Colloids and Micelles

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EPFL

Outline

- Chapter 12 of Mulvaney
- Chapters of Israelachvili
- Interaction between surfaces and particles - Hamaker constant
- Self-assembly and micelle formation

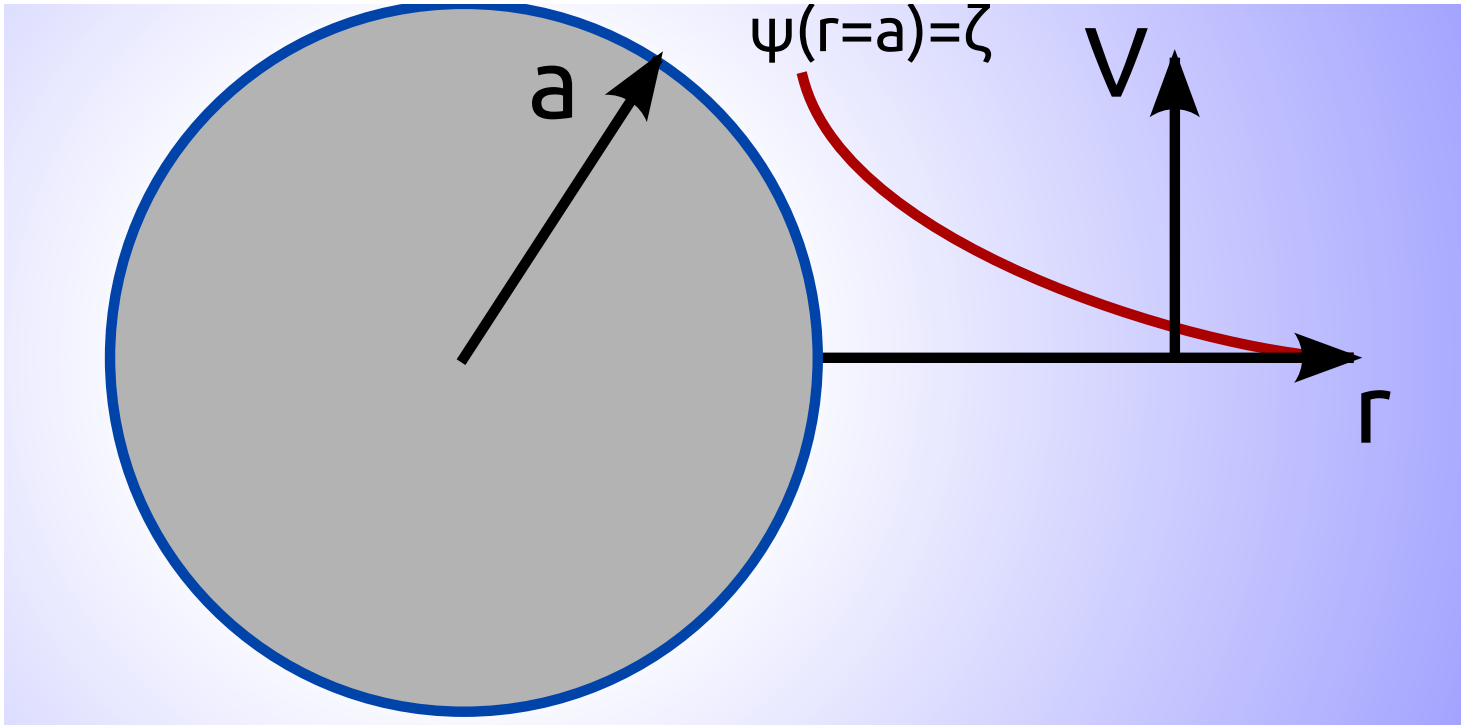
Poisson-Bolztmann for a spherical nanoparticle

- Identical treatment - only boundary conditions change. For a particle of radius a and zeta potential ζ

$$\zeta = \psi(a) = A\frac{e^{-\kappa a}}{a} \rightarrow A = a\zeta e^{\kappa a} \rightarrow \psi(r) = \zeta\frac{a}{r}e^{-\kappa(r-a)}$$

- Small distance $x = r - a$ from a large particle ($a \gg x$)

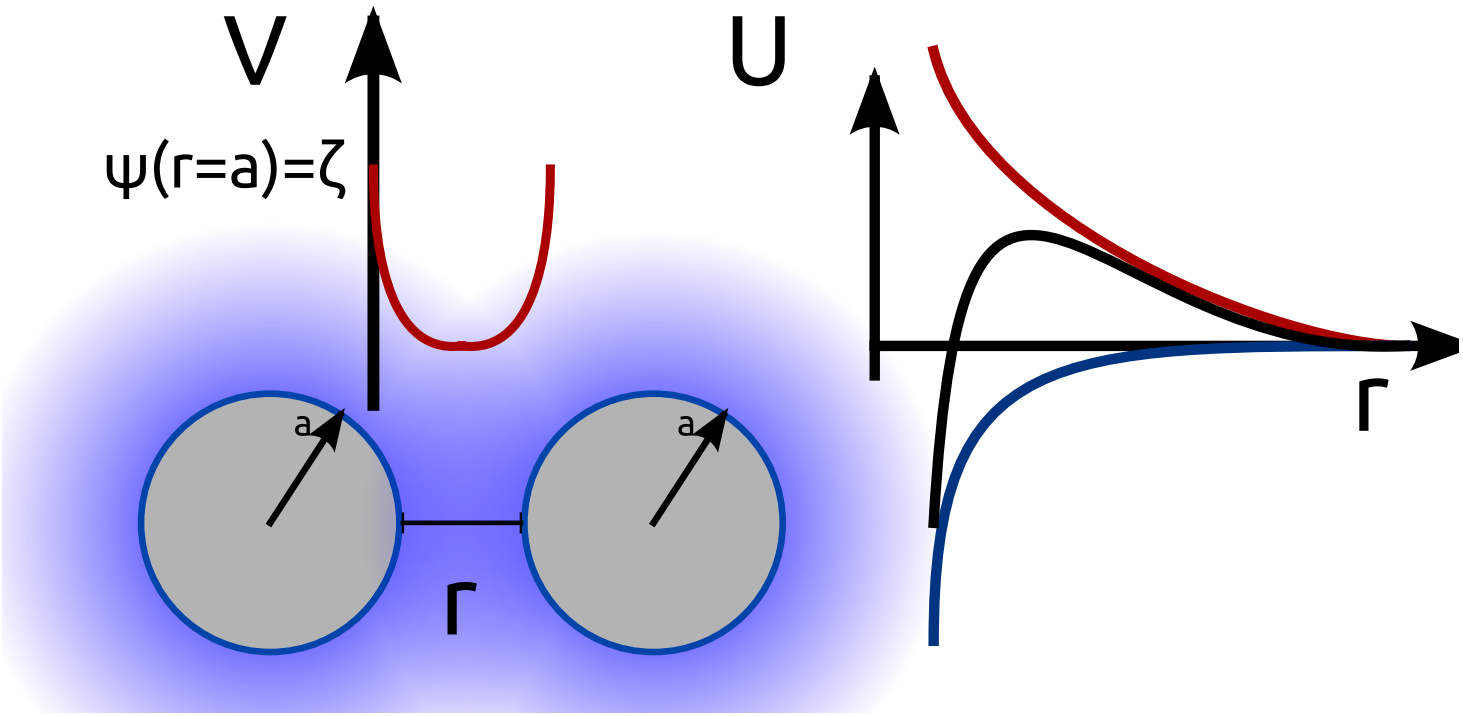
$$\psi(x) \approx \zeta e^{-\kappa x}$$



Interaction between two charged particles

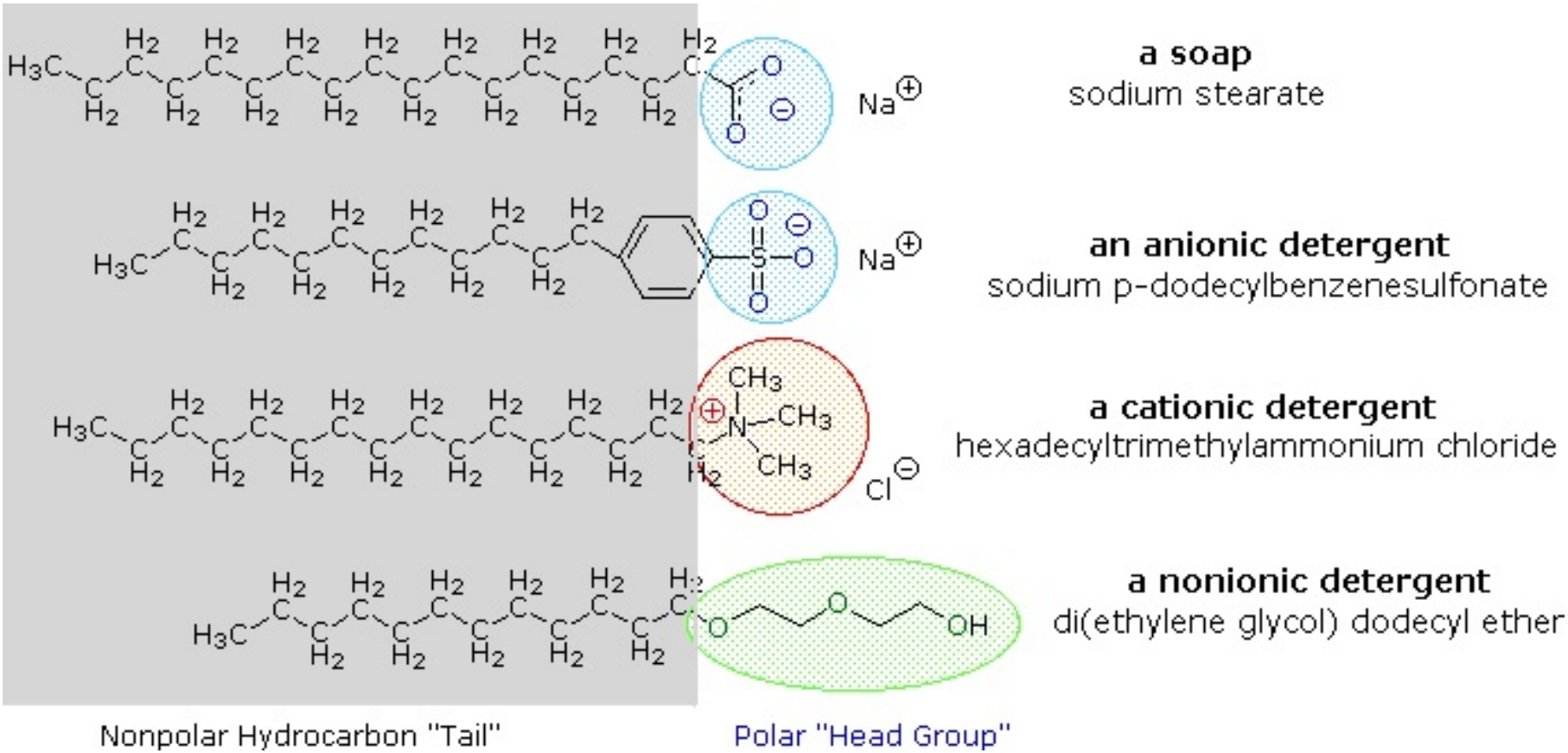
- Particles interact through charge-charge interaction and dispersion forces
  - Overlap of charge distributions lead to effective repulsive interaction between particles of size a
  - At short distances, dispersion leads to attractive force $\approx 1/d^2$ (A: Hamaker constant)

$$U(d) \approx \epsilon_0 \epsilon_r \kappa^2 \zeta^2 \frac{a^2}{d} e^{-\kappa(d-2a)} - \frac{A}{6}\left(\frac{2a^2}{d^2-4a^2} + \frac{2a^2}{d^2} + \ln\left(1-\frac{4a^2}{d^2}\right)\right)$$



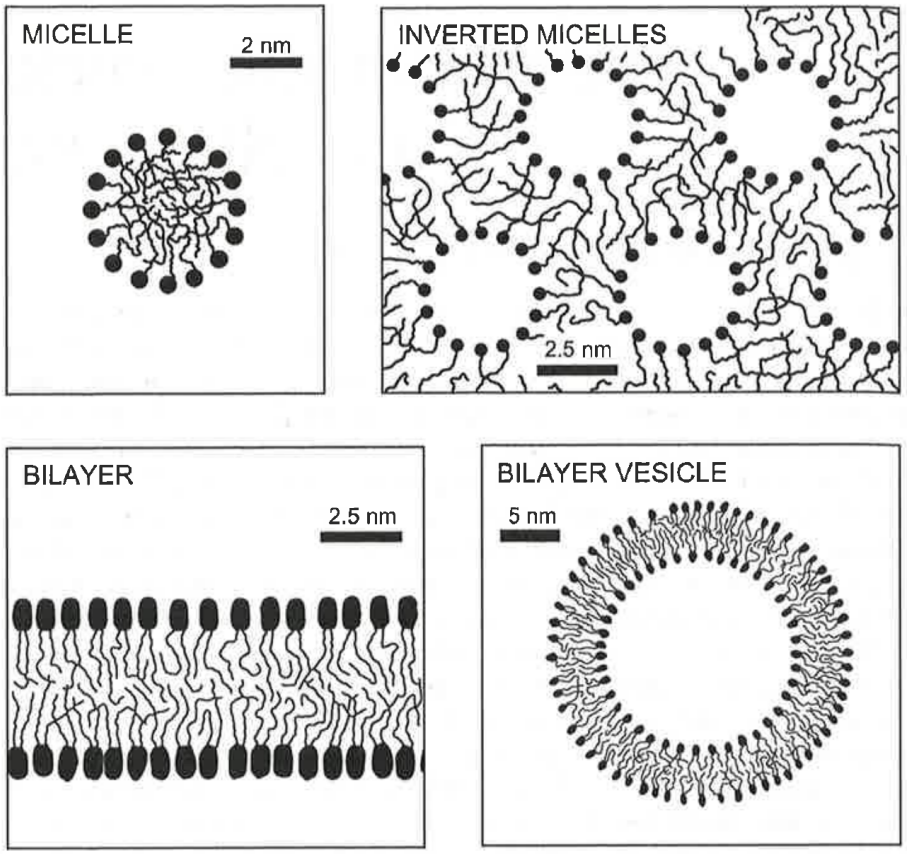
Self-assembly of molecules in solution

- Amphiphilic molecules are characterized by a hydrophilic (charged or strongly polar) head and an hydrophobic tail
- Self-assembly of amphiphilic molecules can generate several families of self-assembled structures. What's the thermodynamic drive?



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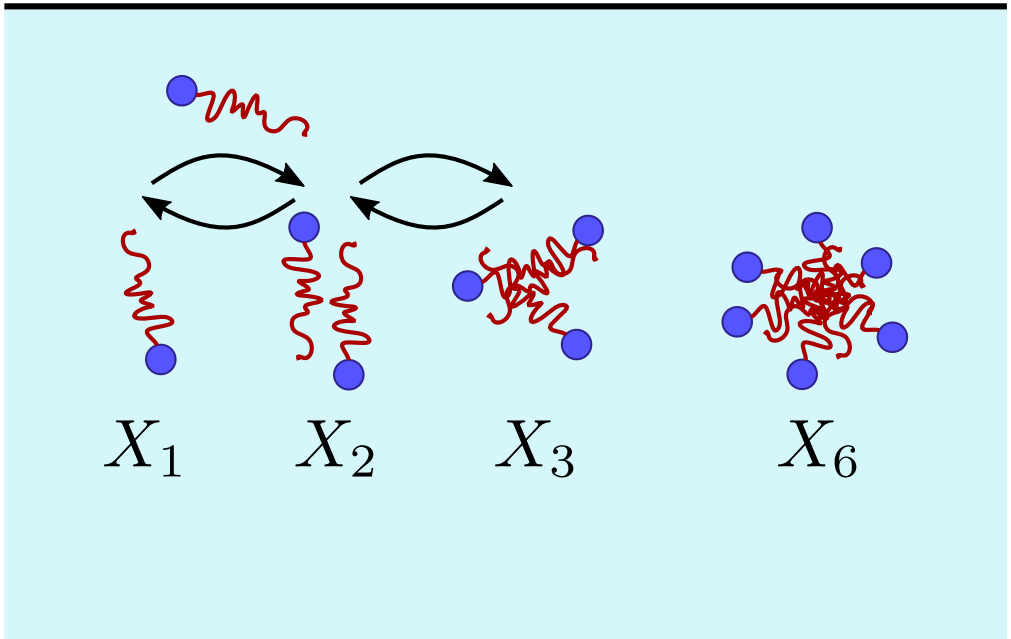
Thermodynamics of self-assembly/1

- Consider a concentration C of amphiphilic molecules. x_N is the concentration of aggregates with N molecules, and X_N the fraction of molecules in such aggregate, that is $X_N = Nx_N$ so that

$$C = \sum_i i x_i = \sum_i X_i$$

- What is the chemical potential of a molecule which is part of a N-aggregate?

$$G_N = G_N^0 + RT \ln x_N \quad \longrightarrow \quad \mu_N = \frac{G_N}{N} = \mu_N^0 + \frac{RT}{N} \ln \frac{X_N}{N}$$



Thermodynamics of self-assembly/2

- At equilibrium the chemical potential has to be the same for each aggregate size of the molecules

$$\mu_N^0 + \frac{RT}{N}\ln\frac{X_N}{N} = \mu_M^0 + \frac{RT}{M}\ln\frac{X_M}{M} \rightarrow \frac{X_N}{N} = \left(\frac{X_M}{M}\exp\frac{\mu_M^0 - \mu_N^0}{RT/M}\right)^{N/M}$$

- If $\mu_N^0 = \text{const}$, then $X_N = NX_1^N$ and since $X_1 < 1$ the number of higher aggregates decays quickly to zero
- PB: what is the size dependence of μ_N^0? Consider a sphere and set $\alpha RT = \gamma\sqrt[3]{36\pi/\rho^2}$

$$G_N \sim N\mu_\infty + \alpha RTN^{2/3} \longrightarrow \mu_N = \mu_\infty + \alpha RTN^{-1/3}$$

we are spreading the surface term over all the molecules in the aggregate

- What would be the expression for a disk or a rod?

Thermodynamics of self-assembly/2

- At equilibrium the chemical potential has to be the same for each aggregate size of the molecules

$$X_N = NX_1^N e^{N\left(\mu_1^0 - \mu_N^0\right)/RT}$$

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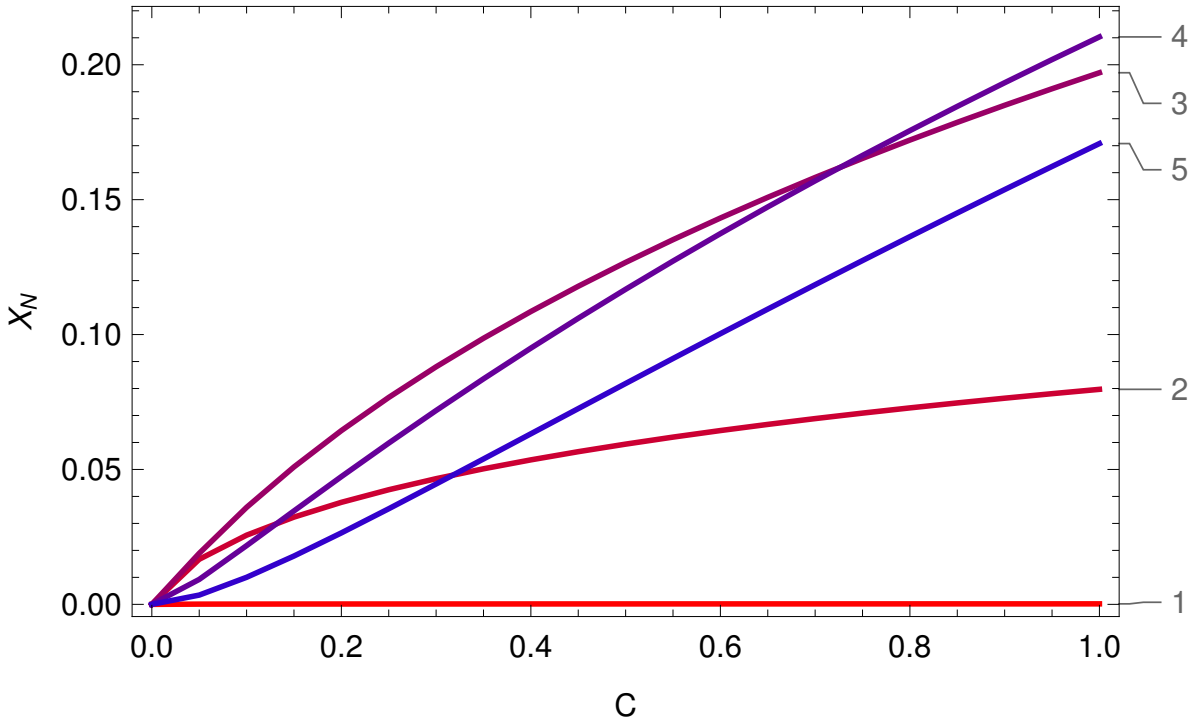
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Critical Micelle Concentration

- Let's see how this pans out in practice

$$X_N = N X_1^N e^{\alpha N\left(1-N^{-1/3}\right)} \sim N\left(X_1 e^{\alpha}\right)^N$$

- Now, if $X_1 > e^{-\alpha}$, the expression for $C = \sum_N X_N$ would diverge! This defines a critical micelle concentration $X_{\mathrm{CMC}} = e^{-\alpha}$. For $X_1 \gtrsim X_{\mathrm{CMC}}$ larger aggregates have to form!
- Now, this is very naive: we cannot control X_1, but only C so story is more complicated - distribution of sizes can be computed numerically

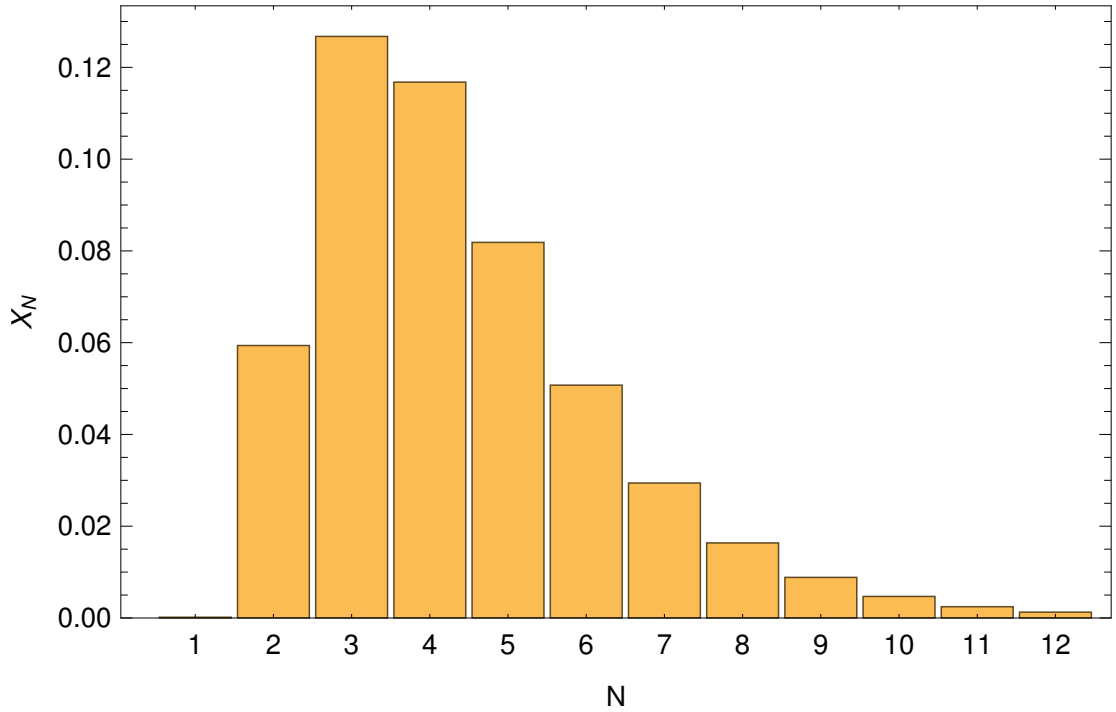


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Aggregation of rods

- The 1D case can be solved analitically, since $\mu_N = \mu_\infty + \alpha RTN^{-1}$

$$X_N = NX_1^N e^{\alpha N\left(1-N^{-1}\right)} \sim Ne^{-\alpha}\left(X_1 e^{\alpha}\right)^N$$

- We first compute the concentration as a function of X_1 and α

$$C = \sum_N Ne^{-\alpha}\left(X_1 e^{\alpha}\right)^N = \frac{X_1}{\left(e^{\alpha}X_1 - 1\right)^2}$$

- Then solve for X_1

$$X_1 = \frac{1 + 2Ce^{\alpha} - \sqrt{1 + 4Ce^{\alpha}}}{2Ce^{2a}} = \frac{2C}{1 + 2Ce^{\alpha} + \sqrt{1 + 4Ce^{\alpha}}} \leq 1$$

- Higher-dimensional aggregates cannot be solved analitically