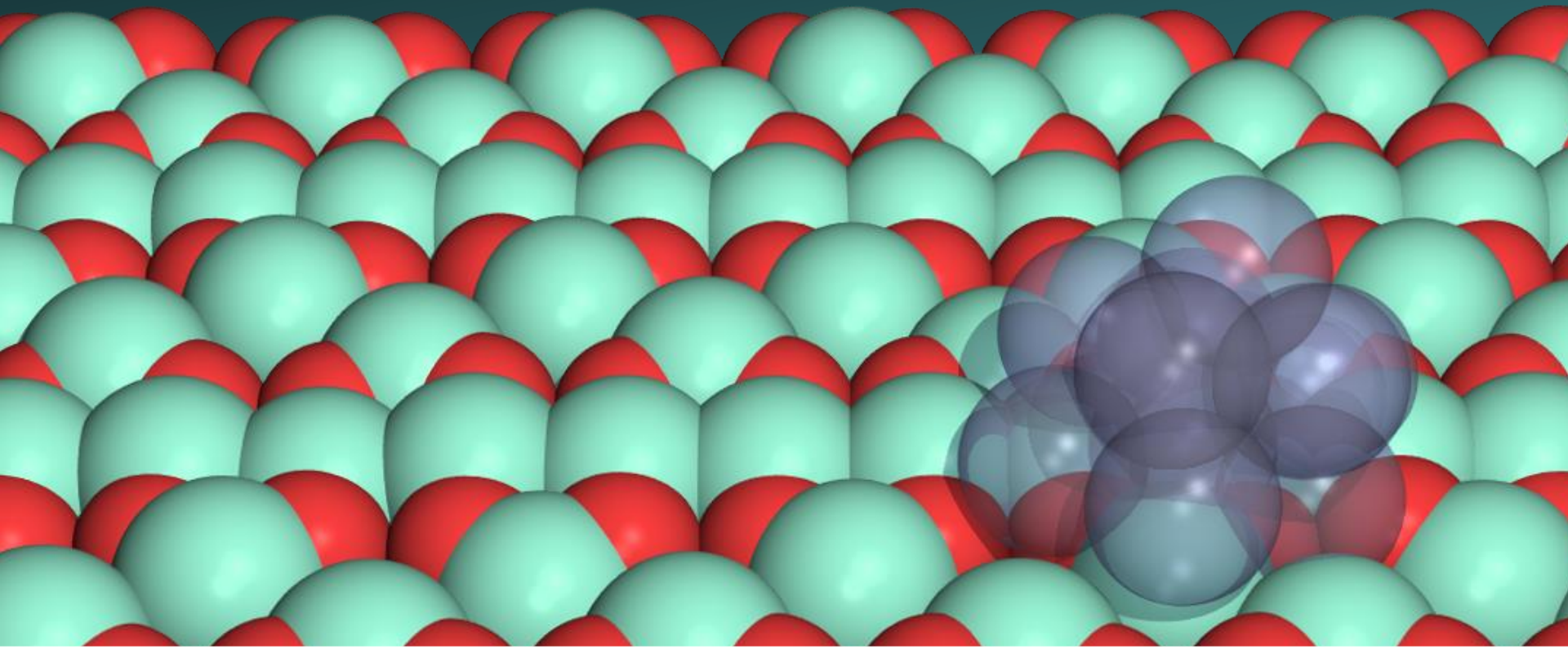
Nanosecond Dynamics in Pt Nanoparticles

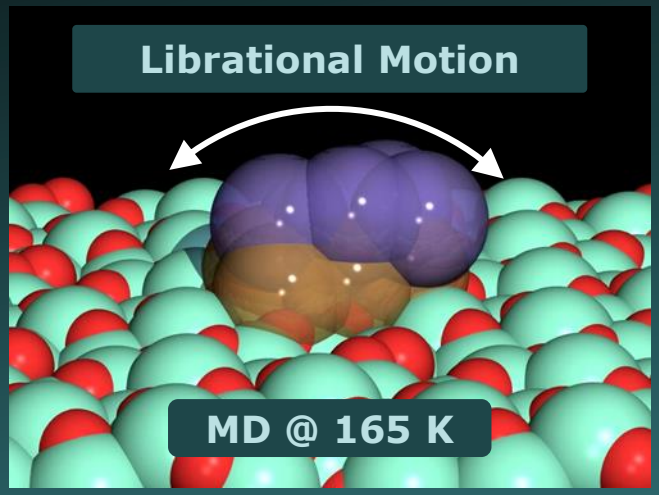
F. Vila, J. M. Moore and J. J. Rehr

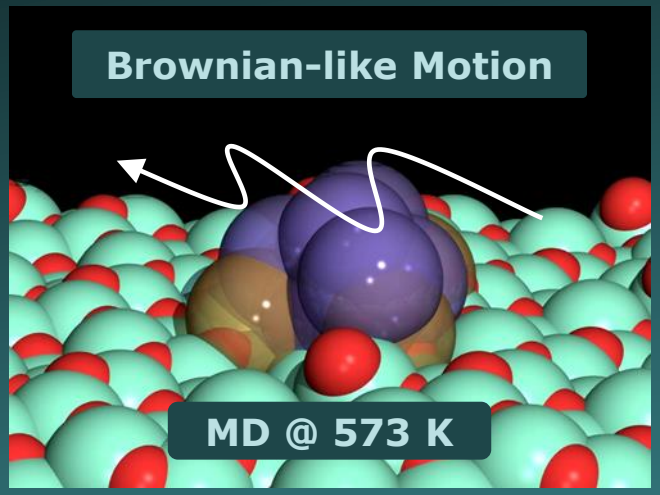


UNIVERSITY OF WASHINGTON

DOE grant DE-FG02-03ER15476 (F.D.V and J.J.R)
NSF REU grant PHY-1262811 (J.M.M.)
With computer support from DOE - NERSC.

Pt nanoparticles: Dynamic structure





Complex dynamics show:

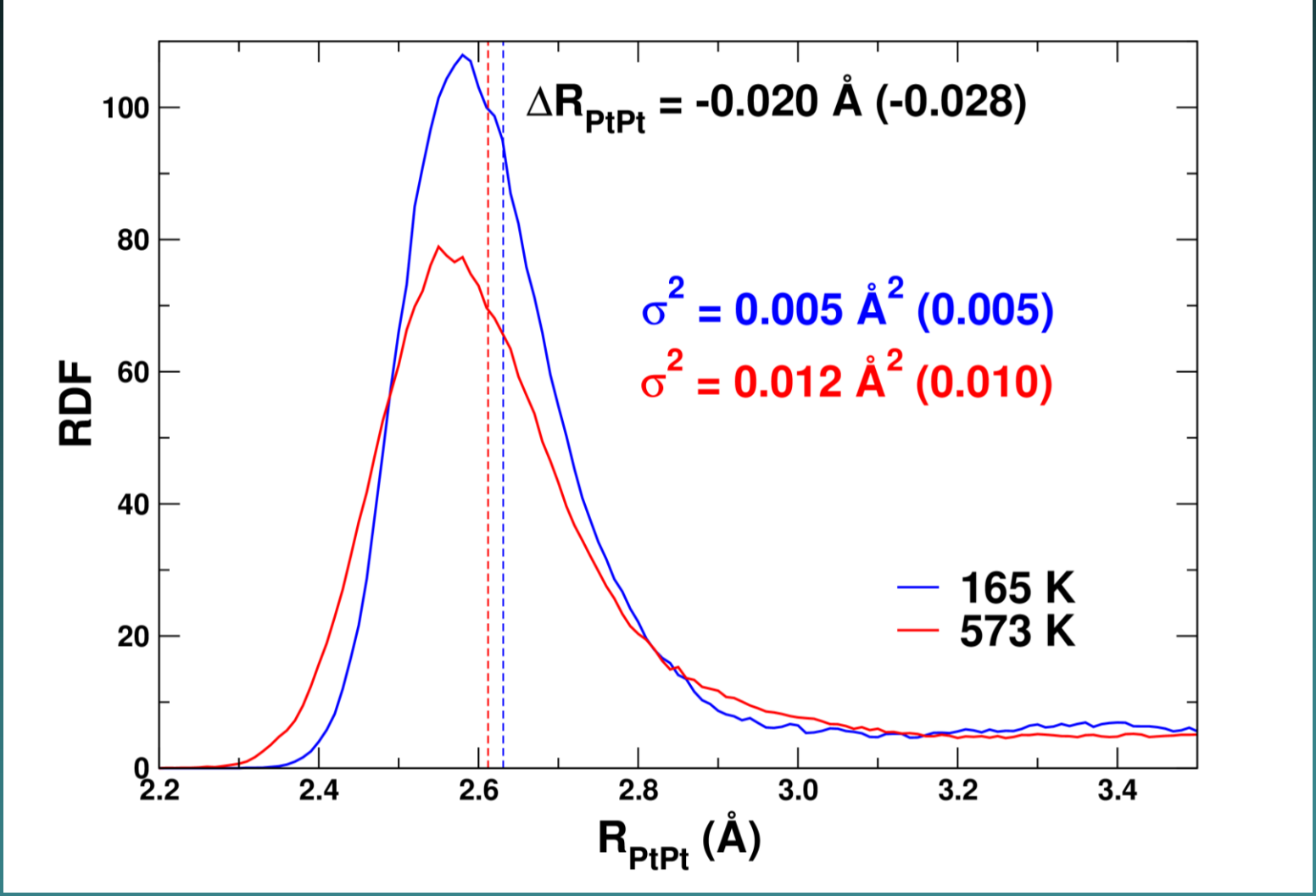
- Multiple-time scales
- Librational motion
- Fluctuating bonding

Simulations explain:

- Large structural disorder
- Negative Thermal Expansion (NTE)
- Change in electronic structure

Vila *et al.* Physical Review B **78**, 121404(R), 2008

DFT/MD Pt-Pt Radial Distribution Function



Very good agreement with expt. NTE and disorder

Need longer simulations

- Three dynamic regimes:
  - Fast bond vibrations (200-400 fs)
  - Stochastic CM motion (2-4 ps)
  - Slow transient bonding (>8 ps)
- DFT/MD simulations:
  - Computationally demanding
  - Difficult to access slow regime
- Option: Model potential?

Model potential

- Sutton-Chen (SC) potential
  - Effective many-body interaction
  - Good for bulk Pt
  - Needs additional interactions to support

- Pros and Cons:
  - Much faster than DFT/MD
  - Larger/longer simulations possible (ns✓, ms?)
  - Model interaction → understanding of physics

  - Might be unphysical
  - Lack electronic structure

Potential form:

Pt-Pt interaction

$$U_{SC} = \epsilon \sum_i \left(\frac{1}{2} \sum_{j \neq i} V_{r_{ij}} - c\sqrt{\rho_i} \right) \qquad V_{r_{ij}} = \left(\frac{a}{r_{ij}} \right)^n \qquad \rho_i = \sum_{j \neq i} \left(\frac{a}{r_{ij}} \right)^m$$

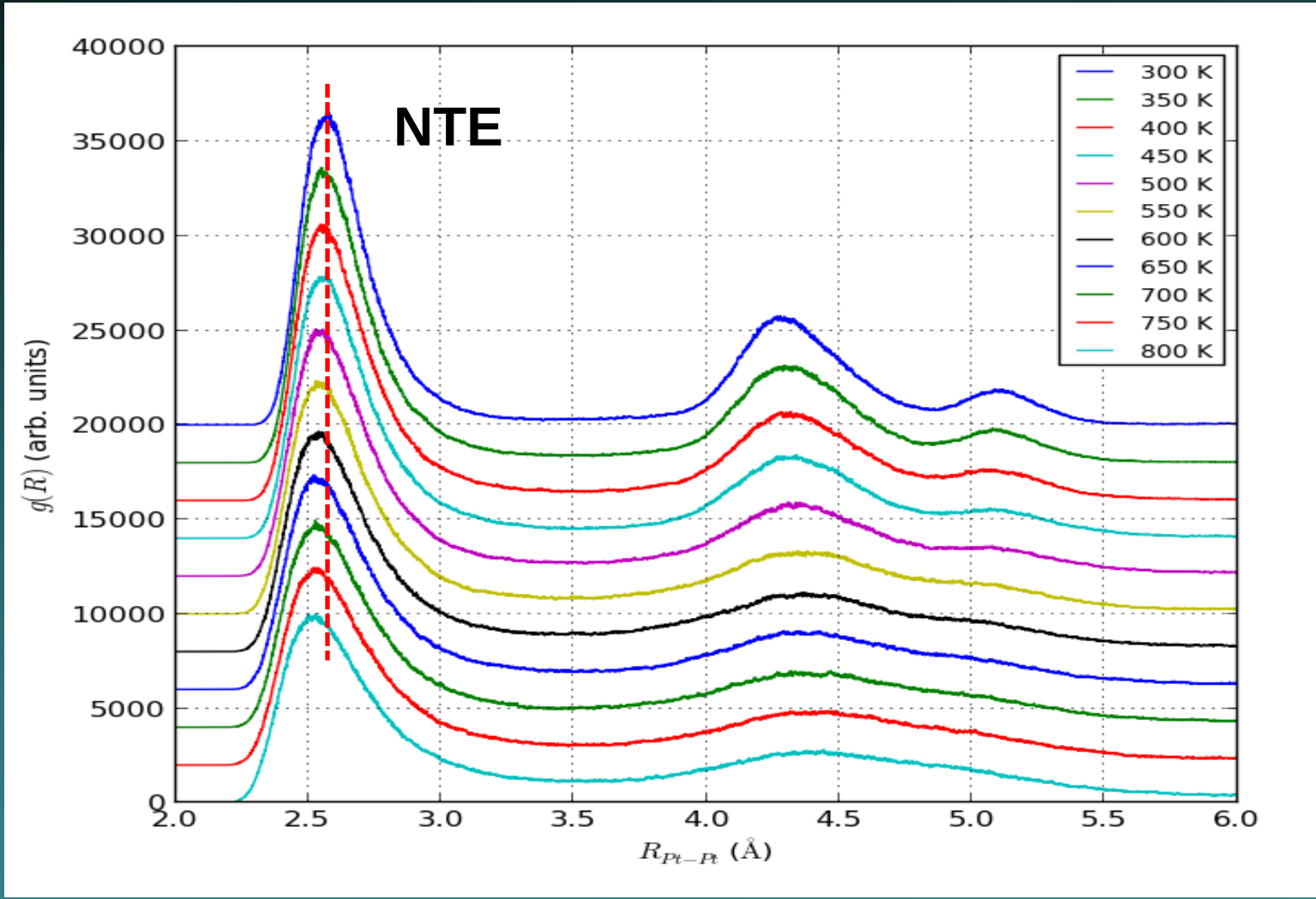
Surface atoms harmonic tethering

$$U_H = \frac{1}{2} k r_e^2$$

Pt-O and Pt-Al interaction

$$U_{LJ} = 4\epsilon \left(\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right)$$

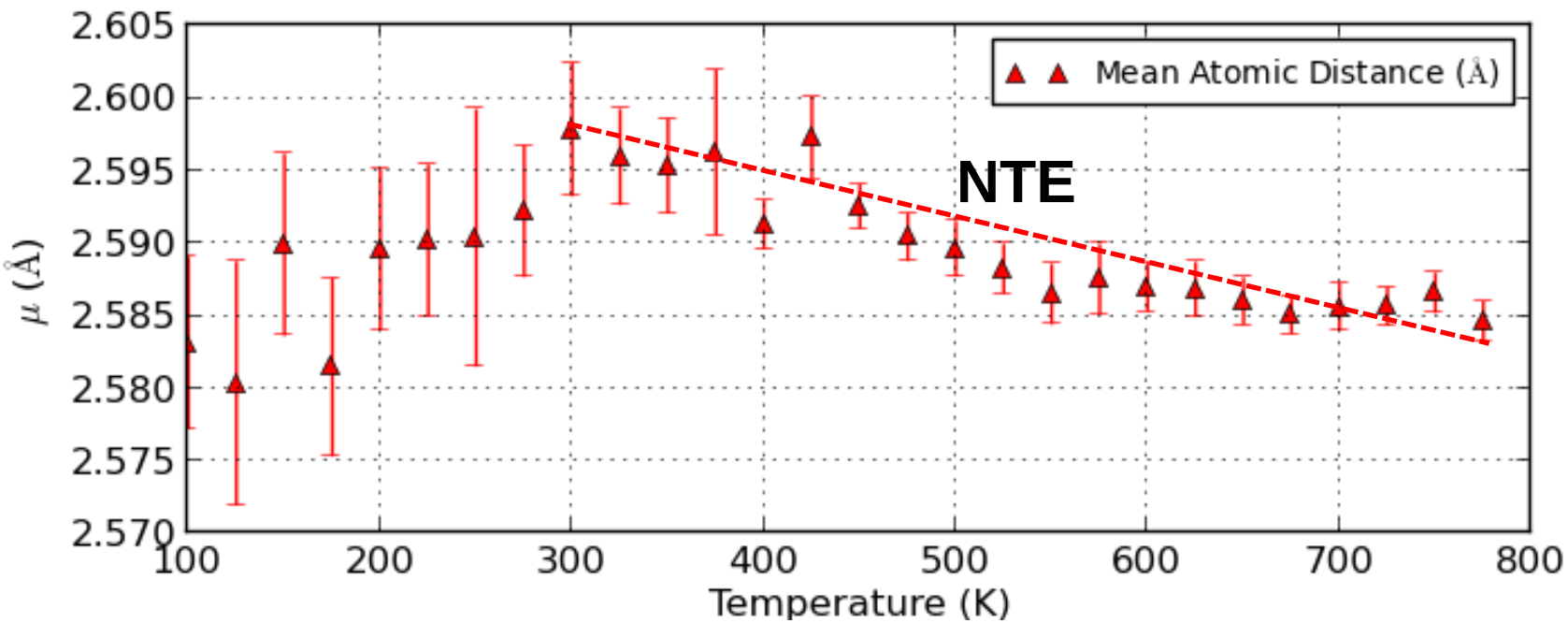
Standard SC Radial Distribution Function



1st shell: NTE

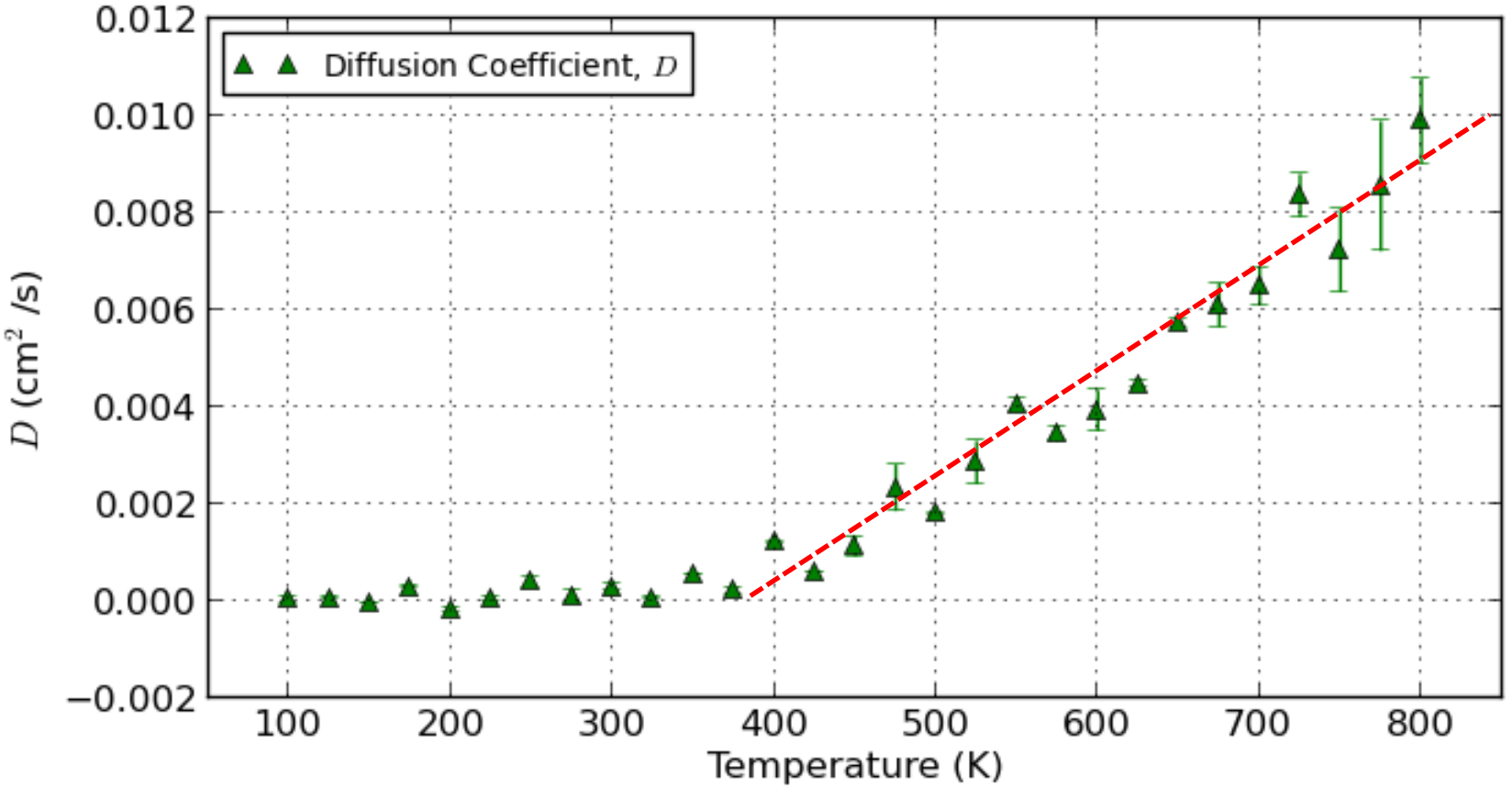
2nd shell: Melting signature

Standard SC Mean Pt-Pt NN distance



NTE: About 0.02 Å (300-800 K)

Standard SC Pt diffusion coefficient



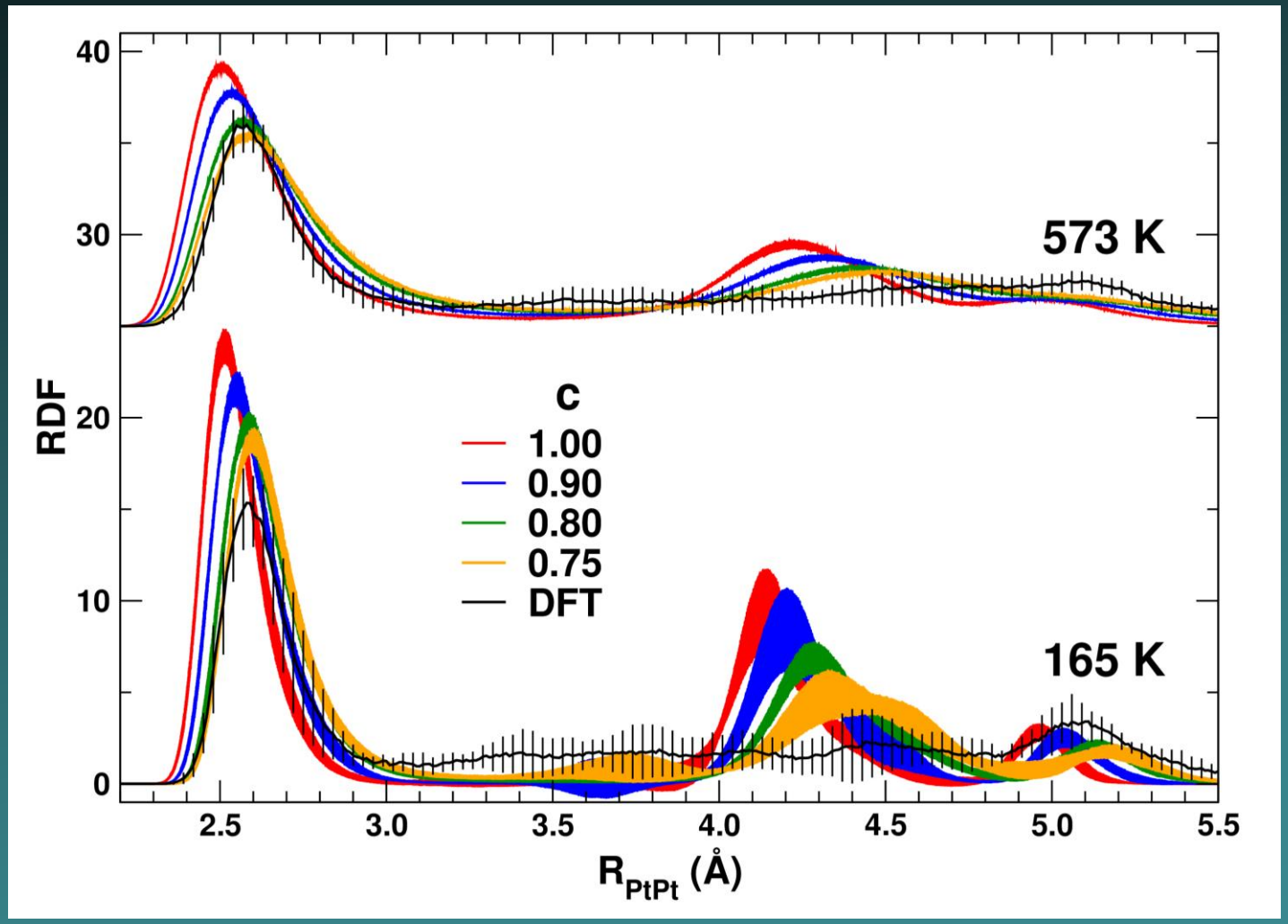
Increase in mobility at ~ 400 K

Sutton-Chen modification

- Standard SC is too structured
- Initial modifications:
  - Reduce "a" scale parameter (to 0.96)
  - Reduce overall attractive part (scale "c")

$$U_{SC} = \epsilon \sum_i \left(\frac{1}{2} \sum_{j \neq i} V_{r_{ij}} - c\sqrt{\rho_i} \right) \qquad V_{r_{ij}} = \left(\frac{a}{r_{ij}} \right)^n \qquad \rho_i = \sum_{j \neq i} \left(\frac{a}{r_{ij}} \right)^m$$

Modified SC: Comparison to DFT/MD



High T: Good 1st shell, improved long range

Low T: Still somewhat structured

Conclusions

- Standard Sutton-Chen:
  - Good qualitative properties
  - Easy access to ns regime
  - Needs modification for nanoparticles
- Modified Sutton-Chen
  - Much better at high T
  - Still somewhat structured at low T

Nanosecond Dynamics in Pt Nanoparticles

F. Vila, J. M. Moore and J. J. Rehr

Acknowledgements:

Rehr Group

S. T. Hayashi
K. Jorissen
J. J. Kas
E. Klevak
A. J. Lee
S. Story

A. Frenkel

S. Bare

S. Kelly

UNIVERSITY OF WASHINGTON

DOE grant DE-FG02-03ER15476 (F.D.V and J.J.R)
NSF REU grant PHY-1262811 (J.M.M.)
With computer support from DOE - NERSC.