## Thermodynamics of interfaces

Thermodynamics of interfaces and adsorption, surface tension, contact angle, wetting. Interaction between surfaces and stabilisation mechanisms (foams, emulsions).



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- 1. Concepts (surface tension, disjoining pressure, adsorption)
- 2. Wetting (contact angle, line tension, Wenzel and Cassie models)
- 3. (De)stabilization mechanisms in dispersed systems (gas in liquid: Foams)

## REFERENCES

Colloidal Domain Intermolecular and Surface forces



Physical Chemistry of Surfaces Capillarity and Wetting Phenomena The Physics of Foams





Capillarity and Wetting Phenomena Drops, Bubbles, Pearls, Waves

Springer



Some slides from Dominque Langevin and Douglas Durian

#### Introduction - Wetting



Fig. 1: A water droplet resting on superhydrophobic cotton.





#### Rain drops on Window



#### Leidenfoster effect



#### **Introduction - Surfaces**

#### Surface properties of Materials vs. Bulk properties





µ-Fluidics Nano-Fluidics





Foams / Emulsions

Particles@Interfaces Particles@Membranes

- 1. Interface
  - Intrinsic profile
  - L= *f*(size of object) < 1 nm



$$\rho(z) = \frac{1}{2} [\rho_1 + \rho_2 + (\rho_1 - \rho_2) \tanh(2 z/L)]$$





2. Interfacial tension  $\gamma$ (cohesive energy) nearest neighbours exchanges

$$E = A \int_{-\infty}^{+\infty} f_E(z) dz = E_1 + E_2 + \Delta E$$

$$\Delta E = \gamma A$$
 A is the





#### 2. Interfacial tension

2Dimensional version of P vs V (piston)



#### Interfacial tension Table

#### Energy cost/unit area

 $k_B T/R^2 = 4x10^{-21}/(0.3x10^{-9})^2 = 44 \text{ mN/m}$ 

(M. Gradzielsky)

Liquid Helium	0.2	mN/m
Octane	21	mN/m
Benzene	28	mN/m
Glycol	48	mN/m
Water	73	mN/m

Silica (SiO2)

76 mN/m

Metals (above Tm)

#### Aluminium Silver Iron

700 mN/m 1000 mN/m 1500 mN/m

#### 3. Capillarity: Laplace equation



$$\Delta p = -\gamma \nabla \cdot \hat{n}$$
$$= 2\gamma H$$
$$= \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$





$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

#### Nanobubble's pressure



Cite this: Soft Matter, 2011, 7, 40

www.softmatter.org

**TUTORIAL REVIEW** 

Very small bubbles at surfaces—the nanobubble puzzle

100 nm in water the extra pressure in the bubble is 1.45 MPa or  $\sim$ 14.3 atmospheres and for a 10 nm radius bubble, the extra pressure is 14.5 MPa.

#### Characteristic length scales





Capillary origami

#### wikipedia

#### 4. Van der Waals interactions

Hamaker constants calculated on the basis of the Lifshitz theory

Two media 1 and 2 interacting across a medium 3:

 $A_H = A_{H,0} + A_{H,v}$ 

$$A_{H,0} = \frac{3}{4} k_B T \left( \frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3} \right) \left( \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3} \right)$$
$$A_{H,v} = \frac{3h_P v_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{0.5}(n_2^2 + n_3^2)^{0.5}[(n_1^2 + n_3^2)^{0.5} + (n_2^2 + n_3^2)^{0.5}]}$$



 $A_{H,0} < (3/4)k_B T$ 

where  $k_B$  is the Boltzmann constant,  $h_P$  is the Planck constant (6.626 10<sup>-34</sup> J.s) and  $\nu_e$  is the main electronic absorption frequency ( $\approx 3 \ 10^{15} \ s^{-1}$ ).

Free energy per unit area between two planar surfaces spaced by a distance h due to Van der Waals long range force is:

 $V_{VdW} = -\frac{A_H}{12\pi h^2}$  (long range)

A<sub>H</sub>>0 attractive

A<sub>H</sub><0 repulsive

Symmetry → Attraction (Foam Lamella) *thinning* 

Asymmetry → Repulsion (Wetting on solid) *thickening* 

#### 5. Disjoining pressure

Free energy of a film L on a substrate S (or G/L/G or L1/L2/L1 systems)



## Up to now pure (L, S, G) systems, now binary or more systems

$$dU = T \cdot dS - p \cdot dV + \sum_{i} \mu_{i} \cdot dn_{i}$$

Surface (interface):

$$n_{i,s} = n_i - n_{i,\alpha,b} - n_{i,\beta,b}$$
  

$$V_s = V - V_{\alpha,b} - V_{\beta,b}$$
 (interphase)

$$U_s = U - U_{\alpha,b} - U_{\beta,b}$$

$$S_s = S - S_{\alpha,b} - S_{\beta,b}$$

$$dU_S = T \, dS_S - p \, dV_S + \sigma \, dA + \sum_i \mu_i \, dn_{i,S}$$

"the fundamental equation of colloid and interface science"



Advances in Colloid and Interface Science Volume 256, June 2018, Pages 163-192 CHINADO CHINAD

#### Historical perspective

The chemical (not mechanical) paradigm of thermodynamics of colloid and interface science George Kaptay 🛛







$d\sigma_{SV} = -\Gamma d\mu + S dT$	(Gibbs adsorption)
$(d\sigma_{SV}/d\mu)_T = -\Gamma$	$\boldsymbol{\mu}$ is the chemical potential
$d\mu = k_B T dln(c)$	(dilute)

 $\Gamma = -1/k_{B}T (d\sigma_{SV}/dlnc)_{T}$ 

When surface active species interact with each others this equation is not valid anymore



Reviews of Modern Physics, Vol. 71, No. 3, April 1999 Kaganer, Möhwald, and Dutta: Structure and phase transitions in Langmuir monolayers

#### Summary Part 1: Concepts

- Interface
- Interface tension
- Capillarity
- Disjoining Pressure (VdW, EDL, DLVO + ....)
- Adsorption
- 3D to 2D concepts



Ζ



## 1. Concepts (surface tension, disjoining pressure, adsorption)

- 2. Wetting (contact angle, line tension, Wenzel and Cassie models)
- 3. (De)stabilization mechanisms in dispersed systems (gas in liquid: Foams)

#### 3 Phases, 3 Interfaces, 1 contact line (triple line)



 $S_0 = \sigma_{SG} - \sigma_{SL} - \gamma$ , initial (or dry) spreading coefficient

Young equation  $\cos \alpha_E = (\sigma_{SG} - \sigma_{SL}) / \gamma$ . (Horizontal f

(Horizontal force balance)



$$E(\alpha) = \sigma_{SG}A - \sigma_{SG}A_0 + \sigma_{SL}A_0 + \gamma A_{LG}.$$

Constant Volume (area is changing)

$$A_0 = \pi R_0(\alpha)^2 \sin^2 \alpha.$$
  

$$A_{LG} = 2\pi R_0(\alpha)^2 (1 - \cos \alpha)$$
  

$$R_0(\alpha) = V^{\frac{1}{3}} \left[ \frac{\pi}{3} (2 - 3\cos \alpha + \cos^3 \alpha) \right]^{-\frac{1}{3}}$$

Minimum in free Energy  $E(\alpha)$ :

Young Equation

$$\cos \alpha_E = (\sigma_{SG} - \sigma_{SL}) / \gamma.$$

## b) Solid particle on liquid surface



Particle keeps constant Volume and Area

$$E(\alpha) = \gamma A + 2\pi R^2 \left[ \sigma_{SG} (1 - \cos \alpha) + \sigma_{SL} (1 + \cos \alpha) - \frac{1}{2} \gamma \sin^2 \alpha \right].$$

$$(\sigma_{SG} - \sigma_{SL})/\gamma = -z_0/R = \cos \alpha_E.$$

The imbalance due to  $\alpha \neq \alpha_E$  produces a force  $F_l = -\frac{dE}{ds}$ , where *s* represents the displacement of the contact line on the solid

 $F_l(\alpha) = 2\pi R_d \gamma(\cos\alpha_E - \cos\alpha) = 2\pi R_0(\alpha) \sin\alpha \gamma(\cos\alpha_E - \cos\alpha).$ 





Self-running droplet

For a spherical particle, the displacement of the contact line is the longitudinal coordinate  $s = R\theta(\theta)$  is the polar angle in spherical coordinates.

 $F_l(\alpha) = 2\pi R \sin \alpha \gamma (\cos \alpha_E - \cos \alpha).$ 



#### Free Energy and Force on the line



R=1  $\mu$ m silica/water/air , E =10<sup>6</sup>...10<sup>7</sup> k<sub>B</sub>T PARTICLE:

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R=1 nm silica/water/air , E =1...10 k_BT
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Stocco, A. Nobili, M. Advances in Colloid and Interface Science 2017



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# ANALISTICAL STATE



Fig.6 A large heavy solid object floating on a liquid surface, separated by a large amount of small solid particles at the liquid/gas interface

cannot hold any weight. Now, let us substitute easily accessible parameters into Eq.(6i): r = 1 µm, f = 0.8,  $g = 9.81 \text{ m/s}^2$ ,  $\sigma_{L/G} = 0.07 \text{ J/m}^2$ ,  $\Theta = 60^\circ$ , resulting to  $\left(\frac{m \cdot g}{A}\right)_{max} = 56 \text{ kN/m}^2$  (note: area of a sandal of an adult male is about 300 cm<sup>2</sup> = 0,03 m<sup>2</sup>. Multiplying the two latter values and dividing the result by the value of g, the maximum mass of the adult male in sandals hold by the above force is 171 kg. So, if still water is covered by a large amount of micron-sized particles, it can easily hold an adult male in a sandal in a way that nor the sandal neither the foot of the male becomes wet (see the Bible claiming Jesus walking on water).

#### Historical perspective

The chemical (not mechanical) paradigm of thermodynamics of colloid and interface science George Kaptay 🛙

#### It was not a miracle!



7. Line tension k (important for bilayers, membranes...) for macroscopic drops



 $\cos \alpha_{eq} = (\sigma_{SG} - \sigma_{SL}) / \gamma.$ 











$$E(\alpha) = \gamma A + 2\pi R^2 \left[ \sigma_{SG} (1 - \cos \alpha) + \sigma_{SL} (1 + \cos \alpha) - \frac{1}{2} \gamma \sin^2 \alpha + \frac{k}{R} \sin \alpha \right]$$

$$\cos \mathcal{A}_{eq} = \cos \alpha_{eq} + \frac{k}{\gamma R} \frac{\cos \mathcal{A}_{eq}}{\sin \mathcal{A}_{eq}} \qquad \text{(particle)}$$





- Minimum could vanish
- Metastable states
- Particles behaves differently depending upon the original location

Important for: nanodrops and nanobubbles high aspect ratio and nano- particles And for lipid domains in membranes



### How the wetting state is related to VdW , EDL, disjoining pressure ?





### How the wetting state is related to VdW , EDL, disjoining pressure ?





How the wetting state is related to VdW , EDL, disjoining pressure ?



Interfacial tension and contact angle of the droplet give the potential P at h<sub>m</sub> !

Does the equilibrium contact angle change with the drop (bubble) size?

Does the equilibrium contact angle change with the particle size?



S<sub>0</sub><0

 $\alpha_{\mathsf{E}}$ 

 $\sigma_{SL}$ 

 $\sigma_{\text{SG}}$ 

7. Line tension k (important for bilayers, membranes...) for macroscopic drops



 $\cos \alpha_{eq} = (\sigma_{SG} - \sigma_{SL}) / \gamma.$ 











$$E(\alpha) = \gamma A + 2\pi R^2 \left[ \sigma_{SG} (1 - \cos \alpha) + \sigma_{SL} (1 + \cos \alpha) - \frac{1}{2} \gamma \sin^2 \alpha + \frac{k}{R} \sin \alpha \right]$$

$$\cos \mathcal{A}_{eq} = \cos \alpha_{eq} + \frac{k}{\gamma R} \frac{\cos \mathcal{A}_{eq}}{\sin \mathcal{A}_{eq}} \qquad \text{(particle)}$$





Nanobubbles

Size dependent contact angle

-

Lohse, Zhang, Rev Mod Phys 2015





Negative line tension!

Berg et al. PRL 2007

#### Particles at PS-air interface

PRL 109, 196101 (2012)

PHYSICAL REVIEW LETTERS

week ending 9 NOVEMBER 2012

#### Influence of Line Tension on Spherical Colloidal Particles at Liquid-Vapor Interfaces






As we did for the interfacial tension, we can estimate line tension values as nearest neighbours exchanges

Energy cost/unit length

kT/R =4x10<sup>-21</sup>/(0.3x10<sup>-9</sup>)=10<sup>-11</sup> N

Microscopic interpretation: line tension reflects the disjoining pressure





$$\gamma \Sigma + \Pi(h) + \rho g h = P_0$$
  
curvature (= 1/R<sub>0</sub>)

If  $R_0 > ca \ 1 \ \mu m$ , capillarity dominates  $\gamma \ \Sigma > \Pi(h)$ If  $R_0 < ca \ 1 \ \mu m$ , surface forces dominates  $\gamma \ \Sigma < \Pi(h)$ 



### EXPERIMENTS show spherical cap profiles for nanodrops and nanobubbles



Line tension can not be a constant for nanodrops ! It must be length scale dependent!

Stocco Möhwald Langmuir 2015

#### Attractive VdW



Local contact angle increases if *h* decreases

=

Positive line tension



=

Negative line tension

Criterion The contact angle of a nanodrop = local contact angle



This profile tells us all the spectrum of interactions between the two interface (disjoining pressure)

### First Summary Part 2: Wetting

- Wetting states
- Contact angle
- Line tension
- Role of Disjoining Pressure (VdW, EDL, DLVO + ....)
- Contact angle depends on the system size
- line tension is connected to the disjoining pressure





Roughness: Free energy (Wenzel model)

Drop:  $E(\alpha) = \sigma_{SG}A - \sigma_{SG}A_0 + \sigma_{SL}A_0 + \gamma A_{LG}.$  (no roughness)  $E(\alpha) = \sigma_{SG}A - \sigma_{SG}A_s + \sigma_{SL}A_s + \gamma A_{LG}$  $\cos \alpha_W = r \cos \alpha$ , where  $r = A_s / A_0$ G S Particle:



$$E(\alpha) = \gamma \mathbf{A} + 2\pi R^2 \left[ r \gamma_{SL} (1 + \cos \alpha) + r \gamma_{SG} (1 - \cos \alpha) - \frac{1}{2} \gamma \sin^2 \alpha \right]$$

$$A_s = A_0 (1 + 2\phi_s \frac{h_s}{R_s}),$$



Adhesion strength can be tuned by roughness

Minimum is deeper for drops and could vanish for paricles

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### Experiments: rough particles

Polymer NPs coating, smoothing by good solvent exposure



San-Miguel, Behrens Langmuir 2012



For planar solids with area fractions  $\phi$  of materials 1 and 2,  $\phi_1 + \phi_2 = 1$ :

$$E(\alpha) = \phi_1(\sigma_{S1G}A - \sigma_{S1G}A_0 + \sigma_{S1L}A_0) + \phi_2(\sigma_{S2G}A - \sigma_{S2G}A_0 + \sigma_{S2G}A_0) + \gamma A_{LG}$$

At the energy minimum, the "Cassie-Baxter" contact angle is defined as:

 $\cos\alpha_{CB} = \phi_1 \cos\alpha_{E,1} + \phi_2 \cos\alpha_{E,2}$ 

IF 2 is air,  $a_{E,2} = 180^{\circ}$  $\cos \alpha_{CB} = \phi \cos \alpha_{E,1} + (1-\phi) -1 =$ 

 $\cos\alpha_{CB} = \phi \cos\alpha_{E,1} - 1 + \phi$ 

Where  $\phi$  = Post area fraction or hydrophilic area fraction

IF  $\phi$  is close to zero  $\alpha_{CB}$  is close to 180°





Air trapped – « fakir » effect



In presence of an isolated defect of size *d* and force  $f_d = \gamma d [\cos(\alpha_d) - \cos\alpha]$ , (where  $\alpha_d$  is the contact angle on the defect) the contact line on the solid takes the form

 $u(x) = \frac{f_d}{\pi \gamma \sin^2 \alpha} \ln\left(\frac{L}{|x|}\right),$ 

Where *L* is a macroscopic distance related to the system size





 $\phi$  = defect density



Considering the case of isolated defects of size d $W = \frac{1}{2}Ku_m^2 = \frac{f_m^2 \ln(L/d)}{\gamma \pi \sin^2 \alpha}.$ 

In the case of surface roughness, instead, the specific energy W of a topographical defect of size d and height h can be written as:<sup>39</sup>

$$W = \frac{\gamma d^2 \sin^2(\frac{dh}{dy}) \ln(L/d)}{2\pi}.$$
$$\cos \alpha_R - \cos \alpha_A = \phi \ 2W,$$

Contact angle hysteresis is related to the defect energies!

Stocco, A. Nobili, M. Advances in Colloid and Interface Science 2017





### Second Summary Part 2: Macroscopic wetting

- Wenzel Model for rough or structured surfaces
- Cassie Model for heterogeneous surfaces
- Role of surface defects
- Contact angle Hysteresis









1. Concepts (surface tension, disjoining pressure, adsorption)

- 2. Wetting (contact angle, line tension, Wenzel and Cassie models)
- 3. (De)stabilization mechanisms in dispersed systems (gas in liquid: Foams)

### Foams: gas bubbles in a liquid



- Vertex
  - region where four Plateau borders meet
  - the point shared by four neighboring bubbles
- Plateau border
  - scalloped-triangular channel where three films meet
  - the edge shared by three neighboring bubbles



### Plateau's rules for dry foams

- for mechanical equilibrium:
  - i.e. for zero net force on a Plateau border,
  - zero net force on a vertex,
  - and  $\Sigma \Delta P=0$  going around a closed loop:
  - (1) films have constant curvature & intersect three at a time at 120°
  - (2) borders intersect four at a time at  $\cos^{-1}(1/3)=109.47^{\circ}$ 
    - rule #2 follows from rule #1
    - both are obviously correct if the films and borders are straight:





# Liquid distribution

- division of liquid between films-borders-vertices
  - Repulsion (between interfaces) vs surface tension
  - wet vs dry





### 5. Disjoining pressure

Free energy of a foam film (suspended film L)



Energy per unit area  $V_{VdW} = -\frac{A_H}{12\pi h^2}$  Attractive 1-30 nm  $V_{EDL} = \frac{64k_BTc_{ion,bulk}}{\kappa} \left( \tanh \frac{e\psi_0}{4k_BT} \right)^2 \exp(-\kappa h)$  Repulsive By surfactants

 $E(h) = \gamma + \gamma + P(h)$ Disjoining pressure  $\Pi(h) = -\frac{dP}{dh}$ (+)Repulsion Electrostatic (Electric Double Layer) Repulsive Force Interaction Energy Distance (nm) Total Force (-)Attraction London-van der Waals Attractive

Energy per unit area

1-1000 nm



Interfaces can be stabilised by surfactants, polymers or particles. The latter are the corresponding "Pickering" Aqueous Foams

### Foam Destabilisation Mechanisms (Dynamics)

- Drainage (gravity): decrease of  $\boldsymbol{\epsilon}$
- Coalescence: van der Waals,  $-A_H/12\pi d^2$
- Coarsening



elasticity

- $dP/dR = -\gamma/R^2 + 2K_s/R^2$
- P = bubble pressure R = bubble radius  $\gamma = surface tension$  $K_s = d\gamma/dln(A) = surface elasticity$



### Colloidal scale ------ Wetting -----Macroscopic scale



- 1. Is it really just wetting (Young equation)?
- 2. How colloids attach onto the water interface?





Thermal hopping of the contact line over surface defects



### Contact angle of NP is $\alpha_{E}$ ? In general NO. *f*(size, roughness, line tension)

Spontaneous adsorption? In general NO. VdW and EDL are repulsive

Fully packing? To be investigated

Contact angle induced curvature? Not really



Hierarchically structured material



hydrophobic

"Pickering" -Aqueous Foams



### In situ-contact angle by Ellipsometry (or by X-ray, Neutron @ILL)



3 parameters: R, h,  $\phi$  $\alpha$ =arccos(h/R)

2 fitting parameters

Spread layers,  $\Gamma$  known [mass/area] =  $f(\phi, R)$ 



In-situ  $\alpha$  measurements for spread particle layers!



### Adsorbed Particle Layer



Energy input to overcome an Electrostatic barrier

#### NO full pack

Data are more scattered for adsorbed layer when compared to Spread layers

Brewster angle microscopy → Interfacial Network



# Surface Tension - $\gamma(c)$ water dispersions





$$\label{eq:gamma} \begin{split} \Delta \gamma &= \Gamma^{10} \\ \text{2D percolation} \end{split}$$

- Fractal
- Particle network

t = 28

t = 48

t = 68

### Surface Elasticity – Oscillating drop/bubble experiments



0.1 wt %

65

A. Stocco et al, Soft Matter 2009



Films

Int<mark>e</mark>rface

Bubbles

### Free Suspended Foam Film

V= 5µL







c=0.05 wt %

c=0.5 wt %




## Fumed Silica aqueous foams production

Turbulent mixing DRY •  $\varepsilon = 0.2-0.1$ 

- Bubble size R =10-70  $\mu$ m
- Polydispersity 20%

By shaking WET

• ε = 0.34-0.2

- Bubble size R =100-300  $\mu$ m
- High Polydispersity > 20%

Foamability

c > 0.3 wt. % - shaking

c > 0.1 wt. % - t. mixing



A. Saint-Jalmes EPJB, 1999

## Foams: MLS multiple light scattering Diffusing Wave Spectroscopy



 $I_s \sim I^* / L \sim R / \sqrt{\epsilon}$ /\* = photon transport mean free path

No absorption and optically thick medium



 $\begin{array}{ll} \text{correlation function } <\!\!I_s(\tau) \; I_s(0)\!\!> \\ \text{single} & \tau_0 \; \text{relaxation time} \\ & \Gamma_1 \; \text{first cumulant} \end{array}$ 





D. Durian et al, PRA, 1996





Foam stability DRY ε=0.2 and c\*>0.7wt % WET

ε=0.34 and c\*>0.5 wt%



### **DWS-** Dynamic Scattering

J. Crassous and A. Saint-Jalmes, Uni. Rennes



Two modes in DWS:

A2 - Bubble : Slow mode (multiple scat.)

A1- Free particles: Fast mode - single scat.

A1 is related to c\_particle = 0.0002-0.01 wt.%

A. Stocco et al, PCCP 2011

## Wet Foams: X- $\mu$ CT



c = 0.9 wt. %

A. Stocco et al, Soft Matter 2011



DRY Foams Final mean diameter = 25  $\mu$ m

Low surface coverage! 4-8 mg/m<sup>2</sup>

Loose network (a)

#### WET Foams

*Appearance of few big bubbles Final mean diameter = 25-*30 μm

### Arrested coarsening mechanism



#### A. Stocco et al, Soft Matter 2011

Summary Part 3: Foam stability and dynamics

- Hierarchical levels in foams (macroscopic, bubble, film, interface)
- For c>c\*, particle stabilized foams are infinitely stable
- Surface elasticity and surface tension  $\gamma$  and the formation of an interfacial network rule foam stability vs. Coarsening.
- Particle networks in films and at the interface are observed





# Thank you !