Perspectives for the understanding of complex deposits on surfaces

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Study of **particulate fouling**, i.e. the accumulation of solid inorganic particles on a surface. Focus on spherical **colloidal particles**.

Example of systems affected by particulate fouling:

- Fouling in heat exchangers (reduction of heat transfer efficiency)
- Fouling in the automotive industry (by soot particles in combustion engines)

Other possible sources of fouling:

- Fouling in the membrane filtration (organic macromolecules in water treatment facilities)
- Fouling in the medical field (blood vessel clogging, deposition in human lungs, contaminant resuspension in hospitals)
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   - Two-way coupling
   - Multilayer resuspension
Plan

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   - Multilayer resuspension
Guidelines to study particulate fouling

- Fouling can be described with 4 underlying phenomena:
  - Deposition
  - Resuspension
  - Agglomeration
  - Clogging

Three key interactions at play:
- particle-fluid, particle-particle and particle-surface interactions

Interplay between two fundamental mechanisms:
1. **Transport step**: hydrodynamic transport of particles to the surface
2. **Attachment step**: adhesion due to the particle-surface interaction
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Experimental evidence of particle deposition

- Analysis of experimental data available

  - Evolution of the deposition rate with fluid (velocity, pH, ionic strength), particle (concentration, size, potential) and wall (potential, roughness) properties

(a) Compilation of various experimental data on the deposition rate (from Papavergos & Hedley, Chem Eng Res Des, 1984)

(b) Sherwood number for latex particles depositing on calcite surfaces expressed as a function of pH (from Darbha et al., Langmuir, 2010)
Experimental evidence of particle deposition (2)

- Analysis of experimental data available
  - Evolution of the deposition rate with fluid (velocity, pH, ionic strength),
    particle (concentration, size, potential) and wall (potential, roughness)
    properties
  - Three typical features for the deposit morphology

⇒ Intricate coupling between particle-fluid, particle-surface and particle-particle
interactions
Various levels of description for the particle phase:

- **Adsorption model (no fluid):**
  RSA or Ballistic models (to generate random packing of particles)

- **Models for particle transport with fluid**
  - **Lagrangian approaches:**
    Explicit tracking of particles with a complexity (and computational cost) that depends on the level of description of particle motion
    - MD Methods
    - Discrete Element Methods
    - Langevin Dynamics
    - Brownian Dynamics
    - Dissipative Particle Dynamics
    - One-particle pdf approach
  - **Lattice-Boltzmann Methods**
  - **Eulerian approaches:**
    Fast evaluations of macroscopic properties (particle concentration), but requires proper formula for the deposition rate (boundary condition)
A one-point pdf formulation for particle deposition (1)

Description by a two-step process:

- **A transport step:**
  - → Eulerian calculation of the fluid phase (RANS calculation)
  - → Lagrangian tracking of particles (stochastic method)

Evolution of each particle state-vector $Z = (x_p, U_p, U_s)$

- $x_p$: particle position, $U_p$: particle velocity, $U_s$: velocity of the fluid seen by particles along their trajectory
- Use of a Langevin equation

\[
\begin{align*}
\frac{dx_p,i}{dt} &= U_{p,i}dt \\
\frac{dU_p,i}{dt} &= \frac{U_{s,i}-U_{p,i}}{\tau_p} dt + K_{Br}dW_i' + (gdt) \\
\frac{dU_s,i}{dt} &= A_i(t, U_{s,i})dt + B_i(t, U_{s,i})dW_i
\end{align*}
\]

- Refinement accounting for interactions of particles with the near-wall coherent structures *Guingo and Minier, Phys. Fluids, 2008, Vol. 20, 053303*
- **Validated on several configurations**
A one-point pdf formulation for particle deposition (2)

Description by a two-step process:

- **A transport step:**
    - Eulerian calculation of the fluid phase (RANS calculation)
    - Lagrangian tracking of particles (stochastic method)
  - **Validated on several configurations**

- **An attachment step:**
  - Particle-surface interactions modelled using the DLVO theory (Derjaguin and Landau, Verwey and Overbeek) which accounts for:
    - van der Waals forces
    - electrostatic forces
  - Refinements accounting for the presence of surface roughness:
    - Smooth plate with hemispherical asperities
    - Additivity of interaction energies
Description by a two-step process:

- **A transport step:**
    - Eulerian calculation of the fluid phase (RANS calculation)
    - Lagrangian tracking of particles (stochastic method)
  - **Validated on several configurations**

- **An attachment step:**
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    - van der Waals forces
    - electrostatic forces
  - Refinements accounting for the presence of surface roughness

- **Coupling using an energetic approach** due to different scales involved:
  - Comparison of the kinetic energy $E_{Kin}$ and the energy barrier $E_{Barr}$ (maximum repulsive interaction obtained with a DLVO calculation)
Single particle deposition (1)

- Numerical results obtained for single particle deposition
  - Introduction of surface roughness in particle-surface interactions
  - Analysis of the effect of surface roughness on particle-surface interactions
  - Validation of the new model by comparison with experimental data

Normalized deposition rate of 0.8 $\mu m$ polystyrene particles on PMMA surfaces (experimental data from Sjollema and Busscher, Colloids & Surfaces, 1990)

- (●) experimental measurements,
- (—) numerical results on smooth surface,
- (- -) numerical results for rough surfaces (5 up to 50nm covering 8% of the surface)

$\Rightarrow$ Non-zero deposition rates in repulsive conditions are reproduced
Single particle deposition (2)

- Numerical results obtained for single particle deposition
  - Introduction of surface roughness in particle-surface interactions
  - Analysis of the effect of surface roughness on particle-surface interactions
  - Validation of the new model by comparison with experimental data

Deposition of hematite particles on polypropylene (Čerović et al, J. Colloid Interface Sci., 2009)

⇒ The overall deposition rate is increased by singularities (bends, box)
Multilayer deposition (1)

- Extension of the model for multilayer deposition
- Development of a new modelling approach to clogging

- Assumptions made for the first modelling steps:
  - Dilute suspension
  - No reentrainment
  - No influence of deposits on the fluid

- Use of a two-step process with an energy-balance approach for the coupling of both steps (similar to deposition):
  - Changed transport step (no fluid motion around deposits): modelled using the same stochastic Lagrangian approach already used for hydrodynamic transport of particles
  - Modified attachment step (to account for particle-particle interactions): modelled using the DLVO theory and a statistical description of the fouled surface (surface covered by deposited particles, size of deposited particles).
Multilayer deposition (2)

- Extension of the model for multilayer deposition
- Development of a new modelling approach to clogging
- Qualitative validation of the new modelling approach

250 nm alumina particles on silicon substrates (data from Perry et al, Microfluid Nanofluid, 2008): Only one layer at $pH = 3$, Multilayer deposit at $pH = 9$ and 9.5, No fouling at $pH \geq 10$

![Graphs showing surface coverage and maximum particle/cluster size](image)

(c) Surface covered by particles
(d) Maximum particle/cluster size

**Figure:** Numerical results for the clogging behaviour of silicon substrates by alumina particles: — $pH$ 3, - - $pH$ 9, -- $pH$ 10
Multilayer deposition (3)

- Extension of the model for multilayer deposition
  - Development of a new modelling approach to clogging
  - Possibility to simulate channel blockage

![Figure](clogging.png)

**Figure:** Clogging of a microchannel through sequential deposition of small particles (a,b,c) until the flow passage becomes blocked by a larger particle (d)

⇒ **Tractable simulations in 3-D cases until complete flow blockage**
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Experimental evidence of resuspension mechanisms

- Two different mechanisms

Rolling motion (mainly small particles)

'Burst-type' resuspension (large particles)

Figure: Snapshots of an entrained glass particle ($d_p = 30 \mu m$, $d_p^+ = 7$) from a rough substrate as recorded by Jiang et al. (from Jiang et al., Pow Tec, 2008)

Figure: Sequence of PIV images superposed with PTV vectors showing the resuspension of a polystyrene particle ($d_p = 538 \mu m$, $d_p^+ = 10$) (from van Hout, J Fluid Mech, 2013)
Modelling approaches for particle resuspension

Various models depending on the level of description of particle dynamics

- **Empirical formulas:**
  Providing macroscopic information (useful in Eulerian approaches) but highly dependent on the conditions studied

- **Force-balance approach**
  Reentrainment due to the rupture of equilibrium (lift, rolling or sliding motion)
  Adapted for both Lagrangian and Eulerian (extraction of macroscopic laws) calculations

- **Kinetic PDF approaches (RRH, Rock’n’Roll theories)**
  Reentrainment due to oscillations around the contact point due to turbulent fluid fluctuations

- **Dynamic PDF approaches**
  Reentrainment accounting for the whole dynamics of rolling particles

- **DEM methods**
  Possibility of performing very fine calculations with rolling, sliding and lifting motions
A one-point PDF approach for colloidal resuspension

- **Model**
  - Introduction of surface roughness for adhering particle-surface contact forces
  - Mechanism retained for particle resuspension: *rolling motion*

Analysis of the effect of surface roughness on the reentrainment process:
- Reduction of adhesion energies with nanoscale roughness
- Rocking of particles on microscale roughness

Equation of particle motions:
Streamwise velocity approximated using the angular velocity: \( U_{p,\parallel} \approx R_{part} \omega \)
Angular velocity given by the balance between moments exerted on particles:

\[
I \frac{d\omega}{dt} \approx M_O(F_{drag,\parallel}) - M_O(F_{adh})
\]

with \( I = 7m_{part}R_{part}^2/5 \) the moment of inertia, \( M_O(F_{drag,\parallel}) = 1.4 \times R_{part} \times F_{drag,\parallel} \) and \( M_O(F_{adh}) = F_{adh} \times a_0 \) the hydrodynamic and adhesion moments.
Results obtained on particle reentrainment (1)

- Numerical results obtained with the one-point PDF approach
  
  Statistical description of surface roughness using $R_{asp}$ and $S_{cov}$
  $\Rightarrow$ Statistical information on the adhesion force (or energy)

Validated on several test cases:
For instance, adhesion between 10 $\mu m$ polystyrene particles and aluminum polished substrate:
- experimental data (from Zhou et al., Powder Technol., 2003, Vol. 135-136, 82-91), – predictions with $R_{asp} = 250$ nm ($S_{cov} = 0.5$ %)

$\Rightarrow$ Possibility to retrieve complex distributions of the adhesion force
Main results obtained for particle resuspension

- Numerical results obtained with the one-point PDF approach
  - Introduction of surface roughness for adhering particle-surface contact forces
  - Validation of the new model by comparison with experimental data

![Graphs showing resuspension data for different particle sizes and exposure times.](image)

**Figure**: Fraction of alumina or graphite particles remaining on stainless steel substrates after a 1 s exposure to an airflow with varying friction velocity:
- numerical results ($R_{asp}^{large} = 2 \mu m, S_{cov}^{large} = 3.1 \%$ and $R_{asp}^{small} = 5 \text{ nm}, S_{cov}^{small} = 3 \%$)

⇒ Relatively correct predictions of particle resuspension from rough substrates
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State-of-the-art in the formation of complex deposits

- Relatively extensive experimental data on deposition and resuspension from monolayers
- Satisfactory predictions provided that modelling approaches properly account for the coupling between hydrodynamic transport, physico-chemistry of interfaces as well as with surface roughness

⇒ Importance of having accurate and consistent descriptions of particle-fluid, particle-surface and particle-particle interactions
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Deposit morphology

**Experimental data:**

- Recent experimental data in microfluidics on the growth of complex deposits with colloidal particles
- Existing works on the formation of deposits for large particles (dust, sand, etc.)
  ⇒ Characterisation of the morphology in terms of fractal dimension $d_F$, coordination number $N_C$, porosity $\rho$, etc.

But **lack of information** on the evolution of the deposit morphology with fluid, particle and surface properties (especially for colloidal particles)
  ⇒ Need of experimental study similar to those already done for particle agglomeration and fragmentation

Need of experimental studies the mechanisms at play in the formation of a given deposit morphology
  → how particles stick to a deposited cluster? Do they stick immediately or roll for a certain time? To what extent these mechanisms impact the morphology?
Deposit morphology

- Modelling approaches:
  - Recent breakthrough in the effect of fluid velocity and particle-particle interactions on the deposit morphology using very fine Lagrangian methods (often DEM)
  
  - Limitation of such DEM simulations:
    particle either stick or roll until reaching a stable position
    No effect of surface roughness on rolling motion (possibly leading to different PDF of the contact angle between particles)

  $\rightarrow$ need to include the effect of surface roughness in such methods, or to use multi-scale approaches (PDF of the contact angle given by a finer calculation)
Need of experimental (and later numerical) studies on several topics:

- **Cohesion forces and deformation:**
  Need to quantify the role played by surface deformation in cohesion forces with respect to particle size and nature (properties).
  Importance of plastic deformation (which requires development of new contact theories)?

- **Restructuring:**
  Need to evaluate the role played by deposit restructuring for colloidal particles (largely studied in the case of large inertial particles such as sand)
  → Is restructuring realistic for colloidal particle with low energy at impact?
  Possibility to study these effects in particle agglomeration/fragmentation
Deposit consolidation (1)

- Experimental evidence of deposit consolidation:
  - Consolidation in heat exchangers (superheaters, nuclear power plants, ...)
  - Ash deposit in gasifiers:

  ![Deposit Image](image)

  **Figure**: Deposit formed on a cool surface (from Drift&Pels, ECN-04-077) showing a compact layer (ash particles and condensed tar) and a porous layer (char particles)

- Various possible mechanisms for consolidation:
  - Ostwald ripening
  - Dissolution/precipitation of oxides in solution
  - Sintering
  - Boiling-induced precipitation
Deposit consolidation (2)

- Model for particle consolidation
  - Complexity and variety of mechanisms involved
  - Lack of fine (microscopic) numerical/experimental studies of consolidation phenomena
  - Existing models are restricted to macroscopic effects related to consolidation (mostly thermal conductivity)

- Constraints related to the Lagrangian module in *Code_Saturne*
  - No detailed information on the cluster structure
Deposit consolidation (3)

- Model for particle consolidation
  - Evolution of the force between particles as a function of the cluster time since deposition and cluster height

\[
F_{p-p}^{deltap} = F_{p-p,DLVO} \times (1 - f(h, t)) + F_{consol}^{p-p} \times f(h, t)
\]

\[
f(h, t) = 0.5 \times \left(1 - \tanh \left(\frac{h - h_{consol}}{k_{consol} \times h_{consol}}\right)\right)
\]

with \(h_{consol}\) the height of consolidated deposits at time \(t\)
and \(k_{consol} = 0.1\) (\(k_{consol} \to 0\) for structures with only two layers)

⇒ Need for detailed experimental/numerical studies on consolidation to provide the evolution of inter-particle forces in clusters
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Two-way coupling

- Experiments:
  - Need of fine measurements of the effect of complex colloidal deposits on fluid motions and near-wall turbulence (using PIV/PTV methods)
Two-way coupling

- Modelling approaches
  - DNS with finite-sized particles:
    ⇒ Exact calculation of particle motions, but high computational costs
  - Moving boundary approach:
    ⇒ Particle motion around smoothed surfaces, but complex evolution with resuspension
  - Porous media (for Eulerian calculations of the fluid):
    ⇒ Modifications of the fluid motions at the mesh scale using Darcy law:

⇒ Need for a consistency between the calculation of particle and fluid phases
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Multilayer resuspension

- Coupling between various mechanisms:
  - Hydrodynamic multilayer resuspension
  - Resuspension after impaction
  - Fragmentation after impaction

Figure: Illustration of the three dust emission mechanisms proposed by Kok et al., Rep Prog Phys, 2012
Multilayer resuspension

- **Hydrodynamic multilayer resuspension**
  - **Experimental data:**
    - Smaller particles are harder to remove
    - Breakage of clusters around weak cohesion zones
    - \( \Rightarrow \) complex dependence on deposit morphology and intricate screening/hiding effects

- **Modelling approaches:**
  - Empirical models
  - Extended kinetic PDF approaches (accounting for changes of hydrodynamic/adhesion forces with the layer number)
  - Fine DEM methods (with rotational and translational motion)

**Figure:** Snapshots of particle reentrainment from an initially nearly spherical cluster exposed to shear flow (from Iimura et al., Chem Eng Sci, 2009)
Multilayer resuspension

- Resuspension after impaction (or splashing)
  - Experimental data:
    Mostly for large cohesionless particles (sediments, sand, dusts)
    High speed video recording

![High-speed images of the splashing of millimetres particles](image)

**Figure**: High-speed images of the splashing of millimetres particles: the time between two images is 4 ms (from Beladjine et al., Phys Rev E, 2007)

- Modelling approaches
  DEM with force/energy propagation

![Snapshots of compression wave propagation](image)

**Figure**: Snapshots of compression wave propagation obtained with a 2D DEM model (from Bourrrier, Gran Mat, 2008)
Multilayer resuspension

- **Fragmentation after impaction**
  - Recent experimental data (2007):
    Mostly on **colloidal particles** (significant adhesion forces)
    Characterisation of agglomerate after impact using TEM showing the effect of impact velocity, agglomerate structure (compact agglomerates are harder to break), deposit nature
  - Modelling approaches:
    MD-like methods

⇒ Dependence of splashing and impact fragmentation on several properties: impacting particle (velocity, angle), deposit (structural ordering, visco-elastic properties)
Limitations and perspectives

- Need of fine PIV/PTV measurements to highlight the mechanisms (rolling, sliding, lifting?) of multilayer resuspension
  \[ \Rightarrow \] development of refined models (DEM, dynamic PDF)

- Need of experimental data for splashing with colloidal particles (if significant) and coupling between splashing and impact fragmentation

- Experimental quantification of the **relative importance** of hydrodynamics, splashing and impact fragmentation in multilayer resuspension both for colloidal and large inertial particles
  \[ \Rightarrow \] Refinement of modelling approaches (DEM, dynamic PDF) to account for the whole range of possible mechanisms
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Further readings

Thank you for your attention

Any question?
Appendix

- General remarks and definitions
- Particle-fluid interactions
  - Modelling of the fluid phase
  - Modelling approaches for particle motions
  - One-particle PDF approach
- Particle-surface interactions
  - DLVO theory
  - Accounting for surface roughness
  - Other parameters influencing adhesion
  - Contact forces
Size separation of particles

Particle sizes

- 1 Å
- 1 nm
- 1 µm
- 1 mm

**Atoms**
**Molecules**
**Macro-molecules**
**Viruses**
**Bacteria**
**Algae**

**Colloidal**
**Suspended**

**Clays**
**Silt**
**Sand**
Equations for fluid motions

- Fluid motions described by the continuity and Navier-Stokes equations, given by (for incompressible flows):

\[ \nabla \cdot \mathbf{v} = 0 \]

\[ \left( \frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{v} + \mathbf{F} \]

- Turbulent flows:
  \[ \Rightarrow \text{Fluctuations of } \mathbf{v}(t, x) \text{ in time and in space over a continuous wide range of scales} \]

- Computational Fluid Dynamics (CFD):
  solving Navier-Stokes equations using numerical methods
Modelling approaches for fluid motions

- Various numerical methods can be used for turbulent flow simulations:
  - Direct Numerical Simulation (DNS):
    - Exact solutions over the entire range of turbulent scales
    - High computational costs (proportional to $Re^3$)
    - Untractable in complex 3D cases
  - Large-Eddy Simulation (LES):
    - Solving only the largest scales of turbulence, model for the small-scales
    - Lower computational costs than DNS but higher than RANS
  - Reynolds-Averaged Navier-Stokes (RANS):
    - Solving only the first two moments of the velocity field: $\mathbf{v} = \langle \mathbf{v} \rangle + \mathbf{v}'$
    - Time-averaged velocity $\langle \mathbf{v} \rangle$ given by the mean Navier-Stokes equation:
      $$\left( \frac{\partial \langle \mathbf{v} \rangle}{\partial t} + \langle \mathbf{v} \rangle \cdot \nabla \langle \mathbf{v} \rangle \right) = -\nabla \cdot \left( \langle \mathbf{v}' \otimes \mathbf{v}' \rangle \right) - \frac{1}{\rho} \nabla \langle p \rangle + \nu \nabla^2 \langle \mathbf{v} \rangle + \langle \mathbf{F} \rangle$$
    - Model for the Reynolds stress tensor $\langle \mathbf{v}' \otimes \mathbf{v}' \rangle$
    - Tractable in complex 3D situations
Modelling approaches to surface fouling

- Adsorption model (no fluid)
  - RSA
  - Ballistic models

- Models with fluid transport
  - Eulerian approaches
  - Lattice-based Monte-Carlo methods
  - Lagrangian approaches
    - Molecular Dynamics
    - Distinct Element Methods
    - Langevin Dynamics
    - Brownian Dynamics
    - Dissipative Particle Dynamics
    - One-particle pdf approach

- Classification of the modelling approaches
Random Sequential Adsorption (RSA)

- **Principle**
  - Sequential deposition (one particle at a time)
  - Particle position generated randomly above a plate
  - Irreversible deposition if no contact with already adsorbed particles
  - Refinements to account for lateral particle-particle interactions
  - Refinements for the particle-surface interactions
  - Refinements for particle diffusion (DRSA)

- **Main results**
  - Study of the kinetics of monolayer formation
  - Study of blocking effects
    - Extraction of constitutive laws
Ballistic models

- Principle
  - Sequential deposition (one particle at a time)
  - Particle position generated randomly above a plate
  - Rolling motions of particles upon deposition

- Main results
  - Study of the deposit morphology
    - Random close packings with rolling motions
    - Random loose packings without rolling motions
Eulerian approaches

- **Principle**
  - Use of convective-diffusion equation for particle transport

\[
\frac{\partial c}{\partial t} + \nabla \cdot (cv) = \nabla \cdot (D \cdot \nabla c - c \tau F)
\]

with \( c \) the particle concentration, \( v \) the fluid velocity, \( D \) the diffusion matrix (including the hydrodynamic and possible turbulent effects), \( \tau \) the characteristic timescale and \( F \) the external forces (such as DLVO interactions)

→ Closure relations for \( D \) and \( F \) (range of validity?)

- **Boundary conditions**
  - Perfect sink model (\( c = 0 \) at the surface), non-penetration models (flux \( j = 0 \) at the surface), etc.
Eulerian approaches

- **Principle**
  - Use of convective-diffusion equation for particle transport
    \[
    \frac{\partial c}{\partial t} + \nabla \cdot (cv) = \nabla \cdot (D \nabla c - c \tau F)
    \]
    with \( c \) the particle concentration, \( v \) the fluid velocity, \( D \) the diffusion matrix (including the hydrodynamic and possible turbulent effects), \( \tau \) the characteristic timescale and \( F \) the external forces (such as DLVO interactions)
    
    \[\rightarrow \text{Closure relations for} \ D \text{ and} \ F \text{ (range of validity?)} \]

- **Boundary conditions**
  - Perfect sink model (\( c = 0 \) at the surface), non-penetration models (flux \( j = 0 \) at the surface), etc.

- **Main results**
  - Fast evaluation of macroscopic clogging properties
    \[\rightarrow \text{Good evaluations of breakthrough curves and jamming limits} \]
  - Only limited information on macroscopic details (here concentration)
  - No insights into microscopic details
Lattice-Based Monte-Carlo methods

- **Principle**
  - Simple “Toy” models for particle transport
  - Discretisation over a lattice
    - Particle motions according to probabilities to move from one site to another site
  - Macroscopic properties obtained through averaging over many realisations

- **Main results**
  - Access to mesoscopic details of multilayer formation (local mechanisms)
  - Good predictions of the monolayer formation
  - Dependence of multilayer growth on electrostatic properties recovered

Return
Molecular Dynamics (MD)

- **Principle**
  - Solving directly the Newtonian equations of motion for all molecules:

  \[ m_i \frac{dv_i}{dt} = \sum_j F_{j \rightarrow i} \]

  with \( F_{j \rightarrow i} \) the force of particle labelled \( j \) on the one labelled \( i \)

- **Main results**
  - Detailed microscopic results
  - But only tractable for small system (due to high computational costs)
    - Small time steps (for rapid fluctuations)
    - Very dilute suspensions (limited number of particles)
Distinct Element Methods (DEM)

- **Principle**
  - Solving directly the equations of both translational and rotational motions for all particles:

\[
m_i \frac{dv_i}{dt} = \sum_j F_{j\rightarrow i}
\]

\[
l_i \frac{d\Omega_i}{dt} = \sum_j M_{j\rightarrow i}
\]

with \( m_i \) the particle mass, \( v_i \) the particle velocity, \( F_{j\rightarrow i} \) the forces acting on the particle, \( l_i \) the particle inertia, \( \Omega_i \) the particle angular velocity and \( M_{j\rightarrow i} \) the torque exerted on the particle.

- **Main results**
  - DEM simulation of particulate clogging in porous media
  - Study on the deposit morphology
  - But, as for MD simulations, only tractable for small system (due to high computational costs)
Langevin Dynamics

- Principle
  - Langevin-type equations of particle motion

\[ m_i \frac{dv_i}{dt} = \sum_j \tilde{F}_{j \rightarrow i} + \eta_i(t) - \gamma_i v_i \]

with \( \tilde{F}_{j \rightarrow i} \) the forces with slow variations acting on particles, \( \eta_i \) a noise term for rapidly fluctuating variables and \( \gamma_i v_i \) the fluid drag force.
Brownian Dynamics

- **Principle**
  - Limiting case of LD with a force-balance approach:

  \[
  0 = \sum_j \tilde{F}_{j\rightarrow i} + \eta_i(t) - \gamma_i v_i
  \]

  with \(\tilde{F}_{j\rightarrow i}\) the forces with slow variations acting on particles, \(\eta_i\) a noise term for rapidly fluctuating variables and \(\gamma_i v_i\) the fluid drag force.

  leading to a formulation on particle positions \(X_{p,i}\) only:

  \[
  dX_{p,i} = \frac{1}{\gamma_i} \sum_j \tilde{F}_{j\rightarrow i} + \sqrt{2D}dW_i
  \]

- **Simplifications:**
  - Sequential BD methods (consecutive single particle deposition)
  - Ranged BD methods (interparticle interactions only within a limited distance)

- **Main results**
  - Microscopic details (such as the shadow effect)
  - Multilayer and monolayer formation captured by the coupling between particle-particle, particle-fluid and particle-surface interactions.
Dissipative Particle Dynamics

Principle

Description of the motion of a collection of DPD mesoscale “particles”, representing an ensemble of colloidal particles

\[ m_i \frac{d\hat{v}_i}{dt} = \sum_j \left( \hat{F}_{j \rightarrow i}^C + \hat{F}_{j \rightarrow i}^D + \hat{F}_{j \rightarrow i}^R \right) + \hat{F}_{\text{ext}} \]

with \( \hat{v}_i \) the mesoscale “particle” velocity, \( \hat{F}_{j \rightarrow i}^C \), \( \hat{F}_{j \rightarrow i}^D \), and \( \hat{F}_{j \rightarrow i}^R \) the conservative, dissipative and random (Brownian) forces (if particle \( j \) is within the radius of influence of particle \( i \)), and with \( \hat{F}_{\text{ext}} \) the external forces.
Dissipative Particle Dynamics

- Principle
  - Description of the motion of a collection of DPD mesoscale “particles”, representing an ensemble of colloidal particles

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- Main results
  - Coarse-grained molecular dynamics method
  - Correct predictions of the accumulation of platelet in blood flows
One-particle pdf approach

- **Principle**
  - Equation of motions described using modelled forces, obtained through mean-field approaches
  - State vector associated to each particle
    \[ m_i \, dv_i = F_i \, dt + K_i \, dW_i \]
    with \( F_i \) and the diffusion coefficients \( K_i \) are models for the forces acting on particles.

- **Main advantages**
  - Tractable in 3-D industrial cases
Classification of the modelling approaches to surface fouling

- **Microscopic**
  - RSA
  - Ballistic model
    - Moment (or Eulerian) approach
    - MD or DEM
    - LD or BD
    - One-particle PDF

- **Mesoscopic**
  - DNS (fluid)
  - DPD

- **Macroscopic**
  - No fluid
    - Ballistic model
  - No fluid
    - RSA

- **No fluid**
Classification of the modelling approaches to surface fouling (2)

RANS (fluid)
- Microscopic
  - MD or DEM
- Mesoscopic
  - LD or BD
  - DPD
  - One-particle PDF
- Macroscopic
  - Moment (or Eulerian) approach
- No fluid
  - Ballistic model
  - RSA

⇒ Need for consistent approaches for fluid and particle motions

Return

Christophe Henry  Perspectives for the understanding of complex deposits on surfaces
Equations of particle motions

Newton’s law, which for negligible relative Reynolds number \( R_p = d_p U_R / \nu_f \), where \( U_R = U_s - U_p \) reduces to:

\[
dx_p = U_p dt \\
dU_p / dt = F_1 + F_2
\]

- **Undisturbed field: \( F_1 \)**
  - Pressure gradient forces
    \[
    \frac{\pi d_p^3}{6} \rho_f \frac{DU_s}{Dt}
    \]
  - Buoyancy forces
    \[
    \frac{\pi d_p^3}{6} (\rho_p - \rho_f) g
    \]
- **Disturbance field: \( F_2 \)**
  - Drag forces
    \[
    3\pi d_p \rho_f \nu_f (U_s - U_p)
    \]
  - Added-mass forces (inertia added to the fluid due to particle acceleration)
    \[
    \frac{\pi d_p^3}{12} \rho_f \left( \frac{DU_s}{Dt} - \frac{dU_p}{dt} \right)
    \]
  - Basset forces (viscous effects + boundary layer development due to particle acceleration)
    \[
    \frac{3d_p^2}{2} \rho_f \sqrt{\pi \nu_f} \left( \int_{-\infty}^{t} \frac{d}{d\tau} (U_s - U_p) \frac{d\tau}{\sqrt{t-\tau}} \right)
    \]
Equations of particle motions (2)

- For heavy particle $\rho_p \gg \rho_f$:
  
  Drag and gravity forces are predominant
  
  $\begin{align*}
  dx_p &= U_p \, dt \\
  dU_p &= \frac{U_s - U_p}{\tau_p} \, dt + g \, dt
  \end{align*}$

  where $\tau_p$ is the particle relaxation time scale related to drag forces:
  
  $\tau_p = \frac{4 \rho_p d_p^2}{3 \rho_f C_D |U_R|} \quad \rho_p \gg \rho_f \quad \rightarrow \quad \frac{\rho_p d_p^2}{18 \rho_f}$

- For colloidal particles:
  
  Gravity is negligible compared to Brownian motion
  
  $\begin{align*}
  dx_p &= U_p \, dt \\
  dU_p &= \frac{U_s - U_p}{\tau_p} \, dt + K_{Br} \, dW \\
  \text{with} \quad K_{Br} &= \sqrt{\frac{2 k_B T}{m_p \tau_p}}
  \end{align*}$
Formalism for the one-particle pdf approach

Lagrange formalism

\[ dx_{p,i} = U_{p,i} dt \]
\[ dU_{p,i} = \frac{U_{s,i} - U_{p,i}}{\tau_p} dt + K_{Bro} dW_i' \]
\[ dU_{s,i} = A_i(t, U_{s,i}) dt + B_i(t, U_{s,i}) dW_i \]

- Drift term: forces with slow variations
  \[ A_i(t, U_{s,i}) = -\frac{1}{\rho_f} \frac{\partial \langle P \rangle}{\partial x_i} + (\langle U_{p,j} \rangle - \langle U_{p,j} \rangle) \frac{\partial \langle U_{f,i} \rangle}{\partial x_j} - \frac{U_{s,i} - \langle U_{f,i} \rangle}{T_{L,i}} \]
  where \( T_{L}^* \) is the fluid Lagrangian time scale (* refers to modifications due to crossing-trajectory effects).

- Diffusion term: forces with rapid fluctuations
  \[ B_i(t, U_{s,i}) = \sqrt{\langle \epsilon \rangle} \left( C_0 b_i \tilde{k}/k + 2/3(b_i \tilde{k}/k - 1) \right) \]
  where \( b_i = \frac{T_L}{T_{L,i}} \) is the correction factor from Csanady’s formulae
  and \( \tilde{k} = \frac{3}{2} \frac{\sum_{i=1}^{3} b_i \langle u_{f,i}^2 \rangle}{\sum_{i=1}^{3} b_i} \) is a modified kinetic energy accounting for anisotropy in the turbulent kinetic energy.
Near-wall hydrodynamic model

- 1D Formulation accounting for the random succession of near-wall coherent structures along particle trajectories
- Langevin equation for the wall-normal velocity $V_p$

$$
\begin{align*}
    dy_{p,i} &= V_{p,i} \, dt \\
    dV_{p,i} &= \frac{V_{s,i} - V_{p,i}}{\tau_p} \, dt + K_{Bro} \, dW_i
\end{align*}
$$

where the fluid velocity seen by the particle is described by a succession of motions:

$$
\begin{align*}
    V_s &= -V_{struc} & \text{sweep} \\
    V_s &= V_{struc} & \text{ejection} \\
    dV_s &= -\frac{V_s}{T_L} \, dt + K_{ext} \, dW & \text{diffusion} \\
    dV_s &= A_{int} \left( y_p^+ \right) \, dt - \frac{V_s}{T_L} \, dt + K_{int} \left( y_p^+ \right) \, dW & \text{internal layer}
\end{align*}
$$
Van der Waals interactions: origin

- Interaction between spontaneous polarisations of nearby dipoles
  - Keesom interactions between two permanent dipoles

\[
\text{H} - \delta^+ \quad \text{Cl} - \delta^- \quad \text{H} \quad \text{Cl} - \delta^+ \quad \delta^+ \quad \delta^- 
\]

- Debye interactions between one permanent dipole and a corresponding induced dipole

- London dispersion interactions between two transient dipoles.

- Retardation:
  Arise when the separation distance is high, leading to a non-instantaneous interaction between dipoles (due to the finite light velocity)
Van der Waals interactions: modelling approaches

- **Molecular scale:**
  London molecule-molecule interaction $\propto 1/h^6$

- **Macroscopic scale**

  ![Diagram showing modelling approaches]

  - **Hamaker approach**
    (Microscopic approach)
    Pairwise summation of intermolecular interactions
    With/without retardation
    - Complex geometry
      - Derjaguin integration method
        Derived from plate-plate interaction for small separations
    - Simple geometry
      - Surface element integration
        Numerical integration over the exact topography

  - **Lifshitz approach**
    (Macroscopic approach)
    Continuum theory based on electromagnetic properties
Electrostatic Double-Layer interactions: origin

- **Origin of the electrical double-layer:** Screening of the surface charge by ions present in the solution

- **Description by the Stern-Grahame model:**
  
  Competition between:

  - Chemical reactions occurring at the surface (ad/de-sorption of protons, or ions)
  
  - Electrostatic affinity of ions in the solution (described by the Poisson-Boltzmann equation)

\[ \nabla^2 \psi = - \frac{1}{\varepsilon_r \varepsilon_0} \sum_i n_i^0 z_i e \exp \left( \frac{-z_i e \psi}{k_B T} \right) \]

(\( \varepsilon_0 \): permittivity of vacuum, \( \varepsilon_r \): material dielectric permittivity, \( n_i^0 \): number density of ions of valency \( z_i \), \( e \): elementary charge, \( k_B \): Boltzmann constant, \( T \): temperature).
Electrostatic Double-Layer interactions: modelling approaches

- Macroscopic interactions:

  - Static description
    - Simple geometry
      - Constant charge approximation
        - Linear Poisson-Boltzmann equation
          - Small potentials
    - Constant potential approximation
      - Non-linear Poisson-Boltzmann equation
        - All potentials

  - Dynamic description
    - Double-layer relaxation
      - Complex geometry
        - Linear superposition approximation
          - Summation of the contribution from each surface
        - Derjaguin integration method
          - Derived from plate-plate interaction for small separations
Sphere-plate geometry: Gregory formula valid at small separations, and Czarnecki formula valid at larger separations

\[
U_{SP}^{VdW} = -\frac{A_{Ham} R_{part}}{6h} \times \left( \frac{1}{1 + \frac{14h}{\lambda} + \frac{5\pi h^3}{4.9\lambda R_{part}^2}} \right) \quad \text{if } h < \frac{\lambda}{2\pi}
\]

\[
U_{SP}^{VdW} = A_{Ham} \frac{2.45\lambda}{60\pi} \left( \frac{h - R_{part}}{h^2} - \frac{h + 3R_{part}}{(h + 2R_{part})^2} \right) - A_{Ham} \frac{2.17\lambda^2}{720\pi^2} \left( \frac{h - 2R_{part}}{h^3} - \frac{h + 4R_{part}}{(h + 2R_{part})^3} \right) + A_{Ham} \frac{0.59\lambda^3}{5040\pi^3} \left( \frac{h - 3R_{part}}{h^4} - \frac{h + 5R_{part}}{(h + 2R_{part})^4} \right)
\]

Sphere-sphere geometry: Gregory formula valid at small separations

\[
U_{SA}^{VdW} = -\frac{A_{Ham} R_{part} R_{asp}}{6h(R_{part} + R_{asp})} \times \left( 1 - \frac{5.32h}{\lambda} \ln \left( 1 + \frac{\lambda}{5.32h} \right) \right)
\]
DLVO interaction: EDL formulae

- Sphere-sphere and sphere-plate geometries: Bell et al formula valid at all separations, for small potentials and $\kappa R_i \geq 5$

$$U_{SA}^{EDL} = 2\pi \varepsilon_0 \varepsilon_r \left( \frac{k_B T}{ze} \right)^2 \times \frac{R_{part} R_{asp} (r - R_{part})(r - R_{asp})}{r[(R_{part} + R_{asp})r - R_{part}^2 - R_{asp}^2]} \times [\Omega_1 \ln(1 + \Gamma) + \Omega_2 \ln(1 - \Gamma)]$$

with the reduced potentials $\Phi = ze \varphi / k_B T$ and:

$$\Omega_1 = \Phi_1^2 + \Phi_2^2 + \Lambda \Phi_1 \Phi_2$$

$$\Omega_2 = \Phi_1^2 + \Phi_2^2 - \Lambda \Phi_1 \Phi_2$$

$$\Lambda = \sqrt{\frac{R_{part} (r - R_{part})}{R_{asp} (r - R_{asp})}} + \sqrt{\frac{R_{asp} (r - R_{asp})}{R_{part} (r - R_{part})}}$$

$$\Gamma = \sqrt{\frac{R_{part} R_{asp}}{(r - R_{part})(r - R_{asp})}} \times e^{\kappa (R_{part} + R_{asp} - r)}$$

Lift of the small potential approximations with the potential from Ohshima et al:

$$Y = 8 \times tanh \left( \frac{\Phi}{4} \right) \times \left( 1 + \sqrt{1 - \frac{2R_i \kappa + 1}{(R_i \kappa + 1)^2} tanh^2 \left( \frac{\Phi}{4} \right)} \right)^{-1}$$
Dynamics of the DLVO interaction: charge regulation

EDL interactions: overlap of two double-layers

- **Static interaction:**
  - Constant potential CP approximation (used here)
  - Constant charge CC approximation

- **Dynamic interaction:**
  Variations of charge and potential upon interaction
  - Constant regulation CR approach:
    Use of a regulation parameter as a linearised sum of the CP and CC interactions
  - Electrostatic and chemical approach:
    Kinetics of the chemical reactions at the surface
    Equations for the electrostatic affinity of ions in the double-layer

- **Limits (restraining its use in the present case):**
  - Increase of the energy barrier
  - Intricate coupling with surface roughness
Existing models for adhesion forces

Various methods exist to describe the adhesion between two bodies:

- **Surface energy ($\gamma$) methods**
  - **JKR model:**
    Adhesion force inside the contact area (given by surface deformation)
    Valid provided that $\mu_T = \left(\frac{R_{part}\Delta \gamma^2}{E^2 z_0^3}\right)^{1/3} \gg 1$ (soft spheres)
    \[
    F_{ad} = 3\pi \frac{R_1 R_2}{R_1 + R_2} \gamma
    \]

- **DMT model:**
  Inclusion of non-contact forces in the vicinity of the contact area
  Valid provided that $\mu_T \leq 1$ (hard spheres)
  \[
  F_{ad} = 4\pi \frac{R_1 R_2}{R_1 + R_2} \gamma
  \]

- **Maugis-Pollock model:**
  Transition from JKR to DMT theories

- **Hamaker approach**
  VDW interaction energy at contact $z_0 = 0.169 \ nm$ (no deformation)
Model for surface roughness

The attachment step has been refined to account for surface roughness (see Henry et al, Langmuir, 2011, Vol. 27(8), pp. 4603-4612)

- Generation of surface roughness:

  Rough surfaces described by smooth plates covered by spherical asperities
  
  - Hemispherical asperities only within a certain cut-off radius (interactions are negligible further than $10/\kappa$):

  $$S_{\text{eff}} = 2.5\pi(2R_{\text{part}} + R_{\text{asp}} + 10/\kappa)(R_{\text{asp}} + 10/\kappa)$$

- Number of asperities within the surface $S_{\text{eff}}$ given by a Poisson distribution with mean $\frac{S_{\text{eff}} \times S_{\text{cov}}}{\pi R_{\text{asp}}^2}$

- Hemispherical asperities placed randomly on the surface

- Polydispersion in the size of asperities

$\Rightarrow$ Statistical representation using two physical parameters: $R_{\text{asp}}$ and $S_{\text{cov}}$
Model for the interaction energies between rough surface.

The attachment step has been refined to account for surface roughness (see Henry et al, Langmuir, 2011, Vol. 27(8), pp. 4603-4612)

- Model for surface roughness:
  - Hemispherical asperities only within a certain cut-off radius (interactions are negligible further away)
  - Hemispherical asperities placed randomly on the surface

- Interaction energy:
  - Still described using the DLVO theory
  - Assuming the additivity of interaction energies: formula

\[ U_{DLVO}^{Sphere-Surface} = (1 - S_{cov}) U_{DLVO}^{Sphere-plate} + \sum_{asperities} U_{DLVO}^{Sphere-asperity} \]

⇒ Statistical information (such as the probability density function PDF, mean, max, min) on the energy barrier using Monte-Carlo evaluations