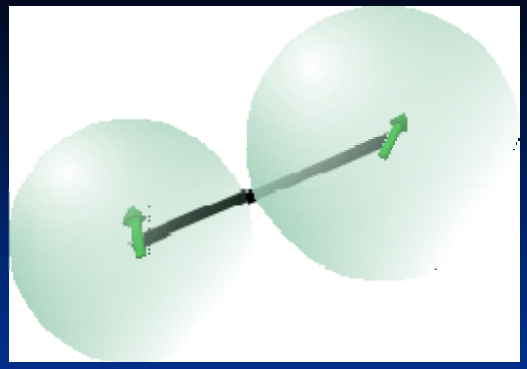
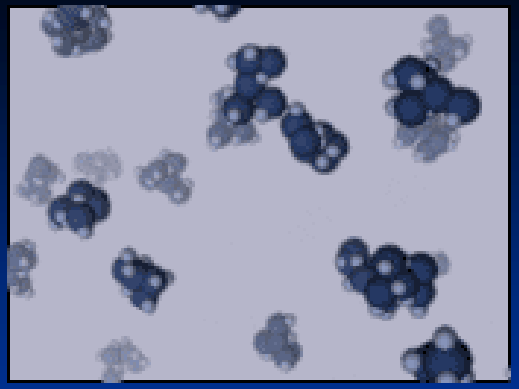
R.E.U./P.C.C.M. 2008

By Eric Sanchez

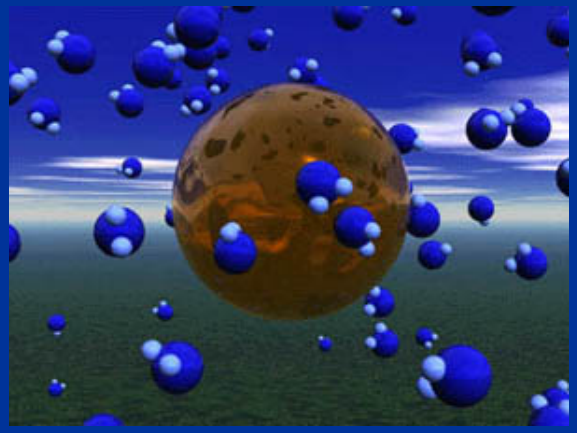
Princeton University

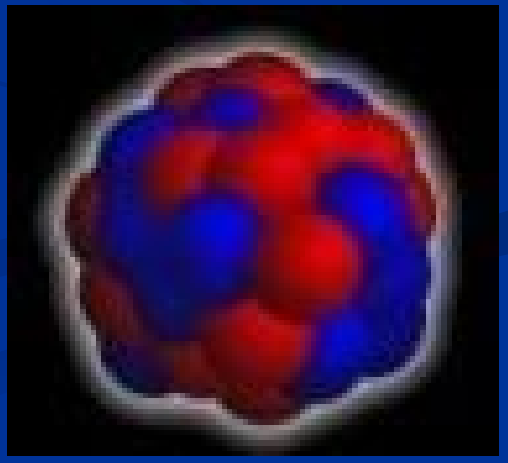
August 4, 2008





Nucleation and Freezing: An investigation of subcooled systems in the Coarse Grain (Marrink/Martini) model





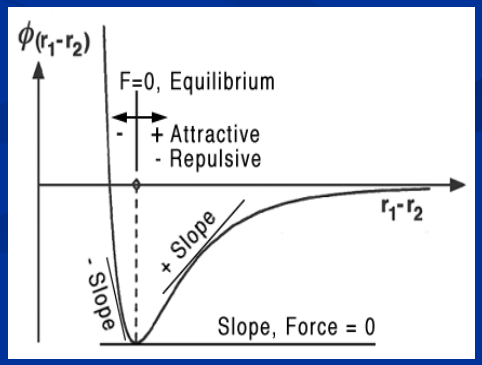
Questions and topics for Summer research

- For pure solvent systems, at what temperature do we see freezing?
- Does the nucleation of molecules (CG particles) affect the temperature at which we see freezing?
- Can we use the tools we have to obtain "snap shots" in time and examine how a system behaves at the temperature extremes and in between?

Background into model and analyses…

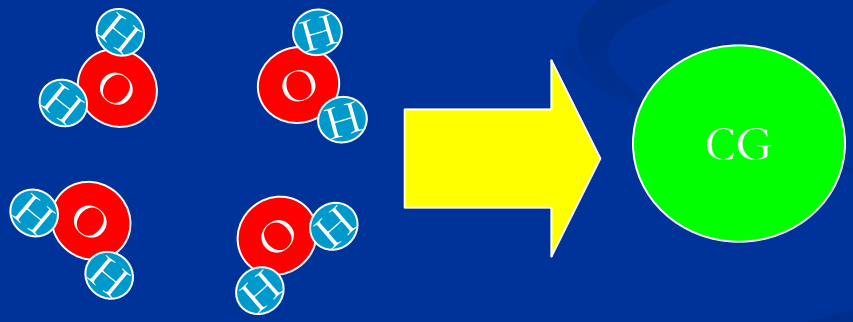
- First off… preliminary concepts and terms
  - Nucleation – particles within the system that have clustered together (i.e. enter a solid phase)
  - Sub-cooled systems
- What is the CG (Marrink/Martini) model?
  - What kind of systems does it attempt to model?
    - Lennard-Jones systems (Lennard-Jonesium) governed by a 12-6 potential energy function given by :

$$U_{LJ}=4\varepsilon\left[(\sigma_{ij}/r_{ij})^{12}-(\sigma_{ij}/r_{ij})^{6}\right]$$



Background into model and analyses…

- How does it model interactions among particles?
  - Force Fields – short range interactions
    - Bonded interactions -$V_{bond}(R)=1/2[K_{bond}(R-R_{bond})^2]$
    - Charged groups -$U_{el}(r)= q_i q_j/4\pi \varepsilon_0 \varepsilon_r r$
    - L-J for nonbonded interactions - $U_{LJ}(r)=4\varepsilon[(\sigma_{ij}/r_{ij})^{12} – (\sigma_{ij}/r_{ij})^6]$
  - Molecule mapping - Interaction centers for different molecule types (i.e. 4 to 1 mapping)



- How do we actually simulate these systems
  - Simulation Package: Gromacs 3.3

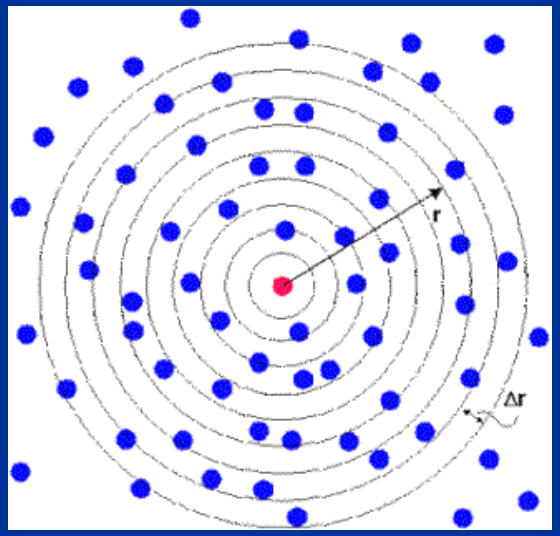
Analyses…

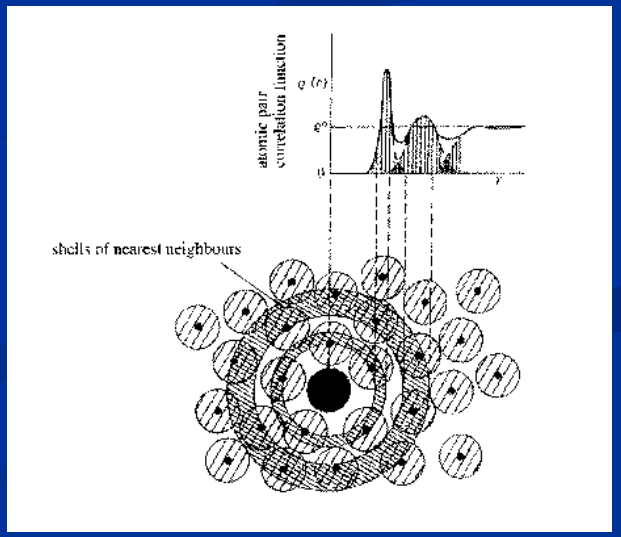
- For this model, what tools will we be using to verify whether a system freezes or not?
  - Indicators of freezing
    - Radial Distribution Function
    - Diffusion coefficients (MSD Vs. Time)
    - A combination of programming and visual inspection

Radial Distribution Function

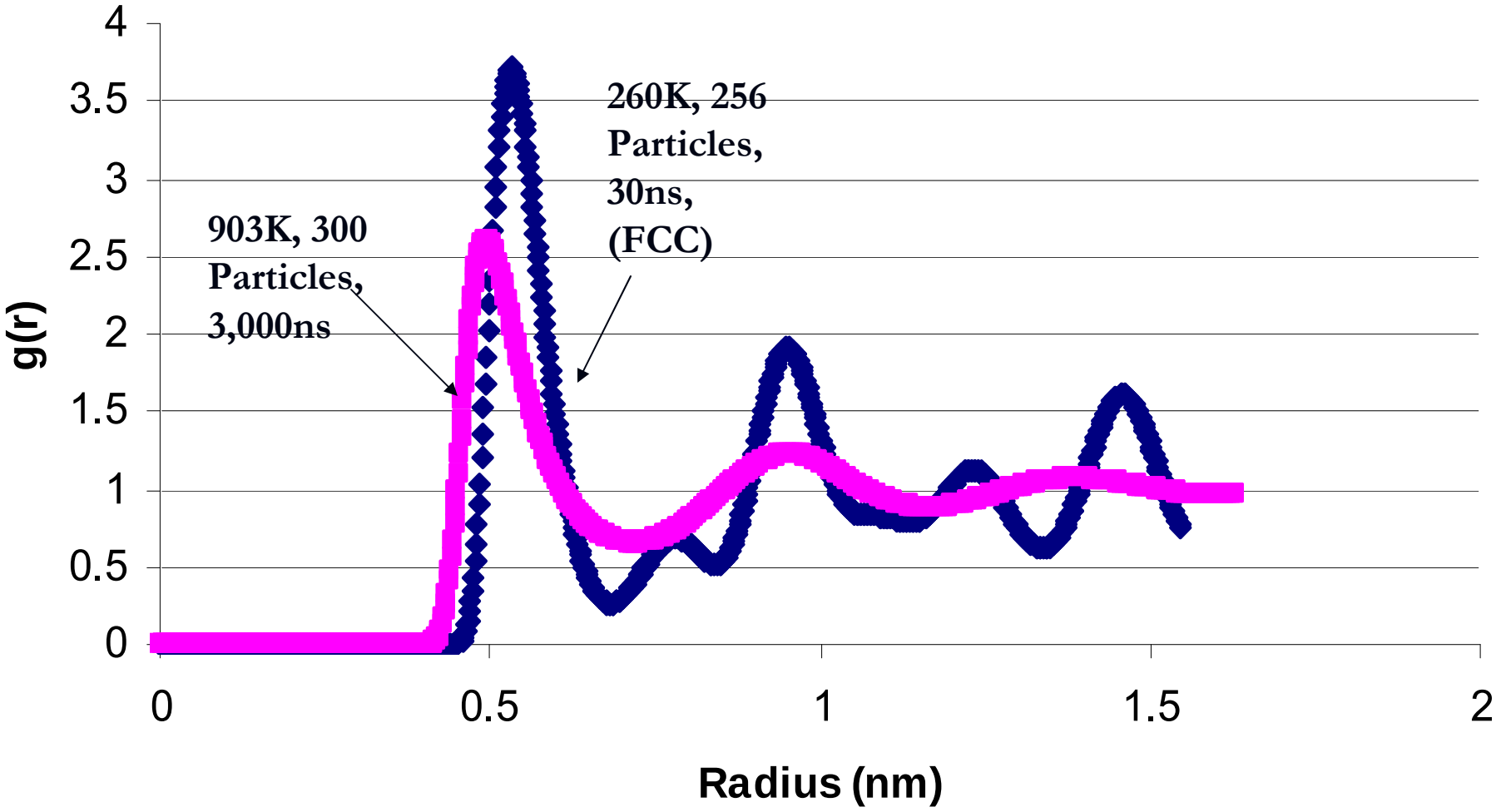
- What is the R.D.F. and how does it help us to determine freezing in our model?
  - Pair Correlation Function
    - Concentric shells of width Δr
    - Distance r between particle i and j^{th}

$$\Sigma\ 4\pi r^2\, g(r)\rho\ \Delta r$$

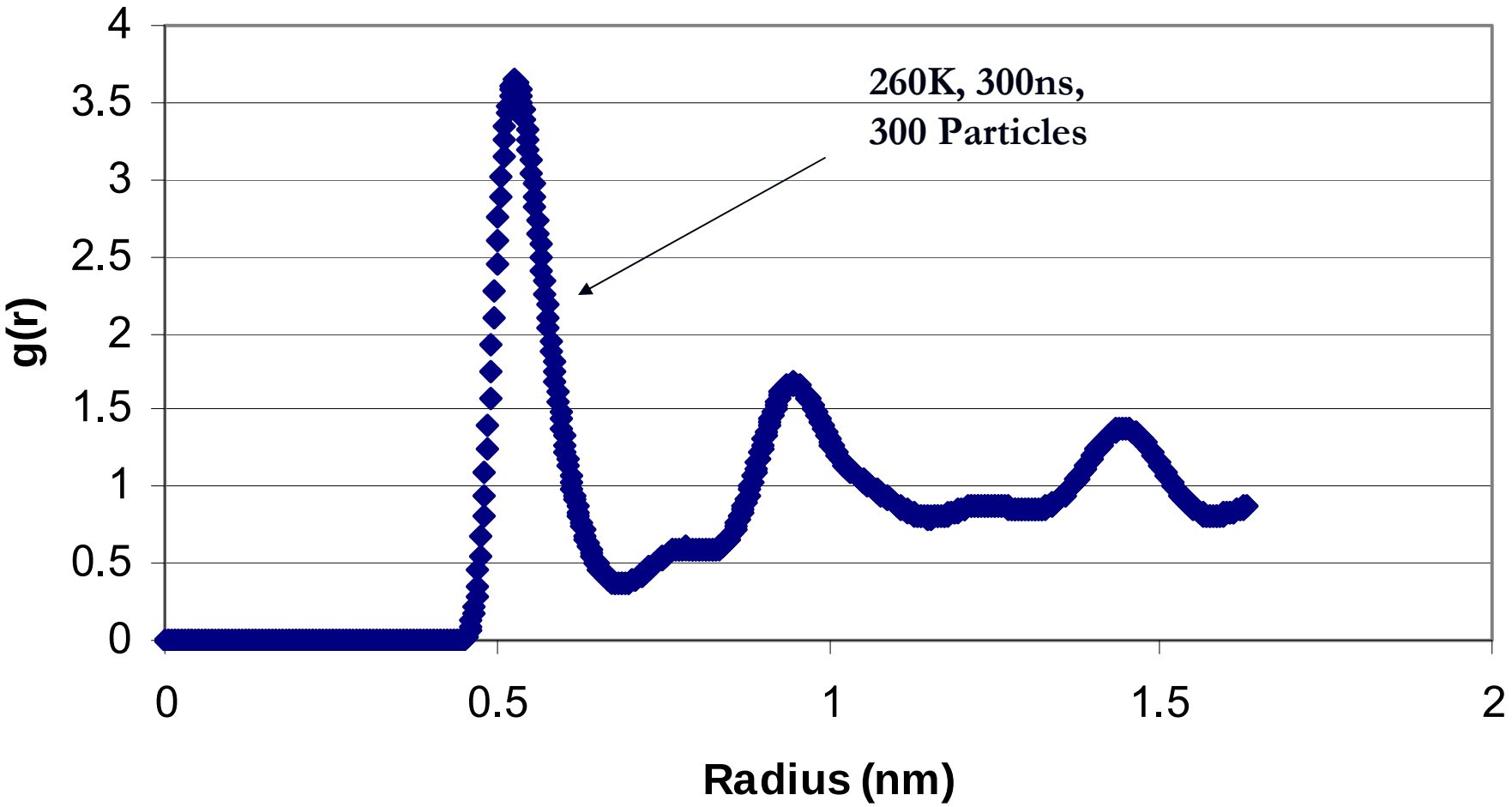




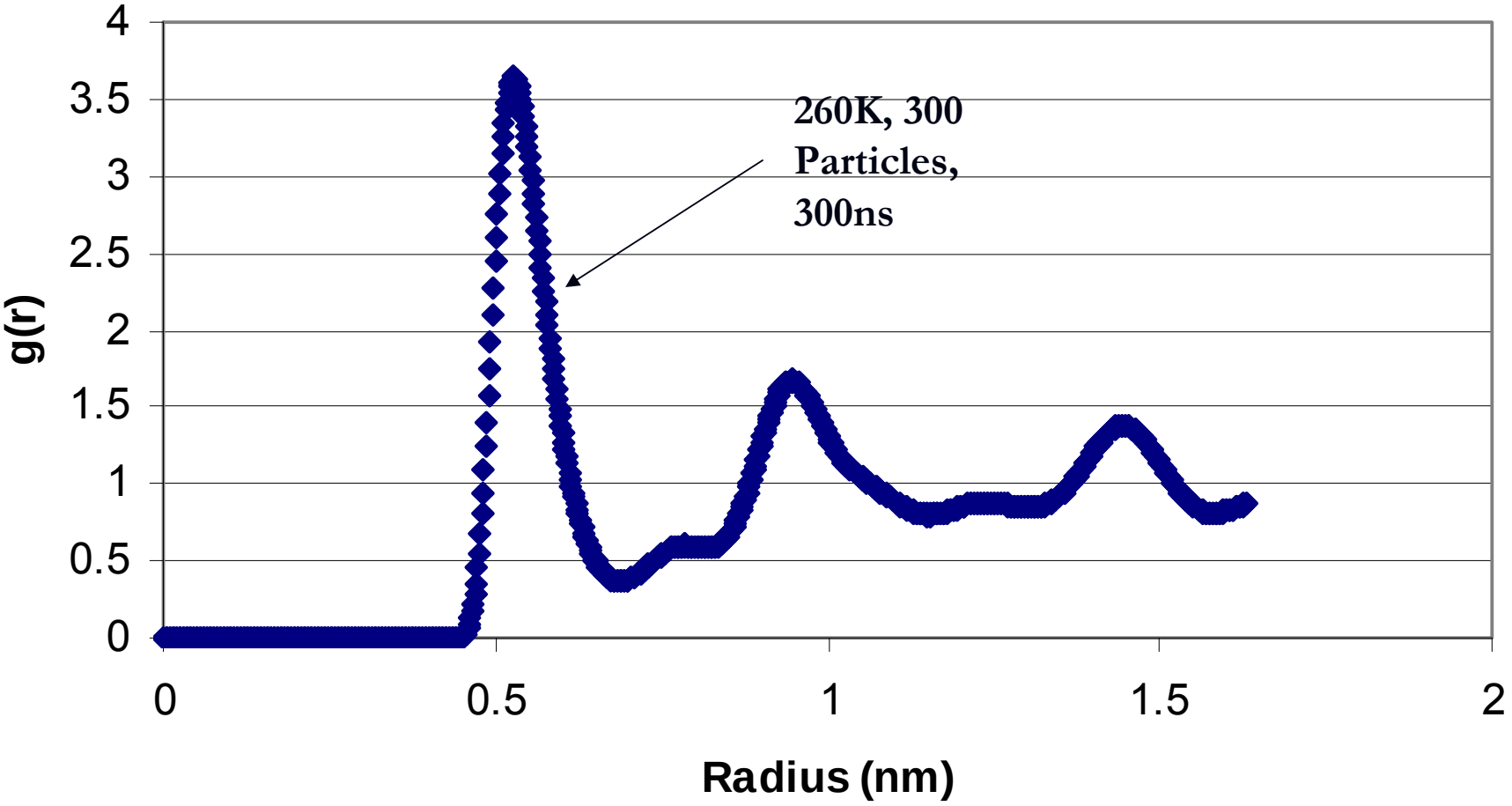
Radial Distribution Function



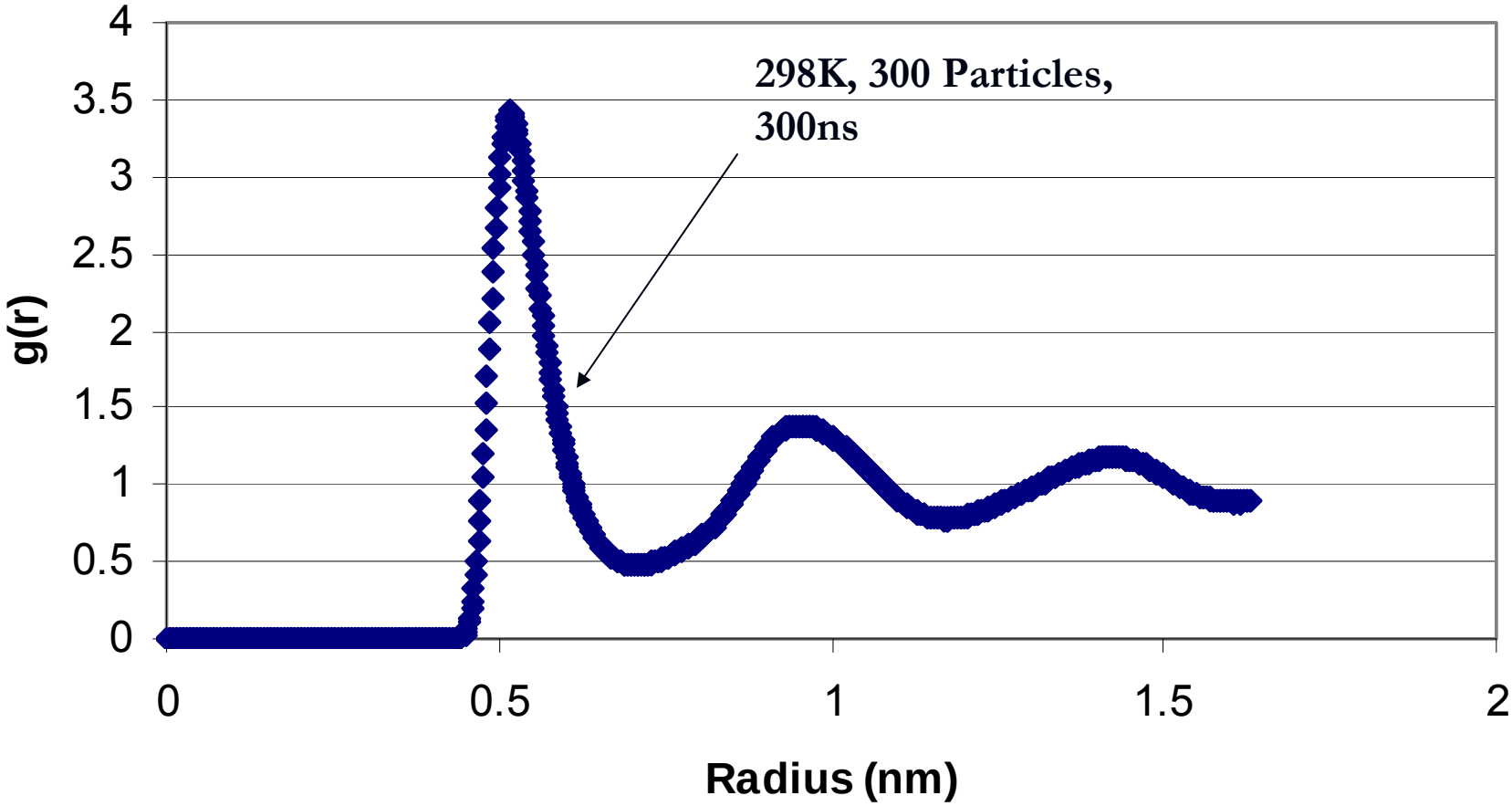
Radial Distribution Function : Simulation Data



Radial distribution Function Simulation Data



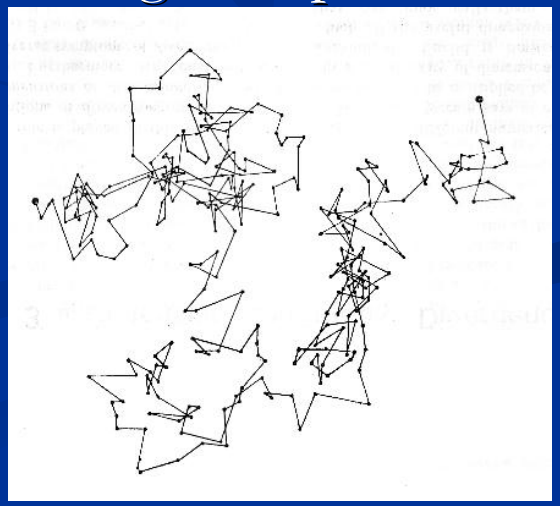
Radial distribution Function Simulation Data



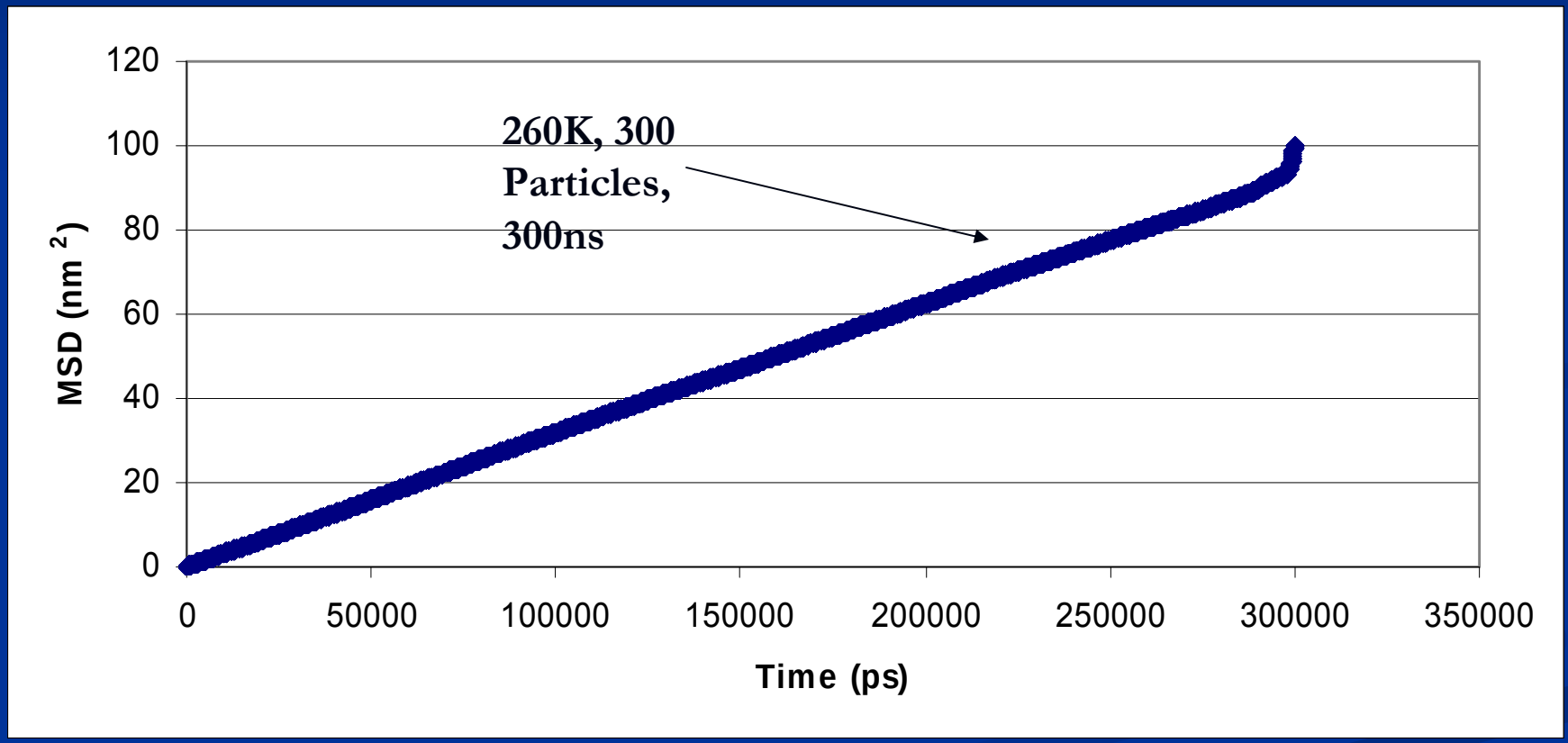
Mean Squared Displacement

- Preliminary information
  - We study pure solvent systems (i.e. water in cubic boxes)
- Apparent random (Brownian) motion of particles in the system of interest
  - Phenomenon occurs in the cores of stars at high temperature
- What is Mean squared displacement?
  - It is given by the Einstein relation:

$$\langle r^2 \rangle = 6\,D\,t + C$$

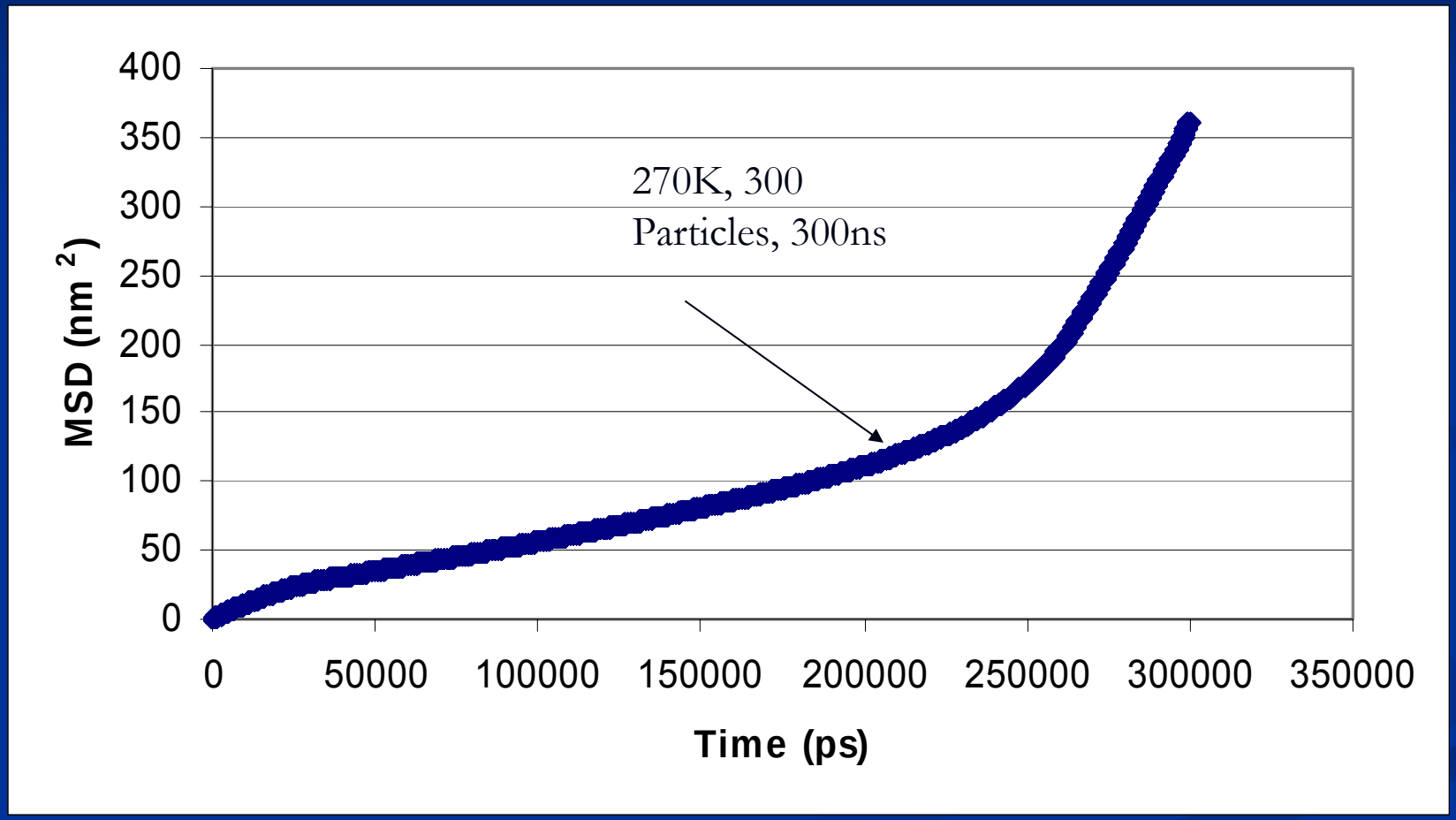


Mean Squared Displacement Simulation Data



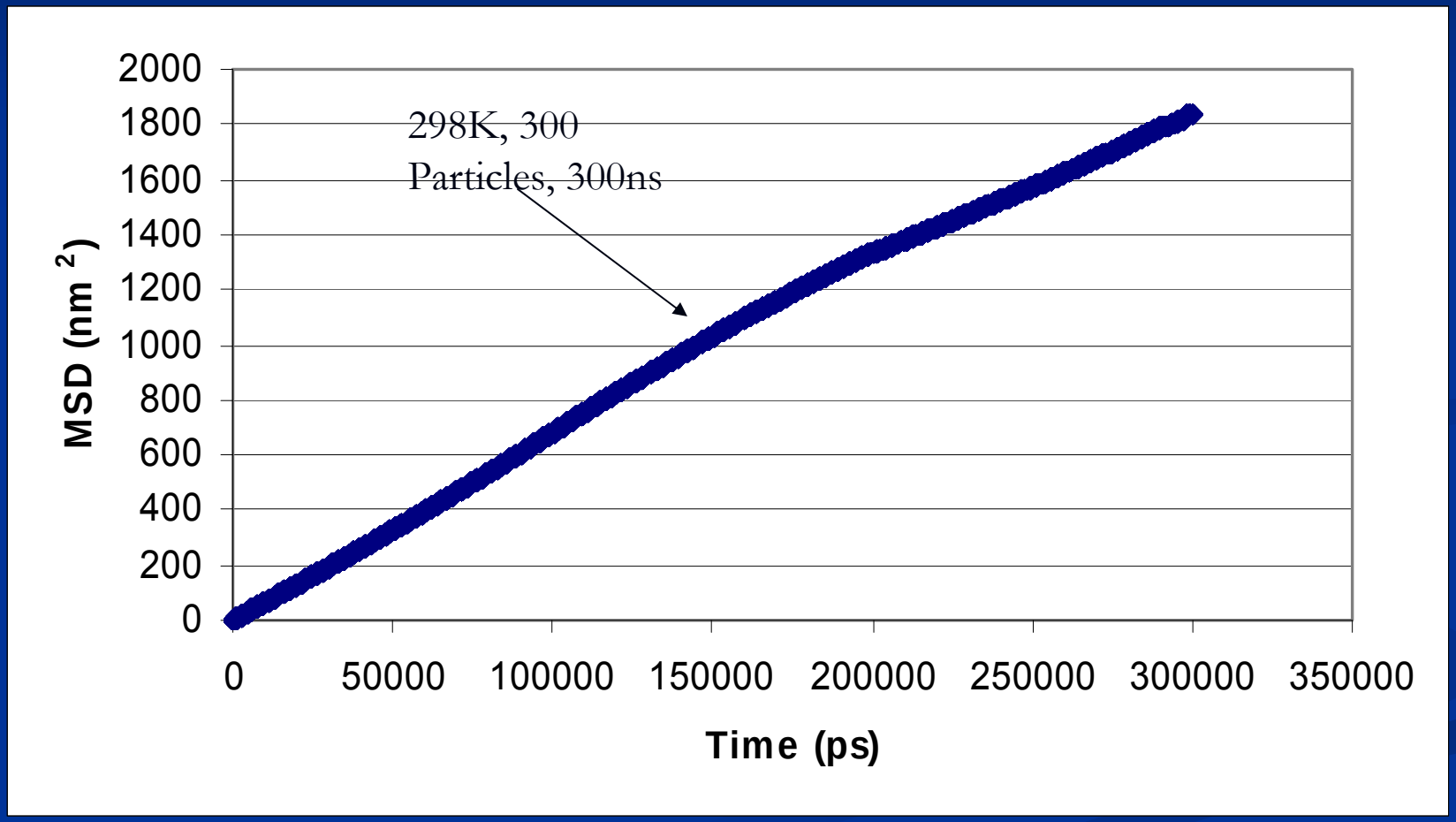
Diffusion Coefficient for 260K:
$0.0513\ (\pm 0.0020) \times 10^{-5}\ cm^2/s$

Mean Squared Displacement Simulation Data



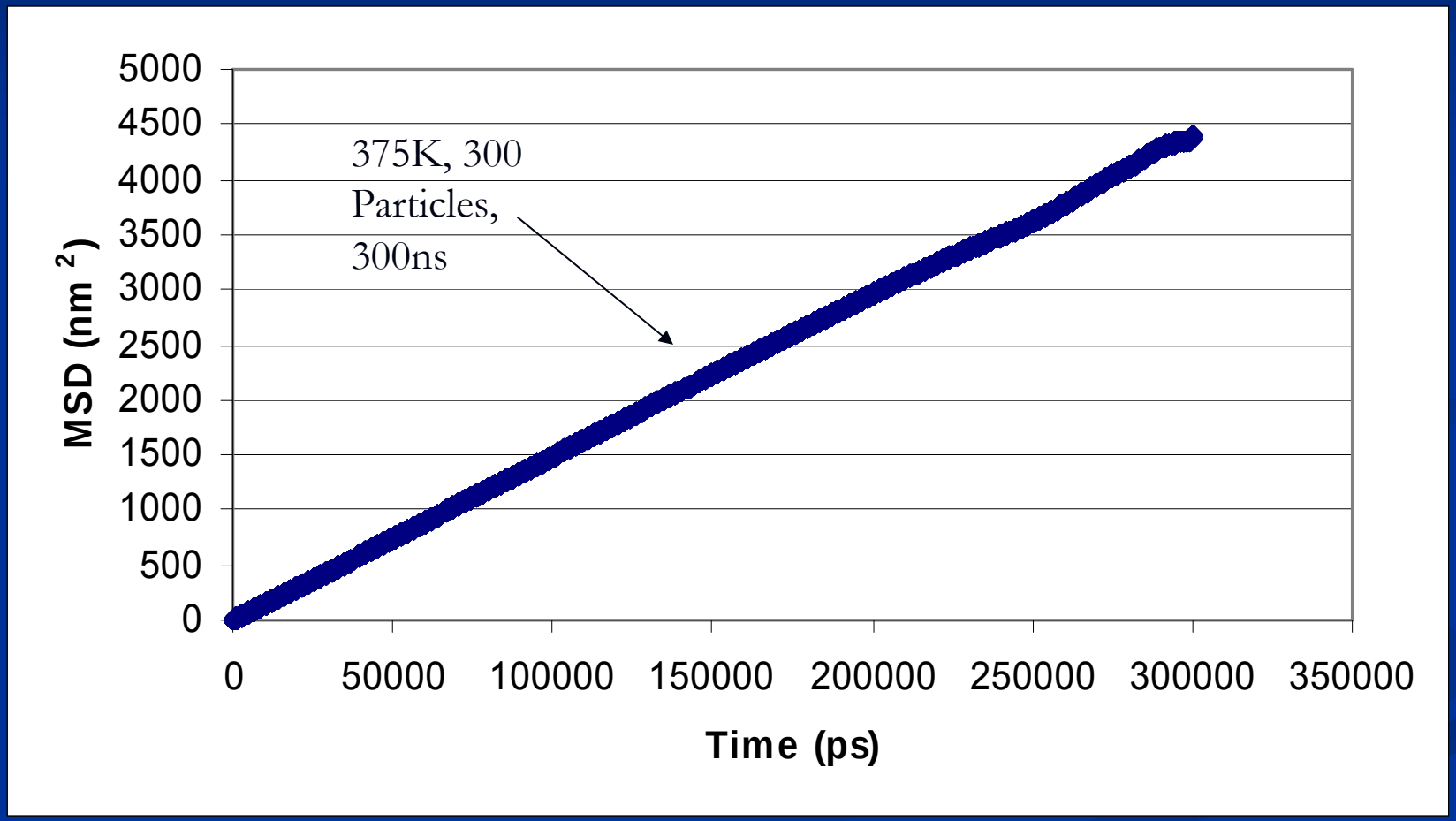
Diffusion Coefficient for 270K:
$0.1118(\pm 0.1041) \times 10^{-5}\ cm^2/s$

Mean Squared Displacement: Simulation Data



Diffusion Coefficient for 298K:
$1.0478(\pm 0.3093) \times 10^{-5}$ cm^2/s

Mean Squared Displacement: Simulation Data



Diffusion Coefficient for 375K:
$2.4201(\pm 0.1676) \times 10^{-5}\ cm^2/s$

Conclusions

- For systems studied, we determined that a system freezes at around 260K, based on comparison of RDF's at this temperature and above.
- Nucleation does play a key role on how a system freezes at subcooled temperatures for this model but technique used to find nuclei needs to be refined and take into consideration system size and nuclei size
- For Diffusion coefficients, the trends are as expected and provide further evidence of freezing at the indicated temperature

Future Work…

- Increase the number of particles in our pure solvent system
- Determine when freezing occurs for larger systems of particles
- Study surfactant systems in solvent systems such as water
- Investigate the effects of nucleation of water molecules on the self- assembly of micelles
- Improve the nucleation code to incorporate more sophisticated methods to determine nucleation and structure type, namely "order parameters" such as spherical harmonics

Special Thanks to…

- Prof. A.Z. Panagiotopoulos
- Prof. Nicholas Kioussis
- Samantha Sanders
- Justin Speth
- Andew Ferguson
- Panagiotopoulos group
- Prof. Jay Benziger
- Shannon Swiley