# Complex Disordered Systems

## Surfactants

Francesco Turci

# Hydrophobicity and amhiphiles

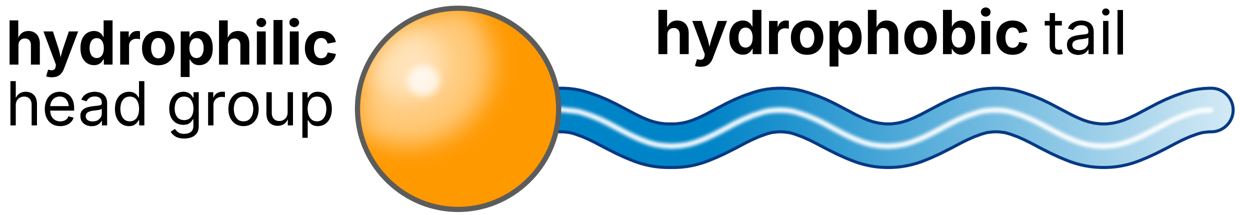
Water is the standard solvent for a lot of chemistry and (almost all) biology.

Molecules in water can be classified by their **affinity** to water:

- **Hydrophilic** (“water-loving”) molecules interact favorably with water (e.g., via hydrogen bonding or dipole interactions).
- **Hydrophobic** (“water-fearing”) molecules do not interact favorably with water (e.g., non-polar molecules).

**Amphiphiles** are molecules that contain both hydrophilic and hydrophobic parts. They include:

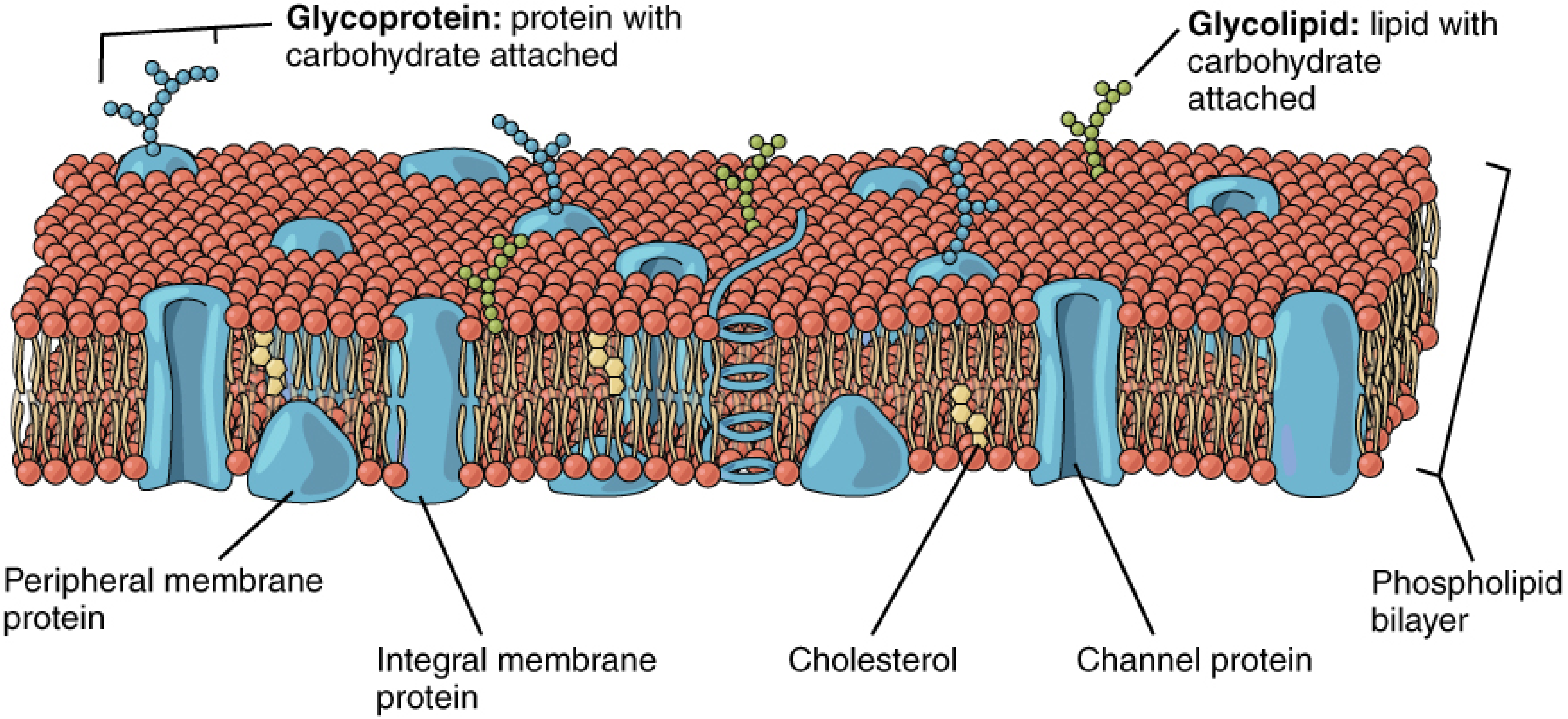
- Surfactants (detergents, soaps, *SURFace ACTive AgeNT*)
- Lipids (cell membranes)
- Some proteins (with hydrophobic and hydrophilic amino acids)



Schematic model of a surfactant

Downloading package: ipython

# Hydrophobicity and amphiphiles



Phospholipid **bilayers** form the cellular membranes. They **self-assemble**!

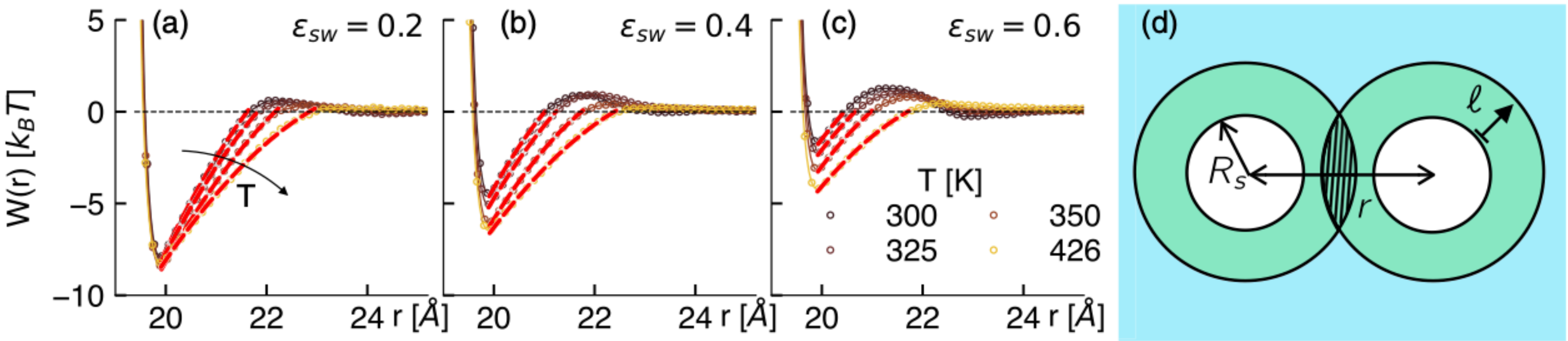
Downloading package: ipython

# Hydrophobicity in brief

The hydrophobic interactions is a topic of active research.

Various approaches

- (from to 1950s) structural approach: water forms cages around molecules. When the cage is disrupted, entropy increases. Solutes come together to minimise the disruption.
- (from 2000s) interfaces approach: water is a fluctuating medium. Large hydrophobic solutes create interfaces that suppress fluctuations. Solutes come together to minimise the interface area.
- (current research) avoided criticality: water is close to a liquid-vapour critical point. Local curvature and interactions promote large density fluctuations. Solutes interact on scales controlled by these fluctuations.



Effective hydrophobic interactions between spherical solutes of variable solute-solvent affinities $\varepsilon_{sw}$. A depletion-like construction produces a surface tension-controlled interaction. from Wilding & Turci PRR (2025)

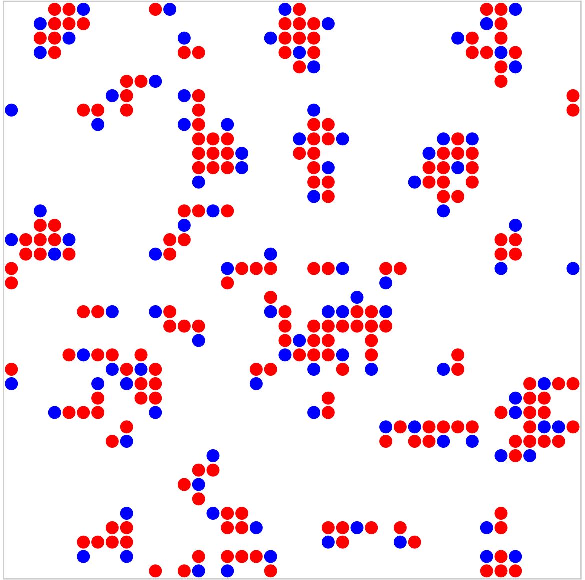
In all cases, the hydrophobic effect originates in **fluctuations of the solvent**, i.e. the way the solvent explores the available configuration.

# Self assembly of surfactants

Temperature (kT) 0.51

Number of Chains 103

Pause



# Self assembly of surfactants

- Surfactants are at the molecular scale so they are *nanometer* sized
  - Diffusion is **fast** (e.g. use $D = \frac{k_B T}{6\pi\eta R}$ to compare a colloid to a surfactant molecule)
  - $\rightarrow$ quickly explore possible conformations and minimise free energy.
- The amphiphilic structure means that special orientations can be achieved to satisfy the energetic constraints.
- The molecules spontaneously form structures: this is called **self-assembly**.
- Underlying phase transitions typically **drive** the self-assembly.

# Aggregation: general case

- Consider a generic problem of aggregation of particles (generic)
- Simple model: we have cluster of size $N$ and a free energy cost $\epsilon_N$ pto add a particle to the cluster.
- Let $\mu_1$ and $\mu_N$ be the chemical potential of isolated particles and aggregates of size $N$ respectively.
- In equilibrium, $\mu_1 = \mu_N := \mu$

We can express $\mu$ in terms of

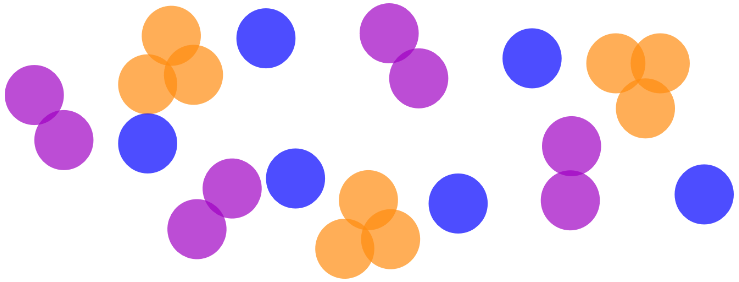
- the interaction energy from being in the aggregate $\epsilon_N$
- the entropy of the aggregate as a whole $\propto \text{ number of aggregates} \times \ln \text{ number of aggregates}$

# Aggregation: general case

- Let the overall **volume fraction** to be $\phi$
- Call $X_N$ the volume fraction in an aggregate of size $N$, so that $\sum_N X_N = \phi$.
- The numbers of aggregates of size $N$ per unit volume is then simply $X_N/N$

ⓘ **Example**

- Suppose $\phi = 0.1$ (10% of the volume is particles).
- Let $X_3 = 0.06$, $X_2 = 0.04$ (so $\sum X_N = 0.06 + 0.04 = 0.1 = \phi$).
- Then the **number of trimers** is $0.06/3 = 0.02$ (fraction of solution volume in separate trimer aggregates).
- The **number of dimers** is $0.04/2 = 0.02$.



—

The uniform chemical potential is then

$$\mu = \{\text{energy per particle in aggregate of size N}\} + \{\text{entropy of mixing per particle in aggregate of size N}\}$$

or

$$\mu = \epsilon_N + \frac{k_B T}{N} \ln \frac{X_N}{N}$$

# Aggregation: general case

From

$$\mu = \epsilon_N + \frac{k_B T}{N} \ln \frac{X_N}{N}$$

we can rewrite this as

$$X_N = N \exp\left(\frac{N(\mu - \epsilon_N)}{k_B T}\right)$$

and eliminate $\mu$ by evaluating the expression for for $N = 1$ and plugging it back to get

$$X_N = N X_1^N \exp\left(\frac{N(\epsilon_1 - \epsilon_N)}{k_B T}\right)$$

The fraction of solutes in the aggregated state is large only if $\epsilon_1 > \epsilon_N$., i.e. there is an energetic advantage.

# Aggregation: general case

$$X_N = N X_1^N \exp\left(\frac{N(\epsilon_1 - \epsilon_N)}{k_B T}\right)$$

means that knowing the form of $\epsilon_N$ is key to predicting aggregation behaviour.

- Consider an aggregate of $N$ particles of total radius $r \approx (Nv)^{1/3}$ where $v$ is the volume of a single particle.
- Then $\epsilon_N$ is the free energy per particle of the aggregate of size $N$,

$$G_N/N = \frac{1}{N}(\text{ bulk free energy} + \text{surface free energy})$$

- Assuming that there is a surface free energy cost (a surface tension) $\gamma$ we write

$$\epsilon_N = \frac{G_N}{N} = \epsilon_\infty + \frac{1}{N}\gamma r^2 = \epsilon_\infty + \gamma\left(\frac{v^2}{N}\right)^{1/3}$$

which is a **monotonically decreasing** function of $N$.

Define $\alpha k_B T = \gamma v^{2/3}$ and extract a relation between $X_N$ and $X_1$ parametrised solely by $\alpha$, i.e.

$$\text{number of aggregates of size N per unit volume} = \frac{X_N}{N} \sim (X_1 e^\alpha)^N$$

# Aggregation: general case

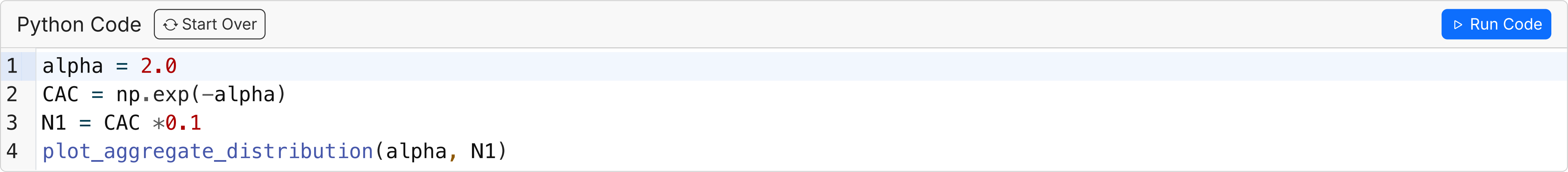
$$\text{number of aggregates of size N per unit volume} = \frac{X_N}{N} \sim (X_1 e^{\alpha})^N$$

This presents us with a few cases depending on $\alpha = \gamma v^{2/3}/k_B T$

- $X_1 e^{\alpha} < 1$: Few isolated particles, and $(X_1 e^{\alpha})^N$ becomes vanishingly small for large $N$
- $X_1 e^{\alpha} = 1$ **(critical point)**: Aggregates of all sizes become equally probable. The system undergoes phase separation into a dilute phase of isolated monomers (with $X_1$ pinned at $e^{-\alpha}$) in coexistence with a dense phase of very large aggregates.
- $X_1 e^{\alpha} > 1$: Above the critical aggregation concentration, the system cannot remain homogeneous and phase separates. The volume fraction $\phi$ at which this occurs is called **critical aggregation concentration**, or CAC.

$$\mathrm{CAC} = X_1^* = e^{-\alpha} = \exp\left(-\frac{\gamma v^{2/3}}{k_B T}\right)$$

# Aggregation: general case



```python
alpha = 2.0
CAC = np.exp(-alpha)
N1 = CAC *0.1
plot_aggregate_distribution(alpha, N1)
```

# Aggregation: surfactants case

Earlier we assumed that the free energy per particle was

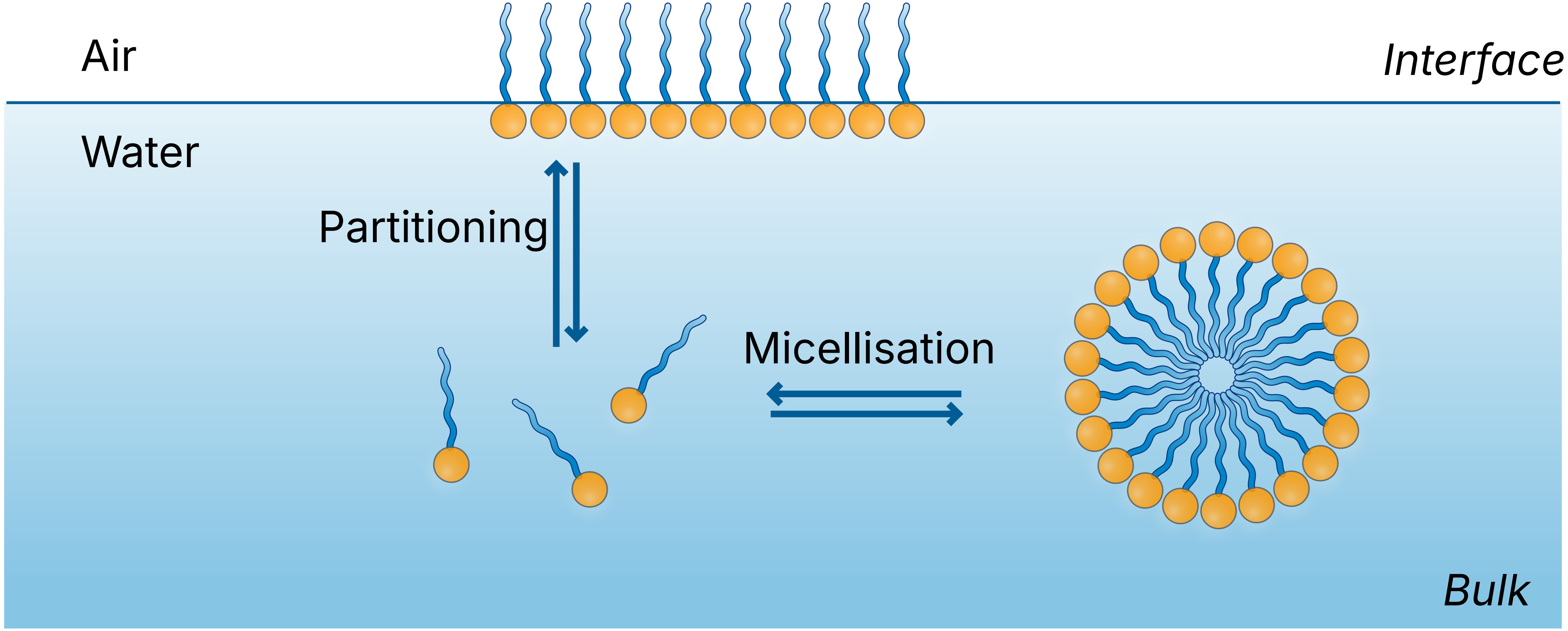
$$\epsilon_N = \epsilon_\infty + \gamma \left( \frac{v^2}{N} \right)^{1/3}$$

a monotonically decreasing function of $N$.

For surfactants, it is not necessarily the case.

- Typically $\epsilon_N$ has a minimum at some finite $N = N^*$ resulting from the fact that beyond a certain size, the aggregate becomes **unfavourable** (e.g., due to packing constraints, curvature energy, etc).
- Therefore the distribution of aggregates of size $N$ is **peaked** around $N^*$.
- This leads to the formation of **micelles**: aggregates of a characteristic size.

# Aggregation: surfactants case



Surfactants in solution: normally, this is done in water in the presence of an interface with air. Due to their nature as amphiphiles, the surfactants typically sit at the air-water interface in a dynamical, equilibrium process that exchanges monomers between the bulk and the surface. The bulk surfactants, when the concentration is larger than a critical value, also self-assemble into micellar structures, which are at equilibrium with the isolated single surfactants.

# Critical micellar concentration (CMC)

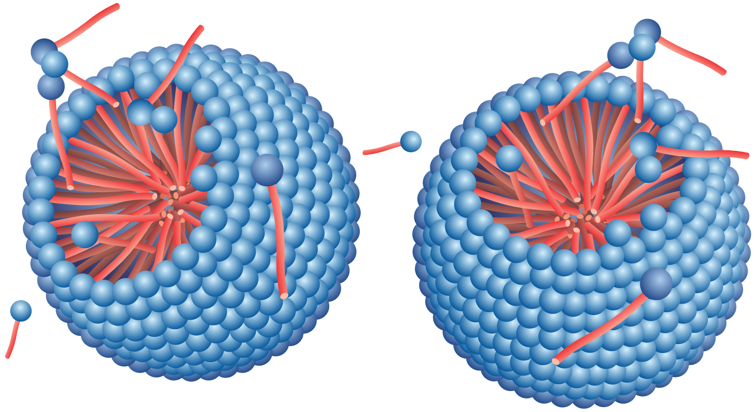
The addition of surfactants to water initially reduces the water-air surface tension, but when the surface is saturated, further addition leads to crossing the a critical micellar concentration (CMC) and micelle formation.

- **Below** the CMC, almost all surfactant molecules are present as **monomers**
- **Above** the CMC, additional surfactant molecules predominantly form **micelles** of size $N^*$ while the monomer concentration remains nearly constant.

The aggregation in water follows specific patterns:

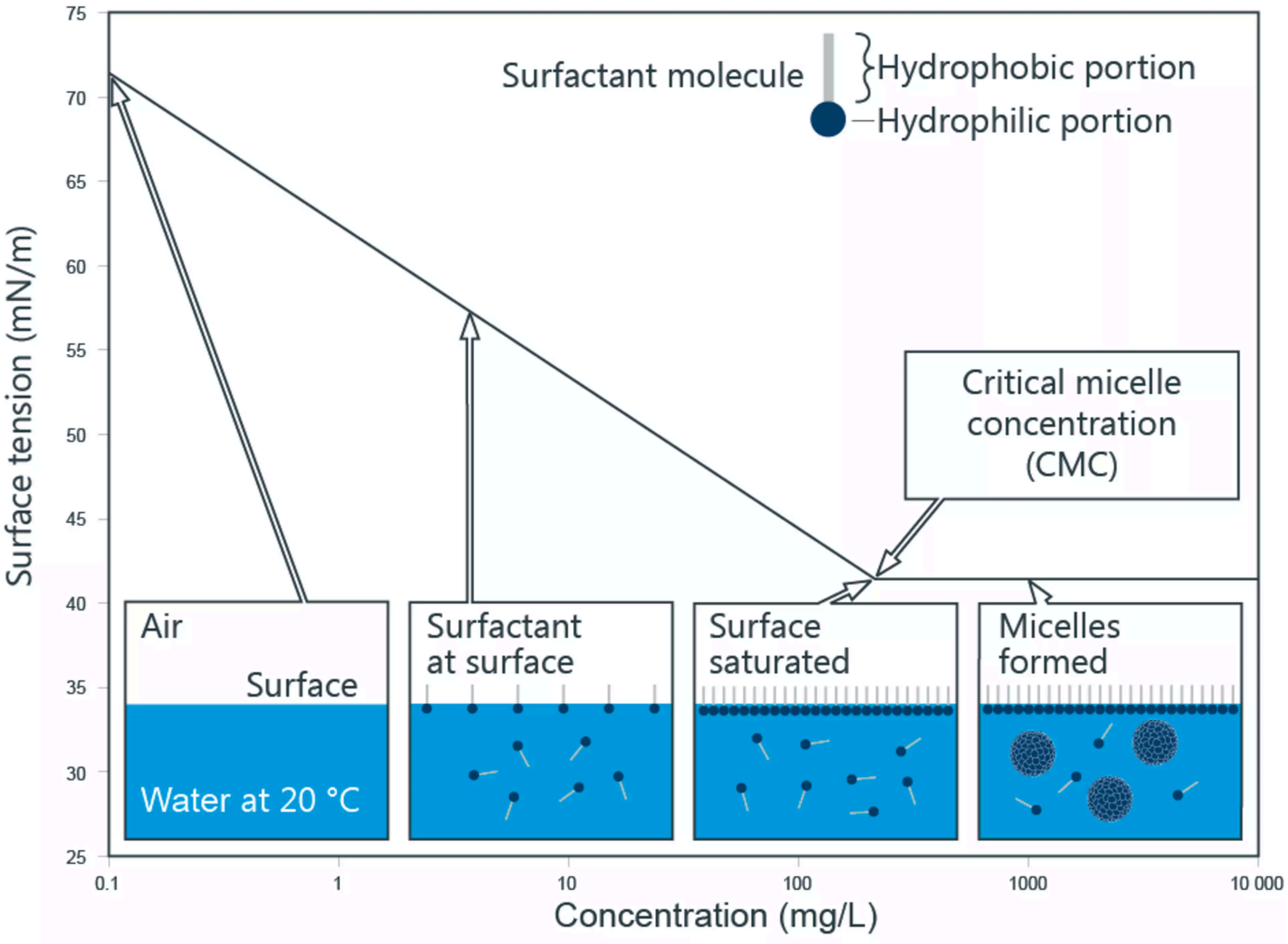
- hydrophobic tails cluster together to avoid water
- hydrophilic heads face the water

The structure on the micelle surface (formed by the heads) is disordered and fluid-like, similar to a 2D liquid.



Schematic of micelles (from DataPhysics Instruments).

# Critical micellar concentration (CMC)

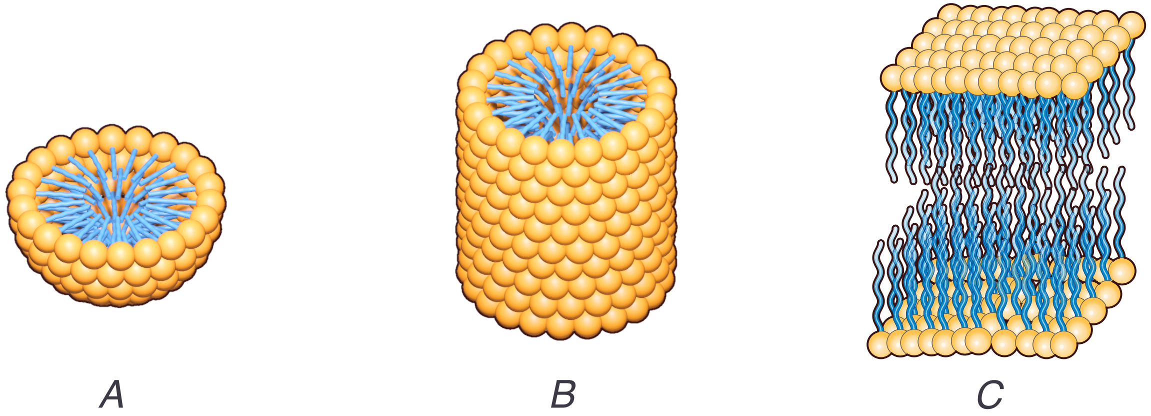


Surface tension of a surfactant solution with increasing concentration, formation of micelles, from Kruss Scientific

# Shape of surfactant assemblies

- Geometric model of a surfactant molecule:
  - **optimal headgroup area $a_0$**: depends on chemical structure, pH and temeprature.
  - **volume $v$ of the hydrophobic part**: The hydrophobic part usually consists of hydrocarbon chains. Its volume $v \propto n$ the number of carbon atoms in the chain.
  - **critical chain length $\boldsymbol{l_c}$** : the effective length of the chain, taking into account chain flexibility, temperature, branching and chemical structure. It also scales like $l_c \propto n$.

A balance between energy and entropy leads to different self-assembled structures .



Different types of self assembled structures: (A) spherical micelles, (B) cylindrical micelles and (C) bilayers.

# Spherical micelle

For a spherical micelle of radius $R$ with aggregation number $N$ , the total volume and surface area are given by

$$
\begin{aligned}
Nv &= \frac{4\pi}{3}R^3 \\
Na_0 &= 4\pi R^2
\end{aligned}
$$

Therefore $$=<

$$

where we used the fact that the radius $R$ cannot be larger than the critical chain length $\mathrm{l}_\mathrm{c}$. We thus obtain for the critical packing parameter $P$

$$P = \frac{v}{a_0 l_c} < \frac{1}{3}$$

# Cylindrical micelles

For a cylindrical micelle the total volume and surface area are given by

$$Nv = \pi R^2 L$$

and

$$Na_0 = 2\pi RL$$

Therefore $\frac{v}{a_0} = \frac{R}{2} < \frac{l_c}{2}$ again using $R < l_C$.

We thus obtain for the critical packing parameter $P = \frac{v}{a_0 l_c}$ that

$$\frac{1}{3} < P < \frac{1}{2}$$

Below the lower limit spherical micelles are formed.

# Bilayers lamellar)

For a bilayer (with separation $D$ between the layers) the total volume and surface area are given by

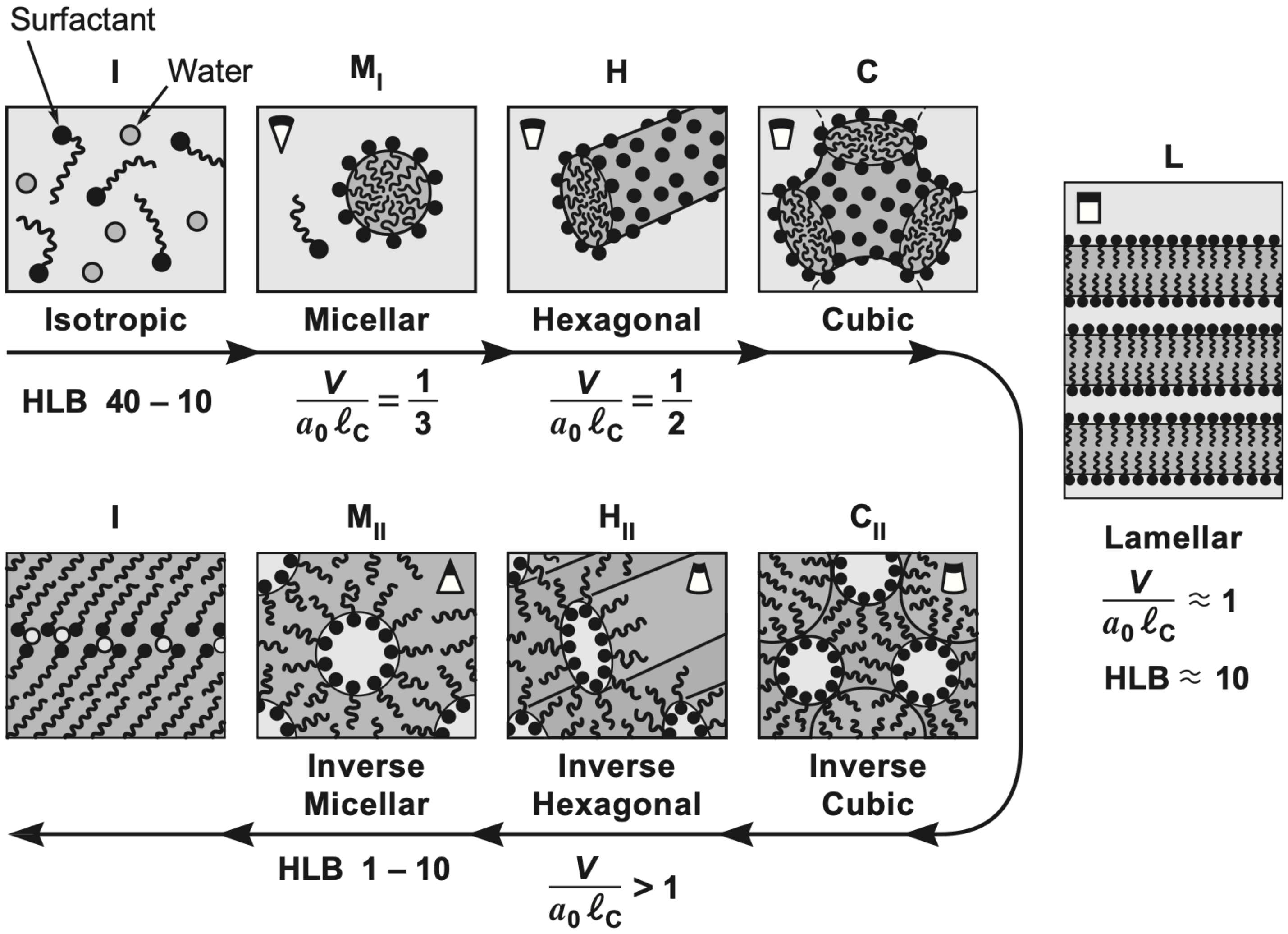
$$\begin{aligned} Nv &= AD \\ Na_0 &= 2A \\ \frac{v}{a_0} &= \frac{D}{2} < l_c \quad (\text{ using } D < 2l_c) \end{aligned}$$

We thus obtain for the critical packing parameter $P = \frac{v}{a_0 l_c}$ that

$$\frac{1}{2} < P < 1$$

Below the lower limit cylindrical micelles are formed.

# Packing parameter summary



**Mesophases** formed by surfactants as we vary the packing parameter $P = \frac{v}{a_0 l_c}$, from Israelachvili, J. N., Intermolecular and Surface Forces, 3rd Edition, Academic Press, 2011.