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Calculation of double layer interaction between colloidal aggregates

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ABSTRACT

This paper examines the interaction between the electric double layers of aggregates. Commonly, rather simplified models are used like the approximation of primary particle interaction (APPI), which just considers the interaction of the closest pair of primary particles having a double layer as if they were isolated. However, for nanoparticles the double layer thickness may be in the same order of magnitude as the particle size or even larger, what leads to a considerable double layer overlap inside the aggregates and between two interacting aggregates. Consequently, such approximations will fail. The paper presents a numerical scheme for the double layer interaction of arbitrarily shaped aggregates, which can e.g. help to establish criteria for the applicability of approximate models. The calculation employs a singularity method, which is based on the linearised Poisson–Boltzmann equation. Additionally, a linear model for charge regulation is implemented. The impact of charge regulation and double layer thickness were studied for fractal DLCA aggregates and hexagonal closed-packed aggregates.

1. Motivation

It is commonly accepted that the macroscopic properties of suspensions are determined by concentration, size and shape of the particles as well as by the interparticle forces. The latter are of particular relevance for colloidal material and affect i. a. the microscopic structure, the viscosity and the stability of the suspension. The interactions between the particles may be attractive or repulsive. The main attractive component is the van-der-Waals interaction, whereas the repulsion is (at least in aqueous systems) primarily due to the interaction between the electric double layers surrounding any charged particle in a liquid medium. For spherical particles the total effect of van-der-Waals and double layer interaction is described by the DLVO theory named after Derjaguin, Landau, Verwey und Overbeek (e.g. [1]).

Particulate material especially with particles in the colloidal size range (<1 μm) is frequently encountered in form of aggregates, e.g. carbon black or fumed silica. The structure of the aggregates strongly depends on factors like the particle concentration, the flow conditions and the interparticle forces in the aggregation process. Consequently there exists a huge variety of potential particle configuration within an aggregate.

Hitherto, there is no clear understanding on how the aggregate structure affects the double layer interaction between two aggregates. That is mainly due to the absence of simple analytical expressions for the interaction between aggregates and the diversity of aggregate configurations. In particular the formation of double layers inside an aggregate and the interaction with the double layers of neighboring aggregates involves the overlap of the double layers and correspondingly charge regulation. For that reason double layer interaction is intrinsically a many-body phenomenon.

A common approximation (e.g. [2–6]) for the interaction of aggregates is to ignore any interaction term but that of the closest pair of primary particles, which is assumed to have a double layer as in the isolated case (approximation of primary particle interaction – APPI). However, its validity has not been examined sufficiently for aggregates of nanoparticles, i.e. particles whose size is in the typical range of the double layer thickness (e.g. the Debye length of a 0.001 M NaCl solution is 10 nm). There is no quantitative criterion that can be employed. Another approximation consists in adding up all pairwise interactions between the primary particles. As in APPI the individual double layers are considered unchanged compared to the isolated case (e.g. [7,8]). Quantitative limits of this approach are not discussed. Therefore, this paper addresses the calculation of the double layer interaction energy between aggregates by refining an existing calculation scheme [9]. It employs this method for a qualitative discussion on the impact of charge regulation and double layer thickness for selected aggregate geometries. Eventually comparison is made with the approximate solutions.

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Nomenclature

Symbols

$\mathbf{A}$	coefficient matrix
A	surface (m^2)
a	radius of primary particles (m)
a_{jl}	coefficient (–)
b_j	coefficient (–)
c	ion concentration (mol/L)
F	Faraday constant (C/mol)
h	minimum surface distance (m)
J	surface specific free energy (J/m^2)
K	regulation capacity (C/V)
N	aggregation number (–)
$\mathbf{n}$	normal vector directed to sphere centre (–)
n_{cp}	number of control points per particle (–)
n_{oc}	number of off-centre singularities per particle (–)
q	weight (V·m)
R	gas constant (J/mol/K)
R	distance between singularity and control point (m)
$\mathbf{r}$	position vector (m)
r_{agg}	radius of aggregates (m)
r_{kl}	centre-to-centre distance between primary particles k and l (m)
S	parameter for charge regulation (C)
T	temperature (K)
V_{DL}	interaction free energy (J)
ε_m	static permittivity of the liquid medium (C/V/m)
κ	Debye-Hückel parameter (m^{-1})
ν_i	valency of ion i (–)
σ	surface charge (C)
ψ	electric potential (V)

Indices

0	surface
*	normalised
∞	bulk
cp	control point
oc	off-centre
iso	isolated

Abbreviations

APPI	approximation of primary particle interaction
BEM	boundary element method
DLCA	diffusion limited cluster–cluster aggregation
FDM	finite difference method
FEM	finite element method
hcp	hexagonal closed-packed
ME	multipole expansion
PBE	Poisson–Boltzmann equation
PS	porous sphere

2. Theory of double layer interaction

2.1. Basic equations

Double layers result from the spontaneous charging of particle surfaces in a liquid medium (e.g. due to adsorption or dissociation). They are built of fixed charges on the surface and in the Stern layer and of mobile ions in the diffuse layer. For the sake of simplification the existence of the Stern layer is ignored within this paper. Double layers of neighboring particles interact with each other because of the electrostatic and osmotic forces between the ions and the surfaces. The interaction energy is determined by the concentration of ions c_i (or mobile charges) inside the diffuse layer and by the corresponding potential field $\psi(\mathbf{r})$. The relationship between these parameters can be described by the Poisson–Boltzmann equation (PBE), when any effect related with the discreteness of charge and the ion volume is ignored:

$$\Delta\psi = -\frac{1}{\varepsilon_m}\sum \mathrm{F}\nu_i c_i^\infty \exp\left(-\frac{\nu_i\psi\mathrm{F}}{\mathrm{R}T}\right) \tag{1}$$

Here F, R and T are the Faraday constant, the gas constant and the absolute temperature, respectively. The parameter ε_m is the static permittivity of the liquid, c_i^∞ the bulk concentration of the ionic species i and ν_i its valency.

Analytical solutions of the Poisson–Boltzmann Eq. (1) exist only for simple geometries and/or symmetrical electrolytes. Even for an isolated sphere there is no exact analytical solution. For that reason the PBE is frequently employed in its linearised expression (Debye–Hückel approximation):

$$\Delta\psi = -\kappa^2\psi \tag{2}$$

where κ is the Debye–Hückel parameter:

$$\kappa^2 = \frac{\mathrm{F}^2\cdot\sum \nu_i^2 c_i^\infty}{\varepsilon_m \mathrm{R}T} \tag{3}$$

The inverse $1/\kappa$, the Debye length, is a rough estimate for the thickness of the double layer. By means of the linearised PBE (2) the potential field ψ inside the diffuse layer can be analytically solved for several geometric situations. For an isolated sphere with the surface potential $\psi_0{}^{iso}$ one obtains [10]:

$$\psi^{iso} = \psi_0^{iso}\frac{a}{r}\cdot e^{-\kappa(r-a)} \tag{4}$$

Interaction of double layers occurs only when their diffuse parts overlap, what results in changes of the ion concentration and of the potential distribution. These alterations in the diffuse layers affect the dissociation and adsorption equilibria and thus the surface charge distribution. Strong overlap may even change the sign of the surface charge σ_0 [11–14]. The way and the extent of the charge regulation is very material specific. In general, a non-linear relationship between the surface charge and the surface potential has to be established. For that reason, most papers refer to the two limiting cases of a constant surface potential and a constant surface charge [11,12,15–17].

In order to calculate the interaction energy it is necessary to assume a model for the charge regulation. Carnie et al. proposed a linear approach [18]:

$$\sigma_0 = S - K\psi_0 \tag{5}$$

which is appropriate, when the linearised PBE is used. The regulation parameters S and K allow for a broad variation of charge regulation regimes: When the regulation capacity K vanishes the constant charge (CC) case is obtained. For very huge regulation capacities ($K \gg \varepsilon_m\kappa$) the surface potential keeps constant (CP). Additionally, Carnie et al. introduced a "canonical intermediate" case of charge regulation [18,19], which is achieved when $K = \varepsilon_m\kappa$.

The set of basic equations is completed by the following boundary condition:

$$\sigma_0 = \varepsilon_m \cdot \nabla\psi \cdot \mathbf{n}, \tag{6}$$

This equation holds true for small permittivities of the particles ($\varepsilon_P \ll \varepsilon_m$). If this restriction is not fulfilled, the potential distribution inside the particles has to be described as well. According to Carnie and Chan [18], the error in using Eq. (6) for particles with a