Molecular Dynamics Simulations of Supported Pt Nanoclusters

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A Brief Outline

- Introduction and Background

- Constructing a Physical Model

- Details of the Simulation

- Results and Conclusions

- Summary and Acknowledgements

What is Nanocatalysis?

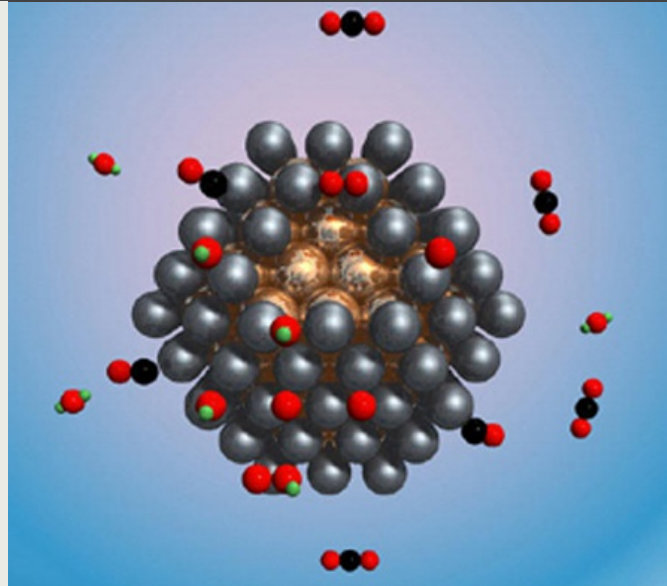The application of nanoscale materials for increasing catalytic activity.

Increase surface area of catalyst.

Objectives:

- 100% selectivity

- extremely high activity

- low energy consumption

- long lifetime.

Applications:

- Catalytic converters

- Petroleum reformation

- Gasification of biomass for biofuels

Previous Investigation of Nanoclusters

- Many properties of nanocatalysts not very well understood.

- X-ray absorption spectroscopy experiments have found unusual characteristics of supported nanoclusters.

- DFT/MD calculations employed to investigate behavior of nanoclusters

- Dynamic methods are ideal to probe the complex, dynamical nature of nanoscale catalytic processes

Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations
F. Vila, J. J. Rehr, J. Kas, R. G. Nuzzo, A.I. Frenkel

Operando Effects on the Structure and Dynamics of Pt_nSn_m/γ -Al_2O_3 from Ab Initio Molecular Dynamics and X-ray absorption Spectra
Fernando D. Vila, John J. Rehr, Shelly D. Kelly, Simon R. Bare

The Goal

DFT/MD calculations are extremely effective for these systems

But, they are extremely computationally intensive:

2×10^4 cpu h required for a time evolution of only 8.5 ps!

The objective of this simulation is to employ a model potential to replicate the results of the ab-initio DFT/MD calculations at a fraction of the time cost, with the ability to probe the dynamics of long time evolutions.

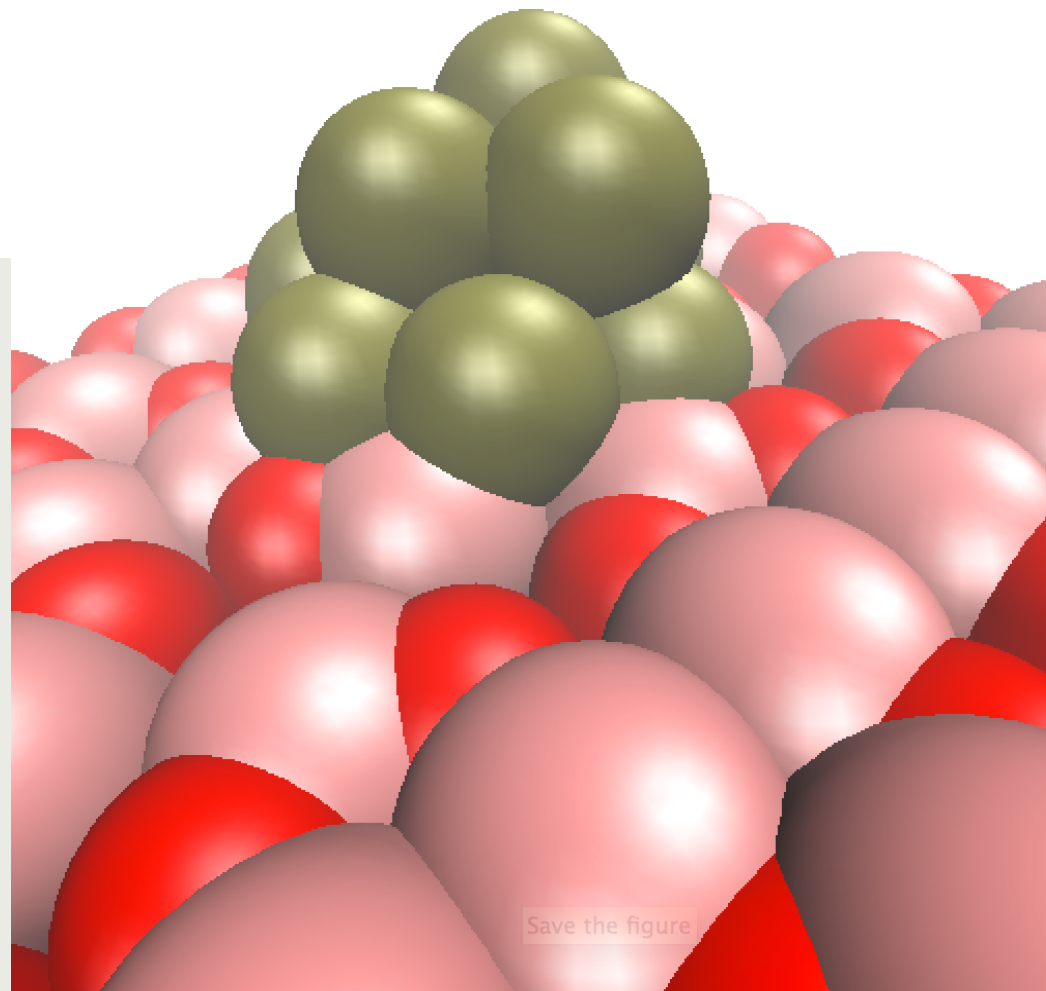3DMD CPU times for an evolution of 50 ps (in seconds) vs. system size.

With surface

CPU Time vs. Num Atoms

• • CPU Time

—— Least squares fit
3.997e-03x^2 + 4.762e-02x
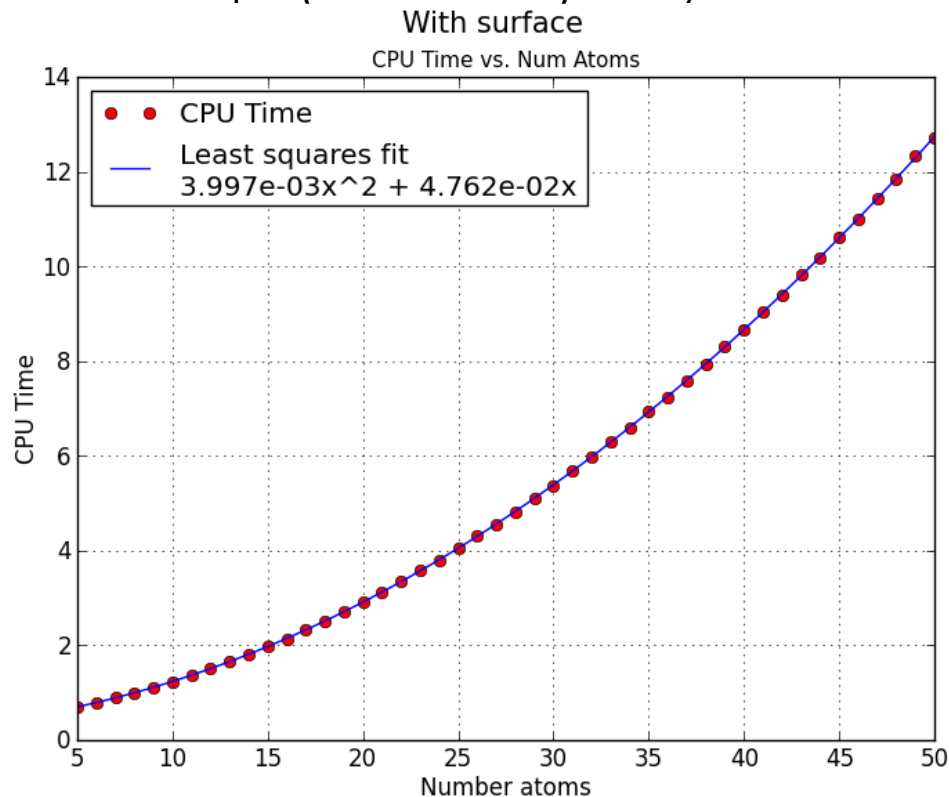
Total number of atoms in the systems used for these measurements:
N+74 surface atoms

Constructing a Physical Model

□ A look at our system

□ Potentials

□ Thermodynamics

The System

Pt$_{10}$ cluster supported by γ-Al$_2$O$_3$ monolayer surface

The Cluster: A Sutton-Chen Potential

$$U_{Tot} = \varepsilon \sum_i \left[\frac{1}{2} \sum_{j \neq i} V(r_{ij}) - c\sqrt{\varrho_i} \right]$$

$$V(r_{ij}) = \left(\frac{a}{r_{ij}} \right)^n$$

$$\varrho_i = \sum_{j \neq i} \left(\frac{a}{r_{ij}} \right)^m$$

Model for the Pt$_{10}$ nanocluster, an approximate many-body potential.

The Sutton-Chen potential was designed specifically for transition metals and their alloys.
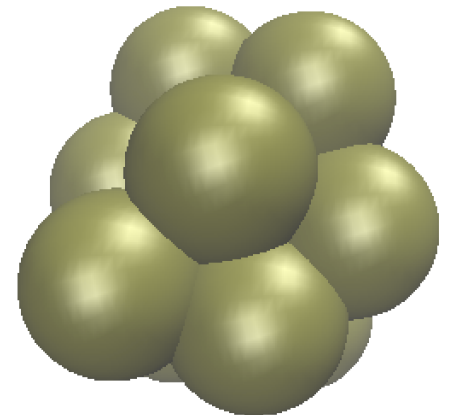
For Platinum:

$$\varepsilon = 1.9835 \times 10^{-2} \ eV$$
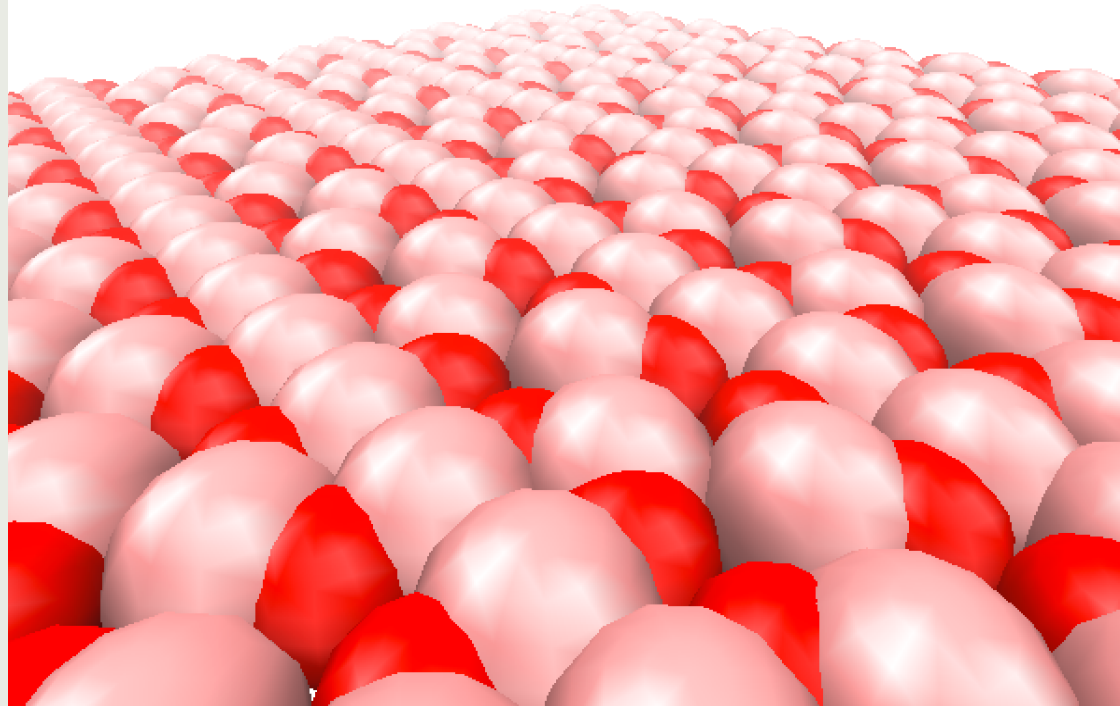$$a = 3.92 \ \breve{A}$$
$$c = 34.408$$
$$n = 10$$
$$m = 8$$

The Surface: A Harmonic Potential

$$U_H = \frac{1}{2}k\,r^2 \qquad k = 6.0\ \frac{eV}{\mathring{A}^2}$$

The γ-Al_2O_3 surface is a monolayer of atoms oscillating about fixed positions.

These oscillations are described by a simple harmonic potential.

Cluster-Surface Interaction:
A Lennard-Jones Potential

$$U_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$
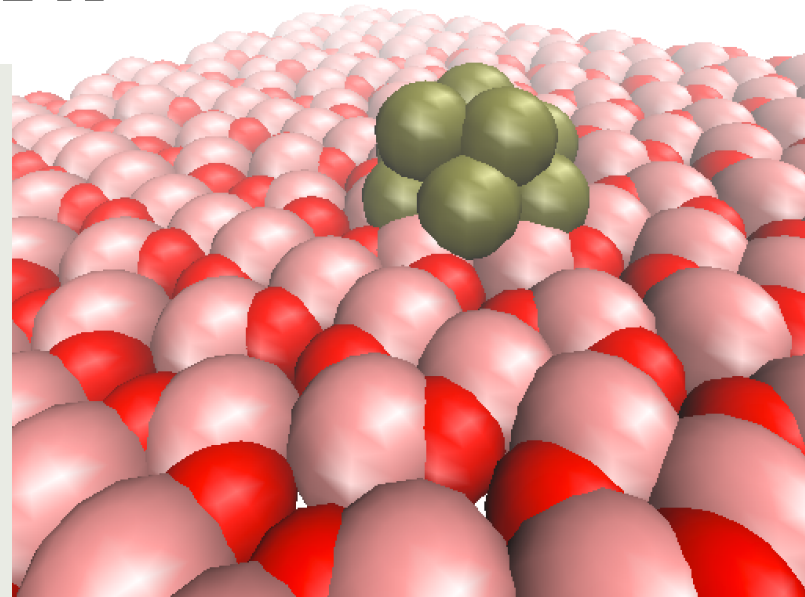
Pt-O:

$\varepsilon = 0.228\ eV$
$\sigma = 1.866\ \check{A}$

Pt-Al:

$\varepsilon = 0.044\ eV$
$\sigma = 2.42\ \check{A}$

The parameters for the Pt-O and Pt-Al interactions were obtained by reverse-engineering radial distribution functions of ab-initio calculations.
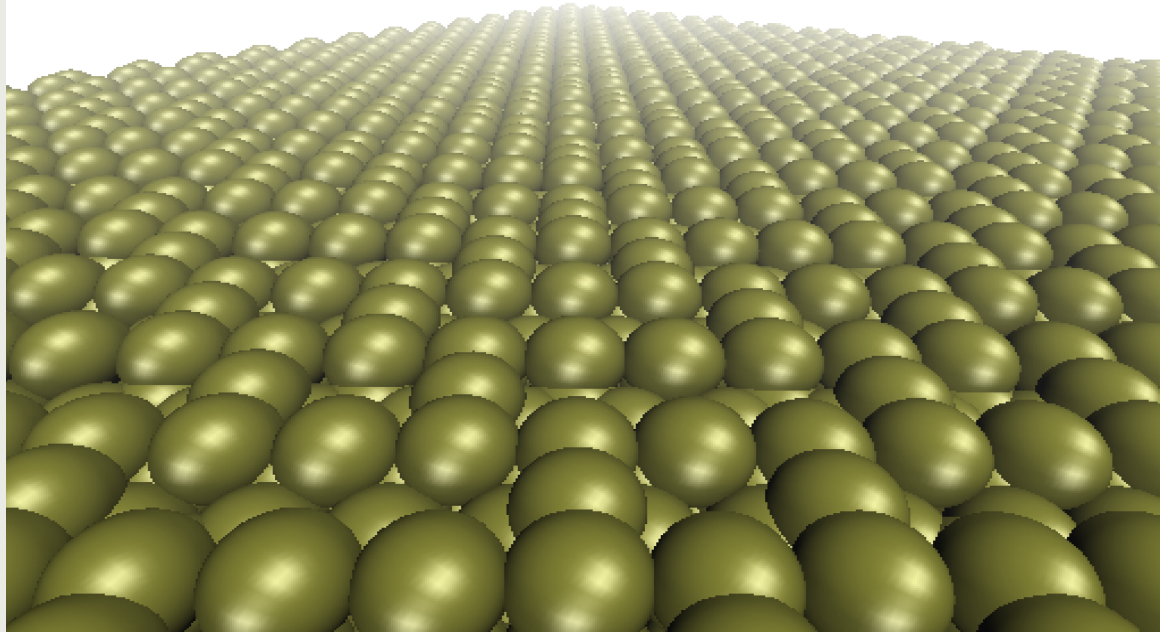
Thermodynamics of the Nanocluster

The thermal properties of nanoparticles differ substantially from those of macroscopic condensed matter.

The mean energy of the system is not sharply defined, but rather fluctuates according to the number of atoms in the system, due to finite size effects.
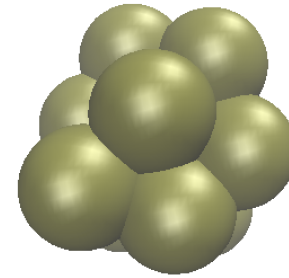
VS

Details of the Simulation

- Velocity-verlet integration scheme

- Velocity-scaling thermostat

- Nosé-Hoover thermostat

- Visualization

Velocity-Verlet Algorithm

The velocity-verlet integration scheme is derived from a Taylor's expansion of Newton's Laws of motion.

It can be shown that the algorithm produces an error of $O(h^3)$.

$$r(t+h) = r(t) + h\,v(t) + \frac{1}{2}h^2\frac{F(t)}{m}$$

$$v(t+h) = v(t) + \frac{1}{2}h\frac{F(t) + F(t+h)}{m}$$

$$F_{Cluster} = -\frac{\partial}{\partial r}(U_{SC} + U_{LJ})$$

$$F_{Surface} = -\frac{\partial}{\partial r}(U_{H} + U_{LJ})$$

Thermostats

Velocity-scaling: scale the velocities by a factor λ.

The frequency at which the rescaling occurs is ad-hoc. Our system thermalizes every 200 fs.

The Nosé-Hoover thermostat introduces a virtual variable ζ into the equations of motion.

The Nosé-Hoover thermostat is the preferred method for constant temperature MD simulations.

$$K = \frac{1}{2} \sum_i^N m_i v_i^2$$
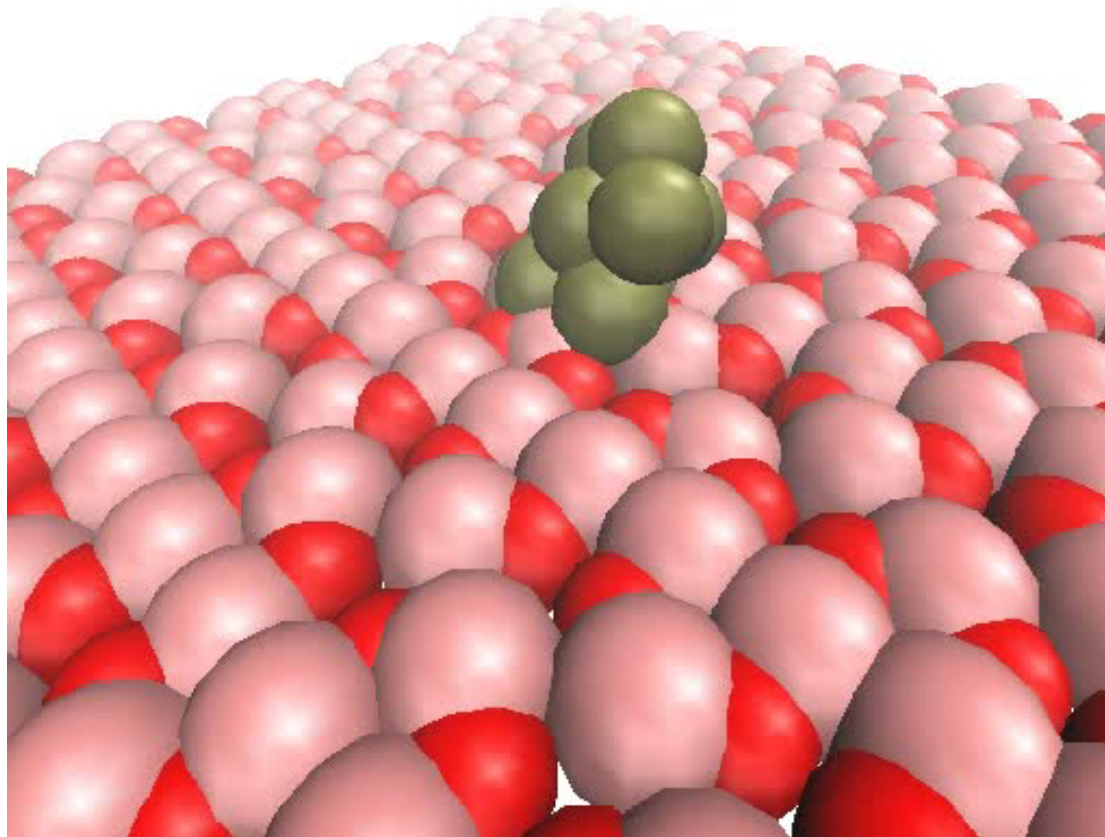
$$K = \frac{1}{2} N_{DoF} \, k_B \, T_{inst}$$

$$\lambda = \sqrt{\frac{T_0}{T_{inst}}}$$

$$Q = N_{DoF} \, k_B \, T_0 \, \tau^2$$

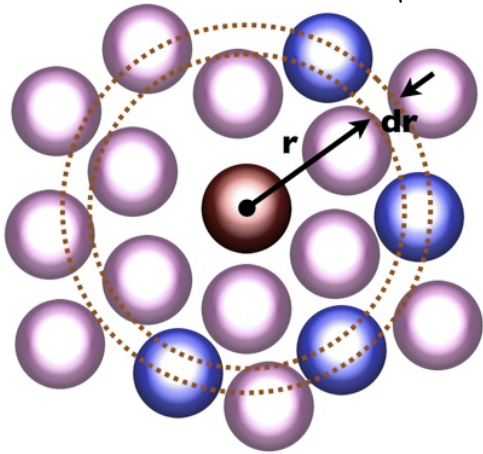$$\zeta = \frac{2K - N_{DoF} \, k_B \, T_0}{Q}$$

Visualization

Results and Conclusions

- Radial distribution functions

- Debye-Waller factors

- Energy and temperature fluctuations
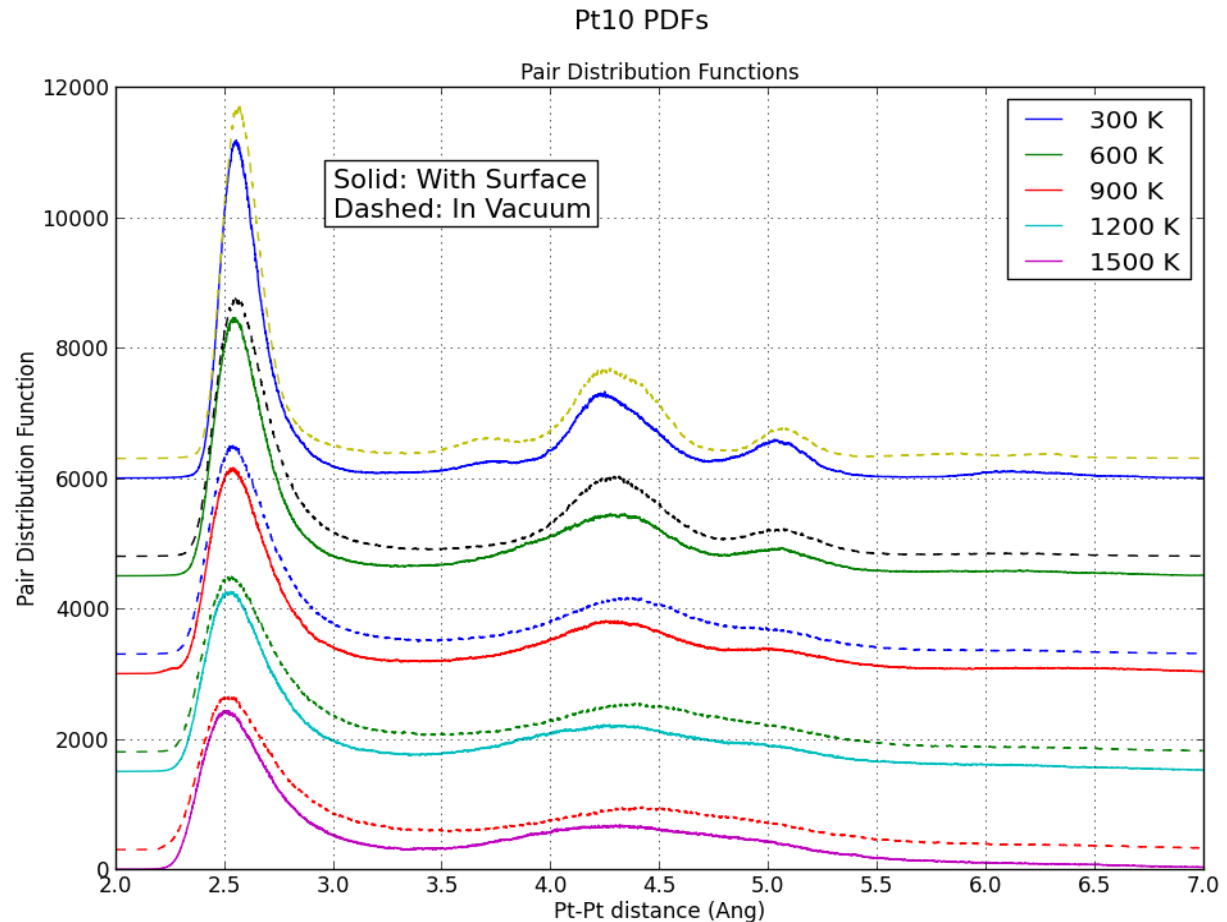
- Diffusion coefficients

- Structural disorder

Pt-Pt Radial Distribution Functions

$$g(r) = 4\pi r^2 \varrho dr$$

Can see 1st, 2nd, 3rd, shells at low temperatures.

Broadening of RDF is a sign of increasing disorder.

Pt10 PDFs

Pair Distribution Functions

Solid: With Surface
Dashed: In Vacuum

- 300 K
- 600 K
- 900 K
- 1200 K
- 1500 K

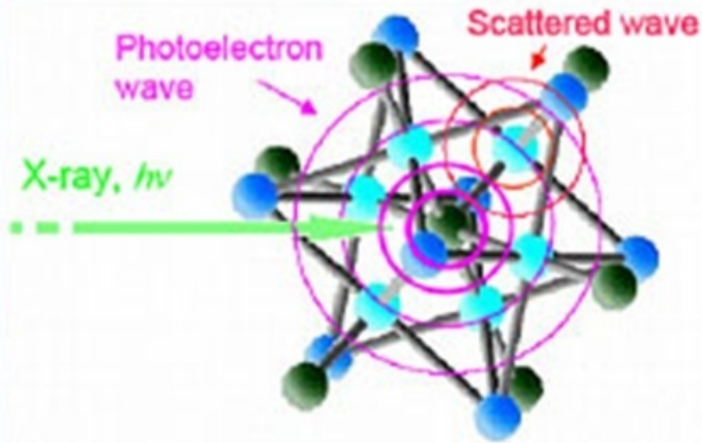Pair Distribution Function

Pt-Pt distance (Ang)

Pt-O RDFs

The Pt-O RDFs give an indication of where the Pt atoms are with respect to the Alumina surface.

The first peak of the system are the surface-bound platinum atoms.
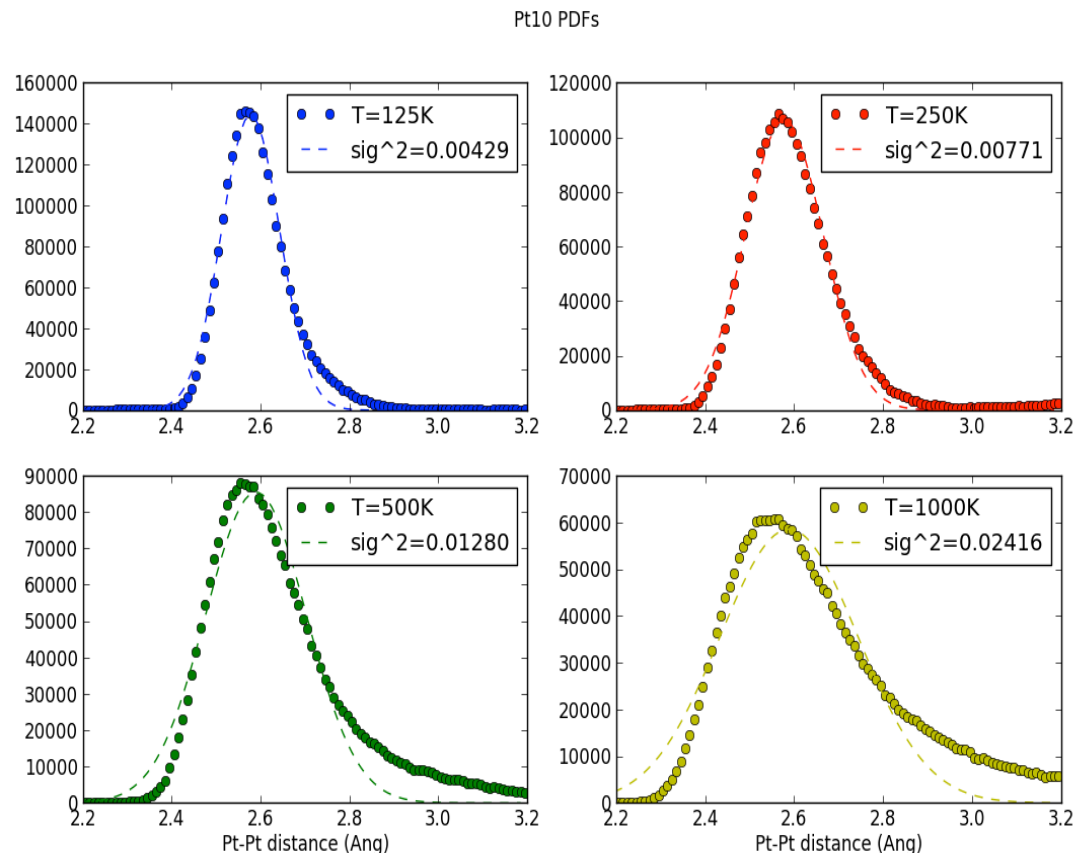

Pt-O

Pair Distribution Functions
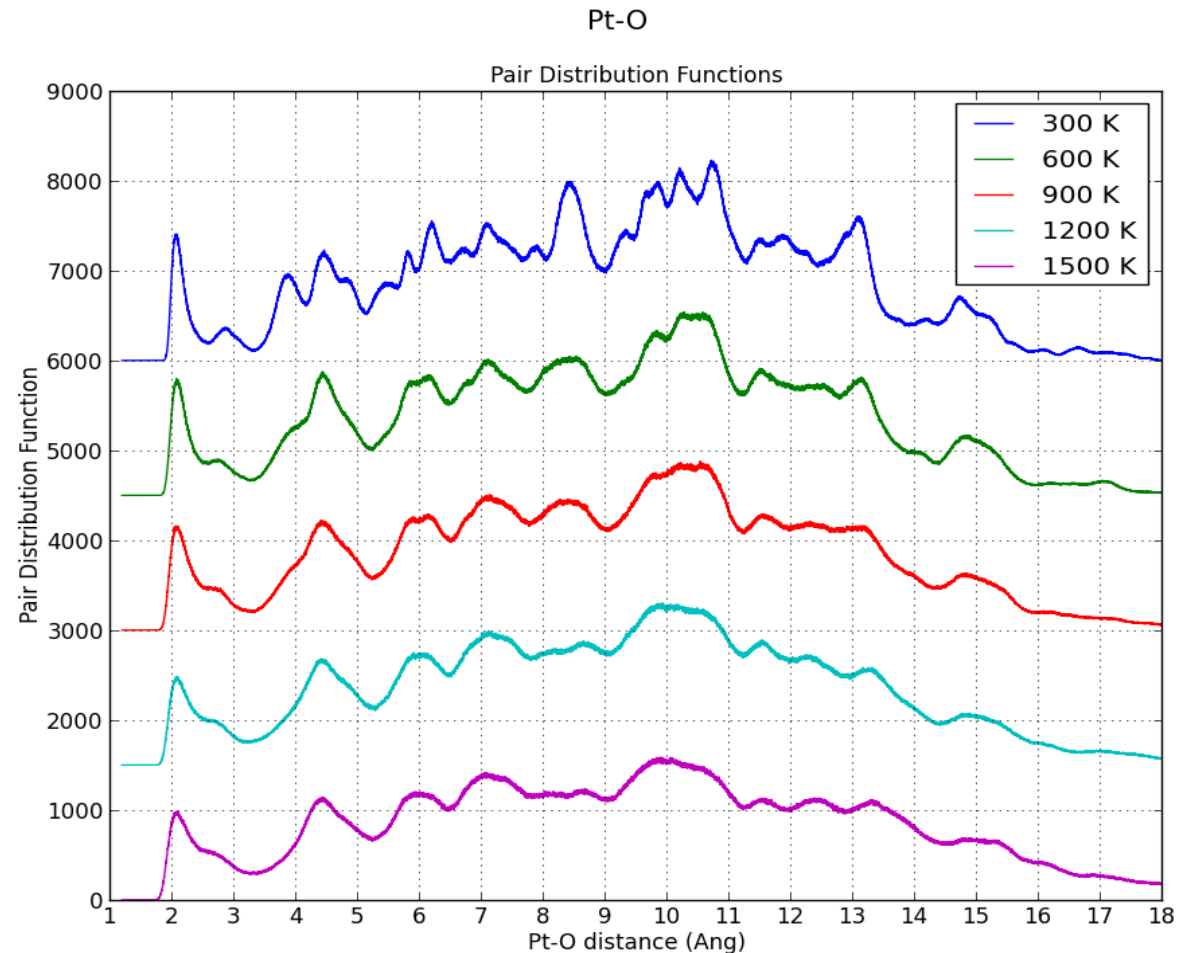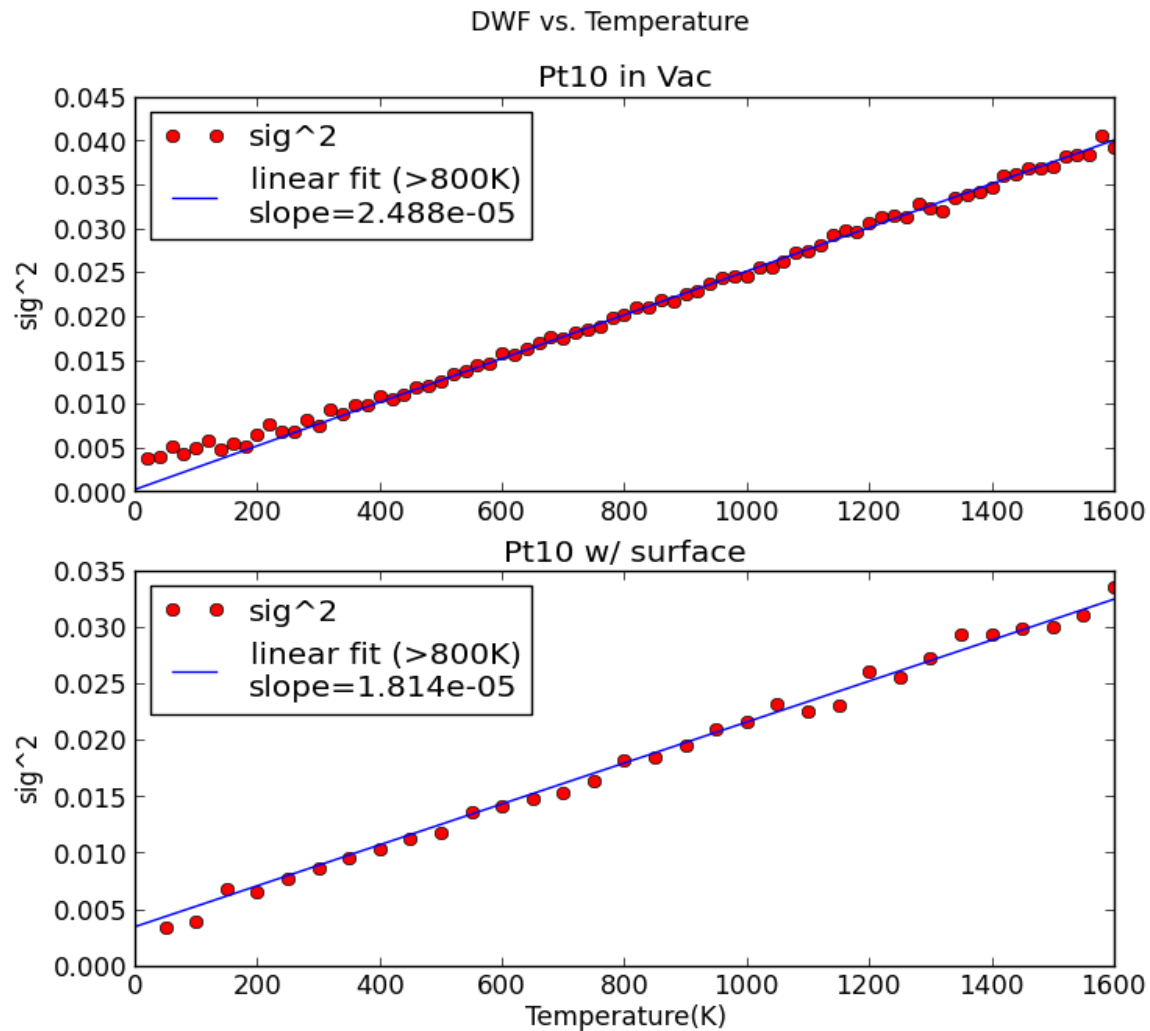
Debye-Waller Factor

The DW factor generalizes the thermal motion of the atoms in the cluster.

The DW factor is directly proportional to the σ^2 obtained from the first shell of the RDF.

Pt10 PDFs

DW Factors vs. Temperature
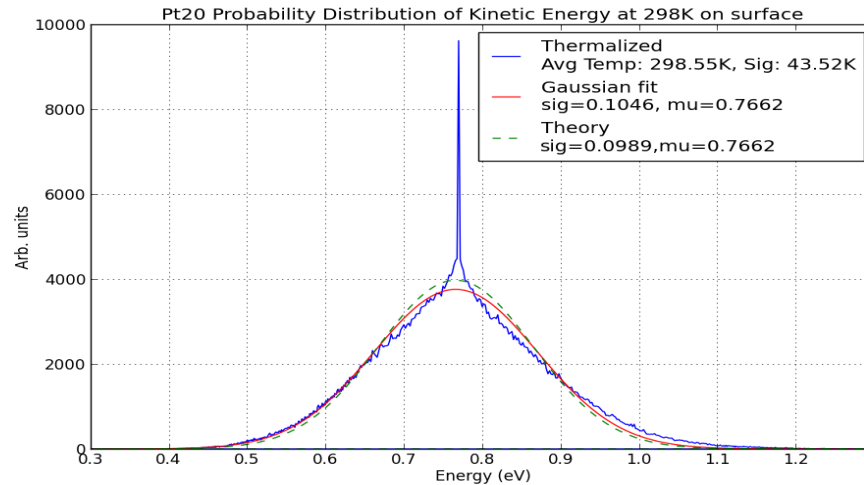

DWF vs. Temperature

Energy Fluctuations: Velocity-Scaling

A look at the probability distribution of the kinetic energy of the system reveals fluctuations proportional to $(3N)^{-1/2}$ as predicted by theory.
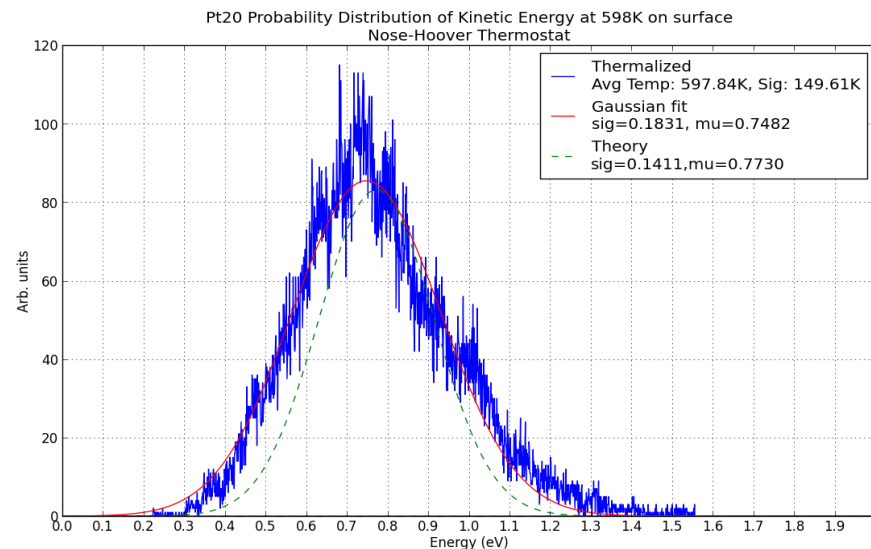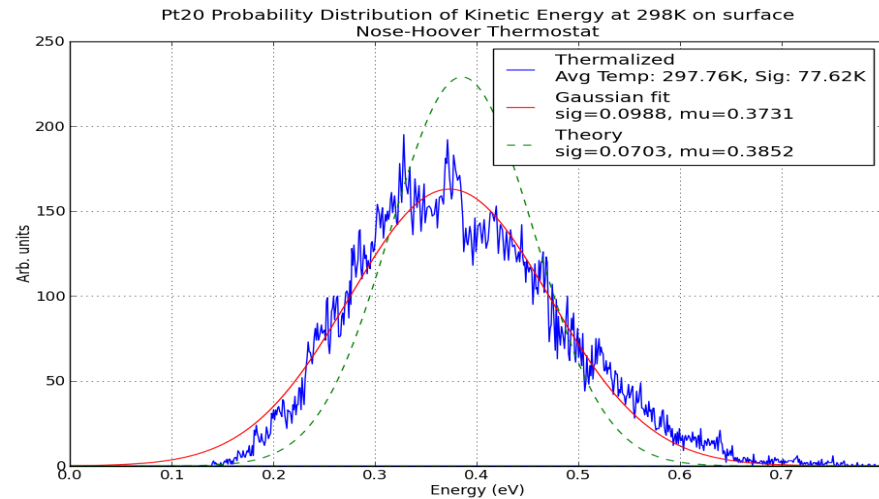
The sharp peak demonstrates the tendency of the velocity-scaling thermostat to bias the expected energy for a given temperature.
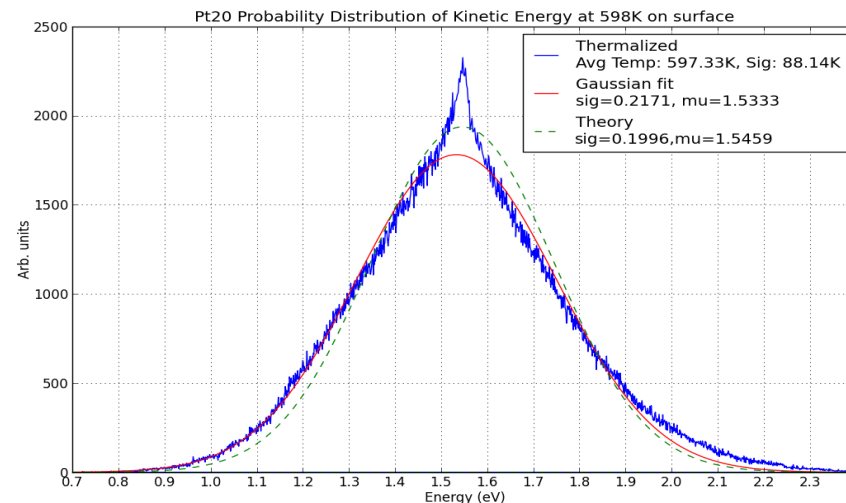
Energy Fluctuations: Nosé-Hoover

The fluctuations of the Nosé-Hoover thermostat give correct mean temperatures, but have fluctuations slightly greater than predicted by theory.

However, the system is no longer biased to be strictly in thermodynamic equilibrium at low temperatures.

Pt20 Probability Distribution of Kinetic Energy at 298K on surface
Nose-Hoover Thermostat

Thermalized
Avg Temp: 297.76K, Sig: 77.62K
Gaussian fit
sig=0.0988, mu=0.3731
Theory
sig=0.0703, mu=0.3852

Pt20 Probability Distribution of Kinetic Energy at 598K on surface
Nose-Hoover Thermostat

Thermalized
Avg Temp: 597.84K, Sig: 149.61K
Gaussian fit
sig=0.1831, mu=0.7482
Theory
sig=0.1411,mu=0.7730

The Diffusion Coefficient

The diffusion coefficient describes the motion of the atoms within the nanocluster, e.g. how often atoms exchange relative positions.
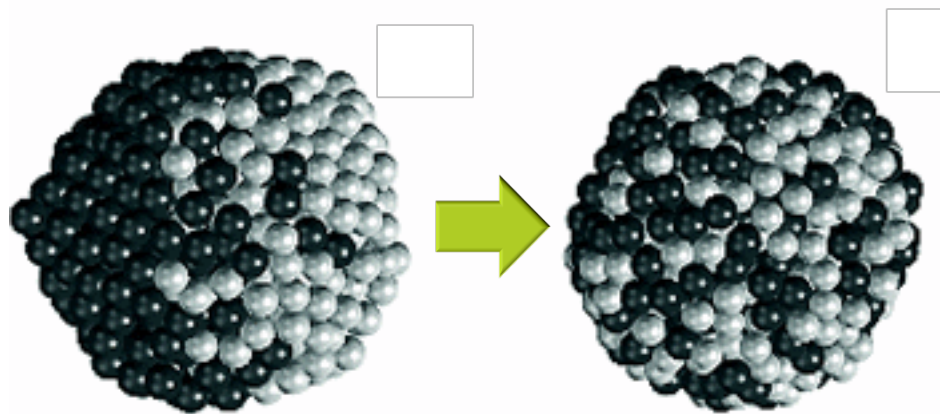
The diffusion coefficient also gives an indication of how an adsorbed nanoparticle migrates to another site on a surface.

The Green-Kubo method uses the particle velocity autocorrelation function to calculate the coefficient.

$$D = \lim_{t \to \infty} \frac{1}{6t} \left(\frac{1}{N} \sum_{i}^{N} |r_i(t) - r_i(0)|^2 \right)$$
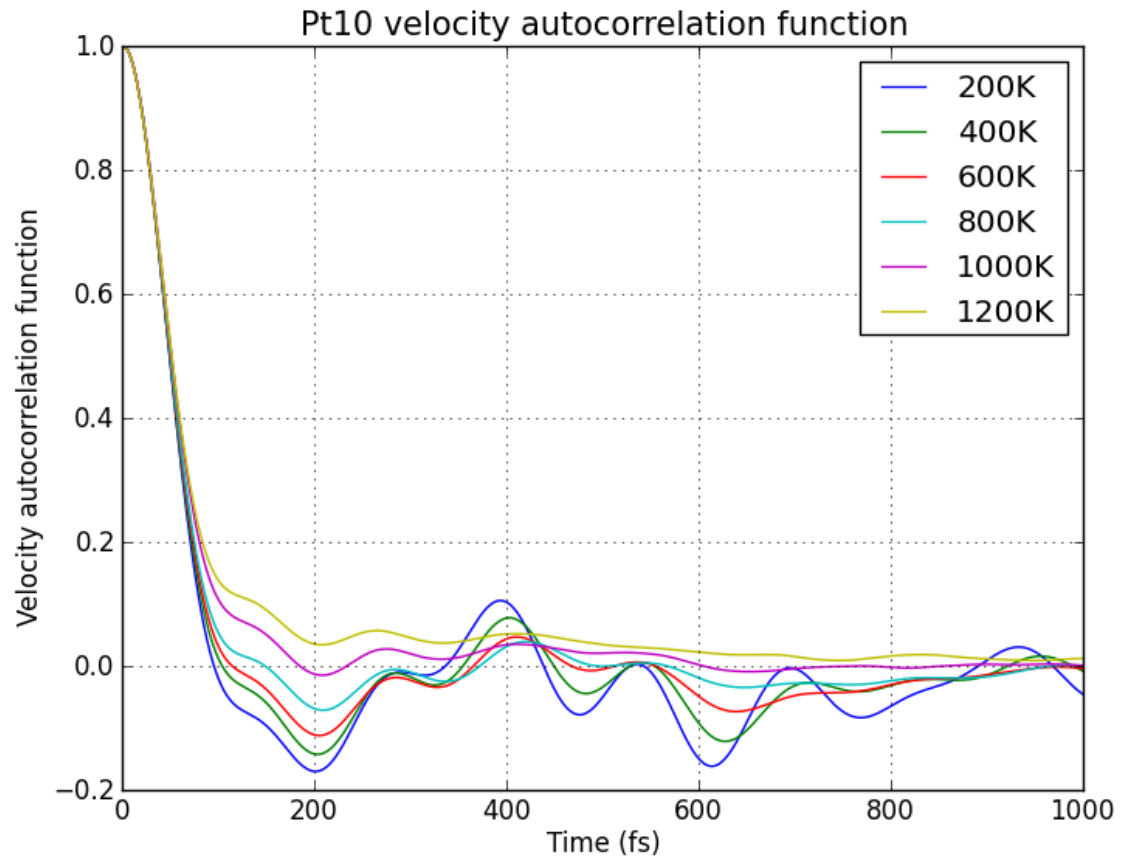
Or equivalently:

$$D = \frac{1}{3} \int_{t=0}^{\infty} \left[\frac{1}{N} \sum_{i}^{N} v_i(0) \cdot v_i(t) \right] dt$$

Velocity Autocorrelation Function

The velocity autocorrelation function gives an indication of the timeframe in which an atom loses "memory" of its initial velocity as the system is perturbed by other forces.

Higher temperatures predictably cause the atom to lose its information faster.

Pt10 Diffusion Coefficients

The diffusion coefficients plotted against temperature obey two different power laws as seen in the Arrhenius plot below.

The slope of a linear fit corresponds to an activation energy. The blue slope (higher temperatures) corresponds to an activation energy of ~0.2 eV, and the slope in red corresponds to ~0.05 eV.

0.2 eV is the approximate amount of energy needed to break the bond of a Pt-O pair.
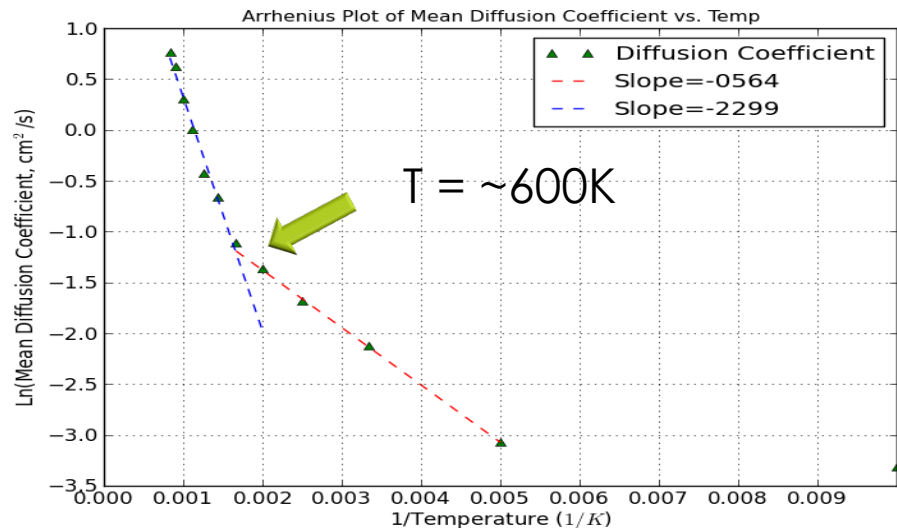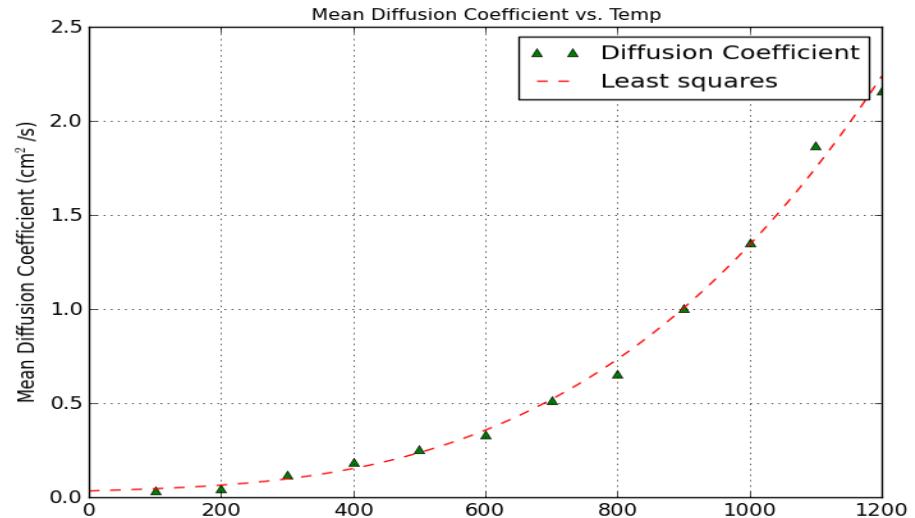
Structural Disorder

Above shows a typical Pt-Pt pair trajectory with respect to time. The high frequency oscillations are due to atomic vibration, while the low frequency oscillations are due to structural disorder.

Below is a power spectrum of the trajectory with the high and low frequency components separated. Although the vibrational component of the disorder roughly doubles with a doubling of temperature, the increase in structural disorder is substantial.

Typical Pt-Pt pair trajectory oscillations

Pt-Pt pair trajectory power spectrum by low and high frequency components

Disorder

Vibrational
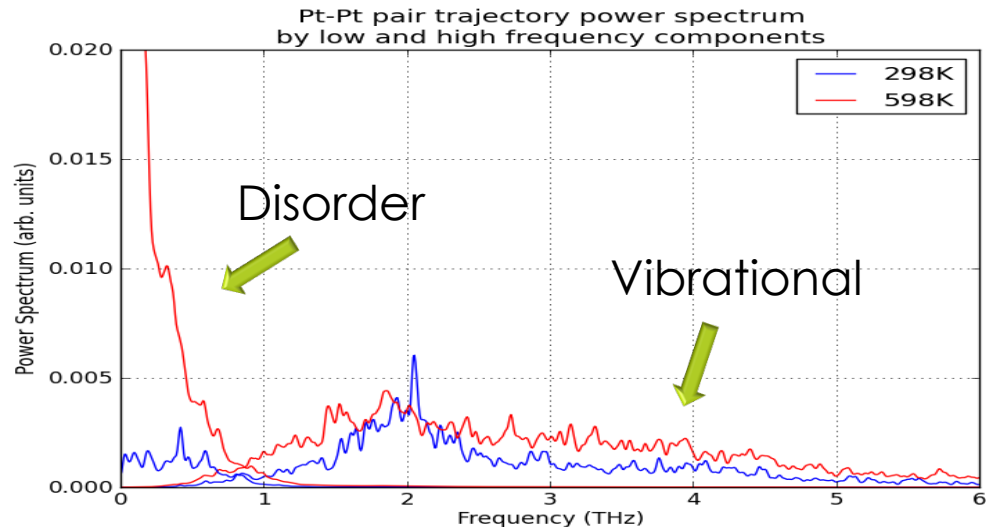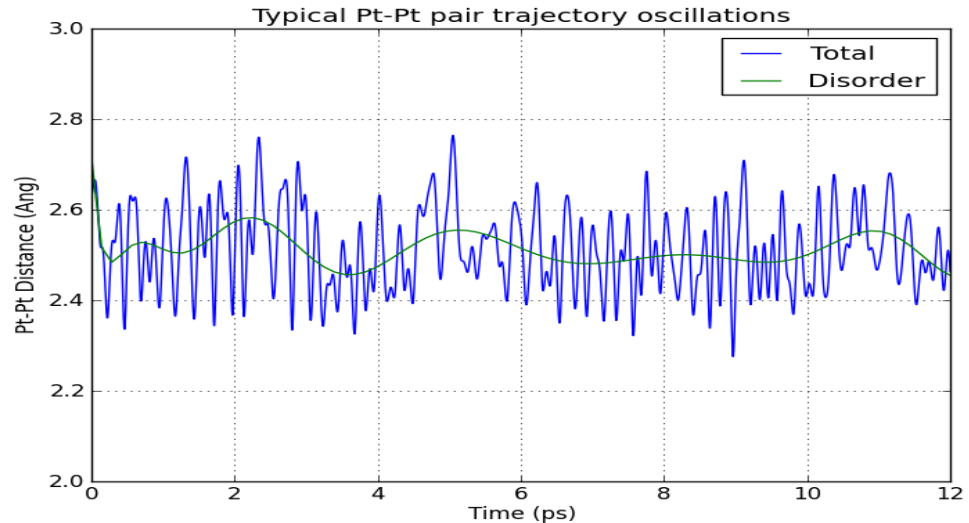
Summary

- We have employed a molecular dynamics simulation program to investigate the behavior of Pt10 nanoclusters supported on γ-Al_2O_3.

- A carefully-chosen model potential can produce results comparable to ab-initio DFT/MD calculations, with the added opportunity of exploring dynamics at much longer time evolutions.

- The calculated results may indicate high temperature cluster-surface interactions are effecting the physical and chemical behavior of the cluster (increased disorder, diffusion, etc.)

Acknowledgements

This effort would not be possible without the outstanding mentorship of

Dr. Fernando D. Vila

and

Dr. John J. Rehr.

Thank you.

Energy Fluctuations in Time

A look at the structure of the Nose-Hoover thermostat reveals a low-frequency periodic oscillation of energy about thermodynamic equilibrium.

DFT/MD calculations cannot capture these long-period energy fluctuations. This is another advantage of using a model potential.

Pt20 Kinetic Energy vs. Time, Nose-Hoover 598K Thermostat

Pt20 Kinetic Energy vs. Time, Velocity-Scaled 598K Thermostat
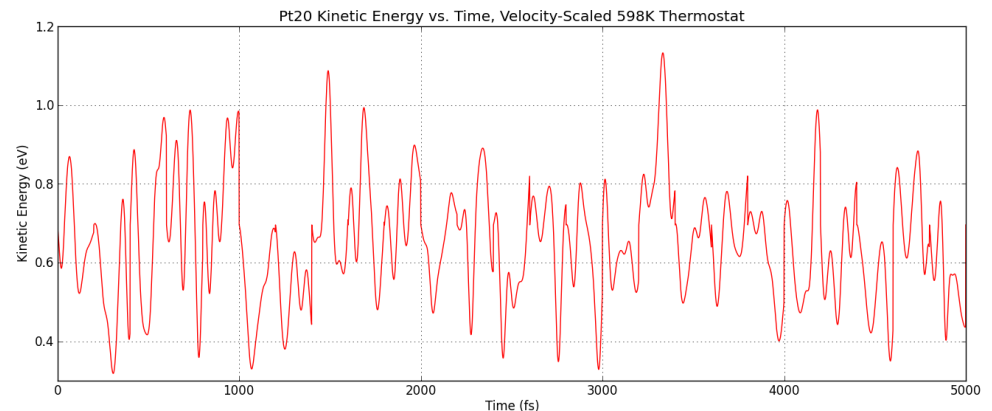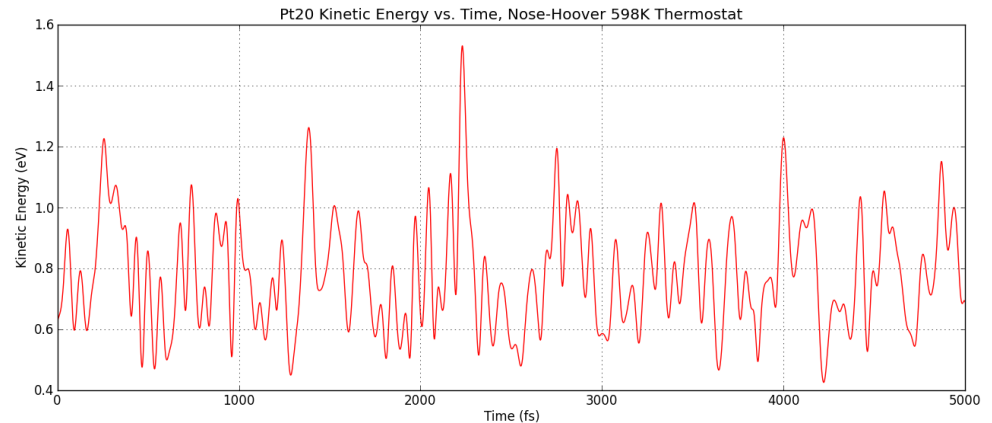
Thermodynamics (cont.)

The energy fluctuations of the system arise from the probability of an atom interacting with the heat bath (i.e. the Alumina support).

The probability is related to the entropy of the system, which depends on the number of distinguishable configurations of the nanocluster, Ω.

$$P(\mathrm{E},T) \approx \Omega\,(\mathrm{E})e^{-\beta \mathrm{E}} = e^{-\beta F(\mathrm{E},T)}$$

$$k \ln \Omega(\mathrm{E}) = \mathrm{S}(\mathrm{E})$$

$$F(\mathrm{E},T) = \mathrm{E} - T\,\mathrm{S}(\mathrm{E})$$

$$\mathrm{S}(\mathrm{E}) \approx 3Nk\,\ln\!\left(\frac{\mathrm{E}}{\mathrm{E}_0}\right)$$

$$\sigma_{\mathrm{E}}^2 = k\left[\frac{\partial^2 \mathrm{S}(\mathrm{E})}{\partial \mathrm{E}^2}\right]^{-1}$$

$$\sigma_{\mathrm{E}} \approx \frac{\mathrm{E}}{\sqrt{3N}} \qquad \mathrm{E} = \frac{3}{2}NkT$$

Nosé-Hoover Thermostat

The **Nosé-Hoover thermostat** introduces a virtual variable ζ into the equations of motion.

The **Nosé-Hoover thermostat** is the preferred method for constant temperature MD simulations.

$$Q = N_{DoF}\, k_B\, T_0\, \tau^2$$

$$\zeta = \frac{2K - N_{DoF}\, k_B\, T_0}{Q}$$

$$r(t+h) = r(t) + h\, v(t) + \frac{1}{2}h^2\left(\frac{F(t)}{m} - \zeta(t)\, v(t)\right)$$

$$v\left(t+\frac{h}{2}\right) = v(t) + \frac{1}{2}h\left(\frac{F(t)}{m} - \zeta(t)\, v(t)\right)$$

$$\zeta(t+h) = \zeta(t) + \frac{h}{2Q}\left(K(t)+K\left(t+\frac{h}{2}\right) - 2N_{DoF}\, k_B\, T_0\right)$$

$$v(t+h) = \frac{2}{2+h\,\zeta(t+h)}\left(v\left(t+\frac{h}{2}\right) + \frac{h}{2}\frac{F(t+h)}{m}\right)$$