Modeling of Particle Contacts in Aggregated Nanoparticles

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PhD Thesis

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Zusammenfassung

In dieser Arbeit "Modeling of Particle Contacts in Aggregated Nanoparticles" werden mechanische Interaktionen zwischen aggregierten Nanopartikeln aus der Gasphase sowie deren Auswirkungen auf Prozessierung und ihre Charakterisierung aufgezeigt. Darüber hinaus werden verschiedene Methoden entwickelt oder bestehende Methoden angepasst, um strukturelle Eigenschaften der Partikel und deren Filme zu beschreiben. Mit Hilfe dieser Modelle können Vorhersagen über Filmeigenschaften wie Porosität, Porengrößenverteilung oder elektrischer Widerstand erstellt werden und genauere Aussagen über die Partikel-Partikel Kontakte in heterogenen Partikeln (bestehend aus mehreren Komponenten) anhand von Bildanalyse getroffen werden.

Aggregierte Nanopartikel sowie deren Filme bestehen aus scheinbar willkürlich angeordneten Primärpartikeln mit Durchmessern von wenigen Nanometern. Diese spezielle Anordnung resultiert in einer Struktur, die sich durch eine sehr hohe Porosität und durchgängige Poren auszeichnet und es somit beispielsweise Fluidmolekülen ermöglicht, die gesamte Oberfläche der Partikel zu erreichen. Diese Eigenschaften machen diese Partikelstrukturen besonders für die Katalyse sehr attraktiv. Partikel, welche sich in Filmen strukturieren, zeichnen sich zudem durch eine hohe Zahl von Perkolationspfaden (kontinuierliche Kette von verbundenen Partikeln) aus, entlang derer bspw. Ladungsträger wie Elektronen transportiert werden können.

Die nähere Betrachtung der Struktur von aggregierten Partikeln zeigt, dass sie einer gewissen Regelmäßigkeit folgen, welche mit der fraktalen Theorie beschreibbar ist. Dabei ist diese Struktur im Wesentlichen durch zwei Kontaktarten zwischen Primärpartikeln bestimmt: (1) ungebundene Partikelkontakte durch schwache, physikalische Kräfte (beispielsweise Kapillarkräfte oder van der Waals Kräfte) und (2) Sinterbrücken, bestehend aus stabilen kovalenten Bindungen. In heterogenen Partikeln (bestehend aus mindestens zwei verschiedenen Komponenten) können sich zudem beide Kontaktarten sowohl innerhalb von gleichen, als auch zwischen verschiedenen Komponenten ausbilden. Im Fokus dieser Arbeit stehen diese verschiedenen Kontaktarten und die Untersuchung ihrer Auswirkung auf Prozessierung (homogene Partikel), bzw. ihre Charakterisierung (heterogene Partikel).

Aufgrund der geringen Größe der Primärpartikel wird die mathematische Modellierung, bzw. Simulation angewandt, welche eine sehr hohe Auflösung aller relevanter Parameter ermöglicht. Dazu werden zunächst Nanopartikel Aggregate unter Berücksichtigung experimentell ermittelter Primärpartikel- und Aggregatgrößenverteilungen erstellt. Anschließend werden der Einfluss von mechanischer Belastung auf Partikelfilme und die resultierende Restrukturierung mit Hilfe der Diskreten Elemente Methode (DEM) untersucht. Dabei werden Primärpartikel als Sphären approximiert und ihre Interaktionen mit Hilfe von speziell auf Nanopartikel angepassten Kontaktmodellen berechnet. Diese Methode ermöglicht die Komprimierung von Partikeln simulativ zu reproduzieren. So erstellte Filmmodelle entsprechen experimentell erzeugten Filmen mit sehr hoher Genauigkeit in Hinblick auf Porosität und Porenstruktur bei gegebenen Komprimierdruck. Des Weiteren ermöglichen diese Filmmodelle die Analyse der exakten Perkolationspfade. So kann der elektrische Widerstand von Nanopartikelfilmen berechnet und mit experimentellen Werten verglichen werden. Der Verlauf des elektrischen Widerstands in Abhängigkeit des Komprimierdrucks mit dem die Schichten erstellt werden, stimmt sehr gut mit den Experimenten überein.

Die Arbeit zeigt zudem wie sich die Kontakte in heterogenen Aggregaten beschreiben lassen. Vor Allem die Anzahl der heterogenen Kontakte zwischen den verschiedenen Komponenten lässt sich dabei über die Anzahl von Primärpartikel je Cluster einer Komponente während der Aggregatgenerierung einstellen. Dadurch folgt der Zusammenhang aus heterogener Koordinationszahl (heterogene Kontakte je Primärpartikel) und Primärpartikel je Cluster exakt der analytischen Vorhersage. Auf Basis dieses Modells und der resultierenden Erkenntnisse werden 2D-Projektionen von heterogenen Aggregaten erstellt. Die direkte Korrelation der 2D-Parameter und der exakten 3D-Parameter (Koordinationszahl, Primärpartikel je Cluster) ermöglicht es, die 3D-Heterogene-Koordinationszahl anhand von experimentellen 2D-Bildanalysen zu ermitteln. Dadurch werden die analytischen Methoden zur Charakterisierung von beispielsweise Transportprozessen (Masse, Ladung) um eine sehr detaillierte Möglichkeit erweitert, die exakten Kontakte aufzulösen.

Die gezeigten Modelle und Methoden eröffnen den Herstellern von Batterieelektroden, Gas Sensoren oder Katalysatoren Zugang zu einer neuen Möglichkeit die Kontakte zwischen Partikeln, die poröse Struktur und die Perkolationspfade in aggregierten Nanopartikeln zu untersuchen und erleichtern es somit diese Partikelstrukturen auf ihre Anwendung zu optimieren.

Abstract

In this thesis "Modeling of Particle Contacts in Aggregated Nanoparticles", the different interaction forces between aggregated nanoparticles from the gas phase as well as their effects on processing and their characterization are shown. Various methods are developed or existing methods adapted to describe structural properties of particles and films of such particles. These models can be used to predict film properties such as porosity, pore size distribution or electrical resistance as well as to make more accurate predictions about particle-particle contacts in multicomponent particles (heterogeneous particles) using image analysis.

Aggregated nanoparticles and their films consist of apparently randomly arranged primary particles of a few nanometers in diameter. The arrangement of these primary particles, however, results in a structure characterized by a very high porosity and continuous pores which, for example, allows fluid molecules to reach the entire surface of the particles. This makes aggregated particles particularly attractive in catalysis. Another special property of these particles is the high number of percolation paths along which charges such as electrons can be conducted. A closer look at the particles shows that they follow a certain regularity which can be described with the fractal theory. The structure of the particles is essentially determined by two types of contact between primary particles: (1) non-bonded particle contacts by weak physical forces (including capillary forces and van der Waals forces) and (2) sinter bridges consisting of stable covalent bonds. In heterogeneous particles (consisting of at least 2 different components), both contact types can exist within the same component and between the different components. This thesis focuses on these different contact types and their effects on processing (homogeneous particles) and characterization (heterogeneous particles) are investigated.

Due to the small size of the primary particles, mathematical modeling and simulation is applied, which enables a very high resolution of all relevant parameters. Therefore, nanoparticle aggregates are first created using the Diffusion Limited Cluster Aggregation (DLCA) theory under consideration of experimentally determined primary particle and aggregate size distributions. The influence of mechanical stress on particles and the resulting restructuring is investigated using the

Discrete Element Method (DEM). In the DEM simulations, primary particles are approximated as spheres and their interactions are calculated using contact models specially designed for nanoparticles. This method makes it possible to reproduce the compaction of particle films in computer simulations. Created this way, film models correspond to experimentally generated films with very high accuracy with regard to porosity and pore structure at given compaction pressure. Furthermore, these film models enable the analysis of the exact percolation paths. For example, the electrical resistance of nanoparticle films can be calculated and compared with experimental values. The resulting electrical film resistance at a specific compaction pressure corresponds very well to the experiments.

The thesis also shows how the contacts in heterogeneous aggregates can be described. Especially the heterogeneous contacts between the different components can be controlled by the number of primary particles per clusters of one component during aggregate generation. Thus, the relationship between heterogeneous coordination number (heterogeneous contacts per primary particle) and primary particles per cluster follows the analytical prediction exactly. 2D projections of heterogeneous aggregates are created on the basis of this model. The direct correlation of the 2D parameters and the exact 3D parameters (coordination number, primary particles per cluster) makes it possible to determine the 3D heterogeneous coordination number using experimental 2D image analysis. Thus, the analytical methods for the characterization of, for example, transport processes (mass, charge) are extended by a very detailed possibility to resolve the exact contacts between primary particles.

The models and methods shown give manufacturers of battery electrodes, gas sensors or catalysts access to a new way of investigating the contacts between particles, the porous structure and the percolation paths in aggregated nanoparticles and thus facilitate the optimization of these particle structures for their application.

Danksagung

Mein besonderer Dank gilt meinem Betreuer und Gutachter Herrn Prof. Lutz Mädler, der mich sowohl im Studium als auch während der Promotion stets begleitet und gefördert hat. Ohne seine Inspiration und seinen Anspruch an meine Arbeit, wäre diese Dissertation nicht möglich gewesen. Vielen Dank für die vielen fachlichen und persönlichen Gespräche, die mich immer dazu angeregt haben besser zu werden und die meine Erfahrung an der Universität Bremen stark geprägt haben.

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Preface

The results presented in this dissertation were obtained during my time as a PhD-student from January 2015 until February 2019 in the division Reactive Spraying in the specialization of Mechanical Engineering at the Faculty of Production Engineering of the University of Bremen. During this time, I was supervised by Prof.-Dr.-Ing. habil. Lutz Mädler.

The thesis contains only my own research, if not explicitly stated otherwise. Single sections of this thesis have been peer-reviewed and published as followed:

In chapter 4, the sections 4.1.2, 4.2.2 and 4.4 have been published in the peer-reviewed journal "Powder Technology":

Baric, V., Colombi Ciacchi, L., Mädler, L. Compaction-Induced Restructuring of Aggregated Nanoparticle Films using the Discrete Element Method. *Powder Technology* **342**, 773-779 (2019).

Valentin Baric carried out all simulations in the manuscript. Sven O. Schopf (University of Bremen) contributed the nitrogen desorption isotherm experiments to obtain the experimental porosity and pore size distribution. Tobias Wollborn (University of Bremen) measured the aggregates mobility diameter that was used to obtain the aggregate size distribution.

Chapter 5 was published in "Particle & Particle Systems Characterization":

Baric, V., Grossmann, H.K., Koch, W., Mädler, L. Quantitative Characterization of Mixing in Multicomponent Nanoparticle Aggregates. *Particle & Particle Systems Characterization* **0**, 1800177 (2018).

Valentin Baric carried out the simulations and the development of the analytic model. Henrike K. Großmann carried out the experiments. The experiments were characterized by both authors to obtain experimenter independent results.

Section 2.2.3 was published in the peer-reviewed journal "Granular Matter":

Laube, J., Baric, V., Salameh, S., Mädler, L., Colombi Ciacchi L. A New Contact Model for the Discrete Element Method Simulation of TiO$_2$ Nanoparticle Films under Mechanical Load. *Granular Matter* **20**, 28 (2018).

Jens Laube developed the models and carried out the DEM simulations. Valentin Baric has simulated the initial particle films and Samir Salameh carried out the AFM-experiments.

Section 2.2.3 was published as the final report for the corresponding DFG priority program SPP 1486 "Particles in Contact - Micro Mechanics, Micro Process Dynamics and Particle Collective".

Contents

Glossary

Agglomerate Collective of several aggregates. The aggregates interact with each other by weak forces such as van der Waals forces, capillary forces and solvation forces. Agglomerates have a fractal structure and are variable in size. They can range from two aggregates to a whole film of millions of aggregates. The electrical conductivity in agglomerates is primarily determined by highly resistive non-bonded particle contacts.

Aggregate Collective of a few tens of primary particles, which are bonded by sinter bridges. The primary particles are organized as fractals, or more specifically quasi-fractals. Aggregates are formed by Diffusion Limited Cluster Aggregation.

Aggregate size Number of primary particles within an aggregate.

Cluster Collective of 5–8 primary particles connected *via* sinter bridges. All primary particles are of the same component. Cluster formation is described by Particle Cluster Aggregation (PCA) which are later combined to aggregates (Cluster Cluster Aggregation (CCA)).

Cluster-cluster aggregation Second step of the DLCA in which clusters diffuse and join clusters. Eventually, this results in aggregates.

Cluster size The number of primary particles in one cluster.

Component One specific material in a mixture of multiple materials.

Coordination number The number of particle-particle contacts per primary particle.

Diffusion Limited Cluster Aggregation Model of the process that forms aggregates. Clusters of primary particles fluctuate due to particle diffusion and collide with other clusters.

Heterogeneous aggregate An aggregate that consists of primary particles from (at least) two different components connected *via* sinter bridges.

Heterogeneous contact Contact between primary particles of different components. This contact can be *via* chemical bonds (sinter bridge contact) or *via* weak physical bonds (non-bonded contact).

Heterogeneous coordination number The number of heterogeneous contacts per primary particle.

Homogeneous contact Contact between primary particles of the same component. This contact can be *via* chemical bonds (sinter bridge contact) or *via* weak physical bonds (non-bonded contact).

Homogeneous coordination number The number of homogeneous contacts per primary particle.

Inaccessible primary particle Primary particle with less visible surface area (top view) than the defined threshold Ψ. This primary particle is excluded from further analysis (2D projection of the simulated particles).

Invisible primary particle Primary particle without any visible pixel from top view (2D projection of the simulated particles).

Mixing Establishing particle-particle contacts in heterogeneous particles. Mixing can be achieved within aggregates (sinter bridge contacts), between aggregates (non-bonded contacts) or on an atomic level (not considered in this thesis).

Non-bonded contact A contact type between two primary particles. These contacts are characterized by physical forces, such as van der Waals forces, capillary forces and solvation forces. The forces of a non-bonded contact are incapable of restoring the original relative primary particle locations after displacement. This contact definition is independent of the components of the particle pair.

Non-bonded tunneling contact Non-bonded particle contact between primary particles whose surfaces do not touch and do not intersect. Electrons can tunnel through this distance to establish an electrical contact.

Particle Generic term that includes primary particles, aggregates and agglomerates.

Particle contact Connection between two primary particles that allows the transport of charge, heat, mass, force and torque. Usually, this contact is defined by a threshold distance of the two primary particles, that allows a minimum distance between the surfaces. In this thesis, a pair of particles are in contact if the surfaces are closer than 1 % of the average particle radius.

Particle film Collective of aggregates and agglomerates. Films usually have dimensions exceeding the dimensions of primary particles and agglomerates by several orders of magnitude. Films are characterized by structural porosity resulting from the fractal nature of aggregates and agglomerates.

Particle-cluster aggregation First step of the DLCA in which primary particles diffuse and join clusters and hence, form clusters.

Percolation path Consecutive particles that form a continuous chain of particle-particle contacts, connecting two defined locations of an agglomerate or film (for example two electrodes in a gas sensor).

Primary particle The smallest building block of aggregated nanoparticles. Primary particles are usually single crystals and often spherical (in this thesis they are considered spherical).

Relaxed film Film without external constraints. Sinter bridges and particle-particle contacts are in equilibrium state (no strain, stress or overlap). Relaxed films preserve their structure (porosity, pore size distribution) over time.

Rigid aggregate Model for aggregates in DEM. Sinter bridges are infinitely rigid. They cannot bend or break. The relative particle locations within the aggregate remain constant at all times.

Single particle simulation Model for aggregates in DEM. Single particles neglect any sinter bridge contact and only apply the non-bonded contacts for all particle-particle contacts.

Sinter bridge contact A contact type between two primary particles. These contacts are characterized by chemical bonds, the so-called sinter bridges. This connection can restore the original relative primary particle position after displacement. This contact definition is independent of the components of the particle pair.

Straight line resistance The electrical resistance of a series of films in one direction. Therefore, the width of the line equals the width of one film, while the length corresponds to the electrode spacing of a gas sensor.

Surface-surface contact A threshold definition for an electrical contact. An electrical contact between non-bonded primary particles is only establish, if the surfaces are in touch or intersect.

Acronyms

μCT	Micro-Computational Tomography
AFM	Atomic Force Microscopy
BCLW	Bell, Cameron, Lucas and Washburn
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CCA	Cluster-cluster aggregation
CFD	Computational Fluid Dynamics
CG	Coarse Grained
CPS	CPS disc centrifuge
CPT	Colloidal Probe Technique
DEM	Discrete Element Method
DFSP	Double Flame Spray Pyrolysis
DFT	Density Functional Theory
DLCA	Diffusion Limited Cluster Aggregation
DLVO	Derjaguin-Landau-Verway-Overbeek
DMA	Differential Mobility Analysis
DSMC	Direct Simulation Monte Carlo
EDX	Energy Dispersive X-Ray Spectroscopy
EELS	Electron Energy Loss Spectroscopy
FSP	Flame Spray Pyrolysis
GSMC	Grand Canonical Monte Carlo
HAADF	High-Angle Annular Dark Field
HPC	High performance computing

ITO	Indium-Tinoxide
JKR	Johnson-Kendall-Roberts
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
LB	Lattice-Boltzmann
LIGGGHTS	LAMMPS Improved for General Granular and Granular Heat Transfer Simulations
LTO	Lithium-Titanateoxide
MD	Molecular Dynamics
MMC	Metal-matrix-composites
PCA	Particle-cluster aggregation
PEPT	Positron Emission Particle Tracking
PP	Polypropylene
PSD	Pore size distribution
PVC	Polyvinylchlorid
PVP	Polyvinylpyrrolidon
RMSE	Root mean square error
SA	Sequential algorithm
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
VAFS	Vapor Assisted Flame Synthesis
XRD	X-Ray Diffraction
XRM	X–Ray Microscopy

List of Dimensionless Numbers

Symbol	Description	Unit
Kn_Z	Knudsen number Zhang	-
Kn	Knudsen number	-
Pe	Péclet number	-

List of Greek Symbols

Symbol	Description	Unit
Γ	Distance CCA	m
Θ	Contact angle of water meniscus	°
Φ_i	Rotational displacement	m
$\Phi_{sb,n}$	Rotational displacement sinter bridge in normal direction	m
$\Phi_{sb,t}$	Rotational displacement sinter bridge in tangential direction	m
α	Ratio of collision and coalescence time	-
α_D	Number of angles for the calculation of the diffusion coefficient	-
β	Angle of three phase water line	°
γ_L	Surface tension of the liquid	J m^{-2}
γ_n	Non-bonded normal damping coefficient	Ns m^{-1}
δ_{CPT}	Penetration distance CPT	m
δ_n	Normal displacement	m

Symbol	Description	Unit
δ_t	Tangential displacement	m
δ_{ij}	Particle-particle overlap	m
λ	Molecular mean free path	m
λ_sb	Sinter bridge radius factor	-
λ_t	Period of the saw tooth-pattern tangential friction	m
μ	Critical exponent	-
μ_f	Dynamic viscosity fluid	kg (ms)^{-1}
$\mu_\text{r,wall}$	Rolling friction coefficient particle-wall contact	-
$\mu_\text{t,wall}$	Tangential friction coefficient particle-wall contact	-
ν_sb	Poisson's ratio of the sinter bridge	-
π	Pi	
ρ	Local particle density (unity within a particle, zero outside a particle)	-
$\rho_\text{e,Film}$	Specific electrical resistivity of the particle film	Ωm
$\rho_\text{e,p}$	Specific electrical resistivity of a material	Ωm
ρ_p	Density of the particles	kg m^{-3}
σ_G	Geometric standard deviation	-
σ_a	Arithmetic standard deviation	m or -
σ_e	Electrical conductivity	S
σ_sb	Tensile stress	Pa
$\sigma_\text{sb,c}$	Tensile strength	Pa
σ_solv	Decay length solvation force	m
τ_r	Rolling friction stiffness non-bonded contact	N m^{-2}
τ_sb	Shear stress	Pa
$\tau_\text{sb,c}$	Shear strength	Pa
τ_t	Tangential friction stiffness non-bonded contact	N m^{-2}
ϕ	Porosity	-
ϕ_BJH	Porosity obtained from BJH analysis	-
ϕ_cont	Porosity of the continuous film compaction	-
ψ	Threshold for accessible primary particles	-
$\tilde{\psi}$	Threshold best matching experiments	-

List of Latin Symbols

Symbol	Description	Unit
A_{H}	Hamaker constant	J
A_{Rect}	Total area of the rectangular grid	$\mathrm{m^2}$
A_{ij}	Contact area	$\mathrm{m^2}$
A_{p}	Projected area	$\mathrm{m^2}$
$A_{\mathrm{projection},i}$	Projected area of a particle (in pixels)	-
A_{sb}	Cross section of the sinter bridge	$\mathrm{m^2}$
$A_{\mathrm{visible},i}$	Visible area of a particle (in pixels)	-
$\hat{A}_{\mathrm{c}}$	Normalization constant	-
$C_{\mathrm{C}}(Kn)$	Cunningham slip correction	-
$C(r)$	Radial distribution function	-
D	Diffusion coefficient	$\mathrm{m^2s^{-1}}$
D_{f}	Fractal dimension	-
D_{fm}	Fractal dimension of mobility	-
D_{s}	Euclidean dimension of space	-
E_{kin}	Kinetic energy	J
E_{sb}	Young's modulus sinter bridge	Pa
E_{wall}	Young's modulus of the wall	Pa
F	Force	N
F_{CPT}	Force from the Colloidal Probe Technique	N
F_{adh}	Adhesion force	N
F_{cap}	Capillary force	N
F_{n}	Normal force	N
F_{nb}	Non-bonded force	N
$F_{\mathrm{nb,n}}$	Non-bonded force (normal direction)	N
$F_{\mathrm{nb,r,max}}$	Maximum rolling friction force	N
$F_{\mathrm{nb,t}}$	Non-bonded force (tangential direction)	N
F_{sb}	Sinter bridge force	N
$F_{\mathrm{sb,n}}$	Sinter bridge force (normal direction)	N
$F_{\mathrm{sb,t}}$	Sinter bridge force (tangential direction)	N
F_{solv}^{0}	Force amplitude solvation force	N

Symbol	Description	Unit
F_{solv}	Solvation force	N
F_{vdw}	Van der Waals force	N
I	Moment of inertia	m^4
I_{FSP}	Intersection distance FSP	m
J	Polar moment of inertia	m^4
L_0	Straight-line flow length	m
$L_{\text{sb},0}$	Initial length of the sinter bridge	m
$L_{\text{sb,n}}$	Normal displacement of the particles connected *via* a sinter bridge	m
$L_{\text{sb,t}}$	Tangential displacement of the particles connected *via* a sinter bridge	m
M	Cummulated mass	kg
$M_{\text{sb,n}}$	Torque on sinter bridge normal direction	Nm
$M_{\text{sb,t}}$	Torque on sinter bridge tangential direction	Nm
$N_{\text{p,a}}$	Particles per aggregate	-
N	Number of particles	-
$N_{\text{c,3D}}$	Number of clusters in 3D	-
N_{grid}	Number of gridpoints	-
$N_{\text{p,3D}}$	Cluster size in 3D	-
$N_{\text{p,c,2D}}$	Cluster size in 2D	-
$N_{\text{p,c,3D}}$	Number of primary particles in 3D	-
$N_{\text{p,c}}$	Cluster size	-
N_{p}	Number of primary particles	-
N_{walker}	Number of walkers (zeno)	-
$dN_{\text{p,c}}$	Deviation of cluster size	-
$\tilde{N}_{\text{p,c,3D}}$	Computed cluster size from correlation	-
P_{p}	Gridpoints within particles	-
P_{total}	Total gridpoints	-
Q_0	Number based cummulated probability distribution	-
Q_2	Area based cummulated probability distribution	-
R	Gas constant	$\text{J mol}^{-1}\text{K}^{-1}$
$R_{\text{e,Film}}$	Film electrical resistance	Ω
$R_{\text{e,Sensor}}$	Sensor electrical resistance	Ω
$R_{\text{e,Tunnel}}$	Electrical tunneling resistance	Ω
$R_{\text{e,V}}$	Electrical resistance of the resistor in series with the film	Ω
$R_{\text{e,bulk}}$	Bulk electrical resistance of a particle	Ω
$R_{\text{e,corner}}$	Electrical resistance of film with electrodes at the corners	Ω
$R_{\text{e,nb}}$	Electrical resistance of a non-bonded contact	Ω

Symbol	Description	Unit
$R_{e,sb}$	Electrical resistance of a sinter bridge contact	Ω
$R_{e,straightLine}$	Electrical resistance of a straight line connecting the gas sensor electrodes	Ω
SSA_{filter}	Specific surface area of a glass fiber filter	$m^2\ g^{-1}$
SSA_{powder}	Specific surface area of particle powder or film	$m^2\ g^{-1}$
SSA_{sample}	Specific surface area of a sample (filter and powder)	$m^2\ g^{-1}$
T	Temperature	K
U_0	Voltage drop	V
U_{Film}	Voltage drop across the film	V
V_{eq}	Equivalent volume of simulated and experimental films	m^3
V_m	Molecular volume	$m^3\ mol^{-1}$
V_p	Cummulated volume of the particles	m^3
$V_{p,f}$	Pore volume of the filter	m^3
$V_{p,pfilm}$	Specific pore volume of the particle film	$m^3\ kg^{-1}$
$V_{p,sample}$	Pore volume of the sample (powder and filter)	m^3
V_{tot}	Total volume of the simulation domain	m^3
$a_{0,2D}$	Fitting constant	-
a_0	Fitting constant	-
$a_{1,2D}$	Fitting constant	-
a_1	Fitting constant	-
a_2	Fitting constant	-
a_3	Fitting constant	-
b_0	Initial number of sinter bridges	-
b_{broken}	Number of broken sinter bridges	-
b_t	Number of broken sinter bridges due to tangential stress	-
c	Coordination number	-
c_{2D}	Coordination number in 2D	-
$c_{Het,2D}$	Heterogeneous coordination number in 2D	-
$c_{Het,2D,norm}$	Heterogeneous coordination number in 2D, normalized to coordination number in 2D	-
$c_{Het,3D}$	Heterogeneous coordination number in 3D	-
$c_{Het,max,3D}$	Maximum heterogeneous coordination number in 3D	-
$c_{Het,min,3D}$	Minimum heterogeneous coordination number in 3D	-
c_{Het}	Heterogeneous coordination number	-
c_{Hom}	Homogeneous coordination number	-
$c_{mean,3D}$	Mean coordination number in 3D	-
c_{nb}	Non-bonded coordination number	-
c_r	Coefficient of restitution	-

Symbol	Description	Unit
dc_{Het}	Deviation of coordination number	-
$\bar{c}_{\text{Het,3D}}$	Computed heterogeneous coordination number in 3D	-
d, d_{ij}	Distance between the particle surfaces	m
d_{Pore}	Pore diameter	m
d_{Tunnel}	Electron tunneling distance	m
d_0	Distance of the centers of mass of two primary particles	m
d_{h}	Particle distance considering the thickness of the water layer	m
f_{c}	Cutoff function	-
f_{d}	Friction factor	kg s^{-1}
f_{d}^{*}	Dimensionless drag	-
$f_{\text{d,CD}}$	Friction factor Chan & Dahneke	kg s^{-1}
$f_{\text{sb,d}}$	Sinter bridge distance threshold	-
$f_{\text{visible},i}$	Visible fraction of a particle	-
h	Water layer thickness	m
h_{n}	Compressed water layer thickness	m
h_{rise}	Water rising level	m
i	Particle index	-
j	Particle index	-
k_{B}	Boltzmann constant	J K^{-1}
k_{f}	Fractal prefix	-
k_{fm}	Fractal prefix of mobility	-
k_{n}	Normal contact stiffness	N m^{-2}
l_{cap}	Inner radius of meniscus	m
m_i	Mass of a particle i	kg
m_{p}	Mass of a particle	kg
n_{S}	Number of straight lines	-
p	Compaction pressure	Pa
p_{d}	Packing density	-
$p_{\text{d,c}}$	Percolation threshold	-
$p_{\text{g,0}}$	Saturation pressure of a gas	Pa
$p_{\text{g}}/p_{\text{g,0}}$	Relative humidity	-
p_{g}	Pressure of a gas	Pa
q_0	Number based probability distribution	m^{-1}
q_2	Area based probability distribution	m^{-1}
r	Incremental distance	m
r_{H}	Hydrodynamic radius	m
r_{S}	Smoluchowski radius	m
r_{cap}	Outer radius of meniscus	m

Symbol	Description	Unit
r_{d}^2	Squared residuum	-
r_{g}	Radius of gyration	m
r_{k}	Kelvin radius	m
r_{m}	Mobility radius	m
r_{p}	Primary particle radius	m
r_{ph}^*	Derjaguin approximation of the radius	m
r_{ph}	Radius of the primary particle with water layer	m
r_{sb}	Radius of the sinter bridge	m
t	Time	s
Δt	Time step	s
t_{c}	Collision time	s
t_{f}	Coalescence time	s
t_{layer}	Thickness of isolating layer	m
v_0	Straight-line imbibition velocity	m s^{-1}
v_{n}	Normal velocity	m s^{-1}
v_{z}	Thermophoretic velocity	m s^{-1}
w_{fil}	Mass fraction of the filter	-
x_{Film}	Width of the film (x-direction)	m
x_{Het}	Ratio of the two components in heterogeneous aggregates	-
x_{Sensor}	Width of the sensor (x-direction)	m
y_{Film}	Length of the film (y-direction)	m
y_{Sensor}	Length of the sensor (y-direction)	m
z_{AFM}	Distance of the cantilever motion	m
z_{Film}	Height of the film	m
z_{Sensor}	Height of the sensor	m

List of Vectors

Symbol	Description	Unit
$\mathbf{C}_{\mathrm{diff}}$	Random diffusion force vector	N
$\mathbf{F}$	Force vector	N

Symbol	Description	Unit
$\mathbf{F}_{\text{adh}}$	Adhesion force vector	N
$\mathbf{F}_{\text{cap}}$	Capillary force vector	N
$\mathbf{F}_{\text{n}}$	Normal force vector	N
$\mathbf{F}_{\text{nb,n}}$	Non-bonded normal contact force vector	N
$\mathbf{F}_{\text{nb,n,d}}$	Non-bonded normal damping force vector	N
$\mathbf{F}_{\text{nb,n,r}}$	Non-bonded normal repulsive force vector	N
$\mathbf{F}_{\text{nb,t}}$	Non-bonded tangential contact force vector	N
$\mathbf{F}_{\text{sb,t}}$	Sinter bridge tangential force vector	N
$\mathbf{F}_{\text{sb,n}}$	Sinter bridge normal force vector	N
$\mathbf{F}_{\text{solv}}$	Solvation force vector	N
$\mathbf{F}_{\text{th}}$	Thermophoretic force vector	N
$\mathbf{M}_{\text{nb,r}}$	Non-bonded rolling torque vector	N m
$\mathbf{M}_{\text{sb,n}}$	Sinter bridge normal torque vector	N m
$\mathbf{M}_{\text{sb,t}}$	Sinter bridge tangential torque vector	N m
$\mathbf{a}_i$	Acceleration vector of a primary particle i	m s^{-2}
$\mathbf{n}_{ij}$	Unit vector in normal direction	-
$\mathbf{r}_0$	Position vector of the center of mass	m
$\mathbf{r}_i$	Position vector of a primary particle i	m
$\mathbf{t}_{ij}$	Unit vector tangential direction	-
$\mathbf{v}_i$	Velocity vector of a primary particle i	m s^{-1}
$\mathbf{w}_i$	Vector of rotational displacement of a primary particle i	m