Dynamic Structural Disorder In Supported Nanoparticles

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Previous Work

Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations

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Physical Review B **78**, 121404(R), 2008

Complex dynamics:
multiple-time scales, librational motion, fluctuating bonding

Simulations explain:
large structural disorder, Negative Thermal Expansion (NTE).

Librational Motion

MD @ 165 K

Brownian-like Motion

MD @ 573 K
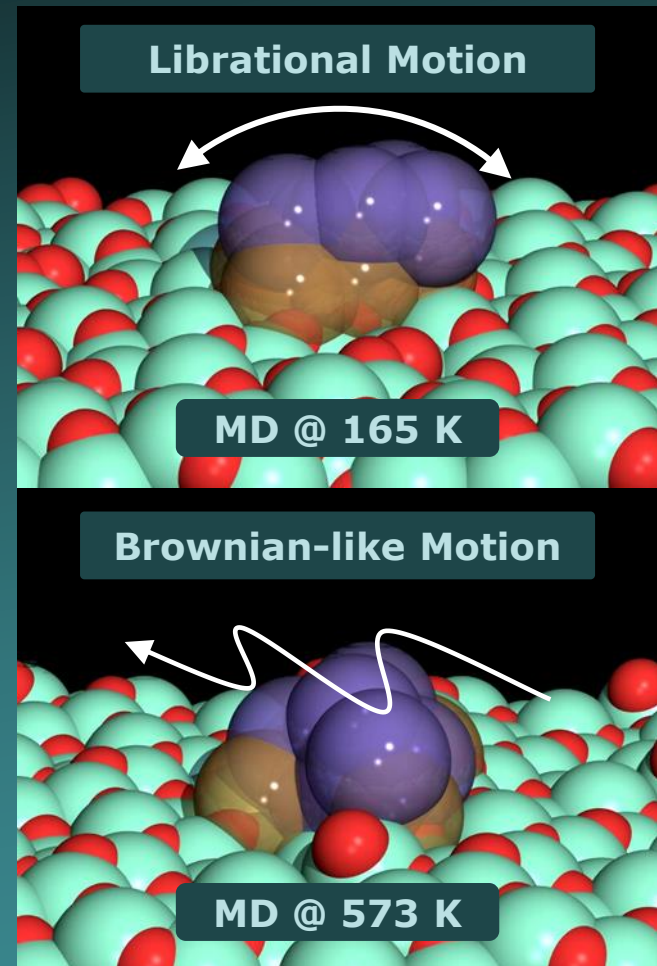
Pt_{10} on γAl_2O_3

Problem: Alumina-supported PtSn catalysts
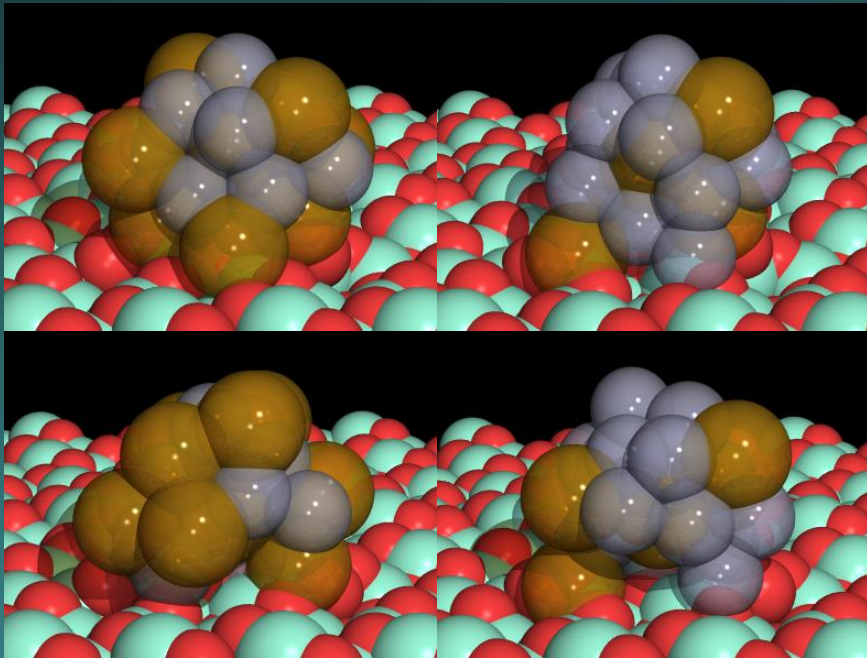
- **Nanoscale physics:**
  - **Differ from condensed matter**
  - **Experience surface effects, inhomogeneous**

- **Experimental probes:**
  - **Yield only averaged properties**

- **Need better understanding of:**
  - **Dynamical segregation**
  - **Transient bonding**

Theoretical Probe: DFT/MD

Atomistic electronic and structural information

Initial structures: randomly Sn-substituted Pt$_{20}$ cluster

DFT/MD

VASP
PBE Functional
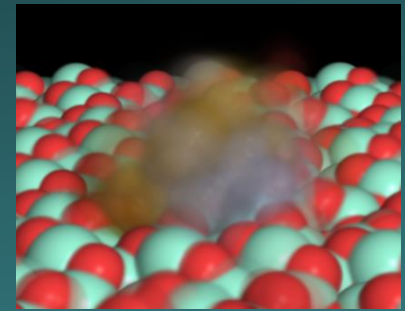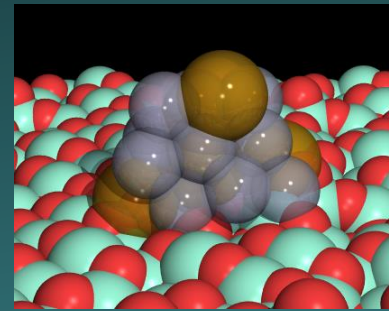**396 eV Cutoff**
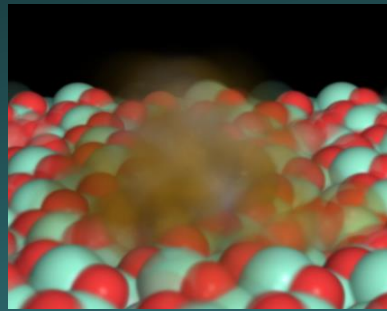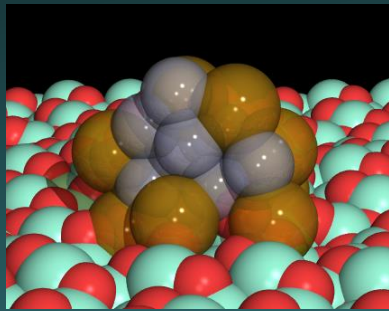**3 fs Steps**
3 ps Equilibration
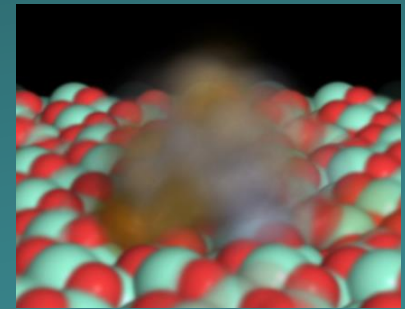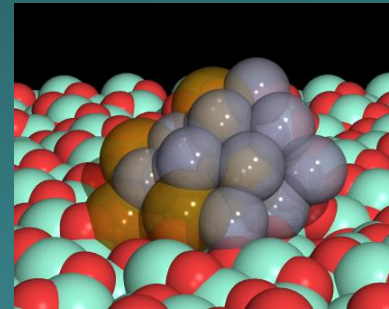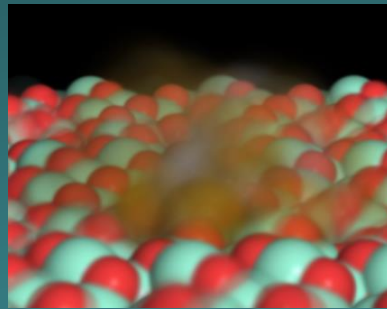**9 ps Runs (4/Temp)**
298 and 598 K

Structure: Segregation and Disorder

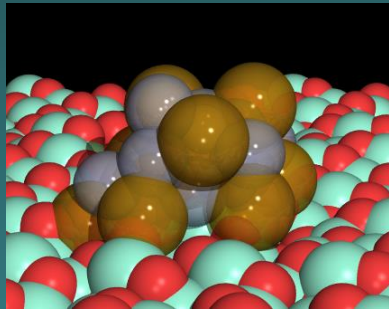

Pt$_{10}$Sn$_{10}$

Pt$_{15}$Sn$_5$

298 K

598 K

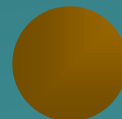Snapshot   Time Elapsed   Snapshot   Time Elapsed

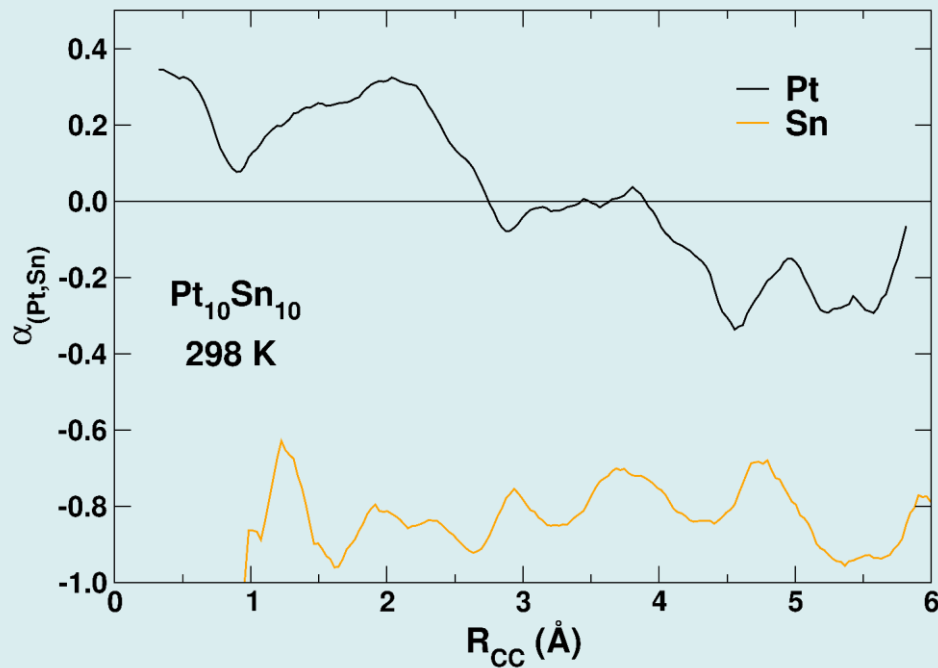Pt   Sn   Al   O

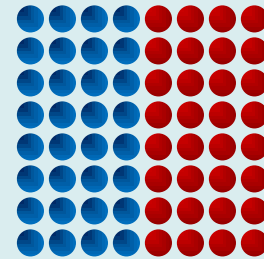# Inhomogeneous Structure: Surface Segregation

Cowley short-range order parameter

$$\alpha_A = 1 - {}^{n_{AB}}\!/\!_{n_{AM}x_B}$$

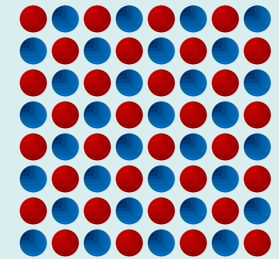$$n_{AM} = n_{AA} + n_{AB}$$
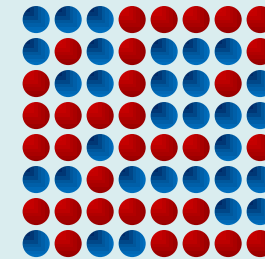

Correlated

$$0 < \alpha_A \leq 1$$

Anticorrelated

$$-1 \leq \alpha_A < 0$$

Random

$$\alpha_A \cong 0$$

Pt — Favors **Pt** NN in **core** and **Sn** NN near **surface**

Sn — **Always** favors Pt NN

Dynamic Structural Disorder (DSD)

Pair (Radial) Distribution Function (PDF/RDF):

$$g(R) = \frac{1}{N(N-1)} \sum_{i \neq j} \left\langle \delta\left(R - \left|\vec{R}_i(t) - \vec{R}_j(t)\right|\right) \right\rangle$$

Near neighbor (NN) PDF: $\tilde{g}(R)$ ($g(R)$ normalized within $R < R_c$)

Mean NN distance: **Mean-Square Radial Displacement (MSRD):**

$$\overline{R} = \langle R \rangle = \int dR \, R \, \tilde{g}(R) \qquad \sigma^2 = \left\langle \left(R - \overline{R}\right)^2 \right\rangle = \int dR \, \left(R - \overline{R}\right)^2 \tilde{g}(R)$$

Partition into Vibrational and Disorder:
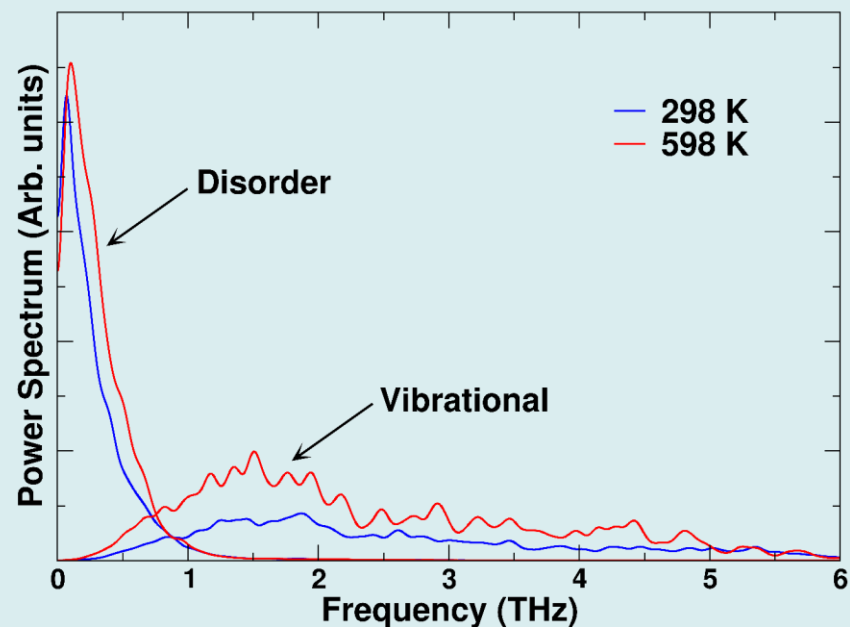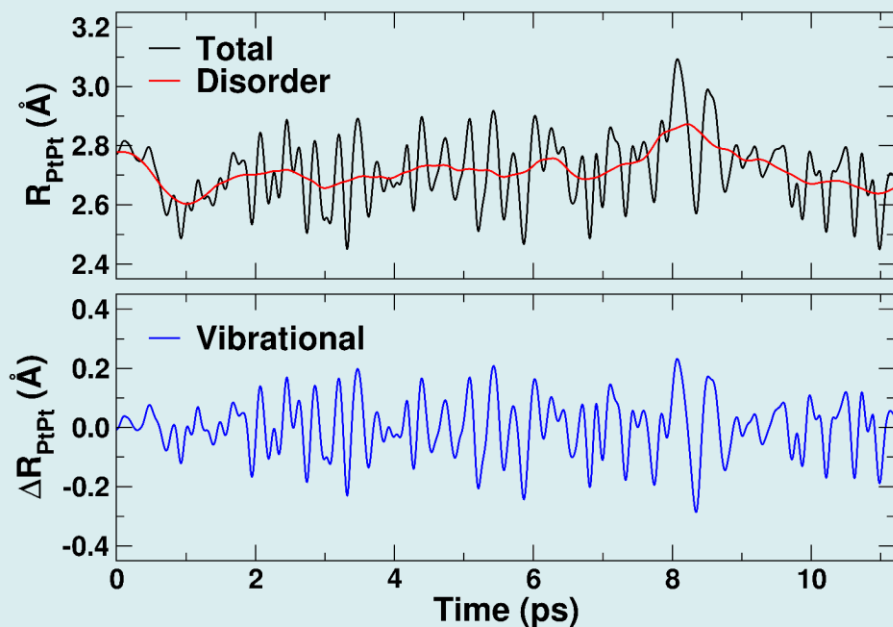
$$\sigma^2 = \sigma_{vib}^2 + \sigma_{dis}^2$$

Dynamic Disorder: Fluxional Bonds
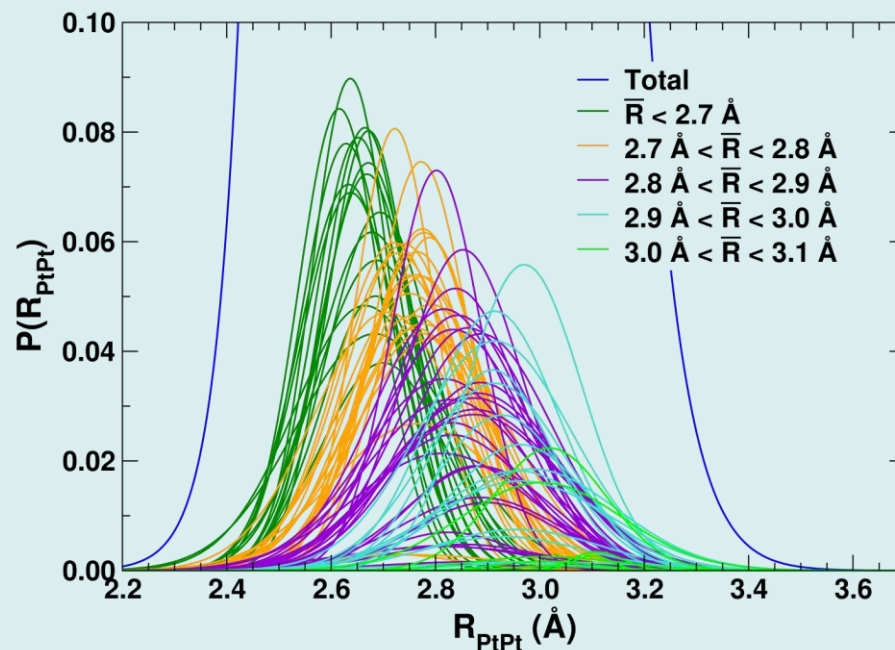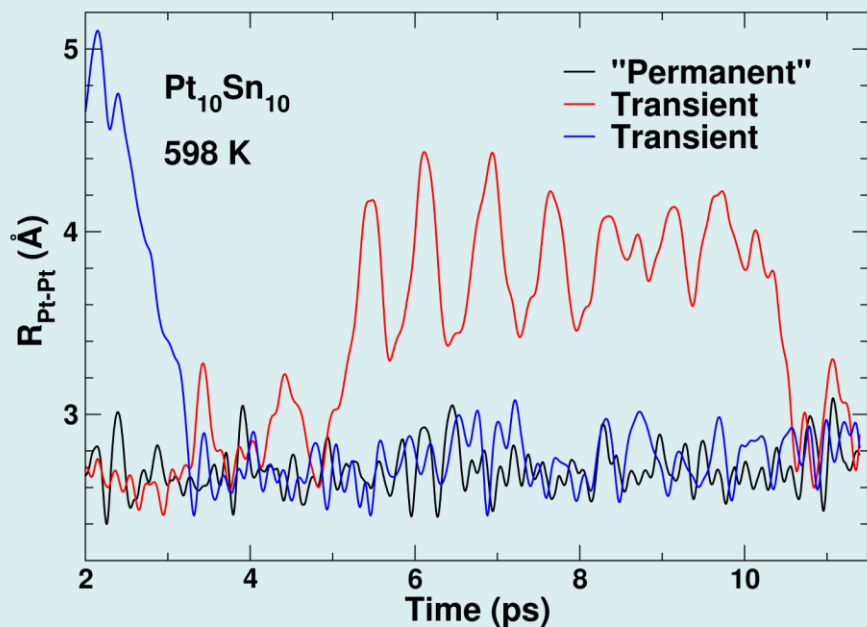
Fluxional Pt-Pt bonds (period > 6-8 ps) – **Large DSD**

Complex R_{PtPt} distribution – **Many inhomogeneous bonds**

Dynamic Disorder: Anomalous Behavior
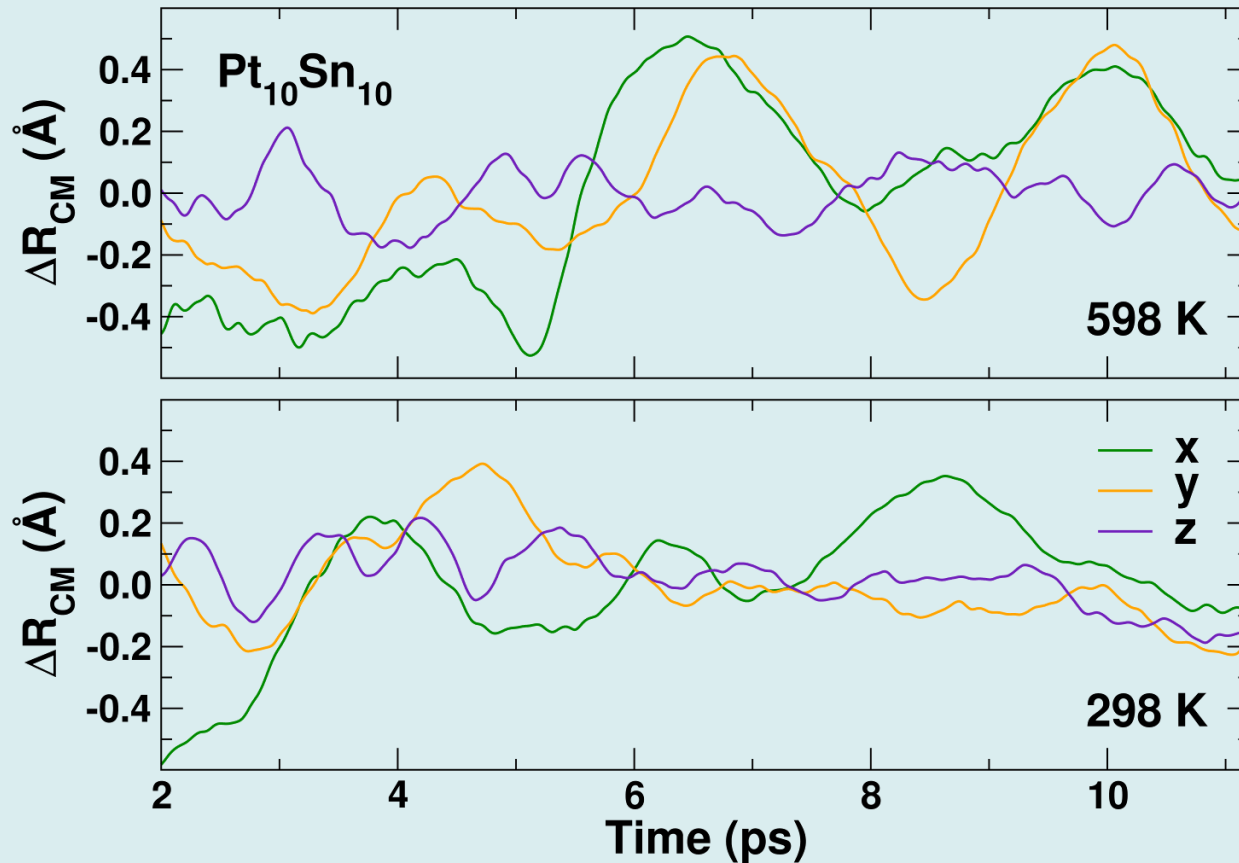

Traj. decomp. into **Vibrational** and **Disorder** components

Vibrational –   **Normal** behavior (200-400 fs periods)

Disorder –   Large, **anomalous**

Dynamic Disorder: Center of Mass Fluctuations

Librational (CM) motion mainly **parallel** (x,y) to support **Sub-THz** regime (2-4 ps periods)

Summary and Implications

- **Three dynamic regimes:**
    - **Fast bond vibrations**
    - **Stochastic CM motion**
    - **Slow fluxional bonding**

- **Disorder:**
    - **Dynamic, anomalous behavior**

- **Catalysis:**
    - **Must account for surface segregation**

- **XAFS Analysis:**
    - **Better models for systems with DSD**

Dynamic Structural Disorder
In Supported Nanoparticles

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Supported by:

Thank you...

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