INVESTICE DO ROZVOJE VZDĚLÁVÁNÍ

MOLEKULÁRNÍ POHLED NA ELECTROSPINNING

(Kapaliny ve vnějším elektrickém poli)

Ivo NEZBEDA

E. Hala Lab. of Thermodynamics, Acad. Sci., Prague, Czech Rep.

PROJEKT OPTIS PRO FT, reg. č.: CZ.1.07/2.2.00/28.0312 JE SPOLUFINANCOVÁN EVROPSKÝM SOCIÁLNÍM FONDEM A STÁTNÍM ROZPOČTEM ČESKÉ REPUBLIKY

Electrospinning

is one of the **electrodeposition** methods used to produce **fibers** from solutions by applying an **electric field**.

There are two different methods:

Needle/capillary electrospinning

i) – a droplet of liquid is formed at the tip of a needle/capillary.

ii) Needleless electrospinning

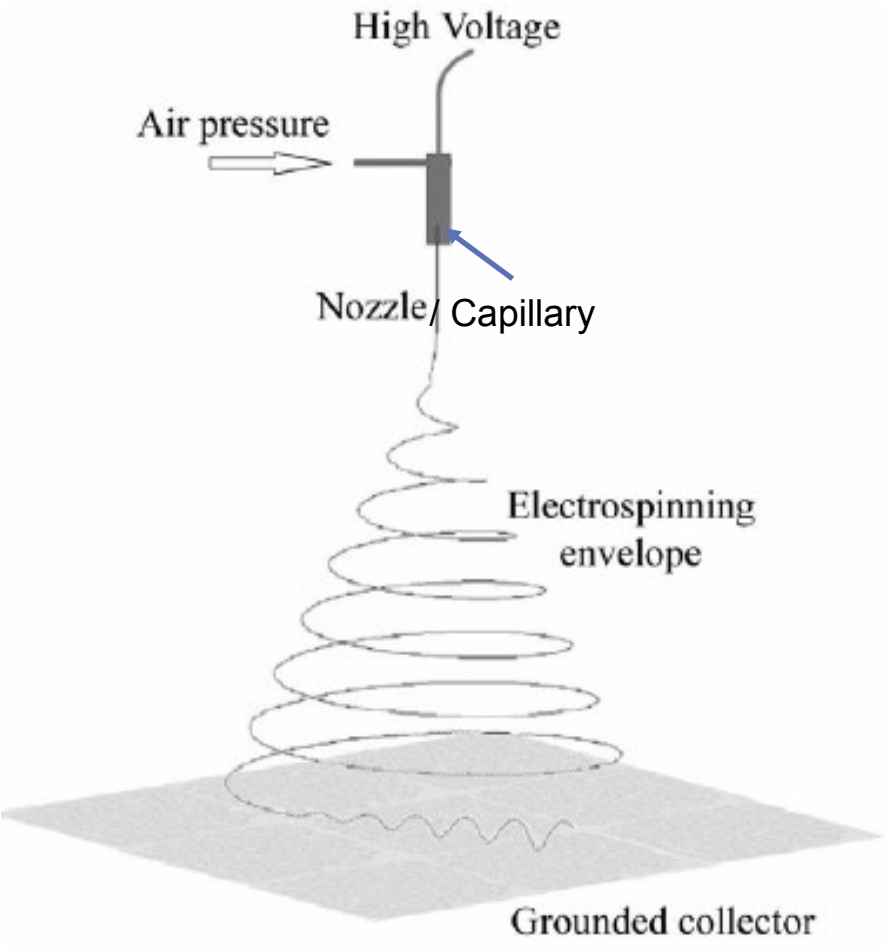
iii) – several polymeric jets emerge spontaneously from the free liquid surface.

WARNING/terminology:

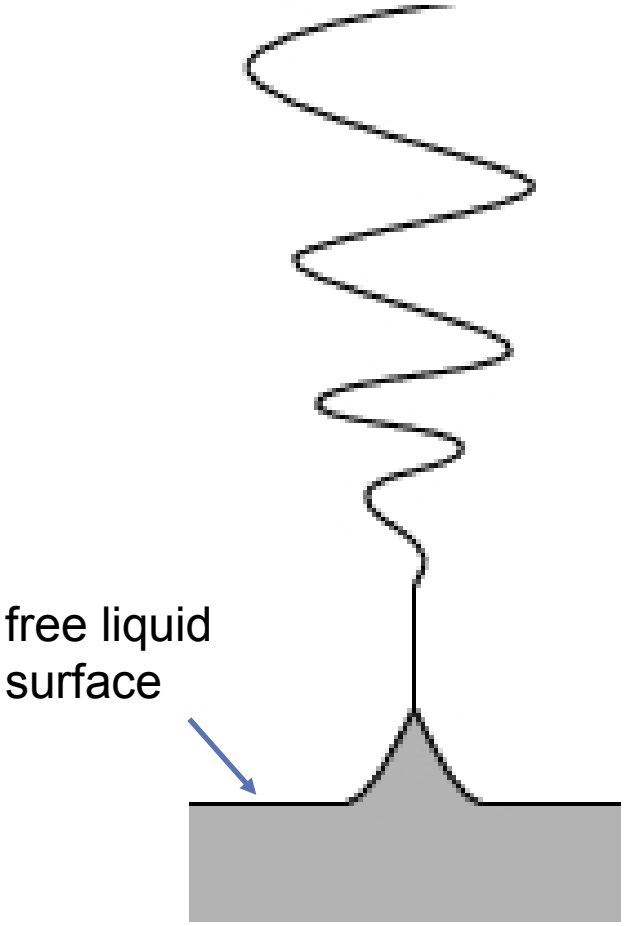
In general, electrospinning means NEEDLE SPINNING !!

(see, e.g., papers in scientific literature)

CAPILLARY/NEEDLE SPINNING



NEEDLELESS SPINNING



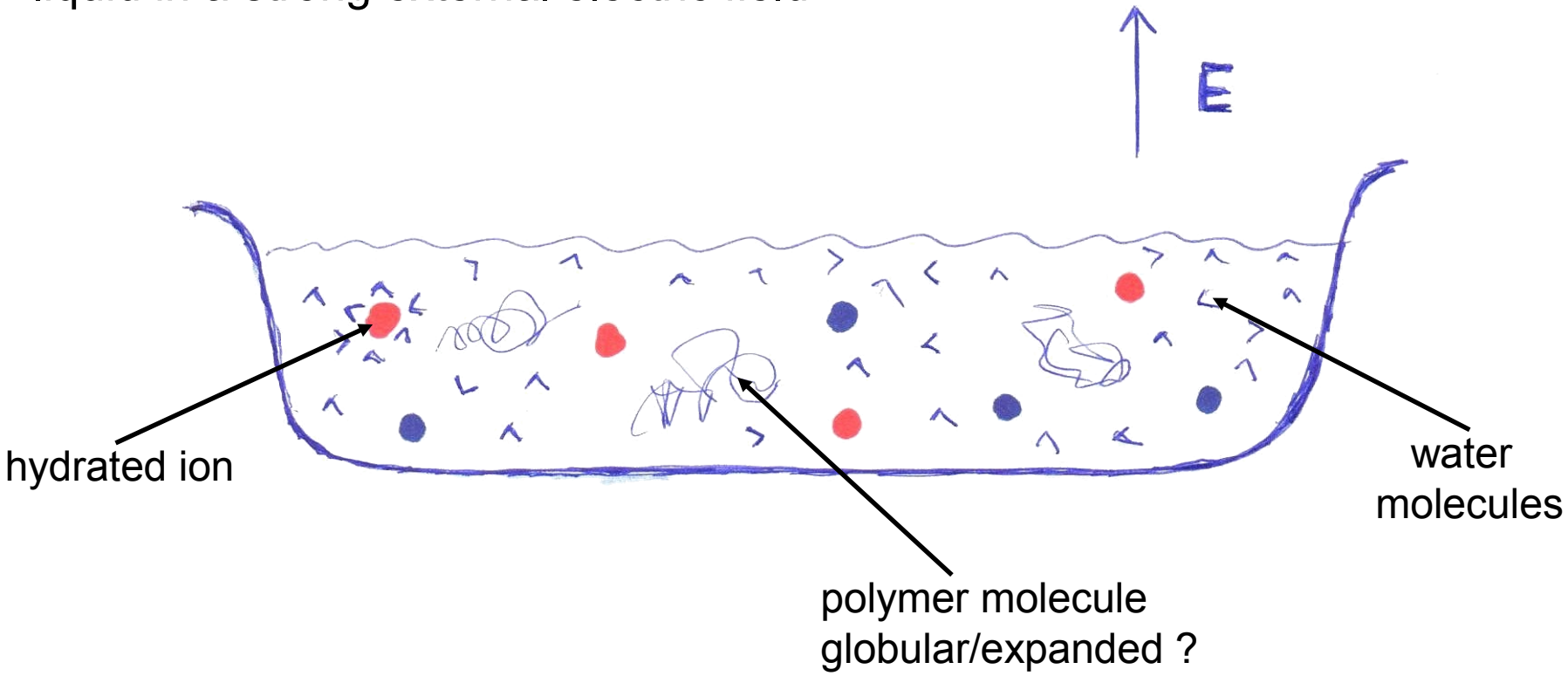
ELMARCO – synonym for electrospinning

Problem of primary interest:

Relation between the properties/quality of the fiber and the solution (its composition, etc.)

PHYSICAL PICTURE OF ELECTROSPINNING:

liquid in a strong external electric field



PRIMARY QUESTION:

What mechanism makes it possible to form the jet of polymer molecules?

OUTLINE

ART I:

otivation/Problem specification
olution – macroscopic approach
– molecular approach
tatistical mechanics – basics
olecular simulations – basics

ART II:

odeling of electrospinning – molecular simulations
feasibility study
experiment and its interpretation

INSIGHT INTO THE ELECTROSPINNING MECHANISM

QUESTION:

When the technology to produce nanofibers is available, is there any reason at all why to study molecular mechanisms of the electrospinning process?

GENERAL PROBLEMS:

How to produce nanofibres possessing the properties desired for applications?

1. filter media, composite materials, biomedical applications, (tissue engineering, scaffolds, bandages, drug delivery, wound dressings), heat and sound insulation, water desalination, etc.

What conditions are needed to produce a fibre in general?

2. Polymer molecules may leave the solution in the form of **spray, jet**, or **stream**

THERE IS ONLY A NARROW WINDOW IN THE MULTIDIMENSIONAL SPACE OF CONDITIONS (material, thermodynamic,…) AT WHICH NANOFIBERS CAN BE

EVIDENT TASK FOR SCIENTIFIC/ENGINEERING COMMUNITY:

Locate the window (in dependence on all the involved parameters)

CONTEMPORARY SOLUTION (state-of-the-art):

TRIAL-AND-ERROR approach is used making use of experienced technicians

⇓

A reasonable solution (time consuming and costly) is, usually but not always, found

⇓

Efficiency of the running technological processes is questioned and its increase is badly demanded.

WAY TOWARDS THIS GOAL:

DEVELOP THEORY !

UNDERSTANDING ELECTRO-SPRAYING/SPINNING PROCESS:
TYPICAL PROBLEM OF ELECTRO-HYDRODYNAMICS
(MACROSCOPIC APPROACH)

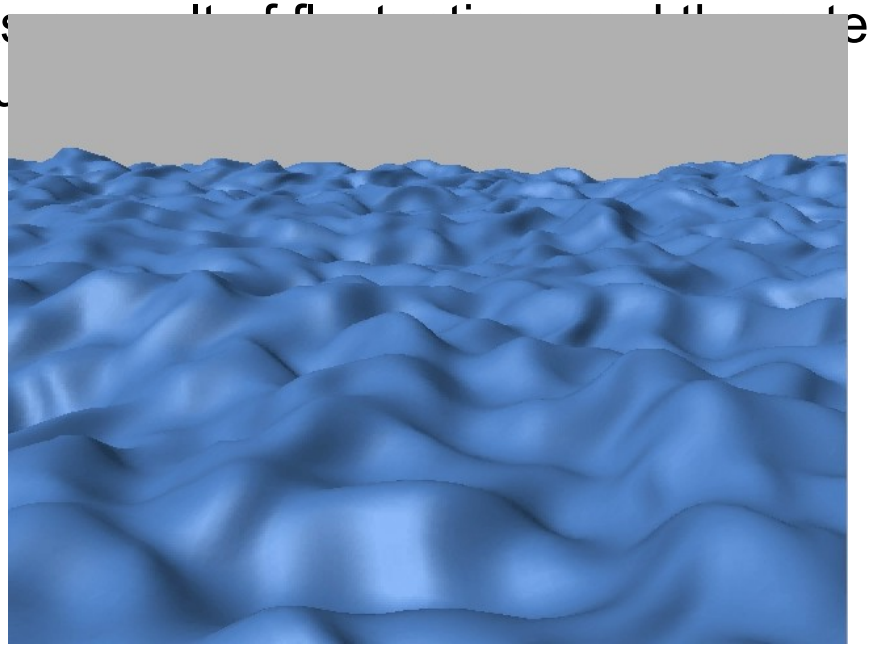
Basic principles were laid by Taylor:
formation of the (Taylor) cone and loss of its stability

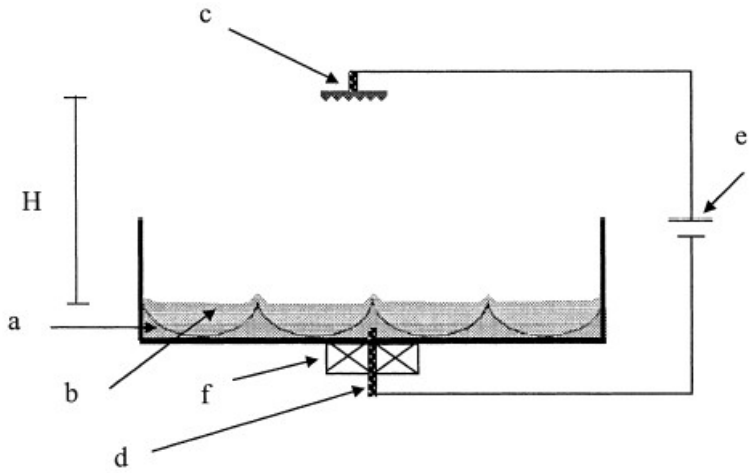
Electrospinning from free liquid surface

Very approximate model description using electrohydrodynamics in 1-D was developed by
Lukas D., Sarkar A., Pokorny P., J. Appl. Phys. 103 (2008), 309.

Idea:

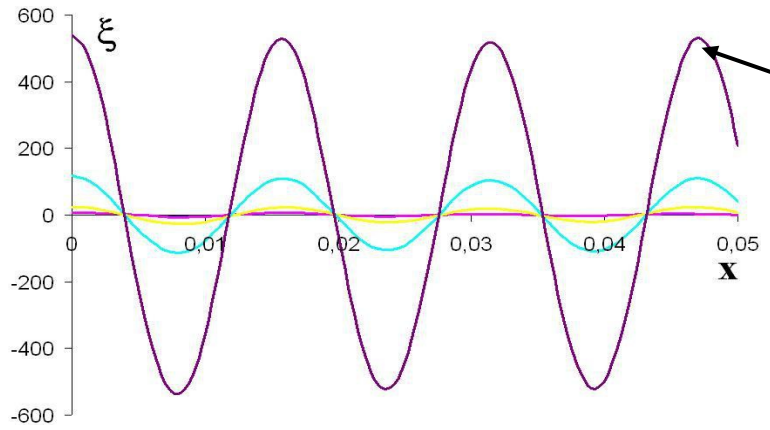
As a result of fluctuations and the external field, rippling (waves) develop on the su





Macroscopic theory - result:

Field strength increment can lead to an unlimited growth of the wave amplitude.



Theoretical description/model:
solved as a 1-dim problem

Formation of Taylor cone

RESULT:

There exists a certain critical field strength, *E*c, which marks the loss of stability

***E*c = function(surface tension, dielectric constant, viscosity…)**

all of them as a function of composition, etc.

That's all what the macroscopic theory can say

SCOPIC (PHENOMENOLOGICAL) APPROACH:

ach that expresses mathematically the results of observed phenomena
aying (unable to pay) detailed attention to their fundamental significance.

OPIC APPROACH:

er as a collection of a huge number of interacting particles (molecules, ions

explain/predict the properties of matter by means of the properties of these
particles

REACH IT?

TE (intuitive) IDEA:

n a set of equations of motions and use then all gears of numerical analysi
rful computers to find the solution.

SIBLE?

TECHNICAL REASON

1 mol of matter contains N ~ 10^{23} particles.
Number of operations needed to solve N equations is of the order N^3
One operation takes about 1nsec

To solve the given set of equations we need about 10^{60} sec ~ 10^{53} years
(more than the existence of the Universe!)

FUNDAMENTAL REASON

To solve differential equations we have to specify the boundary conditions.

Quantum mechanics tells us that, as a consequence of Heisenberg's uncertainty principle, there is a fundamental limit to the precision with which certain pairs of physical properties
of a particle, such as position and momentum, can be known simultaneously.

⇓

In general,

NO PHYSICAL QUANTITY CAN BE DETERMINED WITHOUT

MICROWORLD

MACROWORLD

few molecules

Quantum chemistry

Properties of
-individual mol.s
-dimers, trimers, ..

generalization

(approximation)

collection of a huge number of molecules; N ~ 1023

Many-body Hamiltonmian

continuous matter

Sample of matter in test tube (material parameters)

STARTING POINT:

Fluids (i.e. gases and liquids) are viewed as a collection of N mutually interacting molecules confined to a volume V at a temperature T and are defined by a total intermolecular potential energy (Hamiltonian)

$U=U(q1, q2, ..., qN) = U(1,2,\ldots,N)$

where qi stands for generalized coordinates of molecule i.

All properties of fluids, i.e. both structural and thermodynamic, are then derived from U.

THE PRIMARY GOAL of the statistical mechanics of matter is to develop methods for - ***explaining*** and ***predicting*** the experimentally measurable quantities of a given substance in terms of the properties of its elementary constituent particles.

To seek 'numerical' agreement with experiment should apply ONLY to computer generated data.

MICROWORLD

few molecules

Quantum chemistry

Properties of
-individual mol.s
-dimers, trimers, ..

generalization

(approximation)

collection of a huge number of molecules; N ~ 1023

Many-body Hamiltonmian

STAT. MECH. MACHINERY

(approximate) Theoretical calculations

Macroscopic properties

MACROWORLD

continuous matter

Sample of matter in test tube (material parameters)

Fluid mechanics
Thermodynamics
……

Macroscopic properties

STARTING POINT:

Fluids (i.e. gases and liquids) are viewed as a collection of *N* mutually interacting molecules confined to a volume *V* at a temperature *T* and are defined by a total intermolecular potential energy (Hamiltonian)

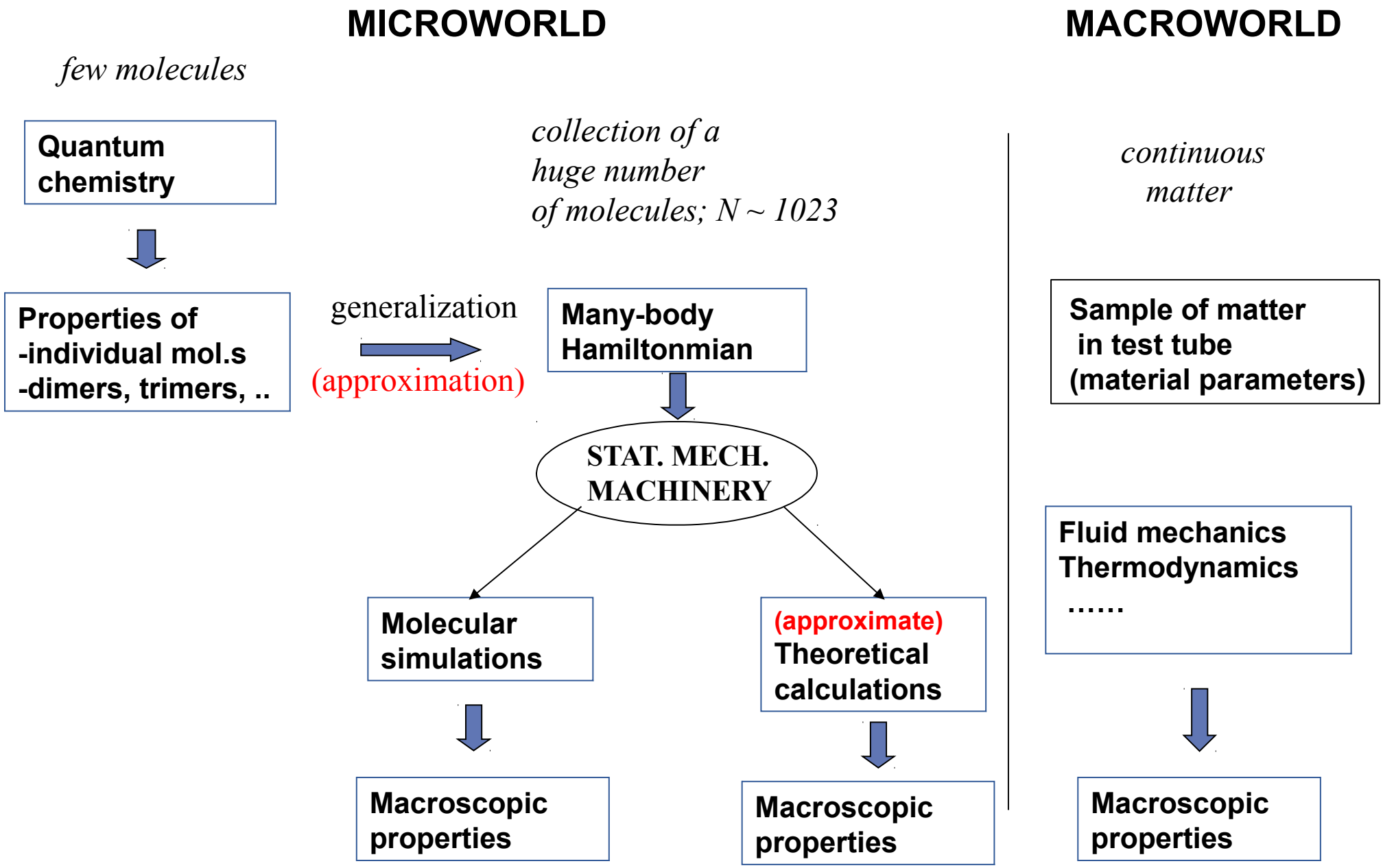
$U=U(q1, q2, ..., qN) = U(1,2,\ldots,N)$

where *qi* stands for generalized coordinates of molecule *i*.

All properties of fluids, i.e. both structural and thermodynamic, are then derived from *U*.

THE PRIMARY GOAL of the statistical mechanics of matter is to develop methods for - ***explaining*** and ***predicting*** the experimentally measurable quantities of a given substance in terms of the properties of its elementary constituent particles.

To seek 'numerical' agreement with experiment should apply ONLY to computer generated data.


MICROWORLD
MACROWORLD
few molecules
collection of a huge number of molecules; N ~ 1023
continuous matter
Quantum chemistry
Properties of -individual mol.s -dimers, trimers, ..
generalization
(approximation)
Many-body Hamiltonmian
STAT. MECH. MACHINERY
Molecular simulations
(approximate) Theoretical calculations
Macroscopic properties
Macroscopic properties
Sample of matter in test tube (material parameters)
Fluid mechanics Thermodynamics .....
Macroscopic properties

MOLECULAR SIMULATIONS:

What do we call molecular simulation ?

A class of (numerical) methods (computer experiments) in which **the geometry, position, and interaction energy of every molecule** is explicitly accounted for when a given MACROSCOPIC system (i.e., a system of ~ 10^k, k = 2,.. 5, molecules) is modeled.

Examples: thermodynamics of pure fluids and their mixtures (e.g., phase equilibria)

reaction kinetics

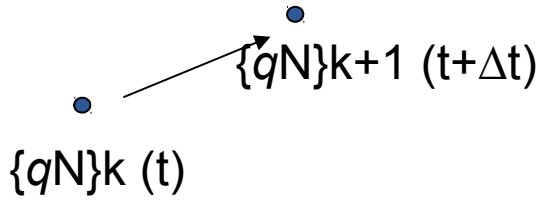
structure of the interface
molecular rearrangement at the level of picosenconds
processes at explosion

experiments at conditions hardly reachable on the Earth

colloidal systems, flow in porous media, etc.

MOLECULAR SIMULATIONS: walk in the configuration space

{*q*N} ≡ (q1, q2, ..., qN) ; qi ... position vector of particle *i*



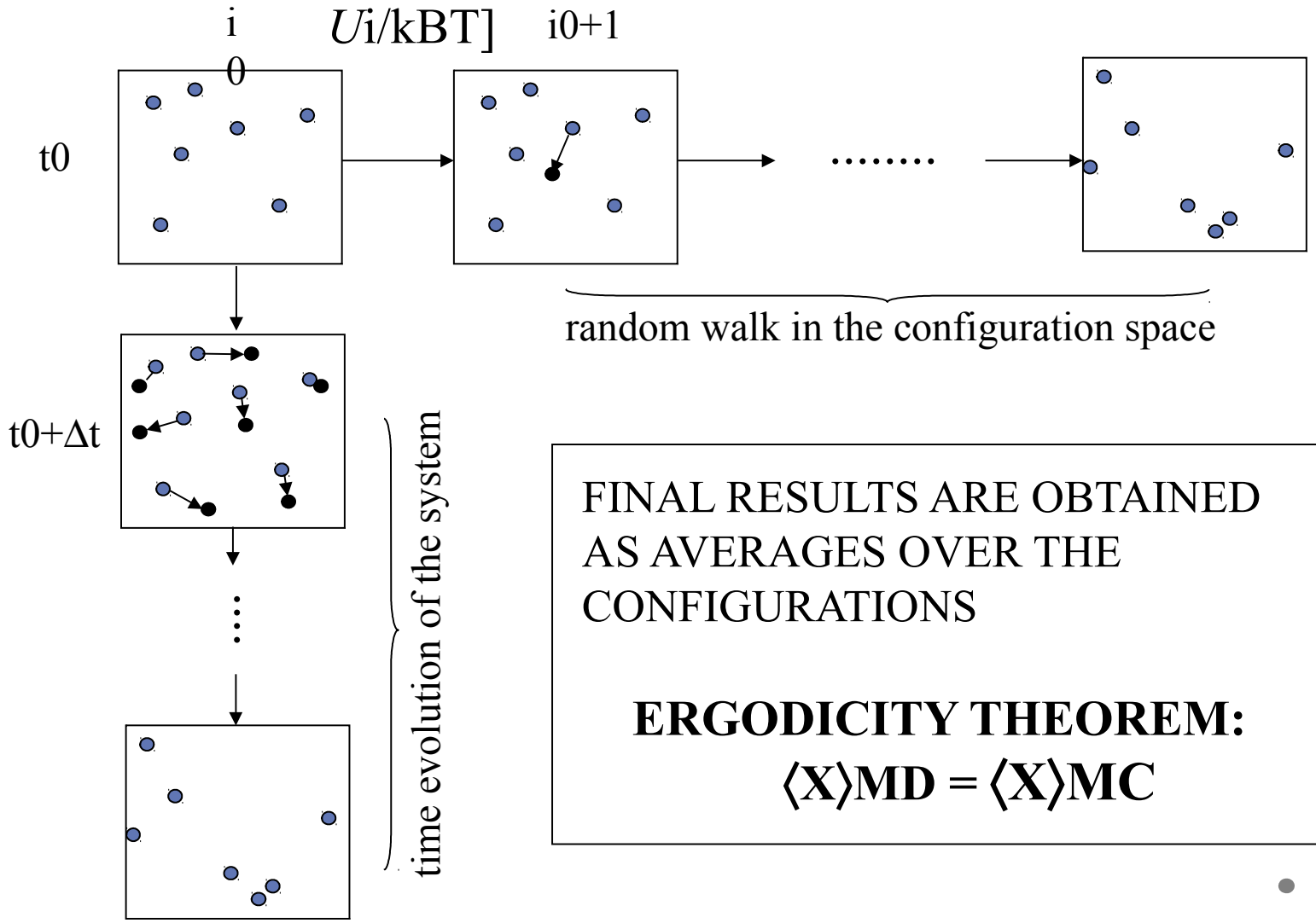
1. **Molecular dynamics**: deterministic evolution given by the equations of motion
2. **Monte Carlo**: probabilistic evolution (random walk)

In both cases the walk is determined uniquely by the interaction Hamiltonian, *i.e.*, the total potential energy, $U=U(\{q\mathrm{N}\})$.

TWO WAYS OF PERFORMING MOLECULAR SIMULATIONS

MONTE CARLO

Generation of the Markov chain with occurrence probability of configurations ~ exp[-*U*i/kBT]



FINAL RESULTS ARE OBTAINED AS AVERAGES OVER THE CONFIGURATIONS

ERGODICITY THEOREM:

⟨X⟩MD = ⟨X⟩MC

ps)* Δt = 1 to 20 nsec

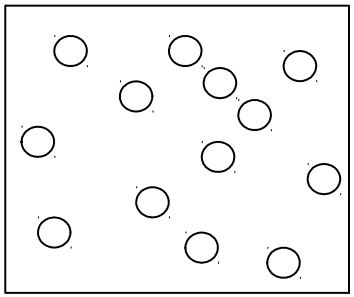
THREE BASIC PROBLEMS OF SIMULATIONS:

1. Choice of $U(\{q\mathrm{N}\})$, *i.e.*,
   define/characterize the investigated matter at the level of molecules

2. In computer we have to work with FINITE systems.
   Problem: **All** theories are valid in the thermodynamic limit,
   i.e., for infinitely large systems: $\mathrm{N} \rightarrow +\infty$, $\mathrm{V} \rightarrow +\infty$, $\mathrm{N/V}=\mathrm{const}$

3. Walks in the configuration space mimic the Mother Nature.
   ⇓
   Development of the system (configurations) may be analyzed:
   - measure physical quantities (**WHAT & HOW?** Not always trivial matter!)
   - qualitative understanding of the process at the molecular level

FINITE SYSTEM –particles closed in a box



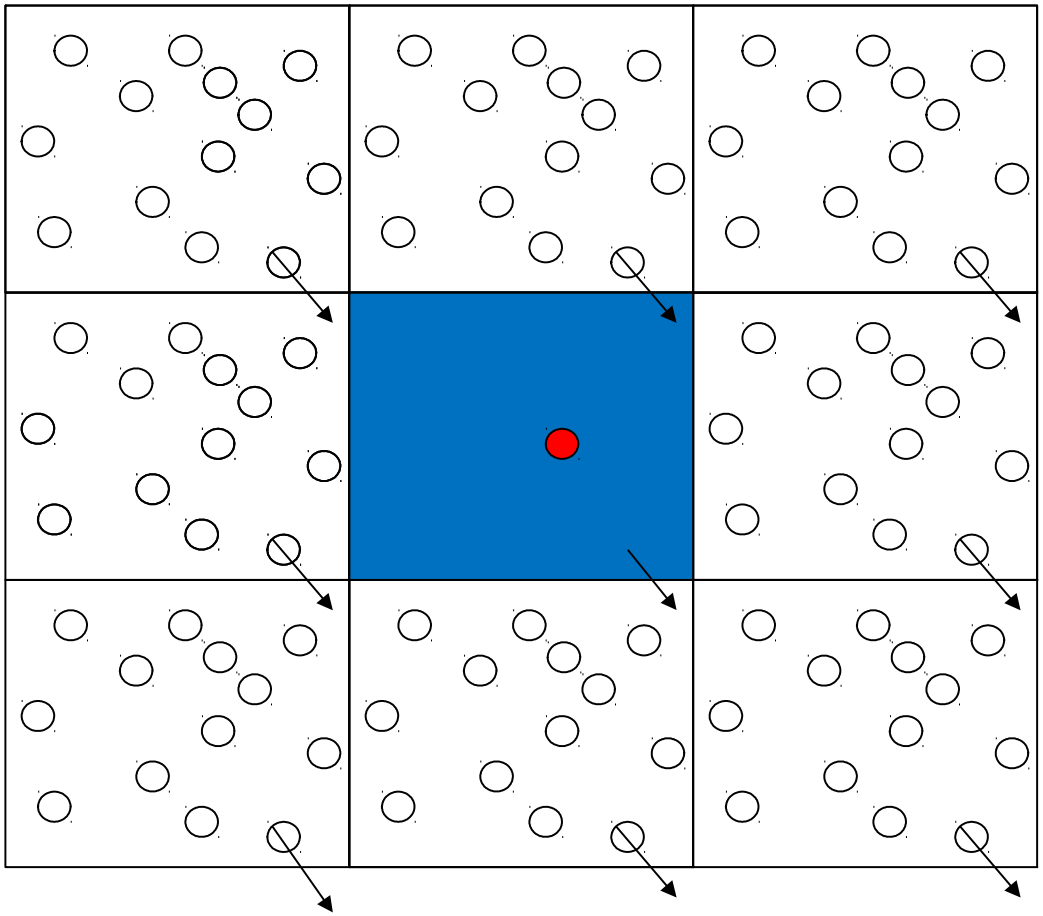
IDEA: consider a very large box to accommodate as much particles as possible

PROBLEMS:

- Technical: there are limits imposed by the hardware (capacity, speed, etc.)
- Even for a very large systems (thousands of molecules) a very large number molecules will feel the effect of the walls

SOLUTION: Periodic boundary conditions

PERIODIC BOUNDARY CONDITIONS:

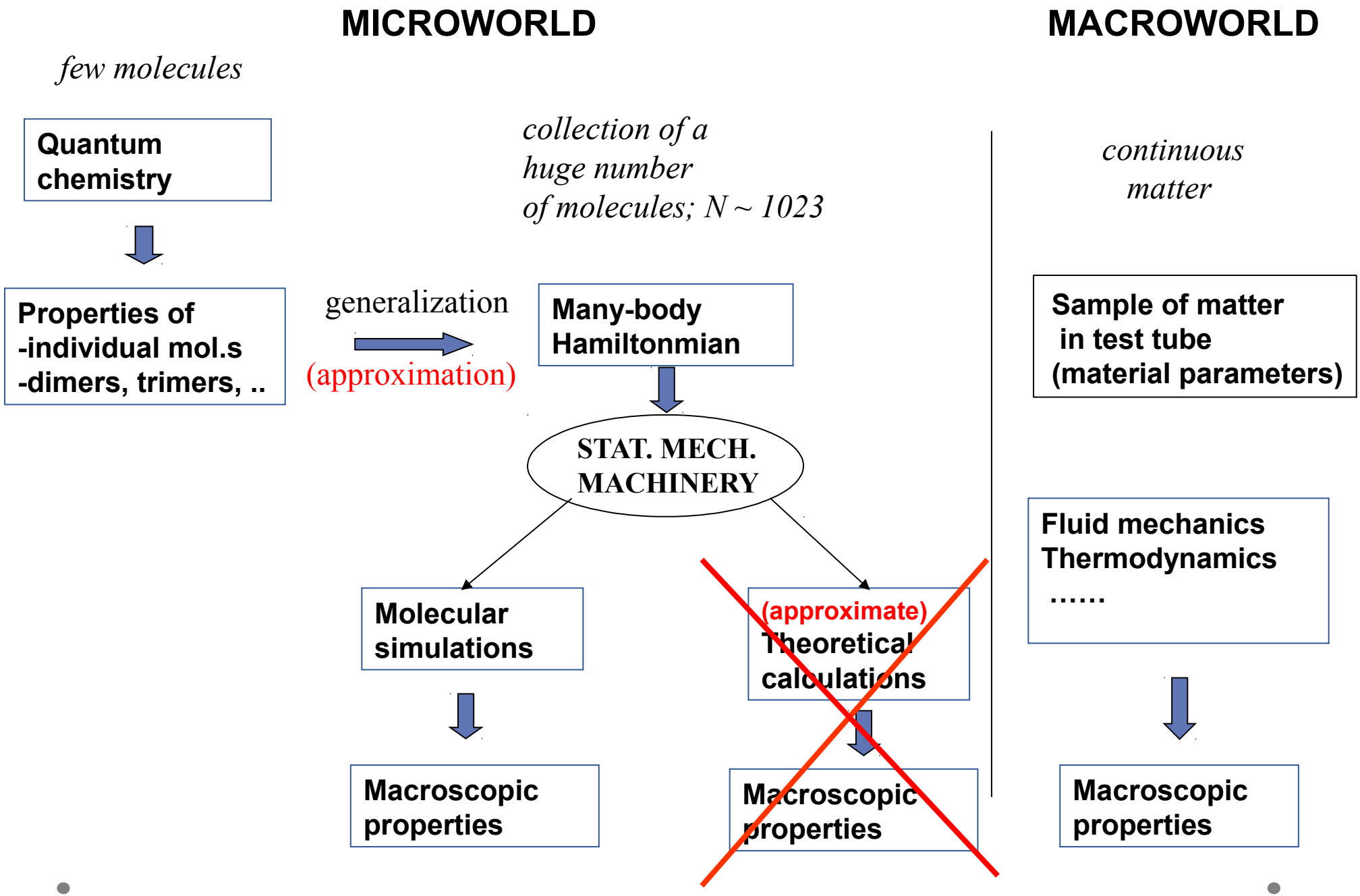


$$U(1,\ldots,N) = \sum_{(i)} [\sum_{(j\neq i)} u_{ij} + \sum_{(j)} u_{ij}]$$

over all particles in the cell

particle *i* with all others in the cell

over all particles outside the basic cell


MICROWORLD
MACROWORLD
few molecules
collection of a huge number of molecules; N ~ 1023
continuous matter
Quantum chemistry
Properties of -individual mol.s -dimers, trimers, ..
generalization
(approximation)
Many-body Hamiltonmian
STAT. MECH. MACHINERY
Molecular simulations
(approximate) Theoretical calculations
Macroscopic properties
Macroscopic properties
Sample of matter in test tube (material parameters)
Fluid mechanics Thermodynamics .....
Macroscopic properties

1953 The advent of molecular simulations:

Equation of State Calculations by Fast Computing Machines
[Metropolis,N., Rosenbluth,A.W., Rosenbluth,M.N., Teller,A.H., Teller,E.;
J. Chem. Phys. 21, 1087 (1953)]

Although this provided molecular physicists with an experimental tool enabling them for the **first time to test and verify their methods and predictions**, future extensions and applications were not on the agenda.

Even 15 years later, in the late 1960's, the role of such computer experiments was not yet quite clear, their potential still not envisaged, and those who were experimenting with these computer simulations were not fully accepted by the molecular physics community;
It was suggested that they be called machinests, they were just operating machines, nothing more.

As remarked 50 years later by one of the members of the Los Alamos team, M. Rosenbluth, in his talk given at a conference celebrating 50th anniversary of the Metropolis algorithm:

"… there was a toy available so why not to use it for various 'scientific games', and this was just one of them. Nothing more, no clear idea and intentions for further development."

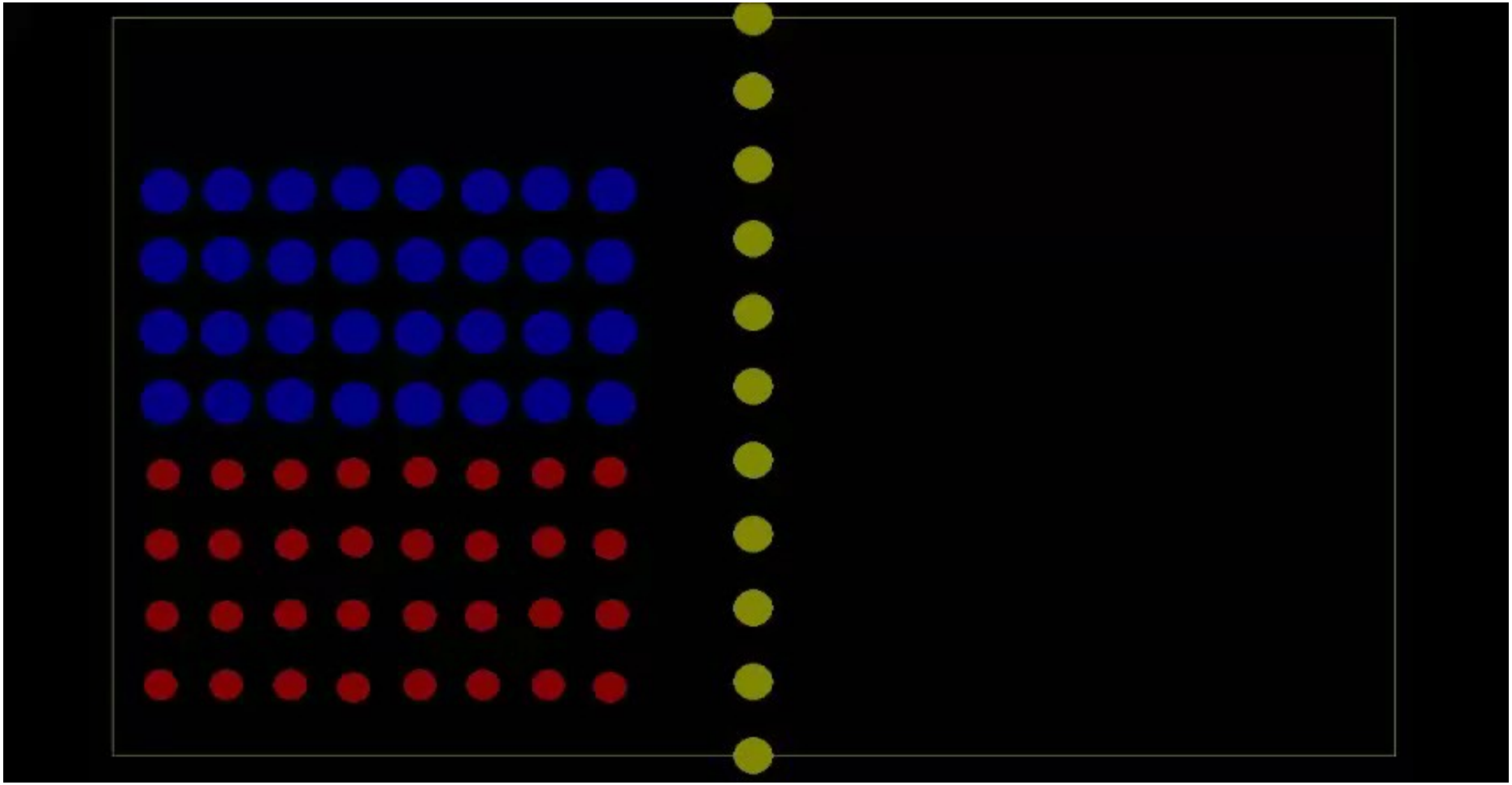
Only the fast development of computers, their power and speed, and their general availability opened eyes of scientific community, and not only of theoreticians dealing with molecules and molecular systems, but mainly applied scientists and engineers found a tool **to model and study problems otherwise defied.**

THREE BASIC PROBLEMS OF SIMULATIONS:

1. Choice of $U(\{qN\})$, *i.e.*,
   define/characterize the investigated matter at the level of molecules

2. In computer we have to work with FINITE systems.
   Problem: **All** theories are valid in the thermodynamic limit,
   i.e., for infinitely large systems: $N \rightarrow +\infty$, $V \rightarrow +\infty$, $N/V=\text{const}$

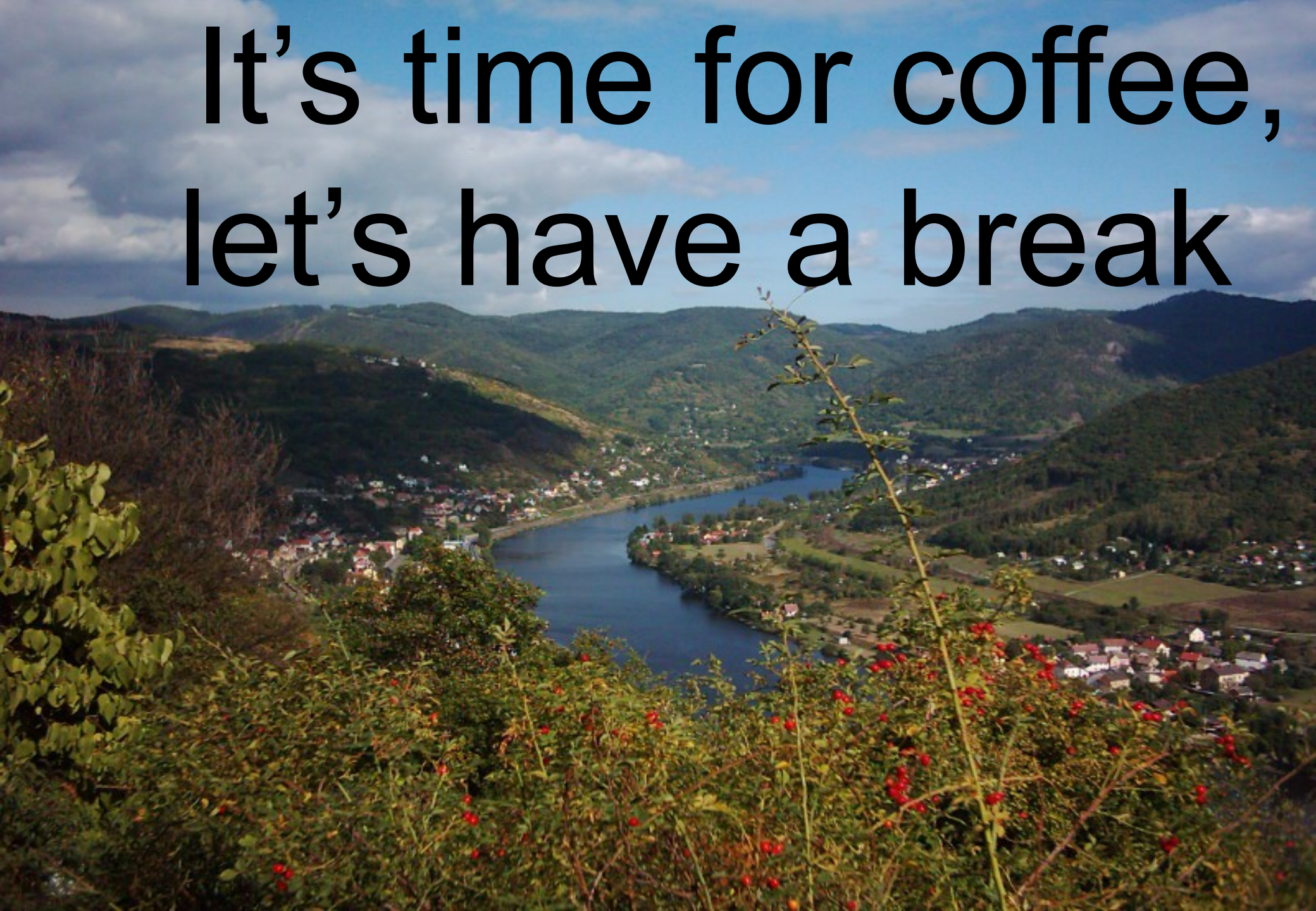
3. Walks in the configuration space mimic the Mother Nature.
   ⇓
   Development of the system (configurations) may be analyzed:
   - measure physical quantities (**WHAT & HOW?** Not always trivial matter!)
   - qualitative understanding of the process at the molecular level

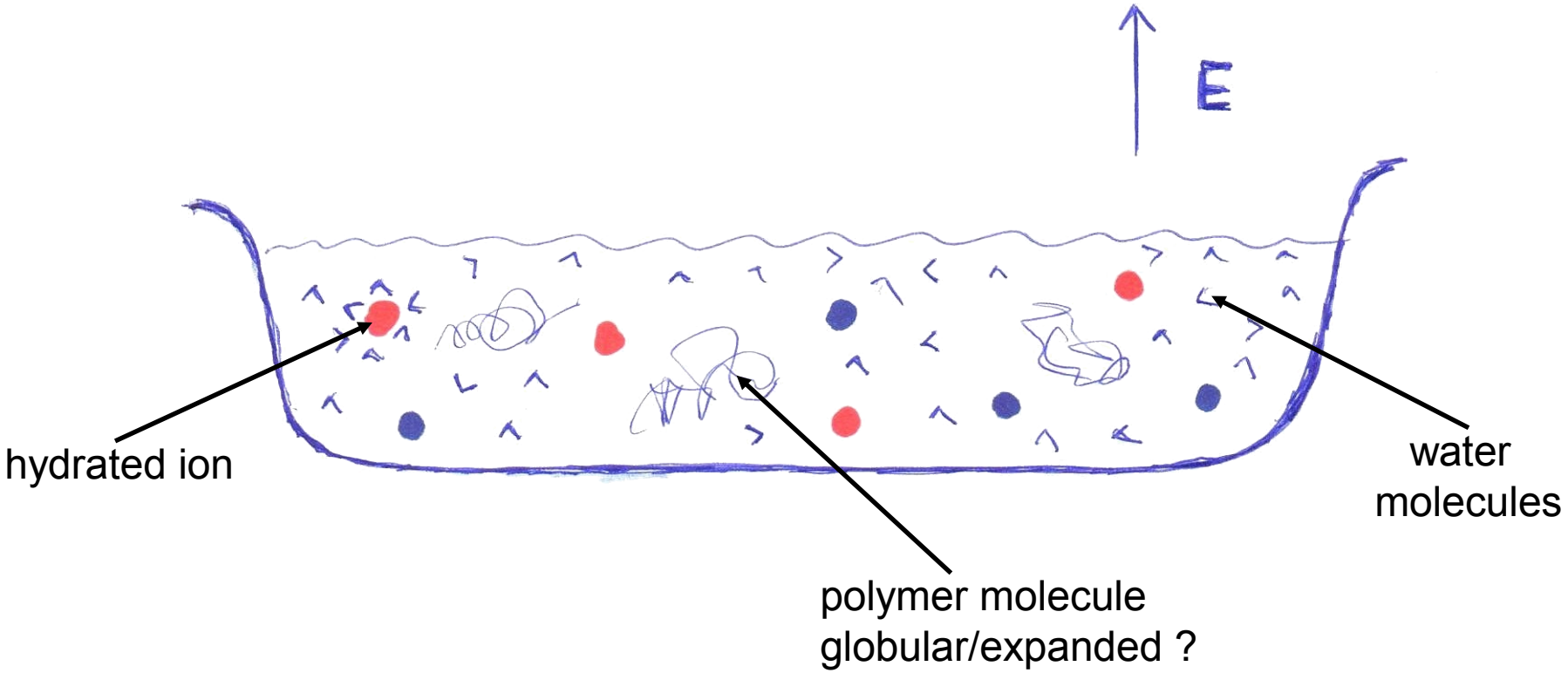


STATEMENT/CLAIM/VISION:
(Am Chem Soc)

By the year of 2020,
at least 25% of all thermophysical properties of fluids will have been etermined solely by molecular simulations without any reference to laboratory experiments.

WE WILL SEE …


It’s time for coffee,
let’s have a break

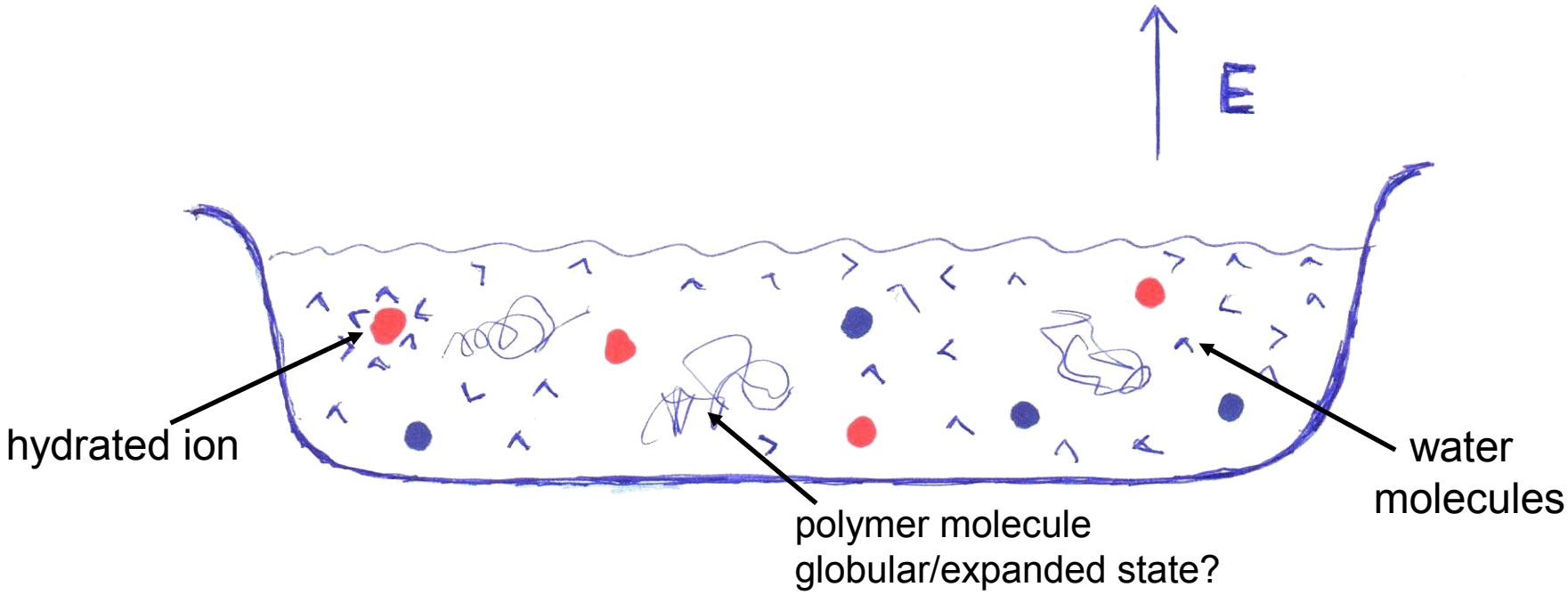


PRIMARY QUESTION (naïve qualitative analysis):

What mechanism makes it possible to form the jet of polymer molecules?

1. Are bare ions pulled out by the field and drag the polymer along?
2. Is it water, whose molecules get polarized and oriented, what drives the process?
3. How do polymer molecules get out of the solution? What is the role of the polymer molecules at all?

SOLUTION IN AN EXTERNAL FIELD

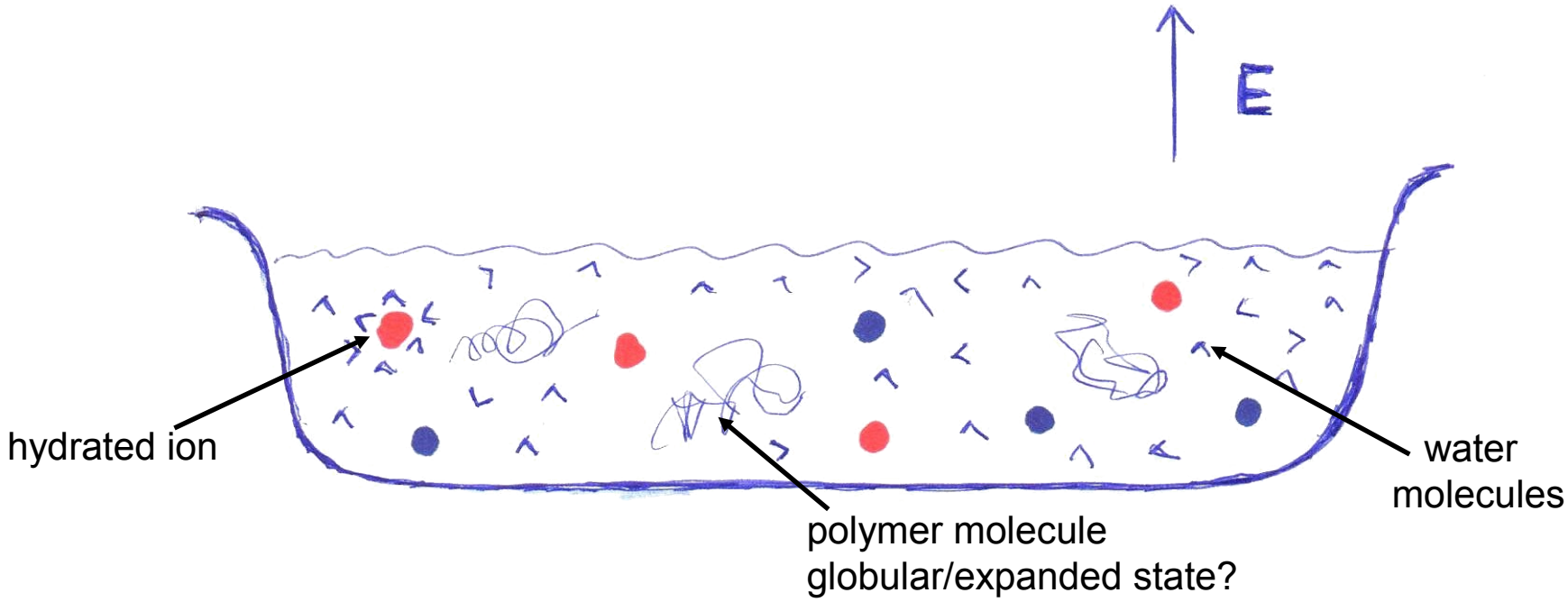


What happens after an external electric field is switched on?

WHY TO STUDY THIS PROBLEM ON A MOLECULAR SCALE?

Because this setup may elucidate fundamental physics behind the electrospinning process!

SOLUTION IN AN EXTERNAL FIELD



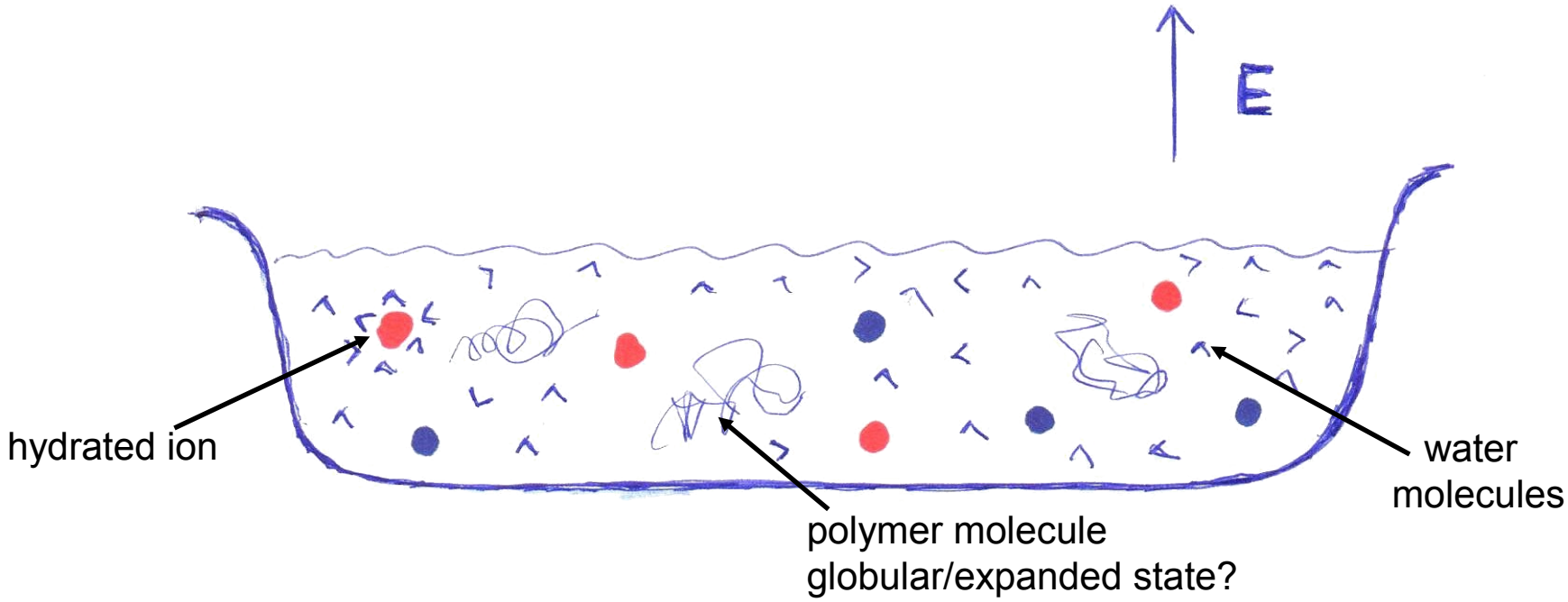
What happens after an external electric field is switched on?

MODERATE FIELD:

Level of liquid will be raised by

$$h \approx \left(\frac{\Delta V}{H}\right)^2 (1 - \frac{1}{\epsilon})\frac{1}{\rho g} \approx \left(\frac{\Delta V}{H}\right)^2 \frac{1}{\rho g}$$

SOLUTION IN AN EXTERNAL FIELD



What happens after an external electric field is switched on?

STRONG FIELD:

Transport of matter will occur – spraying, jetting, or streaming

Stage #1: ATTEMPT TO MODEL THE PROCESS

MOLECULAR DYNAMICS FEASIBILITY STUDY

PROBLEM/QUESTION: Can the process be studied by simulations at all?

Effect of the strength of the electric field

CASE A: pure water

3456 water molecules, TIP3P model;

Simulation cell 5.9494 nm × 5.9494 nm × 9.9747 nm

particle mesh Ewald; **periodic boundary conditions**

T = 298.15 K

simulation length: 150 ps

CASE B: diluted aqueous electrolyte solution

3392 water molecules (TIP3P) + 32 ion pairs Na^+ + Cl^- [Joung 2008]

molality: 0.5237 mol/kg

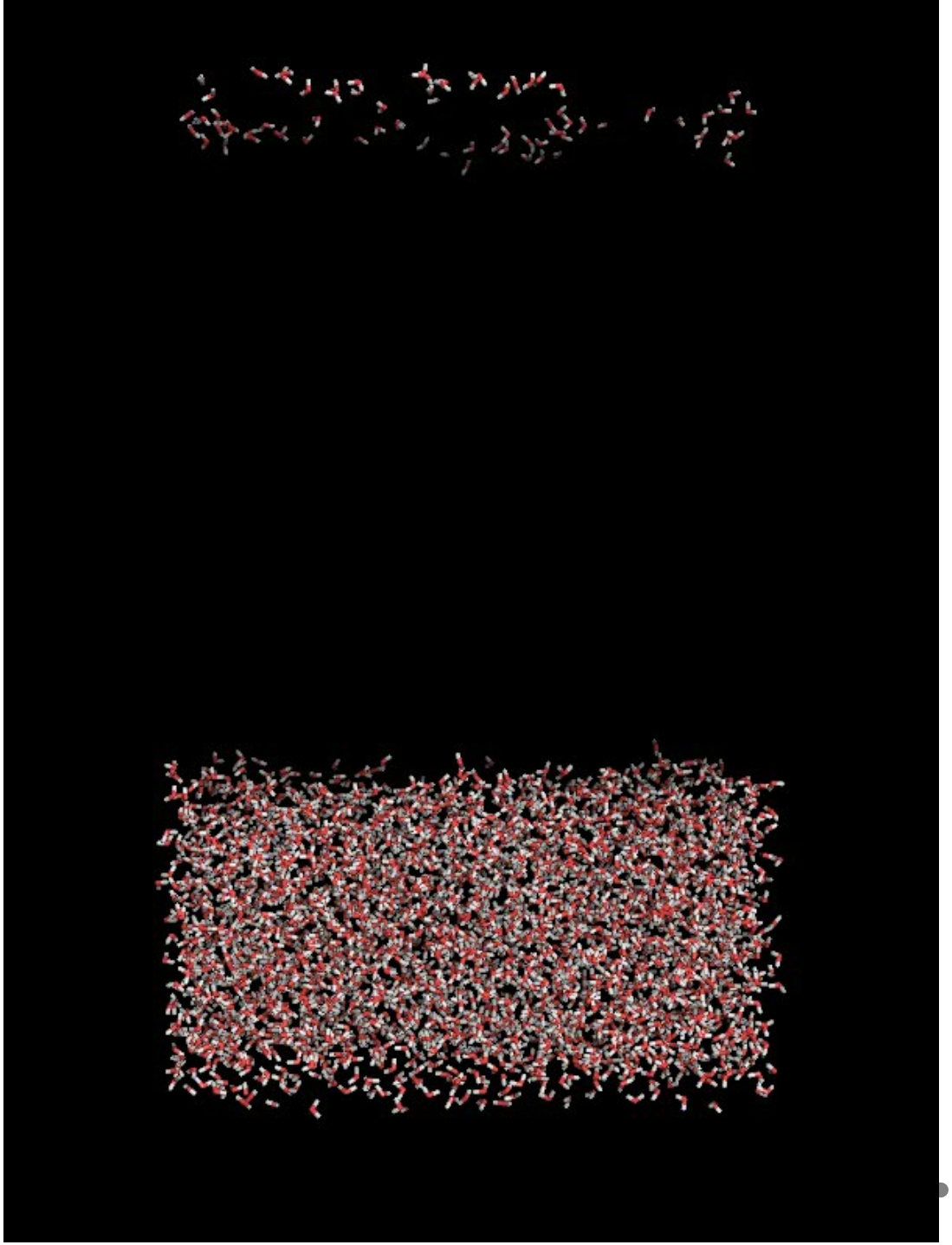
particle mesh Ewald; **periodic boundary conditions**

T = 298.15 K

simulation length: 150 ps

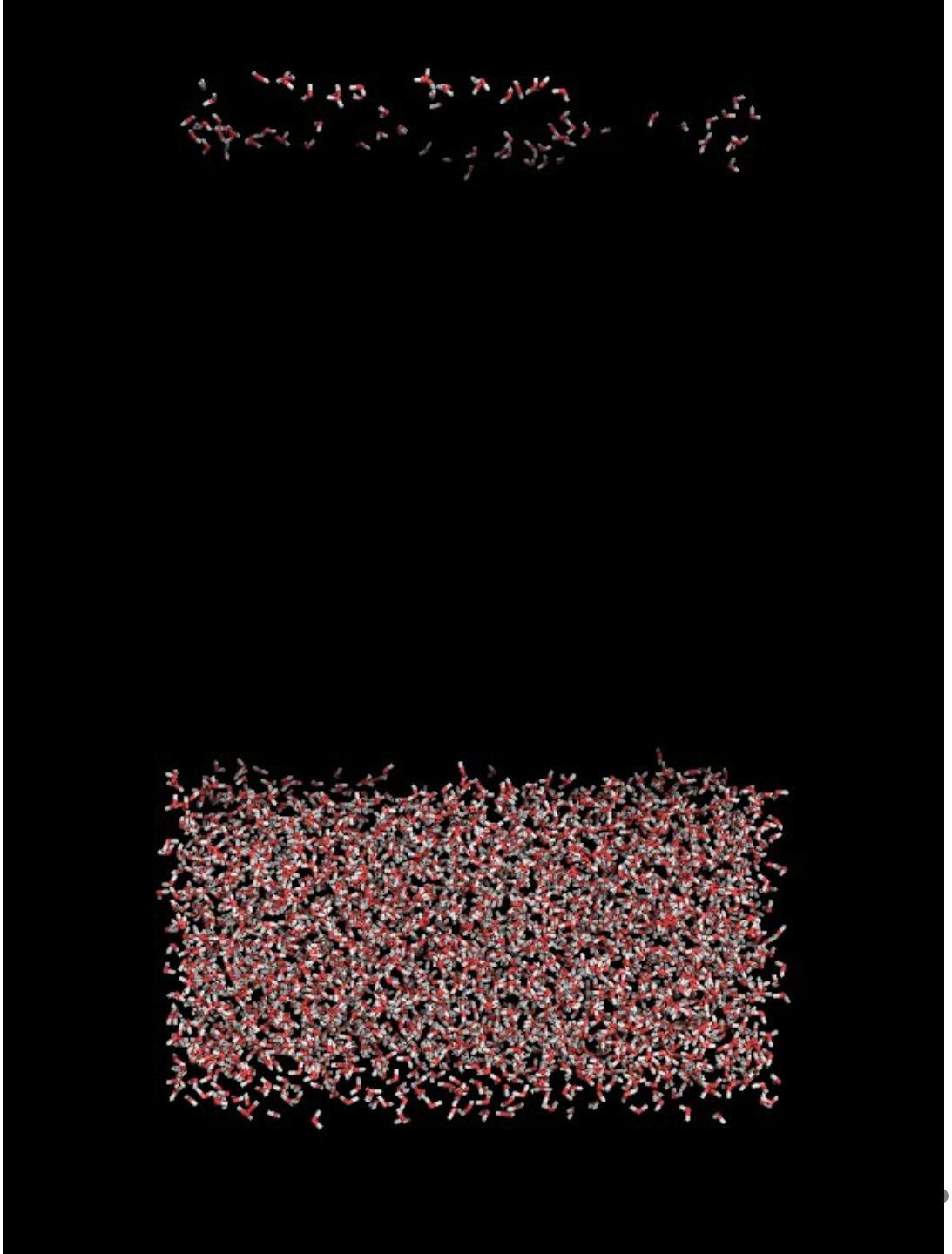
PURE WATER
no electric field

Numerous studies can be found in literature (simple VLE)



PURE WATER
electric field; *Ez* = 1.0 V/nm

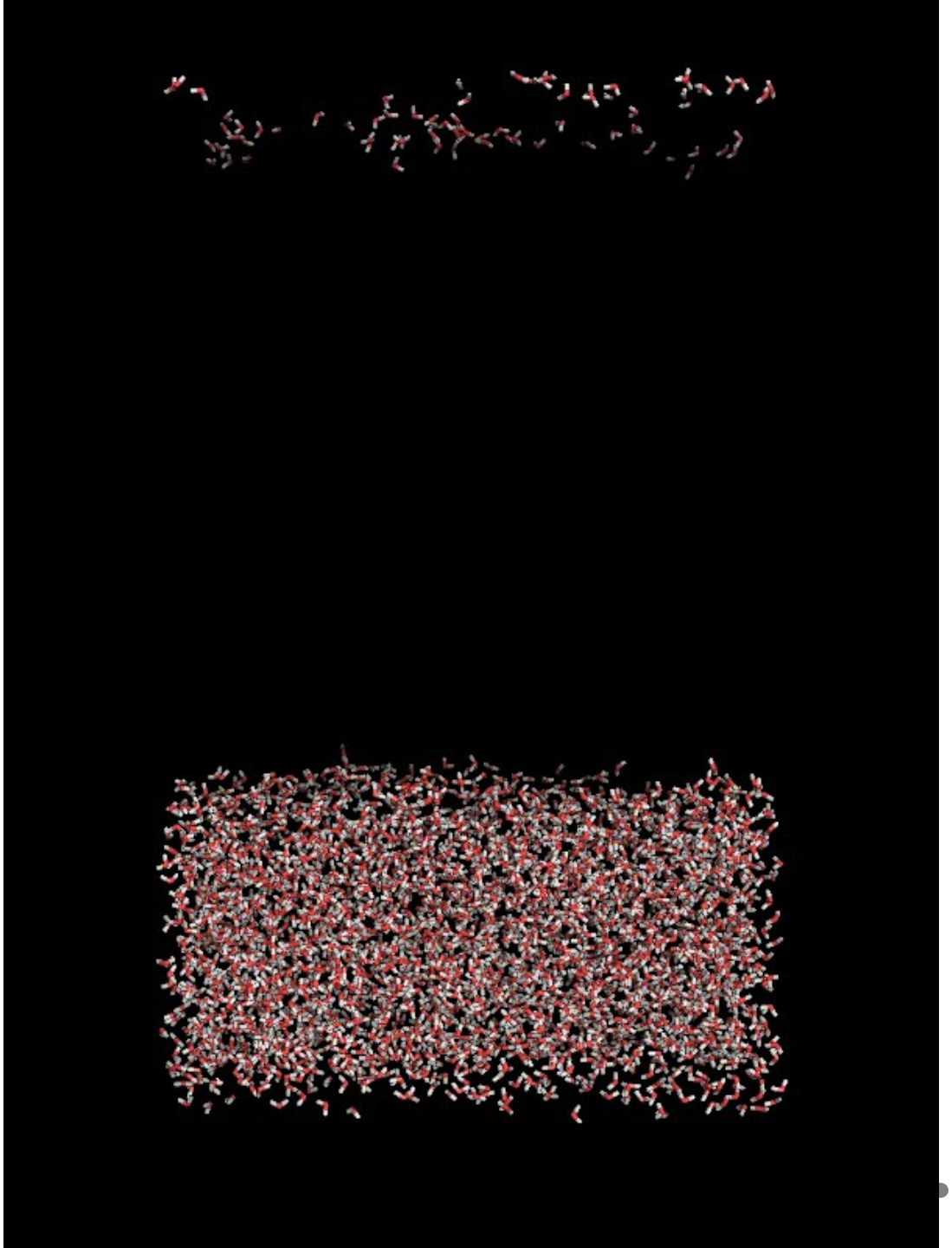
OBSERVATION:
Deformation of the surface is observed (signs of creation of the Taylor cones)



PURE WATER
electric field; *Ez* = 1.5 V/nm

RESULT:
In full agreement with the observation of the effect of the external field on evaporation

Onset of jetting



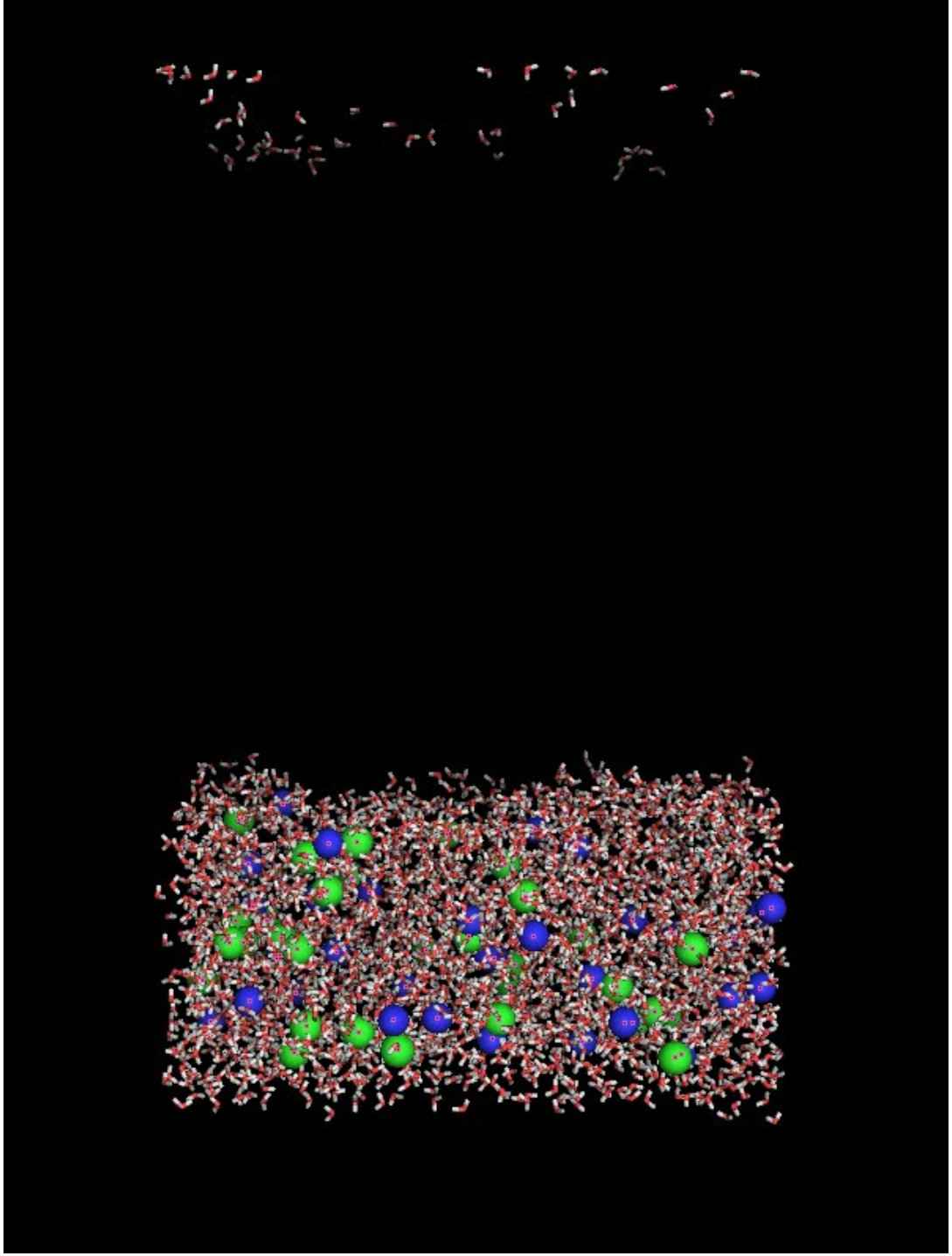
AQUEOUS ELECTROLYTE
no electric field

OBSERVATION:
Ions stay away from the surface

direction of the field

green spheres: Cl^-

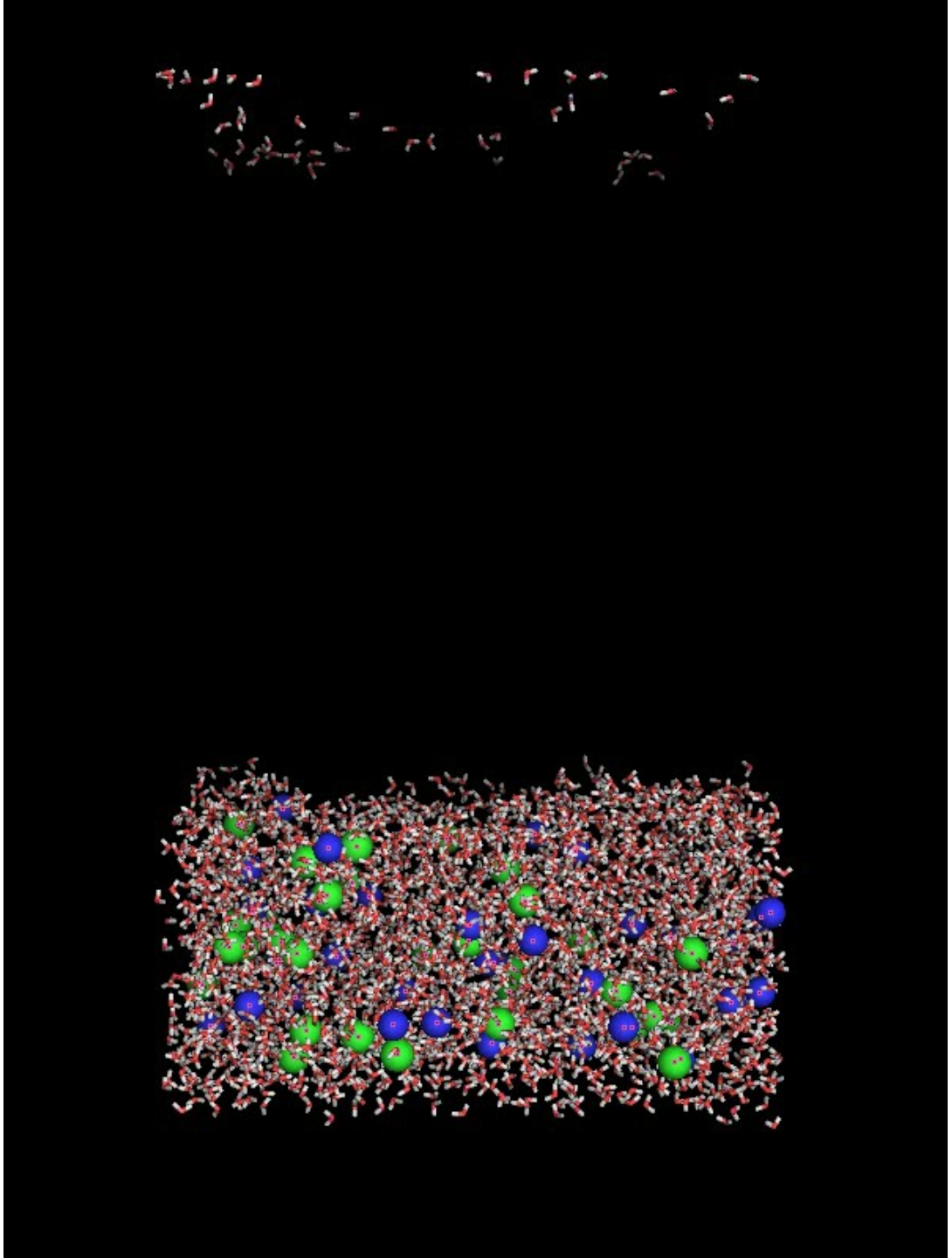
blue spheres: Na^+



AQUEOUS ELECTROLYTE
electric field; *Ez* = 1.0 V/nm

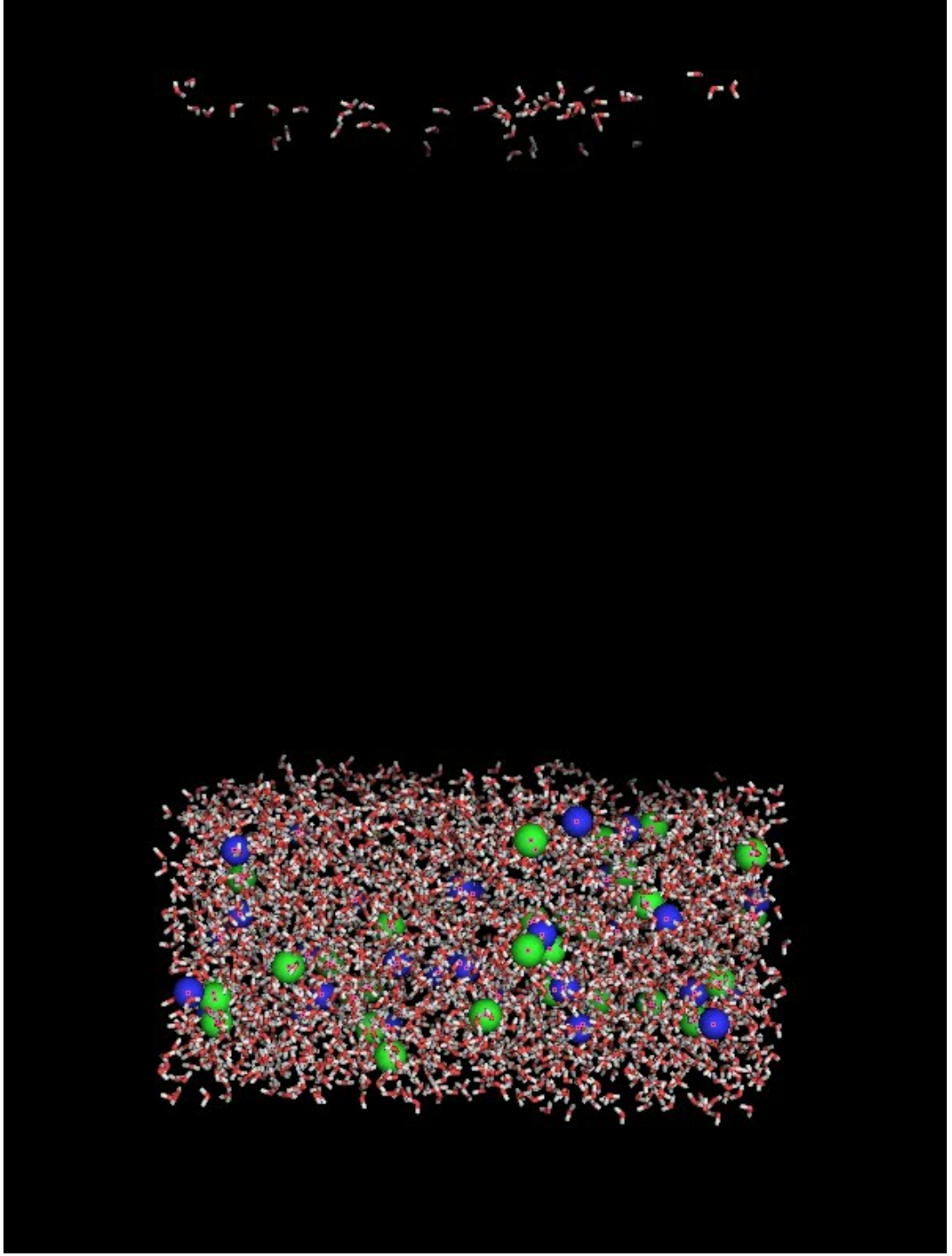
OBSERVATION:

1. Ions still stay away from the surface
2. Surface deformation is observed
   (see pure water in the field)



AQUEOUS ELECTROLYTE
electric field; *Ez* = 1.5 V/nm

OBSERVATION:
Water molecules form first a "bridge" upon which ions ride!



#2: QUALITATIVE UNDERSTANDING

ULATIONS: TECHNICAL DETAILS

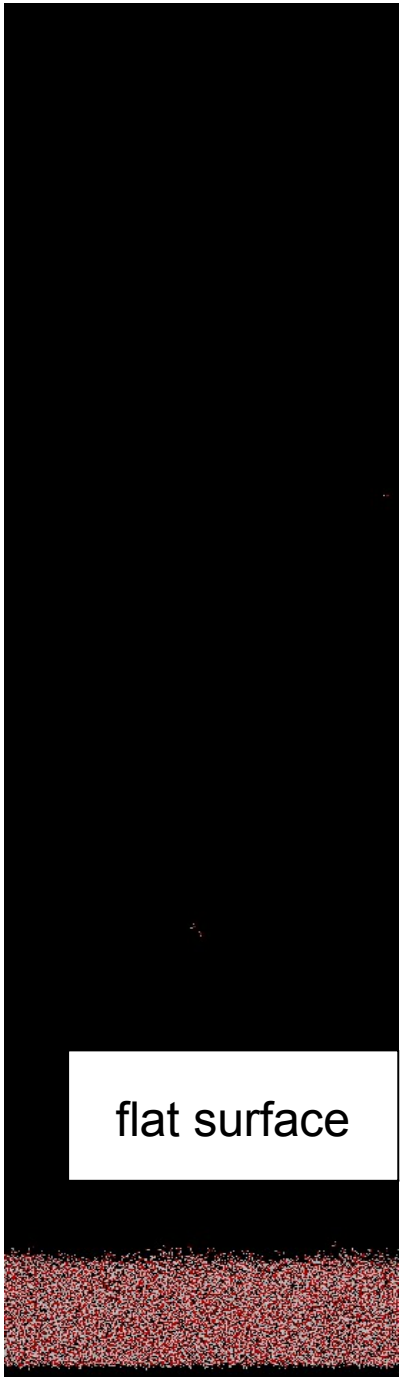
vater; Na+, Cl- ions (model of Joung, 2008)
water molecules + various number of ion pairs (0, 1, 2, 4, 8, 16, 32)

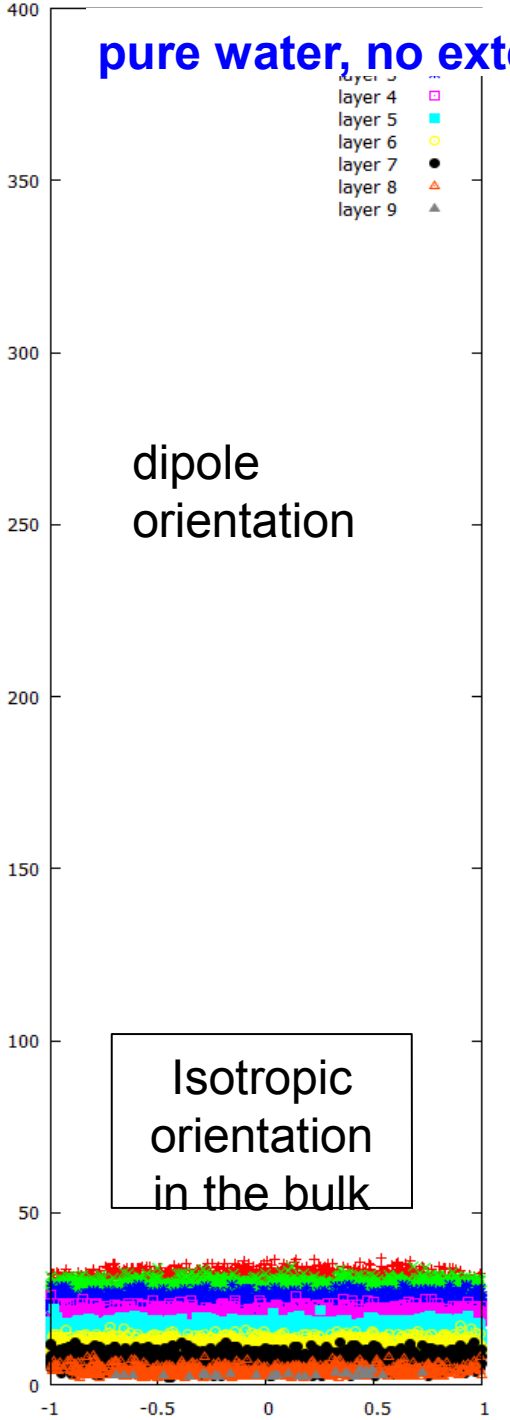
walls 40 nm apart
e: 11.899 nm x 11.899 nm
e wall potential to keep the solution at the bottom

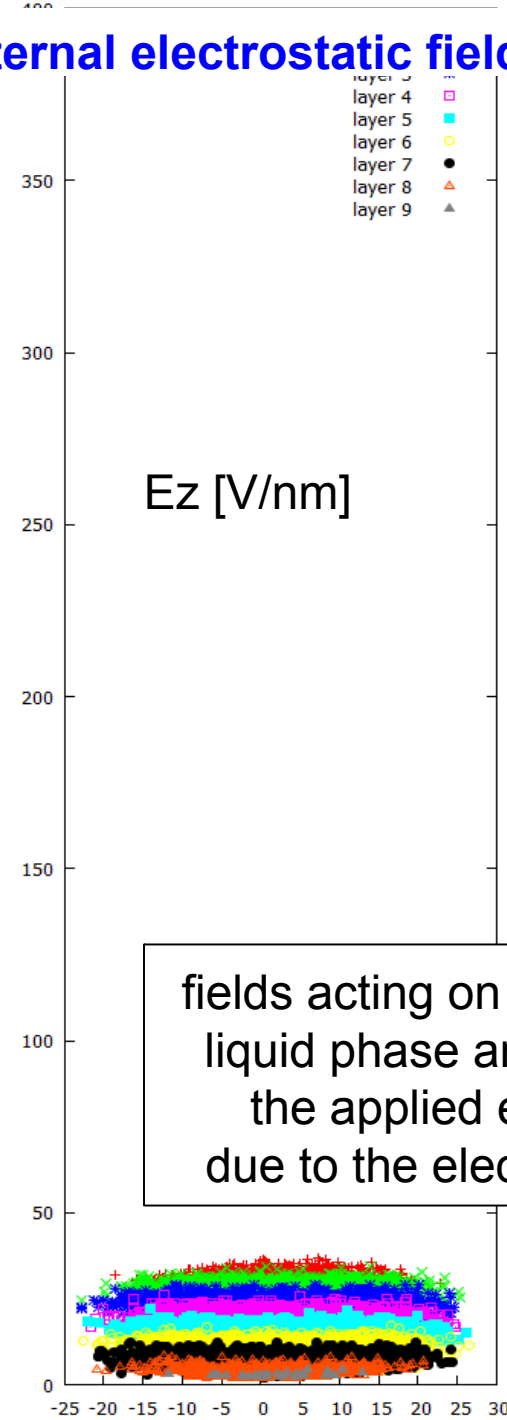
cutoff of the interactions at 2.5 nm; particle mesh Ewald
og integrator, time step 2 fs

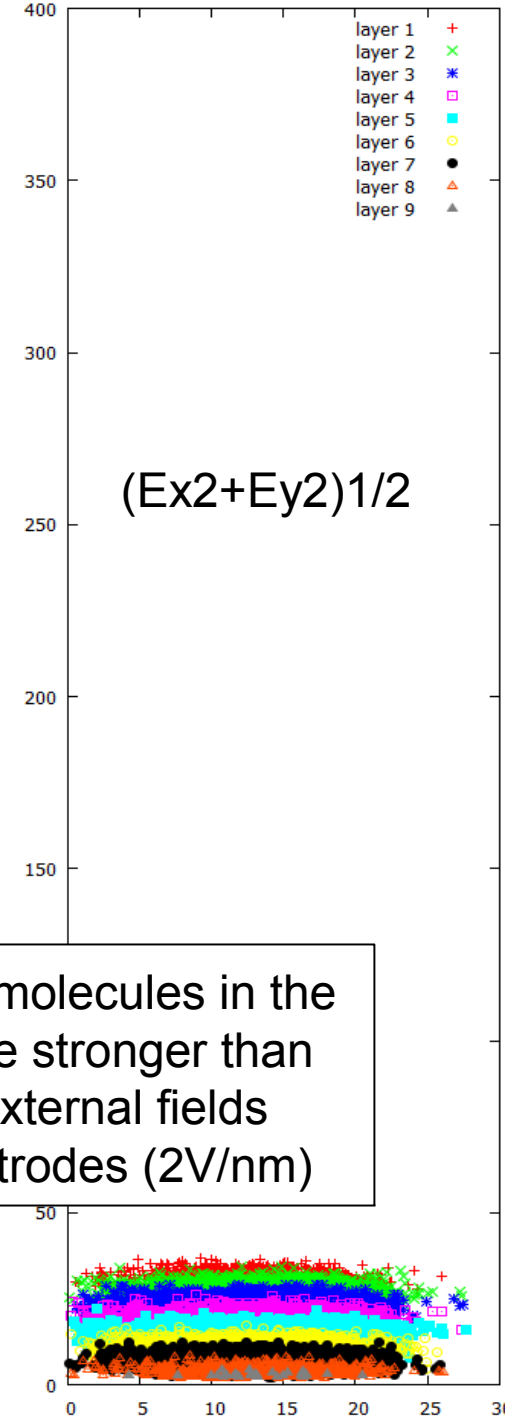
ol:
steps of equilibration (no field) with thermostat (Berendsen coupling) at 29
steps of NVE equilibration

pure water, no external electrostatic field



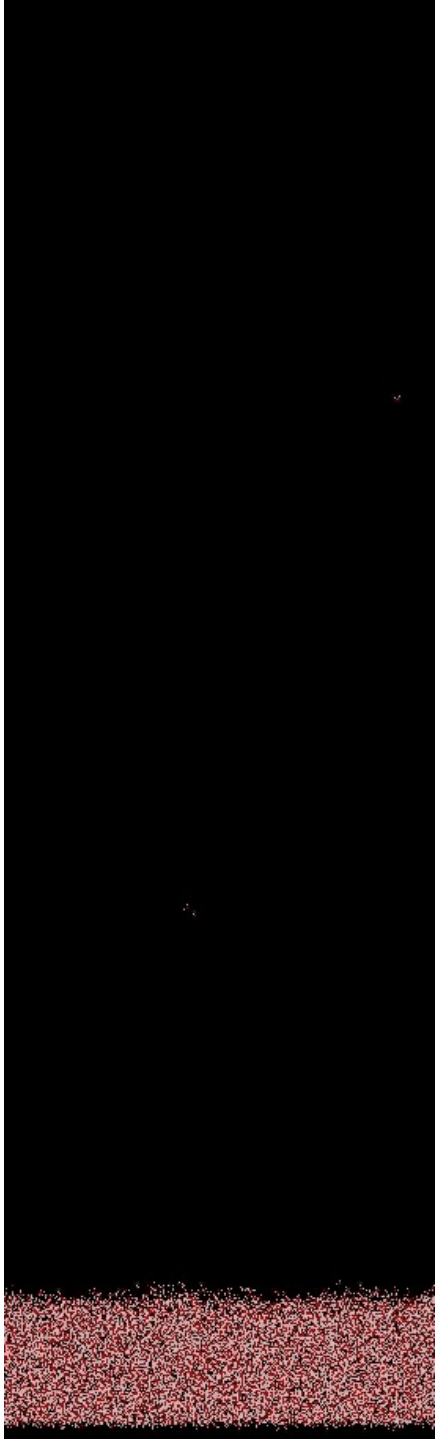






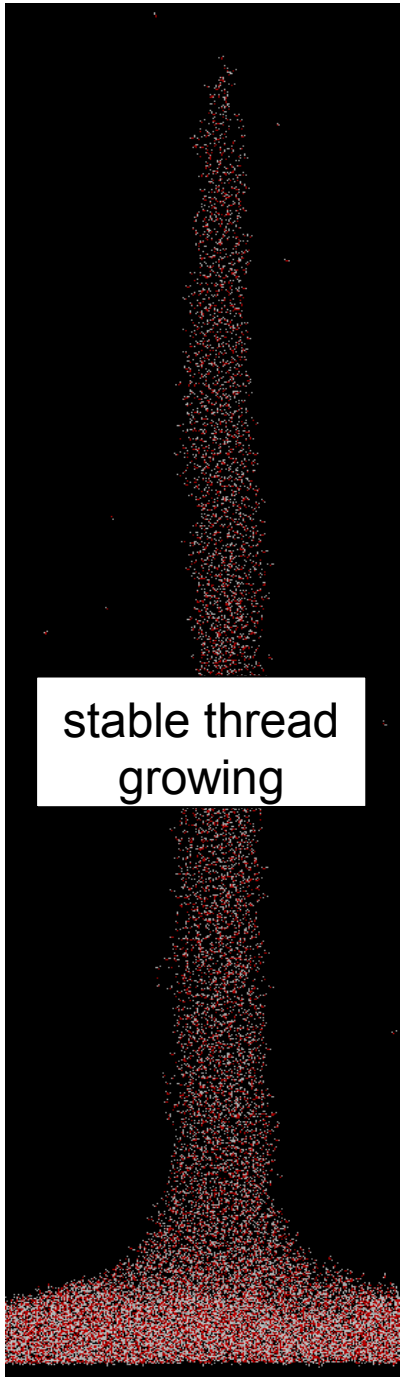
Isotropic orientation in the bulk

fields acting on molecules in the liquid phase are stronger than the applied external fields due to the electrodes (2V/nm)

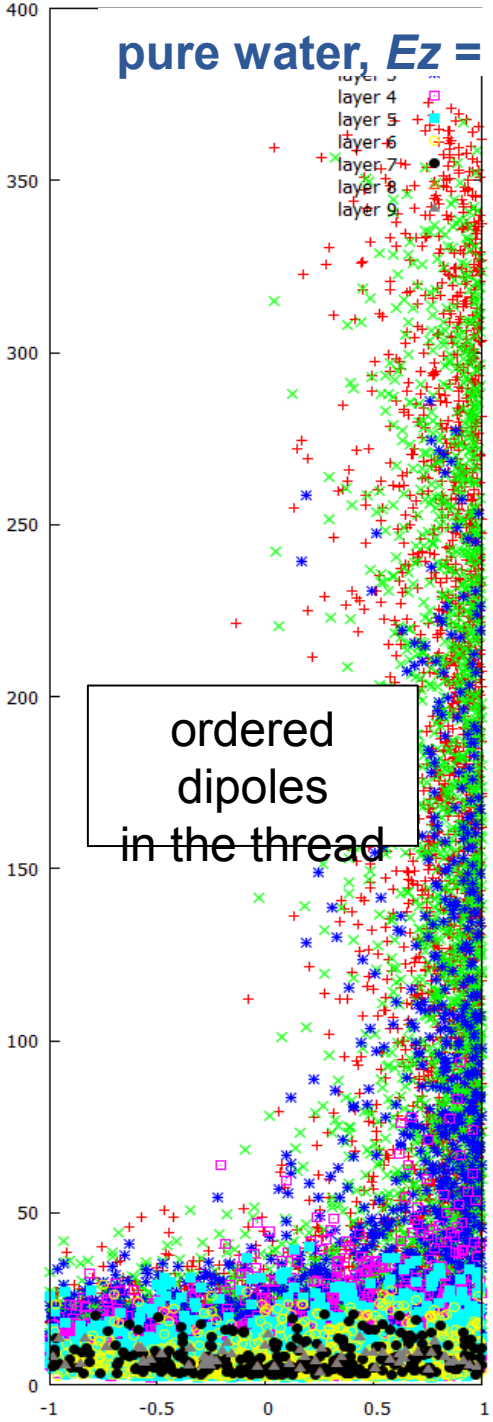


pure water, *Ez* = 2 V/nm, germ of a thread

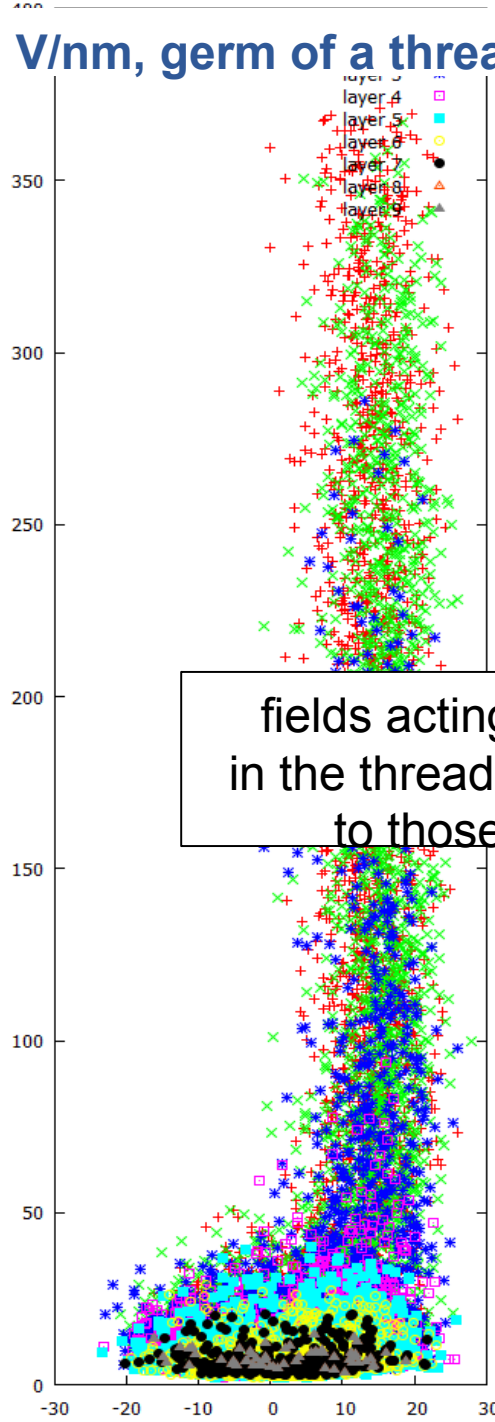
pure water, *Ez* = 2 V/nm, germ of a thread

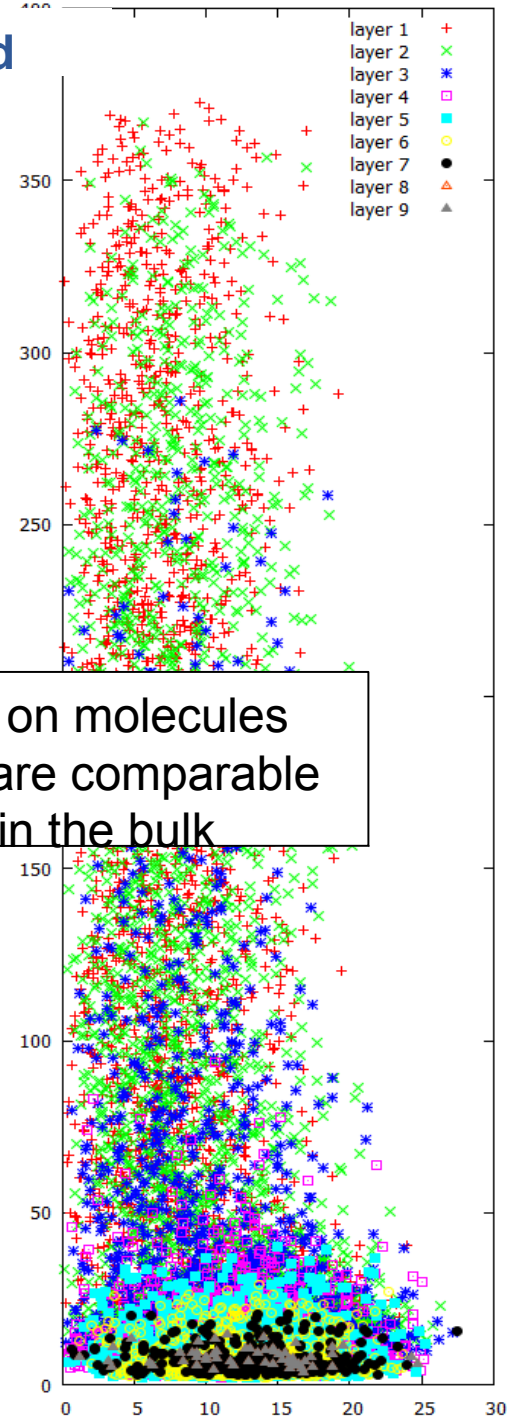


stable thread growing

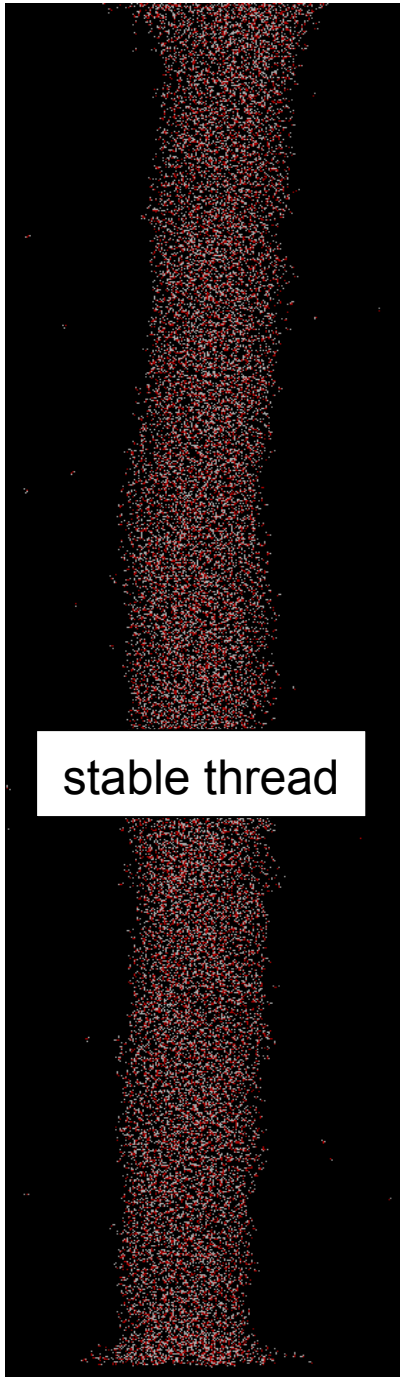


ordered dipoles in the thread





fields acting on molecules in the thread are comparable to those in the bulk

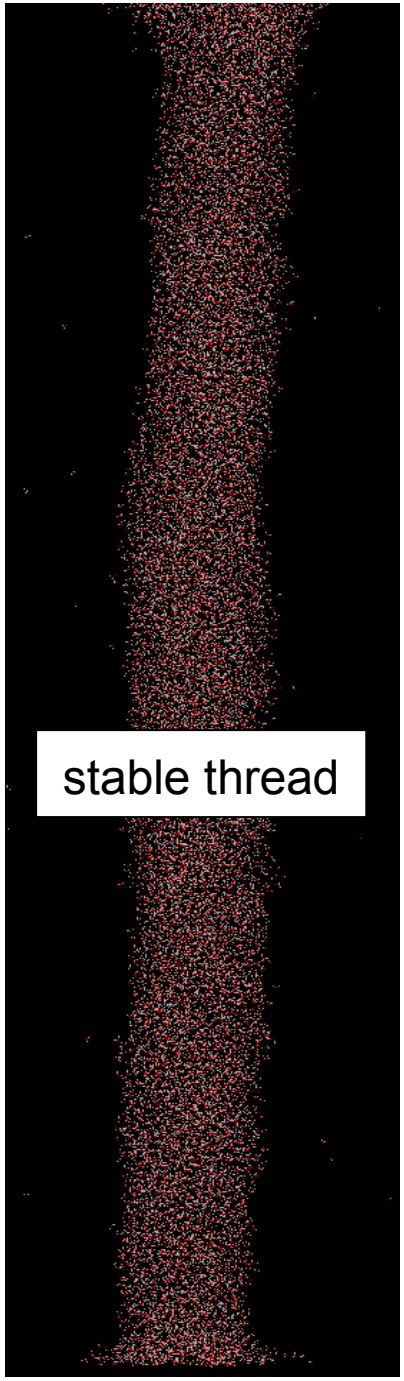


stable thread

pure water, *Ez* = 2 V/nm, thread

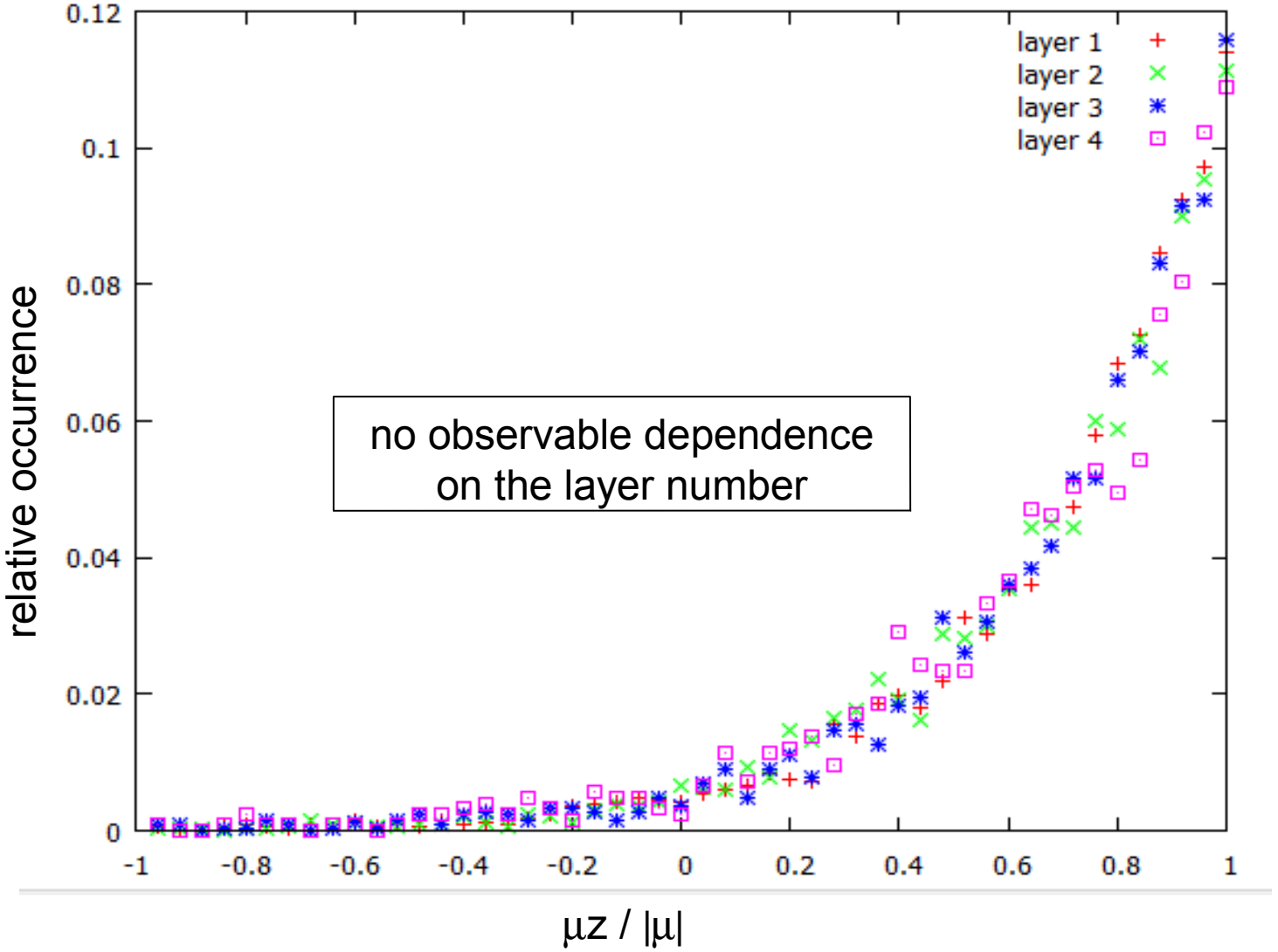
ordered dipoles in the thread

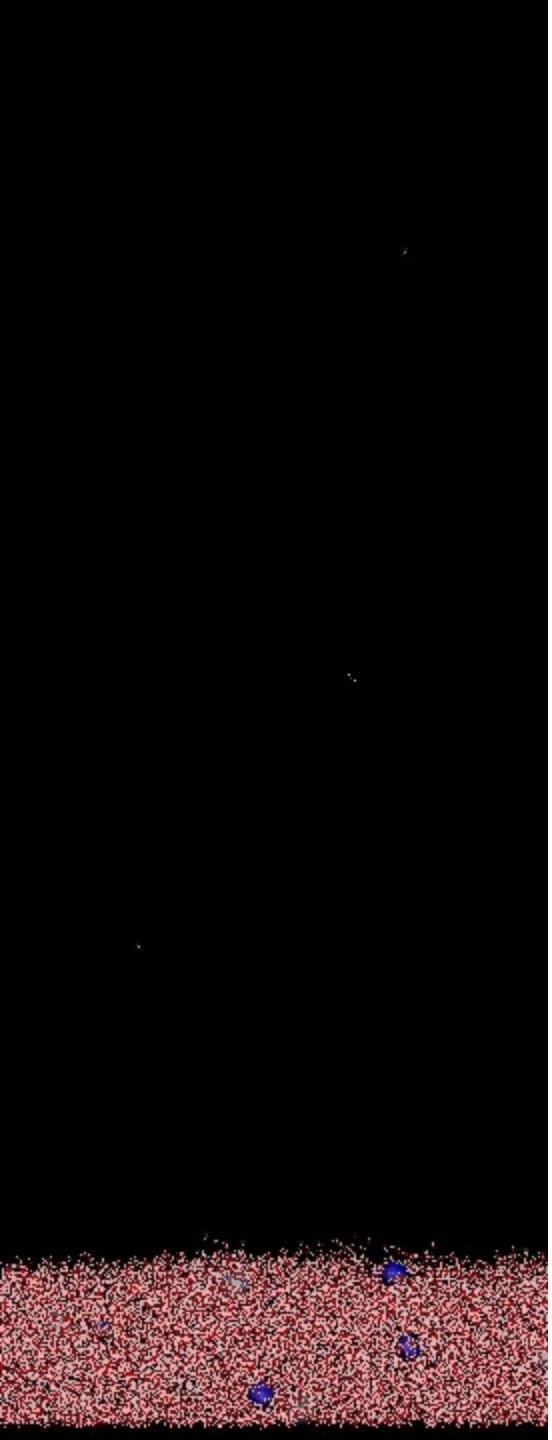
dependence of these properties on the layer number is not observed



pure water, *Ez* = 2 V/nm, thread

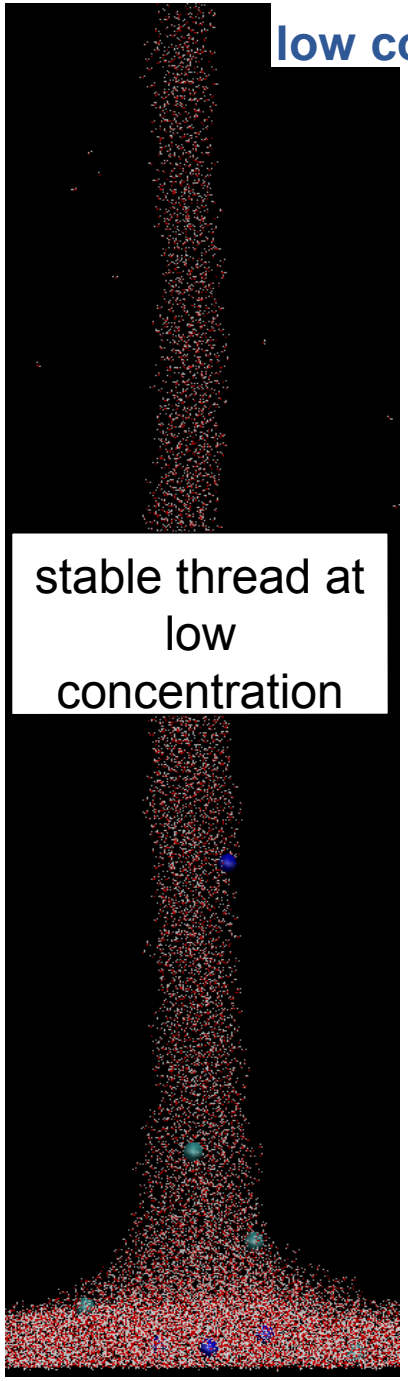
orientation of molecules in the layers





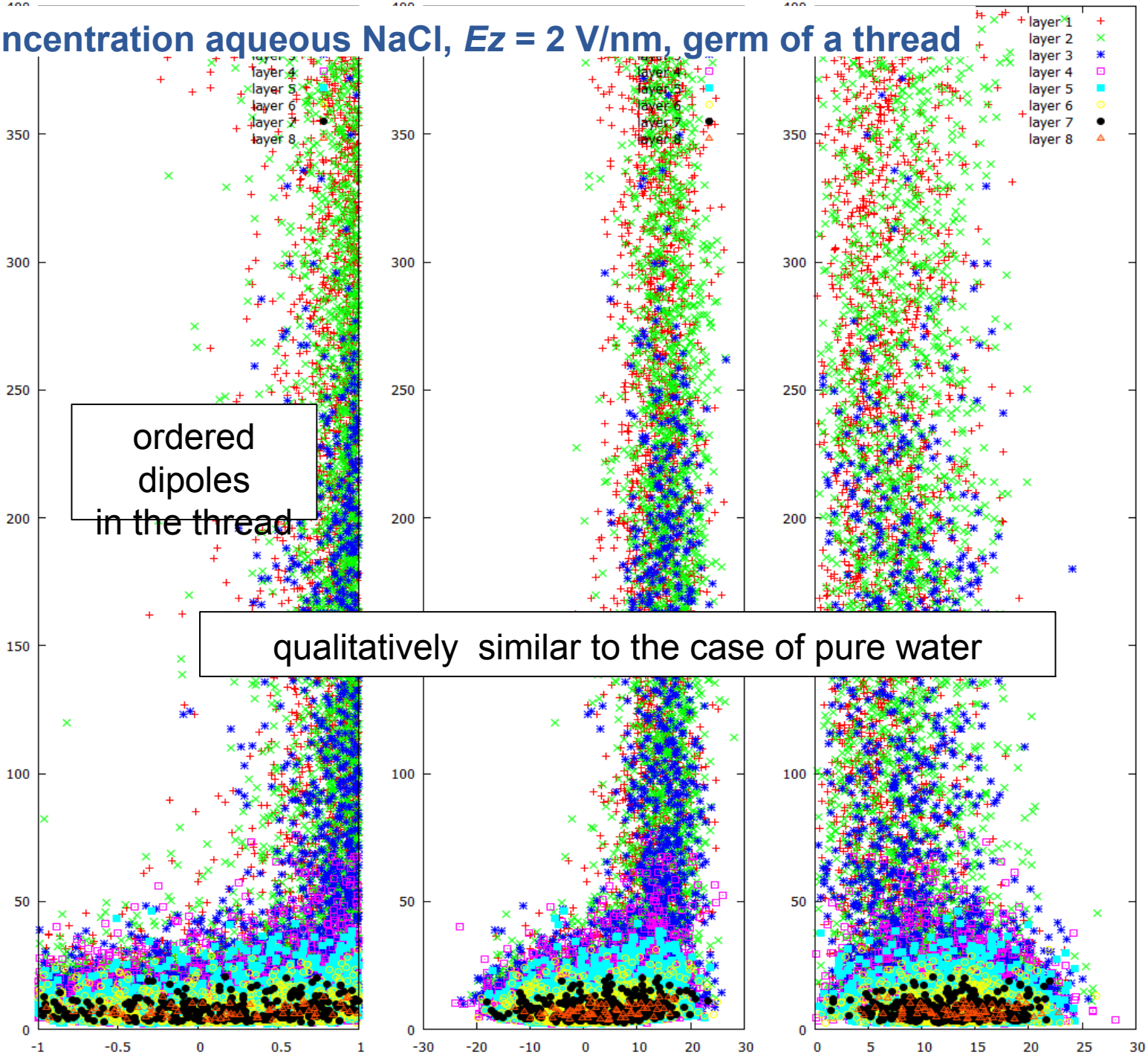
EXTERNAL ELECTRIC FIELD
Low ion concentration

low concentration aqueous NaCl, *Ez* = 2 V/nm, germ of a thread



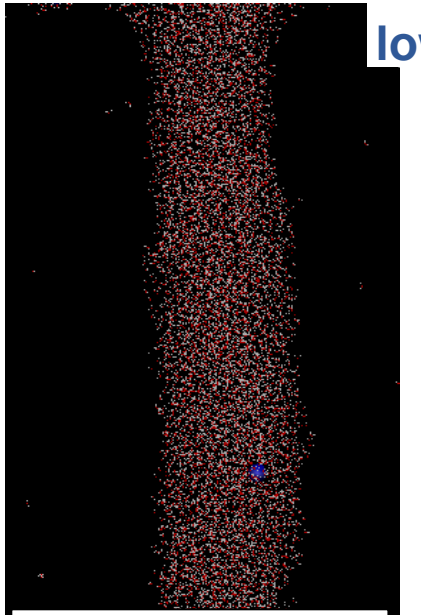
stable thread at low concentration

ordered dipoles in the thread

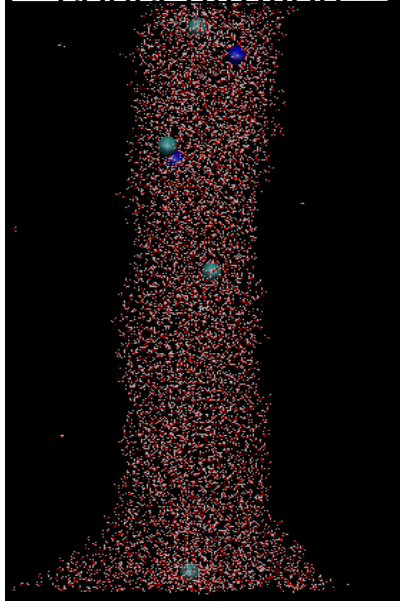


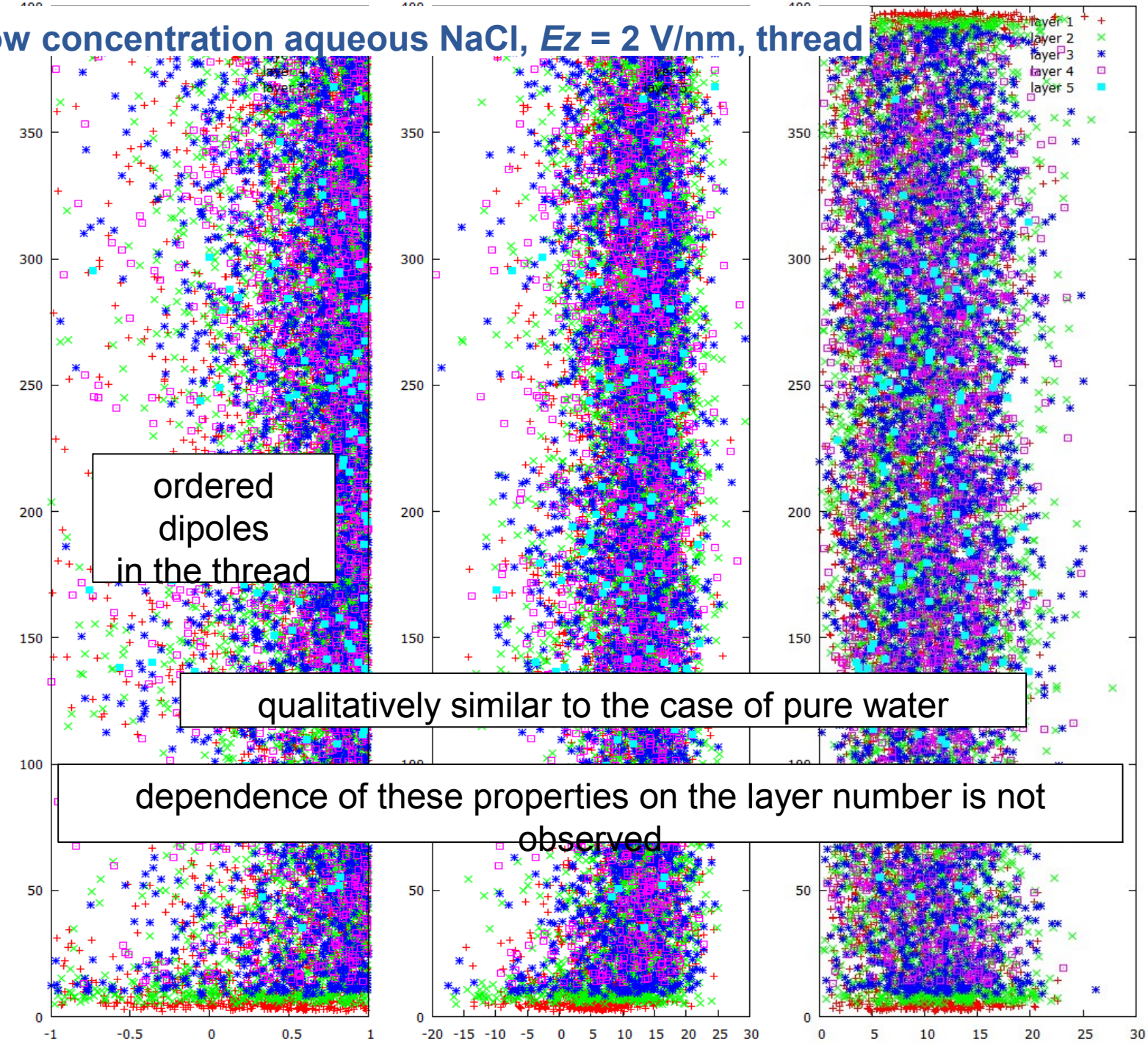
qualitatively similar to the case of pure water

low concentration aqueous NaCl, *Ez* = 2 V/nm, thread



stable thread at low concentration

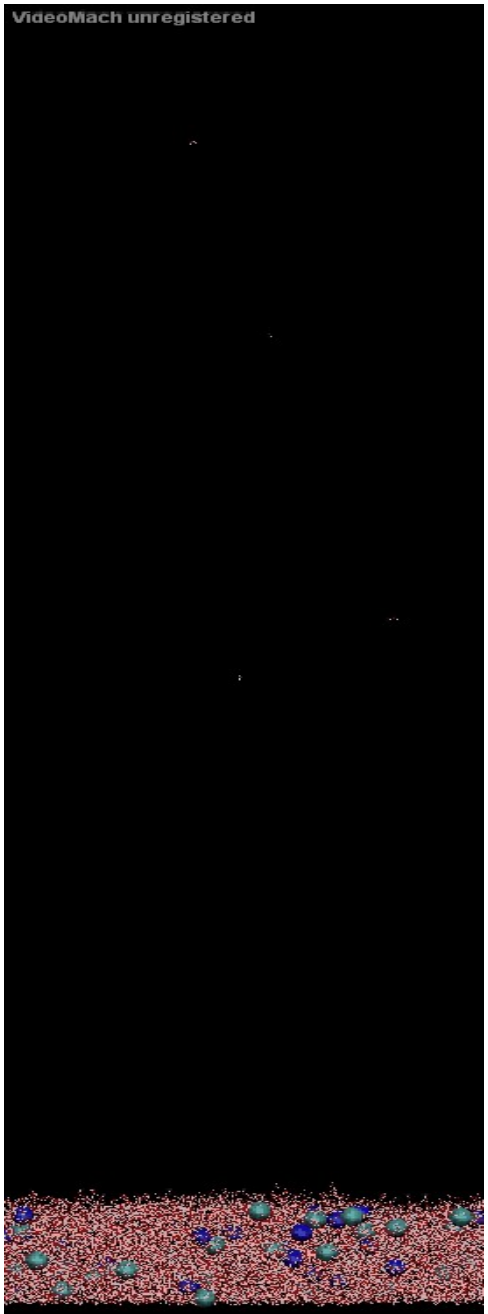




ordered dipoles in the thread

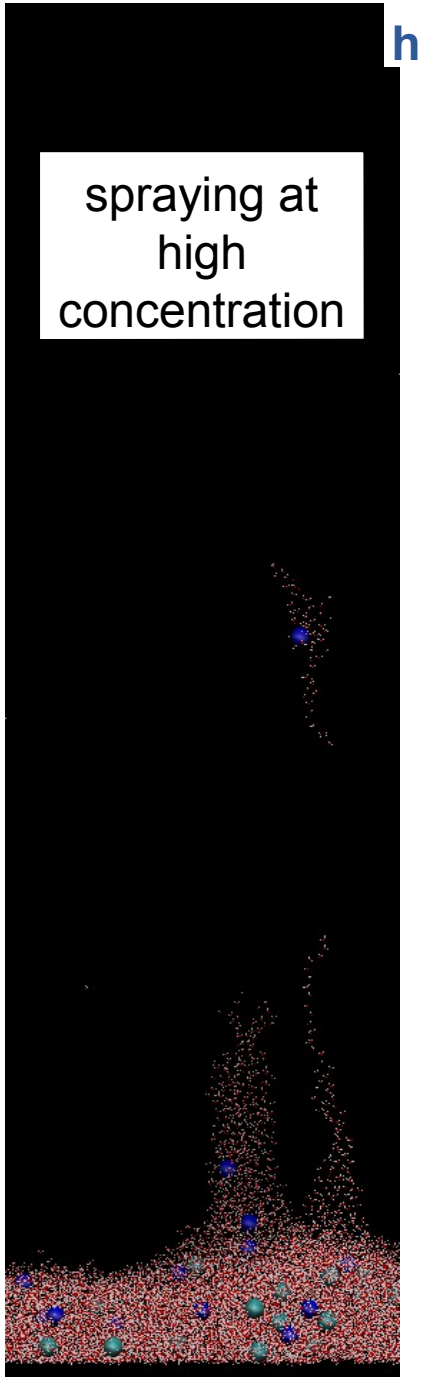
qualitatively similar to the case of pure water

dependence of these properties on the layer number is not observed

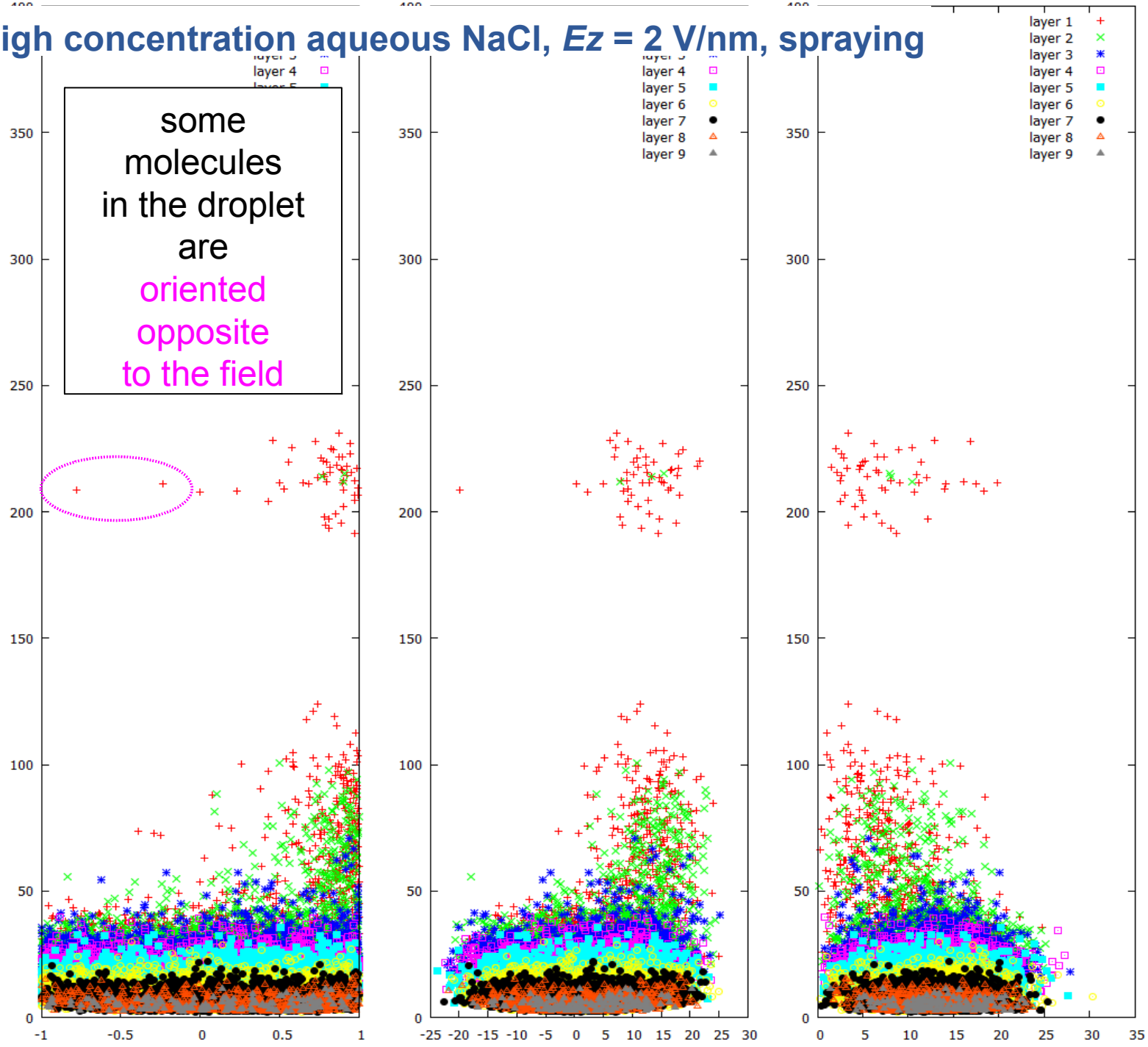


EXTERNAL ELECTRIC FIELD
High ion concentration

high concentration aqueous NaCl, *Ez* = 2 V/nm, spraying



some molecules in the droplet are oriented opposite to the field



CONCLUSION:

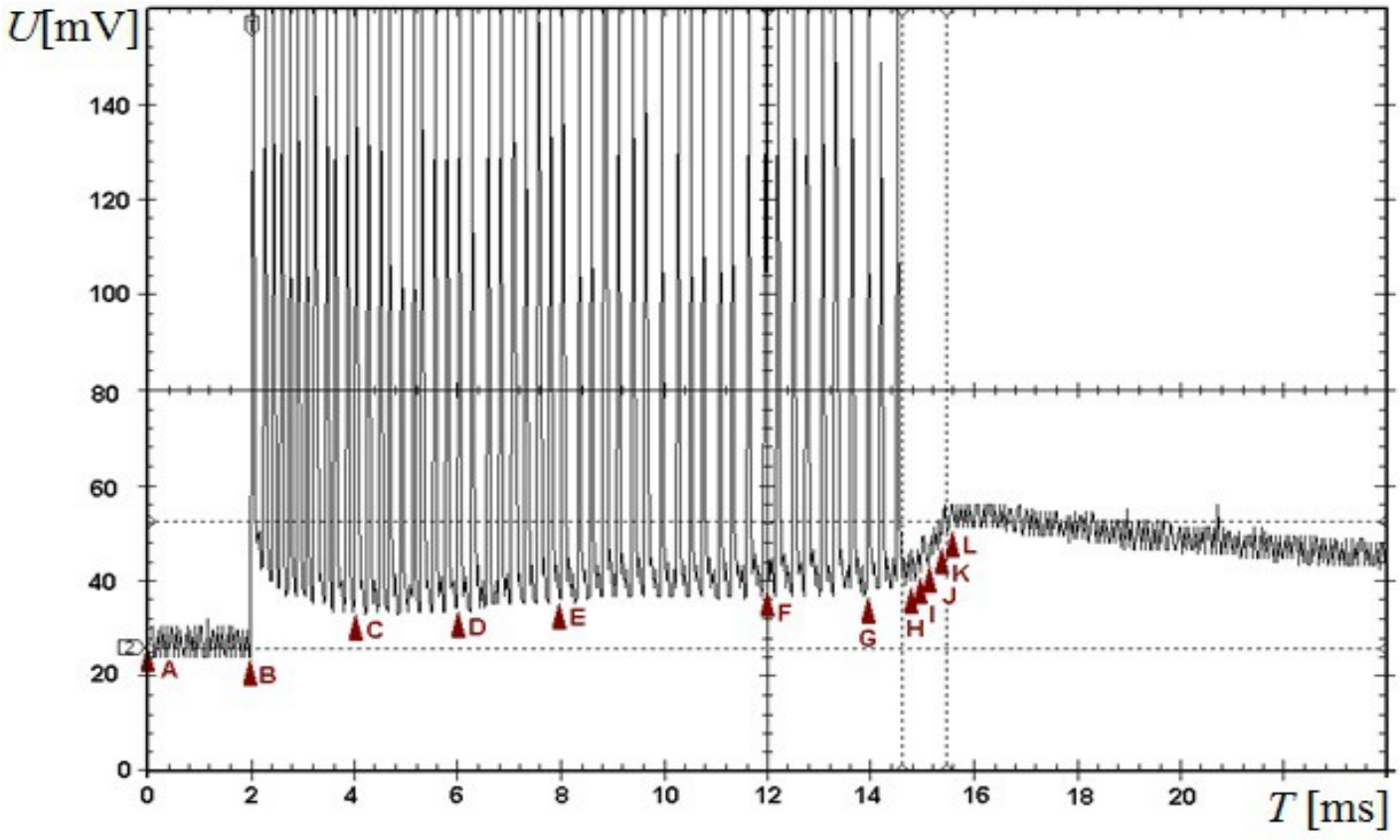
FROM EXPERIMENTS WE LEARNT THAT

- Adding salt may enhance/support jetting, but
- too much salt may lead to spraying only.

CONECTION OF THE RESULT TO REALITY:

EXPERIMANTAL OBSERVATION:

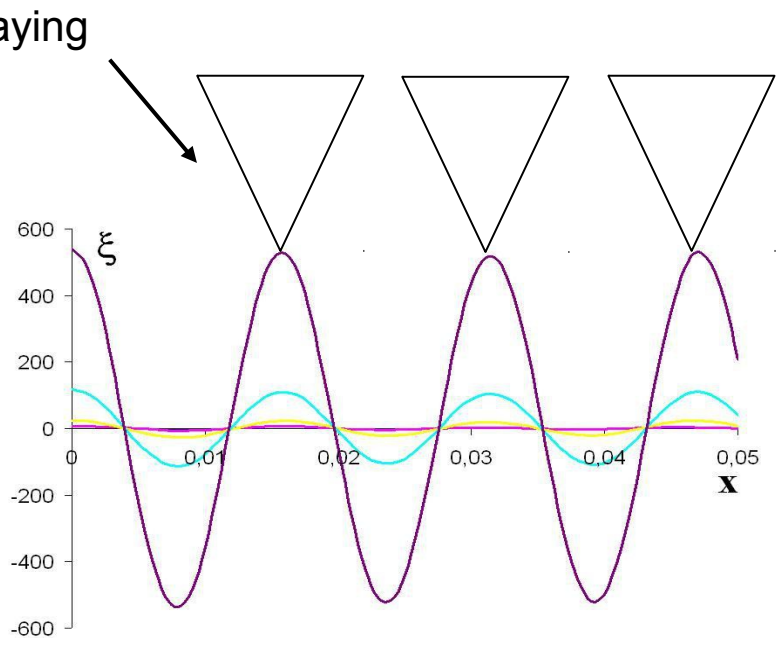
For a certain limited time interval a periodic transfer of the charge is observed in the form of pulses (TU Liberec experiments)



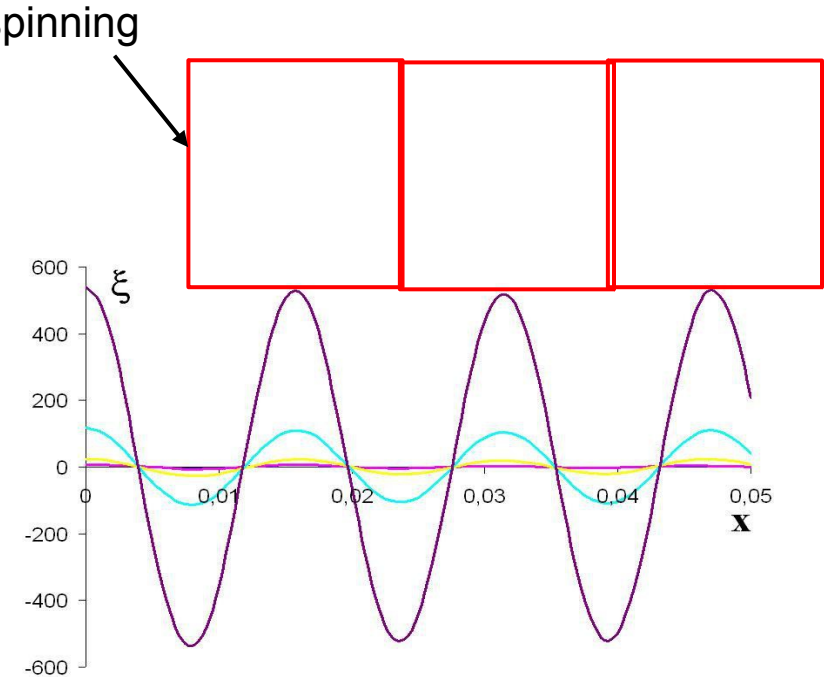
SUGGESTED INTERPRETATION (based on our simulations):

- *in the initial stage (rapid oscillations), due to the high ion concentration in the jet we observe spraying (disintegration of the jet)*
- *as the concentration of the ions decreases, the jet becomes stable and spinning is observed (continuous fiber)*

spraying



spinning



WORKING HYPOTHESIS:

It is the ion concentration what governs the process and gives rise to the observed phenomena

SUMMARY OF OBSERVATIONS

1. **Spinning is NOT driven by *ions***

2. **Spinning seems to be driven by the *solvent***

3. **High concentration of ions in the thread leads to its disruption**

4. Molecular properties across the thread do not change

5. Polymer molecules seem to play the role of dummy agents, it's water and ions that facilitate polymer


THANK YOU
for your attention