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UMI
Collision Efficiency Of Colloidal Particles and Morphology of Deposits: Implications for Membrane Filtration

by

Volodymyr Valentinovich Tarabara

A THESIS SUBMITTED
IN PARTIAL FULFILMENT OF THE
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Master of Science

Approved, Thesis Committee:

Mark R. Wiesner, Professor, Chair
Environmental Science and Engineering

Joseph B. Hughes, Associate Professor
Environmental Science and Engineering

S. Scott Collis, Assistant Professor
Mechanical Engineering and Materials Science

Rudolf H. Riedl, Faculty Fellow
Electrical and Computer Engineering

Houston, Texas

January, 2001
ABSTRACT

Collision Efficiency of Colloidal Particles and Morphology Deposits: Implications for Membrane Filtration

by

VOLOYMYR V. TARABARA

On-lattice Monte Carlo simulations were performed to investigate the effect of collision efficiencies $\alpha$ of particles on the morphology of heterodeposits. The model predicts that the structure and surface chemistry of such deposits are determined by particles with large and small values of $\alpha$, correspondingly. The case of homodeposition onto a rough substrate was also studied. The best "memory" of the deposit measured as a rate of decay of the Fourier amplitude corresponding to the wavelength of the initial roughness, was found to correspond to intermediate values of $\alpha$.

Cross-flow membrane filtration experiments using monodisperse latex suspensions were performed for validation of the Sethi's extended model. A slightly more complex structure at the cake-suspension interface was hypothesized to explain differences between model calculations and experiments. A representation of the cake with a gradually changing solids concentration allowed for better matching of the extended model and experimental results for particles diffusively depositing onto membrane.
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Нашему Св-кровищу
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\[ \alpha_{\text{red}-\text{red}} = 10^{-2}, \quad \alpha_{\text{red}-\text{black}} = 10^{-3}, \quad \alpha_{\text{black}-\text{black}} = 10^{-1}; \quad d_p = 0.1 \mu m \]

b) \[
\alpha_{\text{red}-\text{red}} = 10^{-2}, \quad \alpha_{\text{red}-\text{black}} = 10^{-2}, \quad \alpha_{\text{black}-\text{black}} = 10^{-1}; \quad d_p = 0.1 \mu m
\]

c) \[
\alpha_{\text{red}-\text{red}} = 10^{-1}, \quad \alpha_{\text{red}-\text{black}} = 10^{-3}, \quad \alpha_{\text{black}-\text{black}} = 10^{0}; \quad d_p = 0.1 \mu m
\]

d) \[
\alpha_{\text{red}-\text{red}} = 10^{-1}, \quad \alpha_{\text{red}-\text{black}} = 10^{-3}, \quad \alpha_{\text{black}-\text{black}} = 10^{-1}; \quad d_p = 0.1 \mu m
\]

e) \[
\alpha_{\text{red}-\text{red}} = 10^{-2}, \quad \alpha_{\text{red}-\text{black}} = 10^{-1}, \quad \alpha_{\text{black}-\text{black}} = 10^{-2}; \quad d_p = 0.1 \mu m
\]

f) \[
\alpha_{\text{red}-\text{red}} = 10^{-3}, \quad \alpha_{\text{red}-\text{black}} = 10^{-5}, \quad \alpha_{\text{black}-\text{black}} = 10^{-2}; \quad d_p = 0.1 \mu m
\]

g) \[
\alpha_{\text{red}-\text{red}} = 10^{-2}, \quad \alpha_{\text{red}-\text{black}} = 10^{-5}, \quad \alpha_{\text{black}-\text{black}} = 10^{-1}; \quad d_p = 0.1 \mu m
\]
h) \[ \alpha_{\text{red-red}} = 10^{-2}, \quad \alpha_{\text{red-black}} = 10^{-3}, \quad \alpha_{\text{black-black}} = 10^{-1}; \quad d_p = 0.5\mu m \]

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<th>Description</th>
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<td>BA</td>
<td>Ballistic Aggregation</td>
</tr>
<tr>
<td>CF</td>
<td>Constant Flux</td>
</tr>
<tr>
<td>CP</td>
<td>Constant Pressure</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DLA</td>
<td>Diffusion-Limited Aggregation</td>
</tr>
<tr>
<td>DLVO</td>
<td>Derjaguin-Landau-Verwey-Overbeek Theory</td>
</tr>
<tr>
<td>FPA</td>
<td>Fracture Profile Analysis</td>
</tr>
<tr>
<td>GSPD</td>
<td>Growth Sites Probability Distribution</td>
</tr>
<tr>
<td>MFA</td>
<td>Multifractal Analysis</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle Size Distribution</td>
</tr>
<tr>
<td>RLA</td>
<td>Reaction-Limited Aggregation</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
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1. Introduction

A large proportion (often 40-90%) of trace chemical compounds may be adsorbed on marine (Martin and Dai 1995) and freshwater (Guo and Santschi 1997) colloids via covalent, electrostatic, or hydrophobic interactions (Stumm and Morgan 1996). When associated with colloids and other particles, pollutants may either be deposited onto sediments or within porous media or they may be transported by particulates over long distances from a contamination source (McCarthy and Zachara 1989), (Buffie and Leeuwen 1992). Effective separation methods are needed to recover the adsorbed pollutants.

Membrane filtration is often the method of choice for purifying (or concentrating) and fractionating colloids and solutes of moderate-to-high molecular weight (Blatt, Dravid et al. 1970), (Belfort 1984), (Wiesner and Chellam 1999). During filtration, the materials being separated may deposit onto the membrane surface. This fouling layer of materials accumulated on and/or near the membrane surface imparts a hydrological resistance to the permeate flow, in addition to the inherent resistance imparted by the membrane itself. The fouling layer consists of a) so-called “cake”, a layer of substantially different rheological properties from that of the overlying suspension, and b) concentration-polarization layer, a transition layer between the cake and the bulk suspension. Generally, the resistance to permeate flow exerted by the fouling layer is a complex function of a) concentration, size, shape and density
of particles, b) physical and chemical properties of the liquid phase, c) parameters of external fields applied to the system (such as transmembrane pressure and tangential flow), d) surface chemistry of particles, e) morphology and surface chemistry of the membrane, and f) membrane module design. Detailed understanding of mechanisms of formation and properties of the fouling layer (cake) would result is in the ability to predict membrane module performance and to minimize fouling (Belfort, Davis et al. 1994), (Wiesner 1999).

The goal of the present work was to expand our knowledge of particle deposition in membrane systems and, specifically, to explore the role of deposit morphology in the fouling process. In approaching this problem, membrane filtration experiments, computer modeling of membrane fouling, and Monte Carlo simulations of particle deposition were performed.

Filtration experiments performed in the present work were aimed at the experimental validation of a previously proposed (Sethi and Wiesner 1997) extended model for membrane fouling that incorporated particle transport mechanisms of Brownian diffusion, shear-induced diffusion, inertial lift and concentrated flowing layers. The model predicts a range of particles sizes for which the relative cake build-up is maximized due to a superposition of two effects: a) net minimum in back-transport mechanisms, and b) an increase in specific cake resistance with a decrease in particle size. Discrepancies were found between experimental results and (extended) model. This finding was a motivation to modify the extended model to account for more complex structure
at the cake-suspension interface. A representation of the cake with a gradually changing solidosity allowed for better matching of the extended model with experimental results in the case of small, diffusively depositing particles.

Total cake resistance, the most important factor determining the membrane system performance, is correlated with properties of the solvent, with properties of the particulate phase as well as with characteristics of the membrane module. To establish this correlation, the influence of key operational parameters (particle size, cross-flow velocity, fluid viscosity, etc.) on the cake morphology had to be studied. For this purpose, Monte Carlo simulations of particle deposition were performed. This approach has proven to be a useful tool in studying the structure of deposits (Meakin, Ramanial et al. 1986), (Kim and Rajagopalan 1991), (Veerapaneni 1996), (Meakin 1999). In the present work, the hypothesis that morphology of fouling layers is determined by long-range transport of particles and short-range chemical interactions between particles was tested. A Monte Carlo deposition model was developed in which collision efficiency ($\alpha$) served as a parameter to account for short-range chemical interactions that dominate the attachment stage of the deposition. Further, the influence of $\alpha$ on the morphology of deposits was investigated.

Another factor that may, in some cases, have a dominant influence on the morphology of deposits is the profile of the underlying substrate onto which the deposition occurs. The “memory” of a depositing (fouling) layer with respect to the substrate (membrane) has important implications not only for colloidal fouling of membranes and membrane manufacturing, but also for controlling
undesirable deposition on rough surfaces and scaling within water pipes. In the present work, the influence of $\alpha$ on the decay of the initial roughness over the course of deposition was studied. The case of a diffusive long-range transport regime as representative of the colloidal deposition from the suspended phase was considered.
2 Literature Review

2.1 Flux decline in Cross-flow Membrane Filtration of Colloidal Suspensions

2.1.1 Background

With membrane filtration gaining popularity as a unit process in water treatment, the physical chemical processes involved in filtration become a focus of intensive research (Belfort, Davis et al. 1994), (Wiesner and Chellam 1999).

A major limitation of membrane filtration is the problem of membrane fouling. At the initial stage of filtration, permeate flux is directly proportional to the transmembrane pressure. When contaminants are present in the water, higher pressures produce a nonlinear dependence of flux on pressure drop. Eventually, permeate flux reaches a limiting value and permeate flux becomes independent of the pressure drop.

Two modes of operation associated with different membrane module geometries are used - dead-end filtration and cross-flow filtration. In dead-end operation all fluid introduced to the membrane must pass through the membrane to exit the membrane module. In cross-flow filtration (Figure 2.1), as name implies, the feed stream is directed tangentially to the membrane surface and a portion of the tangentially flowing “concentrate” exits the module while the rest of the fluid exits as permeate. The goal of the tangential flow is to arrest the growth of the fouling layer and thereby retain a higher permeate flux.
Figure 2.1 Schematic of cross-flow filtration. Tangential flow effectively reduces the buildup of rejected materials on the membrane surface (adapted from Sethi (Sethi and Wiesner 1997))

A better understanding of the fouling process would aid in predicting the performance of membrane systems and minimizing fouling.

2.1.2 Formation and Properties of Fouling Layer

Fouling occurs as a result of transport of materials to the membrane surface in the course of filtration. In ultra- and microfiltration the materials retained by the membrane are particulates or macromolecules. A layer of particles accumulated on and/or near the membrane surface imparts a hydrological resistance to the permeate flow in addition to the resistance imparted by the membrane. The total hydrologic resistance of the fouled membrane may be approximately treated as several resistances in series:
\[ R_{\text{tot}} = R_m + R_{\text{plug}} + R_{\text{cake}} + R_{\text{CP}} \]  \hspace{1cm} (2.1.1)

where

- \( R_m \) - membrane resistance, the intrinsic property of the membrane.

- \( R_{\text{plug}} \) - resistance due to adsorption of particles on pore walls and resulting pore plugging. This type of fouling occurs at the initial stage of filtration and is irreversible.

- \( R_{\text{cake}} \) - resistance imparted by the immobilized layer of particles deposited on the membrane.

- \( R_{\text{CP}} \) - resistance of the concentration polarization layer of particles accumulated near membrane.

Thus, effect of membrane fouling includes several phenomena:

- a) pore plugging, which occurs at the initial stages of filtration,
- b) formation of concentration polarization layer,
- c) cake buildup, which may or may not occur depending on the filtration regime chosen.

Generally, \( R_{\text{cake}} \) and \( R_{\text{CP}} \) are complex functions of

- a) concentration, size, shape and density of particles,
- b) surface chemistry of particles,
- c) morphology and surface chemistry of the membrane,
- d) physical and chemical properties of the liquid phase,
- e) parameters of external fields present in the system (transmembrane pressure and cross-flow included),
f) membrane module design.

The following sections present an overview of several models for predicting steady-state permeate flux and/or transient permeate flux.

2.1.3 Review of Models Based on Different Particle Transport Mechanisms

2.1.3.1 Film Theory

Blatt et al. (Blatt, Dravid et al. 1970) proposed a model in which at steady state the convective transport of particles to the membrane surface is balanced by diffusive flux of particles from the interface to the bulk solution. The material balance is then given by a one-dimensional convective-diffusion equation:

\[ J \frac{d\phi}{dx} - D \frac{d^2\phi}{dx^2} = 0 \]  \hspace{1cm} (2.1.2)

where \( \phi \) – foulant solid fraction,

\( x \) - distance from the membrane surface,

\( J \) - water flux,

\( D \) - particle diffusion coefficient.

Integration of equation (2.1.2) across the polarization boundary leads to

\[ J\phi - D \frac{d\phi}{dx} = 0 \]  \hspace{1cm} (2.1.3)

Here,

\( J\phi \) - the particle flux toward the membrane, and
\[ D \frac{d\phi}{dx} \] particle flux away from the membrane by back diffusion.

Integration of (2.1.3) gives

\[ J = \frac{D}{\delta} \ln \left( \frac{\phi_\infty}{\phi_b} \right) = K \ln \left( \frac{\phi_\infty}{\phi_b} \right) \]  

(2.1.4)

where

\[ \phi_\infty, \phi_b \] particle volume fractions at the edge of the cake layer and in the bulk suspension, correspondingly.

\[ \delta \] boundary layer thickness

\[ K = \frac{D}{\delta} \] length-averaged mass transfer coefficient which is usually estimated from the Leveque solution (Porter 1972):

\[ K = 0.81 \left( \frac{\dot{\gamma}_0 D}{L} \right)^{\frac{1}{3}} \]  

(2.1.5)

where \( L \) - the tube or channel length, and

\[ D \] Brownian diffusivity of a particle, given by Einstein-Sutherland equation:

\[ D = \frac{kT}{f} \]  

(2.1.6)

\( f \) being the frictional coefficient. For spherical rigid colloidal particle of size much bigger then hydrated layer \( f = 6\pi \mu a_p \).

The length-averaged permeate flux is equal then

\[ J = 0.114 \left( \frac{\dot{\gamma}_0 k^2 T^2}{\mu_0 \alpha_p^2 L} \right)^{\frac{1}{3}} \ln \left( \frac{\phi_\infty}{\phi_b} \right) \]  

(2.1.7)

If particles are nonadhesive, \( \phi_\infty \) has been chosen to be equal to the maximum packing density of nondeformable monodisperse particles typically
taken to be 0.60 +/- 0.02.

2.1.3.2 Inertial lift

Particles rotating in the fluid experience a lift force. The rotation may result from a velocity gradient or may be caused by particle contact with or rebound from a surface. The difference in pressures on different sides of the rotating particle gives rise to a lift force. The analysis for low Reynolds numbers results in the following expression for the lift force (Saffman 1965):

\[ \bar{F} \propto \mu D \bar{u} - \bar{v} \sqrt{\text{Re}_g} \]  \hspace{1cm} (2.1.8)

where \( \text{Re}_g \) - shear Reynolds number:

\[ \text{Re}_g = \frac{D^2}{v} \frac{du}{dy} \]  \hspace{1cm} (2.1.9)

Belfort and coworkers (Green and Belfort 1980) have proposed that the backtransport of particles from the membrane to suspension may be a factor in accounting for higher than predicted permeate fluxes, thereby resolving the so-called "flux paradox". In the approximation of very dilute suspension and fast laminar flow over thin fouling layer, the following expression for the lifting velocity was obtained:

\[ J = v_{lo} = \frac{0.036 \rho_a a^3 \gamma_o^2}{\mu_o} \]  \hspace{1cm} (2.1.10)

Thus, inertial lift velocity is expected to be significant for the case of sufficiently high velocity gradients and/or particle size. By this analysis, particles of a given size should not reach the membrane if the permeate flux is below
some critical value.

2.1.3.3 Surface Transport

In the surface transport models, the steady state is considered to be a result of a balance between particle deposition due to permeation drag and convective transport of particles along the membrane surface toward the filter exit. To analyze this process quantitatively, the force and torque balances on the particle is performed. Knowledge of tangential and hydrodynamic (lift, drag and buoyant) forces acting on particle as well as surface morphology of the cake (and, initially, the membrane) is needed for this analysis. Usually, the protrusion height distribution is taken to be randomly distributed. The minimal protrusion height necessary for a particle to be deposited was estimated (Stamatakis and Tien 1993):

\[
h_{\text{min}} = \frac{d_p}{2} \left[ 1 - \frac{1}{\left( \frac{F_p}{F_q} \right)^{\frac{1}{2}} + 1} \right]
\]

(2.1.11)

where \( F_p \) - tangential force,

\( F_q \) - normal force on the particle

Under the simplifications of negligible gravitational, lift and adhesive forces, the following expression for steady-state permeate drag has been
obtained (Belfort, Davis et al. 1994):

\[ J = 2.4 a_p \dot{\gamma} (a_p^2 p \dot{\epsilon}_c) \frac{2}{5} \cot \theta \]  

(2.1.12)

where \( \theta \) - angle of repose.

Diffusive transport of particles is not considered in the surface models, and therefore, the applicability of these models is limited to large particles.

2.1.3.4 Shear-induced hydrodynamic diffusion

Shear-induced diffusion occurs as a result of interparticle interactions in shear flows. It was first measured by Eckstein et al. (Eckstein, Bailey et al. 1977) for \( 0.2 < \phi_b < 0.45 \):

\[ D_s = 0.3 \dot{\gamma}_0 a_p^2 \]  

(2.1.13)

Zydny and Colton (Zydny and Colton 1986) replaced Brownian diffusivity \( (D_B \propto d_p^{-1}) \) with shear-induced diffusivity \( (D_s \propto d_p^2 \dot{\gamma}_0) \), which lead for the following expression for the length-averaged permeate flux:

\[
\begin{cases}
\text{for } \phi_w - \phi_b \ll \phi_w : & J = 0.078 \dot{\gamma}_0 \ln \left( \frac{\phi_w}{\phi_b} \right) \left( \frac{a_p}{L} \right)^4 \frac{1}{3} \\
\text{for } \phi_b \ll \phi_w : & J = 0.126 \dot{\gamma}_0 \left( \frac{a_p \phi_w}{L \phi_b} \right)^{\frac{1}{3}} 
\end{cases}
\]  

(2.1.14)

Davis and Sherwood (Davis and Sherwood 1990) considered shear-
induced diffusion as a dominant transport mechanism and incorporated concentration dependence of viscosity (Einstein equation)

$$\mu(\phi) = \mu_0(1 + \frac{5}{2}\phi) \quad (2.1.15)$$

and shear-induced diffusivity (Leighton and Acrivos 1987)

$$D_s(\phi) = 0.33\dot{\gamma} a_0^2 \phi^2 (1 + 0.5e^{8.8\phi}) \quad (2.1.16)$$

into their model. For suspension of nonadhesive monodisperse rigid spheres with $\phi_s < 0.1$ and $\phi_w = 0.6$ they found

$$J = 0.072\dot{\gamma}_0 \left( \frac{a_0^4 \phi_w}{L \phi_b} \right)^{\frac{1}{3}} \quad (2.1.17)$$

### 2.1.4 Extended Model

The shear-induced diffusivity models of Davis and Acrivos (Davis and Leighton 1987) and Romero and Davis (Romero and Davis 1990) were extended by Sethi and Wiesner (Sethi and Wiesner 1997) to consider Brownian diffusion and inertial lift as well as shear-induced diffusivity and concentrated flowing layers as the transport mechanisms in a transient model of cross-flow microfiltration (Figure 2.2). In the extended model (as in the previous models) Darcy's law is employed to relate permeate flux and cake resistance:

$$J = \frac{\Delta P}{\mu_o (R_m + R_c)} = \frac{J_m}{(1 + R_c / R_m)} \quad (2.1.18)$$
where $\Delta P =$ transmembrane pressure,

$R_m =$ membrane resistance,

$R_c =$ cake resistance, and

$J_m =$ clean membrane flux $= \Delta P / \mu_0 R_m$.

Cake resistance for flat slit geometry was estimated using Carman-Kozeny correlation:

$$R_c = R^* \delta_c = \frac{45 \varphi_c^2}{d_p^2 (1 - \varphi_c)^3} \delta_c$$

(2.1.19)

where $\varphi_c =$ the packing density or solidosity of the cake and $\delta_c =$ cake thickness. $\varphi_c$ was taken to be constant and equal to 0.58. Thus, $R_c$ grows linearly with $\delta_c$ in this model.

To formulate the model, the following equations were employed (in the following expressions axes $x$ and $y$ are in the direction along and normal to the membrane, correspondingly):

a) microscopic momentum balance.

$$\dot{\gamma} = \left| \frac{du}{dy} \right| = \frac{\tau_w}{\mu_0 \mu(\varphi)}$$

(2.1.20)

where

$\tau_w =$ wall shear stress,

$\mu(\varphi) =$ relative viscosity.
It was estimated from experimental correlation (Leighton and Acrivos 1987):

\[ \mu(\phi) = \left( 1 + \frac{1.5\phi}{1 - \phi/\phi_c} \right)^2 \]  

(2.1.21)

The derivation of (2.1.20) was based on several assumptions:

- the particle flowing layer is thin, so that shear stress can be taken as constant; suspension flow is fully developed and in steady-state,

- permeate velocity is much smaller than cross-flow velocity so that concentration and velocity profiles change only slowly with \( x \),

- viscosity is concentration-dependent but the suspension still behaves as a Newtonian fluid.

\textit{b) microscopic particle mass balance}

By omitting the axial diffusion term a reduced form of convective diffusion
equation
\[ - \frac{\partial (u\varphi)}{\partial x} - \frac{\partial (v\varphi)}{\partial y} + \frac{\partial}{\partial y} \left( D \frac{\partial \varphi}{\partial y} \right) = \frac{\partial \varphi}{\partial t} \]  (2.1.22)

was obtained and further simplified by:

- omitting the first term \( -\frac{\partial (u\varphi)}{\partial x} \) describing axial convection (Romero and Davis 1988) because it is small relative to lateral convection term, and

- omitting transient term \( \frac{\partial \varphi}{\partial t} \) because it relates to other terms in (2.1.22) as

\[
\frac{\text{bulk suspension volume fraction}}{\text{average volume fraction within the flowing layer}} \ll 1.
\]

Thus, (2.1.22) was reduced to
\[
\left[ D_b + D_s(\varphi) \right] \frac{d\varphi}{dy} + v_w \varphi = 0
\]  (2.1.23)

c) integrated form of microscopic particle mass balance

By integrating (2.1.23) across the entire cake layer results in the following PDE describing the net transport of particles towards the membrane was obtained:

\[
\frac{\partial}{\partial x} \left[ \delta_c + \delta \int (\varphi - \varphi_b) dy + (\varphi_c - \varphi_b) \delta_c \right] + \frac{\partial}{\partial x} \left[ \delta_c + \delta \int u(\varphi - \varphi_b) dy = (v_w - v_l) \varphi_b \right]
\]  (2.1.24)

The first term in (2.1.24) corresponds to the accumulation of particles at x, the second term - the removal of particles in the axial direction and the third term - to the accumulation of particles in the cake due to the permeate flux.
The local velocity can be determined from (2.1.20). To do that the concentration as a function of distance from membrane should be determined. This is done by integration of (2.1.23) using (2.1.16) and (2.1.21) (Leighton and Acrivos 1987).

After substituting the expression for local velocity into (2.1.24) one arrives at the following expression for particle flux balance:

$$\frac{\partial}{\partial t} \left[ \frac{I_1}{v w} + (\varphi_c - \varphi_b) \delta_c \right] + \frac{\partial}{\partial x} \left( \frac{\tau_w}{\mu_o v_w^2} I_2 \right) = (v_w - v_l) \varphi_b$$  \hspace{1cm} (2.1.25)

where

$$I_1 = \frac{\tau_w a^2 p H_o^2}{\mu_o (H_o - \delta_c)^n} I_{11} + \frac{kT}{6 \pi \mu_o a_p} I_{12}$$  \hspace{1cm} (2.1.26)

$$I_2 = \frac{\tau_w^2 a^4 p H_o^2}{\mu_o^2 (H_o - \delta_c)^{2n}} I_{21} + \frac{kT \tau_w a p H_o^2}{6 \pi \mu_o^2 (H_o - \delta_c)^n} (I_{22} + I_{23}) + \frac{k^2 T^2}{36 \pi^2 \mu_o^2 a_p^2} I_{24}$$  \hspace{1cm} (2.1.27)

$$I_{11} = \int \frac{\dot{\varphi}(\varphi)(\varphi - \varphi_b)}{\mu(\varphi)} d\varphi$$  \hspace{1cm} (2.1.28)
\[ I_{12} = \int_{\varphi_b}^{\varphi_e} \left( \frac{\varphi - \varphi_b}{\varphi} \right) d\varphi \]  
(2.1.29)

\[ I_{21} = \int_{\varphi_b}^{\varphi_w} \int_{\varphi_w}^{\varphi_b} \frac{\hat{D}_{sh}(\varphi')}{\mu^2(\varphi')\varphi'} d\varphi' \left( \varphi - \varphi_b \right) \frac{\hat{D}_{sh}(\varphi)}{\mu(\varphi)} \frac{d\varphi}{\varphi} \]  
(2.1.30)

\[ I_{22} = \int_{\varphi_b}^{\varphi_w} \int_{\varphi_b}^{\varphi_w} \frac{\hat{D}_{sh}(\varphi')}{\mu^2(\varphi')\varphi'} d\varphi' \left( \varphi - \varphi_b \right) \frac{d\varphi}{\varphi} \]  
(2.1.31)

\[ I_{23} = \int_{\varphi_b}^{\varphi_w} \int_{\varphi_b}^{\varphi_w} \frac{d\varphi'}{\varphi'\mu(\varphi')} \left( \varphi - \varphi_b \right) \frac{\hat{D}_{sh}(\varphi)}{\mu(\varphi)} \frac{d\varphi}{\varphi} \]  
(2.1.32)

\[ I_{24} = \int_{\varphi_b}^{\varphi_w} \int_{\varphi_b}^{\varphi_w} \frac{d\varphi'}{\varphi'\mu(\varphi')} \left( \varphi - \varphi_b \right) \frac{d\varphi}{\varphi} \]  
(2.1.33)

Non-dimensionalization of (2.1.25) gives:
\[
\frac{d}{d\hat{x}} \left[ \frac{I_{11}(1 + \beta \hat{\delta})}{Pe_s(1 - \hat{\delta})^n} + \frac{I_{12}(1 + \beta \hat{\delta})}{Pe_b} + (\phi_c - \phi_b) \hat{\delta} \right] \\
+ \frac{d}{d\hat{x}} \left[ (1 + \beta \hat{\delta})^2 \left( \frac{I_{21}}{Pe_s^2(1 - \hat{\delta})^{3n}} + \frac{I_{22} + I_{23}}{Pe_b Pe_s(1 - \hat{\delta})^{2n}} + \frac{I_{24}}{Pe_b^2(1 - \hat{\delta})^n} \right) \right] \\
= \left[ \frac{1}{1 + \beta \hat{\delta}} - \frac{\nu_{lo}}{(1 - \hat{\delta})^{2n}} \right] \phi_b
\] (2.1.34)

where all dimensionless variables are defined in Table 2.1

Sethi used the MacCormack method based on a predictor-corrector methodology to solve (2.1.34) recast as

\[
g \frac{d \hat{\delta}}{d\hat{x}} + h \frac{d \hat{\delta}}{d\hat{x}} = f
\] (2.1.35)

where

\[
g = \frac{I_{11}}{Pe_s} \left[ \frac{\beta}{(1 - \hat{\delta})^n} + \frac{n(1 + \beta \hat{\delta})}{(1 - \hat{\delta})^{n+1}} \right] + \frac{\beta I_{12}}{Pe_b} + (\phi_c - \phi_b)
\] (2.1.36)

\[
h = 2\beta(1 + \beta \hat{\delta}) \left[ \frac{I_{21}}{Pe_s^2(1 - \hat{\delta})^{3n}} + \frac{(I_{22} + I_{23})}{Pe_b Pe_s(1 - \hat{\delta})^{2n}} + \frac{I_{24}}{Pe_b^2(1 - \hat{\delta})^n} \right] \\
+ (1 + \beta \hat{\delta})^2 \left[ \frac{3nI_{21}}{Pe_s^2(1 - \hat{\delta})^{3n+1}} + \frac{2n(I_{22} + I_{23})}{Pe_b Pe_s(1 - \hat{\delta})^{2n+1}} + \frac{nl_{24}}{Pe_b^2(1 - \hat{\delta})^{n+1}} \right]
\] (2.1.37)
\[
f = \varphi_b \left[ \frac{1}{1 + \beta \hat{\delta}} - \frac{\hat{v}_{lo}}{(1 - \hat{\delta})^{3n}} \right]
\]

(2.1.38)

Table 2.1. Definitions of dimensionless variables (Sethi and Wiesner 1997)

<table>
<thead>
<tr>
<th>Dimensionless variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \hat{\delta} ) = ( \frac{\delta_c}{H_o} )</td>
<td>Dimensionless cake thickness</td>
</tr>
<tr>
<td>( \beta ) = ( \frac{H_o \rho_c \gamma^2}{R_m} )</td>
<td>Dimensionless resistance</td>
</tr>
<tr>
<td>( \hat{v}_w ) = ( \frac{v_w}{J_m} = \frac{1}{1 + \beta \hat{\delta}} )</td>
<td>Dimensionless permeate velocity for flat slit</td>
</tr>
<tr>
<td>( \hat{v}_w ) = ( \frac{v_w}{J_m} = \frac{1}{1 - \hat{\delta} \left[ 1 + \beta \ln \left( \frac{1}{1 - \hat{\delta}} \right) \right]} )</td>
<td>Dimensionless permeate velocity for inside-out hollow fiber</td>
</tr>
<tr>
<td>( Pe_b = \frac{6 \pi \mu_c a_p J_m H_o}{kT} )</td>
<td>Brownian diffusion based Péclét number</td>
</tr>
<tr>
<td>( Pe_s = \frac{\mu_o J_m H_o}{\tau_{wo} a_p^2} )</td>
<td>Shear-induced diffusion based Péclét number</td>
</tr>
<tr>
<td>( \hat{v}<em>{lo} = \frac{v</em>{lo}}{J_m} )</td>
<td>Dimensionless inertial lift velocity (in absence of cake layer)</td>
</tr>
<tr>
<td>( \hat{t} = \frac{J_m (t - t_{cr})}{H_o} = \frac{J_m t}{H_o} - \hat{t}_{cr} )</td>
<td>Dimensionless time</td>
</tr>
<tr>
<td>( \hat{x} = \frac{\mu_o J_m x}{H_o^2 \tau_{wo}} )</td>
<td>Dimensionless distance</td>
</tr>
</tbody>
</table>
2.2 Morphology of Colloidal Aggregates and Deposits²

The formation of dendritic and chain-like aggregate structures by irreversible coagulation has been known for many years (Usher 1924), (Rees 1951), (Dezelic, Wrischer et al. 1960). But it was not until 1970 that the random nature of particle collisions was recognized to be source of the chain-like structures observed (Sutherland 1970).

Considerable simulation-based research has been carried out on the formation of aggregates and deposits. Much of this research and associated aggregation models have been reviewed by Meakin (Meakin 1988), (Meakin 1999). Briefly, in a system where diffusive forces dominate, two aggregation regimes are typically recognized - diffusion limited aggregation (DLA) (Witten and Sander 1981), (Meakin 1983), (Racz and Vicsek 1983), (Bushell and Amal 1998) and reaction-limited aggregation (RLA) (Kolb and Jullien 1984), (Julien and Kolb 1984). DLA is controlled by the diffusion rate of particles which attach at the first contact with another particle or cluster. In contrast, RLA is controlled by the chemical reactivity of particles - it takes, on average, \( \frac{1}{\alpha} \) collisions, where \( \alpha \) is the collision efficiency, for a particle (or cluster) to attach to another particle, a cluster, a surface, or a mass of previously deposited particles (a deposit). Aggregation has been reported to shift from being reaction-limited to being diffusion-limited, as the colloid concentration decreases with time (Family,

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²Deposition (on the linear substrate) may be considered as a limiting case of particle-particle aggregation where one of the aggregating particles is infinitely big.
Meakin et al. 1985). If particles (or clusters) follow linear trajectories then ballistic aggregation (BA) or deposition takes place, (Vold 1963), (Meakin, Ramanlal et al. 1986). The intermediate case can be represented using a biased random walk algorithm (Houi and Lenormand 1984), (Tassopoulos, O'Brien et al. 1989). This algorithm uses a skewed probability distribution that a particle will move in a given direction. The favored direction or bias in movement results from external forces acting in one direction as opposed to forces of a stochastic nature. A specific probability distribution function is determined from the relative values of forces acting on the particle.

In experimental studies of aggregates (Forrest and Witten 1979), (Cho, Colin et al. 1993), (Francois and Haute 1985), (Kimpel and Hogg 1986), (Kranenburg 1994), (Waite, Schafer et al. 1999) and deposits (Kim and Rajagopalan 1991), (Veerapaneni 1996), (Zahn and Zosch 1997) these objects were identified as fractals. Fractal description has proven to be the most general and very fruitful approach to analyzing aggregate and deposit structures. In the following chapter a brief description of a fractal concept is presented.

### 2.2.1 Concept of Fractal Geometry

The notion of fractal dimension was introduced by Benoit Mandelbrot in 1975 (Mandelbrot 1975) to describe a class of objects that display a power law dependence on scale for one or more properties. Geometrically this so called
"self-similar" behavior is manifested as a pattern that is repeated at larger and smaller scales. For example the Sierpinski gasket (Figure 2.3) is an object obtained by a simple iterative process where the object is seen to be triangular and consists of an assemblage of 3 triangles at all scales. At any scale a larger assemblage of 3 smaller scale objects can be constructed and the object can be subdivided into 3 subassemblages. The fractal dimension $D_f$ of such an object is defined by the equation:

$$M(L) = AL^{D_f}$$  \hspace{1cm} \text{(2.2.1)}

where $M$ - mass of the object, defined as $M(L) = \rho(L) \cdot L^2$, $L$ - side length, and $A$ - amplitude, which is depended on the definitions of $M$ and $L$.

![Diagram of Sierpinski gasket formation](image)

**Figure 2.3** Formation of a Sierpinski gasket fractal. After (Takayasu 1990)
Length, mass and density of this object are indicated in Figure 2.3 for each iteration step.

Fractals may be classified as non-random and random or as ideal and non-ideal fractals. The Sierpinski gasket is an ideal fractal with a strictly repeating geometry. Fractals encountered in nature are typically non-ideal. Non-ideal fractals are not fractals; they are self-similar only in statistical sense and exhibit upper as well as lower bounds in length beyond which they no longer behave like fractals.

The concept of fractal geometry has proved to be extremely useful in characterizing the objects which were formed in the absence of a scale setting factor, i.e. "scale-free" objects. For example there is often no characteristic scale in turbulent flows, aside from the molecular collision mean free path and the scale of the whole system, where the walls or other confinement structures occur. So far from its boundaries the turbulent fluid can become fractal. Other physical and chemical processes in nature which lead to formation of "scale-free" fractal objects are electrochemical deposition, diffusion-limited aggregation, dielectric phenomena, viscous fingering to mention just a few.

2.2.1.1 Methods for Calculating Fractal Dimension

One of the simplest methods of calculating $D_f$ is the so-called "sandbox" algorithm. This method uses the definition (2.2.1) of $D_f$. The mass of an object $M_L$ (or number $N_L$ of elementary particles of equal size) contained within boxes
of increasing size \( L \) centered around the same point of the fractal is calculated. A plot of \( \ln(M_L) \) or \( \ln(N_L) \) as a function of \( \ln(L) \) yields a straight line with slope \( D_f \) if the object is fractal as equation (2.2.1) suggests.

In the case of a deposit of average height \( \bar{h} \) forming on a substrate, the fractal dimension of the deposit can be estimated by plotting average height of the deposit \( \bar{h} \) versus the number of deposited particles for the growing deposits. For the dependence \( \bar{h} \propto N^\phi \) the power \( \phi \) is related to fractal dimension \( D_f \) by

\[
D_f = d - d_s + \frac{1}{\phi} \tag{2.2.2}
\]

where \( d \) - smallest Euclidean dimension of the space the fractal is embedded in, and

\( d_s \) - dimension of the surface of active adsorption sites

The method of Fourier profile analysis (FPA) was proposed by Passoja and Amborski (Passoja and Amborski 1978) who employed discrete Fourier transform to analyze one-dimensional fracture profiles in steels.

By definition the Fourier transform of a function \( f(x) \) is

\[
F(k) = \int_{-\infty}^{\infty} f(x)e^{-2\pi ikx} \, dx \tag{2.2.3}
\]

The discrete form of equation (2.2.3) is

\[
F(k) = \sum_{k} f(\beta \Delta_x)e^{-2\pi i k \Delta_x} \Delta_x \tag{2.2.4}
\]

where \( \Delta_x \) is the separation between the neighboring points.

Fracture profiles were considered as spectra (of microstructural information) and the authors applied signal-processing algorithms to analyze
them. Spectral bands and higher-order harmonics observed in power spectrum of a fracture profile were assigned to fundamental lengths of the microstructure.

In a subsequent work (Mandelbrot, Passoja et al. 1984), the link between a power spectrum and fractal dimension of the fracture was established. The dependence of the integrated power spectrum on the wave number has the form

\[ \Sigma_n = k_n^{-q}, \] where

\( k_n \) - wave number and

\( q = b - 1 = 6 - 2D_f \)

Thus, the fractal dimension \( D_f \) of a profile may be deduced by plotting the data on doubly logarithmic plot. \( \Sigma_n \) is calculated by integrating the power spectrum from high frequencies to low (the higher limit of integration being the frequency correspondent to the wave number \( k_n \)).

The method of FPA was employed in the later work by Mecholsky et al. (Mecholsky, Passoja et al. 1988). Fracture surfaces of alumina materials with different grain size, porosity, and toughness and glass-ceramics with different microstructures were examined and were identified to be fractal. The log-log plot had straight central portion from which \( D_f \) was calculated.

Mitchell and Bonnell (Mitchel 1990) have applied FPA to the STM images of vapor deposited gold, copper fatigue fracture surface, and single crystal silicon fracture surface. The lower limit in length at which the fractal model held was found to be 12A on all surfaces examined, suggesting that this limit was
related to STM tip geometry. The fact the model worked at nanometer scale allowed for conclusion that FPA may be used to study atomistic processes.

2.2.1.2 Multifractal Analysis

In contrast to smooth distributions of scalar quantities (temperature, electrical potential, growth probability etc.) in Euclidian objects the distribution of these quantities over fractals often possesses infinitely many singularities. What is meant by singularity here is that the scalar value scales with the size of the region over which it is calculated with a local exponent $\beta$. Hence, infinitely many $\beta$s, each corresponding to the distribution of a given kind of singularity are needed to characterize the distribution of a scalar quantity defined on a fractal object. Identification of these exponents is the essence of multifractal analysis and may be considered as a decomposition of a distribution into many “sub-distributions”, each characterized by its own fractal dimension (i.e. exponent).

Hereinafter, the measure (distribution) of a scalar quantity would be considered to be normalized and, hence, may be treated as a probability distribution. The general form of a scaling law is

$$P_i(\varepsilon) \propto \varepsilon^{\alpha_i} \quad \text{ (2.2.5)}$$

where $\varepsilon$ is size of the $i^{th}$ box at which the probability is calculated.

The number of boxes with the exponent $\alpha$ in the interval $[\alpha, \alpha + d\alpha]$ scales according to the following relationship
$N_{\beta}(\varepsilon) \propto \varepsilon^{-f(\beta)} \quad (2.2.6)$

Exponent $f(\beta)$ may be interpreted as a fractal dimension of a subset of boxes characterized with an $\beta$ in the interval $[\beta, \beta+\delta \beta]$. Although $\beta$ and $f(\beta)$ may be directly calculated from (2.2.5) and (2.2.6), these values are not easy to estimate. An alternative method is based on the notion of q-th order moments of the measure $M_q$ and their scaling exponents $\tau_q$ defined as

$M_q = \sum_i P_i^q = \sum_P n(P)P^q \propto \varepsilon^{\tau(q)} \quad (2.2.7)$

where $n(P)$ - the number of boxes with probability $P$. Substitution of (2.2.5) and (2.2.6) into (2.2.7) and approximation of the logarithm of the sum by the logarithm of a maximum element in the sum yields

$\tau(q) = q\beta(q) - f(\beta) \quad (2.2.8)$

Thus, according to (2.2.8), $f(\beta)$ is the Legendre transform of $\tau(q)^3$. The value of $\beta(q)$ corresponding to the maximum element in the sum in (2.2.7) and thus, must satisfy the requirement that

$\frac{d}{d\beta} [q\beta(q) - f(\beta)] = 0 \quad (2.2.9)$

so that

$q = f'(\beta) \quad (2.2.10)$

From (2.2.7), (2.2.8) and (2.2.10):

---

3 There exits an analogy between multifractal and thermodynamics functions: $q$ corresponds to $1/kT$, $\tau(q)$ - to free energy, $\beta$ - to internal energy, and $f(\beta)$ - to entropy (Lee and Stanely 1988)
\[ \beta(q) = \frac{d[\tau(q)]}{dq} = \frac{\sum_i P_i^q \ln(P_i)}{\sum_i P_i^q \ln(\varepsilon)} \]  \hspace{1cm} (2.2.11) 

When \( \tau(q) \) and \( \beta(q) \) are known, \( f(\beta) \) is computed from (2.2.8).

For \( q=0 \), \( M_0 \) reduces to the number of boxes with non-zero probability and

\[ M_0 = e^{\tau(0)} \rightarrow \tau(0) = \frac{\ln(M_0)}{\ln(\varepsilon)} = \frac{\ln(N)}{\ln(\varepsilon)} = -D_f \]  \hspace{1cm} (2.2.12) 

Also from (2.2.7) and normalization requirement (2.2.13)

\[ \sum_i P_i = 1 \]  \hspace{1cm} (2.2.13) 

it follows that \( \tau(1) = 0 \).

The general features of multifractal functions \( \beta(q) \) and \( f(\beta) \) derived as described above can be deduced. From (2.2.7) and the fact that \( P_i \) is not bigger than 1, it can be seen that \( \tau(q) \) should monotonously increase with \( q \). One also can see from (2.2.10) that \( f(\beta) \) has a maximum at \( q=0 \):

\[ f(0) = -\tau(0) = D_f \]  \hspace{1cm} (2.2.14) 

This may be interpreted as a consequence of the fact that any subset of a fractal should have fractal dimension less than fractal dimension of the fractal itself.

The multifractal analysis has proven to be very useful in analyzing such phenomena as turbulence (Meneveau and Sreenivasan 1991), fracture (Herrmann 1991), distribution of percolation clusters of growth site distribution on DLA (Coniglio, Arcangelis et al. 1989), and effects of fractal geometry on the heterogeneous catalysis processes (Lee and Lee 1997).
There are several pitfalls to avoid when using multifractal analysis. First of all, when the probability is small, it may not scale. Second of all, the accuracy of the computation of multifractal spectrum depends to a great extend on the completeness of information about the measure to be analyzed. Specifically, “locations” with very small probabilities are often hard to identify\(^4\) so that determination of negative moments, which are, according to (2.2.7) dominated by small probabilities, are prone to considerable error. Another problem, encountered in this work (see chapter 4.2.9), is that lack of complete knowledge of a measure results in the absence of scaling for small probabilities when \(\varepsilon\) is not higher than certain threshold value.

2.2.2 Deposition. Mechanisms and Modeling.

It is convenient to consider deposition as consisting of two sequential steps of transport and attachment (O’Melia and Stumm 1967), (Elimelech, Gregory et al. 1995). This approach allows, to a certain extent, for a separate consideration of physical and chemical processes involved. This is possible because colloidal interactions have a short range and become significant only at very close distances between particles. It should be noted though that “this distinction between transport and attachment, or physics and chemistry, is not perfectly sharp”\(^5\) (O’Melia and Tiller 1991). Transport of particles to the deposit is

---

4 The choice of method of calculation of a measure is of crucial importance here (Vicsek 1992).
5 On the one hand, transport of particles at certain separation between them involves van der Waals forces, while, on the other hand, physical forces may control attachment provided
considered (Wiesner 1999) to result from the superposition of diffusive transport processes:

- Brownian diffusion (Smoluchowski 1917)

- turbulent diffusion (Corrsin and Limley 1956), (Delichatsios and Probstein 1975), (Dabros and Ven 1983)

- shear-induced diffusion (Leighton and Acrivos 1987)

and convective transport processes such as:

- by interception and gravity (Ison and Ives 1969), (Fitzpatrick 1972), (Rajagopalan and Tien 1977), (Yuu and Jotaki 1978), (Tardos and Pfeffer 1980), (Yoshimura and Ueda 1980).

- due to electrostatic attraction (Valioulis and List 1984), (Boluk and Ven 1989), (Peters, Cooper et al. 1989)


Near-field forces acting between particles will be discussed in chapter 2.2.4.

In the light of this approach the following factors determining the structure of deposits may be discriminated:

1) The specific mode of long-range transport of particles to the deposit. The interplay between deterministic and diffusive forces acting on a transported particle determine particle's trajectory and, thereby, effect

weakness of chemical interaction between particles
the morphology of the deposit. This category encompasses all external force fields and all properties of the suspension which determine the interaction between the suspension and the external fields - temperature, densities of fluid and suspended particles, fluid viscosity etc. The relative importance of ballistic (deterministic) and diffusive (stochastic) particle transport in the system may be characterized by Péclet number \( Pe = \frac{vL}{D} \).

2) Properties of the suspended particles - the particle size distribution (PSD), shape and surface chemistry of particles.

3) Properties of the carrying fluid - ionic strength, pH, ε.

4) The nature of interaction between flow and deposit including effects of collisions of particles with deposits.

5) "Post-deposition" changes, i.e. surface diffusion of already deposited particles, chemical reactions at the surface of the deposit, compaction of the deposit due to break-up etc.

Quantitatively, transport and surface reactivity of particles may be characterized by Péclet number \( Pe \) and collision efficiency \( \alpha \) (discussed later in chapter 2.2.4), correspondingly. Generally, \( D_f \) increases with decrease in efficiency \( \alpha \) of collisions between particles and with decrease in fractal dimension of particles' trajectories. An increase in polydispersivity of suspension results in an increase in fractal dimension.
2.2.3 On- and Off-Lattice Models. Algorithms and Associated Complexities.

Advances in information technology stimulated an explosive growth of research in the field of computer modeling of aggregation processes. The size of the modeled aggregates has increased from 3000 to 100,000,000 particles (Kaufman, Vespignani et al. 1995). But even with the technology available today, it is still impossible to build a simulated aggregate while accounting for all factors (see chapter 2.2.1) which possibly influence the aggregation process.

Depending on the mechanism of aggregation, the existing models fit into one of two categories - particle-cluster or cluster-cluster models. Cluster-cluster models incorporate both particle-particle and cluster-cluster addition processes as well as particle-cluster aggregation (Meakin and Djordjevic 1986). Modeling homo- and heterocoagulation in the frame of cluster-cluster model, Stoll et al (Stoll and Pefferkorn 1996) have assumed that the diffusion coefficient of cluster cluster’s reactivity and aggregation ability were given by

\[ D_n = D_t n^{1/D_t} \]  
\[ R_n = R_t n^\sigma \]  
\[ A_n = A_t n^\gamma = D_t R_t n^{1/D_t + \sigma} \]  

where

\( n \) - cluster size,
$D_r$ - fractal dimension of the cluster,

$\sigma$ and $\gamma$ - scaling exponents.

Another possible approach to account for cluster size in cluster-cluster aggregation model is to make collision efficiency dependent on the sizes of two colliding clusters (Family, Meakin et al. 1985).

The off-lattice models produce more realistic structures on short-length scales. Thus, the off-lattice algorithm is the algorithm of choice when the local microstructure of an aggregate should be captured to analyze anisotropy or investigate asymptotic scaling relationships. For the structures generated by lattice models the minimal scale at which the meaningful structure analyses can be performed is of the order of 10 particles. The lattice models, however have an advantage of being more efficient, and, as was shown for the case of cluster-cluster aggregation (Meakin and Wasserman 1984), accurate enough - fractal dimension has the same value for both lattice and off-lattice models.

2.2.4 Collision efficiency

It is convenient to describe the attachment step in aggregation and deposition in terms of a collision efficiency $\alpha$. Collision efficiency is defined as the probability that the approaching particle is not immediately attached to another particle or cluster but is reflected or detached. For example, the collision efficiency of 0.1 implies that it would take, on average, 10 collisions for

6 Another frequently used term is sticking probability
the particle to be attached.

In quantitative description of aggregation and deposition $\alpha$ is incorporated as a multiplier in expressions for reaction rates (O'Melia and Tiller 1991). For example, the rate of aggregation is given by

$$\frac{dn}{dt} = -k_{agg} n^2 = -\alpha_{agg} \beta n^2$$

(2.2.18)

where

$n$ - number concentration of particles in suspension at time $t$,

$k_{agg}$ - second order rate constant,

$\alpha_{agg}$ - collision efficiency for aggregation,

$\beta$ - mass transport coefficient.

Analogously, the rate of deposition

$$\frac{dn}{dL} = -k_{dep} n = -\alpha_{dep} \eta n$$

(2.2.19)

where

$n$ - number concentration of particles in suspension at time $t$,

$k_{dep}$ - second order rate constant,

$\alpha_{dep}$ - collision efficiency for deposition,

$\eta$ - mass transport coefficient.

The fundamental origin of $\alpha$ may be described in terms of the potential of interaction between particles. The DLVO theory (Derjaguin and Landau 1941), (Verwey and Overbeek 1948) assumes that the potential energies of electrostatic repulsion $V_e$ and van der Waals’ attraction $V_a$ are additive to produce the total potential energy. The balance between attractive van der
Waals forces and repulsive electrostatic forces may lead to two minima in total potential. Particles may be associated in a (deep) primary minimum state or (shallow) secondary minimum state.

Smoluchowski (Smoluchowski 1917) derived the following expression for the initial rate of disappearance of rapidly aggregating (no repulsion) primary particles in perikinetic conditions:

\[
-\left( \frac{dn}{dt} \right)_{t \to 0} = 8\pi RDn_0^2 \tag{2.2.20}
\]

where \( R \) - distance between particles,

\( n_s \) - the concentration of single particles and \( n_s = n_0 \) at \( t = 0 \),

\( D \) - diffusion coefficient.

Fuchs (Fuchs 1934) considered the same system but with non-zero repulsive interactions and found that

\[
-\left( \frac{dn}{dt} \right)_{t \to 0} = \frac{8\pi RDn_0^2}{W} \tag{2.2.21}
\]

Thus the rate of coagulation has been slowed down by a factor of \( W \), the so-called stability ratio. In the model for the stability ratio, \( W \) is calculated from the relative magnitude of attractive and repulsive potential:

\[
W_{\text{coagulation}} = 2a \int_{2a}^{\infty} \frac{e^{-TR}}{r^2} dr \tag{2.2.22}
\]

where

\( a \) - particle radius,

\( V \) - potential energy of interaction,
$kT$ - thermal energy.

The collision efficiency $\alpha$ is defined as a value reciprocal to $W$: $\alpha = \frac{1}{W}$.

Thus, the collision efficiency for coagulation

$$\alpha_{\text{coagulation}} = \left[ 2a \int_2^{\frac{\nu}{2a}} e^{\frac{6T}{r^2}} dr \right]^{-1}$$

(2.2.23)

In case when aggregation occurs due to particle attachment in secondary minimum, it can be shown (Reynolds and Goodwin 1987) that assuming a Boltzmann distribution of particles’ energies, the collision efficiency factor is given by

$$\alpha_{\text{flocculation}} = \left[ \frac{(2a + H_{s_{\text{min}}}) \int_{2a + H_{s_{\text{min}}}}^{\frac{\nu}{2a + H_{s_{\text{min}}}}} e^{\frac{6T}{r^2}} dr}{\frac{\nu_{s_{\text{min}}}}{1 - e^{\frac{6T}{r^2}}}} \right]^{-1}$$

(2.2.24)

where

$H_{s_{\text{min}}}$ - the distance from the particle surface at which the secondary minimum occurs, and

$V_{s_{\text{min}}}$ - depth of the secondary minimum.

The factors determining the potential of interaction between particles, and, as a consequence, very often determining the value of $\alpha$, are the chemistry of the aqueous phase and the surface chemical properties of the particles. The corresponding measurable physical values for the aqueous phase are ionic
strength and the pH of the solution. Particles suspended in solution are usually charged as a result of the ionization or dissociation of surface groups or the adsorption of ions from solution. Thus, the functionality of the surface groups and the nature of the adsorbed material determine the surface potential of the particles which can be measured experimentally.

The fact that $\alpha$ for natural particles was observed to vary in a wide range, from about 0.001 to 1 (O'Melia and Tiller 1991), is due to the wide variability in parameters affecting $\alpha$. The values of ionic strength for different aquatic environments range from 0.0001M (mountain springs) to 0.7M (oceans). pH may vary from 3 to 9 and aquatic humic substances range in molecular weight from 500 to perhaps 50,000 daltons (O'Melia and Tiller 1991).

The fact that the conditions for particle attachment have an influence on the short-range structure of the deposit has been known from experiments for some time (Usher 1924). The influence of collision efficiency on aggregate structure has been experimentally investigated (Schulthess, Benedek et al. 1980), (Soler, Garcia et al. 1982), (Sattler 1983).

Compact RLA-type aggregate structures were observed in low ionic strength waters, while in high ionic strength marine systems, a loose aggregate structure was observed and was attributed to a higher collision efficiency (Leppard, West et al. 1997), (Leppard, Baffle et al. 1986).

Dissipative forces due to non-elastic deformations may also become a factor if the kinetic energy of colliding particle is high, which is often the case with deposition and aggregation of aerosol particulates (Clement, Kulmala et al.
From the point of view of applicability of the concept of collision efficiency to the deposition in natural environment, it is important to know how many chemically different depositing fractions are present in the suspension. As Buffle *et al.* argue (Buffle, Wilkinson et al. 1998) chemical heterogeneity strongly depends on types of colloids involved. They pointed out that in case of inorganic colloids, homoaggregation models that assume that all particles have similar surface properties have been reasonably successful (O'Melia 1990), (Filllela and Buffle 1993). In natural waters, most inorganic colloids are covered by a similar adsorbed layer of fulvic compounds. This adsorbed layer will largely determine the surface charge of the compact colloid and give suspensions a more homogeneous appearance in terms of surface chemistry. These researchers conclude. (Buffle, Wilkinson et al. 1998), that

"...to a first approximation, inorganic colloids can be considered as a single class of colloidal compounds, irrespective of their nature, for which only size polydispersivity has to be considered".

### 2.2.5 Heteroaggregation and Heterodeposition

A more common situation in natural and industrial systems is the presence of more than one sort of chemically distinct particles. Examples are abundant, some of them are:

a) Estuarial sediments are a mixture of water, sand, fines and organic material.
b) In CVD technological processes, it is impossible, or even not needed, to totally exclude presence of impurities.

c) Coagulation of some of colloids requires the presence of colloids of a second type.

Hence, one has to take into account possible interactions between different depositing fractions. The knowledge of the mechanisms governing deposition of multicomponent mixture would provide a better understanding of and, potentially, control over deposition process and properties of the deposits.

In their pioneering work, Meakin and Djordjevic (Meakin and Djordjevic 1986) studied aggregation in two monomer systems interpreted in the context of a diffusion limited cluster-cluster aggregation model. The influence of the relative concentrations of the two monomers on the aggregation rate as well as the effect of difference in monomers’ functionality on the structure and growth kinetics of aggregates were investigated. Large clusters were shown to have a fractal-like geometry but their effective fractal dimensionality depended on the composition of the mixture. A single large cluster was formed only in a restricted composition range. In this range, a dynamic scaling of the form \( N_r(t) = \frac{f\left(\frac{s}{t^2}\right)}{s^2} \) (the generic scaling law for self-affine fractals (Vicsek 1992)) holds for polymerization kinetics in the gelling region, and is “quite general and applicable to a very wide range of aggregation and polymerization processes” (Meakin and Djordjevic 1986).

Meakin and Miyazima (Meakin and Miyazima 1988) have found that in the
system of two chemically different monomer types that can only react with each other but not with themselves, the fractal structures are produced with fractal dimensions between DLA and RLA values, depending on the concentrations of the individual species present.

The study of Meakin and Djordjevic (Meakin and Miyazima 1988) has been extended by Stoll and Pefferkorn to study 2D (Stoll and Pefferkorn 1996) and 3D (Stoll and Pefferkorn 1993) heterocoagulation kinetics as the function of the frequency of inefficient random encounters between similar particles of identical functionality. The major finding from this work was that 2D heterocoagulation is less sensitive to the collision efficiency than is 3D coagulation. This underscores the importance of the surface aggregation in the destabilization of hydrophobic colloids. Authors speculate (Stoll and Pefferkorn 1996) that

“Colloidal powders such as fertilizers or insecticides transported in the atmosphere may in fact accumulate at air-water interfaces, aggregate prior to immersion, and then promote a three-dimensional aggregation within the liquid phase”.

The deposition of mud/sand mixtures has been investigated in settling column experiments for different types of mud at different sand contents (Toorman and Berlamont 1993), (Torfs, Mitchener et al. 1996). Density profiles, settling rates and pore water pressures were measured. The structure of a bed was found to be dependent on input concentration and rate, sand content and sedimentological, chemical and biological properties of the mud. It was shown that the non-cohesive fraction segregates when the suspension concentration is low (which is the case for suspended sediment in estuaries) and sand content is
high. As the concentration increases and solid volume fraction reaches value \( \varphi_{\text{gel}} \), known as gel point, the cohesive particles coagulate and a continuous network structure is formed with effective stresses being developed through the structure. For many types of estuarine muds, \( \varphi_{\text{gel}} = 0.03 - 0.07 \). Increasing the sand content lead to an increase in \( \varphi_{\text{gel}} \). As soon as a network is formed, the non-cohesive fraction is trapped within. The amount of sand that a mud could hold within its matrix depended on the type of mud: mineralogical and chemical composition, the organic content and biological processes. At the critical sediment volume, the structure collapses under its own weight and consolidation occurs.

Hong et al. (Hong, Hsu et al. 1997) have studied the uniformity of CVD films as a function of collision efficiencies of particles constituting the depositing material. The direct simulation Monte Carlo method was used to model the interactions between molecules and between molecules and wall. The concentration ratio of two film-forming species was found to have a significant effect on the uniformity of the films. A more uniform film was formed when the species of low \( \alpha \) dominated the mixture.

2.2.6 Effects of Fragmentation, Restructuring and Consolidation.

In many industrial and natural processes involving aggregation and

---

7 Measured sediment porosities at the interface are typically greater that 0.90 and may be as high as 0.99 (Janke, Emerson et al. 1988).
deposition, the effects of break-up, restructuring (and consequent consolidation of a deposited layer for the case of deposition) play a determining role. Examples include:

a) In membrane fouling, the density profile of the fouling cake determines the resistance to the permeate flow, the key parameter from the point of view of membrane performance.

b) Knowledge of a density profile of a deposit is needed to assess the deposit's resistance to erosion which may lead to release of deposit-bound contaminants.

c) With land disposal becoming the important issue, a good prediction of consolidation of a dredged material is important for optimization of disposal process.

However, very few papers on the modeling of consolidation present the computed density profiles.

Recently, in the frame of the MAST III Cosinus project (http://sun-hydr-01.bwk.kuleuven.ac.be/COSinus/cosinus.html), a study has been carried out aimed at understanding and modeling the behavior of near-bed suspensions of high concentrated fine-grained cohesive sediments. A unified theory for settling and consolidation has been developed (Toorman 1996), (Toorman 1999). This model allows the computation of the density and/or stress history within the deposited mud layer. It has been shown in this work that the sedimentation and self-weight consolidation processes can be described by the general one-dimensional sediment mass balance equation
\[
\frac{\partial \varphi_s}{\partial t} = \frac{\partial S}{\partial z} = \frac{\partial}{\partial z}\left( w_0 \varphi_s + \frac{w_0}{\gamma_v - \gamma_w} \frac{\partial \sigma'}{\partial z} + D_s \frac{\partial \varphi_s}{\partial z} \right)
\]

(2.2.25)

\[w_0 = k \varphi_s \left( \frac{\gamma_v}{\gamma_w} - 1 \right)\]

where

\(t\) - time,
\(z\) - vertical Eulerian coordinate,
\(\varphi_s\) - solids volume fraction,
\(S\) - sediment flux. \(S = w_0 \varphi_s\), with \(w_0\) being the average settling rate of the particles,
\(\sigma'\) - vertical effective stress,
\(D_s\) - diffusivity coefficient, which includes Brownian diffusion and other effects, such as differential settling,
\(\gamma_v\) and \(\gamma_w\) - unit weights of the sediment and water, respectively, and
\(k\) - permeability.

The equation (2.2.25) has been solved using closure equations for permeability \(k\), diffusivity \(D_s\) and effective stress \(\sigma'\) and validated against experimental data.

Even for non-cohesive sediments with negligible diffusion, and thus very steep density gradients, the model worked well (Figures 2.4, 2.5). The biggest simplification of the models considered so far was the supposition that particles and clusters attach irreversibly. In reality, as soon as the aggregate becomes sufficiently big, the break-up occurs. The extreme complexity of short-range
Figure 2.4. Computed density profiles for spherical glass beads. dashed line, analytical solution (Kynch's sedimentation theory); full line, finite-element solution. Initial height. From (Toorman 1999)

Figure 2.5. Comparison between experimental (dashed lines) and experimental data. computed (full lines) density profile evolution for a China clay suspension. Experimental data from (Huysentruyt 1995). Modeling data from (Toorman 1999)
interactions between particles is a limiting factor in describing break-up process. Computer modeling as well as experimental efforts have being undertaken to provide an insight into this problem.

Elminyawi et al. (Elminyawi, Gangopadhyay et al. 1991) have recently obtained a numerical solution of the Smoluchowski aggregation-fragmentation equation (Smoluchowski 1916) and have found a scaling form of the cluster size distribution.

Both break up and restructuring lead to an increase in fractal dimensions of aggregates (Kolb 1986), (Jullien and Meakin 1989). Specifically, in the case of 3D reaction-limited cluster-cluster aggregation, three-stage spontaneous restructuring lead to an increase in fractal dimension from 1.95-2.1 (typical values for this aggregation regime) up to approximately 2.25 (Jullien and Meakin 1989).

2.2.7 Effect of the morphology of substrate on the surface profile evolution in the course of deposition and etching.

The interest in the study of the morphology of surfaces growing on the substrates with different profiles has been stimulated by the development of applications involving thin solid film deposition such as chips fabrication, thermal resistance coating (for example, in aerospace engineering), magnetic recording devices etc.
V.K. Singh has investigated the effect of the roughness of underlying substrates on the microstructure of chemical vapor deposited (CVD) films (Singh and Shaqfeh 1993). An initial two-dimensional roughness in the starting surface was represented by a sinusoidal wave of the form \( z = \cos(\beta y) \), where the amplitude of the roughness is unity and \( \beta \) is the wave number. A large \( \beta \) corresponds to a large rate of change in the height of the substrate, or higher roughness. All wave numbers were shown to grow in the small time regime, for all values of \( \alpha \) but 0. At longer times, the mechanism of cusp formation is shown to arrest this growth. The cusp formation was believed to be responsible for the formation of void-free film under the conditions of low \( \alpha \). The amplitude of surface roughness was shown to decay quicker with time for higher \( \beta \). It was shown that larger columns “shadowed” smaller adjacent columns which, for low \( \alpha \), resulted in halving of the wave number and slowing down the decay of surface roughness.

In subsequent work (Singh, Ford et al. 1997), these researchers have extended the results of their study of evolution of a film surface to considering the effect of etching. In their model, surface re-emission and surface diffusion were considered as surface transport mechanisms. Collision efficiency \( \alpha \) was used as a parameter for re-emission. It was demonstrated that for etching, unlike for deposition, surface roughness always decays with time, the rate of decay being proportional to \( \alpha \). The presence of surface diffusion resulted in removing of sharp edges from the film profile.
The dependence of uniformity of CVD film coverage of substrate of different geometry on the stickiness coefficient was investigated by Hong et al (Hong, Hsu et al. 1997). The direct simulation Monte Carlo method was used to model the interactions between molecules and between molecules and the wall. The substrate had a trench shape (rectangular or wide mouth) as is the case in the manufacturing of the integrated circuits. It was found that the major factors in determining the uniformity of coverage were the stickiness coefficient and the geometry of the substrate. The uniformity of the film thickness is improved if the stickiness coefficient is small. Also, the CVD system containing two film-forming species of different stickiness coefficients was simulated. In this case, the uniformity was dominated by the species with larger stickiness coefficient. When two stickiness coefficients were equal, the uniformity was similar to that of film formed from species of one stickiness coefficient. Other parameters - Knudsen number (characteristic of rarefaction of the gas), ratio of diameters and ratio of masses of two molecules - did not influence much the uniformity of coverage. The concentration ratio of two film-forming species was found to have a significant effect on the uniformity - the latter was improved when the species of low $\alpha$ dominated the mixture.
3. Experimental Methods

3.1 Membrane module and system parameters

The ultrafiltration membrane set-up was constructed based on the SEPA cross-flow flat slit membrane cell (Osmonics, Minnetoka, MN; SEPA CF) operating in cross-flow configuration (Figure 2.6) (Hovinga 1999). Transmembrane pressure was regulated by a pressurized air cylinder. The feed suspension was pumped in a recycle loop over the membrane by a pulse-free centrifugal pump (Pulsafeeder, Rochester, NY; EC-J1). A stainless steel needle valve was used to control the feed flow that had a range 0-3 L/min. The temperature was kept constant at 20.0° ±0.1° Celsius using a cooling loop. The feed concentration was kept constant by pumping either permeate, or concentrated particle suspension back into the feed tank. On-line spectrophotometry at $\lambda=245$nm (Spectra-Physics, San Jose, CA; Spectra 100) and photon-correlation spectroscopy (PCS 4700a, Malvern Instruments, Malvern, UK) were used to control bulk concentration of particles in the suspension and aggregation state of the particles, correspondingly. The initial permeate flow rate was 5.3 ml/min, which corresponded to permeate velocity of $\sim4.15 \times 10^{-3}$ cm/sec, while the cross-flow velocity was kept constant at 11.6 cm/sec. The initial transmembrane pressure was adjusted to yield the same initial permeate flux for all experiments.
Figure 2.6. Flow chart of the membrane filtration set-up\textsuperscript{8}

\textsuperscript{8} Modified from (Hovinga 1999)
3.2 Suspensions

Spherical latex particles (Bangs Laboratories Inc., Fishers, IN) were suspended in ultrapure water with an electrical resistance greater than 8 MΩ-cm. A Milli-Q system (Millipore Corporation, Bedford, MA) was used to produce ultrapure water. The feed suspension had pH of 6.4. The samples of suspension were taken periodically from the filtration module in the course of filtration experiments to check the particle size distribution.

3.3 Membranes

All experiments were performed using polysulphone membranes chemically modified to have a hydrophylic surface (Hydranautics, Oceanside, CA). In the first set of experiments, when the dependence of the transient and steady state permeate flux on the particle size was investigated, a membrane with a molecular weight cutoff of 7,000 Daltons (pore diameters ~2nm) and an effective area of 21.4 cm² was used. The second set of experiments aimed at a comparison of CF and CP regimes was performed using a membrane with a molecular weight cutoff of 50,000 Daltons (pore diameters ~30nm). The effective membrane area was 129.6 cm². Before each experiment, the membrane was compressed at 621 kPa transmembrane pressure until the clean water flux through it was stabilized. The time of compression varied for different membranes and was in the range of 30-90 minutes.
4. Results and Discussion

4.1 Transient Permeate Flux in Cross-flow Membrane Filtration

A previously proposed (Sethi and Wiesner 1997) extended model for membrane fouling incorporates particle transport mechanisms of Brownian diffusion, shear-induced diffusion, inertial lift and concentrated flowing layers. The model predicts a range of particles sizes where the relative cake build-up is maximized due to a net minimum in back-transport mechanisms superimposed on the effect of increasing of specific cake resistance with a decrease in particle size (Figure 4.1.1a). Simulations comparing CF and CP modes of operation (Figure 4.1.1b) suggest increasing benefits for CP operation as particle size decreases.

In this chapter the results of experimental validation of the extended model are presented. In particular, the effects of particle size on the transient behavior of permeate flux are examined. Differences between predicted and observed fluxes are interpreted in terms of cake properties and additional transport mechanisms, possibly not accounted for by the extended model. Further, the model was modified to incorporate the possibility of varying the morphology of the cake surface. Two additional parameters describing the cake surface - cake solid fraction at the wall and thickness of the transition zone, were introduced. The dependence of permeate flux behavior on the values of these two
parameters is presented.

4.1.1 Experimental Validation of Sethi’s Model. Effect of particle size

To verify the predicted dependence of the transient and steady-state permeate flux on the particle size, a set of cross-flow membrane filtration experiments with monodisperse latex suspensions of particles 0.02μm, 0.12μm and 0.68μm in diameter was carried out in a CP regime. Values of operational parameters used in the experiments are summarized in the Table 4.1. The corresponding results are depicted in Figure 4.1.2 (a-c).

Two major differences between predicted and observed results are a) slight overprediction of steady-state flux for 0.68μm and 0.02μm particles, and b) considerable underprediction of transient as well as steady-state permeate flux for 0.12μm particles. In what follows, an interpretation of the observed discrepancies is presented.

In the course of filtration of 0.02μm and 0.12μm particles the suspension in the recycled feed loop tended to become more concentrated as detected by an increase in UV absorbance. To keep the bulk concentration of particles constant, millipore water was pumped into the feed tank. In the case of the 0.68μm particles, UV absorbance decreased with time, and the concentrated suspension was added to the feed side of the module. One possible explanation for this unexpected result is the presence of a “fluff” layer at the cake-suspension interface (Stolzenbach, Newman et al. 1992). Under this
Figure 4.1.1a The influence of particle size on the normalized length-averaged permeate flux as predicted by Sethi (Sethi and Wiesner 1997). Performed at various times, for flat slit and inside-out hollow fiber filters.

Figure 4.1.1b. Comparison between constant pressure and constant flux modes of operation for different particle sizes from Sethi (Sethi and Wiesner 1997).
assumption, the solid fraction of the uppermost layer of the cake is less\(^9\) than that for perfectly packed spheres (0.58) and particles may be removed from the suspension by \textit{interfacial aggregation} (Stolzenbach, Newman et al. 1992) when moving across the fluff layer in a direction tangential to the cake-suspension interface. Interfacial aggregation, together with the fact that the backtransport due to differences in solid fraction between the cake wall and the bulk suspension are less when the fluff layer is present, may explain the observed overprediction of steady-state permeate flux for 0.68\(\mu\)m and 0.02\(\mu\)m particles.

Another feature of the flux behavior observed experimentally is that flux in the initial stage is underpredicted for particles of all sizes. This observation is also consistent with the hypothesis of a fluff layer; initially, the cake is not compressed by it is own weight and yields a more porous layer.

If the presence of the fluff layer is assumed, the solid fraction at the wall, \(\phi_{\text{wall}}\), and thickness of the transition zone between compacted part of the cake with \(\phi=0.58\) and the wall, i.e. thickness of the fluff layer \(\Delta\), are the unknowns to be determined (see next chapter).

The considerable underprediction of flux for 0.12\(\mu\)m particles may originate either due to the additional backtransport mechanism not accounted by the model, or due to a cake structure different than that assumed by the model. Recently, Lee and Clark have concluded from their experimental work (Lee and Clark 1998) that the theoretical prediction of Carmen-Kozeny equation (employed by our model) underestimates the specific cake resistance for larger

\(^9\) In fact, a solid fraction of 0.01 is known to be sufficient for the 3-dimensional continuous network to be formed in a K-ilite suspension (Williams and Williams 1989)
particle sizes and overestimates for smaller particle sizes. This may shift the minimum for the permeate flux to the smaller particle sizes and the observed

<table>
<thead>
<tr>
<th>Parameter</th>
<th>for 20nm particles</th>
<th>for 116nm particles</th>
<th>for 680nm particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average transmembrane pressure, kPa</td>
<td>490</td>
<td>496</td>
<td>519</td>
</tr>
<tr>
<td>Bulk suspension volume fraction</td>
<td>0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slit half-height, mm</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average cross-flow velocity at inlet, cm/s</td>
<td>11.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane length, cm</td>
<td>2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average membrane resistance, 1/cm</td>
<td>$1.38 \times 10^{10}$</td>
<td>$1.14 \times 10^{10}$</td>
<td>$1.41 \times 10^{10}$</td>
</tr>
</tbody>
</table>

*Table 4.1 Values of operational parameters used in filtration experiments*

absence of minimum of performance for 0.12μm particles would be explained.

Another factor to take into account is that the model assumes a no-slip condition at the cake boundary. It is possible that a non-zero cross-flow at cake-suspension interface favors the scavenging of intermediate-size particles. This effect would be less for smaller particles because they form cakes with higher resistance and a no-slip condition at the cake boundary may be a reasonable approximation. For bigger particles, a slip velocity would only enhance the
tubular pinch effect resulting in a decrease in the potential for scavenging. The resuspension effect may be also at maximum for the medium-sized particles; big particles have more inertia and are not as easily resuspended while specific area of interaction of slipping layer of fluid and uppermost part of the cake is minimal for small particles which also decreases the potential for resuspension. The time to reach steady-state is underpredicted by model for 0.02μm and 0.68μm particles, while for 0.12μm particles the steady-state was reached at the predicted time.
Figure 4.1.2 (a,b,c) Comparison of modeled and observed decline in specific permeate flux in CP filtration of a) 0.02μm, b) 0.12μm, and c) 0.68 μm latex particles
4.1.2 Formulation of Modified Extended Model.

The Sethi's model (see chapter 2.1.4) was modified to account for a slightly more complex morphologies of the cake. In the modified model presented here, $\varphi_c$ is considered to be a function of the cake depth. This dependence is modeled by Fermi-Dirac distribution function:

$$f(x) = \frac{1}{1 + e^{-b}}$$  \hspace{1cm} (4.1.1)

$$0 \leq f(x) \leq 1, \text{ and } f(x) = 0.5, \text{ for } x = a$$

Here, $x$ is a distance from the membrane surface: $0 \leq x \leq \delta_{(i)}^{(n)}$, where $\delta_{(i)}^{(n)}$ is cake thickness at the $i^{th}$ grid point and at the $n^{th}$ time step.

Two parameters, $a$ and $b$ determine the $x$ value at which $f(x)$ decreases by a factor of 2 and how steep the transition from $(f(x))_{\text{max}}$ to $(f(x))_{\text{min}}$ occurs, correspondingly.

Thus, the specific cake resistance $R_{c(n)}^{(i)}$ becomes a function of the cake depth at which it is calculated:

$$R_{c(n)}^{(i)}(x) = \frac{45\varphi^{(i)}_{c(n)}(x)^2}{d_p^2(1 - \varphi^{(i)}_{c(n)}(x))^3} \hspace{1cm} (4.1.2)$$

where

$$\varphi^{(i)}_{c(n)}(x) = \varphi_{\text{min}} + \frac{\varphi_{\text{max}} - \varphi_{\text{min}}}{e^{-\frac{\Delta_{(n)}^{(i)}}{k}} + 1} \hspace{1cm} (4.1.3)$$
Here $\varphi_{\text{max}} = 0.58$, while $\varphi_{\text{min}} = \varphi_{\text{wall}}$ is the cake solid fraction at the cake-suspension interface, i.e. at the "wall". $\varphi_{\text{wall}}$ is used in the modified model as a fitting parameter.

The meaning of $\zeta$ and $\Delta$ values is explained in the Figure 4.1.3. Fermi-Dirac function is symmetrical so it is possible to write (Figure 4.1.3):

$$f(1000) = \varphi_{\text{min}} + \varepsilon(\varphi_{\text{max}} - \varphi_{\text{min}})$$

$$f(300) = \varphi_{\text{min}} + (1-\varepsilon)(\varphi_{\text{max}} - \varphi_{\text{min}})$$

It can be shown that $k = 2\ln\left(\frac{1-\varepsilon}{\varepsilon}\right)$. The $k(\varepsilon)$ dependence is shown on Figure 4.1.3. As can be seen, the choice of $k = 10$ was made to insure that $\varepsilon \leq 0.01$. Taking into the account that the total cake thickness at a given grid point and at a given moment of time is

$$\delta_n^{(i)} = \zeta_n^{(i)} + \frac{\Delta_n}{2}$$  \hspace{1cm} (4.1.4)
Figure 4.1.3 Fermi-Dirac distribution function
(4.2.3) may be rewritten as

$$\varphi_{c(n)}^{(i)}(x) = \varphi_{\min} + \frac{\varphi_{\max} - \varphi_{\min}}{1 + e^{-\frac{x - (\delta_{c(n)}^{(i)} - \delta_{l(n)}^{(i)})}{10}}} \frac{\delta_{c(n)}^{(i)} + \delta_{l(n)}^{(i)}}{2}$$  (4.1.5)

It should be noted that the dependence of the thickness of the transition zone $\Delta$ on the position along the membrane surface is neglected in this approach. The assumption hinges on the supposition that differences in values of permeate flux corresponding to different positions along the membrane are insufficient to result in differences in $\Delta$ values.

At each time step $n$, the total cake resistance $R_{c(n)}^{(i)}$

$$R_{c(n)}^{(i)} = \int_{0}^{x} R_{c(n)}^{(i)}(x) dx$$  (4.1.6)

the dimensionless cake resistance

$$\beta_{c(n)}^{(i)} = \frac{H_{0} R_{c(n)}^{(i)}}{R_{m}} = \frac{H_{0} R_{c(n)}^{(i)}}{R_{m} \delta_{c(n)}^{(i)}}$$  (4.1.7)

and dimensionless permeate velocity

$$v_{w(n)}^{(i)} = \frac{1}{1 + \beta_{c(n)}^{(i)} \delta_{c(n)}^{(i)} H_{0}} = \frac{1}{1 + \frac{\beta_{c(n)}^{(i)} \delta_{c(n)}^{(i)}}{H_{0}}}$$  (4.1.8)

are computed for each grid point $i$.

Numerical values of integrals were evaluated using routines nag_quad_1d_gen and nag_quad_2d (NAG FORTRAN 90 Library, release 3. www.nag.com)
4.1.3 Effect of Surface Morphology of the Cake.

Modeling Results

Figures 4.1.4 and 4.1.5 illustrate changes brought to a permeate flux behavior by introducing a fluff layer at the cake-suspension interface.

To find values of $\phi_w^{opt}$ and $\Delta^{opt}$ which correspond to the best match between experimental results and the model, the model was run for 36 different pairs of values of $\phi_w$ and $\Delta$ for all 3 particles sizes (20nm, 116nm, and 680 nm). 36 pairs were composed by combining 6 values of $\phi_w$: 0.58 (random packing), 0.48, 0.38, 0.28, 0.18, 0.08, and 6 values of $\Delta$: 0 (no transition zone), 10, 50, 100, 500, and 1000 particle diameters. Time values when experimental points were read and time values for which permeate flux was calculated in the model were not the same. Thus, to estimate the proximity of the model outcome to the experimental result, the linear interpolation between two modeled flux values closest in time to a given experimental point was used. For each experimental point the difference between experimental flux value and (interpolated) modeled flux value was computed. Squares of these differences for all points in a given experiment were added to obtain a single value characterizing the goodness of fit. Plot of these values against $\phi_w$ and $\Delta$ in case of 20nm and 680nm particles is shown on Figure 4.1.6 ($a,b$).
Figure 4.1.4 Modeled decline in specific permeate flux in CP filtration of 0.02μm latex particles as a function of fluff layer parameters:

$\phi_w = a) 0.48$, b) 0.38, c) 0.28, d) 0.18 e) 0.08
$D_p=20\text{nm}, \phi_w=0.08$, influence of $\Delta$.

- Experiment
- Ext. model
- $\Delta=0$
- $\Delta=10$
- $\Delta=50$
- $\Delta=100$
- $\Delta=500$
- $\Delta=1000$

Specific Number of Particles per m$^3$ vs. Time (s)
In case of 20 nm particles the best fit is realized for $\phi_w = 0.48$ and $50 < \Delta < 100$ (1 $\mu$m - 2 $\mu$m). Both steady-state value of flux and time when steady state is achieved are better predicted with this set of fluff layer parameters.

For 680 nm no significant improvement can be achieved by introducing the fluff layer. This could be explained by the fact that values of pseudo-Péclet number (defined in chapter 2.2.2) for the experimental conditions in the present work were as follows: $N_{pe}(20 \text{nm}) \sim 3.9 \times 10^{-2}$, $N_{pe}(116 \text{nm}) \sim 1.3 \times 10^0$, $N_{pe}(680 \text{nm}) \sim 4 \times 10^1$. High $N_{pe}$ for 680 nm particles means that the deposition was essentially ballistic. Under the ballistic conditions, the formation of a loose layer of particles at the suspension-cake interface is not probable. On the other hand, for 20 nm particles the diffusive character of deposition promotes formation of less-connected structure at the interface.

In the case of 0.12 $\mu$m particles, the modifications of the structure of cake-suspension interface can not explain the experimental results (Figure 4.1.6). In fact, for all $\phi_w < 0.58$ and $0 < \Delta < 1000$ tested (only $\phi_w = 0.38$ for $\Delta = 0, 10, 100, 1000$ combinations are shown in Figure 4.1.6) the steady-state flux is even lower than that given by already underpredicting extended model. Additional backtransport mechanisms, different structures of the bulk of the cake and/or inadequacies in the permeability model may be the source of this discrepancy.
Figure 4.1.5 Modeled decline in specific permeate flux in CP filtration of 0.68μm latex particles as a function of fluff layer parameters:

\[ \phi_m = \text{a) 0.48, b) 0.38, c) 0.28, d) 0.18 e) 0.08} \]
Figure 4.1.6 Difference between experimental and modeled permeate flux values for 20 nm particles calculated as a sum of squared differences between individual measurements and model prediction.
Figure 4.1.7 (a, b) Modeled decline in specific permeate flux in CP filtration of 0.12μm latex particles as a function of fluff layer parameters.
4.2 Monte Carlo Simulation of the effect of collision efficiency of particles on the deposit morphology

To establish a correlation between key operational parameters in membrane filtration and properties of the fouling layer and, hence, a membrane system performance, Monte Carlo simulation of particle deposition were performed. A focus of the presented study was the dependence of morphology of colloidal deposits on the particles' collision efficiency. This part of the presented work is a continuation and extension of the research carried out by Veerapaneni (Veerapaneni and Wiesner 1994), (Veerapaneni and Wiesner 1997), (Veerapaneni 1996) in that it has as an objective study of the influence of short-range transport on the morphology of colloidal deposits, while in Veerapaneni’s work the influence of the long-range transport was investigated.

4.2.1 Deposition Algorithm

The Monte Carlo simulation of deposition from a monodisperse suspension is performed using on-lattice model similar in many respects to those reported by previous investigators (Veerapaneni and Wiesner 1994), (Racz and Vicsek 1983). The particles are introduced to simulation space one by one on a release line (Figure 4.2.1) 20 units above the level of the highest particle in the deposit at random horizontal positions along the deposit. The horizontal coordinate $x$, of the new particle was sampled from the uniform
probability distribution:

\[ x_i = \text{nint}(\text{rand}(0) \cdot (L + 1) + 0.5) \]  \hspace{1cm} (4.2.1)

where

\text{rand}(0) - UNIX intrinsic function; returns random numbers between 0 and 1,

\text{nint}(A) - integer elemental function; returns the nearest integer to the real value A (i.e. A is rounded), and

\( L \) - length of the deposit.

As can be seen from (4.2.1), \( x_i = 1, 2, 3, \ldots, L + 2 \). The total number of columns in the lattice was \( L + 2 \). The first \( (x_i = 1) \) and the last \( (x_i = L + 2) \) columns were used to establish periodical boundary conditions in the horizontal direction: the first column was identical to the \((L + 1)^{th}\) column, while the second column was identical to the \((L + 2)^{th}\) column. As a result, if a particle reaches, for example, the left border of the lattice it would disappear there and re-appear at the right border at the same elevation. Also, the width of the lattice was chosen to be much bigger than a characteristic lateral size of the biggest deposit substructures (columns, branches) to minimize the influence of boundaries. The boundary conditions in the vertical direction - the line of initial growth sites (hereinafter referred to as substrate) and "free surface" of the deposit - inevitably have some influence on the deposit in the vicinity of these boundaries.

As soon as a particle is released it has an option of moving in one of 8 directions. Which direction is chosen depends on the force balance on the particle (Figure 4.2.2)
Figure 4.2.1 Schematic of a computer-generated deposit and the simulation workspace ¹⁰

¹⁰ Modified from (Veerapaneni and Wiesner 1994)
Figure 4.2.2 Forces acting on the particle

The force balance determines the non-uniform probability distribution in the following manner:

\[ P(1) = \frac{1 + \frac{V_z + V_{pf}}{V_d}}{8 + N_{Pr}} \]  \hspace{1cm} (4.2.2)

\[ P(7) = \frac{1 + \frac{V_{pf}}{V_d}}{8 + N_{Pr}} \]  \hspace{1cm} (4.2.3)

\[ P(i) = \frac{1}{8 + N_{Pr}} \quad i = 2,3,4,5,6,8 \]  \hspace{1cm} (4.2.4)

\[ \sum_i P(i) = 1 \]  \hspace{1cm} (4.2.5)

In the formulas above, \( N_{Pr} \) is a dimensionless Péclét-like quantity.
(Veerapaneni and Wiesner 1994) characterizing the relative importance of ballistic (deterministic) and diffusive (stochastic) particle transport in the system:

\[ N_{pe} = \frac{V_{xcf} + V_{pff} + V_s}{V_d} \quad (4.2.6) \]

Associated particle velocities \( V_{xcf}, V_{pff}, V_d \) and \( V_s \) are due to cross-flow fluid drag, permeate fluid drag, gravity drag, and diffusion correspondingly and are determined as follows:

\[ V_{xcf} = V_{cf}(1 - \gamma_{cf}V_{cf}) = V_{cf}\left(1 - \frac{\rho_f V_{cf} d_p}{24 \mu}\right) \quad (4.2.7) \]

\[ V_{pff} = V_{pf}(1 - \gamma_{pf}V_{pf}) = V_{pf}\left(1 - \frac{\rho_f V_{pf} d_p}{24 \mu}\right) \quad (4.2.8) \]

\[ V_d = \frac{kT}{3\pi \mu d_p^2} \quad (4.2.9) \]

\[ V_s = \frac{d_p^2 g (\rho_p - \rho_f)}{18 \mu} \quad (4.2.10) \]

where

- \( d_p \) - diameter of the particle,
- \( g \) - acceleration due to gravity,
- \( \rho_p, \rho_f \) - density of particle and fluid respectively,
- \( \mu \) - fluid viscosity,
- \( V_{pf}, V_{cf} \) - velocity of permeate flow and cross-flow respectively, and
- \( \gamma_{pf}, \gamma_{cf} \) - correction coefficients for permeate flow and cross-flow respectively.

\( N_{pe} \) depends strongly on the particle size. For a simple case of no
convective flow, it can be seen from (4.2.7)-(4.2.10), that \( N_p \propto d_p^4 \).

Another value important from the point of view of the model's applicability is particle's Reynolds number defined as:

\[
\text{Re}_p = \frac{d_p \sqrt{V_{\text{ref}}^2 + (V_{\text{ref}} + V_s)^2}}{\mu/\rho} \tag{4.2.11}
\]

Stokes' law (4.2.10) is only valid for creeping flow around the particle. For creeping flow the condition \( \text{Re}_p \ll 1 \) should be satisfied.

The kill line is set at the very top of the simulation space to make the simulation as realistic as the model formulation permits. When diffusion dominates and/or collision efficiency is low, it may take a long time (many elementary steps) for a particle to attach. Discarding such a particle too early may result in artificial changes introduced to the structure of a simulated deposit.

The collision efficiency \( \alpha \) was used to model the attachment process. Attachment was considered to be a sequence of collision events. In the model, attaching particles do not change the arrangement of already deposited particles and, once attached, they are considered to be attached permanently - neither resuspension, no "rolling" follows. The dependence of \( \alpha \) on the angle of incidence was not considered either. Unlike in the approaches to modeling of collision efficiency reported in the literature (Kim and Rajagopal 1991), (Meakin and Julien 1987), (Julien and Kolb 1984), (Meakin and Family 1987) in this work the collisions which did not result in the attachment were followed by
the reflection of particle in the direction which was determined by local structure of deposit and forces acting on the particle. An assumption was made that relative importance of diffusive and convective forces for a particle detached from any location in the deposit was the same as for the free particle in the suspension. Detachment rules are summarized in the Figure 4.2.4

Figure 4.2.4 Illustration of the detachment rules employed in the model

- means active site, - free site, occupied site and - adsorbing particle.

- a possible direction of detachment

Nearest neighbors of occupied sites were considered to be active sites, i.e. the sites where attachment may occur. In this model, detachment to an active site was forbidden.

The following assumptions were made in the model:

1) The suspension is monodisperse.
2) Particles are spheres.

3) No restructuring occurs. Here, restructuring means only breakup of the deposit under the influence of external forces or its own weight. A broader interpretation of restructuring is possible (Kim and Rajagopalan 1991), when the effects of multiple attachments ($\alpha \leq 1$) are considered to be also restructuring.

4) Simplistic consideration of interaction between depositing particle and the previously deposited particle.

5) Interactions between depositing particles and between particles already in the deposit are not considered.

For all simulations reported in this work, the simulation space was a square 1000x1000 lattice, unless specified otherwise. The number of deposited particles varied with deposition conditions in the approximate range $4.1 \times 10^4 + 4.3 \times 10^3$. All simulations were performed on Sun Ultra10 Workstation (333MHz UltraSparc-Ili 2MB ECache). Table 4.2 shows some typical values of CPU time required to perform simulations with different sets of deposition parameters.

4.2.2 Aggregation Algorithm

To model the DLA process the following modifications were introduced to the deposition algorithm described above:

a) Instead of a line of initial attachment sites, a “seed” particle was placed
in the middle of the 1000x1000 lattice.

b) The release “line” was a circle with a radius \( r_{\text{max}} + 20 \), where
\[
 r_{\text{max}} = \sqrt{m_0^2 + n_0^2}.
\]

\( m_0 \) and \( n_0 \) being the abscise and ordinate of the deposited particle which is remotest from the “seed”. The polar angle of the location of the next released particle was sampled with random number generator. Thus, the coordinates of a new particle released at the release line were determined as follows:

\[
m_{\text{new}} = \text{int}\left[ r_{\text{max}} \cos\left(\frac{\text{rand}(0)}{2\pi}\right)\right], \quad n_{\text{new}} = \sqrt{1 - m_{\text{new}}^2}
\]

(4.2.13)

c) Periodical boundary conditions were introduced for all four borders of the lattice.

4.2.3 Characterizing the Structure of Deposits

In this work, the fractal dimension of deposits was calculated from the upper surface properties by plotting average height of the deposit \( \bar{h} \) versus the number of deposited particles for the growing deposits. For the dependence \( \bar{h} \propto N^\phi \), the power is related to fractal dimension \( D_f \) by (2.2.2) : \( D_f = d - d_s + \frac{1}{\phi} \).

Here, \( d = 2 \) and \( d_s = 1 \).

An attempt was made to use a sandbox method to calculate fractal dimension \( D_f \) of deposits. A square lattice up to 2500x2500 in size was
employed. Thirty sandboxes (overlapping in general case) distributed homogeneously over the deposit were built. Caution was exercised in assuring that the boundaries were not approached too closely to minimize their influence. The results obtained using sandbox method were in agreement with those of first method. However, the scatter in calculated $D_f$ values was much higher than that obtained when using $\ln(\bar{h}) = d \ln(N)$ method. Probably, the

<table>
<thead>
<tr>
<th>Deposition parameters</th>
<th>$N_{Pc}$</th>
<th>$\alpha$</th>
<th>Particles released</th>
<th>Particles deposited</th>
<th>CPU Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>low $N_{r}$, low $\alpha$</td>
<td>1.22*</td>
<td>10^{-4}</td>
<td>0.01</td>
<td>279607</td>
<td>166442</td>
</tr>
<tr>
<td>low $N_{r}$, high $\alpha$</td>
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<td>1</td>
<td>(59.5%)</td>
<td>56551</td>
<td>41913</td>
</tr>
<tr>
<td>high $N_{r}$, low $\alpha$</td>
<td>1.22*</td>
<td>10^{-4}</td>
<td>1</td>
<td>419890</td>
<td>419890</td>
</tr>
<tr>
<td>high $N_{r}$, high $\alpha$</td>
<td>1.22*</td>
<td>10^{-4}</td>
<td>1</td>
<td>428259</td>
<td>428259</td>
</tr>
</tbody>
</table>

Table 4.2 CPU requirements
sandbox method should be applied to analyzing the deposits of even bigger size to completely exclude the influence of boundaries and give more accurate results.

In case of aggregation modeling boundary conditions do not influence structure of a modeled aggregate and the sandbox method was successfully used though to calculate fractal dimension of the computer generated aggregates. Values of $D_f$ obtained were consistent and accurate.

**4.2.4 Effect of Particle Size and Permeate Flow Velocity**

In the recent years, the influence of the transport properties on deposition patterns has been a subject of considerable amount of research. In most of the cases, particles were considered to be perfectly sticky with $\alpha = 1$, i.e. it was assumed that all of the collisions resulted in attachment. In other words, the focus was on the transport, while surface processes received simplistic treatment for not to complicate the interpretation of the results. One goal of the present work is to study the effect of surface chemistry of particles on deposit characteristics. Nevertheless, simulation were also performed with perfectly cohesive particles for the purpose of comparison of this model with those reported in the literature. Simulated deposits formed from perfectly cohesive particles ($\alpha = 1$) at different values of $N_A$ are presented in Figure 4.2.5 (a-d). Operational parameters were as follows:
\[
\begin{align*}
\alpha &= 1 \\
\rho_p &= 1.960 \cdot 10^3 \frac{\text{kg}}{\text{m}^3} \\
\rho_f &= 0.998 \cdot 10^3 \frac{\text{kg}}{\text{m}^3} \\
\mu &= 1.002 \cdot 10^{-3} \frac{\text{kg}}{\text{m} \cdot \text{s}} \\
T &= 273.15^0 \text{K} \\
V_{\sigma} &= 0
\end{align*}
\]

(4.2.14)

4.2.5 Effect of Surface Chemistry on Deposit's Morphology

Simulated deposits formed from particles with different collision efficiencies are presented in Figures 4.2.6 (a-d). Operational parameters were as follows:

\[
\begin{align*}
d_p &= 0.5 \mu m \\
\rho_p &= 1.960 \cdot 10^3 \frac{\text{kg}}{\text{m}^3} \\
\rho_f &= 0.998 \cdot 10^3 \frac{\text{kg}}{\text{m}^3} \\
\mu &= 1.002 \cdot 10^{-3} \frac{\text{kg}}{\text{m} \cdot \text{s}} \\
T &= 273.15^0 \text{K} \\
V_{\sigma} &= V_{\tau} = 0
\end{align*}
\]

(4.2.15)

Visual examination leads to the conclusion that a decrease in \( \alpha \) results in the deposits becoming denser with a thicker columnar structure. Though both an increase in \( N_{\tau} \) and a decrease in \( \alpha \) result in denser deposits, the nature of
**Figure 4.2.5 (a-d)**

Simulated deposit formed of perfectly cohesive particles ($\alpha = 1$) at different values of $N_{p_r}$: a) $1.31 \cdot 10^{-4}$, b) $1.31 \cdot 10^{-2}$, c) $1.31 \cdot 10^{0}$, d) $1.31 \cdot 10^{+4}$
"densification" is different in these two cases as can be seen from the comparison of Figure 4.2.5 and Figure 4.2.6.

An increase in $N_p$, leads to relatively homogeneous spreading of the deposit so that density of the deposit does not depend on the location in the deposit where the density is measured; provided that the measured volume is bigger than volume of several particles. A decrease in collision efficiency, on the other hand, results in non-homogeneous spreading of the deposit, thick deposit branches with long voids between them being formed\textsuperscript{11}. These voids tend to be elongated in the direction of growth. It may be concluded that the changes in the short-range structure of the deposit occur as a result of changing $\alpha$, while no such changes are induced by changes in $N_p$.

The aggregation model was also run, mainly with a purpose of calibrating presented results against results of the models reported in the literature. Two aggregates were generated (Figure 4.2.7a,b), for two different collision efficiency values : $\alpha = 0.1$ and 1. The sandbox method was employed to compute fractal dimensions of the aggregates. The obtained values $D_f$ are presented in Table 4.3. The $D_f$ value for the case of $\alpha=1$ is in perfect agreement with previously reported results (Witten and Sander 1981), (Vicsek 1992) suggesting that the algorithm and analysis are correct.

\textsuperscript{11} In both cases the growth is not isotropic as there is a preferential direction in the system - the direction of growth.
Figure 4.2.6 (a-d)

Simulated deposit formed of 0.5\(\mu\)m particles with different collision efficiencies: \(\alpha = a) 0.50, b) 0.10, c) 0.05, and d) 0.03\)
Figure 4.2.7 (a,b)

Simulated aggregates formed of 0.1 $\mu$m particles with different collision efficiencies $\alpha$: a) 1, b) 0.1
<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$D_f$</th>
<th>$\delta D_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.700</td>
<td>0.001</td>
</tr>
<tr>
<td>0.1</td>
<td>1.761</td>
<td>0.002</td>
</tr>
<tr>
<td>0.01</td>
<td>1.951</td>
<td>0.001</td>
</tr>
</tbody>
</table>

**Table 4.3** Fractal dimension values for generated aggregates

To compare the long-range structure of the deposits quantitatively the fractal dimension $D_f$ of each deposit was calculated by plotting logarithm of average height of deposit $\bar{h}$ versus logarithm of the amount of deposited particles $N$. There were several runs of the model for each combination of $\alpha$ and $N_{p_e}$. Specifically, three runs were done for all combinations of $\alpha$ and $N_{p_e}$ when $N_{p_e} > 1.06 \cdot 10^{-2}$ and six runs were done for all combinations of $\alpha$ and $N_{p_e}$ where $N_{p_e} < 1.06 \cdot 10^{-2}$. This was because of the higher scatter in data when DLA limit was approached (i.e. for the case of low $N_{p_e}$ values). The fractal dimension was obtained by averaging the results of these three/six runs. The dependence of $D_f$ on $\alpha$ for different $N_{p_e}$ values is summarized in Figure 4.2.8. Error bars correspond to a 90% confidence interval. Operational parameters were the same as indicated above in this section.

For the perfectly cohesive particles ($\alpha=1$) the following fit (4.2.16) of the
fractal dimension to the Péclét number was proposed earlier (Veerapaneni and Wiesner 1994).

**Figure 4.2.8** Fractal dimension of deposit as a function of Péclét number for two different collision efficiencies: $\alpha=0.1$ and $\alpha=1$

\[
D_f = \begin{cases} 
    1.7 & \log(N_{Pr}) \leq -1.7 \\
    1.8130 + 0.0873erf(\log(N_{Pr})) & -1.7 \leq \log(N_{Pr}) \leq 3.0 \\
    \rightarrow 2 & \log(N_{Pr}) \geq 3.0
\end{cases} \tag{4.2.16}
\]

where the theoretical limit of 2 for ballistic deposition has been substituted for an asymptote of approximately 1.9 observed in the simulations. The comparison between these results and results obtained in this work is shown in Figure 4.2.9.
In limit of low \( N_p \), values both models predict the theoretical DLA (diffusion-limited aggregation) limit of 1.7, while in the ballistic limit the theoretical limit of 2.0 was reached in the model presented here. The latter may explain the discrepancy seen in Figure 4.2.9.

![Graph showing fractal dimension of deposits of perfectly cohesive particles (\( \alpha = 1 \)) as a function of Péclet number.](image)

**Figure 4.2.9** Fractal dimension of deposits of perfectly cohesive particles (\( \alpha = 1 \)) as a function of Péclet number

Instead of using fit (4.2.16) the data were fit by the hyperbolic tangent function dilated and translated as needed (4.2.17). The fit was performed using
non-linear least-square regression\textsuperscript{12}. The results of the fit are represented in Figure 4.2.8 as dashed lines. The values for coefficients found are summarized in Table 4.3.

Different researchers (Dickinson 1989), (Kim and Rajagopalan 1991) reported contradicting results when investigating whether collision efficiency has an influence on the long-range structure of the deposit. The results obtained in this work clearly support the idea that $\alpha$ is one of the key parameters determining both short-range and long-range structure of a deposit.

$$f(x) = a + k_1 \tanh(k_2(x-b)) = a + k_1 \frac{e^{k_2(x-b)} - e^{-k_2(x-b)}}{e^{k_2(x-b)} + e^{-k_2(x-b)}}$$

(4.2.17)

<table>
<thead>
<tr>
<th></th>
<th>$\alpha=0.1$</th>
<th>$\alpha=1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>1.917 ± 0.001</td>
<td>1.876 ± 0.001</td>
</tr>
<tr>
<td>$b$</td>
<td>-1.962 ± 0.033</td>
<td>-2.156 ± 0.034</td>
</tr>
<tr>
<td>$k_1$</td>
<td>0.076 ± 0.001</td>
<td>0.111 ± 0.001</td>
</tr>
<tr>
<td>$k_2$</td>
<td>1.531 ± 0.129</td>
<td>0.672 ± 0.026</td>
</tr>
</tbody>
</table>

Table 4.4 Coefficients and their standard deviations for the fit (4.2.17)

\textsuperscript{12} The Visual Basic program which does the regression and finds standard deviations of regression coefficients was written and kindly provided by Prof. M. Tomson.
4.2.6 Effect of Lateral Flow Velocity and Collision Efficiency.

Simulated deposits formed at non-zero values of cross-flow velocity are presented in Figure 4.2.10. The values assigned to parameters describing suspension properties, fluid properties, permeate and cross-flow velocity were as follows (4.2.14):

\[
\begin{align*}
&d_p = 1 \mu m \\
&\rho_p = 1.960 \cdot 10^3 \frac{kg}{m^3} \\
&\rho_f = 0.998 \cdot 10^3 \frac{kg}{m^3} \\
&\mu = 1.002 \cdot 10^{-3} \frac{kg}{m \cdot s} \\
&T = 273.15^0 K \\
&V_{\nu} = 0 \\
&V_{cf} = 0.5 \frac{\mu m}{s}
\end{align*}
\]
Figures 4.2.10 (a-b) Simulated deposit formed at non-zero cross-flow velocity for different values of cross-flow velocity $v_c < v_b$. 
Due to the no-slip condition (tangential component of fluid velocity should be zero at the membrane surface) the deposits initially grow almost normally to the surface (Figure 4.2.10). It means that at the initial stage of filtration, fouling cakes formed in cross-flow regime have the structure similar to that of cakes formed in dead-end filtration. In effect, there are two more considerations which make the similarity even closer. Firstly, the realistic no-slip surface is not the membrane surface but some surface in the bulk of the cake. No-slip surface moves in the direction from the membrane as cake growth progresses so that only top layer of the fouling cake experiences the shear stress. Secondly, the profile of tangential velocity is not parabolic as would be the case in the absence of the cake but a more complex function.

An additional restructuring due to lower values of $\alpha$ results in lowering the fractal dimension of deposits. Lower fractal dimension means lower surface roughness and denser deposits, which results in the no-slip surface being closer to the cake-suspension interface. Thus, changes introduced into structure of cakes formed in shear flows by lowering the collision efficiency of particles $\alpha$ make the similarity between dead-end and cross-flow operation regimes even closer.

4.2.7 Deposition from Heterosuspensions

A logical first step in simulating the more realistic case of heterodeposition is to simulate the deposition of just two different sorts of particles. In this work,
deposits composed of two sorts of particles, each sort having its own surface chemistry, were modeled.

Generally, a system with \( N \) sorts of particles with different surface chemistries, is characterized by \( \frac{N(N-1)}{2} \) different collision efficiencies. In a system with two sorts of particles, say red and black ones, will be 3 collision efficiencies: \( \alpha_{\text{red-red}} \), \( \alpha_{\text{black-black}} \), and \( \alpha_{\text{red-black}} \). In fact, there are 2 \((2N\) in a general case) more alphas to consider - \( \alpha_{\text{red-substrate}} \) and \( \alpha_{\text{black-substrate}} \), but these are important only in the processes occurring in the vicinity close to the substrate (in the region several particle diameters thick adjacent to the substrate). Another parameter in the case of heterodeposition is a fraction (or relative concentration) \( f_i \) of each sort of particles. Although \( f_i \) is an important factor in determining the deposit's structure (see chapters 2.2.5, 2.2.7), for all results reported here the fraction was considered to be the same, \( f_i = 0.5 \). That was done because the subject of this work was to study primarily the influence of surface chemistries of particles. Factoring out such an important factor as \( f_i \) made a task of interpretation of results much easier.

In this model, at the time of release of a new particle a random number was sampled from a uniform probability distribution. If the value of this random number was less than \( f_i \) than a particle was considered to be from class 1 (red), if the number was bigger than \( f_i \) - from class 2 (black). When a particle of class \( i \) reaches a deposit and encounters an active site of a particle of class \( j \), the particle attaches with a probability \( \alpha_{ij} \). Figure 4.2.11(a,b) illustrates growth sites
for a modeled heterodeposit.

4.2.7.1 Structure of a Heterodeposit for Different Combinations of Collision Efficiencies

Deposits with different combinations of the parameters involved were modeled (Table 4.5). In this chapter, resulted deposition patterns are discussed. Two features of the deposition patterns - degree of segregation and "color" of the deposit's surface are used to characterize deposits.

The case $\alpha_{br} \geq \alpha_{bb}, \alpha_{rr}$ is trivial - red particles attach to black ones and vice versa and the chessboard-like pattern would result (Figure 4.2.12d, sim. #6). Thus, the non-trivial case $\alpha_{br} \leq \alpha_{bb}, \alpha_{rr}$ is of most interest. For certainty, the probability of sticking between black particles ($\alpha_{bb}$) was taken to be bigger than that between red ones ($\alpha_{rr}$): $\alpha_{bb} \geq \alpha_{rr}$, and initial surface was assumed to consist of red particles.

First, the case $\alpha_{bb} \neq \alpha_{rr}$ was studied. Different degrees of segregation were found for this case. Absolute values of collision efficiencies had a major influence on the relative distribution of particles of different types in the deposit (compare Figures 4.2.12e and 4.2.12f, sim.#10,12).

In the case when $\alpha_{br}$ is at least 1 to 2 orders of magnitude smaller than the smallest of $\alpha_{bb}$ and $\alpha_{rr}$ particles with smaller $\alpha$ segregate on the surface of branching structures formed by particles with bigger $\alpha$ (e.g. Figure 4.2.12a,
The decrease in value of $\alpha_r$ with a fixed values of $\alpha_r$ and $\alpha_b$, resulted in higher degree of segregation, but not in changes in the segregation pattern - particles from less cohesive fraction filled the spaces between branching structures formed from more cohesive particles. This general trend held for a wide range of values of $\alpha$: from $\alpha_r = 10^{-3}$ (Figure 4.2.12a, sim#1) to $\alpha_r = 10^{-5}$ (Figure 4.2.12 g).

In the other case when $\alpha_b = \alpha_r$, relatively independent growth of red and black structures is observed (Figure 4.2.12c, sim.#4 and sim#5, not shown) with the deposition pattern being symmetrical in respect to reds and blacks, as anticipated. Of course, the symmetry was not observed in the vicinity of the substrate, because of the influence of the all-red substrate.

Also, two heterodeposits differing only in particle size were compared. In first one, all particles - red and black - were 0.1µm (Figure 4.2.12a, sim#1), while in another deposit, all particles were 0.5µm (Figure 4.2.12h, sim.#7). The deposition pattern changed in a predictable fashion - the homogeneous spreading occurred in a deposit with smaller particles, as a result of the increase in Péclét number. However, the segregation pattern, when on the
Figure 4.2.11  (a,b)  a) Growth sites for a heterodeposit grown on 300x160 lattice. dark blue sites are sites of adsorption to yellow particles, orange sites are sites of adsorption to red particles. b) Close-up of the
heterodeposit shown in a).

surface the less cohesive particles are predominantly found, remained unchanged.

<table>
<thead>
<tr>
<th>number of simulation</th>
<th>Dp, μm</th>
<th>$\alpha_{rr}$</th>
<th>$\alpha_{br}$</th>
<th>$\alpha_{bb}$</th>
<th>Fraction</th>
<th>&quot;color&quot; of membrane</th>
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</thead>
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<td>$10^{-2}$</td>
<td>$10^{-1}$</td>
<td>0.5</td>
<td>red</td>
</tr>
<tr>
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<td>$10^{-3}$</td>
<td>$10^{-1}$</td>
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<td>$10^{-5}$</td>
<td>$10^{-2}$</td>
<td>0.5</td>
<td>red</td>
</tr>
<tr>
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<td>$10^{-1}$</td>
<td>$10^{-2}$</td>
<td>0.5</td>
<td>red</td>
</tr>
<tr>
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<td>$10^{-3}$</td>
<td>$10^{-1}$</td>
<td>0.5</td>
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<td>0.5</td>
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</tr>
<tr>
<td>9</td>
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<td>$10^{-5}$</td>
<td>$10^{-1}$</td>
<td>0.5</td>
<td>red</td>
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<tr>
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<td>$10^{-2}$</td>
<td>0.5</td>
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<tr>
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<td>$10^{-2}$</td>
<td>0.5</td>
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</tr>
<tr>
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<td>$10^{-0}$</td>
<td>0.5</td>
<td>red</td>
</tr>
</tbody>
</table>

Table 4.5 Performed simulations with different combinations of heterodeposition parameters
4.2.7.2 Physical Interpretation of Different Combinations of Collision Efficiencies

In this chapter, when establishing a correspondence between the physical properties of particles and different sets of collision efficiency values only effects of charge and hydrophobicity will be considered. The effects of sterical and other possible interactions will be neglected for simplicity.

Two different scenarios - one when electrostatic interactions are dominant and another one when particles (or molecules) carry very small charges and hydrophobic forces dominate interparticle interactions - will be considered separately.

a) Electrostatic interactions are more important.

If red and black particles carry electrical charges q1 and q2 correspondingly and q1 and q2 have opposite signs then a trivial case occurs as discussed above - $\alpha_{br} > \alpha_{bb}, \alpha_{rr}$ (Figure 4.2.12d), whatever the relative hydrophobicity of red and black particles may be. Not only van der Waals forces but also electrostatic forces are attractive in this case.

If particles from different sets carry the charge of the same sign (and absolute value of charge carried by a red particle is higher, because of stipulation that $\alpha_{bb} \geq \alpha_{rr}$), then $\alpha_{rr} < \alpha_{br} < \alpha_{bb}$. The value of $\alpha_{br}$ depends on the relative hydrophobicity of red and black particles.

b) Hydrophobic interactions are more important.
If both sorts of particles, reds and blacks, are hydrophobic/hydrophilic (and

Figure 4.2.12 (a-h)

Simulated heterodeposits

a) $\alpha_{\text{red-red}} = 10^{-2}$, $\alpha_{\text{red-black}} = 10^{-3}$, $\alpha_{\text{black-black}} = 10^{-1}$; $d_p = 0.1\mu m$

b) $\alpha_{\text{red-red}} = 10^{-2}$, $\alpha_{\text{red-black}} = 10^{-2}$, $\alpha_{\text{black-black}} = 10^{-1}$; $d_p = 0.1\mu m$

c) $\alpha_{\text{red-red}} = 10^{-1}$, $\alpha_{\text{red-black}} = 10^{-3}$, $\alpha_{\text{black-black}} = 10^{-1}$; $d_p = 0.1\mu m$

d) $\alpha_{\text{red-red}} = 10^{-2}$, $\alpha_{\text{red-black}} = 10^{-1}$, $\alpha_{\text{black-black}} = 10^{-2}$; $d_p = 0.1\mu m$

e) $\alpha_{\text{red-red}} = 10^{-3}$, $\alpha_{\text{red-black}} = 10^{-5}$, $\alpha_{\text{black-black}} = 10^{-2}$; $d_p = 0.1\mu m$

f) $\alpha_{\text{red-red}} = 10^{-1}$, $\alpha_{\text{red-black}} = 10^{-3}$, $\alpha_{\text{black-black}} = 10^{-0}$; $d_p = 0.1\mu m$

g) $\alpha_{\text{red-red}} = 10^{-2}$, $\alpha_{\text{red-black}} = 10^{-3}$, $\alpha_{\text{black-black}} = 10^{-1}$; $d_p = 0.1\mu m$

h) $\alpha_{\text{red-red}} = 10^{-2}$, $\alpha_{\text{red-black}} = 10^{-3}$, $\alpha_{\text{black-black}} = 10^{-1}$; $d_p = 0.5\mu m$
$\alpha_{\text{red-red}} = 10^{-2}, \alpha_{\text{red-black}} = 10^{-3}, \alpha_{\text{black-black}} = 10^{-1}$
b) \[ \alpha_{\text{red-red}} = 10^{-2}, \alpha_{\text{red-black}} = 10^{-2}, \alpha_{\text{black-black}} = 10^{-1} \]
\( \alpha_{\text{red-red}} = 10^{-1}, \alpha_{\text{red-black}} = 10^{-3}, \alpha_{\text{black-black}} = 10^{-1} \)
Close-up. $\alpha_{\text{red-red}} = 10^{-2}, \alpha_{\text{red-black}} = 10^{-1}, \alpha_{\text{black-black}} = 10^{-2}$
\( \alpha_{\text{red-red}} = 10^{-3}, \alpha_{\text{red-black}} = 10^{-5}, \alpha_{\text{black-black}} = 10^{-2} \)
"g"

\[ \alpha_{\text{red-red}} = 10^{-2}, \alpha_{\text{red-black}} = 10^{-5}, \alpha_{\text{black-black}} = 10^{-1} \]
h)

\[ D_p = 0.5 \text{um}, \alpha_{\text{red-red}} = 10^{-2}, \alpha_{\text{red-black}} = 10^{-3}, \alpha_{\text{black-black}} = 10^{-1} \]
black particles are more hydrophobic/hydrophilic than reds are, again because of the stipulation that $\alpha_{bb} \geq \alpha_{rr}$, then $\alpha_{rr} < \alpha_{br} < \alpha_{bb}$. Where exactly "in between $\alpha_{rr}$ and $\alpha_{bb}$", the $\alpha_{br}$ is depends on the relative charge of red and black particles.

If red particles are hydrophobic while black ones are hydrophilic (or vice versa) then the case of $\alpha_{br} \leq \alpha_{bb}, \alpha_{rr}$ (modeled in this work) may be represented. This situation may be realized when a mixture of polystyrene (latex) and silica particles having hydrophobic and hydrophilic functionality, correspondingly, is depositing.

A variety of combinations is possible in the gray area when neither electrostatic, nor hydrophobic interactions dominate. Generally, $\alpha_{br} \leq \alpha_{bb}, \alpha_{rr}$ holds when reds and blacks carry the same charge and are both hydrophobic or both hydrophilic.

4.2.7.3 Characterization of Surface of a Deposit

To quantitatively characterize the surface segregation effect, knowledge of the surface per se is required. The approach to defining the deposit’s surface used in this work was to compute the growth-site probability distribution (GSPD) (Vicsek 1992). The surface may be defined then as a set of all sites with a probability higher then a given value.

The method is based on the deposition algorithm used to form a deposit. Instead of releasing new particles, probe particles, (referred to in the text simply
probes,) were released at the very top of a lattice containing deposit. The only difference between probes and particles was that a probe disappears at the moment when a "regular" particle would attach to the deposit. While regular particles modify the deposit by attaching to it, probes just explore the deposit by touching it. Thus, probes are transported in the same way as are regular particles. A probe has size, and density, and its surface chemistry is characterized by a collision efficiency \( \alpha_{\text{probe}} \). By changing \( \alpha_{\text{probe}} \), it is possible to vary the ability of a probe to enter sinuous fjords in the deposit. At the location in the deposit touched by a probe the last time before it disappears, a counter increases its value by one. After a certain number of probes are released, the counter values are read and are plotted in the same format as the one used to plot the deposit. Figure 4.2.13 (a-f) represents the surface of the deposit depicted on Figure 4.2.11a, for probes with different collision efficiencies. The higher the number of probes released, and the lower the collision efficiency \( \alpha_{\text{probe}} \), the more counters have non-zero readings and, hence, more detailed information about the surface is obtained. In this work, 50000 probes were released for each value of \( \alpha_{\text{probe}} \). Figure 4.2.15 illustrates a) how accurately the surface was determined, and b) degree of particle segregation on the surface. With \( \alpha_{\text{probe}} \) decreasing, more and more inner regions of the deposit appear accessible to the probes. As can be seen from Figure 4.2.15, red particles a) dominate the easily accessible regions of the deposits, and b) become even more abundant on the surface of remote, hardest to reach, corners of the deposit's fjords.
Figure 4.2.13 (a-f)

Surface of the deposit shown on Figure 4.12a represented by growth sites touched at least 1 time by probe particles with collision efficiency $\alpha$: a) $10^0$, b) $10^{-1}$, c) $10^{-2}$, d) $10^{-3}$, e) $10^{-4}$, f) $10^{-5}$
c) Collision efficiency of probe particles $\alpha=10^{-2}$

d) Collision efficiency of probe particles $\alpha=10^{-3}$
Figure 4.2.13 (a-d)

Simulated heterodeposit (a) and heteroaggregate (c) color-coded (b and d, correspondingly) according to the time of arrival
a)

\[ \alpha_{\text{red-red}} = 10^{-2}, \alpha_{\text{red-black}} = 10^{-3}, \alpha_{\text{black-black}} = 10^{-1} \]
c) \( \alpha_{\text{red-red}} = 10^{-2}, \alpha_{\text{red-black}} = 10^{-3}, \alpha_{\text{black-black}} = 10^{-1} \)
In an attempt to explain such segregation patterns, particles in the deposits were color-coded according to the time of their attachment. (Figure 4.2.13 b,d). The periphery of the deposits, i.e. their surface, is, naturally, composed of particles, which were the latest to attach. Taking this into account, a mechanistic explanation of the observed segregation pattern may be made. Because particles with smaller collision efficiency (red ones in this work) bounce more before attachment than the ones with a larger collision efficiency (blacks in this work), and, because, consequently, reds have more chances to get into the fjords without being attached to the fjords's walls, it is red particles that attach last and cover the surface.

Figure 4.2.15 Percentage of red particles on the surface and amount of growth sites detected by probes on the surface as a function of $\alpha_{\text{probe}}$. 
4.2.8 Effect of Substrate Morphology

It was found in this work that the changes in deposit morphology induced by variations in collision efficiency differ from those induced by differences in long-range transport (chapter 4.2.5). This finding was a motivation for the study of diffusion-limited deposition from monodisperse suspensions of particles of variable cohesiveness onto a rough substrate. The influence of collision efficiency on the decay of the initial roughness in the course of deposition was studied in a series of Monte Carlo simulations.

Fourier profile analysis was employed to characterize the decay of the initial substrate profile in the course of the deposition as a function of particle's collision efficiency. The profile of the starting surface was represented by the \( \cos^2 x \) function:

\[
A_i = A_0 + A_m \cos^2 \left( \frac{2\pi n}{L'} i \right)
\]  \hspace{1cm} (4.2.18)

where

- \( A_i \) - amplitude of the substrate roughness at \( i^{th} \) location along the substrate
- \( L' = L + 2 \), where \( L \) - length of the substrate,
- \( i \) - location along the substrate. \( i = 1, 2, ..., L' \),
- \( A_m \) - maximum amplitude of the substrate roughness,
- \( A_0 \) - constant which allows for substrate elevation (to make the deposition algorithm simpler. \( A_0 \) has no specific physical meaning. \( A_0 = 3 \) in all cases),
Figure 4.2.16  Simulated deposits formed of 0.5\(\mu\)m particles with different collision efficiencies (\(\alpha=0.01, 0.1\)) at the sinusoidal substrate
\( n_0 \) - number of waves in the substrate profile of length \( L' \).

Visual inspection of upper surfaces of deposits (Figure 4.2.16) immediately suggests that collision efficiency strongly effects the evolution of the deposit profile on an uneven substrate. The deposit profiles were recorded 100 times in the course of deposition. The lattice was divided into 100 horizontal bands of equal width. As soon as the highest particle in the deposit reached the level of the next band, the deposit profile would be recorded. The illustration of how well the deposit "remembers" the morphology of an underlying substrate for different values of \( \alpha \) is represented in Figure 4.2.17.\(^{13}\)

Treating the deposit profile as a signal and using appropriate signal processing tools allow for a quantitative comparison of the deposition patterns corresponding to different \( \alpha \) values. The Fourier transform spectra were calculated for each of the profiles using the fft (fast-fourier transform) tool available from the Matlab toolbox.

\(^{13}\) In the Figure 4.2.17 the evolution of roughness of the upper surface of the deposit is shown. One hundred of deposit profiles (deposit profile = contour of upper surface) were recorded at different stages of deposition. Each time the average height of the deposit grown so far was subtracted from the profile so that the resulting curve represented deviation of deposit height from the average for each point along the deposit length, or, in other words, it represented roughness of deposit's upper surface. These resulting curves were plotted here against the maximum heights of the deposit at the times of growth when these curves were recorded. The figure is a 2D projection of the 3D graph.
Figure 4.2.17 The evolution of roughness of the upper surface of the deposit for two different collision efficiencies: $\alpha = 0.02, 0.10$. Dimensions: Length of deposit (distance), Height of deposit (distance'), where distance is measured in particle diameters, and distance' is measured in particle diameters and normalized by the amplitude of the initial roughness of the substrate.
The link between space and frequency domains as given by Fourier transform is as follows:

\[
\begin{aligned}
A_{\omega}(w) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(x) e^{-i\omega x} \, dx \\
A(x) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} A(\omega) e^{i\omega x} \, d\omega
\end{aligned}
\]  

(4.2.19)

where

\[
\begin{align*}
\dim(A) &= \text{distance} \\
\dim(x) &= \text{distance} \\
\dim(w) &= \frac{\text{rad}}{\text{distance}} \\
\dim(A_{\omega}) &= \text{distance}^2
\end{align*}
\]

Figure 4.2.18 illustrates the changes in the Fourier spectrum with deposit height for different alphas. In this graph the 0th frequency component is subtracted from all the spectra (which is equivalent to subtracting the average height in the space domain). The band \( A_{\omega} \) corresponding to the wavelength of the substrate is a prominent feature in this graph. The decay of the amplitude of this component is a characteristic of the deposit’s “memory” of the morphology of the substrate.

Five runs of the deposition program were done for each of the following seven values of collision efficiency \( \alpha \): 0.01, 0.03, 0.07, 0.10, 0.20, 0.50, 1.00.

The dependence of the Fourier amplitude \( A_{\omega} \) on the deposit heights shown on the Figure 4.2.19. The \( A_{\omega} \) values were normalized by the maximum value of \( A_{\omega} \) - the value which corresponds to the substrate with no deposit on it.
Figure 4.2.18 The degradation of the Fourier transform spectrum of the deposit profile for different collision efficiencies: \( \alpha = 0.02, 0.05, 0.1, 1.0 \).

Dimensions:

- Frequency \( \left( \frac{\text{rad}}{\text{distance}} \right) \),
- Fourier Amplitude \( (\text{distance}^2) \),
- Height of deposit \( (\text{distance}) \), where distance is measured in particle diameters, and \( \text{distance}' \) is measured in particle diameters and normalized by the amplitude of the initial roughness of the substrate.
Each of these dependencies were fit with an exponential curve
\[ A_w = e^{-kH_d}, \]
where \( H_d \) - height of the deposit, and \( k \) - decay coefficient.

Technically, the linear fit was used to approximate the function
\[ \ln(A_w) = -kH_d. \]
From these fits the values of decay coefficient \( k \pm \delta k \) were found, where \( \delta k \) corresponded to a 95% confidence interval. The reciprocal value of \( k \), \( h_{\text{decay}} \) has a simple physical meaning - \( A_w \) decreases by the factor of \( e = 2.727 \) when deposit height reaches \( h_{\text{decay}} \) value. Thus, \( h_{\text{decay}} \) represents how well the deposit preserves the initial profile of substrate. The higher \( h_{\text{decay}} \), the better “memory” the deposit has. The dependence of \( h_{\text{decay}} \) on the collision efficiency of particles which form the deposit is represented in Table 4.6 and Figure 4.2.17.

The error in determination of \( h_{\text{decay}} \) was found by differentiating the relationship \( h_{\text{decay}} = \frac{1}{k} \):

\[ \left| \delta h_{\text{decay}} \right| = \frac{\delta k}{k^2} \]  \hspace{1cm} (4.2.20)

As can be seen, the deposits formed of particles with intermediate collision efficiencies \( \alpha \) best preserve the shape of the underlying substrate. A possible explanation for this observation is that at one extreme (at low values of \( \alpha \)) particles bounce so many times before being eventually attached that they fill the “valleys” of the substrate very quickly. At another extreme (at values of \( \alpha \) close to 1 near the immediate attachment limit) - the branches of the deposit coalesce readily at relatively low deposit heights which also leads to a limiting
Figure 4.2.19 Decay of the $A_p$ component of the deposit profile Fourier transform in the course of the deposit growth as a function of collision efficiency $\alpha$.

Figure 4.2.20 Decay height as a function of collision efficiency $\alpha$. 
influence of boundary conditions on the deposit surface morphology.

<table>
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<th>$\alpha$</th>
<th>$h_{\text{decay}}$</th>
<th>$\delta h_{\text{decay}}$</th>
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<td>0.507</td>
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| Table 4.6 Decay height as a function of collision efficiency $\alpha$. |

4.2.9 Multifractal Analysis of Growth Site Probability Distribution over Deposits

To investigate the effect of fractal dimension of deposits and processes governing deposit formation on the properties of the surface of the deposit, multifractal analyses of growth site probability distributions (GSPDs) over different deposits were performed. Four simulated deposits formed at different $N_{pe}$ and four simulated deposits formed from particles with different $\alpha$ were investigated. Fractal dimensions in the set of deposits formed at different $N_{pe}$ were approximately the same as these in the set of deposits formed from particles with different $\alpha$ so that the effect of the formation process on the GSPD
could be studied separately from the effect of fractal dimension. In fact, a deposit formed of particles with \( \alpha = 1.000 \) transported to deposit at \( N_{pe} = 7.0 \times 10^{-2} \) was common for both sets and all other deposits were obtained either by variation of \( \alpha \) or by variation of particle’s density (and thereby \( N_{pe} \)). The GSPD for all deposits were obtained using random walkers algorithm described in chapter 4.2.7.3. Random walkers (probes) with collision efficiency of \( 10^{-4} \) were released until a total of 50000 probes disappeared on a deposit’s surface. For each location at the deposit surface the number of contacts by a probe was calculated and divided by 50000 so that the normalized GSPD was obtained. Normalized GSPDs for all 8 deposits are represented on Figure 4.2.21 (a, b).

On this figure:

\[
\text{Probability of attachment} = \frac{\text{Number of attachments at site } X}{\text{Total number of attachments}}
\]

\[
\text{Fraction of attachment sites} = \frac{\text{Number of sites } X}{\text{Total number of attachment sites}} \times 100\%
\]

As can be seen from the comparison of 4.2.21.a and 4.2.21 b, for deposits formed from very neutral (non-cohesive, low \( \alpha \)) particles the least accessible sites do not dominate GSPD in contrast to the case of deposits formed at very ballistic conditions (high \( N_{pe} \)) characterized by the same fractal dimension. This result reflects the fact that a decrease in \( \alpha \) leads to a formation of a deposit which has not only a higher fractal dimension but also a surface with a distribution of adsorption sites which is more homogeneous in terms of their accessibility. This observation was further tested using MFA.
Figure 4.2.21 (a, b) GSPDs for deposits formed at different (a) $N_{pe}$, and (b) $\alpha$. 
To calculate the multifractal spectrum the following algorithm was followed for each of the deposits:

1) the total $2^{10} \times 2^{10}$ lattice with GSPD was divided into $(2^{10}/2^n)^2$ smaller squares $\varepsilon = 2^n$ lattice units in size, $n=1,2,\ldots,10$.

2) For each $n$ the total probability for each box was calculated.

3) For each $n$ moments were calculated using (2.2.7):

$$M_q = \sum_i p_i^q$$

$q = -p, -p+\delta, -p+2\delta$.

4) For each $q$ the scaling exponent $\tau(q)$ for the $q^{\text{th}}$ moment was calculated as a slope of $\ln(M_q)$ vs $\varepsilon$ dependence (according to 2.2.7)

5) $\beta(q)$ was calculated from (2.2.11)

6) $f(\beta)$ was calculated from (2.2.8)

It was found that in case of negative $q$ (corresponding to sites with low probability), the moments did not scale at small $n$ (i.e. at small $\varepsilon$). The less $q$, the stronger the deviation from linearity as shown on Figure 4.2.22. Only when $\varepsilon$ was higher than a certain value, the scaling was observed. Thus, in computing multifractal spectra only higher $\varepsilon$ regions of $\ln(M_q)$ vs $\varepsilon$ dependence with less nonlinearity were considered. The error introduced by this procedure is associated with finite size effects when $\varepsilon$ approaches the size of the whole fractal object under consideration. In this particular case, the periodical
boundary conditions imposed during the growth of a deposit and calculating its GSPD, were selected with the goal of decreasing the finite size effects. It is this consideration that served as a validation for considering only higher ε region. The scaling appears only when a box size exceeds ca. 100 particle sizes which corresponds to a size of deposit's macro-structures (columns). Cut-off values of $M(q)$ are determined by (2.2.7) dependence. The smallest probability value is $10^{-5}$ which corresponds to a site visited just once by a probe particles.
Figure 4.2.23 (a, b) Multifractal spectra of simulated deposits. Influence of a) $\alpha$, and b) $N_{pe}$. 
This term will dominate the sum in (2.2.7) and, raised to the power of q, will give the cut-off value observed in Figure 4.2.22. E.g. \((10^{-5})^{20}=10^{100}\).

Multifractal spectra calculated according to the algorithm described above are presented on the Figure 4.2.23 (a, b). The spectrum of deposit which is common to both sets is depicted in red. As can be seen from the figures, the spectra for deposits formed at different \(N_{pe}\) are wider than their counterparts with the same fractal dimensions but formed of particles with lower collision efficiencies. This observation corroborates the conclusion drawn from comparison of GSPDs in Figure 4.2.21 (a, b). The wider \(f(\beta)\) spectra (i.e. the wider range of \(\beta\) values needed to characterize a deposit) correspond to a wider range of local environments present in the deposit's GSPD and reflects higher heterogeneity of the deposit. This may have important implications for application of deposited films as catalytic surfaces.

The following notes should be made concerning the results reported on in this chapter:

1) A random walk algorithm was employed to obtain the GSPD. An inherent drawback of this approach is that low-probability parts of GSPD are underrepresented. Hence, the part of the \(f(\beta)\) spectrum where \(f(\beta)<0\), corresponding to negative \(q\), should be interpreted with caution.
2) Preparing bigger deposits (bigger than $2^{10} \times 2^{10}$) to insure that $\varepsilon \ll 1$
condition holds will improve reliability of results.

3) It was reported in the literature (Lee and Lee 1997) that the multifractal spectrum of GSPD of diffusion-limited aggregate depends on the size of the aggregate. This circumstance complicates the analysis of sensitivity of a multifractal spectrum due to differences in deposit formation history and its fractal dimension.

4) The multifractal spectra were calculated for just one simulated deposit.
Preparing several deposits under the same set of conditions ($\alpha$, $N_{pe}$) and averaging calculated multifractal spectra would provide a more statistically reliable result.

5) Multifractal spectra depend on the collision efficiency of the probes which was the subject of extensive study by Lee and Lee (Lee and Lee 1997). Therefore, the multifractal spectra obtained here can only compared and relative but not absolute conclusions can be drawn.
Chapter 5

Summary

The extended model of membrane filtration was verified experimentally. Model was found to describe reasonably well (slightly overpredicting) steady-state permeate flux for small (20nm) and big (580nm) particles. However, steady-state flux for medium-sized particles (116nm) was considerably underpredicted by the model.

The presence of the fluff layer at cake-suspension interface was hypothesized to explain the differences found between modeling and experimental results. The fluff layer was described by two parameters - cake solid fraction at the wall and thickness of the zone transition of transition between the bulk of the cake with solidosity of $\phi_c=0.58$ and the cake wall.

Incorporation of the fluff layer into the extended model allowed for a better matching of modeling and experimental results for 0.02µm particles. All 3 factors - longer (than predicted) time to reach steady state, higher permeate flux observed at the initial stages of filtration and lower steady-state permeate fluxes observed could be explained. The best fit for this case should be with $\phi_{wall} \sim 0.48$ and $\Delta \sim 10\mu m$. For 680nm particles, it was not possible to match the model and experimental results by varying $\Delta$ and $\phi_{wall}$.

In the case of 0.12µm particles, the modifications of the structure of cake-suspension interface can not explain the considerable difference between
predicted \((-0.09\text{Flux}_{\text{initial}})\) and observed \((-0.55\text{Flux}_{\text{initial}})\) steady-state flux. Additional backtransport mechanisms, different structure of the bulk of the cake and/or inadequacies in the permeability model may be the source of these discrepancies.

Monte Carlo simulations of deposition from a monodisperse suspension using on-lattice model were performed. The dependence of the deposit morphology on the surface chemistry of particles was studied.

The effect of surface chemistry was modeled using a "lump" parameter - collision efficiency \(\alpha\). It was shown that variations in \(\alpha\) result in changes in the long-range structure of the deposit. To analyze these changes quantitatively, the fractal dimensions of the deposits formed from particles with \(\alpha=0.1\) in different far-field transport regimes (different \(N_{\text{Pe}}\)) were calculated and compared with fractal dimensions of deposits formed of perfectly cohesive (\(\alpha=1.0\)) particles at corresponding \(N_{\text{Pe}}\). It was observed that at large values of \(N_{\text{Pe}}\), compact deposits were formed and \(D_f \to 2\) for both values of \(\alpha\). In the case of small \(N_{\text{Pe}}\) values though, substantial differences in the morphology were observed. For \(\alpha=1.0\), \(D_f\) converged to \(-1.77\) (1.7 being the theoretical value for diffusion-limited growth), while for \(\alpha=0.1\), \(D_f\) was considerably higher and converged to \(-1.84\).

Changes in short-range structure are also induced by changes in \(\alpha\), as could be concluded from visual examination of the simulated deposits. But
these changes differ from those induced by changes in long-range transport ($N_{p_0}$). In the former case, a decrease in $\alpha$ results in thickening of deposit branches, which is in sharp contrast with the latter case, where an increasingly ballistic character of deposition leads to formation of an increasingly dense web-like structure, more homogeneously distributed in space.

Simulations of deposits composed of two subsets of particles, each subset having its own surface chemistry ($\alpha$), were performed. Relative concentrations of particles from the two subsets were taken to be 0.5 to simplify the analysis of results and factor out influence of $\alpha$ on the morphology. Different combinations of values of the three collision efficiencies characterizing this process ($\alpha_{11}, \alpha_{12}, \alpha_{22}$) led to different degrees and patterns of segregation of particles from different subsets.

The non-trivial case $\alpha_{12} < \alpha_{11}, \alpha_{22}$ was studied in detail. Physically, the condition $\alpha_{12} < \alpha_{11}, \alpha_{22}$ corresponds to the situation when two sorts of particles have the same charge and/or different hydrophobicities. The model predicts that the structure of the deposit is mostly determined by particles with larger values of $\alpha$. The overall pattern of segregation is determined by all three alphas - $\alpha_{11}$, $\alpha_{12}$, $\alpha_{22}$ - by both their relative and absolute values. In particular, it was observed that
a) in the case when $\alpha_{11}, \alpha_{22} < 0.1$ and $\alpha_{12}$ is 1 or more orders of magnitude smaller than the smallest of $\alpha_{11}$ and $\alpha_{22}$, the particles with smaller $\alpha$ segregate at the surface of branching structures formed by particles with bigger $\alpha$, and

b) when $\alpha_{11}, \alpha_{22} > 0.1$, no segregation occurs. The deposits formed under the latter conditions are not realistic though, because at such high $\alpha$ values very thin and branching deposits form so that break-up and restructuring processes can not be neglected.

Generally, the application of the developed deposition algorithm is limited to modeling of the interfaces only, because restructuring is not considered.

The effect of roughness of the underlying substrate on the deposit morphology was also studied. A sinusoidal profile was chosen to represent the roughness. To quantify the effect of the morphology of the substrate, a Fourier analysis of the profile of the upper surface of the simulated deposit was performed at different stages of the deposit growth. It was shown that deposits formed from particles with intermediate values of $\alpha$ have the best "memory", i.e. they better preserve the initial profile of a substrate than do deposits formed from particles with lower or higher values of $\alpha$. In the case studied here of 0.5$\mu$m silica particles depositing in stagnant water at 20$^\circ$C under the influence of gravity only, it was found that the slowest decay of a Fourier component correspondent to the roughness of initial substrate is achieved at intermediate values of $\alpha$ ($\sim$0.1) of collision efficiency.
Chapter 6

Conclusions

Current membrane filtration models appear to be inadequate to describe permeate flux behavior. Poor description of fouling cake morphology may be a reason for the lack of a consistent method of predicting membrane performance.

Although the transient behavior of permeate flux for particles of several orders of magnitude is reasonably described by the multi-transport model considered in this work, the fouling behavior for medium-sized particles (~100nm) differs considerably from theoretical predictions. A more complex description of cake morphology allows for better coherence between experimental observation and theory.

Heterogeneous deposition is common for many natural and industrial systems. The Monte Carlo heterodeposition model predicts that the structure of a fouling layer is mostly determined by particles with larger values of $\alpha$. In a particular case when particles from two subsets carry a charge of the same sign and/or have different hydrophobicity (hydrophilicity), particles with smaller values of $\alpha$ dominate the surface chemistry of the fouling layer. Depositing cohesive particles form a network-like structure which is filled in by or coated with the non-cohesive fraction. From the prospective of membrane filtration, this result implies that heterogeneous structure of the bulk of cake determining to a
big extent the cake's resistance to permeate flux may be predicted based on the knowledge of the properties of the particles which form the cake.

Knowledge of effects of the collision efficiency and the mode of the long-range transport of depositing particles on the connection between membrane profile and morphology of a fouling layer may be used for problem-specific design of membrane modules and for membrane manufacturing. In the case of diffusively depositing particles studied here, it was found that the slowest decay of a Fourier component correspondent to the roughness of initial substrate is achieved at intermediate values of collision efficiency ($\alpha_{opt} \approx 0.1$). Lower values of $\alpha_{opt}$ are expected for more diffusive long-range transport regime.
Chapter 7

Engineering Significance and Research Needs

7.1 Engineering Significance

The structure of the cake/solution interface plays a significant role in determining cake-limited permeate flux. Yet, no simple experimental methods are available for gaining information about the morphology of the interface. In this situation, the approach combining modeling of the transient permeate flux (chapter 4.2), modeling of the cake/solution interface morphology (chapter 4.1) and controlled experiments (chapter 3) may be helpful for gaining knowledge of the structure of the fouling layer and, consequently, for prediction of the permeate flux behavior. Dead-end filtration of cohesive material is deemed to be the experimental set-up most suited for this approach, as it is under the conditions of high $\alpha$ and low shear rate when the formation of cake with low solid fraction at the wall $\phi_w$ is favored.

Modeling of the morphology of the very top layer of the deposit, i.e. deposit/solution interface, provides the information about the surface accessible for the adsorbing contaminants as well as propensity of the deposit to break-up or to capture the adsorbed contaminants in the bulk of the deposit. Heterodeposition modeling may improve the understanding of the relationship
between the structure of deposit and its functionality, which also has implications for the partitioning of contaminants from solution.

The structure of the cake on the intermediate size scale (10-100 particle diameters) which is the scale of sub-regions of the cake where particles from different depositing fractions segregate may be a factor determining the total hydraulic resistance of the cake. In this regard, heterodeposition modeling may be a useful predictive tool to get an estimate of the resistance of the cake.

Knowledge of effects of the collision efficiencies of depositing particles on the connection between profile of the substrate and morphology of the deposited film can provide better understanding of and control over natural and engineered deposition processes. The “memory” of a depositing layer with respect to the substrate has important implications for controlling undesirable deposition on rough surfaces, colloidal fouling of membranes and scaling in water pipes as well as for such applications as membrane production and thin layer deposition. In electronics industry, for example, chemical vapor deposition is used for chips manufacturing with a substrate having a shape of a rectangular trough. The substantial gain in quality of coverage may potentially be achieved by choosing the suspension composition to control the important properties of the film.
7.2 Research Needs

A set of controlled dead-end filtration experiments using a mixture of two sorts of well characterized particles may be performed for experimental validation of heterodeposition modeling results. For example, a suspension of polystyrene and silica particles may be used for this purpose. Surface of particles may be chemically modified and ionic strength of solution may be changed to vary collision efficiency values. Using particles of different colors (e.g. black/white) would allow for visual examination of deposit structure with optical microscopy.

A conclusion that diffusionally transported particles of intermediate collision efficiency preserve the initial profile of the membrane the best merits an experimental validation. Membranes with turbulence-inducing corrugated surface may be used to study the effect of collision efficiency of particles of different sizes on the permeate flux behavior.

To verify a conclusion that for progressively lower collision efficiency of particles the kinetics of permeate flux decline in cross-flow mode more and more resembles this in dead-end mode, a cross-flow and dead-end filtration experiments can be performed for particles with different values of collision efficiency.
Appendix A.

Fouling layer on the polysulfone membrane
Appendix B.

Membrane filtration experimental data
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<th>Q 0.97L/m²</th>
<th>Q 0.47L/m²</th>
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<th>Q 0.97L/m²</th>
<th>Q 0.47L/m²</th>
<th>Q 0.11L/m²</th>
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**Calculations**

- **Flow Rate:** 1.96 + 1.10 (1/m³)
- **Height of Water:** 2.4 (m)
- **Type:** Hydraulic
- **Flow Rate:** 1.96 + 1.10 (1/m³)
- **Height of Water:** 2.4 (m)
- **Type:** Hydraulic

**Design:** 1.96 + 1.10 (1/m³)
- **Height of Water:** 2.4 (m)
- **Type:** Hydraulic

**Date:** Jan 14, 1999

**Mode:** Control Pressure

**Pressure:** 73 (psig)

**Flow:** 2.4 (m³)

**Height of Water:** 2.4 (m)

**Type:** Hydraulic

**Flow Rate:** 1.96 + 1.10 (1/m³)
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**Calculated Data**

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- **Particle Size Distribution (cm)**: not measured
- **Vendor**: Boeing Aerospace
- **Preform Time**: 6/11/99

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- **Max:** 14.3 (m/m)
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**Calculated Data**

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- **Discharge:** 0.1 (mm)
- **Discharge:** 6.0 (mm)

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- **Volume:** Polyethylene

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- **Date:** Jan 25, 1999
- **Mode:** Constant Pressure
- **Type:** Hawkman
- **Vendor:** Hawkman
- **Resistance:** 1.7E+10 (Ω/m)
- **K-factor:** 2.1 (m/s)
- **Pressure:** 75 (PSI)

**Flow:** 3.8 (m³/s)

**Pressure:** 75 (PSI)

**Flow:** 3.8 (m³/s)

**Pressure:** 75 (PSI)
Appendix C.

Calibration of Flowmeters
Appendix D.

Linear fit of the dependence of Fourier amplitude of deposit profile on the deposit height for different values of collision efficiency
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<td>$+/-$</td>
</tr>
<tr>
<td>$m$</td>
<td>-0.282293</td>
</tr>
<tr>
<td>$b$</td>
<td>-0.047595</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.791235</td>
</tr>
</tbody>
</table>
\[ \alpha = 0.5 \]

![Graph with data points and regression line]

<table>
<thead>
<tr>
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<th>Value</th>
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</thead>
<tbody>
<tr>
<td>( n )</td>
<td>100</td>
</tr>
<tr>
<td>( \text{ave } x )</td>
<td>3.59625</td>
</tr>
<tr>
<td>( \text{ave } y )</td>
<td>-1.201928</td>
</tr>
<tr>
<td>( \text{ESD} )</td>
<td>0.275033</td>
</tr>
<tr>
<td>( \text{conf. interval} )</td>
<td>0.95</td>
</tr>
<tr>
<td>Factor t-test</td>
<td>1.984467</td>
</tr>
<tr>
<td>( y = mx + b )</td>
<td>(+/-)</td>
</tr>
<tr>
<td>( m )</td>
<td>-0.281915 0.037848</td>
</tr>
<tr>
<td>( b )</td>
<td>-0.18809 0.146647</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.807014</td>
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</tbody>
</table>
\( \alpha = 1.00 \)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>( n )</td>
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</tr>
<tr>
<td>( \text{ave } x )</td>
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</tr>
<tr>
<td>( \text{ave } y )</td>
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<tr>
<td>( \text{ESD} )</td>
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<tr>
<td>( \text{conf.interval} )</td>
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<tr>
<td>( \text{Factor t-test} )</td>
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<tr>
<td>( y = mx + b )</td>
<td>+/-</td>
</tr>
<tr>
<td>( m )</td>
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</tr>
<tr>
<td>( b )</td>
<td>-0.191067</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.760422</td>
</tr>
</tbody>
</table>
Appendix E.
Heterodeposition program

PROGRAM heterodeposition
!
USE my_subroutines
!
! DESCRIPTION:
!
! The program does Monte Carlo simulation of colloid heterodeposition on
! a one-dimensional substrate.
!
! Features:
! 1) flow field parallel to the bed may be introduced
! 2) periodical boundary conditions
! 3) particles of 2 sorts with different sticking probabilities
!
! RECORD OF CORRECTIONS:
!
! Dept. Environmental Science and Engineering, Rice University
!
! Programmer: Date of correction: Changes:
! ========= ============= ===============
! V. Tarabara Apr 25 00 Original code
!
! ---"--- Apr 27 00 If particle is discarded at
! the top of domain then next released particle has the same color
!
! ---"--- May 01 00 Added code to compute fractal
! dimension. Moduled the code
!
! ---"--- May 08 00 now subtracts (hei/10) from
! h_bar when calculating PD
!
! ---"--- Oct 17 00 commented the code
!
! DICTIONARY OF VARIABLES:
!
! ARRAY - array containing deposit and space above it. Array values
! may be:
! "0" - red particles (type=1)
"1" - attachment sites ("active" sites) for red particles
"2" - empty spot
"5" - black particles (type=2)
"6" - attachment sites ("active" sites) for black particles
alpha - current value of collision efficiency b/wn particles
(chosen from alphas 11, 12, 22
dependent on which particles are in contact
alpha11 - collision efficiency b/wn red particles
alpha22 - collision efficiency b/wn black particles
alpha12 - collision efficiency b/wn red and black particles
black_deposited - counts deposited black particles
d (m) - diameter of the particle
FD - fractal dimension of deposit
FD_delta - error in "FD"
f_d_dim - dimension of vectors "height_vector" and
"part_deposited_vector" needed to calculated fractal dimension
flag1 - signals that particle was discarded at the top of the domain
fraction - determines the fraction of particles of a given color
h_bar - average height of deposit
hei - height of the workspace
i - counter
j - counter
i_fd - counter
j_fd - counter
k1 - probability for a particle to move in the direction of grav.force
k2 - probability for a particle to move in direction of the flow
k3 - probability for the particle to move in of the other 6 directions
len - len of the workspace
level - height level where fractal dimension is calculated
mera - tracks program progress, mera~(height of deposit)/(height of domain)
mera_old - holds old value of "mera" variable
mu (kg/m/sec) - viscosity of the fluid
m_old - remember value of array at the site where particle is going to move to
Npe - Péclet-like number
n_max - height of the highest particle in the deposit
n_max_old - temporal variable to hold old n_max value while searching
for a higher particle
n_old - remember value of array at the site where particle is going to move to
! PID - holds a process ID at the UNIX machine where the program is run
! rand - intrinsic UNIX random number generator. 0<mg<1
! red_deposited - counts deposited red particles
! Re_p - particle Reynolds number
! ro_squared - correlation coefficient R**2. For FD determination
! Ro_f (kg/m^3) - density of the fluid
! Ro_p (kg/m^3) - density of the particle
! slope - slope in h_bar=h_bar(red_deposited+black_deposited)
dependence.
! Needed to compute FD
! slope_delta - error in "slope"
! T (K) - fluid temperature
! t_factor - t_factor for 95% confidence interval in linear least-square
! fit for FD determination
! type - determines the particle's type (color)
! type=1 - red particles
! type=2 - black particles
! type_repeat - temporal variable. Holds value of "type" in case when a
! particle reaches kill line at the top of the domain
! to ensure next released particle has that color
! U1 - random number. Used to determine whether attachment was successful
! U10 - random number. Used to determine type of particles
! Vcf (m/sec) - cross-flow velocity
! Vpf (m/sec) - permeate flow velocity
! Vpcf (m/sec) - particle velocity due to cross-flow drag
! Vppf (m/sec) - particle velocity due to permeate flow drag
! Vg (m/sec) - settling velocity of the particle
! Vd (m/sec) - diffusive velocity

IMPLICIT NONE

! Declare constants

REAL, PARAMETER :: PI=3.1415926
REAL, PARAMETER :: Kb=1.3805d-23
REAL, PARAMETER :: G=9.81

! Declare locals

INTEGER :: i, j, n, m, k, red_deposited, black_deposited
INTEGER :: n_max, n_max_old
INTEGER :: tt, qq, bb, ii, jj, ii1, i2, i3, i4, j1, j2, j3, j4

INTEGER :: m_old, n_old
INTEGER :: len, hei
INTEGER, DIMENSION (::,:), ALLOCATABLE :: ARRAY
INTEGER :: PID, GETPID
INTEGER :: type, type_repeat, check
INTEGER :: mera
INTEGER :: flag1
INTEGER :: j_fd, fd_dim, level

REAL :: rand
REAL :: U1, U10, k1, k2, k3
REAL :: Vcf, Vpf, Ro_f, Ro_p, Mu, T, d
REAL :: Vpcf, Vppf, Vg, Vd, Npe, Re_p
REAL :: alpha, alphall, alpha12, alpha22, fraction
REAL :: mera_old
REAL :: i_fd
REAL :: h_bar
REAL :: PD, FD_delta, slope, slope_delta, ro_squared, t_factor
REAL, DIMENSION (:), ALLOCATABLE :: height_vector
REAL, DIMENSION (:), ALLOCATABLE :: part_deposited_vector

! Begin execution

! Initialize variables

OPEN(unit=8, file='in_bin.dat', status='old')
READ(8,*) Vcf, Ro_p, Ro_f, Mu, T, d, len, hei, alphall, alpha12, alpha22, &
   & fraction, Vpf
CLOSE(8)

! Check inputs
WRITE (*,*) '-----Check Inputs-----'
WRITE (*,*) 'Vcf=', Vcf, 'm/s'
WRITE (*,*) 'Vpf=', Vpf, 'm/s'
WRITE (*,*) 'Ro_p=', Ro_p, 'kg/m^3'
WRITE (*,*) 'Ro_f=', Ro_f, 'kg/m^3'
WRITE (*,*) 'Mu=', Mu, 'kg/m/s'
WRITE (*,*) 'T=', T-273.15, 'Celsius'
WRITE (*,*) 'd=', d, 'm'
WRITE (*,*) 'len=', len, 'particle diameters'
WRITE (*,*) 'hei=', hei, 'particle diameters'
WRITE (*,*) 'alphall=', alphall
WRITE (*,*) 'alpha12=', alpha12
WRITE (*,*) 'alpha22=', alpha22
WRITE (*,*) 'fraction=', fraction
WRITE (*,*) '-------------------'

Vpcf=Vcf*(1-Ro_f*Vcf*d/24/Mu) ! Define particle's velocities
Vppf=Vpf*(1-Ro_f*Vpf*d/24/Mu)
$V_g = d^{**2} g^{*} (R_o_p - R_o_f)/18/Mu$

$V_d = K_b*T/3/PI/Mu/d^{**2}$

```
WRITE (*,*) 'Vpcf=', Vpcf
WRITE (*,*) 'Vg=', Vg
WRITE (*,*) 'Vd=', Vd
WRITE (*,*) 'Vppf=', Vppf
```

$$N_p = (Vpcf+Vg+Vppf)/V_d$$

```
WRITE (*,*) 'Npe= ', Npe
```

$$R_e_p = d*sqrt(Vpcf**2+(Vg+Vppf)**2)*R_o_f/Mu$$

```
WRITE (*,*) 'Re_p=', Re_p
IF (Re_p >= 0.1) WRITE (*,*) 'Re_p>0.1; Model not valid'
```

```
WRITE (*,*) '--------------------------'
PID=GETPID()
WRITE (*,*) 'PID = ', PID
WRITE (*,*) '--------------------------'
```

```
WRITE (*,*) 'Press "Return" to start'
READ (*,*)
```

```
! Define probabilities
k1 = (1+(Vg+Vppf)/Vd)/(8+Npe)
k2 = 1/(8+Npe)
k3 = (1+Vpcf/Vd)/(8+Npe)
```

```
! Open files to write output to
OPEN (unit=1002, file='p050801', status='unknown') ! clean deposit
! deposit with active zones
OPEN (unit=1003, file='p050801_zones', status='unknown')
OPEN (unit=1998, file='p050801_have_ln', status='unknown')
OPEN (unit=1999, file='p050801_part_ln', status='unknown')
```

```
ALLOCATE (ARRAY(len+2,hei))
```

```
! Initialize the entire array to two
ARRAY=2
```

```
! initialize cells adjacent to substrate to 1
DO i=1,len+2
    ARRAY(i,1)=1
    ARRAY(i,2)=1
END DO
```

```
! zero all counters
r_max=1
```
red_deposited=0
black_deposited=0
qq=0
mera_older=0
i_fd=4.5
j_fd=0
fd_dim=(9.5-i_fd)*4

ALLOCATE (height_vector(fd_dim), part_deposited_vector(fd_dim))

outer: DO

qq=qq+1 ! counts released particles

! computing fractal dimension
level=hei/10*(i_fd+0.25)
computeFD: IF (n_max==level) THEN
  i_fd=i_fd+0.25
  j_fd=j_fd+1
  CALL h_average (ARRAY,len, hei, n_max, h_bar)
  height_vector(j_fd)=log(h_bar-hei/10)

part_deposited_vector(j_fd)=log(real(red_deposited+black_deposited))
END IF computeFD

IF (n_max>hei-20) EXIT ! deposit is formed

m=nint(rand(0)*(len+1)+0.5) ! sample initial horizontal position
n=n_max+10

U10=rand(0)
color: IF (real(n_max) <= hei/10 ) THEN ! sample color
  type=1 ! red padding
ELSE
  IF (flag1==1) THEN
    type=type_repeat
    flag1=0
  ELSE IF (U10 <= fraction) THEN
    type=1
  ELSE
    type=2
  END IF
END IF color

inner: DO

! Choose a direction to move
CALL direction (m, n, k1, k2, k3)

! Check whether kill line at the top of domain is reached
IfKillLineReached: IF (n==hei) THEN
    flag1=1
    type_repeat=type ! remember color of the particle to be discarded
    CYCLE outer ! discard the particle
END IF IfKillLineReached

! wrap around (periodical boundary condition)
IF (m==1) m=len+1
IF (m==len+2) m=2

! remember value of array at the site where particle is going ! to move to
check=ARRAY(m,n)
m_old=m
n_old=n

IfActiveSiteReached: IF (check==1 .OR. check==6) THEN
    SELECT CASE (check) ! choose appropriate alpha
    CASE(1)
        IF (type==1) alpha=alpha11
        IF (type==2) alpha=alpha12
    CASE(6)
        IF (type==1) alpha=alpha12
        IF (type==2) alpha=alpha22
    END SELECT

    U1=rand(0)
    IfAttachement: IF (U1<= alpha) THEN ! attached or not?
        EXIT inner ! yes
    ELSE ! no, detachment follows
        CALL detachment (len, hei, ARRAY, Vg, Vppf, Vpcf, Vd,
        check,&
        & n_old, m_old, m, n)
    END IF IfAttachement
    END IF IfActiveSiteReached
END DO inner

AssignColor: SELECT CASE (type) ! assign value according to color
    CASE (1)
        ARRAY(m,n)=0
IF (real(n_max) >= hei/10) red_deposited = red_deposited + 1
CASE (2)
    ARRAY(m,n)=5
    IF (real(n_max) >= hei/10) black_deposited = black_deposited + 1
END SELECT AssignColor

CALL adSites (ARRAY, len, hei, m, n) ! redefine attachment sites

! Periodical boundary conditions (pbc)
 PeriodicalBC: IF (m<3 .OR. m>=len) THEN
    CALL pbc (ARRAY, len, hei, m, n)
END IF PeriodicalBC

! reassignment of n_max if needed
 IsItTheHighestParticle: IF (n /= n_max) THEN
    n_max_old = n_max
    n_max = n
    DO i=2,len+1
       ! checking for for higher particles in the deposit
       IF (ARRAY(i,n+1)==0 .OR. ARRAY(i,n+1)==5) THEN
          n_max = n_max_old
          EXIT
       END IF
    END DO
END IF IsItTheHighestParticle

mera=nint(real(n_max)/real(hei-20)*100) ! output progress
IsItTimeToComputeFD: IF (real(mera)/5==int(mera/5)) THEN
    IF (real(mera)/5 /= 0) THEN
       IF (real(mera)==mera_old) CYCLE outer
       WRITE (*,77) real(mera)
       mera_old = real(mera)
    END IF
END IF IsItTimeToComputeFD

77 FORMAT (1x, F6.1, '% completed')

END DO outer

t_factor=1.96 ! the value for 20 measurements and 95% confidence interval

CALL least_squares_fit (fd_dim, part_deposited_vector, height_vector, &
 & t_factor, slope, slope_delta, ro_squared)

FD=1+t_factor/slope
FD_delta = slope_delta / slope**2

SELECT CASE (len)
CASE (300)
   WRITE (1003, 1001) ARRAY
CASE (1000)
   WRITE (1003, 2001) ARRAY
END SELECT

DO i=1, len+2
   DO j=1, hei
      IF (ARRAY(i, j) == 1 .OR. ARRAY(i, j) == 6) ARRAY(i, j) = 2
   END DO
END DO

SELECT CASE (len)
CASE (300)
   WRITE (1002, 1001) ARRAY
CASE (1000)
   WRITE (1002, 2001) ARRAY
END SELECT

WRITE (1998, *) height_vector
WRITE (1999, *) part_deposited_vector

1001 FORMAT (/,,1x,302(I3,1x))
2001 FORMAT (1000(/,,1x,102(I3,1x))

! Check inputs again
WRITE (*, *) '-------Check Inputs again-------'
WRITE (*, *) 'Vcf=', Vcf, 'm/s'
WRITE (*, *) 'Vpf=', Vpf, 'm/s'
WRITE (*, *) 'Ro_p=', Ro_p, 'kg/m^3'
WRITE (*, *) 'Ro_f=', Ro_f, 'kg/m^3'
WRITE (*, *) 'Mu=', Mu, 'kg/m/s'
WRITE (*, *) 'T=', T-273.15, 'Celsius'
WRITE (*, *) 'd=', d, 'm'
WRITE (*, *) 'len=', len, 'particle diameters'
WRITE (*, *) 'hei=', hei, 'particle diameters'
WRITE (*, *) 'alpha11=', alpha11
WRITE (*, *) 'alpha12=', alpha12
WRITE (*, *) 'alpha22=', alpha22
WRITE (*, *) 'fraction=', fraction
WRITE (*, *) '-------------------------'
WRITE (*, *) 'Vpcf=', Vpcf
WRITE (*, *) 'Vg=', Vg
WRITE (*,*) 'Vd=', Vd
WRITE (*,*) 'Vppf=', Vppf
WRITE (*,*) 'Npe=', Npe
WRITE (*,*) 'Re_p=', Re_p

! Print output
WRITE (*,*) '---------------------------------------'
WRITE (*,*) 'The total amount of released particles=', qg-1
WRITE (*,*) 'The amount of red particles deposited=', red_deposited
WRITE (*,*) 'The amount of black particles deposited=', black_deposited

WRITE (*,*) '---------------------------------------'
WRITE (*,*) 'The fractal dimension FD = ', FD,'+-',FD_delta
WRITE (*,*) 'Correlation coefficient R**2 = ', ro_squared

END PROGRAM heterodeposition
Appendix F.

Multifractal analysis program

MODULE precision_for_MFA
  INTRINSIC KIND
  INTEGER, PARAMETER :: wp=KIND (1.0D0)
END MODULE precision_for_MFA

PROGRAM MFA

USE precision_for_MFA, ONLY : wp
USE procedures_for_MFA
!
! DESCRIPTION:
!
! The program calculates multifractal spectrum (MFS) of scalar value
! distribution over 1000x1002 array. Written to calculate MFS of
growth
! site probability distributions (GSPDs) over simulated deposits.
GSPls
! were obtained by the method of probes ([1],p.159). Approach to
! calculating MFS is described in details in [2]. [3] may be a
useful
! reference as well
!
! To be compiled with module mfa_sub.f90
!
!
! FEATURES:
!
! 1) Takes an input file with an array 1000x1002 and pads it
! to 1024x1024 array. Periodicity is employed so that padding
values
! for the array are taken from the opposite border of the same
array.
! This is justifiable for the case when array contains growth
site
! probability distribution over deposits)
!
! 2) Restrictions on q:
!  <a> q_min<=q<=q_max
!  <b> q_max<-308/log_10(p_min), where p_min is a smallest value
! in the array. This restriction is a result of the limited
! exponent range (10^-308) - 10^308) of Sun Sparc (64 bits)
! 3) By choosing variable "points" (2<=points<=10) it is possible to
! account for poor scaling. For example, by choosing points=4
one
! forces the linear least-squares subroutine to use only 4 points
(corresponding to 4 divisions of the array resulting in biggest subarrays: 1024x1024, 512x512, 256x256, and 128x128).

LITERATURE:


RECORD OF CORRECTIONS:

Dept. Environmental Science and Engineering, Rice University

Programmer: Date of correction: Changes:

V. Tarabara Aug 14 00 Original code
---"--- Oct 17 00 Commented the code
---"--- Oct 27 00 "Trimmed" version
---"--- Oct 31 00 Took off hard-wired limits on the range of q.
---"--- Nov 08 00 Correction: used natural log instead of log of base 10, for easier to interpretation of scaling. Changed log of base 10

DICTIONARY OF VARIABLES:

A_q - A(q) function
A_q_delta - error in beat(q) function
F_A - multifractal spectrum f(A) (dispersion relation)
F_A_delta - error in f(A)
fraction
hei - height of the padded array
boxes_y - number of squares along vertical direction of array at a given division
! Input_Array - an array containing the distribution to be analyzed
! divider - vector with values of dividers used to divide domain
!   into subdomains
! len - length of the padded array
! boxes_y - number of squares along horizontal direction of
!   array at a given division
! log_divider - log(size)
! log_Sigma - log(M_q)
! Measure - input array padded to become 1024x1024 array
! Measure_Norm - an array containing normalized distribution to be
! analyzed
! points - number of points to use in fit when determining t(q) from
!   log(M(q))-log(epsilon) dependence
! rol1 - correlation coefficient for linear least squares fit
! temp1 - temporal variable needed to pad an array
! temp2 - temporal variable needed to pad an array
! slope - slope value, an output of linear least squares fit
! subprogram
! slope_delta - error in slope
! sum - sum of elements in the array
! tau_q - scaling function tau(q)
! tau_q_delta - error in scaling function tau(q)
! t_factor - t_factor for linear least squares analysis
!
!
IMPLICIT NONE

! Declare locals

INTEGER :: i,j,ii,kk, nn,n,k, nn_old
INTEGER :: istat
INTEGER :: len,hei,temp1,temp2
INTEGER :: boxes_y, boxes_x
INTEGER :: sum
INTEGER :: points
INTEGER, DIMENSION (1002,1000) :: Input_Array
INTEGER, DIMENSION (1024,1024) :: Measure
INTEGER, DIMENSION (10) :: divider
INTEGER :: steps
INTEGER :: status1

REAL (wp), DIMENSION (1024,1024) :: Measure_Norm
REAL (wp), DIMENSION (:), ALLOCATABLE :: tau_q, tau_q_delta
REAL (wp), DIMENSION (:), ALLOCATABLE :: F_A, F_A_delta
REAL (wp), DIMENSION (:), ALLOCATABLE :: A_q, A_q_delta
REAL (wp), DIMENSION (10) :: log_divider,log_divider_trimmed
REAL (wp), DIMENSION(:,:), ALLOCATABLE :: log_Sigma,
log_Sigma_trimmed
REAL (wp), DIMENSION(:,:), ALLOCATABLE :: fraction, fraction_trimmed
REAL (wp) :: slope, slope_delta, rol, t_factor, t_factor_trim, q
REAL (wp) :: q_min, q_max, q_step

! Begin execution

WRITE (*,10,advance='NO') 'Input q_min. q_min= '
READ (*) q_min
WRITE (*,10,advance='NO') 'Input q_max. q_max= '
READ (*) q_max
WRITE (*,10,advance='NO') 'Input q_step. q_step= '
READ (*) q_step
WRITE (*,10) 'Input number of points to use when determining'
WRITE (*,10) 'tau(q) from log(M(q))-log(epsilon) dependence.'
WRITE (*,10,advance='NO') 'points= '
READ (*) points

steps=(q_max-q_min)/q_step+1

ALLOCATE (tau_q(steps),tau_q_delta(steps), F_A(steps),&
 & F_A.delta(steps), A_q(steps), A_q.delta(steps))
ALLOCATE (log_Sigma(10,steps), fraction(10,steps))
ALLOCATE (log_Sigma_trimmed(points,steps),
fraction_trimmed(points,steps))

! Begin execution

! Read input file with distribution
OPEN (unit=88, file='pattern_probelt1',status='unknown',
iostat=status1)
input1: IF (status1/=0) THEN
    WRITE (*,*) 'Error opening file pattern_probelt1. IOSTAT=', status1
    WRITE (*,*) 'Shutting down...'
ELSE
    READ(88,209) Input_Array
    CLOSE(88)
END IF input1

! Open files to write output to:
OPEN (unit=22, file='tau',status='unknown')
OPEN (unit=33, file='tau_q_delta',status='unknown')
OPEN (unit=44, file='A_q',status='unknown')
OPEN (unit=55, file='A_q_delta',status='unknown')
OPEN (unit=66, file='F_A',status='unknown')
OPEN (unit=77, file='F_A_delta',status='unknown')
OPEN (unit=888, file='log_divider',status='unknown')
OPEN (unit=999, file='log_Sigma',status='unknown')

nn=10

DO i=1,10
   divider(i)=2**i
END DO
len=1024
hei=1024
sum=0
Measure_Norm=0
i=0
j=0
ii=0
q=0
tau_q=0.
tau_q_delta=0.
F_A=0.
F_A_delta=0.
A_q=0.
A_q_delta=0.
q=q_min-q_step ! initial value of q

! Conversion Input_Array -> Measure
!
!
! Conversion Input_Array -> Measure
along1: DO i=1,len
   across1: DO k=1,hei
      padding1: SELECT CASE (i)
         CASE (:1002)
            temp1=i
         CASE (1003:)
            temp1=i-1002
       END SELECT padding1
   padding2:SELECT CASE (k)
      CASE (:1000)
         temp2=k
      CASE (1001:)
         temp2=k-1000
       END SELECT padding2
   Measure(i,k)=Input_Array(temp1,temp2)
   END DO across1
   END DO along1

!
! calculate the total sum of elements of the measure
along2: DO i=1,len
   accross2: DO k=1,hei
      sum=sum+Measure(i,k)
END DO accross2
END DO along2

! normalize the measure
along3: DO i=1,len
   accross3: DO k=1,hei
      Measure_Norm(i,k)=real(Measure(i,k))/sum
   END DO accross3
END DO along3

!!$  ! delete low probability elements from the measure
!!$  ! WARNING! This introduce an error into negative moments dominated
!!$  ! by the
!!$  ! small probabilities
!!$
!!$  DO i=1,len
!!$    DO k=1,hei
!!$      IF (Measure_Norm(i,k)<=4.E-5) Measure_Norm(i,k)=0
!!$    END DO
!!$  END DO

! divide domain into squares

DO kk=1,10

   boxes_y=hei/divider(kk)
   IF (int(len/divider(kk))==len/divider(kk)) THEN
      boxes_x=len/divider(kk)
   ELSE
      boxes_x=int(len/divider(kk))+1
   END IF

   print *, 'boxes_y=', boxes_y
   print *, 'boxes_x=', boxes_x

   CALL Qth_order_moments (nn, Measure_Norm, divider, kk, boxes_y,&
      & boxes_x, log_Sigma, fraction,q_min,q_max,q_step,steps)
   log_divider(kk)=log(real(divider(kk))/1024)/log(10.)

END DO

WRITE (888,*) log_divider
WRITE (999,*) (log_Sigma(n,1), n=1,10)

t_factor=2.36  ! the value for 10 measurements and 95%
! confidence
! interval
t_factor_trim=3.18  ! for 4 measurements

DO i=-(steps-1)/2, (steps-1)/2  
j=j+1  
q=q+q_step  

IF (i<=steps-1/2) THEN  
nn_old=nn  
nn=points  

DO ii=1,points  
log_divider_trimmed(ii)=log_divider(ii+10-points)  
fraction_trimmed(ii,j)=fraction(ii+10-points,j)  
log_Sigma_trimmed(ii,j)=log_Sigma(ii+10-points,j)  
END DO  

CALL least_squares_fit (nn, log_divider_trimmed ,&  
& log_Sigma_trimmed, j, t_factor_trim, slope,&  
& slope_delta, rol,steps)  
tau_q(j)=slope  

IF (j==1) print *, 'tau_q(1)=', tau_q(j)  
tau_q_delta(j)=slope_delta  

CALL least_squares_fit (nn,log_divider_trimmed,&  
& fraction_trimmed, j, t_factor_trim,&  
& slope, slope_delta, rol, steps)  
A_q(j)=slope  
A_q_delta(j)=slope_delta  

nn=nn_old  
ELSE  

CALL least_squares_fit (nn, log_divider , log_Sigma, j,&  
& t_factor, slope, slope_delta, rol,steps)  
tau_q(j)=slope  
tau_q_delta(j)=slope_delta  

CALL least_squares_fit (nn, log_divider , fraction, j,&  
& t_factor, slope, slope_delta, rol,steps)  
A_q(j)=slope  
A_q_delta(j)=slope_delta  

END IF
\[ F_A(j) = q^{A}(q(j) - \tau_q(j)) \]
\[ F_A \_\delta(t) = \sqrt{((q^{A}(q \_\delta(t))) ^ 2 + (\tau_q \_\delta(t))) ^ 2)} \]

END DO

WRITE (22, 1001) tau_q
WRITE (33, 1001) tau_q \_\delta
WRITE (44, 1001) A_q
WRITE (55, 1001) A_q \_\delta
WRITE (66, 1001) F_A
WRITE (77, 1001) F_A \_\delta

10 FORMAT (a50)
1001 FORMAT (201(//,1x,F10.5,1x))
2009 FORMAT (1000(//,1x,1002(I10,1x)))

END PROGRAM MFA

MODULE procedures \_\_for_MFA

! Module with subroutines for program Multifractal \_Analysis in
! file mfa \_sub.f90

IMPLICIT NONE

CONTAINS

! ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

SUBROUTINE Qth \_order \_moments (nn, Norm \_Measure, k, kk, boxes \_y, &
 & boxes \_x, log \_Sigma, fraction, q \_min, q \_max, q \_step, steps)

USE precision \_for_MFA, ONLY : wp

IMPLICIT NONE

! Declare calling parameters:
INTEGER, INTENT(IN) :: boxes \_y, boxes \_x, kk, nn, steps
REAL (wp), DIMENSION (1024,1024), INTENT (IN) :: Norm \_Measure
INTEGER, DIMENSION (10), INTENT (IN) :: k
REAL (wp), DIMENSION (10, steps), INTENT (OUT) :: log \_Sigma,
fraction
REAL (wp), INTENT (IN) :: q \_min, q \_max, q \_step
! Declare locals:
INTEGER : i, j, ii, jj, q, count
REAL (wp), DIMENSION (nn,boxes_x,boxes_y) :: Norm_Measure_3D
REAL (wp) :: sum_local, qq
REAL (wp), DIMENSION (10,steps) :: M_q, Nom_beta_q, Denom_beta_q

Norm_Measure_3D=0.
M_q=0
count=0
qq=q_min-q_step

! 3rd dimension of Normalized Measure introduced. 3rd dimension contains dividers
IF (k(kk)==1) THEN
   DO i=1,boxes_x
      DO j=1,boxes_y
         Norm_Measure_3D(kk,i,j)=Norm_Measure(i,j)
      END DO
   END DO
ELSE
   DO i=1,boxes_x
      DO j=1,boxes_y
         sum_local=0.
         DO ii=i+k(kk)*(i-1),k(kk)*i
            DO jj=j+k(kk)*(j-1),k(kk)*j
               sum_local=sum_local+Norm_Measure(ii,jj)
            END DO
         END DO
         Norm_Measure_3D(kk,i,j)=sum_local
      END DO
   END DO
END IF

DO q=-(steps-1)/2, (steps-1)/2
   count=count+1
   qq=qq+q_step

   logMq: DO i=1,boxes_x
      DO j=1,boxes_y
         IF (Norm_Measure_3D(kk,i,j)>0) THEN ! discard squares with zero probability

M_q(kk,count)=M_q(kk,count)+Norm_Measure_3D(kk,i,j)**(qq)
Nom_beta_q(kk,count)=Nom_beta_q(kk,count)+&
   & Norm_Measure_3D(kk,i,j)**(qq)*&
   & log(Norm_Measure_3D(kk,i,j))/log(10.)
Denom_beta_q(kk,count)=Denom_beta_q(kk,count)+&
   & Norm_Measure_3D(kk,i,j)**(qq)
   END IF
   END DO
END DO
END IF
END IF
END DO
END DO logMq
log_Sigma(kk,count)=log(M_q(kk,count))/log(10.)
fraction(kk,count)=Nom_beta_q(kk,count)/Denom_beta_q(kk,count)
END DO

END SUBROUTINE Qth_order_moments

!--------------------------------------------------------------------------

SUBROUTINE least_squares_fit (nn, ikxes, ygreks, q, t, slope,&
 & slope_delta, ro, steps)

! Adapted in modified form from S.Chapman's "Fortran 90/95 for
! Scientists and Engineers"

USE precision_for_MFA, ONLY : wp

IMPLICIT NONE

! Declare calling parameters:

INTEGER, INTENT (IN) :: q,steps,nn
INTEGER :: nn ! Number of input data pairs (x,y)
REAL (wp), DIMENSION (nn), INTENT(IN) :: ikxes
REAL (wp), DIMENSION (nn,steps), INTENT(IN) :: ygreks
REAL (wp), INTENT(OUT) :: slope, ro

! Declare locals:

INTEGER :: i,qqq
REAL (wp), DIMENSION (nn) :: x ! An input X value
REAL (wp), DIMENSION (nn) :: y ! An input Y value
REAL (wp), DIMENSION (nn) :: y_calc
REAL (wp) :: slope1 ! Slope of the line
REAL (wp) :: sum_x ! Sum of all input X values
REAL (wp) :: sum_x2 ! Sum of all input X values squared
REAL (wp) :: sum_y2 ! Sum of all input Y values squared
REAL (wp) :: sum_xy ! Sum of all input X*Y values
REAL (wp) :: sum_y ! Sum of all input Y values
REAL (wp) :: x_bar ! Average X value
REAL (wp) :: y_bar ! Average Y value
REAL (wp) :: y_int !
REAL (wp) :: SSresiduals
REAL (wp) :: SSregression
REAL(wp) :: SSxx, SSyy
REAL(wp) :: RSD=0 ! Relative Standard Deviation
REAL(wp) :: t ! t-factor to determine confidence limit
REAL(wp) :: slope_delta

qqq=0
sum_x=0.
sum_x2=0.
sum_y2=0.
sum_xy=0.
sum_y=0.
SSregression=0.
SSresiduals=0.

DO i=1,nn
  x(i)=ikses(i)
  y(i)=ygreks(i,q)
  sum_x = sum_x + x(i)
  sum_y = sum_y + y(i)
  sum_x2 = sum_x2 + x(i)**2
  sum_y2 = sum_y2 + y(i)**2
  sum_xy = sum_xy + x(i) * y(i)
END DO

! x_bar = sum_x / real(nn)
y_bar = sum_y / real(nn)
slope1 = (sum_xy - sum_x * y_bar) / (sum_x2 - sum_x * x_bar)
slope=slope1
y_int=y_bar-slope*x_bar

SSxx=sum_x2-nn*x_bar**2
SSyy=sum_y2-nn*y_bar**2
RSD=sqrt(abs(SSyy-slope**2*SSxx)/(nn-2))

slope_delta=t*RSD/sqrt(SSxx) ! = delta(Slope)

! Calculation of Correlation Coefficient
DO i=1,nn
  y_calc(i)=x(i)*slope1+y_int
  SSregression=SSregression+(y_bar-y_calc(i))**2
  SSresiduals=SSresiduals+(y(i)-y_calc(i))**2
END DO
ro=1-SSresiduals/SSregression

END SUBROUTINE least_squares_fit

END MODULE procedures_for_MFA
References


