Foundation of Multiscale Modelling: Kinetics

(Seminars / Labs)

Lesson 1

Teaching assistants (TAs):   Alexey Tsukanov, a.tsukanov@skoltech.ru
Georgii Paradezhenko, g.paradezhenko@skoltech.ru

February, 2022.

Outline

- Seminars / labs organization
- Structure of homework (HW), grading
- Final project: topics will be uploaded
- Modelling at different scales: examples
- Molecular dynamics: approaches and method
- Molecular dynamics: HW1, task 1.

Homeworks, seminars, grading
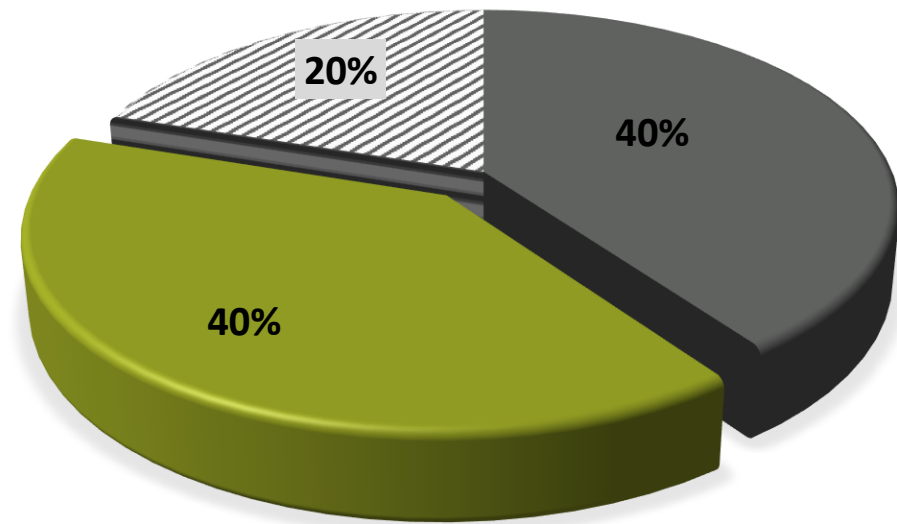
6 seminars / labs in total:

- Once per week (on every Friday).
- From 4 to 7 p.m.
- After each seminar → HW

5 homeworks (HWs)

- HW includes about 4-5 tasks (including analytical and programming problems → use **Python / Jupyter**)
- Each HW = **14 (12 + 2*) points**

  = 60 + 10* points

+ **Additional HW 6*** [optional]

(also allows getting extra points)

Total points: 150 pp = 100%

40%

40%

20%

◨ Final Project (60 points) - end of the term

▧ Homeworks (60 points)

▨ Exam (30 points) - beginning of March

Seminars, projects, grading

Seminars will be organized as follows:

- **First part:** Analysis of previous HW, typical mistakes and troubles, discussion of solutions, etc.

- **Part II:** Presentation with an explanation of the methods, approaches and tools necessary to solve the problems of the next HW.
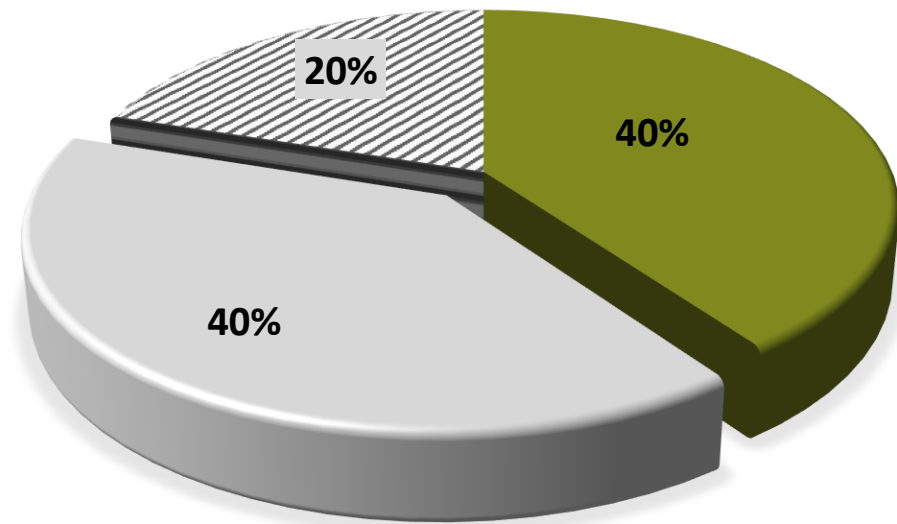
Final exam

- Will be in the middle of March

- Gives up to 30 points

Project

- Will be at the end of the term

- Gives up to 60 points (40% of total)

Total points: 150 pp = 100%

- 🟩 Final Project (60 points) - end of the term

- ⬜ Homeworks (60 points)

- ▥ Exam (30 points) - beginning of March

Seminars and homeworks

Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
this week	**15:00 HW 1** is **available** in Canvas **Lecture**		**Lecture**	**Seminar / Lab** * **16:00 – 19:00**		
next week	**15:00** HW 2 is **available** in Canvas **Lecture**		**Lecture** **Upload** your solutions **HW 1** (**till 23:59:59**)	**Seminar / Lab** **16:00 – 19:00**		

week 1

etc… week 2

Note: Each day of **delay** leads to **-25%** discount of total grade for the HW (–3 points per day)
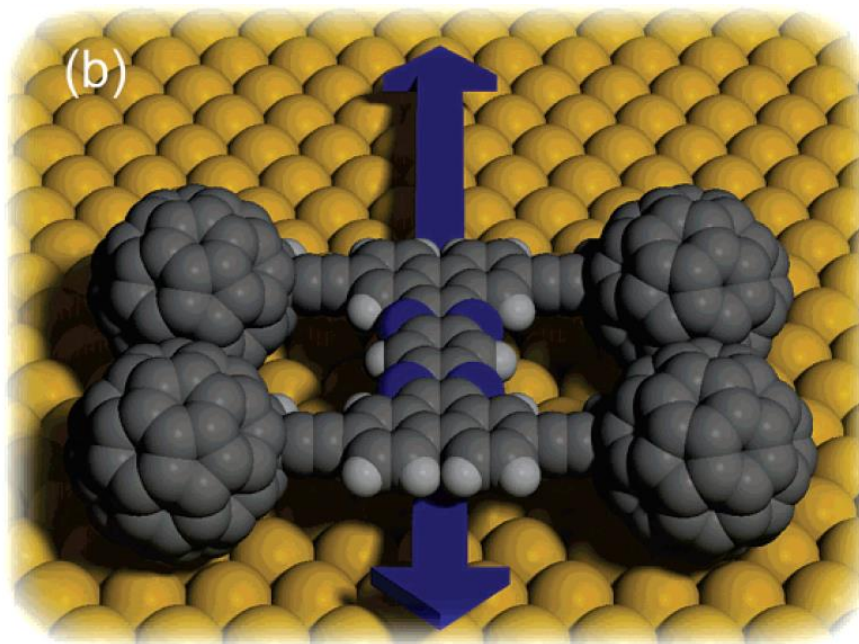
Final Project
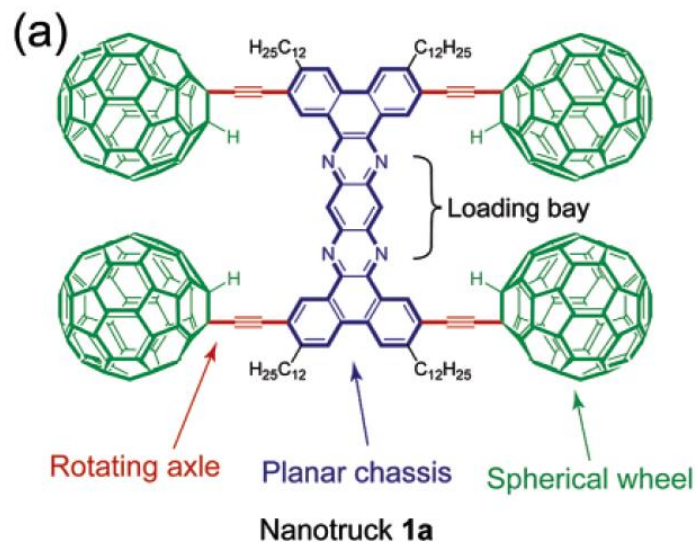
EXAMPLES of Project topics (including projects 2019-2021):

1. Modelling of molecular dynamics and kinetics in LAMMPS. Time-correlation functions and the computation of transport coefficients

2. Problem of parking for hard particles (cars). The irreversible parking problem

3. Aging and ergodicity breaking in sub-diffusion (TAMSD vs EAMSD)

4. Resonant activation over a fluctuating barrier

5. Langevin equation with the solid friction

6. Event-driven simulations of granular gases

7. Direct simulation Monte Carlo of rough granular particles

8. Scaled Brownian motion

9. Generation of correlated noise with given time-correlation function

10. Modelling of molecular dynamics and kinetics of polar fluid in external electric field. Time-correlation functions and dielectric properties.

11. Modelling of molecular dynamics and kinetics in system with an exchange.

12. Fast solvers for aggregation kinetic equations.

Final Project

"Nanoscale Modelling of Fullerene-Wheeled Single Molecular Nanomachines"

(a)

H₂₅C₁₂   C₁₂H₂₅

Loading bay

H₂₅C₁₂   C₁₂H₂₅

Rotating axle   Planar chassis   Spherical wheel

Nanotruck **1a**

(b)

Shirai, Y., Osgood, A. J., Zhao, Y., Yao, Y., Saudan, L., Yang, H., ... & Tour, J. M. (2006). Surface-rolling molecules. *Journal of the American Chemical Society*, *128*(14), 4854-4864.
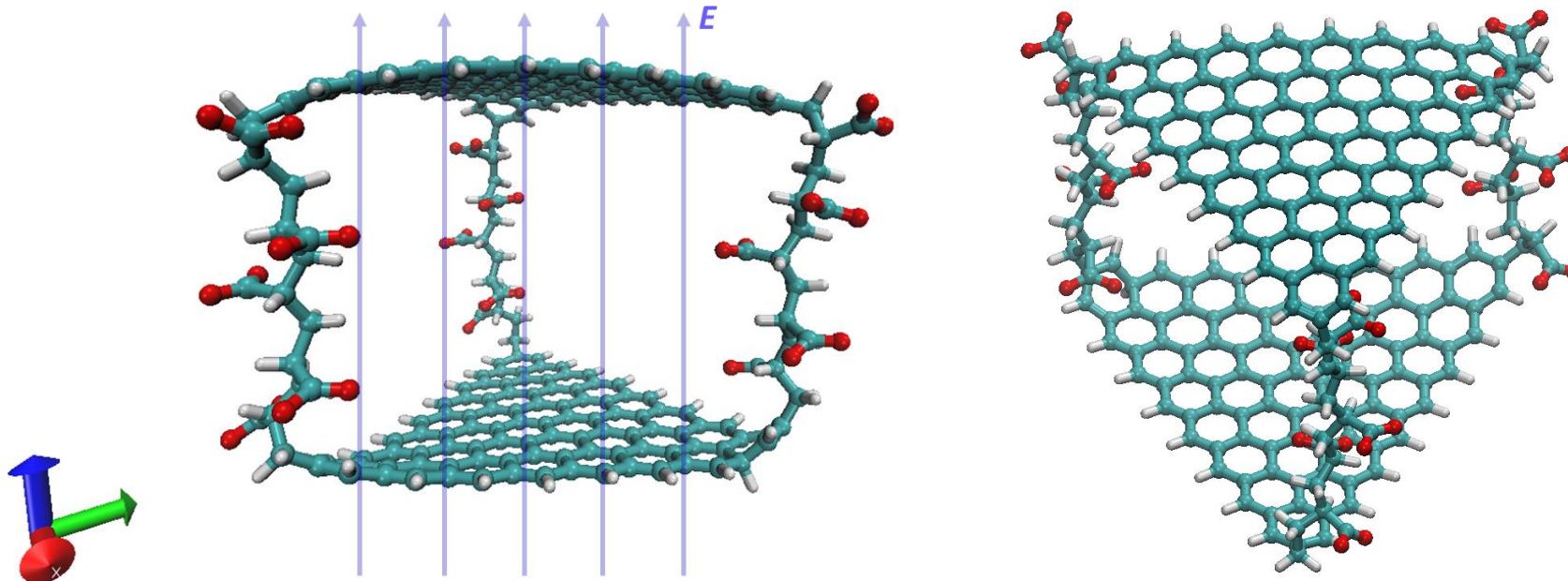
2022 year topics will be uploaded in two weeks

In would be better if You suggest topic you are interesting in!

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Final Project

EXAMPLES of Project topics (including projects 2019-2020):

"Nanoscale Modelling of Polyelectrolyte-based Nanotweezers"

2022 year topics will be uploaded in two weeks

In would be better if You suggest topic you are interesting in!

Introduction: Modelling at different scales, examples and methods

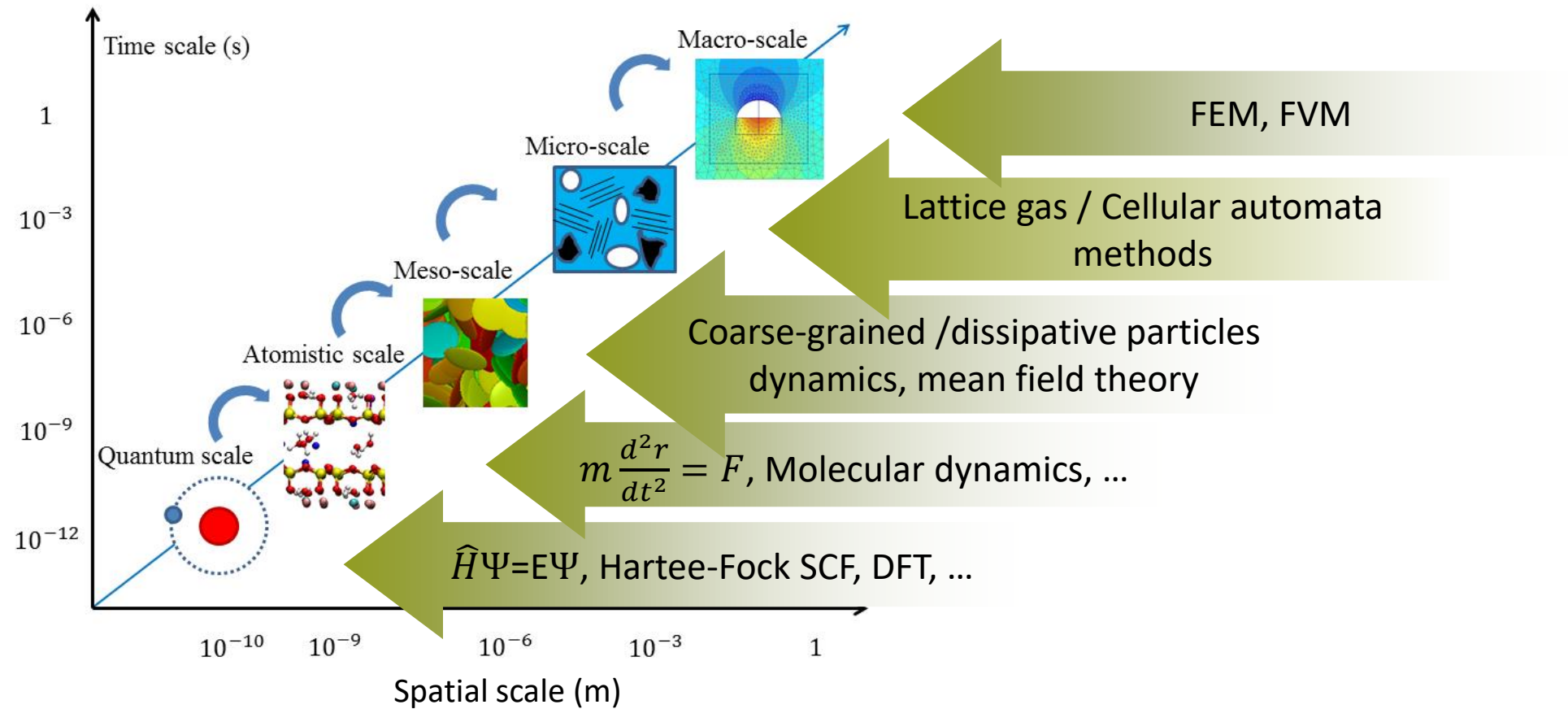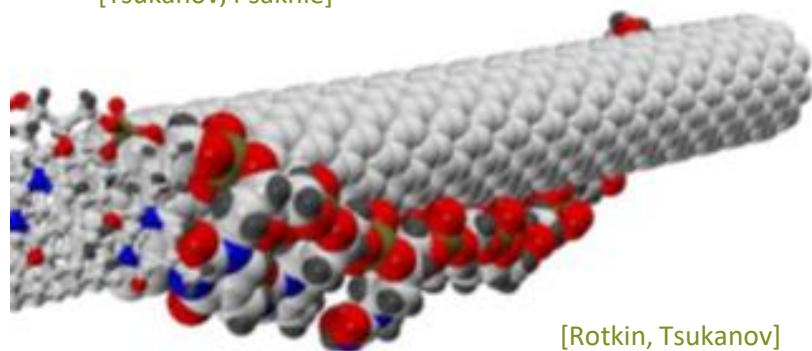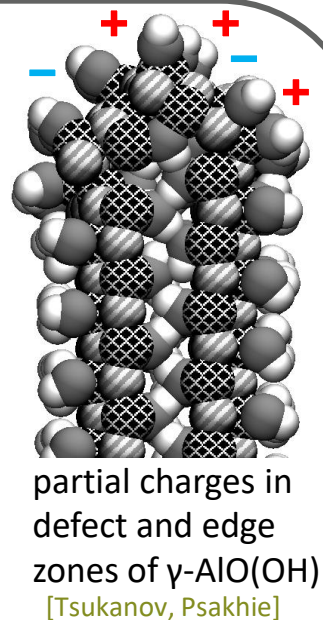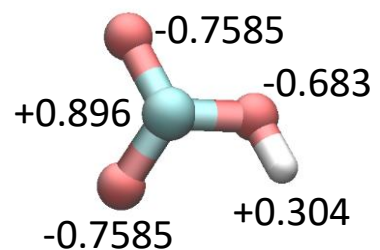# Multiscale Modelling: Scales and methods

Image from site of **Andrew J. Whittle's Research Group MIT**
[https://ajw-group.mit.edu/multiscale-modeling-clays]

Modelling at different scales: Examples

Quantum + atomic scales models >>

partial atomic charges of small molecules
[Tsukanov, Psakhie]

partial charges in defect and edge zones of γ-AlO(OH)
[Tsukanov, Psakhie]

dielectric response of SC and Me CNT @ polycytosine (RNA)
[Rotkin, Tsukanov]

Nanoscale >> (molecules, nanostructures)

nanotribology
[Brilliantov, Tsukanov]

cold-sintering of bimetallic nano-composite
[Tsukanov, Lerner]

competitive adsorption
[Tsukanov, Psakhie]

NP interaction with a cell or bacteria
[Tsukanov, Lozhkomoev]

Complex biological nanosystems
[Tsukanov, Psakhie]

grafted polyelectrolytes
[Brilliantov, Tsukanov]

nanomaterial with selective permeability
[Tsukanov, Shilko]

phase transformations in nanoconfinement
[Tsukanov, Shilko]

Modelling at different scales: Examples

Meso- and microscale models >>
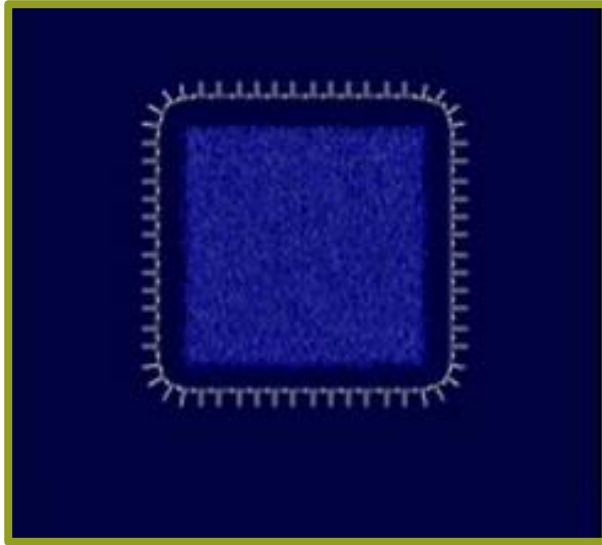
[Tsukanov, Grachev]

Hybrid model of HPP$_{3D}$ cellular automata (variation of lattice Boltzmann method, **LBM**) with explicit elastic surface (shell) in gravitational field

https://www.youtube.com/watch?v=I4wX7LNzm7U
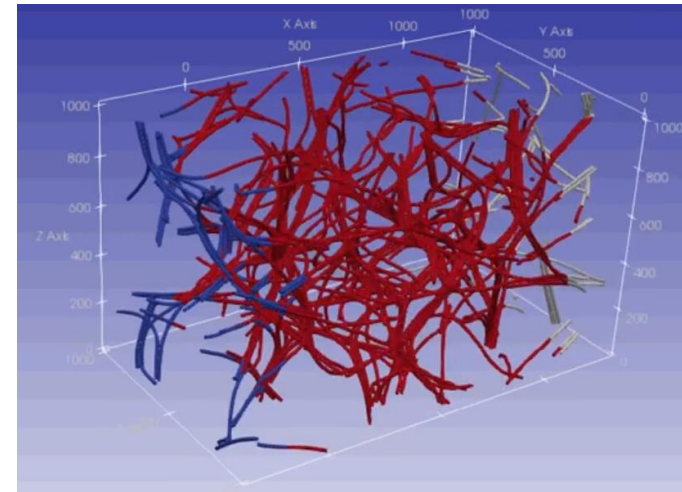
[Igor Ostanin]

Mechanical load (stretching) of carbon nanotubes assembly
[by Igor Ostanin]

Modelling at different scales: Examples

Macroscale models (meters) >>
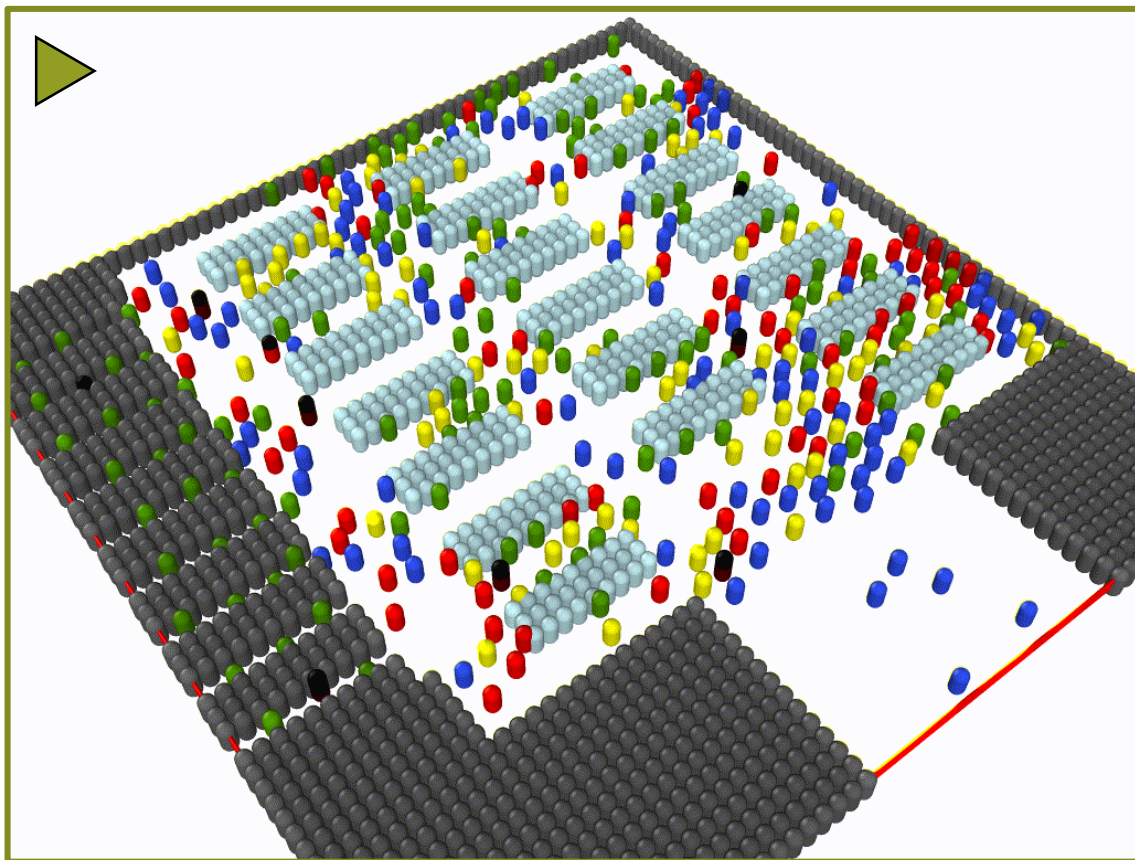
Pedestrians Dynamics (based on social forces model) of visitors behavior in the supermarket with infection transmission model (e.g. COVID-19)

[Brilliantov, Tsukanov]

Macroscale models (kilometers) >>
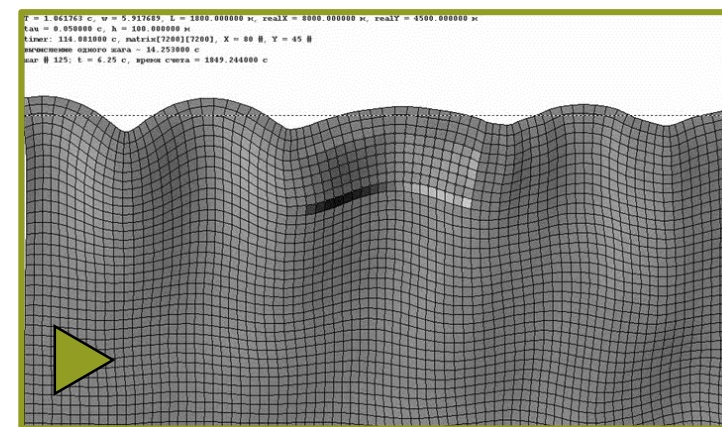
Distance along profile, km

Depth, km
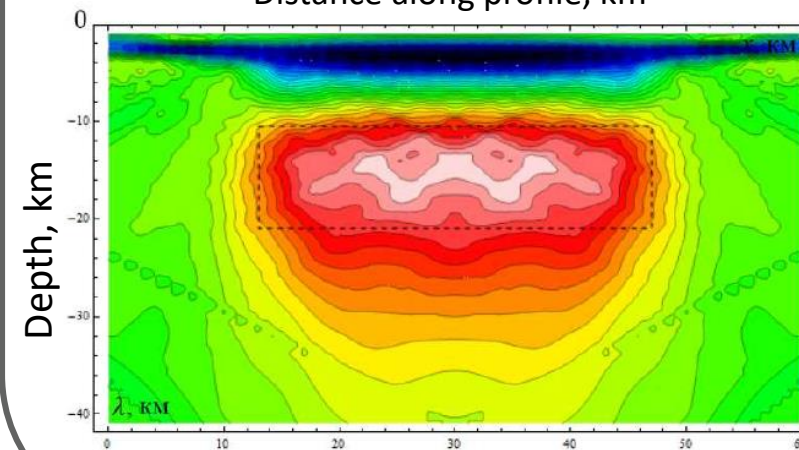
[Tsukanov, Gorbatikov]

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Method of **molecular dynamics** (MD)

(HW 1, task 1)

Classical molecular dynamics

Writing the II-nd Newtons law for each of N atoms, we get the system of N coupled **ordinary differential equations** (ODE):

$$m_i \frac{d^2}{dt^2} \vec{r_i} = \vec{F_i}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

$$i = \overline{1, N}$$

Force field *F* is **conservative**:

- depends only on atom coordinates, doesn't depend on atoms velocities,
- work done by *F* is independent on trajectory, depends on initial and final positions

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de Broglie

$$e^-: \lambda \sim 1\text{Å}$$
$$\sim 10^{-10} \, m$$

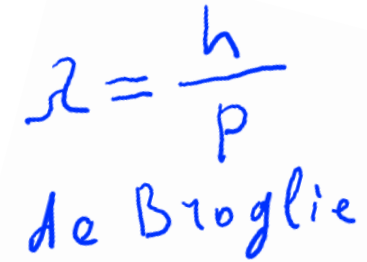Force field *F* is **conservative**:
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$$\frac{m}{2}2v\frac{dv}{dt} + \frac{dU}{dr}\frac{dr}{dt} = 0$$

$$mv\,a - F\,v = 0$$

$$ma = F\ - \text{II-nd Newtons law}$$

$\Rightarrow$ System evolves *microcanonically*
$\Rightarrow$ **Hint**: if full energy is not conserved in simulation – find out, where is a mistake in the algorithm!
     (* – *in one-dimensional case for single particle in conservative force field*)

Classical molecular dynamics: pair potential

Pairwise energy summation:

$$U = \frac{1}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} U_{ij} + (U_0) \qquad (U_0 \text{ conventionally is zero})$$

Pair potential of two atom interaction depends only on distance between atoms:

$$U_{ij} = U_{ij}(|\vec{r_i} - \vec{r_j}|)$$

U is function only of atoms positions.

Common features:

- **repulsion at short distances**
- **attraction at intermediate and long distances**
- **tends to zero as distance tends to infinity**

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$\vec{f}_{ij} = -\vec{f}_{ji}$

(III Newton law)

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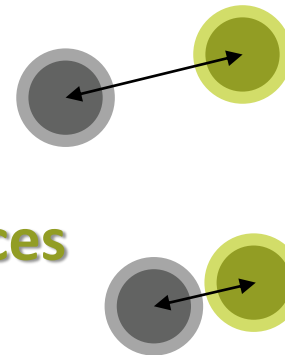
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$$(\text{III Newton law})$$

$$\sum_{i=1}^{N}\sum_{j=i+1}^{N} U_{ij}$$

twice less iterations

Classical molecular dynamics: Lennard-Jones

LJ (potential 6-12) is two-parameter potential for parameterization of pair interaction between two atoms (*of fixed types; more types – more pairs of LJ parameters – may be calculated with Lorentz-Barthelot combining rules*).

LJ uses a minimal set of parameters – **energy scale ε** and **length scale σ**.

$$U_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] = \varepsilon \left[\left(\frac{r_0}{r}\right)^{12} - 2 \left(\frac{r_0}{r}\right)^{6} \right]$$

Attraction term $\sim r^{-6}$ describes the effective dipole–dipole interactions of atoms due to electron correlation dispersion (London dispersion forces). Due to calculation reasons in LJ potential repulsion is described by $\sim r^{-12}$ which allows simple evaluation by getting a square of r^{-6} term.

Lennard-Jones potential $r_0 = 1$, $\varepsilon = 1$
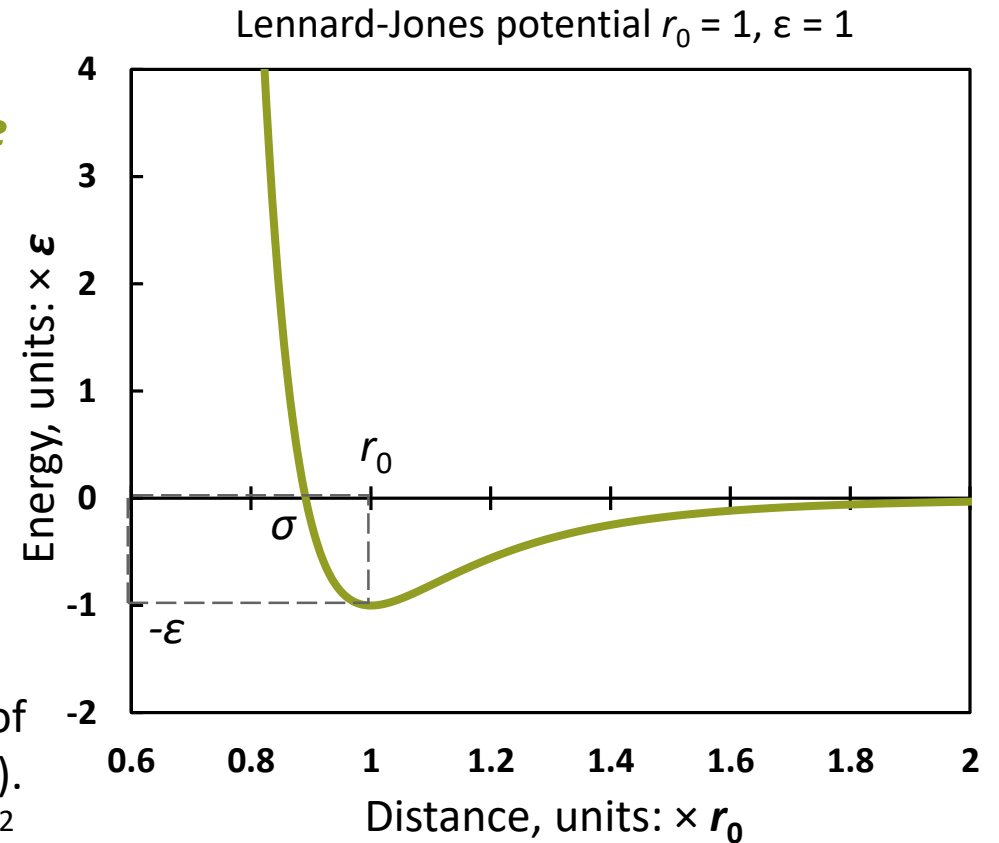
Pair potential: Lennard-Jones

- Renormalize distance **r**, time **t**, temperature **T**, pressure **p** and so on by the following way

$$\tilde{t} = \frac{t}{\sigma}\sqrt{\frac{\varepsilon}{m}}$$

$$\tilde{T} = \frac{k_B T}{\varepsilon}$$

$$\tilde{p} = \frac{\sigma^3}{\varepsilon}p$$

$$\tilde{r} = {r}/{\sigma}$$

$$\tilde{\rho} = \rho\sigma^3$$

we get identical Lennard-Jones systems!

The Lennard-Jones model for a given material is always equal to the Lennard-Jones model for another material at different conditions of temperature and pressure.
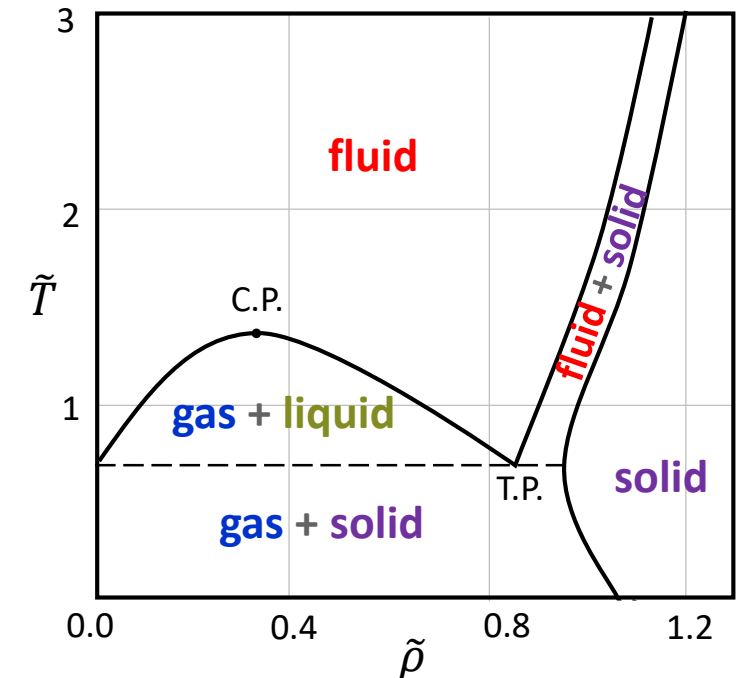
Molecular dynamics: numerical solution

A system of N coupled ODE of second order:

$$m_i \frac{d^2}{dt^2}\vec{r_i} = \vec{F_i}(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) = -\nabla U(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)$$

$$i = \overline{1, N}$$

In case N is large, and e.g. system doesn't have symmetry and periodicity (liquid, amorphous…) it is impossible to find an analytical solution!

Second order ODE needs the certain initial values of coordinates and velocities to be defined, as well as boundary conditions.

In other words, we need to have specified positions at t_0 and t_1, or both positions and velocities at t_0 for all particles ($6N$ values) to uniquely identify the dynamic of the system.

Numerical solution: simple Verlet algorithm

Let time is (uniformly) discretized with timestep δt > 0:

Numerical solution: simple Verlet algorithm

Let time is (uniformly) discretized with timestep δt > 0:

Recall Taylor expansion:

$$\varphi(t + \delta t) = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{d^n}{dt^n} \varphi(t)\, \delta t^n = \sum_{n=0}^{N} \frac{1}{n!} \frac{d^n}{dt^n} \varphi(t)\, \delta t^n + \bar{\bar{o}}(\delta t^{N+1})$$

$$\boldsymbol{r}(t + \delta t) = ?$$

$$\boldsymbol{r}(t - \delta t) = ?$$

Numerical solution: simple Verlet algorithm

Let time is (uniformly) discretized with timestep δt > 0:

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$$\boldsymbol{r}(t + \delta t) = \boldsymbol{r}(t) + \frac{d\boldsymbol{r}(t)}{dt} \delta t + \frac{1}{2} \frac{d^2\boldsymbol{r}(t)}{dt^2} \delta t^2 + \frac{1}{6} \frac{d^3\boldsymbol{r}(t)}{dt^3} \delta t^3 + \bar{\bar{o}}(\delta t^4)$$

$$\boldsymbol{r}(t - \delta t) = \boldsymbol{r}(t) - \frac{d\boldsymbol{r}(t)}{dt} \delta t + \frac{1}{2} \frac{d^2\boldsymbol{r}(t)}{dt^2} \delta t^2 - \frac{1}{6} \frac{d^3\boldsymbol{r}(t)}{dt^3} \delta t^3 + \bar{\bar{o}}(\delta t^4)$$

Taking a sum of this two relations it can be obtained a formula for atomic positions at the next time step:

$$\boldsymbol{r}(t + \delta t) + \boldsymbol{r}(t - \delta t) = 2\boldsymbol{r}(t) + \frac{d^2\boldsymbol{r}(t)}{dt^2} \delta t^2 + \bar{\bar{o}}(\delta t^4)$$

The odd terms compensate each other

$$\boldsymbol{r}(t + \delta t) = 2\boldsymbol{r}(t) - \boldsymbol{r}(t - \delta t) + \boldsymbol{a}(t)\delta t^2 + \bar{\bar{o}}(\delta t^4)$$

Where acceleration at present timestep can be found from 2nd Newton's law: $\boldsymbol{a}(t) = -\frac{1}{m} \text{grad}\, U\big(\boldsymbol{r}(t)\big)$,

Velocity can be evaluated via symmetric finite difference: $\boldsymbol{v}(t) = \frac{\boldsymbol{r}(t+\delta t) - \boldsymbol{r}(t-\delta t)}{2\delta t}$.

Numerical solution: velocity Verlet algorithm

Again use Taylor expansion for future timestep (but up to third term):

$$\boldsymbol{r}(t+\delta t) = \boldsymbol{r}(t) + \frac{d\boldsymbol{r}(t)}{dt}\delta t + \frac{1}{2}\frac{d^2\boldsymbol{r}(t)}{dt^2}\delta t^2 + \bar{\bar{o}}(\delta t^3)$$

$$\boldsymbol{r}(t+\delta t) = \boldsymbol{r}(t) + \boldsymbol{v}(t)\delta t + \frac{\boldsymbol{a}(t)}{2}\delta t^2 + \bar{\bar{o}}(\delta t^3)$$

1) Calculate $\boldsymbol{r}(t+\delta t)$

$$\boldsymbol{v}(t+\delta t) = \boldsymbol{v}(t) + \boldsymbol{a}(t)\delta t + \frac{1}{2}\frac{d\boldsymbol{a}(t)}{dt}\delta t^2 + \bar{\bar{o}}(\delta t^3)$$

2) Calculate $\boldsymbol{a}(t+\delta t)$

$$\frac{d\boldsymbol{a}}{dt} \approx \frac{\boldsymbol{a}(t+\delta t) - \boldsymbol{a}(t)}{\delta t}$$

$$\boldsymbol{a}(t+\delta t) = -\frac{1}{m}\operatorname{grad} U\big(\boldsymbol{r}(t+\delta t)\big),$$

$$\boldsymbol{v}(t+\delta t) \approx \boldsymbol{v}(t) + \boldsymbol{a}(t)\delta t + \frac{1}{2}\big(\boldsymbol{a}(t+\delta t) - \boldsymbol{a}(t)\big)\delta t = \boldsymbol{v}(t) + \frac{1}{2}\big(\boldsymbol{a}(t+\delta t) + \boldsymbol{a}(t)\big)\delta t$$

3) Calculate $\boldsymbol{v}(t+\delta t)$

- Velocity Verlet allows to control velocity and therefore allows thermostatting.

Boundary conditions. PBC.

- To estimate some macroscopic quantity of molecular system (for example, *elastic moduli, compressibility, self-diffusion coefficient, coefficient of thermal expansion…*) we need large enough number of atoms.

- In many cases the use of periodic boundary conditions (PBC) allows to reach representative "volume" with comparatively small number of atoms

To apply PBC in your MD simulator (HW1) you need:

1. **Check atoms coordinates and "wrap" them to the simulation box (every time step).**

2. **Calculating forces, the shortest distance between particles must be used, taking into account periodic boundaries.**
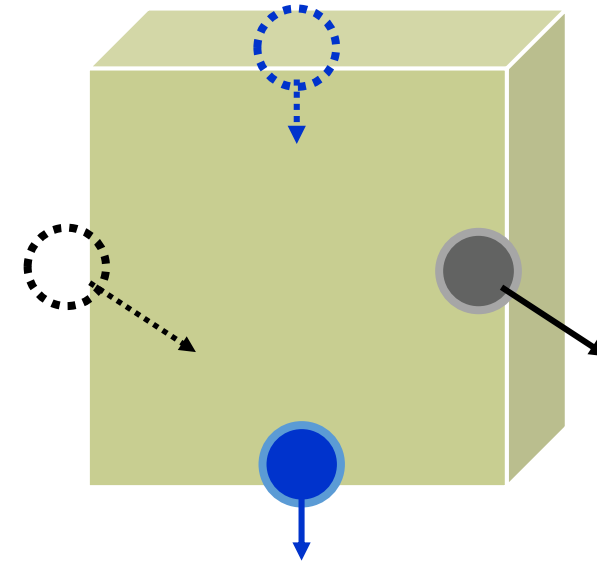
if a particle leaves the main region, it returns (re-enter) from the opposite side with the same momentum = "coordinates wrapping":

```
if x > Lx → x-=Lx
          …
if x < Lx → x+=Ly
          …
if y… z…
          …
```

Initial conditions and equilibration
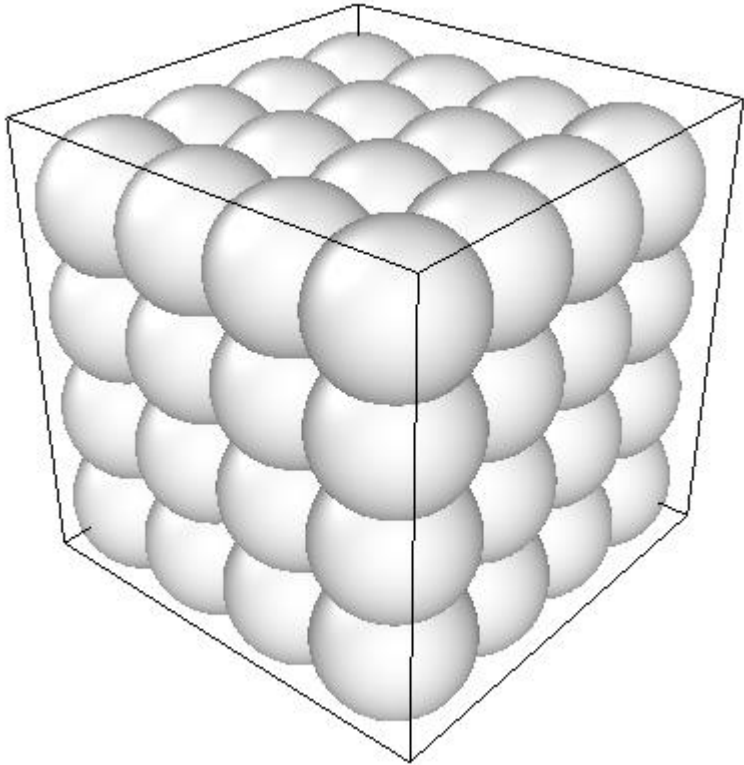
Initialize: select positions and velocities since velocity Verlet algorithm need both $\mathbf{r}_i$ and $\mathbf{v}_i$ to be specified at $t = 0$.

Hint: avoid overlap and short distances, it is reasonable to set initial positions in uniform 3D grid
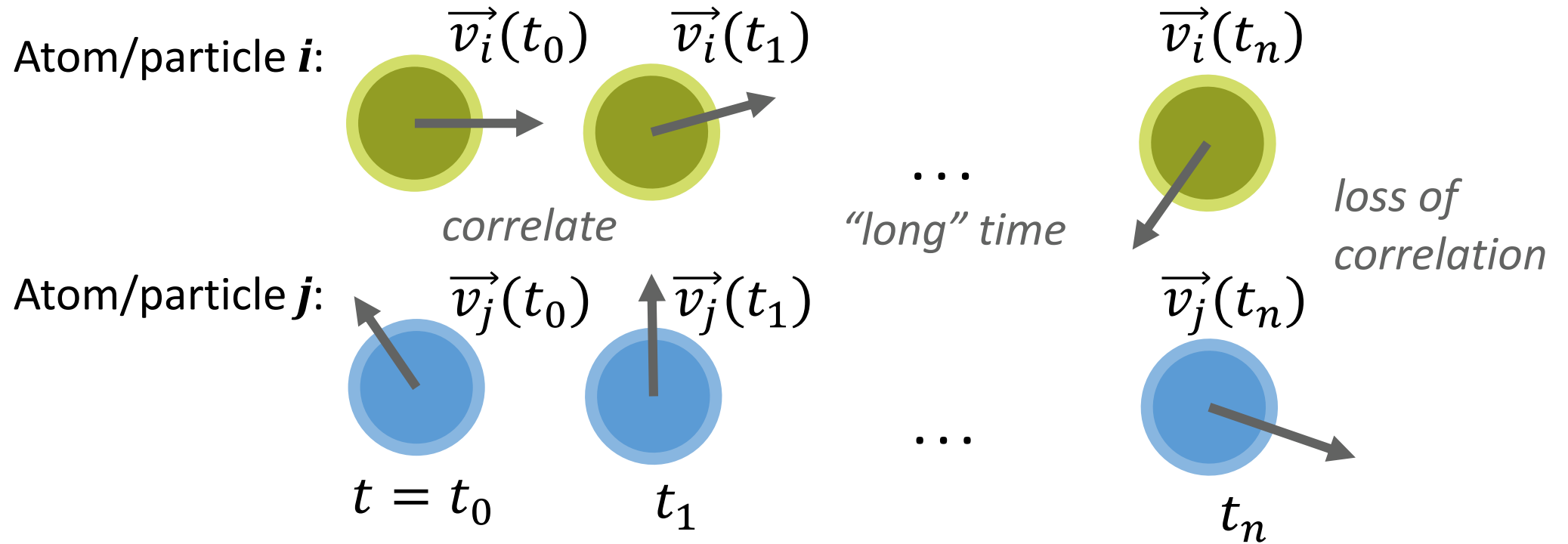
Equilibrate: let the system reach equilibrium (i.e. distribute velocity, distribute energy over degrees of freedom and lose memory of initial conditions)

Average: accumulate quantities of interest (e.g. VACF)

Hint: do not accumulate VACF before equilibration of the system

Velocity autocorrelation function

Atom/particle $\boldsymbol{i}$:

$\vec{v_i}(t_0)$ $\vec{v_i}(t_1)$ $\vec{v_i}(t_n)$

correlate *"long" time* *loss of correlation*

Atom/particle $\boldsymbol{j}$:

$\vec{v_j}(t_0)$ $\vec{v_j}(t_1)$ $\vec{v_j}(t_n)$

$t = t_0$ t_1 t_n

Velocity autocorrelation function (VACF) is a function of time:

$$K_v(t) = < \vec{v}(0) \cdot \vec{v}(t) >$$

is ensemble-averaged scalar product of velocity vectors.

Velocity autocorrelation function

Behaviour of VACF (as a function of time) characterizes molecular thermal motion (*see Lecture notes*):

$$VACF(\boldsymbol{t}) \sim \exp(-\frac{\boldsymbol{t}}{\tau_C})$$

Gas

Crystal

Liquid
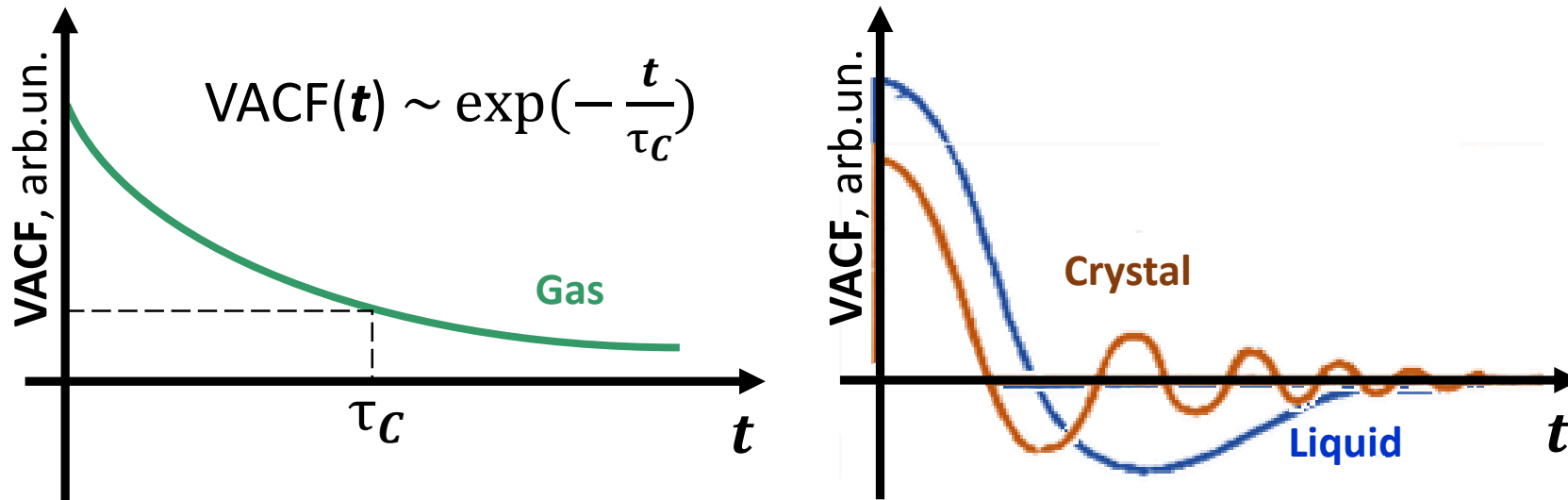
Velocity autocorrelation function depends on aggregate state of the mater.

In **HW1** (**task 1**): $\sim\exp(-\frac{t}{\tau_C})$ should be obtained for LJ system in gas phase.

HOMEWORK 1

Task 1 (**check the actual formulation of the task in the Canvas**)
Write a simple Molecular Dynamics simulation program which uses the Verlet algorithm as described below. Simulate a gas of 64 spheres in a box 16×16×16 with the periodic boundary conditions (PBC). The interaction between the spheres happens according to the Lennard-Jones (LJ) potential. For simplicity, you may set ε = 1 and σ = 1.

- **Hint 1**. It is highly recommended to compute the total energy of the system after each step. If this value changes too much that would be a sign of programming errors.
- **Hint 2**. Don't forget to set an initial distribution of velocities and coordinates of the particles. The recommended way for the initial distribution of the particles is to put them in the vertices of a simple cubic lattice. That minimizes the potential energy. Hence the original kinetic energy sets the temperature.
- **Hint 3**. The forces which define the acceleration can be obtained as corresponding derivatives from the Lennard-Jones potential.
- **Hint 4**. The balls could interact "across" the boundaries in the case of the periodic boundary conditions. Compute the forces from the shortest distance between the two particles ("across" the PBC if necessary).

HOMEWORK 1

Task 1 (continuation)

(a) Equilibrate the system and check that the Maxwell distribution of velocities is obeyed.

(b) Calculate and plot the normalized velocity autocorrelation function (VACF) Kv(t) as a function of time for the low density of particles (the simulation of a gas).

- **Hint**. You should get that Kv(t) $\sim$ exp($-$t/τ) for small density.

(check the actual formulation of the task in the Canvas/HWs…)

Some recommendations on MD, useful links:

- **Book**: Understanding Molecular Simulation (Academic Press) by **D. Frenkel** and **B. Smit.**

- **Book**: Computer Simulation of Liquids (Oxford Science Publications) by **M. P. Allen** and **D. J. Tildesley**.

- Link to **MDAnalysis** module for Python: https://www.mdanalysis.org/mdanalysis/documentation_pages/overview.html

- Link to **OVITO** package homepage: https://www.ovito.org/

- Link to **Visual Molecular Dynamics** (VMD) download page: https://www.ks.uiuc.edu/Development/Download/download.cgi?PackageName=VMD

- **Open** materials of **MIT course** "Atomistic computer modeling of materials" by **G. Ceder** and **N. Marzari**.

Thank you for your attention!

NEXT: Georgii Paradezhenko's presentation >>