Sedimentation & Rheology of Clay Suspensions: Sticky & Repulsive

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Motivation - geomorphology
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Muddy landscapes:
Shaped by mud sedimentation/erosion
Motivation - from geomorphology to physics

Goal:
Understand the physics of mud sedimentation/aggregation
What is mud?:
- mud = silt + clay + $H_2O$ + organic matter
- mud: complex fluid
Approach - physics point of view

Simplification

mud: clay + $H_2O$ (clay suspension)
Processes involved

• Sedimentation & Flow
• Chemistry: particle shape, interparticle forces
• Mechanics & Rheology
• …much more
Main goal: Understand the sedimentation of clay suspensions using a materials approach
Experimental Setup

Two types of particles:
- Glass beads \( \rightarrow \) \( D_p \sim 10 \, \mu m; \rho = 2.4 \, g/cm^3; \) spheres
- Kaolinite clay \( \rightarrow \) \( D_k \sim 10 \, \mu m; \rho = 2.6 \, g/cm^3; \) sheet mineral

- Volume fraction \( \phi \) ranging from 0.8 to 8\% \( \rightarrow \) *dilute regime*
- Interparticle potential \( \rightarrow \) repulsion/attraction using salts

Sedimentation time vary from hours to days.
Particle Characterization
Tuning interparticle potential

Zeta potential $\zeta_p$ as a function of salt concentration

- $\zeta_p$ quantifies degree of electrostatic repulsion between particles
- Red line closer to zero is the most attractive solution
- Glass beads (green dot) are mostly repulsive

- Addition of NaCl $\rightarrow$ **Attractive** suspensions
- Addition of $(NaPO_3)_6$ $\rightarrow$ **Repulsive** suspensions
Sample videos

Glass beads in DI water
(\(\phi = 10\%\))

Kaolinite in DI
(\(\phi = 4\%\))

Kaolinite + (NaPO\(_3\))\(_6\)
(\(\phi = 4\%\))

behavior expected of non-attractive suspensions

Solid-like behavior

Similar to glass beads (non-attractive)
Let’s quantify these observations
Measurements

Image analysis to obtain:
1) Concentration (density) profiles
2) Interface position & width (spreading)

Concentration profiles

*E. coli*: $0.75 \times 10^9$ cells/mL
($\phi = 0.1\%$)
Concentration profiles

Glass beads in DI water
\( \phi = 8\% \)  

Kaolinite in DI
\( \phi = 1.6\% \)  

Kaolinite + \((\text{NaPO}_3)_6\)
\( \phi = 1.6\% \)

- \( \phi_{\text{max}} \) is the maximum volume fraction near jamming front
- Vastly different behavior between attractive and repulsive systems
- Adding \((\text{NaPO}_3)_6\) returns repulsive behavior but times scales are different \( \rightarrow \) particle size effects
Concentration profiles: Glass Beads

Glass beads in DI water

\[ v_0 = \frac{4\Delta \rho g a^2}{18\mu} \approx 75.6 \, \mu m/s \]

- Particle size (a) at 10 \( \mu m \); viscosity at 1 \( cp \)
- Follow sedimentation front
- \( \phi_{\text{max}} \) is the maximum volume fraction near jamming front
Macroscopic model for concentration

- Sedimentation described by conservation of species $c_i$ and particle flux $J$

$$\frac{\partial c}{\partial t} + \nabla \cdot J = 0 \quad \text{with} \quad J = cV(c) - D(c)\nabla c$$

Landau & Lifshitz (1975)

*Velocity is concentration dependent → competition between convection and dispersion*

$$\frac{\partial c}{\partial t} + \frac{\partial (cV(c))}{\partial h} = \frac{\partial}{\partial h} \left( D(c) \frac{\partial c}{\partial h} \right)$$

$c \rightarrow \text{particle concentration} \ (\phi = c \times \text{particle volume})$

$D(c) \rightarrow \text{hydrodynamic dispersion coefficient}$

$V(c) \rightarrow \text{settling particle (front) velocity}$

Batchelor JFM (1972); Martin Phys. Fluids (1994)
Macroscopic model for concentration

• IF $U(c)$ is linear in $c$ and $D$ is constant, THEN one obtain Burgers’ equation which leads to:

$$C(h, t) = \Lambda_1 + \frac{(\Lambda_2 - \Lambda_1)}{1 + \psi(h, t) \exp[(w_2 - w_1)(h - V_{St})/2D]}.$$  

$$h(x, t) = \frac{1 - \text{erf}[(x - v_2 t)/\sqrt{4Dt}]}{1 - \text{erf}[(x - v_1 t)/\sqrt{4Dt}]} \quad \Lambda_1 = C(0, t) \quad \psi(h, t) = 1 \quad w_1 = U(\Lambda_1)$$  

$$\Lambda_2 = C(L, t) \quad V_s = (w_1 + w_2)/2 \quad w_2 = U(\Lambda_2)$$

$$V(c) = V_0(1 - c^p) \approx V_0(1 - pc)$$
Macroscopic model for concentration

Fitting model to data:
- Sedimentation speed $V_s = 61 \, \mu m/s$
- Dispersivity $D = 4 \times 10^{-5} \, m^2/s$

Single glass bead (10 \, \mu m)
- Settling speed $V_0 = 75 \, \mu m/s$

$$H(\phi) = \frac{V_s}{V_0} \approx 0.8$$

*Hindering settling function $H(\phi) = \frac{V_s}{V_0} < 1$
Macroscopic model for concentration

Fitting model to data:
- Sedimentation speed $V_s = 0.55 \, \mu\text{m/s}$
- Dispersivity $D = 1.9 \times 10^{-5} \, \text{m}^2/\text{s}$

Single disk ($a = 10 \, \mu\text{m}$)
- Drag force $F_D \approx 16 \mu a V$ (Shail & Norton 1968)
- Terminal velocity:

\[
V_0 = \frac{\pi (\Delta \rho) a h g}{16 \mu} \approx 0.031 \, \mu\text{m/s}
\]

\[
H(\phi) = \frac{V_s}{V_0} \sim 17.3 (>1!!)
\]

What causes this behavior with repulsive disks?
Macroscopic model for concentration

Kaolinite in DI
(\(\phi = 1.6\%\), attractive sample)

- Working on developing models to describe this type of sedimentation behavior
- Clues may be found in rheology
Growth of jamming front

- Common behavior among different samples
- Initial linear follow by exponential growth

\[ h(t) = \frac{\phi_0}{\tau} \left( 1 - e^{\frac{t}{\tau}} \right) \]
Conclusion - Sedimentation

- Sedimentation:
  - glass beads diffuse front $\neq$ repulsive clay diffuse front
  - beads jamming front = repulsive clay
  - attractive system $\Rightarrow$ colloidal gel
  - Importance of $\zeta_p$ in sedimentation behavior

- Colloidal gel properties: rheology
Rheology of Kaolinite Suspensions

Can rheology inform sedimentation?
Clay Rheology

\[ \zeta_p \sim -50 \text{ mV} \]

\[ \sigma (\text{Pa}) \]

\[ \gamma (\text{s}^{-1}) \]

Repulsive system \(\Rightarrow\) Newtonian fluid
Clay Rheology

\[ \zeta_p \sim -30\ mV \]
\[ \zeta_p \sim -50\ mV \]

\[ \eta \ (Pa) \]
\[ \gamma \ (s^{-1}) \]

Repulsive system \(\Rightarrow\) Newtonian fluid
Attractive system \(\Rightarrow\) thixotropic fluid
Clay Rheology: Attractive System

- Hysteresis in stress curve is a sign of a structured fluid
  - Thixotropic, viscoelastic colloidal gel

- The loops in this sample are peculiar → large shear rates should erase structure
Rheological models

- Direction of the loop is counterintuitive
- Fielding et al. showed a structure parameter could capture this, but didn’t fit model to data

Main goal:
Starting from a basic structure parameter model, can we get good qualitative fit?
A “simple” model

For models of the form

\[ \dot{\sigma} = f(\sigma, \dot{\gamma}, \xi) \]

\[ \frac{d\xi}{dt} = g(\xi, \dot{\gamma}) \]

5 parameters needed to be viscoelastic & thixotropic (without major unphysical effects):

\[ \frac{\dot{\sigma}}{G_A} + \frac{\sigma}{\eta_A} = \left( \xi + \frac{\eta_\infty}{\eta_A} \right) \dot{\gamma} + \frac{\eta_\infty}{G_A} \ddot{\gamma} \]

\[ \frac{d\xi}{dt} = k_1 (1 - \xi) - k_2 \xi |\dot{\gamma}| \]

List (5): \( \eta_\infty, \eta_A, G_A, k_1, k_2 \)

(Blackwell & Ewoldt, JNNFM 2014)
Fitting to clay data

- Can qualitatively capture the main features of the data
- Model not robust enough
Model finding

• But there are many choices of where to add parameters
• Create a master model with many reasonable choices of additions:

\[
\frac{\dot{\sigma}}{G_\infty + G_A \xi^p} + \frac{\sigma}{\eta_c + \eta_A \xi^q} = \frac{\eta_\infty + \eta_c + \eta_A \xi^q}{\eta_c + \eta_A \xi^q} \dot{\gamma} + \frac{\eta_\infty}{G_\infty + G_A \xi^p} \ddot{\gamma}
\]

\[
\frac{d\xi}{dt} = k_1 (1 - \xi^{n_1}) - k_2 \xi^{n_2} |\dot{\gamma}|^{m_2} + k_3 \xi^{n_3} |\dot{\gamma}|^{m_3}
\]

List (15): \(\eta_\infty, \eta_c, \eta_A, G_\infty, G_A, p, q, k_1, n_1, k_2, n_2, m_2, k_3, n_3, m_3\)

• This is clearly overly complex, so we must downselect… but how?

(Barnes, JNNFM 1997)
(Mewis & Wagner, ACIS 2009)
(de Souza Mendes, Soft Matter 2011)
Model finding & Neural Networks

- Neural net makes testing a huge number of choices computationally feasible
- Bayesian Inference Criterion (BIC) to penalize having too many parameters

- Gradient descent (adjusting parameters based on the gradient of the objective function) efficiently explores parameter space
- Reduction to matrix operations reduces computational expense
- Makes exploring all parameter combinations possible in reasonable computation time

(Freund & Ewoldt, JoR 2015)
Conclusions & Perspectives

- Interparticle forces and particle shape significantly affect the sedimentation dynamics of clay suspensions
  - Type of salt and local chemistry $\rightarrow$ sedimentation $\rightarrow$ formation of geological structures
  - Small amounts of salt leads to the formation of colloidal gels
  - Formation, destruction, history of structure
  - Constitutive models are still not robust enough

- Neural networks (and machine learning) may be useful for model discovery
  - Improve rheological models
  - upscaling

- NEED Model Systems
- Local ecology/biology
Sample videos

Particle Suspension ($\phi = 0.14\%$)
- *no Bacteria*

Particle Suspension ($\phi = 0.14\%$)
- *with Bacteria ($\phi = 0.2\%$)*

Image $\Delta t = 10$ minutes

Videos at 10x real time

Duration = 38 hours

Duration = 40 hours

- Bacteria hinder particle sedimentation process
Sample results

- *E. coli* volume fraction $\phi = 0.2\%$
- Particle volume fraction $\phi = 0.14\%$

- Bacteria settle much slower than passive particles
- Bacteria hinders passive particle sedimentation
- Presence of particles does not affect bacteria sedimentation
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