

# Introduction to surfactants

- What are surfactants and why do we need them?
- Thermodynamics of interfaces
  - Surface Excess
  - Gibbs adsorption equation
- Adsorption from solution
  - Adsorption isotherms
- Equations of state
- States of monolayers
- Self-assembly of amphiphiles
- Effect of surfactants on wetting

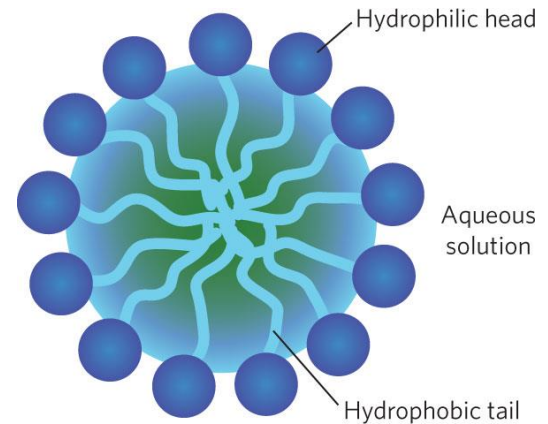
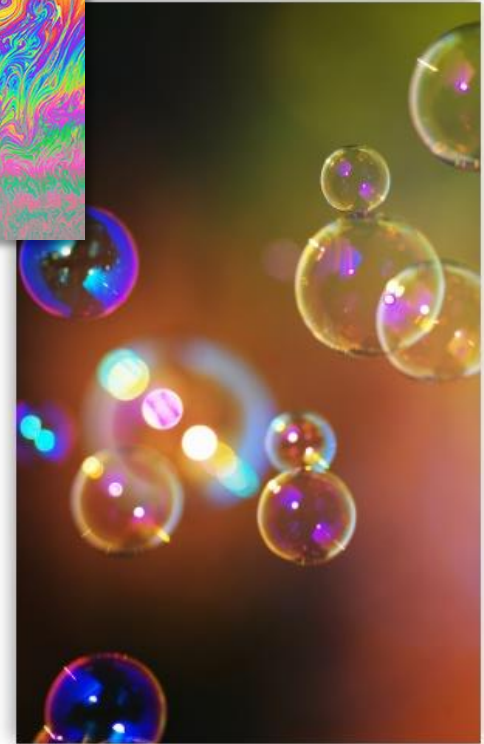
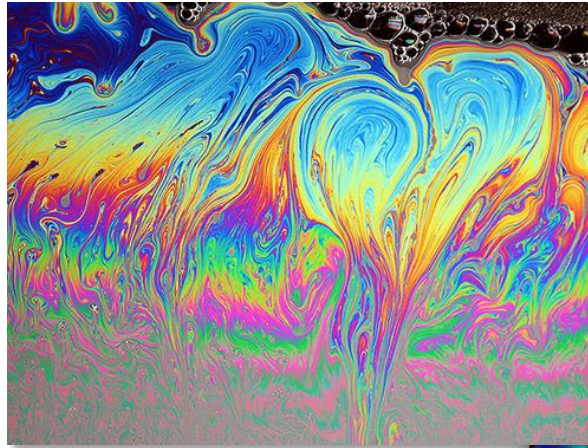
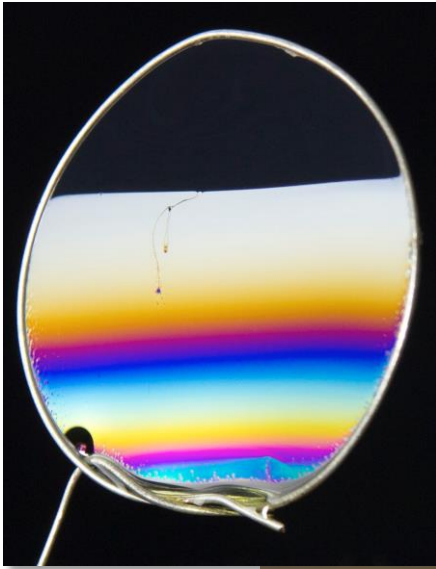


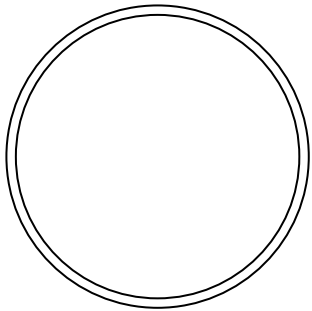
image: [www.nature.com/nmat/](http://www.nature.com/nmat/)

# Soap films and soap bubbles



# Soap bubbles

- Why is it not possible to make stable bubbles with pure water? What is the role of soap?
- Estimate the % reduction in energy cost of a soap bubble with soap compared to no soap



radius of the bubble:

$$R = 5 \text{ cm}$$

thickness of the liquid film:

$$h = 10 \text{ }\mu\text{m}$$

surface tension water-air:

$$\gamma_{\text{water}} = 70 \text{ mN/m}$$

surface tension soap water:

$$\gamma_{\text{soap}} = 25 \text{ mN/m}$$

- To make a soap bubble we blow air onto a soap film suspended onto a wire. Why do we get no bubbles if we don't blow sufficiently strongly?
- What happens to the liquid when you burst a soap bubble? Sketch the situation

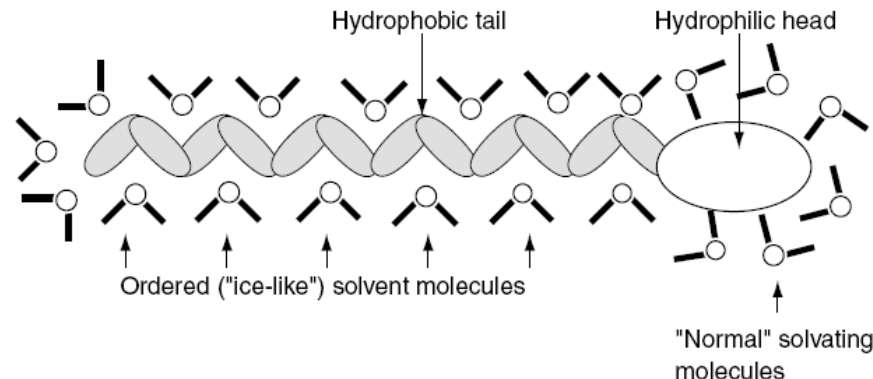
**Now watch the slow motion video of bursting bubbles:**

**<http://youtu.be/blNe2Ae5a2c?t=10s>**

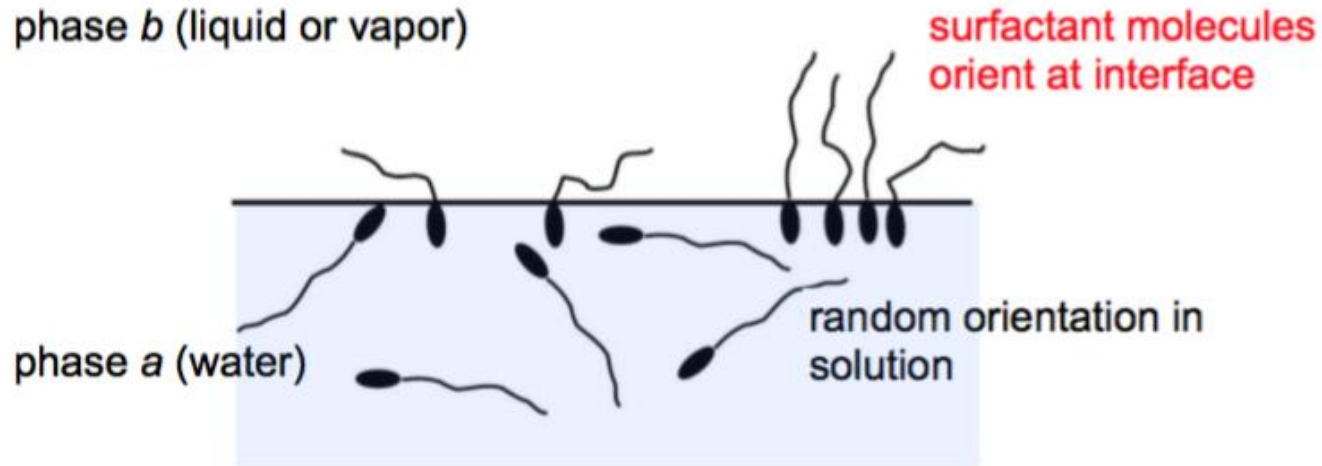
# Surface Active Agents

“Surface active” = surfactant molecules **adsorb** at liquid-gas or liquid-liquid interfaces

Energetically favorable to be at interface because of molecular structure: typical surfactant is **amphiphilic**, i.e., it combines hydrophilic groups and hydrophobic groups



# Surfactants adsorb at fluid interfaces

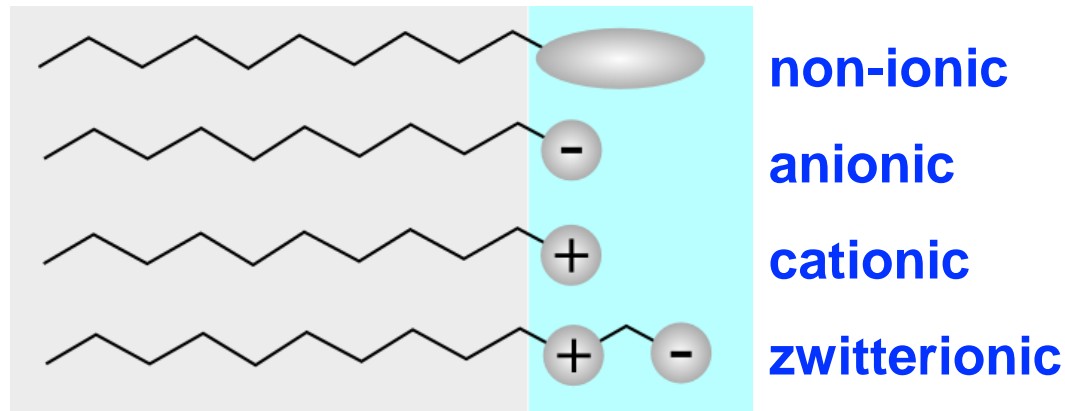


surfactants adsorbing at interfaces (e.g. air/water or oil/water) take a preferred orientation so as to minimise unfavourable interactions between aqueous phase and hydrophobic “tails”

# Molecular structure of surfactants

The major applications of surfactants are in **aqueous media**

The classification depends on the nature of the hydrophilic group



The hydrophilic group determines the main differences between surfactants, and therefore the effect of the surfactant type:

- **NON-IONIC**: stability in varying pH
- **ANIONIC**: detergents, adsorption on polar surfaces
- **CATIONIC**: adsorption on surfaces
- **ZWITTERIONIC**: found in cell membranes

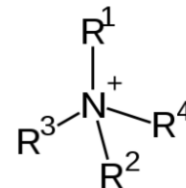
# Major applications of surfactants

Industrial	Consumer
Agricultural crop applications	Adhesives
Building materials	Cleaning fluids
Cement additives	Cosmetics
Coal fluidization	Disinfectants
Coating and leveling additives	Foods and beverages
Electroplating	Household cleaning and laundering
Emulsion polymerization	Paints
Graphic arts	Pharmaceuticals
Industrial cleaning	Photographic products
Leather processing	Soaps, shampoos, creams
Lubrication	Waxes and polishes
Mold release agents	
Ore flotation	
Paper manufacture	
Petroleum recovery	
Printing and printing inks	
Surface preparations	
Textiles	
Waterproofing	

# Molecular structure – Hydrophilic group (*head*)

Surfactants are classified according to their head group. Most commonly used hydrophilic compounds in commercial surfactants:


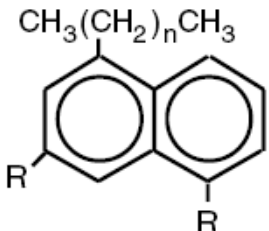
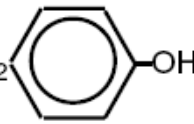
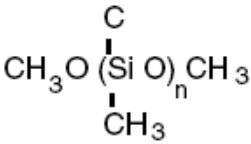
Class	General structure
Sulfonate	$\text{R-SO}_3^-$
Sulfate	$\text{R-OSO}_3^-$
Carboxylate (soap)	$\text{R-COO}^-$
Phosphate	$\text{R-OPO}_3^{2-}$
Hydroxyl	$\text{R-OH}$
Ether	$\text{R-O-R'}$
Polyoxyethylene (POE)	$\text{R-OCH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}$
Polyols	Sucrose, glycerol, ethylene glycol, etc
Ammonium	$\text{R}_x\text{H}_{4-x}\text{-N}^+$ , $x = 1-3$
Quaternary ammonium	$\text{R}^1 \text{R}^2 \text{R}^3 \text{R}^4\text{-N}^+$



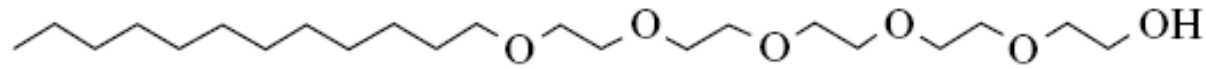


# Molecular structure – Hydrophobic group (*tail*)

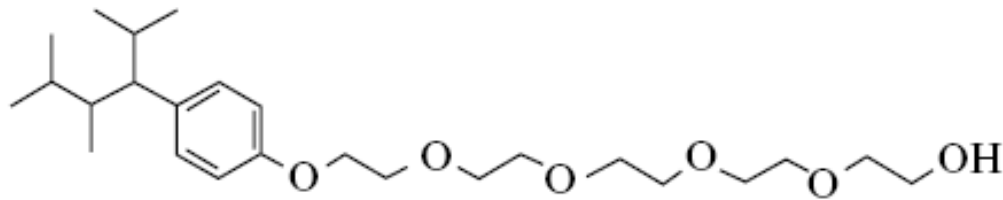
- The hydrophobic group of most surfactants is made up of hydrocarbons
- Typically linear chain
- Also aromatic groups
- Most commonly used hydrophobic materials in commercial surfactants:

$\text{CH}_3(\text{CH}_2)_n$ Natural fatty acids ( $n = 12-18$ )	$\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ Petroleum paraffins ( $n = 8-20$ )
$\text{CH}_3(\text{CH}_2)_n\text{CH}=\text{CH}_2$ Olefins	$\text{CH}_3(\text{CH}_2)_n\text{CH}_2$  Alkylbenzenes ( $n = 6-10$ , linear or branched )
 Alkylaromatics ( $n = 1-2$ for water soluble, $= 8$ or $9$ for oil soluble surfactants )	$\text{CH}_3(\text{CH}_2)_n\text{CH}_2$  Alkylphenols ( $n = 6-10$ , linear or branched )
$\text{CH}_3\underset{\text{X}}{\text{CH}}\text{CH}_2\text{O}\underset{\text{CH}_3}{\text{CH}}(\text{CH}_2)_n$ Polyoxypropylene ( $n =$ degree of oligomerization, $\text{X} =$ oligomerization initiator )	$\text{CF}_3(\text{CF}_2)_n\text{COOH}$ Fluorocarbons ( $n = 4-8$ , may be branched or H-terminated )
	 Silicones

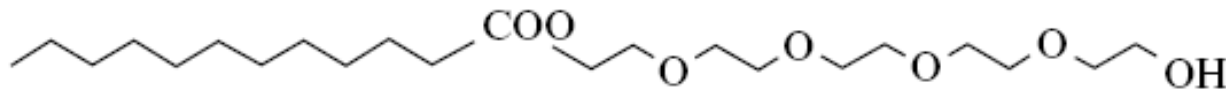
**Non-ionic** surfactants: Used in detergents, food products, pharmaceuticals, cosmetics, pesticides, etc.



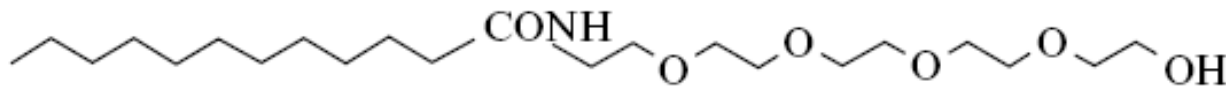
Fatty alcohol ethoxylate



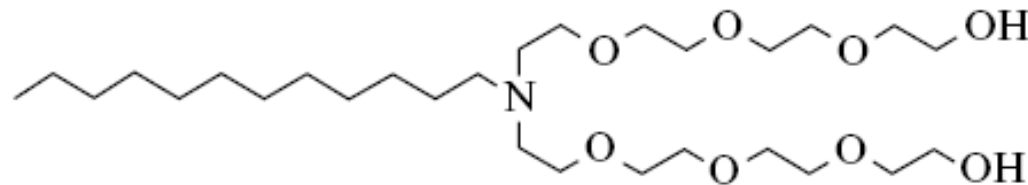
Alkylphenol ethoxylate



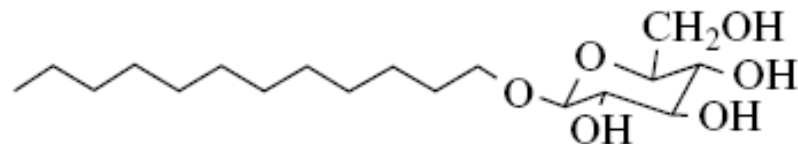
Fatty acid ethoxylate



Fatty amide ethoxylate

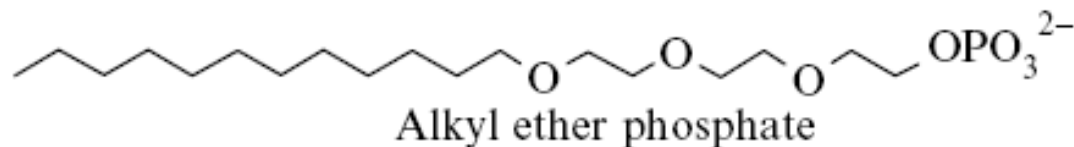
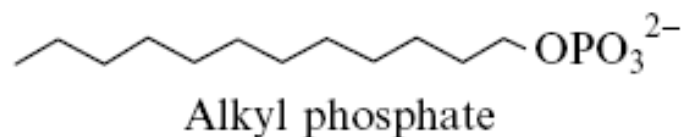
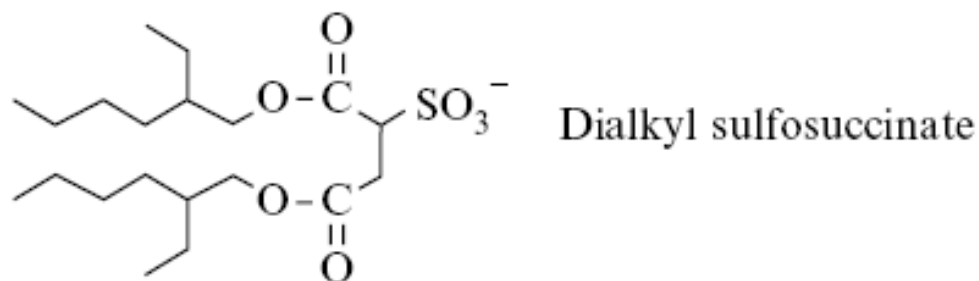
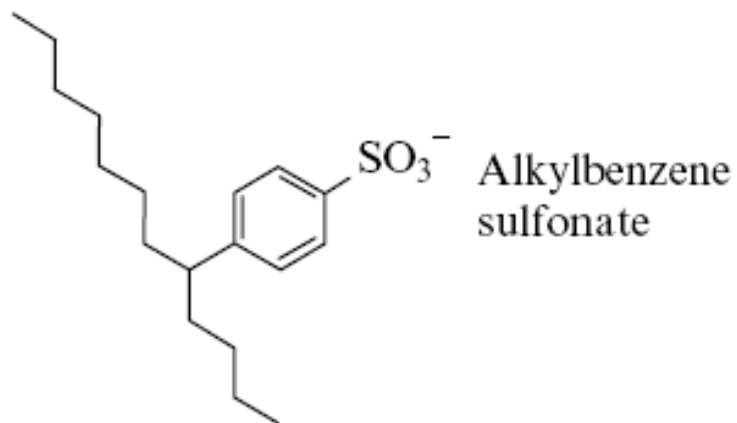
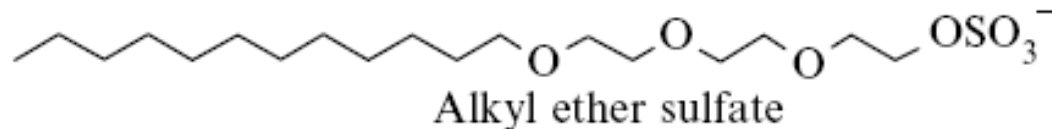
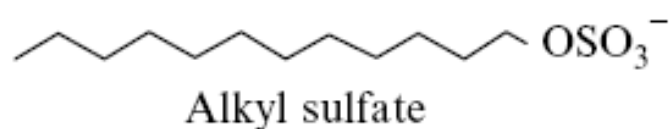
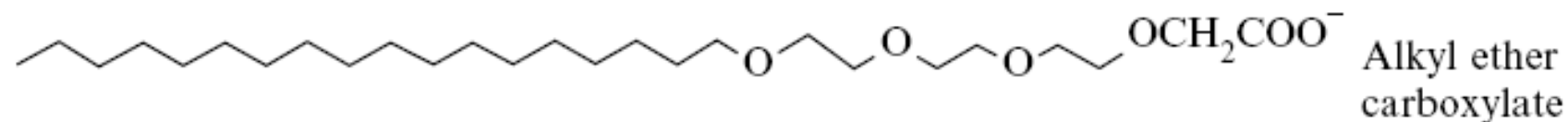


Fatty amine ethoxylate

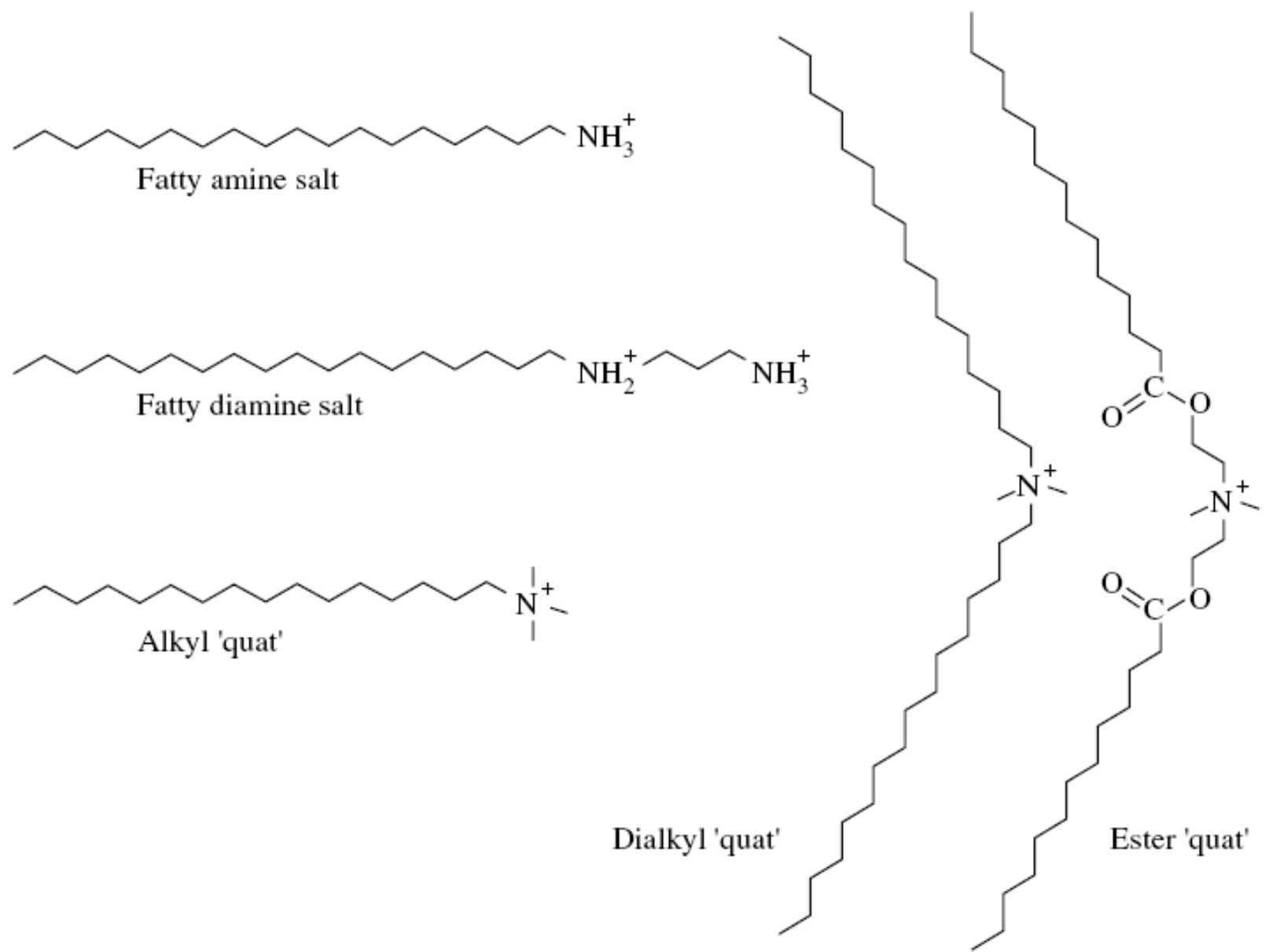


Alkyl glucoside

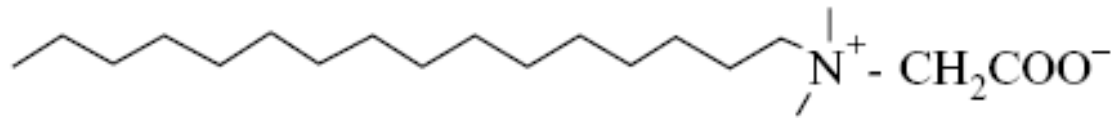
# Anionic surfactants: used in pesticide formulations and toothpastes



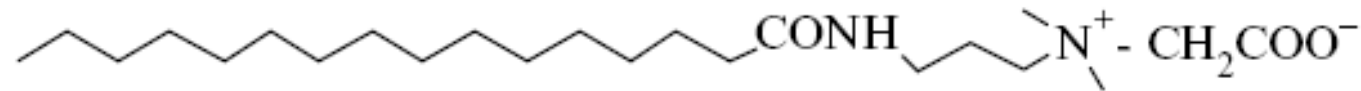
# Cationic surfactants: used in hair and fabric conditioners



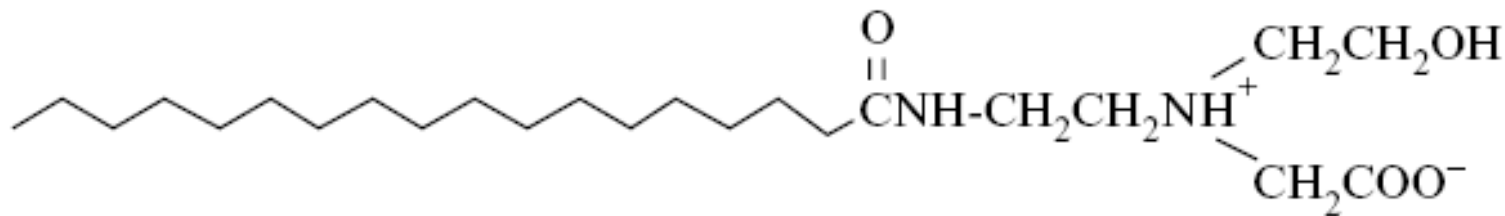
# Zwitterionic Surfactants: found in cell membranes and used in drug delivery and cosmetics



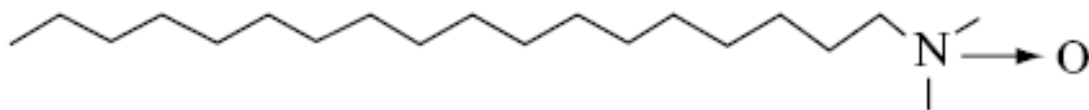
Betaine



Amidobetaine



'Imidazoline'



Amine oxide

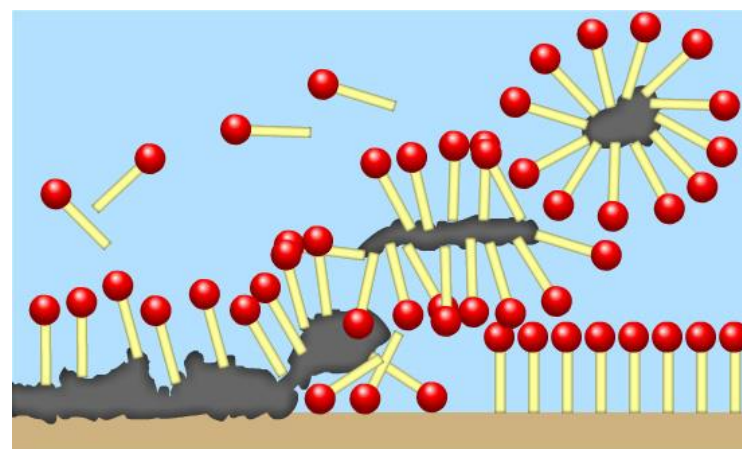
# Why do we need surfactants?

**Surfactants are used as detergents, emulsifiers, encapsulants, lubricants, etc**

Grease does not mix with water because the main interactions between water molecules are hydrogen bonding, whilst those between molecules of oils and fats are dispersion forces.

To get water and grease to mix we use **surfactants as detergents**. The hydrophobic 'tail' can form van der Waals bonds with non-polar grease molecules, whilst the polar 'head' can form hydrogen bonds with water.

This is an example of the 'like dissolves like' rule.



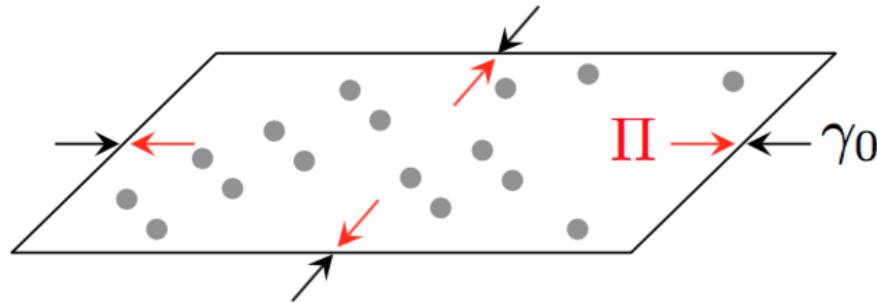
The non-polar tails of detergent molecules mix with grease, while the polar heads mix with water, thus forcing the grease and water to mix

# Problems with surfactants

- **dermatological problems** (emulsification of lipids on skin can cause removal of protective layer; loss of water by the skin)
- **biocidal effects**
- **environmental issues**
  - aquatic toxicity
  - biodegradability
  - bioaccumulation
- **research into “green” surfactants or alternatives**

# Thermodynamics of interfaces

Surfactants decrease the surface tension



$$\gamma = \gamma_0 - \Pi$$

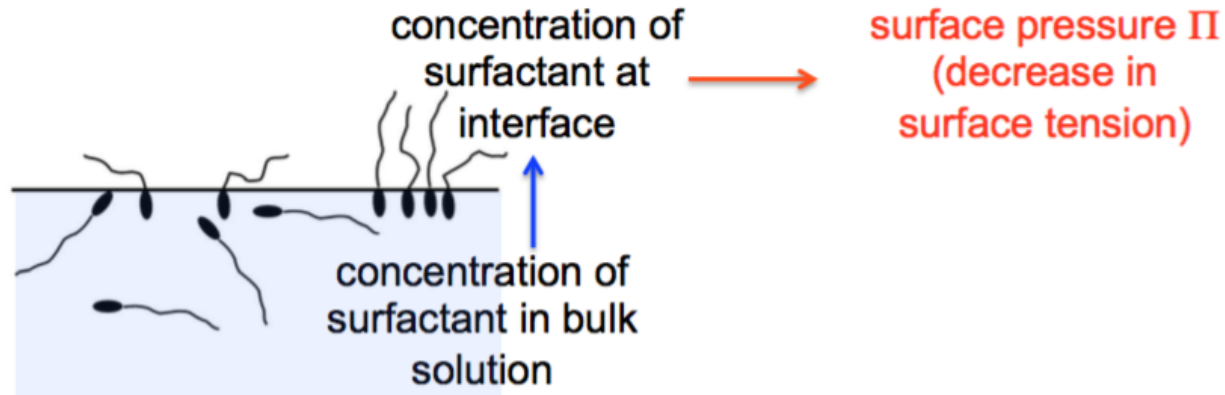
$\gamma$  : surface tension (function of surfactant concentration)

$\gamma_0$  : surface tension of fluid-fluid interface (no surfactants)

$\Pi$  : surface pressure of surfactant monolayer

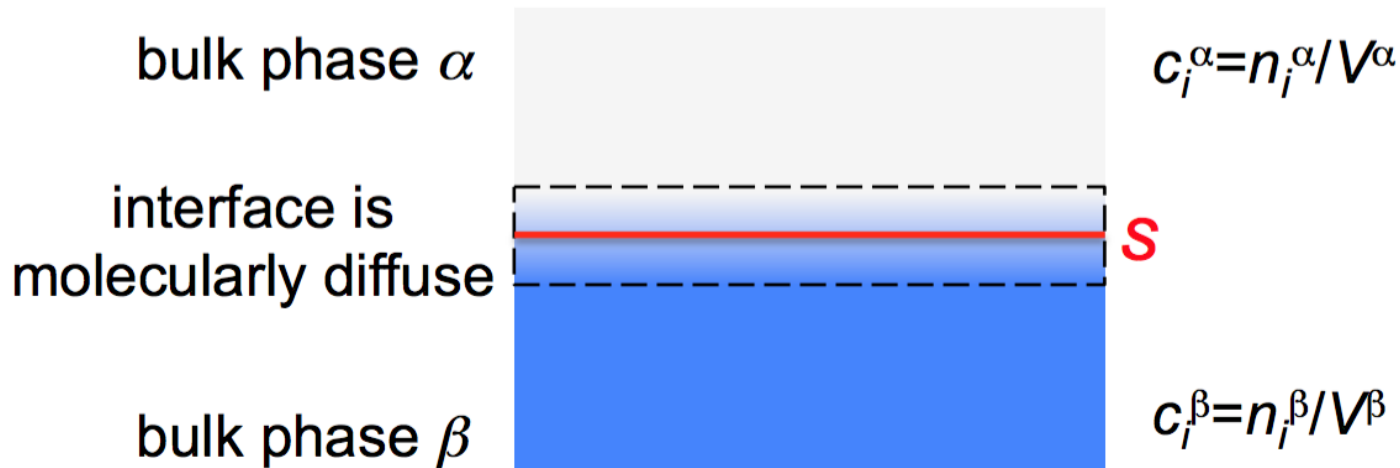


# Thermodynamics of interfaces



- Surfactants adsorbing from solution: **Gibbs monolayer**
- How much surfactant adsorbs at a fluid/fluid interface from a solution of concentration  $c$ ?
  - Can we increase  $c$  indefinitely?
- How much does the surface tension decrease as a function of concentration of surfactant at interface?

# Thermodynamics of interfaces



define: **Gibbs dividing surface**

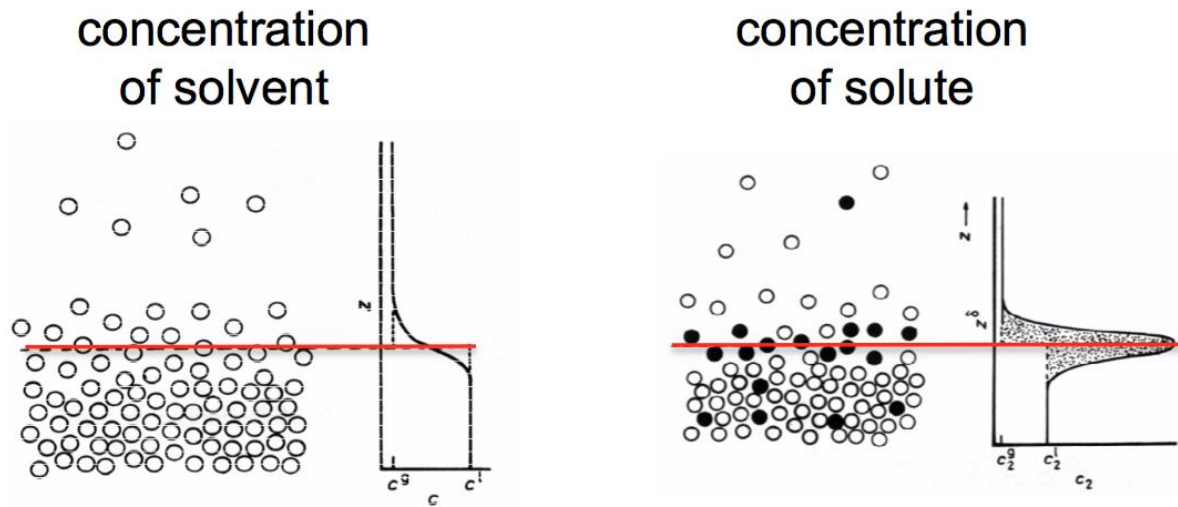
with volume  $V^s = 0$

and area  $A$

$n_i^s$  number of moles of component  $i$  on surface

**$\Gamma_i = n_i^s / A$  surface excess of component  $i$**

# Thermodynamics – Surface excess



The surface excess  $\Gamma$  is the excess material at the interface compared to the bulk:

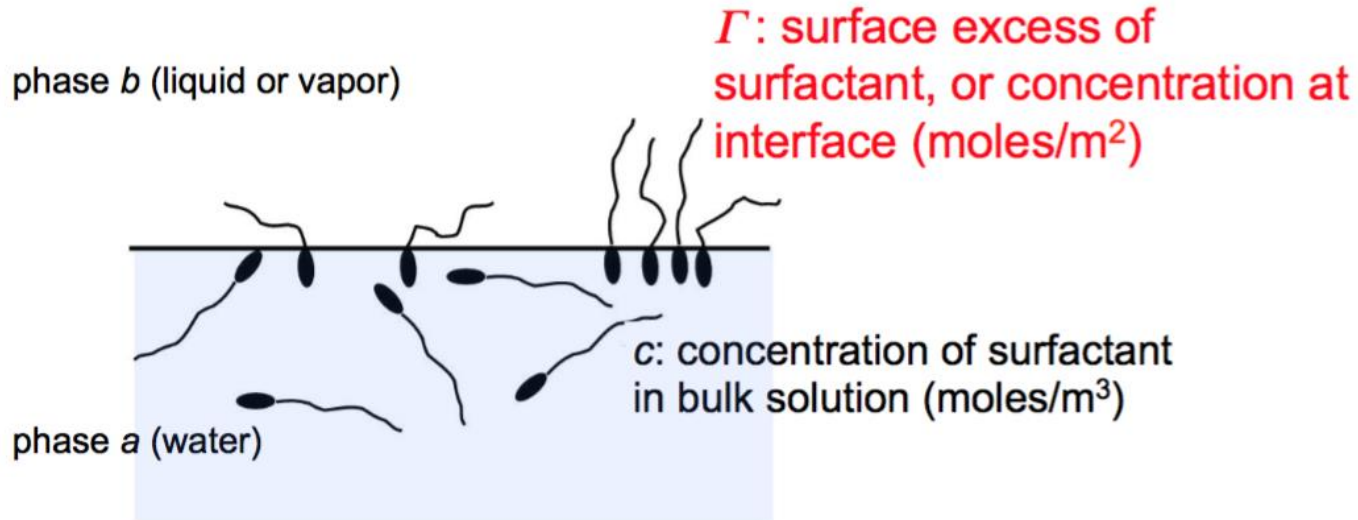
$\Gamma_i > 0$  interfacial excess (e.g. surfactant)

$\Gamma_i < 0$  interfacial depletion (e.g. salt)

The location of the Gibbs dividing surface can be chosen so that the surface excess of solvent is  $= 0$ .

Measurement of surface excess: radioactive tracers, neutron reflectivity

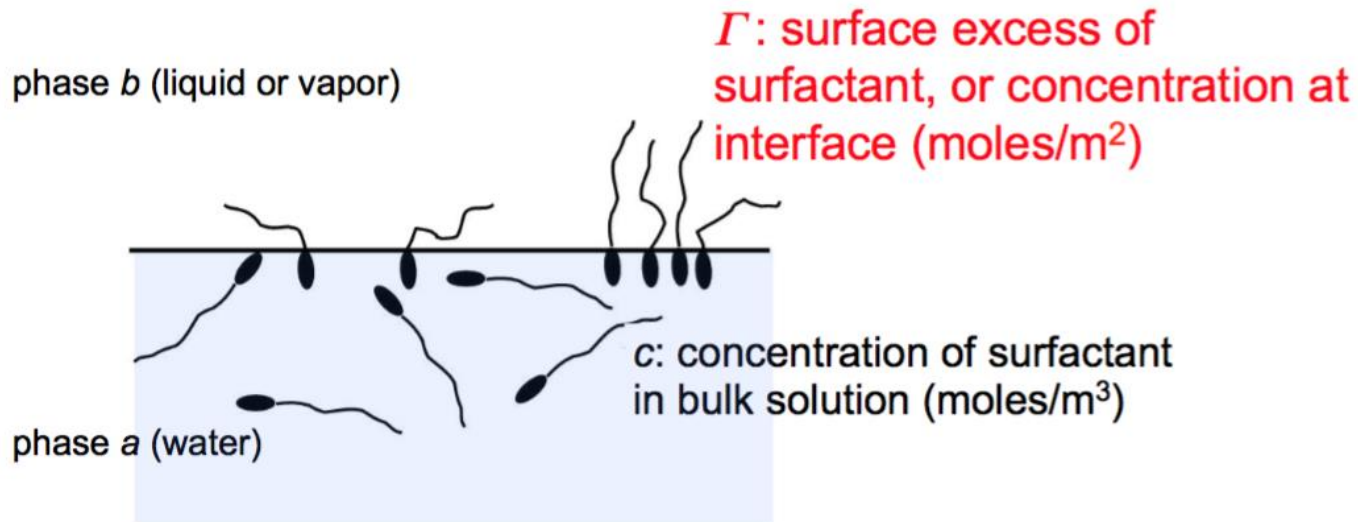
# Adsorption from solution



$$d\gamma = -\sum_i \Gamma_i d\mu_i \quad \text{Gibbs adsorption equation}$$

relates change in surface tension to surface excess and change in chemical potential (i.e. concentration) of the bulk surfactant solution

# Adsorption from solution



$$d\gamma = -\Gamma d\mu \quad \text{Gibbs adsorption equation}$$

(one component)

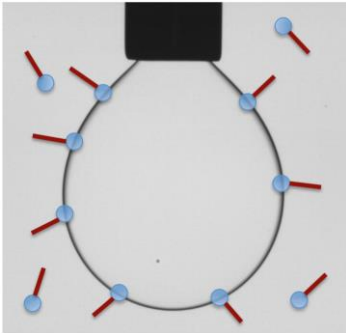
$$\mu = RT \ln a = RT \ln c$$

$a$ : activity; for dilute solution  $a \approx c$  concentration

$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln c} \quad \text{adsorption isotherm } \Gamma(c)$$

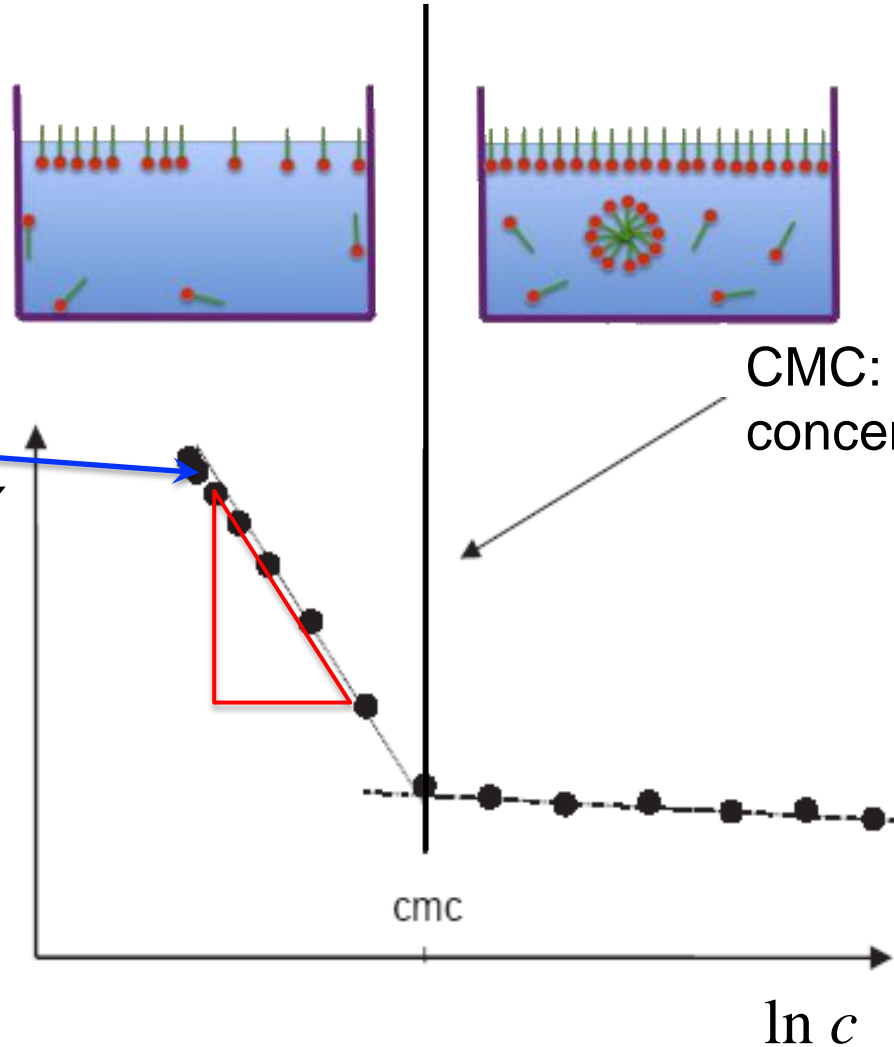
# Adsorption from solution

each data point is  
a measurement  
with different bulk  
concentration  $c$

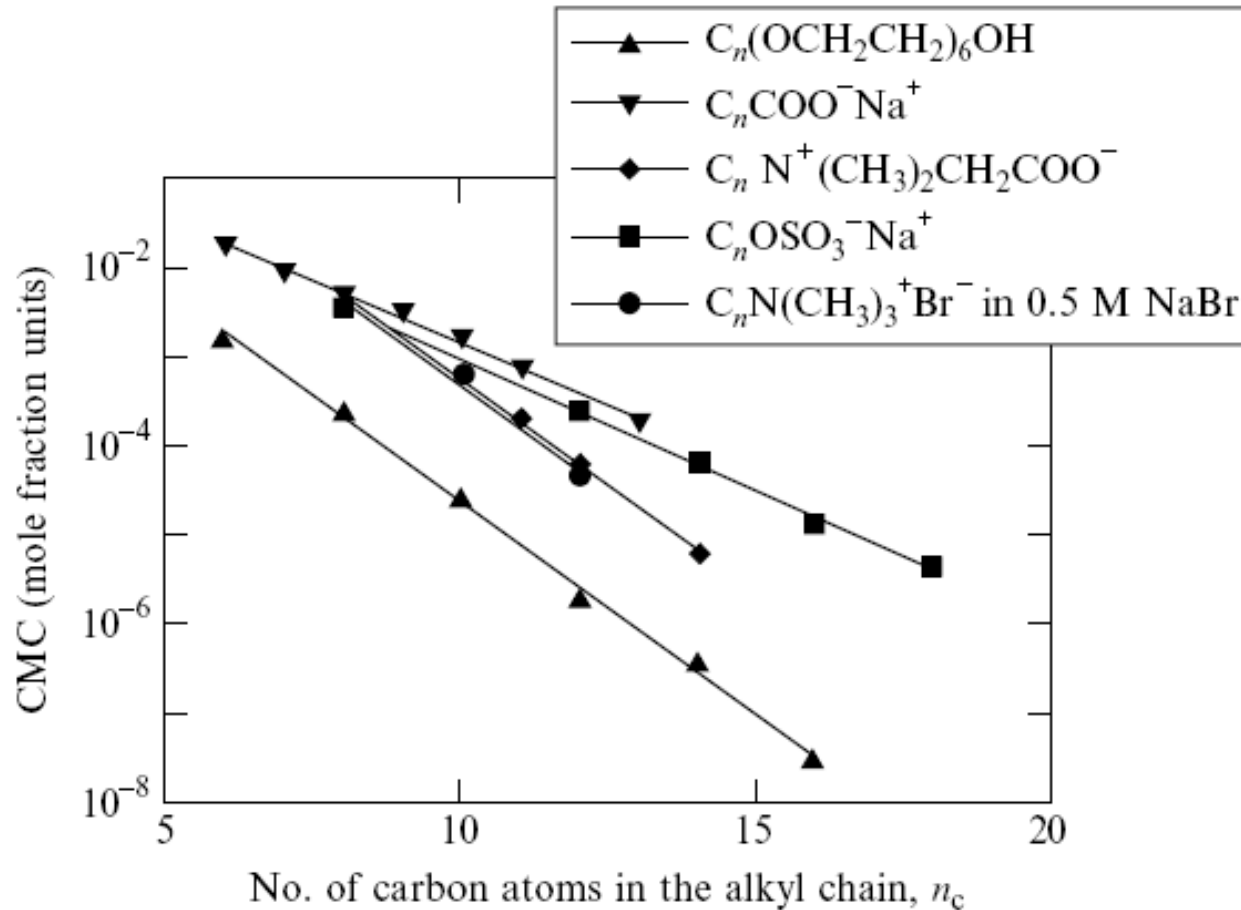


$$\Gamma = -\frac{1}{RT} \frac{d\gamma}{d \ln c}$$

can obtain surface  
concentration of  
surfactant



# CMC depends upon chemical structure



- CMC decreases exponentially with **alkyl chain length**
- for a variety of headgroups

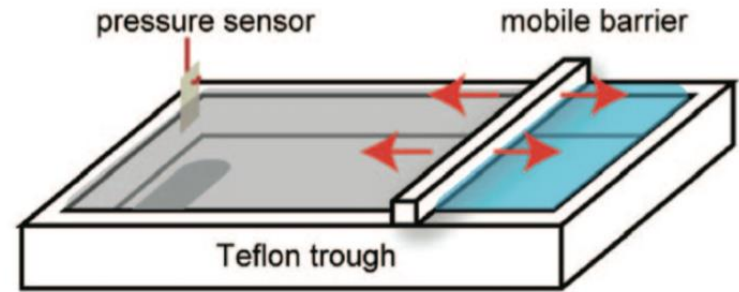
# Insoluble monolayers

- Some amphiphiles have very low CMC → always form micelles in water (example: phospholipids)
- They are called **insoluble surfactants**
- Can form monolayers at water/air or water/oil interface
- Can be deposited on interface from a volatile spreading solvent (e.g. chloroform)
- Spread monolayers are called **Langmuir monolayers**
- (in contrast with monolayers formed by spontaneous adsorption, called Gibbs monolayers)
- <https://wordhistories.net/2017/10/06/oil-on-troubled-waters/>

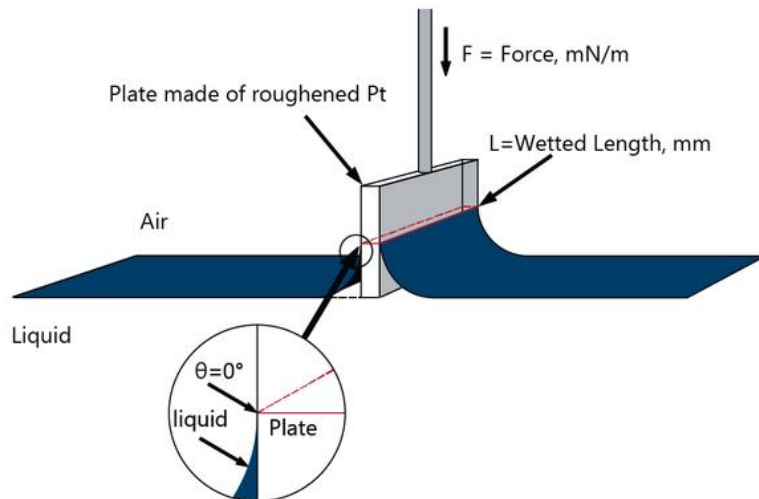


# Langmuir trough

- trough (Teflon) containing the aqueous subphase
- moving barrier: change area  $A$  and compress the surfactant monolayer
- surface pressure sensor to measure  $\gamma$  continuously
- $n^s$  is constant,  $A$  changes  $\rightarrow \Gamma = n^s/A$  **changes**
- Used to determine  $\Pi$  as a function of  $\Gamma$



## Surface pressure sensor: Wilhelmy plate



$$F = L\gamma \cos \theta \approx L\gamma$$

$$\gamma = \gamma_0 - \Pi$$

# Surface equation of state $\Pi(\Gamma)$

How much does the surface tension decrease as a function of the concentration of surfactant on the interface?

$$\gamma = \gamma_0 - \Pi$$

$\Pi(\Gamma)$  is the **surface equation of state**:

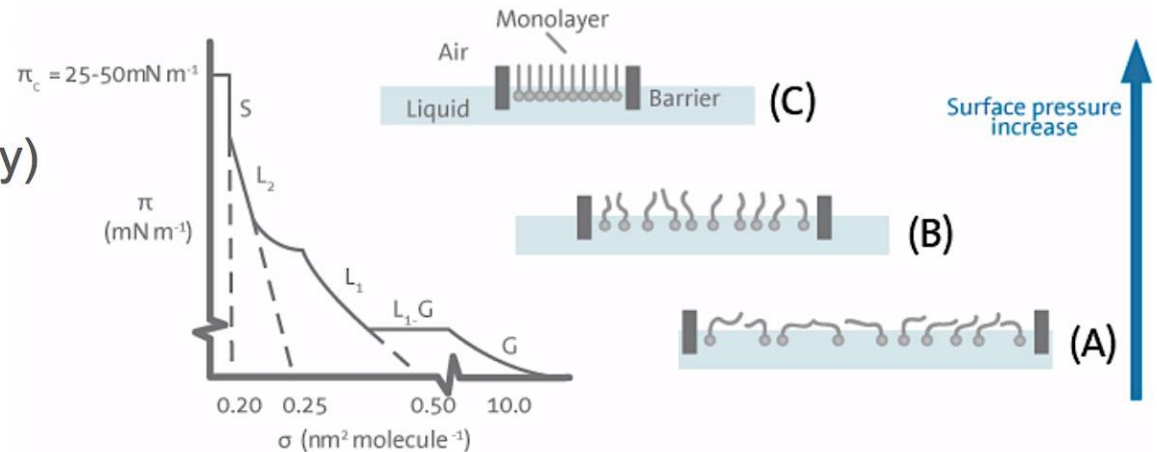
$$\gamma(\Gamma) = \gamma_0 - \Pi(\Gamma)$$

surface excess (or area density)

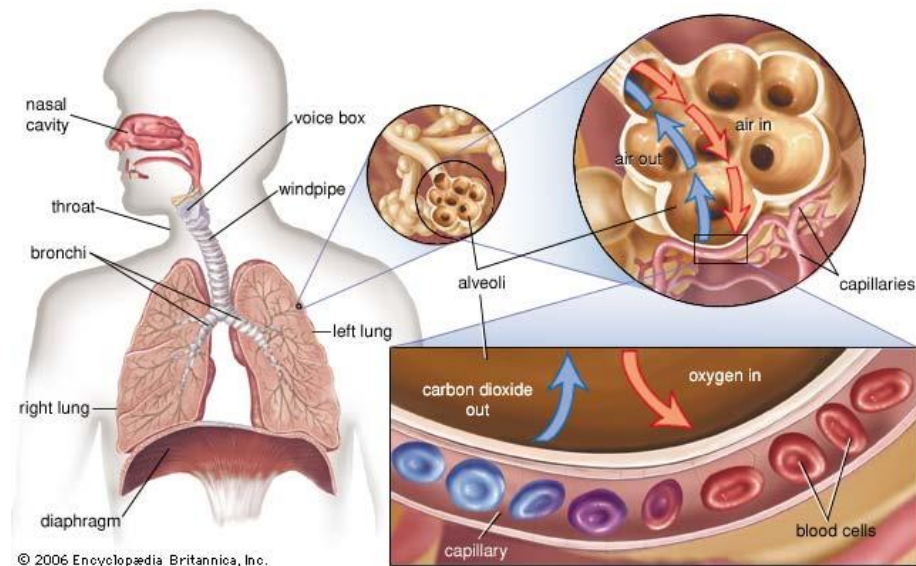
$$\Gamma = n^s/A$$

area per molecule

$$\sigma = 1/\Gamma = A/n^s$$

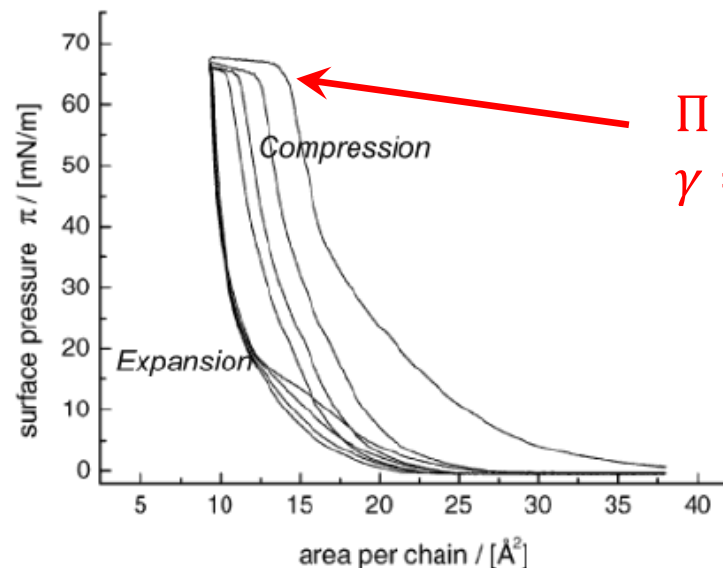


# Example: lung surfactants



- Alveoli: sites of gas exchange at water-air interface ( $O_2$  comes in;  $CO_2$  goes out)
- During breathing: compression/expansion of water-air interface
- Work against surface tension!
- Alveoli are lined with surfactant monolayer, which reduces surface tension, hence reduces work of breathing

Typical isotherm of a model lung surfactant lipid mixture DPPC/POPG/PA on water at 23 C



$$\Pi \approx 65 \text{ mN/m}$$

$$\gamma = \gamma_0 - \Pi \approx 8 \text{ mN/m}$$

# Models for surface equation of state

At **infinite dilution**:

$$\Pi A = n^s RT$$
$$\Pi = \Gamma RT$$

2D analogue of ideal gas equation  $pV = nRT$

At **higher concentrations**:

$$\Pi(A - A_0) = n^s RT$$

**Volmer equation.**  $A_0$  is **molecular co-area** (measures effective cross-sectional area of adsorbed molecule).

At **even higher concentrations**:

$$\left( \Pi - \frac{\alpha}{A^2} \right) (A - A_0) = n^s RT$$

In analogy to the **van der Waals** equation of state for gases, it accounts for intermolecular interactions through parameter  $\alpha$ .

# Gibbs adsorption equation

Adsorption isotherm is related to surface equation of state through Gibbs adsorption equation  $-d\gamma = \Gamma d\mu$

Example: Infinite dilution case (ideal gas)

$$\Pi = \Gamma RT$$

Recast Gibbs adsorption equation in terms of  $\Pi$ :

$$-d\gamma = -d(\gamma_0 - \Pi) = d\Pi = \Gamma d\mu$$

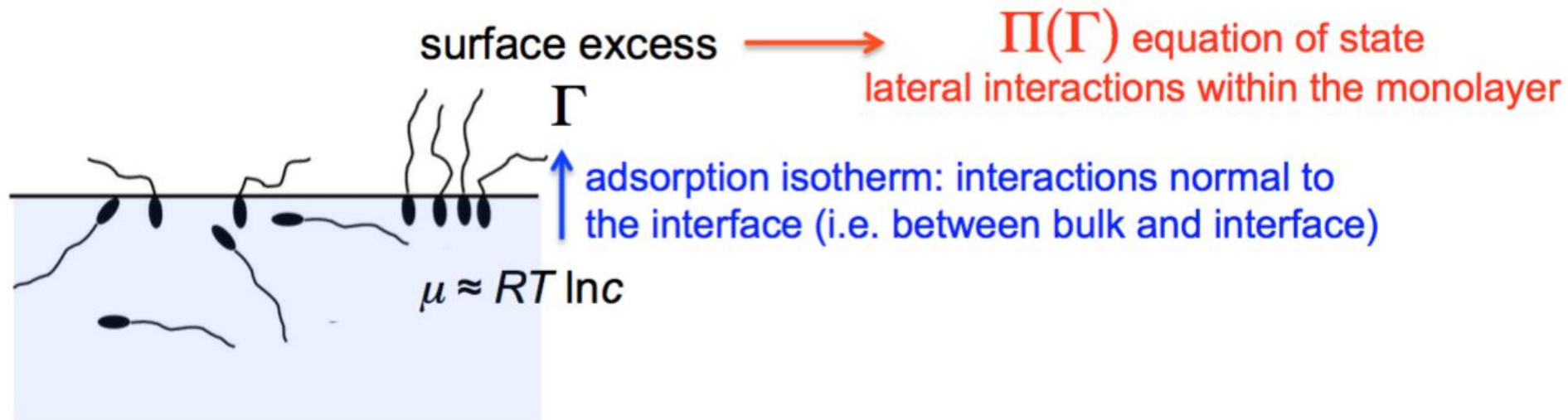
Use relationship between  $\mu$  and  $c$  at low  $c$ :  $\mu \approx RT \ln c$

$$d\Pi = \Gamma d\mu = \Gamma RT d(\ln c)$$

Adsorption isotherm:

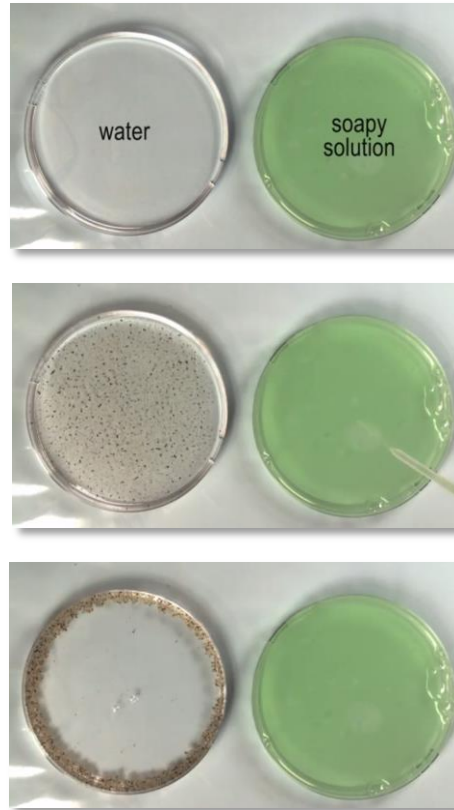
$$\Gamma = \frac{1}{RT} \frac{d\Pi}{d(\ln c)} = -\frac{1}{RT} \frac{d\gamma}{d(\ln c)} \therefore$$

# Thermodynamics of interfaces – SUMMARY



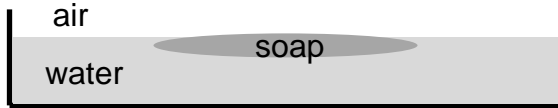
- How much surfactant adsorbs at a fluid/fluid interface from a solution of concentration  $c$ ? **Adsorption isotherm**
  - Can we increase  $c$  indefinitely? **NO: critical micellar concentration**
- How much does the surface tension decrease as a function of concentration of surfactant at interface? **Equation of state**

# Surface tension gradients and the Marangoni effect

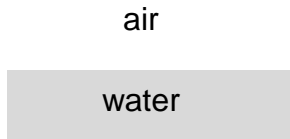


<http://www.youtube.com/watch?v=gTGr25ypiDQ>

# The Marangoni effect

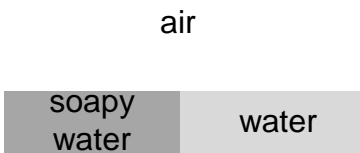
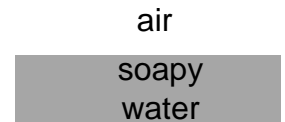


**Why does the addition of soap cause the pepper particles to move? Let's find out:**



1. First consider the surface of water. In what direction(s) does the force on the water-air interface due to surface tension point? Draw the vectors.

2. Now consider the surface of soapy water. Is the force on the soapy water-air interface due to surface tension larger or smaller than for pure water? Draw the vectors:

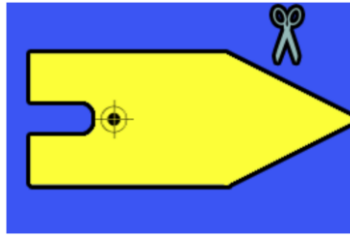


3. In the experiment, a region of the interface has the surface tension of soapy water, and the other region has the surface tension of pure water. Use (1) and (2) to draw the vectors for the two regions of the interface (pay attention to direction and magnitude). There is a net force on the interface. In which direction?



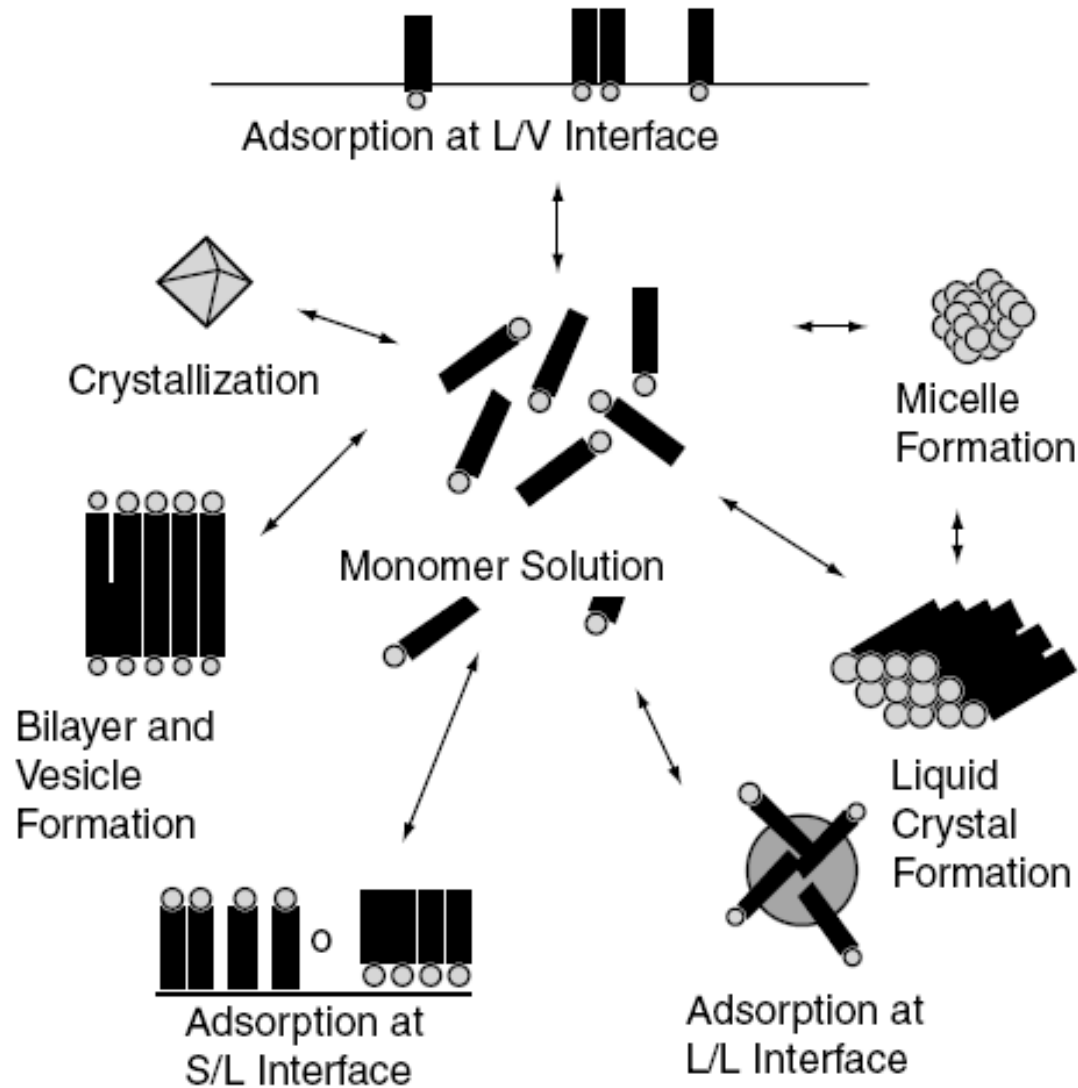
# Surface tension gradients and the Marangoni effect

Try this at home:  
the soap boat experiment



<http://www.youtube.com/watch?v=rq55eXGVvis>

# Self-assembly of surfactants



# Why do micelles form? – Hydrophobic Interaction

## Examples of hydrophobic interaction

a) water and oil are immiscible, with strong **driving force to expel hydrocarbons from water**

b) self-assembly of surfactants

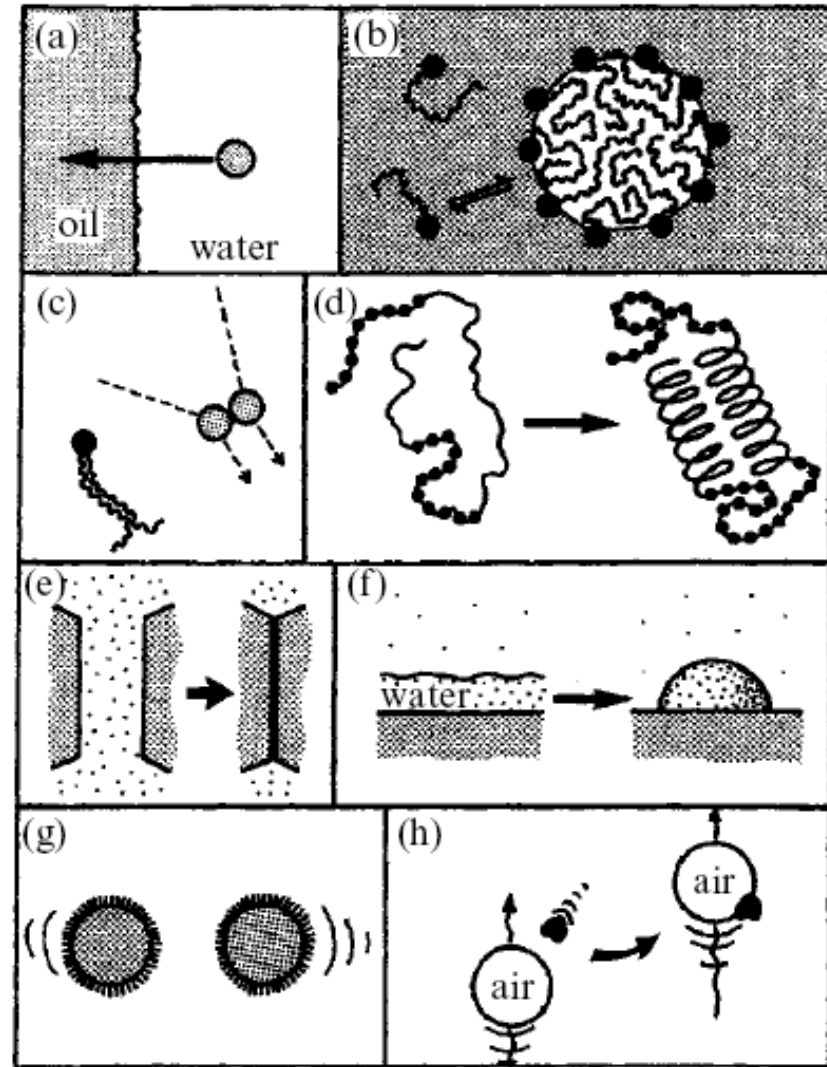
c) other types of hydrocarbon chain association

d) strong adhesion between hydrophobic surfaces in water

f) non-wetting of water on hydrophobic surfaces

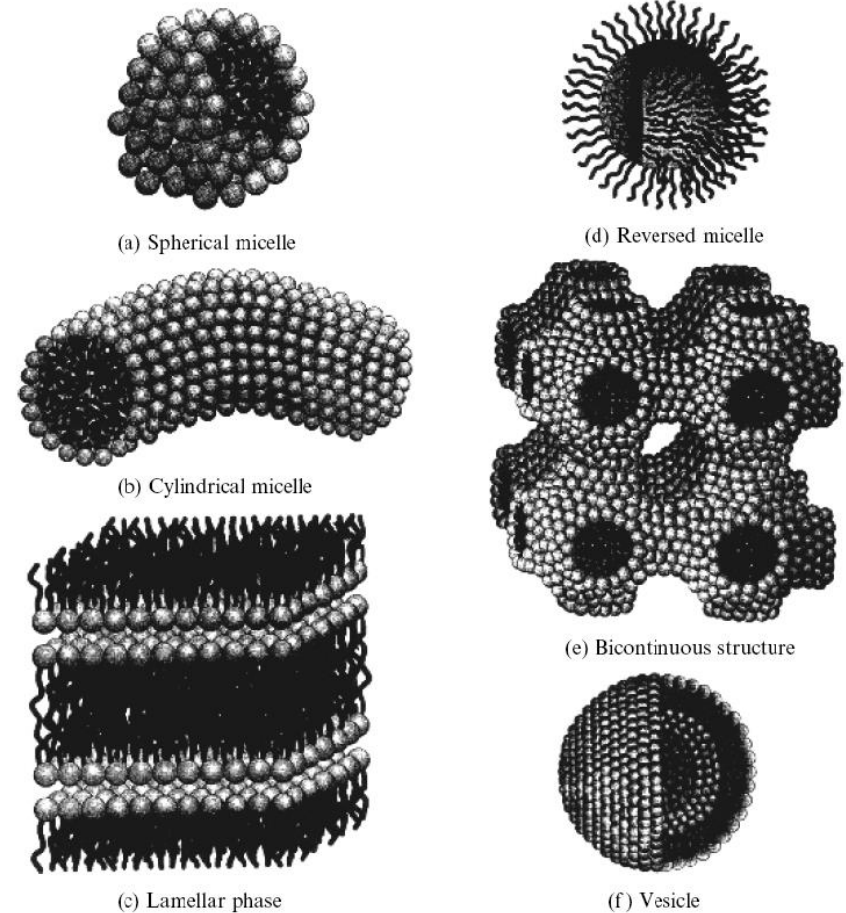
g) rapid coagulation of hydrophobic particles in water

h) attachment of hydrophobic particles to air bubbles



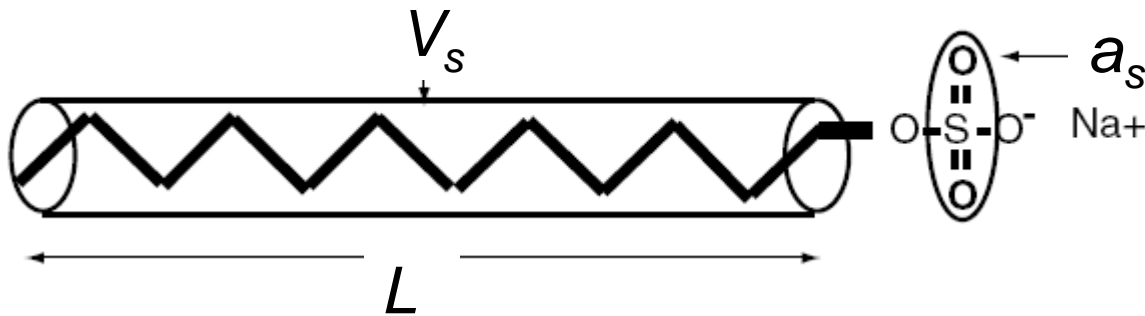
# Self-assembly of surfactants

- surfactant self-assembly leads to different structures
- which depend on:
  - shape, type & concentration of surfactant
  - ratio of polar/non-polar solvent



# Surfactant packing parameter

Surfactant packing parameter  $P$  allows prediction of shape & size of surfactant aggregates that will produce a minimum in free energy for a given surfactant structure

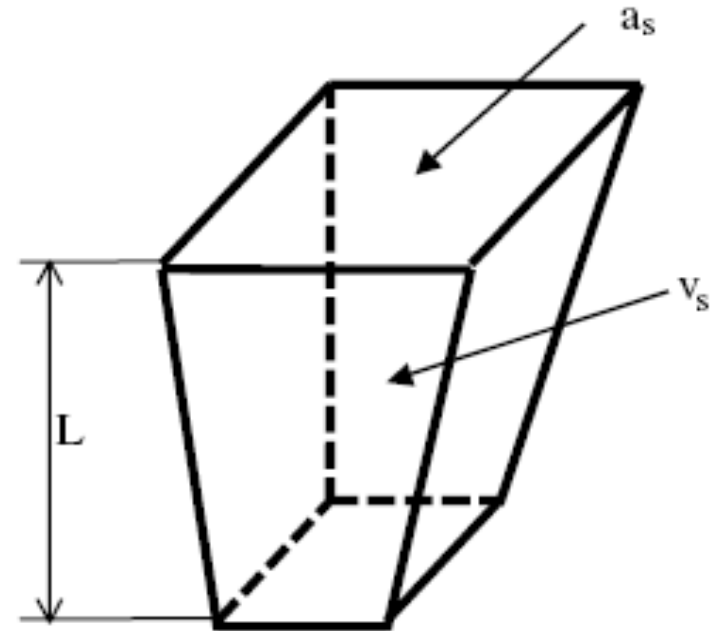


$$P = \frac{V_s}{a_s L}$$

$V_s$  = volume of hydrophobic tail,

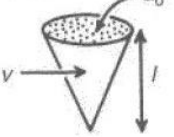
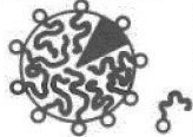

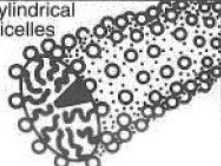

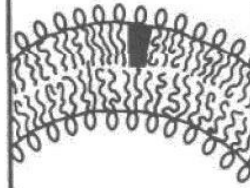

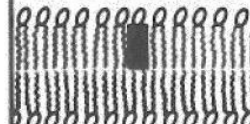
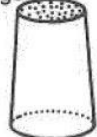
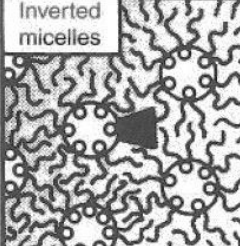
$a_s$  = optimal surface area occupied by surfactant monomer at the micelle-water interface

$L$  = maximum extended chain length



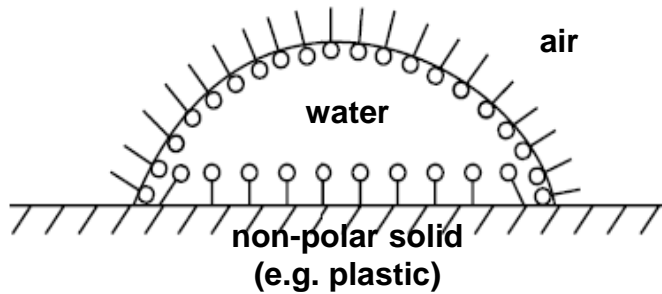
# Surfactant shape and self-assembly shape

Expected aggregate characteristics in relation to surfactant packing parameter  $P$  (critical value  $P_c$ )

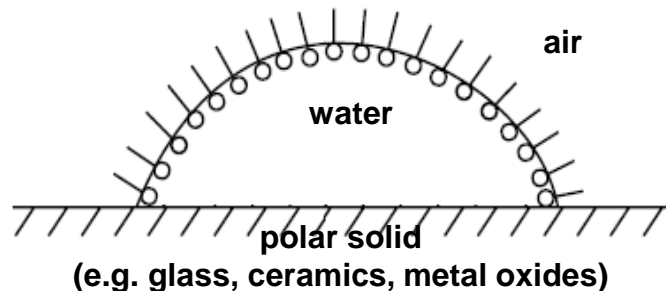
$P$	Surfactant Shape	Self-Assembly Shape
$< 1/3$	cone 	Spherical micelles 
$1/3-1/2$	Truncated cone 	Cylindrical micelles 
$1/2-1$	Truncated cone 	Flexible bilayers, vesicles 
$\sim 1$	Cylinder 	Planar bilayers 
$> 1$	Inverted truncated cone or wedge 	Inverted micelles 

$P_c$	General Surfactant Type	Expected Aggregate Structure
$< 0.33$	Simple surfactants with single chains and relatively large head groups	Spherical or ellipsoidal micelles
$0.33-0.5$	Simple surfactants with relatively small head groups, or ionics in the presence of large amounts of electrolyte	Relatively large cylindrical or rod-shaped micelles
$0.5-1.0$	Double-chain surfactants with large head groups and flexible chains	Vesicles and flexible bilayer structures
$1.0$	Double-chain surfactants with small head groups or rigid, immobile chains	Planar extended bilayers
$> 1.0$	Double-chain surfactants with small head groups, very large and bulky hydrophobic groups	Reversed or inverted micelles

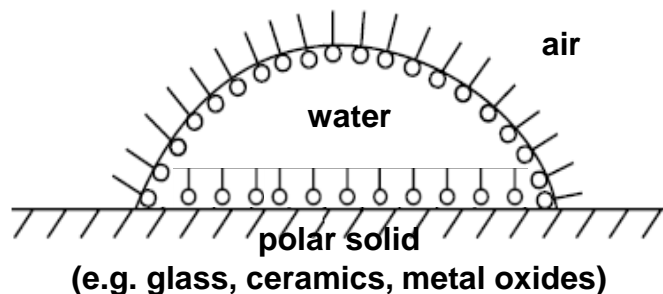
# Surfactant adsorption on solid surfaces



**1. Non-polar surface:** surfactant adsorbs at SL (due to hydrophobic effect) and LV interfaces. Result: **decrease in  $\theta$  ; increased wetting.**



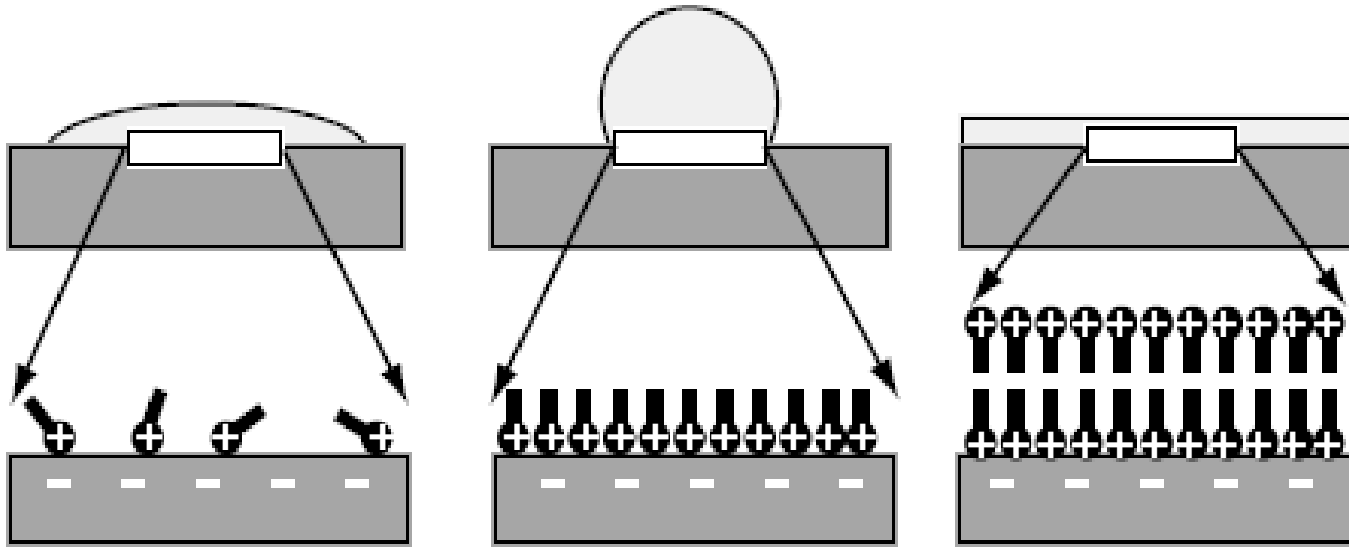
**2. Polar surface. (a) Surfactant and surface have same charge.** Surfactant adsorbs at LV interface. Surfactant is repelled by like-charged surface. Result: **decrease in  $\theta$  ; increased wetting.**



**2. Polar surface. (b) Surfactant and surface have opposite charge.** Surfactant adsorbs to SL (due to opposite charge) and LV interface. Result: **increase in  $\theta$  ; decreased wetting. Autophobic effect.**

# Surfactant adsorption on solid surfaces

When an **ionic surfactant** in water adsorbs on an **oppositely charged** solid surface, the orientation of molecules will be such that one may observe a contact angle cycle as the adsorption increases:



The initial surface will be hydrophilic and have a small contact angle

As adsorption proceeds, surface becomes more hydrophobic and contact angle increases to a maximum

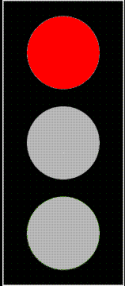
Further adsorption (if it occurs) will reverse the process leading to more polar surface and smaller contact angle.



# Introduction to surfactants

- recall: definition of surfactant
- understand: mechanism of surfactant adsorption at interfaces
- understand: difference between non-ionic, ionic, zwitterionic surfactant
- understand: surface pressure and surface tension reduction
- recall: definition of Gibbs dividing surface and surface excess
- understand: significance of Gibbs adsorption equation
- apply: adsorption isotherm  $\Gamma(c)$
- understand: effect of critical micellar concentration on adsorption from solution
- recall: difference between Gibbs monolayer and Langmuir monolayer
- understand: surface equation of state of monolayers
- apply: surface equations of state to compute  $\Pi$  from surface excess  $\Gamma$
- understand: Marangoni effect
- recall: structures formed by surfactant self-assembly
- understand: effects of surfactants on wetting of solids

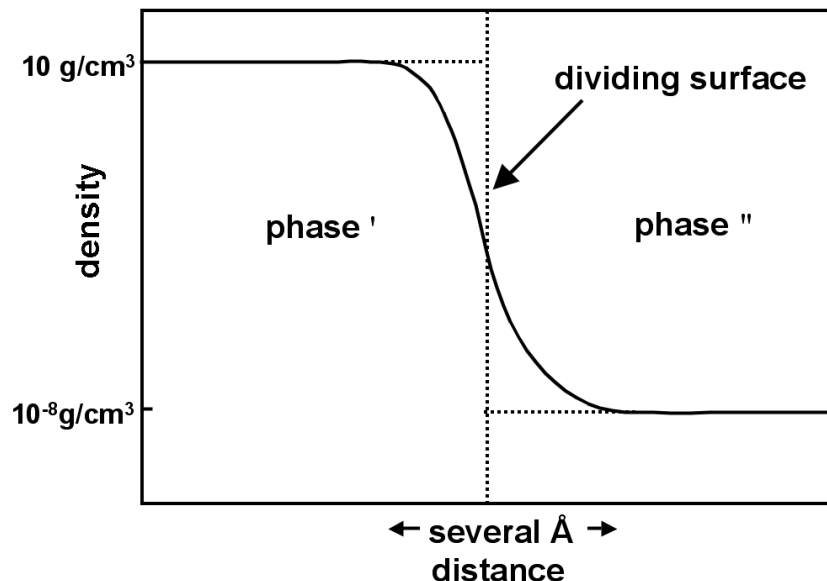
# Some extra notes on derivation of Gibbs Eqn



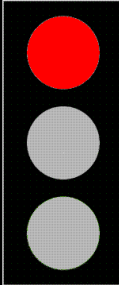
# Interfacial Thermodynamics

The Interfacial energy is denoted by  $\gamma$  (with typical units of [mJ/m<sup>2</sup>]) note its an alternative representation of the surface tension. It is defined as the reversible work needed to create unit area of surface, at constant temperature, volume (or pressure), and chemical potentials.

Use liquid-vapor surface as an example, i.e., consider a system composed of a liquid and a vapor phase at equilibrium, separated by an interface.



*dividing surface, hypothetical system*



# Interfacial excess properties

## Examples:

interfacial excess internal energy,  $U^s$ :

$$U^s = U - U' - U''$$

and interfacial excess no. of moles of component i:  $n_i^s = n_i - n_i' - n_i''$

Exception: no interfacial excess volume,

$$V = V' + V''$$

Internal energies of phases ' and '' are written (as usual):

$$dU' = TdS' - PdV' + \sum_i \mu_i' dn_i'$$

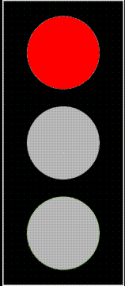
$$dU'' = TdS'' - PdV'' + \sum_i \mu_i'' dn_i''$$

and interfacial excess internal energy (no volume change) is written:

$$dU^s = TdS^s + \gamma dA + \sum_i \mu_i^s dn_i^s$$

$$dU = T(dS' + dS'' + dS^s) - P(dV' + dV'') + \gamma dA + \sum_i \mu_i (dn_i' + dn_i'' + dn_i^s)$$

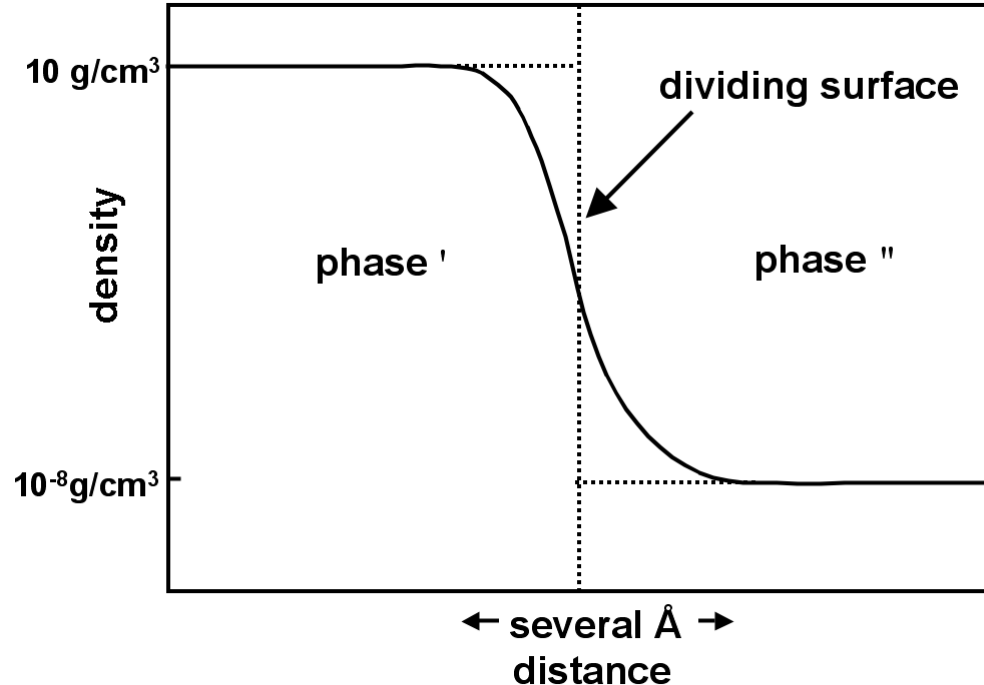
$$dU = TdS - PdV + \gamma dA + \sum_i \mu_i dn_i$$

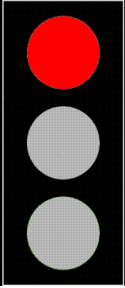


All other thermodynamic properties can be written from the previous relation: e.g. Gibbs free energy,  $G = U + PV - TS$

$$dG = dU + PdV + VdP - TdS - SdT = -SdT + VdP + \gamma dA + \sum_i \mu_i dn_i$$

**Note!** The surface excess quantities are *arbitrary*, since they depend on precisely where the dividing surface is located within the diffuse region associated with the interface. We shall see later how this issue may be addressed.





## Gibbs adsorption equation and isotherm

The expression for  $dU^s$ , is written only in terms of extensive independent variables ( $dS^s$ ,  $dA$ ,  $dn_i^s$ ), while the intensive variables ( $T$ ,  $\gamma$ ,  $\mu_i$ ) are constant in the equilibrated system. This makes integration of  $dU^s$  straightforward:

$$U^s = TS^s + \gamma A + \sum_i \mu_i n_i^s$$

Re-differentiating yields:

$$dU^s = TdS^s + S^s dT + \gamma dA + Ad\gamma + \sum_i \mu_i dn_i^s + n_i^s d\mu_i$$

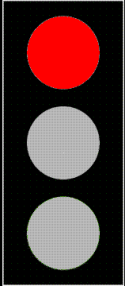
Comparing with the expression for  $dU^s$ , we conclude:

$$S^s dT + Ad\gamma + \sum_i n_i^s d\mu_i = 0$$

We now define the following *specific interfacial excess quantities*:

$$s^s \equiv S^s / A \quad \text{and} \quad \Gamma_i \equiv n_i^s / A$$

where  $\Gamma_i$  is referred to as the adsorption of component i



and obtain:  $d\gamma = -s^s dT - \sum_i \Gamma_i d\mu_i$  **Gibbs adsorption equation**

At constant temperature, this simplifies to the **Gibbs adsorption isotherm**. For a two-component system, *at constant T* it can be written:

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2$$

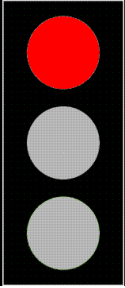
This may be simplified further by the use of the Gibbs-Duhem equation:

$$n'_1 d\mu_1 + n'_2 d\mu_2 = 0$$

It is conventional to take components 1 and 2 to be the solvent and solute, respectively, and to eliminate  $\mu_1$  from the adsorption equation:

$$\frac{d\gamma}{d\mu_2} = \left( \Gamma_1 \frac{n'_2}{n'_1} - \Gamma_2 \right)$$

The l.h.s. of the above equation is measurable, therefore the **r.h.s. cannot be arbitrary**.



## Approximate forms of the Gibbs adsorption isotherm

The chemical potential may be expressed as:  $\mu_2 = \mu_2^\circ + kT \ln a_2$ , where  $a_2$  is the activity and  $\mu_2^\circ$  is the standard state chemical potential. For ideal solutions,  $a_2 = c_2$ , where  $c_2$  is the molar concentration. For dilute solutions,  $a_2 = k_0 c_2$ , where  $k_0$  is Henry's Law constant. In both of these cases,  $d\mu_2 = RT d(\ln c_2)$ . Thus, in both those cases the Gibbs isotherm may be written:

$$\frac{1}{RT} \frac{d\gamma}{d \ln c_2} = \left( \Gamma_1 \frac{n'_2}{n'_1} - \Gamma_2 \right)$$

In particular, in dilute solutions,  $n'_2 \ll n'_1$ , so that we can write:

$$\frac{1}{RT} \frac{d\gamma}{d \ln c_2} = -\Gamma_2$$

This is the most commonly used form of the Gibbs adsorption isotherm.