Smoothed Dissipative Particle Dynamics Model for Predicting Self-Assembled Nano-Cellulose Fibre Structures

David Vidal and Tetsu Uesaka
FPInnovations, Pointe-Claire, Québec, CANADA

Nano-cellulose fibres in suspension/gel states are known to have complex structures, depending on, e.g., concentration and ionic strength. These complex structures pose both opportunity (creating novel functional structures) and challenges (difficult rheology and processability). To better assess their impacts on the formation of nano-cellulose structures, a novel particle-based method has been proposed based on Smoothed Dissipative Particle Dynamics. This numerical approach treats both fluid and solid phases, in a unified way, as a set of particles exchanging momentum and/or interacting through Derjaguin-Landau-Verwey-Overbeek (DLVO) potentials. Additionally, nano-cellulose fibres are represented as strings of solid particles connected through extensional/bending springs. Brownian motion is also accounted for as a dissipative term. Preliminary results already showed that self-assembled structures created by the nano-cellulose fibres are extremely sensitive to the type of interactions (e.g., electrostatic force interactions), the intensity and spatial distance of the interactions, and the concentration and configuration of nano-cellulose fibres. By using this method, it is thus possible to investigate the...
impacts of hydrodynamics (e.g., shear), temperature, and ionic strength of the suspension on the formation of structures.

Acknowledgments

The financial contribution of Tekes, the Finnish Funding Agency for Technology and Innovation, through the Forestcluster Ltd is gratefully acknowledged. The authors would also like to express their gratitude to Dr. Hellen Erkki and Dr. Jukka Ketoja, both from VTT, for their continuous support.
Smoothed Dissipative Particle Dynamics Model for Predicting Self-assembled Nano-Cellulose Fibre Structures

David Vidal & Tetsu Uesaka
FPInnovations

Re-engineering Paper project (EffTech)
Objectives

- Nano-cellulose suspensions/gels have complex structures, depending on, e.g., concentration and ionic strength

- These complex structures pose both:
  - opportunities - creating novel functional structures
  - challenges - difficult rheology and processability

Predict and understand the formation of structures of nano-fibrillated cellulose (NFC) under flow conditions → rheology
Methodology

• Develop a 3D unified solid-liquid numerical model based on Smoothed Particle Hydrodynamics (SPH) to simulate fibril dynamics

(Image from S. Lindström)
Available Particle Methods

**Atomistic approach:**
- Molecular Dynamics (MD) — Adler & Wainright, 1957

**Mesoscopic approaches:**
- Brownian Dynamics (BD) — Ermak, 1975
- Dissipative Particle Dynamics (DPD) — Hoogerbrugge & Koelman, 1992

**Macroscopic approaches:**
- Monte-Carlo (MC) — Metropolis & Ulam, 1949
- Particle-in-Cell Method (PIC) — Harlow, 1963
- Discrete Element Method (DEM) — Cundall & Strack, 1971
- Smoothed Particle Hydrodynamics (SPH) — Lucy, 1977
- Stokesian Dynamics (SD) — Brady & Bossis, 1988
- Lattice Gas/Lattice Boltzmann Method (LBM) — McNamara & Zanetti, 1988
- Stochastic Rotation Dynamics (SRD) — Malevanets & Kapral, 1999
- Smoothed Dissipative Particle Dynamics (SDPD) — Espanol & Revenga, 2003
Proposed Model

• Unified interaction approach → no “coupling” required between solid and liquid phases
• Elongated solid particles can be dealt with a collection of spheres hooked together
• Additional forces can be added:
  – Colloidal (electrostatic, Van der Walls, Born repulsion) & Brownian
  – Stretching & bending → fiber flexibility
• High parallel content required for computation

An improved SPH method seems the best approach: Smoothed Dissipative Particles Dynamics
Unified Interaction Approach

Exchange momentum through:
- pressure
- shear stress
- thermal fluctuations (SDPD)

Interacting fluid-solid particles
- Interact through:
  - truncated Lennard-Jones potential

Interacting fibril particles
- Interact through:
  - stretching & bending (spring) forces
  - Born + DLVO potentials
  - lubrication force
Smoothed Particle Hydrodynamics (SPH)

- Particles represent volumes of fluid which have a spatial distance \( (h) \) over which their properties (e.g. \( \rho \)) are “smoothed” by a *kernel function* \( (W) \).
- From a given initial & boundary conditions, particle properties are evolved in time.
- This is a CFD approach, but can be seen as a particle method.

\[
f(x_a) = \int_{\Omega} f(x) \delta(x_a - x) dx
\]

\[
\lim_{h \to 0} W(x_a - x, h) dx = \delta(x_a - x)
\]

\[
f(x_a) \approx \int_{\Omega} f(x) W(x_a - x, h) dx
\]

\[
\approx \sum_{b=1}^{N_a} m_b f(x_b) W(x_a - x_b, h)
\]
Fiber Flexibility

\[ F_{strecth}^k = k_s \sum_l (r_{kl} - l_0) e_{kl} \]

\[ k_s = \frac{\pi d_s}{4} E \]

\[ d_s = \frac{3 \sqrt{2}}{\pi} dx \]

\[ F_{bend}^k = -\frac{k_b}{2} \frac{\partial}{\partial r_k} \sum_l (e_{l+1,l} - e_{l,l-1})^2 \]

\[ k_b = \frac{A}{l_0} \]

What are E & A for NFC?
An “Educated Guess” from MD

Stretching simulations

Bending simulations

(J. Liam McWhirter, Sami Paavilainen et al.)
Solid-solid Potential Interactions

$$F_{\text{Bom}} = \frac{A\sigma^6}{7560} \left( \frac{1}{(d_s + r)^7} - \frac{7(4d_i + r)}{(d_s + r)^8} - \frac{7(3d_s - r)}{r^8} - \frac{1}{r^7} \right)$$

$$F_{\text{vdW}} = \frac{A d_s}{24} \left( \frac{1}{r^2} \right)$$

$$F_{\text{el}} = C e^{-\kappa r}$$

What are $\kappa$, $A$, $\sigma$ & $C$ for NFC?
An “Educated Guess” from MD

(J. Liam McWhirter, Sami Paavilainen et al.)
Time Integration Convergence Criteria

**CFL condition:**

\[ dt \leq 0.25 \frac{h}{c_s} \quad \text{with } c_s \approx 10 V_{\text{max}} \]

**Viscous diffusion condition:**

\[ dt \leq 0.125 \frac{\rho h^2}{\mu} \]

**Acceleration condition:**

\[ dt \leq 0.25 \min_i \left( \frac{h}{\|a_i\|} \right)^{\frac{1}{2}} \]

\[ dt \sim 1-10 \, \text{ps} \]
Example of Code Instability
Fibrils under Couette Flow

Side view

Short nano-fibrils submitted to Couette Flow
Fibrils under Couette Flow

Perspective view

Short nano-fibrils submitted to Couette Flow
Larger Simulations…

Short nano-fibrils submitted to Couette Flow
Impact of Solid Content & Ionic Strength

$$\eta \mu_{medium} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m}$$
Thixotropic Effects

- κ⁻¹=1 nm
- κ⁻¹=10 nm

Φ=2.5%
Conclusions

• A SDPD method has been established to study:
  – the rheology of NFC suspensions as a function of solid content, ionic strength, shear rate, temperature,…
  – the formation of self-assembled structures (e.g. NCC)

• Preliminary results predict the important impact of solid content and ionic strength

• Further validations are required…
Acknowledgments

• Funding organizations:

[Logos for ForestCluster and TEKES]

• Managers of REP:
  – Dr. Jukka Ketoja
  – Dr. Erkki Hellèn

[Logos for VTT]
Thank you for your Attention!

Questions?