Molecular dynamics simulation of reverse micelles: problems after 25 years of investigations

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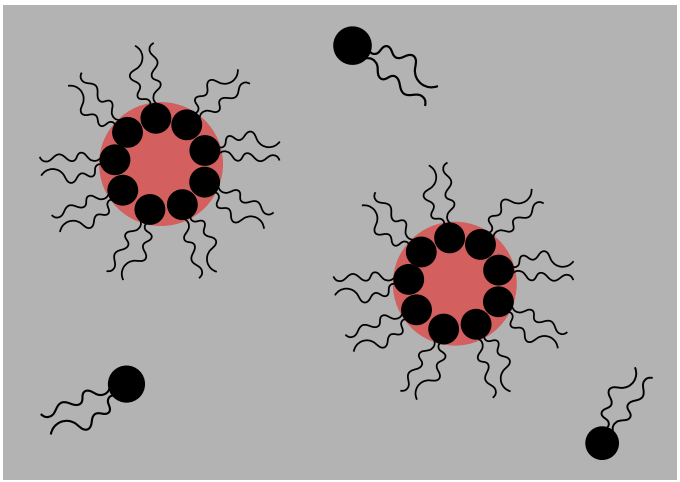
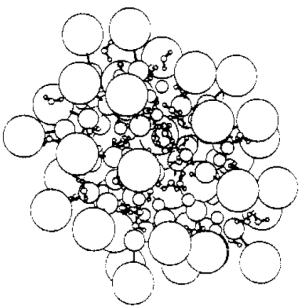
Reverse micelles

Reverse micelles form in nonpolar solutions of definite surfactants



Reverse micelles: first simulation...

...was carried out in 1988 (Brown and Clarke):



36 surfactant molecules

72 water molecules

1079 nonpolar solvent molecules

1403 atoms

$\mathbf{1.6 \cdot 10^{-10}}$ seconds — time scale

22 hours — calculating time

205 CPUs

Today, 1 hour and 1 CPU are required for similar simulation

Modern supercomputers

10^5–10^7 atoms (1000 times more than in 1988)

10^{-7}–10^{-6} seconds of time scale (3000 times more than in 1988)

10^3–10^5 CPU/GPU cores (app. 50 times more than in 1988)

Evident question

Is it possible to completely investigate all properties of reverse micelles: **shape, structure, distribution of components, energy profiles**, etc — by molecular dynamics simulation at some modern supercomputer during several days/weeks ?

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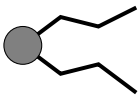
Is it possible to completely investigate all properties of reverse micelles: **shape, structure, distribution of components, energy profiles**, etc — by molecular dynamics simulation at some modern supercomputer during several days/weeks ?

There are some problems,

and increased calculation power of modern supercomputers is not sufficient to solve these problems

Prepare to MD: Initial geometry

Step 1. Choice of constant number of particles **N**:

250  **+53**  **+900** 

Prepare to MD: Initial geometry

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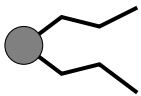
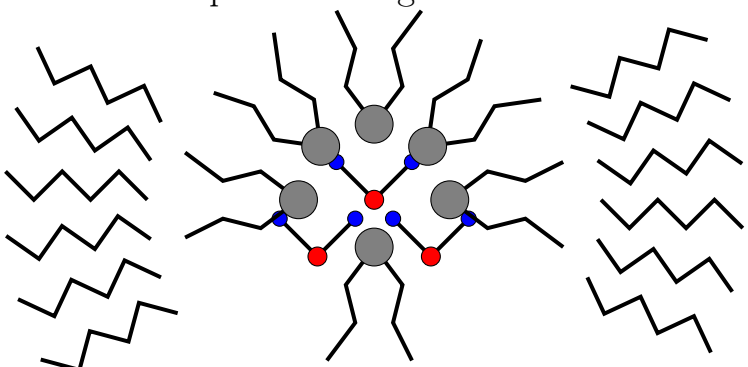
250  **+53**  **+900** 

Step 2. Choice of spatial arrangement of these molecules:



Initial geometry for proteins

First question: how many molecules?

Simple answer: 1 main molecule

Second question: how to distribute this molecule?

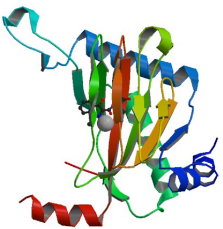
Answer: There are two possible ways

Initial geometry for proteins

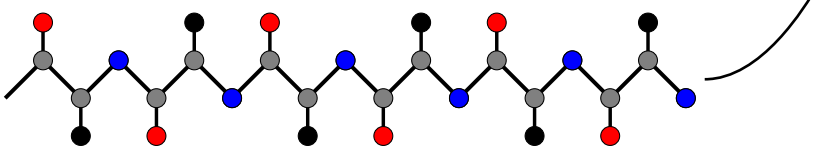
Way 1. Use X-Ray structural analysis:

Protein data bank gives tertiary structure

http://www.rcsb.org/pdb/home/home.do ⟶



Way 2. Try to use protein primary structure:



Primary structure becomes tertiary structure during MD

if we have quite appropriate simulation technique

Initial geometry for reverse micelles

First question: how many molecules?

Two types of main molecules − water and surfactant

$\boldsymbol{x}$ water and $\boldsymbol{y}$ surfactant molecules

$\boldsymbol{x}$ and $\boldsymbol{y}$ are independent

Second question: how to distribute these molecules?

There are two possible ways

1. Preassembled micelle
2. Random distributed molecules

Initial geometry for reverse micelles

How to choose $\boldsymbol{x}$ *waters* and $\boldsymbol{y}$ *surfactants*?

1. Try to use information from experiment
2. Try to guess $\boldsymbol{x}$ and $\boldsymbol{y}$

We should remember that experiment information is available

only for widely investigated reverse micelles

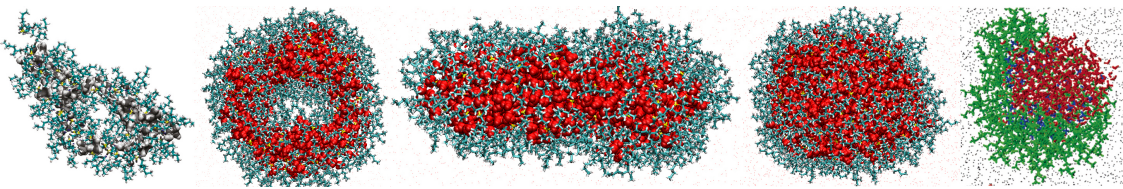
Accuracy of $\boldsymbol{x}$ and $\boldsymbol{y}$ is not sufficient

even if reverse micelles are widely studied

Initial geometry for reverse micelles

Single aggregate will form at any $\boldsymbol{x}$ and $\boldsymbol{y}$

There are 5 structures at different $\boldsymbol{x}$ and $\boldsymbol{y}$

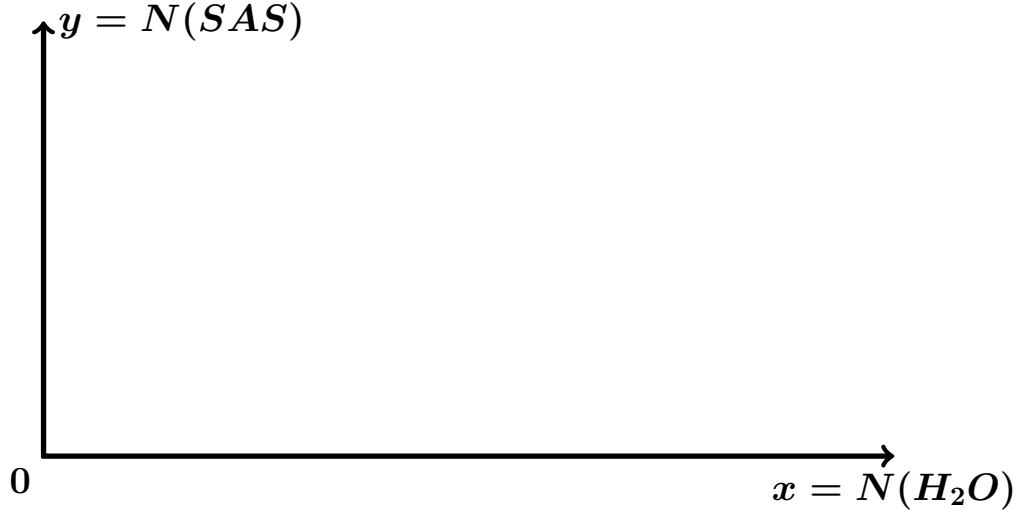


Complicated structure — Vesicle — Ellipsoid — Sphere — Water/oil contacts

$\boldsymbol{x}$ rises while $\boldsymbol{y}$ remains

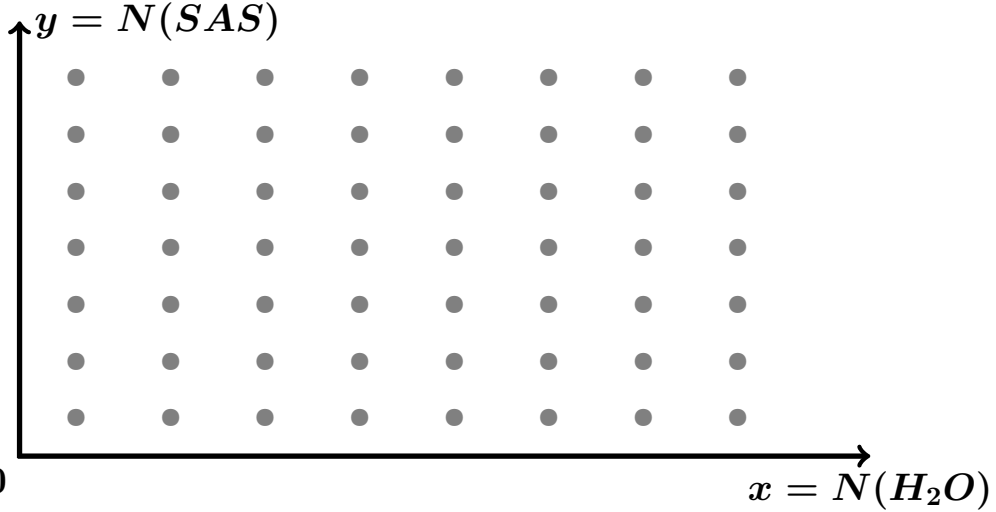
Initial geometry for reverse micelles

Because of the accuracy of $\boldsymbol{x}$ and $\boldsymbol{y}$ is not sufficient:



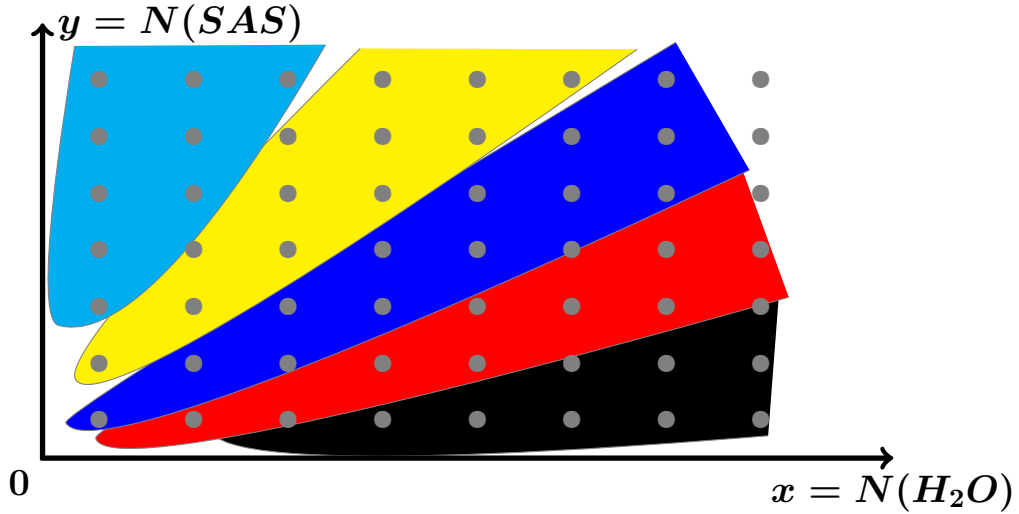
Initial geometry for reverse micelles

Choose any $\boldsymbol{x}$ and $\boldsymbol{y}$:



Initial geometry for reverse micelles

Structure depends of $\boldsymbol{x}$ and $\boldsymbol{y}$:



Initial geometry for reverse micelles

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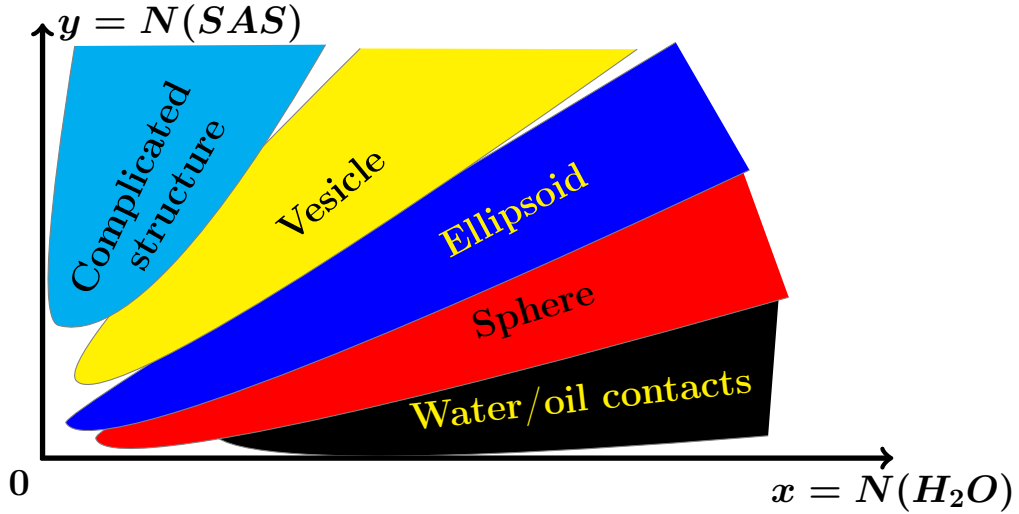
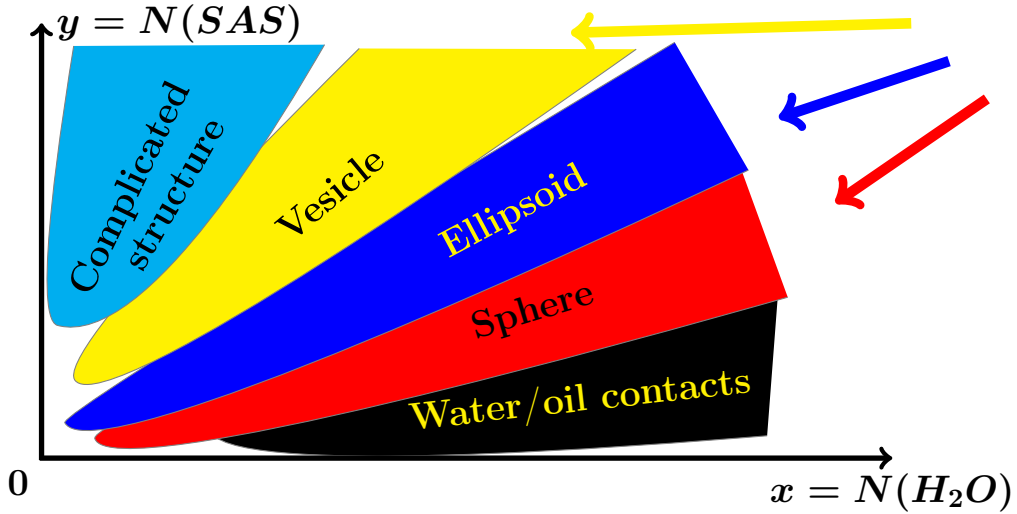


Initial geometry for reverse micelles

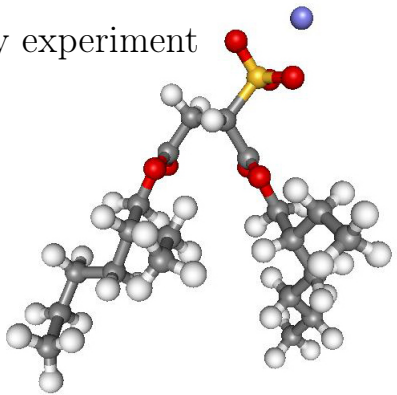
Compare structure with experiment:



Reverse micelles of Aerosol OT

Reverse micelles of Aerosol OT:

1. are the most widely investigated by experiment
2. have spherical shape



Reverse micelles of Aerosol OT

Cell size: 12–15 nanometers

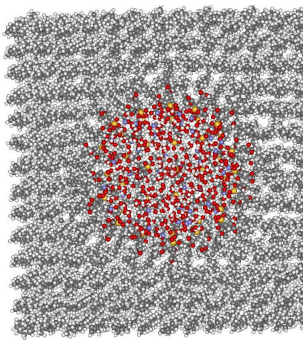
30000–300000 atoms

Preassembled micelle as initial geometry

Time scale — 20–50 nanoseconds

Cores of CPU: 8

(*at Institute of Problems of Chemical Physics, RAS*)

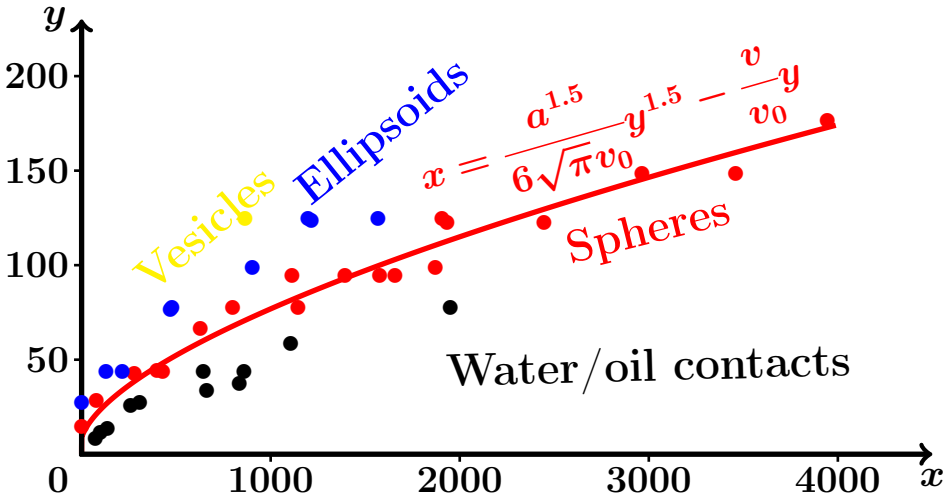


Cores of CPU: 64–1024 (*at Joint Supercomputer Center, RAS*)

Number of calculations: 20–50

Reverse micelles of Aerosol OT

Save the micelles with spherical shape:



Thank you for attention!