Complementing ultrafast imaging experiments with insights from atomistic simulations

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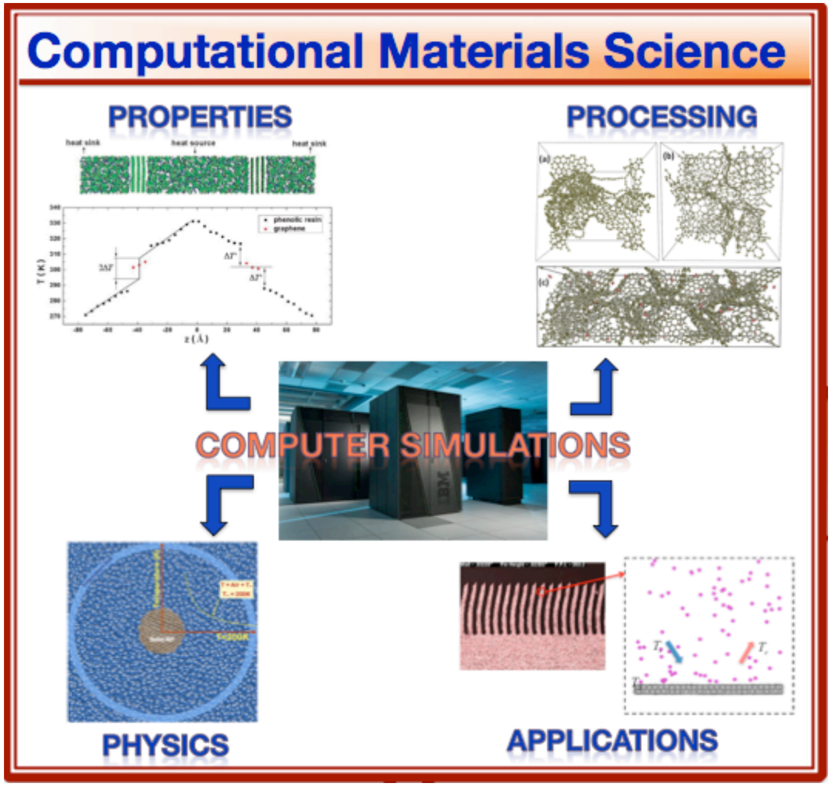
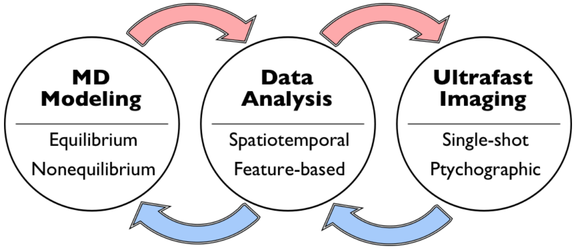


Courtesy: Raghavan Ranganathan, RPI

MAUI

"Modeling, Analysis, and Ultrafast Imaging"

MAUI: Modeling, Analysis, and Ultrafast Imaging

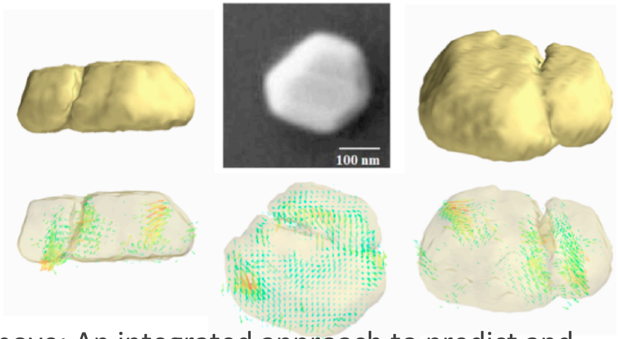


MD Modeling
Equilibrium
Nonequilibrium

Data Analysis
Spatiotemporal
Feature-based

Ultrafast Imaging
Single-shot
Ptychographic

Above: Simulation and experiment are integrated through a common language of data analysis.



Above: An integrated approach to predict and validate material response to external stimuli shows density and distortion vectors that lead to identification of cracks along slip planes.

Scientific Achievement

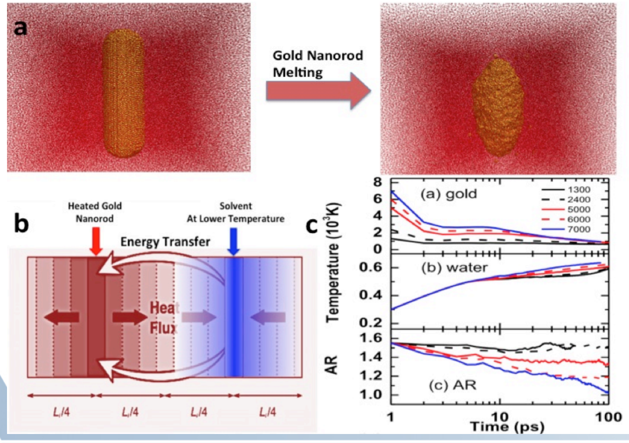
Integrated Imaging, Modeling, and Analysis of Ultrafast Energy Transport in Nanomaterials

Significance and Impact

Understanding lattice vibrations in individual nanoparticles can enable energy applications such as photocatalysis, photonics, thermoelectrics, semiconductor design, groundwater photo remediation, and heat transfer in battery interfaces.

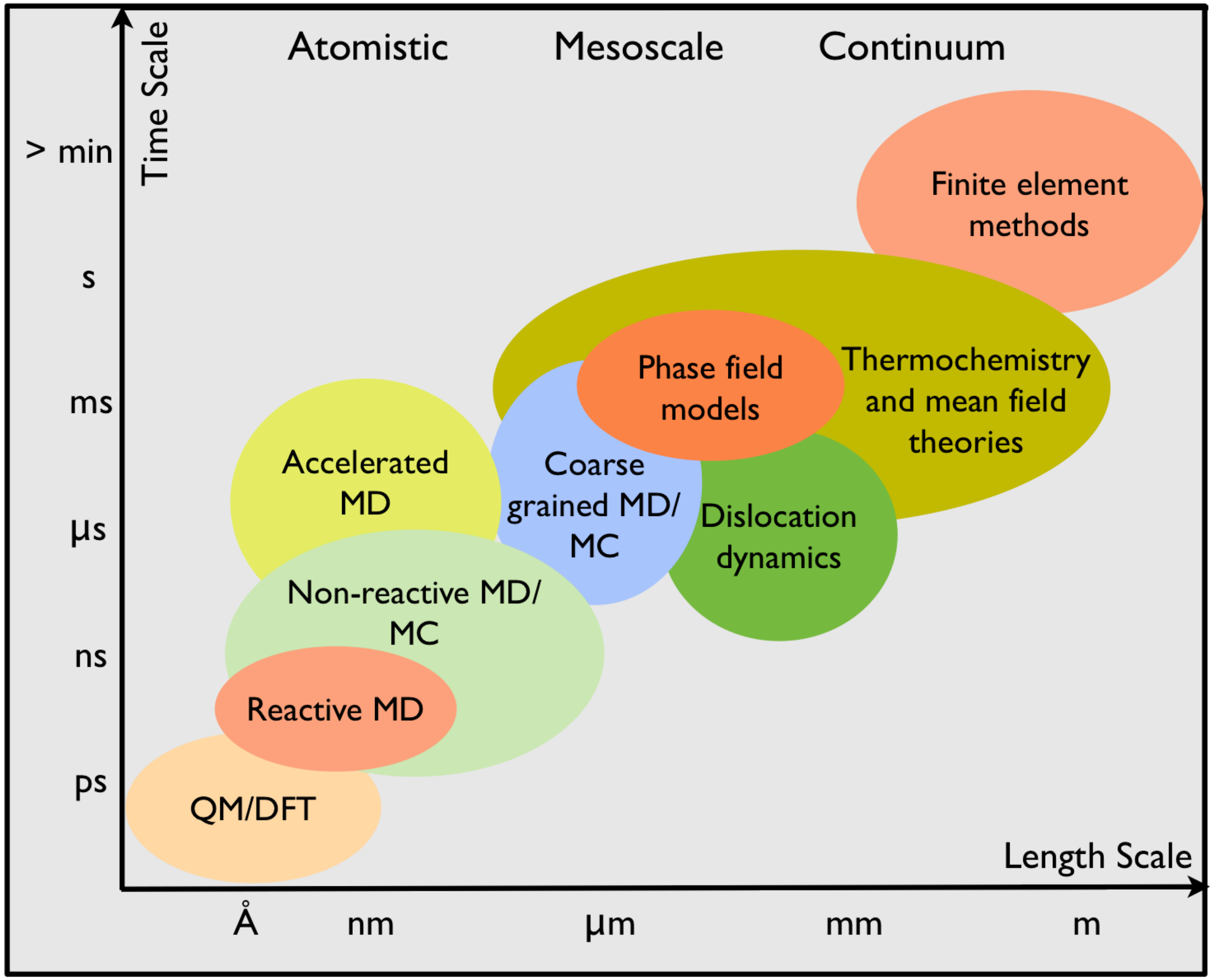
High Level Research Details

- Modeling: MD will be used to model the phonon transport and lattice thermal conductivities for the proposed systems.
- Analysis: In order to combine the reverse (image reconstruction) with the forward (simulation) models, data transformations between model spaces will be investigated.
- Ultrafast imaging: We will conduct laser pump-probe imaging experiments to study the structure dynamics originating from electron-phonon interactions.



Left: (a) Million-atom MD simulation showing a laser-heated gold nanorod in water (b) Typical schematic of an NEMD simulation to compute heat transport (c) Temperature dissipation and aspect ratio in our preliminary MD calculations.

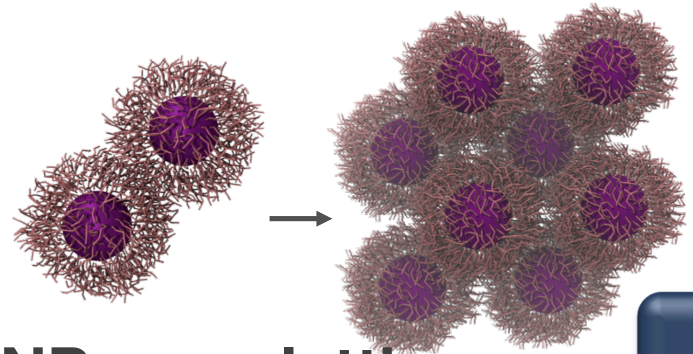
Molecular dynamics: accessible length and time scales



- With dedicated HPC systems classical molecular dynamics (MD) for micron length and time scales possible.
- For several interfacial phenomena, nanoscale regime required for significant deviations from bulk behavior.
- Classical and reactive MD offer powerful tools to investigate underlying physics and reaction kinetics.
  - No assumptions like mesoscale or continuum models.
  - Faster than DFT.

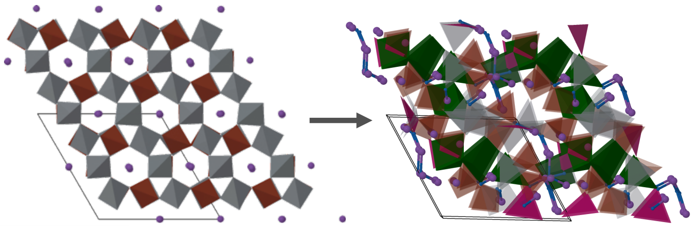
Molecular dynamics is an ideal technique to gain atomistic insights into materials phenomena

Self assembly



NP superlattices

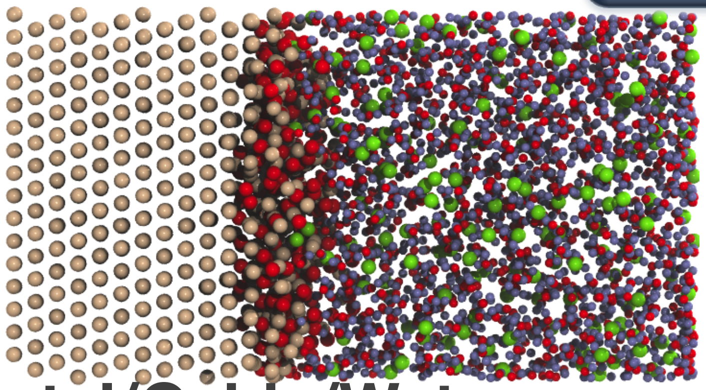
Pressure induced structural transitions



Ceramics

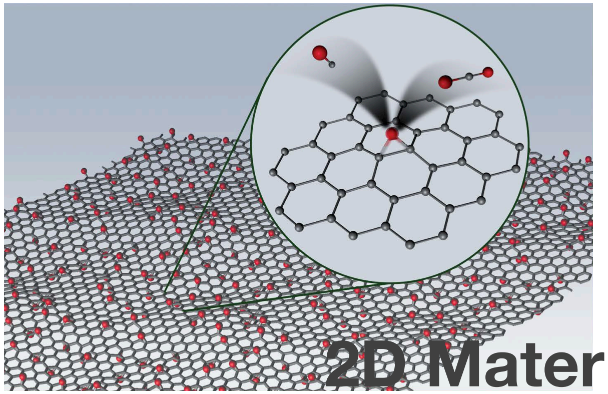
Molecular Dynamics

Corrosion



Metal/Oxide/Water

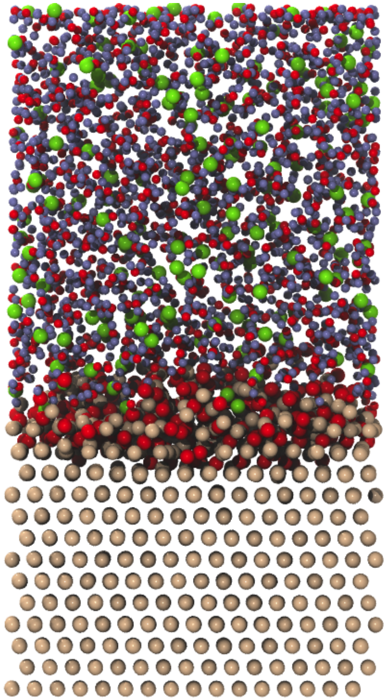
Reaction Mechanisms



2D Materials

Courtesy: Badri Narayanan, ANL

Force-field is the “heart” of molecular dynamics



$$-\frac{\partial V}{\partial r_i} = m_i \frac{\partial^2 r_i}{\partial t^2}$$

$$V = f(r_i) \rightarrow$$

Force-field
Interatomic potential

Success of molecular dynamics hinges on the accuracy, robustness, and transferability of force field

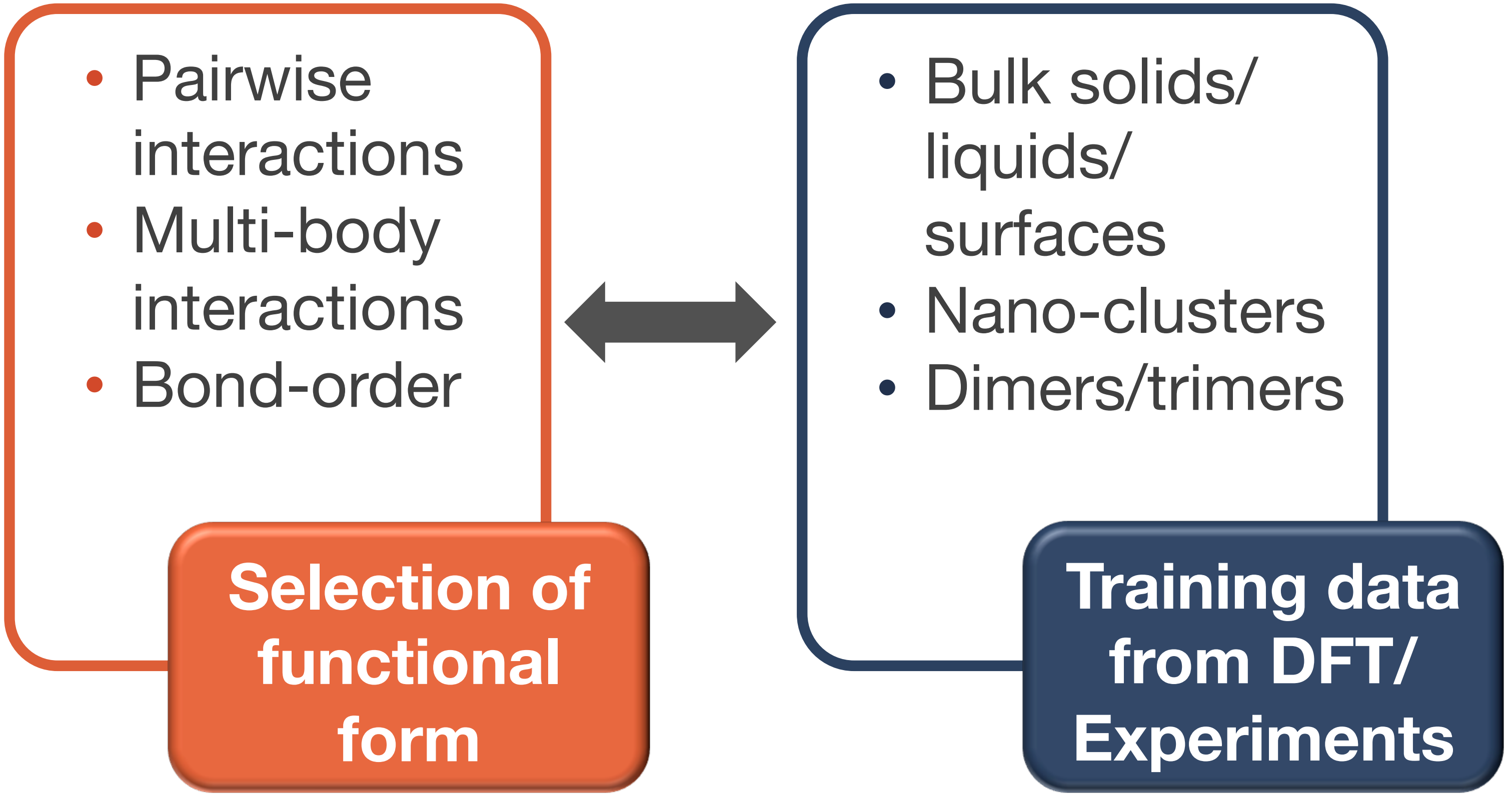
Courtesy: Badri Narayanan, ANL

Force-field parameterization

- Simplistic forms: Lennard Jones $V = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$ 2 parameters
- Complex (Realistic) forms: ReaxFF

$$E = \sum_{\substack{i,j \\ i \neq j}} E_{b,ij} + \sum_{i} E_{ov,i} + \sum_{i} E_{un,i} + \sum_{i} E_{lp,i} + \sum_{\substack{i,j,k \\ i<j<k}} E_{v,ijk} + \sum_{i,j} E_{vdW,ij} + \sum_{i,j} E_{C,ij}$$

upto 600 parameters



- Pairwise interactions
- Multi-body interactions
- Bond-order

Selection of functional form

- Bulk solids/ liquids/ surfaces
- Nano-clusters
- Dimers/trimers

Training data from DFT/ Experiments

Courtesy: Badri Narayanan, ANL

Integrated imaging and simulation to probe nanocatalytic activity of gold

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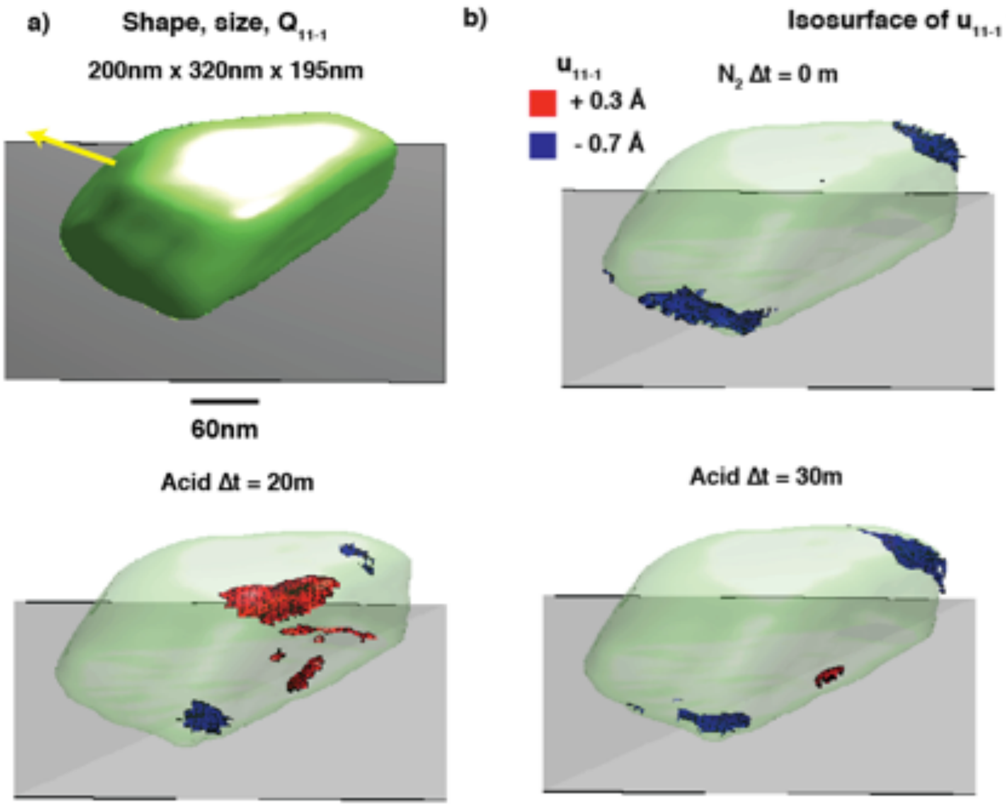
Nanocatalytic activity on gold surfaces

- Purpose: Investigate origin of lattice strain in gold nanoclusters facilitating ascorbic acid decomposition
- Methodology: Reactive MD simulations
- Key result: Identification of a mechanistic sequence of processes/reactions during ascorbic acid decomposition on gold

Simulation background

Ascorbic acid decomposition

$$C_6H_8O_6 + 0.5\ O_2 \xrightarrow{Au_{NC}} H_2O + C_6H_6O_6$$



Reconstructed CDI images of gold + ascorbic acid system.

Experimental observation:

- Reversible lattice distortions in gold nanocrystals upon exposure to 0.1M and 1M ascorbic acid solutions.
- The lattice strain was seen to be at a maximum near the edges of the top and bottom {111} oriented facets.

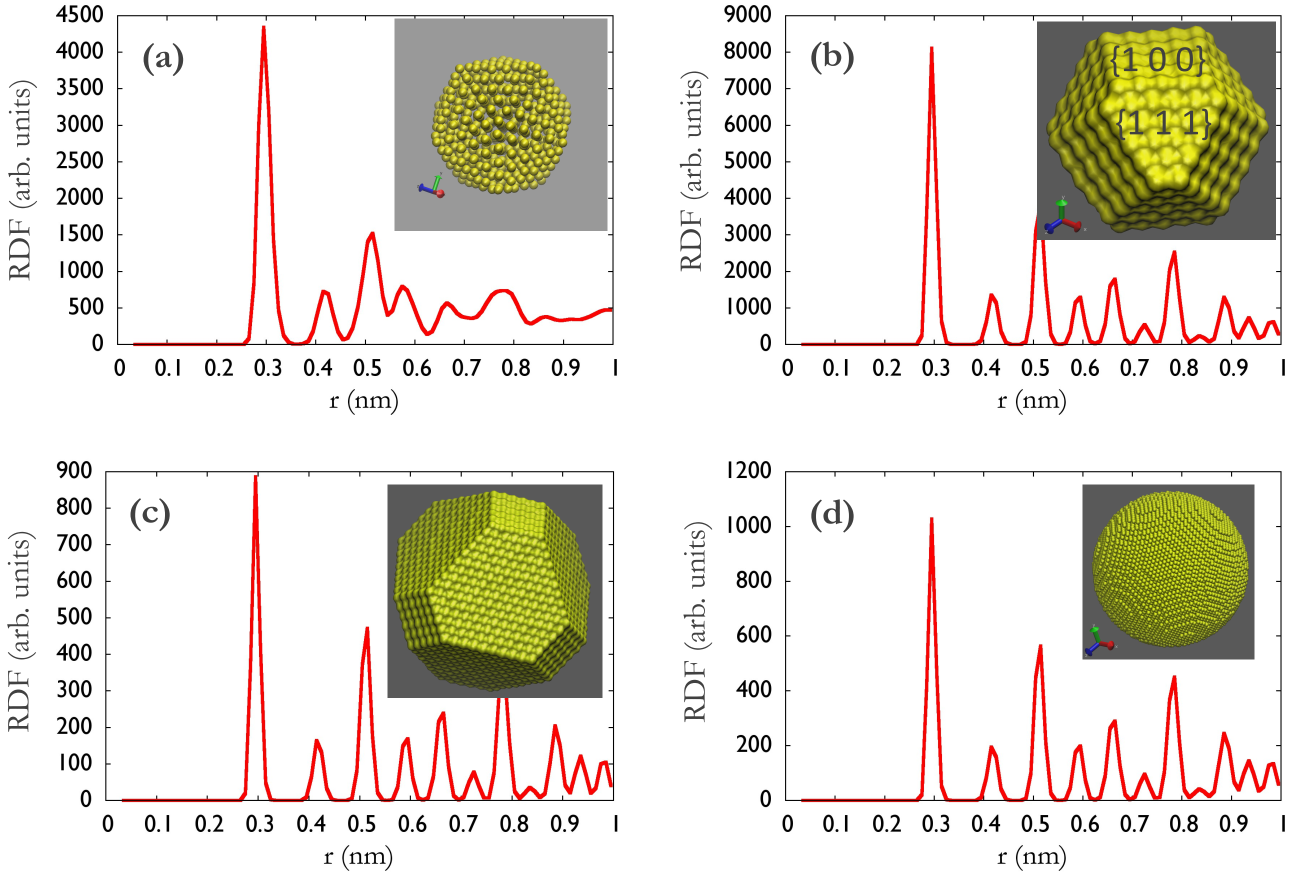
Reactive MD:

- Goal - Investigate the atomic scale processes underlying gold-catalyzed ascorbic acid decomposition.
- The reactive MD simulations are performed using the ReaxFF force field.

Information collected:

- Bond orders of every pair of atoms.
- Atomic trajectory.
- Analysis yields temporal data about molecular species and reaction pathways in simulation.

Equilibrated gold NP structures



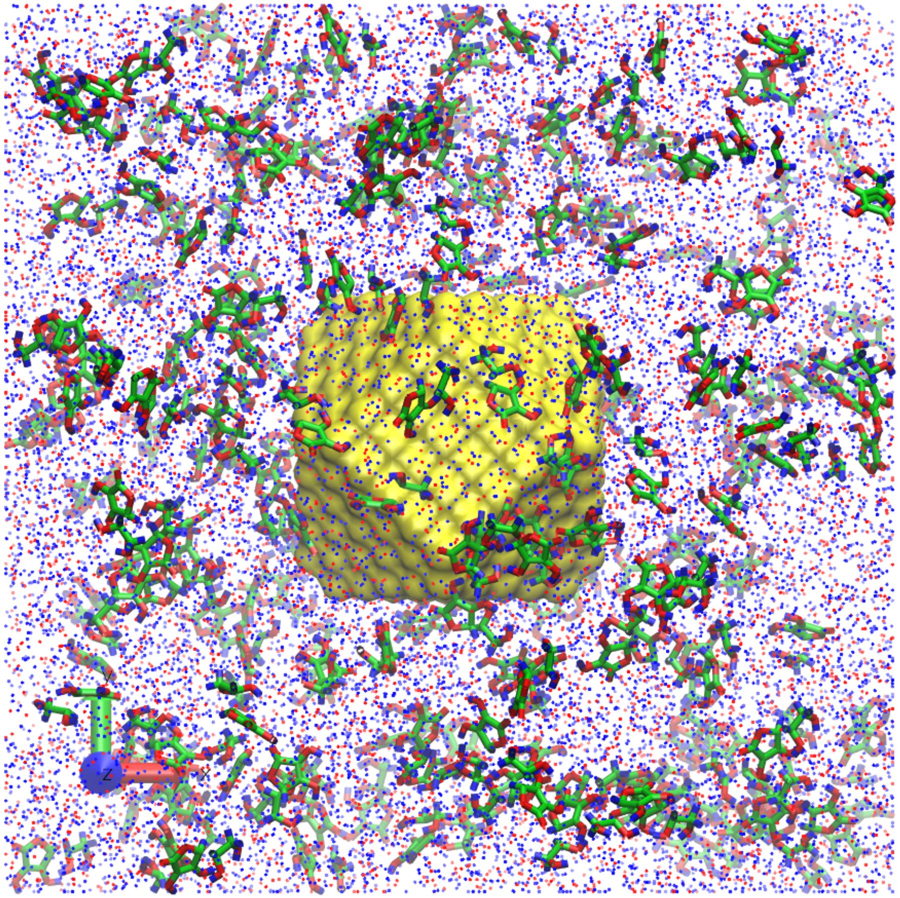
(a) Icosahedron
561 atoms
r_{Au} = 12.32 Å

(b) Truncated octahedron
490 atoms
r_{Au} = 10.68 Å

(c) Truncated octahedron
5010 atoms
r_{Au} = 29.55 Å

(d) Sphere: 36132 atoms
r_{Au} = 52.94 Å

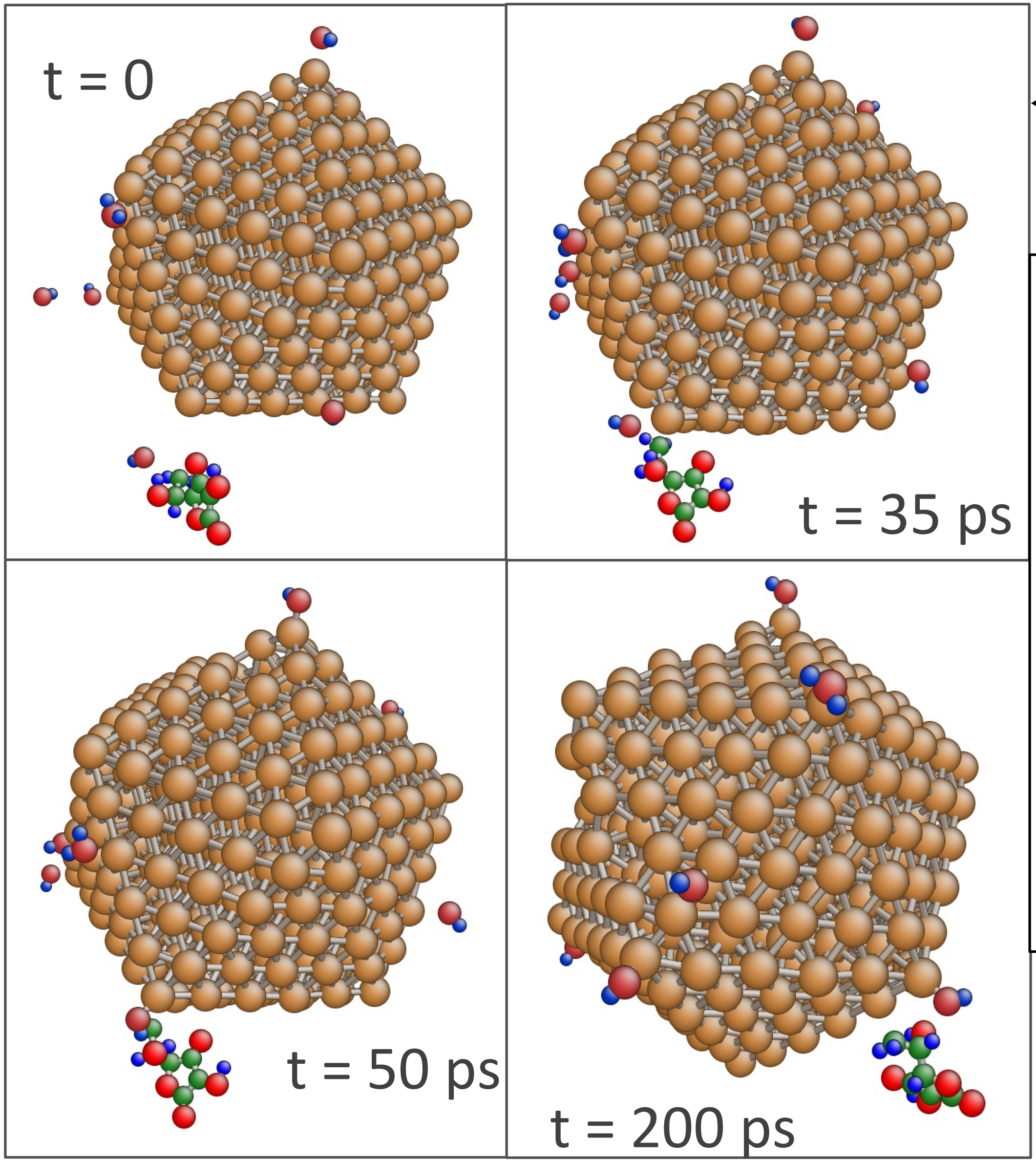
Sample schematic of simulated system
1M acid + water + gold (truncated octahedron)



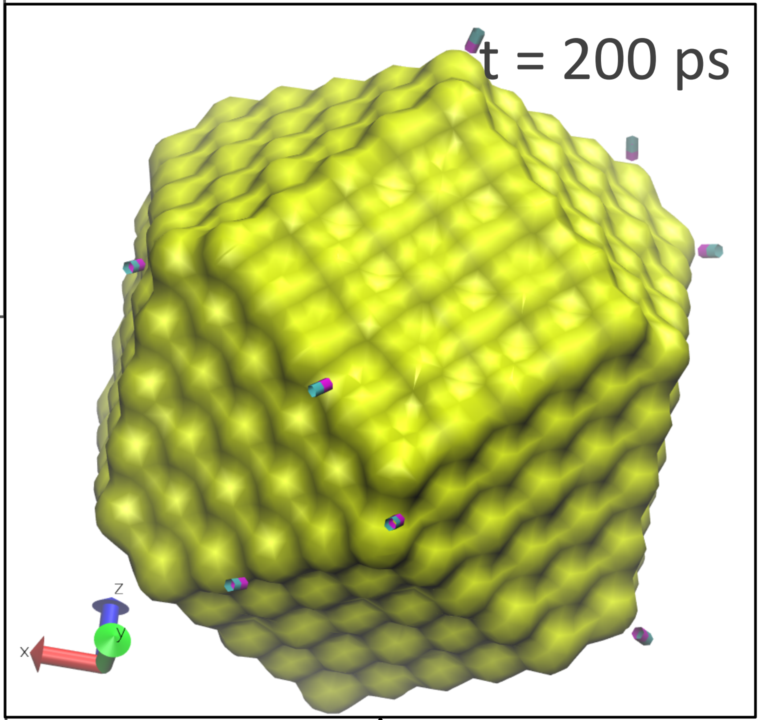
Yellow - Gold
Green - Carbon

Red - Oxygen
Blue - Hydrogen

OH ion chemisorbs on gold, acid physisorbs



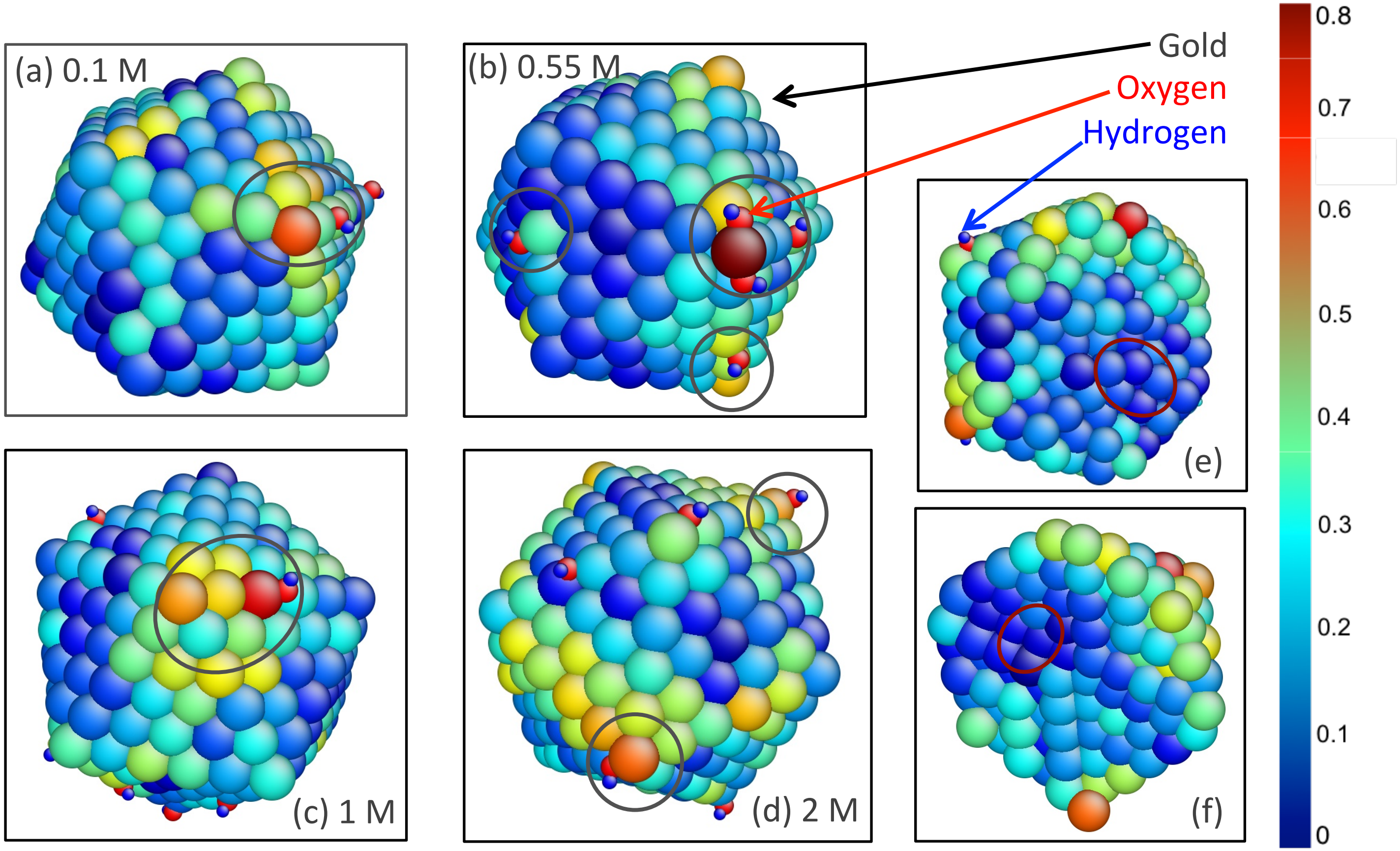
561-atom icosahedron in a 2 M acid solution



490-atom truncated octahedron in a 1 M acid solution

Effect of acid molarity

Displacement of Au atoms after 200 ps



Effect of acid molarity

- Maximum strain on Au at corner and edge sites.

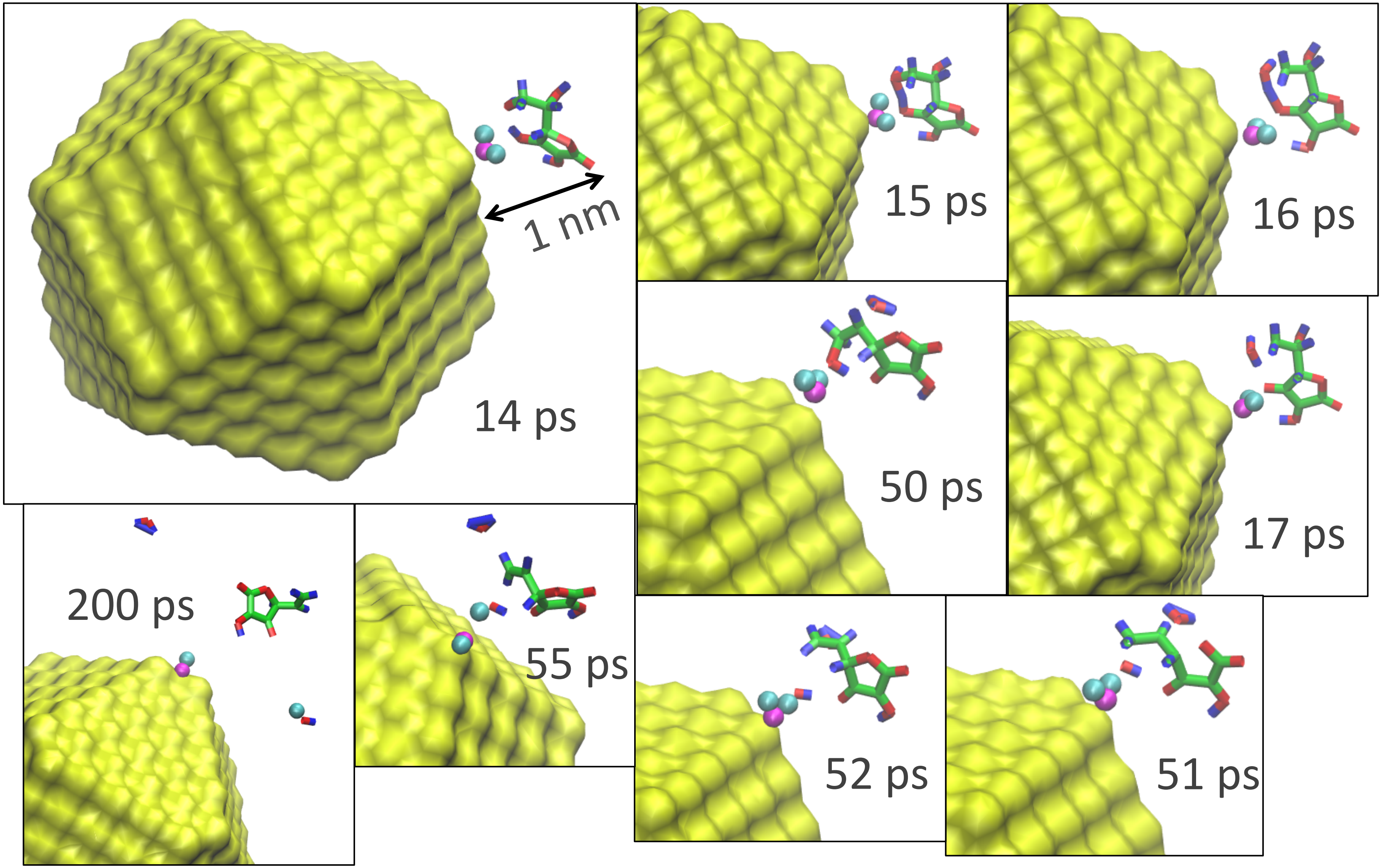
- Displacement magnitude is independent of molarity (between 0.64 and 0.80 Å).
  - Observed values are comparable with experiments.

- Strain depends on chemical adsorption and strength of O-Au bond (no Au-C bonds are seen).

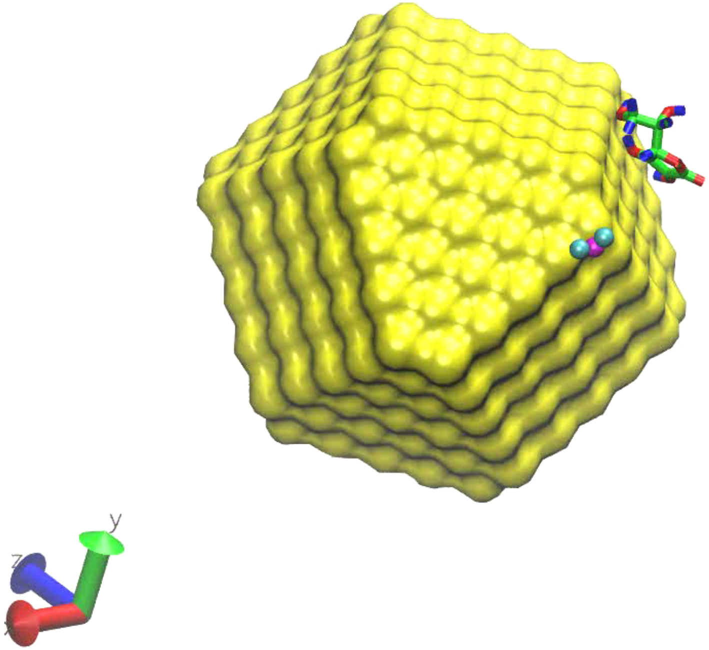
- For comparison there are no adsorbed OH's in the absence of ascorbic acid.

- Presence of acid affects dissociation of water near the gold surface.

Adsorption pathway



Adsorption pathway movie



Summary

- Purpose: Investigate origin of lattice strain in gold nanoclusters facilitating ascorbic acid decomposition

- Methodology: Reactive MD simulations

- Key results:
  - Identification of a mechanistic sequence of processes/reactions during ascorbic acid decomposition on gold.
  - Strain values and location are comparable with experiments.

Ultrafast vapor nanobubble cavitation around intensely heated nanoparticles

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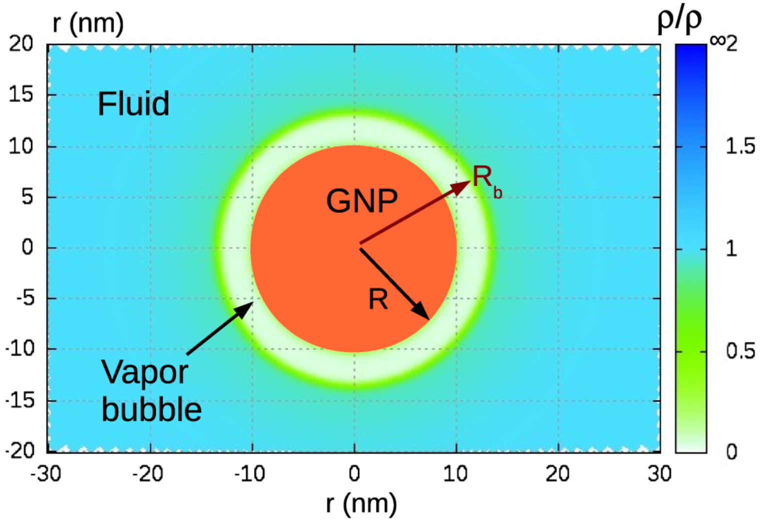
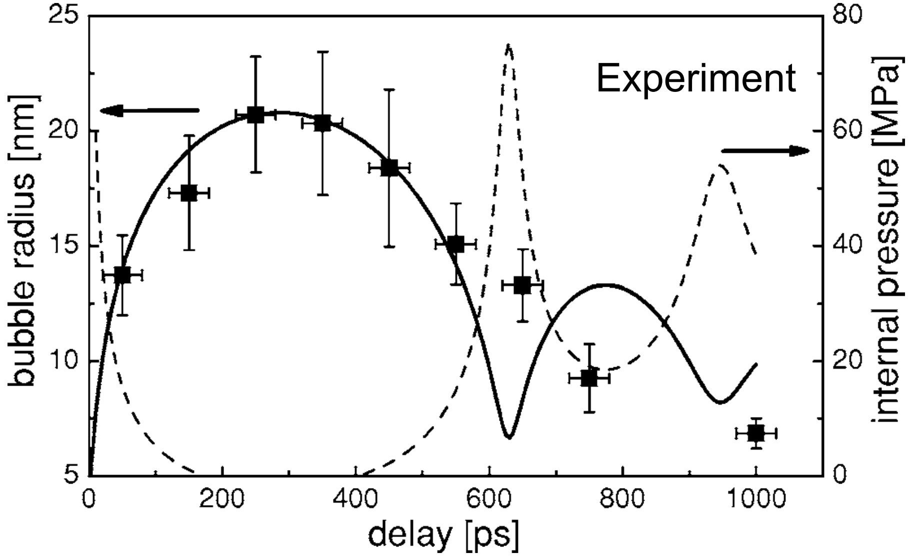


Lombard et al., Phys Rev. Lett. 112(10) (2014) 105701.



Kotaidis et al., Appl. Phys. Lett. 87(21) (2005) 213102.

Model system

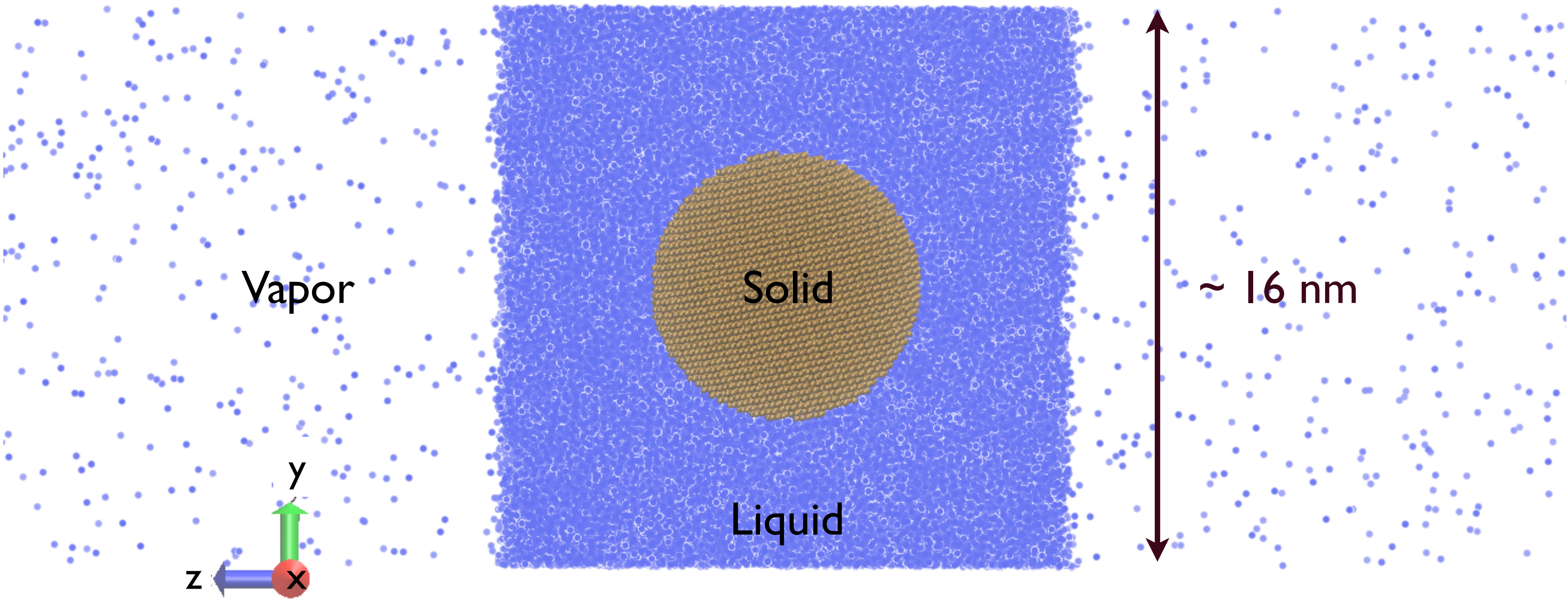
- Finitely extensible spring (FENE) to model nanoparticle (NP) - solid may be heated to any temperature without melting.
- Lennard-Jones (LJ) potential modeling the fluid.

$$\boxed{V(r) = -0.5kR_0^2 \ln[1-(r/R_0)^2]}$$

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

ϵ = 0.5758 kcal/mol

σ = 0.3 nm

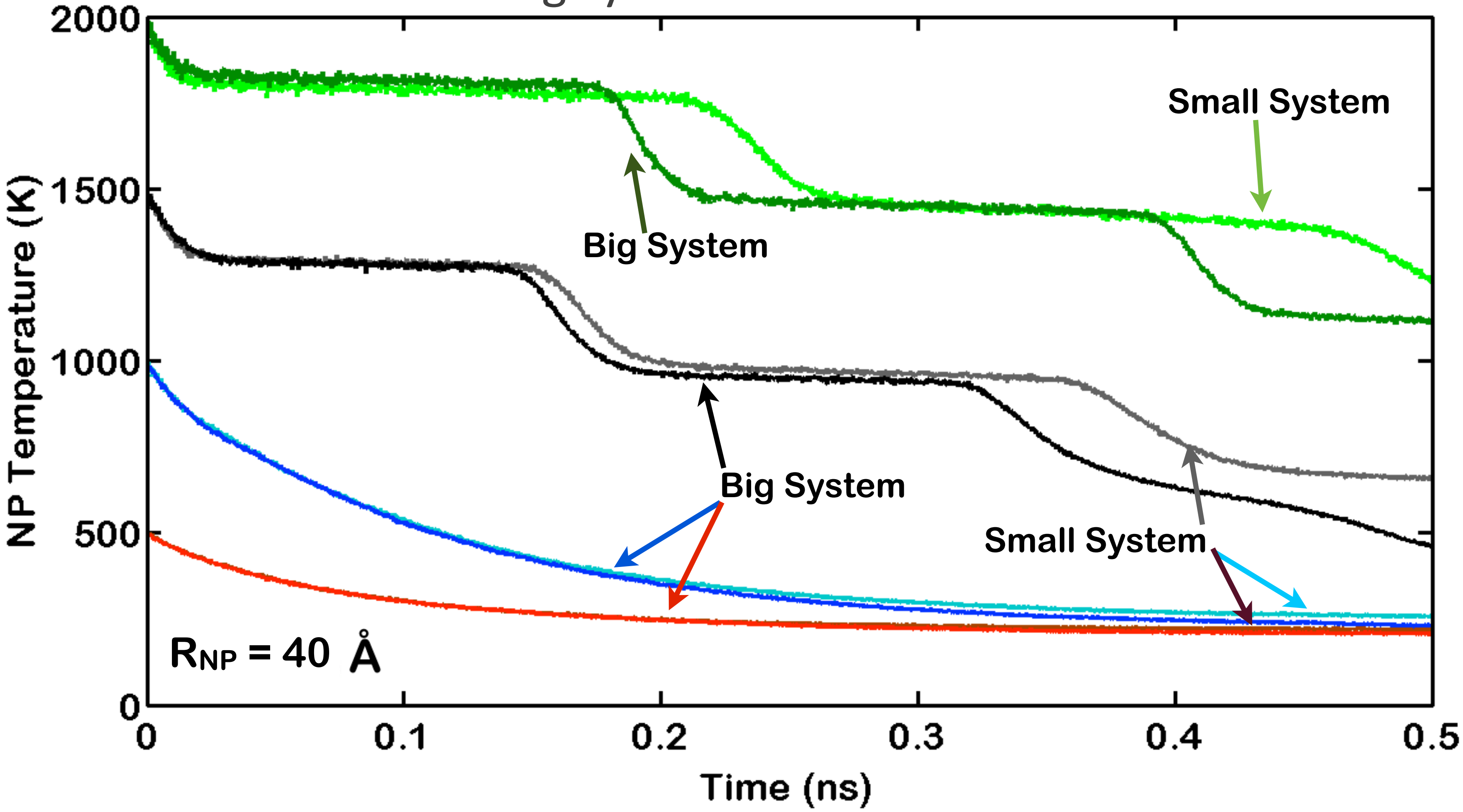


Nanoparticle cooling curves

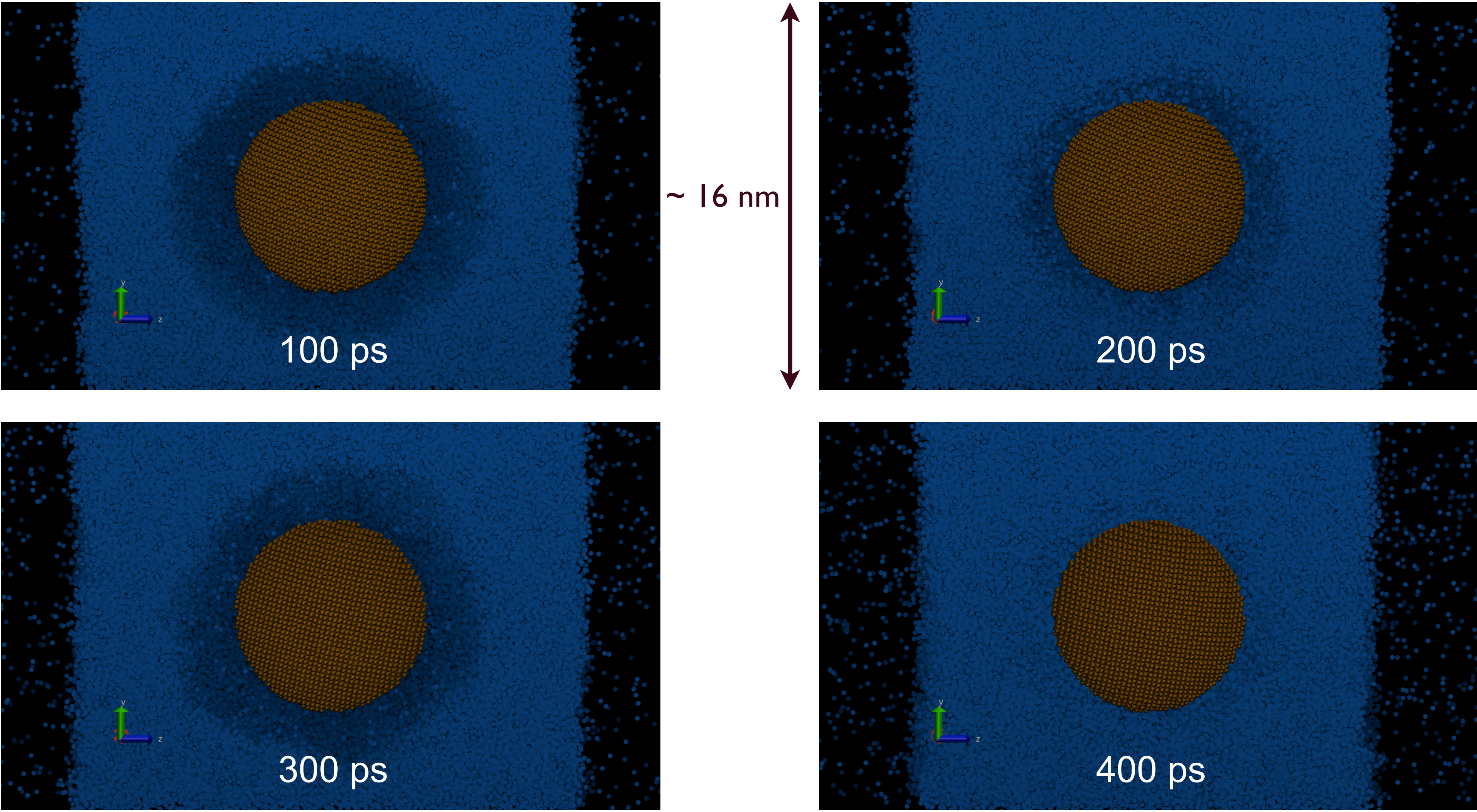
X-Y cross-section area

Small system - 16 × 16 nm^2

Big system - 23 × 23 nm^2

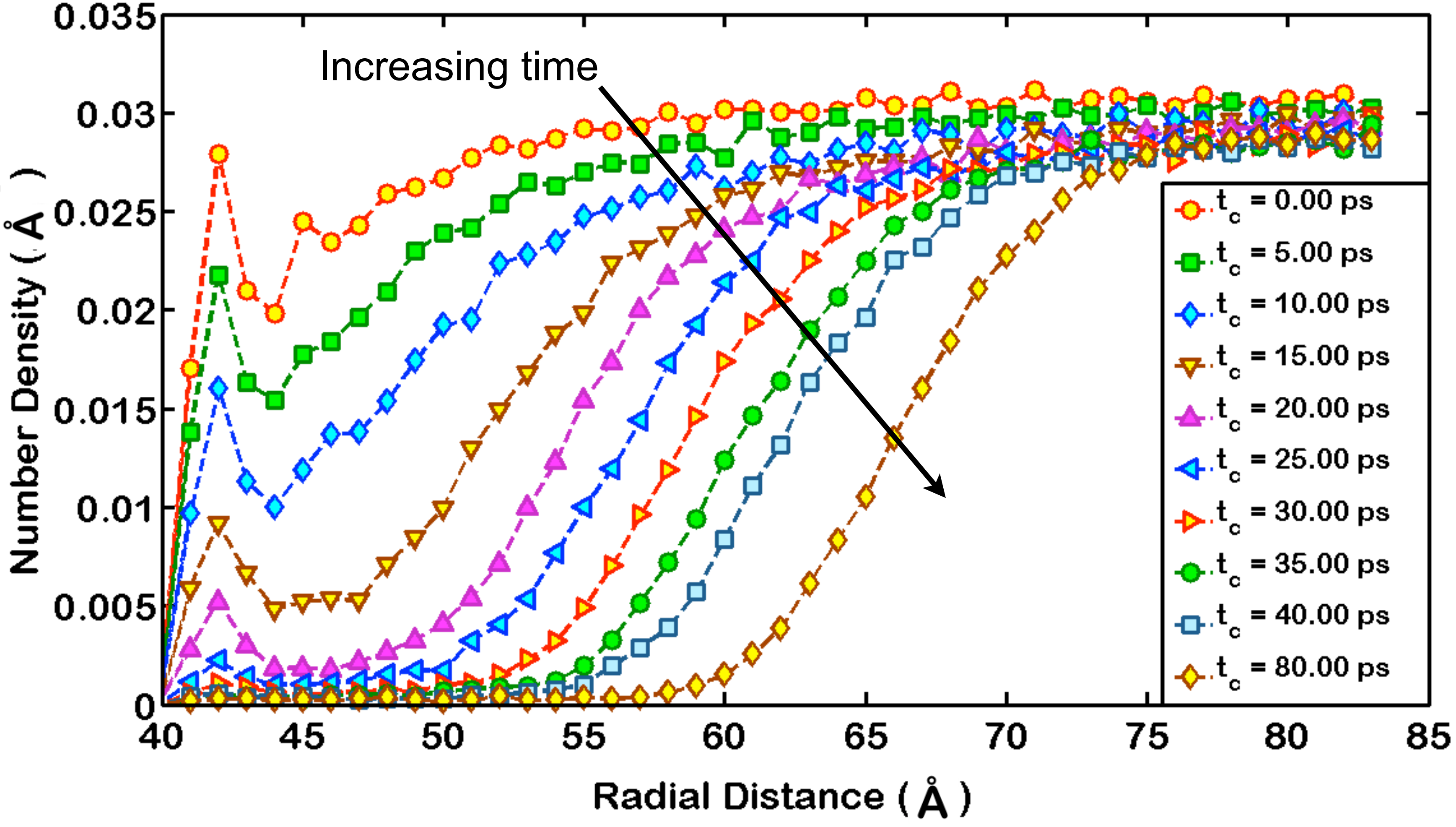


Nanoscale vapor cavitation demonstrated via MD for the first time



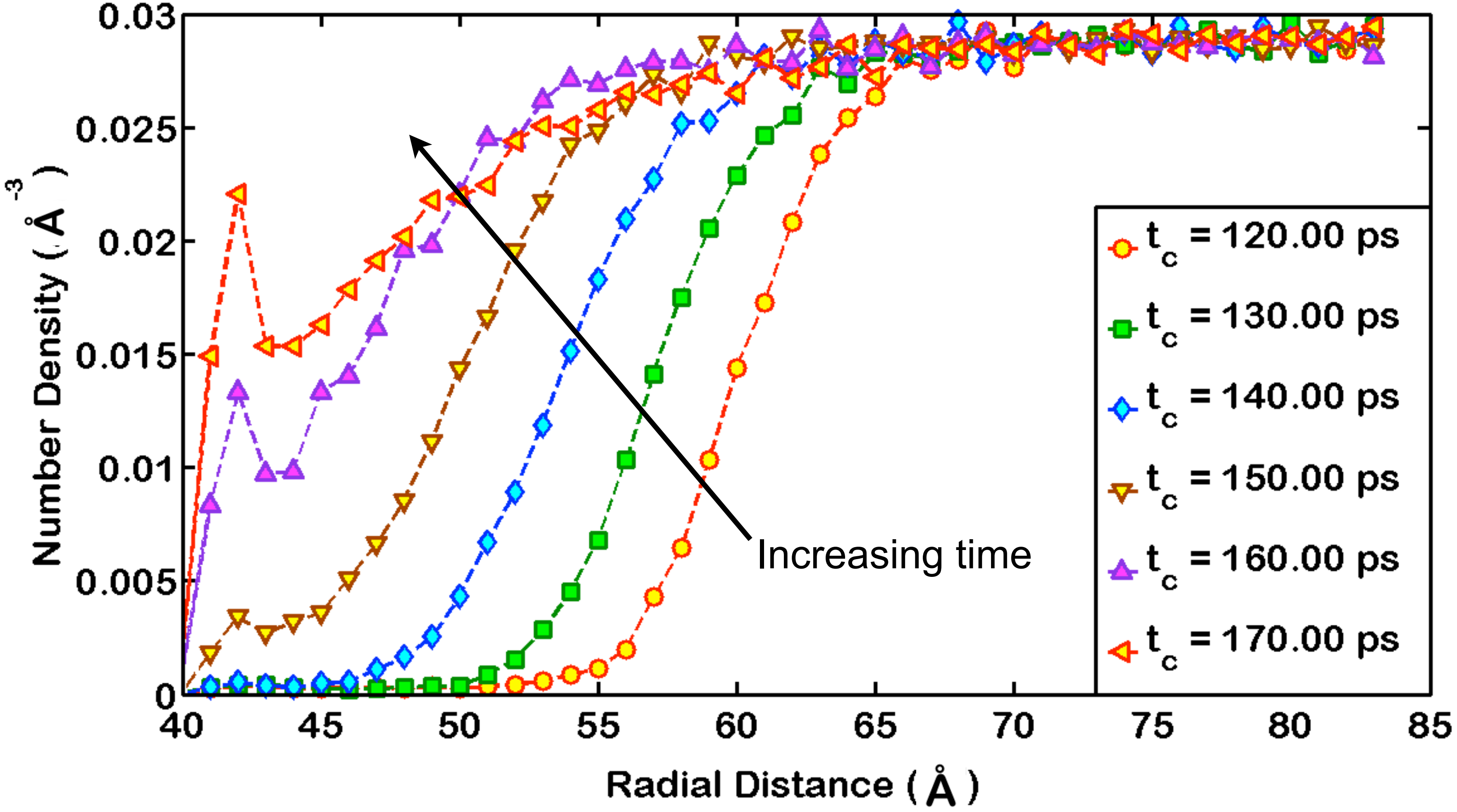
Initial T_{NP} = 1500 K

Formation of vapor upon cooling of NP – density profiles



Initial T_{NP} = 1500 K

Collapse of vapor upon cooling of NP – density profiles

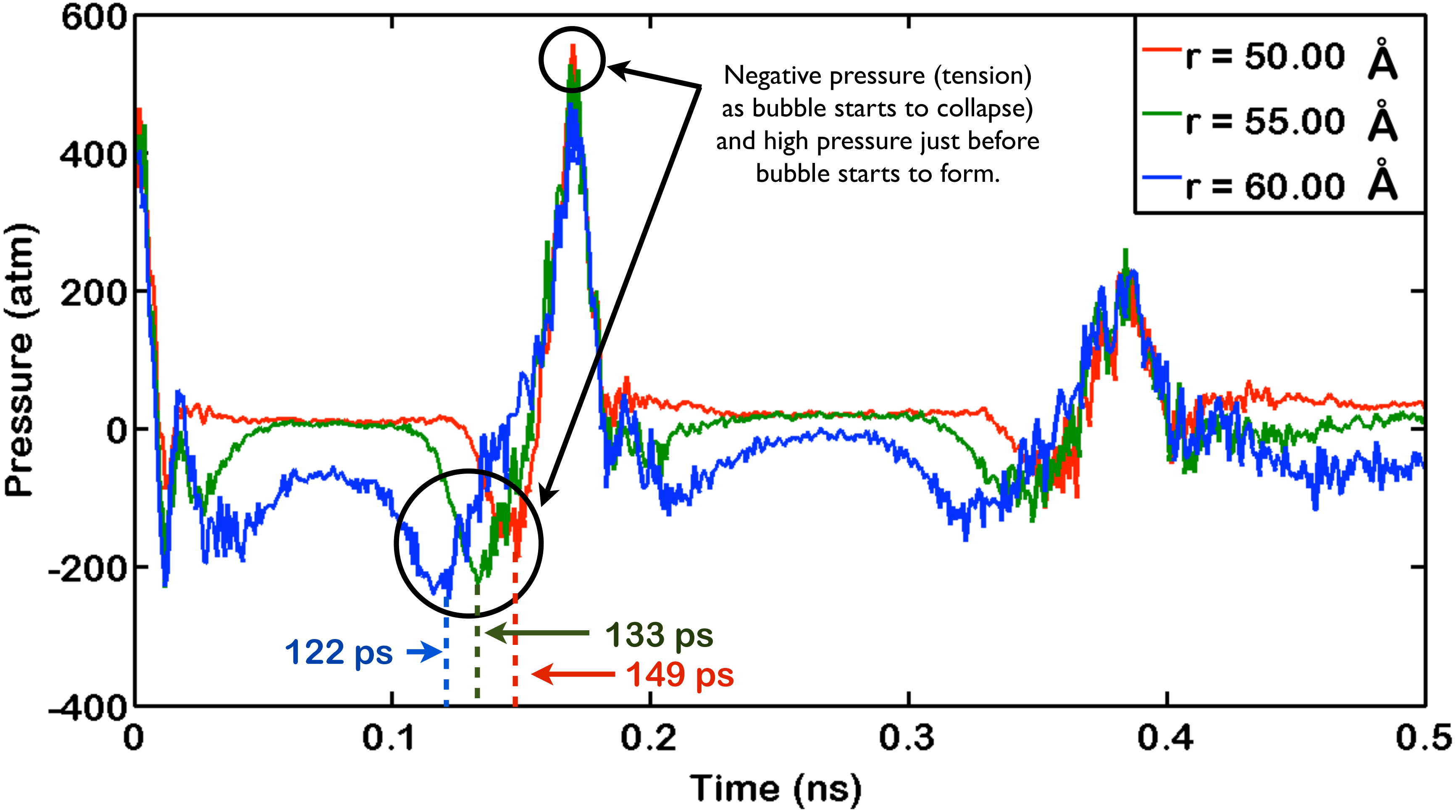


Initial T_{NP} = 1500 K

Hydrostatic pressure in spherical shells of the liquid

Initial T_{NP} = 1500 K

Shell thickness = 5 A°

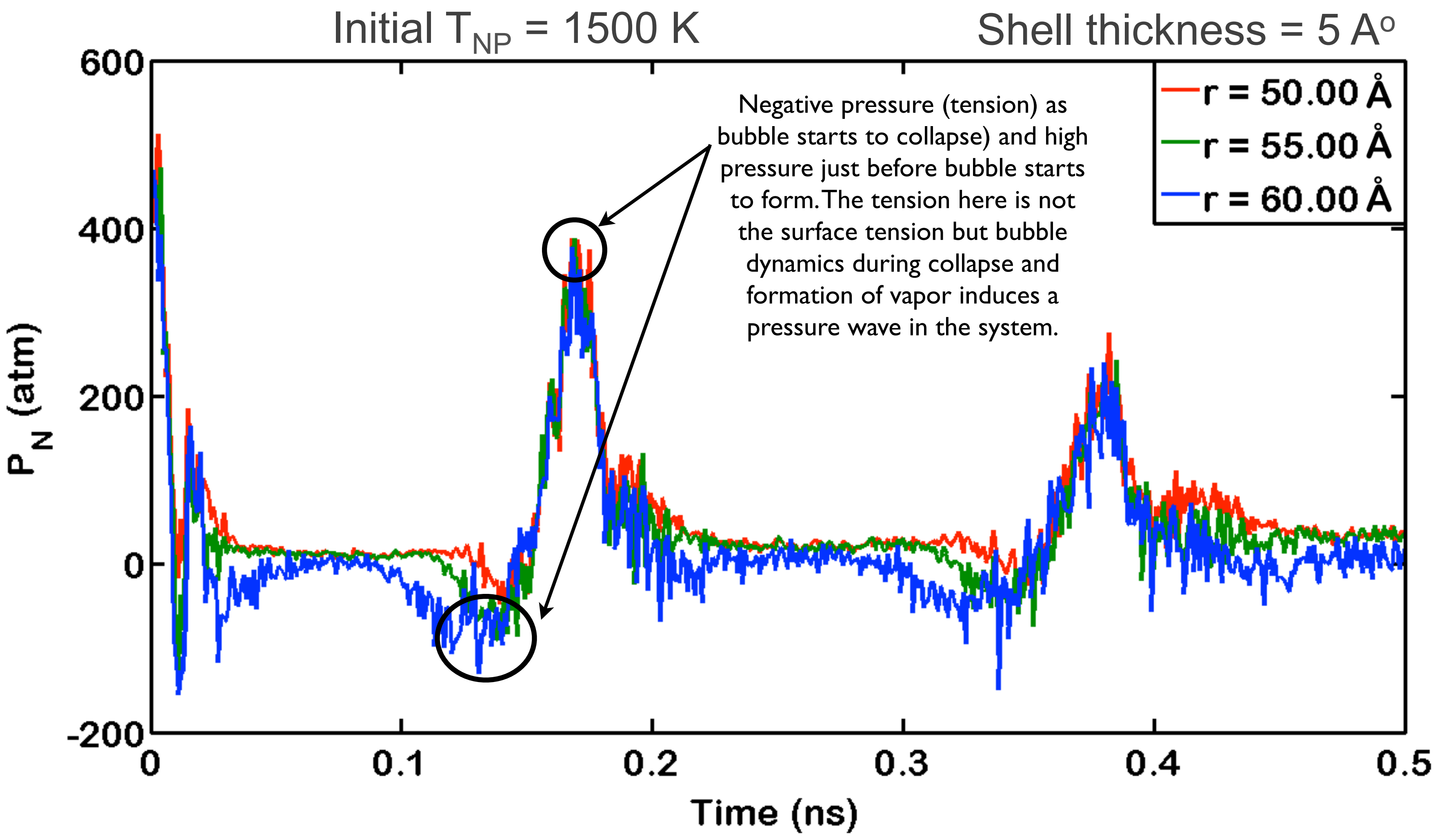


Negative pressure (tension) as bubble starts to collapse) and high pressure just before bubble starts to form.

Speed of bubble collapse = ~ 37 m/s

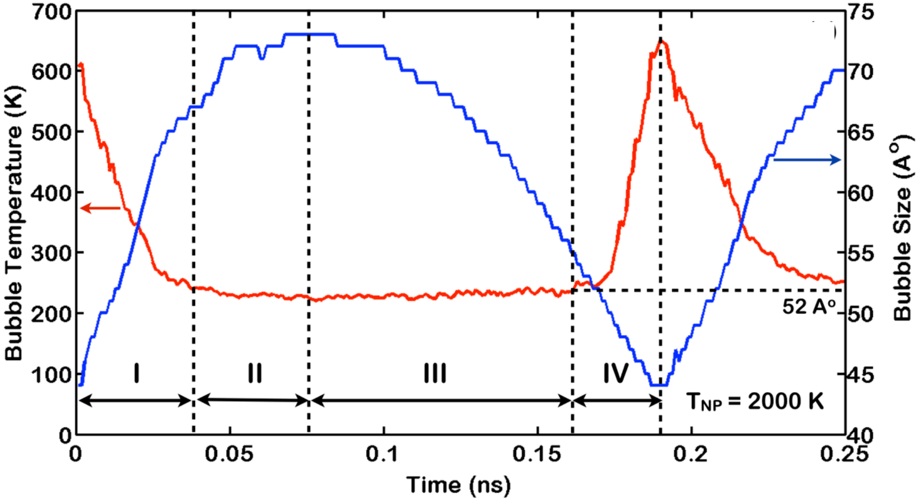
Consistent with bubble velocity calculations from bubble size evolution

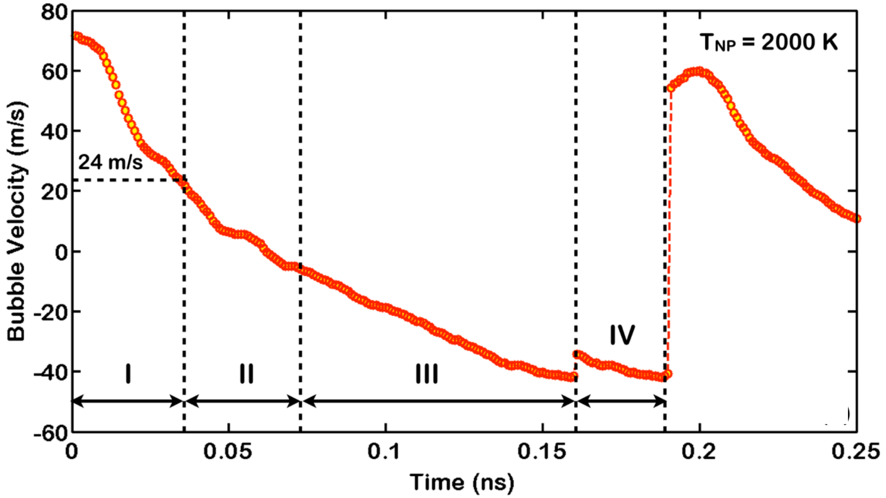
Hydrostatic pressure in spherical shells of the liquid



Negative pressure (tension) as bubble starts to collapse) and high pressure just before bubble starts to form. The tension here is not the surface tension but bubble dynamics during collapse and formation of vapor induces a pressure wave in the system.

Cavitation dynamics – 4 regimes





I - adiabatic/rapid expansion

II - isothermal expansion

III - isothermal collapse

IV - rapid heating due to liquid reestablishing the contact with hot nanoparticle.

Summary

- Bubble dynamics during collapse and formation of vapor induces a pressure wave in the system.

- The evolution of the bubble can be represented in 4 stages:
  - (I) adiabatic expansion;
  - (II) isothermal expansion;
  - (III) isothermal collapse and
  - (IV) rapid heating due to interaction with hot nanoparticle.

Final note

- MD simulations can complement imaging experiments in a wide variety of scenarios.

  - Investigate reactions on nanoscale surfaces.
  - Investigate lattice dynamics.
  - Investigate phase change.

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