

Modeling and visualization of molecular dynamic processes

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1. Formulation of the problem

Two many-particle molecular dynamic problems are regarded within this work . These problems are important in practical applications. They are:

- Modelling of movement of a metal nanosize grain in gas
- Creation of carbon chains from monatomic components

These problems have been investigated in order to check the possibility to solve them by using existing methods and programs and to test the correspondence between computations and theory. For both problems large systems had been modelled, hence their solution requires large computational resources. To perform the computations and to visualize the results special software was selected and studied.

1.1. LAMMPS

To perform the computations we used software package LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) [1]. It is open source (GPL) software created specially for parallel computer clusters. LAMMPS is based on classical molecular dynamics, it uses classical equations of Newton:

$$\frac{d^2\vec{r}}{dt^2} = -grad U(\vec{r})$$

This program uses MPI on systems with distributed memory and was coded with C++. LAMMPS is active developing project with technical support (mail list).

We can model following systems using LAMMPS: atomic systems, charged particle systems, polymers, organic molecules, proteins, DNA, metals, granular materials, coarse mesogrid models, ellipsoidal particles, point dipoles, combination of everything listed above.

LAMMPS is distributed in a source code, the source code is compiled and the created executable file can be used on computers with similar configuration. An MPI realisation and fast Fourier transform packages should be additionally installed.

To start the computation the following command should be used:

```
mpiexec -n <num_processors> lammmps_exec <input.file
```

We used MPICH as MPI realisation here.

Input file is a text file that contains all the information about the system (volume, initial parameters, timestep length, number of timesteps, types and masses of atoms etc.)

At the output we have a text or binary file. We can make it to be large (one file for all timesteps) or many small files (one file per each timestep). Output files can have different formats used in popular MD-applications.

Output information is determined by user and can contain system thermodynamical parameters, coordinates, speed and other info about every atom, computing of parameters with an algorithm written by user.

Disadvantages of LAMMPS include inability to create molecular systems (only atomic systems can be created automatically) , you have to write a data file for molecules using another software. LAMMPS has no graphical interface (only command prompt), it cannot determine automatically coefficients of interaction potentials. There is no built-in software to make plots and visualize the results of computations.

1.2. Hardware for computation

All the computations were performed on the basis of the distributed scientific complex of grid technologies at SPbSU (Gridzone.ru). Four computational nodes were used (two-processor machines), connected via Gigabit LAN. Operational system was Scientific Linux 5.2.

1.3. Visualisation

Two packages were used for visualisation: VMD [2] and GNUPlot [3].

VMD is a freeware program for visualizing of output data of different MD simulators. It can be improved by Tcl scripts. VMD needs graphical interface and gives high-quality visualizations.

GNUPlot is an open source program for building 2D and 3D plots, it works both with graphical interface and command prompt, gives output in many popular formats (gif, jpeg, png etc.).

2. Modelling of movement of a nanosize metal grain in argon in two dimensions.

2.1. Problem

The problem is to model a movement of a metal grain in inert gas and to observe a track of the grain and a gas distribution in this track.

Note: The size of the grain and the free path of argon atoms are of the same order of magnitude, so we cannot use the usual principals of aero- or hydrodynamics in our case, we have to solve equations of molecular dynamics!

This is only a 2 dimensional model and computations are rather boring. The real problem is a 3 dimensional one, so it would require 100 times more time to compute it in the case considered.

2.2. System parameters

| | |
|------------------------------------|---|
| Medium: argon (Ar) | Grain: nickel (Ni) |
| Free path – 750 Å | Diameter – 520 Å |
| Temperature – 300 K | Atomic mass Ni $m=4201.78$ g/mole |
| Pressure – 101 kPa | Grain mass: $M = 4.52 \cdot 10^{-18}$ g |
| Atomic mass Ar – 39.948 g/mole | Speed: 325-1625 m/s |
| Number of atoms $\approx 550\,000$ | Number of atoms ≈ 700 |

Model volume – orthogonal box, size 75000 by 30000 Å

Boundary conditions – periodical

Note: *Nickel atoms form not a grain, but a hollow sphere (for faster computing), that is why we introduce strange atomic mass. The mass of the sphere is equal to the mass of the grain. Atoms do not move with respect to each other, but travel as a whole in the direction of X axis.*

2.3. Potential used for simulation

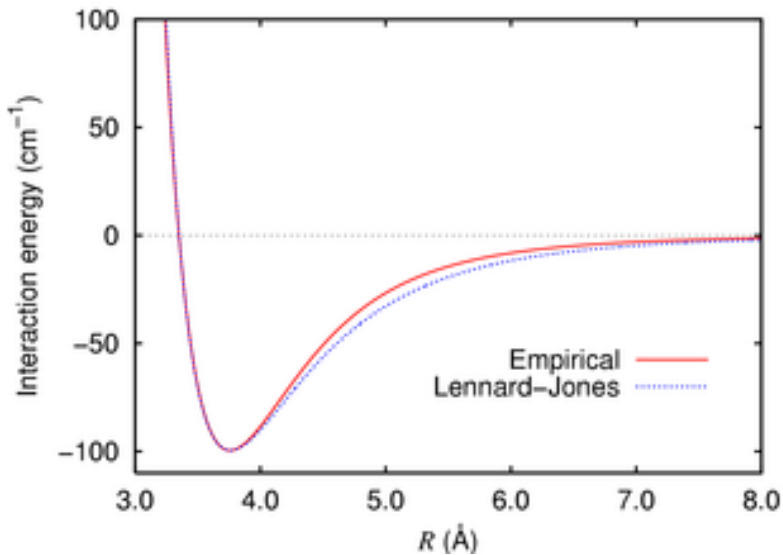
Lennard Jones potential describes interaction between argon atoms (Ar-Ar), between argon and nickel (Ar-Ni).

I.e. it holds for those atoms, that do not participate in chemical reactions.

This potential is described by the formula:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

And has the following graph:



ϵ here is a characteristic interaction energy,

σ is a characteristic interaction distance.

We use also a cut parameter - maximum distance where potential is crucial.

2.4. Parameters of the potential

Argon-argon interaction $\epsilon=0.185$ kcal/mole; $\sigma=3.54\text{\AA}$; $\zeta=9$ Å [4];

Argon-nickel interaction $\epsilon=1.842$ kcal/mole; $\sigma=3.04\text{\AA}$; $\zeta=9$ Å [5];

Nickel atoms are fixed with respect to each other;

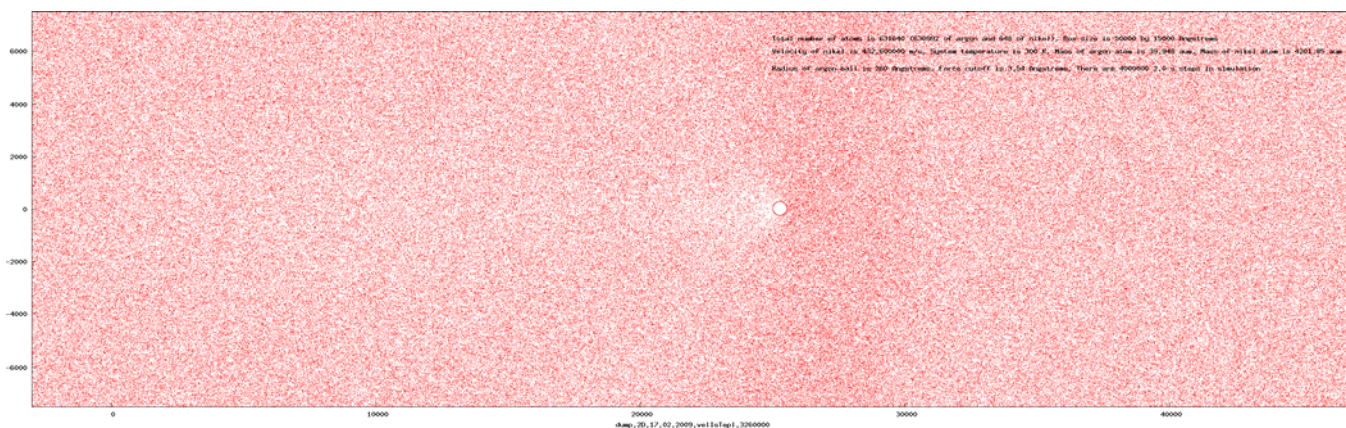
ϵ here is a characteristic interaction energy,

σ is a characteristic interaction distance.

ζ is a cut parameter.

2.5. Visualization of results in GNUPlot

Speed of the grain is 433 m/s, plot is graduated in angstroms:



Speed of the grain is 650 m/s, plot is graduated in angstroms:



2.6. Used resources and output

Computing time for a model with one grain speed value was 10 hours for 3.5 mln. steps, 1.5 fs each step.

Output data: 200 - 300 text files containing coordinates of atoms (one file per 10000 steps, one step in a file), 3.5 GB HDD space used.

Note: such output method was chosen because of output limitation of C language (2GB per one file on 32 bit processor)

Visualisation:

Gif images were produced by GNUPlot. Although VMD is simpler and gives better pictures, it works only with graphical interface, so it was impossible to make pictures on a remote server (where output files were stored), and we used GNUPlot 4.2. A bash-script was written to read a text file and draw gif images in GNUPlot (one image per a text file).

3. Creation of carbon chains from monatomic components (gas phase)

3.1. Problem

The problem is modelling of breaking covalent bonds in carbon molecules and creation of carbon chains on the basis of usage of AIREBO potential. All these problems were computed in case of small systems (10 000 atoms) to test possibilities of computational methods. For interactions with buffer gas usual LJ potential was used.

3.2. AIREBO (adaptive intermolecular reactive empirical bond-order) potential [5][6]

It is used to model reactions between carbon and hydrogen. This potential is called empirical, because almost all its components came from fitting experimental results and not from theory.

The basic formula is:

$$E = E^{REBO} + E^{LJ} + E^{tors}$$

Bond-order part is a short-range potential and describes covalent bonds.

$$E_{ij}^{REBO} = V_{ij}^R(r_{ij}) + b_{ij} V_{ij}^A(r_{ij})$$

It consists of repulsive and attractive pairwise potentials. Indexes i and j correspond either to hydrogen or to carbon. b_{ij} is a bond-order term. A variety of chemical effects that affect the strength of covalent bonding interaction are all accounted for in this term (i.e. presence of neighbouring atoms and bonds, type of hybridisation etc.).

The LJ component...

$$E_{ij}^{LJ} = S(t_r(r_{ij}))S(t_b(b_{ij}^*))C_{ij}V_{ij}^{LJ}(r_{ij}) + [1 - S(t_r(r_{ij}))]C_{ij}V_{ij}^{LJ}(r_{ij}), \quad V_{ij}^{LJ}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

...consists of LJ potential and spline (S) and cosine (C) switch functions which depend on the distance between atoms and presence of neighbouring atoms. Switches make less or switch off LJ repulsion if a bond is created.

Torsional potential...

$$E^{tors} = \frac{1}{2} \sum_i \sum_{j \neq i} \sum_{k \neq i,j} \sum_{l \neq i,j,k} w_{ij}(r_{ij})w_{jk}(r_{jk})w_{kl}(r_{kl}) \times V^{tors}(\omega_{ijkl}), \quad V^{tors}(\omega) = \epsilon \left[\frac{256}{405} \cos^{10} \left(\frac{\omega}{2} \right) - \frac{1}{10} \right].$$

...describes bond interactions, it depends on dihedral angle constructed by 4 neighboring atoms. It contains bond weights (cosine spline switches (w)) varying from 0 to 1.

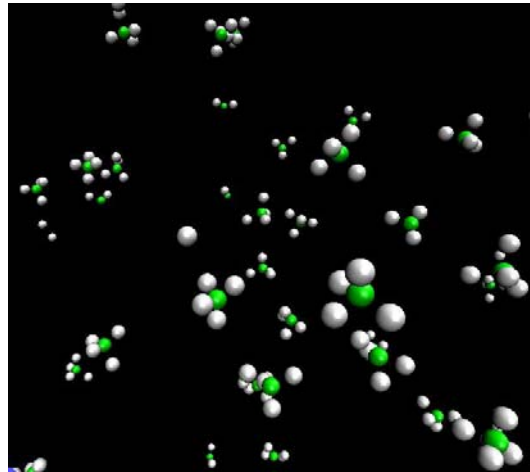
All switches are selected in a way to make the whole potential as smooth as possible during the creation and breaking of covalent bonds.

3.3. Checking of AIREBO potential in simple simulations

3.3.1. Modelling methane (CH₄) in a box

Parameters:

- cubic box 100 Å
- pressure 4MPa
- temperature 300 K
- 512 molecules
- time of simulation is 200 fs

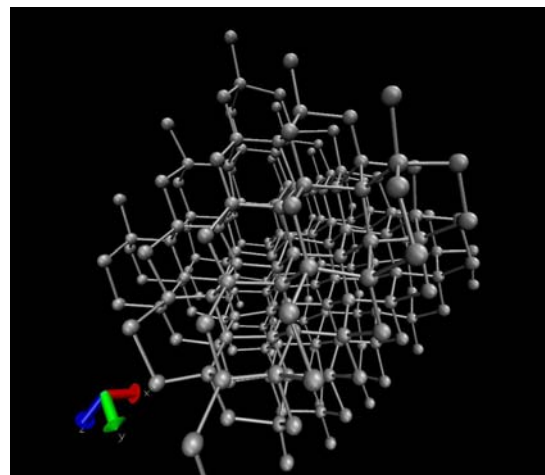


This simulation was visualized via VMD. We can see thermal motion and oscillations of methane molecules. The chosen potential is good for this simple simulation.

3.3.2. Modelling diamond

Parameters:

- cubic box 10 Å
- lattice 3.35 Å
- temperature 300 K
- 216 atoms
- time 1000 fs



This simulation was also visualized in VMD. We can see lattice oscillations of carbon atoms in diamond. AIREBO fits well for modelling rigid carbon also.

3.4. Creation of carbon chains from monatomic components (microcanonical ensemble)

This simulation was done twice: with buffer gas and without it.

Note: *In these two simulations the total energy of the system is fixed. When new bonds are created, an extra energy is emitted, so the system is heated up. If we have no energy receiver (buffer gas), the extra energy breaks bonds of neighbouring atoms, so the bonds are unstable. Buffer inert gas receives extra energy hence the bonds are not breaking (they are more stable).*

3.4.1. Without buffer gas

initial parameters:

temperature 100 K

760 hydrogen + 760 carbon atoms

pressure 5 MPa

box – 80*40*40 Å

boundary – periodical

time – 150 ps

In this simulation carbon and hydrogen atoms interact with one another and we see no chains, but only hydrocarbon radicals and hydrogen molecules, a very few bonds are created.

3.4.2. With buffer gas (argon)

initial parameters:

temperature 100 K

7260 argon + 2904 carbon atoms

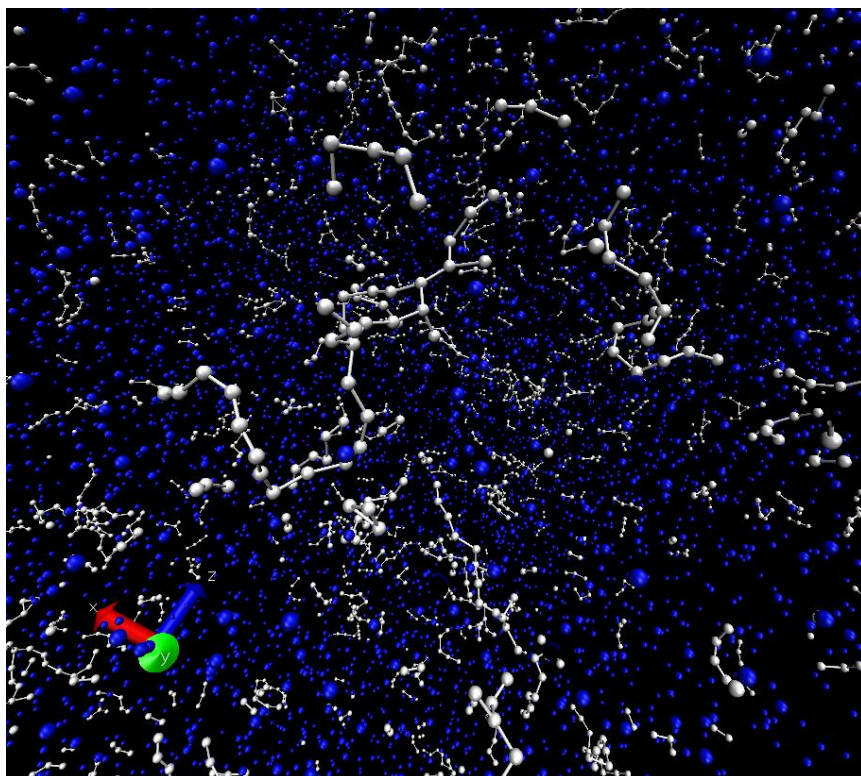
pressure 5MPa

box – cube 260 Å

boundary – periodical

time – 150 ps

We see only short chains at the picture. It means that buffer gas receives extra energy, but hence it is also heating it gives up energy receiving at some moment, we should cool the system also.



3.5. Creation of carbon chains from monatomic components with buffer gas (canonical ensemble, fixed temperature)

initial parameters:

temperature 100 K (fixed)

7260 argon + 2904 carbon atoms

pressure – 5Mpa

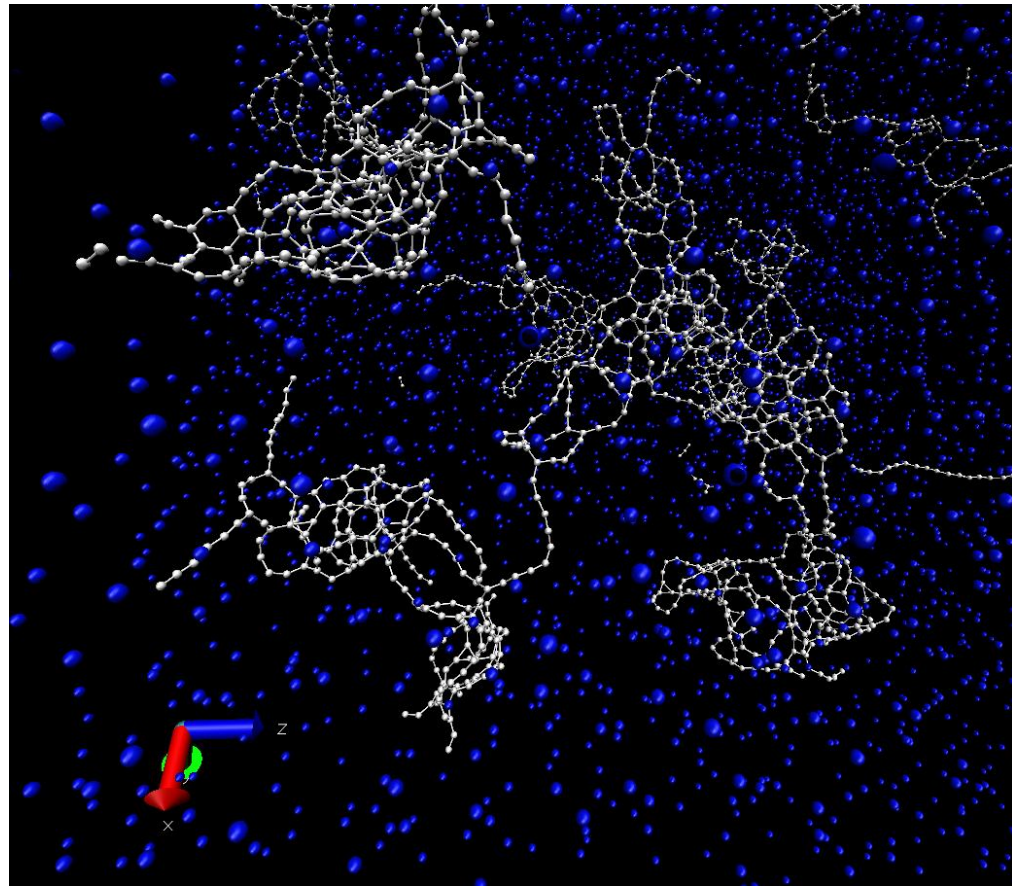
boundary – periodical

box – cube 260 Å

At the picture we see much more complex chains, there are also pentagons, hexagons and heptagons.

So it is clear that good heat receiver causes longer chains.

Note: In this simulation temperature is fixed and energy is not, so the total system energy decreases. Canonical ensemble computations are provided by special NVT (number of atoms, volume and temperature) fixing function in LAMMPS (it performs constant NVT integration to update positions and velocities at each timestep for atoms in the group using a *Nose/Hoover temperature thermostat*) [8]. Buffer gas is used here only as an atmosphere rather than a heat receiver.



4. Conclusion

1. A parallel version of LAMMPS was installed, investigated and adjusted on the computer cluster.
2. A proper software for visualization was chosen.
3. This software was used to solve applied problems:
 - A. Modelling of movement of a nanosize grain in a gas
 - B. Creation of carbon chains from monatomic components

This research will be continued and results will be applied to another problem in nanophysics.

5. References

- [1] <http://lammmps.sandia.gov/features.html>
- [2] <http://www.ks.uiuc.edu/Research/vmd/>
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- [8] Hoover, Phys Rev A, 31, 1695 (1985)

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