reality. The deviation between the atomistic and the experimental contact angle is generally known from former investigations [23, 206] and is not definitively related to differences of the material properties, but could also be due to environmental effects like surface contamination [211, 212].

4.6 The influence of roughness on the interparticle forces

Having shown in the last section that the discrepancy between the force trends with humidity is probably not due to a differing hydrophilicity, it has to be noted that the shape of commonly produced nanoparticles deviates from ideal spheres. In this case, the onset of steric repulsion and thus the separation distance at maximum contact force are dominated by the local asperities [97, 117]. Therefore, if the adsorbate layer thickness is comparable to the surface roughness, even large changes of the humidity (and thus of the water coverage) have little influence on $D$. In fact, through explicit calculation of force-displacement curves between rough particle models exhibiting asperities with a height of 0.5 nm and a width of 0.5 to 1.7 nm radius depending on the particle size (Fig. 4.27), we obtain slightly positive and
roughly constant $D$ values (cf. (Fig. 4.28)). This increase of the interparticle distance $D$ by the incorporation of asperities leads to a significant reduction of the capillary forces and even to an almost elimination of the force oscillations \cite{127}. This effect is strongest for the 50 nm particles. Here, water menisci build nearly exclusively between the asperities (Fig. 4.27), whose size therefore dominates (i.e. limits) the adhesion force \cite{116,118}. Note, however, that even for the rough particles we can distinguish between the two contributions of capillary and solvation effects to the interparticle forces (Fig. 4.27 and Appendix section A.7 for further particle orientations, sizes and roughness values).

As a consequence of the modified $D$, we also compute maximum attractive forces which do not vary with humidity over the whole range of investigated water coverages (Fig. 4.29). These constant adhesion forces at varying humidities for rough particles now agree well with our experimental findings and show that the irregular particle shape is a key to rationalize the humidity-dependence of our FSP-produced TiO$_2$ nanoparticles.

### 4.7 The influence of particle size on the interparticle forces

As a direct outcome of our analysis, from Fig. 4.12 it is apparent that the F-D curves normalized by the particle diameter present nearly identical values for all particle sizes. This demonstrates that the capillary force contribution scales linearly with particle size also for diameters below 100 nm, extending the trend predicted by classical models valid for microscopic and macroscopic sizes \cite{50,110,123,125}. Furthermore, the point of meniscus breakdown, and thus the range of action of the capillary forces, is nearly invariant with particle size, as already anticipated in Fig. 2.5. These two statements also hold for mixed particle sizes (8 nm and 4 nm), where the capillary forces can be calculated using the Derjaguin approximation

$$R_{Cap} = 2R^* = 2 \frac{R_1 R_2}{R_1 + R_2}.$$  \hspace{1cm} (4.8)

In contrast, the amplitudes of the oscillatory solvation forces are less pronounced at larger particle sizes in relation to the capillary forces, or occur only for some particular orientations where specific crystal facets face each
4.7. THE INFLUENCE OF PARTICLE SIZE

Figure 4.27: Forces between rough particles. Top left: Scheme for the creation of asperities on the particle surfaces. Top right to bottom right: Representative force displacement curves between two 4 nm and two 8 nm particles and between two caps of 50 nm particles all decorated with asperities of 0.5 nm height and covered with 16.2 water molecules per nm$^2$. The insets display volumetric density isosurfaces of the crystal and water phase of the respective simulated particle models at a surface distance of approximately 1 nm and a cutout of the asperities in contact.

Figure 4.28: Analysis of the meniscus geometry between two rough 4 nm particles at a distance of $d - 2R = 1.6$ nm covered with 10.2 (left) and 25.2 (right) water molecules per surface nm$^2$. The respective upper part of the charts shows the iso-value lines of the radially-averaged water density around the two particles considering different mutual orientations, while in the lower part a geometrical fit of the meniscus geometry to the iso-density line at 0.5 g/cm$^3$ is displayed.
Figure 4.29: Variation of the capillary force contribution with humidity for rough 4 nm particle models [3]. The values predicted by our modified capillary model (blue symbols) are compared with explicitly calculated maximum attractive forces along different orientations after subtraction of the corresponding forces in bulk water (black crosses), and plotted over parametrized force-humidity curves at constant particle-particle separation \( D \) (grey lines). The humidity-values are adopted from the respective water coverages of the smooth particle models.

Other. This underlines a decreasing influence of the solvation forces with growing particle size.

Figure 4.30 shows the development of the interparticle forces with particle size, presented for the coverage of 16.2 water molecules per nm\(^2\) (corresponding to an air humidity of approximately 65-75%, Fig. 4.14). Reported are the absolute values of the forces in correspondence of the minimum of the F-D curves computed with MD, at separation distances \( \delta \) between 0.6 and 0.7 nm, which we define here as \( F_{\text{max}} \). The total adhesion forces from the MD simulations (black crosses in Fig. 4.30) are significantly higher than the capillary forces calculated from our modified capillary theory within the circular approximation (blue curve in Fig. 4.30) because of the additional contribution due to solvation. As explained above, this contribution diminishes for larger sizes and is also dependent on the specific orientation of the particles. However, at all sizes, including the largest ones (20 and 50 nm) the explicitly calculated forces are never lower than the analytical capillary force prediction calculated for negative values of the particle separation \( D \).

Conventional capillary theory with a typical \( D \) value of 0.0 nm [125, 139], on the other hand, is expected to be valid at large particle radii. We suggest that an intuitive way of reconciling the validity of the conventional theory in
4.7. THE INFLUENCE OF PARTICLE SIZE

Figure 4.30: Maximum interparticle forces against the particle size for smooth and rough particles which are decorated with asperities of 0.5 nm height [3]. In comparison the development of the capillary forces at the same particle distance is shown for the modified circular approximation (blue line) considering the surface adsorbed water layer and thus a negative particle distance \( D = -0.34 \) nm (cf. Fig. 4.15) and for the unmodified circular approximation (green line) assuming direct particle contact with \( D = 0.0 \) nm [125,139].

the microscopic size scale with our observed behaviour of the adhesion forces is to postulate that the surface roughness dictates the minimum separation distance between (wet) larger particles. For very small particles, negative \( D \) values can occur even in the presence of roughness, especially for particle orientations presenting a good degree of surface crystallinity, as a consequence of the interpenetration of the water adsorption layers. For larger particles, roughness asperities would prevent overlap of the water layers, so that \( D \) is pinned to zero or positive values. This seems to be confirmed by the results we have obtained for rough particle models (red crosses in Fig. 4.30). For smaller particles, the total forces are in the range predicted by capillary theory with \( D \) values between zero and -0.34 nm, plus a small additional effect of solvation (not as large as in the case of smooth particles). With our rough model of 50 nm particles we have computed a much smaller adhesion force, even smaller than the predicted capillary force with \( D \) equal to 0.0 nm. In fact, one needs to take into account that water menisci are formed almost exclusively between the asperities and not homogeneously distributed across the whole particle-particle cross-section [116][118].

Coming back to the interparticle contact model outlined in Fig. 1.3, we can now fill the non-contact term \( F_{nc} \) of the model using our quantitative
predictions of the capillary and solvation forces. The variation of these contributions with different conditions and properties can be respected precisely by using our generated knowledge of the influence of particle size, humidity and roughness on the interparticle forces.
Chapter 5

Parametrization of a discrete element method contact model

The detailed analysis of the adhesion forces between our TiO\textsubscript{2} nanoparticles and of the influence of different environmental conditions in the previous chapter now allows us to develop a comprehensive non-contact adhesion force model for the use in discrete element method simulations. This model should be capable to mimic the adhesion forces acting between particles in polydisperse assemblies and under varying environmental conditions with a high degree of precision and flexibility. However, to correctly reproduce the mechanical behaviour of nanoparticles, we still have to quantify the missing components illustrated in Fig. 1.3, namely the normal contact force, the tangential sliding force and the rolling torque. Due to the complex cross-linking inside nanoparticle films, we expect the correct incorporation of these types of forces to be equally important to the realistic representation of the mechanical film behaviour as the adhesion forces. Similar to the adhesion forces, it is not clear if the macroscopic equations developed for repulsion and frictional forces still hold at the nanoscale, which leads us to conducting again extensive all-atom MD simulations using our atomistic particle model and accounting for nano size effects. To respect the operation under ambient conditions, we cover the surfaces again by condensed water molecules, which we assume to crucially determine the nature of the forces as in the case of adhesion. Together with our findings concerning the non-contact forces, we
will then use the results from these simulations to parametrize a constitutive force model for the use in discrete element method simulations.

5.1 Sliding and rolling friction forces

To obtain a comprehensive understanding of the nature of the tangential forces we perform all-atom sliding and rolling simulations of differently oriented 4 and 8 nm particles at different tangential velocities and different normal loads $F_N$.

Methods: To analyse the friction forces acting between two particle surfaces during relative tangential displacement, single particles are placed and relaxed for 1 ns on our TiO$_2$ slab with a size of approximately 16x14 nm. After their relaxation, the particles are dragged in a steered all-atom molecular dynamic (MD) simulation with a timestep of 1 fs at a constant speed of 0.1-1 m/s and over a distance of 5 nm in parallel direction to the slab surface, while the atom positions of the slab are kept fixed. The dragging force acting on the particle center and resulting from a constantly displaced spring with a spring-stiffness of 160 N/m is recorded every $10^{-6}$ nm and averaged over 10,000 points to receive one force point per 0.01 nm of dragging distance. To force sliding of the particle against the slab surface, the angular momentum acting on the particle is zeroed out, while it stays unchanged to enable rolling of the particle.

Figure 5.1 shows the tangential force displacement curves resulting from the sliding (left) or rolling (right) of a 4 nm particle over the slab model at a pulling speed of 1 m/s. From these force curves it becomes obvious that, rather than finding a constant sliding force during the tangential displacement, the particle exhibits a stick-slip behaviour. This stick-slip depends on the atomistic roughness of the surfaces, which is typical for the friction of microscopic contacts as already shown both theoretically [89, 91, 151, 153, 155, 158, 165] and experimentally [148, 150, 153, 154, 156, 158, 160, 213]. Furthermore, we see that the force amplitude is significantly higher at the sliding displacement than at the rolling displacement and that we measure tangential forces even at negative normal loads which is due to the adhesion forces between the particle and the slab as found in the previous chapter.

To put these qualitative findings into more quantitative terms we search
5.1. SLIDING AND ROLLING FRICTION FORCES

Figure 5.1: Top: Schematic view of the forces and displacements acting on an atomistic 4 nm particle during a tangential sliding (left) or rolling (right) displacement on a slab. Bottom: Respective tangential force displacement curves at a pulling velocity of 1 m/s and different normal loads $F_N$ for sliding (left) and rolling (right) displacement. The force curves are shifted on the $y$-axis for clarity with the tangential force of 0 nN being marked by a dashed black line respectively. The black crosses denote the fitted local maxima of the force curves and the black continuous lines show the respective coarse grained force models.

for the local maxima of the tangential sliding force curves in accordance to other works \cite{158,160} by applying a low-pass smoothing function with a cut-off frequency of $f_{cut} = 2.8 \text{ nm}^{-1}$, which keeps only the largest oscillations of the force curves. In the resulting smoothed force curve we then locate the peaks and find the maximum values of the original force curve in the range between ± half the distance to the next minimum around the maximum peaks of the smoothed curve. Averaging the force values and the spacings between the found local force maxima of a single force curve then gives us the mean maximum tangential force $F_{t,max}$ and the mean wavelength $\omega_t$ of the respective curve. These are used to construct a coarse graining sawtooth curve as can be seen on the left in Fig. 5.1. Because the amplitudes of the tangential rolling forces are much smaller and approach towards the same order of magnitude as the thermal fluctuations (cf. Fig. 5.1 right), we take
the maximum values from the smoothed curve directly in this case instead of from the original curve and approximate the mean of the maximum forces $F_{r,\text{max}}$ by a constant value.

From the analysis of all force curves we find that the frequency of the force oscillations is independent of the applied normal load $F_N$ with a value of approximately 0.5 nm (See Appendix section A.8) related to the spacing of the surface adsorbed water molecules [148], while the amplitude depends strongly on the normal load (see Fig. 5.4). The simulation of different pulling speeds (See Appendix section A.8) shows that the influence of the velocity on both the magnitude and the shape of the tangential forces [155, 165, 167, 168, 214] is negligible compared to the much stronger influence of the normal force. This leads to the conclusion that we can use a tangential force model without the frequently applied damping term for the later use in our DEM simulations. Furthermore, we find that the torque arising from torsion between two particles is significantly lower than the rolling and sliding forces (See Appendix section A.8) and can therefore be also neglected.

5.2 Steric repulsion

Before analysing the tangential forces in more detail, now we first look again at the repulsive contact forces in normal direction between the two surfaces. Even though we have already fitted the repulsive part between two particles roughly by a Van der Waals term in the previous chapter, the integration of the tangential forces into the comprehensive particle model now demands for a more thorough analysis of this type of forces. To this aim we average the $z$-position of the particles over the whole length of the sliding and rolling simulations and plot the averaged $z$ values against the respective acting normal force as is shown in Fig. 5.2 for all orientations of a 4 nm particle in both sliding and rolling mode. In this plot the applied normal load $F_N$ is shifted by the non-contact adhesion force $F_{nc}$ at equilibrium between the sphere and the slab as determined in the previous chapter, to account for the overall acting normal force $F_n$.

It becomes clear that the true repulsive force between the surfaces follows as expected an atomistic repulsion with a ninth order dependence, due to the steric repulsion of single atoms in the contact-zone. However, as we will see below, we will need a dependence of the contact area on the nor-
5.2. STERIC REPULSION

Figure 5.2: Applied normal force vs. averaged z-height from different rolling and sliding simulations of a 4nm particle on a slab as shown in figure 5.1. The normal forces are shifted by $F_{nb} = 2.1 \text{nN}$ to account for the average adhesion forces from the non-contact term acting between the sphere and the slab, while the z-values are shifted individually to coincide at an externally applied load of $F_N = 0 \text{nN}$. The coloured lines show fits with different $z$-exponents, where the fits with the exponents 1 and $3/2$ are restricted to the values below $F_n = 5 \text{nN}$ to best represent the values around the equilibrium position without external load.

Figure 5.2: Applied normal force vs. averaged z-height from different rolling and sliding simulations of a 4nm particle on a slab as shown in figure 5.1. The normal forces are shifted by $F_{nb} = 2.1 \text{nN}$ to account for the average adhesion forces from the non-contact term acting between the sphere and the slab, while the z-values are shifted individually to coincide at an externally applied load of $F_N = 0 \text{nN}$. The coloured lines show fits with different $z$-exponents, where the fits with the exponents 1 and $3/2$ are restricted to the values below $F_n = 5 \text{nN}$ to best represent the values around the equilibrium position without external load.

Normal forces for the further fitting of the frictional forces and the ninth order term approaches to distances much larger than the geometric contact of the particles, which results in an overestimation of the theoretical contact areas at the force equilibrium. We therefore decide to proceed with a 1.5th order dependence between the normal forces $F_n$ and the particle overlap $\delta_n$ representing Hertzian stress [33] as defined in equation (2.5). This relationship describes the contact forces in the region around the equilibrium position with reasonable agreement.

The fitting of this Hertz contact law to the force-displacement values below $F_n = 5 \text{nN}$ yields a fitted contact stiffness of $k_n = 24.5 \text{nN/nm}^2$ and $k_n = 33.7 \text{nN/nm}^2$ for the 4 and the 8 nm particles against the slab respectively and a size independent equilibrium overlap of approximately $\delta_n(F_N = 0) = 0.15 \text{nm}$. The found elastic stiffness is much lower than the stiffness of rutile TiO$_2$ [215] but comparable to that of frozen water [216] due to the dominant influence of the surface adsorbed ice-like water shell.

In addition to the elastic stiffness we determine the damping in normal direction between two particles by monitoring the relaxation of two atomistic particles after initial displacement and comparing the decay of the oscillation
CHAPTER 5. PARAMETRIZATION OF A DEM MODEL

Figure 5.3: Distance $d$ between the particle centers against the relaxation time after the radial separation of two atomistic particles at different orientations (coloured continuous lines) and of two discrete element particles (black dashed line). In the discrete element simulations a relative damping coefficient of $\gamma^* = 5.0\times10^6$ Ns/m$^3$·$R^2$ is used to match the time dependent behaviour of different particle sizes as shown here for 4 nm (top) and 8 nm (bottom) particles.

of the particle distance to the relaxation of two particles in a discrete element simulation.

Methods: To analyse the damping behaviour in normal direction between the particles, two particles are placed at a certain distance larger than the equilibrium distance but where the capillary forces already act. The positions of the particles crystal atoms are then kept fixed in an MD simulation of 0.6 ns to allow the water molecules to form a stable meniscus between the particles. Finally one particle is left free to attach to the second one and the distance of the centers of mass is recorded over an MD simulation of 0.4 ns to monitor the damping of the relative particle displacement.

From this analysis we find that a relative damping coefficient of $\gamma_n = 5.0 \cdot 10^6$ Ns/m$^3$·$R^2$, which scales quadratically with the particle radius due to an increasing interfacial area, best represents the relaxation behaviour of all investigated atomistic particles, if we use the above developed contact models (See Fig. 5.3).

5.3 Contact area dependence of friction forces

As already mentioned in chapter 2, a deviation from the macroscopic Amonton’s law of friction for microscopic contacts due to the interaction between
single asperities is frequently reported in the literature \cite{85,157,158,158-165,217,218}. This deviation leads to the linear dependence of the friction forces on the contact area $A$

$$F_t = \tau A, \quad (5.1)$$

via the shear strength $\tau$. To test this hypothesis we calculate the contact area from the penetration depth $\delta_n$ in equation (2.5) with the specified contact stiffness $k_n$ and the non-contact forces $F_{nc}$ and insert the resulting equation into equation (5.1). If we fit this non-linear relationship between the tangential and the normal forces to the sliding friction peak forces between the particles and the slab, we find a much better agreement compared to a linear relationship as can be seen in the upper panel of Fig. 5.4. The fitted sliding shear strengths of $\tau_t = 0.76 \pm 0.11 \text{nN/nm}^2$ and $\tau_t = 0.57 \pm 0.2 \text{nN/nm}^2$ for the 4 and 8 nm particles respectively are in line with the reported range of shear strengths between 0.27 and 0.91 nN/nm$^2$ for atomistic friction \cite{159,160,162} and deviate only slightly from each other due to the measuring uncertainty of the simulations resulting from different particle shapes, individual simulation trajectories and varying adhesion forces. Applying the same equation to the rolling friction, we obtain a rolling shear strength of $\tau_r = 0.23 \pm 0.05 \text{nN/nm}^2$ and $\tau_r = 0.13 \pm 0.03 \text{nN/nm}^2$ for the 4 and the 8 nm particles respectively. Compared to the sliding shear strength, the rolling shear strength differs much more between the particle sizes in relation to its absolut value, which is due to the increasing sphericity of the atomistic model with rising particle size. To take this effect into account and to reflect the experimental conditions with slightly irregularly shaped particles as well as possible (cf. Fig. 4.1) we perform the same rolling simulations with a polygonal 8 nm particle exhibiting in total 32 edges (See inset of Fig. 5.4). These simulations result in a rolling shear strength of $\tau_r = 0.23 \pm 0.06 \text{nN/nm}^2$, which is in perfect agreement to the value of the less regular 4 nm particle.

5.4 Discrete element method contact model

Using our previous findings we can now build a comprehensive contact force model (Fig. 5.5) to describe the mechanical interactions between polydisperse nanoparticles taking into account molecular features which are characteristic for the nanoscopic contacts. In this model the non-contact normal
Figure 5.4: Average of the peak tangential forces from the sliding (top) and rolling (bottom) simulations as shown in figure 5.1 against the respective applied load for different particle sizes and orientations. The continuous lines represent fits to the forces by assuming a linear relationship between the tangential forces and the contact area using the Hertzian stress relation between the normal force $F_n$ and the normal overlap $\delta_n$ with a contact stiffness of $k_n = 24.5$ nN/nm$^2$ and $k_n = 33.7$ nN/nm$^2$ and an additional adhesion force from the non-contact term of $F_{nb} = 2.1$ nN and $F_{nb} = 4.0$ nN for the 4 and 8 nm particles respectively. The inset shows the atomistic model of the polygonal 8 nm particle used for the rolling simulations.
5.4. CONTACT MODEL

Figure 5.5: Applied contact force model as developed in the former chapters. The non-contact term $F_{nc}$ (light green) consists of the capillary and solvation forces and acts on the particle centers always when the particle separation is below a certain cutoff. The repulsive normal contact term $F_n$ (light blue) consists of a spring-dashpot model and acts only when the particles are in contact. The tangential sliding term $F_t$ (orange) consists of a spring-slider model and acts also only when the particles are in contact. The rolling friction torque $M_r$ (magenta) consists of a pure slider model and acts also only when the particles are in contact.

force $F_{nc}$ results from a capillary and a solvation force term as found in chapter 4. The capillary forces are calculated as already mentioned by

$$F_{cap} = \pi \gamma L^2 (R + h)^* \sin(\beta)$$

$$\left[2 \sin(\Theta + \beta) + 2 (R + h)^* \sin(\beta) \left(\frac{1}{r_m} - \frac{1}{l_m}\right)\right], \quad (5.2)$$

with the thickness of the surface-adsorbed water layer $h$ taken from the adsorption isotherm (Figs. 4.14 and 4.15), the surface tension of the water $\gamma_L$ depending on the humidity and particle size (Fig. 4.17), the contact angle $\Theta = 0^\circ$ and the star denoting the Derjaguin approximation. The curvature of the meniscus is calculated from the circular approximation by

$$r_m = \frac{4 (R + h)^* (1 - \cos(\beta)) + D}{2 \cos(\Theta + \beta)}, \quad (5.3)$$

$$l_m = 2 (R + h)^* \sin(\beta) - r_m [1 - \sin(\Theta + \beta)] \quad (5.4)$$

and the Kelvin equation (4.4) with the interparticle distance $D$ depending on the combination of the two single particle sizes including the adsorbed
As we have seen in chapter 4, the solvation forces depend strongly on the local surface structure and deviate largely between different particle orientations. Furthermore, the determination of the correct shape of the solvation forces is complex and very sensitive to small changes of the material, surface or solvent, which leads us to take a step back and facilitate the calculation of the solvation forces by a semiempirical decaying cosine function related to equation (2.20):

$$F_{\text{solv}} = F_{\text{solv,0}} \cos \left( \frac{2\pi(d - 2R)}{\sigma_{\text{solv}}} \right) e^{-\frac{(d - 2R)}{\sigma_{\text{solv}}}}.$$ (5.5)

In this equation, the wavelength is $\sigma_{\text{solv}} = 0.21$ nm due to the water spacing inside the water shell and the force amplitude $F_{\text{solv,0}}$ is dependent on the particle size. This force amplitude cannot be directly compared to the corresponding term in equation (2.20), as this equation was found for surfaces which do not interact with the solvent molecules. Our particle surfaces, on the contrary, do interact with the solvent molecules and the solvation force contribution is thus significantly larger than the pure influence of the bulk solvent pressure. The direct adjustment of $F_{\text{solv,0}}$ to the respective average of the actual force amplitudes arising from our atomistic simulations therefore yields a reasonable way to describe the solvation force contribution for all occurring particle sizes in a simple and robust framework.

The normal contact force $F_n$ can be matched best by a spring-dashpot model as applied in the Hertz-Mindlin theory [84] as found in section 5.2:

$$F_n = F_{n}^k + F_{n}^d = k_n \sqrt{(R + \Delta R_{\text{rep}})^* \delta_n \delta_{ij} n_{ij} - \gamma_n v_n}.$$ (5.6)

In this model the original particle radius $R$ is increased by the constant value $\Delta R_{\text{rep}}$ to account for the repulsion inside the surface-adsorbed water shell. Furthermore, an equilibrium distance $d - 2R = 2\Delta R_{\text{equi}} = 2 \cdot 0.285$ nm, where the sum of all normal forces acting between the particles is zero, is defined from the equilibrium positions in the atomistic force-distance curves between single particles (Fig. 4.12). The stiffness of the elastic spring $k_n$ between the particles can then be calculated individually for every particle size combination, to match the equilibrium position of the particles at an
5.4. CONTACT MODEL

overlap \( \delta_n = 2(\Delta R_{rep} - \Delta R_{equi}) \):

\[
k_n = \frac{F_{nc,\text{equi}}}{\sqrt{(R + \Delta R_{rep})^2 2(\Delta R_{rep} - \Delta R_{equi}) 2(\Delta R_{rep} - \Delta R_{equi})} ,
\]

(5.7)

with the non-contact force at the equilibrium distance \( F_{nc,\text{equi}} \). For \( 2(\Delta R_{rep} - \Delta R_{equi}) = 0.15 \) nm (see section 5.2) this results in a spring stiffness between 20 to 45 nN/nm\(^2\) depending on the particle size. The absolute normal damping coefficient \( \gamma_n \) is calculated from the squared effective particle radius by

\[
\gamma_n = \gamma^* \gamma_n (R + \Delta R_{rep})^2 ,
\]

(5.8)

with the relative damping constant \( \gamma^* \gamma_n \) found to be approximately \( 2 \cdot 10^6 \) Ns/m\(^3\).

Furthermore, we have found the tangential friction force \( F_t \) to be best fit by a modified spring-slider model derived from the tangential model developed by Mindlin and Deresiewicz \[84\]

\[
F_t = F^k_t = k_t \delta_t \mathbf{t}_{ij} ,
\]

(5.9)

with

\[
F^k_{t,\text{max}} = \tau_t A ,
\]

(5.10)

\[
k_t = \frac{F^k_{t,\text{max}}}{\omega_t}
\]

(5.11)

and

\[
\delta_t \rightarrow 0 \text{ if } F_t > F^k_{t,\text{max}} ,
\]

(5.12)

with the relative tangential displacement vector \( \mathbf{t}_{ij} \). This model results in a sawtooth curve with a wavelength \( \omega_t \), which we have determined in section 5.1 to be approximately 0.5 nm, and in a maximum tangential force \( F^k_{t,\text{max}} \) depending linearly on the contact area \( A \) by the sliding shear strength \( \tau_t \), that we have found in section 5.3 to be 0.65 nN/nm\(^2\). The contact area, in turn, can be determined from the particle overlap \( \delta \) and the particle size.

The rolling resistance torque \( M_r \) is described by a simple slider model \[87,172\]

\[
M_r = (R + \Delta R_{rep})^* \tau_r A ,
\]

(5.13)

which represents the less pronounced oscillations during rolling with reason-
Table 5.1: Parameters used in this work for the discrete element method simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvation force wavelength: ( \sigma_{\text{solv}} )</td>
<td>0.21 nm</td>
</tr>
<tr>
<td>Solvation force amplitude: ( F_{\text{solv},0} )</td>
<td>-11 nN - 2.4 nN/nm ( \cdot R^* )</td>
</tr>
<tr>
<td>Onset of water repulsion: ( \Delta R_{\text{rep}} )</td>
<td>0.36 nm</td>
</tr>
<tr>
<td>Force equilibrium distance: ( \Delta R_{\text{equi}} )</td>
<td>0.285 nm</td>
</tr>
<tr>
<td>Normal contact stiffness: ( k_n )</td>
<td>Equation (5.7)</td>
</tr>
<tr>
<td>Normal relative damping constant: ( \gamma_n^* )</td>
<td>2 ( \cdot ) 10^6 Ns/m^3</td>
</tr>
<tr>
<td>Sliding shear stiffness: ( \tau_l )</td>
<td>0.65 nN/nm^2</td>
</tr>
<tr>
<td>Sliding sawtooth wavelength: ( \omega_l )</td>
<td>0.5 nm</td>
</tr>
<tr>
<td>Sliding contact stiffness: ( k_l )</td>
<td>Equation (5.11)</td>
</tr>
<tr>
<td>Rolling shear stiffness: ( \tau_r )</td>
<td>0.25 nN/nm^2</td>
</tr>
<tr>
<td>Simulation timestep: ( \Delta t )</td>
<td>5 ( \cdot ) 10^{-13} s</td>
</tr>
</tbody>
</table>

able agreement (Fig. 5.1), and does not compromise the simulation stability. Equivalently to the case of sliding friction, also the rolling friction forces depend linearly on the contact area \( A \) via the rolling shear strength \( \tau_r \), which we have found to be approximately 0.25nN/nm^2.

From the calculation of the Rayleigh time [219], using the smallest occurring particle mass and the respective contact stiffness at the equilibrium distance, we estimate the critical timestep of the simulations to be approximately \( \Delta t_{\text{crit}} = 10^{-12} \) s. This allows us to use a timestep of \( \Delta t = 5 \cdot 10^{-13} \) s keeping the simulations stable over the entire simulation time.

The values of all parameters used in our coarse grained DEM contact model as described above and applied in the following chapter are summarised in Table 5.1. These contact models and parameters result in typical normal and tangential force displacement curves in the DEM simulations as shown in Figure 5.6.
Figure 5.6: Force-displacement curves in the discrete element method simulations for relative normal (top), tangential sliding (middle) and tangential rolling (bottom) displacement resulting from the developed contact model at 70% humidity.
Chapter 6

Validation and application

To make our atomistic findings concerning the forces acting between nanoparticles accessible for other scientific disciplines, we concentrate in this chapter on the validation and application of our contact model. To this aim, we first simulate the stretching of a loosely connected nanoparticle agglomerate and compare the resulting force-displacement curve and the particle trajectory between an all-atom and a DEM simulation. This approach is intended to verify that the choice of parameters from the atomistic simulations of single particle contacts reproduces the correct particle behaviour also in a system consisting of several particles with different sizes. In a second step we simulate an entire atomic force microscopy experiment, by using our contact model in the discrete element method and compare the occurring forces and trajectories to the results of AFM force spectroscopy and combined AFM/TEM experiments. This approach is intended to verify the correct choice of the simulation system and of the boundary conditions and yields a detailed view into the particle dynamics during the AFM experiments providing a further understanding of the mechanical mechanisms occurring inside the nanoparticle films.

For the first step we assemble an all-atom nanoparticle agglomerate consisting of 14 particles with particle sizes between 4 and 10 nm using a TEM image of an FSP-produced TiO$_2$ nanoparticle agglomerate as a guideline. We then stretch the agglomerate by pulling the outer particles apart.

Methods: A nanoparticle agglomerate is generated with the example of a TEM-Image by placing 14 particles of different sizes into contact and relaxing the positions of the particles in an MD simulation of 2 ns with
the atom positions of the four outer particles kept fixed. To investigate
the detachment behaviour of the agglomerate, the two particles on one
side of the agglomerate are moved at a constant speed of 5 m/s away
from the two particles on the other side which are still kept fixed,
while the rest of the particles is left free to move. The forces acting
on the constrained particles are recorded in every simulation step and
averaged over 10,000 steps. To lower the effect of the moment of
inertia due to the high detachment speed, hollow particles with a shell
thickness of 1 nm are used for the creation of the agglomerate, which
does not affect the interparticle forces at the surface.

We then use the particle positions before the stretching to construct the
same agglomerate out of discrete element spheres, which we subsequently
stretch in a DEM simulation according to the same conditions as in the
all-atom simulations.

The results of these two completely independent simulations show a re-
markably high degree of agreement considering both the particle trajectory
and the force displacement curve (Fig. 6.1), which supports our choice of
models and parameters. A major difference between the two simulations is
the earlier breakage of the DEM agglomerate. This can be explained by the
metastable existence of the water meniscus at large particle distances in the
all-atom simulations (Figs. 4.11 and 4.12), which additionally depends on the
detachment velocity. Furthermore, the physisorbed water available on the
surfaces of the unstressed particles can move into the stressed contact region,
which therefore increases the local humidity and represents a multibody-
effect that is not considered by the two-particle simulations above. The
second difference is the higher flexibility of the DEM-agglomerate after the
detachment, which becomes obvious from the bending of the agglomerate in
Fig. 6.1(4) and could be due to a slight underestimation of the rolling shear
strength.

For the second step we perform AFM force spectroscopy measurements
on a particle film as already described in section 4.4 and simulate AFM
force measurements in an equivalent setup to compare the forces exerted
by the particle film on the AFM tip. To simulate the AFM measurement,
we first construct a nanoparticle film containing 200,000 primary particles
in a simulation box with the side length of 140 \( a \), with \( a \) being the sauter
diameter \( a = 6V/A \) of the primary particle size distribution (\( V \) is the total
Figure 6.1: Comparison of the particle trajectory (top) and of the pulling forces (bottom) in a steered agglomerate stretching simulation using the all-atom (upper agglomerate) and the discrete element (lower agglomerate) method both at a humidity of approximately 70%. The positions of the trajectory snapshots are marked by the respective numbers in the force-displacement curve of the pulled particles. A video showing the entire particle trajectory can be found in the Appendix section A.9.
particle volume and $A$ the total surface area).

**Methods:** Rigid nanoparticle aggregates are generated using a Sequential Algorithm (SA) combined with a Cluster-Cluster Aggregation (CCA) as presented in [220]. A primary particle size distribution as taken from TEM image analysis [221] is used as a discretized log-normal distribution. The primary particle diameter ranges from 3–23 nm with a stepsize of 1 nm (median 4.9 nm, $\sigma_G = 1.45$). The aggregate size distribution is calculated out of the mobility diameter from Disc Centrifuge experiments [221] using the mass mobility exponent for FSP synthesized particles [222]. The distribution ranges from 1–128 primary particles with a median of 36 particles and an arithmetic standard deviation $\sigma_s$ of 0.5.

Clusters of a defined amount of primary particles are assembled using the SA and subsequently combined to aggregates of the desired size with a fractal dimension of 1.8. These aggregates are deposited individually in a simulation box according to diffusion and a thermophoretic velocity as described elsewhere [223]. The coefficient of diffusion for polydispersed nanoparticle aggregates is calculated according to Zhang et al. [224]. The program *zeno* is used to determine the hydrodynamic radius [225] and 56 angles are used to calculate the mean projected area.

The application of a thermophoretic velocity of 0.1 m/s [226] results in a film with a porosity of 98% in good agreement to the experimental film porosity of also 98%. We then conduct the approach and retraction of an AFM-tip into this film in a DEM simulation (Fig. 6.2 (top)) using our developed contact model as described in the previous section.

**Methods:** DEM simulations of an AFM force measurement are performed by first relaxing the particle film using our developed contact model in combination with a viscosity term acting on all particles. To mimic the penetration of an AFM-tip, a three-sided pyramid with a side length of 0.8 µm, built out of particles with a diameter of 20 nm is then placed over the nanoparticle film, which does not reproduce the precise geometry of the experimental tips but is a good estimate for our purposes. The pyramid is approached towards the film with a speed of -0.5 m/s until the repulsive force acting on the tip reaches a value of approximately 2 nN, which is comparable to the setpoint in the exper-
imental measurements. After reaching this setpoint value, the velocity of the tip is slowly shifted down and reversed within a time of 0.2 µs to minimize the effect of inertia of the particles and then the tip is retracted at a velocity of 0.5 m/s until the rupture of the film. The simulations are performed using the LIGGGHTS package [227] under periodic boundary conditions, with a frozen bottom layer of aggregates to mimic the underlying sample holder and with the primary particles which belong to the same aggregates kept rigid to account for the stronger binding strength within the aggregates [221,222,228–230].

The different force displacement curves measured at the tip in several individual simulations using different particle films exhibit a good agreement between experiments and simulations regarding the sawtooth shape of the force curve, the distance spanned by the force curve and the height of the final detachment peak (Fig. 6.2 (bottom)). Furthermore, we compare the particle trajectory of the breaking of single particle chains during the tip retraction in Fig. 6.3 to the trajectories from combined AFM/TEM-experiments in Fig. 6.4.

Methods: Dynamic agglomerate behaviour under strain is imaged using a combined AFM / TEM set-up with an Si₃N₄ cantilever (k = 5.3 N/m). These in-situ investigations are performed inside a Phillips CM 200 FG transmission electron microscope equipped with an AFM / TEM holder (Nanofactory Instruments AB) and with a column vacuum of approximately 10⁻⁶ mbar [2].

Although the AFM-TEM experiments are performed in vacuum, while the simulations are performed at 50% humidity, we can see also in this case a very good agreement between simulations and experiments exhibiting the characteristic chain rearrangements of particle rolling and sliding before the final breakage of a primary particle contact. We note, however that the direct comparison of the single particle trajectories is difficult, as the variation between the single experimental observations is very high and a quantitative statement about the rearrangement events is not possible due to the only two dimensional image data in the experimental case. Therefore, only a qualitative comparison of the results is meaningful.

Nevertheless, we also find some discrepancies between the measured and calculated force curves, namely the lack of elasticity in the repulsive part, the weaker pronunciation of the local peaks and an overall U-shape of the
Figure 6.2: Comparison of several representative force displacement curves from AFM force spectroscopy experiments (bottom right) to force displacement curves from DEM simulations at a humidity of approximately 50% (bottom left) with the blue lines representing the approaching forces and the red lines representing the retraction forces. The curves are shifted along the x-axis to meet approximately at the setpoint and along the y-axis with respect to their respective zero-force lines (dashed) for clarity. The positions of the representative particle trajectory snapshots from a single simulation (top) are assigned by numbers in the corresponding topmost simulation force curve. The black dashed square highlights the enlarged volume shown in figure 6.3. Differently coloured particles represent different particle sizes. A video of the entire representative particle trajectory can be found in the Appendix section A.9.
Figure 6.3: Enlargement of the marked volume in figure 6.2 focussing on some rearrangement and detachment events during the simulated retraction of the AFM-tip. Arrows with a "D" denote the detachment of a primary particle contact, while arrows with an "S" denote the sliding and arrows with an "R" denote the rolling of two particles. The positions of the trajectory snapshots are marked by the respective numbers in the detail of the force displacement curve (lower right). Differently coloured particles represent different particle sizes. A video of the entire particle trajectory can be found in the Appendix section A.9.
majority of the force curves in the simulations. For the particle trajectories, in some AFM/TEM experiments the particle chains are slightly more flexible, presenting a higher amount of rearrangements inside single particle chains than in the simulations (See also Appendix section A.10).

We explain these features by a number of different limitations of the simulations compared to the experiments. First of all, with a thickness of approximately 3 µm and a width of approximately half of this value the simulated system is much smaller than the measured films, which reach a thickness of approximately 20 µm. This disparity results in a far smaller penetration depth of the tip during the simulations compared to the experiments, as can be seen for example from the aggregate coverage of the experimental AFM-tip after a single measurement [2]. There is also an influence of the periodic boundaries on the film compaction, as can be seen in Fig. 6.2 (top), where the upper particles are pushed down and dragged up also at the edges of the simulation box and therefore experience the interaction with the AFM-tip of the next periodic image. Another issue is the
much higher tip velocity of 0.5 m/s in the simulations compared to 5 µm/s in the experiments, which results in a much higher influence of the particle inertia during the reversing of the tip movement, and therefore further decreases the elastic energy stored in the film. A quasi-static integration approach or a further coarse graining of the model could address this issue, but are beyond the scope of this work. Finally, the bonding inside the aggregates is physically not clear at the current state. We know that the binding inside the aggregates is much stronger than between the aggregates \[221, 222, 228, 230\]. Nevertheless, completely rigid bonds in the simulations could overestimate the strength of the real bonds, while completely free primary particles severely underestimate the aggregate bonds. The overestimation of the binding strength leads to a prevention of rearrangements inside the aggregates and with this also to less pronounced local peaks in the force displacement curves. A solution to this would be the definition of a new type of aggregate bonds with a certain stiffness and breaking probability based on the physical properties of the real bonds. This topic should be the issue of extensive further theoretical and experimental investigations.

Coming back to the question of the humidity dependence of the contact forces in section \[4.4\] we perform the same simulations as above using the contact model with different humidities. From Fig. 6.5 it becomes clear that the length of the force curves until the final breakage of the particle chain increases largely at lower humidities. This is accompanied by a much deeper penetration during the tip-approach, which can be explained by the smaller range of the capillary forces at lower humidities, resulting in a smaller mechanical resistance of the film. During the penetration, the connectivity inside the film is strongly increased, which then leads to longer particle chains during the detachment.

Furthermore, we analyse the development of the final detachment forces with humidity and surprisingly we find no humidity dependence or even a small increase of the forces with increasing humidity (Fig. 6.5 right). This is in contrast to the maximum adhesion forces produced by the contact model, which show a maximum at low to intermediate humidities for all particle sizes due to the assumption of smooth hydrophilic particles (Fig. 6.5 left). Although the statistics are poor and the analysis of a larger amount of simulation force curves could alter this trend, we conclude from this finding that the development of the final detachment forces is determined by the
Figure 6.5: Force displacement curves from AFM simulations at different humidities starting from the same initial configuration. The curves are shifted along the y-axis with respect to their respective zero-force lines (dashed).

Figure 6.6: F vs. humidity in AFM simulations: Left: Development of the maximum adhesion forces from the DEM contact model with humidity for different particle sizes. Right: Development of the last peak forces in the AFM simulations, where the individual detachment forces are marked by black crosses and the average at constant humidity is marked by the red line.
connectivity and percolation inside the film to a much higher extent than by the specific height of the single contact forces. This finding yields another explanation for the deviations of the experimental and the all-atom results in section 4.4.
Chapter 7

Conclusion and outlook

In this work we have learned that the classical continuum theories, which are frequently applied in the field of colloidal materials, can still be used to predict the mechanical interactions between nanoparticles and their dependence on the surrounding environment, which was not at all expected before. However, to precisely reproduce the correct force strength and the features of the interaction curves, a few peculiarities of the nanoscale have to be respected. This results in the fact that e.g. the adhesion forces between two particles can be rationalized in terms of dispersion, solvation and capillary contributions only if the crucial effects of adsorbate layer formation, structuring and nanoscopic surface roughness are correctly taken into account. An unbiased, quantitative prediction of these contributions relies on the knowledge of four fundamental properties, namely (i) the radial distribution function of the adsorbate molecules around a single particle; (ii) the isotherm of adsorption of the adsorbates linking their vapour pressure to the condensation layer thickness; (iii) the variation of the surface tension of thin liquid films with their thickness and curvature; and (iv) the extent of the surface roughness of the particles under investigation. With the exception of the surface roughness, these properties can be all obtained from accurate atomistic simulations \[192\,196\,197\] (as performed in this work), and at least the first two from experimental measurements that are directly accessible for nanoparticulate materials \[65\,135\,136\]. The determination of the surface roughness is slightly more delicate for the case of non-ideally spherical particles, where the average height of the roughness must be approximated by e.g. the root mean square deviation from the ideal surface. Knowledge
of other, less accessible properties such as the solvent/solid contact angle are neither required, nor play an important role for particles about 10 to 100 times larger than the adsorbate layer thickness. Comparing our results to the adhesion forces between silica nanoparticles as investigated atomistically by Leroch et al. [94], we find an only slightly different trend of the capillary forces with humidity and less pronounced force oscillations at close particle contact. These variations are due to a differently shaped adsorption isotherm and a weaker structuring of water molecules at the SiO$_2$ surface and strongly support our proposed adhesion model.

The independence from macroscopic quantities can be found similarly for the case of tangential friction between the particles, where the forces depend on the contact area via the contact stiffness rather than on the normal load via the coefficient of friction [85,157,165]. In contrast to the empirical coefficient of friction, which varies largely between different systems even if they contain the same material combinations, the contact stiffness depends explicitly on the atomistic interactions inside the sliding zone, namely the interactions in the adsorbate layer. This makes the mechanism highly transferable to other systems where the same adsorbate layer is involved, independently of the underlying material, which means that other hydrophilic particles should behave generally like our system in terms of friction. As a consequence of this contact area dependence, the tangential forces at the equilibrium distance of the particles are significantly higher than predicted from the Coulomb’s law of friction and result in much stiffer particle contacts. Furthermore, the microscopic contact between the particles leads to a pronounced stick-slip behaviour during tangential friction of the particles, due to the atomic roughness of the particle surfaces and the water structuring between the surfaces [150,156,158,160]. This stick-slip implicates highly non-linear tangential forces during sliding of the particles, which can be approximated best by a sawtooth curve rather than by a constant value.

In the case of capillary theory, the incorporation of the adsorbate layer [96,99,137,138,140] leads to negative values of the effective particle-particle separation distance $D$. We have revealed this negative separation to play the governing role on the humidity dependence of the interparticle forces, which can be sensitively tuned by the incorporation of a slight roughness of the surface [97,99,101,101,105,107,116,120,141] or by changing the surface hydrophilicity [24,98,99,101,105,114,115]. It is worth to note that we have
shown that the circular approximation can be safely used to predict the capillary force contributions at the point of maximum adhesion force, because at small particle distances the errors of its geometrical assumptions are negligible. However, due to the increase of these errors at larger particle distances \[24, 141\], the circular approximation underestimates rather severely the actual range of action of capillary forces, as set by the point of meniscus breakdown in the F-D curves. A transition to conventional capillary theory valid at microscopic size scales \[60, 115, 124, 125, 139\] can be only rationalized if the presence of roughness asperities on the surface of the large particles is explicitly taken into account. As the surface roughness on particles in technical applications has a fractal character \[117, 231, 232\], the influence of roughness on the interparticle forces will grow with increasing particle size and must be determined in depth to correctly predict the interparticle adhesion forces \[97, 116, 117, 125, 139, 233, 235\].

Furthermore, we have demonstrated that the linear scaling of interparticle forces with their diameter, which is well established for particle sizes above 100 nm \[50, 110, 123, 125\], extends to the size range down to 4 nm and probably even less. In this range, however, the structuring of the water layers between the particles (i.e. solvation) and the increase of the surface tension become important contributions to the adhesion forces. The solvation forces are independent of the surrounding humidity but depend highly on the local surface conformation in the contact zone. This is due to their molecular nature, which leads to significant variations of the forces between different particle contacts \[126, 127\]. In comparison to these very dominant capillary and solvation forces, we find that the van-der-Waals forces play only a minor role for all particle sizes as can be seen from the pure crystal forces in Figs. 4.3 and 4.4.

The implementation of our findings into a comprehensive contact model, which is used in discrete element method simulations, has shown that the correct reproduction of the mechanical behaviour of nanoparticle films is possible on a physically rigorous basis. This compatibility was enabled by a multiscale approach from quantum mechanical effects all the way up to the mesoscale using combined experimental measurements and atomistic simulations of particle interactions. Due to the stepwise deliberate coarse graining of our atomistic findings, we are now able to simulate significantly larger system sizes and timespans which compare to technically relevant experiments.
At the same time, we can still describe a large portion of the microscopic features characteristic to the nanomechanics between our particles, as was shown by an extensive validation in comparison with experimental results. The gain of simulation speed by this method can be probably best observed in the case of our agglomerate stretching simulations (Fig. 6.1), where the atomistic simulation requires a computation time of $4 \cdot 10^4$ CPU hours on a supercomputer, while the DEM simulation of the same system requires only 0.3 CPU seconds on a local workstation, which is equivalent to a speed up of approximately $10^8$.

Our proposed model can now be used to investigate mesoscopic effects like the influence of porosity, percolation, coordination number, aggregate size and primary particle size distribution on the mechanical properties of nanoparticle films. The observed trend of our AFM simulations with humidity suggests that these mesoscale effects, as expected, play a crucial role in the overall mechanical behaviour of the particle films, and can even compensate opposite trends at the primary particle level. The variation of the mesoscopic configuration of a nanoparticle film can thus be used to selectively adjust its mechanical response. In the example discussed in chapter 1, the mechanical response of a laminated nanoparticle film during a colloidal probe measurement depends crucially on the formerly applied compaction pressure (Fig. 7.1). By using our simulation model we should now be able to link this dependence to the respective changes in the film structure and propose process parameters that meet the needs of possible applications. Based on our findings concerning the dependencies of the interparticle forces on the environment, we suggest that direct tuning of the interparticle forces can be accomplished by acting on any property that influences such dependence, most notably the material’s affinity for different adsorbate molecules or the surface roughness. This could be achieved e.g. by surface functionalization, particle doping, or deliberate insertion of other types of (surface) defects. The substantiated understanding of the interplay between these variables at the nano- and mesoscale, which can be achieved from applying our contact model with different modifications to different systems, will then enable a broad tuning of the nanoparticle film properties for the needs of technical applications such as catalysis, sensorics, filtering, et cetera.

We stress that our analysis is formulated for a realistic solid/vapour couple (here, TiO$_2$/ water), thus capturing effects absent in model systems
such as ideally spherical particles in van-der-Waals solvents. Nevertheless, we have been able to extract conclusions of great generality, which can be potentially applied to a variety of different systems. Still we have to mention some restrictions and open questions to our result.

First of all, the incorporation of the adsorbate layer in our model is only valid for at least moderately hydrophilic materials, where a closed adsorption layer is formed. The amount of water found in the desorption measurements suggests that this is the case for our experimental particles, but we cannot offer a measured contact angle to testify this assumption. Furthermore, the finding that the experimentally measured forces increase after UV irradiation, while the amount of adsorbed water stays constant is difficult to reconcile with our opinion that these two effects should be connected to each other. Anyway, the deviation between the experimentally and theoretically observable contact angles found for water on TiO$_2$ has been controversially discussed in the literature $^{23,206,207,211,212}$ and should be clarified before firm conclusions about the effect of irradiation can be drawn.

Concerning our less hydrophilic model, the downscaling of the partial charges represents a rather rough option to reduce the material hydrophilicity, as both the crystal structure as well as the surface termination remain unchanged. The analysis of a completely different material with lower hydrophilicity would be a better option to analyse a realistic system. However, we intentionally chose this procedure, as it enables us to neglect the influence
of other properties on the interparticle forces.

The determination of the surface/solvent interactions and of the solvent structuring at the surface, which are necessary for the theoretical calculation of the solvation forces, is experimentally challenging for nanoparticles due to their hardly accessible atomistic surface conformation. Therefore, the transfer of our concept of solvation forces to other systems implies some experimental or theoretical efforts which complicate the straightforward application of the model. The more empirical approach used later in our work (See section 5.4) provides a much simpler framework but requires an empirical determination of the force amplitudes. Regardless, this amplitude can be approximated from other properties such as the hydrophilicity and the solvent structuring at the surface, since a higher density excess will lead to a higher force amplitude. The quality of this estimation for a new system would be largely enhanced by a generalization of our contact model to further materials exhibiting different shapes, hydrophilicities and surface terminations. This would yield correlations to properties above the atomistic scale like the adsorption isotherm and the particle shape. We therefore highly recommend the application of our approach to other materials, which are accessible to both the atomistic simulation and the experimental validation, such as SiO$_2$, Al$_2$O$_3$ or SnO$_2$.

The investigation of the tangential forces is performed at a single humidity, so we cannot say with certainty, if the friction at low humidities obeys to the same mechanism. However, our findings from the adhesion forces between the particles show that the force mechanisms do not change with changing humidity and that the forces do not show any discontinuities, which leads us to the expectation that the tangential forces at low humidities can be well predicted from our investigations at higher humidities. Still, the onset of steric repulsion could change for very low humidities due to the changing thickness of the water layer (see Fig. 4.4).

The choice of stiff aggregates in the DEM simulations lacks any physical knowledge about the mechanical properties of the bonds inside the aggregates. Although it is widely accepted that these bonds are much stiffer than the bonds between aggregates [221,222,228,230], it is not clear whether this increased stiffness results from very strong physical bonds or from chemical bonds, such as sintering bridges. However, the importance of incorporating aggregate bonds in our case becomes directly obvious from comparing
our agglomerate stretching simulations to the results of the AFM/TEM experiments. The lack of stiff interparticle bonds in the simulations leads to large rearrangements of all particle contacts and to the formation of a very linear particle chain. The AFM/TEM experiments on the contrary show only rearrangements for a small portion of the particle contacts, resulting in still kinked and branched particle chains. In addition to this, the simulation of the AFM-experiments without the use of stiff aggregates shows extensive chain elongation before detachment and contraction afterwards. This is comparable to the results of Friedlander et al. for loosely bound nanoparticle agglomerates [236, 237], but deviates largely from our experimental findings concerning both the measured forces and the observed particle trajectories. Nevertheless, the simulations that use stiff aggregates seem to slightly underestimate the particle rearrangement observed in the AFM-TEM experiments. Moreover, some preliminary simulations investigating the compression of the particle films shows a lower compressibility of the films than found in the experiments. These findings suggest that an intermediate bond strength between our physical adhesion forces and the stiff bonds is necessary to correctly model the internal binding of aggregates. A thorough analysis of this topic should be conducted in future to complete our model.

In our analysis of the adhesion forces we did not consider the preferential alignment of contacting particles, which could be especially important for the strength of the solvation forces [104, 238]. From additional simulations we find that the solvation force amplitudes, and with this the maximum adhesion forces, increase if the particles are left free to rotate, due to the arrangement into more favorable positions during the detachment (see Appendix section A.1). On the other hand, leaving the particles free does not reproduce the correct solvation forces either, as inside a particle film the particles are much more confined by multiple contacts and cannot rotate easily to their favored alignment. Nevertheless, the aggregation pathway during the film generation could play a role, which we disregard here. In addition to this, we do not consider atomistic surface inhomogeneities in our model due to the coarse graining towards the discrete element method. These inhomogeneities lead to a statistical distribution of the solvation forces, which will result in the breaking of the weakest particle connections in the AFM experiments and cannot be observed by our model. For this reason, we
would expect our DEM simulations to overestimate the forces occurring in the experiments and in the atomistic simulations. Regardless of this expectation, the comparison between the atomistic and DEM simulations of the agglomerate stretching show that the forces are surprisingly similar, which could mean that the two simplifications, the neglect of preferential alignment and the neglect of surface inhomogeneity, compensate each other to a certain extent. To overcome these simplifications we would recommend the implementation of an inhomogenous surface model into the DEM simulations, which introduces a statistical variation of the forces, but will also increase the complexity of the model and raise the computational costs.

Although our atomistic findings suggest that the adhesion forces found experimentally can be best reproduced by the use of a rough surface model, this insight has not been considered in our DEM simulations and could be a possible reason for the higher maximum forces in comparison to the experiments. The reason for not considering roughness so far is the very complex individual dependence of all involved interparticle forces on the roughness of the surface and the inability of our simple contact force model to account for this complexity. A possible solution of this problem could be again the implementation of a surface model with varying properties as already mentioned above. However, the height and distribution of the roughness in our atomistic model show the general influence of asperities very well but are not inspired by any experimental value and can thus be only used for demonstration purposes. The development of such a roughness model would require an extensive analysis of TEM-images together with the development of a sensible statistical distribution function.

Beside these possible refinements, our model also forms the basis for well-grounded further simplifications, which could enhance the simulation speed and robustness and facilitate the correlation between mesoscale and macroscale film properties [36]. Such simplifications would be achieved for example by omitting single components, linearising the adhesion forces [239] or even simply inserting the maximum adhesion values into established cohesion models such as JKR or DMT. To this aim, a comprehensive analysis identifying the components of the contact model, which are really necessary to correctly reproduce the experimental behaviour, would be helpful and is not covered by our work. The selective variation or deactivation of single components like the solvation forces, rolling friction, or the stick-slip be-
Figure 7.2: A multiscale simulation approach using the combination of a microscopic discrete element method solver coupled to a continuum mechanics finite element method (FEM) solver. Reproduced from Ref. [240] with permission from John Wiley and Sons.

haviour of the sliding friction, can yield a good estimate of the importance of these components and of the necessity to include them into future models or not.

Furthermore, despite the already impressive speedup through our DEM coarse graining, the simulation size and speed still represent the limiting factors for large scale applications, as can be seen from the influence of the system size and the velocity of the AFM-tip on the results of our AFM-simulations. Hence, a further coarse graining could be necessary for the application of our model to larger systems. One possibility to increase the simulation speed is represented by the use of mass scaling, or a quasi-static integration approach, which would however crucially change the dynamics of the system and yield only moderate accelerations [241, 242]. On a broader scale, significant acceleration could be achieved by the integration of entire aggregates or even agglomerates into single elements [243, 244], into polymer models [245] or into multiscale simulation approaches [240, 246] (Fig. 7.2). This which would imply a significant increase of the element size and thus an increase of the critical timestep and a decrease of the element number. However, to avoid the neglecting of important mechanisms, such a coarse graining approach should be performed, as in this work, by carefully considering a multitude of possibly influencing factors such as particle shape and hydrophilicity, particle size distribution and aggregate structure, loading
state, humidity and type of solvent, et cetera.

Finally, the coupling of our model to computational fluid dynamics simulations (CFD) could enable the investigation of further applications such as flame simulation or filtering, which are highly important for the production of nanoparticles and of liquid infiltration into particle films.
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CHAPTER 7. CONCLUSION AND OUTLOOK
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In der vorliegenden Arbeit sind Ergebnisse enthalten, die im Rahmen der Betreuung folgender studentischer Arbeiten entstanden sind:


Jens Laube
Appendix A

Background information on simulation and experimental data

Section A.1: Force-displacement curves between smooth particles
Section A.2: Water structure between smooth 4nm particles in contact
Section A.3: Solvation forces between smooth particles
Section A.4: Water density profiles and capillary forces between smooth particles
Section A.5: Surface tension on a flat surface
Section A.6: Less hydrophilic particles
Section A.7: Rough particles
Section A.8: Friction parameters
Section A.9: DEM simulation results
Section A.10: AFM/TEM results

A.1 Force-displacement curves between smooth particles
Figure A.1.1: Force-displacement curves calculated for 4 nm TiO$_2$ particles facing each other along different orientations with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. 

$\langle 111 \rangle$

$\langle 100 \rangle$

$\langle 110 \rangle$

$\langle 010 \rangle$
Figure A.1.2: More force-displacement curves calculated for 4 nm TiO$_2$ particles with different amounts of adsorbed water molecules and facing each other along different arbitrary orientations generated by random particle rotation or free aggregation of particles. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$ [3].
**Figure A.1.3**: Force-displacement curves calculated for 6 nm TiO$_2$ particles facing each other along different orientations with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$ [4].
Figure A.1.4: Force-displacement curves calculated for 8 nm TiO$_2$ particles facing each other along different orientations with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. 

[Diagram of force-displacement curves with different orientations and adsorption densities.]
Figure A.1.5: Force-displacement curves calculated for an 8 nm TiO$_2$ particle together with a 4 nm particle facing each other along the $\langle 100 \rangle$ direction with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$ [4].
Figure A.1.6: Force-displacement curves calculated for 10 nm TiO$_2$ particles facing each other along different orientations with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. 

[Description of the figure: The figure shows multiple graphs with force-displacement curves for different orientations and adsorbed water molecules. The x-axis represents the displacement $d-2R$ in nm, and the y-axis represents the normalized force $F/2R$ in nN/mm. Each curve is labeled with the number of water molecules per square nanometer, and different orientations are indicated by the symbols and colors used in the graph.]

[Referenced text: Further details and citations are provided in the original text.]
Figure A.1.7: Force-displacement curves calculated for 4 nm TiO$_2$ particles facing each other along different orientations with different amounts of adsorbed water molecules. The continuous lines are running average forces, which stem from MD simulations in which the particle-particle distance $d$ is progressively increased at a speed of 0.5 m/s and the particles are left free to rotate towards their favourite conformation. The symbols are average forces computed in 1 ns MD runs restarted from the detachment simulations, where the particle separation distances are kept fixed and the particles are left free to rotate. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. 
Figure A.1.8: More force-displacement curves calculated for 4 nm TiO$_2$ particles facing each other along different orientations with different amounts of adsorbed water molecules. The continuous lines are running average forces, which stem from MD simulations in which the particle-particle distance $d$ is progressively increased at a speed of 0.5 m/s and the particles are left free to rotate towards their favourite conformation. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. 
A.2 Water structure between smooth 4nm particles in contact

Figure A.2.1: Superimposed $g(z)$ (red curve) and $g(z, \alpha)$ (colour plot, with red representing regions higher than in the bulk, on a logarithmic scale) calculated in a cylindrical volume with an area $A = \pi (0.7)^2 \text{nm}^2$ between two smooth 4 nm TiO$_2$ particles in humid air at different separations $\delta$, facing each other along the $\langle 110 \rangle$ direction. Black lines are theoretical predictions from the linear superposition approximation using the $g(z)$ in bulk water over an isolated particle in the same orientation [3].
Figure A.2.2: Same as in Fig. A.2.1
Figure A.2.3: As in Fig. A.2.1 and A.2.2 for other mutual orientations of the particles and at distances corresponding to the minima of potential energy along each orientation [4].
A.3 Solvation forces between smooth particles

Figure A.3.1: Theoretical solvation forces calculated from the water distribution function and the solid-liquid interaction forces as described in the main text and fitted to the oscillatory part of the simulated forces between two 4, 6, 8, 10 and 20 nm particles and between an 8 nm particle and a 4 nm particle respectively by the interaction area A. The oscillatory forces are obtained from the F-D curves at a coverage of 16 water molecules per nm$^2$ by subtracting the capillary forces from our modified capillary theory.
A.4 Water density profiles and capillary forces between smooth particles

Figure A.4.1: Iso-value lines of the radially-averaged water density between two smooth 4 nm TiO$_2$ particles with different amounts of adsorbed water molecules, at a distance $\delta = 0.6$ nm (top panels) and geometrical fit of the meniscus geometry to the iso-density line at 0.5 g/cm$^3$ (bottom panels). Results are shown for water coverages of 5.2, 7.2, 10.2, 13.2, 16.2, 20.2, 25.2, and 30.2 water molecules per nm$^2$, from top left to bottom right [3].
Figure A.4.2: Capillary geometries extracted from the water density isoleine at 0.5 g/cm³ computed from the combined simulation trajectories of different particle orientations of 6 nm particles at a coverage of 16 water molecules per nm² (equivalent to an air humidity of approximately 65%) and at a distance $\delta = 1.0$ nm (a). (b-e): Comparison of the explicitly calculated forces from MD simulations of 6 nm particles at different particle orientations and different air humidities (black crosses) to the capillary forces calculated from the capillary simulations (red line), the modified capillary theory (blue line) and from the conventional capillary theory (green line) using the averaged capillary quantities from the water density profile [4].
Figure A.4.3: Capillary geometries extracted from the water density isoline at 0.5 g/cm³ computed from the combined simulation trajectories of different particle orientations of 8 nm particles at a coverage of 16 water molecules per nm² (equivalent to an air humidity of approximately 65%) and at a distance δ = 1.0 nm (a). (b-e): Comparison of the explicitly calculated forces from MD simulations of 8 nm particles at different particle orientations and different air humidities (black crosses) to the capillary forces calculated from the capillary simulations (red line), the modified capillary theory (blue line) and from the conventional capillary theory (green line) using the averaged capillary quantities from the water density profile \[4\].
Figure A.4.4: (a-f): Comparison of the explicitly calculated forces from MD simulations of 10 nm particles at different particle orientations and different air humidities (black crosses) to the capillary forces calculated from the capillary simulations (red line), the modified capillary theory (blue line) and from the conventional capillary theory (green line) using the averaged capillary quantities from the water density profile [4].
Figure A.4.5: Capillary geometries extracted from the water density isoline at 0.5 g/cm³ computed from the combined simulation trajectories of different particle orientations of 20 nm particles at a coverage of 16 water molecules per nm² (equivalent to an air humidity of approximately 65%) and at a distance δ = 1.1 nm (a). (b): Comparison of the explicitly calculated forces from MD simulations of 20 nm particles at different particle orientations and different air humidities (black crosses) to the capillary forces calculated from the capillary simulations (red line), the modified capillary theory (blue line) and from the conventional capillary theory (green line) using the averaged capillary quantities from the water density profile [4].
Figure A.4.6: Capillary geometries extracted from the water density isoline at 0.5 g/cm³ computed from the combined simulation trajectories of different particle orientations of an 8 nm particle in contact with a 4 nm particle at a coverage of 16 water molecules per nm² (equivalent to an air humidity of approximately 65%) and at a distance $\delta = 1.0$ nm (a). (b-e): Comparison of the explicitly calculated forces from MD simulations of an 8 nm particle in contact with a 4 nm particle at different particle orientations and different air humidities (black crosses) to the capillary forces calculated from the capillary simulations (red line), the modified capillary theory (blue line) and from the conventional capillary theory (green line) using the averaged capillary quantities from the water density profile [4].
Figure A.4.7: Variations of the geometrically fitted values of $R_{Cap}$ (top left), and of the $\gamma_L$ (top right) and $P/P_0$ (bottom) values obtained from classical capillary theory (main text, Equations 2.13-2.16) at different particle separation distances $d - 2R$ and for different water coverages for smooth 4 nm TiO$_2$ particles. Coverages of 5, 7, 10, 13, 16, 20, 25 and 30 water molecules per nm$^2$ are represented with blue crosses, orange dots, black diamonds, lightblue reverse triangles, red squares, green triangles, magenta crosses and cyan circles, respectively.
A.5 Surface tension on a flat surface

Figure A.5.1: The pressure gradient at the liquid/gas interface of a specific water layer thickness (bottom) is calculated from subtracting the pressure gradient at the solid/liquid interface of a thick film (60 water molecules per surface nm$^2$, middle) below a z-height of 1.65 nm from the actual pressure gradient (top) [4].
Figure A.5.2: Resulting pressure gradient at the liquid/gas interface after subtraction of the solid/liquid interface values for different water layers containing 30, 25, 20, 16, 13, 10, 7 and 5 water molecules per surface nm² from top left to bottom right respectively [4].
Figure A.5.3: Work of adhesion between two slab surfaces of with an area of approximately 218 nm$^2$ calculated from the integration of the detachment force displacement curve for different water layers containing 30, 25, 20, 16, 13, 10, 7 and 5 water molecules per surface nm$^2$ from top left to bottom right, respectively. The dark grey area depicts the work considered for two approaching surfaces ($W_a$) while the dark grey plus the light grey area depicts the work considered for the detaching surfaces ($W_d$) [4].
A.6  Less hydrophilic particles

Figure A.6.1: Force-displacement curves calculated for less hydrophilic 4 nm TiO$_2$ particles with rescaled partial charges facing each other along different orientations with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter 2$R$. 
A.7 Rough particles

Figure A.7.1: Force-displacement curves calculated for rough 4 nm TiO$_2$ particles with asperities of 0.5 nm height, facing each other along different orientations with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. The continuous lines are running average forces resulting from MD simulations in which the particle-particle distance $d$ is progressively increased at a speed of 0.5 m/s. The symbols are average forces computed in 1 ns MD runs at fixed separation distances. Right top: Model of two particles with asperities of 0.5 nm facing each other along the $\langle110\rangle$ direction at the distance of the maximum attractive force [3].
Figure A.7.2: Force-displacement curves calculated for rough 4 nm TiO$_2$ particles with asperities of 0.35 nm height, facing each other along different orientations with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. The continuous lines are running average forces resulting from MD simulations in which the particle-particle distance $d$ is progressively increased at a speed of 0.5 m/s. The symbols are average forces computed in 1 ns MD runs at fixed separation distances. Right top: Model of two particles with asperities of 0.35 nm facing each other along the $\langle 110 \rangle$ direction at the distance of the maximum attractive force.
Figure A.7.3: Force-displacement curves calculated for rough 6 nm TiO$_2$ particles with asperities of 0.5 nm height, facing each other along different orientations with different amounts of adsorbed water molecules. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. The continuous lines are running average forces resulting from MD simulations in which the particle-particle distance $d$ is progressively increased at a speed of 0.5 m/s. The symbols are average forces computed in 1 ns MD runs at fixed separation distances.

Figure A.7.4: Force-displacement curves calculated for rough 6 nm TiO$_2$ particles with asperities of 0.25 nm height, facing each other along different orientations. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. The continuous lines are running average forces resulting from MD simulations in which the particle-particle distance $d$ is progressively increased at a speed of 0.5 m/s. The symbols are average forces computed in 1 ns MD runs at fixed separation distances.
Figure A.7.5: Force-displacement curves calculated for rough 8 nm TiO$_2$ particles with asperities of 0.5 nm height, facing each other along different orientations. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. The continuous lines are running average forces resulting from MD simulations in which the particle-particle distance $d$ is progressively increased at a speed of 0.5 m/s. The symbols are average forces computed in 1 ns MD runs at fixed separation distances.

Figure A.7.6: Force-displacement curves calculated for rough 8 nm TiO$_2$ particles with asperities of 0.25 nm height, facing each other along different orientations. The curves are shifted along the y axis with respect to their respective zero-force lines (dashed) and divided by the particle diameter $2R$. The continuous lines are running average forces resulting from MD simulations in which the particle-particle distance $d$ is progressively increased at a speed of 0.5 m/s. The symbols are average forces computed in 1 ns MD runs at fixed separation distances.
A.7. ROUGH PARTICLES

Figure A.7.7: Left: Iso-value lines of the radially-averaged water density between two rough 4 nm particles with an asperity height of 0.5 nm and covered with different amounts of adsorbed water molecules, at a distance $\delta = 1.49$ nm (top panels) and geometrical fit of the meniscus geometry to the iso-density line at 0.5 g/cm$^3$ (bottom panels). Right: Comparison between the F-D curves computed explicitly in MD simulations (black crosses) of the rough particles and the theoretically predicted capillary force contributions with geometrical fits of the MD trajectories with constraints on particle radius and humidity (blue). The blue curves consist of two parts associated to the capillary adhesion between the whole particles (at smaller $d - 2R$) and only between the asperities (at larger $d - 2R$). The magenta curves are the total sum of steric, dispersion, solvation and capillary force contributions. The F-D curves for different particle orientations are shifted to match the position of the maximum attractive force and divided by the particle’s diameter $2R$. Values are shown for a water coverage of 5, 7, 10 and 13 water molecules per nm$^2$, from top to bottom [3].
Figure A.7.8: As in Fig. A.7.7 for water coverages of 16, 20 and 25 water molecules per nm$^2$, from top to bottom.
A.8 Friction parameters

Figure A.8.1: Tangential force wavelength $\omega$ calculated from the averaged distance between the local force peaks for different particles sizes and orientations at sliding (top) and rolling (bottom) friction with a pulling speed of 1 m/s.
Figure A.8.2: Representative tangential force displacement curves for a 4 nm particle at a normal load of $F_N = 1$ nN and different pulling velocities for sliding (left) and rolling (right) movement. The force curves are shifted on the y-axis for clarity with the tangential force of 0 nN being marked by a dashed black line respectively.
Figure A.8.3: Top: Simulation of torsion between two particles by keeping one particle fixed and rotating the second particle at a constant speed of 1 U/ns. Bottom: Resulting torsional torque vs. twisting angle between two particles at different conformations.
A.9 DEM simulation results

Figure A.9.1: Comparison of all-atom and DEM agglomerate stretching as in the main text. To watch a video of the particle trajectory visit [http://nbn-resolving.de/urn:nbn:de:gbv:46-00106093-11](http://nbn-resolving.de/urn:nbn:de:gbv:46-00106093-11).
Figure A.9.2: Comparison between DEM simulations and AFM experiments as in the main text. To watch a video of the particle trajectory visit http://nbn-resolving.de/urn:nbn:de:gbv:46-00106094-13.
Figure A.9.3: Chain detachment in AFM simulation as in the main text. To watch a video of the particle trajectory visit [http://nbn-resolving.de/urn:nbn:de:gbv:46-00106095-14](http://nbn-resolving.de/urn:nbn:de:gbv:46-00106095-14)
A.10 AFM/TEM results

Figure A.10.1: Series of images from our combined AFM/TEM experiments showing the rearrangement and detachment of particle contacts during the retraction of the AFM-tip as in the main text.
Figure A.10.2: Additional series of images from our combined AFM/TEM experiments showing the rearrangement and detachment of particle contacts during the retraction of the AFM-tip.

Figure A.10.3: Additional series of images from our combined AFM/TEM experiments showing the rearrangement and detachment of particle contacts during the retraction of the AFM-tip.
Figure A.10.4: Additional series of images from our combined AFM/TEM experiments showing the rearrangement and detachment of particle contacts during the retraction of the AFM-tip.

Figure A.10.5: Additional series of images from our combined AFM/TEM experiments showing the rearrangement and detachment of particle contacts during the retraction of the AFM-tip.
Figure A.10.6: Additional series of images from our combined AFM/TEM experiments showing the rearrangement and detachment of particle contacts during the retraction of the AFM-tip.