Molecular Dynamics and Accelerated Molecular Dynamics

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Lecture 1

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Overall Outline

Day 1: Molecular dynamics methods

Day 2: Molecular dynamics methods

Day 3: Infrequent events, transition state theory, saddle finding, etc.

Day 4: Accelerated molecular dynamics methods

Molecular Dynamics (MD)

Evolve a system of atoms according to the classical equations of motion (F=ma)

N atoms ---> 6N coordinates {**x**,**p**}

x_i = position of atom i

p_i = momentum of atom i

$v_i = p_i/m_i$ = velocity of atom i

Equations of motion:

$$\frac{\partial x_i}{\partial t} = \frac{p_i}{m}$$

$$\frac{\partial p_i}{\partial t} = -\frac{\partial V}{\partial x_i}$$

Typically, potential V is solely due to interactions among the atoms (but need not be).

Brief History of MD

First MD simulation

B.J. Alder and T.E. Wainwright, 1956 - hard sphere liquid, phase transition

First MD simulations with a continuous potential

G.H. Vineyard et al, 1959 -- radiation damage simulation with a pair potential

A. Rahman, 1964 - Lennard-Jones liquid

Some points

In nature, V comes from the electronic interactions -- the electronic wavefunction. In MD, this is typically swept under the rug, leaving just a relatively simple functional form for V. (Although sometimes we do better than this.)

The system is evolved on the Born-Oppenheimer surface -- i.e., V is for the ground state of the system, and the electronic wavefunction is assumed to instantaneously adapt to the current configuration of atoms ($m_{electron} << m_{nucleus}$).

Why do we do MD?

MD is the highest level (i.e., the largest scale) model that gives dynamics in full atomistic detail in an unbiased fashion.

There is no approximation beyond the choice of interatomic potential and the assumption of (nonrelativistic) classical mechanics.

Interatomic potential + boundary conditions

↓

Integrate equations of motion

↓

Observations, predictions

Gives the "truth" for the chosen interatomic potential -- very appealing.

Why do we do MD? (cont)

With a good-quality potential, we can use MD to interpret experiment, make experimentally testable predictions, and gain a physical understanding of real systems at the atomic level.

Also, MD simulations can themselves be considered to be "experiments."

- test higher-level models
- parameterize higher-level models
- to simply see what happens*

*Often, MD simulations show unexpected, surprising results, forcing the development of better theory, better understanding, and new experiments.

Properties we can calculate/study

Pair distribution function in a liquid
Diffusion constant in a a liquid
Structure factor in a liquid
Pressure vs. volume
Thermal expansion
Melting point
Surface melting
Free energy differences between phases
Defect dynamics and diffusion in solid (*)
Surface diffusion (*)
Surface sputtering
Surface scattering
Thermal conductivity

Shock waves
Detonation
Radiation damage events
Grain boundary structure
Vapor deposition (*)
Fast fracture
Nanoindentation
Fast plastic flow
Grain boundary sliding (*)
Protein structure (*)
Protein function (*)
Protein dynamics (*)

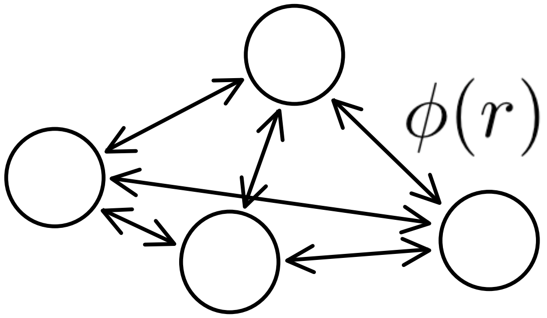
(* = may be limited by MD time scale)

Limited primarily by imagination.

Interatomic Potentials - first pass

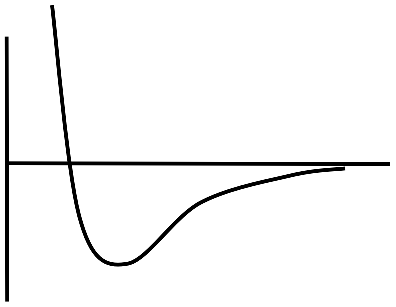
Simplest: pair potential

$$V = \frac{1}{2}\sum_{i\neq j}^{N}\phi(r_{ij})$$



e.g., Lennard-Jones 6-12:

$$\phi(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]$$



σ = length scale
ε = energy scale

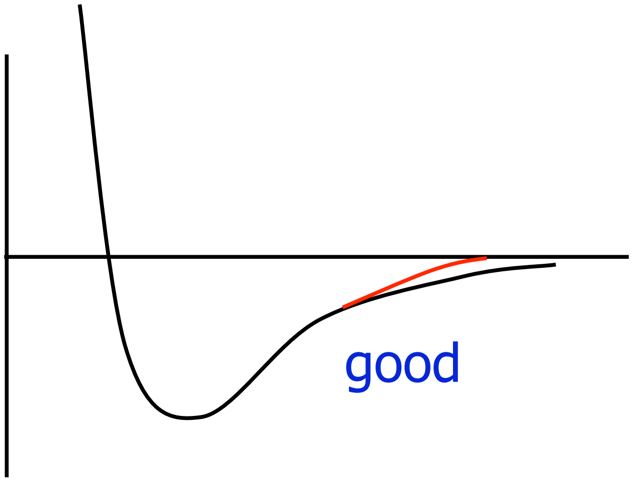
short-range repulsion

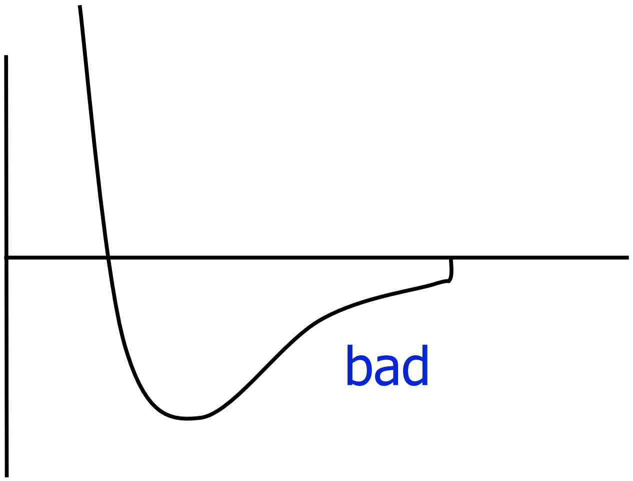
dispersion interactions

LJ is appropriate for argon, for example.

Interatomic potentials

Potential cutoff (typical for non-ionic materials)

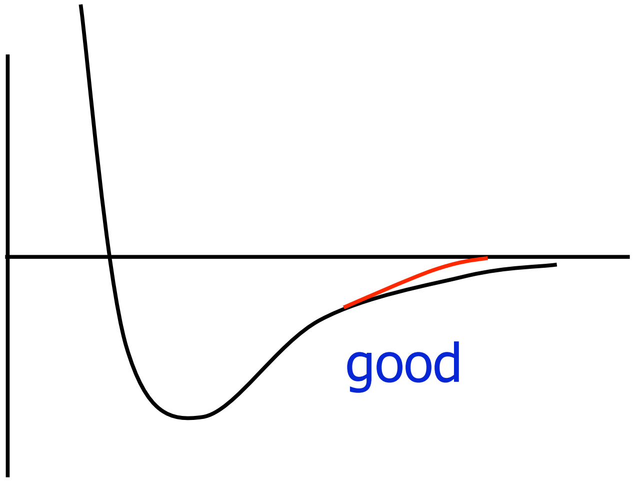




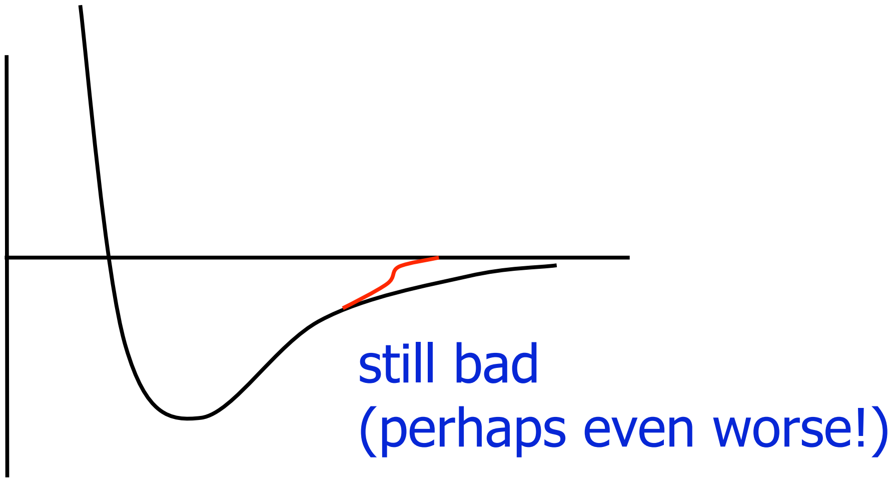
With cutoff, forces depend only on nearby atoms, and overall computational work scales as N.

Interatomic potentials

Potential cutoff (typical for non-ionic materials)



good



still bad
(perhaps even worse!)

With cutoff, forces depend only on nearby atoms, and overall computational work scales as N.

Integrating the equations of motion

For each atom i:

$$\frac{\partial x_i}{\partial t} = \frac{p_i}{m}$$

$$\frac{\partial p_i}{\partial t} = -\frac{\partial V}{\partial x_i}$$

Verlet Algorithm

Most commonly used method for MD these days.

Given **x**(t), **p**(t-Δt/2),

First advance p:

$$p_i(t+\Delta t/2) = p_i(t-\Delta t/2) - \frac{\partial V(\mathbf{x}(t))}{\partial x_i}\Delta t$$

Then advance x:

$$x_i(t+\Delta t) = x_i(t) + \frac{1}{m}p_i(t+\Delta t/2)\Delta t$$

x and p jump over each other, staying out of phase by Δt/2.

This is “leapfrog Verlet.” There are other types of Verlet (e.g., velocity Verlet), but they all give the same integration.

Verlet Algorithm

Simple.

Error term is 4th order.

Symplectic (conserves volume in phase space, as real Hamiltonian dynamics should).

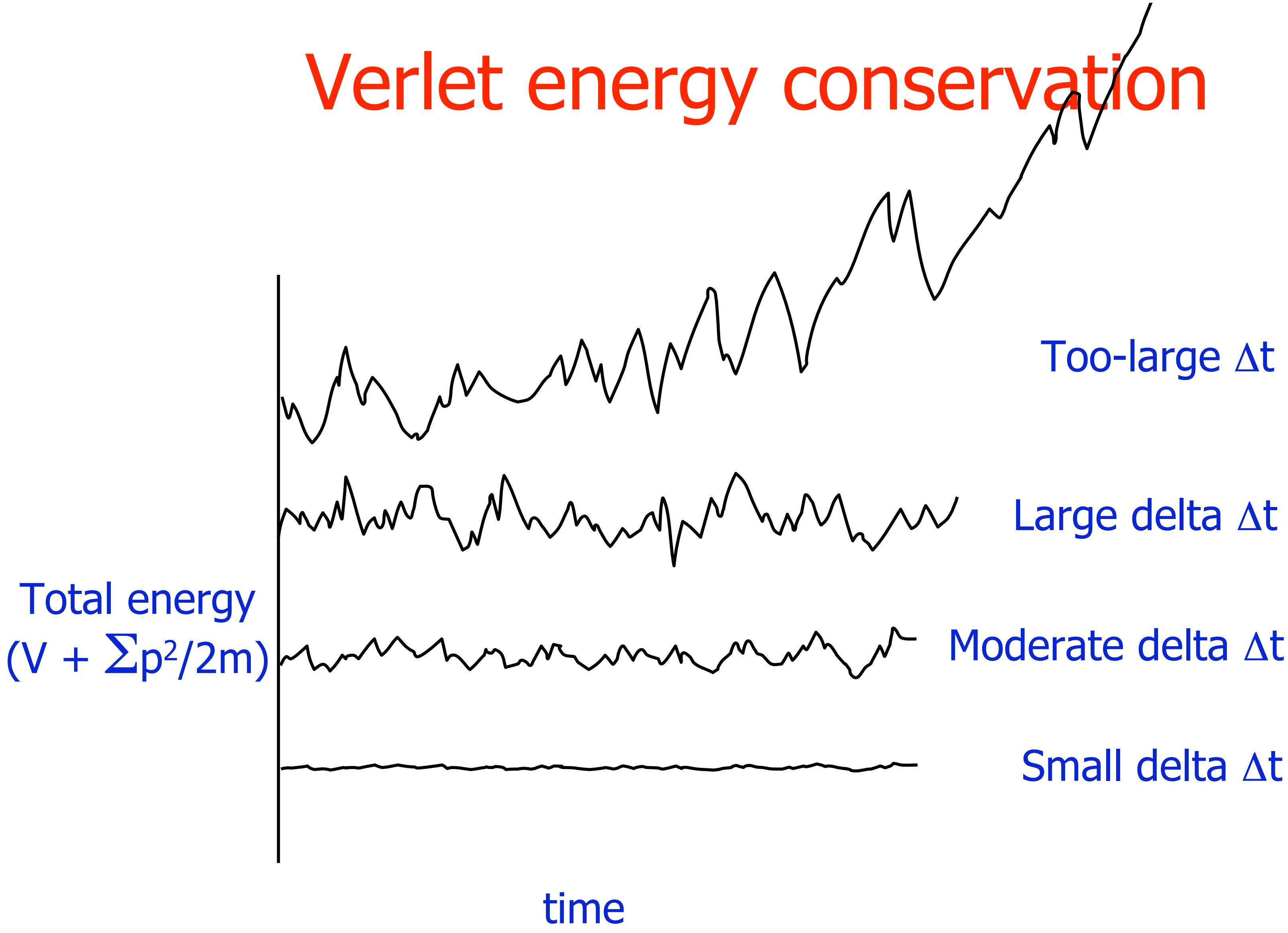
Time reversible.

Within stability limit ($\Delta t <= \sim$period/20), conserves energy for an extremely long time.

Typical time step: metals 2-6 fs, proteins 0.5-1 fs

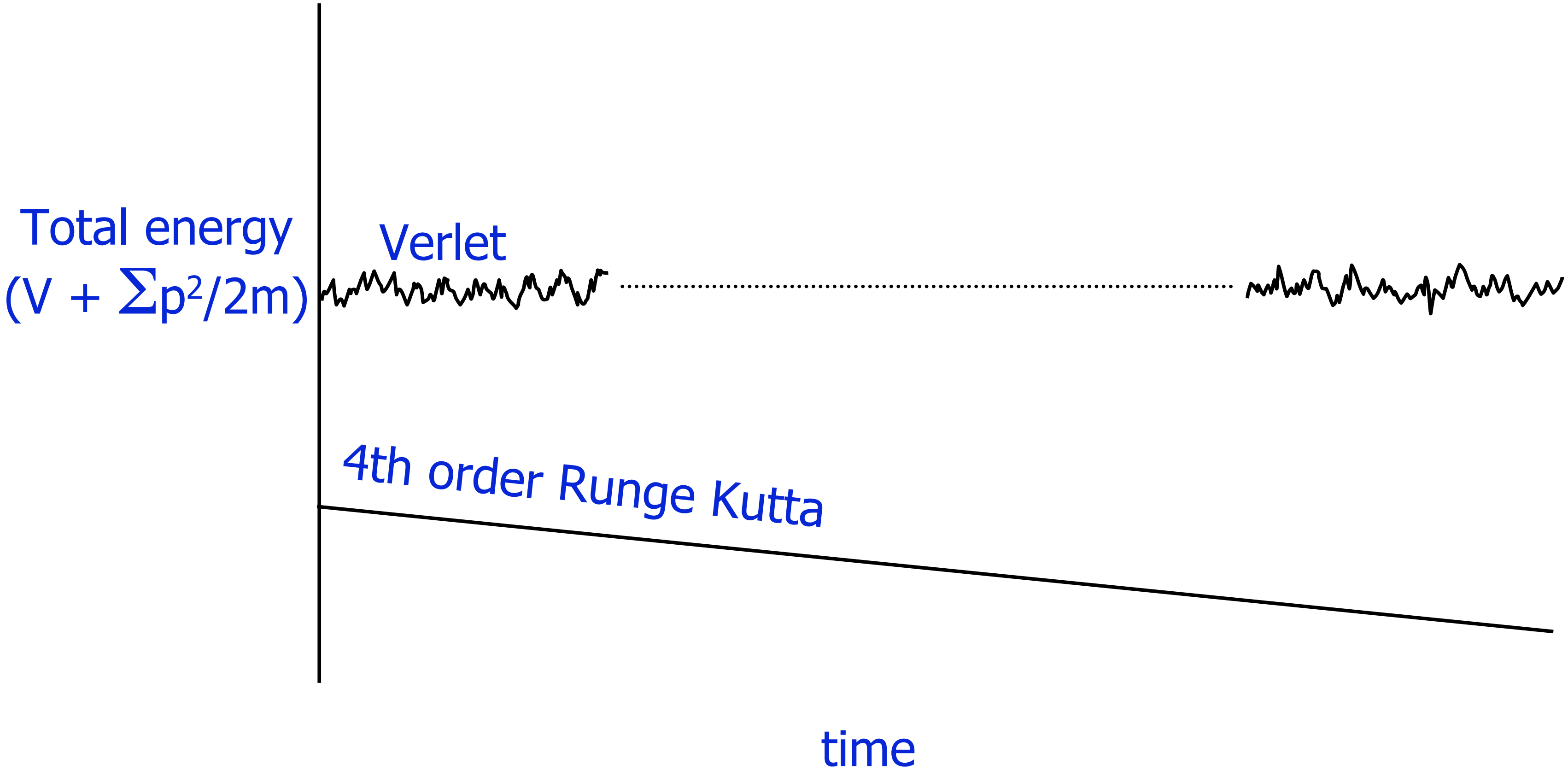
Typically the best choice for most any MD simulation.

Verlet energy conservation

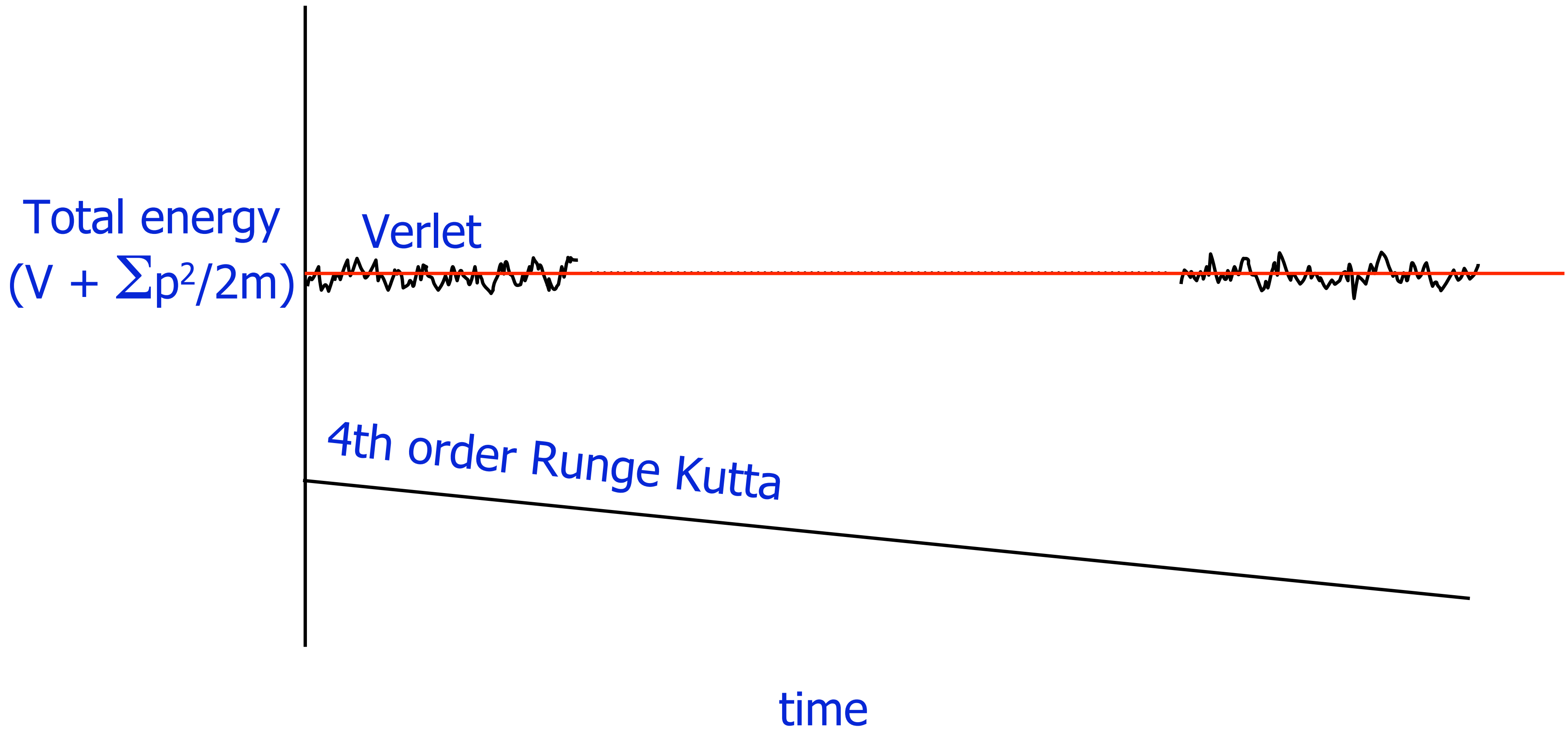


Energy fluctuates, but mean is very stable over long times.

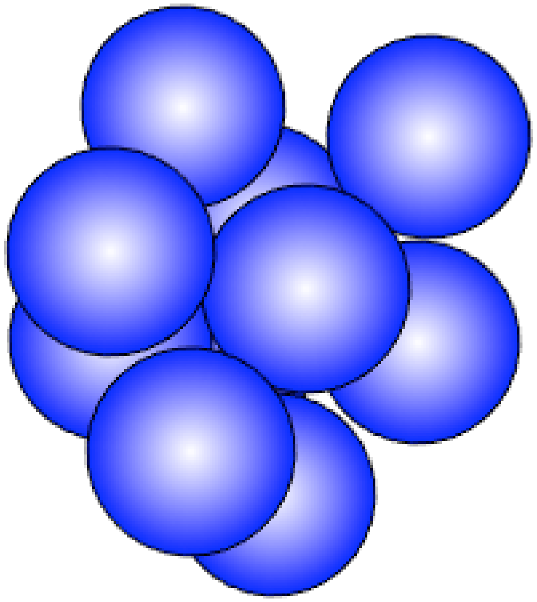
Verlet vs. Runge Kutta



Verlet vs. Runge Kutta

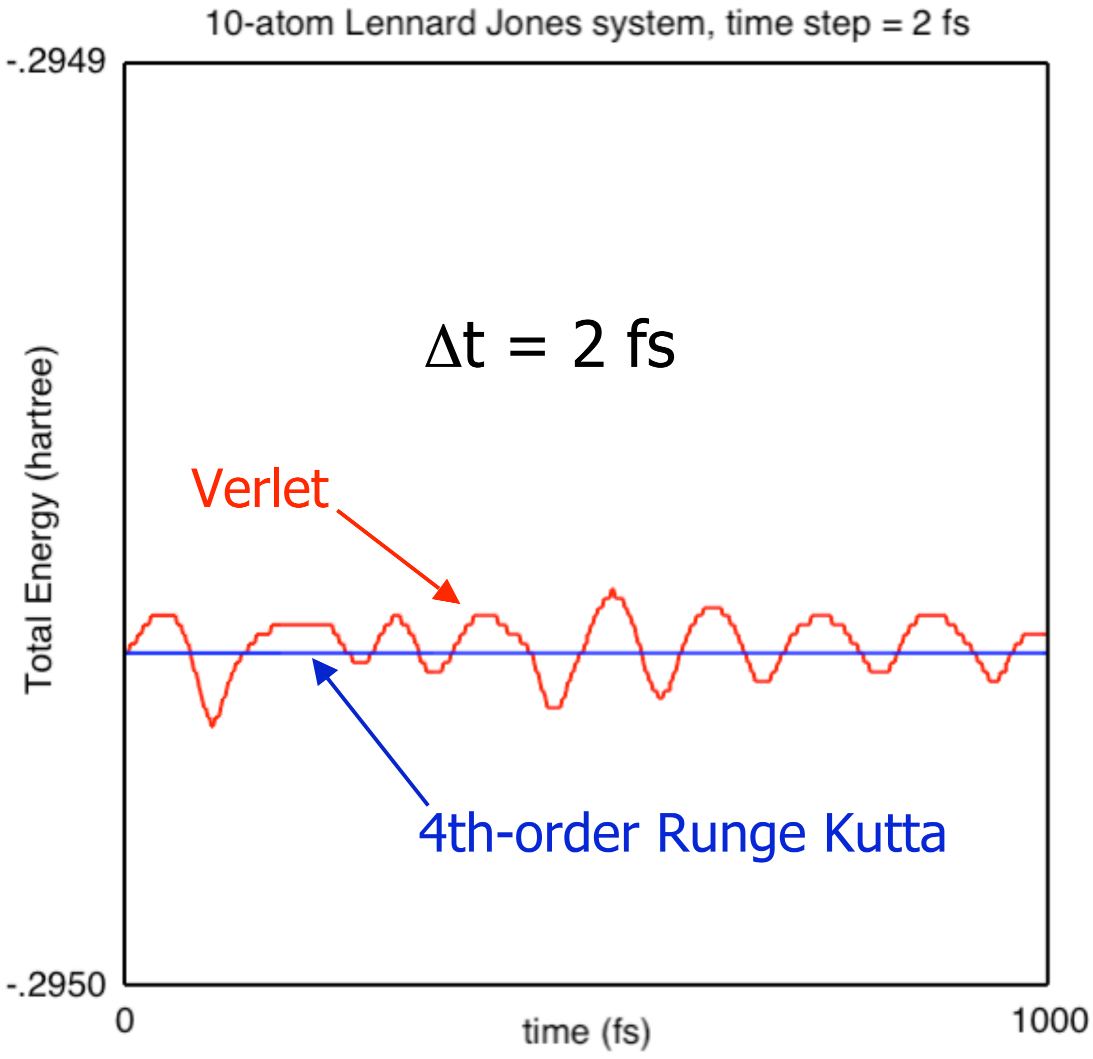


10-atom Lennard-Jones cluster



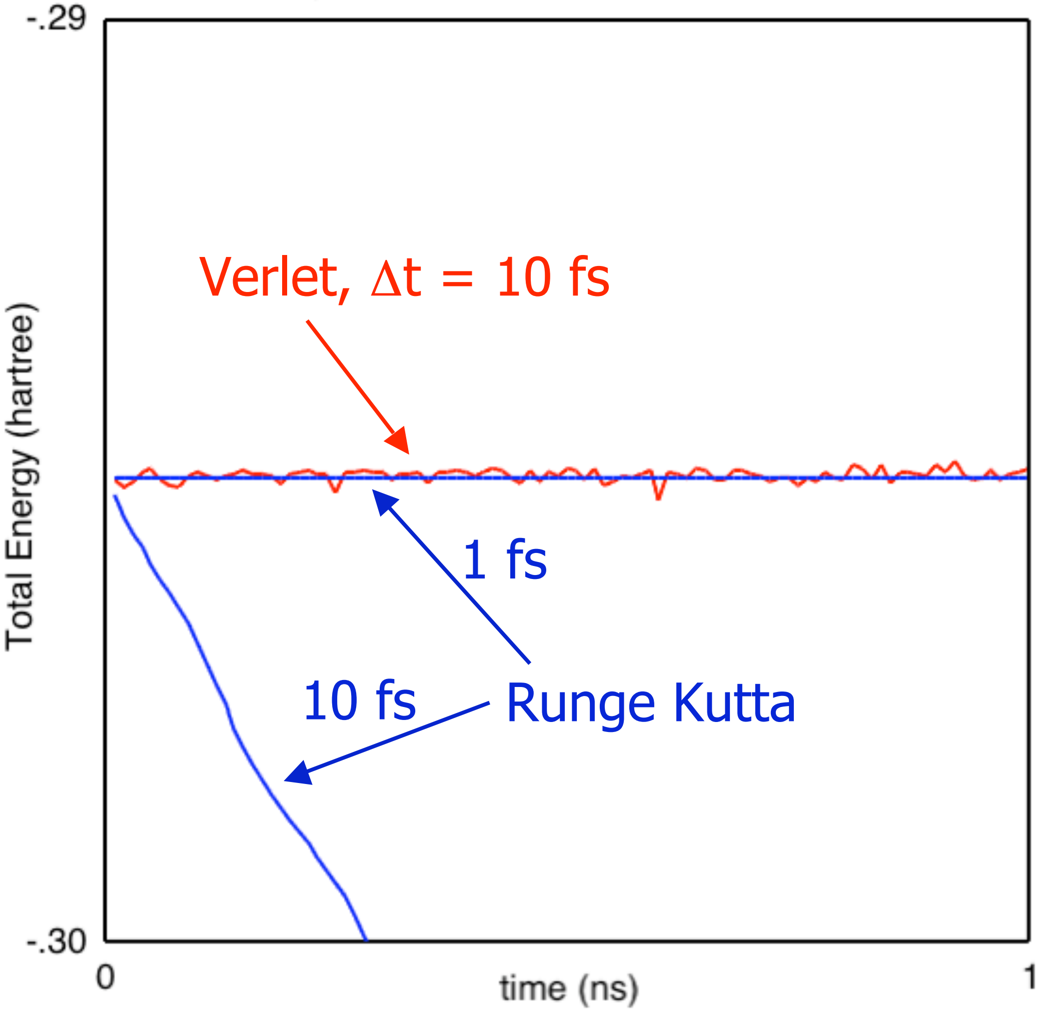
Parameterized to be sort of like silver
Verlet time step = 5 fs
Kinetic temperature ~500K
10 ps movie

Verlet versus Runge Kutta



short time

Verlet versus Runge Kutta



10-atom LJ system, time step = 1,10 fs (RK), 10 fs (Verlet)

Verlet, Δt = 10 fs

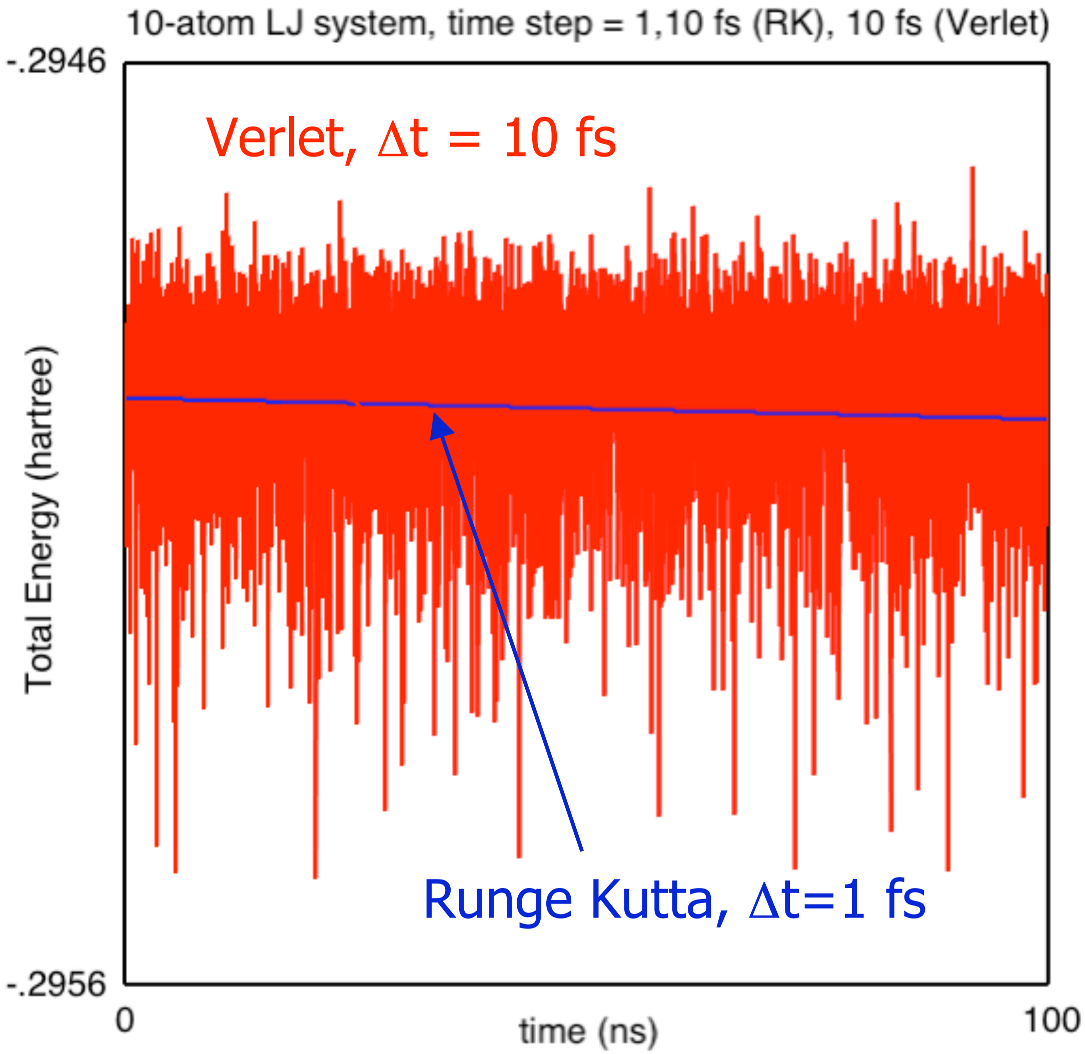
1 fs

10 fs

Runge Kutta

long time

Verlet versus Runge Kutta



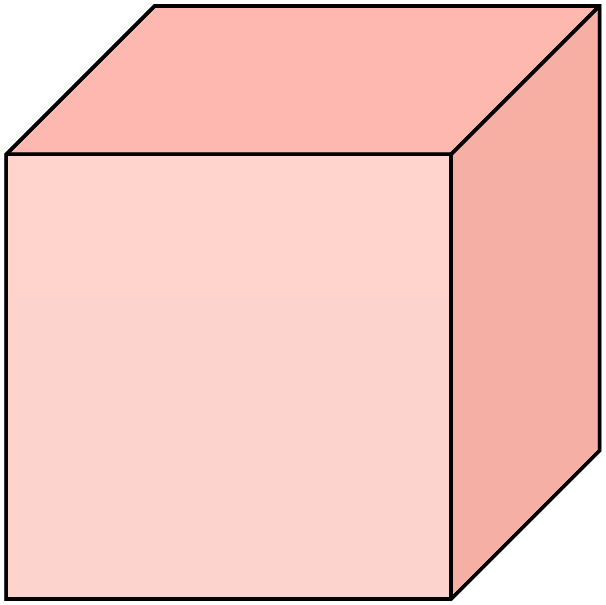
even longer time

Integrators - other point(s)

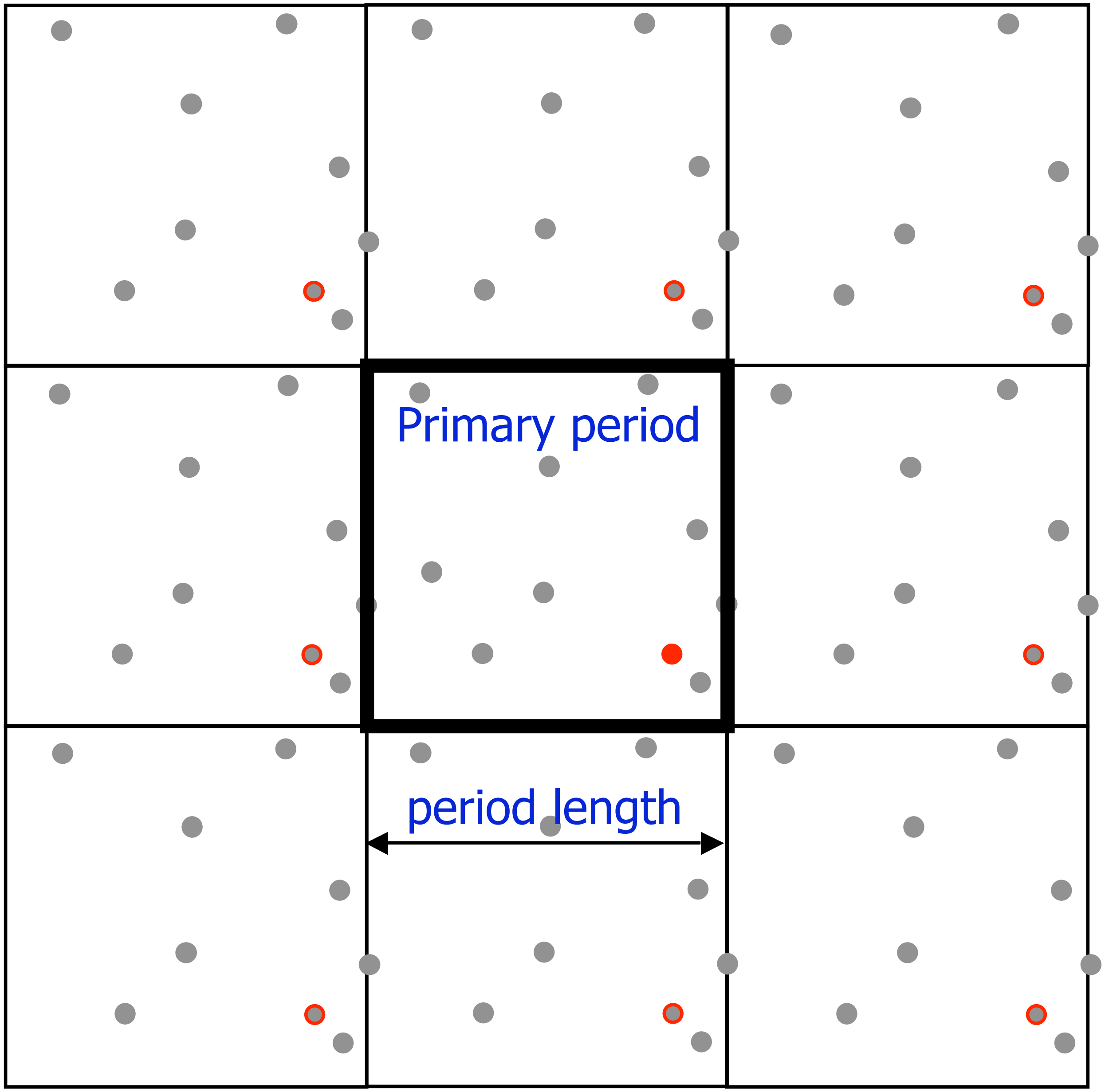
Computational cost is almost always dominated by the cost of the force call (evaluating dV/dx), not by the integrator itself.

Periodic boundary conditions

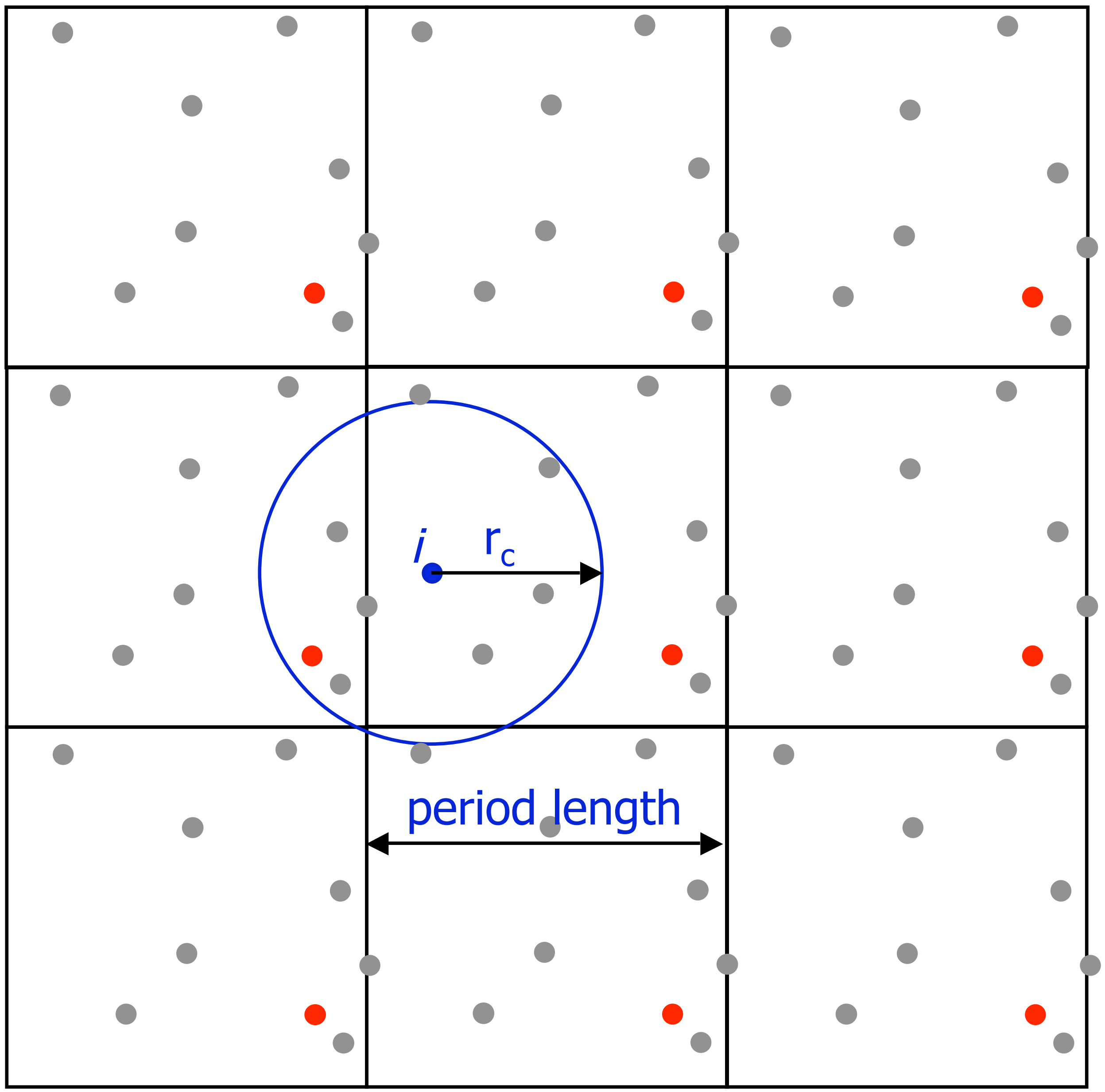
We often use periodic boundary conditions to mimic infinite bulk system -- liquid, solid, surface, …



Periodic boundary conditions


Primary period
period length

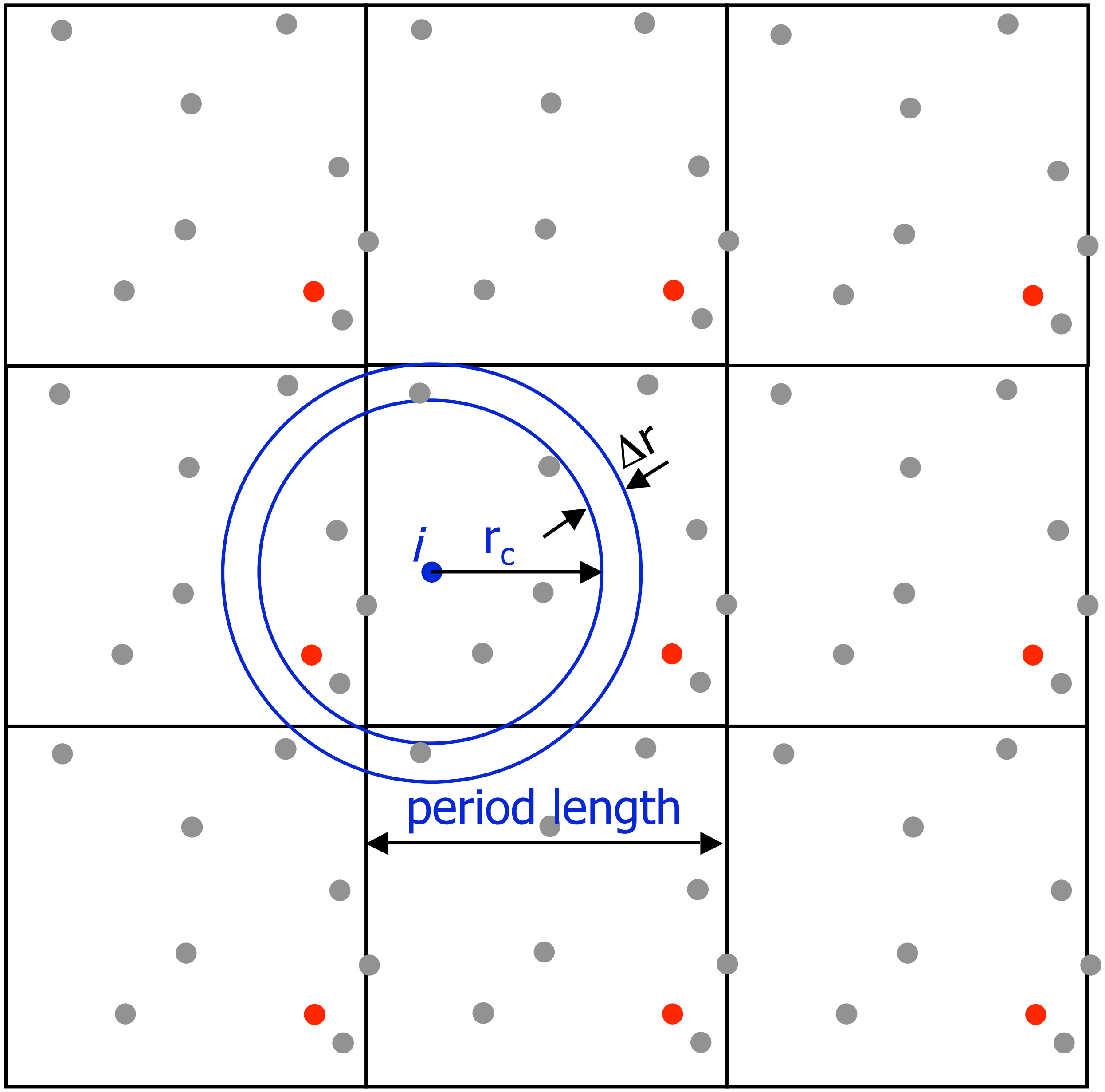
Minimum-image condition



If r_c < period length/2, then only one image of each neighbor will be within cutoff distance of atom i.

This simplifies construction of the neighbor lists, and reduces artificial behavior.

Verlet list

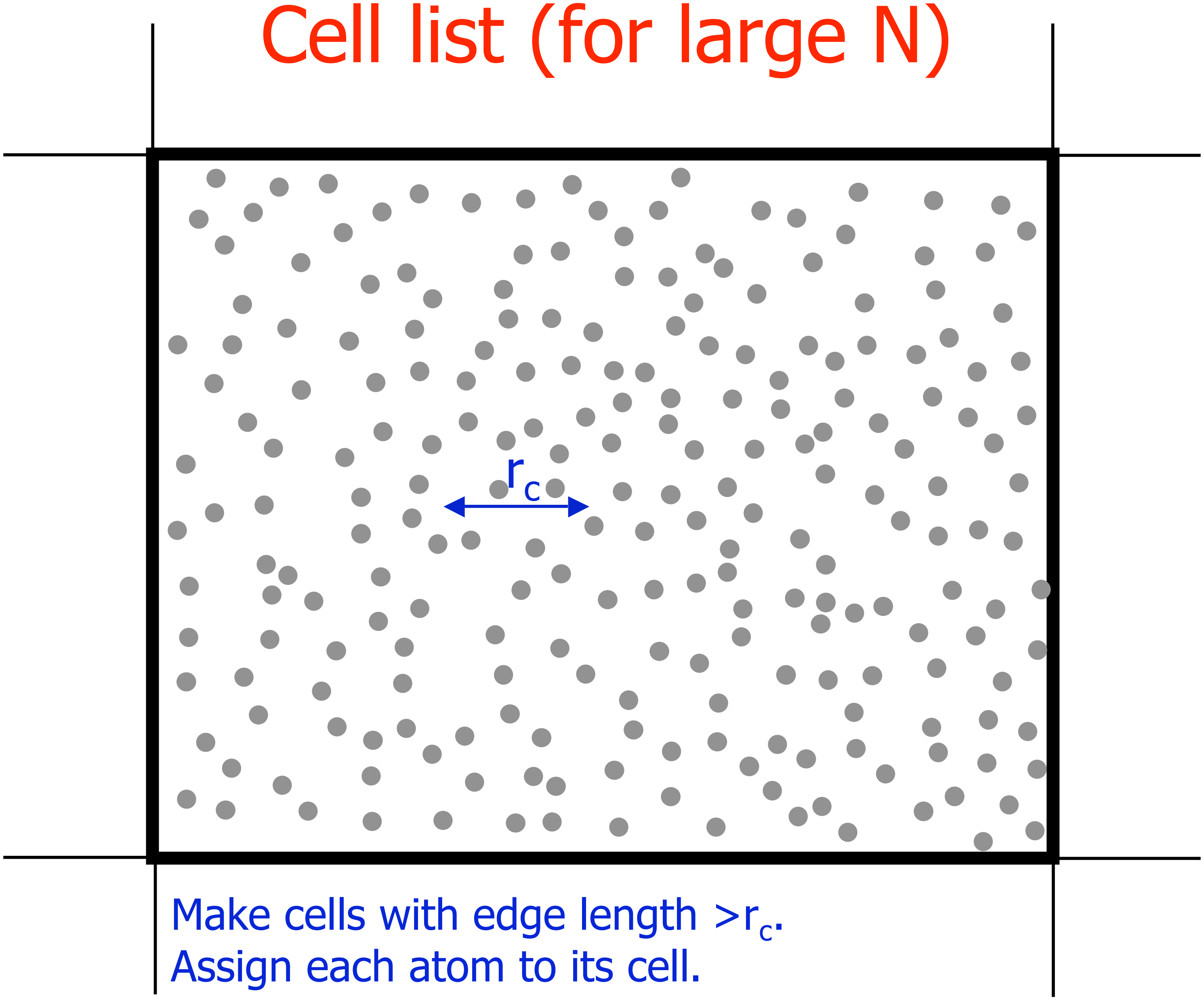


Make list of neighbors within a larger cutoff range.

Compute neighbor distances from this list.

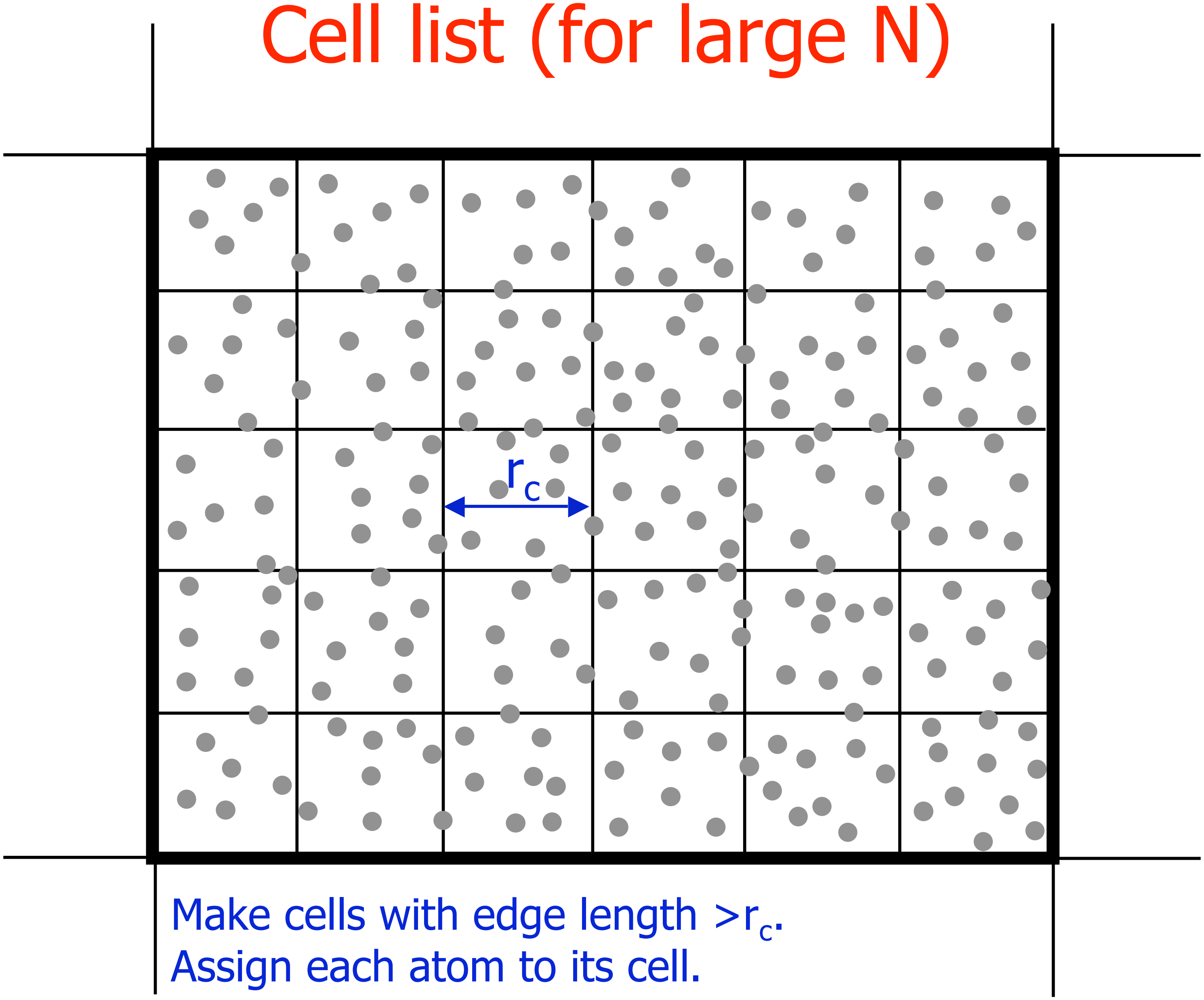
Only update the list after some atom has moved more than Δr
- typically many MD steps.

Cell list (for large N)



Make cells with edge length $>r_c$.
Assign each atom to its cell.
Only search adjacent cells when making neighbor list.
Overall work scales as N.

Cell list (for large N)



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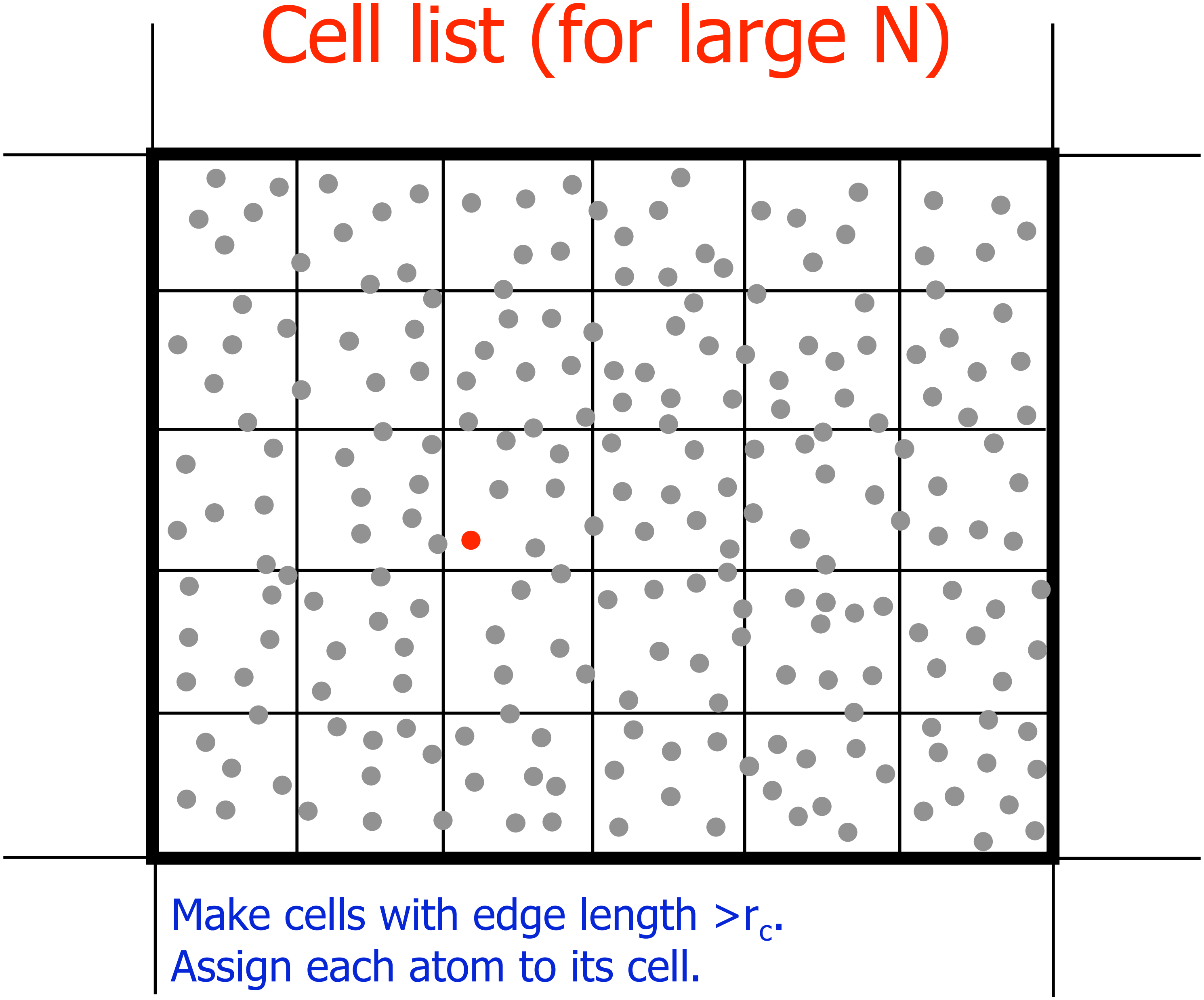
Cell list (for large N)



Make cells with edge length $>r_c$.
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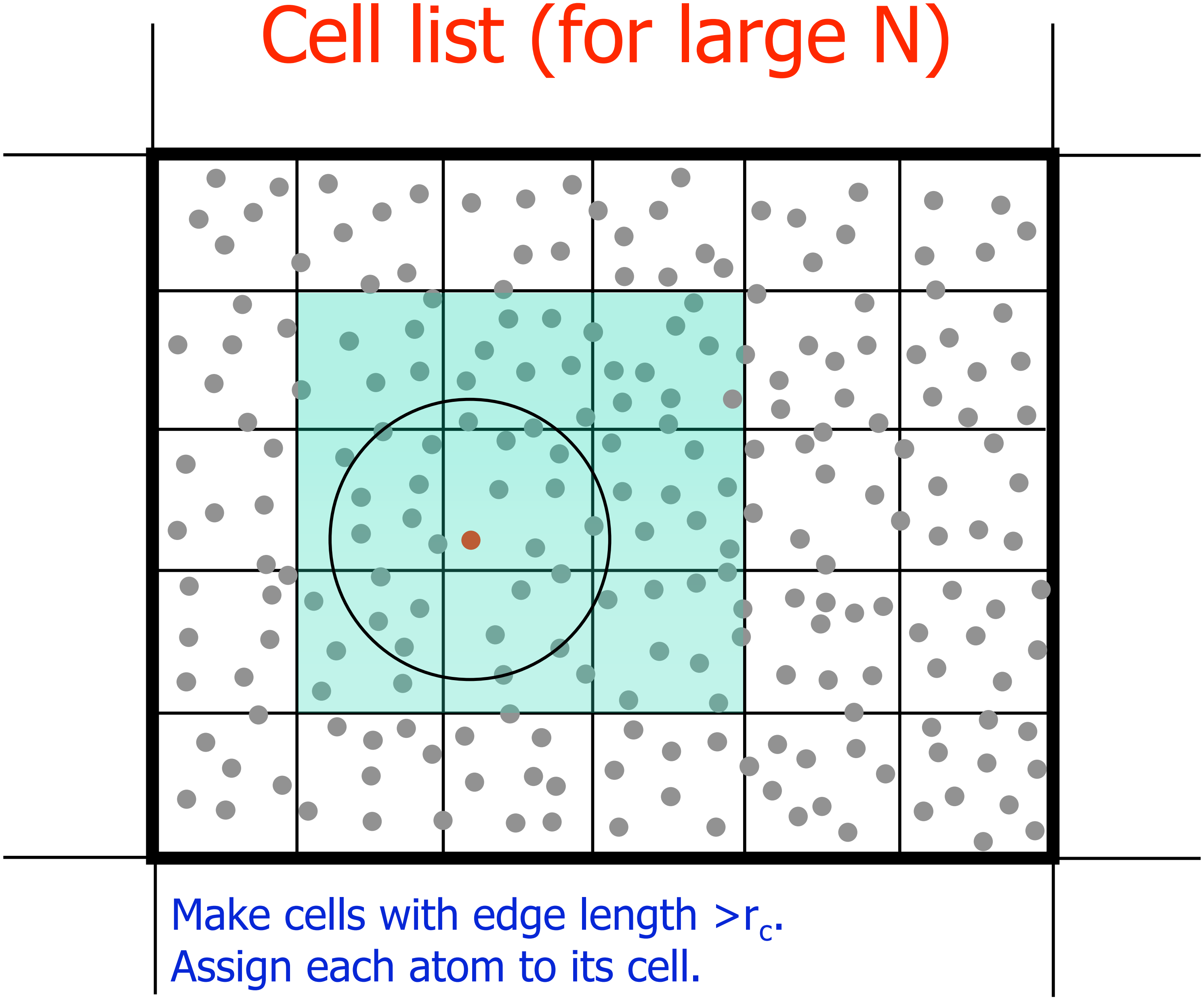
Cell list (for large N)



Make cells with edge length $>r_c$.

Assign each atom to its cell.

Only search adjacent cells when making neighbor list.

Overall work scales as N.

Limitations of MD

- Accuracy of potential
- Length scale - not macroscopic
- Time scale - limited to ns
- Quantum dynamical effects
- Non adiabatic dynamics

Accuracy of potentials

Good systems:

Noble gases (Ne, Ar, …)
Certain fcc metals (Cu, Ag, Ni)

OK systems:

- many metal systems (Pt, Fe, V …)
- ionic systems (NaCl, MgO,…)
- proteins, polymers (but not perfect, and bonds can't break)
- silicon (record number of fits)

Problem systems:

- mixed ionic-covalent systems (e.g., Pt/MgO)
- mixed metallic-covalent systems (e.g., C in Fe)

MD - achievable length scales

10^3 - 10^4 atoms easy on single processor

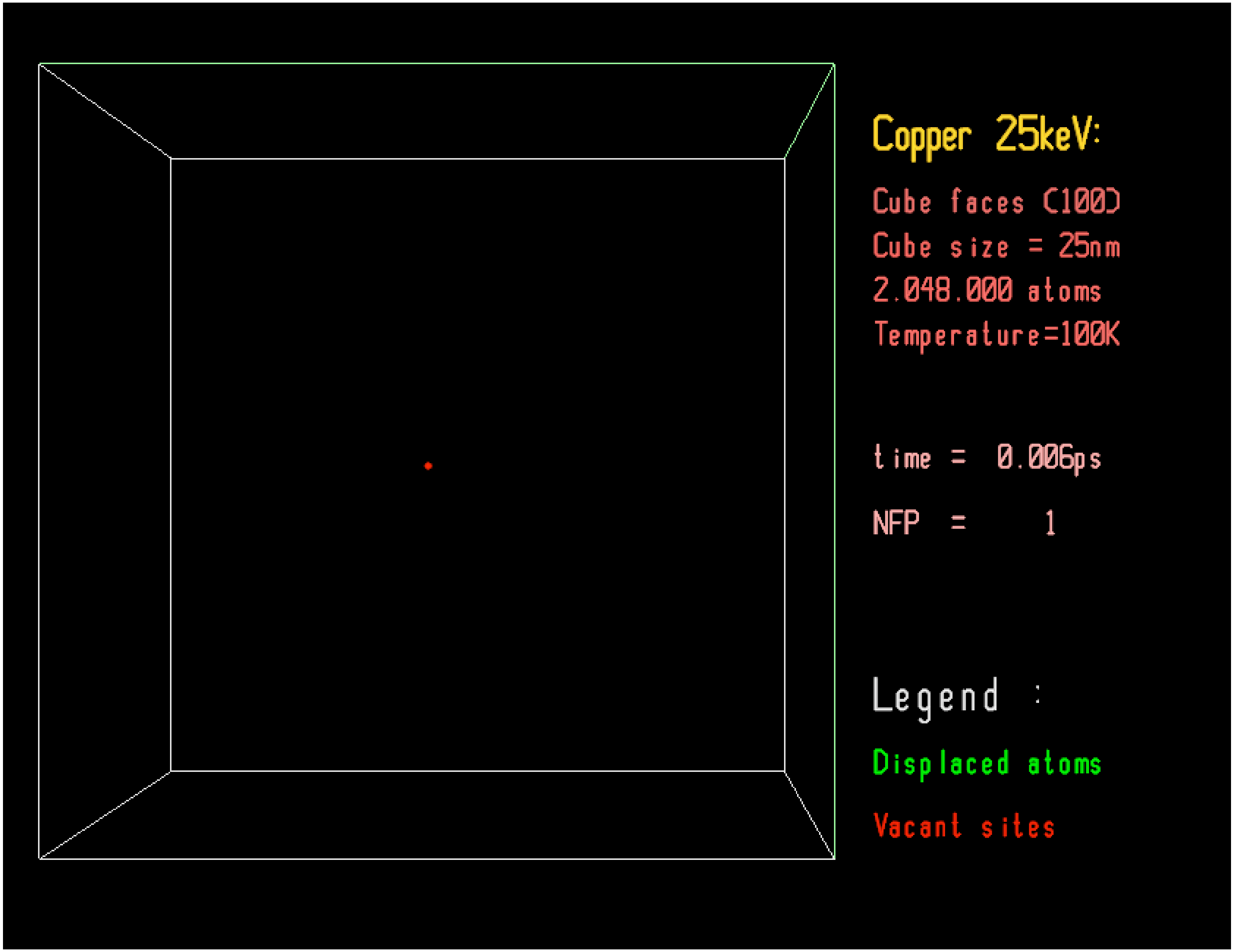
Much larger systems possible via parallelization

Each processor responsible for atoms in a physical cell
Communication required between adjacent cells
>~10^3-10^4 atoms per processor to maintain good efficiency

Million atoms -- now fairly routine

Billion atoms -- possible

Cu Cascade simulation



Copper 25keV:

Cube faces (100)

Cube size = 25nm

2.048.000 atoms

Temperature=100K

time = 0.006ps

NFP = 1

Legend :

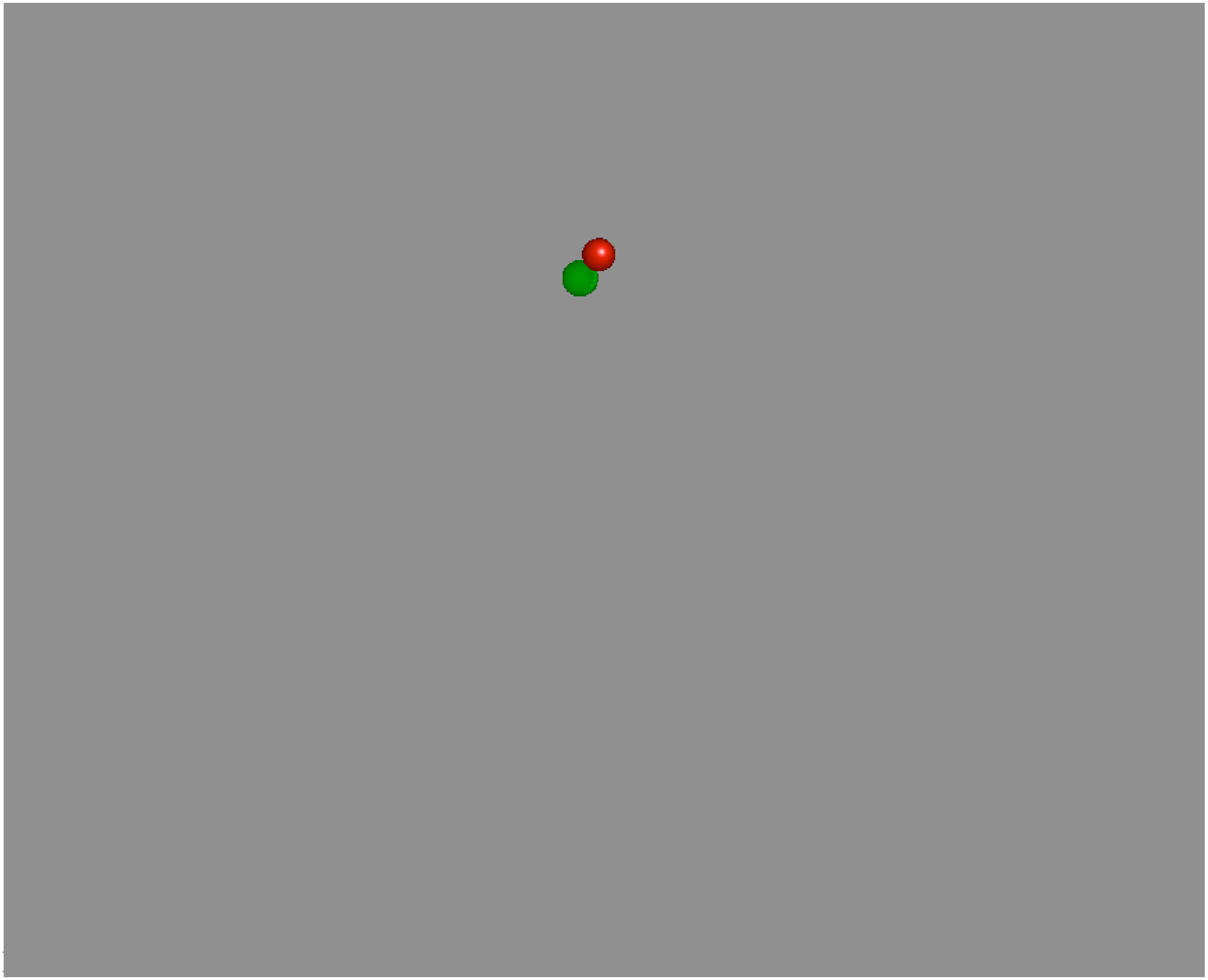
Displaced atoms

Vacant sites

D.J. Bacon
et al
(Liverpool)

Los Alamos

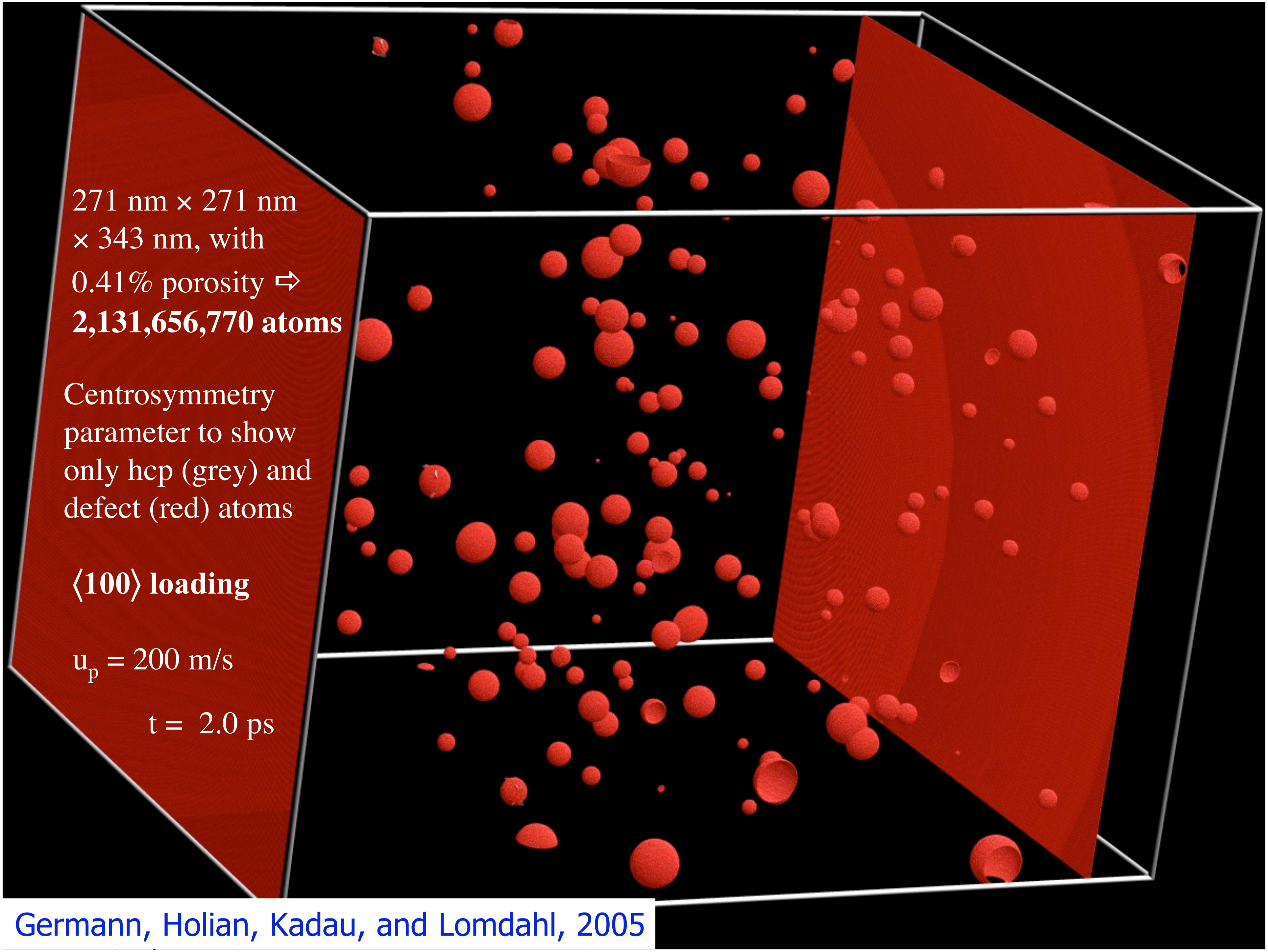
Cu Cascade simulation



25 keV, copper

green=interstitial
red=vacancy

D.J. Bacon et al



271 nm × 271 nm
× 343 nm, with
0.41% porosity ⇨
2,131,656,770 atoms

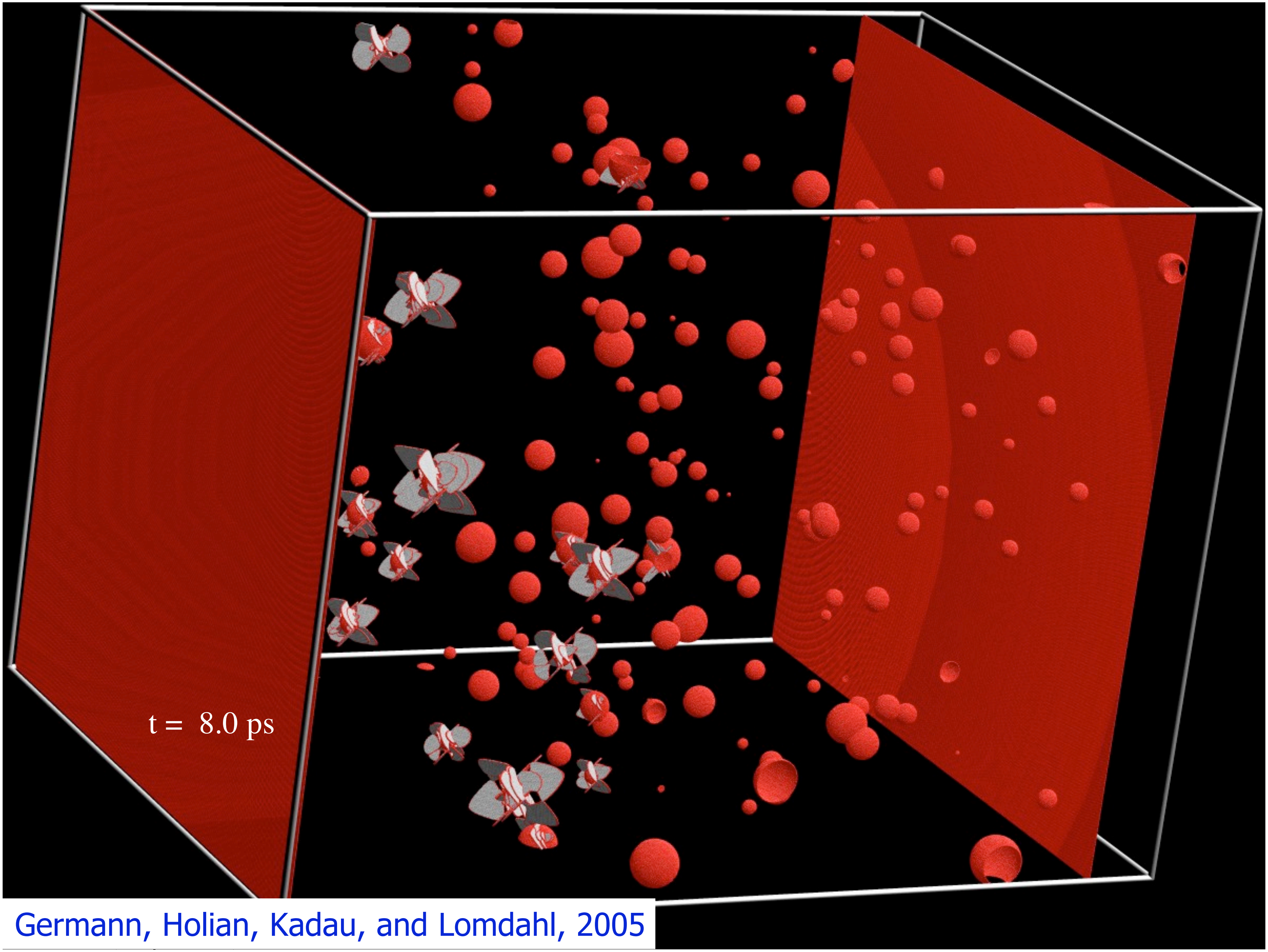
Centrosymmetry
parameter to show
only hcp (grey) and
defect (red) atoms

⟨100⟩ loading

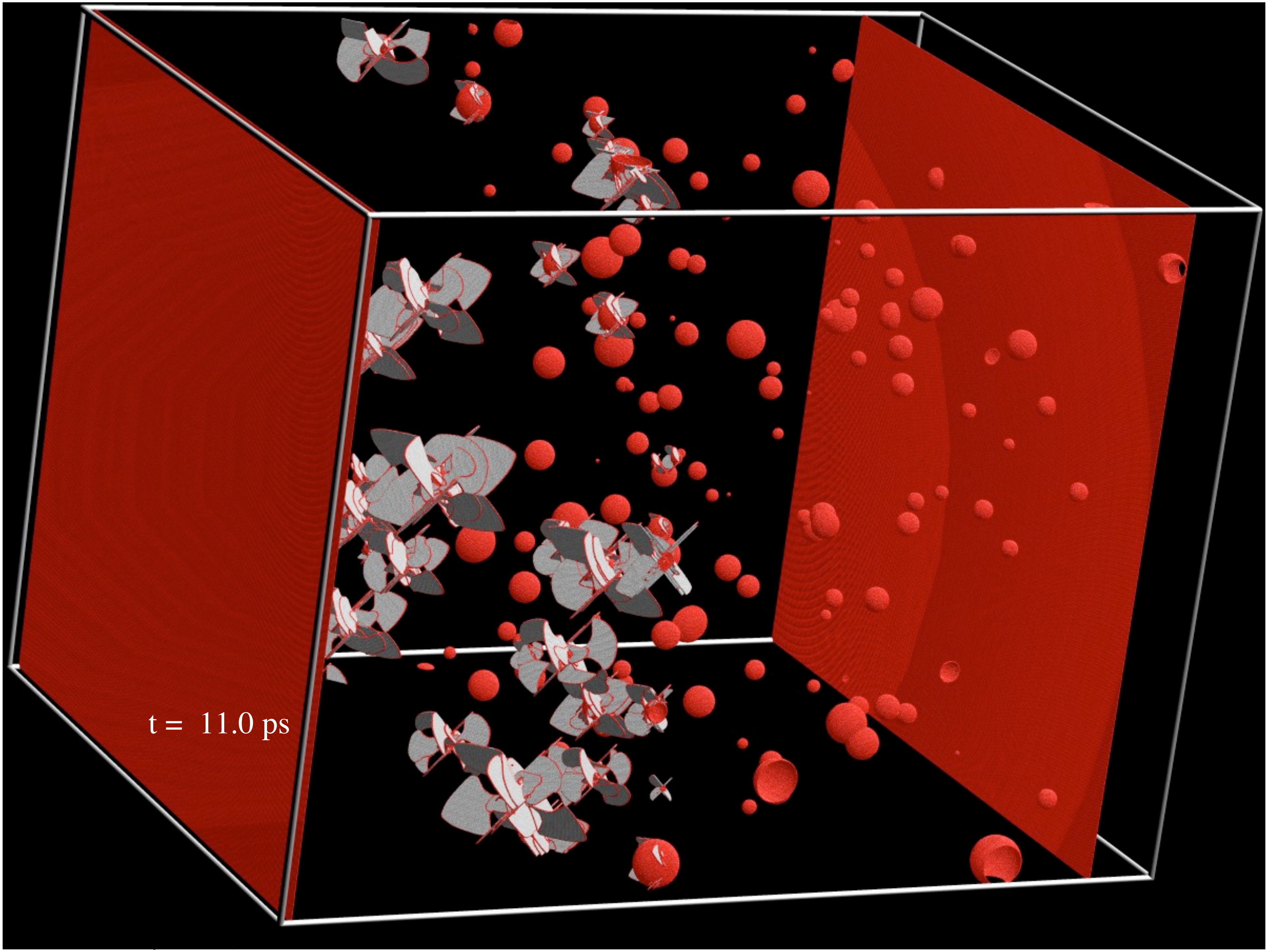
$u_p = 200$ m/s

$t = 2.0$ ps

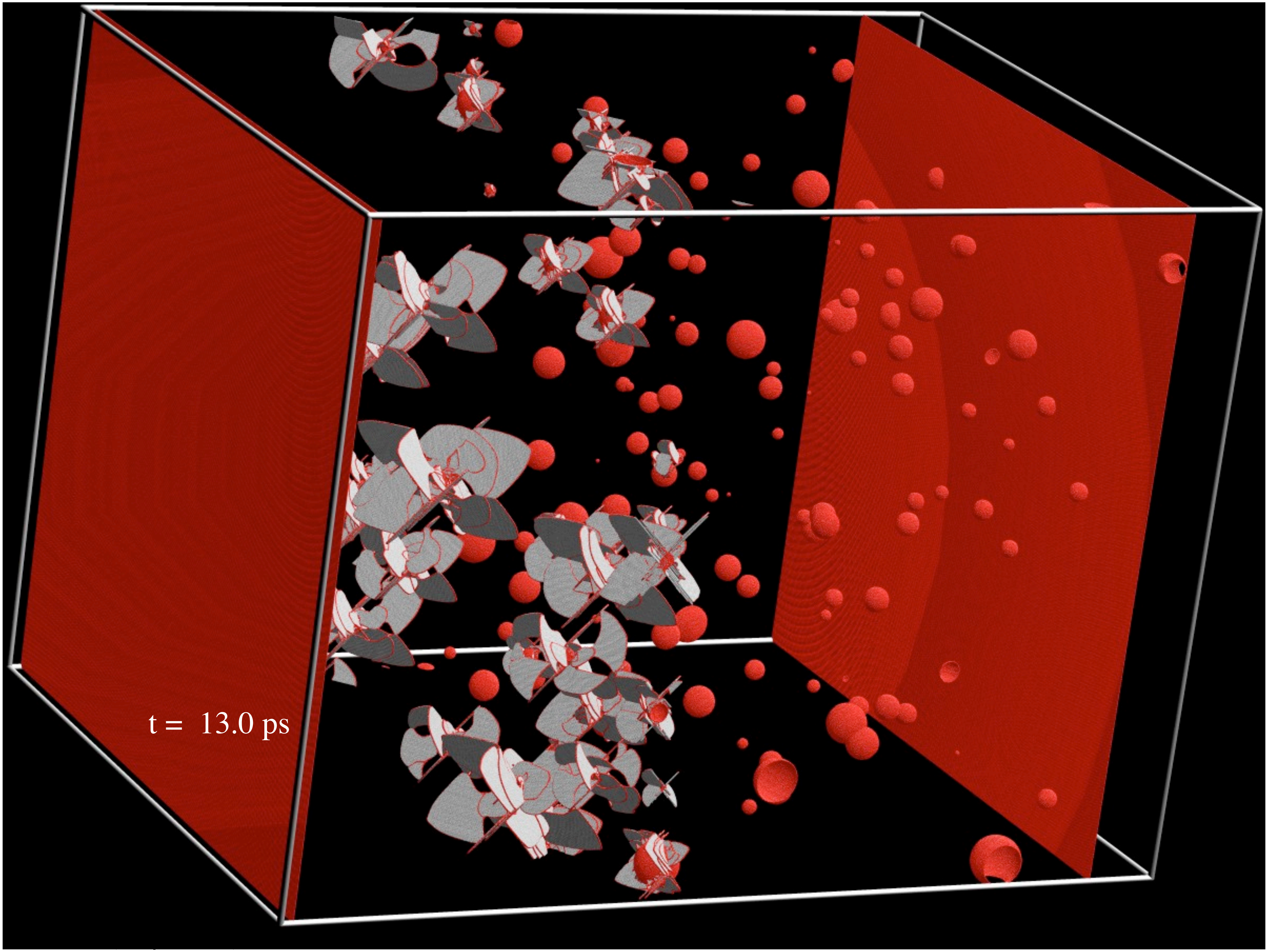
Germann, Holian, Kadau, and Lomdahl, 2005

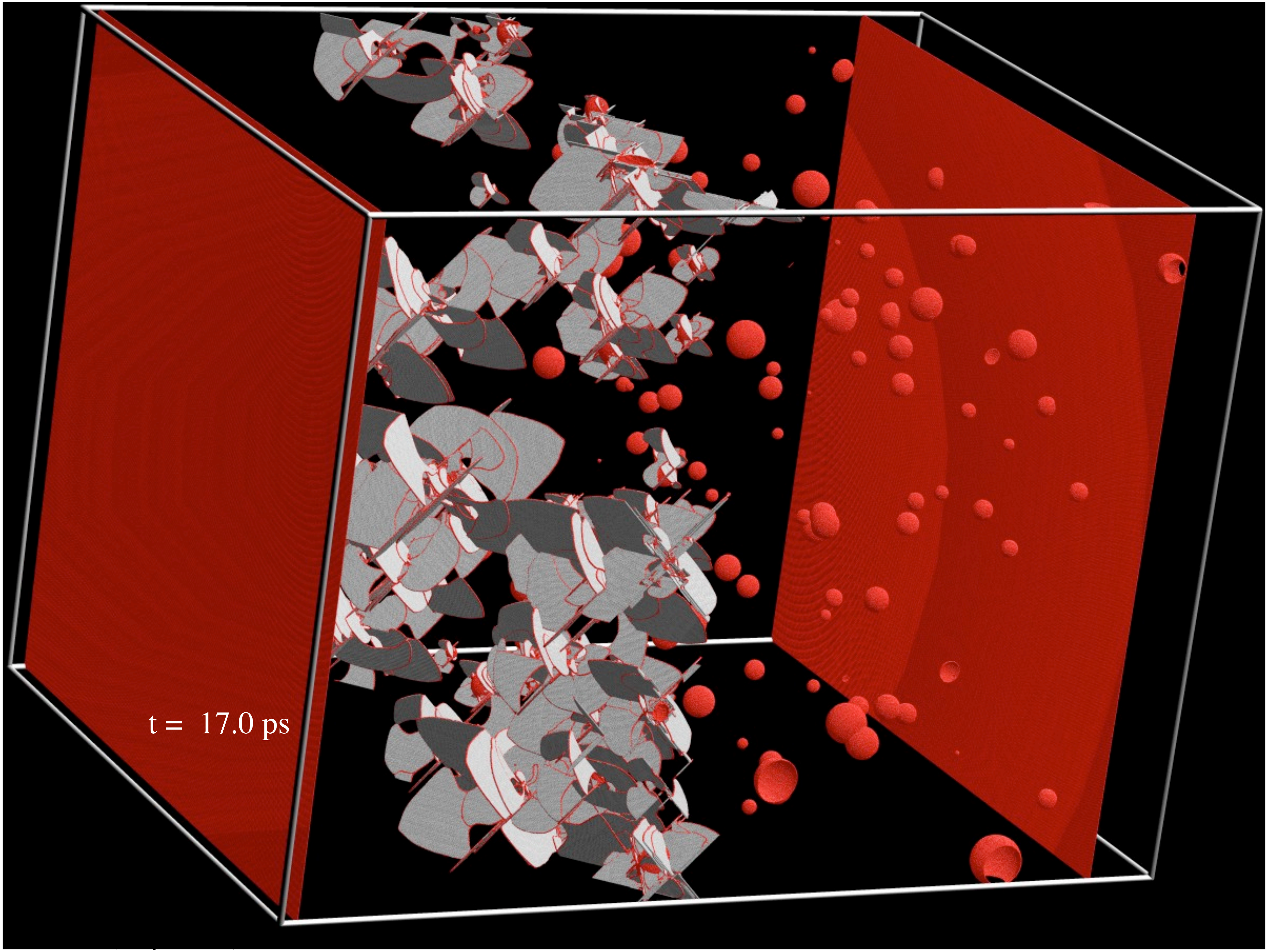


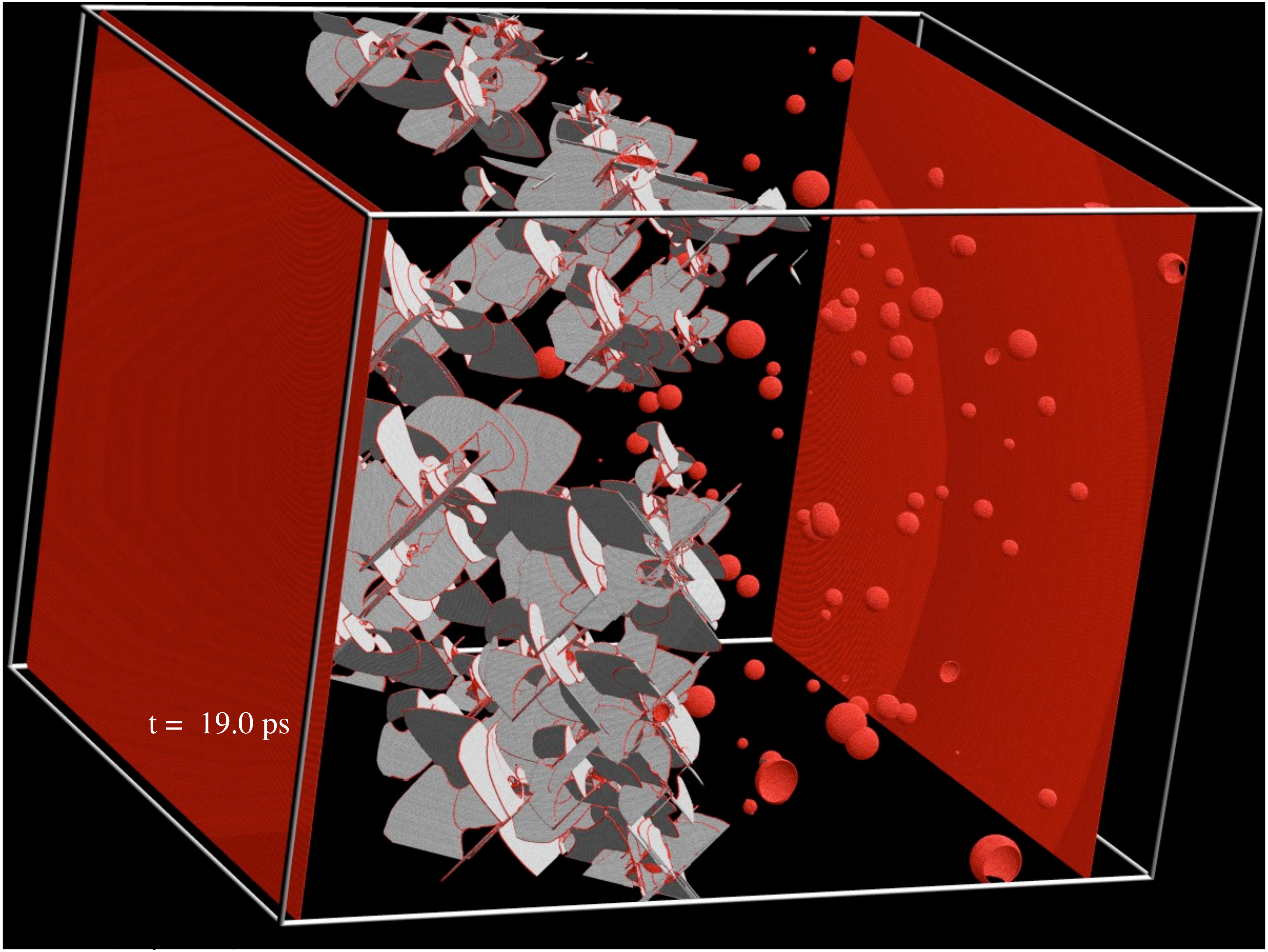
Germann, Holian, Kadau, and Lomdahl, 2005

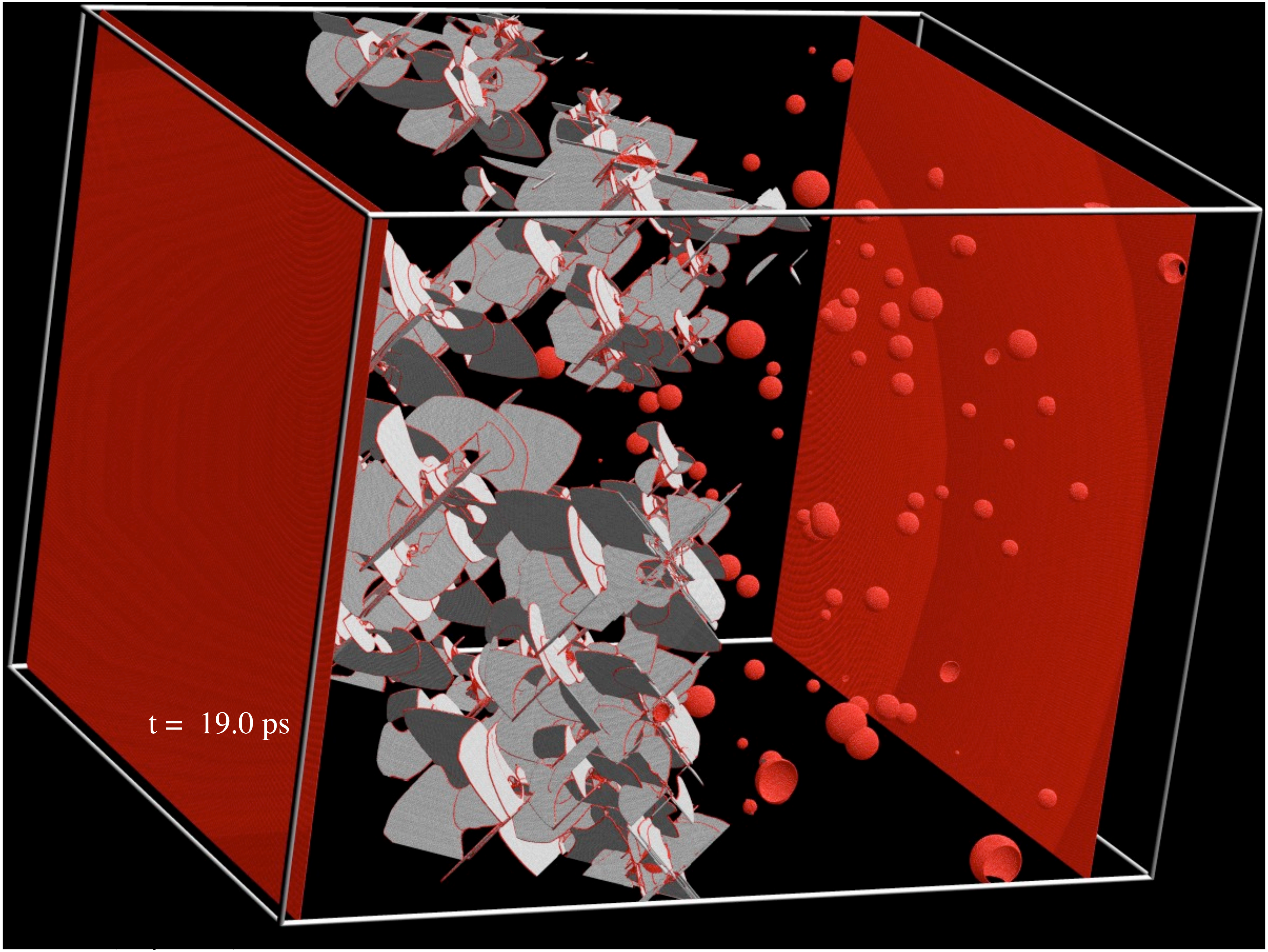


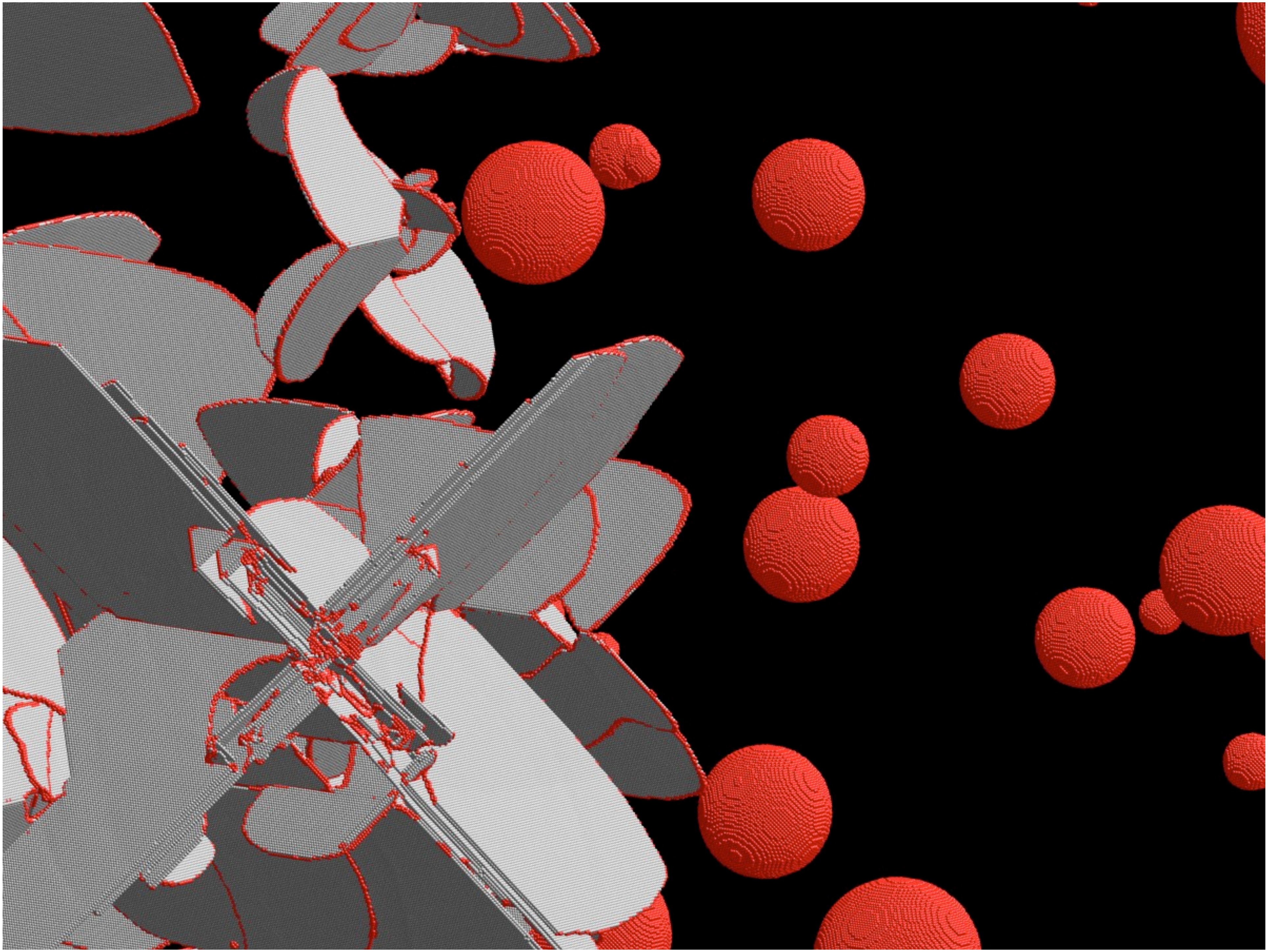
t = 11.0 ps

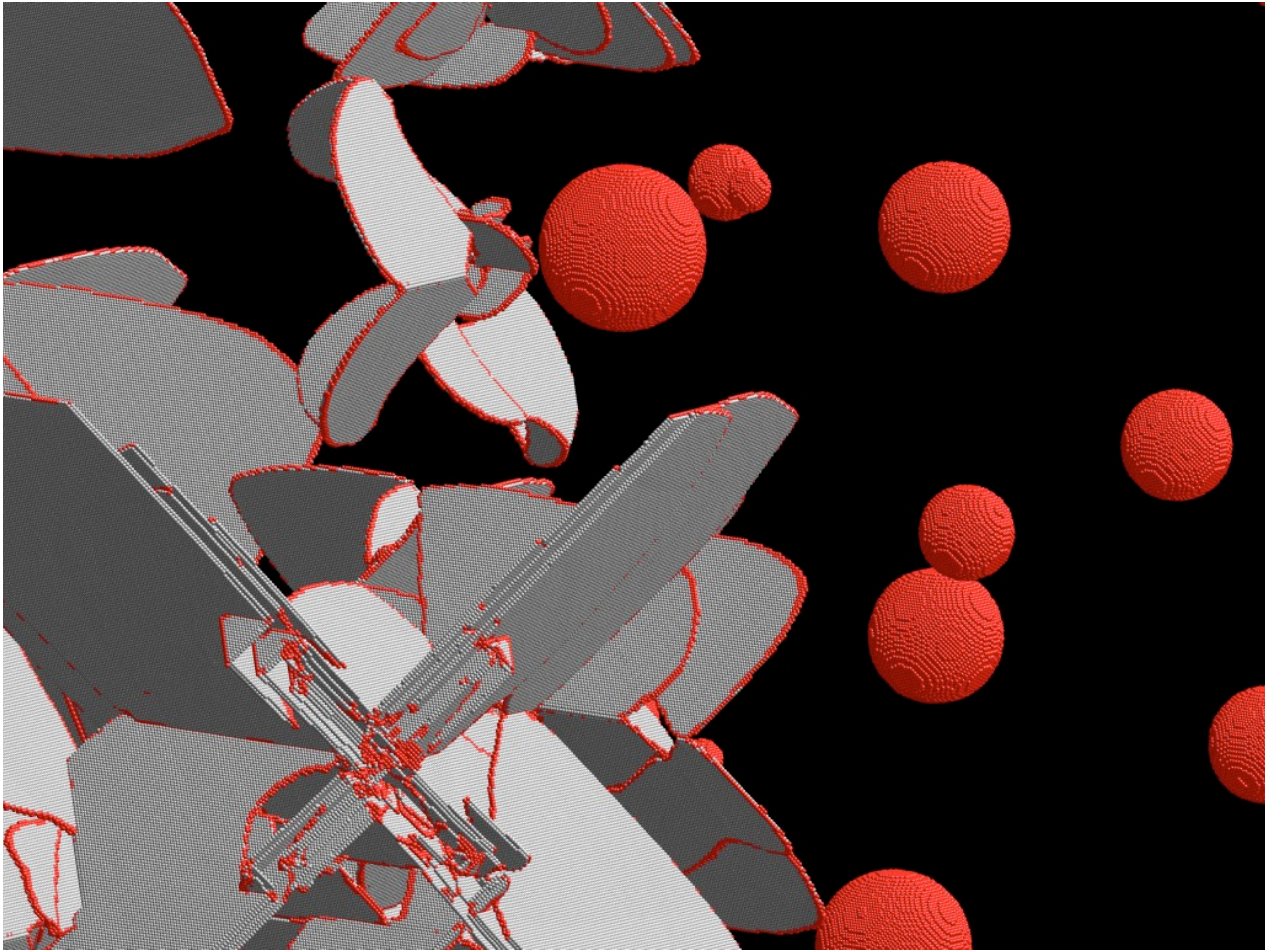

t = 13.0 ps

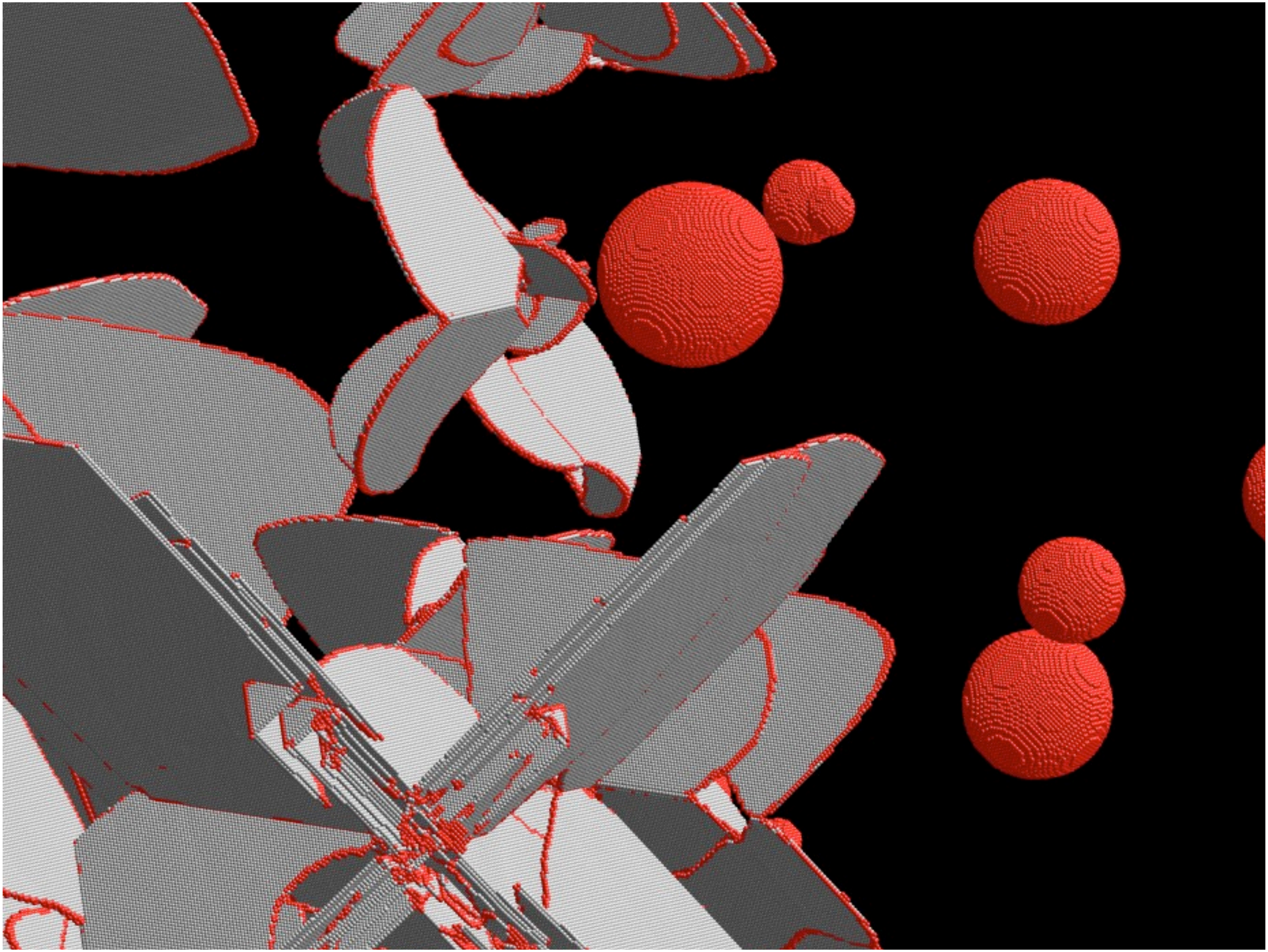

t = 17.0 ps

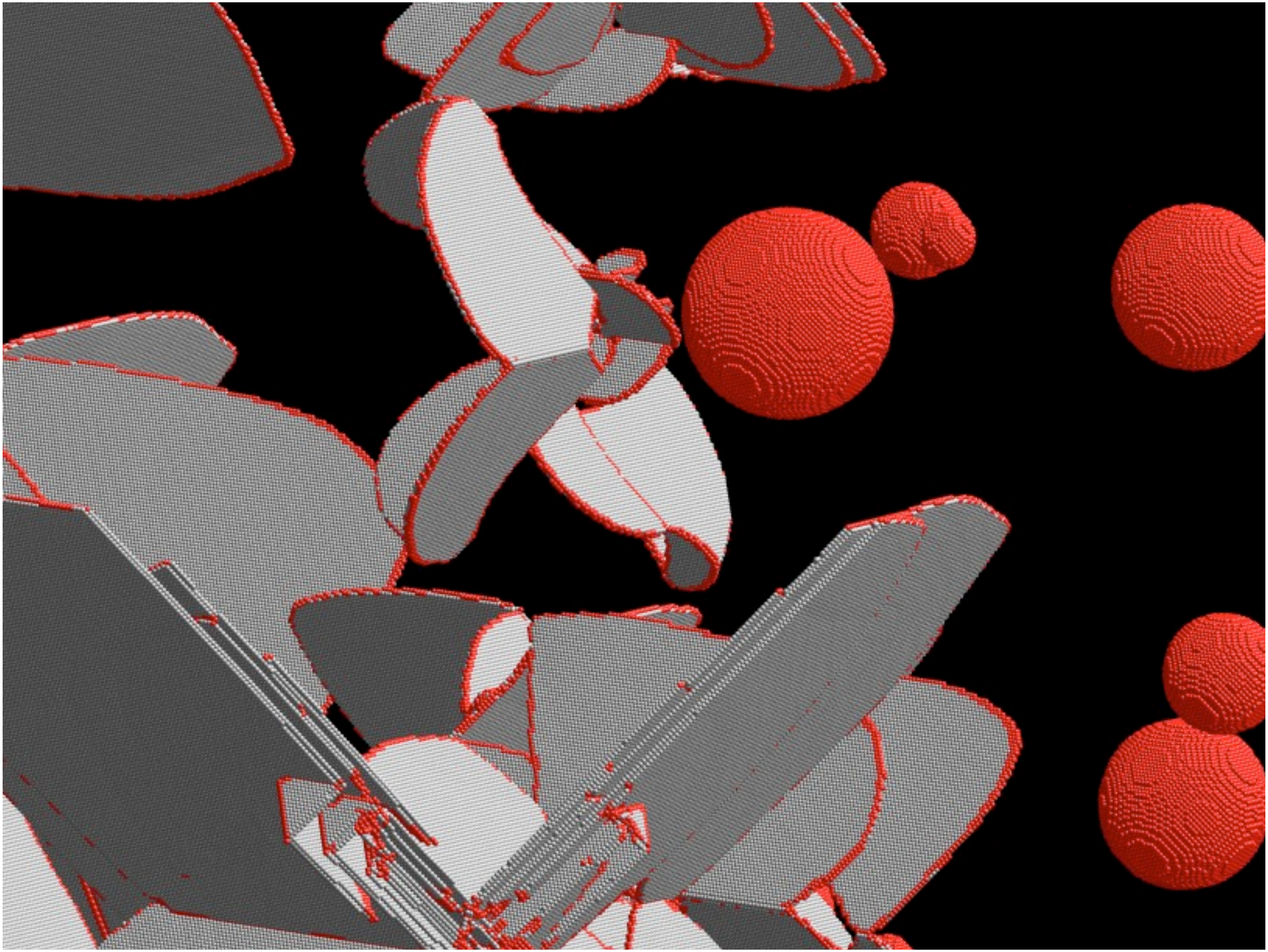

t = 19.0 ps

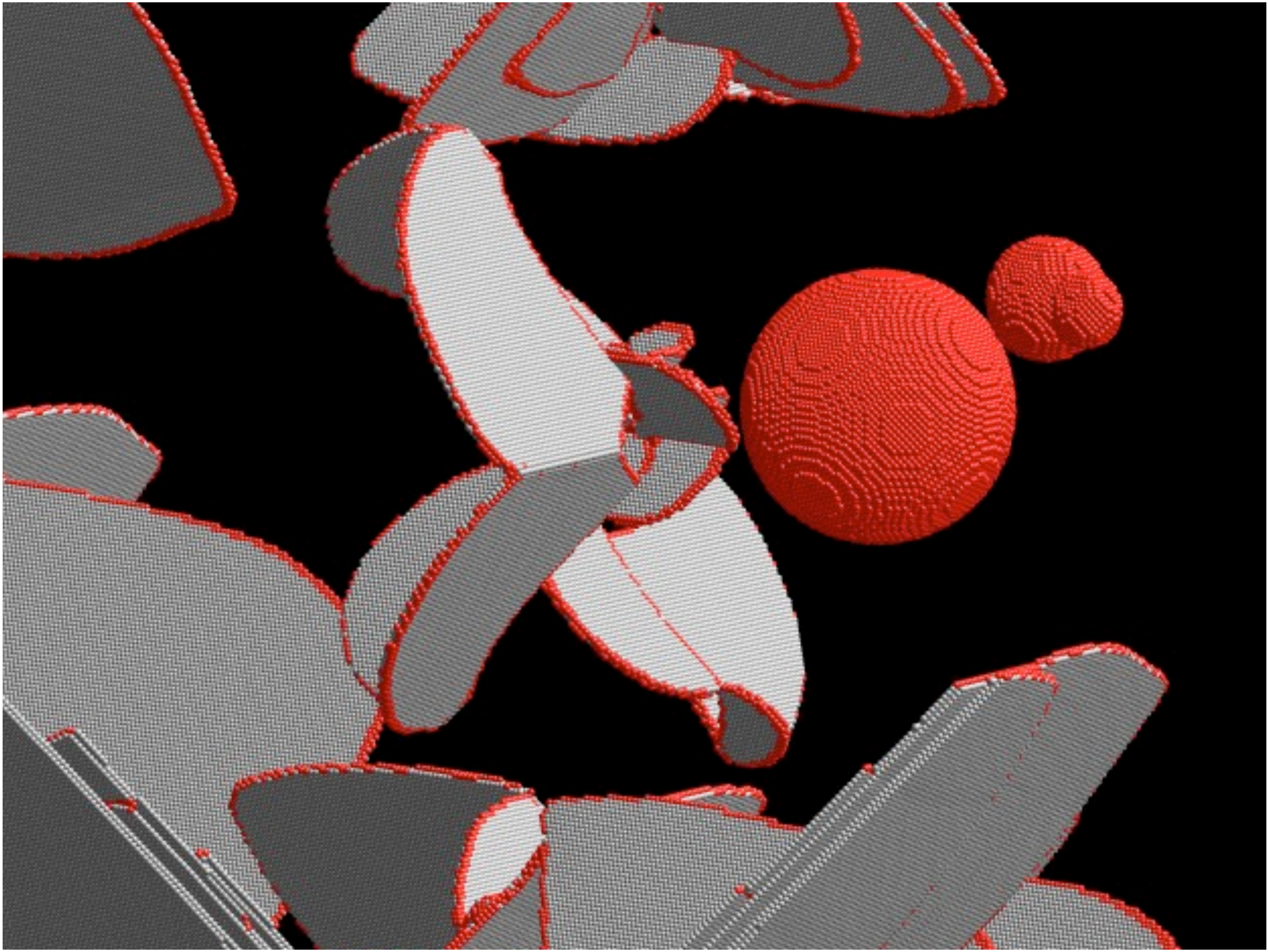

t = 19.0 ps

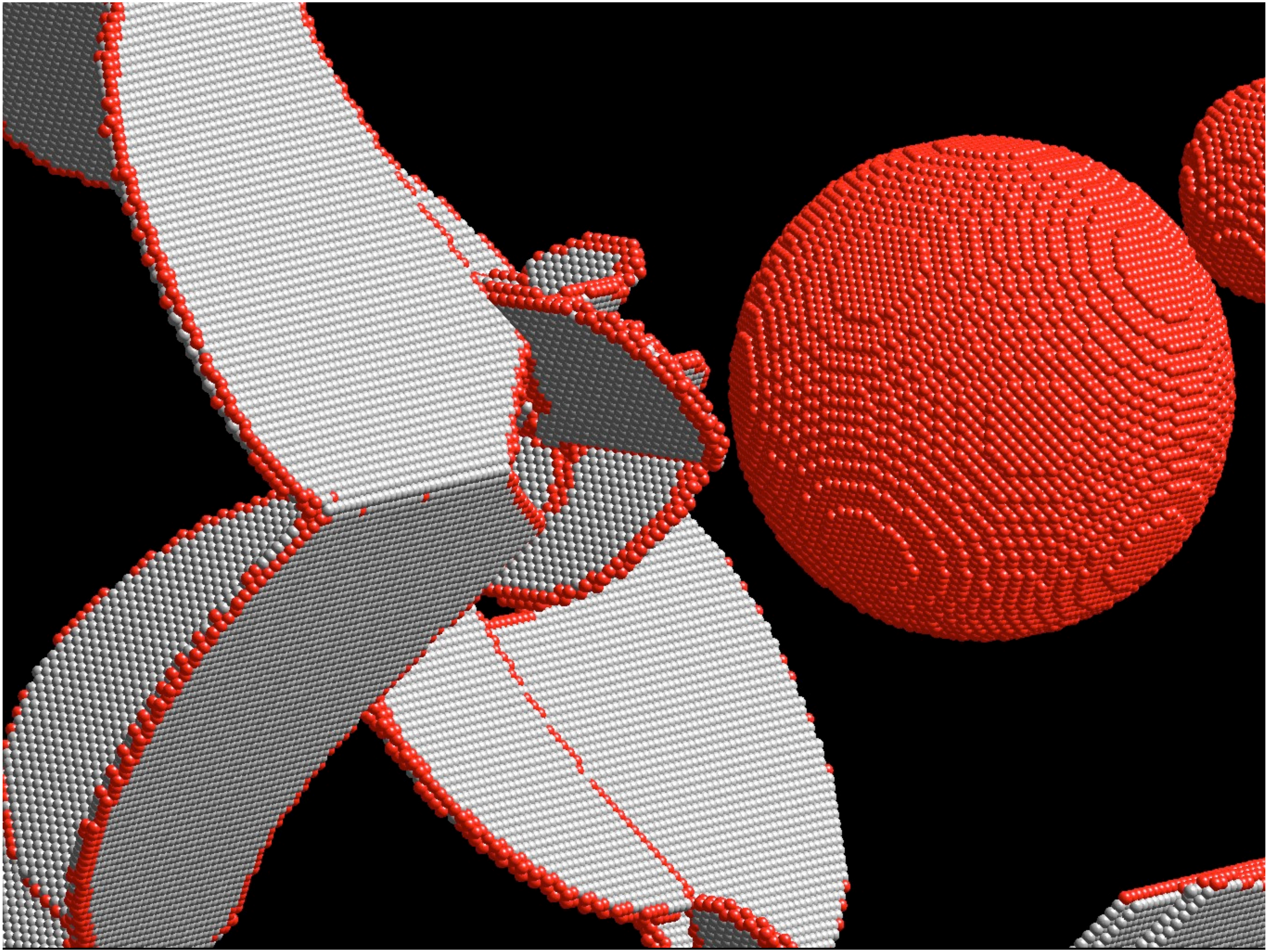


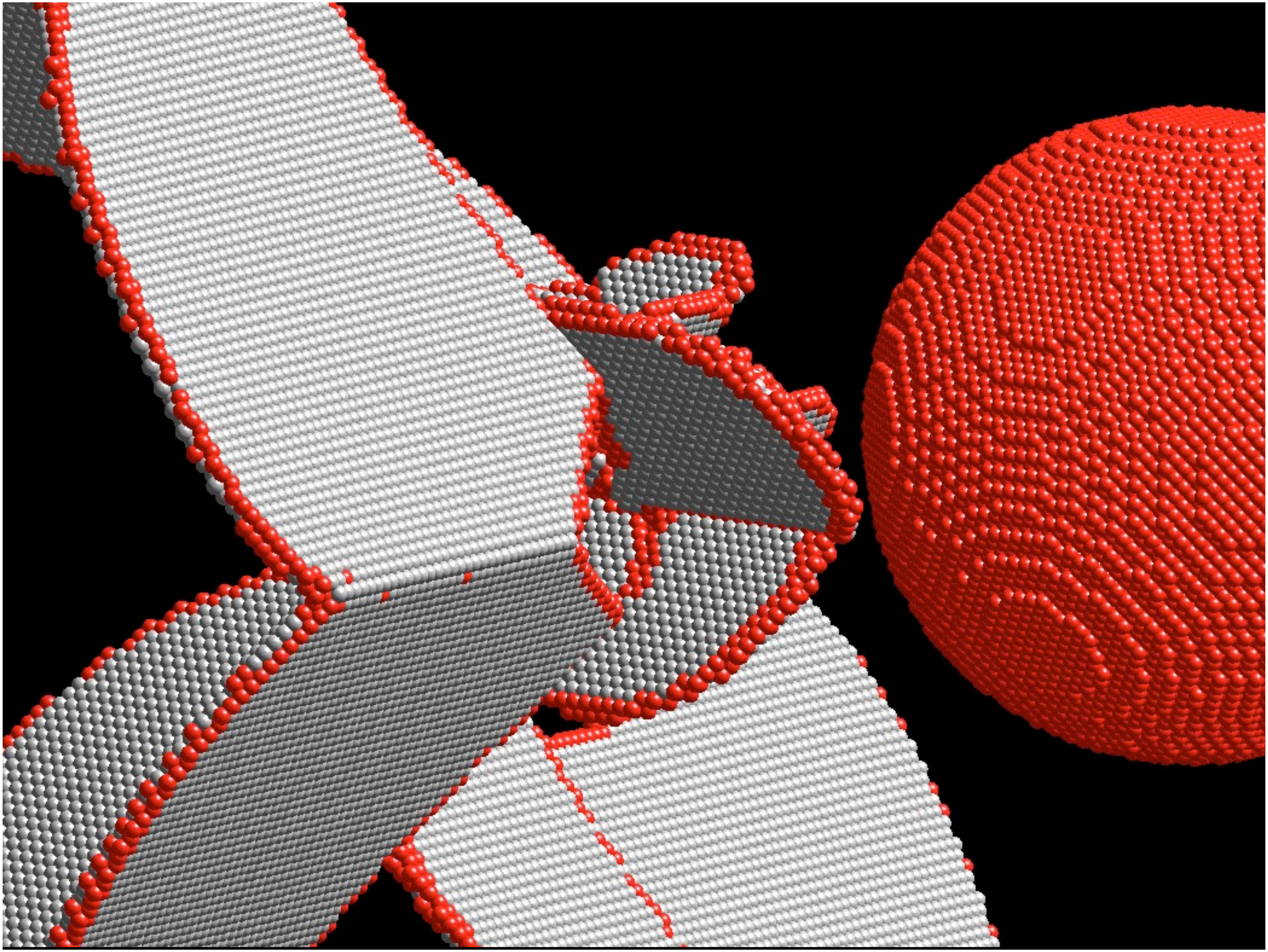




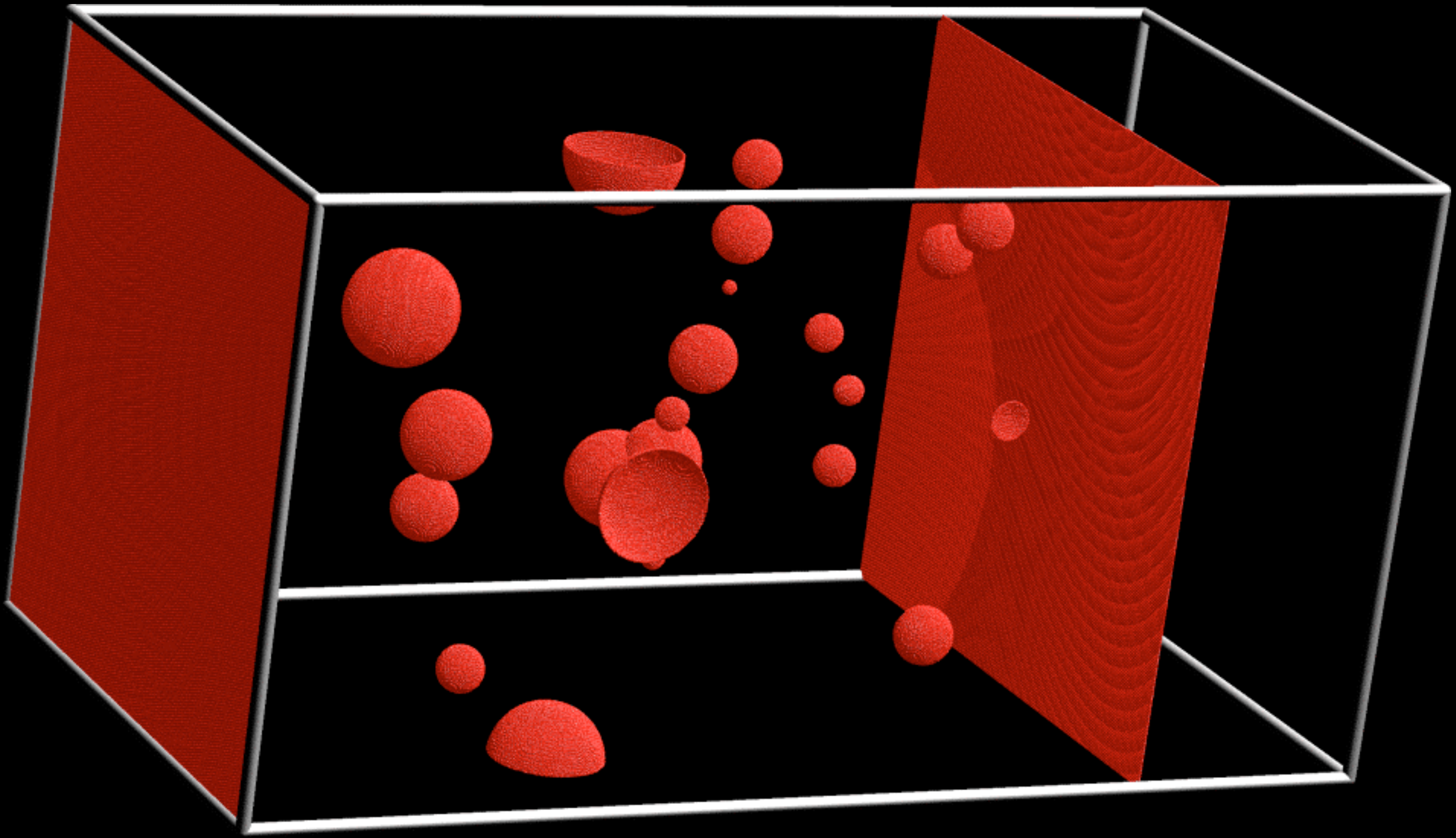






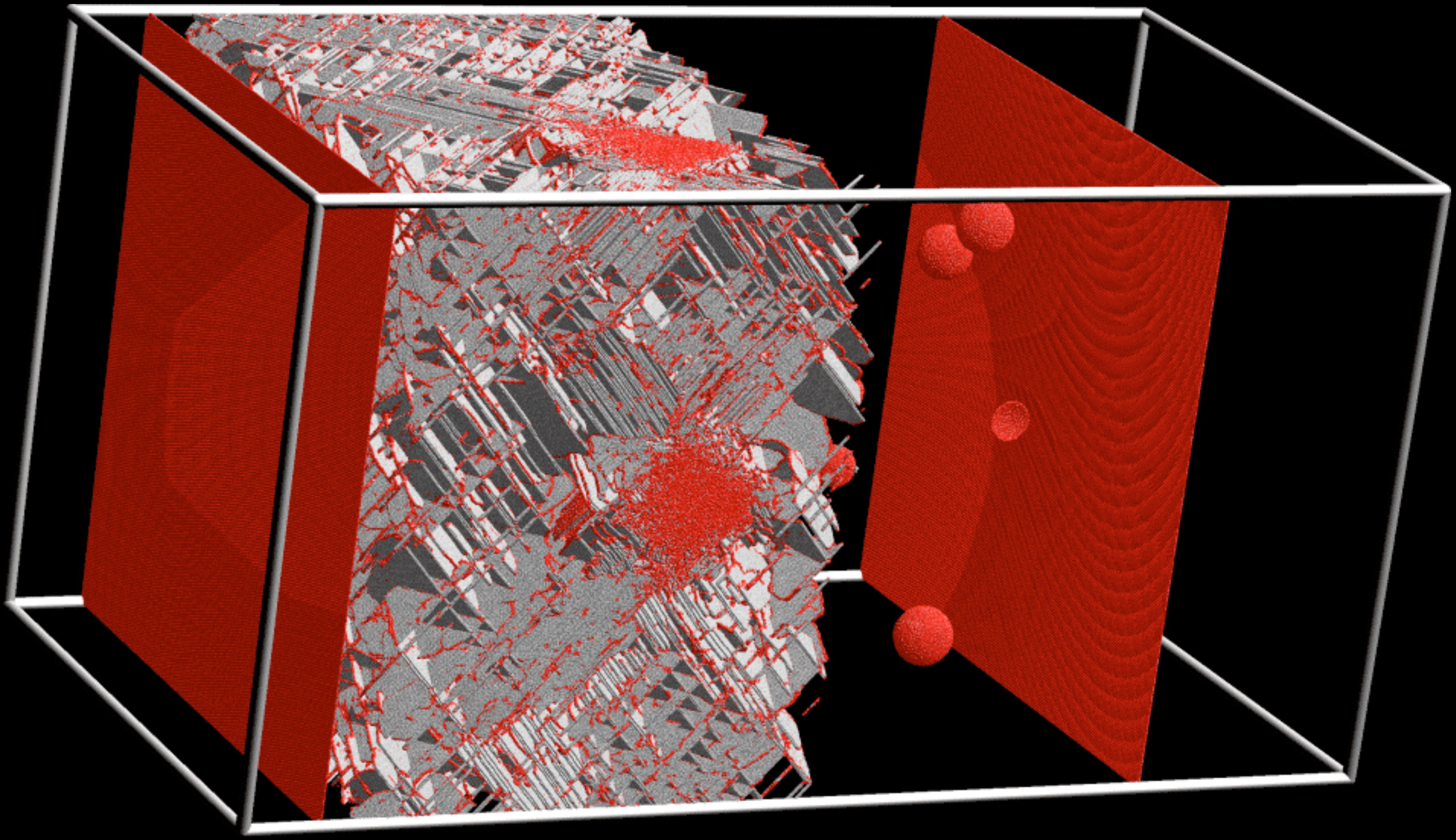


⟨100⟩ loading, u_p = 1 km/s, t = 0 ps

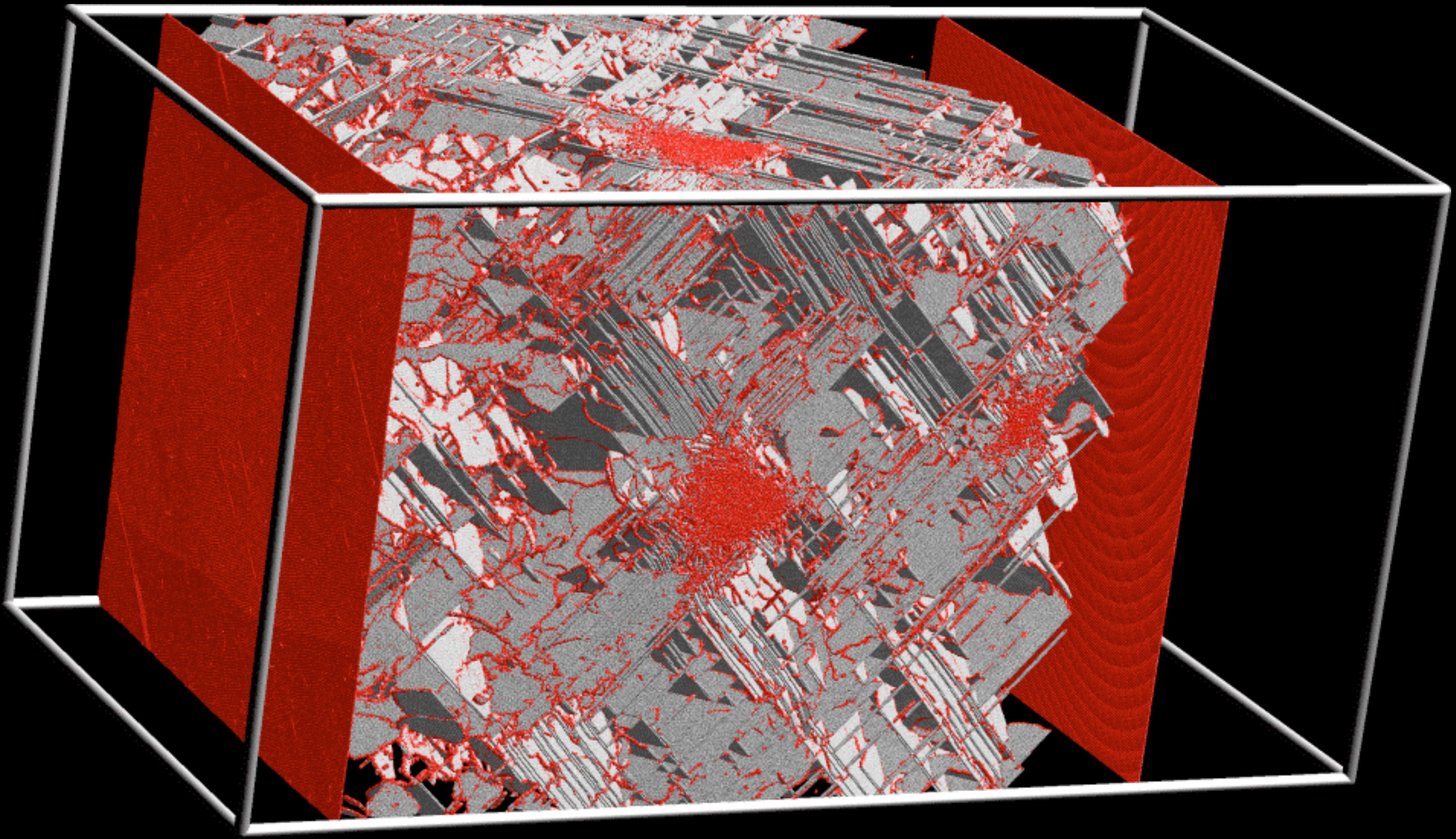


116 nm × 116 nm × 181 nm (1.41% porosity) ⇨ 202,872,066 atoms

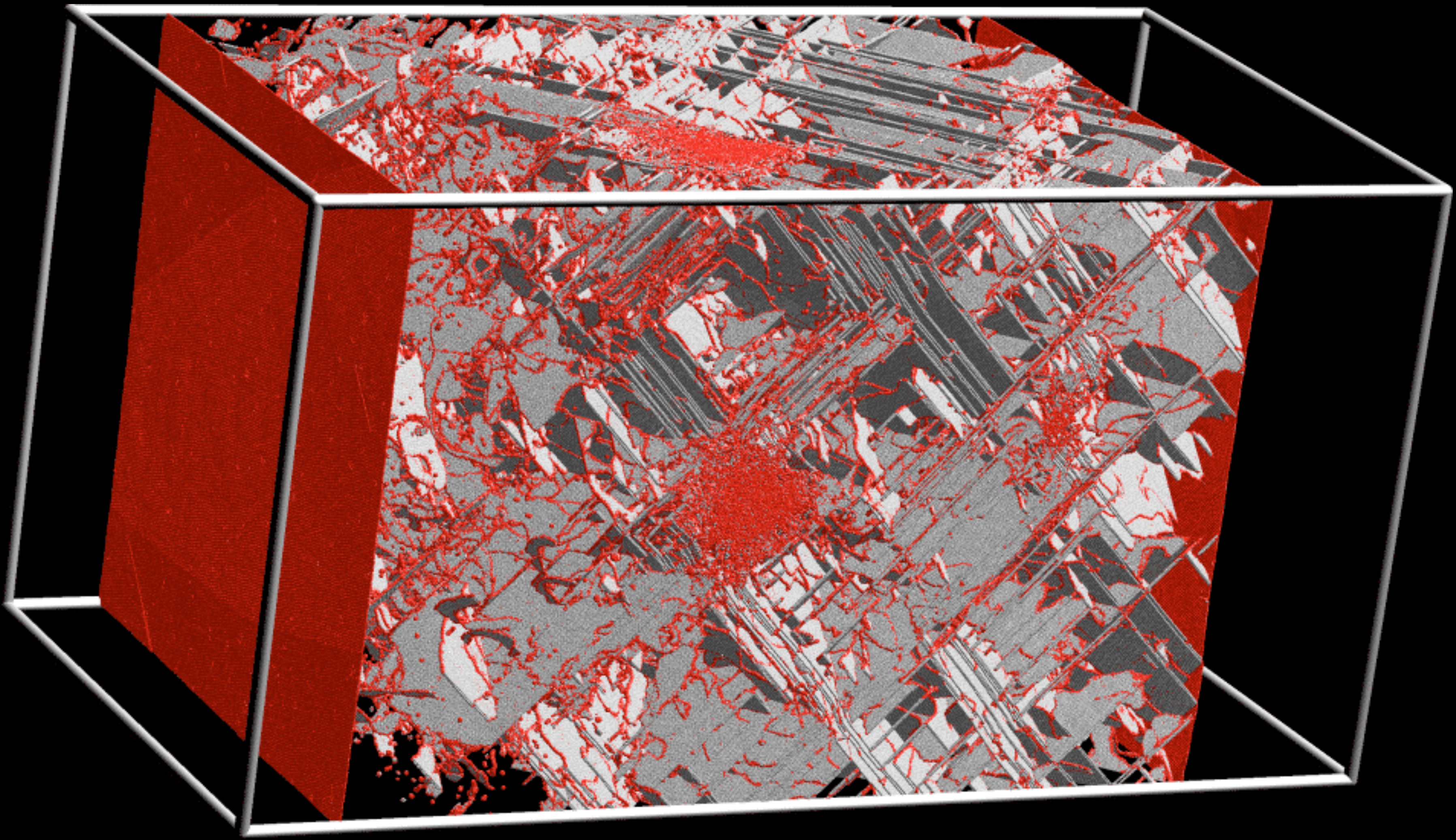
⟨100⟩ loading, $u_p = 1$ km/s, $t = 10$ ps



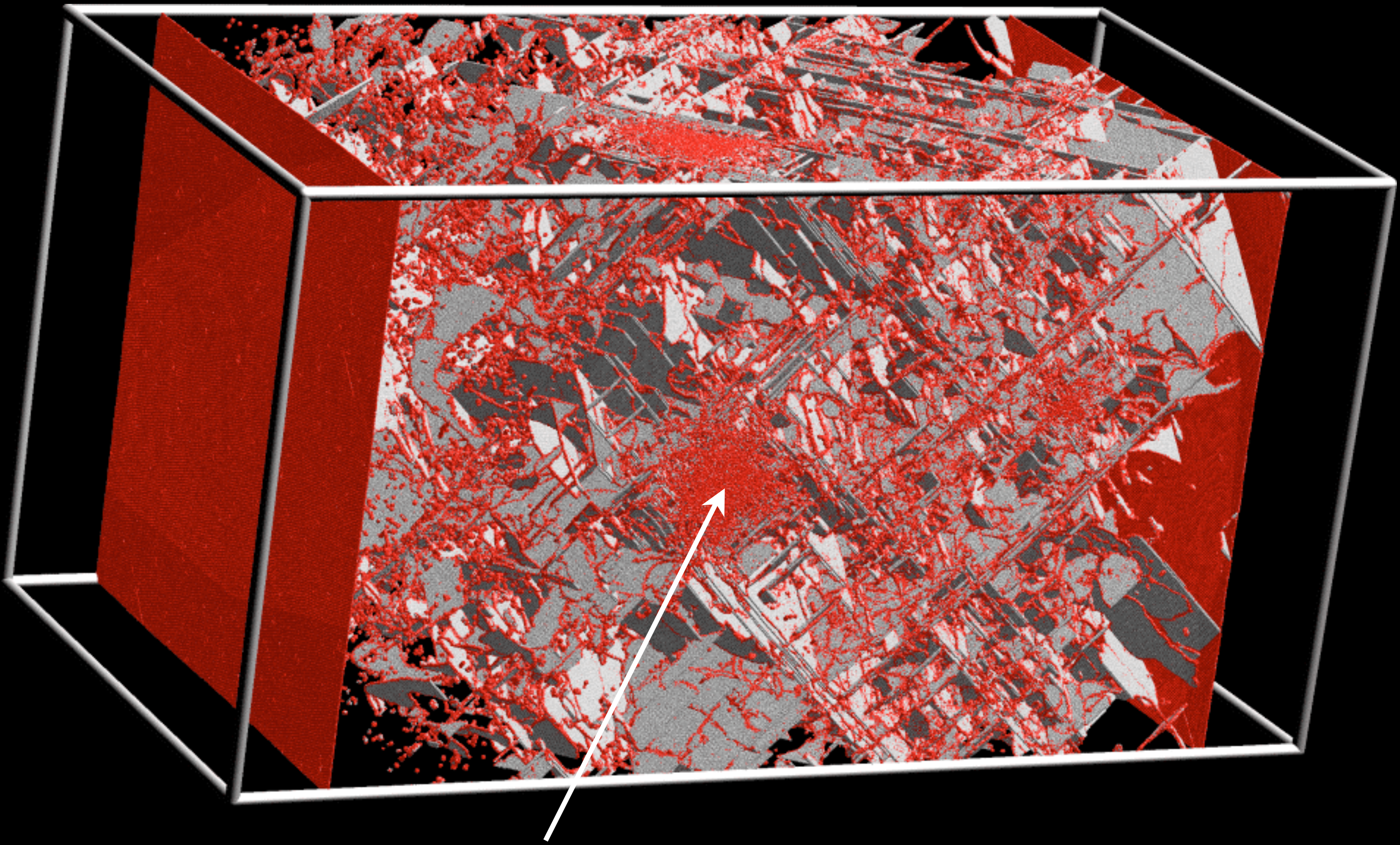
⟨100⟩ loading, $u_p = 1$ km/s, $t = 20$ ps



⟨100⟩ loading, $u_p = 1$ km/s, t = 30 ps

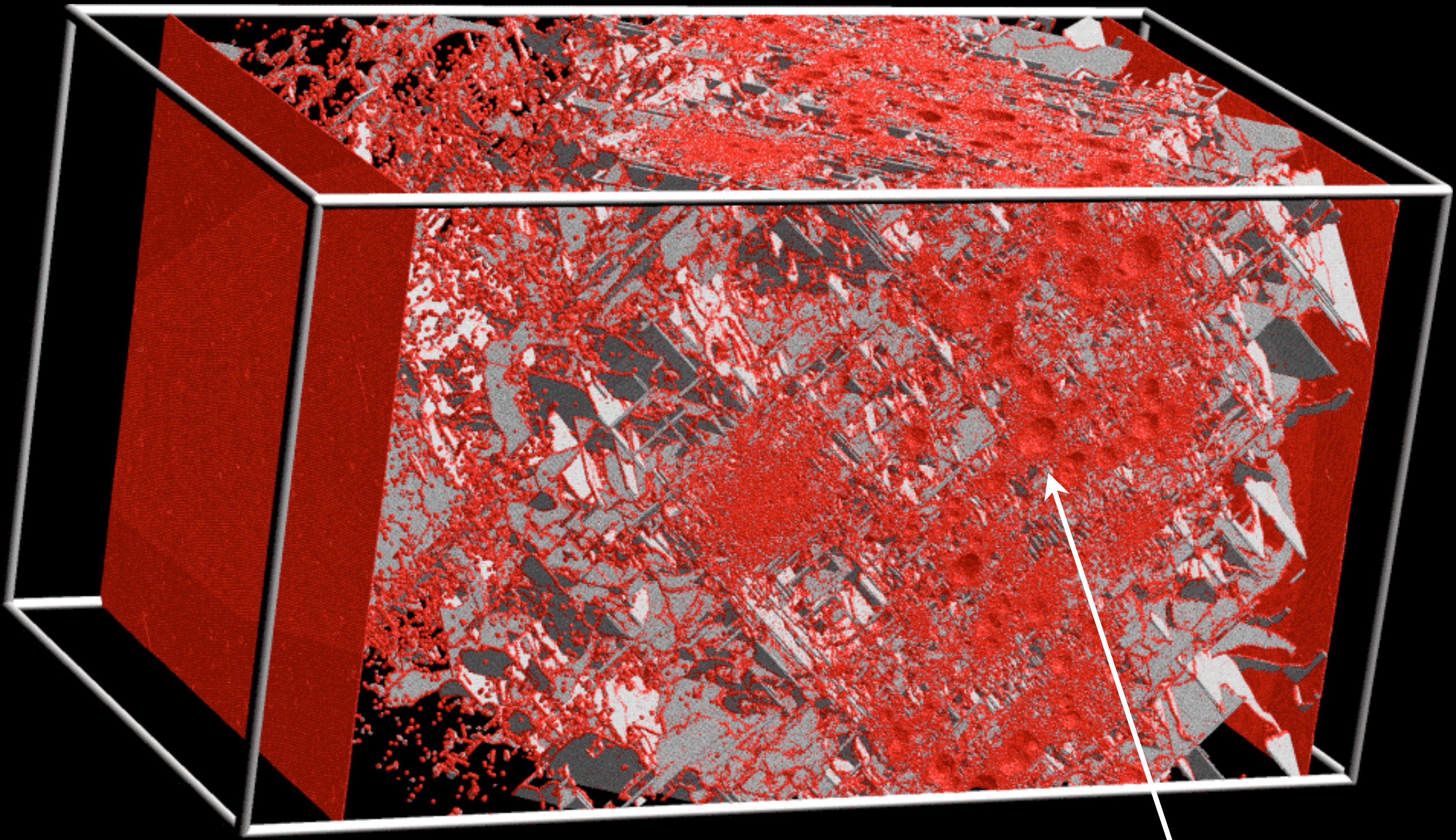


$\langle 100 \rangle$ loading, u_p = 1 km/s, t = 40 ps



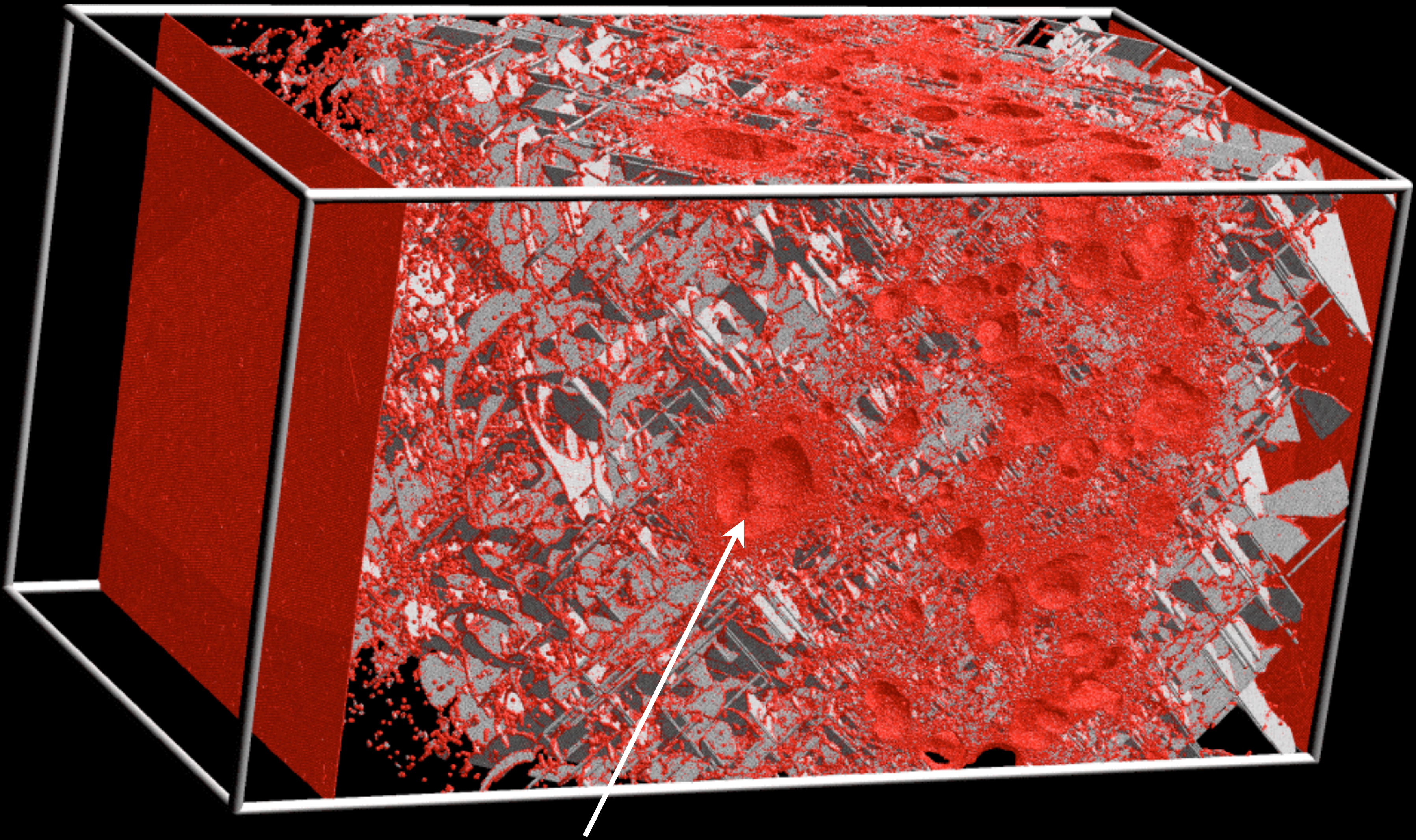
Increased local dislocation density provides "memory" of void locations

⟨100⟩ loading, $u_p = 1$ km/s, $t = 50$ ps



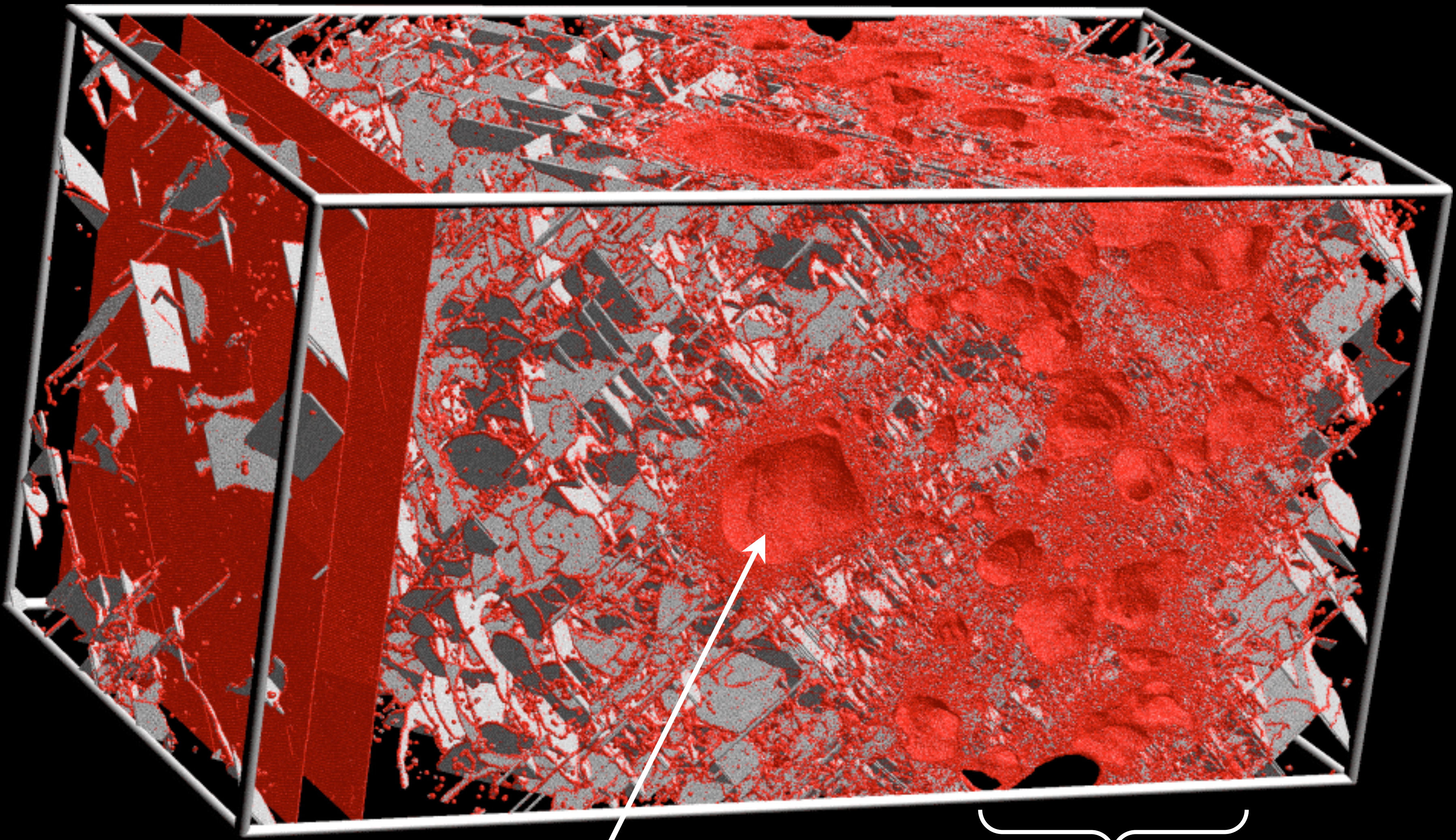
Nucleation of numerous small voids

⟨100⟩ loading, u_p = 1 km/s, t = 60 ps



Re-opening of preexisting void

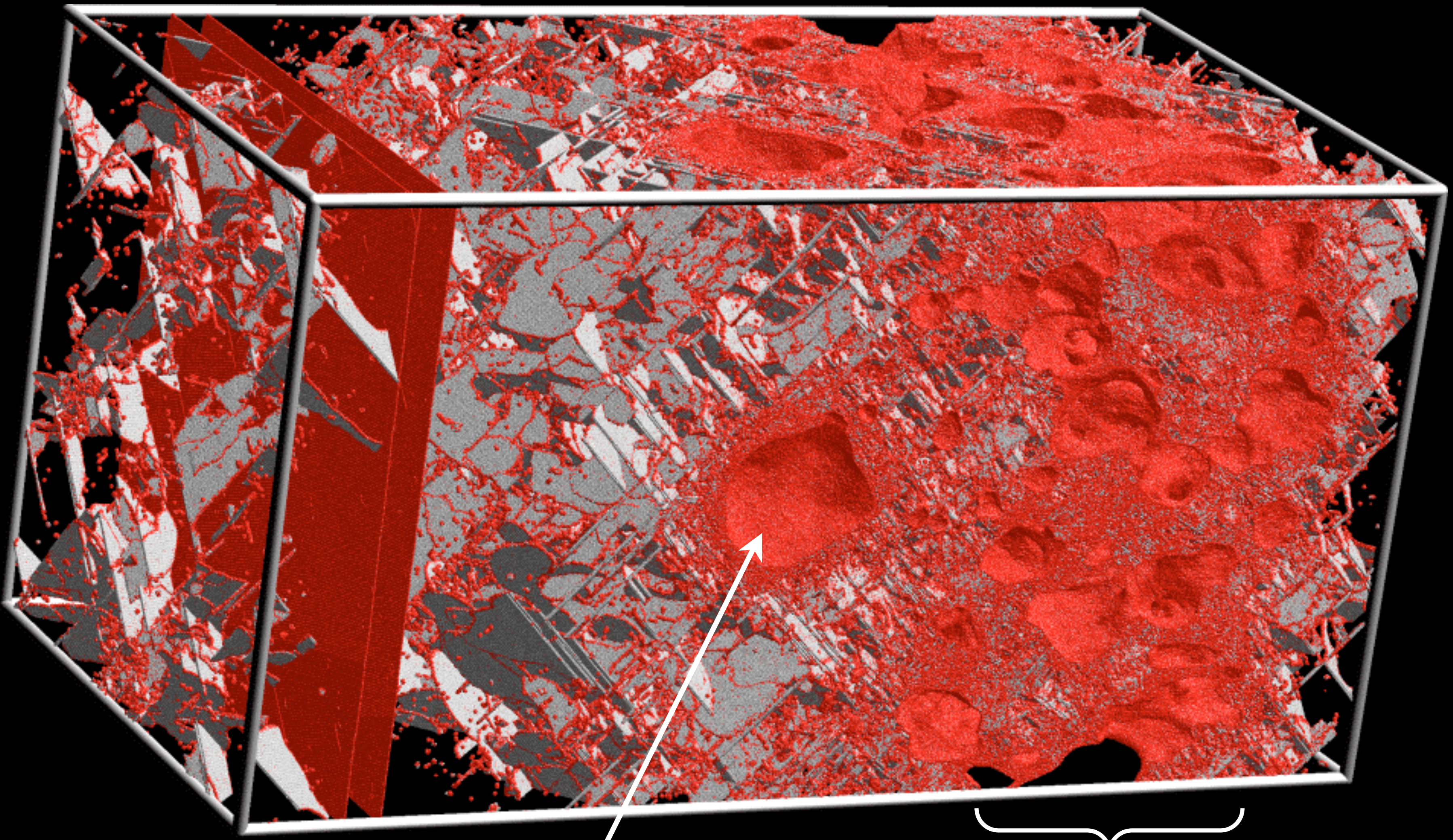
$\langle 100 \rangle$ loading, $u_p = 1$ km/s, $t = 70$ ps



Re-opening of preexisting void

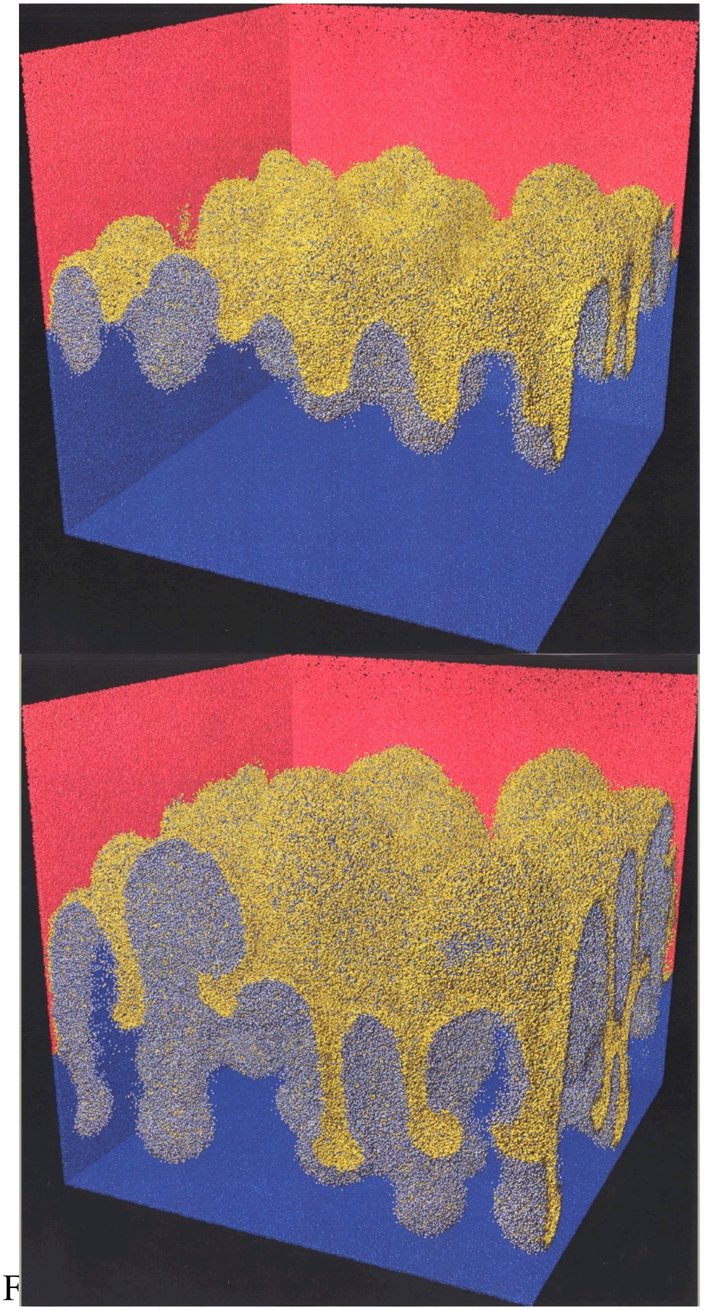
Linkup of voids in main spall zone

⟨100⟩ loading, u_p = 1 km/s, t = 80 ps



Re-opening of preexisting void
Linkup of voids in main spall zone

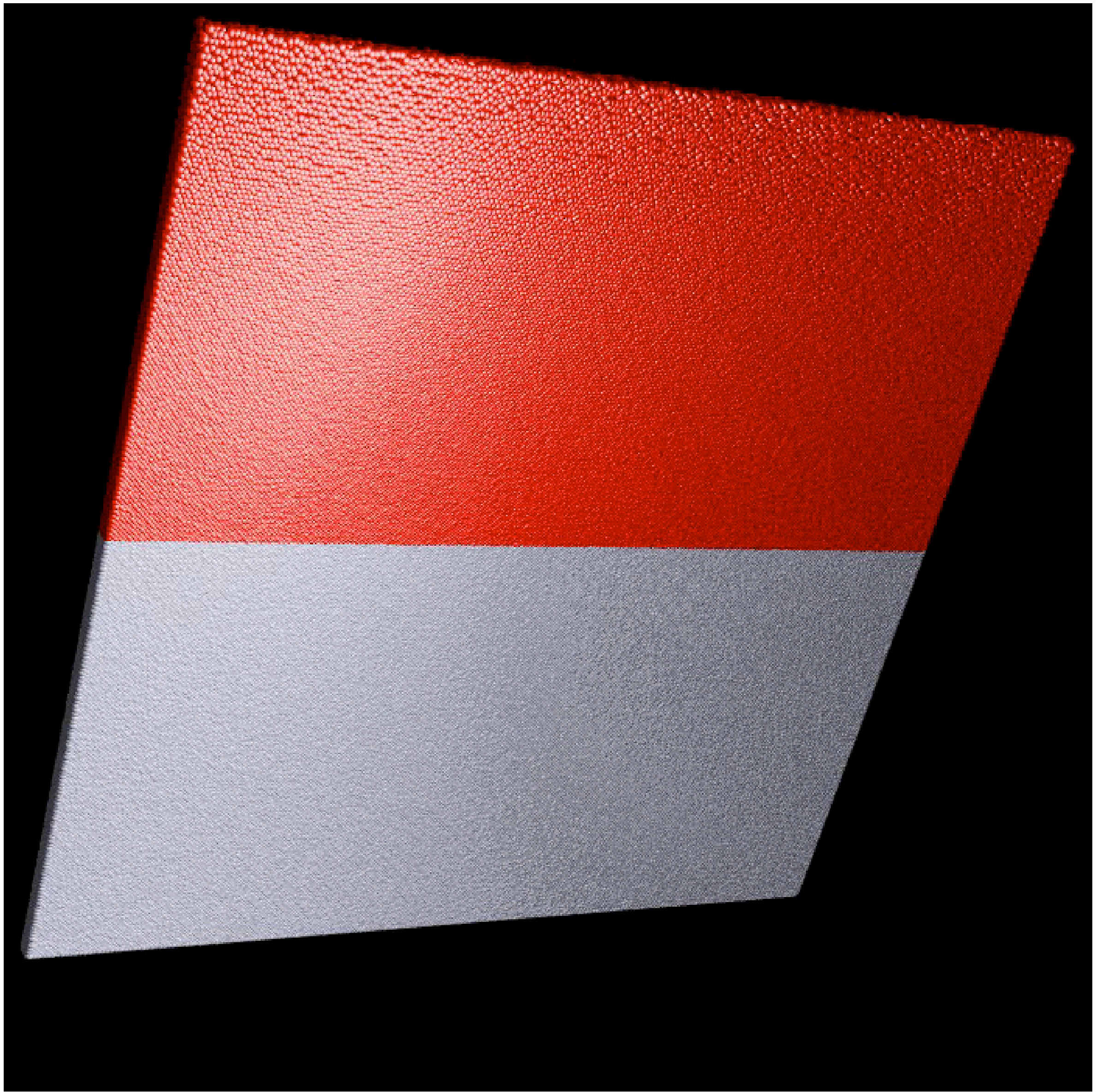
Raleigh-Taylor instability



Kadau et al, PNAS **101**, 5851 (2004)

100 million LJ atoms

Raleigh-Taylor instability



Kadau et al, PNAS **101**, 5851 (2004).

MD - achievable time scales

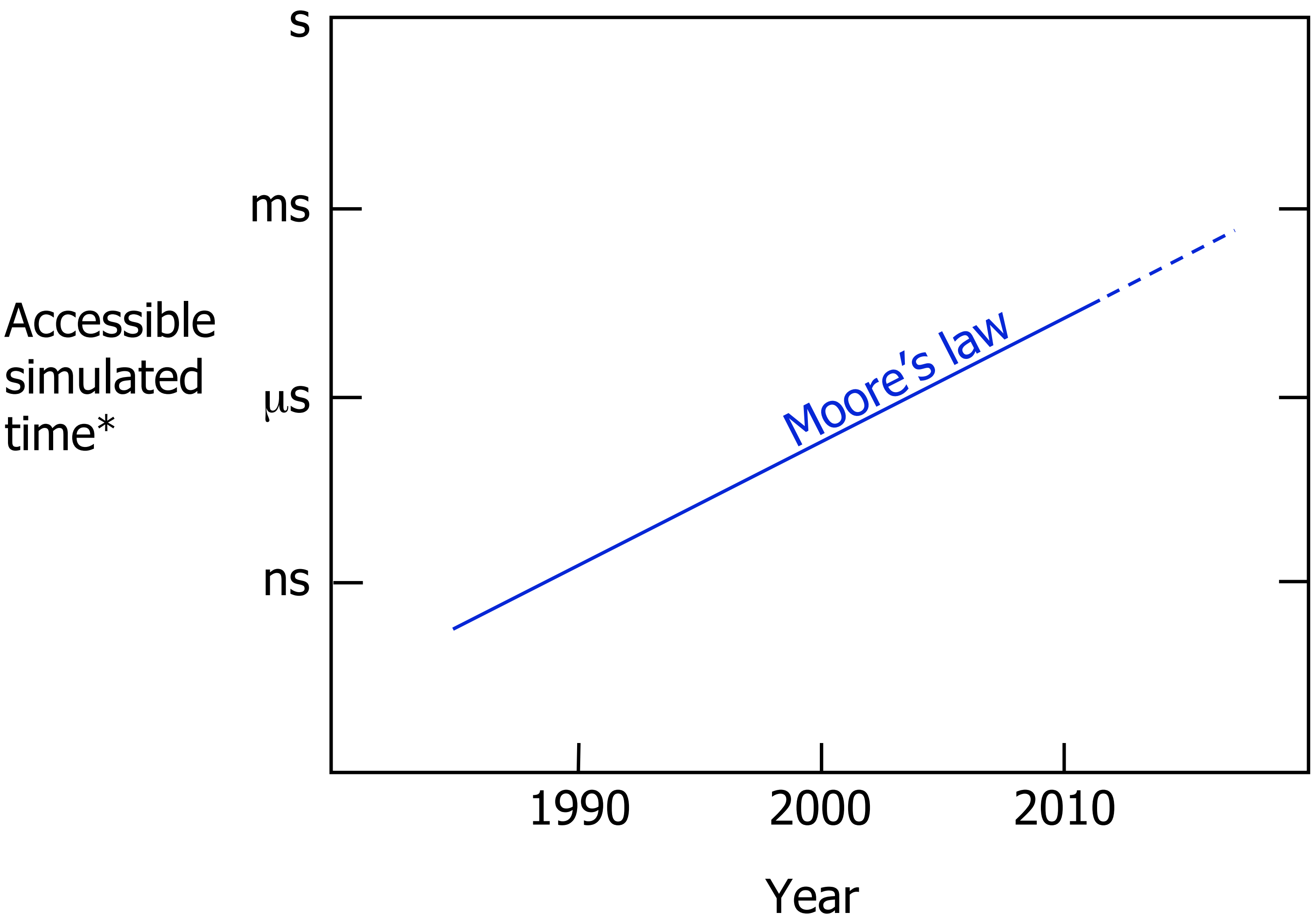
With fast empirical potential

nanoseconds

With first-principles forces (e.g., density functional theory)

few ps

MD may never reach even one millisecond



* 1-week simulation of 1000-atom metal system, EAM potential