Modeling interfacial dynamics in soft interface dominated materials

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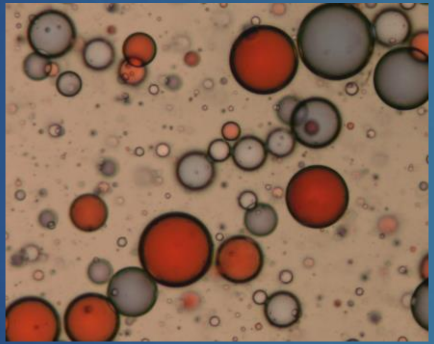
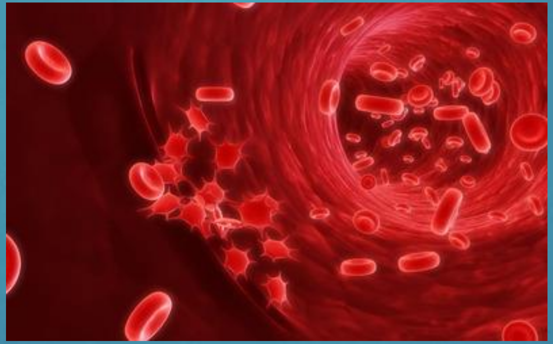
Content

Soft Interface Dominated Materials

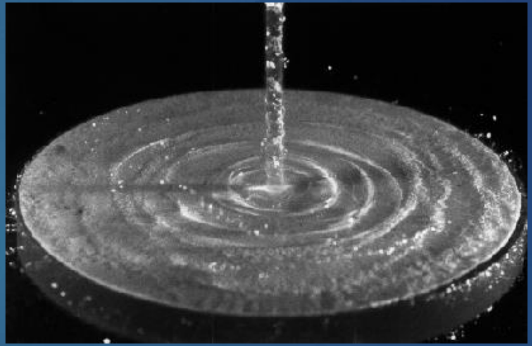
- Materials with high surface/volume ratio (10^3-10^7 m^2/m^3)
- Macroscopic behavior dominated by interfacial properties


Emulsions


Foams

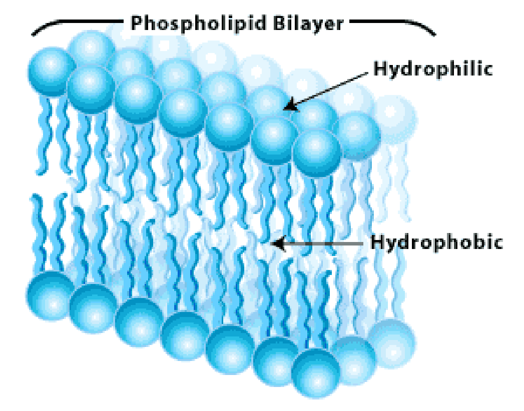

Cells


Microcapsules

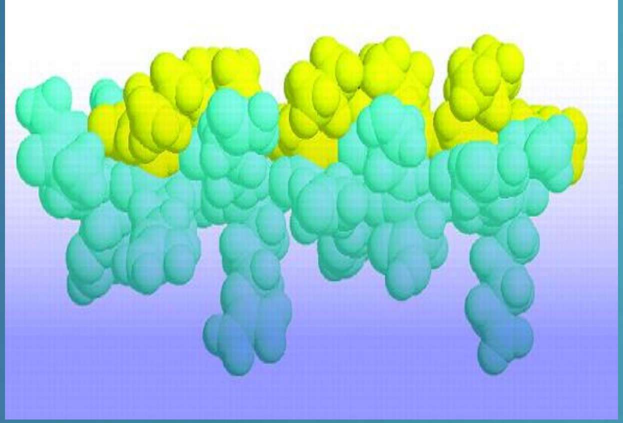

Thin coatings

Soft Interface Dominated Materials

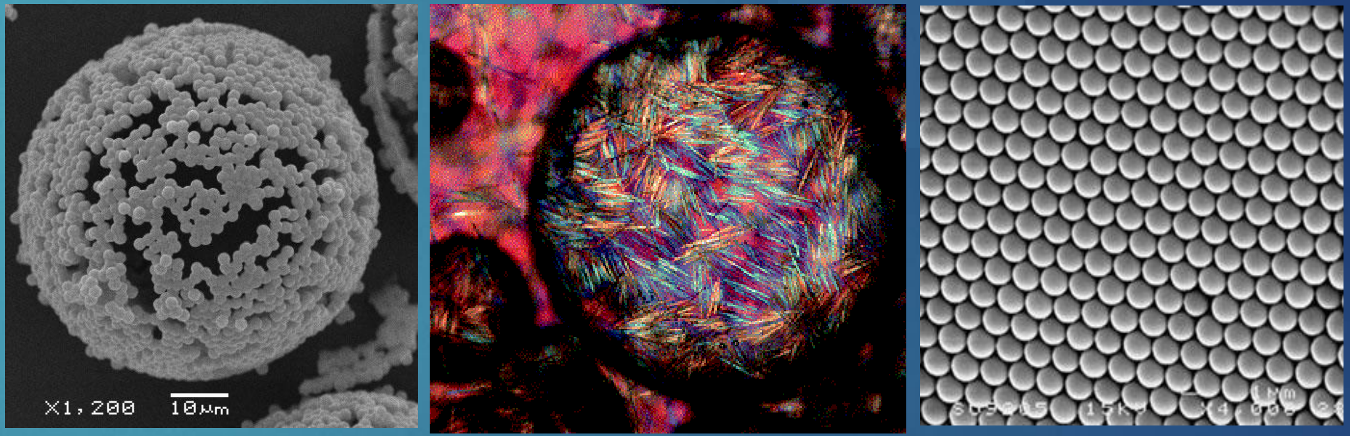
- Interfacial structures



Lipid (bi)layers



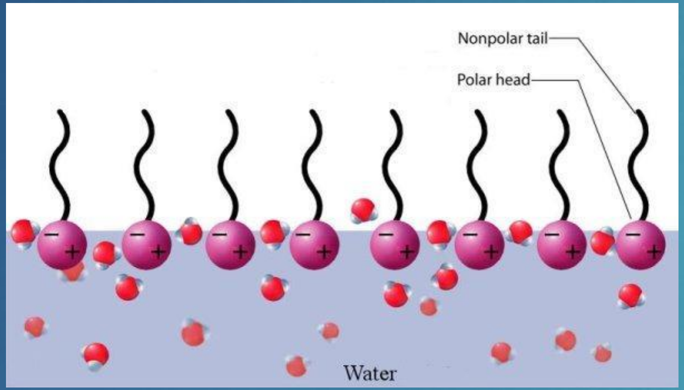
Proteins



Colloidal particles

Soft Interface Dominated Materials

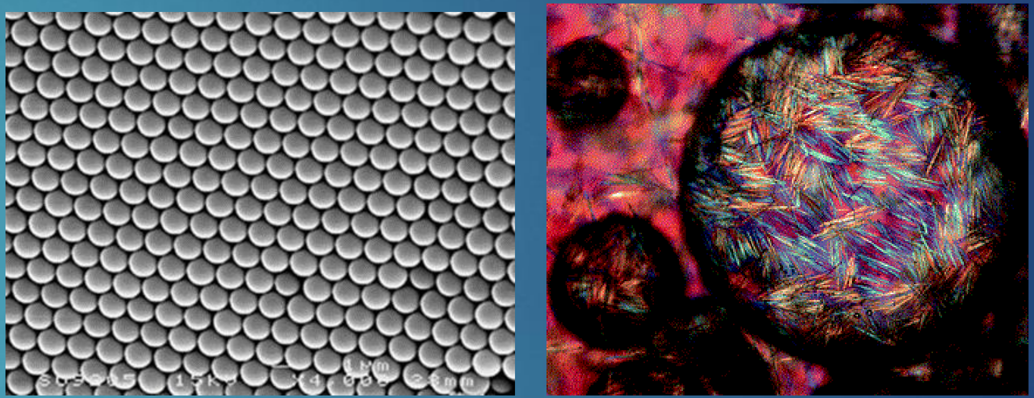
- Interfacial structures:



Simple interfaces

Single or miscible mixtures of low molecular weight surfactants

Liquid (condensed) structures



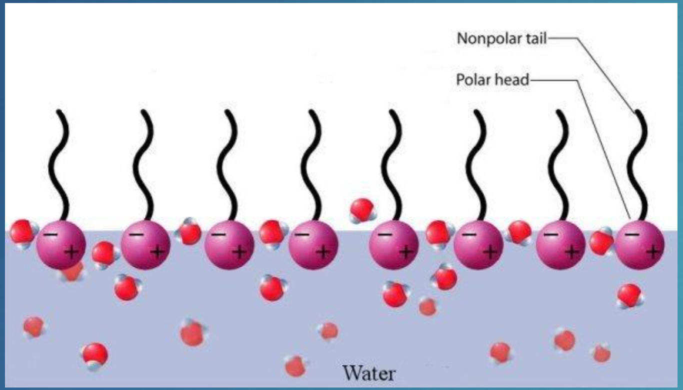
Complex interfaces

Proteins, polymers, colloidal particles, immiscible surfactants

2d gels, glasses, (liquid) crystals, emulsions, suspensions

Soft Interface Dominated Materials

- Simple interfaces:



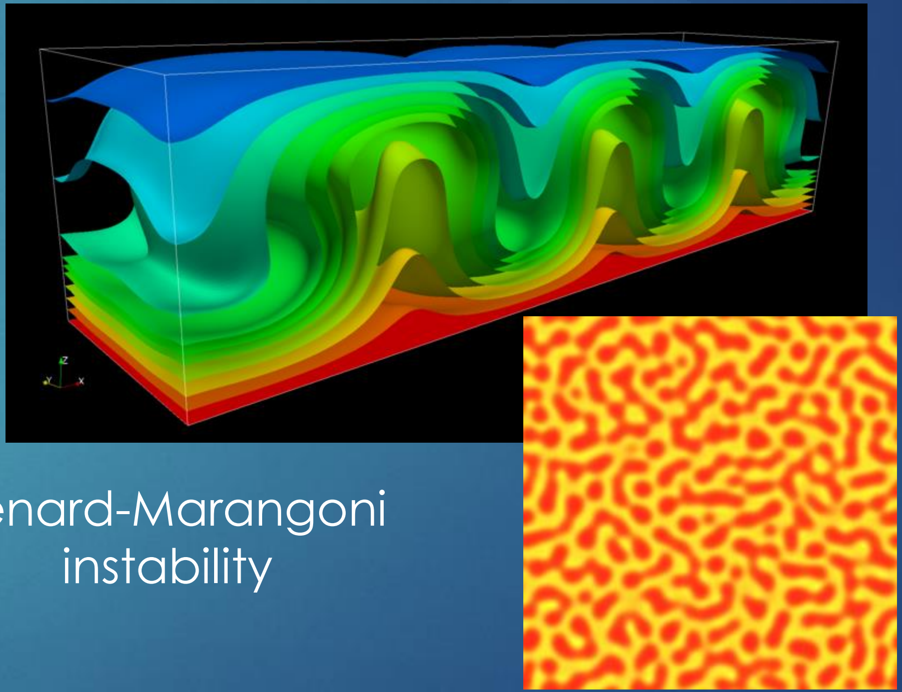
Liquid (condensed) structures

Dominant interfacial property:

surface tension: $\gamma(c^s,T^s)$

Note:
simple interface ≠ simple macroscopic dynamics

Example: Raleigh-Benard convection problem



Benard-Marangoni
instability

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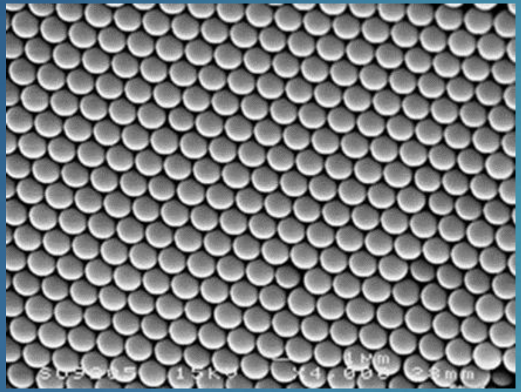
Soft Interface Dominated Materials

- Complex interfaces:



2d gel, glass, (liquid) crystal, suspension, emulsion:

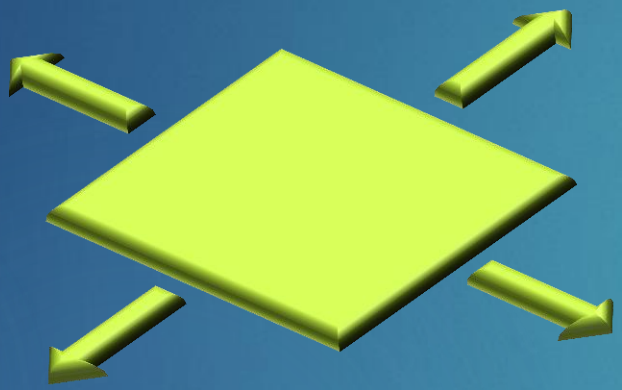
(solid) viscoelastic behavior

Dominant interfacial properties:

- Surface dilatational modulus
- Surface shear modulus
- Bending rigidity

Soft Interface Dominated Materials

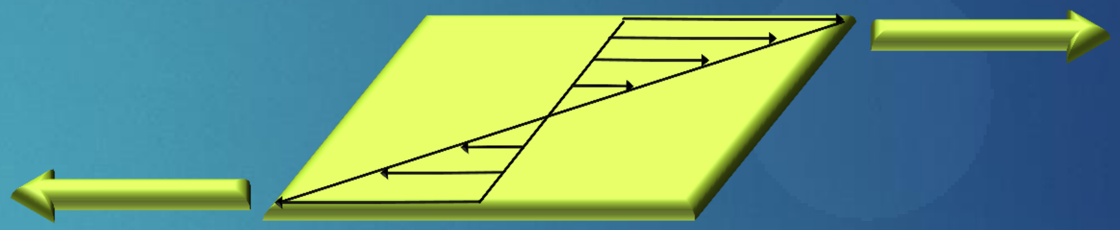
- Complex interfaces:



Surface dilatational modulus:

Resistance against all-sided compression/extension

$$E_d(\omega)=E_d^{'}(\omega)+iE_d^{''}(\omega)$$



Surface shear modulus:

Resistance against in-plane shear

$$G_s(\omega)=G_s^{'}(\omega)+iG_s^{''}(\omega)$$

Soft Interface Dominated Materials

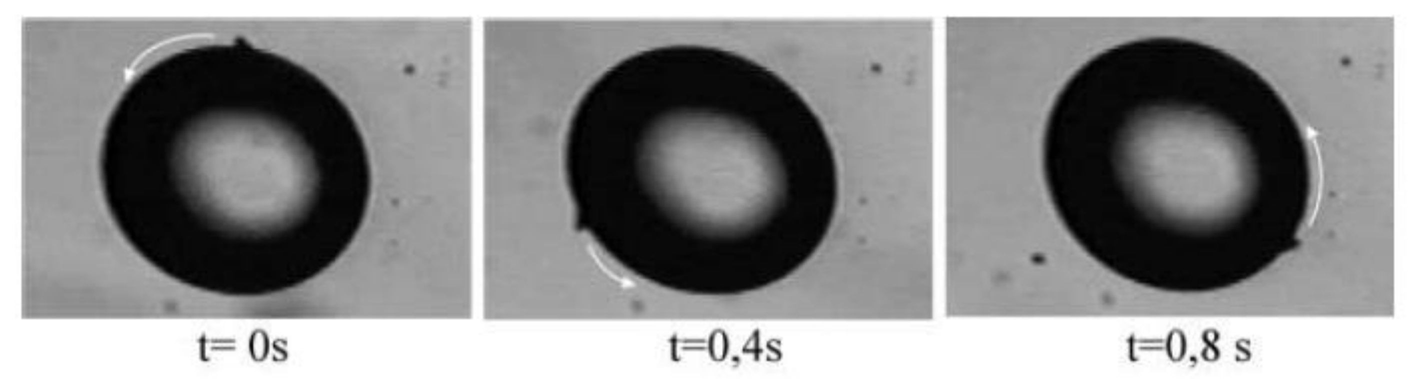
Importance surface shear and dilatational moduli, bending rigidity [1]:

- Dampening of surface waves in free surface flows
- Oscillatory deformation of droplets in shear flow
- Tank-treading of interface of droplets in shear flow
- Break-up of droplets and jets
- Stability of foam and emulsions against coalescence
- (De-)wetting of thin films on a solid
- Late stages (coarsening) of phase separation in immiscible polymer mixtures
- Disproportionation of microbubbles
- Bubble or droplet rise velocities in a quiescent liquid
- Polymer flow instabilities (sharkskin melt fracture)

Soft Interface Dominated Materials

Importance Surface shear and dilatational moduli and bending rigidity:

- Oscillatory deformation of droplets in shear flow
- Tank-treading of interface of droplets in shear flow


t= 0s t=0,4s t=0,8 s

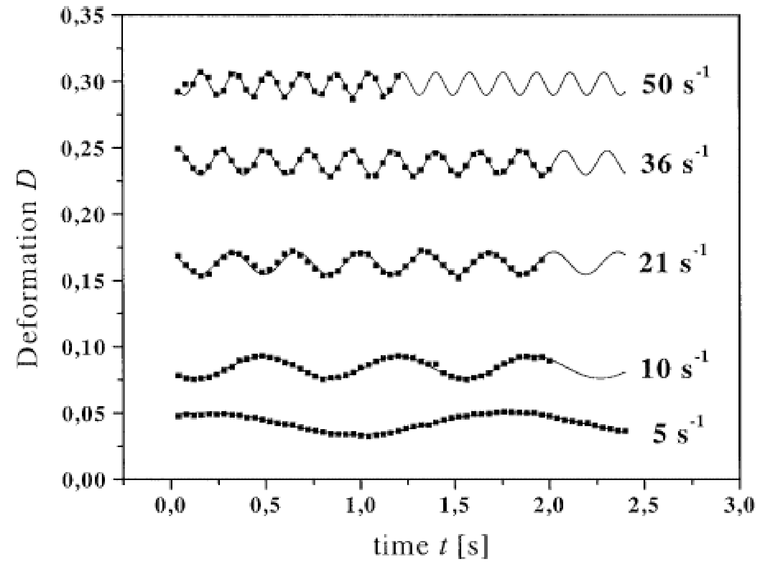


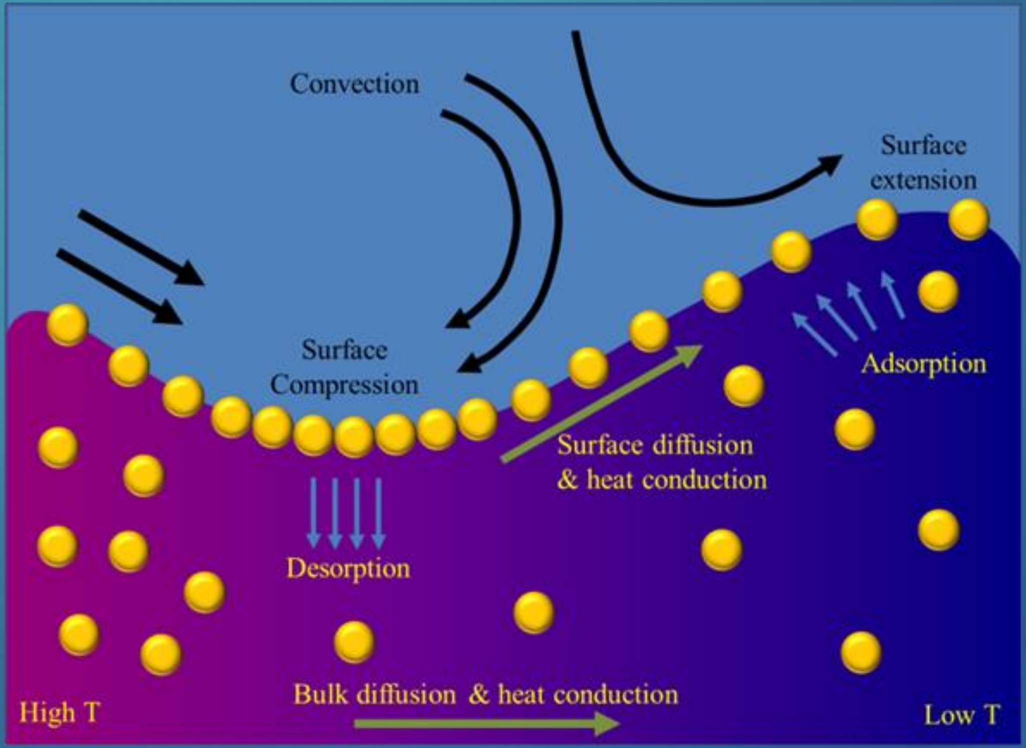
Fig. 17. Sinusoidal deformation of a polyamide microcapsule observed in simple shear flow for different values of the shear rate

Rehage et al., Rheologica Acta (2002) **41** 292.

Soft Interface Dominated Materials

Important:

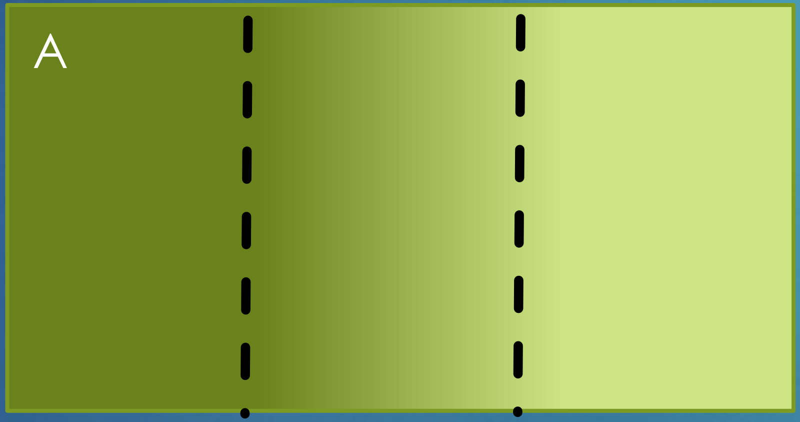
- Often in-plane momentum transfer is coupled to heat and mass transfer along and across the interface.
- Need consistent framework to handle coupled mass, momentum, energy transfer along and across interfaces

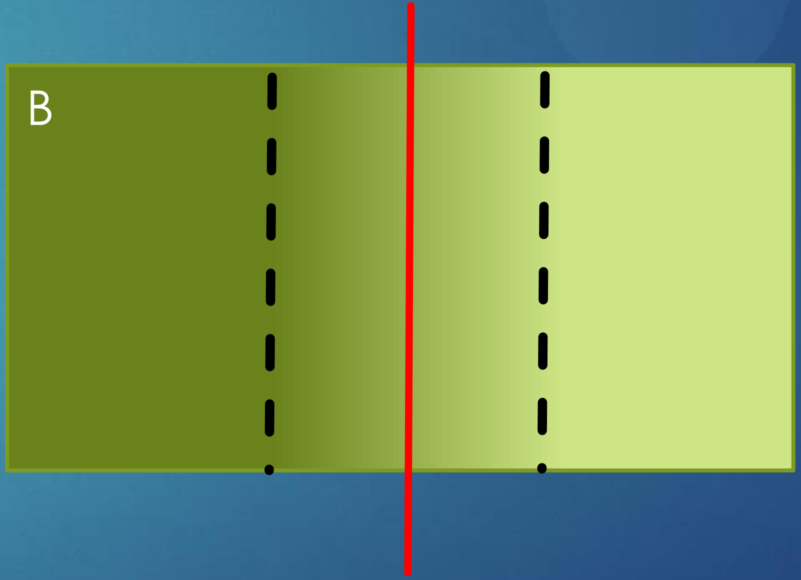


Gibbs Dividing Surface Model

Two important frameworks:

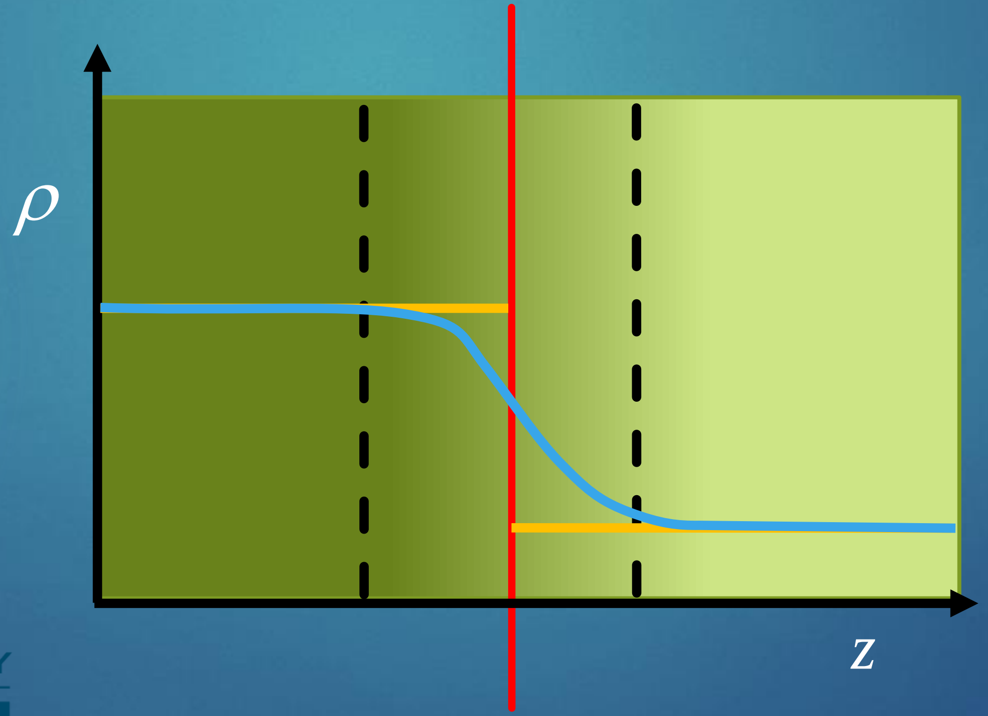
- Diffuse interface or phase field model (A)
- Gibbs dividing surface model (B)





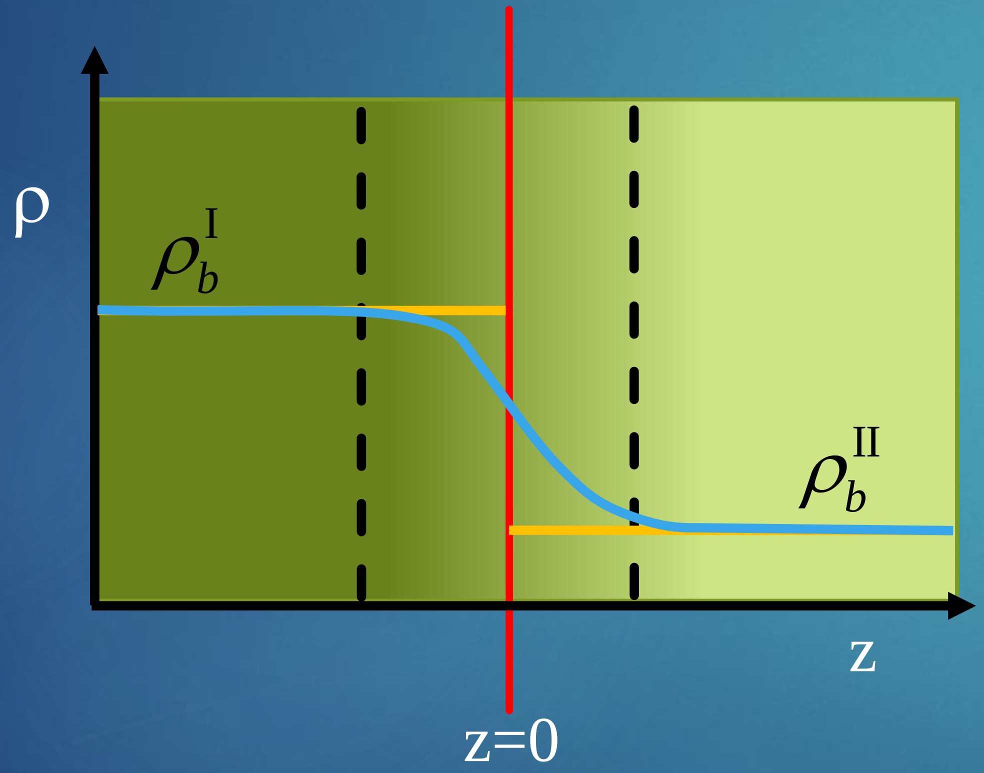
Gibbs Dividing Surface Model

- Sharp 2d interface placed within the interfacial region
- Bulk fields are extrapolated up to this "dividing" surface
- Difference between actual and extrapolated fields accounted for by excess variables



Gibbs Dividing Surface Model

- Example: surface excess density



$$\rho^{s} = \int_{-\infty}^{0} \left(\rho - \rho_b^{\mathrm{I}} \right) dz + \int_{0}^{\infty} \left(\rho - \rho_b^{\mathrm{II}} \right) dz$$

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Surface Excess Variables

- Which variables do we choose?

- System variables for a simple multicomponent single phase system:
  - Overall mass density: ρ
  - Momentum density: $\boldsymbol{m} = \rho \boldsymbol{v}$
  - Internal energy density: $\bar{u}$
  - Component densities: $\rho_{(J)} \quad (J = 1, \ldots, N-1)$

Surface Excess Variables

- Which variables do we choose?

- Common sense suggests we associate an excess variable with each of these:

$$\left\{ \rho^{s}, \boldsymbol{m}^{s}, \bar{u}^{s}, \rho^{s}_{(1)}, \ldots, \rho^{s}_{(N-1)} \right\}$$

ρ^{s} : surface mass density (kg/m^2)

$\boldsymbol{m}^{s} = \rho^{s}\boldsymbol{v}^{s}$: surface momentum density (kgm/m^{2}s)

$\bar{u}^{s}$: surface internal energy per unit area (J/m^2)

$\rho^{s}_{(J)}$: surface mass density of component J (kg/m^2)

Surface Excess Variables

- Number of bulk and surface variables equal!
- Violation of Gibbs phase rule?

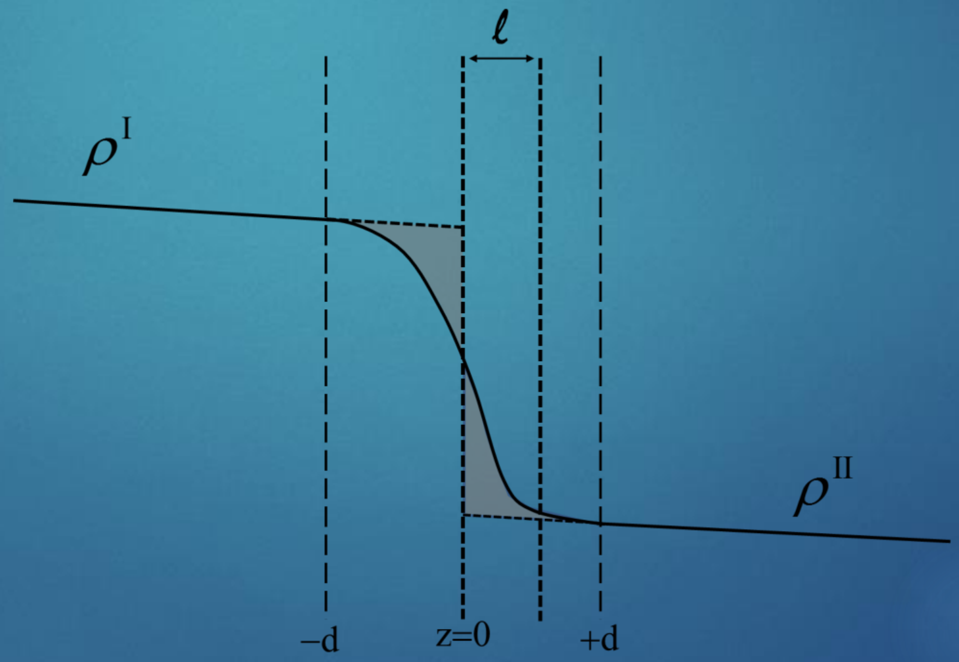
- Note: we have yet to fix the exact location of the dividing surface.
- Single component systems: Often fix position of interface by setting $\rho^S = 0$

- At equilibrium Gibbs phase rule is now satisfied.
- Important note: can only choose $\rho^S = 0$ for the reference configuration!

Surface Excess Variables

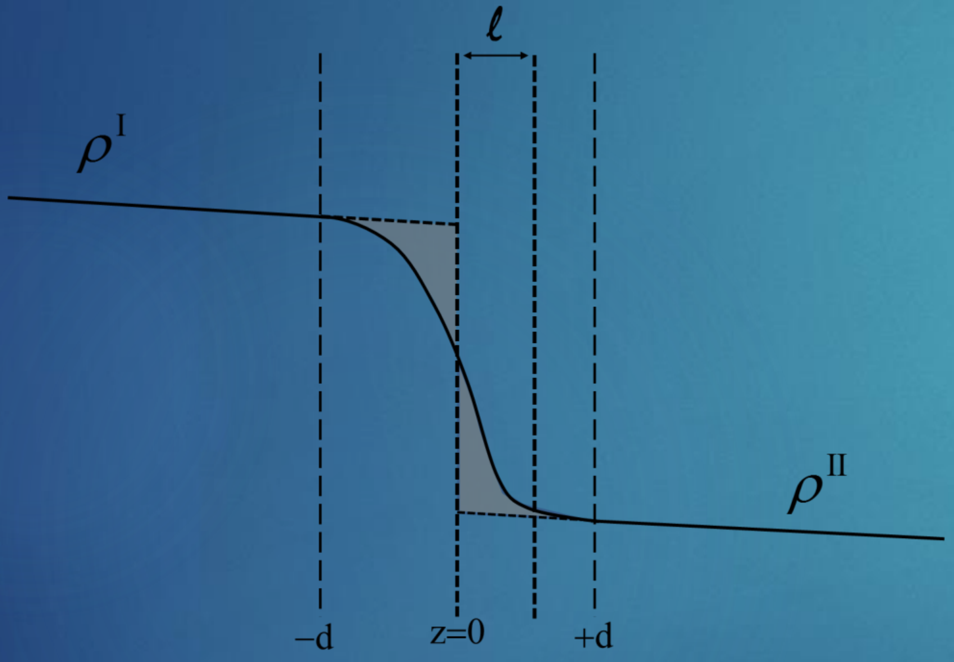
- Choice of the location can be seen as a gauge degree of freedom
- Set of surface densities we just selected is very sensitive to particular choice

- Example: choose $\rho^S = 0$, and displace dividing surface by a small distance



Surface Excess Variables

- Example: choose $\rho^s = 0$, and displace dividing surface by a small distance



$$
\begin{aligned}
\rho^{s}* &= \int_{-\infty}^{\ell}\left(\rho-\rho^{\mathrm{I}}\right)dz+\int_{\ell}^{\infty}\left(\rho-\rho^{\mathrm{II}}\right)dz \\
&= \int_{-\infty}^{0}\left(\rho-\rho^{\mathrm{I}}\right)dz+\int_{0}^{\ell}\left(\rho-\rho^{\mathrm{I}}\right)dz+\int_{0}^{\infty}\left(\rho-\rho^{\mathrm{II}}\right)dz-\int_{0}^{\ell}\left(\rho-\rho^{\mathrm{II}}\right)dz \\
&= -\int_{0}^{\ell}\left(\rho^{\mathrm{I}}-\rho^{\mathrm{II}}\right)dz=-\ell\left(\rho^{\mathrm{I}}-\rho^{\mathrm{II}}\right)
\end{aligned}
$$

Surface Excess Variables

- Similarly we find for the surface momentum density

$$\boldsymbol{m}^{\mathrm{s}}* = \rho^{\mathrm{s}}*\boldsymbol{v}^{\mathrm{s}}* = -\ell\left(\rho^{\mathrm{I}}\mathbf{v}^{\mathrm{I}} - \rho^{\mathrm{II}}\mathbf{v}^{\mathrm{II}}\right)$$

- Eliminate dependence on ℓ with $\rho^{\mathrm{s}}* = -\ell\left(\rho^{\mathrm{I}} - \rho^{\mathrm{II}}\right)$

$$\boldsymbol{v}^{\mathrm{s}} = \frac{\rho^{\mathrm{I}}\mathbf{v}^{\mathrm{I}} - \rho^{\mathrm{II}}\mathbf{v}^{\mathrm{II}}}{\rho^{\mathrm{I}} - \rho^{\mathrm{II}}}$$

Surface Excess Variables

- Other gauge invariant variables:
- Internal energy per unit mass:

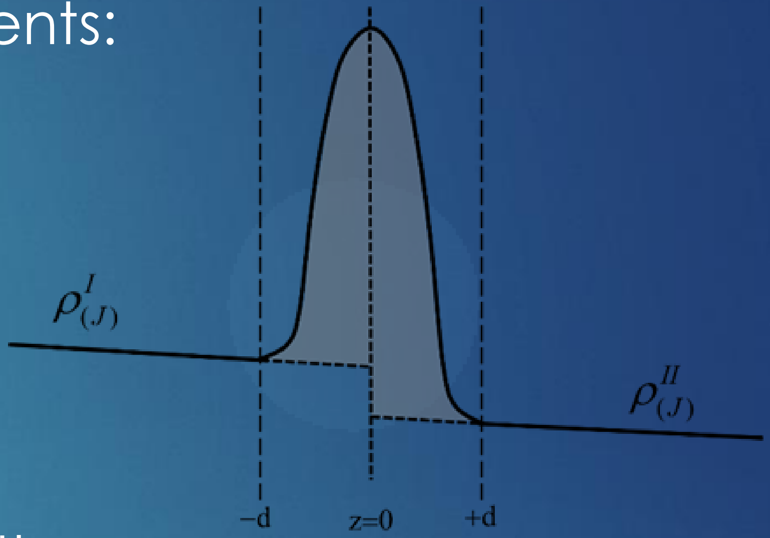
$$u^{\mathrm{s}} = \frac{\bar{u}^{\mathrm{s}}}{\rho^{\mathrm{s}}} = \frac{\rho^{\mathrm{I}}\bar{u}^{\mathrm{I}} - \rho^{\mathrm{II}}\bar{u}^{\mathrm{II}}}{\rho^{\mathrm{I}} - \rho^{\mathrm{II}}}$$

- Surface mass fractions:

$$\omega^{\mathrm{s}}_{(J)} = \frac{\rho^{\mathrm{s}}_{(J)}}{\rho^{\mathrm{s}}} = \frac{\rho^{\mathrm{I}}\omega^{\mathrm{I}}_{(J)} - \rho^{\mathrm{II}}\omega^{\mathrm{II}}_{(J)}}{\rho^{\mathrm{I}} - \rho^{\mathrm{II}}}$$

Surface Excess Variables

- Multicomponent systems with surface active components:



$$\rho^{s} = \sum_{J=1}^{N} \rho^{s}_{(J)}$$

- Setting overall surface density to zero to fix position of the interface means some excess component densities are negative.
- Alternative choice: Fix (in reference configuration)

$$\rho^{s} = \rho^{s}_{\infty}$$

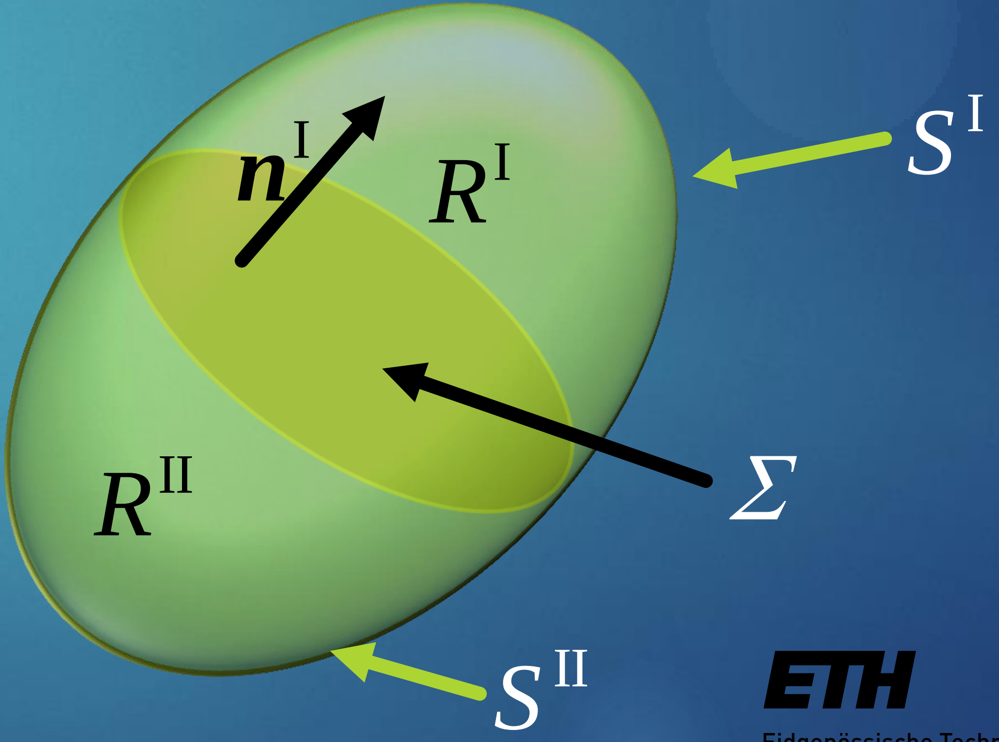
Conservation principles

- Conservation of mass for multiphase system with surface excess mass:
- The total mass of a multiphase system is constant in time

$$\frac{d}{dt}\left[\int_R \rho \mathrm{d}V + \int_\Sigma \rho^{\mathrm{s}} \mathrm{d}\Omega\right] = 0$$

$$R = R^{\mathrm{I}} \cup R^{\mathrm{II}}$$

$\boldsymbol{n}^{\mathrm{M}}$ unit vector normal to Σ, pointing in direction of phase M

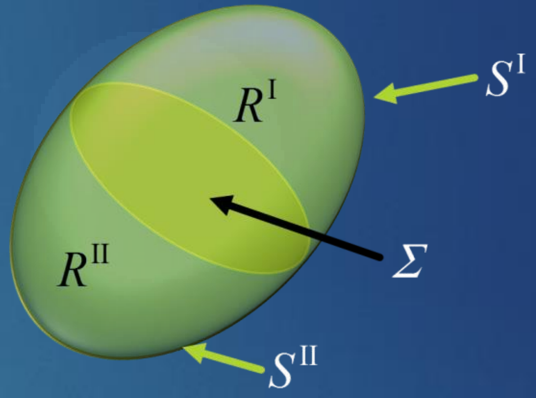


Conservation principles

- Evaluate the time derivative:

$$\int_R\left(\frac{\partial\rho}{\partial t}+\nabla\cdot(\rho\boldsymbol{v})\right)\mathrm{d}V$$

$$+\int_\Sigma\left(\frac{\mathrm{d}_\mathrm{s}\rho^\mathrm{s}}{\mathrm{d}t}+\rho^\mathrm{s}\nabla_\mathrm{s}\cdot\boldsymbol{v}^s+[\![\rho(\boldsymbol{v}-\boldsymbol{v}^\mathrm{s})\cdot\boldsymbol{n}]\!]\right)\mathrm{d}\Omega=0$$



$$[\![\Psi\cdot\boldsymbol{n}]\!]=\Psi^\mathrm{I}\boldsymbol{n}^\mathrm{I}+\Psi^\mathrm{II}\boldsymbol{n}^\mathrm{II}$$

Jump term: contributions from both adjoining bulk phases

Conservation principles

- Since the domain of integration was chosen arbitrarily:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = 0$$

$$\frac{\mathrm{d_s} \rho^{\mathrm{s}}}{\mathrm{d}t} + \rho^{\mathrm{s}} \nabla_{\mathrm{s}} \cdot \boldsymbol{v}^{s} + [\![\rho (\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n}]\!] = 0$$

Equation of continuity

Jump mass balance [2]

Surface material derivative [2]:

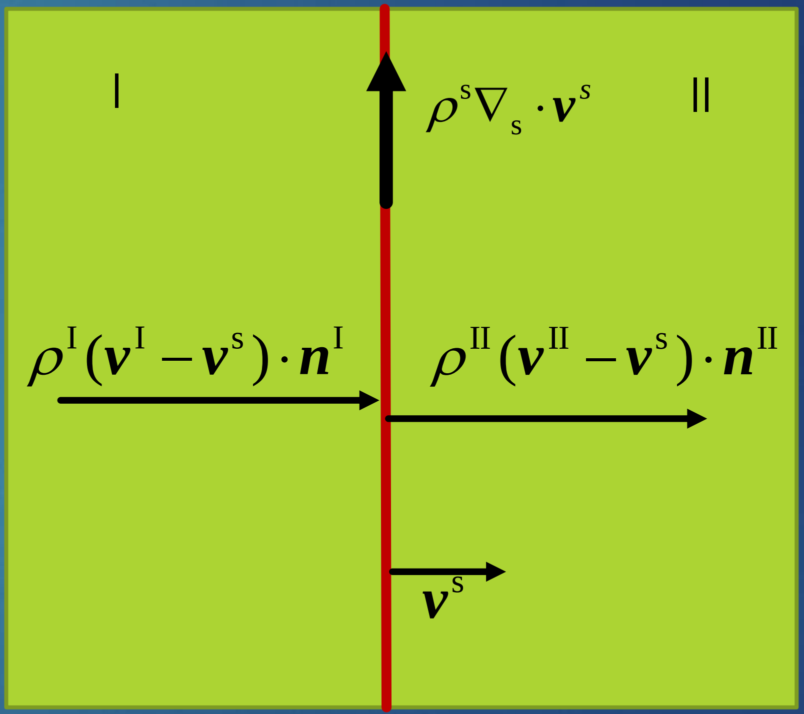
$$\frac{\mathrm{d_s} \rho^{\mathrm{s}}}{\mathrm{d}t} = \frac{\partial \rho^{\mathrm{s}}}{\partial t} + (\nabla_{s} \rho^{s}) \cdot (\boldsymbol{v}^{s} - \boldsymbol{u})$$

$\boldsymbol{u}$ Speed of displacement of interface

Conservation principles

- Overall jump mass balance:

$$\frac{\mathrm{d}_s\rho^s}{\mathrm{d}t}+\underbrace{\rho^s\nabla_s\cdot\boldsymbol{v}^s}_{\text{In-plane convection}}+\underbrace{[\![\rho(\boldsymbol{v}-\boldsymbol{v}^s)\cdot\boldsymbol{n}]\!]}_{\text{Exchange of mass with the adjoining bulk phases}}=0$$



Conservation principles

- Component mass balance (non-reactive):

$$\rho \frac{\mathrm{d}_\mathrm{b}\omega_{(J)}}{\mathrm{d}t} + \nabla \cdot \boldsymbol{j}_{(J)} = 0$$

$$\rho^\mathrm{s} \frac{\mathrm{d}_\mathrm{s}\omega^\mathrm{s}_{(J)}}{\mathrm{d}t} + \underbrace{\nabla_\mathrm{s} \cdot \boldsymbol{j}^\mathrm{s}_{(J)}}_{\text{In-plane diffusion}} + \left[\!\left[\underbrace{\rho\left(\omega_{(J)} - \omega^\mathrm{s}_{(J)}\right)\left(\boldsymbol{v} - \boldsymbol{v}^\mathrm{s}\right)\cdot \boldsymbol{n}}_{\text{Convective exchange with the bulk phases}} + \underbrace{\boldsymbol{j}_{(J)} \cdot \boldsymbol{n}}_{\text{Diffusive exchange with the bulk phases}} \right]\!\right] = 0$$

Mass flux vectors (barycentric):

$$\boldsymbol{j}_{(J)} = \rho_{(J)}(\boldsymbol{v}_{(J)} - \boldsymbol{v})$$

$$\boldsymbol{j}^\mathrm{s}_{(J)} = \rho^\mathrm{s}_{(J)}(\boldsymbol{v}^\mathrm{s}_{(J)} - \boldsymbol{v}^\mathrm{s})$$

$$\boldsymbol{v} = \frac{1}{\rho}\sum_{J=1}^{N} \rho_{(J)}\boldsymbol{v}_{(J)}$$

$$\boldsymbol{v}^\mathrm{s} = \frac{1}{\rho^\mathrm{s}}\sum_{J=1}^{N} \rho^\mathrm{s}_{(J)}\boldsymbol{v}^\mathrm{s}_{(J)}$$

Conservation principles

- Momentum balance:

$$\rho \frac{\mathrm{d}_\mathrm{b} \boldsymbol{v}}{\mathrm{d}t} - \nabla \cdot \boldsymbol{T} - \sum_{J=1}^{N} \rho_{(J)} \boldsymbol{b}_{(J)} = 0$$

$$\rho^\mathrm{s} \frac{\mathrm{d}_\mathrm{s} \boldsymbol{v}^\mathrm{s}}{\mathrm{d}t} - \nabla_\mathrm{s} \cdot \boldsymbol{T}^\mathrm{s} - \sum_{J=1}^{N} \underbrace{\rho^\mathrm{s}_{(J)} \boldsymbol{b}^\mathrm{s}_{(J)}}_{\text{Body forces}} + \left[\!\left[\underbrace{\rho\left(\boldsymbol{v} - \boldsymbol{v}^\mathrm{s}\right)\left(\boldsymbol{v} - \boldsymbol{v}^\mathrm{s}\right)}_{\substack{\text{Inertial stresses} \\ \text{exerted by the bulk}}} \cdot \boldsymbol{n} - \underbrace{\boldsymbol{T} \cdot \boldsymbol{n}}_{\substack{\text{Viscous stresses} \\ \text{exerted by bulk}}} \right]\!\right] = 0$$

Stress tensors:

$$\boldsymbol{T} = -p\boldsymbol{I} + \boldsymbol{\sigma} \qquad \boldsymbol{T}^\mathrm{s} = \gamma \boldsymbol{P} + \boldsymbol{\sigma}^\mathrm{s}$$

Extra stress tensors

$\boldsymbol{P}$: Surface projection tensor

$\boldsymbol{b}_{(J)}, \boldsymbol{b}^\mathrm{s}_{(J)}$: Body forces per unit mass

Conservation principles

- Jump momentum balance:

$$\rho^{\mathrm{s}}\frac{\mathrm{d}_{\mathrm{s}}\boldsymbol{v}^{\mathrm{s}}}{\mathrm{d}t}\underbrace{-\nabla_{\mathrm{s}}\gamma}_{\text{Surface tension gradients}}\underbrace{-2\gamma H\boldsymbol{n}}_{\text{Curvature induced stress}}\underbrace{-\nabla_{\mathrm{s}}\cdot\boldsymbol{\sigma}^{\mathrm{s}}}_{\text{In-plane deviatoric stress}}-\sum_{J=1}^{N}\rho^{\mathrm{s}}_{(J)}\boldsymbol{b}^{\mathrm{s}}_{(J)}+[\![\rho\left(\boldsymbol{v}-\boldsymbol{v}^{\mathrm{s}}\right)\left(\boldsymbol{v}-\boldsymbol{v}^{\mathrm{s}}\right)\cdot\boldsymbol{n}+\overbrace{P\boldsymbol{n}}^{\text{Pressure jump across interface}}\underbrace{-\boldsymbol{\sigma}\cdot\boldsymbol{n}}_{\text{Viscous stress exerted by bulk}}]\!]=0$$

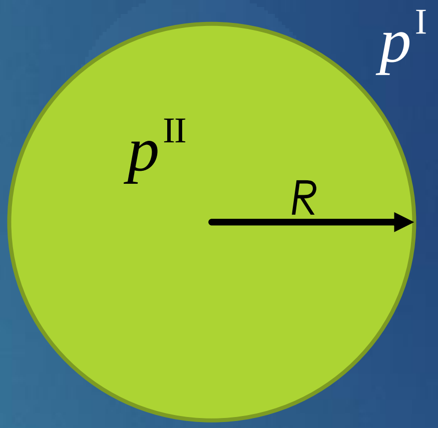
H: Mean curvature of the interface

Conservation principles

- Jump momentum balance: Generalized Laplace equation

When these stresses are negligible:

- in-plane deviatoric stresses
- surface tension gradients,
- inertial and viscous stresses exerted by the bulk



$$2\gamma H\boldsymbol{n} = [\![P\boldsymbol{n}]\!]$$

$$\frac{\gamma}{R} = p^{\mathrm{II}} - p^{\mathrm{I}}$$

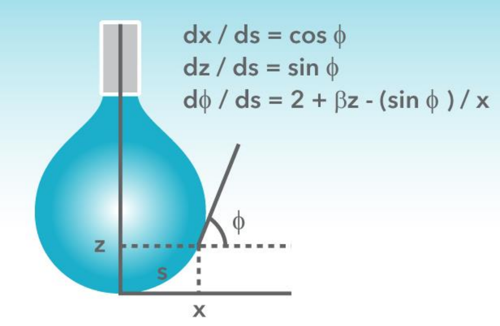
Conservation principles

- Generalized Laplace equation

Important:

- in-plane deviatoric stresses often NOT negligible in complex interfaces

$$\xcancel{2\gamma H\boldsymbol{n} = [\![P\boldsymbol{n}]\!]} \Longrightarrow 2\gamma H\boldsymbol{n} + \nabla_s \cdot \boldsymbol{\sigma}^s = [\![P\boldsymbol{n}]\!]$$



- Important in oscillating drop tensiometry for determining dilatational modulus [1]

Conservation principles

$\boldsymbol{q}, \boldsymbol{q}^{\mathrm{s}}$: Bulk, surface energy flux vectors

- Energy balance:

$$\rho \frac{\mathrm{d}_b u}{\mathrm{d}t} = \boldsymbol{\sigma} : \nabla \boldsymbol{v} - p \nabla \cdot \boldsymbol{v} + \sum_J \boldsymbol{j}_{(J)} \cdot \boldsymbol{b}_{(J)} - \nabla \cdot \boldsymbol{q}$$

$$\rho^{\mathrm{s}} \frac{\mathrm{d}_{\mathrm{s}} u^{\mathrm{s}}}{\mathrm{d}t} = \underbrace{\boldsymbol{\sigma}^{\mathrm{s}} : \nabla_{\mathrm{s}} \boldsymbol{v}^{\mathrm{s}}}_{\text{In-plane viscous dissipation}} + \underbrace{\gamma \nabla_{\mathrm{s}} \cdot \boldsymbol{v}^{\mathrm{s}}}_{\text{Work by surface tension}} + \sum_{J=1}^{N} \underbrace{\boldsymbol{j}^{\mathrm{s}}_{(J)} \cdot \boldsymbol{b}^{\mathrm{s}}_{(J)}}_{\text{Work by body forces}} \underbrace{- \nabla_{\mathrm{s}} \cdot \boldsymbol{q}^{\mathrm{s}}}_{\text{In-plane conduction}} - [\![\underbrace{\rho \left(u + p/\rho - u^{\mathrm{s}} + \tfrac{1}{2} \left| \boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}} \right|^2 \right) (\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n}}_{\text{Convective energy exchange with bulk}} + \overbrace{\boldsymbol{q} \cdot \boldsymbol{n}}^{\text{Conduction surface-bulk}} - \underbrace{\left(\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}} \right) \cdot \boldsymbol{\sigma} \cdot \boldsymbol{n}}_{\text{Viscous friction surface-bulk}}]\!]$$

Conservation principles

- Entropy balance:

$$\rho \frac{\mathrm{d_b} s}{\mathrm{d}t} = -\nabla \cdot \boldsymbol{j}_S + \rho e$$

$$\rho^{\mathrm{s}} \frac{\mathrm{d_s} s^{\mathrm{s}}}{\mathrm{d}t} = \underbrace{-\nabla_{\mathrm{s}} \cdot \boldsymbol{j}_S^{\mathrm{s}}}_{\text{Surface entropy flux}} + \underbrace{\rho^{\mathrm{s}} e^{\mathrm{s}}}_{\text{Surface entropy production rate}} - \left[\!\left[\underbrace{\rho\left(s - s^{\mathrm{s}}\right)\left(\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}}\right) \cdot \boldsymbol{n}}_{\text{Convective entropy exchange with bulk}} + \underbrace{\boldsymbol{j}_S \cdot \boldsymbol{n}}_{\text{Non-convective entropy exchange with bulk}} \right]\!\right]$$

e, e^{s} : Rate of bulk or surface entropy production per unit mass

$\boldsymbol{j}_S, \boldsymbol{j}_S^{\mathrm{s}}$: bulk or surface entropy flux vectors

To satisfy 2nd law of Thermodynamics:

$$e \geq 0 \qquad e^{\mathrm{s}} \geq 0$$

Conservation principles

- Summary:

Bulk balances

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = 0$$

$$\rho \frac{\mathrm{d}_{\mathrm{b}} \omega_{(J)}}{\mathrm{d}t} + \nabla \cdot \boldsymbol{j}_{(J)} = 0$$

$$\rho \frac{\mathrm{d}_{\mathrm{b}} \boldsymbol{v}}{\mathrm{d}t} - \nabla \cdot \boldsymbol{T} - \sum_{J=1}^{N} \rho_{(J)} \boldsymbol{b}_{(J)} = 0$$

$$\rho \frac{\mathrm{d}_{\mathrm{b}} u}{\mathrm{d}t} = \boldsymbol{\sigma} : \nabla \boldsymbol{v} - p \nabla \cdot \boldsymbol{v} + \sum_{J} \boldsymbol{j}_{(J)} \cdot \boldsymbol{b}_{(J)} - \nabla \cdot \boldsymbol{q}$$

$$\rho \frac{\mathrm{d}_{\mathrm{b}} s}{\mathrm{d}t} = -\nabla \cdot \boldsymbol{j}_S + \rho e$$

Surface balances

$$\frac{\mathrm{d}_{\mathrm{s}} \rho^{\mathrm{s}}}{\mathrm{d}t} + \rho^{\mathrm{s}} \nabla_{\mathrm{s}} \cdot \boldsymbol{v}^{s} + \llbracket \rho (\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n} \rrbracket = 0$$

$$\rho^{\mathrm{s}} \frac{\mathrm{d}_{\mathrm{s}} \omega^{\mathrm{s}}_{(J)}}{\mathrm{d}t} + \nabla_{\mathrm{s}} \cdot \boldsymbol{j}^{\mathrm{s}}_{(J)} + \llbracket \rho \left(\omega_{(J)} - \omega^{\mathrm{s}}_{(J)} \right) \left(\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}} \right) \cdot \boldsymbol{n} + \boldsymbol{j}_{(J)} \cdot \boldsymbol{n} \rrbracket = 0$$

$$\rho^{\mathrm{s}} \frac{\mathrm{d}_{\mathrm{s}} \boldsymbol{v}^{\mathrm{s}}}{\mathrm{d}t} - \nabla_{\mathrm{s}} \gamma - 2\gamma H \boldsymbol{n} - \nabla_{\mathrm{s}} \cdot \boldsymbol{\sigma}^{\mathrm{s}} - \sum_{J=1}^{N} \rho^{\mathrm{s}}_{(J)} \boldsymbol{b}^{\mathrm{s}}_{(J)} + \llbracket \rho \left(\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}} \right) \left(\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}} \right) \cdot \boldsymbol{n} + P \boldsymbol{n} - \boldsymbol{\sigma} \cdot \boldsymbol{n} \rrbracket = 0$$

$$\rho^{\mathrm{s}} \frac{\mathrm{d}_{\mathrm{s}} u^{\mathrm{s}}}{\mathrm{d}t} = \boldsymbol{\sigma}^{\mathrm{s}} : \nabla_{\mathrm{s}} \boldsymbol{v}^{\mathrm{s}} + \gamma \nabla_{\mathrm{s}} \cdot \boldsymbol{v}^{\mathrm{s}} + \sum_{J=1}^{N} \boldsymbol{j}^{\mathrm{s}}_{(J)} \cdot \boldsymbol{b}^{\mathrm{s}}_{(J)} - \nabla_{\mathrm{s}} \cdot \boldsymbol{q}^{\mathrm{s}}$$
$$- \llbracket \rho \left(u + p/\rho - u^{\mathrm{s}} + \tfrac{1}{2} \left| \boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}} \right|^2 \right) (\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n} + \boldsymbol{q} \cdot \boldsymbol{n} - \left(\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}} \right) \cdot \boldsymbol{\sigma} \cdot \boldsymbol{n} \rrbracket$$

$$\rho^{\mathrm{s}} \frac{\mathrm{d}_{\mathrm{s}} s^{\mathrm{s}}}{\mathrm{d}t} = -\nabla_{\mathrm{s}} \cdot \boldsymbol{j}^{\mathrm{s}}_{S} + \rho^{\mathrm{s}} e^{\mathrm{s}} - \llbracket \rho \left(s - s^{\mathrm{s}} \right) (\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n} + \boldsymbol{j}_S \cdot \boldsymbol{n} \rrbracket$$

Conservation principles

- What is still missing from this framework:

1. Constitutive equations for bulk and surface fluxes

Bulk balances

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = 0$$

$$\rho \frac{\mathrm{d}_\mathrm{b} \omega_{(J)}}{\mathrm{d}t} + \nabla \cdot \boldsymbol{j}_{(J)} = 0$$

$$\rho \frac{\mathrm{d}_\mathrm{b} \boldsymbol{v}}{\mathrm{d}t} - \nabla \cdot \boldsymbol{T} - \sum_{J=1}^{N} \rho_{(J)} \boldsymbol{b}_{(J)} = 0$$

$$\rho \frac{\mathrm{d}_b u}{\mathrm{d}t} = \boldsymbol{\sigma} : \nabla \boldsymbol{v} - p \nabla \cdot \boldsymbol{v} + \sum_{J} \boldsymbol{j}_{(J)} \cdot \boldsymbol{b}_{(J)} - \nabla \cdot \boldsymbol{q}$$

$$\rho \frac{\mathrm{d}_\mathrm{b} s}{\mathrm{d}t} = -\nabla \cdot \boldsymbol{j}_S + \rho e$$

2. Boundary conditions for bulk-surface coupling

Surface balances

$$\frac{\mathrm{d}_\mathrm{s} \rho^\mathrm{s}}{\mathrm{d}t} + \rho^\mathrm{s} \nabla_\mathrm{s} \cdot \boldsymbol{v}^s + [\![\rho (\boldsymbol{v} - \boldsymbol{v}^\mathrm{s}) \cdot \boldsymbol{n}]\!] = 0$$

$$\rho^\mathrm{s} \frac{\mathrm{d}_\mathrm{s} \omega^\mathrm{s}_{(J)}}{\mathrm{d}t} + \nabla_\mathrm{s} \cdot \boldsymbol{j}^\mathrm{s}_{(J)} + [\![\rho \left(\omega_{(J)} - \omega^\mathrm{s}_{(J)} \right) \left(\boldsymbol{v} - \boldsymbol{v}^\mathrm{s} \right) \cdot \boldsymbol{n} + \boldsymbol{j}_{(J)} \cdot \boldsymbol{n}]\!] = 0$$

$$\rho^\mathrm{s} \frac{\mathrm{d}_\mathrm{s} \boldsymbol{v}^\mathrm{s}}{\mathrm{d}t} - \nabla_\mathrm{s} \gamma - 2\gamma H \boldsymbol{n} - \nabla_\mathrm{s} \cdot \boldsymbol{\sigma}^\mathrm{s} - \sum_{J=1}^{N} \rho^\mathrm{s}_{(J)} \boldsymbol{b}^\mathrm{s}_{(J)} + [\![\rho \left(\boldsymbol{v} - \boldsymbol{v}^\mathrm{s} \right) \left(\boldsymbol{v} - \boldsymbol{v}^\mathrm{s} \right) \cdot \boldsymbol{n} + P \boldsymbol{n} - \boldsymbol{\sigma} \cdot \boldsymbol{n}]\!] = 0$$

$$\rho^\mathrm{s} \frac{\mathrm{d}_\mathrm{s} u^\mathrm{s}}{\mathrm{d}t} = \boldsymbol{\sigma}^\mathrm{s} : \nabla_\mathrm{s} \boldsymbol{v}^\mathrm{s} + \gamma \nabla_\mathrm{s} \cdot \boldsymbol{v}^\mathrm{s} + \sum_{J=1}^{N} \boldsymbol{j}^\mathrm{s}_{(J)} \cdot \boldsymbol{b}^\mathrm{s}_{(J)} - \nabla_\mathrm{s} \cdot \boldsymbol{q}^\mathrm{s}$$
$$- [\![\rho \left(u + p/\rho - u^\mathrm{s} + \tfrac{1}{2} \left| \boldsymbol{v} - \boldsymbol{v}^\mathrm{s} \right|^2 \right) (\boldsymbol{v} - \boldsymbol{v}^\mathrm{s}) \cdot \boldsymbol{n} + \boldsymbol{q} \cdot \boldsymbol{n} - \left(\boldsymbol{v} - \boldsymbol{v}^\mathrm{s} \right) \cdot \boldsymbol{\sigma} \cdot \boldsymbol{n}]\!]$$

$$\rho^\mathrm{s} \frac{\mathrm{d}_\mathrm{s} s^\mathrm{s}}{\mathrm{d}t} = -\nabla_\mathrm{s} \cdot \boldsymbol{j}^\mathrm{s}_S + \rho^\mathrm{s} e^\mathrm{s} - [\![\rho \left(s - s^\mathrm{s} \right) (\boldsymbol{v} - \boldsymbol{v}^\mathrm{s}) \cdot \boldsymbol{n} + \boldsymbol{j}_S \cdot \boldsymbol{n}]\!]$$

Constitutive modelling

- Classical Irreversible Thermodynamics: use entropy balance as a guide [3,4]

$$s^{\mathrm{s}} = s^{\mathrm{s}}\left(u^{\mathrm{s}}, \hat{\Omega}, \omega^{\mathrm{s}}_{(1)}, \dots, \omega^{\mathrm{s}}_{(N-1)}\right) \qquad \hat{\Omega} = 1/\rho^{\mathrm{s}}$$

$$\rho^{\mathrm{s}} \frac{\mathrm{d_s} s^{\mathrm{s}}}{\mathrm{d}t} = \frac{\rho^{\mathrm{s}}}{T^{\mathrm{s}}} \frac{\mathrm{d_s} u^{\mathrm{s}}}{\mathrm{d}t} - \frac{\gamma\rho^{\mathrm{s}}}{T^{\mathrm{s}}} \frac{\mathrm{d_s} \hat{\Omega}}{\mathrm{d}t} - \frac{\rho^{\mathrm{s}}}{T^{\mathrm{s}}} \sum_{J=1}^{N} \mu^{\mathrm{s}}_{(J)} \frac{\mathrm{d_s} \omega^{\mathrm{s}}_{(J)}}{\mathrm{d}t}$$

Surface temperature

Surface chemical potential per unit mass of component J

Eliminate time derivatives using:

- Surface energy balance
- Surface overall mass balance
- Surface component mass balance

Substitute result in surface entropy balance

Constitutive modelling

- Result: bi-linear expression for surface entropy production rate

$$
\begin{aligned}
\rho^{\mathrm{s}} e^{\mathrm{s}} = {} & \frac{1}{T^{\mathrm{s}}} \overline{\boldsymbol{\sigma}}^{\mathrm{s}} : \overline{\boldsymbol{D}}^{\mathrm{s}} + \frac{\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}}}{T^{\mathrm{s}}} \mathrm{tr}\boldsymbol{D}^{\mathrm{s}} - \frac{1}{T^{\mathrm{s}}} \sum_{J=1}^{N} \boldsymbol{j}^{\mathrm{s}}_{(J)} \cdot \boldsymbol{d}^{\mathrm{s}}_{(J)} - \frac{1}{(T^{\mathrm{s}})^2} \left(\boldsymbol{q}^{\mathrm{s}} - \sum_{J=1}^{N} \mu^{\mathrm{s}}_{(J)} \boldsymbol{j}^{\mathrm{s}}_{(J)} \right) \cdot \nabla_{\mathrm{s}} T^{\mathrm{s}} \\
& - \frac{1}{T^{\mathrm{s}}} \left[\!\!\left[\rho \left((u + p/\rho) \left[\frac{T - T^{\mathrm{s}}}{T} \right] + \sum_{J=1}^{N} T^{\mathrm{s}} \left(\frac{\tilde{\mu}_{(J)}}{T} - \frac{\tilde{\mu}^{\mathrm{s}}_{(J)}}{T^{\mathrm{s}}} \right) \omega_{(J)} \right) (\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n} \right.\right. \\
& + \tfrac{1}{2} \rho \left((v - v^{\mathrm{s}})^2 + \frac{v^2 T^{\mathrm{s}} - (v^{\mathrm{s}})^2 T}{T} \right) (\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n} \\
& \left.\left. + \boldsymbol{q} \cdot \boldsymbol{n} \left[\frac{T - T^{\mathrm{s}}}{T} \right] - \left(\boldsymbol{v} - \boldsymbol{v}^{\mathrm{s}} \right) \cdot \boldsymbol{\sigma} \cdot \boldsymbol{n} + T^{\mathrm{s}} \sum_{J=1}^{N} \boldsymbol{j}_{(J)} \cdot \boldsymbol{n} \left(\frac{\tilde{\mu}_{(J)}}{T} - \frac{\tilde{\mu}^{\mathrm{s}}_{(J)}}{T^{s}} \right) \right]\!\!\right] \geq 0
\end{aligned}
$$

With:

$$\overline{\boldsymbol{\sigma}}^{s} = \boldsymbol{\sigma}^{\mathrm{s}} - \tfrac{1}{2} \boldsymbol{P} (\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}})$$

$$\boldsymbol{D}^{\mathrm{s}} = \tfrac{1}{2} \left(\boldsymbol{P} \cdot \nabla_{\mathrm{s}} \boldsymbol{v}^{\mathrm{s}} + [\nabla_{\mathrm{s}} \boldsymbol{v}^{\mathrm{s}}]^{\mathrm{T}} \cdot \boldsymbol{P} \right)$$

$$\tilde{\mu}_{(J)} = \mu_{(J)} - \tfrac{1}{2} v^2$$

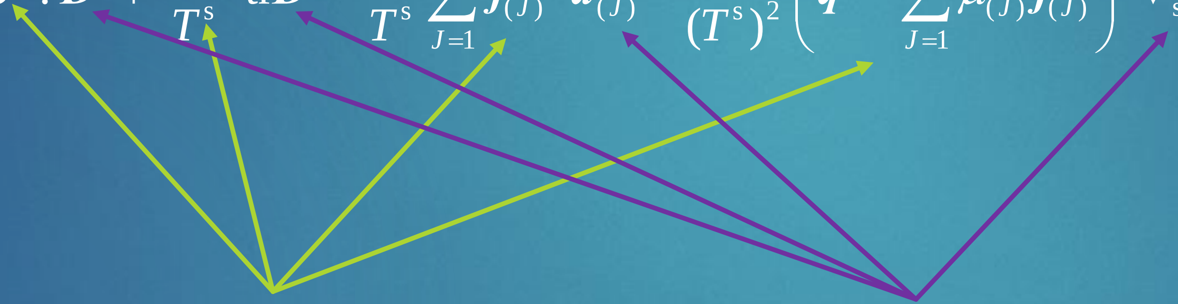
$$\tilde{\mu}^{\mathrm{s}}_{(J)} = \mu^{\mathrm{s}}_{(J)} - \tfrac{1}{2} (v^{\mathrm{s}})^2$$

$$\boldsymbol{d}^{\mathrm{s}}_{(J)} \equiv \nabla_{\mathrm{s}} \mu^{\mathrm{s}}_{(J)} - \boldsymbol{b}^{\mathrm{s}}_{(J)}$$

Constitutive modelling

- First look at system without exchange between bulk and surface

$$\rho^{\mathrm{s}} e^{\mathrm{s}} = \frac{1}{T^{\mathrm{s}}} \overline{\boldsymbol{\sigma}}^{\mathrm{s}} : \overline{\boldsymbol{D}}^{\mathrm{s}} + \frac{\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}}}{T^{\mathrm{s}}} \mathrm{tr}\boldsymbol{D}^{\mathrm{s}} - \frac{1}{T^{\mathrm{s}}} \sum_{J=1}^{N} \boldsymbol{j}^{\mathrm{s}}_{(J)} \cdot \boldsymbol{d}^{\mathrm{s}}_{(J)} - \frac{1}{(T^{\mathrm{s}})^2} \left(\boldsymbol{q}^{\mathrm{s}} - \sum_{J=1}^{N} \mu^{\mathrm{s}}_{(J)} \boldsymbol{j}^{\mathrm{s}}_{(J)} \right) \cdot \nabla_{\mathrm{s}} T^{\mathrm{s}} \geq 0$$



Fluxes

Driving forces

With:

$$\overline{\boldsymbol{\sigma}}^{\mathrm{s}} = \boldsymbol{\sigma}^{\mathrm{s}} - \tfrac{1}{2} \boldsymbol{P}(\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}})$$

$$\boldsymbol{D}^{\mathrm{s}} = \tfrac{1}{2} \left(\boldsymbol{P} \cdot \nabla_{\mathrm{s}} \boldsymbol{v}^{\mathrm{s}} + [\nabla_{\mathrm{s}} \boldsymbol{v}^{\mathrm{s}}]^{\mathrm{T}} \cdot \boldsymbol{P} \right)$$

$$\boldsymbol{d}^{\mathrm{s}}_{(J)} \equiv \nabla_{\mathrm{s}} \mu^{\mathrm{s}}_{(J)} - \boldsymbol{b}^{\mathrm{s}}_{(J)}$$

Constitutive modelling

- Expanding fluxes linearly in terms of driving forces of equal tensorial order:

$$\left.\begin{aligned}\overline{\boldsymbol{\sigma}}^{\mathrm{s}} &= 2\varepsilon_{\mathrm{s}}\overline{\boldsymbol{D}}^{\mathrm{s}}\\ \mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}} &= 2\varepsilon_{\mathrm{d}}\mathrm{tr}\boldsymbol{D}^{\mathrm{s}}\end{aligned}\right\} \quad \boldsymbol{\sigma}^{\mathrm{s}} = \left(\varepsilon_{\mathrm{d}} - \varepsilon_{\mathrm{s}}\right)\left(\mathrm{tr}\boldsymbol{D}^{\mathrm{s}}\right)\boldsymbol{P} + 2\varepsilon_{\mathrm{s}}\boldsymbol{D}^{\mathrm{s}}$$

With: $\overline{\boldsymbol{\sigma}}^{\mathrm{s}} = \boldsymbol{\sigma}^{\mathrm{s}} - \tfrac{1}{2}\boldsymbol{P}(\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}})$

Linear **Boussinesq** model for viscous interface

ε_{s} : Surface shear viscosity

ε_{d} : Surface dilatational viscosity

Compare with bulk Newtonian fluid

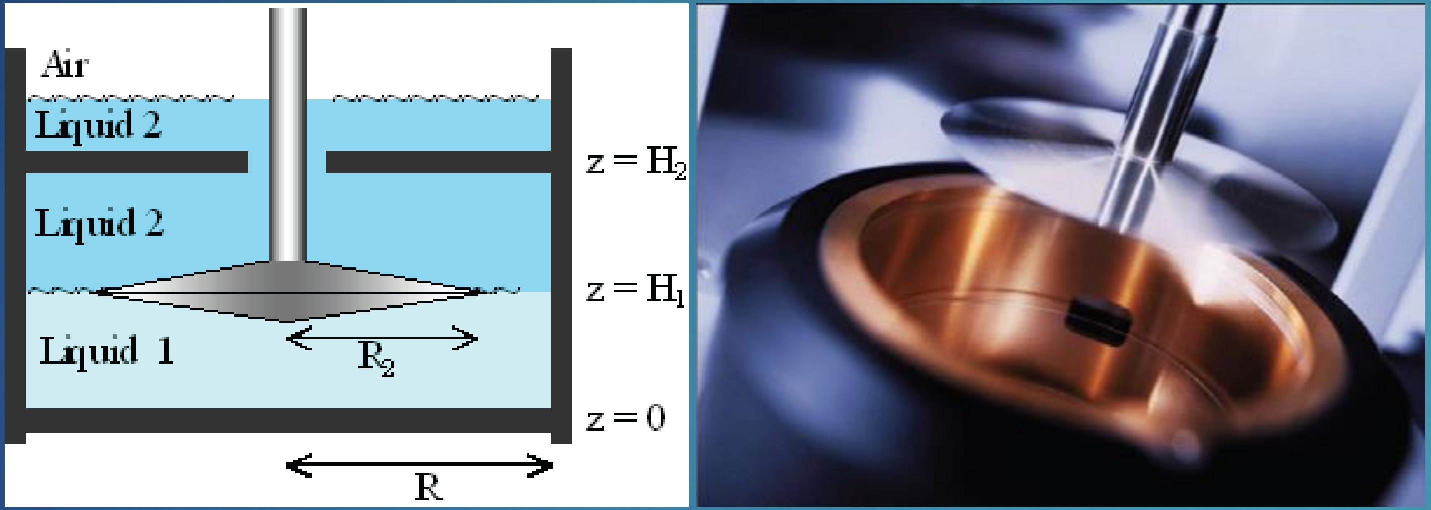
$$\boldsymbol{\sigma} = \left(\lambda - \tfrac{2}{3}\eta\right)\left(\mathrm{tr}\boldsymbol{D}\right)\boldsymbol{I} + 2\eta\boldsymbol{D}$$

$$\frac{\varepsilon_{\mathrm{s}}}{T^{\mathrm{s}}}\overline{\boldsymbol{D}}^{\mathrm{s}} : \overline{\boldsymbol{D}}^{\mathrm{s}} + \frac{\varepsilon_{d}}{T^{\mathrm{s}}}(\mathrm{tr}\boldsymbol{D}^{\mathrm{s}})^{2} \geq 0 \quad \longrightarrow \quad \varepsilon_{\mathrm{s}} \geq 0 \qquad \varepsilon_{\mathrm{d}} \geq 0$$

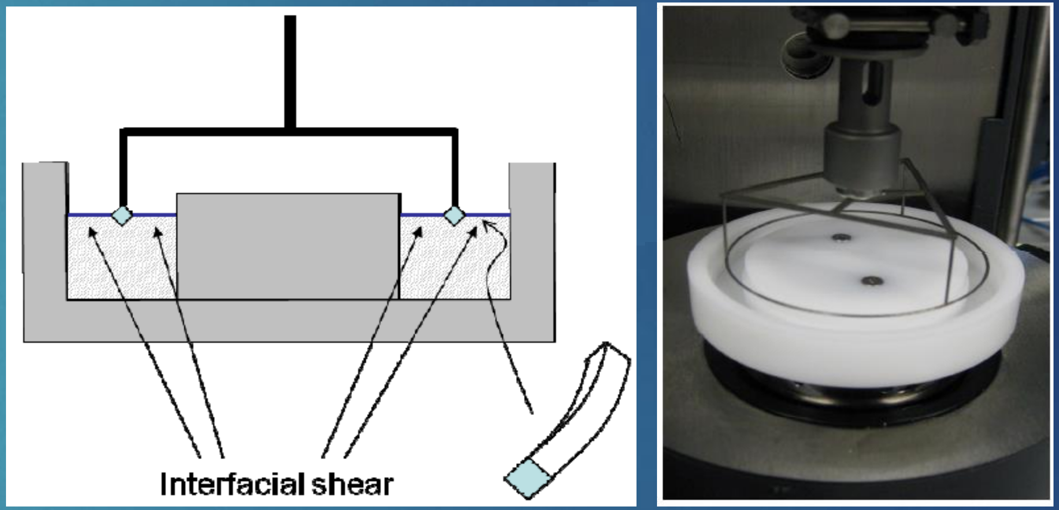
Constitutive modelling

Measuring interfacial shear properties:

Bi-cone geometry



Double wall ring geometry



In steady shear typically analyzed with Linear Boussinesq model

Constitutive modelling

- Fluxes for in-plane heat and mass transfer:

$$-\frac{1}{T^{\mathrm{s}}}\sum_{J=1}^{N}\boldsymbol{j}^{\mathrm{s}}_{(J)}\cdot\boldsymbol{d}^{\mathrm{s}}_{(J)}-\frac{1}{(T^{\mathrm{s}})^{2}}\left(\boldsymbol{q}^{\mathrm{s}}-\sum_{J=1}^{N}\mu^{\mathrm{s}}_{(J)}\boldsymbol{j}^{\mathrm{s}}_{(J)}\right)\cdot\nabla_{\mathrm{s}}T^{\mathrm{s}}\geq 0$$

With: $\boldsymbol{d}^{\mathrm{s}}_{(J)}\equiv\nabla_{\mathrm{s}}\mu^{\mathrm{s}}_{(J)}-\boldsymbol{b}^{\mathrm{s}}_{(J)}$

$$\boldsymbol{j}^{\mathrm{s}}_{(J)}=-\sum_{K}D^{\mathrm{s}}_{(JK)}\boldsymbol{d}^{\mathrm{s}}_{(K)}-\alpha^{\mathrm{s}}_{(J)}\nabla_{\mathrm{s}}\ln T^{\mathrm{s}}$$

$$\boldsymbol{q}^{\mathrm{s}}-\sum_{J=1}^{N}\mu^{\mathrm{s}}_{(J)}\boldsymbol{j}^{\mathrm{s}}_{(J)}=-\sum_{J}\alpha^{\mathrm{s}}_{(J)}\boldsymbol{d}^{\mathrm{s}}_{(J)}-\lambda^{\mathrm{s}}\nabla_{\mathrm{s}}\ln T^{\mathrm{s}}$$

$D^{\mathrm{s}}_{(JK)}$: Surface diffusion coefficient

$\alpha^{\mathrm{s}}_{(J)}$: thermal diffusion coefficient

λ^{s} : surface thermal conductivity

Constitutive modelling

- Fluxes for in-plane mass transfer:

$$\boldsymbol{j}^{\mathrm{s}}_{(J)} = -\sum_K \underbrace{D^{\mathrm{s}}_{(JK)}(\nabla_{\mathrm{s}}\mu^{\mathrm{s}}_{(J)} - \boldsymbol{b}^{\mathrm{s}}_{(J)})}_{\text{Describes ordinary and forced diffusion}} - \underbrace{\alpha^{\mathrm{s}}_{(J)}\nabla_{\mathrm{s}} \ln T^{\mathrm{s}}}_{\text{Soret effect, thermodiffusion}}$$

With:

$D^{\mathrm{s}}_{(JK)}$: Surface diffusion coefficient

$\alpha^{\mathrm{s}}_{(J)}$: thermal diffusion coefficient

When thermodiffusion and forced diffusion are negligible:

$$\boldsymbol{j}^{\mathrm{s}}_{(J)} = -\sum_K D^{\mathrm{s}}_{(JK)}\nabla_{\mathrm{s}}\mu^{\mathrm{s}}_{(K)}$$

Surface equivalent of Fick's law: $\boldsymbol{j}_{(J)} = -\sum_K D_{(JK)}\nabla\mu_{(K)}$

Constitutive modelling

- Fluxes for in-plane heat transfer:

$$\boldsymbol{q}^{\mathrm{s}} - \sum_{J=1}^{N} \mu^{\mathrm{s}}_{(J)} \boldsymbol{j}^{\mathrm{s}}_{(J)} = \underbrace{-\sum_{J} \alpha^{\mathrm{s}}_{(J)} \boldsymbol{d}^{\mathrm{s}}_{(J)}}_{\text{Dufour effect}} - \lambda^{\mathrm{s}} \nabla_{\mathrm{s}} \ln T^{\mathrm{s}}$$

$\alpha^{\mathrm{s}}_{(J)}$: thermal diffusion coefficient

λ^{s} : surface thermal conductivity

When mass transfer is negligible:

$$\boldsymbol{q}^{\mathrm{s}} = -\frac{\lambda^{\mathrm{s}}}{T^{\mathrm{s}}} \nabla_{\mathrm{s}} T^{\mathrm{s}}$$

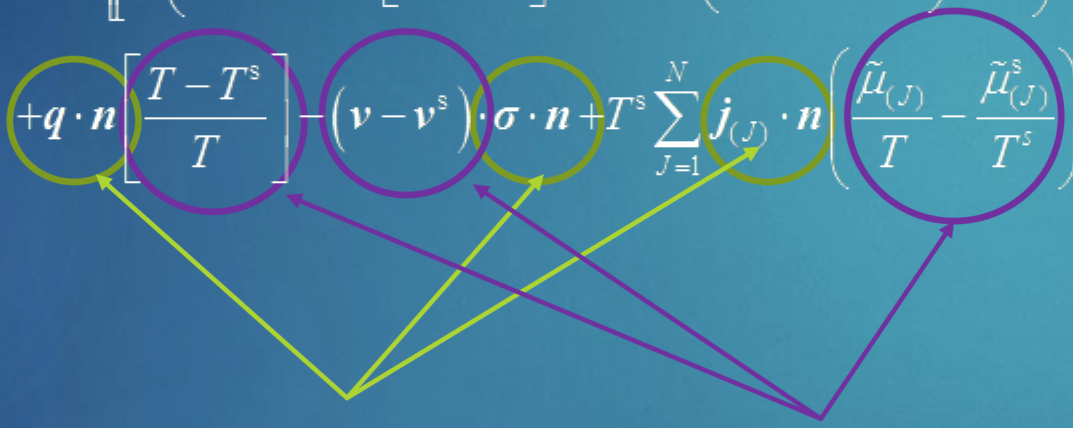
Surface equivalent of Fourier's law: $\boldsymbol{q} = -\dfrac{\lambda}{T} \nabla T$

Constitutive modelling

- Boundary conditions (coupling bulk-interface):

$$-\frac{1}{T^{\mathrm{s}}}\left[\!\left[\rho\left((u+p/\rho)\left[\frac{T-T^{\mathrm{s}}}{T}\right]+\sum_{J=1}^{N}T^{\mathrm{s}}\left(\frac{\tilde{\mu}_{(J)}}{T}-\frac{\tilde{\mu}^{\mathrm{s}}_{(J)}}{T^{\mathrm{s}}}\right)\omega_{(J)}\right)(\boldsymbol{v}-\boldsymbol{v}^{\mathrm{s}})\cdot\boldsymbol{n}+\tfrac{1}{2}\rho\left((v-v^{\mathrm{s}})^2+\frac{v^2T^{\mathrm{s}}-(v^{\mathrm{s}})^2T}{T}\right)(\boldsymbol{v}-\boldsymbol{v}^{\mathrm{s}})\cdot\boldsymbol{n}\right.\right.$$

$$\left.\left.+\boldsymbol{q}\cdot\boldsymbol{n}\left[\frac{T-T^{\mathrm{s}}}{T}\right]-\left(\boldsymbol{v}-\boldsymbol{v}^{\mathrm{s}}\right)\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n}+T^{\mathrm{s}}\sum_{J=1}^{N}\boldsymbol{j}_{(J)}\cdot\boldsymbol{n}\left(\frac{\tilde{\mu}_{(J)}}{T}-\frac{\tilde{\mu}^{\mathrm{s}}_{(J)}}{T^{s}}\right)\right]\!\right]\geq 0$$



Fluxes
(reduced order)

Driving forces

Constitutive modelling

- Boundary conditions (coupling bulk-interface): mass flux

$$-\frac{1}{T^{s}}\left\llbracket \rho\left((u+p/\rho)\left[\frac{T-T^{s}}{T}\right]+\sum_{J=1}^{N}T^{s}\left(\frac{\tilde{\mu}_{(J)}}{T}-\frac{\tilde{\mu}^{s}_{(J)}}{T^{s}}\right)\omega_{(J)}\right)(\boldsymbol{v}-\boldsymbol{v}^{s})\cdot\boldsymbol{n}+\tfrac{1}{2}\rho\left((v-v^{s})^{2}+\frac{v^{2}T^{s}-(v^{s})^{2}T}{T}\right)(\boldsymbol{v}-\boldsymbol{v}^{s})\cdot\boldsymbol{n}\right.$$

$$\left.+\boldsymbol{q}\cdot\boldsymbol{n}\left[\frac{T-T^{s}}{T}\right]-(\boldsymbol{v}-\boldsymbol{v}^{s})\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n}+T^{s}\sum_{J=1}^{N}\boldsymbol{j}_{(J)}\cdot\boldsymbol{n}\left(\frac{\tilde{\mu}_{(J)}}{T}-\frac{\tilde{\mu}^{s}_{(J)}}{T^{s}}\right)\right\rrbracket\geq 0$$

Mass flux

Driving forces

For each phase M (M=I,II):

$$\boldsymbol{j}^{M}_{(J)}\cdot\boldsymbol{n}^{M}+\rho^{M}_{(J)}\left(\boldsymbol{v}^{M}-\boldsymbol{v}^{s}\right)\cdot\boldsymbol{n}^{M}=-\Lambda^{M}_{(J)}\left(\frac{\tilde{\mu}^{M}_{(J)}}{T^{M}}-\frac{\tilde{\mu}^{s}_{(J)}}{T^{s}}\right)-\Lambda^{TM}_{(J)}\left(T^{M}-T^{s}\right)$$

Constitutive modelling

- Boundary conditions (coupling bulk-interface): heat flux

$$-\frac{1}{T^{s}}\left[\!\left[\rho\left((u+p/\rho)\left[\frac{T-T^{s}}{T}\right]+\sum_{J=1}^{N}T^{s}\left(\frac{\tilde{\mu}_{(J)}}{T}-\frac{\tilde{\mu}^{s}_{(J)}}{T^{s}}\right)\omega_{(J)}\right)(\boldsymbol{v}-\boldsymbol{v}^{s})\cdot\boldsymbol{n}+\tfrac{1}{2}\rho\left((v-v^{s})^{2}+\frac{v^{2}T^{s}-(v^{s})^{2}T}{T}\right)(\boldsymbol{v}-\boldsymbol{v}^{s})\cdot\boldsymbol{n}\right.\right.$$

$$\left.\left.+\boldsymbol{q}\cdot\boldsymbol{n}\left[\frac{T-T^{s}}{T}\right]-(\boldsymbol{v}-\boldsymbol{v}^{s})\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n}+T^{s}\sum_{J=1}^{N}\boldsymbol{j}_{(J)}\cdot\boldsymbol{n}\left(\frac{\tilde{\mu}_{(J)}}{T}-\frac{\tilde{\mu}^{s}_{(J)}}{T^{s}}\right)\right]\!\right]\geq 0$$

heat flux

Driving forces

For each phase M (M=I,II):

$$\boldsymbol{q}^{M}\cdot\boldsymbol{n}^{M}+\rho^{M}\left[u^{M}+p^{M}/\rho^{M}+\tfrac{1}{2}(\mathrm{v}^{M})^{2}\right]\left(\boldsymbol{v}^{M}-\boldsymbol{v}^{s}\right)\cdot\boldsymbol{n}^{M}-\boldsymbol{v}^{M}\cdot\boldsymbol{\sigma}^{M}\cdot\boldsymbol{n}^{M}=-\frac{T^{M}-T^{s}}{R_{K}^{M}}-\sum_{J}\Lambda_{(J)}^{TM}T^{M}T^{s}\left(\frac{\tilde{\mu}_{(J)}^{M}}{T^{M}}-\frac{\tilde{\mu}_{(J)}^{s}}{T^{s}}\right)$$

Kapitza resistance

Constitutive modelling

- Boundary conditions (coupling bulk-interface): momentum flux

$$-\frac{1}{T^{\mathrm{s}}}\left[\!\!\left[\rho\left(\left(u+p/\rho\right)\left[\frac{T-T^{\mathrm{s}}}{T}\right]+\sum_{J=1}^{N}T^{\mathrm{s}}\left(\frac{\tilde{\mu}_{(J)}}{T}-\frac{\tilde{\mu}^{\mathrm{s}}_{(J)}}{T^{\mathrm{s}}}\right)\omega_{(J)}\right)(\boldsymbol{v}-\boldsymbol{v}^{\mathrm{s}})\cdot\boldsymbol{n}+\tfrac{1}{2}\rho\left((v-v^{\mathrm{s}})^2+\frac{v^2T^{\mathrm{s}}-(v^{\mathrm{s}})^2T}{T}\right)(\boldsymbol{v}-\boldsymbol{v}^{\mathrm{s}})\cdot\boldsymbol{n}\right.\right.$$

$$\left.\left.+\boldsymbol{q}\cdot\boldsymbol{n}\left[\frac{T-T^{\mathrm{s}}}{T}\right]-\left(\boldsymbol{v}-\boldsymbol{v}^{\mathrm{s}}\right)\boldsymbol{\sigma}\cdot\boldsymbol{n}+T^{\mathrm{s}}\sum_{J=1}^{N}\boldsymbol{j}_{(J)}\cdot\boldsymbol{n}\left(\frac{\tilde{\mu}_{(J)}}{T}-\frac{\tilde{\mu}^{\mathrm{s}}_{(J)}}{T^{s}}\right)\right]\!\!\right]\geq 0$$

momentum flux

Driving forces

For each phase M (M=I,II):

$$\boldsymbol{\sigma}^{M}\cdot\boldsymbol{n}^{M}-\rho^{M}\boldsymbol{v}^{M}\left(\boldsymbol{v}^{M}-\boldsymbol{v}^{\mathrm{s}}\right)\cdot\boldsymbol{n}^{M}=\sum_{N=\mathrm{I}}^{\mathrm{II}}\zeta^{M,N}T^{\mathrm{s}}\cdot\left(\frac{\boldsymbol{v}^{N}}{T^{N}}-\frac{\boldsymbol{v}^{\mathrm{s}}}{T^{\mathrm{s}}}\right)$$

Friction tensors

Constitutive modelling

- Summary

Bulk

$$\boldsymbol{j}_{(J)} = -\sum_{K} D_{(JK)} \nabla \mu_{(K)}$$

$$\boldsymbol{q} = -\frac{\lambda}{T} \nabla T$$

$$\boldsymbol{\sigma} = \left(\lambda - \tfrac{2}{3}\eta\right)\left(\mathrm{tr}\boldsymbol{D}\right)\boldsymbol{I} + 2\eta \boldsymbol{D}$$

Interface

$$\boldsymbol{j}^{\mathrm{s}}_{(J)} = -\sum_{K} D^{\mathrm{s}}_{(JK)} \nabla_{\mathrm{s}} \mu^{\mathrm{s}}_{(K)}$$

$$\boldsymbol{q}^{\mathrm{s}} = -\frac{\lambda^{\mathrm{s}}}{T^{\mathrm{s}}} \nabla_{\mathrm{s}} T^{\mathrm{s}}$$

$$\boldsymbol{\sigma}^{\mathrm{s}} = \left(\varepsilon_{\mathrm{d}} - \varepsilon_{\mathrm{s}}\right)\left(\mathrm{tr}\boldsymbol{D}^{\mathrm{s}}\right)\boldsymbol{P} + 2\varepsilon_{\mathrm{s}} \boldsymbol{D}^{\mathrm{s}}$$

Bulk-Interface coupling

$$\boldsymbol{j}^{M}_{(J)} \cdot \boldsymbol{n}^{M} + \rho^{M}_{(J)}\left(\boldsymbol{v}^{M} - \boldsymbol{v}^{\mathrm{s}}\right) \cdot \boldsymbol{n}^{M} = -\Lambda^{M}_{(J)}\left(\frac{\tilde{\mu}^{M}_{(J)}}{T^{M}} - \frac{\tilde{\mu}^{\mathrm{s}}_{(J)}}{T^{\mathrm{s}}}\right) - \Lambda^{TM}_{(J)}\left(T^{M} - T^{\mathrm{s}}\right)$$

$$\boldsymbol{q}^{M} \cdot \boldsymbol{n}^{M} + \rho^{M}\left[u^{M} + p^{M}/\rho^{M} + \tfrac{1}{2}(\mathrm{v}^{M})^{2}\right]\left(\boldsymbol{v}^{M} - \boldsymbol{v}^{\mathrm{s}}\right) \cdot \boldsymbol{n}^{M}$$
$$-\boldsymbol{v}^{M} \cdot \boldsymbol{\sigma}^{M} \cdot \boldsymbol{n}^{M} = -\frac{T^{M} - T^{\mathrm{s}}}{R^{M}_{K}} - \sum_{J} \Lambda^{TM}_{(J)} T^{M} T^{\mathrm{s}}\left(\frac{\tilde{\mu}^{M}_{(J)}}{T^{M}} - \frac{\tilde{\mu}^{\mathrm{s}}_{(J)}}{T^{\mathrm{s}}}\right)$$

$$\boldsymbol{\sigma}^{M} \cdot \boldsymbol{n}^{M} - \rho^{M} \boldsymbol{v}^{M}\left(\boldsymbol{v}^{M} - \boldsymbol{v}^{\mathrm{s}}\right) \cdot \boldsymbol{n}^{M} = \sum_{N=\mathrm{I}}^{\mathrm{II}} \zeta^{M,N} T^{\mathrm{s}} \cdot \left(\frac{\boldsymbol{v}^{N}}{T^{N}} - \frac{\boldsymbol{v}^{\mathrm{s}}}{T^{\mathrm{s}}}\right)$$

Extension to complex interfaces

- How well do these linear models describe actual systems?

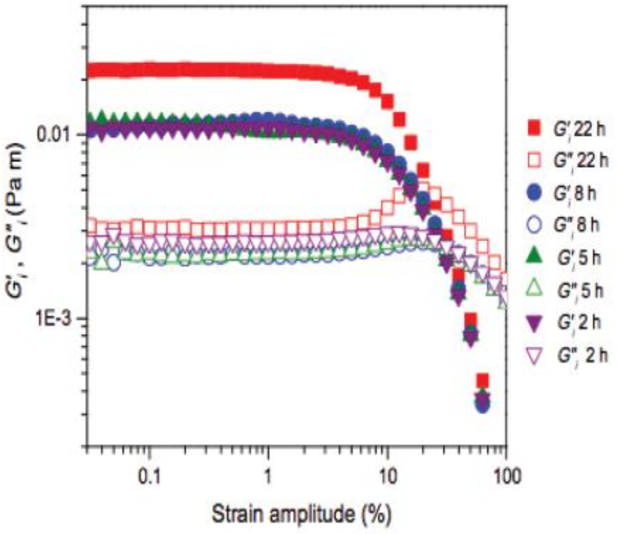


Figure 4: Strain sweep experiments for β-lactoglobulin at different surface ages (frequency 1 Hz, replotted from Torcello-Gómez et al. [7]).

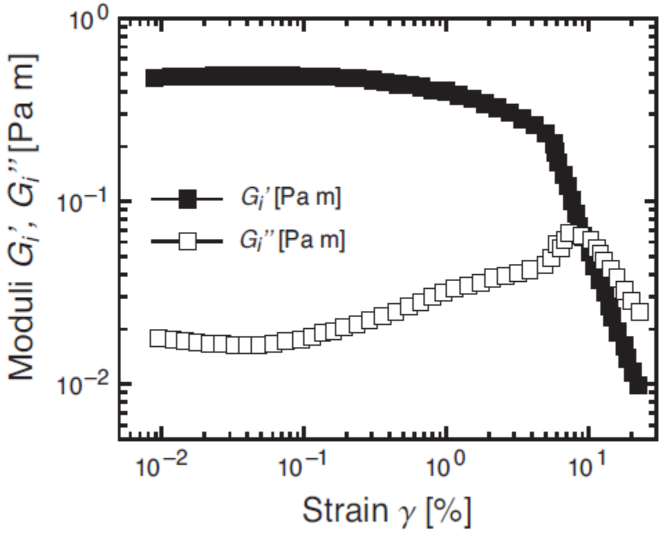


Figure 5: Strain sweep experiments of Silicate nanoparticles (particle diameter 300 nm, 50 mg/m^2, frequency 2 Hz, replotted from Zang et al. [31]).

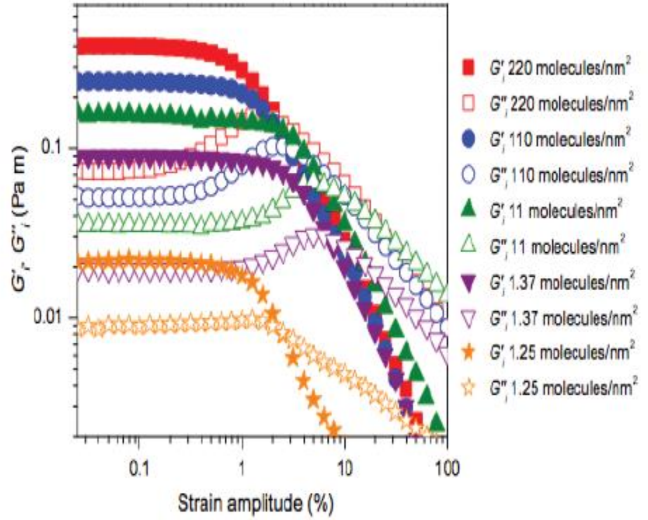


Figure 6: Strain sweep experiments for Span 65 at different surface concentration (frequency 1 Hz, replotted from Torcello-Gómez et al. [7]).

Most complex interfaces display (nonlinear) viscoelastic behavior !!!

Extension to complex interfaces

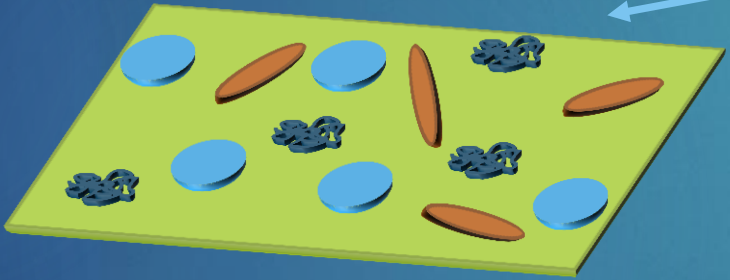
- Complex interfaces have a microstructure which is affected by deformation
- Can account for this by including additional structural variables

$$s^{\mathrm{s}} = s^{\mathrm{s}}\left(\underbrace{u^{\mathrm{s}},\hat{\Omega},\omega^{\mathrm{s}}_{(1)},\ldots,\omega^{\mathrm{s}}_{(N-1)}}_{\text{Simple interface}},\underbrace{\underbrace{\mathit{\Gamma}^{\mathrm{s}}_{1},\ldots,\mathit{\Gamma}^{\mathrm{s}}_{n}}_{\text{Scalars}},\underbrace{\boldsymbol{c}^{\mathrm{s}}_{1},\ldots,\boldsymbol{c}^{\mathrm{s}}_{m}}_{\text{Vectors}},\underbrace{\boldsymbol{C}^{\mathrm{s}}_{1},\ldots,\boldsymbol{C}^{\mathrm{s}}_{k}}_{\text{Tensors}}}_{\text{Surface structural variables}}\right)$$

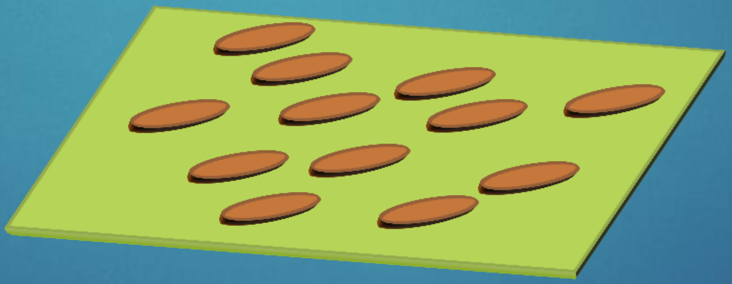
Extension to complex interfaces

- Examples additional structural variables

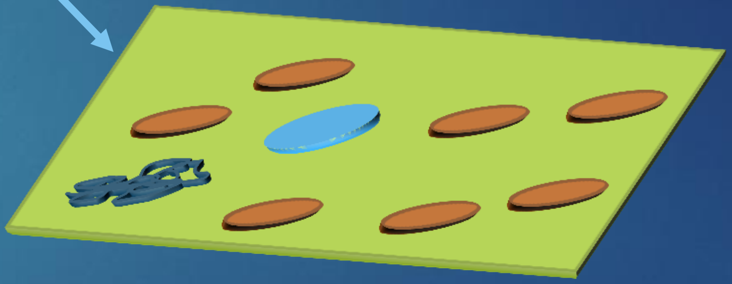
$$s^{\mathrm{s}} = s^{\mathrm{s}}\Big(\underbrace{u^{\mathrm{s}}, \hat{\Omega}, \omega^{\mathrm{s}}_{(1)}, \ldots, \omega^{\mathrm{s}}_{(N-1)}}_{\text{Simple interface}}, \underbrace{\Gamma^{\mathrm{s}}_{1}, \ldots, \Gamma^{\mathrm{s}}_{n}}_{\text{Scalars}}, \underbrace{\boldsymbol{c}^{\mathrm{s}}_{1}, \ldots, \boldsymbol{c}^{\mathrm{s}}_{m}}_{\text{Vectors}}, \underbrace{\boldsymbol{C}^{\mathrm{s}}_{1}, \ldots, \boldsymbol{C}^{\mathrm{s}}_{k}}_{\text{Tensors}}\Big)$$



Surface area fraction of
particles, polymers, ...



Director field, lattice vectors, ...



Orientation tensors

Extension to complex interfaces

- Procedure identical to that for simple interfaces:

$$s^{\mathrm{s}} = s^{\mathrm{s}}\left(u^{\mathrm{s}}, \hat{\Omega}, \omega^{\mathrm{s}}_{(1)}, \ldots, \omega^{\mathrm{s}}_{(N-1)}, \Gamma^{\mathrm{s}}_{1}, \ldots, \Gamma^{\mathrm{s}}_{n}, \boldsymbol{c}^{\mathrm{s}}_{1}, \ldots, \boldsymbol{c}^{\mathrm{s}}_{m}, \boldsymbol{C}^{\mathrm{s}}_{1}, \ldots, \boldsymbol{C}^{\mathrm{s}}_{k}\right)$$

- Take material time derivative

$$\rho^{\mathrm{s}} \frac{\mathrm{d}_{\mathrm{s}} s^{\mathrm{s}}}{\mathrm{d}t} = \frac{\rho^{\mathrm{s}}}{T^{\mathrm{s}}} \frac{\mathrm{d}_{\mathrm{s}} u^{\mathrm{s}}}{\mathrm{d}t} - \frac{\gamma \rho^{\mathrm{s}}}{T^{\mathrm{s}}} \frac{\mathrm{d}_{\mathrm{s}} \hat{\Omega}}{\mathrm{d}t} - \frac{\rho^{\mathrm{s}}}{T^{\mathrm{s}}} \sum_{J=1}^{N} \mu^{\mathrm{s}}_{(J)} \frac{\mathrm{d}_{\mathrm{s}} \omega^{\mathrm{s}}_{(J)}}{\mathrm{d}t} \boxed{- \sum_{n} \frac{\rho^{\mathrm{s}} \Xi^{\mathrm{s}}_{n}}{T^{\mathrm{s}}} \frac{\mathrm{d}_{\mathrm{s}} \Gamma^{\mathrm{s}}_{n}}{\mathrm{d}t} - \sum_{m} \frac{\rho^{\mathrm{s}}}{T^{\mathrm{s}}} \boldsymbol{w}^{\mathrm{s}}_{m} \cdot \frac{\mathrm{d}_{\mathrm{s}} \boldsymbol{c}^{\mathrm{s}}_{m}}{\mathrm{d}t} - \sum_{k} \frac{\rho^{\mathrm{s}}}{T^{\mathrm{s}}} \boldsymbol{W}^{\mathrm{s}}_{k} : \frac{\mathrm{d}_{\mathrm{s}} \boldsymbol{C}^{\mathrm{s}}_{k}}{\mathrm{d}t}}$$

- Use surface energy, mass, and component mass balance to eliminate derivatives of $u^{\mathrm{s}},\ \hat{\Omega},\ \omega^{\mathrm{s}}_{(J)}$
- Substitute result in surface entropy balance

Extension to complex interfaces

- Interface with one tensorial structural variable:

$$\overline{\boldsymbol{\sigma}}^{\mathrm{s}} = 2\varepsilon_{\mathrm{s}}\overline{\boldsymbol{D}}^{\mathrm{s}} + 2L^{\mathrm{s}}\overline{\boldsymbol{W}}^{\mathrm{s}}$$

$$\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}} = \varepsilon_{\mathrm{d}}\mathrm{tr}\boldsymbol{D}^{\mathrm{s}} + 2M^{\mathrm{s}}\mathrm{tr}\boldsymbol{W}^{\mathrm{s}}$$

$$\rho^{\mathrm{s}}\frac{\mathrm{d}_{\mathrm{s}}\boldsymbol{C}^{\mathrm{s}}}{\mathrm{d}t} = 2X_{0}^{\mathrm{s}}\boldsymbol{D}^{\mathrm{s}} + X^{\mathrm{s}}\boldsymbol{W}^{\mathrm{s}}$$

- Expression for the tensor **W**$^{\mathrm{s}}$:

$$\boldsymbol{W}^{\mathrm{s}} \equiv T^{\mathrm{s}}\left(\frac{\partial s^{\mathrm{s}}}{\partial \boldsymbol{C}^{\mathrm{s}}}\right)_{\bar{u}^{\mathrm{s}},\hat{\Omega},\omega_{(J)}^{\mathrm{s}}}$$

$$s^{\mathrm{s}} = s_0^{\mathrm{s}} + \frac{\nu_1}{2T^{\mathrm{s}}}\boldsymbol{C}^{\mathrm{s}}:\boldsymbol{C}^{\mathrm{s}} + \frac{\nu_2}{3T^{\mathrm{s}}}\mathrm{tr}\left(\boldsymbol{C}^{\mathrm{s}}\cdot\boldsymbol{C}^{\mathrm{s}}\cdot\boldsymbol{C}^{\mathrm{s}}\right) + \frac{\nu_3}{4T^{\mathrm{s}}}\mathrm{tr}\left(\boldsymbol{C}^{\mathrm{s}}\cdot\boldsymbol{C}^{\mathrm{s}}\cdot\boldsymbol{C}^{\mathrm{s}}\cdot\boldsymbol{C}^{\mathrm{s}}\right) + \ldots.$$

Extension to complex interfaces

- Interface with one tensorial structural variable:

$$\left.\begin{aligned}
\overline{\boldsymbol{\sigma}}^{\mathrm{s}} &= 2\varepsilon_{\mathrm{s}}\overline{\boldsymbol{D}}^{\mathrm{s}} + 2L^{\mathrm{s}}\overline{\boldsymbol{W}}^{\mathrm{s}} \\
\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}} &= \varepsilon_{\mathrm{d}}\mathrm{tr}\boldsymbol{D}^{\mathrm{s}} + 2M^{\mathrm{s}}\mathrm{tr}\boldsymbol{W}^{\mathrm{s}} \\
\rho^{\mathrm{s}}\frac{\mathrm{d}_{\mathrm{s}}\boldsymbol{C}^{\mathrm{s}}}{\mathrm{d}t} &= 2X_{0}^{\mathrm{s}}\boldsymbol{D}^{\mathrm{s}} + X^{\mathrm{s}}\boldsymbol{W}^{\mathrm{s}}
\end{aligned}\right\} \Longrightarrow
\begin{aligned}
\overline{\boldsymbol{\sigma}}^{\mathrm{s}} &= 2\varepsilon_{s}\overline{\boldsymbol{D}}^{\mathrm{s}} + 2L^{\mathrm{s}}\nu_{1}\overline{\boldsymbol{C}}^{\mathrm{s}} + 2L^{\mathrm{s}}\nu_{2}\overline{\boldsymbol{C}^{\mathrm{s}}\cdot\boldsymbol{C}^{\mathrm{s}}} \\
\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}} &= \varepsilon_{d}\mathrm{tr}\boldsymbol{D}^{\mathrm{s}} + 2M^{\mathrm{s}}\nu_{1}\mathrm{tr}\boldsymbol{C}^{\mathrm{s}} + 2M^{\mathrm{s}}\nu_{2}\left(\boldsymbol{C}^{\mathrm{s}}:\boldsymbol{C}^{\mathrm{s}}\right) \\
\frac{\mathrm{d}_{\mathrm{s}}\boldsymbol{C}^{\mathrm{s}}}{\mathrm{d}t} &= 2\hat{X}_{0}^{\mathrm{s}}\boldsymbol{D}^{\mathrm{s}} + \frac{1}{\tau_{1}}\boldsymbol{C}^{\mathrm{s}} + \frac{1}{\tau_{2}}\boldsymbol{C}^{\mathrm{s}}\cdot\boldsymbol{C}^{\mathrm{s}}
\end{aligned}$$

Extension to complex interfaces

- Interface with one tensorial structural variable:

$$\overline{\boldsymbol{\sigma}}^{s} = 2\varepsilon_{s}\overline{\boldsymbol{D}}^{s} + 2L^{s}\nu_{1}\overline{\boldsymbol{C}}^{s} + 2L^{s}\nu_{2}\overline{\boldsymbol{C}^{s}\cdot\boldsymbol{C}^{s}}$$

$$\mathrm{tr}\boldsymbol{\sigma}^{s} = \varepsilon_{d}\mathrm{tr}\boldsymbol{D}^{s} + 2M^{s}\nu_{1}\mathrm{tr}\boldsymbol{C}^{s} + 2M^{s}\nu_{2}\left(\boldsymbol{C}^{s}:\boldsymbol{C}^{s}\right)$$

$$\frac{\mathrm{d}_{s}\boldsymbol{C}^{s}}{\mathrm{d}t} = \underbrace{2\hat{X}_{0}^{s}\boldsymbol{D}^{s}}_{\text{Drives structure out of equilibrium}} + \underbrace{\frac{1}{\tau_{1}}\boldsymbol{C}^{s} + \frac{1}{\tau_{2}}\boldsymbol{C}^{s}\cdot\boldsymbol{C}^{s}}_{\text{Nonlinear relaxation back to equilibrium}}$$

Nonlinear viscoelastic behavior

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Swiss Federal Institute of Technology Zurich

Extension to complex interfaces

- When deformation is uniform, relaxation effects are linear, and

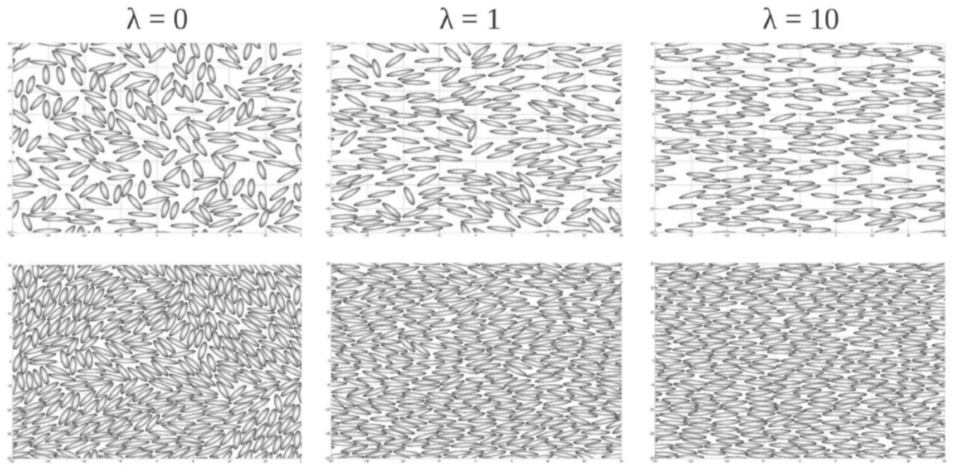
$$\boldsymbol{\sigma}^{\mathrm{s}} \sim \boldsymbol{C}^{\mathrm{s}}$$

$$\frac{\partial \boldsymbol{\sigma}^{\mathrm{s}}}{\partial t} + \frac{1}{\tau_{\mathrm{s}}} \boldsymbol{\sigma}^{\mathrm{s}} = 2\hat{X}_0^{\mathrm{s}} \boldsymbol{D}^{\mathrm{s}}$$

linear Maxwell model

Extension to complex interfaces

- Example: interface stabilized with hard ellipsoids [5]



$$s^s = s^s_{fs} + s^s_{id} + s^s_{excl}$$

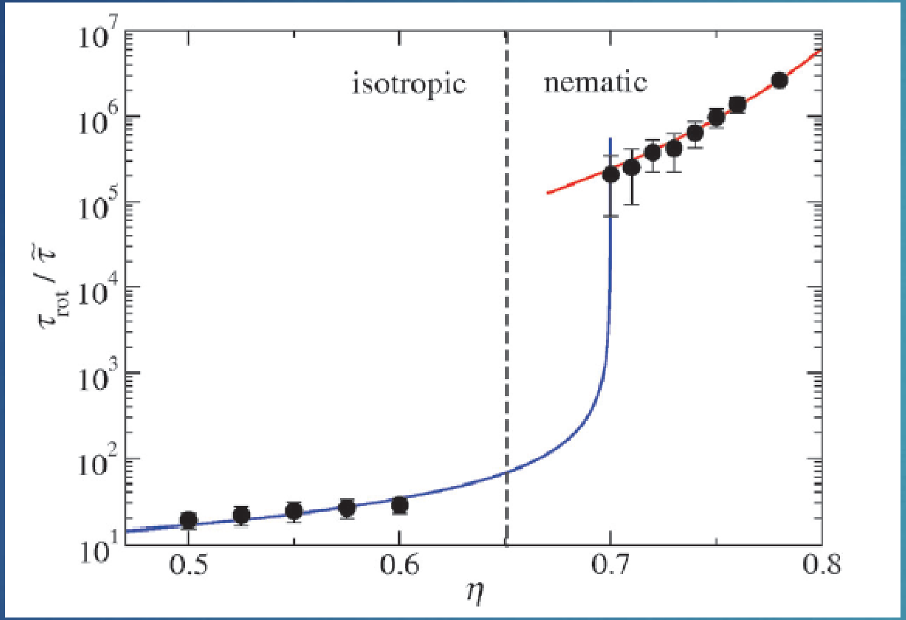
$$s^s_{id} = k_B n_p \left(\tfrac{1}{2} \ln(1 - S_2) + \tfrac{1}{2} S_2 - \tfrac{3}{4}(S_2)^2 + \tfrac{1}{6}(S_2)^3 - \tfrac{1}{8}(S_2)^4 + \tfrac{1}{10}(S_2)^5 - \tfrac{1}{18}(S_2)^6 \right)$$

$$s^s_{excl} = k_B n_p \left(\eta + a\eta^2 \right) \left(b(S_2)^2 + c(S_2)^4 \right)$$

$$S_2 = \sqrt{2\boldsymbol{C}^s : \boldsymbol{C}^s - 2tr\boldsymbol{C}^s + 1}$$

Extension to complex interfaces

- Example: interface stabilized with hard ellipsoids*



Rotational relaxation time determined from EDMD

$$\boldsymbol{\sigma}^s = 2T\left[\boldsymbol{C}^s \cdot \frac{\partial s^s}{\partial \boldsymbol{C}^s} - \left(\boldsymbol{C}^s : \frac{\partial s^s}{\partial \boldsymbol{C}^s}\right)\boldsymbol{C}^s\right]$$

Time evolution structural tensor:

$$\frac{\partial \boldsymbol{C}^s}{\partial t} \underbrace{-(\nabla_s \boldsymbol{v}^s)\cdot\boldsymbol{C}^s - \boldsymbol{C}^s\cdot(\nabla_s \boldsymbol{v}^s)^T}_{\text{Convection}} + 2(\boldsymbol{C}^s : \nabla_s \boldsymbol{v}^s)\boldsymbol{C}^s + \underbrace{\frac{1}{\tau_{eff}}\left(\boldsymbol{C}^s - \tfrac{1}{2}\boldsymbol{I}\right)}_{\text{Relaxation}} = 0$$

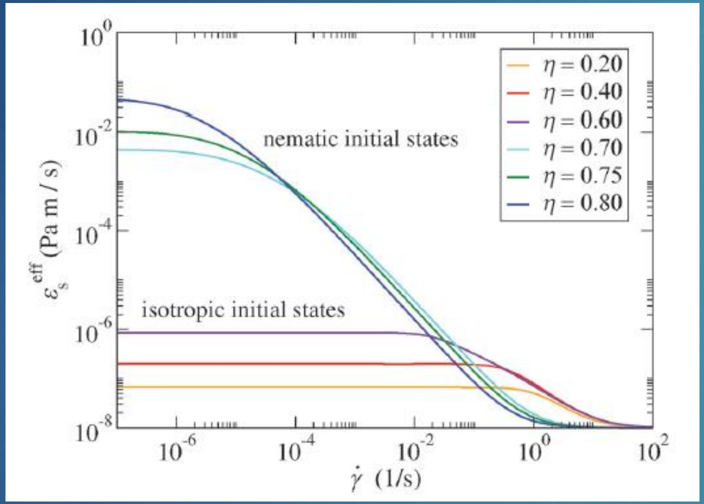
$$\frac{1}{\tau_{eff}} = \frac{f(\eta, S_2)(S_4 - 1)}{k_B n_p}\frac{1}{\tau_{rot}}$$

$$S_4 = \langle \cos 4\theta \rangle$$

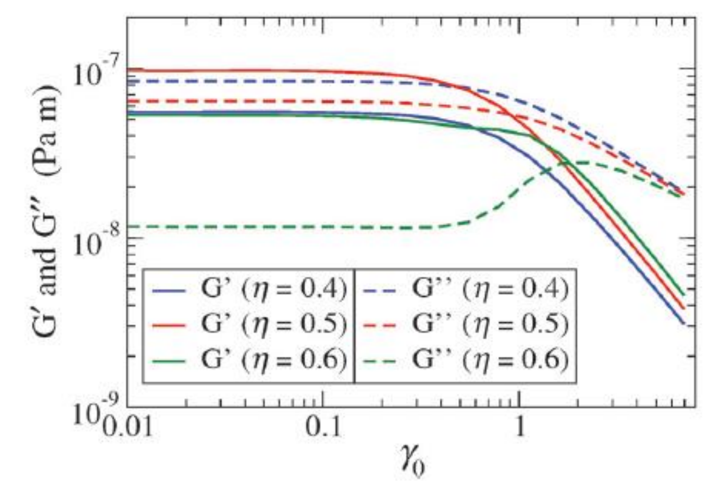
*Developed using GENERIC

Extension to complex interfaces

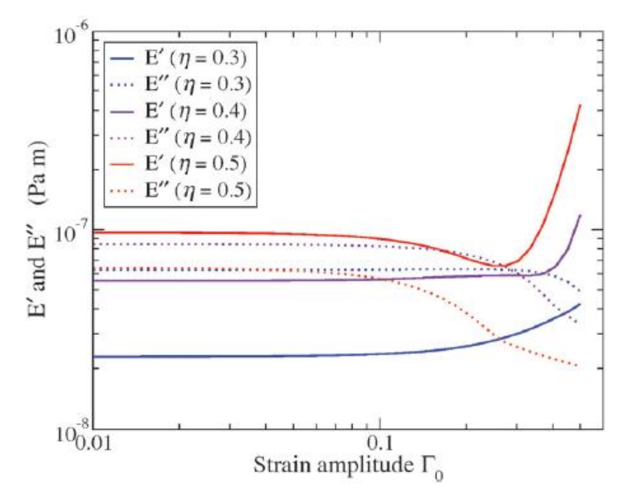
- Example: interface stabilized with hard ellipsoids



Response in simple shear



Response in oscillatory shear



Response in oscillatory dilatation

Other approaches for complex interfaces

- Extended irreversible thermodynamics: $s^{\mathrm{s}} = s^{\mathrm{s}}\left(u^{\mathrm{s}}, \hat{\Omega}, \omega^{\mathrm{s}}_{(1)}, \ldots, \omega^{\mathrm{s}}_{(N-1)}, \mathrm{tr}\,\boldsymbol{\sigma}^{\mathrm{s}}, \boldsymbol{j}^{\mathrm{s}}_{(1)}, \ldots, \boldsymbol{j}^{\mathrm{s}}_{(N-1)}, \boldsymbol{q}^{\mathrm{s}}, \overline{\boldsymbol{\sigma}}^{\mathrm{s}}\right)$

$$\frac{\mathrm{d}_{\mathrm{s}}\overline{\boldsymbol{\sigma}}^{\mathrm{s}}}{\mathrm{d}t} - \overline{\boldsymbol{\sigma}}^{\mathrm{s}}\cdot\left(\nabla_{\mathrm{s}}\boldsymbol{v}^{\mathrm{s}}\right)^{\mathrm{T}} - \left(\nabla_{\mathrm{s}}\boldsymbol{v}^{\mathrm{s}}\right)\cdot\overline{\boldsymbol{\sigma}}^{\mathrm{s}} + \frac{1}{\tau_{\mathrm{s}}}\overline{\boldsymbol{\sigma}}^{\mathrm{s}} + \frac{\alpha_{\mathrm{s}}}{\varepsilon_{\mathrm{s}}}\overline{\boldsymbol{\sigma}}^{\mathrm{s}}\cdot\overline{\boldsymbol{\sigma}}^{\mathrm{s}} = 2\frac{\varepsilon_{\mathrm{s}}}{\tau_{\mathrm{s}}}\overline{\boldsymbol{D}}^{\mathrm{s}}$$

$$\frac{\mathrm{d}_{\mathrm{s}}\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}}}{\mathrm{d}t} + \frac{1}{\tau_{\mathrm{d}}}\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}} + \frac{\alpha_{\mathrm{d}}}{\varepsilon_{\mathrm{d}}}\left(\mathrm{tr}\boldsymbol{\sigma}^{\mathrm{s}}\right)^2 = \frac{2\varepsilon_{\mathrm{d}}}{\tau_{\mathrm{d}}}\mathrm{tr}\boldsymbol{D}^{\mathrm{s}}$$

Surface Giesekus model [1]

- GENERIC

$$\frac{dA}{dt} = \{A, E\} + \{A, E\}^{\mathrm{mint}} + [A, S]$$

Bracket formulation well suited for the construction of nonlinear structural models

Summary

- Introduced Gibbs dividing surface model
- Discussed definition of surface excess variables; distinguished ambiguous/non-ambiguous variables, and choices for location of dividing surface.
- Discussed conservation principles for mass, momentum, energy, and entropy
- Illustrated constitutive modelling within CIT, using the entropy balance; derived constitutive equations for bulk and surface fluxes, and boundary conditions for bulk-interface coupling
- Discussed extension to systems with complex interfaces: CIT with internal structural variables

Outlook

- Structural models for realistic systems (interfaces with attractive particles, 2d emulsions, …
- Flow solvers which can handle these nonlinear equations
- Microscopic simulations for determining surface transport coefficients
- Accurate experimental data to compare models

Literature

[1] Sagis L.M.C., Reviews of Modern Physics, **83**, 1367 (2011).

[2] Slattery J.C., Sagis L.M.C, Oh E.-S., Interfacial Transport Phenomena, 2nd Ed., Springer Verlag, New York, 2007.

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[4] Kjelstrup S., Bedeaux, D., Non-Equilibrium Thermodynamics of Heterogeneous Systems, World Scientific Pub. Co., Singapore, 2008.

[5] Luo A.M., Sagis L.M.C., Öttinger H.C., De Michele C., Ilg P., Soft Matter, **11**, 4383 (2015).

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