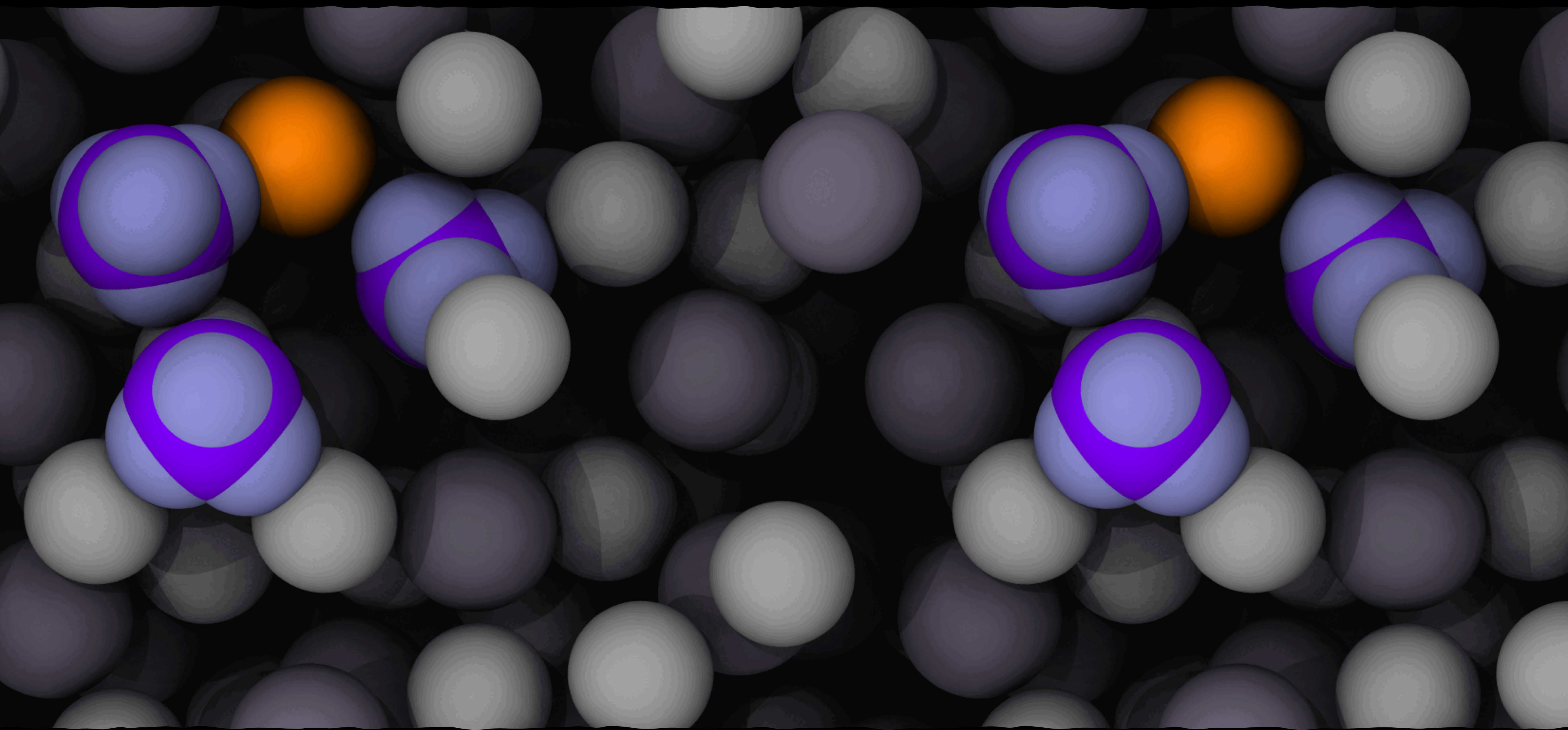
Predicting Properties from First-Principles II:
Total Energy and Force Applications



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RUTGERS

Acknowledgements

Neil Hall

Atul Thakur (now @ UCSD)

Hank Longo

Harender Dhattarwal

Colin Hylton-Farrington

Olivia Martin

Melany Contreras*

Hari Rajesh*

Henry Bilton*

Nistha Sheth*

Funding:

Army Research Office

ACS PRF

ASTROBIOLOGY at NASA
LIFE IN THE UNIVERSE

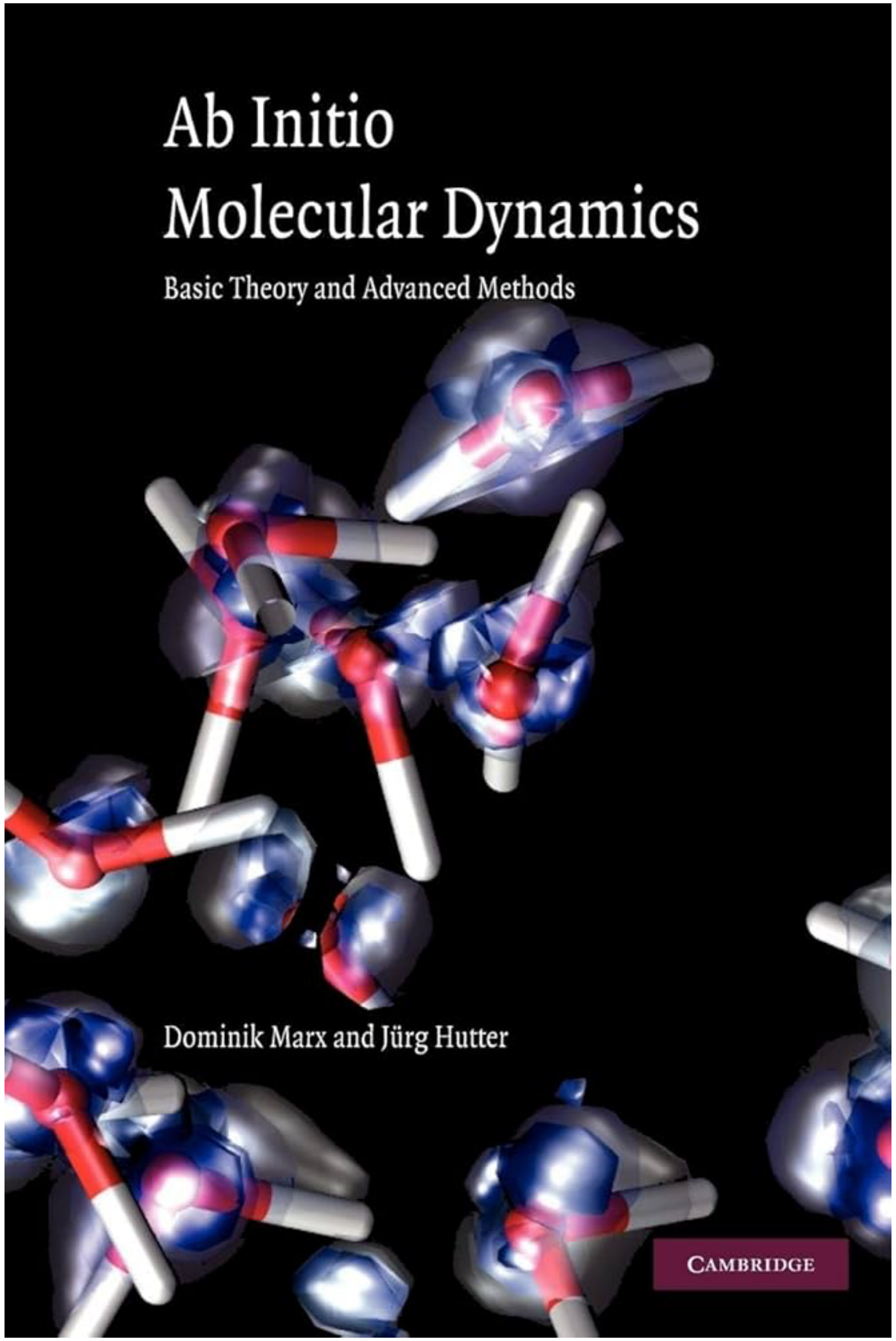
ACCESS

U.S. DEPARTMENT OF ENERGY

NASA Planetary Science Early Career Award

XSEDE
Extreme Science and Engineering Discovery Environment

Good References to Learn More



The Journal of Chemical Physics
ARTICLE
scitation.org/journal/jcp

CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations

Cite as: J. Chem. Phys. **152**, 194103 (2020); doi: 10.1063/5.0007045
Submitted: 10 March 2020 • Accepted: 22 April 2020 •
Published Online: 19 May 2020

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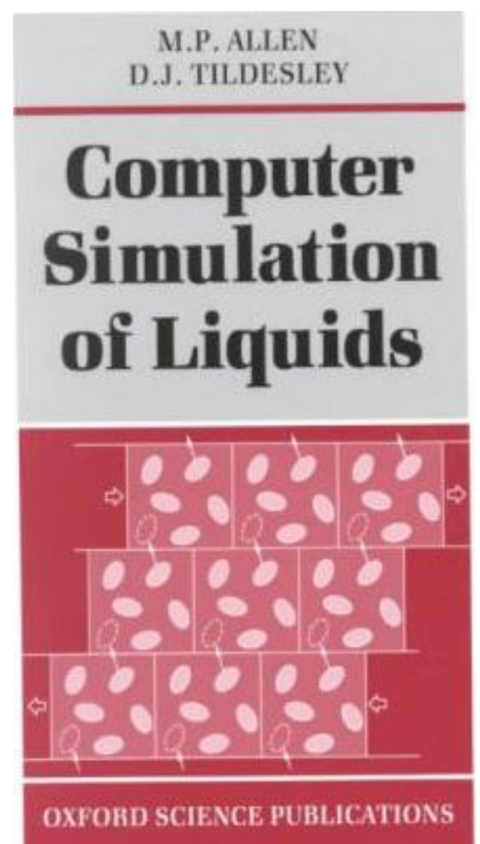
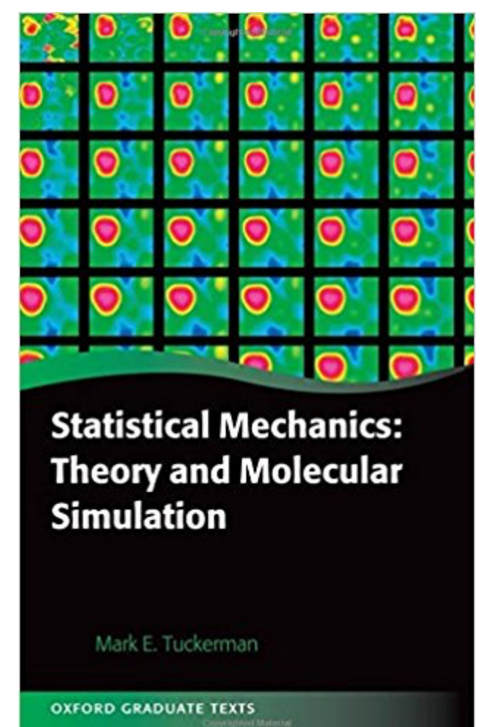
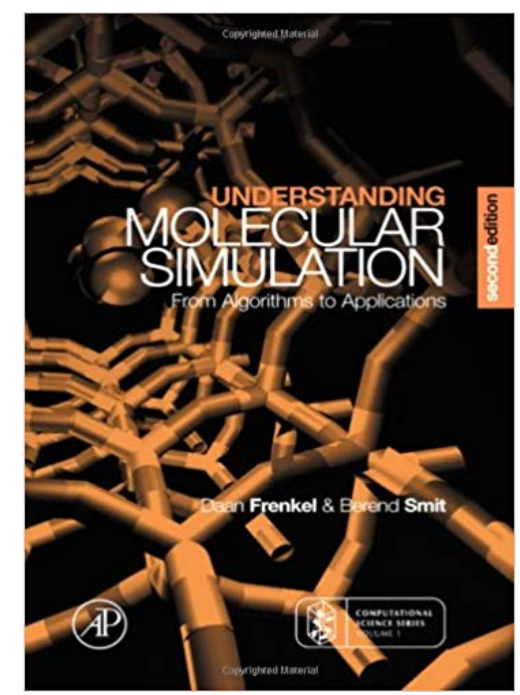


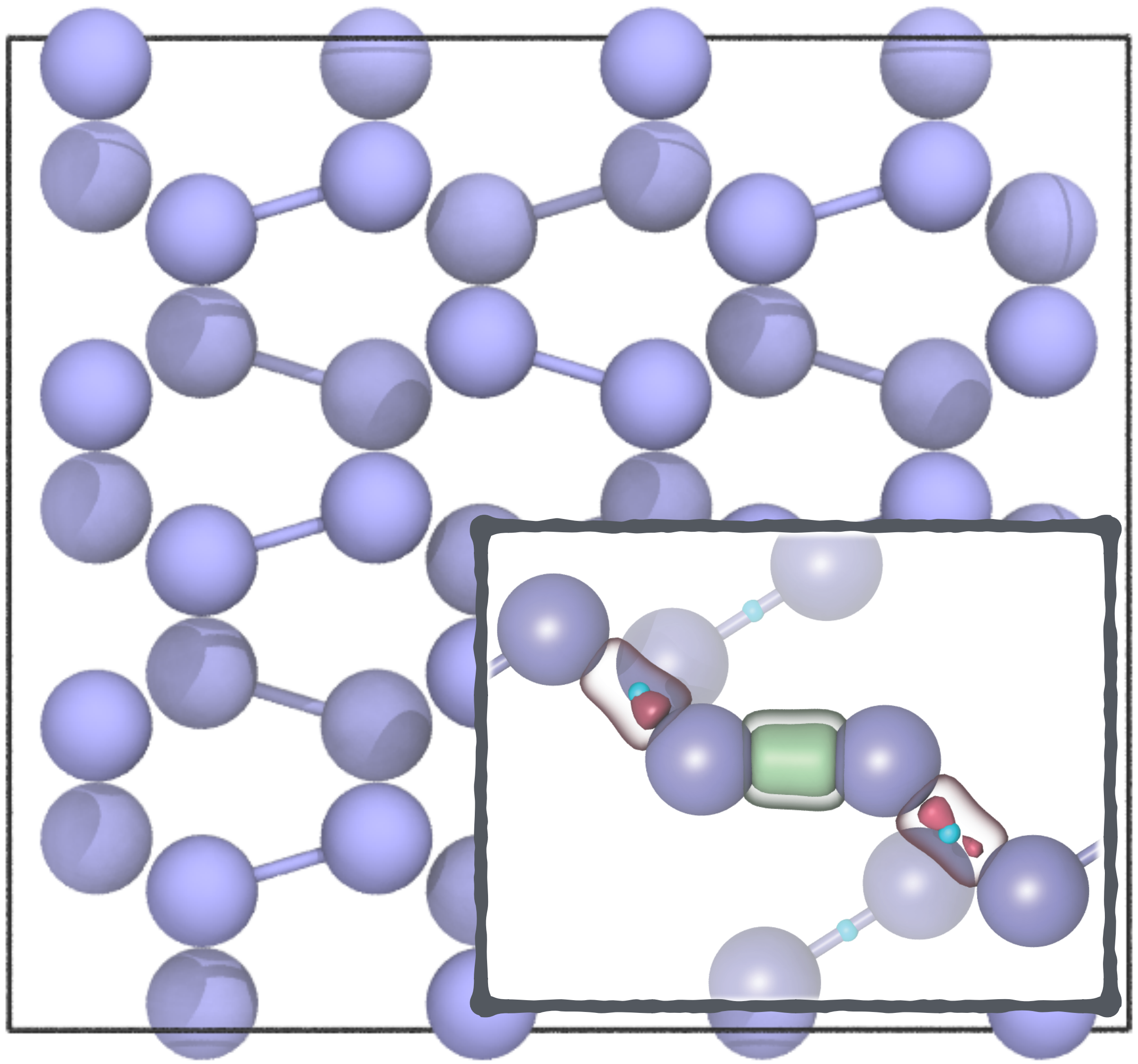




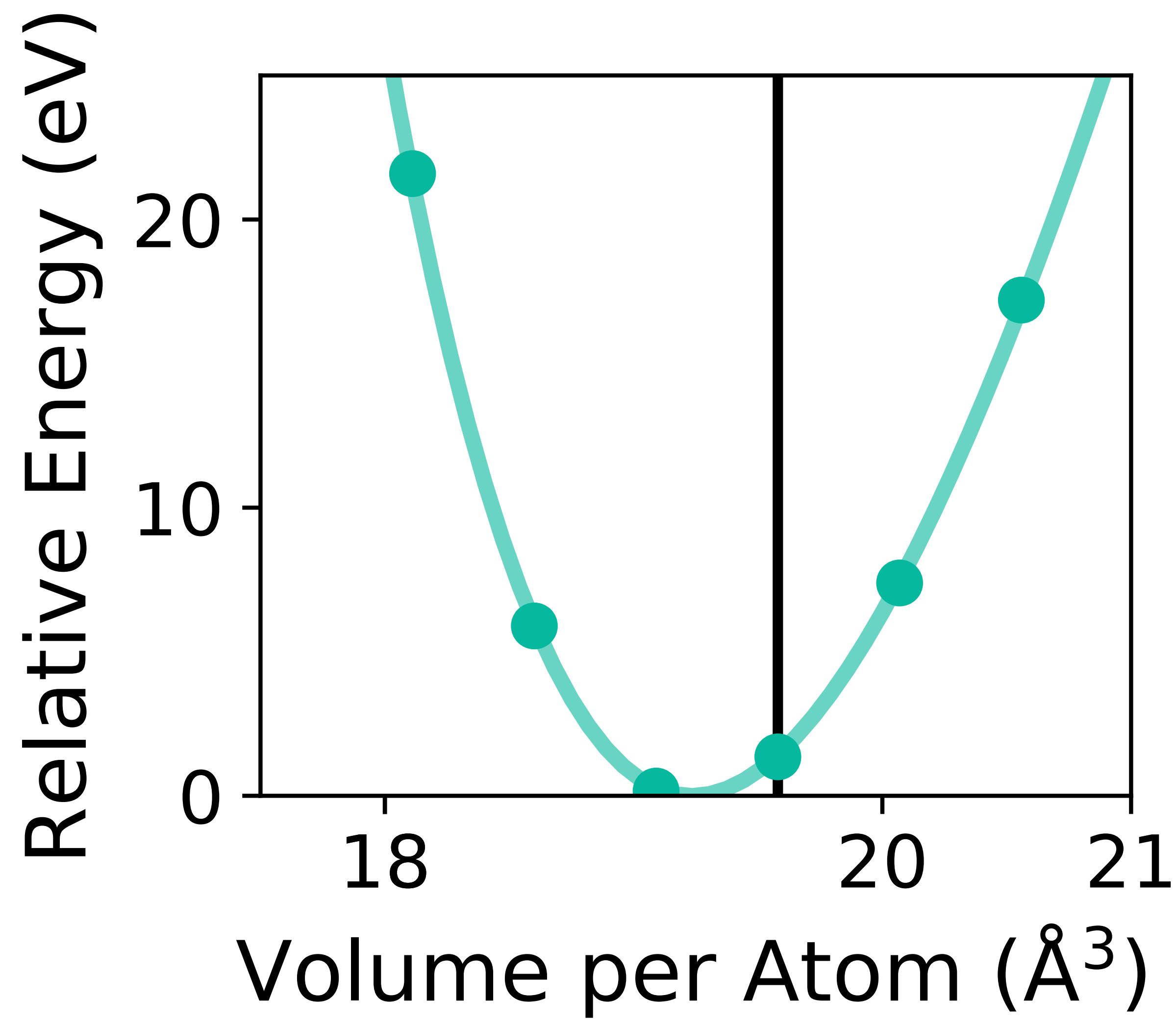
Why think about total energy?

- Many important materials properties depend on total energy

α-Gallium



- **Equation of State & Bulk Moduli**



Murnaghan equation of state:

$$E(V) - E_0 = K_0 V_0 \left[\frac{1}{K_0'(K_0'-1)} \left(\frac{V}{V_0} \right)^{1-K_0'} + \frac{1}{K_0'} \frac{V}{V_0} - \frac{1}{K_0'-1} \right]$$

K_0 = bulk modulus

RCR *et al.* Mol Phys 2018

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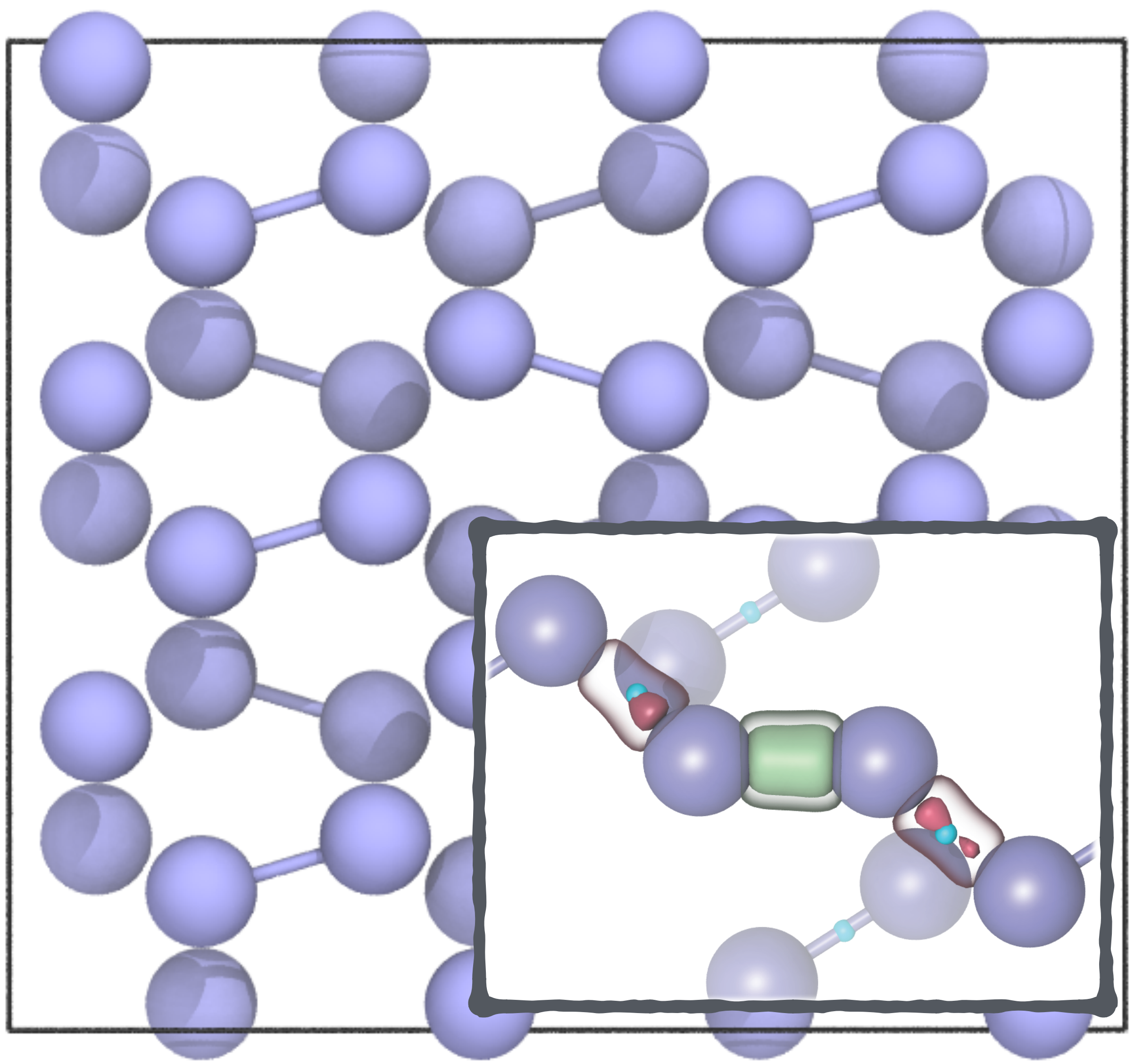

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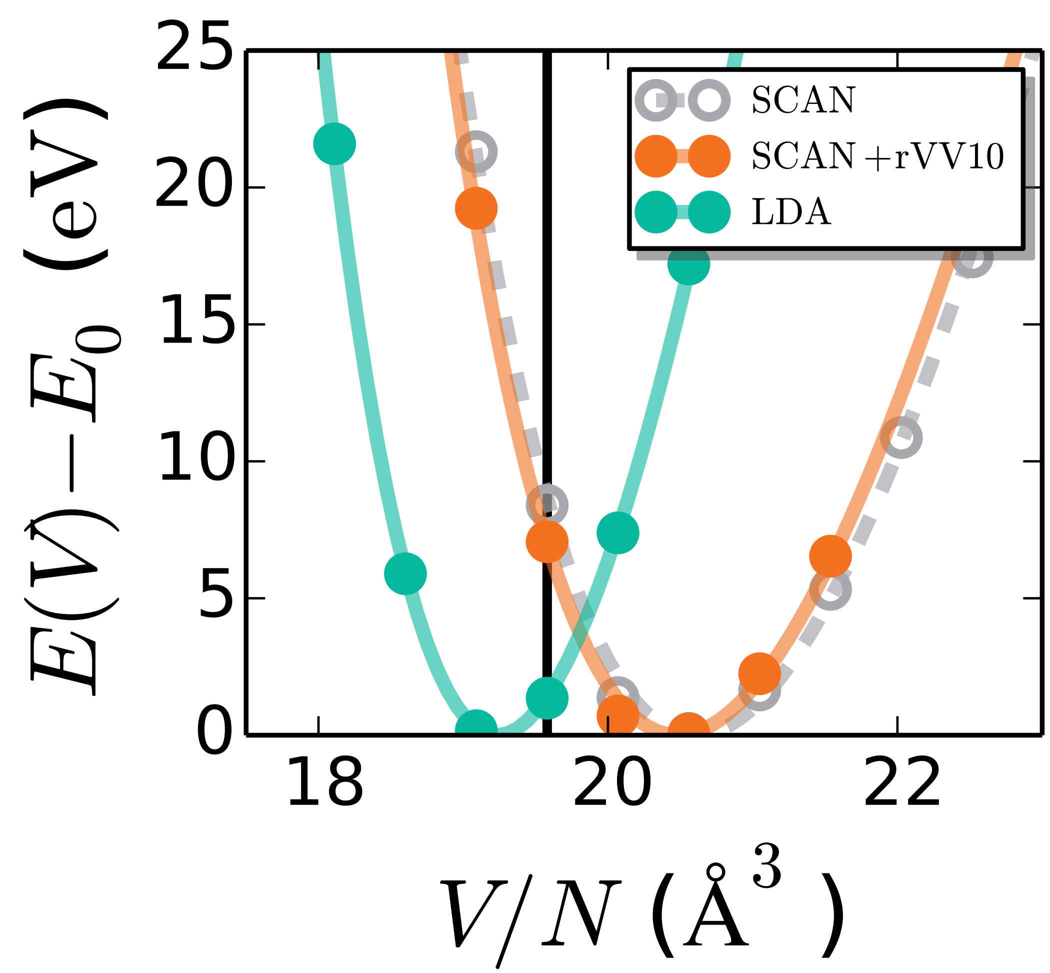

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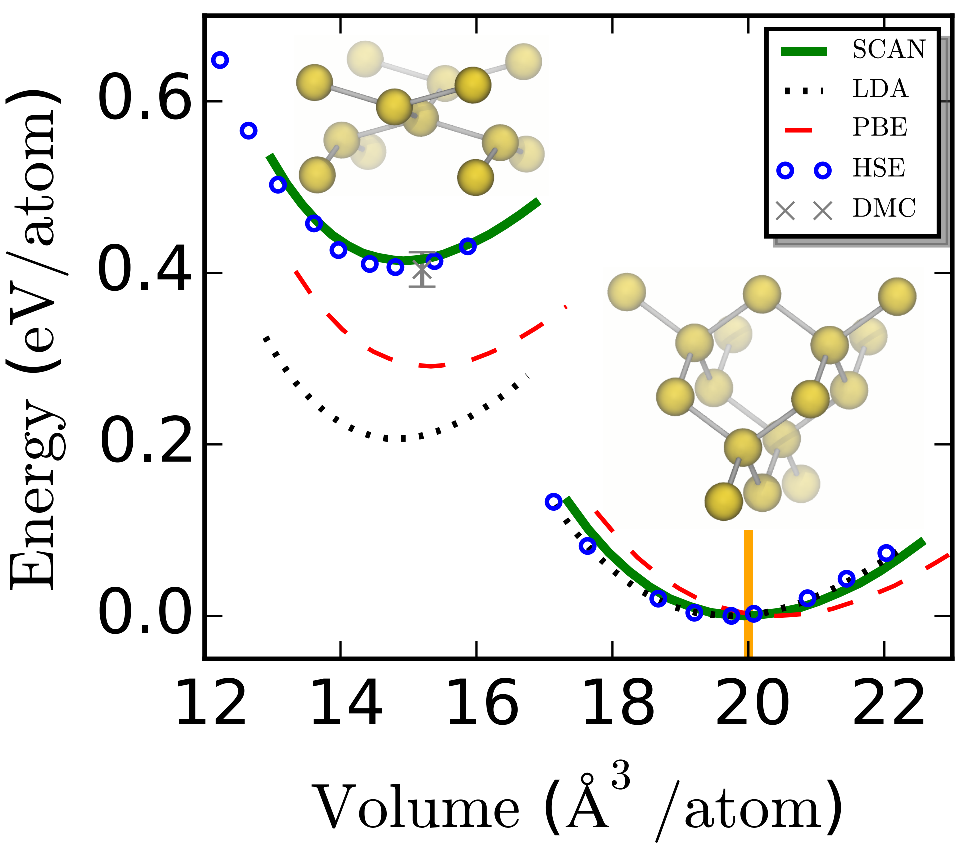
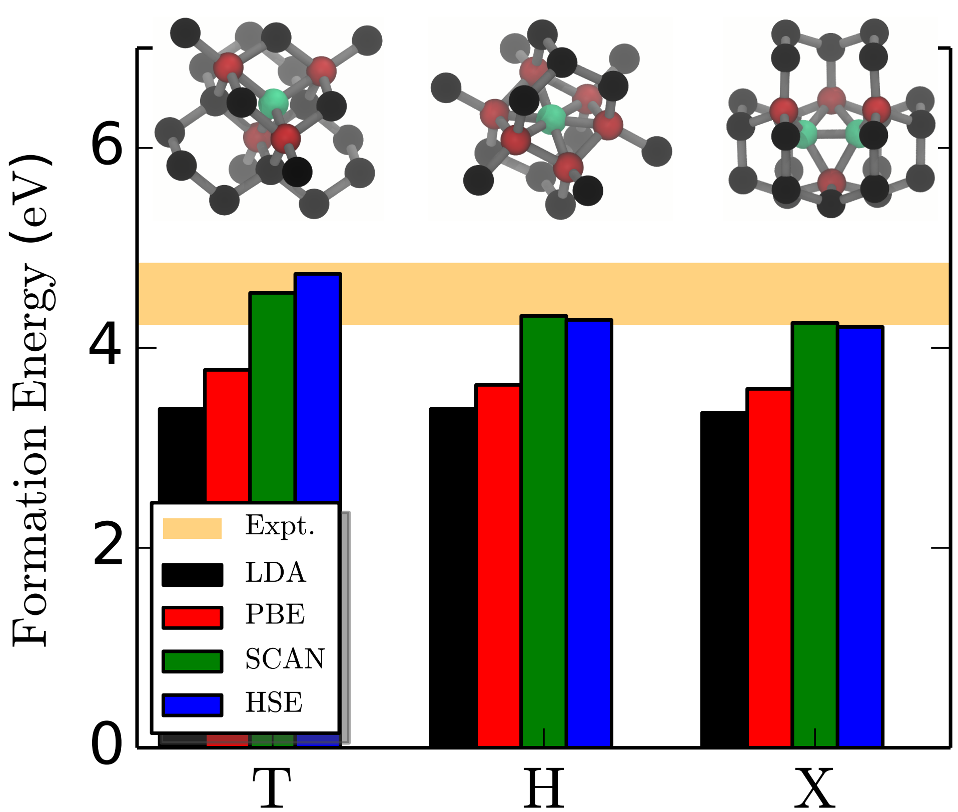
RCR *et al.* Mol Phys 2018

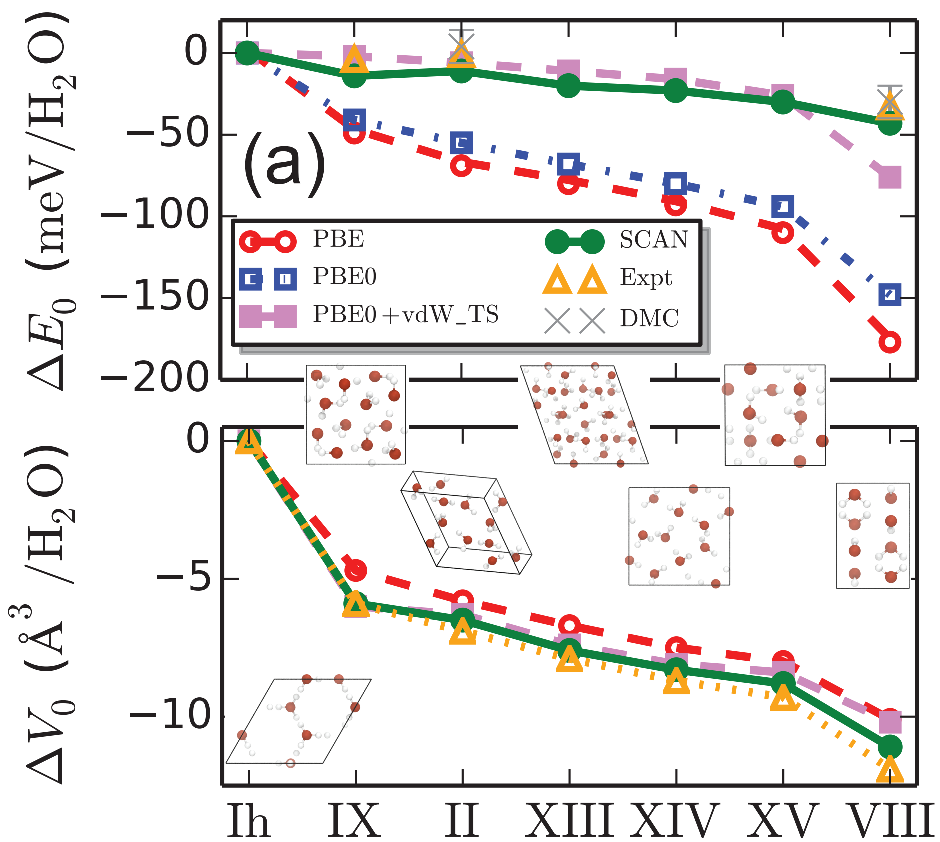
Phase Stability & Defect Formation

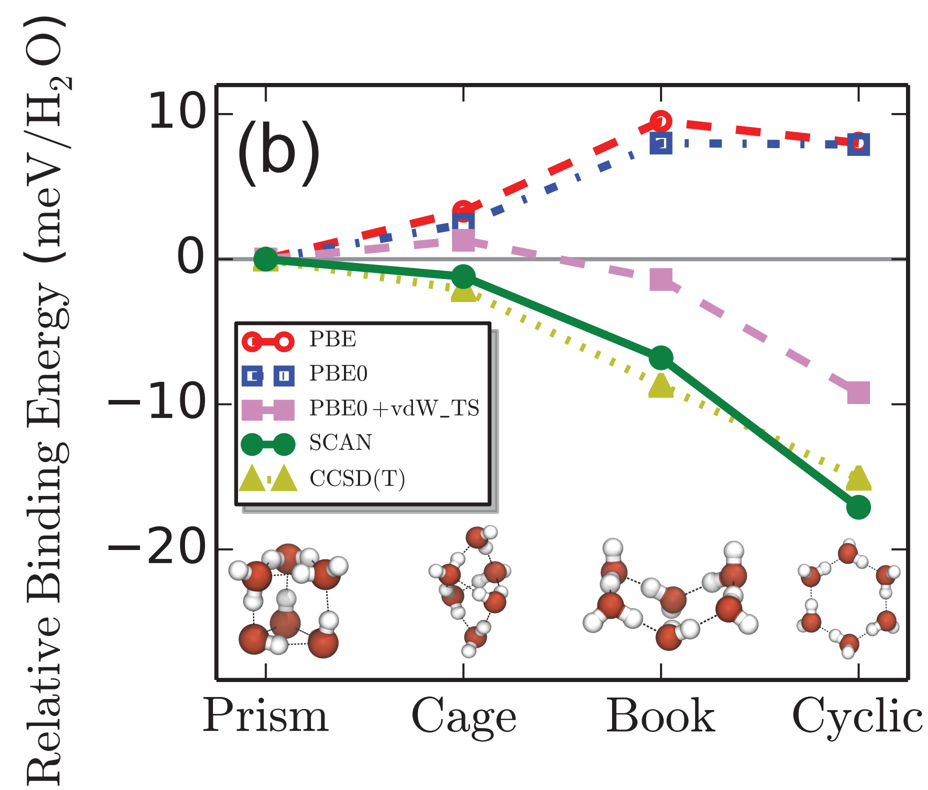
Silicon





Water

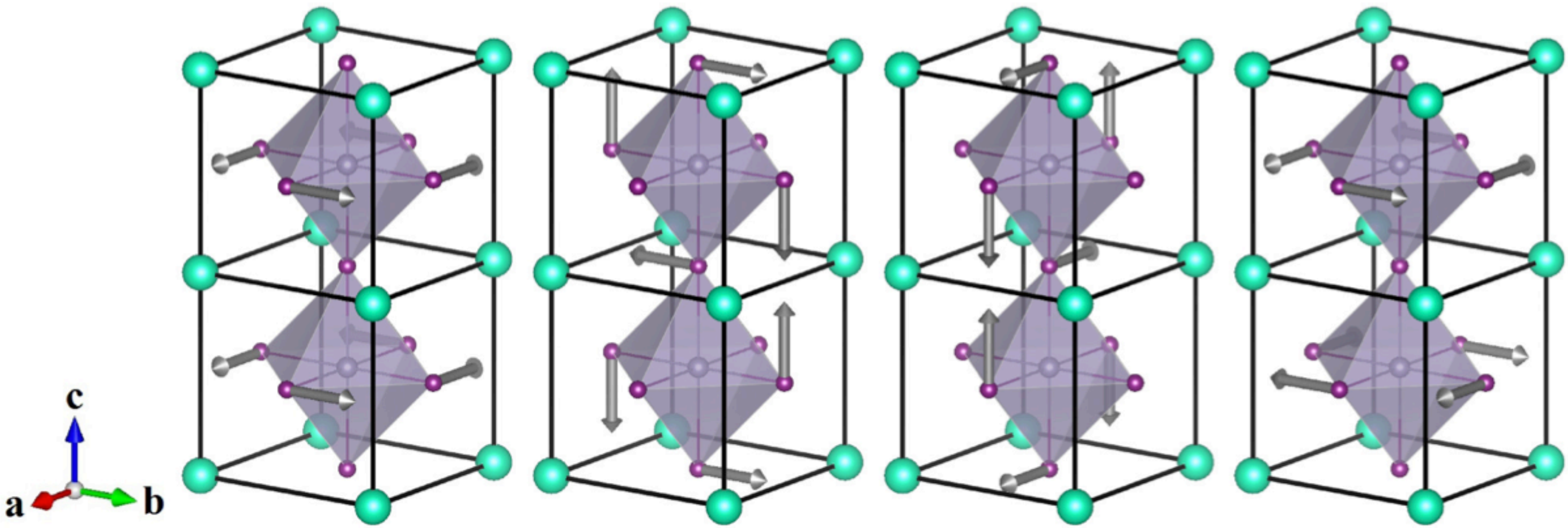




J Sun, RCR, *et al.* Nature Chem 2016

Why care about Forces?

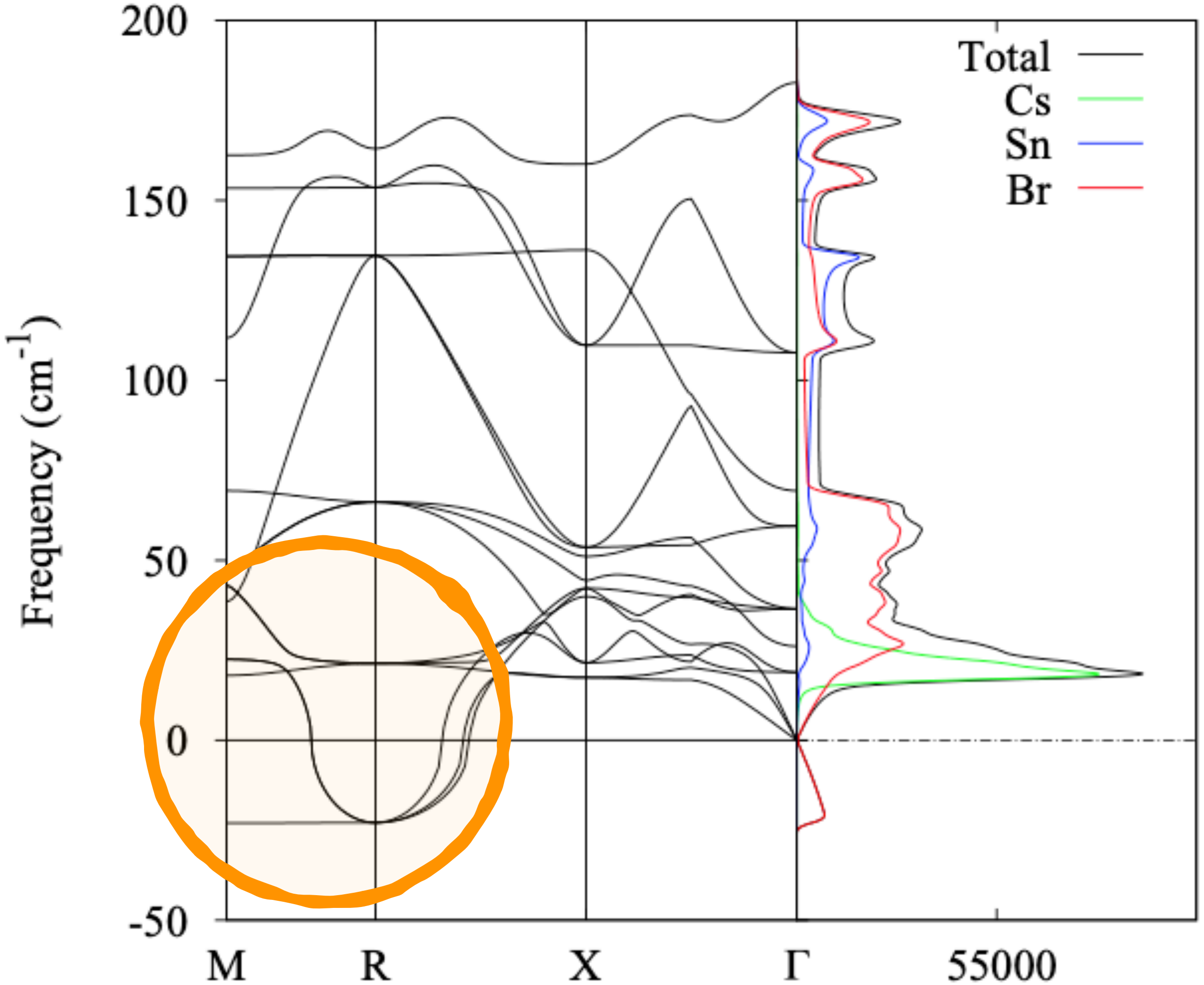
- Forces (derivatives of total energy) tell us how **atoms move**
- Structural relaxation, cell optimization (stresses), mechanics
- **Molecular dynamics** → fluctuations, vibrations, diffusion, reactions
- **Let's look at vibrations (phonons) in a model material, $CsSnBr_3$**

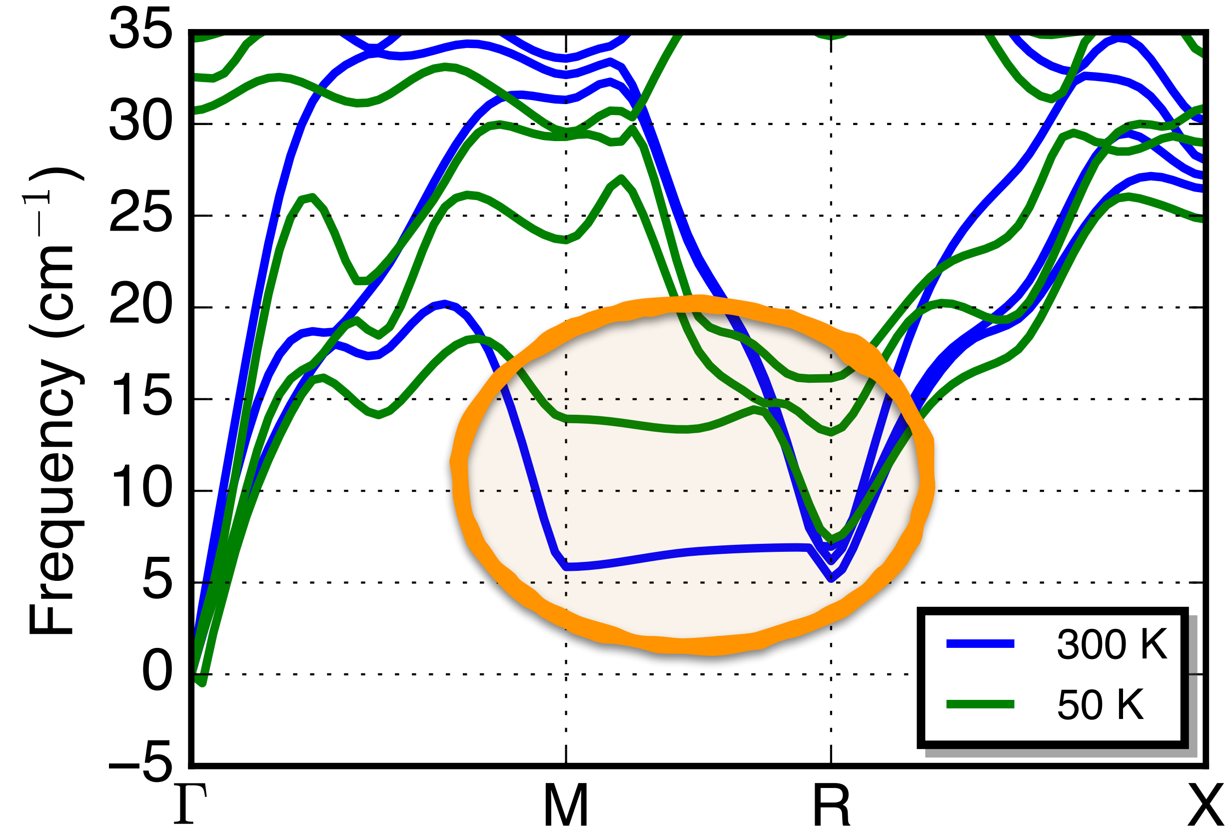


Huang, Lambrecht, Phys Rev B 2014

Phonons from harmonic approximations vs. MD simulations

- Phonon dispersion curves for $CsSnBr_3$





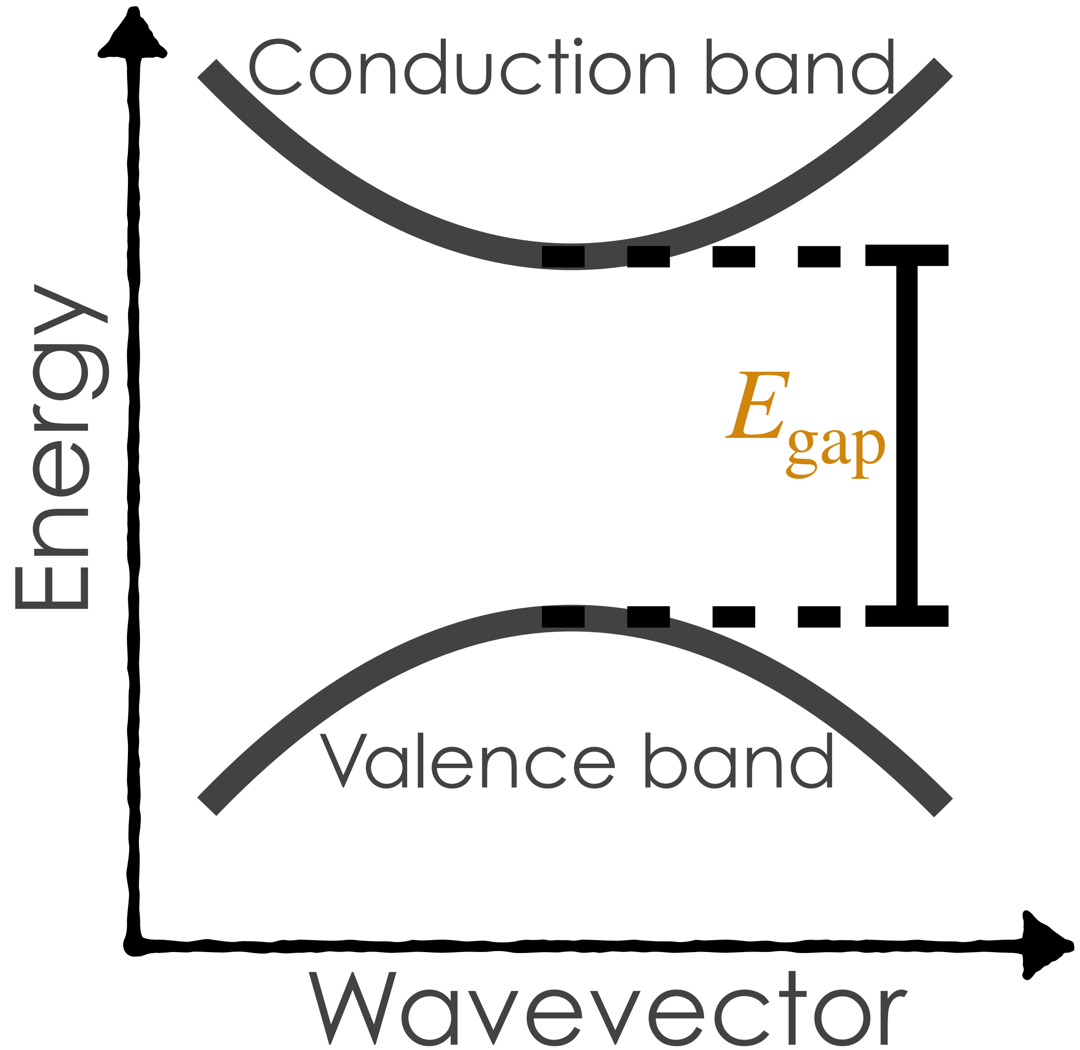
- **Negative frequencies!** = unstable / soft modes

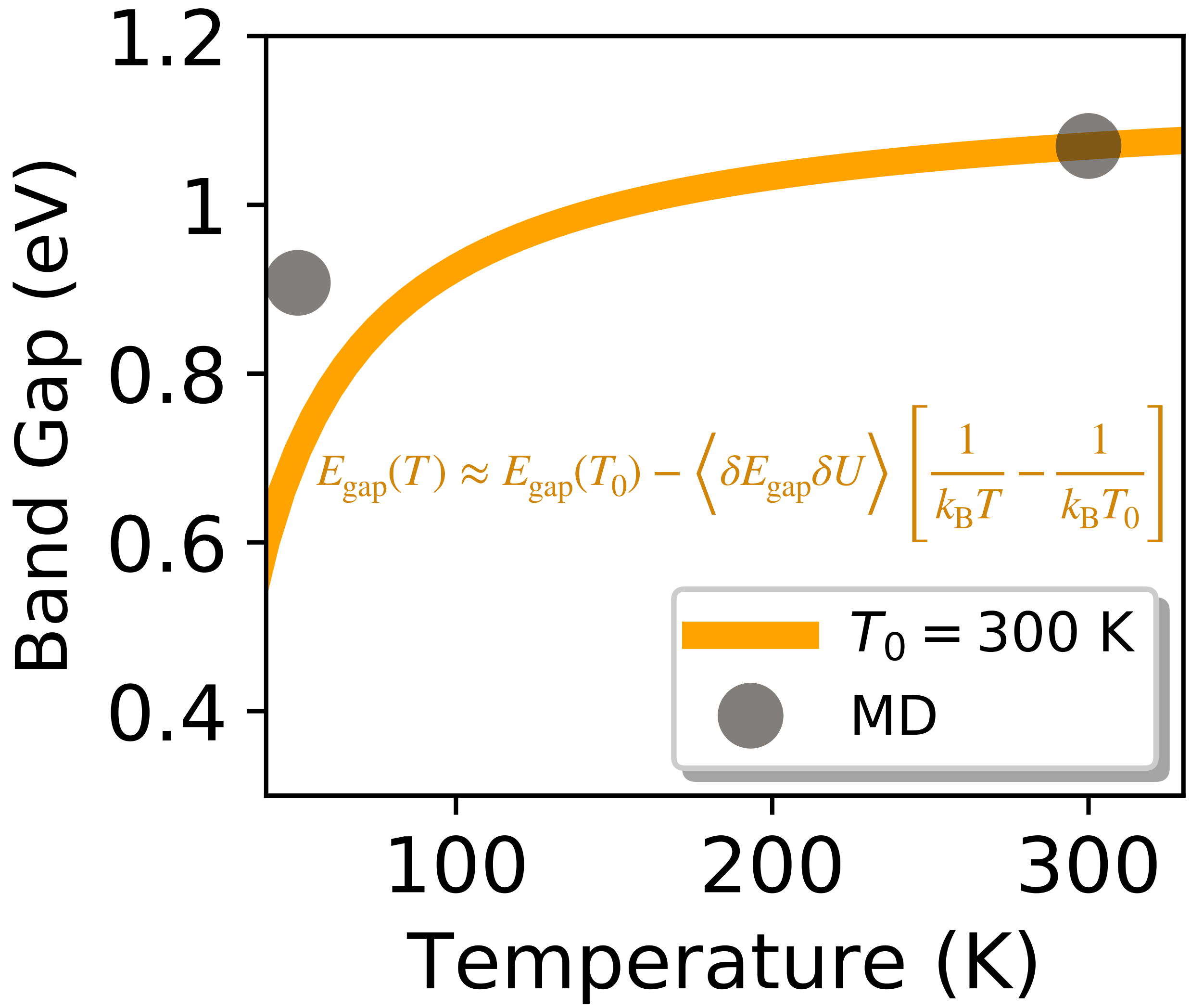
- Anharmonic effects & thermal renormalization included in MD sims

Huang, Lambrecht, Phys Rev B 2014

CM Hylton-Farrington, RCR, *Chem Mater*, 2024

Band gap predictions must include anharmonicity





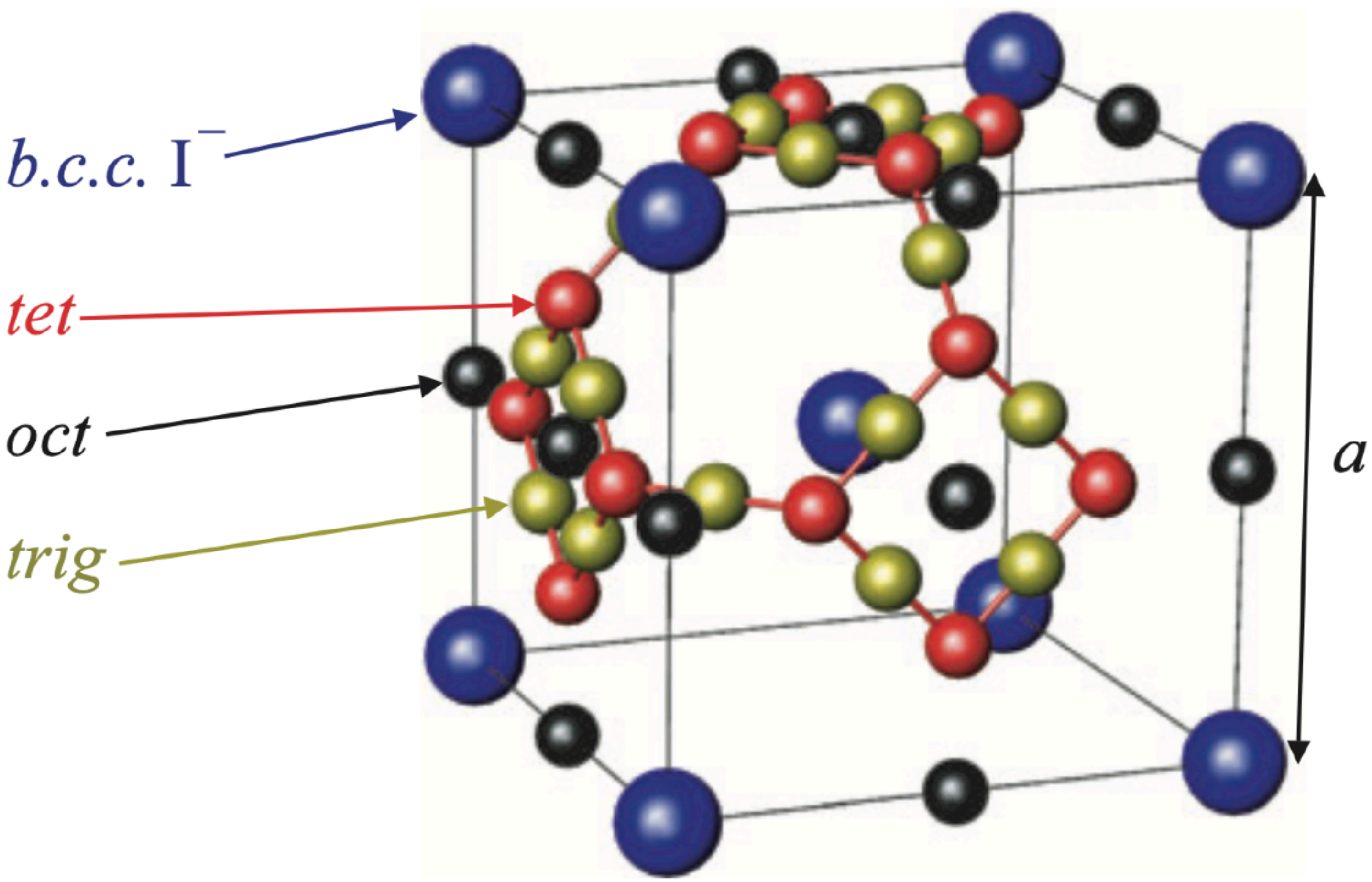
- Cannot describe band gap of anharmonic materials with linear/harmonic theories

- **Need anharmonicity** (from *hidden electronic disorder*)

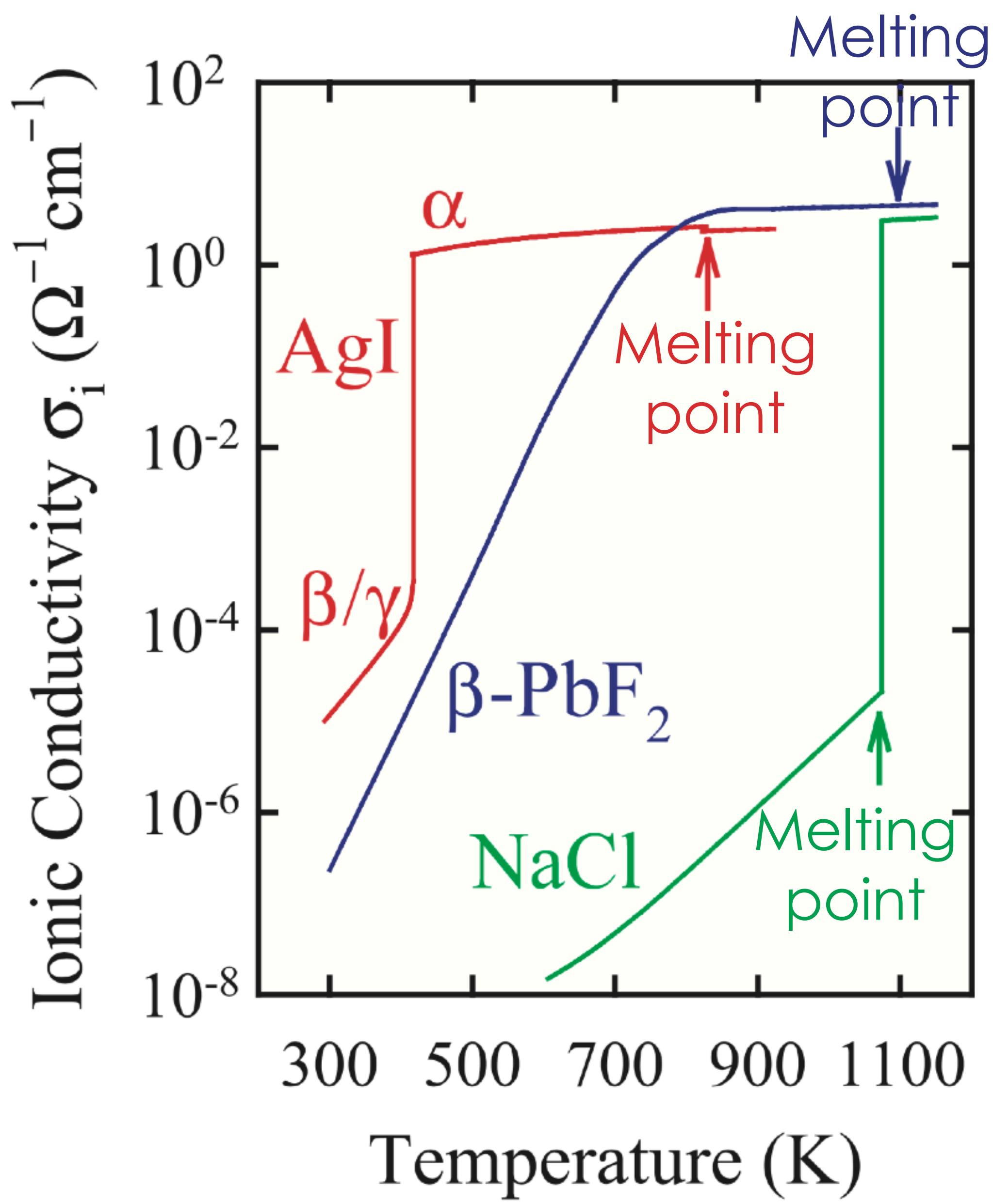
CM Hylton-Farrington, RCR, *Chem Mater*, 2024

Cation diffusion in Silver Iodide

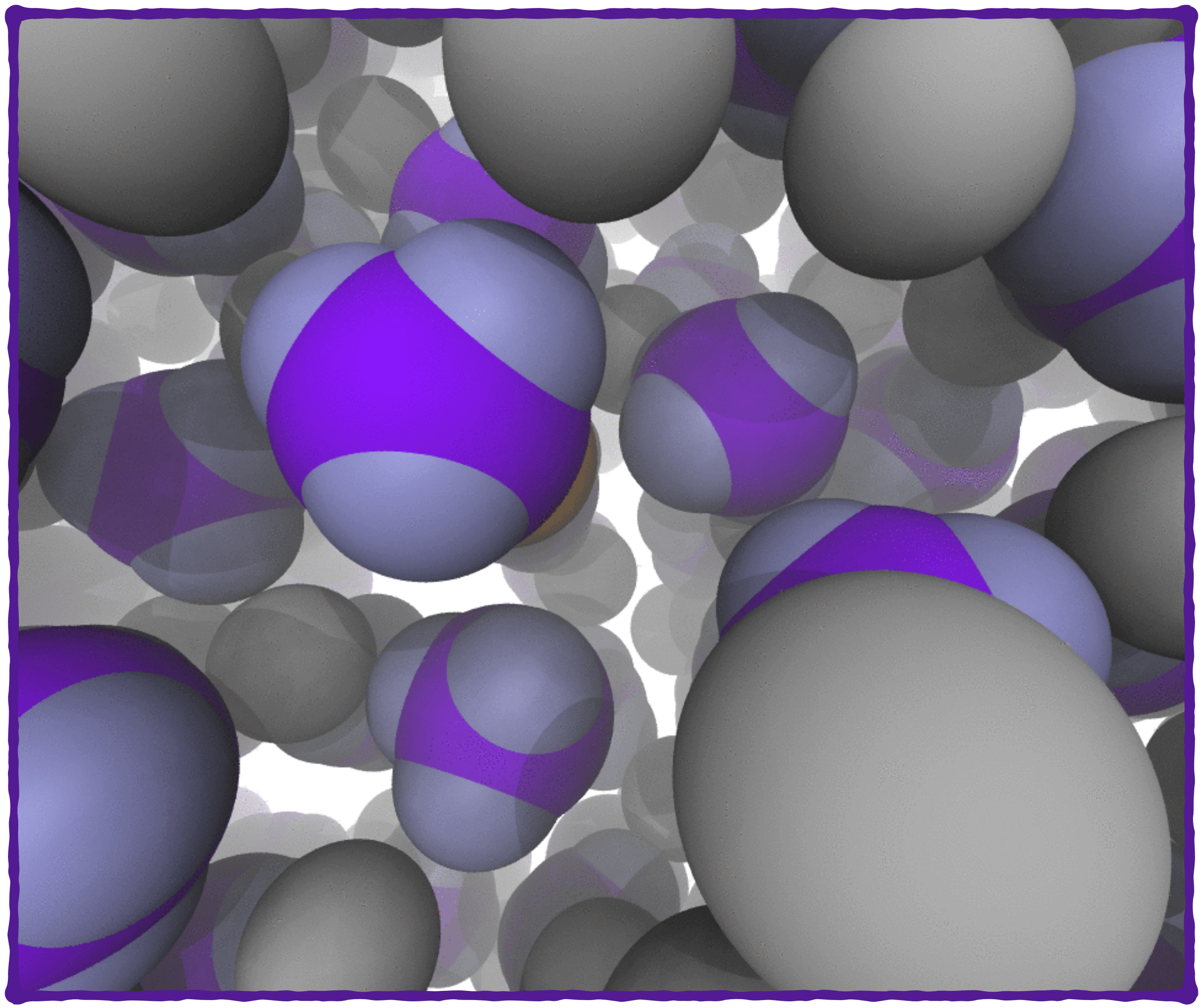
- Iodide sits on cubic lattice, Ag^+ diffuses

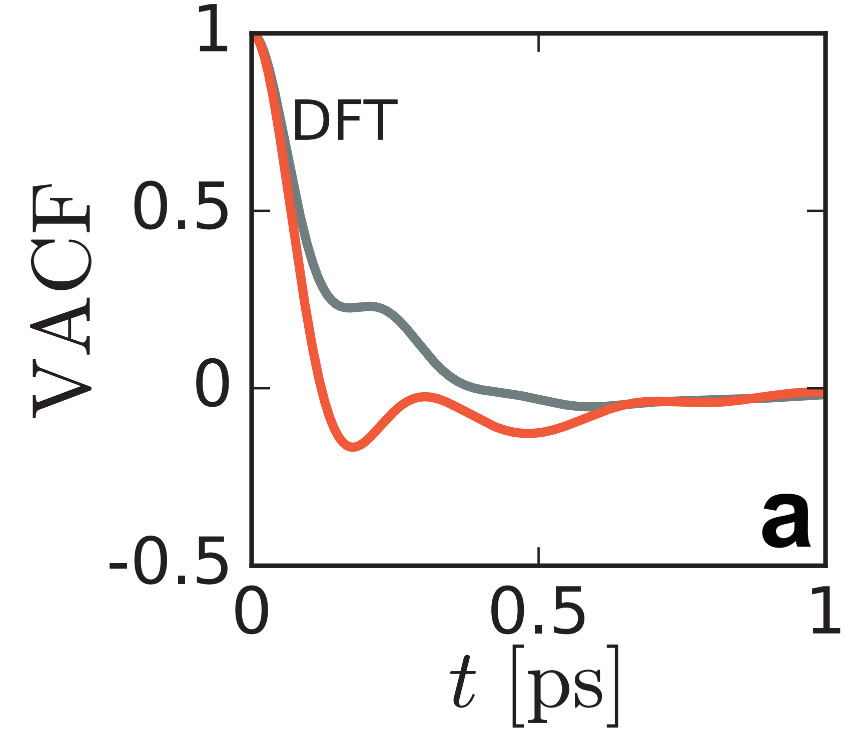


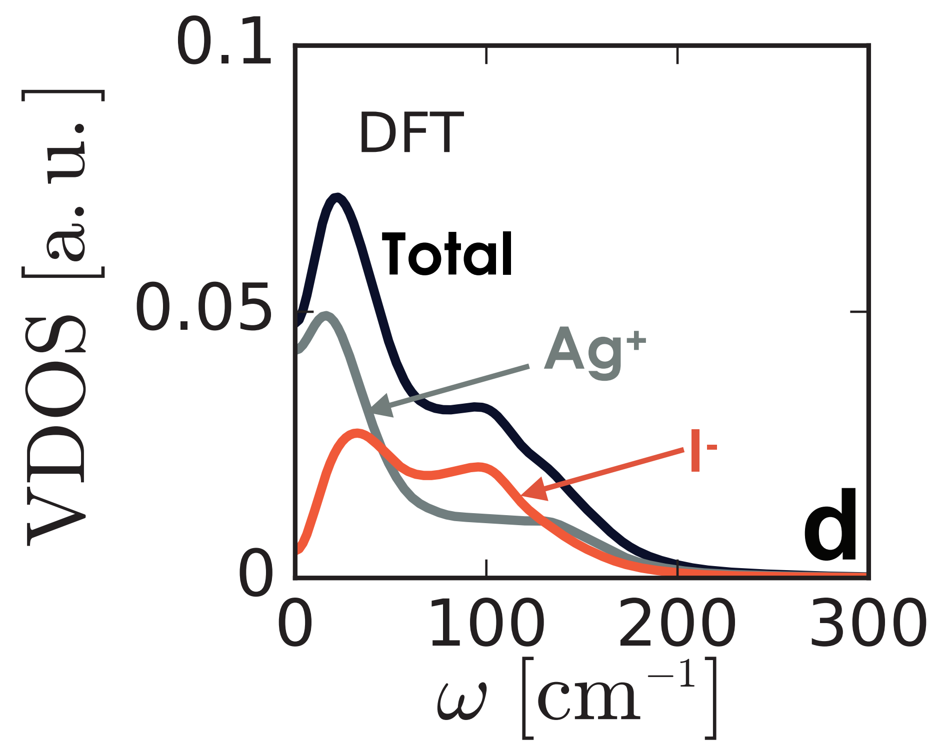
S. Hull, *Rep Prog Phys* 2004



Cation diffusion in Silver Iodide



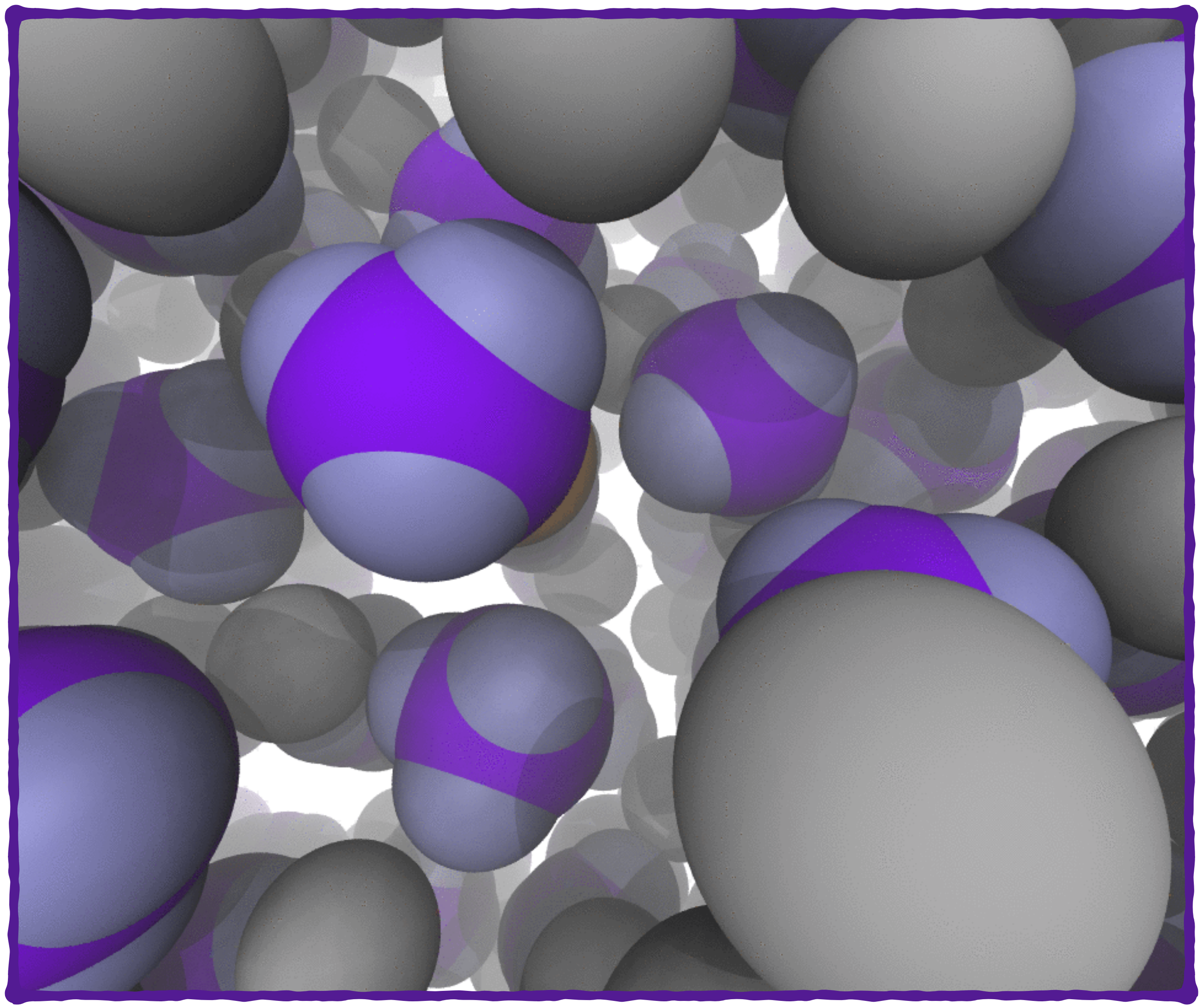


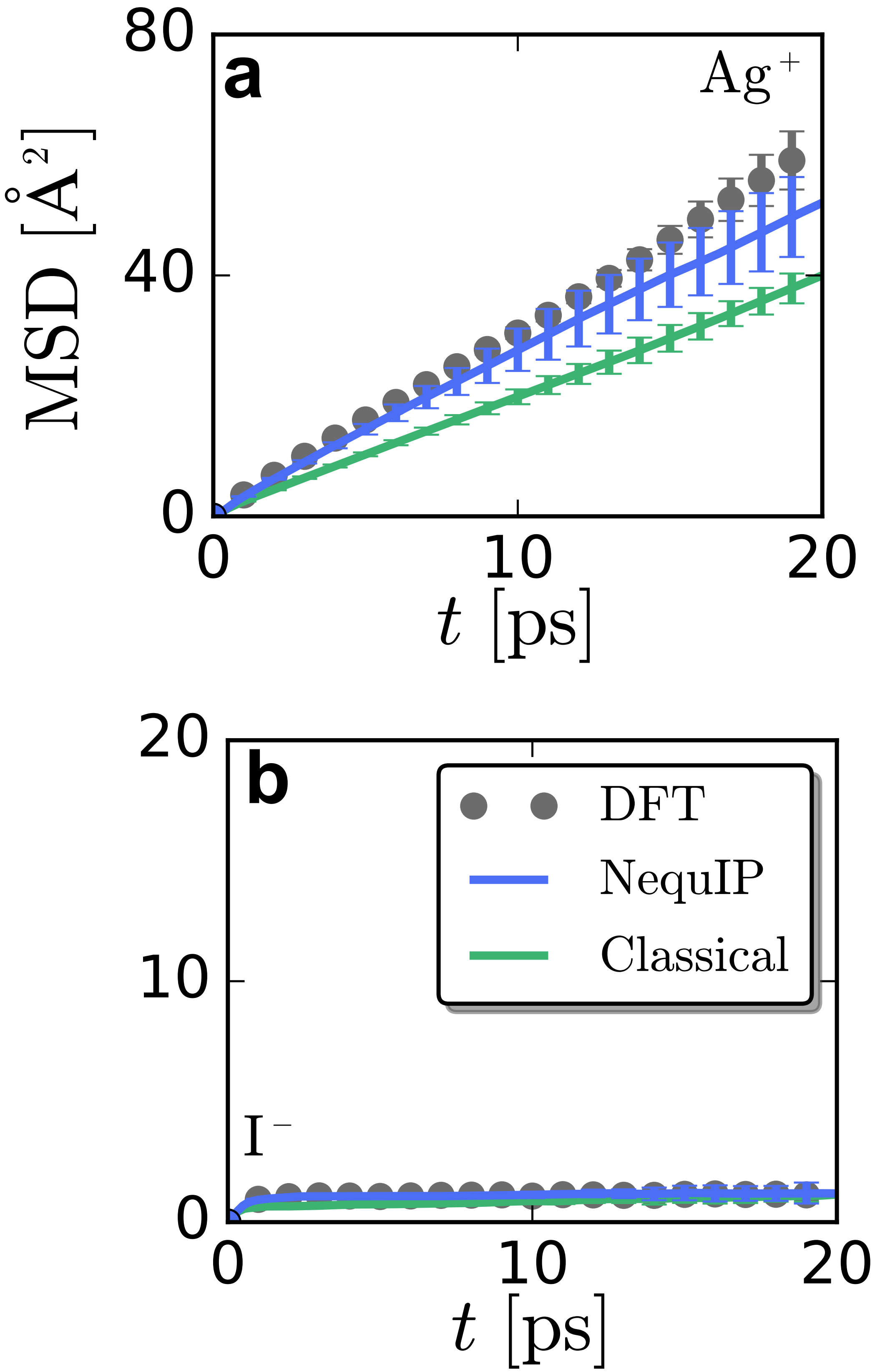


- $\mathrm{VACF}(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$
- $\mathrm{VDOS}(\omega) = \int_{-\infty}^{\infty} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \, e^{-i\omega t} dt \; ; \; \mathrm{VDOS}(\omega = 0) = 3D$

HS Dhattarwal, R Somni, RCR, *Nature Commun* (2024) HS Dhattarwal, RCR, arXiv (2025)

Cation diffusion in Silver Iodide

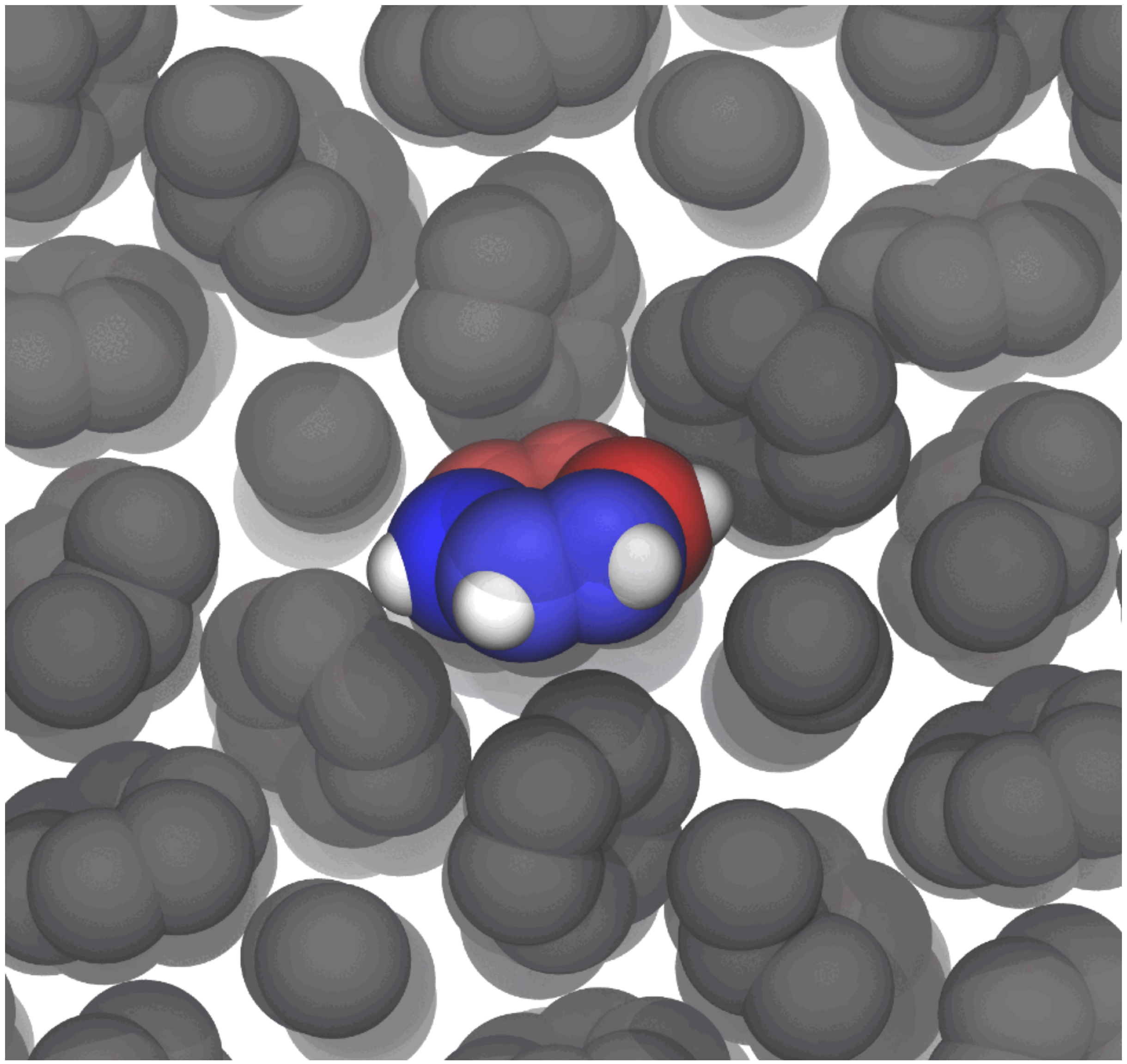


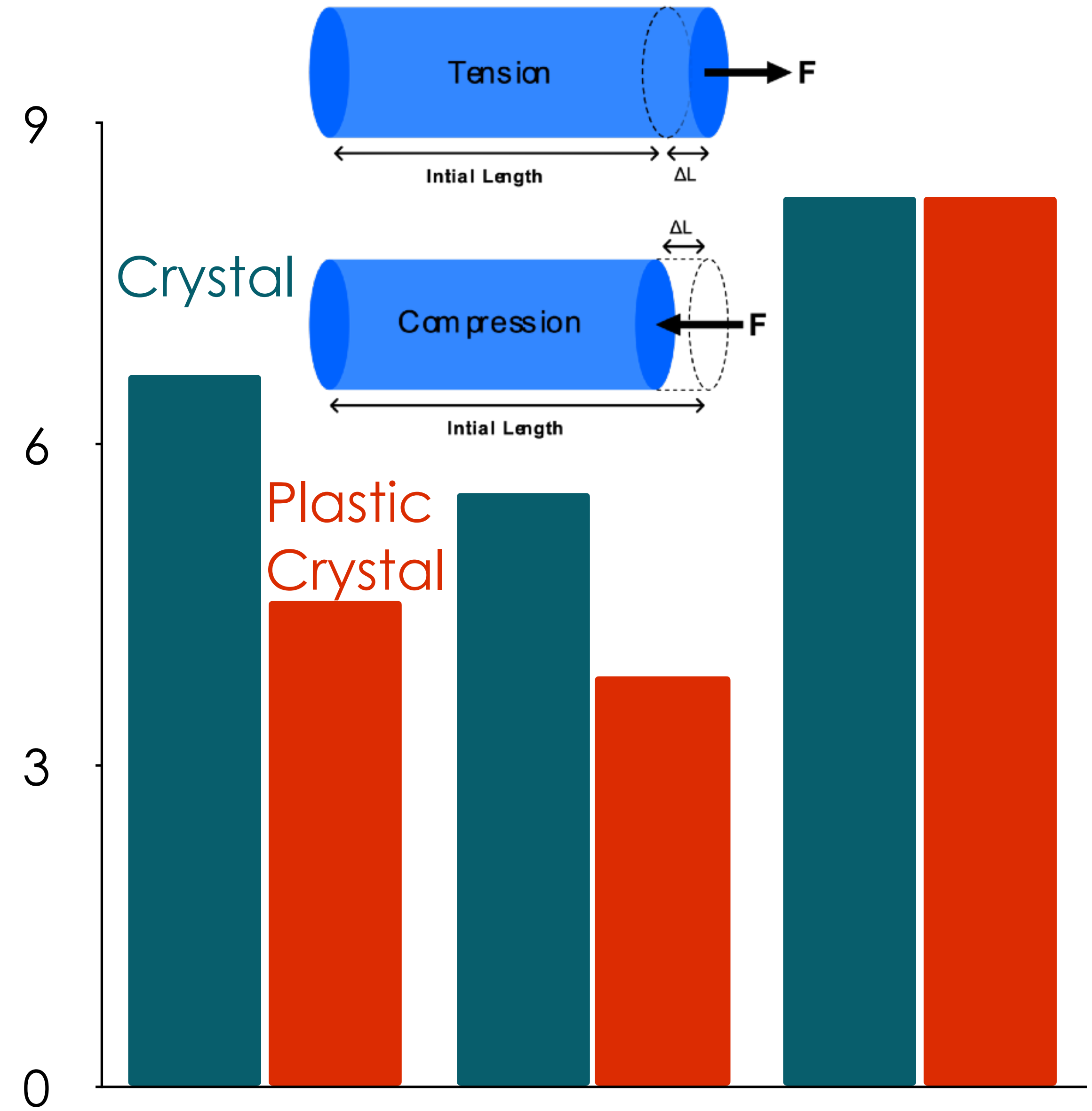


- $\mathrm{MSD}(t) = \left\langle \left| \mathbf{r}(t) - \mathbf{r}(0) \right|^2 \right\rangle$
- $\lim_{t \to \infty} \mathrm{MSD}(t) = 6Dt$

HS Dhattarwal, R Somni, RCR, *Nature Commun* (2024)   HS Dhattarwal, RCR, arXiv (2025)

Rotational Disorder & Mechanics



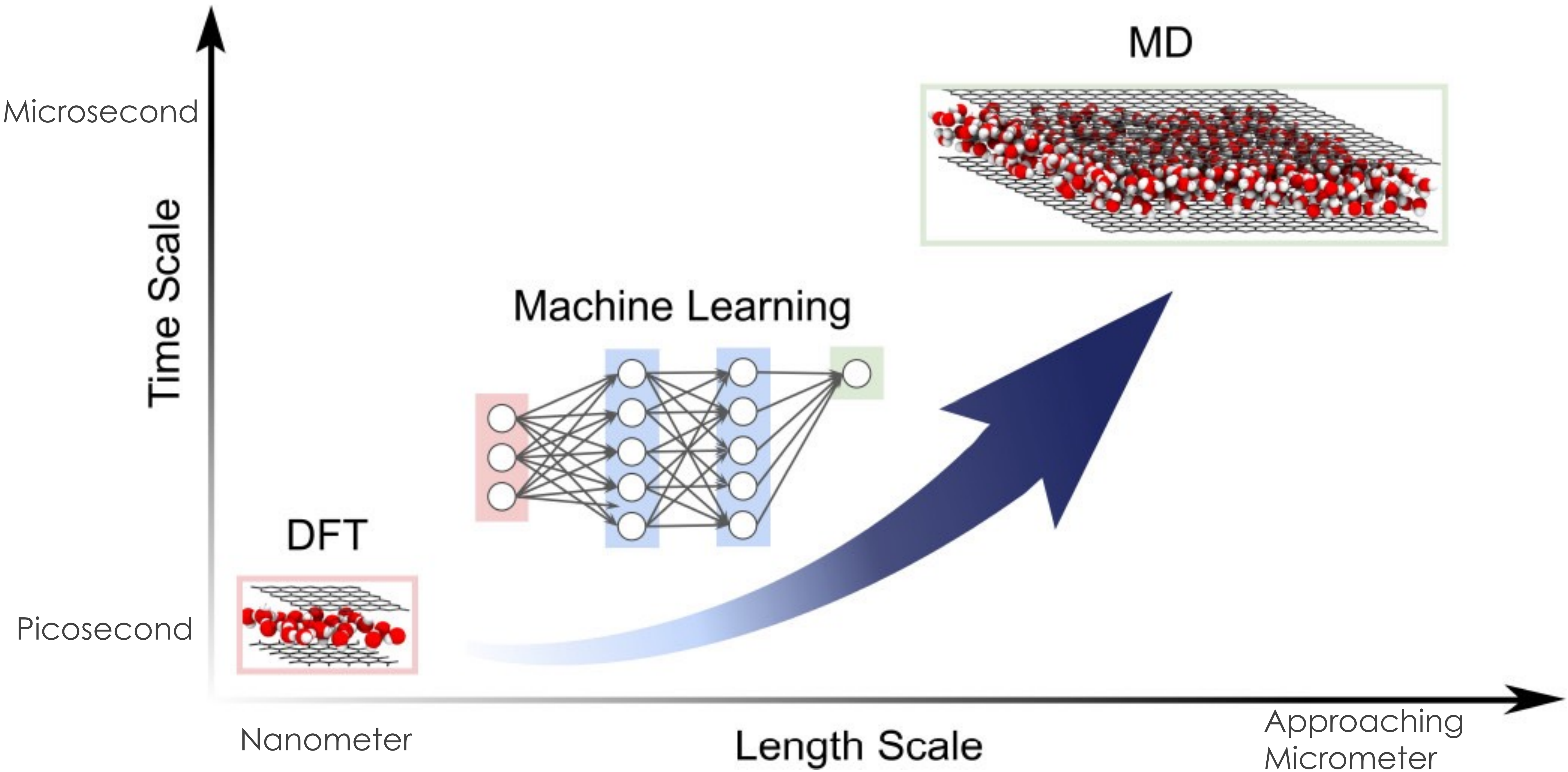


- ***Plastic Crystals*** have translational order & rotational disorder

- Rotational disorder can weaken mechanical properties (e.g. Young's moduli)

AC Thakur, RCR, *ACS Earth & Space Chem* 2024, *JCP* 2024, *ACS Earth & Space Chem* 2023, *Mol Phys* 2021

Bridging the gap with machine learning

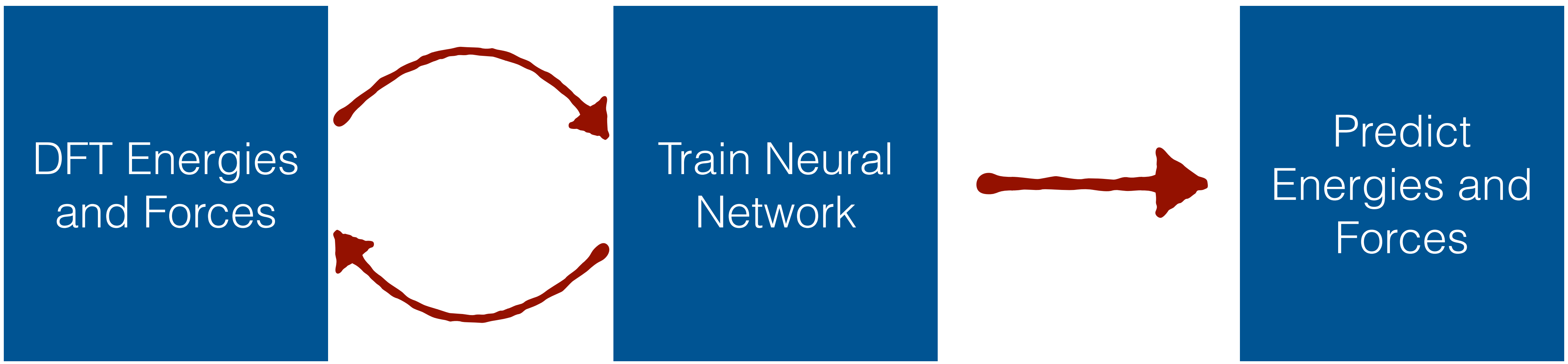


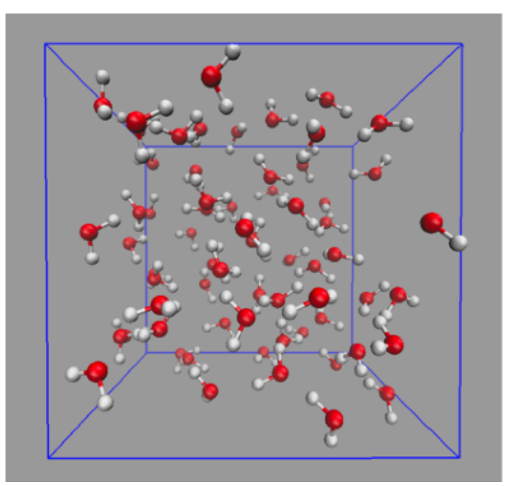
- **Machine learning moves us in the right direction**
- *Still developing techniques that include important physics…*

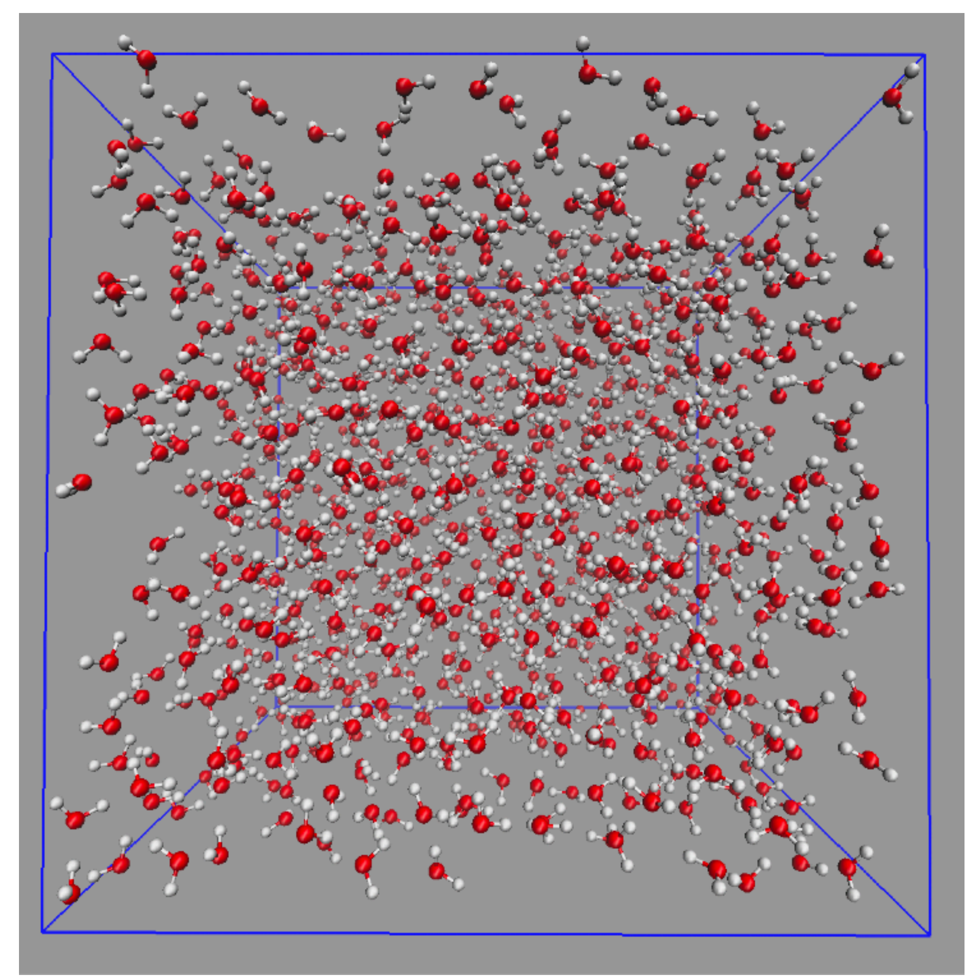
Zhao, Qiu, Guo, *J Phys Chem C* 2022

Use machine learning to model interatomic interactions

- Machine learning to make **neural network potentials**







- Can model large systems with DFT accuracy!

Scalability enables increase in scales reachable in simulations

- Can model huge systems

Pushing the Limit of Molecular Dynamics with *Ab Initio* Accuracy to 100 Million Atoms with Machine Learning

Weile Jia[*], Han Wang[†], Mohan Chen[‡], Denghui Lu[‡], Lin Lin[*¶], Roberto Car[∥], Weinan E[∥], Linfeng Zhang[∥ §]
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Email: jiaweile@berkeley.edu, linlin@math.berkeley.edu
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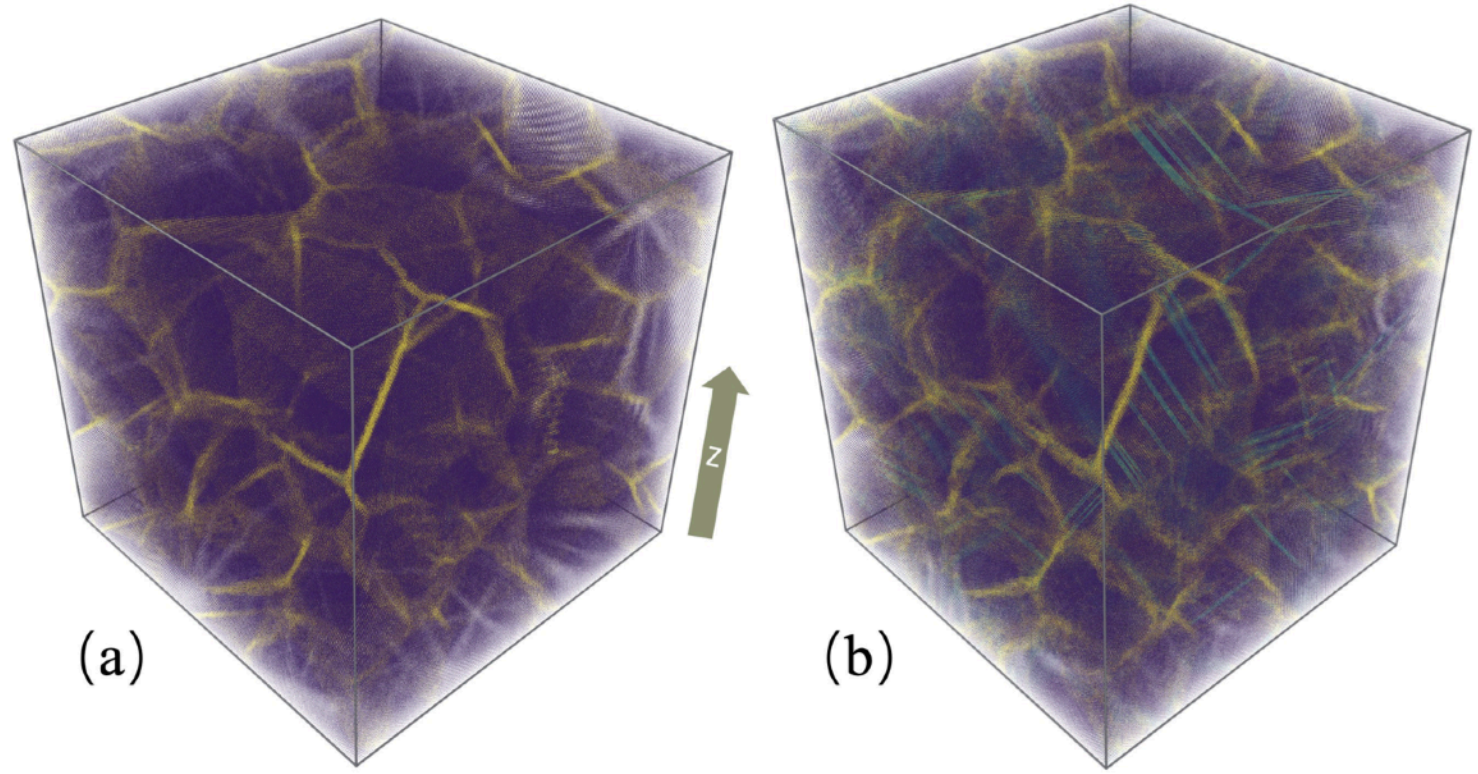
Email: mohanchen@pku.edu.cn, denghuilu@pku.edu.cn
[¶]Lawrence Berkeley National Laboratory, Berkeley, USA
[∥] Princeton University, Princeton, USA

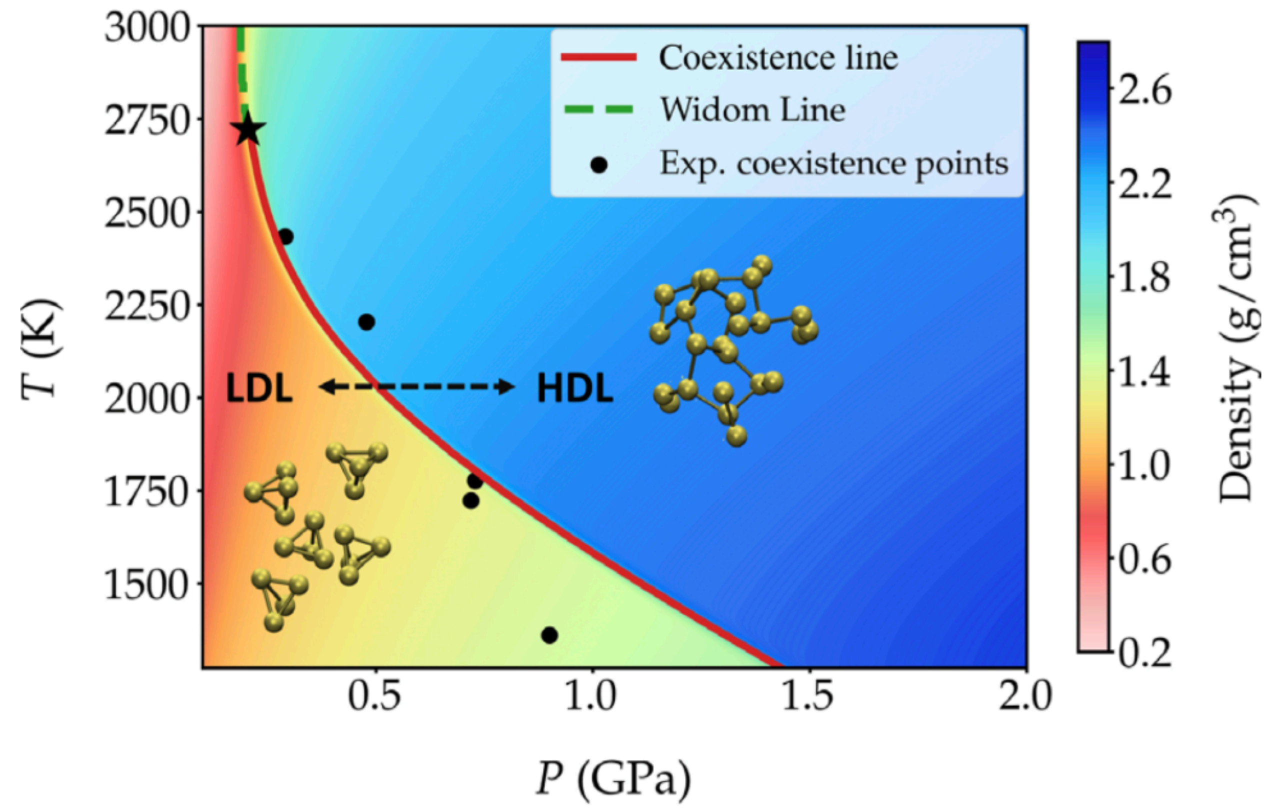


- Can model long timescales for thermodynamics & kinetics

PHYSICAL REVIEW LETTERS **127,** 080603 (2021)

Liquid-Liquid Critical Point in Phosphorus

Manyi Yang, Tarak Karmakar, and Michele Parrinello[*]
Italian Institute of Technology, Via Melen 83, 16152 Genova, Italy



- All at ab initio accuracy!

To the board to discuss
the theory behind these calculations

What are Molecular Dynamics (MD) Simulations?

- Numerical solution of classical equations of motion (Newton's Equations) for a molecular system

$$\mathbf{F} = m\mathbf{a}$$

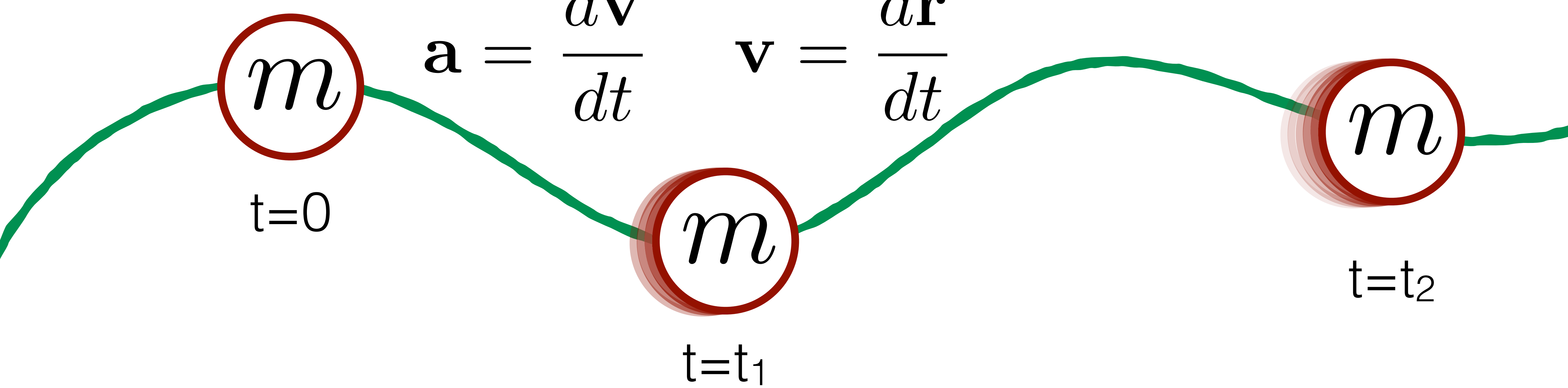
What are Molecular Dynamics (MD) Simulations?

- Numerical solution of classical equations of motion (Newton's Equations) for a molecular system

$$\mathbf{F} = m\mathbf{a}$$

- Given an initial condition (positions and momenta), we can numerically evolve the system in time

$$\mathbf{a} = \frac{d\mathbf{v}}{dt} \qquad \mathbf{v} = \frac{d\mathbf{r}}{dt}$$

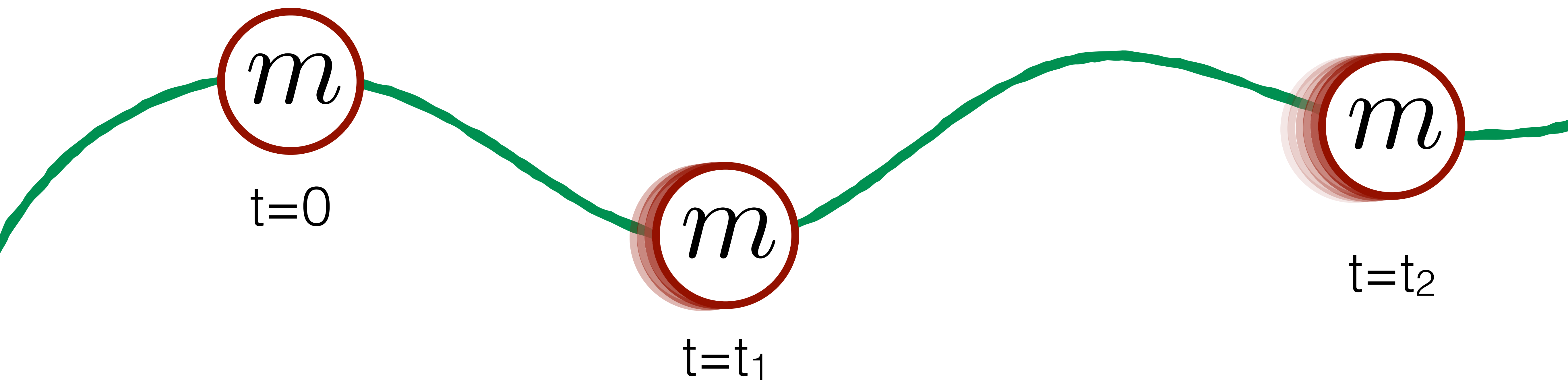


Integrating the equations of motion

- Velocity Verlet algorithm (Taylor expansion)

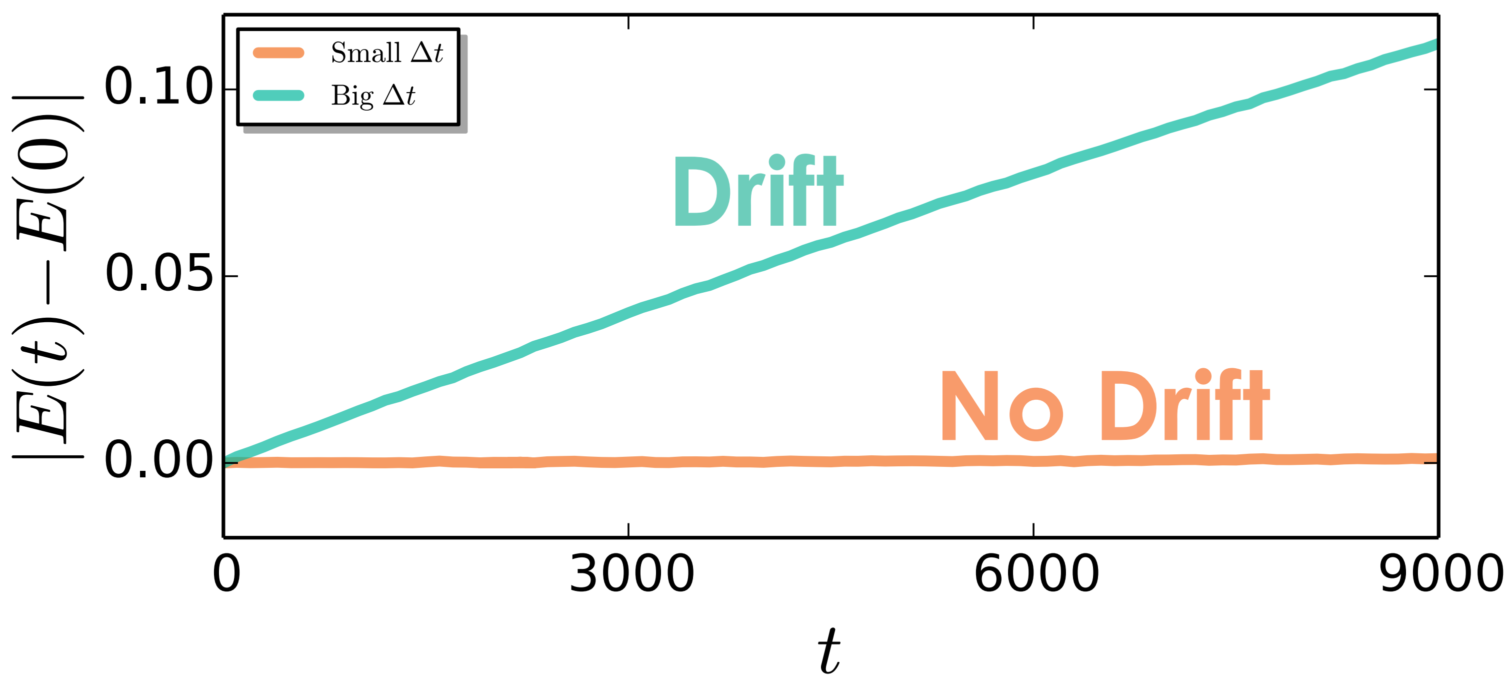
$$\mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2$$

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



How to choose the timestep?

- Want Δt large enough to simulate for long times
- Need Δt small enough to accurately integrate EOM; error $O(\Delta t^2)$



- Δt should conserve constant of motion; here, the energy **E**

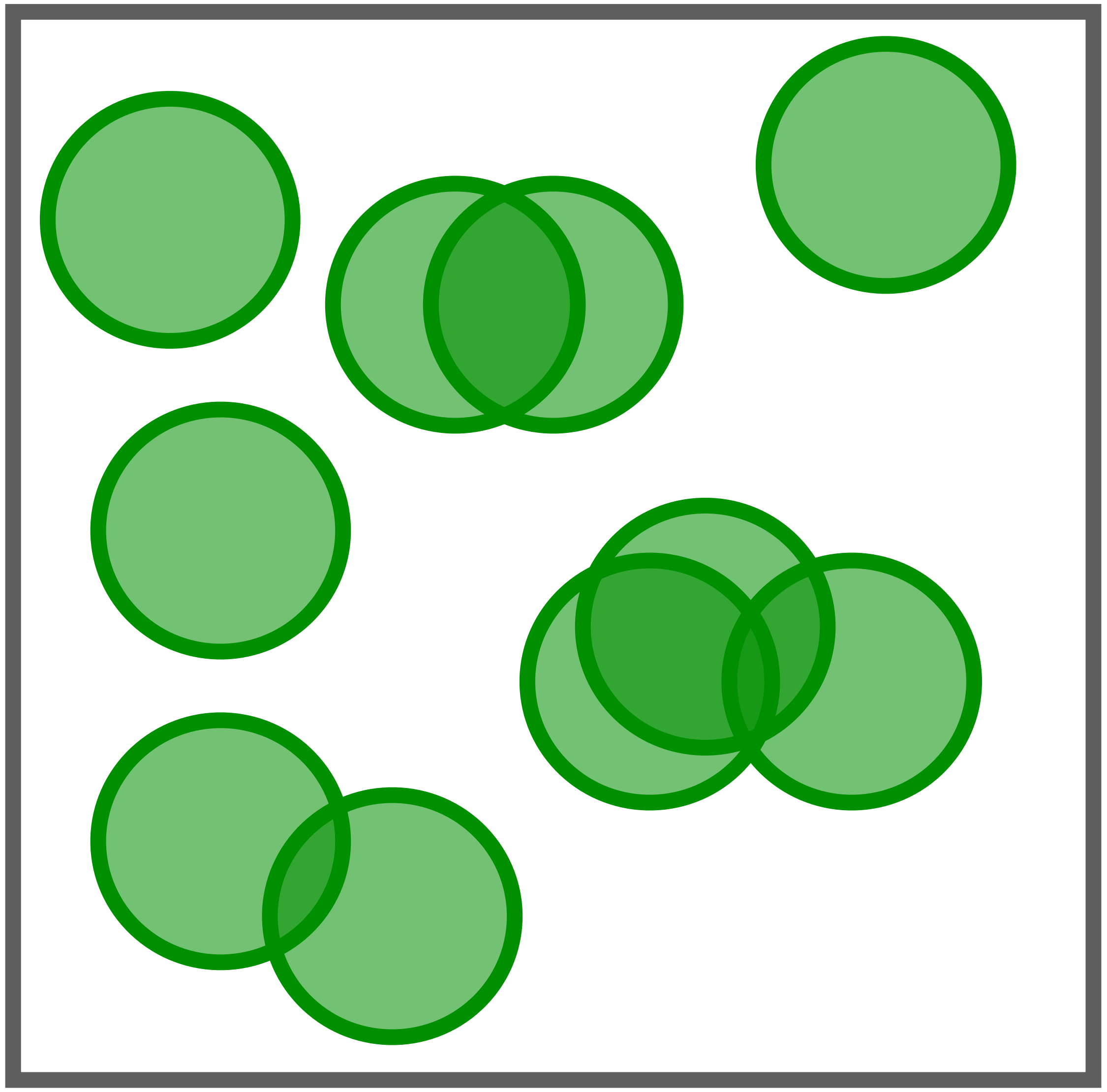
- Typically Δt smaller than fastest timescale in the system

system (fastest motion)	time step (1 fs = 10^{-15} s)
molecules (bond vibrations)	0.5 – 1.0 fs
molecules, rigid bonds (angle bending)	2.0 fs
atoms (translation)	5 – 10 fs
Lennard-Jones system	0.001 (dimensionless units)

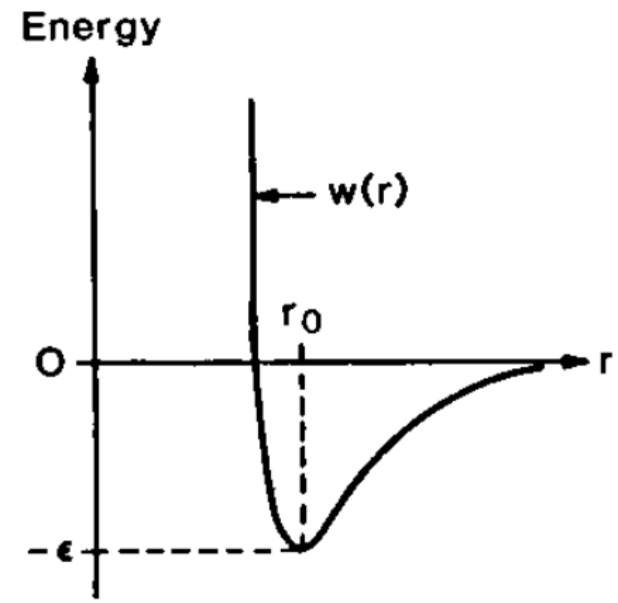
From Scott Shell's (UCSB) lecture notes

Choosing Initial Conditions

- Randomly insert **N** molecules into simulation box



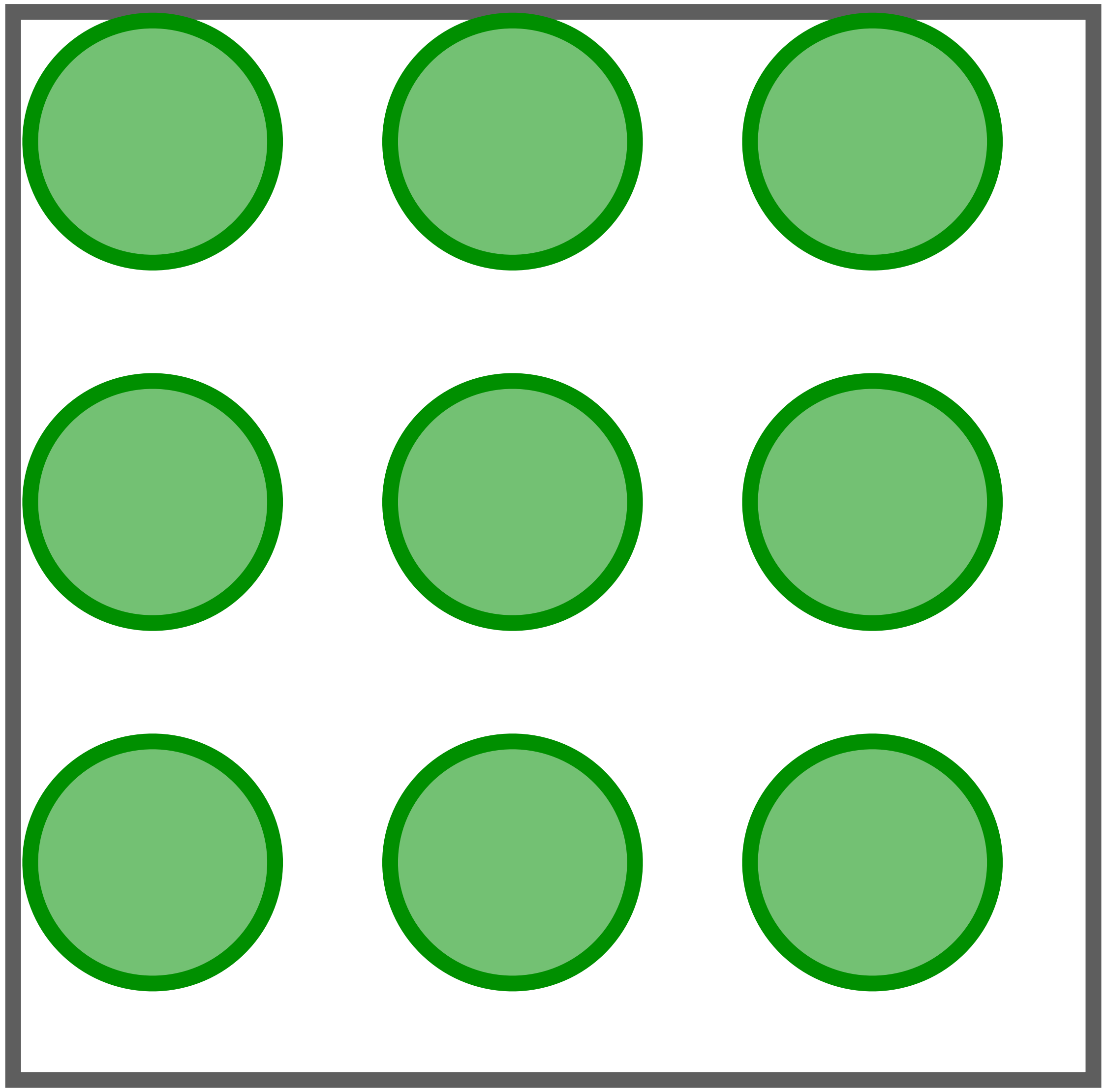
- Almost all intermolecular potentials include an excluded volume core (Pauli exclusion)



- Overlapping cores lead to high energy configurations
- Difficult to equilibrate: **Bad initial condition**
- Could make sure particles don't overlap…

Choosing Initial Conditions

- Put **N** molecules onto a lattice (often cubic)

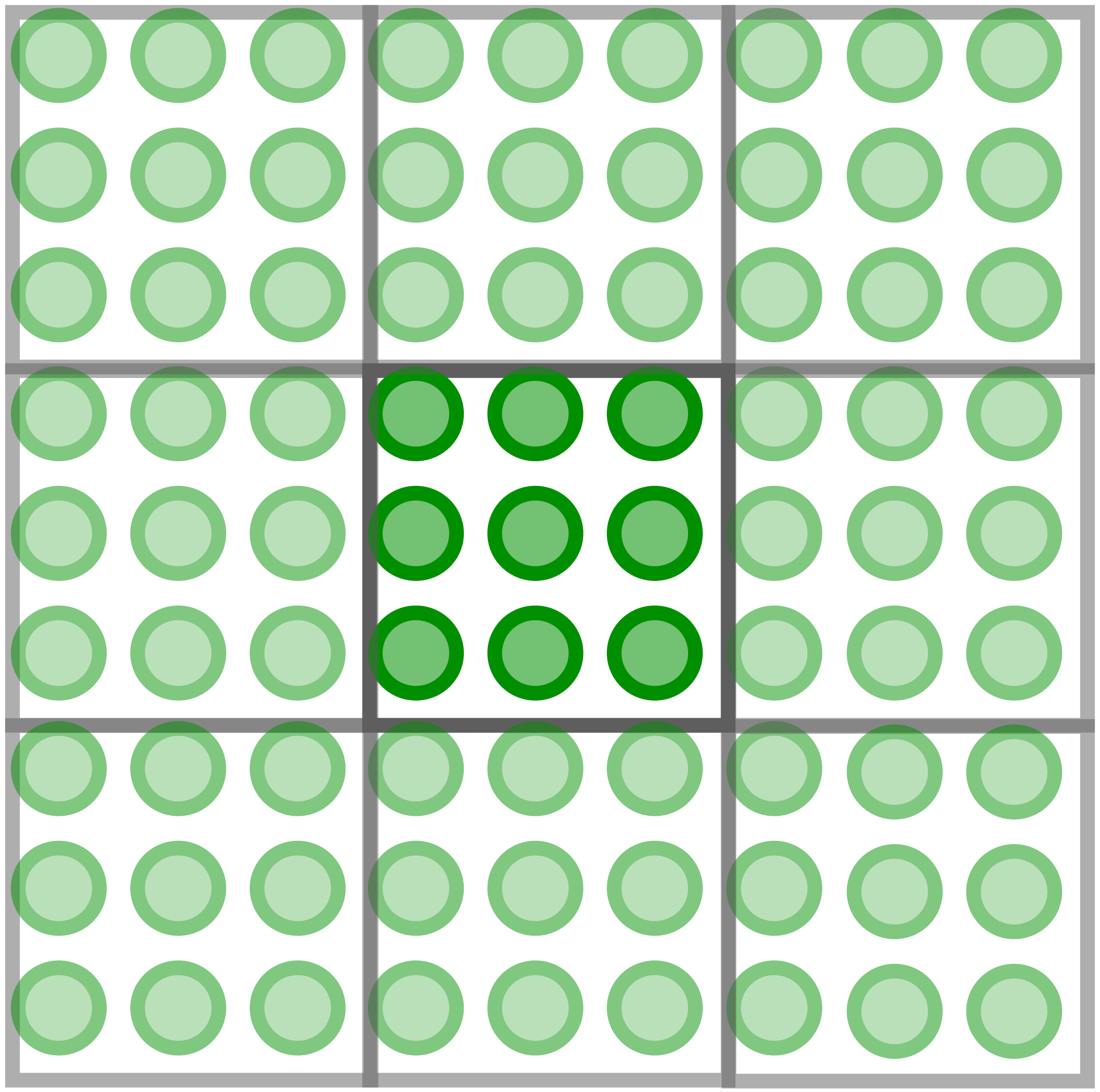


- Lattice will melt if it is not stable at this state point.
- Need to follow time evolution of "melting" to ensure you arrive at the desired state

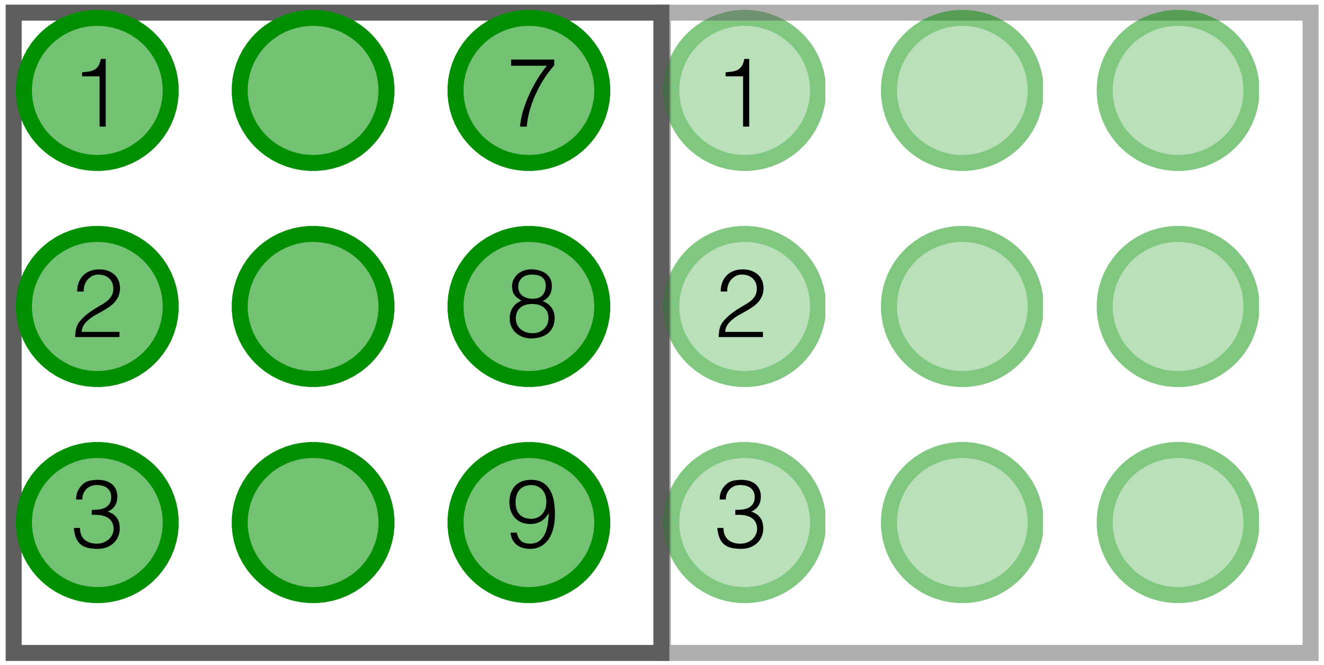
- *Why have I drawn the system off-center?*

Periodic Boundary Conditions

- Want to mimic an **infinite** system with **N** molecules



- Particles “feel” image of other particles outside on other side of boundary



- If particle “leaves” box, it “enters” on other side
- Be careful of artifacts! E.g. long-wavelength fluctuation suppression, finite-size effects,…

Initializing the Momenta

- Choose velocities randomly from a Gaussian distribution

$$P(v_x) = \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{1/2} \exp\left(-\frac{m v_x^2}{2 k_\mathrm{B} T}\right)$$

- Need to correct so that there is no net momentum

$$\mathbf{P}_\mathrm{tot} = \sum_{i=1}^{N} m_i \mathbf{v}_i = 0$$

- System should rapidly equilibrate to Maxwell-Boltzmann distribution if initialized differently (*e.g.* uniform distribution)

Equilibrating the System

- Need to run for a period of time to allow the system to come to equilibrium at the state point of interest
- Monitor thermodynamic & structural quantities to ensure quantities no longer drift and oscillate about average values

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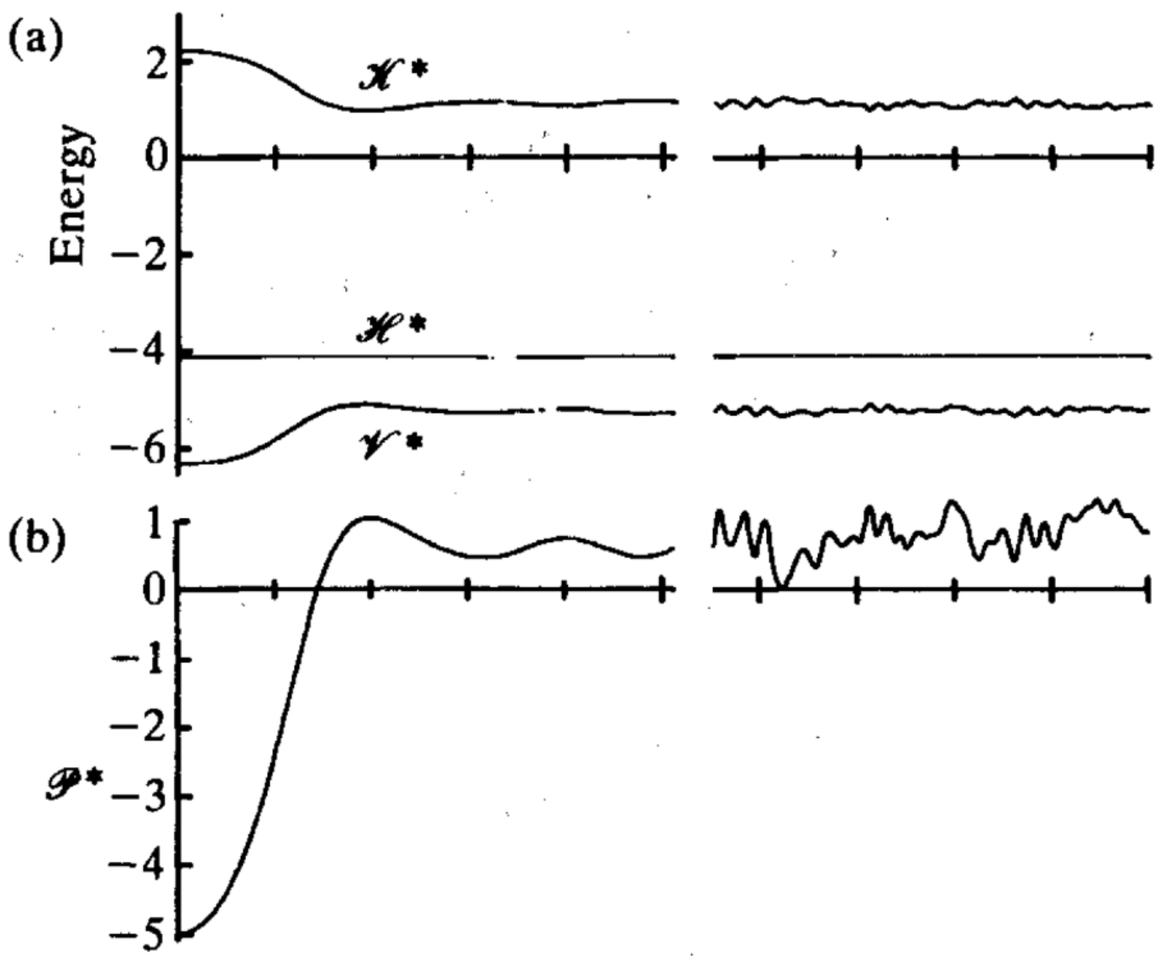

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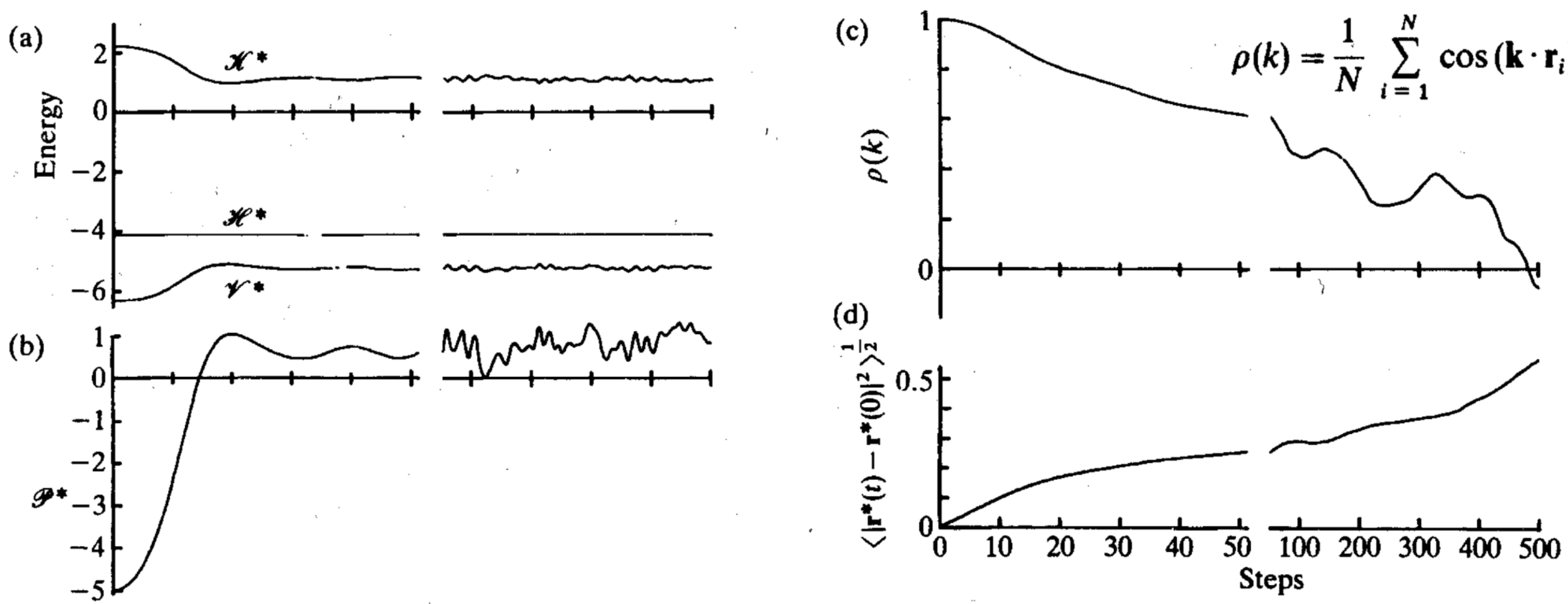

- To speed equilibration from lattice, can often increase **T** to "melt" the lattice, then later decrease to desired **T**

More on Equilibration

- Scale interactions to speed equilibration in some cases
- Starting closer to equilibrium state results in shorter equilibration times
- Difficult to say *a priori* how long is needed for equilibration
- More time typically needed when equilibrating from a lattice or near a phase transition
- **Golden Rule:** examine carefully parameters/observables as the simulation proceeds
- Check as many exact relations as possible, *e.g.* partitioning of kinetic energy in molecular systems
- Once equilibrated, can proceed to **production** phase: accumulating meaningful statistics!

Simulations at Constant Temperature

- Under most experimental situations, we operate at a constant temperature **T**

- How can we do this in a MD simulation?

Simulations at Constant Temperature

- Under most experimental situations, we operate at a constant temperature **T**
- How can we do this in a MD simulation?
- Imagine the system is **weakly coupled** to a **heat bath** (thermal reservoir) at specified temperature **T**
- We will discuss 3 approaches:
  - Constraint Methods
  - Extended System Methods
  - Stochastic Methods

Constraint Method: Velocity-Rescaling

- Rescaling velocities at every step would yield correct **T**, but not preserve fluctuations in KE: *not a canonical ensemble!*

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- **Berendsen thermostat** (1984): scale over some time scale

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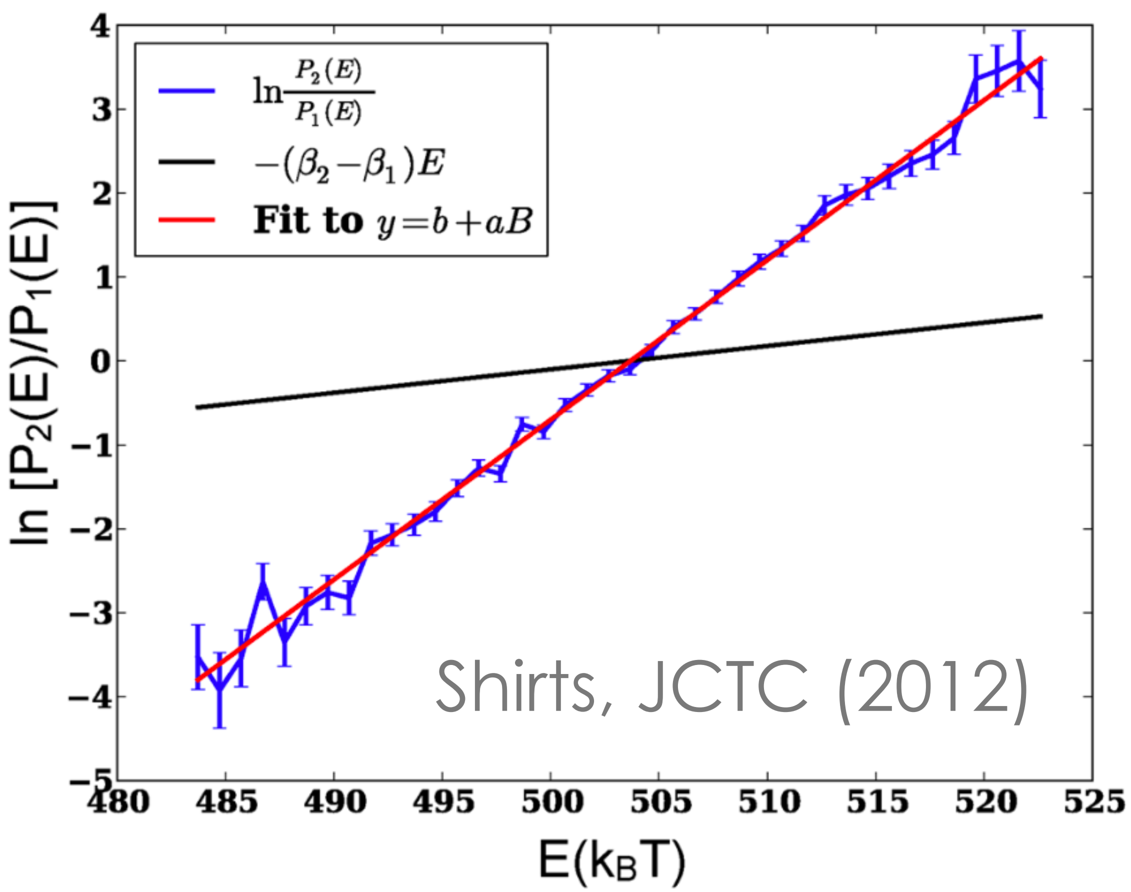

- **Berendsen does not preserve canonical distribution** (incorrect fluctuations in KE)
- Good for fast equilibration…

Canonical Velocity-Rescaling

Andersen, J. Chem. Phys. 1980; Bussi *et al.*, J. Chem. Phys. 2007

- **Andersen thermostat** & canonical velocity-rescaling yield a true canonical ensemble
- Strength of coupling to heat bath specified by collision frequency ν.
- For each particle at each step, if random number between 0 & 1 < $\nu\Delta$t, then particle velocities are reset from a Gaussian

$$P(v_x) = \left(\frac{m}{2\pi k_{\mathrm{B}} T}\right)^{1/2} \exp\left(-\frac{m v_x^2}{2 k_{\mathrm{B}} T}\right)$$

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- **Generates canonical ensemble over long times**
- **Significantly perturbs dynamics**
- Bussi *et al.* canonical velocity-rescaling minimally effects dynamic properties

Nose-Hoover Thermostat

- **Nose (1984)**: rigorously formulated using Lagrangian mechanics (we simplify here)
- Introduce degrees of freedom for bath
  - *s* - "position" of bath
  - p_s - *conjugate "momentum" of bath*
  - *Q - effective "mass" associated with s*

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$$\mathcal{H} = \sum_{i=1}^{N} \frac{m_i s^2 \mathbf{v}_i^2}{2} + U(\mathbf{r}^N) + \frac{p_s^2}{2Q} + k_\mathrm{B} T (3N+1) \ln s$$

- Momenta scaled by s; coupling system to bath
- **Consider microcanonical simulation in *extended system***

$$\Omega = \mathrm{const} \times Q(N, V, T)$$

Nose-Hoover Thermostat

- **Hoover (1986)**: scaling of momenta by *s* is not convenient to implement; Hoover reformulated approach
- Introduce friction coefficient that "replaces p_s"

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}^N) + \frac{\xi^2 Q}{2} + 3Nk_\mathrm{B}T\ln s$$

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- Resulting equations of motion are similar to those for Newton's equations
- Velocity update modified by term (friction x velocity)
- Can develop analogues of Velocity Verlet
- See Martyna, Tuckerman, Tobias, Klein, Mol. Phys. (1996) for more…

Nose-Hoover Thermostat

- **Nose-Hoover Thermostat yields the canonical ensemble**

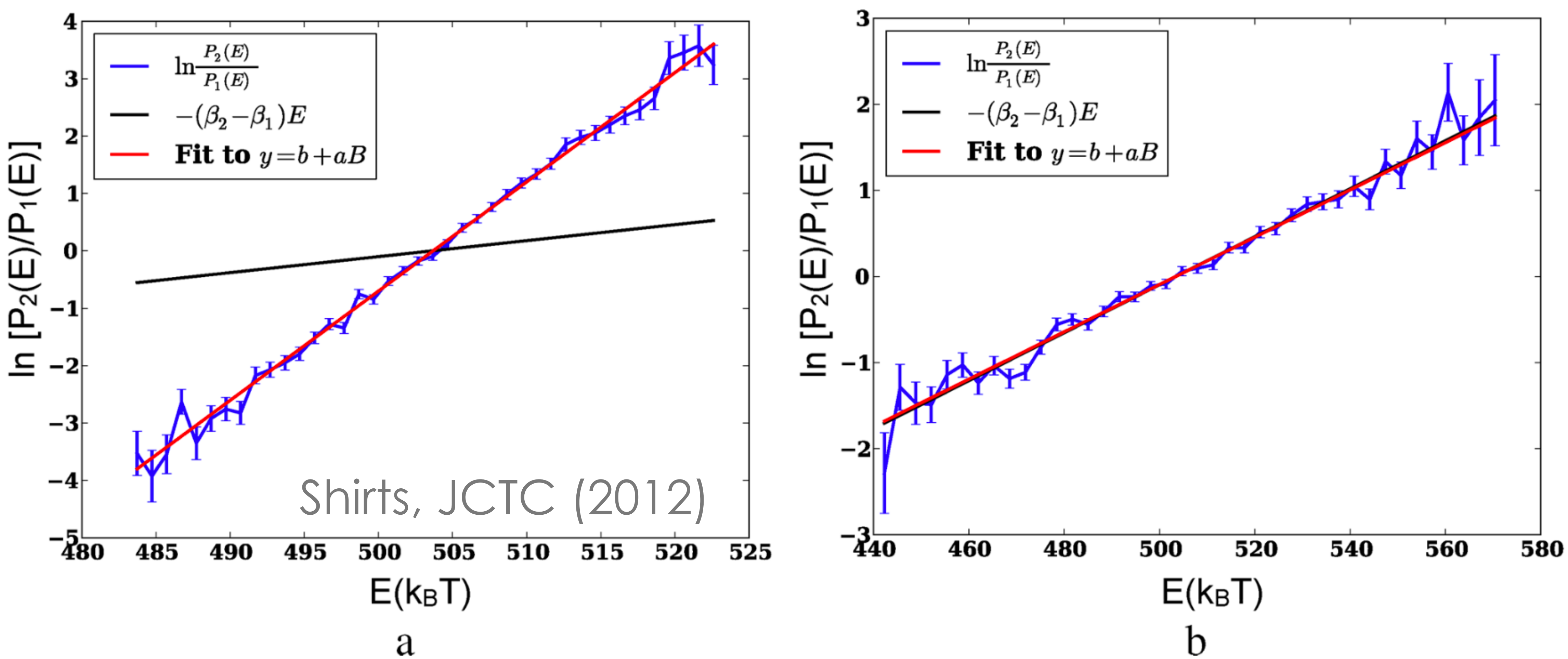

Figure 5. Differences in validation of Berendsen and Nosé–Hoover thermostats. (a) Berendsen temperature control produces simulations deviating greatly from the true distribution; in this case, the slope $\beta_2 - \beta_1$ of the kinetic energy log ratio is 7 times higher than it should be, 68 standard deviations away from the true value. (b) The Nosé–Hoover thermostat, like most others examined here, gives a slope statistically indistinguishable from the proper slope for the kinetic energy portion of the canonical ensemble.

- **Nose-Hoover chains** have been developed to increase robustness and reduce issues with NH approach…

Langevin (Stochastic) Thermostat

- Influence of the bath is captured by a **friction coefficient** and a **stochastic noise** term to mimic collisions with bath

- Modified equation of motion:

$$m_i \mathbf{a}_i = -\frac{\partial U(\mathbf{r}^N)}{\partial \mathbf{r}_i} - \gamma_i m_i \mathbf{v} + (2k_{\mathrm{B}} T \gamma_i m_i)^{1/2} \eta(t)$$

- Stochastic term is Gaussian random variable: $\langle \eta(0)\eta(t) \rangle = \delta(t)$

- Rigorously conserves canonical ensemble

- Introduces stochastic component to trajectories…

Simulations at Constant Pressure

- Can readily extend thermostatting approaches
- Consider coupling to "pressure bath" instead of "temperature bath"

Simulations at Constant Pressure

- Can readily extend thermostatting approaches
- Consider coupling to "pressure bath" instead of "temperature bath"
- Barostats:
  - Volume rescaling (akin to velocity rescaling)
  - Berendsen barostat (doesn't produce NPT ensemble)
  - Extended ensemble: **Andersen barostat (JCP 1980)**
- Need to capture correct volume fluctuations to produce isothermal-isobaric ensemble
- Make predictions regarding density, phase transitions,…