Getting into the skin of thin-skinned emulsion drops stressed by elasticity and capillarity

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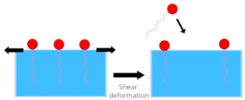
INTRODUCTION : ELASTOCAPILLARY INTERFACES

An increasing number of multi-phase systems exploit complex interfaces with interfacial stresses of multiple origins. Despite growing efforts, simple and reliable experimental characterisation of the interfacial properties remains a challenge, especially when the quantification of dilational interfacial properties is sought. Here we combine theory and Surface Evolver simulations to revisit the use of capillary pressure tensiometry of initially spherical drops attached to a needle in the absence of gravity. We consider a model interface in which stresses arising from a constant interfacial tensionare superimposed with mechanical extra-stresses arising from the deformation of a solid-like, incompressible interfacial layer of finite thickness. We compare our results with an experimental system where the polymeric skin is created via the deposition of poly-electrolyte multi-layers.

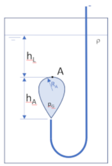


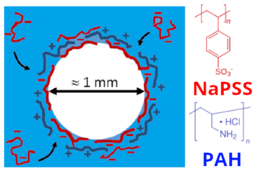
Capillary stress: between interfaces of immiscible fluids loaded with surfactant molecules. At thermodynamical equilibrium, the interfacial energy is characterised by its interfacial tension γ. Elastic response, when adsorption/desorption can be neglected, is refered to as Gibbs elasticity.[1,2]

Elastic stress: solid deformed reversibly from a reference state Ω_0 of null stress, to a deformed state Ω, with a (possibly) anisotropic stress. Material deformation for rubber-like material follows neo-Hooke elasticity.

EXPERIMENTS : POLY-ELECTROLYTES MULTI-LAYERS

Rising bubble elastometry registers bubble inner pressure and shape when subjected to inflation/deflation cycles. It is used to determine interfacial tension for simple interfaces, but also its elastic parameters[3]. Polymer deposition at the interface changes how the drop deforms in these cycles by forming a solid elastic skin. Below, our case study of an air-water interface with successive layer-by-layer depositions of NaPSS and PAH polymers.





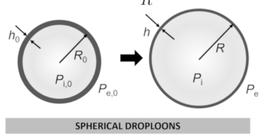
How does the interfacial properties change during the polymer deposition ?
What is the general law describing it ?

THEORY : SPHERICAL DROPS

Pressure difference ΔP at a liquid-liquid interface relates to its radius of curvature R and its interfacial tension γ through the Young-Laplace relation. Extension to elastic interfaces by replacing interfacial tension by total interfacial stress. Explicit expression of the stress depends on the material type.

$$\Delta P_{io} = P_i - P_o = 2\frac{\gamma}{R}$$

$$\Delta P = 2\frac{(\gamma + \sigma_e)}{R}$$



$$\sigma_G = \gamma + 2K_G \ln\left(\frac{R}{R_0}\right)$$

Gibbs elasticity : variation of surfactant molecules concentration at the interface

$$\sigma_{NH} = \gamma + G_{3D}h_0\left(1 - (\frac{R0}{R})^6\right)$$

Neo-Hooke elasticity : some hyperelastic materials (i.e. rubber)

$$\sigma_H = \gamma + 6G_{3D}h_0\left(\frac{R0}{R}) - 1\right)$$

Hooke elasticity : first order approximation of Gibbs and neo-Hooke laws in the small deformation limit

Corresponding normalised pressure-deformation laws :

$$\Delta\tilde{P} = \Delta P_{io}\frac{R_0}{2\gamma_0} = 1 + 2\alpha\ln(\lambda) \quad \text{Young-Laplace-Gibbs}$$

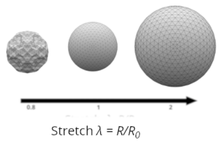
$$= 1 + \frac{\alpha}{3}(1 - \lambda^{-6}) \quad \text{Young-Laplace-Neo-Hooke}$$

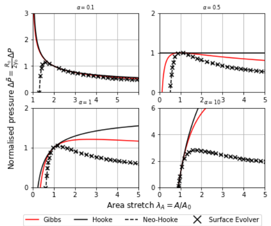
$$= 1 + 2\alpha(\lambda - 1) \quad \text{Young-Laplace-Hooke}$$

Elastocapillary number $\alpha = G_{3D}h_0/\gamma$ (Hooke and neo-Hooke) or K_G/γ (Gibbs)
Stretch ratio $\lambda = R/R_0$

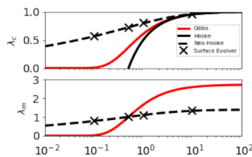
NUMERICAL SIMULATIONS : SURFACE EVOLVER

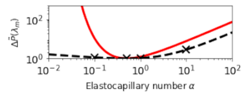
Surface Evolver[4] can be used to study neo-Hookean interfaces. Deformation is computed facet-wise by refering to initial and final shapes.





The model predicts how deflating a bubbloon can reduce the pressure difference across its interface to zero and induce buckling, due to the combined effects of surface tension and elastic stresses. The model also predicts the stretch λ_m for which the pressure difference goes through a maximum. These two features are absent for bubbles without elastic skins.

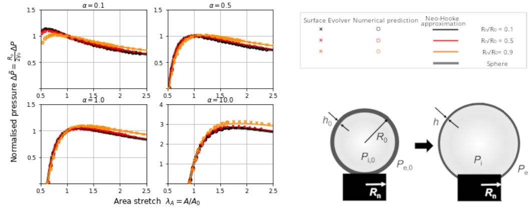




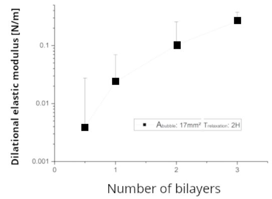
Code available online :
https://git.unistra.fr/gginot/pendant-elastic-droplet

RESULTS : DROPS ON NEEDLES

In pendant capsule elastometry, the spherical geometry is replaced by a truncated geometry. Adapted Young-Laplace-neo-Hooke equation predicts the pressure-deformation relation but not stretch anisotropy at the needle. Theoretical prediction and capsule elastometry equations compare very well with Surface Evolver results.



The simulations show that for small needle radii ($R_n/R_0<0.5$) and small deformations, the pressure-deformation relations are very well described by the sphere theory. We can therefore use the simple analytical relations to obtain the dilational elastic modulus of polymeric skins from experiments, shown here for the example of NaPSS/PAH multi-layers.



CONCLUSION

Surface Evolver is a reliable tool to predict pressure-deformation relations of elasto-capillary problems. In the absence of gravity, pressure-deformation of elasto-capillary drops on needles can be reliably approximated by simple theoretical expressions for spherical drops prodvided that $R_n/R_0<0.5$ and that deformations are small, i.e. shear at the needle is negligible.

Outlook

Check of validity with new physical systems
Impacts on drop-drop interactions and packing properties

Acknowledgements

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