Tver State Technical University

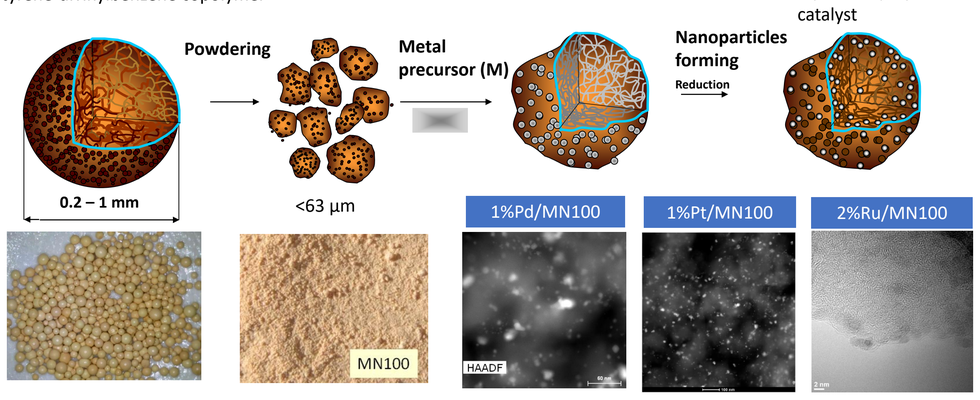
Metal Cluster and Nanoparticle Mobility in Aromatic Polymer Network of Styrene Divinylbenzene

Bykov A.V., Demidenko G.N., Nikoshvili L.Zh., Pinyukova A.O.

E-mail: BykovAV@yandex.ru

ASAM 8 NOVOSIBIRSK

MN100, MN270
Styrene-divinylbenzene copolymer



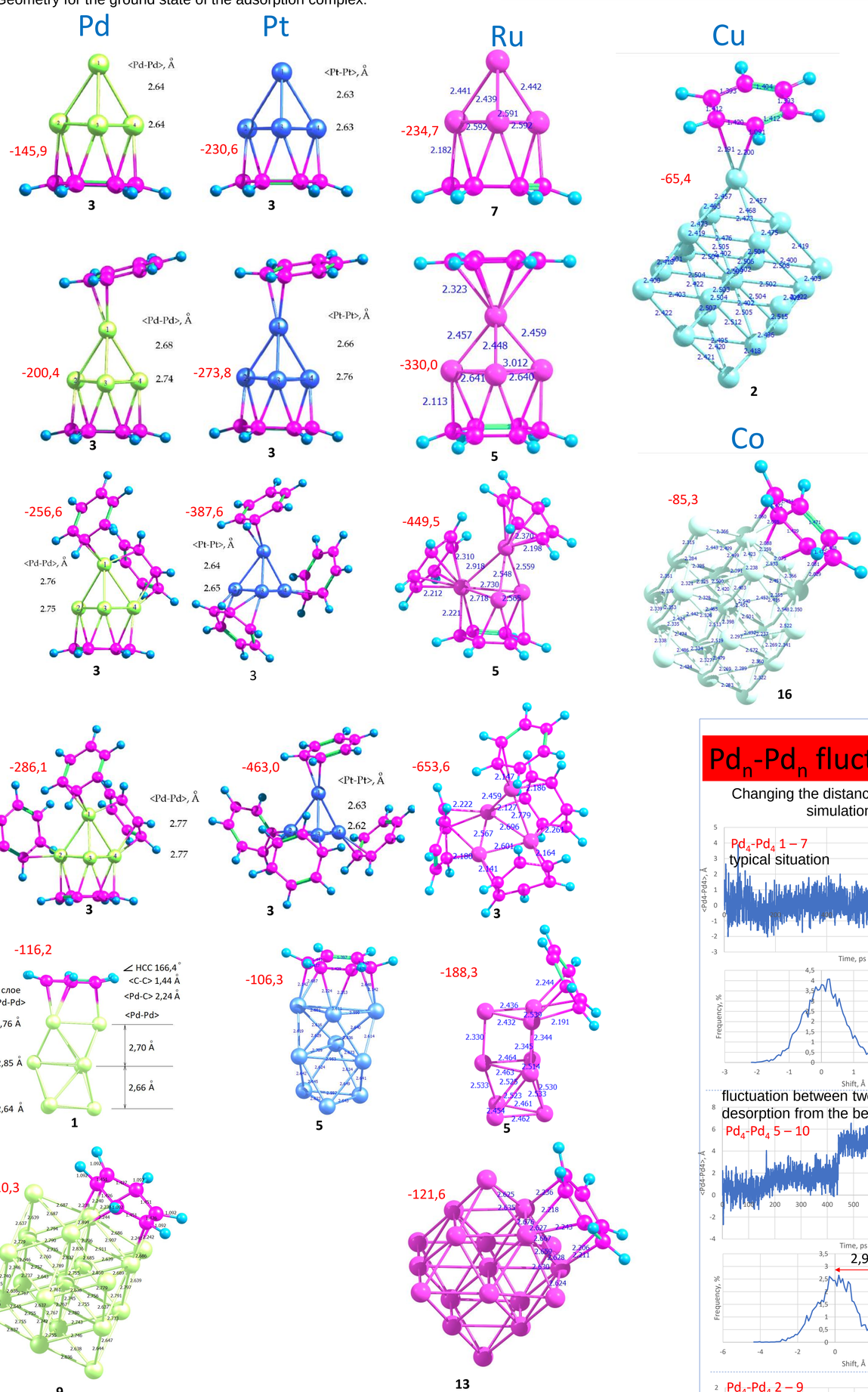
How strongly are metal clusters held by the aromatic polymer matrix?
Can metal clusters migrate through the polymer matrix during gas-phase reduction?

Quantum mechanic calculations — ORCA

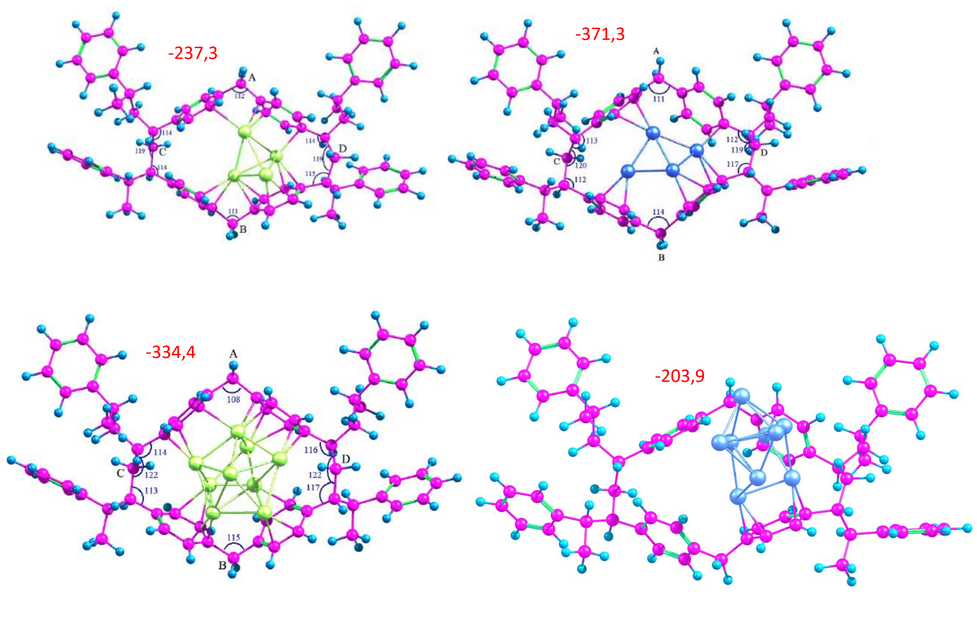
C, H, Pd, Ru, Co, Cu: DFT/ZORA/BP/ZORA-def2-TZVP
Pt: DFT/ZORA/BP/SARC-ZORA-TZVP

Description:
-145,9 – cluster adsorption energy, kJ/mol
3 - multiplicity of the ground state

Geometry for the ground state of the adsorption complex:



Adsorption of a cluster in a micropore:



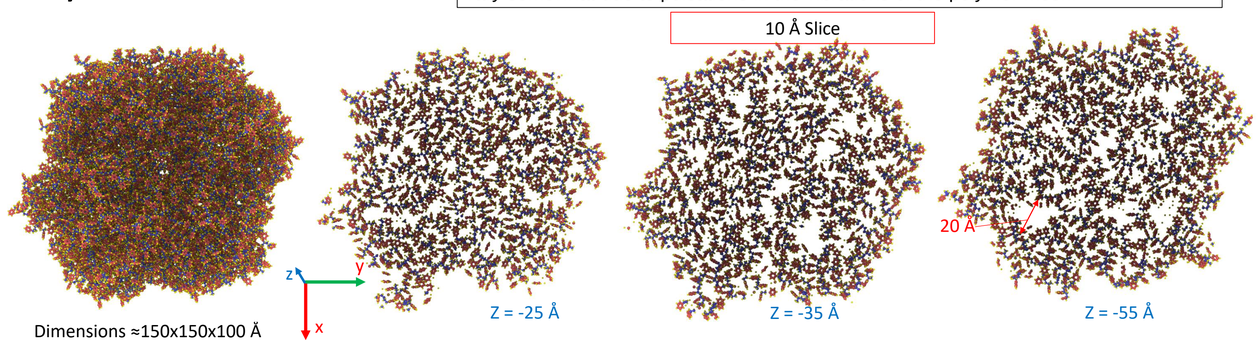
Molecular dynamic simulations — LAMMPS

Styrene-divinylbenzene copolymer was modeled using DREADING potential. The copolymer contains 11%mol divinylbenzene. LJ-metal-metal potentials were calculated to reproduce the cohesion energy of M_{19} clusters according to quantum chemical calculations. The LJ metal-carbon interaction potentials were obtained on the basis of quantum mechanical calculations so as to reproduce the adsorption energies of M19 clusters on the benzene ring and the metal-carbon bond lengths.

Simulation conditions:
Tthermostat: Nose-Hoover; nvt; temperature 573 K (300 °C); Time step: 0,1 fs; total time of each simulation 1 ns

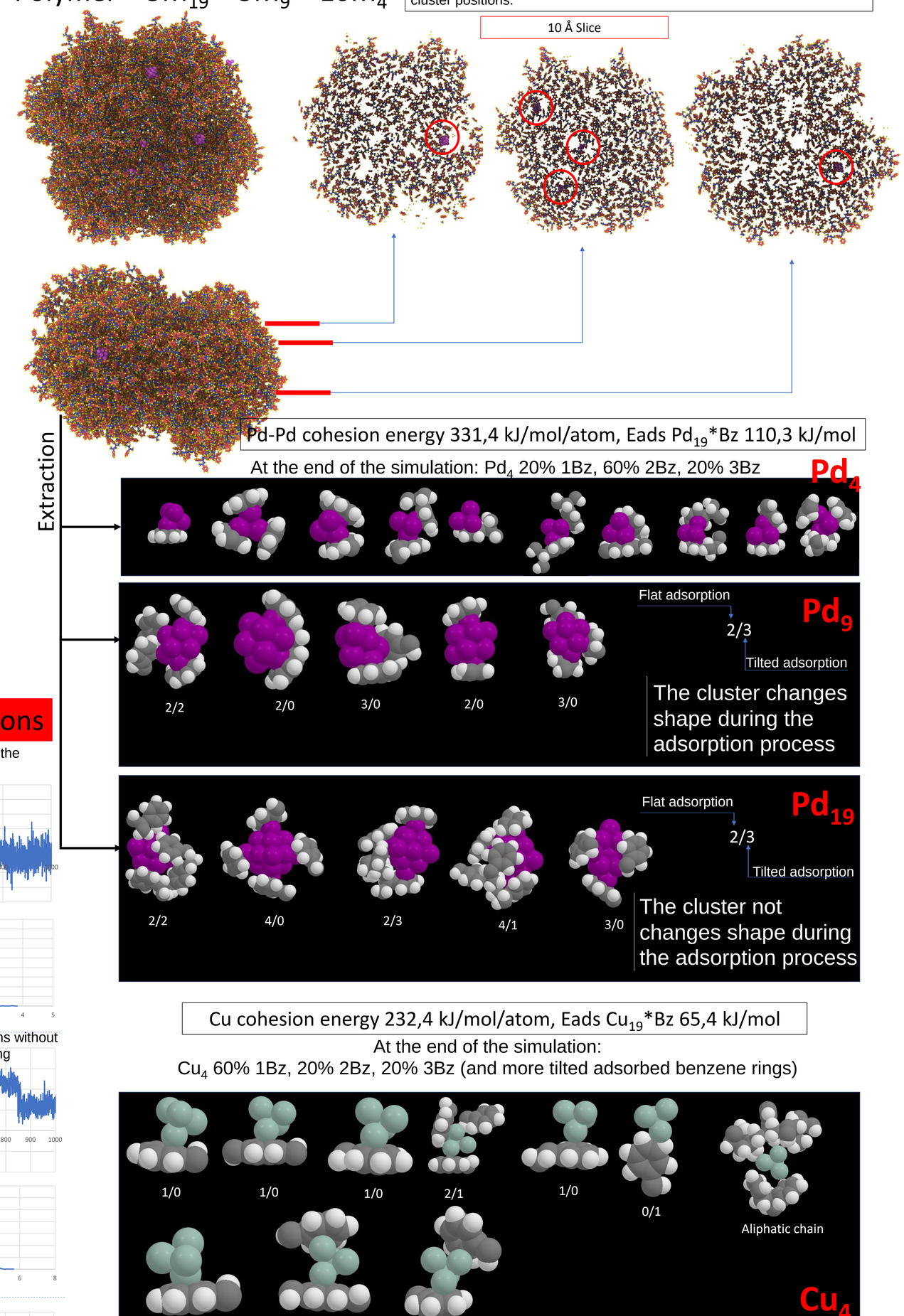
Polymer >74000 atoms

The polymer has a relatively stable system of micro- and mesopores. The pore sizes vary somewhat due to pulsations in the vibrations of the polymer mesh.



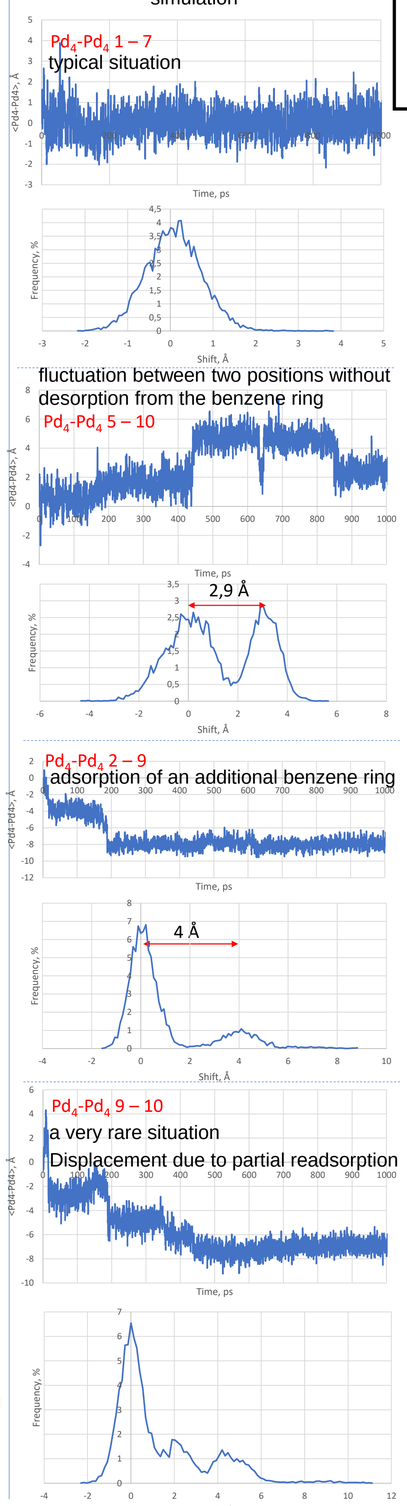
Polymer + $5M_{19}$ + $5M_9$ + $10M_4$

Each simulation had the same polymer conformation and the same metal cluster positions.



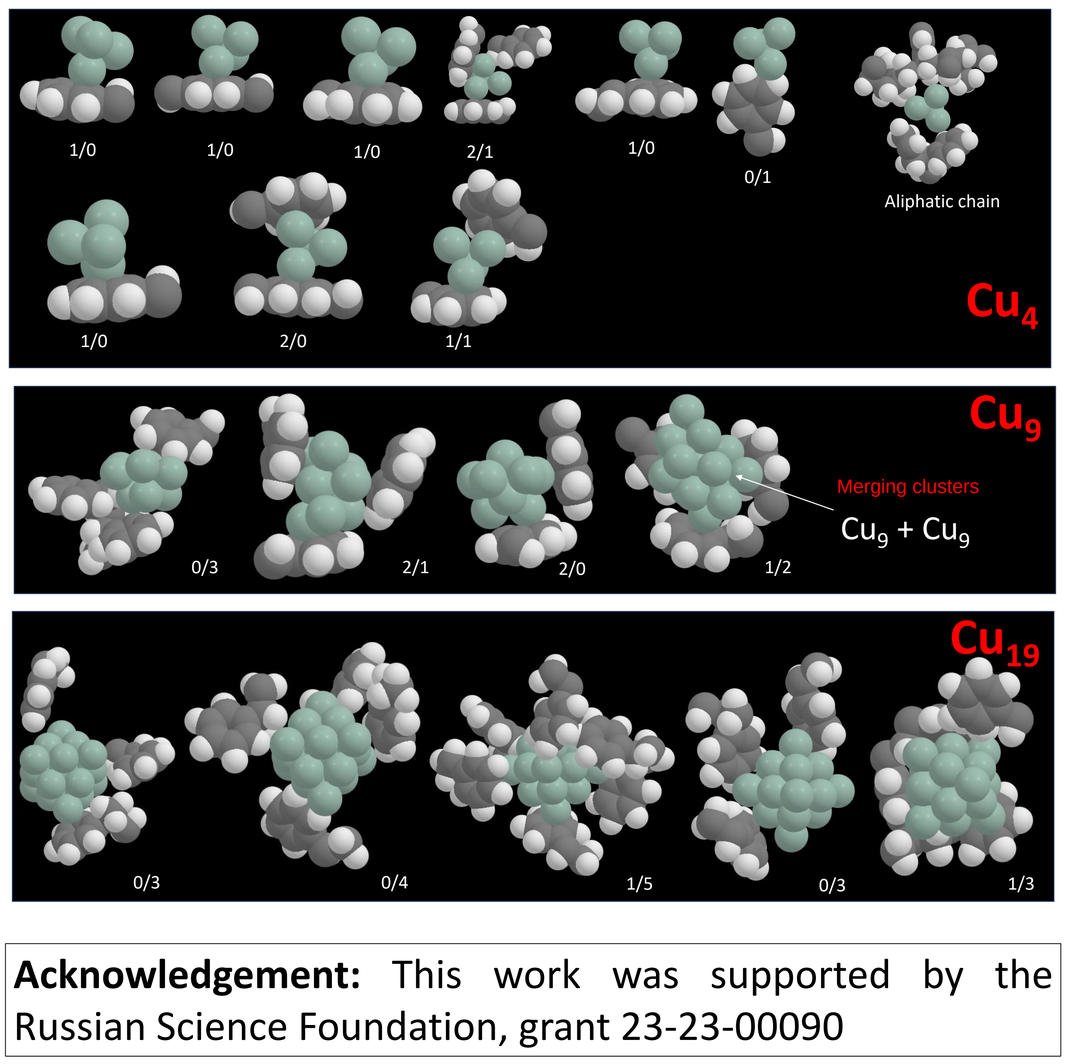
Pd_n-Pd_n fluctuations

Changing the distance during the simulation



Cu cohesion energy 232,4 kJ/mol/atom, Eads Cu_{19}*Bz 65,4 kJ/mol

At the end of the simulation:
Cu_4 60% 1Bz, 20% 2Bz, 20% 3Bz (and more tilted adsorbed benzene rings)



Acknowledgement: This work was supported by the Russian Science Foundation, grant 23-23-00090