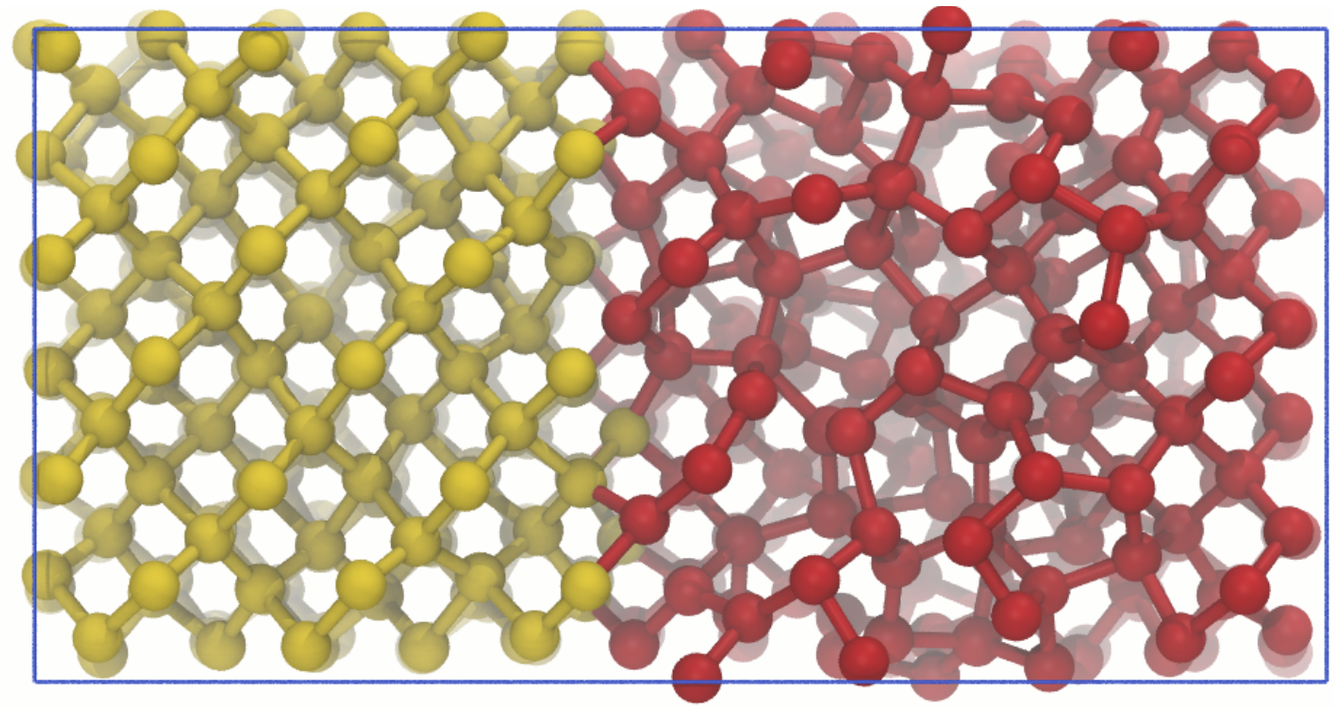
TEMPLE UNIVERSITY

Ab Initio Molecular Dynamics (MD) Simulations



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ICMS
Institute for Computational Molecular Science

CCDM

What are Molecular Dynamics (MD) Simulations?

- Technique to compute statistical and transport properties of many-body systems
- Given initial condition (*positions & momenta of N particles/ nuclei*), evolve system in time following equation of motion

Why MD Simulations?

- We want to do **statistical mechanics**!
- Compute ***observables*** to connect with experiment
- Thermodynamics, structure, dynamics, electronic properties…

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$$\langle O(\mathbf{R}) \rangle = \frac{\int d\mathbf{R} O(\mathbf{R}) e^{-\beta U(\mathbf{R})}}{\mathcal{Z}}$$

- *3N*-dimensional configurational integrals

$$\langle O \rangle = \frac{\sum_n O_n e^{-\beta \varepsilon_n}}{Q}$$

Partition Function:

$$Q = \sum_n e^{-\beta \varepsilon_n}$$

$$\mathcal{H}\psi_n = \varepsilon_n \psi_n$$

- *Summation over **all** states*

How to compute observables?

- Work under assumption of the ***Ergodic Hypothesis:***

$$\langle O \rangle \approx \lim_{\tau \to \infty} \int_0^\tau dt O(t)$$

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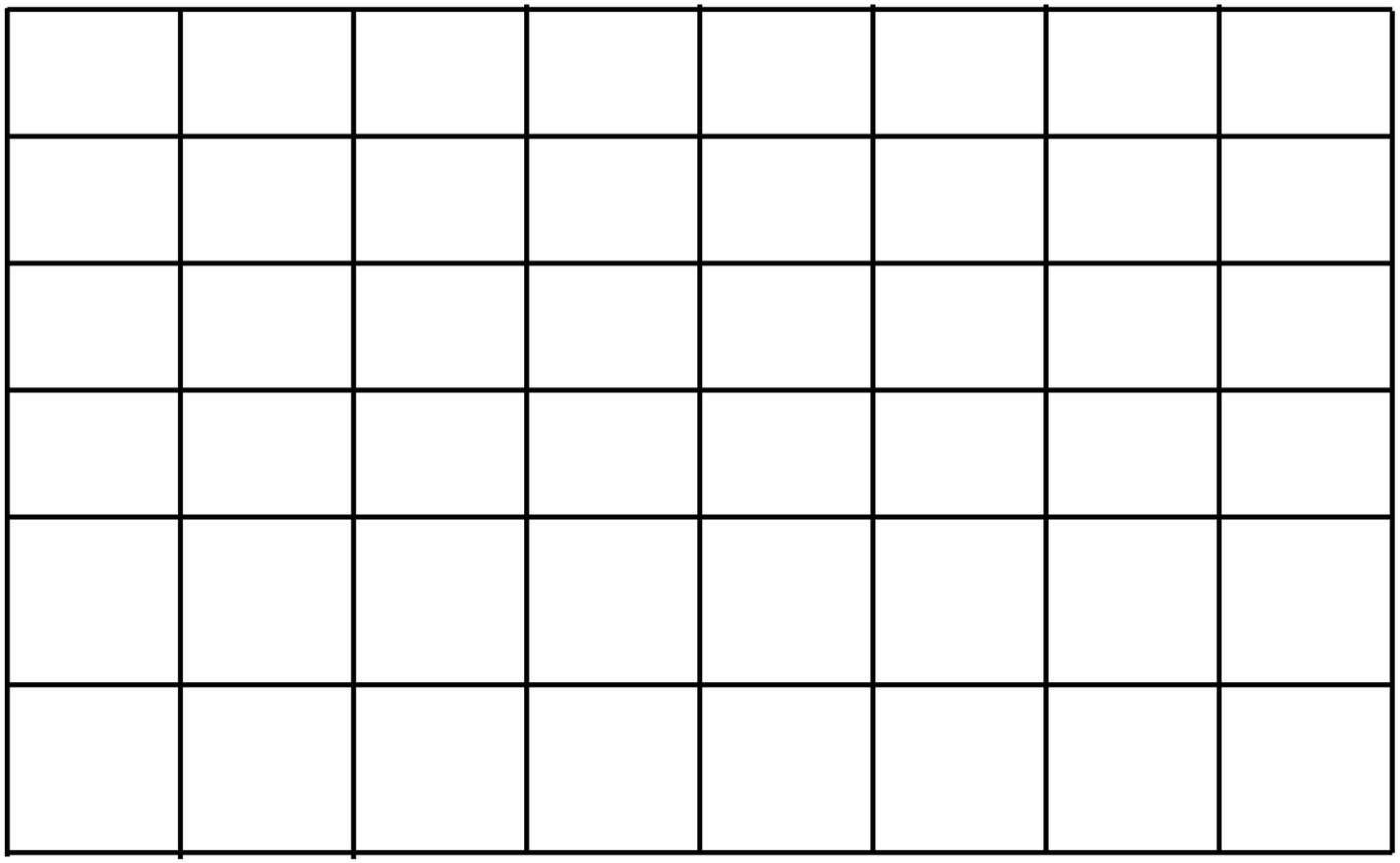

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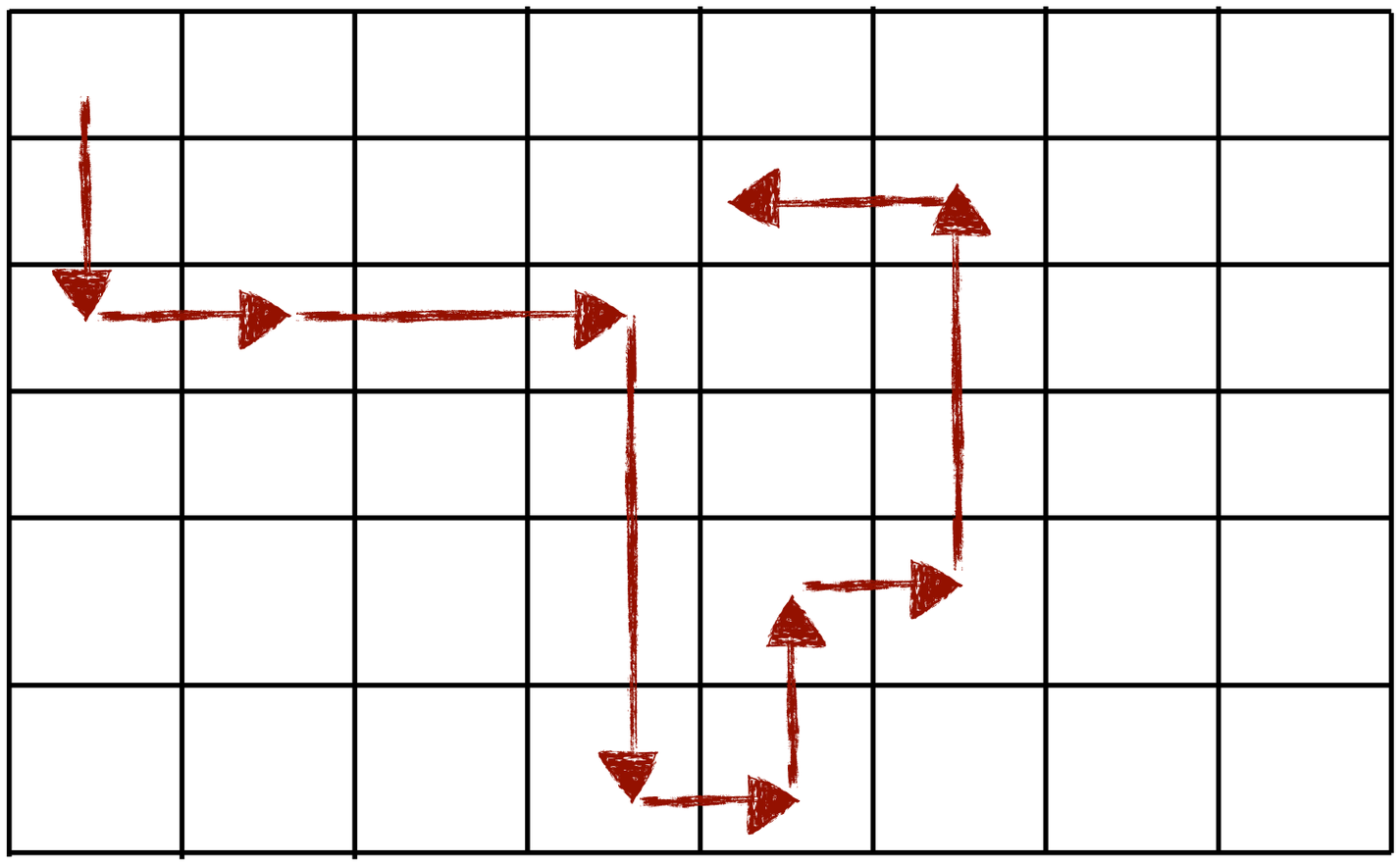

- Long enough trajectories will adequately sample phase space

Simulating the Time Evolution

- Need to evaluate the forces on particles/nuclei
- Classical MD uses empirical potentials
- Numerous approaches exist for *ab initio* MD
- Ehrenfest dynamics
- *Car-Parrinello MD (CPMD)*
- **Born-Oppenheimer MD (BOMD)**

Born-Oppenheimer MD

- Work within the Born-Oppenheimer approximation
  - Separation of nuclear & electronic DoFs

- Nuclei evolve in time
- *Electronic structure* problems is solution to *time-independent* Schrodinger equation: *static problem*

- BOMD equation of motion:

$$m_i \ddot{\mathbf{r}}_i(t) = -\nabla_{\mathbf{r}_i} \min_{\Psi_0} \{\langle \Psi_0 | \mathcal{H}_e | \Psi_0 \rangle\}$$

$$\mathcal{H}_e \Psi_0 = E_0 \Psi_0$$

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F

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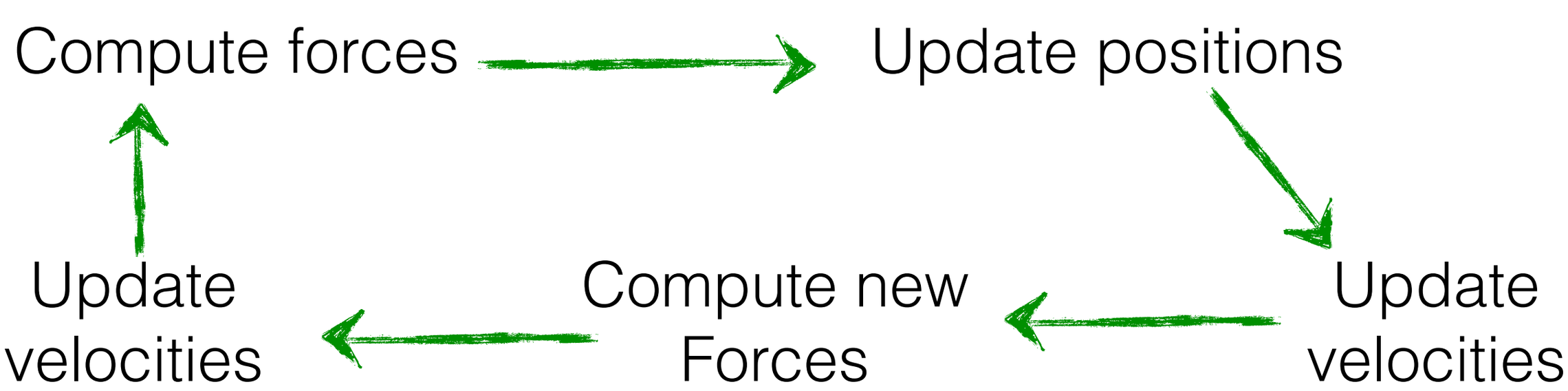
Integrating the equations of motion: the velocity Verlet algorithm

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

$$\mathbf{v}(t+\Delta t) = \mathbf{v}(t) + \frac{\mathbf{F}(t) + \mathbf{F}(t+\Delta t)}{2m}\Delta t$$



- Global error $O(\Delta t^2)$
- Need to carefully choose Δt

Exercise 1, *Timesteps*

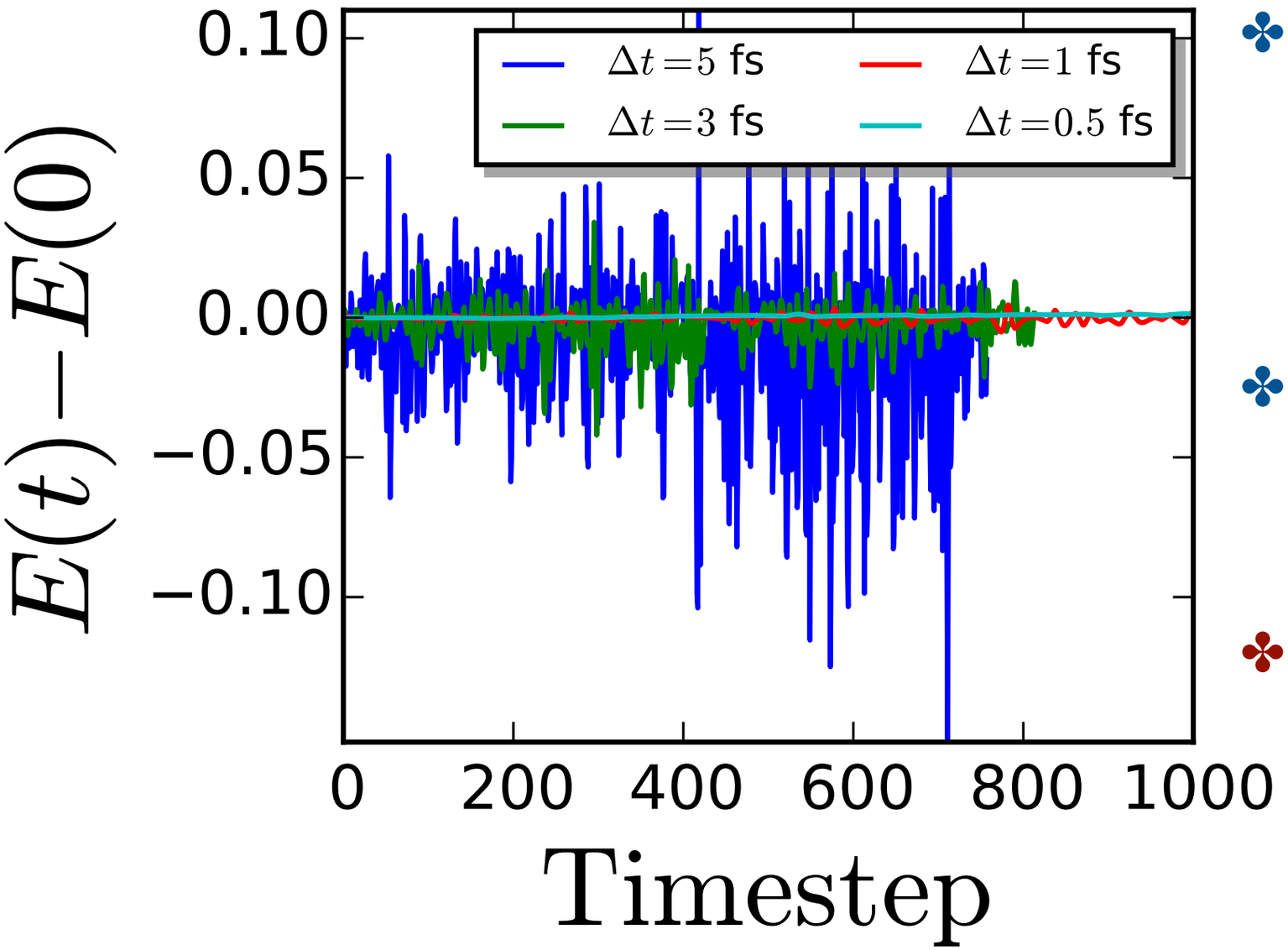
- Run MD simulations of 8-atom liquid Si cell with Δt=0.5-3 fs

- Simulations in microcanonical (**NVE**) ensemble

- Energy is constant of motion: $\frac{\partial E}{\partial t} = 0$

- Integration scheme should conserve energy, error in discrete integration will lead to buildup of errors

Results: Exercise 1, *Timesteps*



- Energy fluctuations (and drift) increase with size of timestep
- Smaller Δt conserves E better
- Tradeoff between accuracy & efficiency

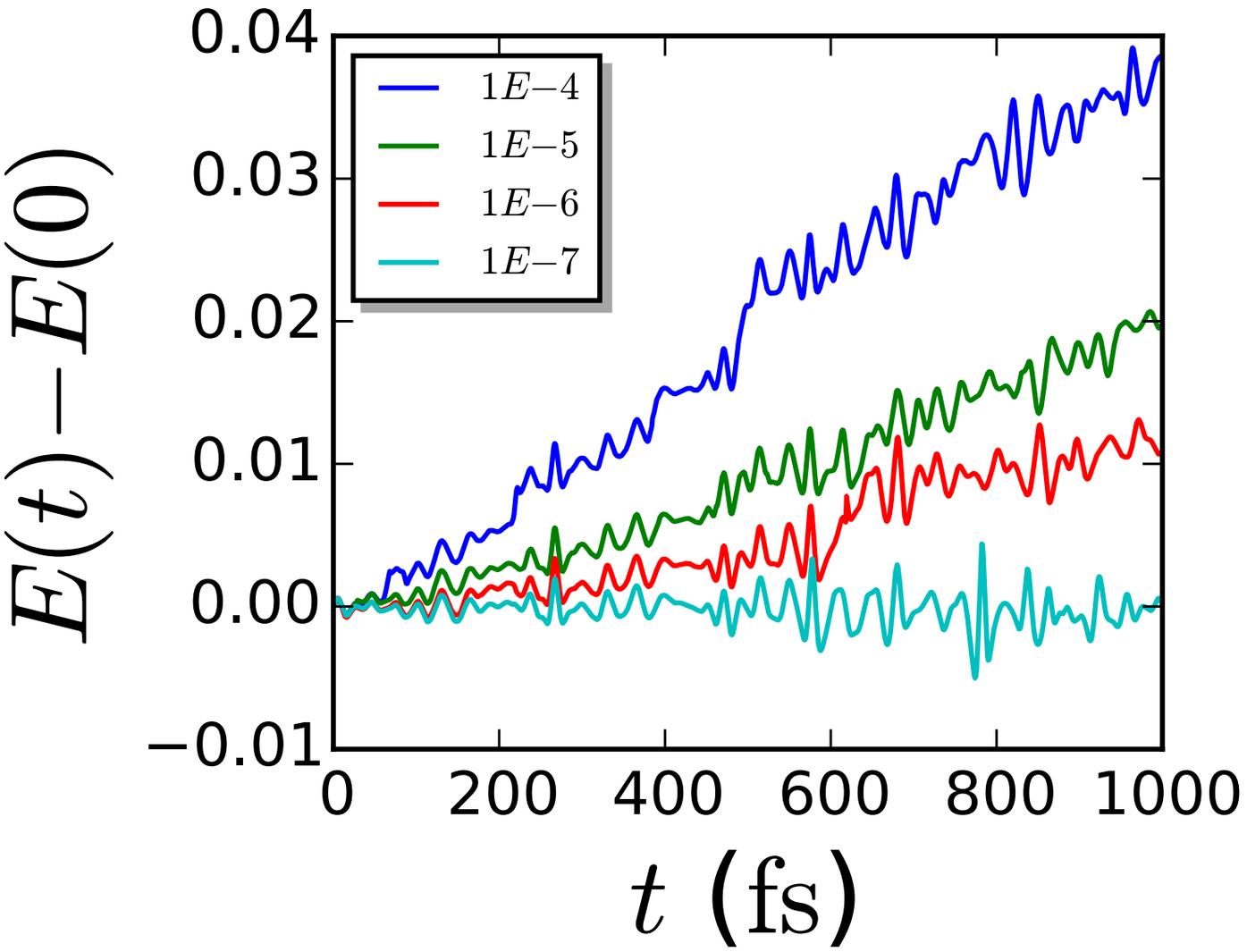
Exercise 2, *Energy Convergence*

- BOMD: Energy (and *forces*) depend on minimization of energy functional

- Sensitive to convergence criteria for self-consistent iteration

- Perform NVE BOMD for convergences of 1E-4 to 1E-7 eV for energy difference between iterations

Results: Exercise 2, *Energy Convergence*



- Energy drift increases significantly with decreasing tolerance
- Tradeoff between accuracy & efficiency

Exercise 3, *Averages*

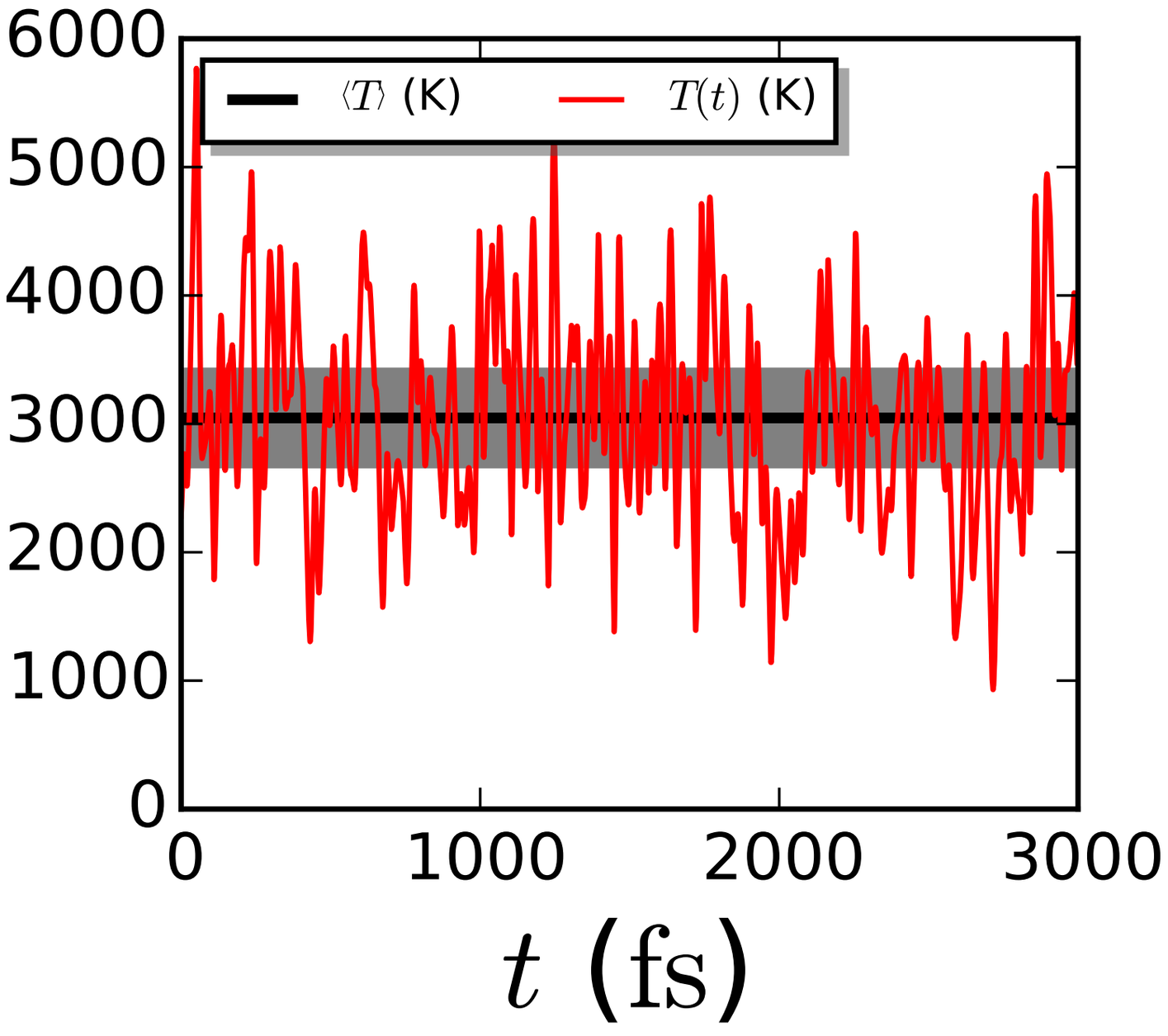
- Compute average thermodynamic, structural, and dynamic observables

- Temperature in NVE ensemble

- Pair correlation functions

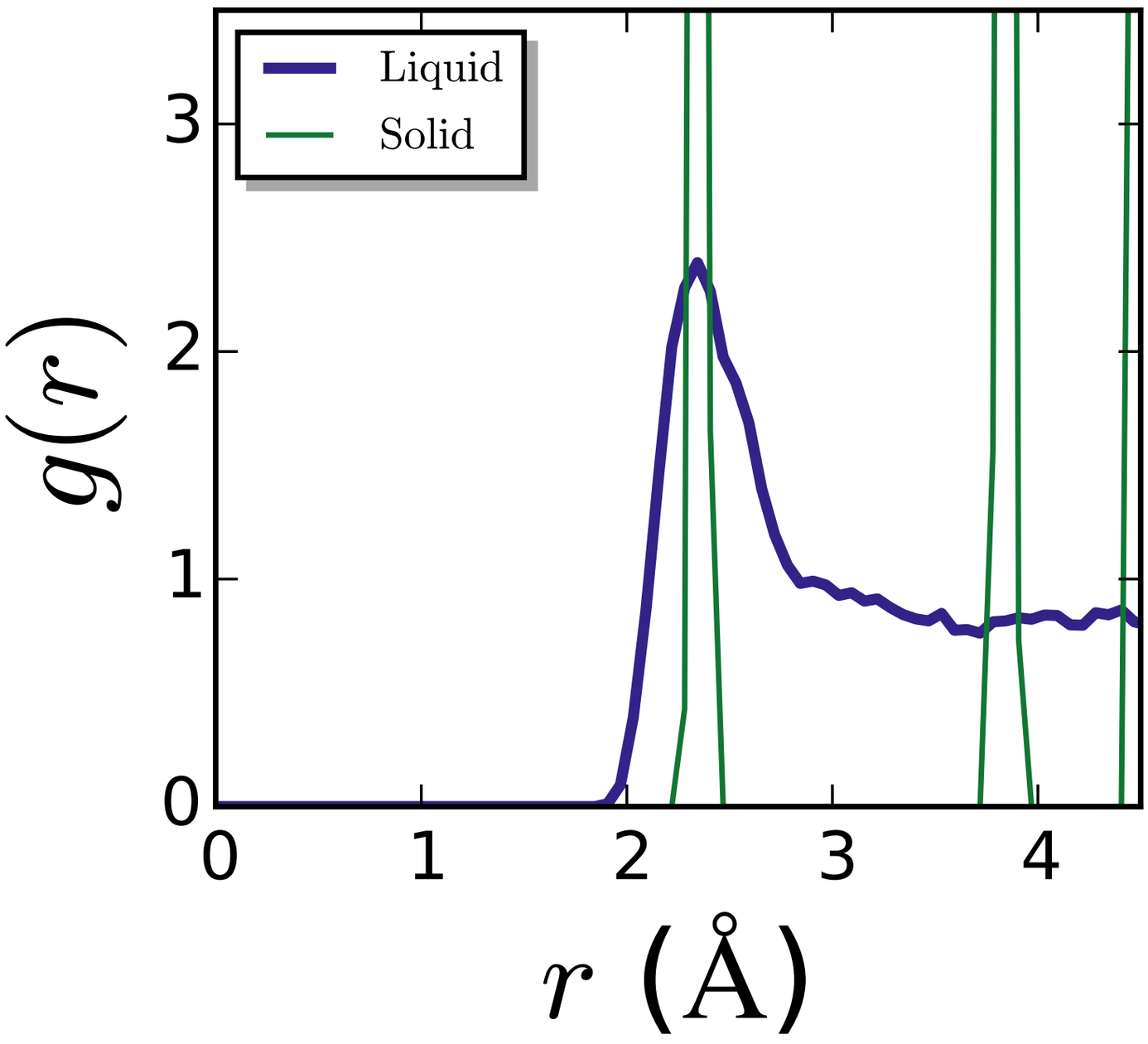
- Diffusion Coefficient: Green-Kubo vs. Einstein relations

Results: Exercise 3a, *Temperature*

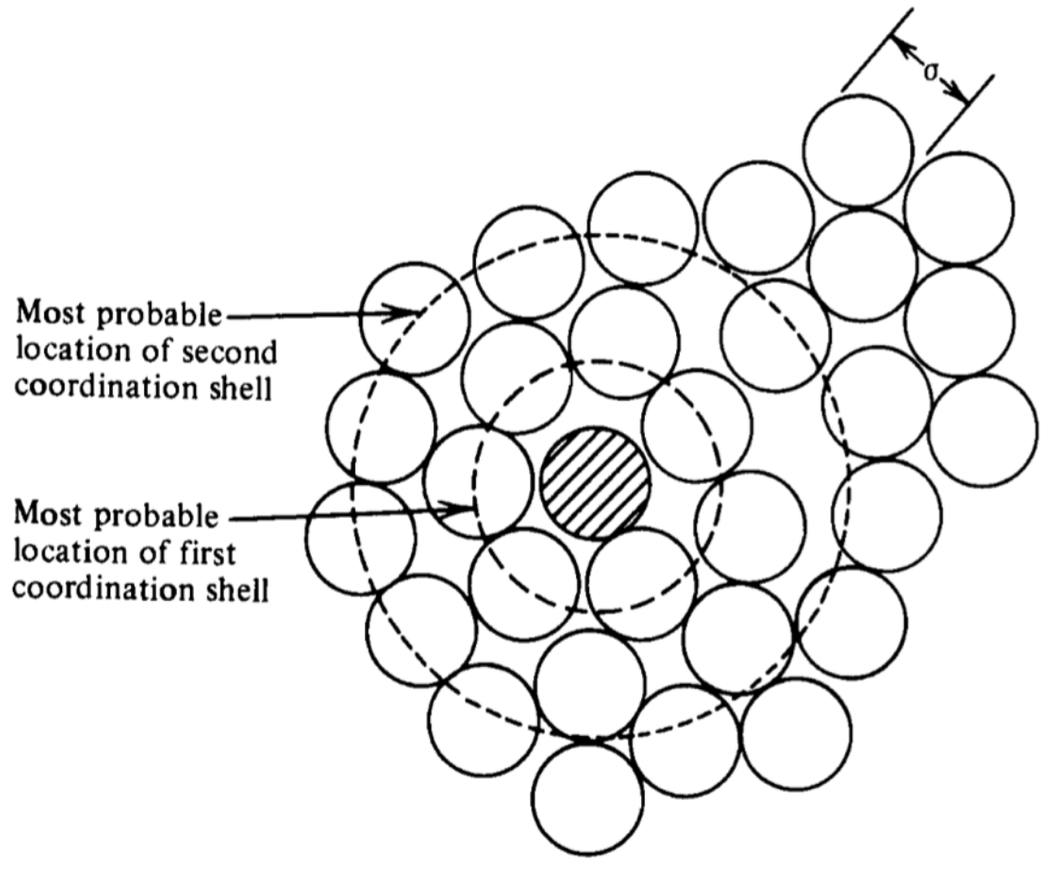


- <T> ~ 3000 K

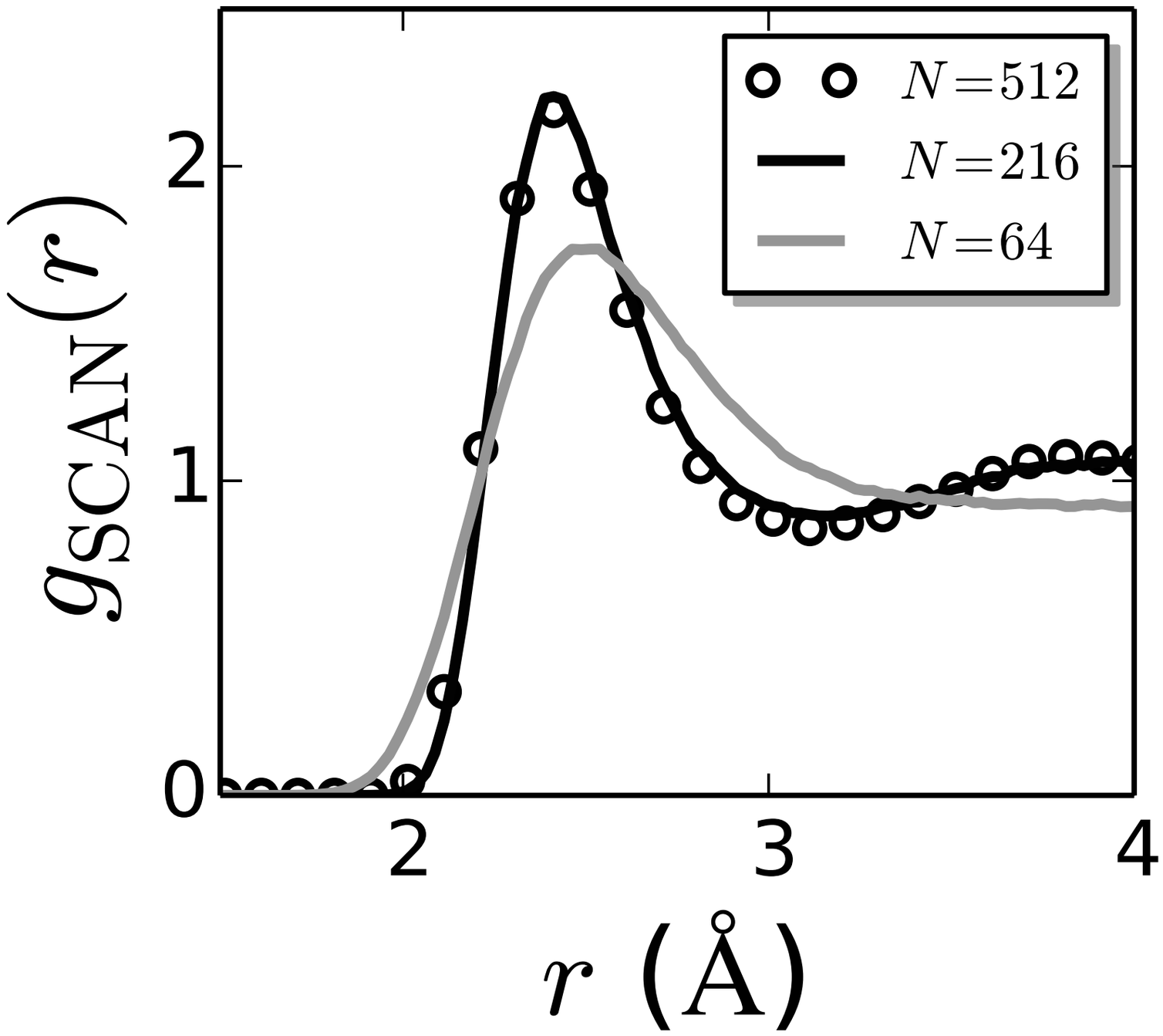
Results: Exercise 3b, *Structure*



- Disordered liquid, ordered solid



Finite size effects in *l*-Si



Exercise 3c, *Dynamics*

- MD also enables computation of dynamic properties

- **Green-Kubo:** Transport coefficients related to integral of time correlation function (TCF)

$$D = \frac{1}{3}\int_0^\infty dt\, \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$$

Exercise 3c, *Dynamics*

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- **Green-Kubo:** Transport coefficients related to integral of time correlation function (TCF)

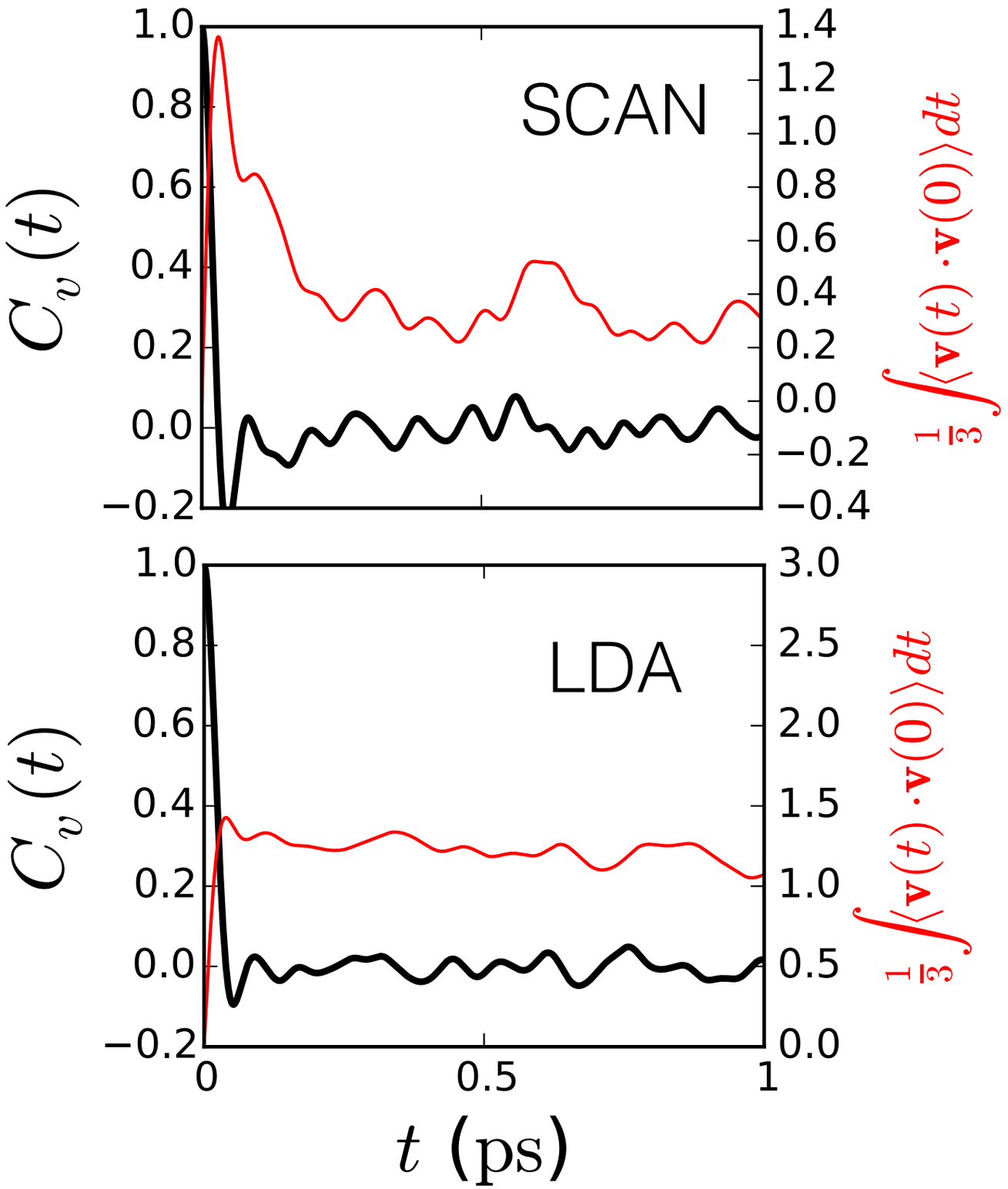
$$D = \frac{1}{3}\int_0^\infty dt\,\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$$

- **Einstein:**

$$6Dt = \lim_{t\to\infty}\langle|\mathbf{r}(t)-\mathbf{r}(0)|\rangle$$

- Should yield equivalent *D* values…

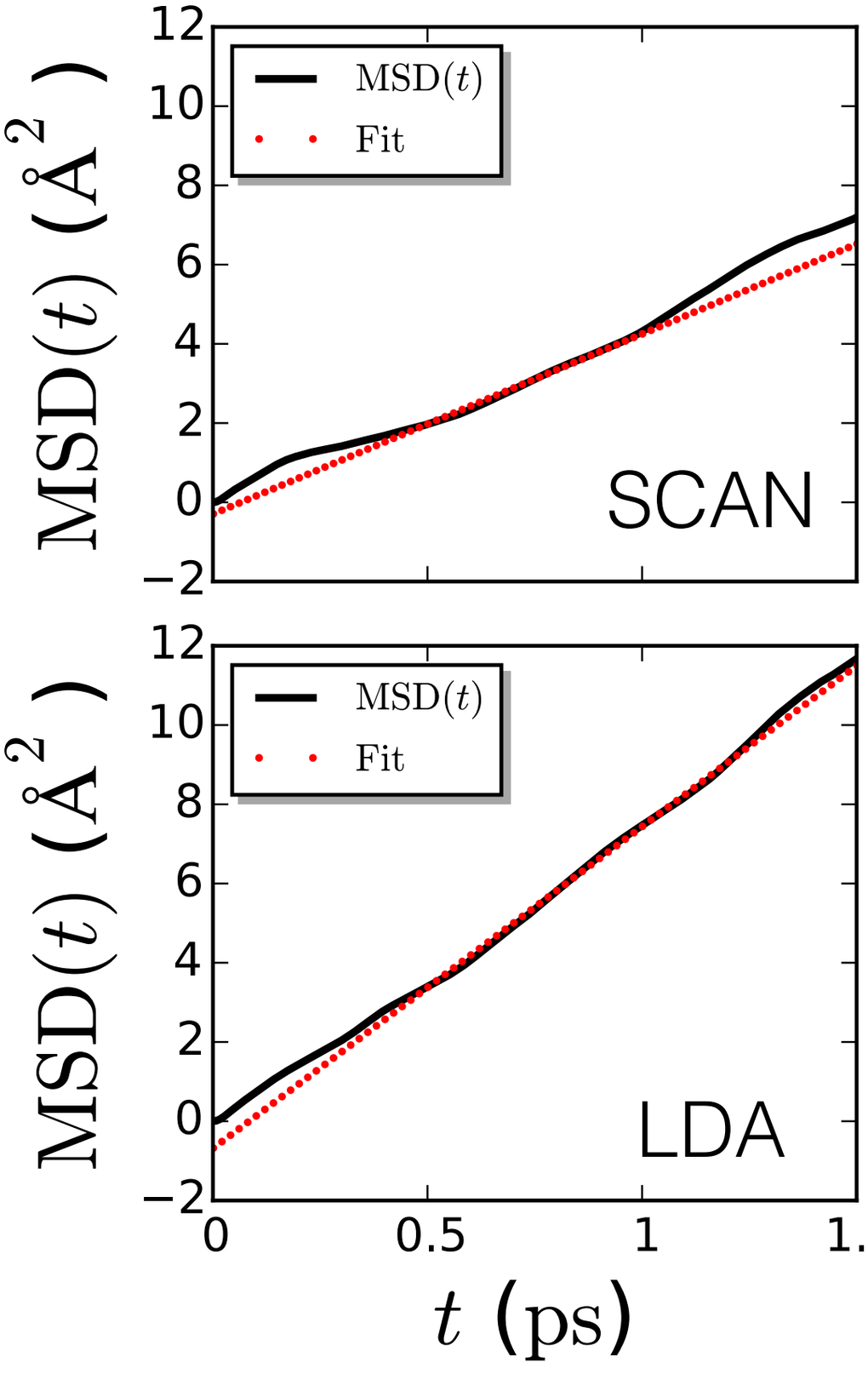
Results: Exercise 3c, *Dynamics from TCFs*



- $D_{SCAN} \sim 0.4$ Å^2 / ps
- $D_{LDA} \sim 1.4$ Å^2 / ps

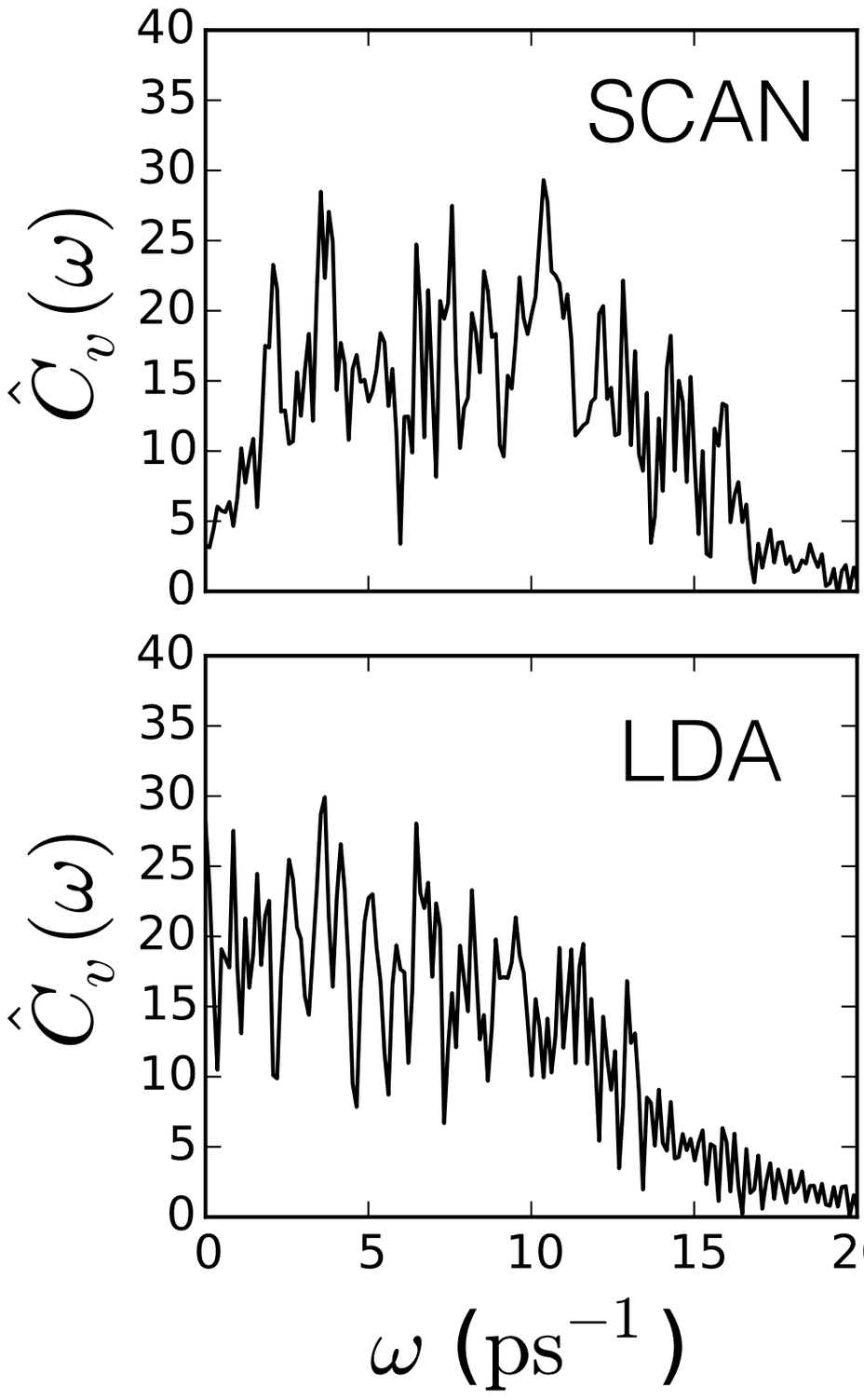
- Green-Kubo type relations typically take longer to converge than MSD, for example…

Results: Exercise 3d, *Dynamics from MSD*



- $D_{SCAN} \sim 0.76$ Å^2 / ps
- $D_{LDA} \sim 1.35$ Å^2 / ps
- Consistent with VACF results
- *Faster dynamics in LDA due to lack of good covalent bonds*

Results: Exercise 3e, *Phonon Density of States*



- Phonon DOS is Fourier transform of velocity autocorrelation function, *C(t)*

- Qualitatively similar
- Need better statistics

- *Can compare with solid in phonon tutorial…*

Exercise 4, *Canonical (NVT) Ensemble*

- *Perform simulations at constant temperature*

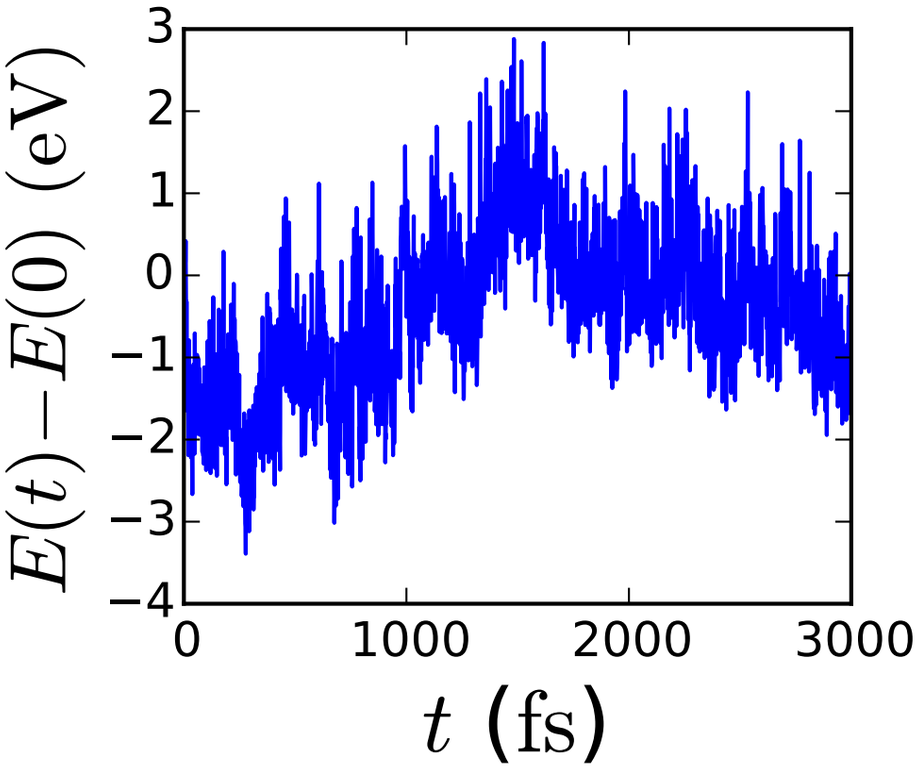
- Use Andersen thermostat (*preserves canonical distribution*)

- Mimics coupling to heat bath (with a prescribed collision frequency)

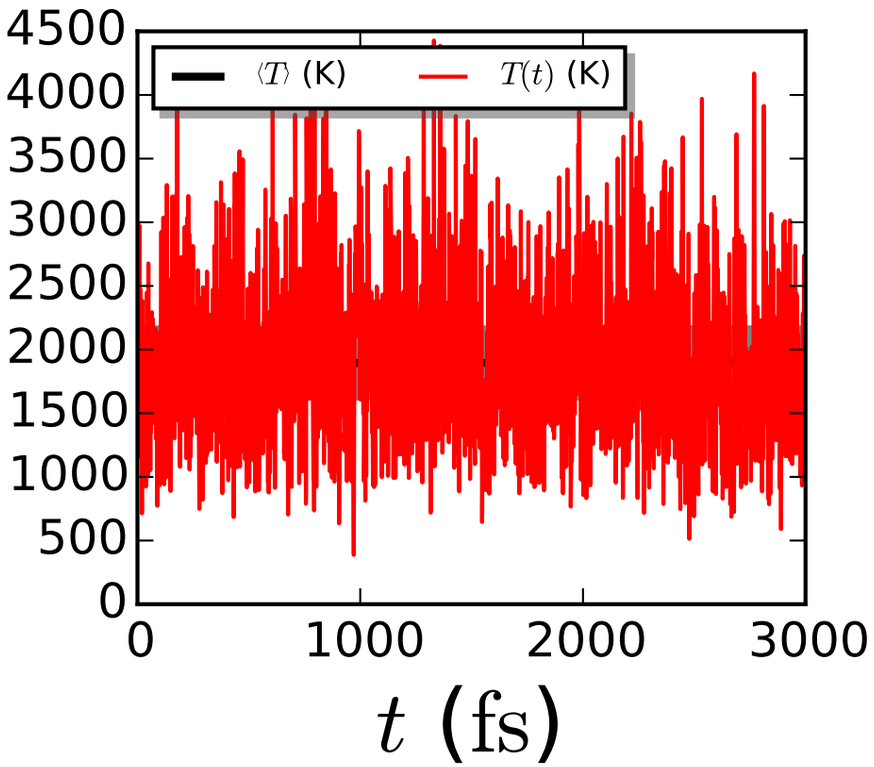
- Particle momenta are reset randomly, following Maxwell-Boltzmann distribution

- **Thermodynamics? Dynamics???**

Results: Exercise 4, *Canonical (NVT) Ensemble*

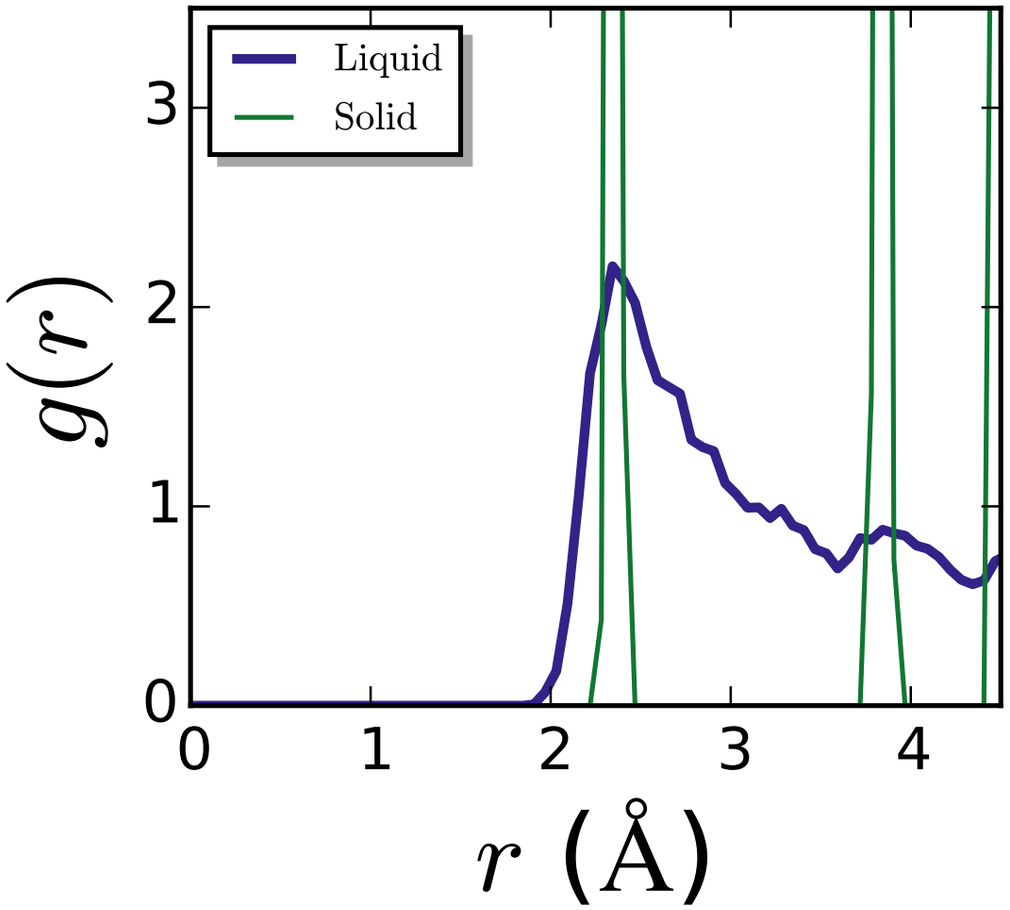


- E is not the conserved quantity
- Can fluctuate…



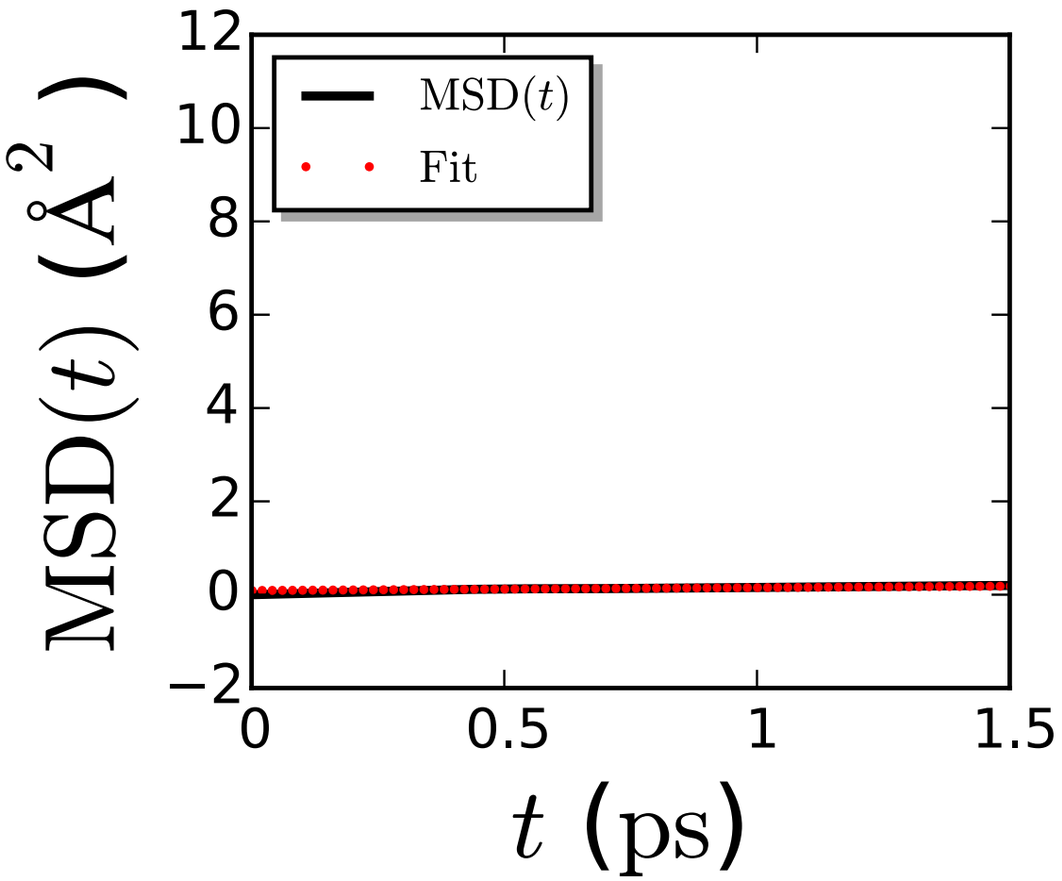
- T fluctuates about constant $\langle T \rangle$
- *Why isn't T constant?*
- Small system, constant T as N tends to infinity…

Results: Exercise 4, *Canonical (NVT) Ensemble*



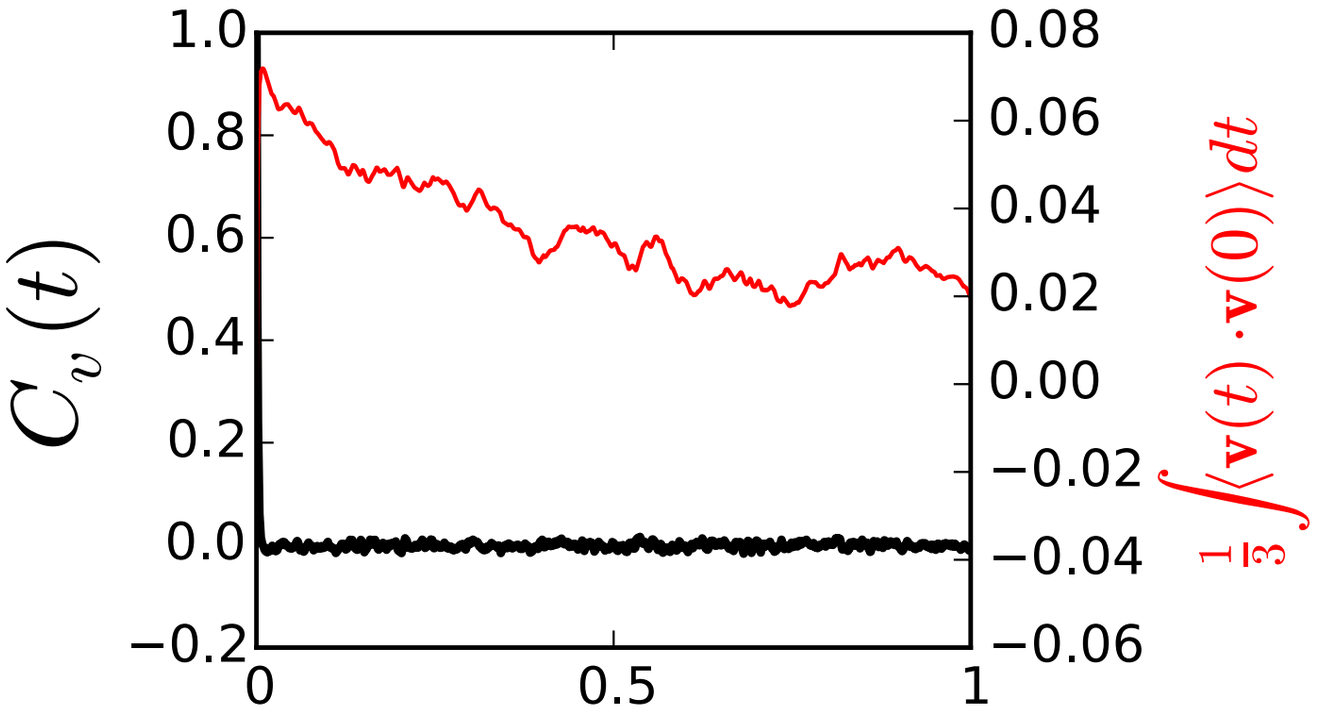
- *Structure is independent of ensemble*

Results: Exercise 4, *Canonical (NVT) Ensemble*



- *Dynamics are severely altered by thermostat*

- Extreme case, others thermostats (and weak coupling) may not significantly alter dynamics…

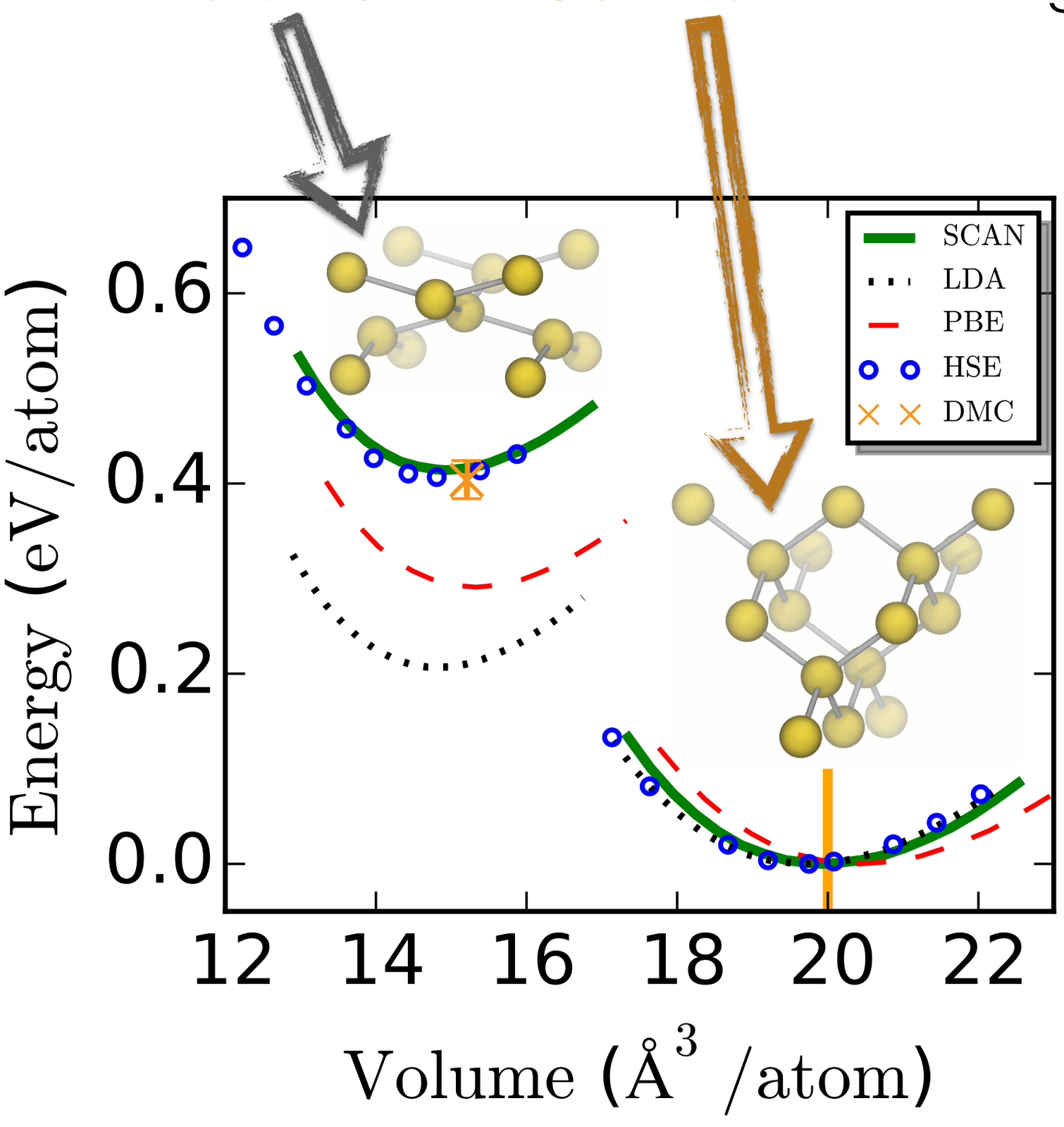


- **Be careful!**

SCAN description of silicon with MD

Background:

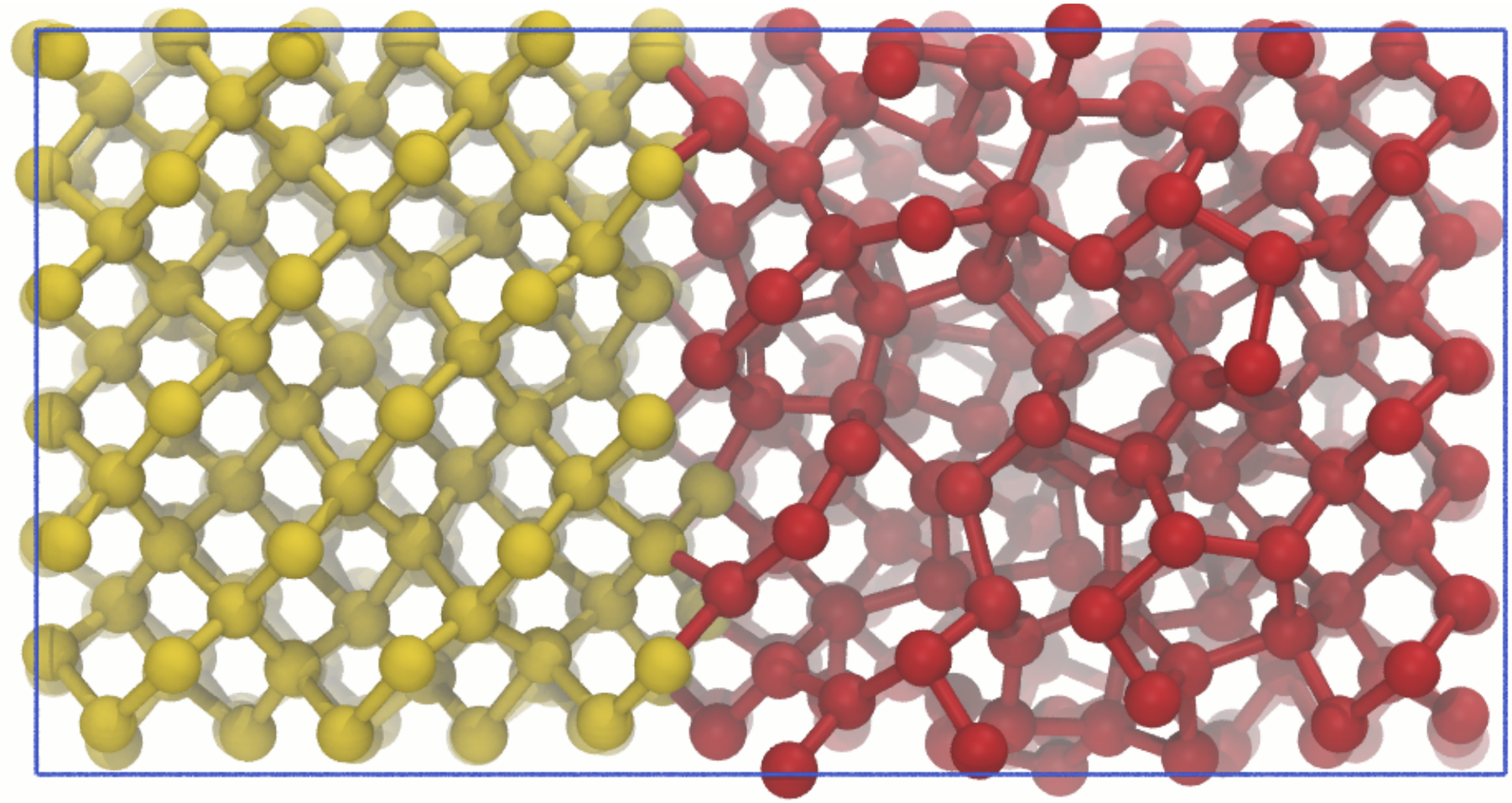
Metallic and **Covalent** Bonding in Solid Silicon



- Si transitions from semiconducting diamond to metallic ß-Sn at P~12 GPa
- SCAN captures structure and energetics with quantitative accuracy
- Distinguishes covalent from metallic bonds

J. Sun, *et al.* Nature Chem. **2016**

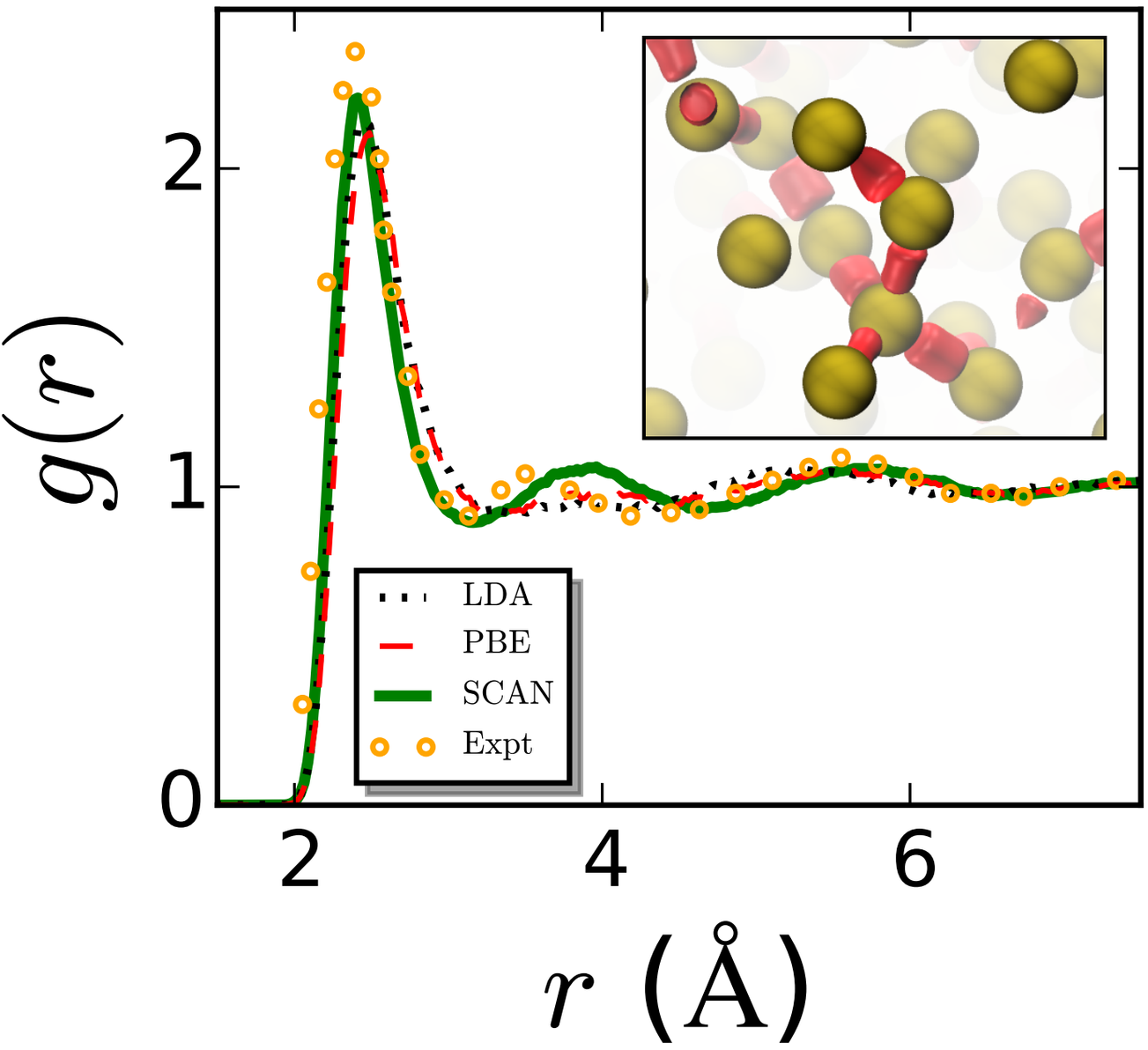
Phase Transitions



- Coexistence: semiconducting solid and metallic liquid
- $T_m \sim 1550$ K, closer to Exp. (1680 K) than previous estimates using LDA: 1200-1300 K

RCR, J. Sun, M. L. Klein, to be submitted

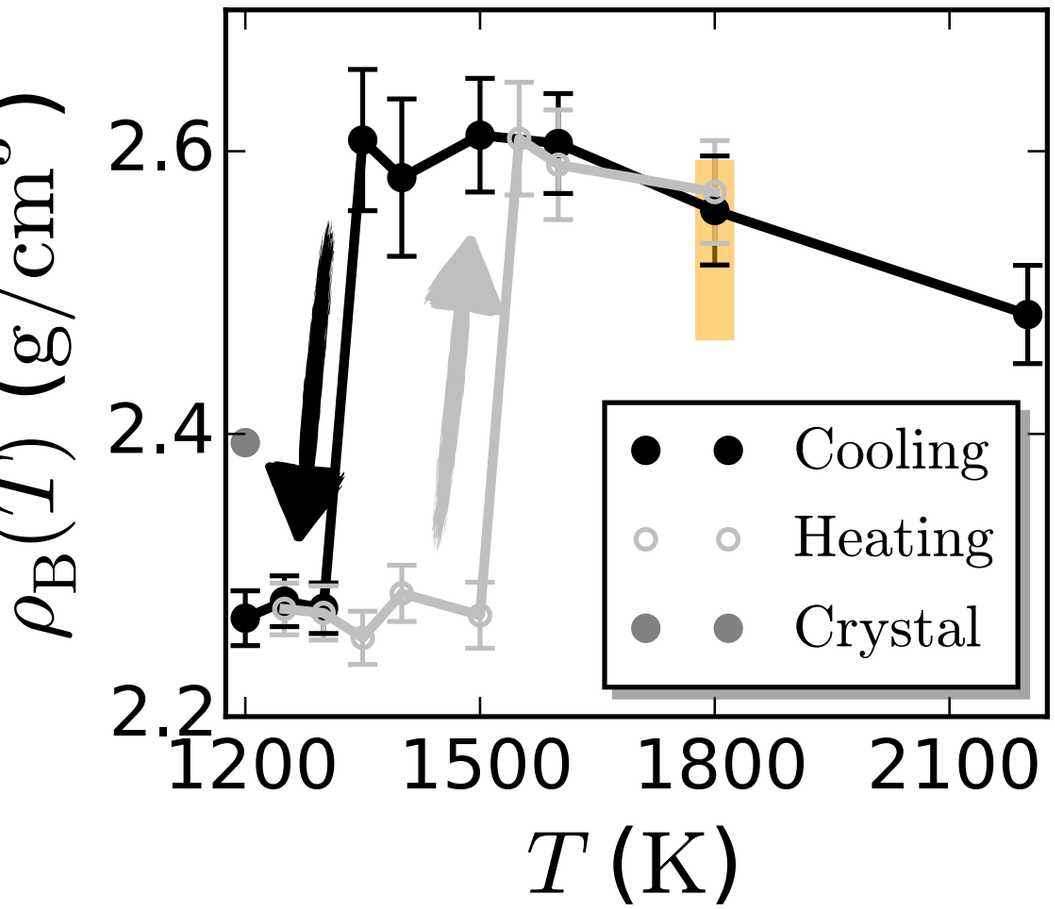
Mixed Interactions: Liquid Silicon



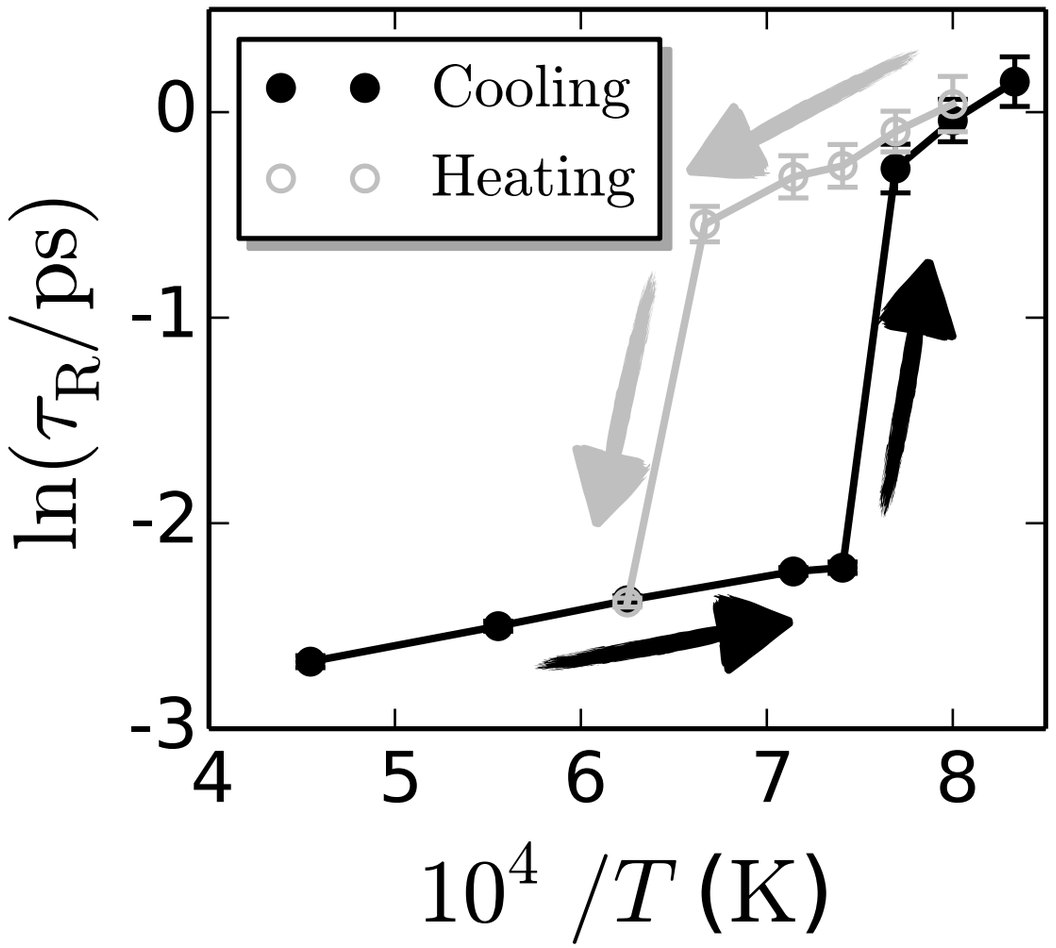
- l-Si is largely metallic; some covalent character
- 2nd peak is absent in LDA/PBE descriptions
- LDA/PBE lack adequate discrimination between metallic and covalent bonding

J. Sun, *et al.* Nature Chem. **2016**

More phase transitions



✤ Thermodynamics



✤ Dynamics

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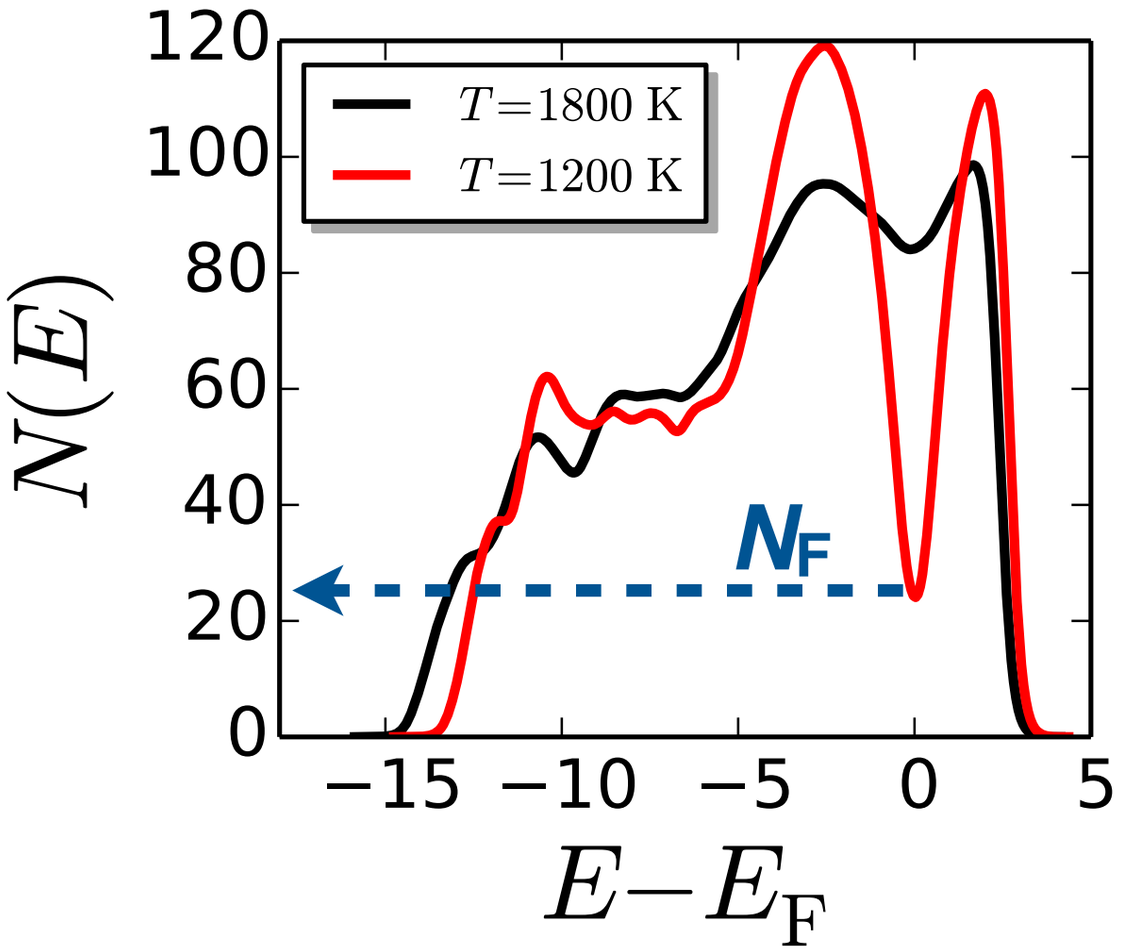
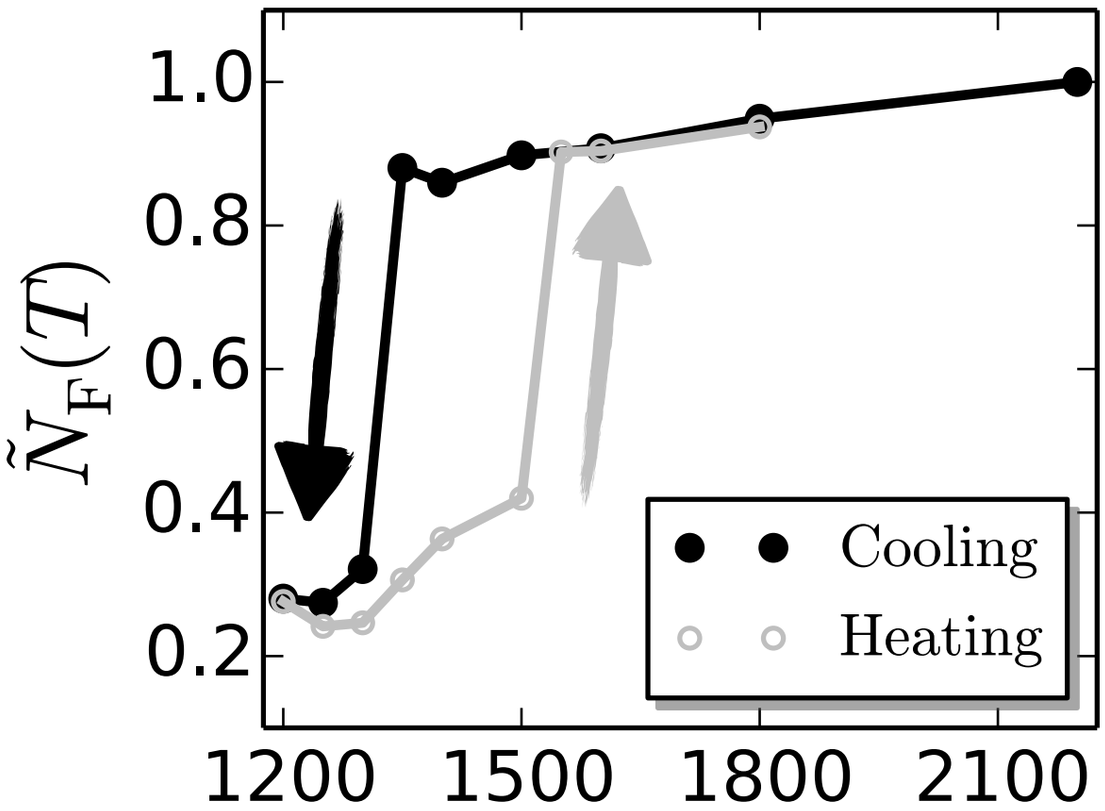
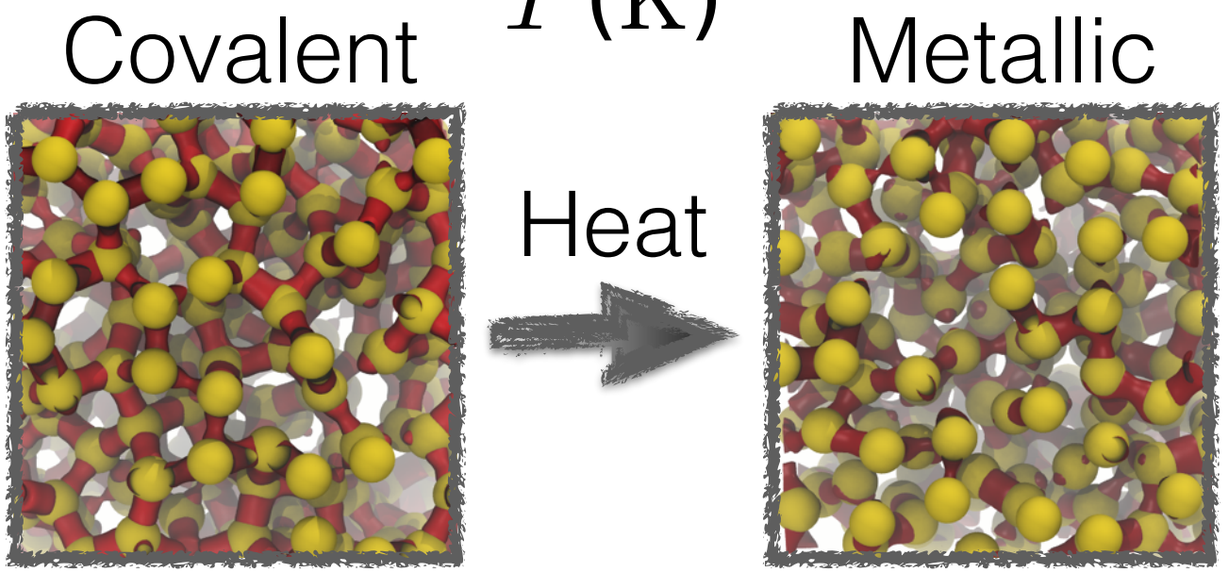
Changes in Electronic Structure





- DOS follows density dependence on T
- Transition from covalent and metallic bonding dominating



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Q & A