Nanoparticles vs surfactants as emulsion stabilizers

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Motivation

- Colloids in multiphase flows are ubiquitous:
  - Food, cosmetics, crude oil.
- Particles can accumulate at interfaces, similarly to surfactant molecules, but they do not need to be amphiphilic!
- They also do not change the surface tension, but interface free energy.
- Interesting features:
  - Blocking of Ostwald ripening allowing long-term stabilization.
  (W Ostwald, Z. Phys. Chem. 37:385, 1901)
  - Complex rheology due to irreversible particle adsorption at interfaces.
- We use a combined multicomponent LB and MD algorithm to study such systems.
D3Q19 multicomponent lattice-Boltzmann:

\[ f^c_i(\vec{x}, t) - f^c_i(\vec{x} + \vec{c}_i, t + 1) = -\Omega^c_i(\vec{x}, t), \quad (1) \]

where \( f^c_i \) is the single particle distribution function for component \( c \) in direction \( \vec{c}_i \) and \( \Omega^c_i \) is the BGK collision operator \((i = 1, \ldots, 19)\).

Shan-Chen model for multicomponent LB:

\[ \vec{F}^c(\vec{x}, t) \equiv -\Psi^c(\vec{x}, t) \sum_{c'} g_{cc'} \sum_{\vec{x}'} \Psi^{c'}(\vec{x}', t)(\vec{x}' - \vec{x}), \quad (2) \]

where \( \Psi^c(\vec{x}) \) is an effective mass, and \( g_{cc'} \) is a force coupling constant. X. Shan and H. Chen. *Phys. Rev. E* 47(3):1815, 1993.

Amphiphiles in LB: density is treated as ordinary fluid. Dipoles describe average orientation at a lattice site.

Method: multicomponent LB with particles

- Particles are discretized on the LB lattice and propagated by MD.

- Modified bounceback interaction.
  - Delete fluid on sites newly covered by a particle, set fluid density at freed sites equal to local average (different from original model, which uses the initial density).
  - Set a “virtual fluid density” on outermost layer of lattice sites inside the particle to prevent unphysical increased fluid density around the particle.
    - As a bonus, this can also be used to set the wettability of particles!

- Particle-particle interaction: lubrication force plus Hertz force (hardcore).

IBM BlueGene/P at JSC: JUGENE

- **compute node**
  - quadcore CPU, 850 MHz
  - 2 GB RAM
- **73,728 compute nodes**
  - 294,912 CPU cores in total
- **3D torus network**
- **Funding:** GSC large scale grant, PRACE

photo: FZ Jülich
BlueGene/P Scaling

- Proper memory alignment is mandatory ⇒ Change 1 line of code and get a speedup of 30.
- Single core performance is a factor 8 -10 less than up to date Intel.
- Matching network topology

- Reducing serial code fraction

![Graph 1](normalized speedup vs number of cores)

- 1 Newtonian fluid component,
  - 1024² × 2048 lattice sites

![Graph 2](normalized speedup vs number of cores)

- Pickering emulsion: 2 fluid species + suspended particles
From spheres to ellipsoids: Interactions

- For modelling hard core interaction we use Hertz and lubrication potentials.

- Hertz potential for two spheres of the same radius $R_i = R_j = R$:
  \[ \phi_H = K_H (2R - r_{ij})^{2.5} \]
  $K_H$: force constant, $r_{ij}$: distance between the two sphere centers

- Rescale potential using the approach of Berne and Pechukas:
  \[ \phi_H = \epsilon (1 - \frac{r_{ij}}{\sigma})^{2.5} \]
  $\sigma = 2R$ and $\epsilon = K_H \sigma^{2.5}$
  \[ \epsilon(\hat{\sigma}_i, \hat{\sigma}_j) = \frac{\bar{\epsilon}}{\sqrt{1 - \chi^2 (\hat{\sigma}_i \hat{\sigma}_j)^2}} \]
  \[ \sigma(\hat{\sigma}_i, \hat{\sigma}_j, \hat{r}_{ij}) = \frac{\bar{\sigma}}{\sqrt{1 - \frac{\chi^2}{2} \left( \frac{(\hat{r}_{ij} \hat{\sigma}_i + \hat{r}_{ij} \hat{\sigma}_j)^2}{1 + \chi \hat{\sigma}_i \hat{\sigma}_j} + \frac{(\hat{r}_{ij} \hat{\sigma}_i - \hat{r}_{ij} \hat{\sigma}_j)^2}{1 - \chi \hat{\sigma}_i \hat{\sigma}_j} \right)}} \]
  \[ \bar{\sigma} = 2R_o, \quad \bar{\epsilon} = K_H \bar{\sigma}^{2.5} \text{ and } \chi = \frac{R_p^2 - R_o^2}{R_p^2 + R_o^2} \]

- Analogous for lubrication correction
Place a particle (with $\theta \approx 9.56^\circ$) just touching an oil-water interface at an angle $\phi$.

- Red line: points where the ellipsoid just touches the flat interface.
- Adsorption trajectories for ellipsoids (aspect ratio $m = 2$):
  - All lines approach the attractor line.
- Red point: equilibrium state of the adsorbed particle.
- Different from theory: semistable particle position perpendicular to the interface possible.

Surface tension

- Force balance for a 3D sphere: \((2\pi R)\sigma = (\pi R^2) \Delta P\).
  \(\Rightarrow\) Young-Laplace equation: \(\sigma = \frac{R\Delta P}{2}\).
- Far away from the droplet interface one fluid is dominant and we can use \(P = c_s^2 \rho = \rho/3\).
- Densities in DdQq LB:
  \[\rho^c(\vec{x}) = \sum_{i=1}^q f_i^c(\vec{x}).\]
- Local density:
  \[\rho(\vec{x}) = \rho^r(\vec{x}) + \rho^b(\vec{x}) + \rho^s(\vec{x}).\]
- We can now measure droplet radius \(R\) and density difference \(\Delta \rho\) to find \(\sigma\) and relate it to our simulation parameters \(\Rightarrow\) linear correlation \(\sigma(g_{br})\).
Now we have: $\sigma = \sigma(g_{br}, \rho^s)$.

Qualitatively: adding surfactant to the binary mixture lowers the overall surface tension.
Curves collapse when we consider: \( \Delta \sigma_{\text{rel}}(\rho^s) = g_{\text{br}} \cdot \frac{\sigma(g_{\text{br}}, \rho^s) - \sigma(g_{\text{br}}, 0)}{\sigma(g_{\text{br}}, 0)} \).

Surfactant effect scales with our interaction strength.
Surface tension with particles

- System size: $256 \times 256 \times 512$ lattice sites, up to 512 particles.
- Particle radius $r = 5.0$ $\Rightarrow$ up to $\sim 67\%$ of droplet covered.
- With or without particles, surface tension tends to the same value. $\Rightarrow$ Particles do not change $\sigma$ – they change interface free energy.
Droplets in shear flow

- Lees-Edwards boundary conditions.
- Shear rate: $\dot{\gamma} = \frac{2v_{\text{shear}}}{h}$.
- Deformation parameter: $D = \frac{L-B}{L+B}$.
- Capillary number: $Ca = \frac{\eta \dot{\gamma} R}{\sigma}$.
Taylor theory – binary fluids

- Taylor: For two fluids of equal density and equal viscosity, and in the small deformation limit the following holds:
  \[ D = \frac{L-B}{L+B} = \frac{35}{32} \text{Ca}. \]

- We now fix our interaction strength \( g_{br} = 0.13 \Rightarrow \sigma \) fixed.
- Linear behaviour of \( D(Ca) \) as predicted by Taylor for low Ca.
Interaction strengths still fixed, increase initial surfactant concentration $\rho^s$.

For same shear rate, $D$ gets larger as we add more surfactant.
▶ Adding surfactant: changes Ca through $\rho^s$ and $\sigma$.
▶ All curves collapse nicely!
Droplet deformation with particles

Shear rates (for water-like fluid): $8.6 \cdot 10^7 \text{ s}^{-1} \leq \dot{\gamma} \leq 5.1 \cdot 10^8 \text{ s}^{-1}$. 
Deformation and shear rate

Taylor law
Deformation and shear rate

The graph shows the relationship between deformation (D) and the Ca parameter. It indicates two distinct regions: 'No breakup' and 'Breakup.' The data points are represented by blue and red dots, with error bars indicating variability. The graph suggests a threshold value for the Ca parameter that distinguishes between the two regions.
Emulsion stabilization with surfactants

Define the time dependent lateral domain size $L(t)$ along direction $i$:

$$L_i(t) \equiv \frac{2\pi}{\sqrt{\langle k_i^2(t) \rangle}},$$

where

$$\langle k_i^2(t) \rangle \equiv \frac{\sum_k k_i^2 S(k, t)}{\sum_k S(k, t)}$$

(3)

is the second order moment of the three-dimensional structure function

$$S(k, t) \equiv \frac{1}{V} \left| \phi'_k(t) \right|^2.$$  

(4)

$\langle \rangle$: average in Fourier space; $V$: number of lattice nodes

$\phi'_k(t)$: FFT of the order parameter fluctuations $\phi' \equiv \phi - \langle \phi \rangle$
Emulsion stabilization with surfactants

- $\rho^s < 0.15$: $L(t) \sim t^\alpha$ (power law)
- $\rho^s < 0.20$: $L(t) \sim (\ln t)^\theta$ (logarithmic)
- $\rho^s > 0.20$: $L(t) \sim A - B \exp(-Ct^D)$ (stretched exponential)
Periodic minimal surfaces

- Amphiphilic Mesophases often form minimal surfaces: the surface area lying inside any drawn boundary is the minimum possible.
- We found triply periodic surfaces with cubic symmetry: the “primitive” (P), “diamond” (D), and “gyroid” (G) surface.
- Transformation between surfaces through a single parameter: Bonnet angle.
- Real-life examples: block copolymer melts.
Individual droplets of one phase covered by particles.
W. Ramsden. *Proc. R. Soc. Lond.*, 72:156, 1903,

“Bijel”: bicontinuous interfacially jammed emulsion gel.
After a fast demixing process the system remains stable.
More colloids stabilise a higher surface area: finer structures.

Fit function: \( L = \frac{3.96}{\alpha} + 10.85 \).
As soon as the surface of the droplets is covered with colloids droplet growth stops. Different growth regimes can be identified for Pickering emulsions:

- Nucleation of fluid droplets.
- Droplet growth and adsorption of particles.
- Coalescence of particle covered droplets.
Higher concentration $\Rightarrow$ larger stabilised surface area $\Rightarrow$ smaller droplets.

Arditty predicts $\sim \alpha^{-1}$. Offset due to finite system size (more particles result in less volume filled by fluid).

Emulsion or bijel?

Contact angle $\theta$ [degrees]

Particle concentration $\alpha$ [volume ratio]

Fluid ratio

Bijel
Emulsion

2:55:93:41:1
Ongoing work: Study of formation of bijel and Pickering emulsions with ellipsoidal particles.

- Influence of aspect ratio?
- Rotational degree of freedom?
Emulsions stabilized by ellipsoidal particles

Two timescales:
1. Emulsion formation
2. Particle reorganisation
Conclusion and Outlook

- We studied the behaviour of individual particles at fluid-fluid interfaces, particle covered droplets under shear, the formation of Bijels and Pickering emulsions.
- Lattice Boltzmann based simulations are a powerful technique to study particle-laden multicomponent flows.
  - Particle-fluid interaction simple
  - Established multiphase/multicomponent models
  - Amphiphiles
  - High scalability $\Rightarrow$ large systems possible (and needed!)
  - Problem: Diffuse interface unrealistically large $\Rightarrow$ high LB resolution.
- Further exploration of particle-covered droplets: change particle concentration, size, wettability, fluid properties.
- Comparison particles / surfactants as emulsifiers: other phases?
- More particle variety: Janus particles, rods, deformable particles.
- More complex inter-particle potentials: charges, magnetic particles.