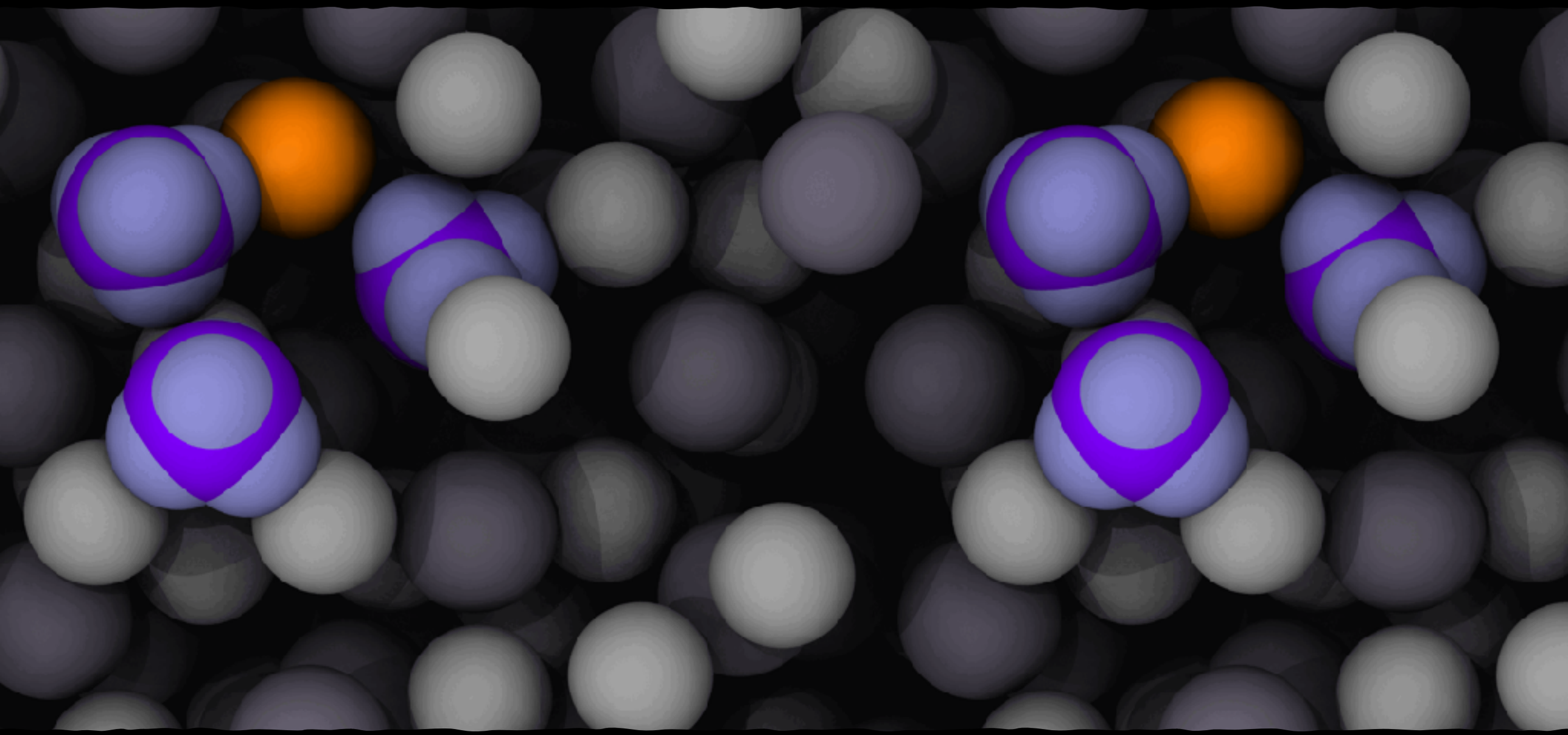
Predicting Properties from First-Principles II:
Total Energy and Force Applications



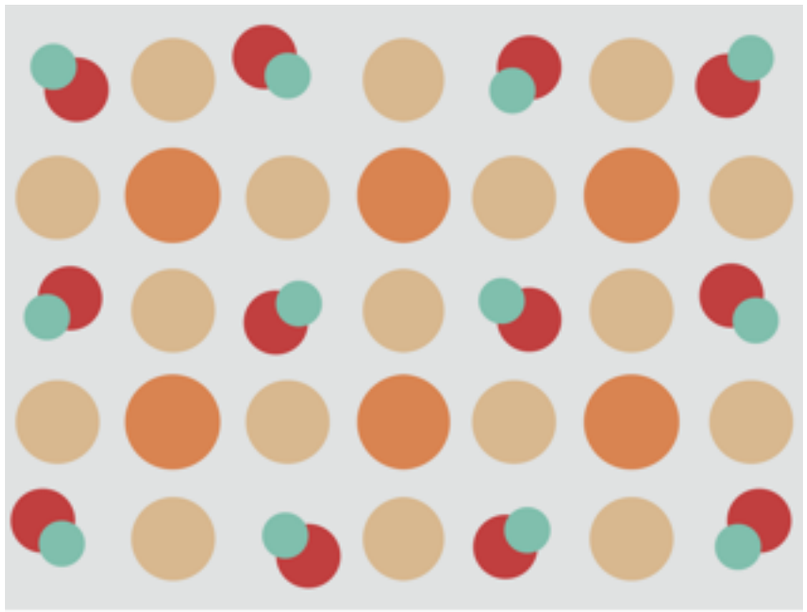
Rick Remsing

RUTGERS

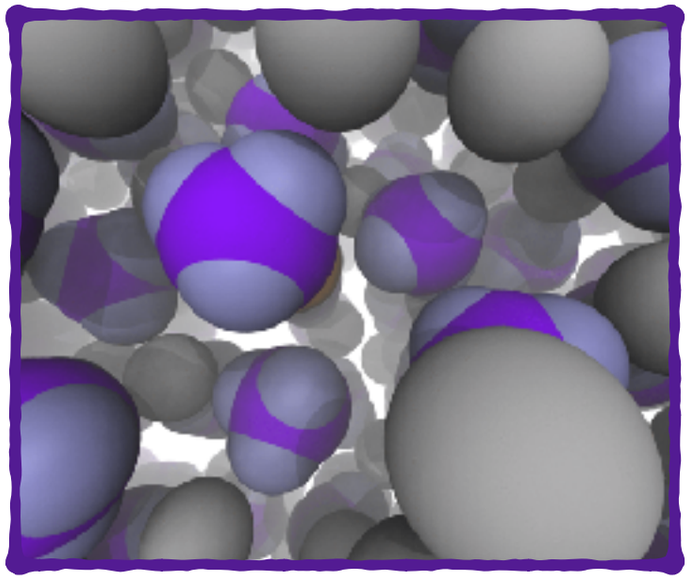
remsinglab.com rick.remsing@rutgers.edu

What we work on

Materials for Energy

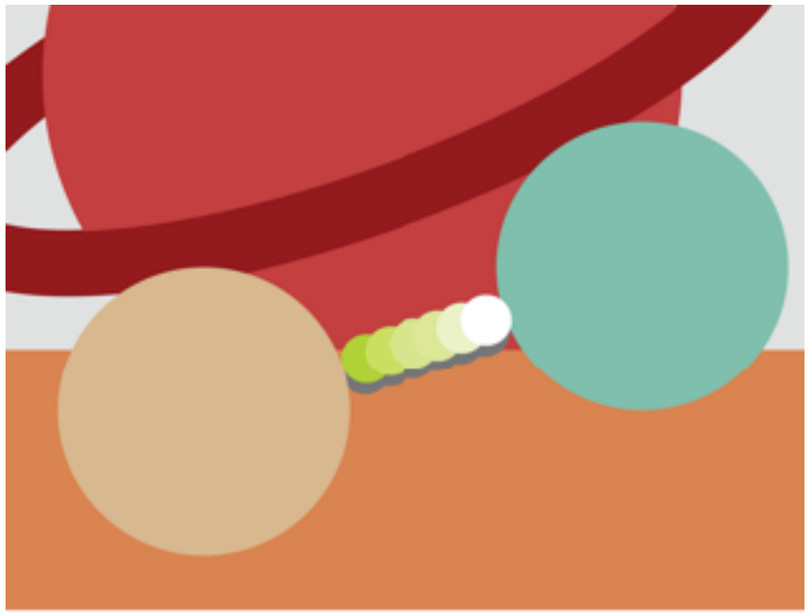


Electrolytes, perovskites, catalysis & defects…

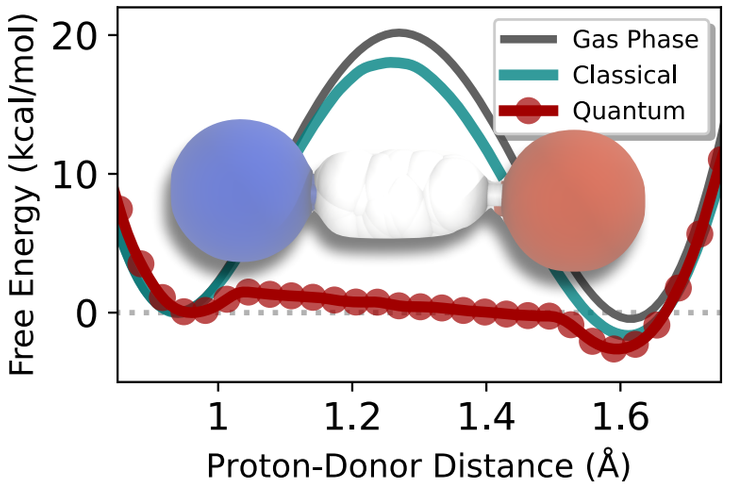


CM Hylton-Farrington, RCR, *Nat Comm* 2026
HS Dhattarwal, R Somni, RCR *Nat Comm* 2024
HS Dhattarwal, RCR, *J Chem Phys* 2025
HS Dhattarwal, RCR, *ChemPhysChem* 2025

Astrobiology & Planetary Science

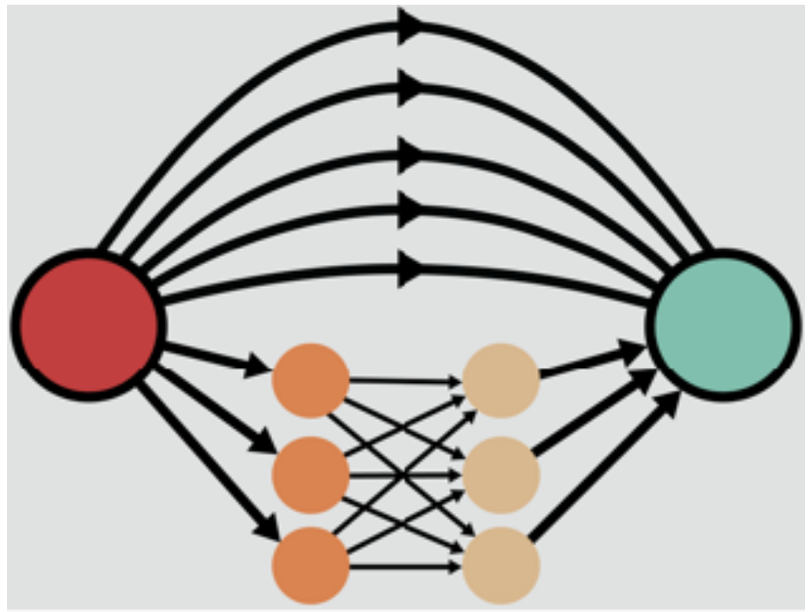


Non-H_2O chem, organic crystals, NQEs, minerals…

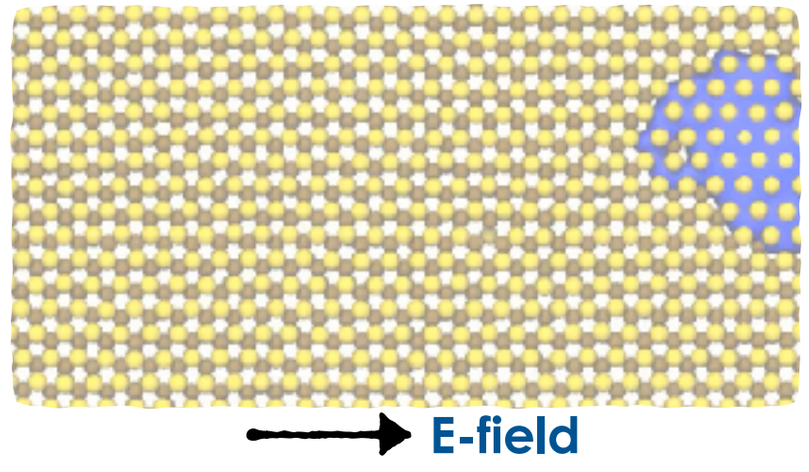


HW Longo, RCR *arXiv* 2024
AC Thakur, RCR, *ACS Earth & Space Chem 2024, JCP 2024, ACS Earth & Space Chem 2023, Mol Phys 2021*

Method Development

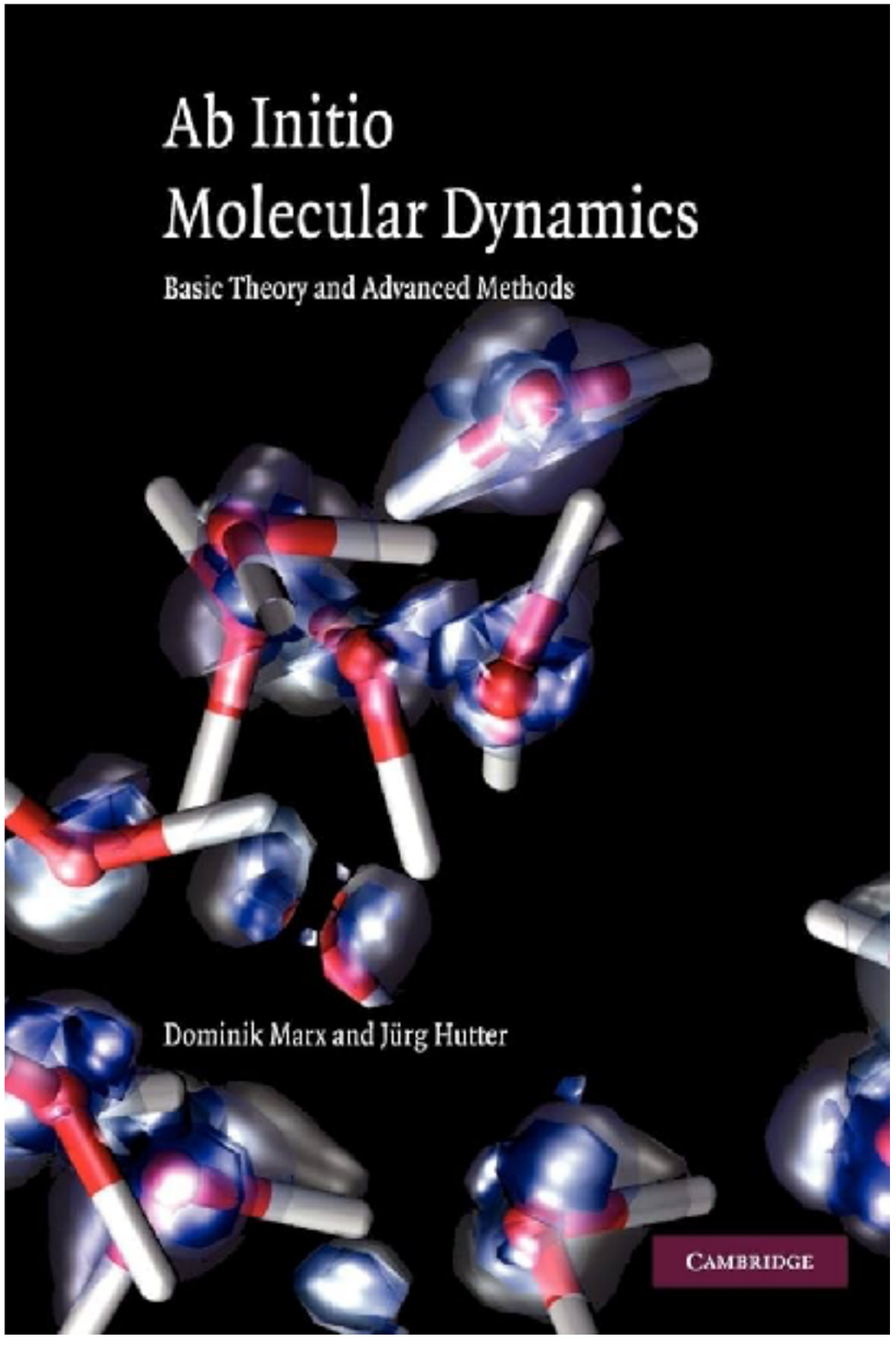


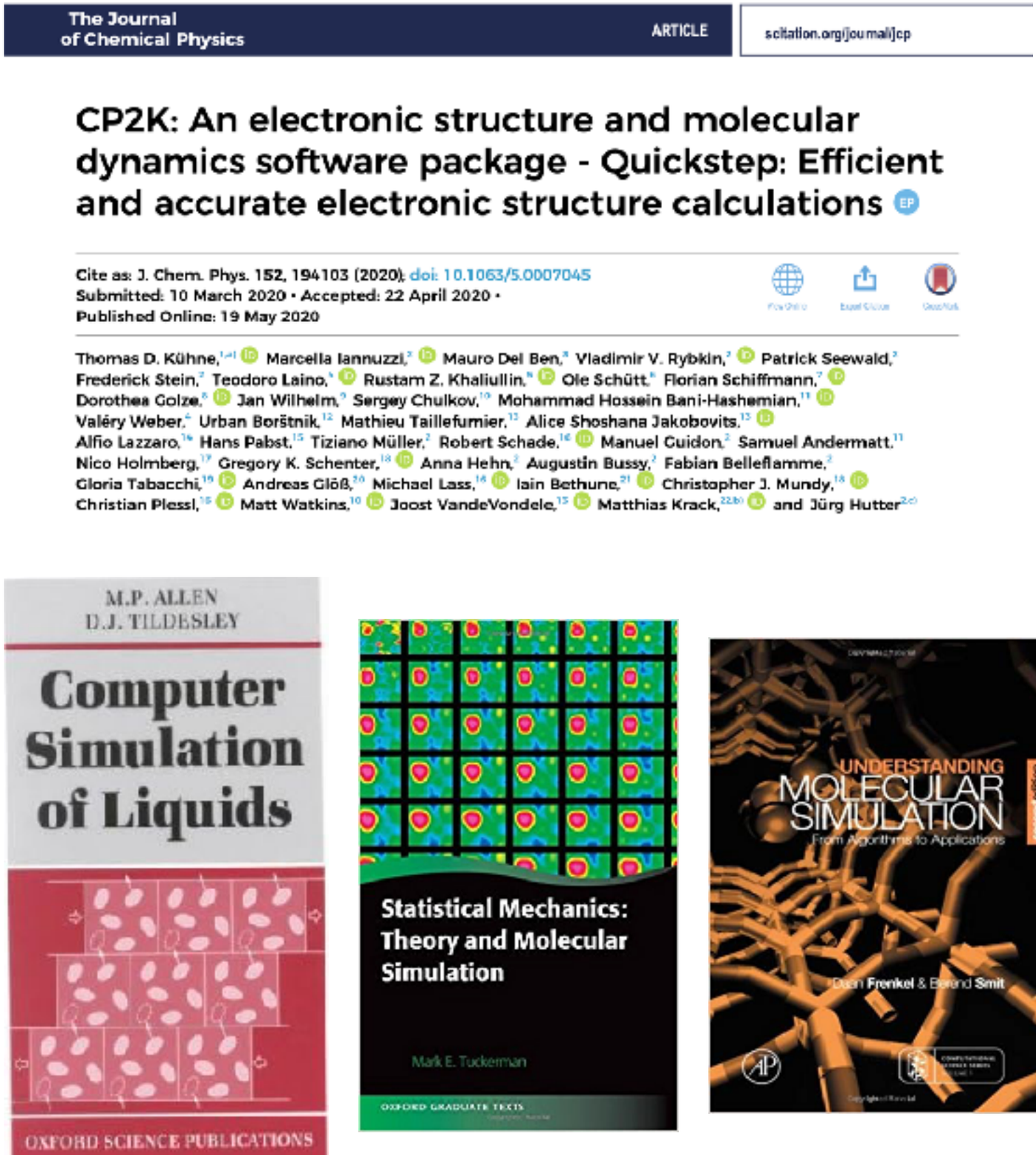
Machine learning, path integrals, nonequilibrium…



A Gao, RCR *Nat Comm* 2022
HS Dhattarwal, A Gao, RCR, *JPCB* 2023
RCR, *JCP 2024*
RCR, JE Bates, *JCP* 2020

Good References to Learn More

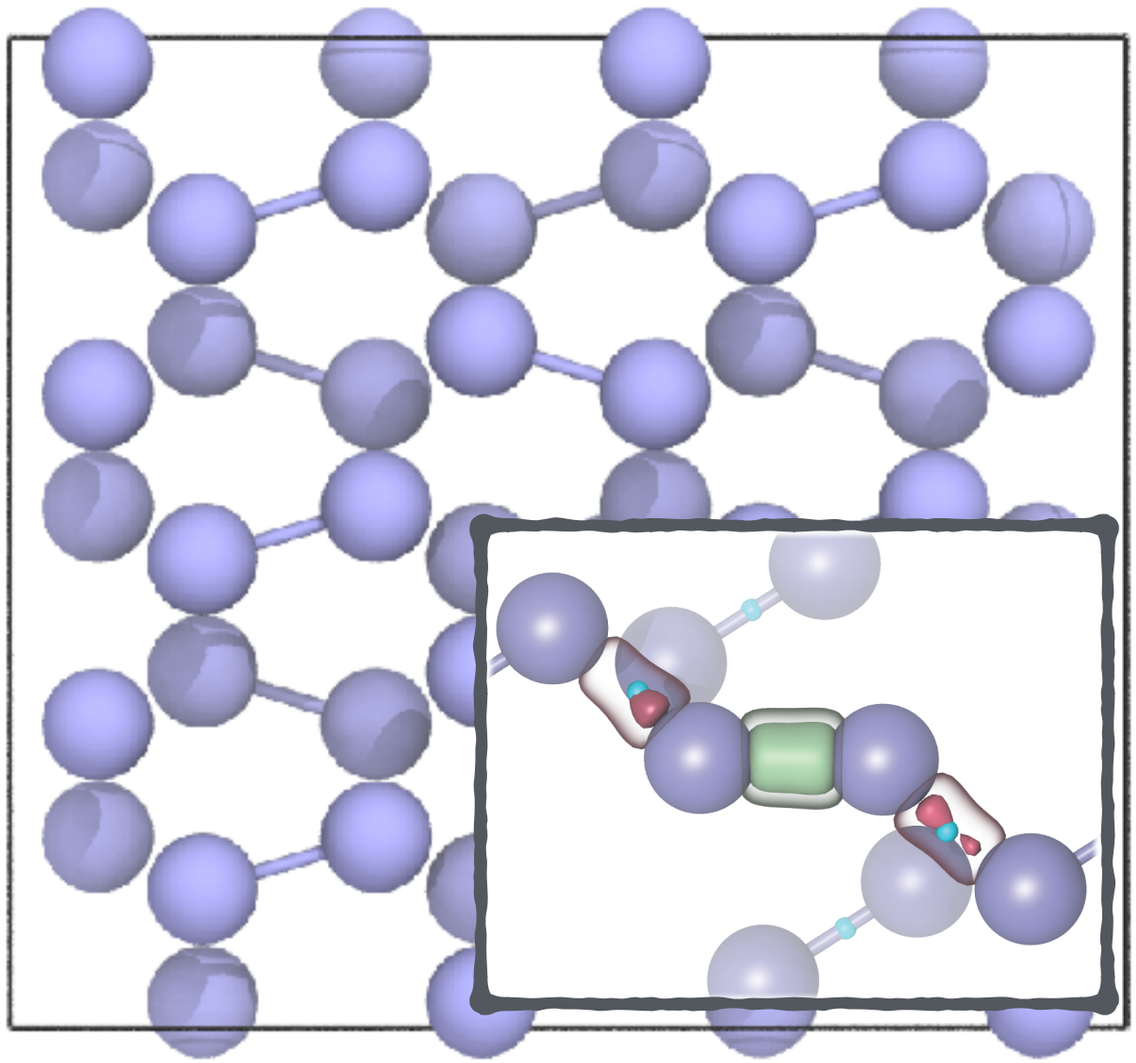




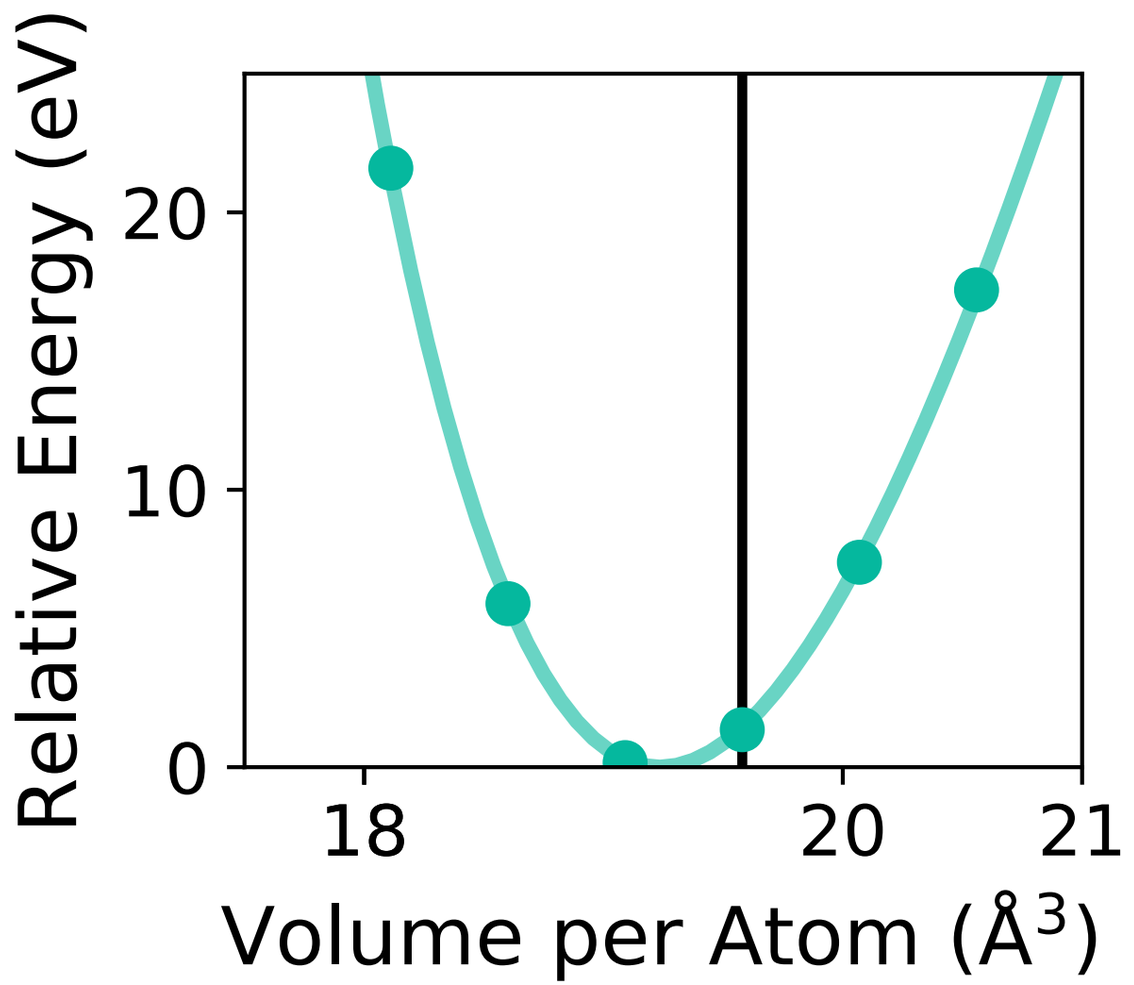
Why think about total energy?

- 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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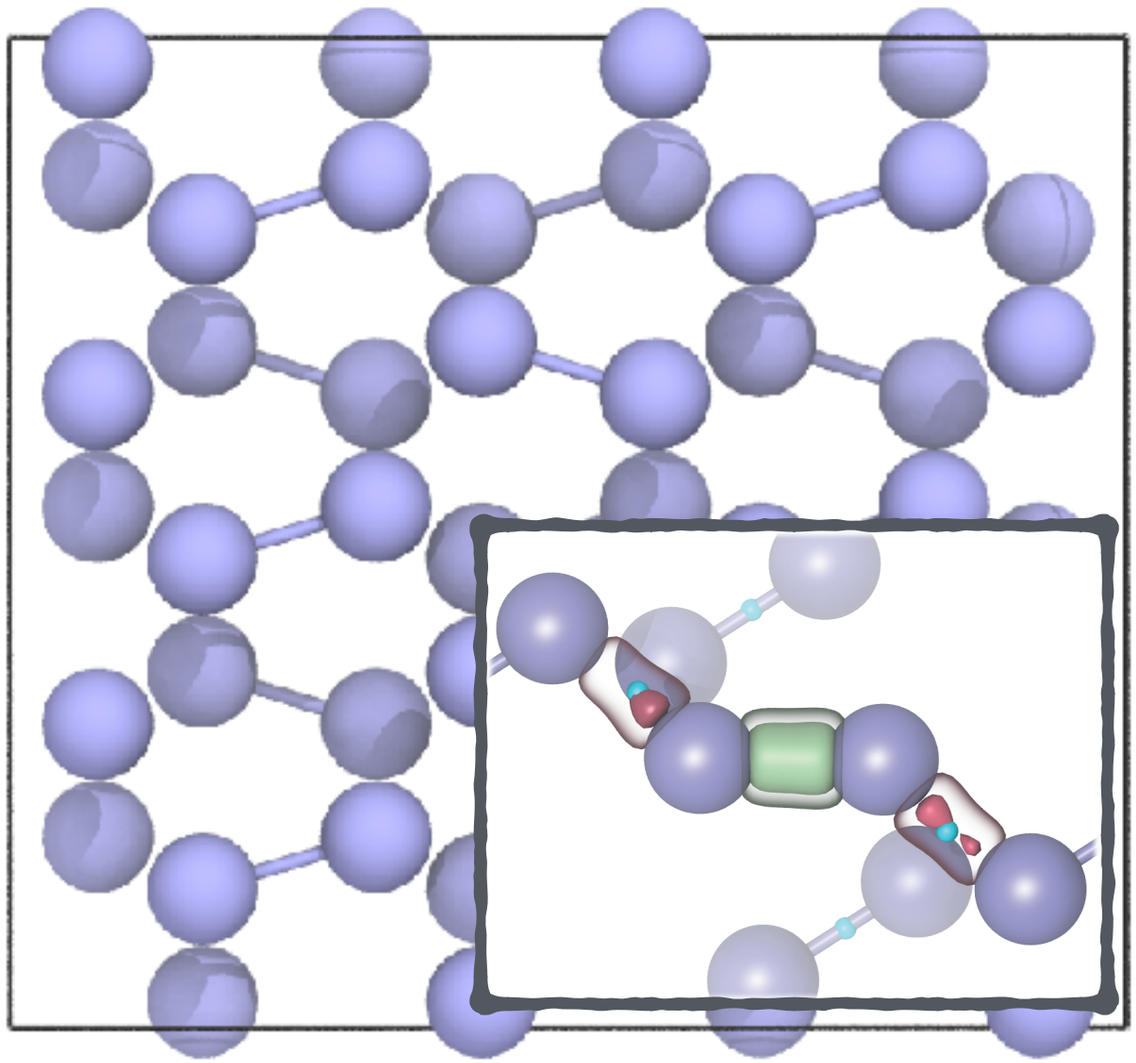
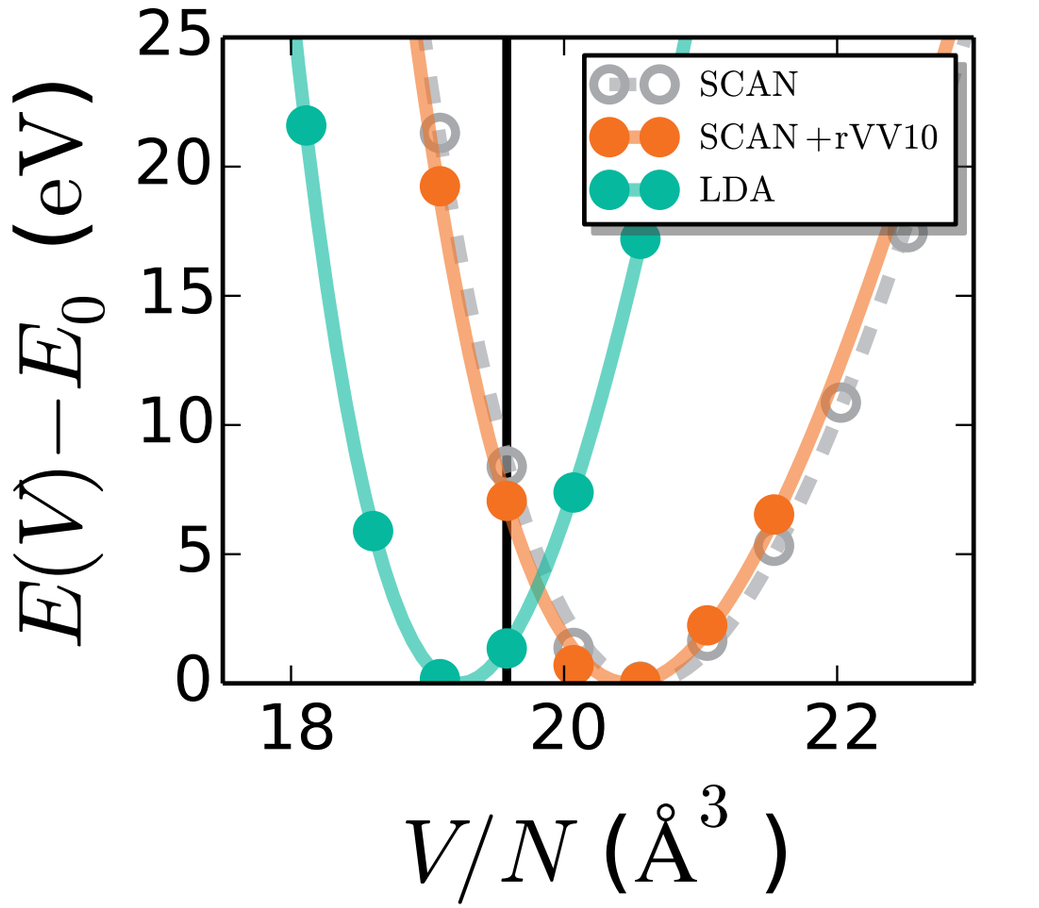
α-Gallium



- **Equation of State & Bulk Moduli**



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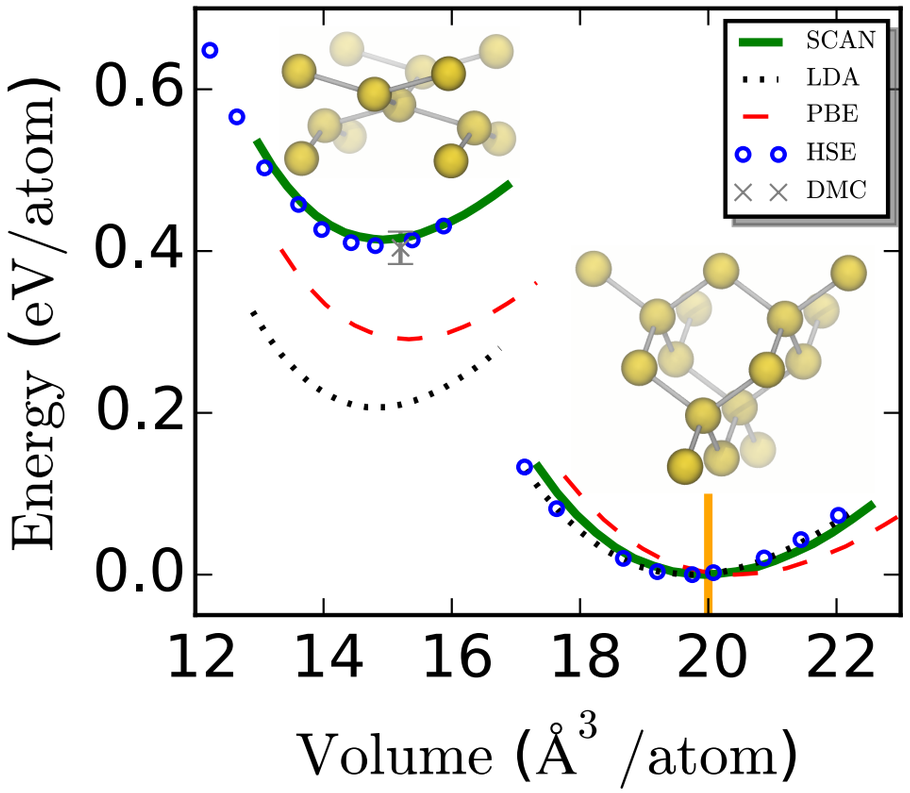
$$E(V) - E_0 = K_0 V_0 \left[\frac{1}{K_0'(K_0' - 1)} \left(\frac{V}{V_0} \right)^{1-K_0'} + \frac{1}{K_0'} \frac{V}{V_0} - \frac{1}{K_0' - 1} \right]$$

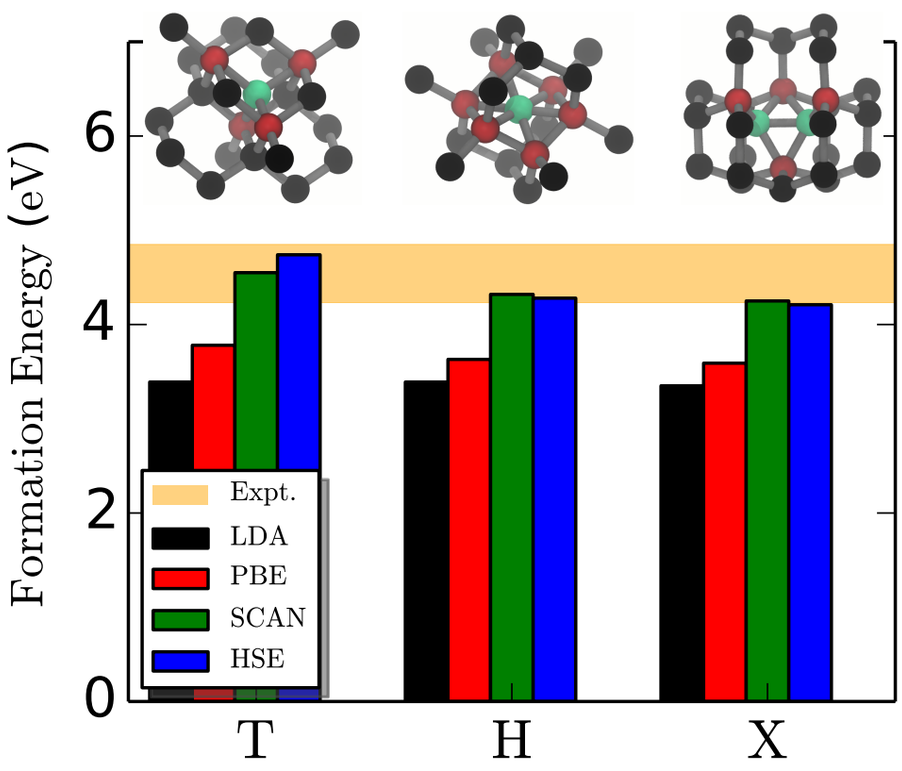
K_0 = bulk modulus

RCR *et al.* Mol Phys 2018

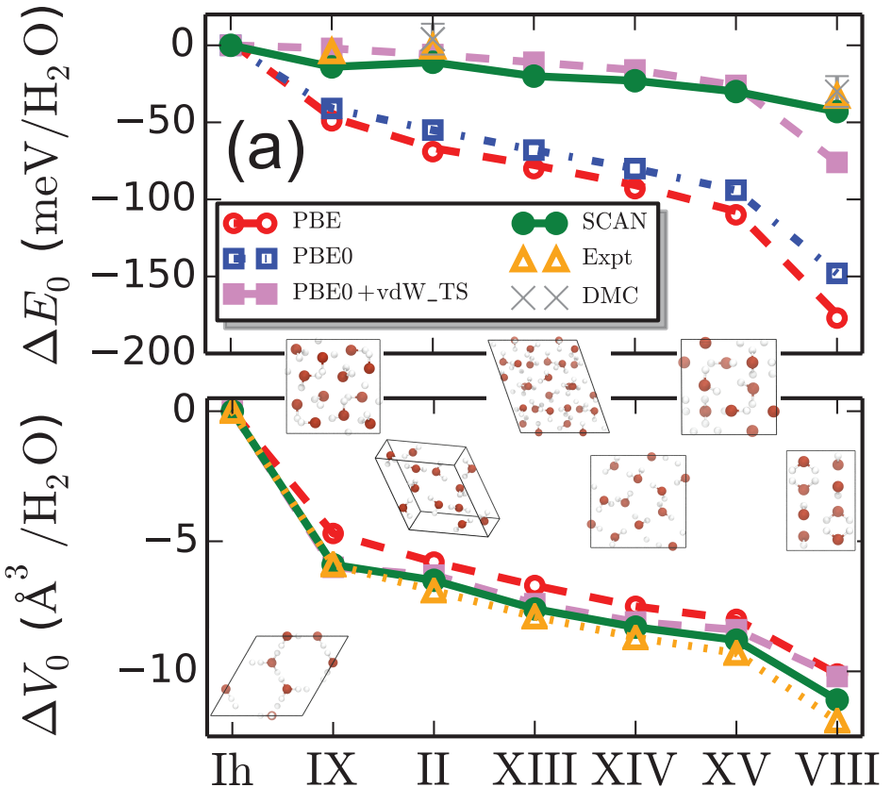
Phase Stability & Defect Formation

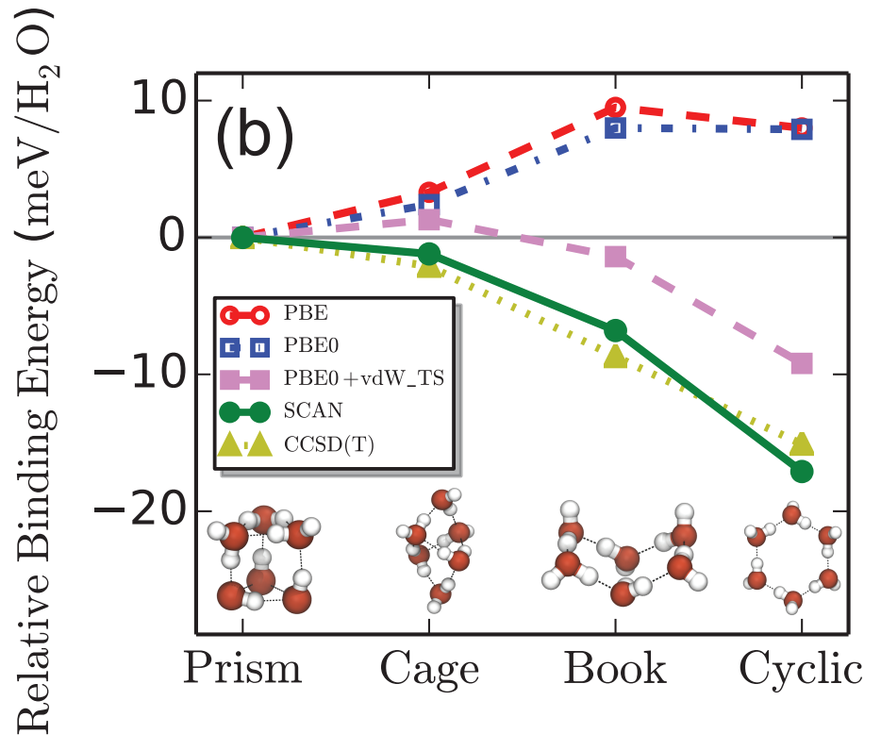
Silicon





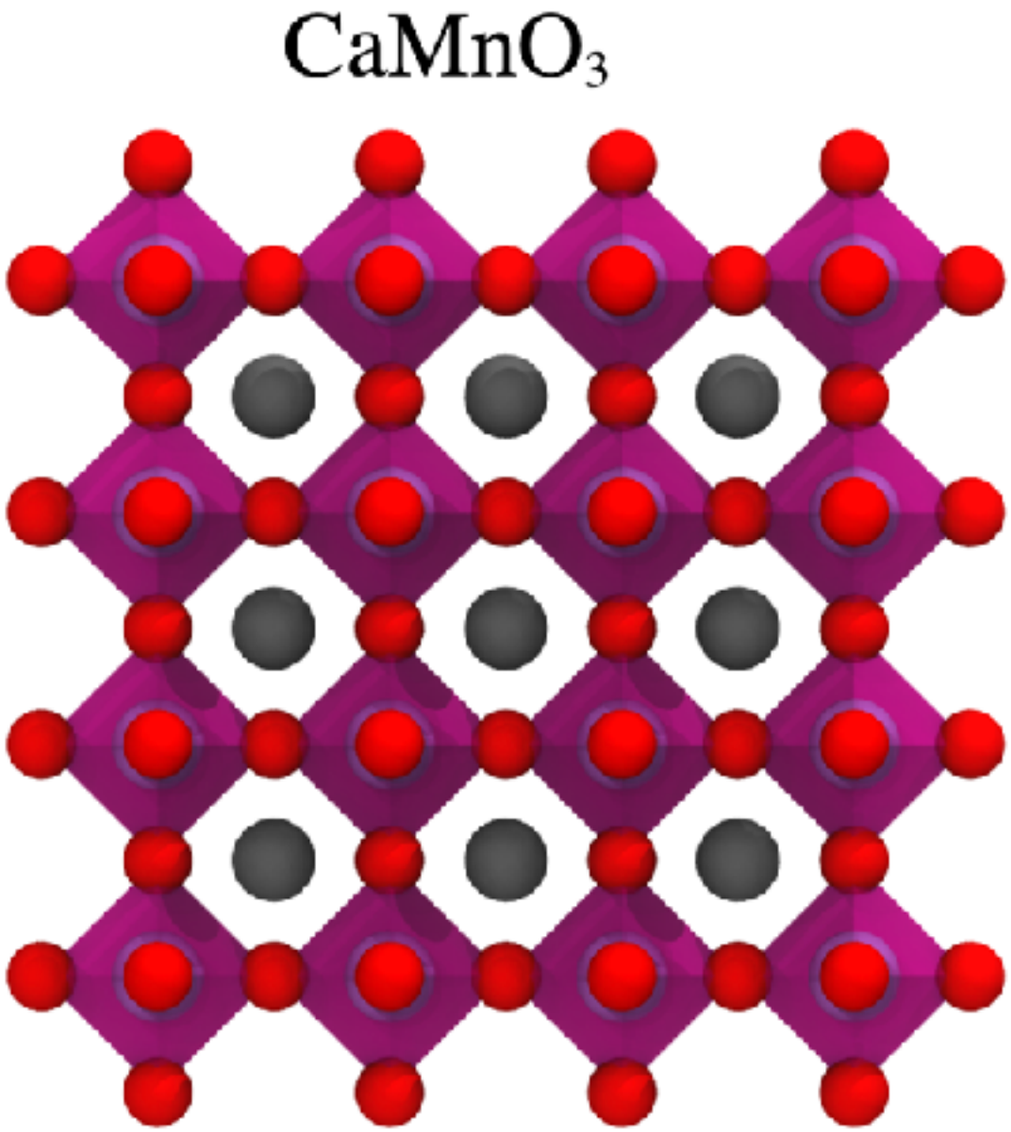
Water





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

Oxygen vacancies in oxide perovskites



- Oxygen vacancy formation

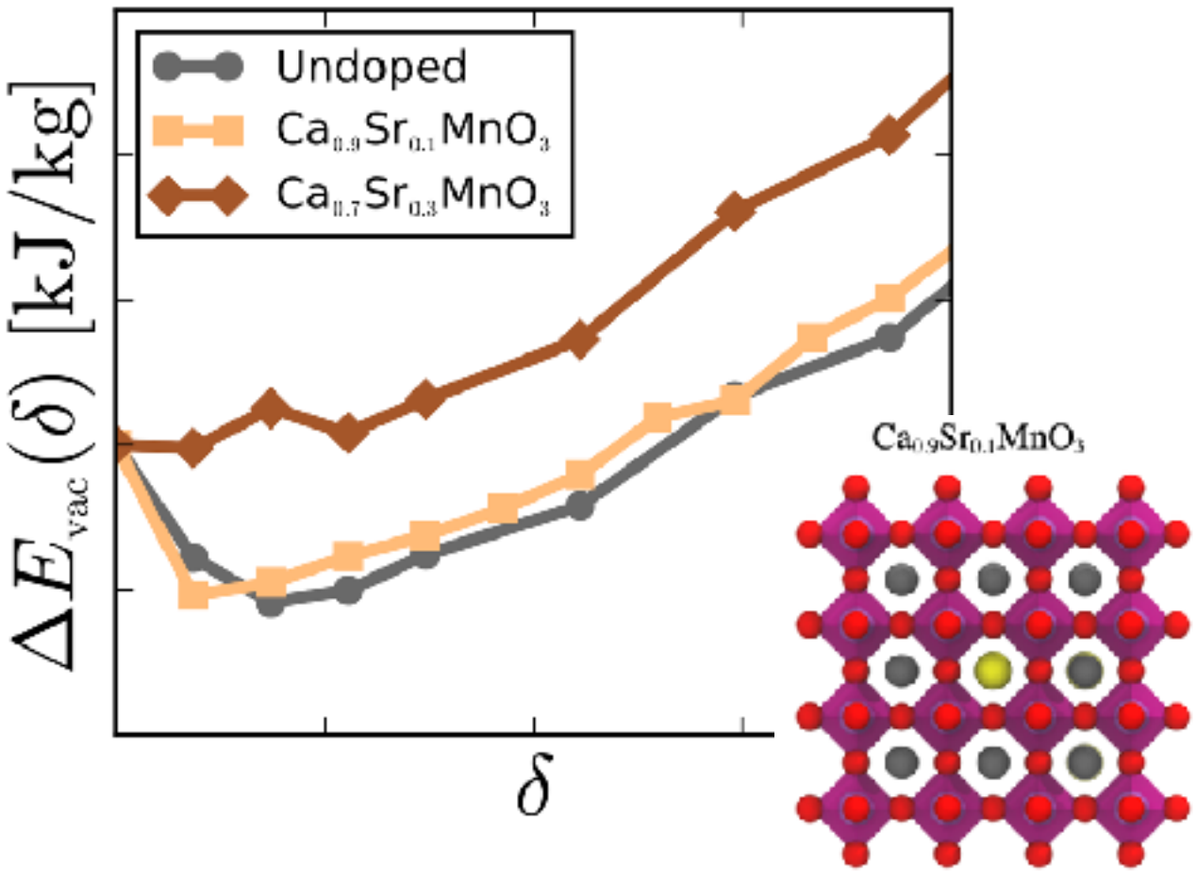
$$nABO_3 \longrightarrow nABO_{3-1/n} + \frac{1}{2}O_2(g)$$

- Energetics of forming vacancies with concentration δ from **total energies**

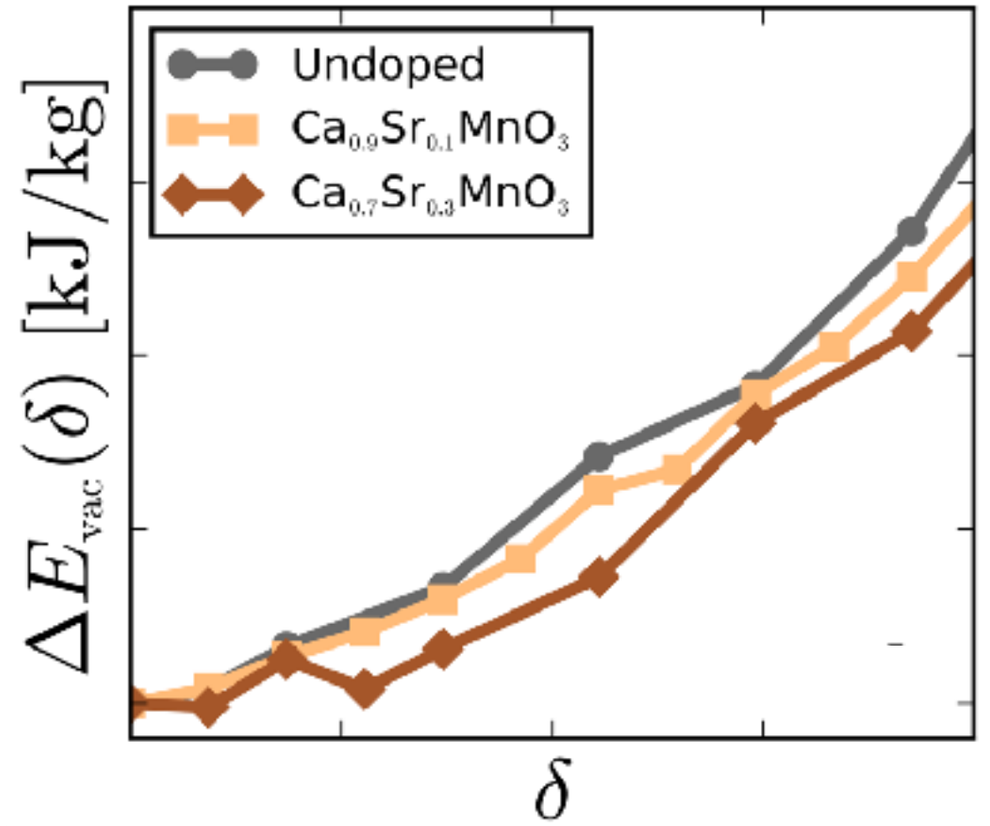
$$\Delta E_{\mathrm{vac}}(\delta) = E_{\mathrm{ABO_{3-\delta}}} - E_{\mathrm{ABO_3}} + \frac{\delta}{2}E_{\mathrm{O_2}}$$

HS Dhattarwal, CM Hylton-Farrington, IG McKendry, C Abram, RCR; arXiv 2026

Oxygen vacancies in oxide perovskites



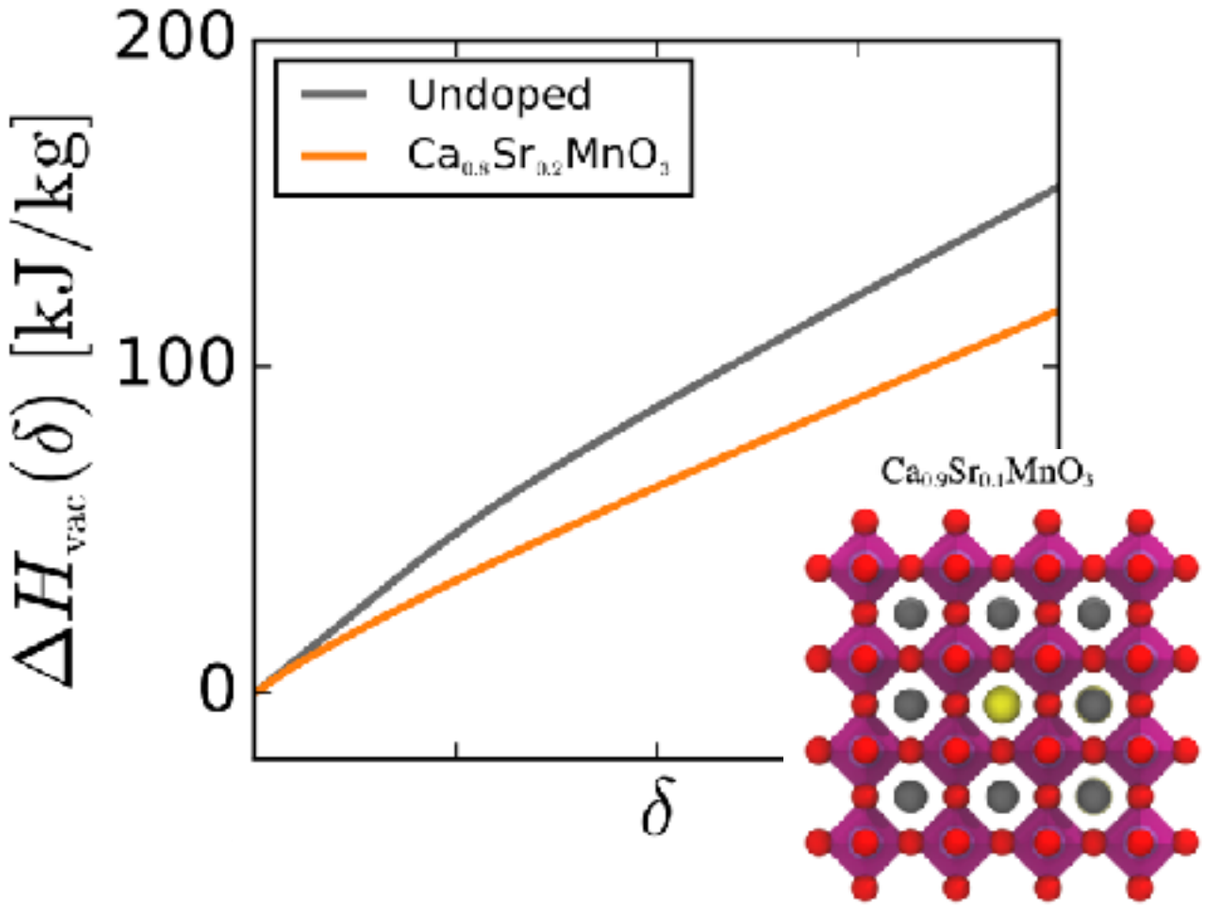
- Minimum = stable with finite concentration of vacancies

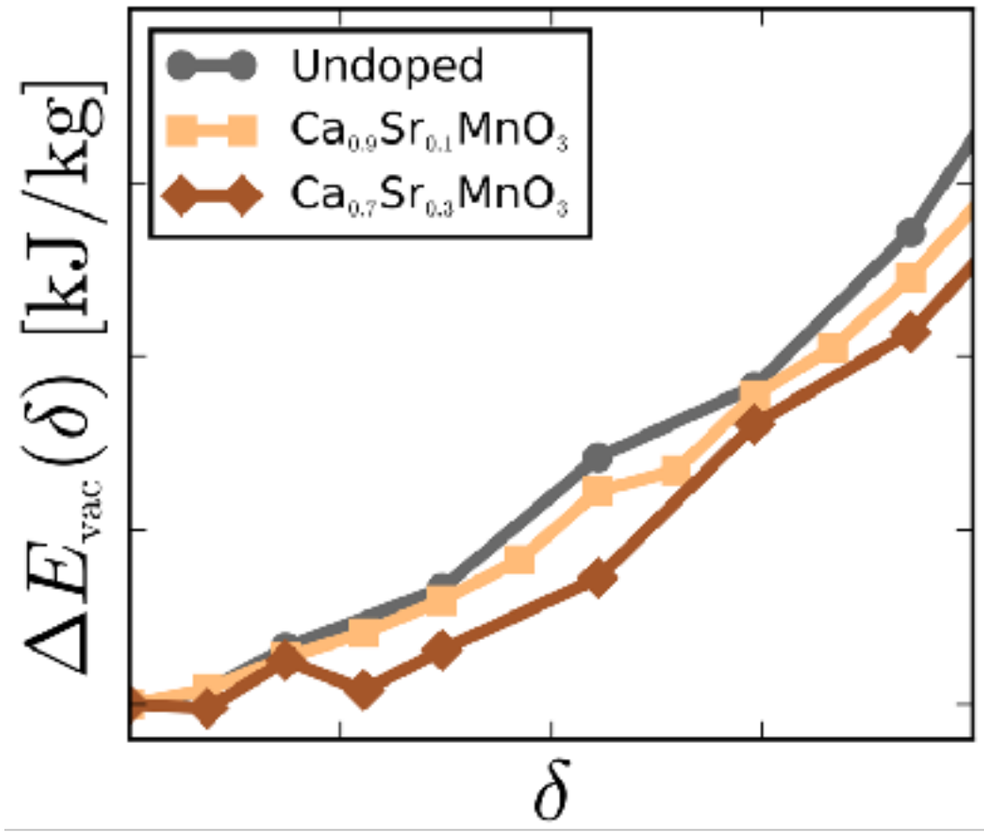


- Shift WRT minimum in ΔE to predict exp. Observable

HS Dhattarwal, CM Hylton-Farrington, IG McKendry, C Abram, RCR; arXiv 2026

Oxygen vacancies in oxide perovskites





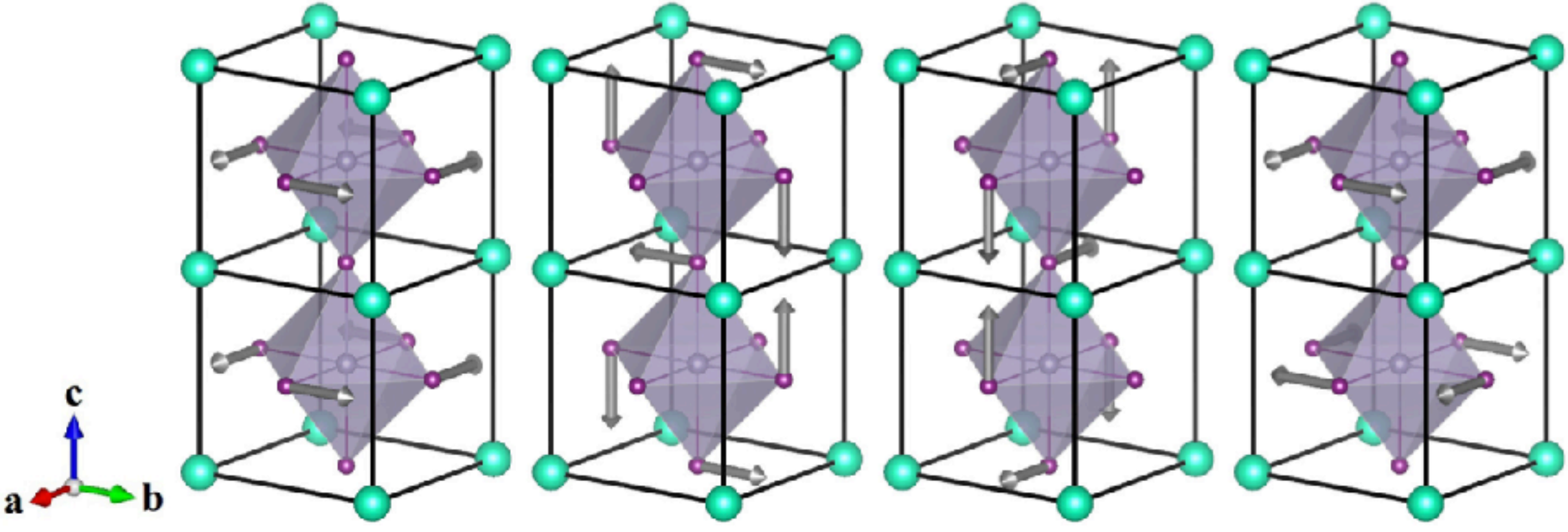
This is with total energy…

… what can we do with forces?!?

HS Dhattarwal, CM Hylton-Farrington, IG McKendry, C Abram, RCR; arXiv 2026

Why care about Forces?

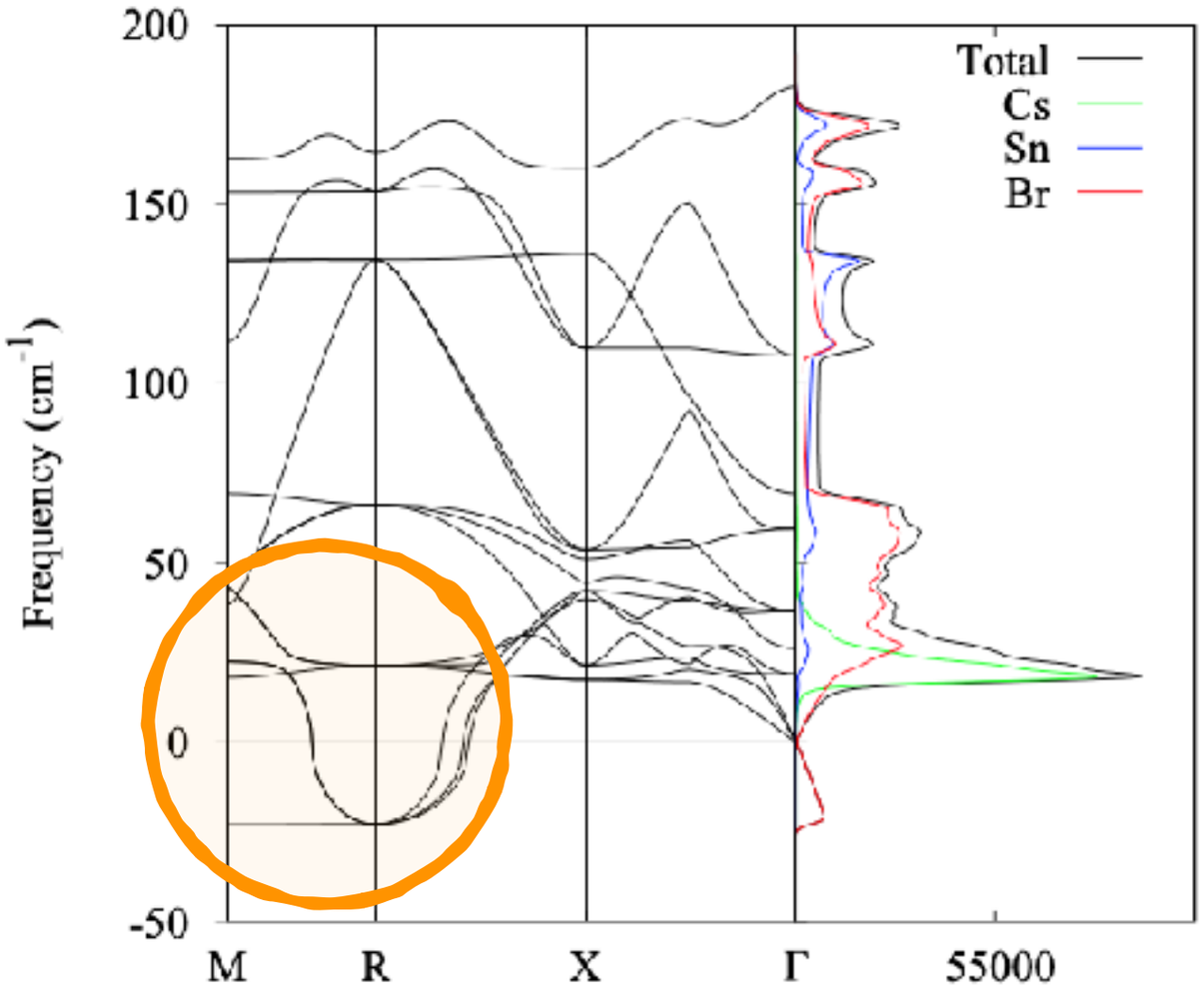
- Forces (derivatives of total energy) tell us how **atoms move**
- Structural relaxation, cell optimization (stresses), mechanics
- **Molecular dynamics** → fluctuations, vibrations, diffusion, reactions
- **Let's look at vibrations (phonons) in a model material, $CsSnBr_3$**

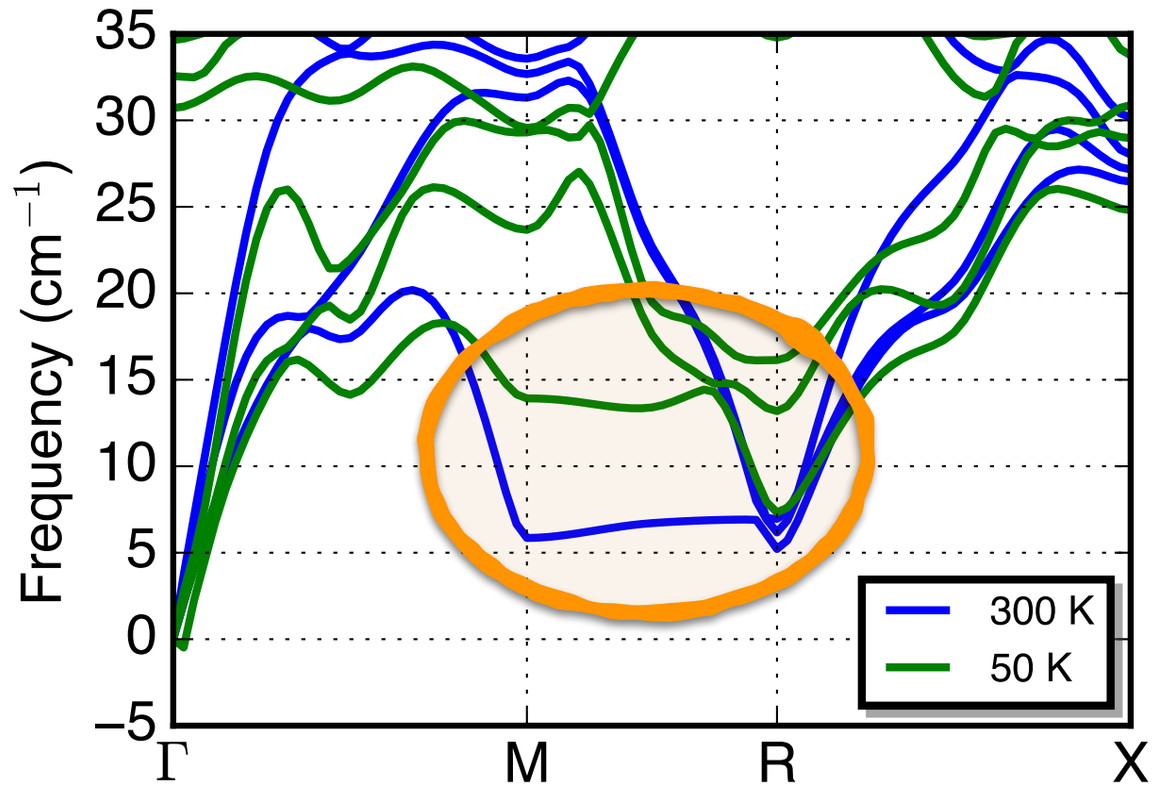


Huang, Lambrecht, Phys Rev B 2014

Phonons from harmonic approximations vs. MD simulations

- Phonon dispersion curves for $CsSnBr_3$





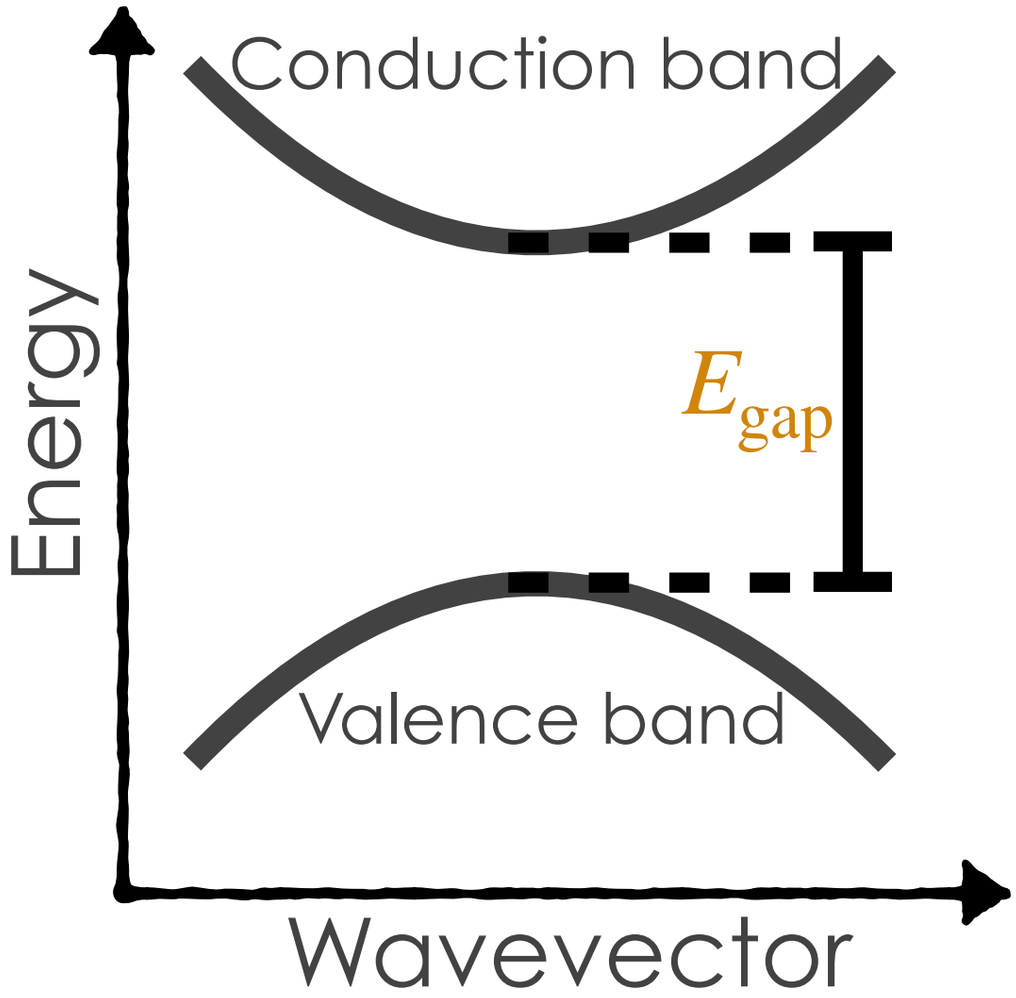
- **Imaginary frequencies!**
  = unstable / soft modes

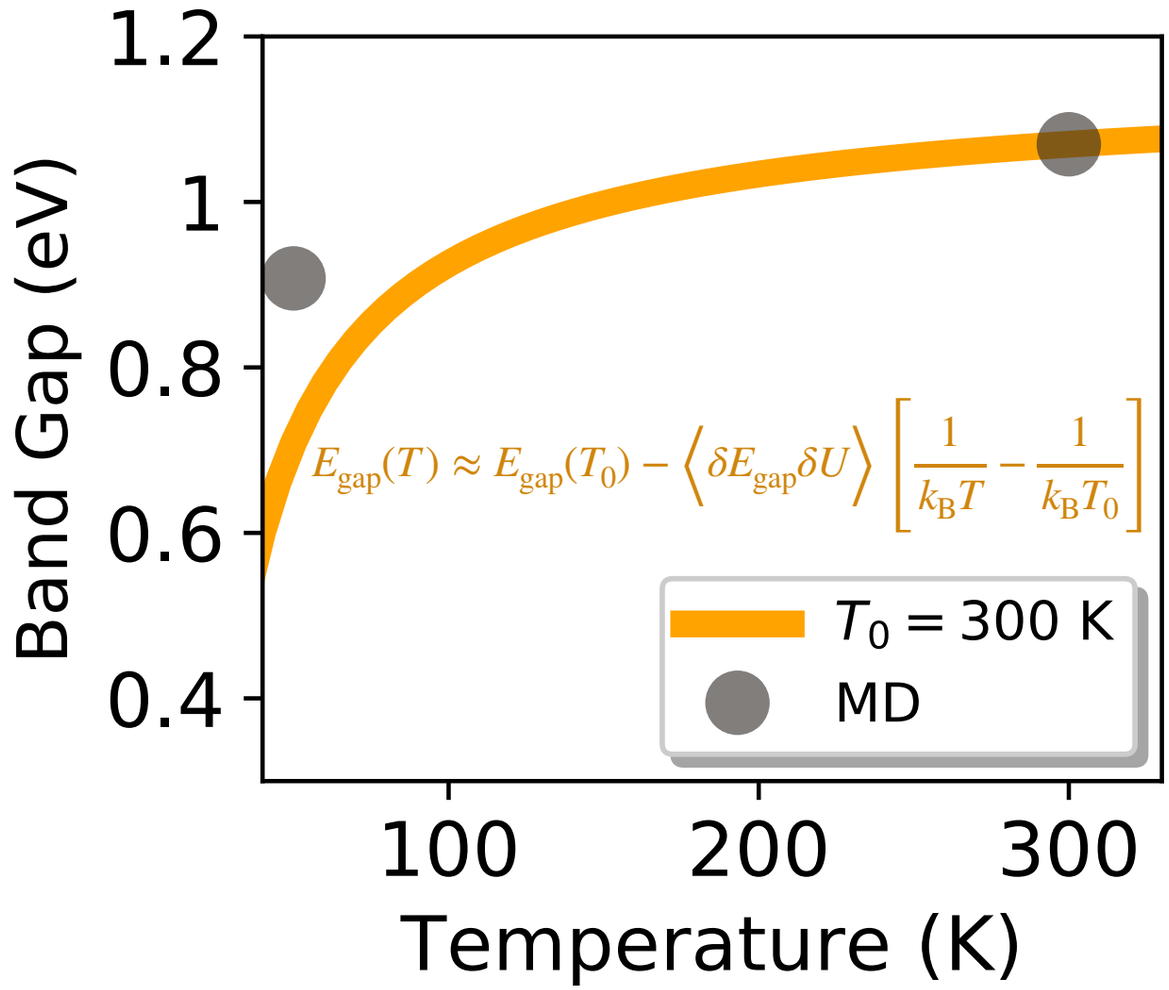
- Anharmonic effects & thermal renormalization included in MD sims

Huang, Lambrecht, Phys Rev B 2014

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

Band gap predictions must include anharmonicity



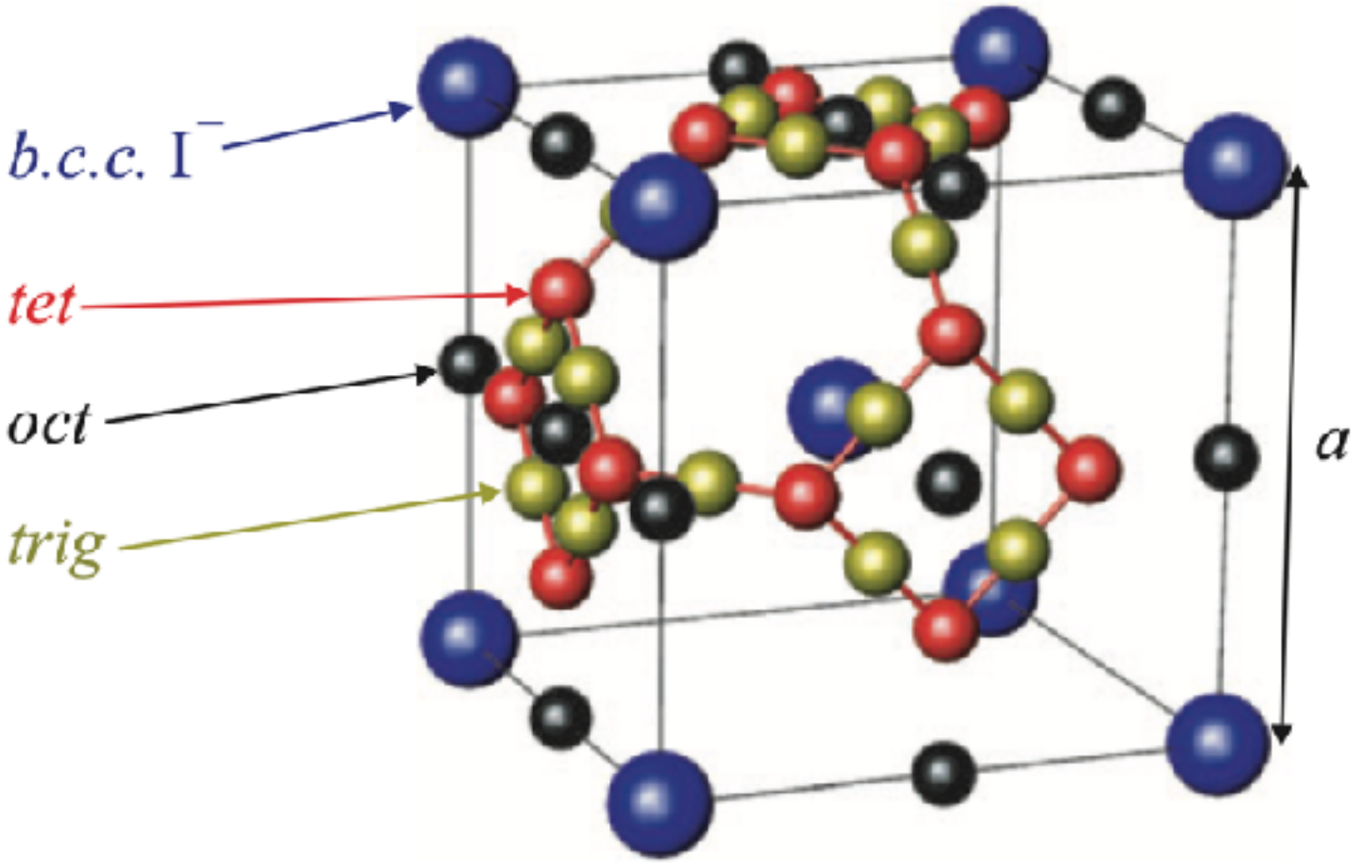


- Cannot describe band gap of anharmonic materials with linear/harmonic theories
- **Need anharmonicity** (from *hidden electronic disorder*)

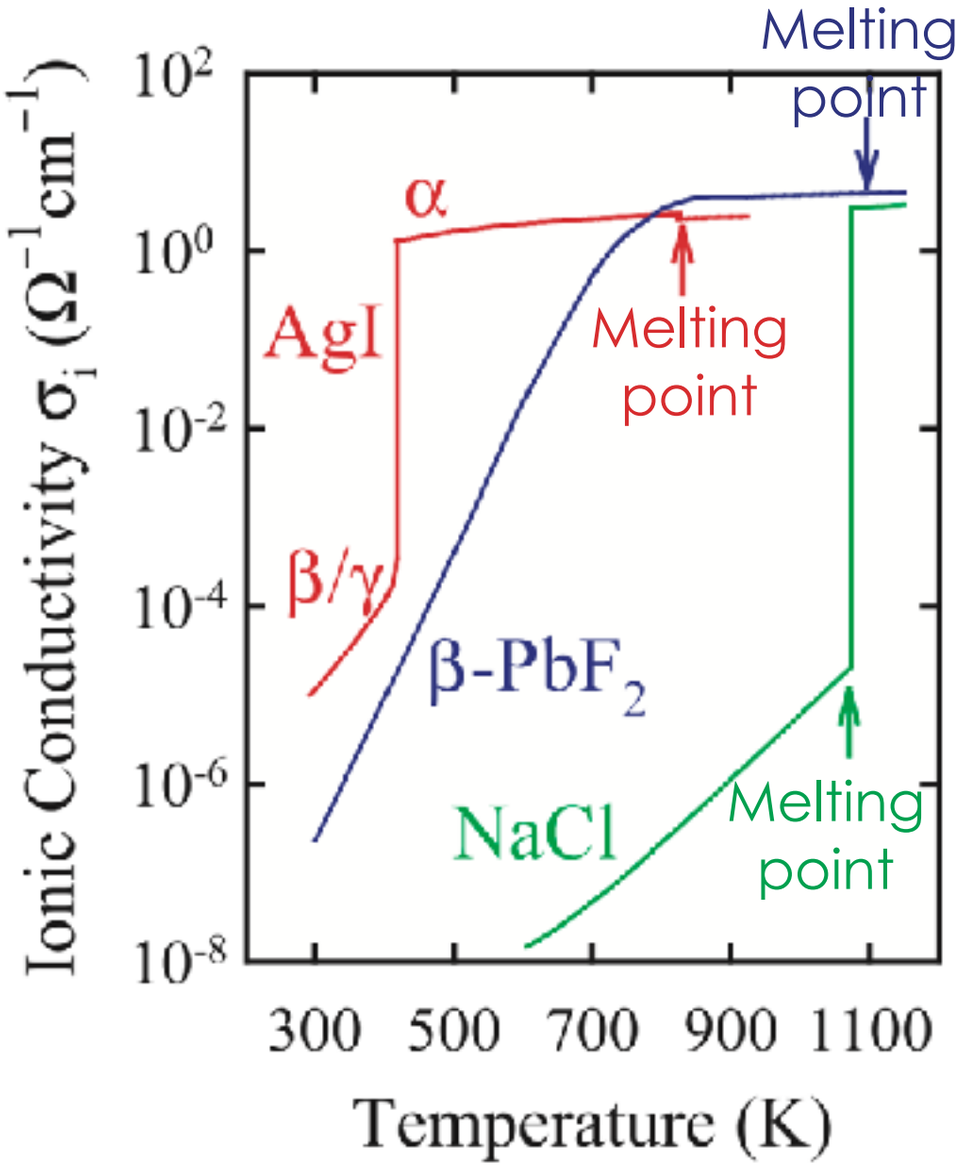
CM Hylton-Farrington, RCR, *Chem Mater*, 2024

Cation diffusion in Silver Iodide

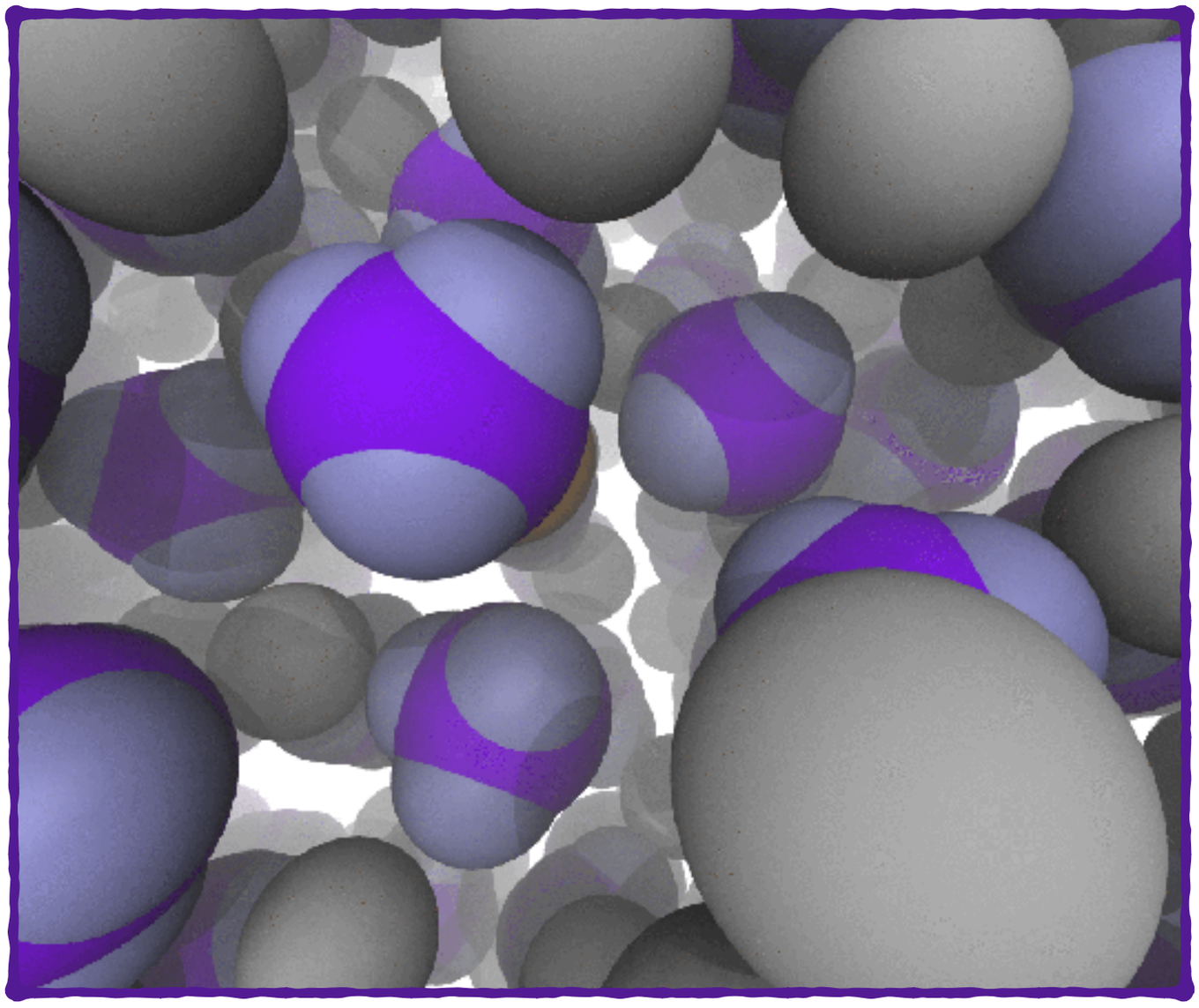
- Iodide sits on cubic lattice, Ag^+ diffuses

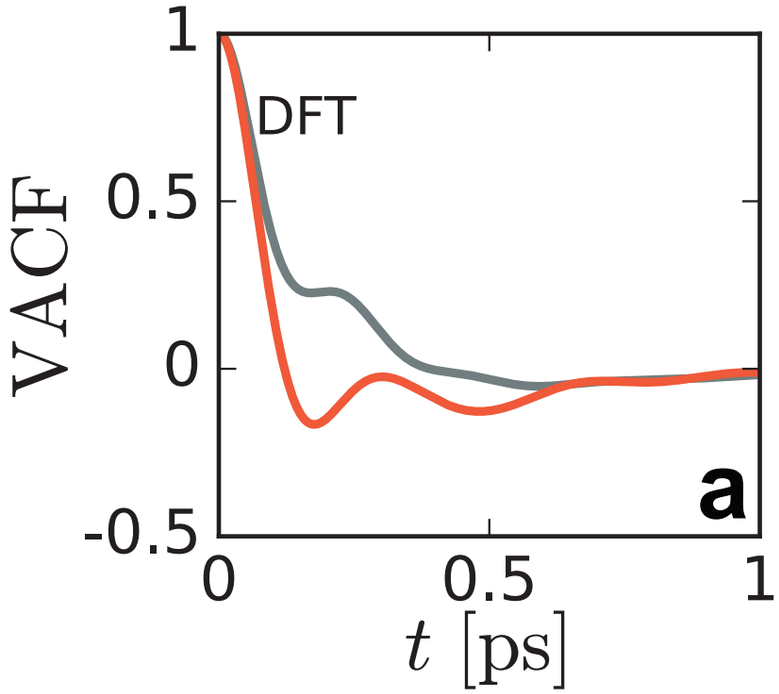


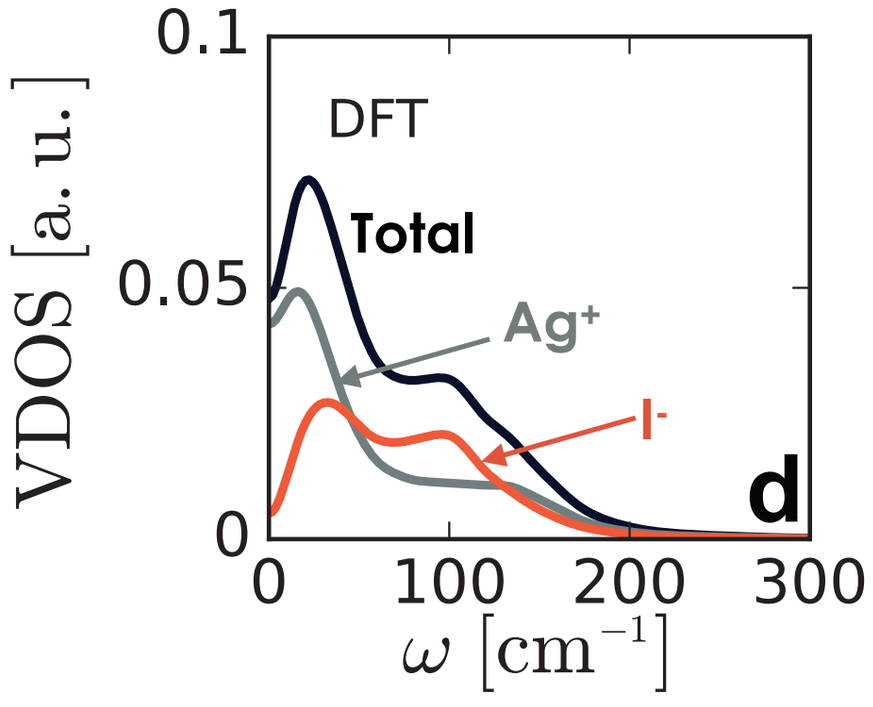
S. Hull, *Rep Prog Phys* 2004



Cation diffusion in Silver Iodide





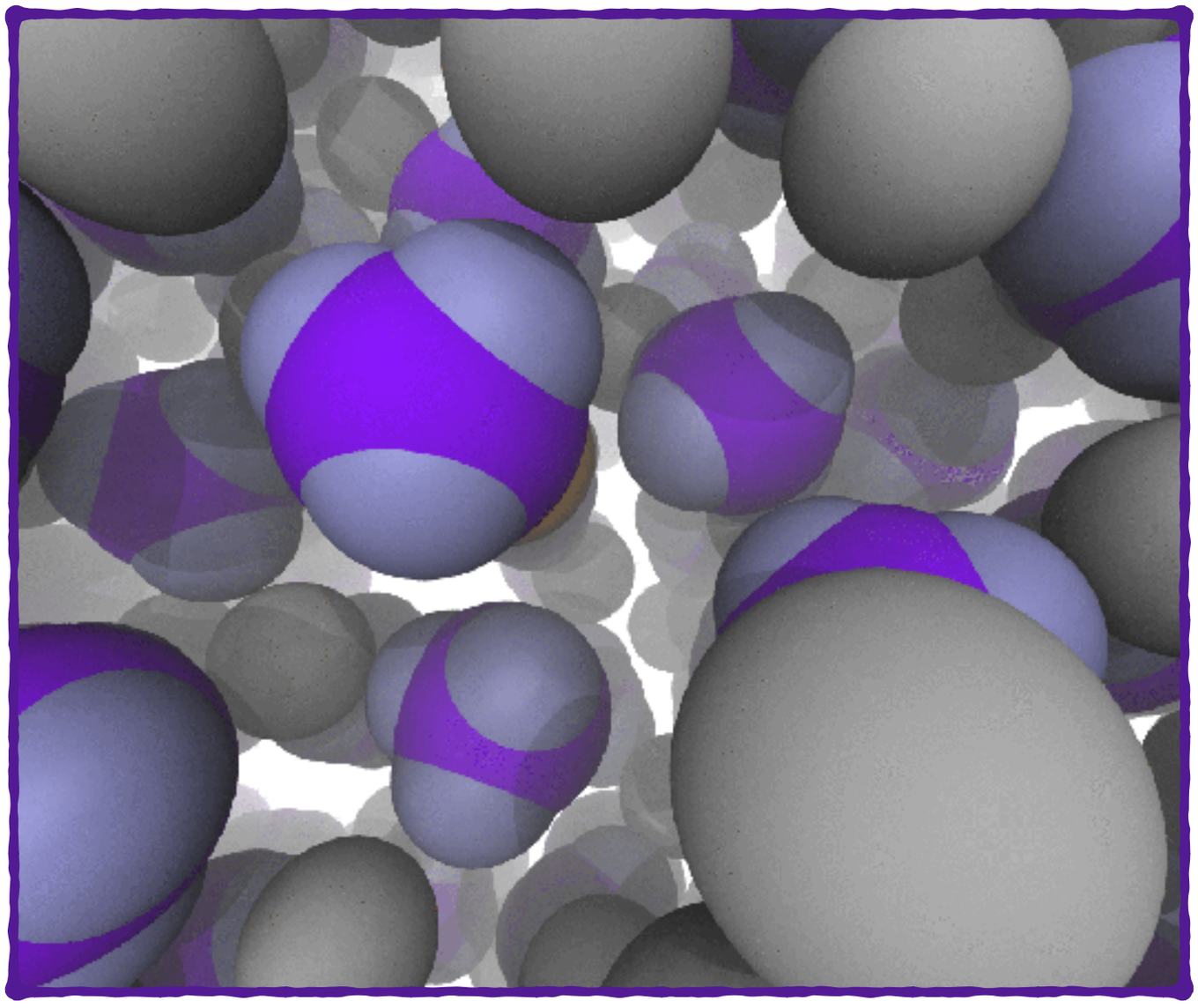


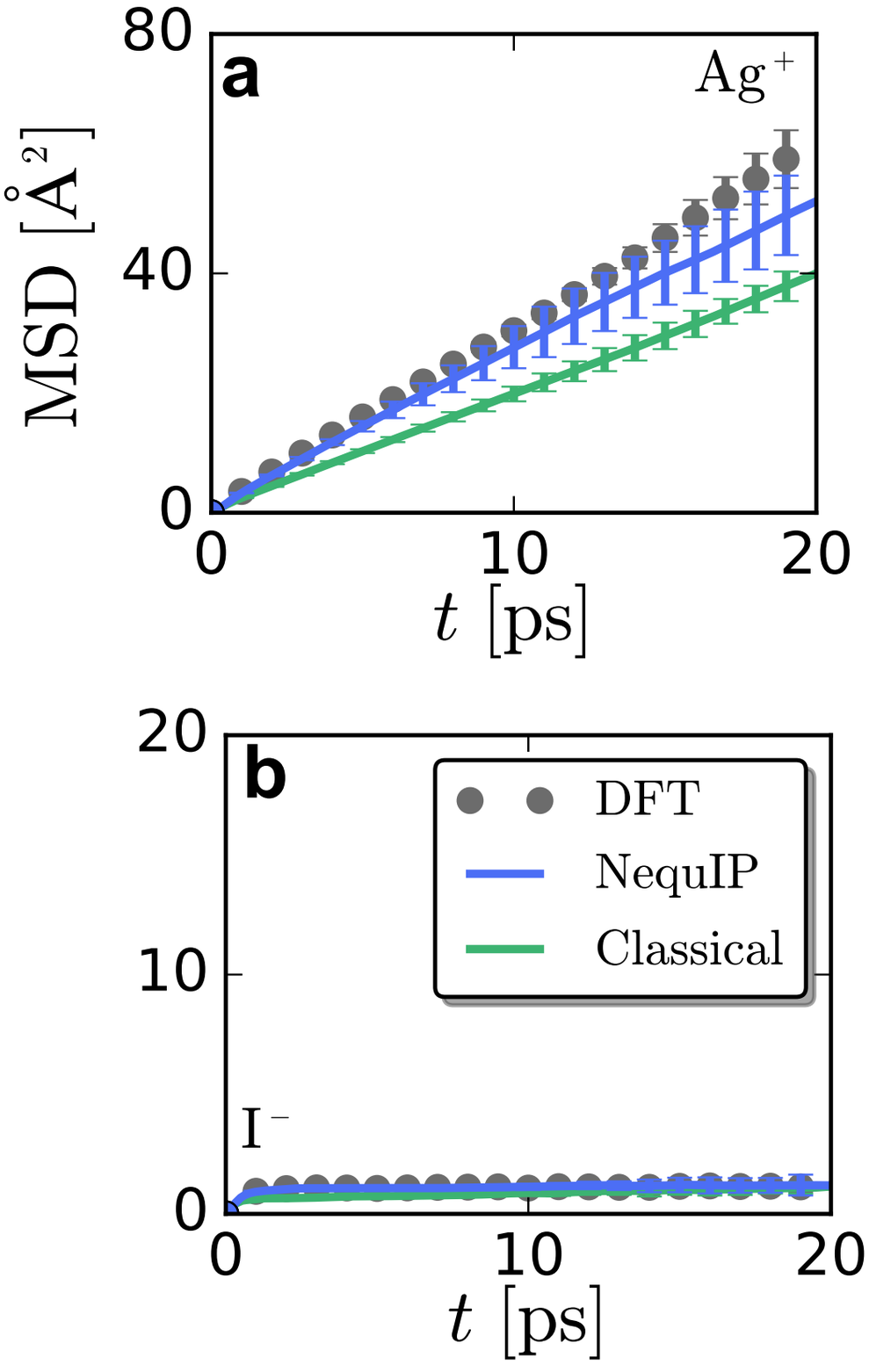
- $\mathrm{VACF}(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$
- $\mathrm{VDOS}(\omega) = \int_{-\infty}^{\infty} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \, e^{-i\omega t} dt \; ; \; \mathrm{VDOS}(\omega = 0) = 3D$

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

HS Dhattarwal, RCR, ChemPhysChem (2025)

Cation diffusion in Silver Iodide



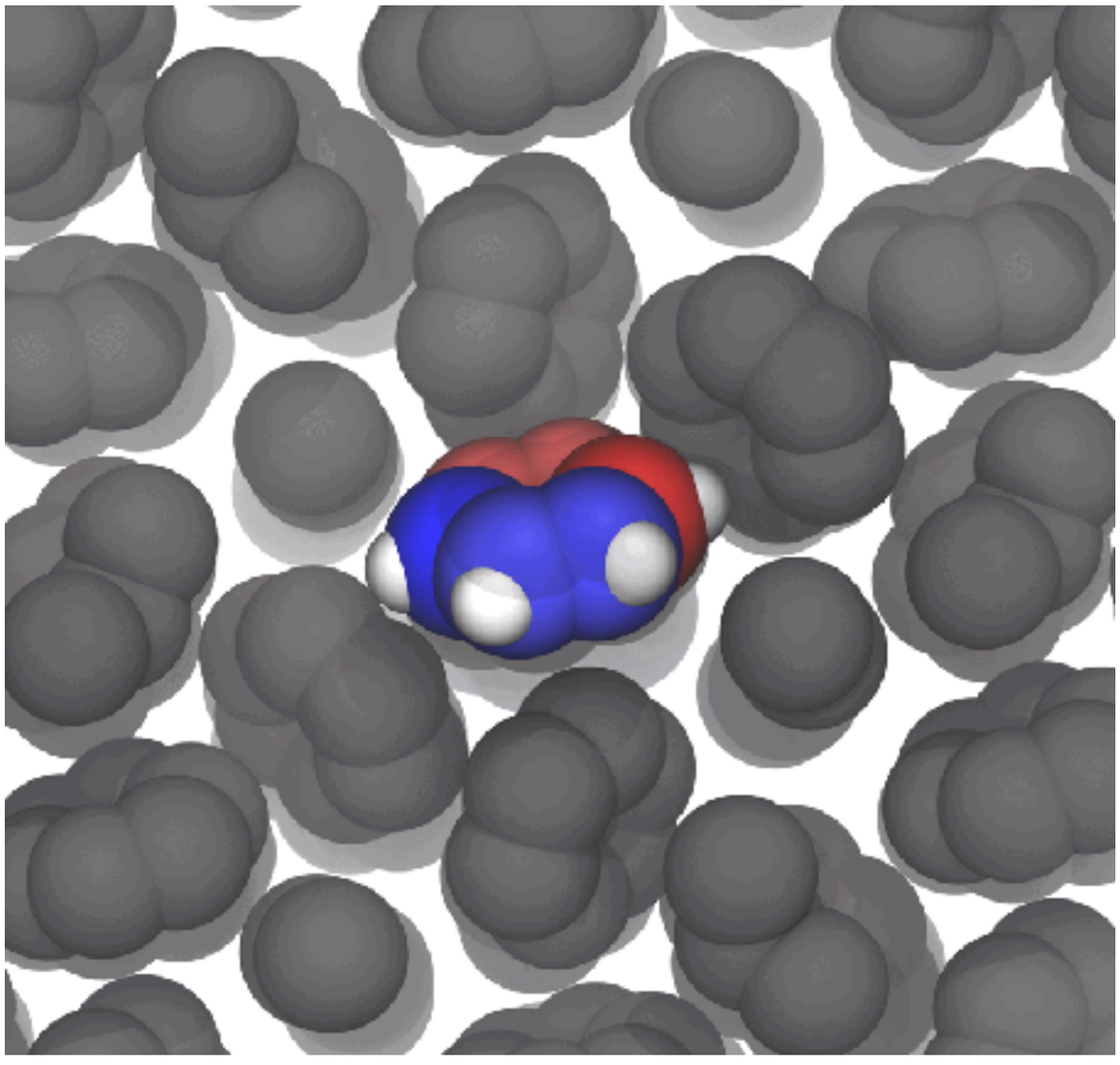


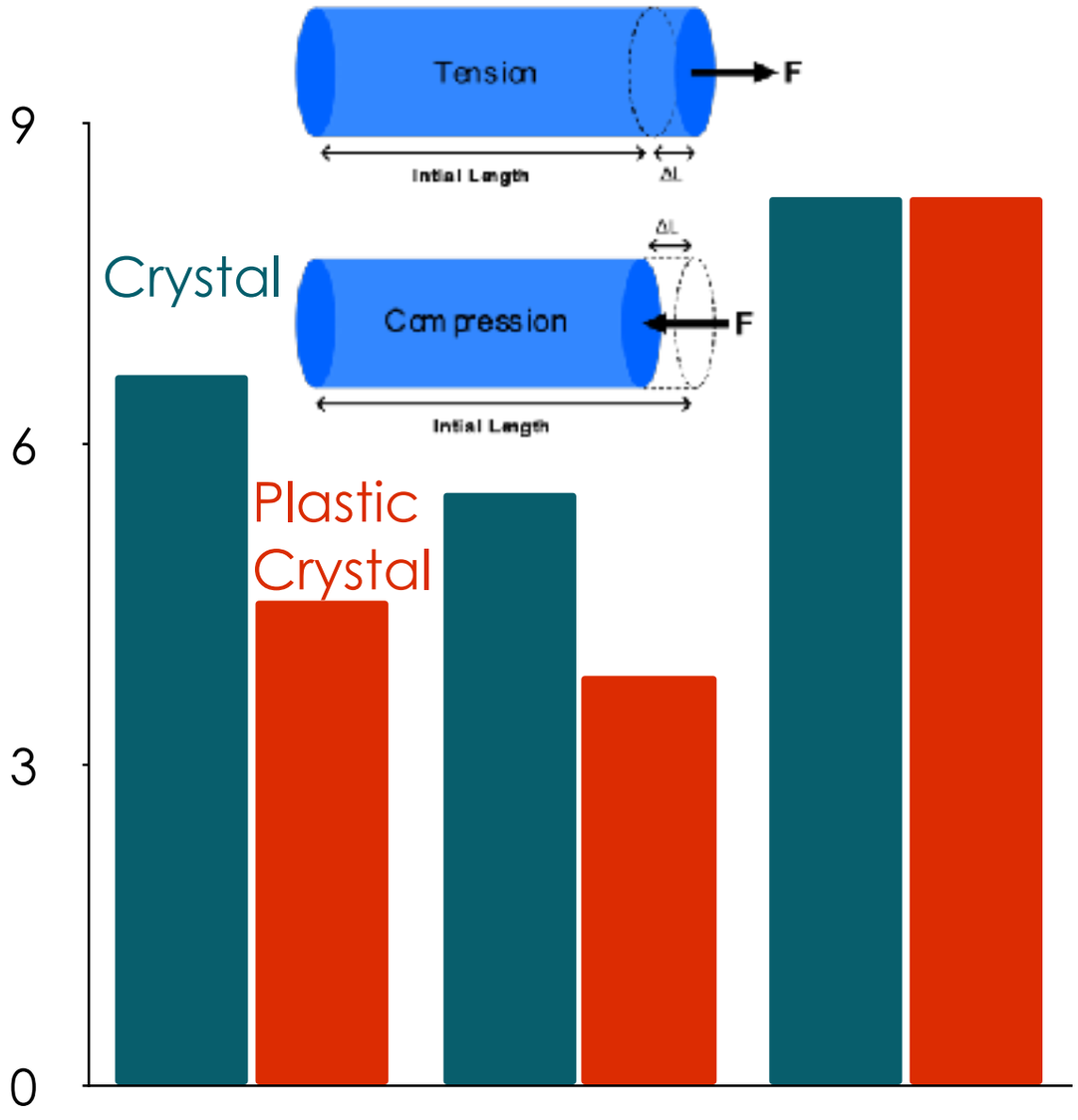
- $\mathrm{MSD}(t) = \left\langle \left| \mathbf{r}(t) - \mathbf{r}(0) \right|^2 \right\rangle$
- $\lim_{t \to \infty} \mathrm{MSD}(t) = 6Dt$

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

HS Dhattarwal, RCR, ChemPhysChem (2025)

Rotational Disorder & Mechanics



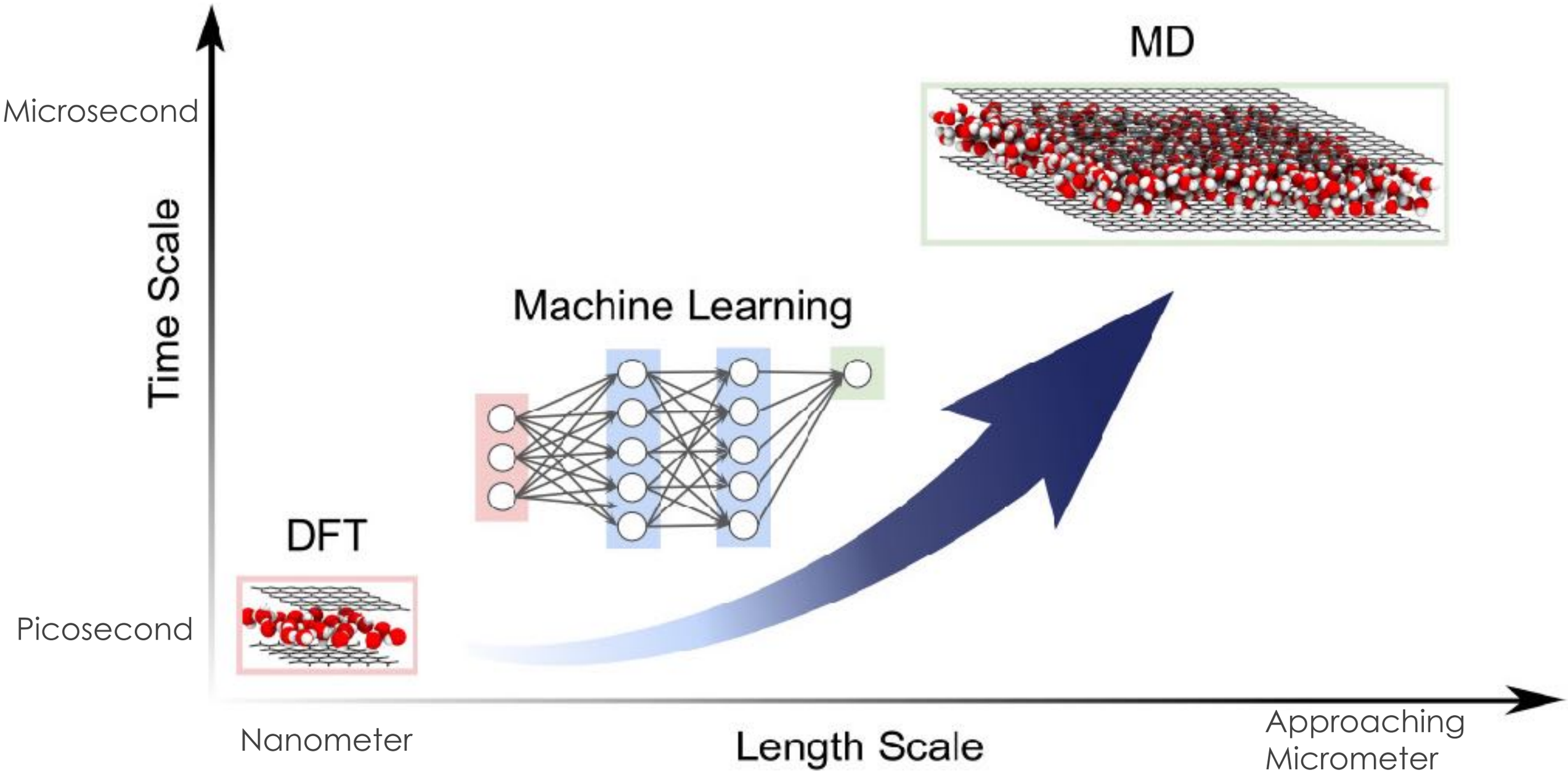


- ***Plastic Crystals*** have translational order & rotational disorder

- 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

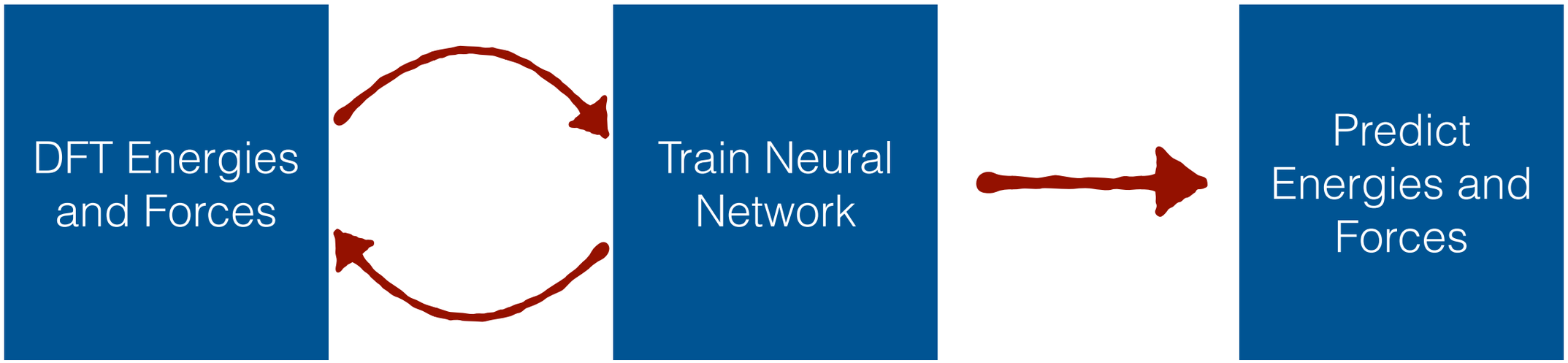


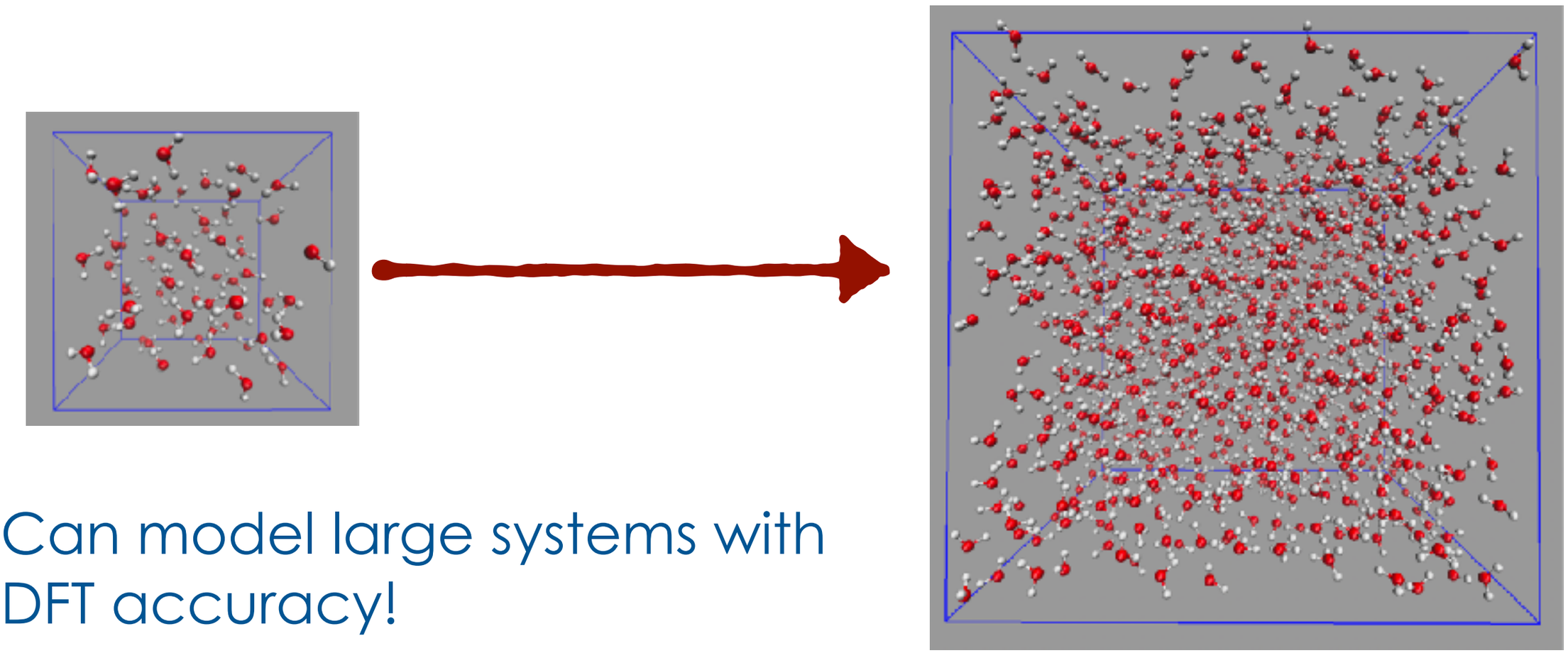
- **Machine learning moves us in the right direction**
- *Still developing techniques that include important physics…*

Zhao, Qiu, Guo,
J Phys Chem C 2022

Use machine learning to model interatomic interactions

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





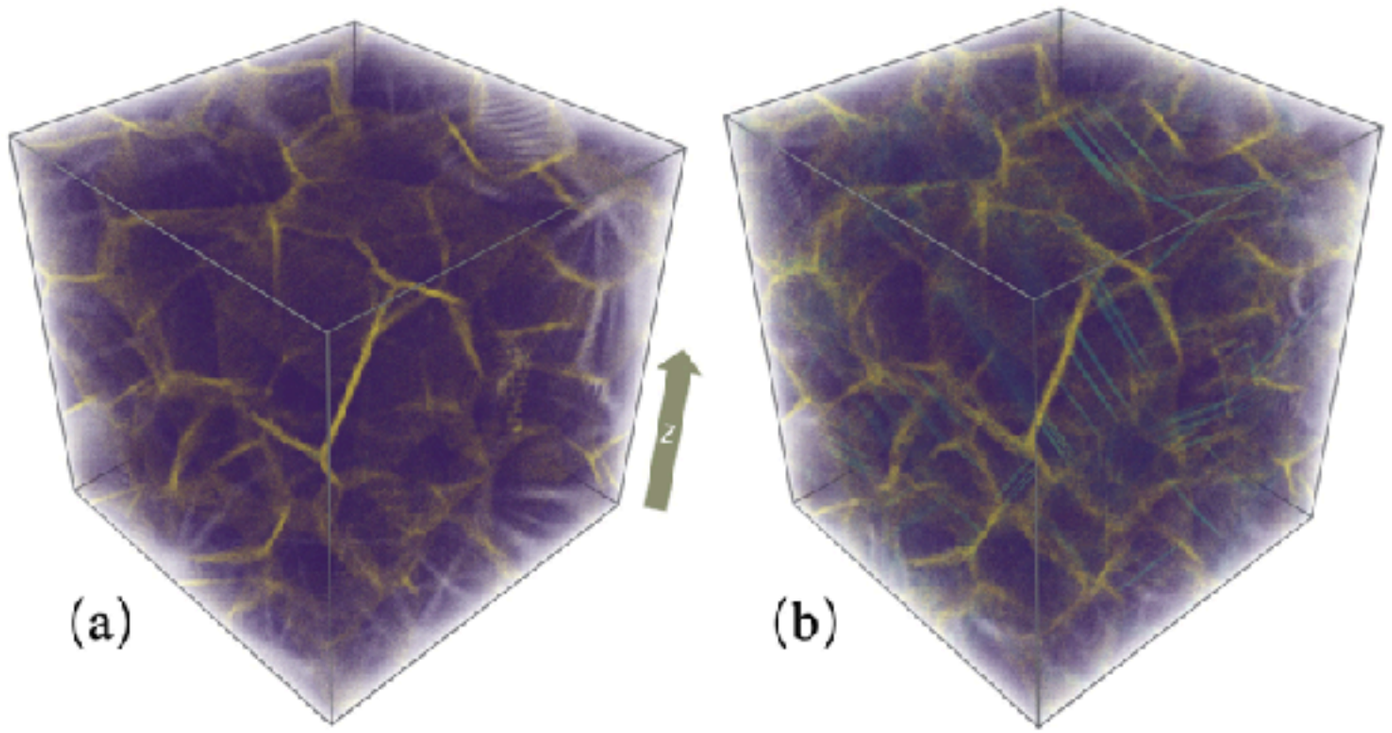
- Can model large systems with DFT accuracy!

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‖ §
*University of California, Berkeley, Berkeley, USA
Email: jiaweile@berkeley.edu, linlin@math.berkeley.edu
† Laboratory of Computational Physics, Institute of Applied Physics and Computational Mathematics, Beijing, China
Email: wang_han@iapcm.ac.cn
‡CAPT, HEDPS,College of Engineering, Peking University, Beijing, China
Email: mohanchen@pku.edu.cn, denghuilu@pku.edu.cn
¶Lawrence Berkeley National Laboratory, Berkeley, USA
‖ Princeton University, Princeton, USA

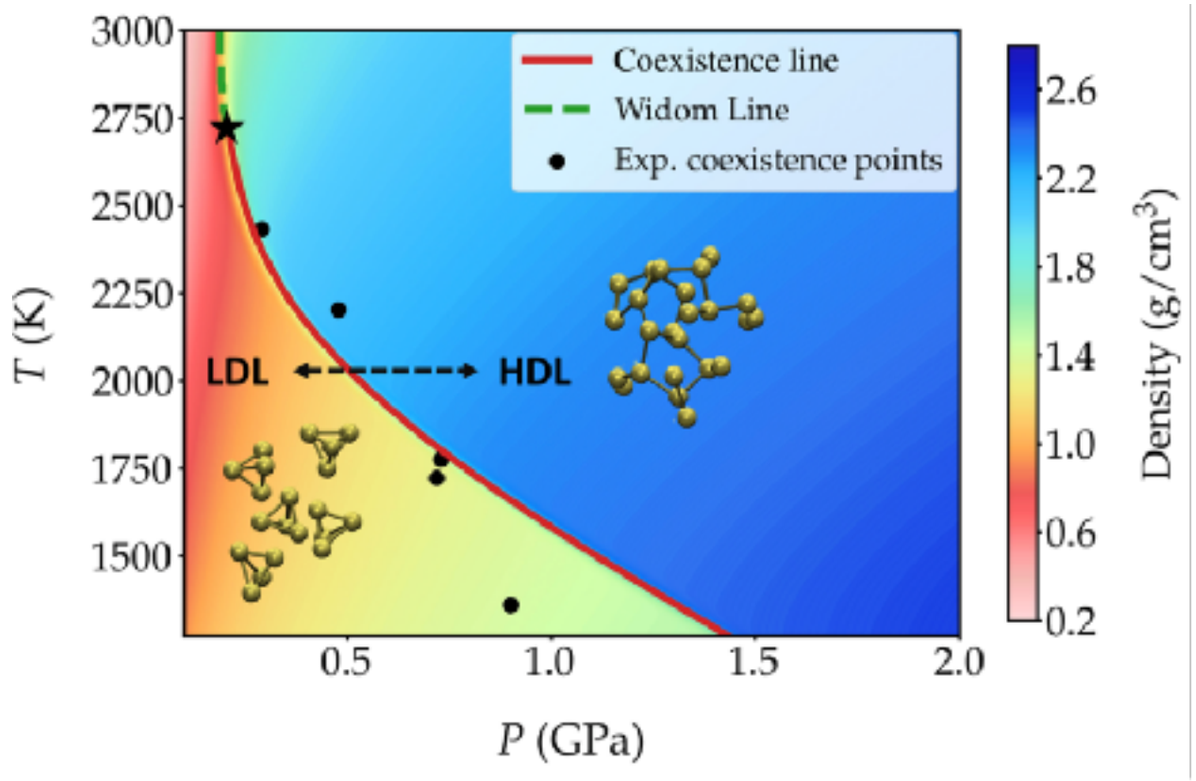


- Can model long timescales for thermodynamics & kinetics

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!

So how do we do calculations in practice?

- Start with a brief review of DFT

$$E_{\mathrm{tot}} = \min_{\Psi_0} \left\{ \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle \right\} = \min_{\{\phi_i\}} E^{\mathrm{KS}}[\{\phi_i\}]$$

  - Replace minimization over all many-body wavefunctions $\{\Psi_0\}$ …
  - … with minimization over orthonormal one-particle Kohn–Sham orbitals $\{\phi_i\}$.
  - **Same ground-state energy and density — but a tractable single-particle problem.**

Kohn-Sham energy functional

$$E^{\mathrm{KS}}[\{\phi_i\}] = T_s[\{\phi_i\}] + \int d\mathbf{r}\, V_{\mathrm{ext}}(\mathbf{r})\, n(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}\, V_H(\mathbf{r})\, n(\mathbf{r}) + E_{\mathrm{xc}}[n]$$

Kinetic | External potential | Hartree | Exchange-Correlation

with the electron density built from occupied orbitals:

$$n(\mathbf{r}) = \sum_i^{\mathrm{occ}} f_i\, |\phi_i(\mathbf{r})|^2$$

Kinetic + external (electron–ion) + Hartree + exchange–correlation.

$T_s[\{\phi_i\}] = \sum_i^{\mathrm{occ}} f_i \langle \phi_i \lvert -\frac{1}{2}\nabla^2 \rvert \phi_i \rangle$	Kinetic energy of the non-interacting KS system
$V_{\mathrm{ext}}(\mathbf{r}) = -\sum_I \frac{Z_I}{\lvert \mathbf{r} - \mathbf{R}_I \rvert}$	External potential: attraction to the nuclei
$V_H(\mathbf{r}) = \int d\mathbf{r}' \frac{n(\mathbf{r}')}{\lvert \mathbf{r} - \mathbf{r}' \rvert}$	Hartree potential: classical electron-electron repulsion
$\nabla^2 V_H(\mathbf{r}) = -4\pi\, n(\mathbf{r})$	Hartree potential satisfies Poisson's equation

Kohn-Sham energy functional

$$E^{\mathrm{KS}} = \sum_i \varepsilon_i - \tfrac{1}{2}\int d\mathbf{r}\, V_H(\mathbf{r})\, n(\mathbf{r}) + E_{\mathrm{xc}}[n] - \int d\mathbf{r}\, \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}\, n(\mathbf{r})$$

Solve the single-particle Schrödinger-like equations self-consistently:

$$\hat{h}_e^{\mathrm{KS}}\, \phi_i = \varepsilon_i\, \phi_i \qquad\qquad \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})} = V_{\mathrm{xc}}(\mathbf{r})$$

Band-structure energy = $\Sigma\varepsilon_i$. GGA approximates E_{XC} from the density and its gradient:

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int d\mathbf{r}\, n(\mathbf{r})\, \epsilon_{\mathrm{xc}}^{\mathrm{GGA}}\big(n(\mathbf{r}), \nabla n(\mathbf{r})\big)$$

Basis Sets

$$\phi_i = \sum_{\nu} C_{i\nu}\, f_\nu(\mathbf{r}_i; \{\mathbf{R}\})$$

- Expand each orbital in simple, well-characterized functions f_ν.
- Coefficients $C_{i\nu}$ are what we actually optimize.
- Energies and forces are computed through these basis functions.

Two common choices: **localized Gaussians** (CP2K) and **plane waves** (QE, VASP, CP2K).

Gaussian-Type Orbitals (GTOs)

$$g(\mathbf{r}) = r^{\,l}\, Y_{lm}(\mathbf{r} - \mathbf{r}_i)\, e^{-\alpha(\mathbf{r}-\mathbf{r}_i)^2}$$

- Atom-centered, defined by exponent α and spherical harmonic *(l, m)*
- α and (*l, m*) are fixed; the coefficients are optimized
- **Compact and localized → sparse, cheap matrix elements**
- Atom-fixed ⇒ Pulay forces when atoms move (more later)
  - "Freely floating Gaussians" in space would avoid Pulay forces

Plane Waves

- Periodicity of the lattice ⇒ natural to expand the periodic part of the orbitals in plane waves.
- Complete, orthonormal set; the label ν is replaced by the reciprocal vector G.
- **Real space ⇄ reciprocal space connected efficiently by FFTs.**
- Improve systematically by raising the cutoff E_{cut} (larger $|\boldsymbol{G}|$).

$$f_{\mathbf{G}}^{\mathrm{PW}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{G}\cdot\mathbf{r}}$$

Pros

- Originless ⇒ Pulay forces vanish exactly, even in a finite basis.
- Unbiased, balanced basis.
- Systematically improvable with a single parameter, E_{cut}.
- Efficient FFTs between real and G-space.

Cons

- Sharp, rapidly-varying densities (core region) need very large G.
- Cannot add basis functions only where needed — it is global.
- → **use pseudopotentials to remove the hard core (next).**

Gaussian and Plane Waves (GPW)

CP2K handles each part of the energy functional in *whichever basis is cheaper to evaluate*.

Gaussian basis

- Kinetic energy
- Non-local pseudopotential
- Short-range local pseudopotential

Plane-wave basis

- Hartree energy E_H
- Long-range part of the local PP
- (density mapped to a grid via FFT)

All-Electron Calculations in CP2K: Gaussian Augmented Plane Waves (GAPW)

Split density into **slowly-varying** and **rapidly-varying, atom-centered** parts

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_I n_I(\mathbf{r}) - \sum_I \tilde{n}_I(\mathbf{r})$$

Smooth, slowly-varying part in plane waves:

$$\tilde{n}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} \tilde{n}(\mathbf{G})\, e^{i\mathbf{G}\cdot\mathbf{r}}$$

Atom-centered, rapidly-varying part in Gaussians:

$$n_I(\mathbf{r}) = \sum_{\mu\nu} P^I_{\mu\nu}\, \phi_\mu(\mathbf{r})\, \phi^*_\nu(\mathbf{r})$$

$$\tilde{n}_I(\mathbf{r}) = \sum_{\mu\nu} \tilde{P}^I_{\mu\nu}\, \tilde{\phi}_\mu(\mathbf{r})\, \tilde{\phi}^*_\nu(\mathbf{r})$$

- **Near atom *I*: $n = n_i$, $\tilde{n} = \tilde{n}_i$. Far from atom *I*: $n = \tilde{n}$, $n_i = \tilde{n}_i$.**
- **Exact in the complete basis set limit; recovers all-electron accuracy.**

Implementation in Periodic Systems

The KS potential has the periodicity of the direct lattice:

$$V^{\mathrm{KS}}(\mathbf{r}) = V^{\mathrm{KS}}(\mathbf{r}+\mathbf{L})$$

So the orbitals take Bloch form, with a lattice-periodic part u_j:

$$\phi_j(\mathbf{r},\mathbf{k}) = e^{i\mathbf{k}\cdot\mathbf{r}}\, u_j(\mathbf{r},\mathbf{k}), \qquad u_j(\mathbf{r},\mathbf{k}) = u_j(\mathbf{r}+\mathbf{L},\mathbf{k})$$

k *is the crystal momentum quantum number and a vector in the first Brillouin zone.*

Plane wave expansion:

$$u_j(\mathbf{r},\mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_j(\mathbf{G},\mathbf{k})\, e^{i\mathbf{G}\cdot\mathbf{r}}$$

$$\phi_j(\mathbf{r},\mathbf{k}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} c_j(\mathbf{G},\mathbf{k})\, e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$

The density follows as a Fourier series over reciprocal-lattice vectors:

$$n(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} n(\mathbf{G})\, e^{i\mathbf{G}\cdot\mathbf{r}}$$

Everything (orbitals, density, potentials) lives on the same ***G****-grid, linked by FFT.*

Approximations/truncations

Discretize the Brillouin-zone integral over a weighted k-point set:

$$\int_{\mathrm{BZ}} d\mathbf{k} \longrightarrow \sum_{\mathbf{k}} w_{\mathbf{k}}$$

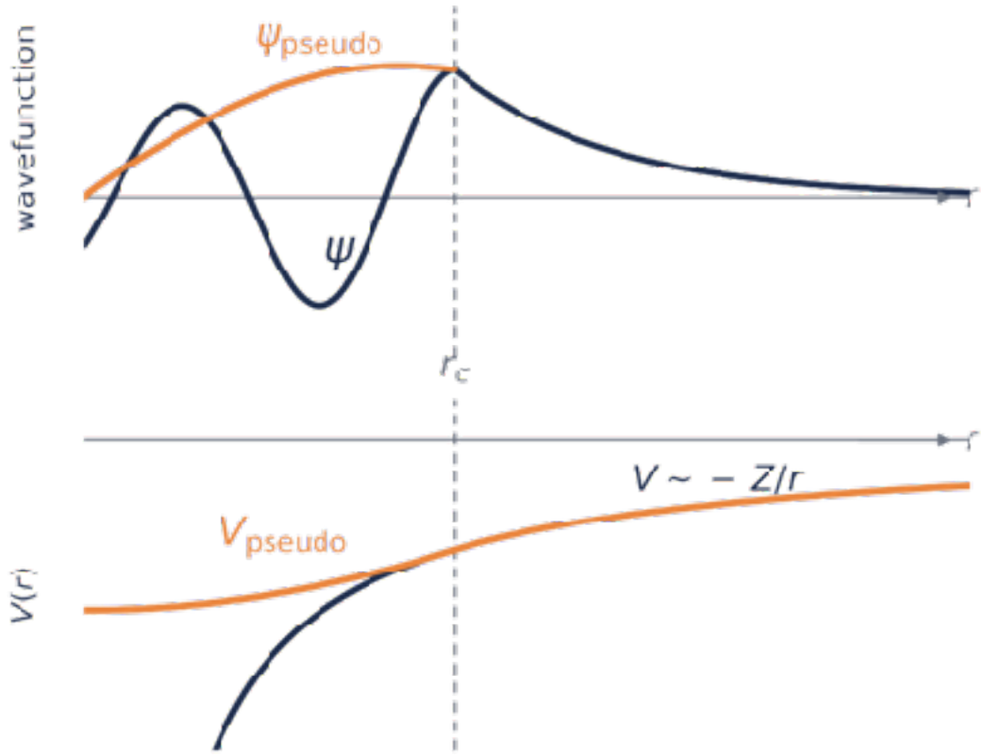
At each **k**, keep only plane waves below the kinetic-energy cutoff:

$$\frac{1}{2}\left|\mathbf{k}+\mathbf{G}\right|^2 \leq E_{\mathrm{cut}} \qquad N_{\mathrm{PW}} \approx \frac{\Omega}{2\pi^2} E_{\mathrm{cut}}^{3/2}$$

- **Precision is controlled by the single parameter E_{cut}.**
- Density cutoff needs ~8x the plane waves required for the orbitals.

Pseudopotentials (PPs)

- Replace core electrons and their rapid spatial variation.
- Pseudo-WF matches the true WF beyond a cutoff radius r_c …
- **… and is smooth & nodeless inside r_c → small plane-wave basis.**
- Removes the feature that makes plane waves expensive.



True vs. pseudo wavefunction and potential, match beyond r_c

- Norm-conserving PPs are angular-momentum dependent (spherical harmonics).
- Written in separable form with a local and a non-local part:

$$\hat{V}^{\mathrm{PP}} = \underbrace{\hat{V}_{\mathrm{loc}}}_{\text{local}} + \underbrace{\hat{V}_{\mathrm{nloc}}}_{\text{non-local}}$$

Now we have: DFT + basis sets + pseudopotentials + PBCs.
Time to compute the energy.

Electrostatic energy

Electron-electron, electron-core, and core-core:

$$E_{\rm es} = \tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \sum_I \int d\mathbf{r}\, V_I^{\rm core}(\mathbf{r})\, n(\mathbf{r}) + \tfrac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}$$

- Could treat with a standard Ewald sum …
- **… but we want a single charge density describing everything, nuclei included.**

Associate a Gaussian charge distribution with each nucleus:

$$n_I^c(\mathbf{r}) = -\frac{Z_I}{(R_I^c)^3\,\pi^{3/2}}\,\exp\left[-\frac{|\mathbf{r}-\mathbf{R}_I|^2}{(R_I^c)^2}\right]$$

Its potential is a screened (erf) Coulomb term:

$$V_I^{\rm core}(\mathbf{r}) = \int d\mathbf{r}'\,\frac{n_I^c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = -\frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}\,\mathrm{erf}\left(\frac{|\mathbf{r}-\mathbf{R}_I|}{R_I^c}\right)$$

Correctly reduces to $-\dfrac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}$ *for distances large compared with* R_c.

Rewrite energy using total density

$$E_{\text{es}} = \tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{n(\mathbf{r})n(\mathbf{r}') + n^c(\mathbf{r})n^c(\mathbf{r}') + 2\,n^c(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
$$+\tfrac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|} - \tfrac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{n^c(\mathbf{r})n^c(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Define core and total charge densities:

$$n^c(\mathbf{r}) = \sum_I n_I^c(\mathbf{r}), \qquad n^{\text{tot}}(\mathbf{r}) = n(\mathbf{r}) + n^c(\mathbf{r})$$

For a neutral cell the divergent G = 0 terms cancel.

$$E_{\text{ES}} = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{n^{\text{tot}}(\mathbf{r})\,n^{\text{tot}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}\sum_{I\neq J}\frac{Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}\,\text{erfc}\left[\frac{|\mathbf{R}_I-\mathbf{R}_J|}{\sqrt{(R_I^c)^2+(R_J^c)^2}}\right] - \sum_I \frac{1}{\sqrt{\pi}}\frac{Z_I^2}{R_I^c}$$

SKETCH POTENTIALS ON BOARD...

Total electrostatic energy in final form

$$E_{\mathrm{ES}} = 2\pi\Omega \sum_{\mathbf{G}\neq 0} \frac{|n^{\mathrm{tot}}(\mathbf{G})|^2}{G^2} + E_{\mathrm{overlap}} - E_{\mathrm{self}}$$

Poisson solved in Fourier space (Ewald)

$$E_{\mathrm{overlap}} = \sum_{I\neq J}{}' \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J - \mathbf{L}|} \operatorname{erfc}\left[\frac{|\mathbf{R}_I - \mathbf{R}_J - \mathbf{L}|}{\sqrt{(R_I^c)^2 + (R_J^c)^2}}\right]$$

Rapidly converging in real space

$$E_{\mathrm{self}} = \sum_I \frac{1}{\sqrt{\pi}} \frac{Z_I^2}{R_I^c}$$

Can readily evaluate self term

Total energy

$$E_{\mathrm{tot}} = E_{\mathrm{kin}} + E_{\mathrm{loc}}^{\mathrm{PP}} + E_{\mathrm{nloc}}^{\mathrm{PP}} + E_{\mathrm{xc}} + E_{\mathrm{ES}}$$

Kinetic + local PP + non-local PP + exchange-correlation + electrostatics

Now we can differentiate to get forces…

Forces from total energy

$$\mathbf{F}_I = -\nabla_I \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle$$

- Finite differences are too costly and too inaccurate for many atoms.
- **Can we get the force analytically? Yes: Hellmann-Feynman theorem**

Hellmann-Feynman Theorem

$$
\begin{aligned}
\nabla_I \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle &= \langle \nabla_I \Psi_0 | \hat{H}_e | \Psi_0 \rangle + \langle \Psi_0 | \nabla_I \hat{H}_e | \Psi_0 \rangle + \langle \Psi_0 | \hat{H}_e | \nabla_I \Psi_0 \rangle \\
&= E_0 \langle \nabla_I \Psi_0 | \Psi_0 \rangle + \langle \Psi_0 | \nabla_I \hat{H}_e | \Psi_0 \rangle + E_0 \langle \Psi_0 | \nabla_I \Psi_0 \rangle \\
&= E_0 \, \nabla_I \langle \Psi_0 | \Psi_0 \rangle + \langle \Psi_0 | \nabla_I \hat{H}_e | \Psi_0 \rangle \\
&= \langle \Psi_0 | \nabla_I \hat{H}_e | \Psi_0 \rangle
\end{aligned}
$$

Orthonormality makes wavefunction derivative terms equal to zero…

if Ψ is an exact eigenfunction:

$$
\mathbf{F}_I = -\langle \Psi_0 | \nabla_I \hat{H}_e | \Psi_0 \rangle
$$

Corrections in practice

Ψ is never an exact eigenstate in practice, creating two corrections:

$$\mathbf{F}_I = \mathbf{F}_I^{\mathrm{HFT}} + \mathbf{F}_I^{\mathrm{IBS}} + \mathbf{F}_I^{\mathrm{NSC}}$$

IBS / Pulay force

From an incomplete basis set whose functions are fixed to moving atoms.

NSC force

From non-self-consistency — the density is never perfectly converged.

- If self-consistency exactly satisfied ⇒ $F_{NSC} = 0$ (but F_{IBS} need not be)
- Pulay force vanishes in the complete basis limit (never happens in practice)
- **Originless basis (plane waves) ⇒ Pulay force vanishes exactly.**
- If N_{PW} changes (e.g. cell changes at fixed E_{cut}) ⇒ Pulay stress nonzero

Important for computing stress tensor: $$\Pi_{\mu\nu} = -\frac{1}{\Omega}\sum_s \frac{\partial E_{\mathrm{tot}}}{\partial h_{\mu s}} h^T_{s\nu}$$

What can we do with forces? Molecular Dynamics Simulations

- In ensemble of interest, *how to compute averages of observables?*

- Ensemble average:

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

$$\beta = 1/k_{\mathrm{B}}T$$

- What does this mean?

$$P(\mathbf{R}) = \frac{e^{-\beta U(\mathbf{R})}}{\int d\mathbf{R} e^{-\beta U(\mathbf{R})}} = \frac{1}{\mathcal{Z}} e^{-\beta U(\mathbf{R})}$$

- We are averaging over a probability distribution…

$$\langle O(\mathbf{R}) \rangle = \int d\mathbf{R} P(\mathbf{R}) O(\mathbf{R})$$

Computing Averages in MD Simulations

- What do we actually do in MD simulations?

- Generate **time evolution** of system and
  - compute ***time averages*** over a (discrete) trajectory

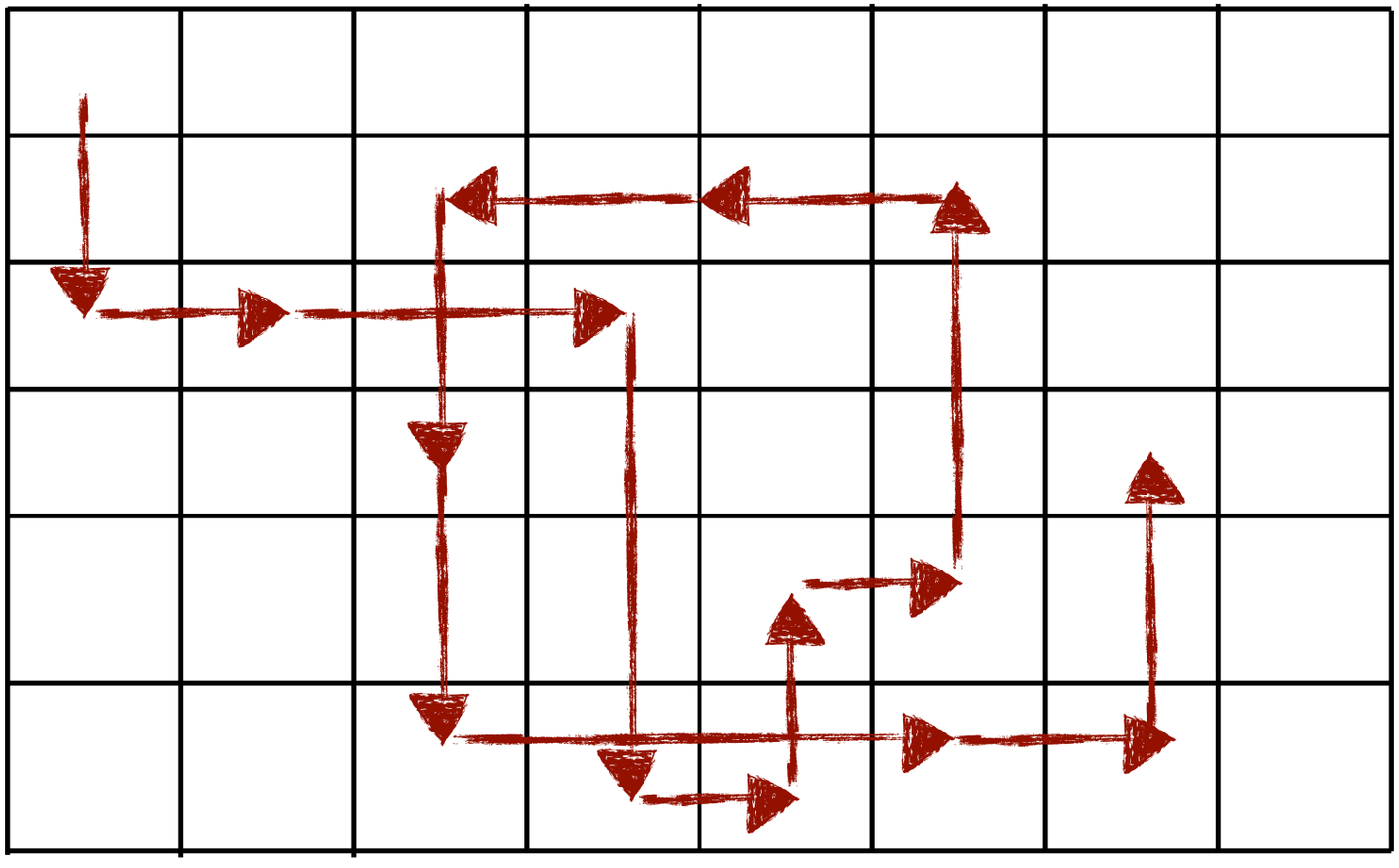
$$\bar{O} = \frac{1}{t}\sum_{\tau=1}^{t} O(\mathbf{R}_\tau)$$

- How is a **time average** related to an **ensemble average**?

Ergodic Hypothesis

The Ergodic Hypothesis

- *Long enough* trajectories will adequately sample phase space



$$\langle O(\mathbf{R}) \rangle = \lim_{t \to \infty} \bar{O}(t) = \lim_{t \to \infty} \frac{1}{t} \sum_{\tau=1}^{t} O(\mathbf{R}_\tau)$$

Ehrenfest dynamics

- Nuclei are classical
- Electrons and their dynamics are quantum
- One-determinant (single-configuration) ansatz for the total wavefunction

$$\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) \approx \Psi(\{\mathbf{r}_i\};t)\,\chi(\{\mathbf{R}_I\};t)$$

Ehrenfest dynamics: coupled mean-field equations

Leads to the coupled mean-field (TDSCF) equations (Dirac 1930)

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}_i;t) = -\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2\Psi + \langle\chi|\,\hat{V}_{n-e}\,|\chi\rangle\,\Psi$$

$$i\hbar\frac{\partial}{\partial t}\chi(\mathbf{R}_I;t) = -\sum_i \frac{\hbar^2}{2M_I}\nabla_i^2\chi + \langle\Psi|\,\hat{H}_e\,|\Psi\rangle\,\chi$$

Electrons & nuclei move in presence of **time-dependent effective fields**

→ **averages!** This is **mean field** description of quantum dynamics

Ehrenfest dynamics

Take the classical limit for the nuclei
→ Newton's equation with Ehrenfest potential V_E

$$M_\alpha \ddot{\mathbf{R}}_\alpha(t) = -\nabla_\alpha V_E\big(\{\mathbf{R}_\alpha(t)\}\big)$$

Electronic state determined from time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \left[-\sum_i \frac{\hbar^2}{2m_e}\nabla_i^2 + V_{n\text{-}e}\big(\{\mathbf{r}_i\},\{\mathbf{R}_\alpha(t)\}\big)\right]\Psi = \hat{H}_e\,\Psi$$

- $\hat{H}_e$ depends parametrically on nuclear positions
- Feedback between classical & quantum DoFs incorporated in both directions at *mean field level*
- Allows transitions between electronic states → can expand WF in basis of electronic states: $\Psi = \sum_{l=0}^{\infty} c_l(t)\Psi_l$

Born-Oppenheimer MD simulations

- Ehrenfest reduces to BOMD if Ψ is restricted to the adiabatic ground state Φ_0 at each instant.
- **Good when the gap $E_1 - E_0 \gg k_B T$ everywhere.**

$$V_E = \int d\mathbf{r}\, \Phi_0^*\, \hat{H}_e\, \Phi_0 \equiv E_0(\{\mathbf{R}_I\}) = V_{\mathrm{BO}}$$

- Solve electronic TISE at each nuclear configuration $\{\mathbf{R}_I\}$ generated during MD simulation to get ground state BO potential energy surface
- Can decouple generating classical nuclear dynamics from computing quantum PES
- Do classical dynamics on nuclei and then solve electronic problem “on the fly” at each instant in time

Born-Oppenheimer MD simulations

Time-dependence of ES imposed/dictated by parametric dependence on classical dynamics of nuclei

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0} \left\{ \left\langle \Psi_0 \middle| \hat{H}_e \middle| \Psi_0 \right\rangle \right\} \qquad \hat{H}_e \Psi_0 = E \Psi_0$$

BOMD neglected nondiagonal *and* diagonal corrections
→ it is *not* adiabatic MD because it does not include diagonal corrections

Represent Ψ_0 w/ set of orbitals $\{\phi_i\}$, constrained minimization becomes:

$$\min_{\phi_i} \left\{ \left\langle \Psi_0 \middle| \hat{H}_e \middle| \Psi_0 \right\rangle \right\}_{\left\{ \left\langle \phi_i \middle| \phi_j \right\rangle = \delta_{ij} \right\}}$$

Born-Oppenheimer MD simulations

Constraints become Lagrange multipliers in the dynamics

$$\mathcal{L} = \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle + \sum_{i,j} \Lambda_{ij} \left(\langle \phi_i | \phi_j \rangle - \delta_{ij} \right)$$

Minimization leads to the BOMD equations of motion:

$$0 = -\hat{H}_e \phi_i + \sum_j \Lambda_{ij} \phi_j$$

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I \min_{\Psi_0} \left\{ \left\langle \Psi_0 \middle| \hat{H}_e \middle| \Psi_0 \right\rangle \right\}$$

Car-Parrinello MD simulations

- BOMD allows large time steps but needs to solve ES problem at each time step
- Ehrenfest MD doesn't need to solve ES problem but needs to propagate electronic dynamics = small time step

- **Car & Parrinello** tried to bridge these two methods with CPMD
- **CPMD** evolves electron dynamics efficiently and tries to get to large time step for nuclear dynamics, but is a *compromise*

- **CPMD** maps two-component quantum/classical problem onto two-component pu classical problem w/ *two separate energy scales*
- Loses physical time info of quantum subsystem dynamics
- Orbitals → classical field

CPMD Equations of Motion

$$M_I \, \ddot{\mathbf{R}}_I(t) = -\nabla_I \, \langle \Psi | \hat{H}_e^{\mathrm{KS}} | \Psi \rangle$$

$$\mu \, \ddot{\phi}_i(t) = -\hat{H}_e^{\mathrm{KS}} \, \phi_i + \sum_j \Lambda_{ij} \, \phi_j$$

Effective mass/fictitious mass/adiabaticity parameter

- Vibrational DOS of nuclear & electronic subsystems need to be sufficiently decoupled so that two subsystems stay decoupled
  → essentially maintaining metastable system

Limitation of CPMD

- Electronic and nuclear vibrational spectra must stay decoupled (metastable adiabatic separation).

$$\omega_e^{\min} \propto \left(\frac{E_{\text{gap}}}{\mu}\right)^{1/2}, \qquad \Delta t_{\max} \propto \left(\frac{\mu}{E_{\text{cut}}}\right)^{1/2}$$

- Needs fine-tuning of μ to maximize Δt while keeping the subsystems separated.
- **If the gap $E_{gap} \rightarrow 0$ then $\mu \rightarrow 0$ and $\Delta t \rightarrow 0$ …**
  use BOMD for metals!

Summary of Equations of Motion

BOMD

Nuclei

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E_{\text{tot}}\{\mathbf{R}_I(t)\}$$

Electrons

$$0 = \hat{H}\phi_i + \sum_j \lambda_{ij}\phi_j$$

CPMD

Nuclei

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E_{\text{tot}}[\rho]$$

Electrons

$$\mu\ddot{\phi}_i = -\hat{H}\phi_i + \sum_j \lambda_{ij}\phi_j$$

Ehrenfest

Nuclei

$$M_I \ddot{\mathbf{R}}_I = -\nabla_I E_{\text{tot}}[\rho]$$

Electrons

$$i\hbar\,\dot{\psi}_n = \hat{H}\psi_n$$

Classical Force Fields

Approximate the ground-state PES directly as a sum of few-body interactions:

$$V_e \simeq V_e^{\mathrm{FF}}(\{\mathbf{R}_I\}) = \sum_I V_1(\mathbf{R}_I) + \sum_{I<J} V_2(\mathbf{R}_I, \mathbf{R}_J) + \sum_{I<J<K} V_3(\mathbf{R}_I, \mathbf{R}_J, \mathbf{R}_K) + \cdots$$

No more electrons! Purely classical mechanics

$$M_I \ddot{\mathbf{R}}_I(t) = -\nabla_I V_e^{\mathrm{FF}}(\{\mathbf{R}_I(t)\})$$

Fast & scalable, but accuracy limited by assumed functional form and parameterization

Machine learned Neural Network Potentials

$$V_e \simeq V_e^{\mathrm{NN}}(\{\mathbf{R}_I\})$$

- Represent the PES with a neural network (or other ML model).
- Train on ab initio energies and forces.
- **Learn the surface to high accuracy, then evaluate far faster than ab initio.**
- **The current revolution in atomistic materials modeling.**

What are Molecular Dynamics (MD) Simulations?

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

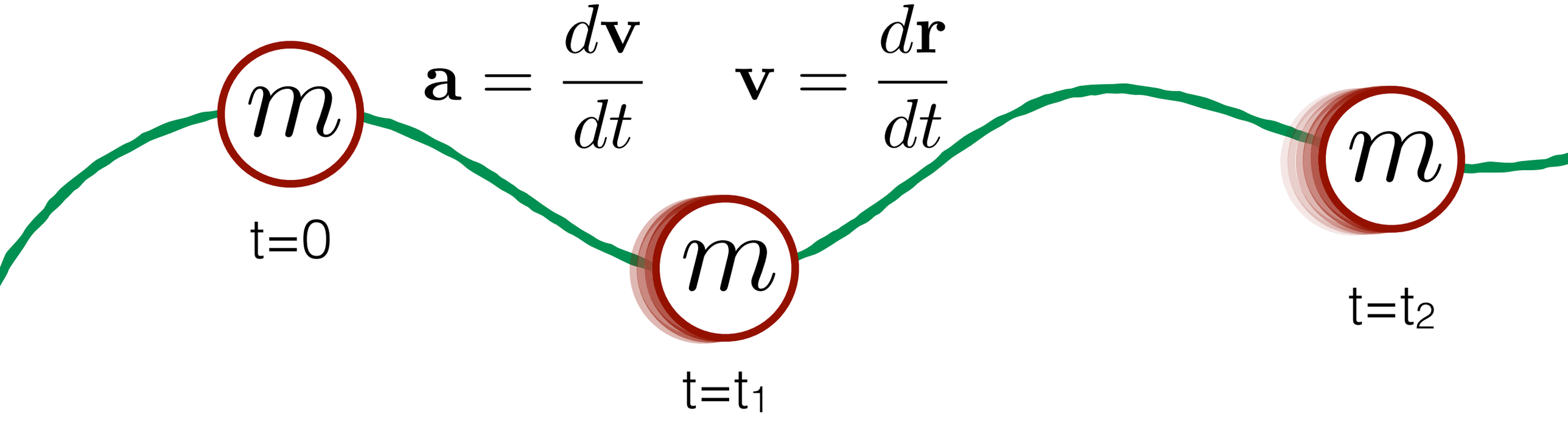
$$\mathbf{F} = m\mathbf{a}$$

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

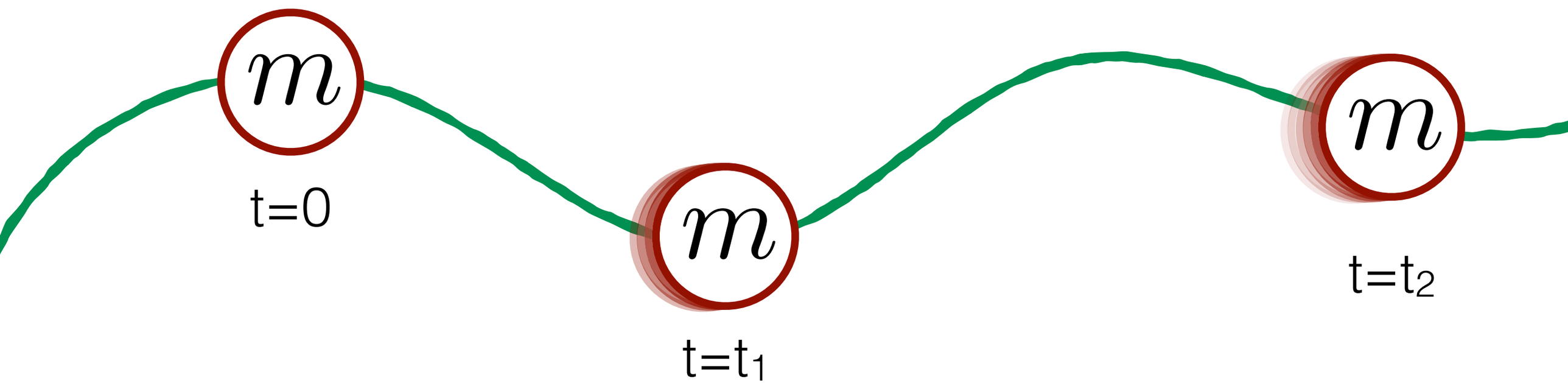


Integrating the equations of motion

- Velocity Verlet algorithm (Taylor expansion)

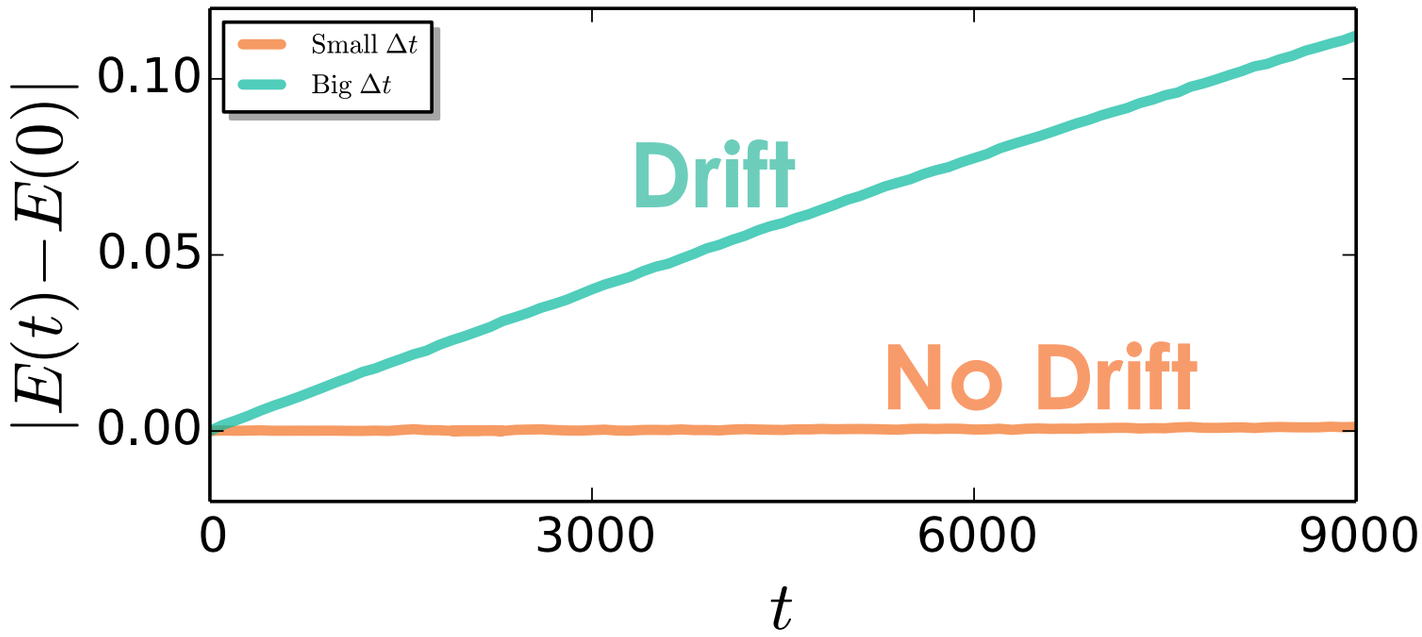
$$\mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{1}{2}\mathbf{a}(t)\Delta t^2$$

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



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**

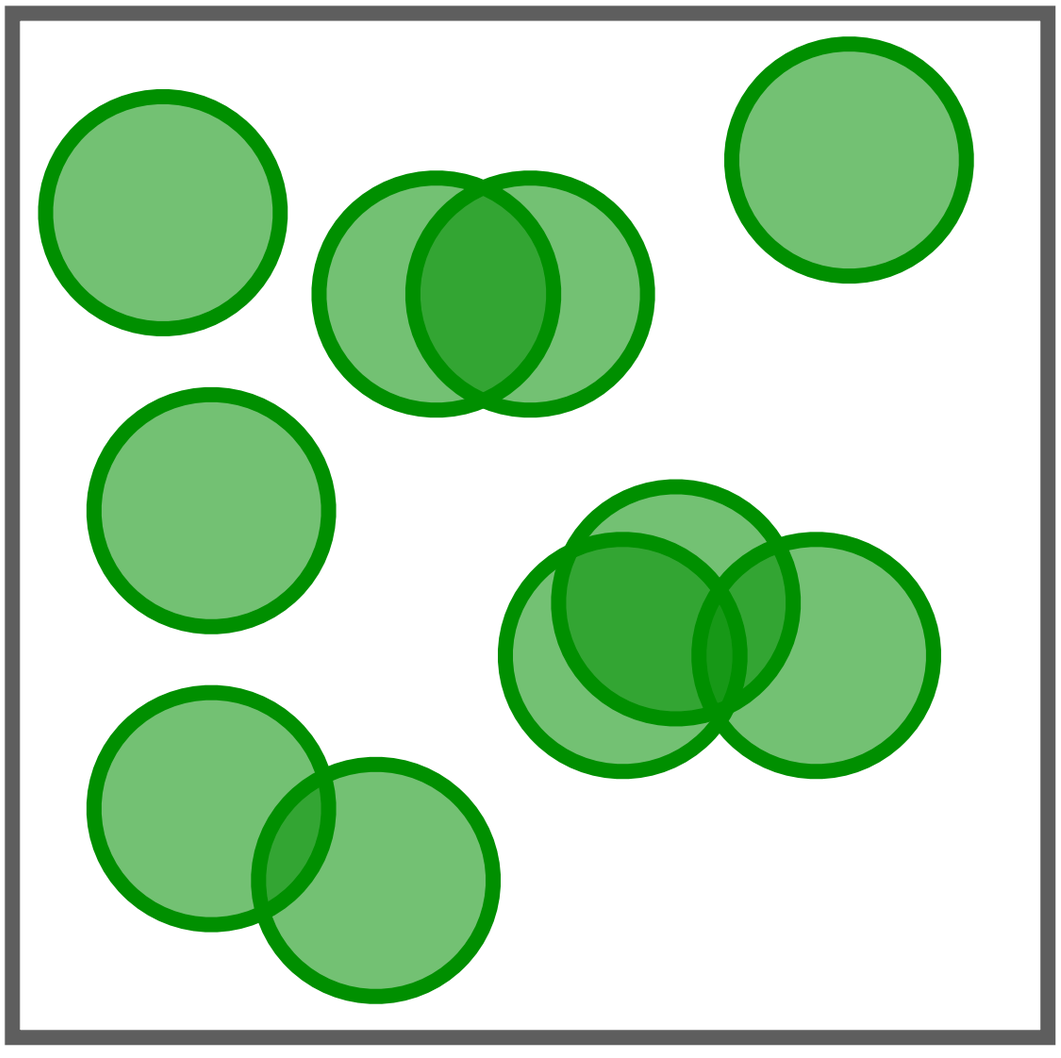
- Typically Δt smaller than fastest timescale in the system

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)

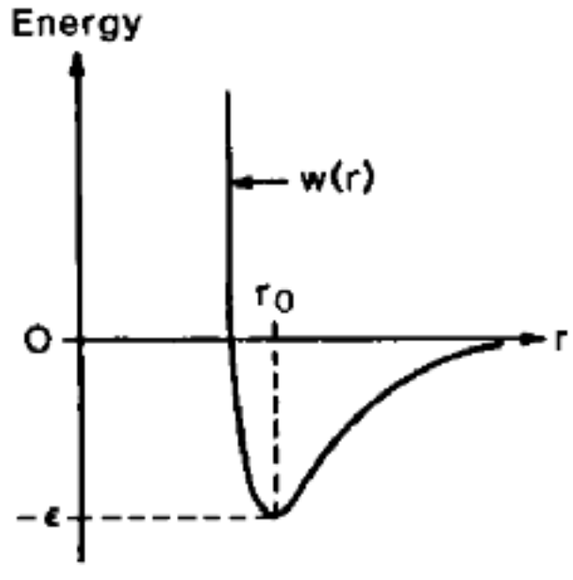
From Scott Shell's (UCSB) lecture notes

Choosing Initial Conditions

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



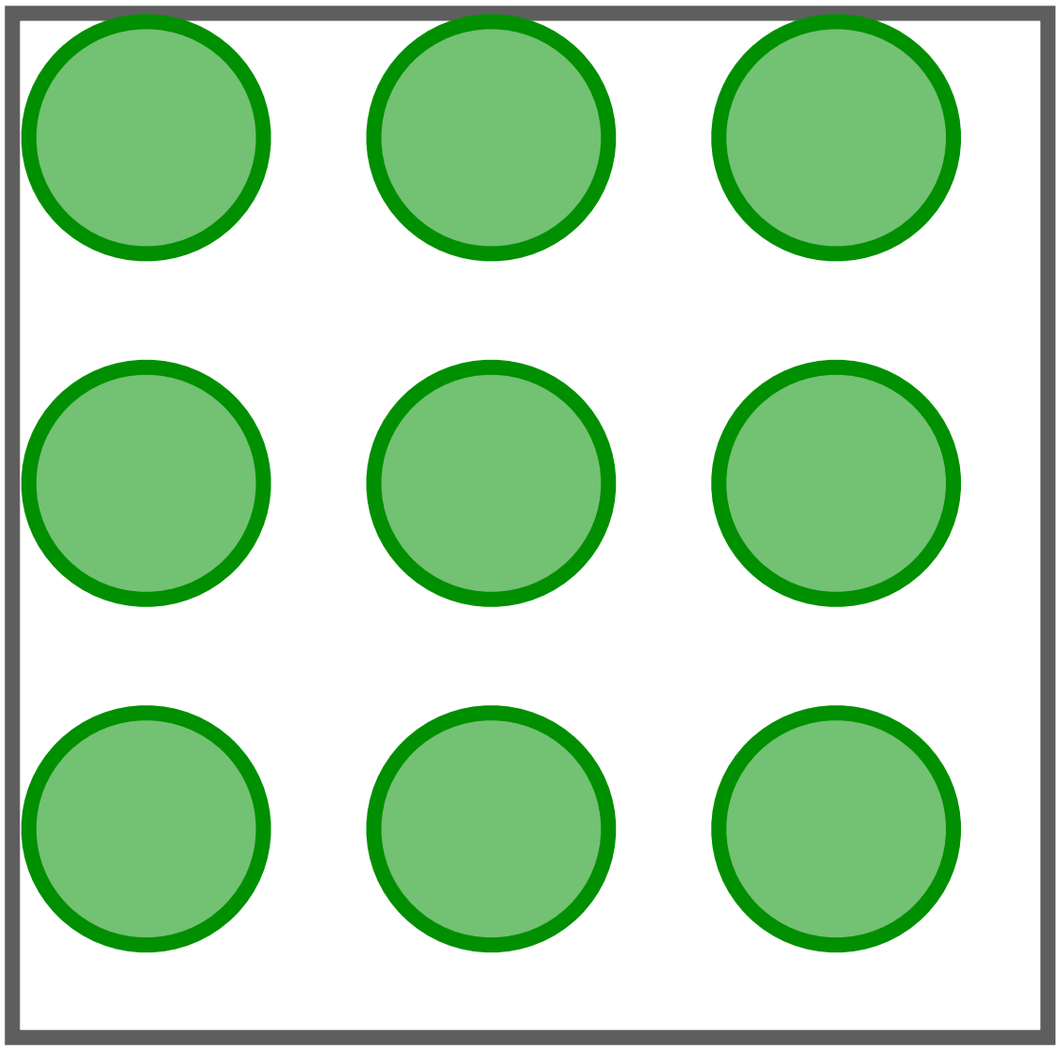
- Almost all intermolecular potentials include an excluded volume core (Pauli exclusion)



- 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)

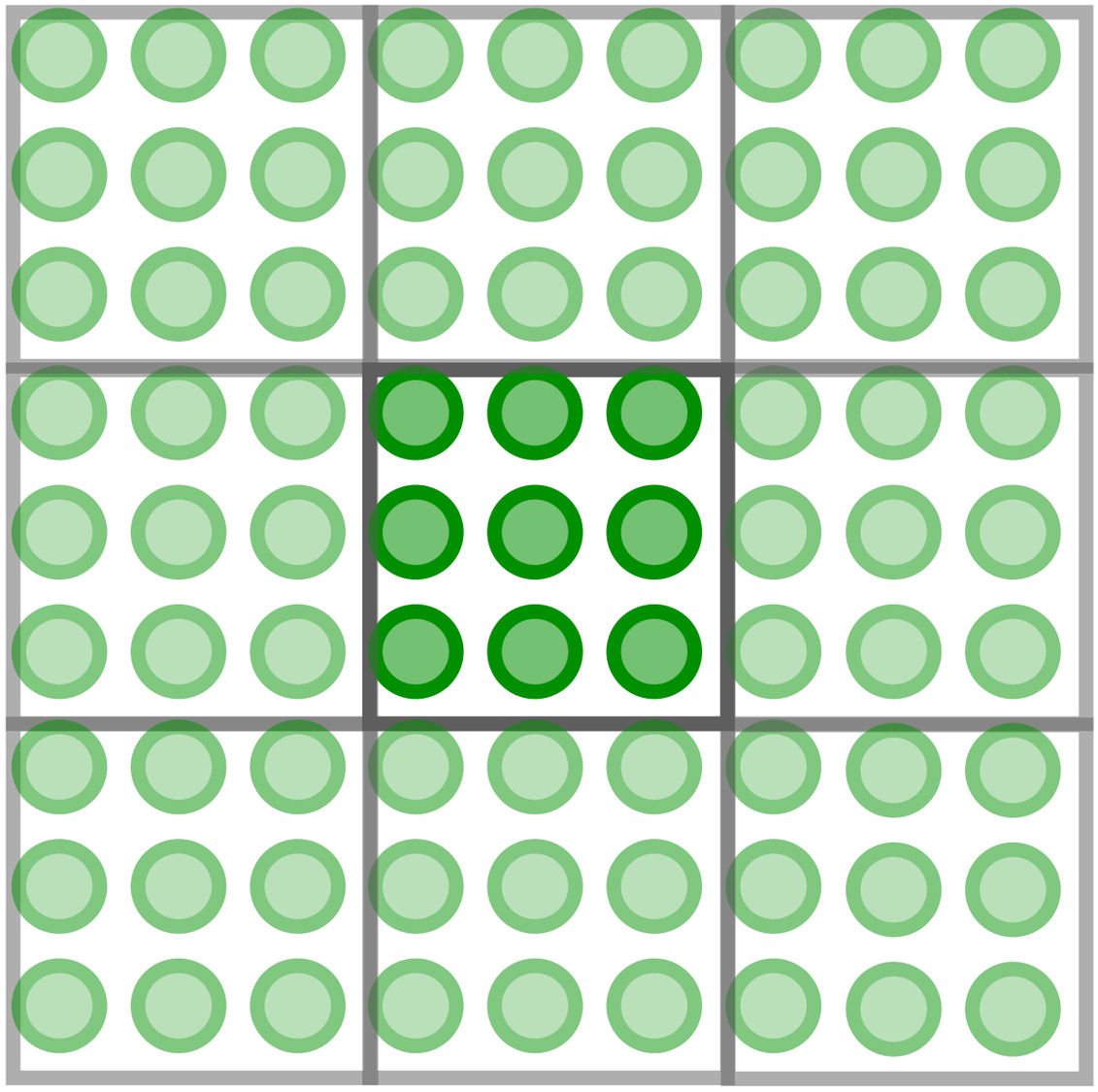


- Lattice will melt if it is not stable at this state point.
- Need to follow time evolution of "melting" to ensure you arrive at the desired state

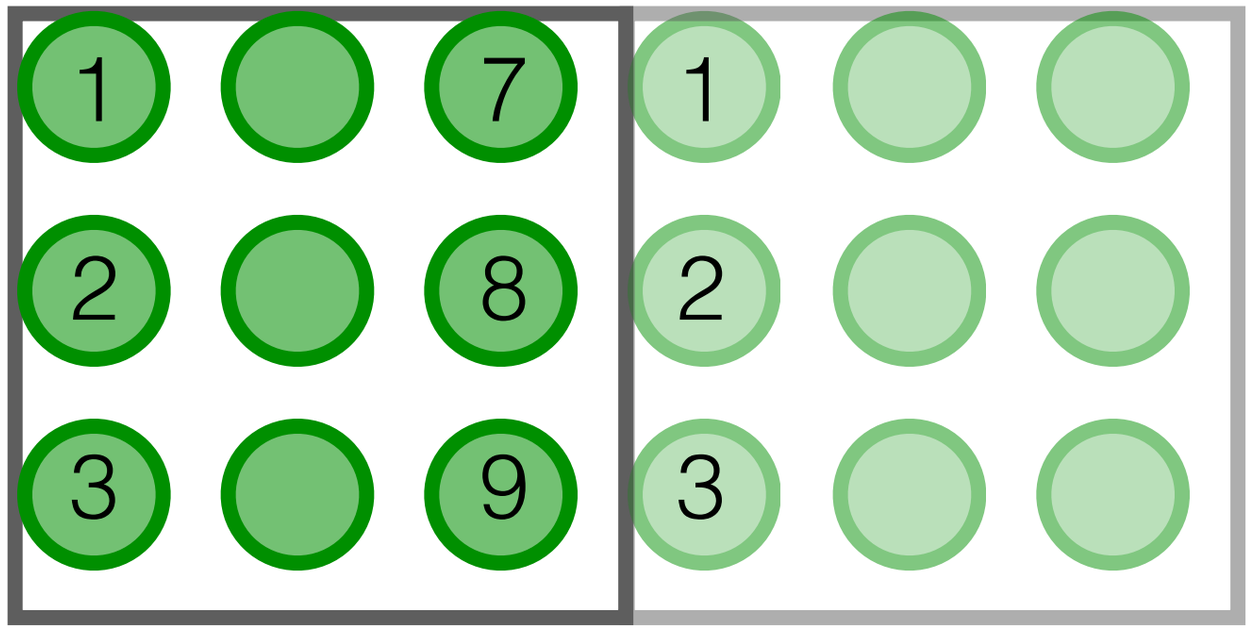
- *Why have I drawn the system off-center?*

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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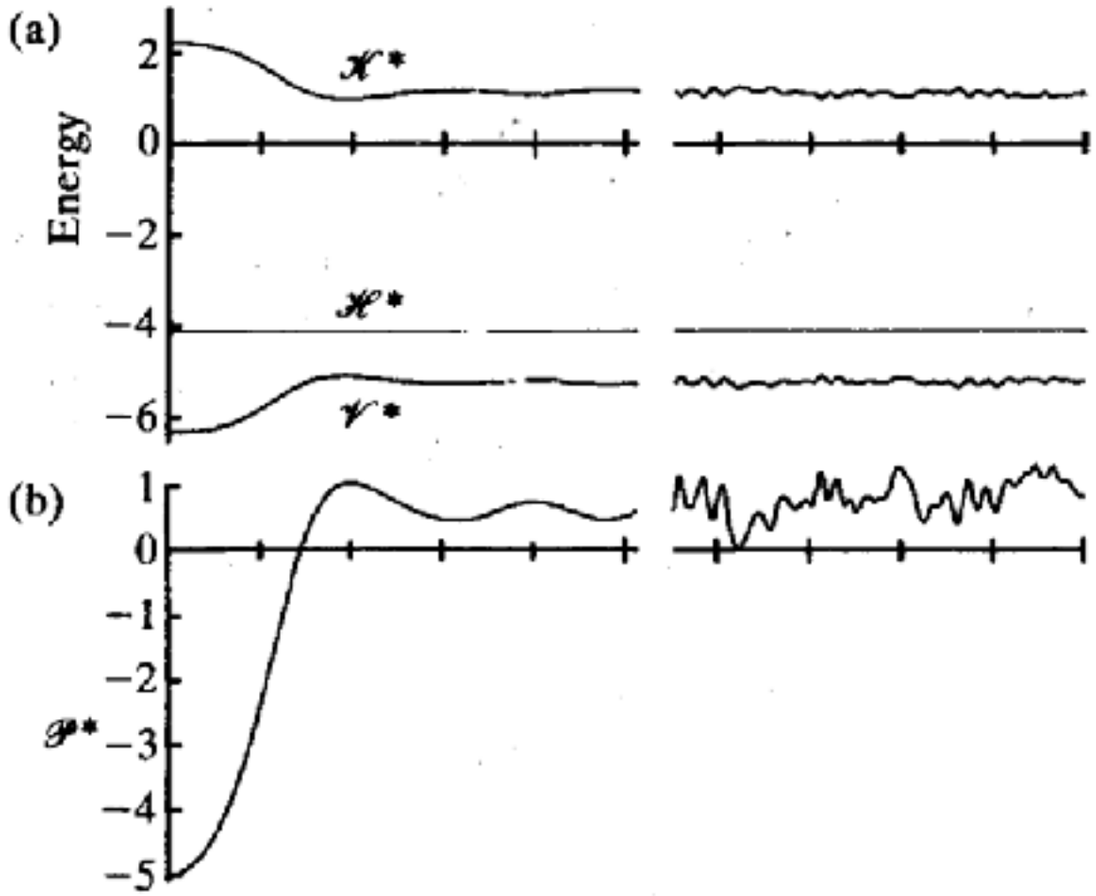

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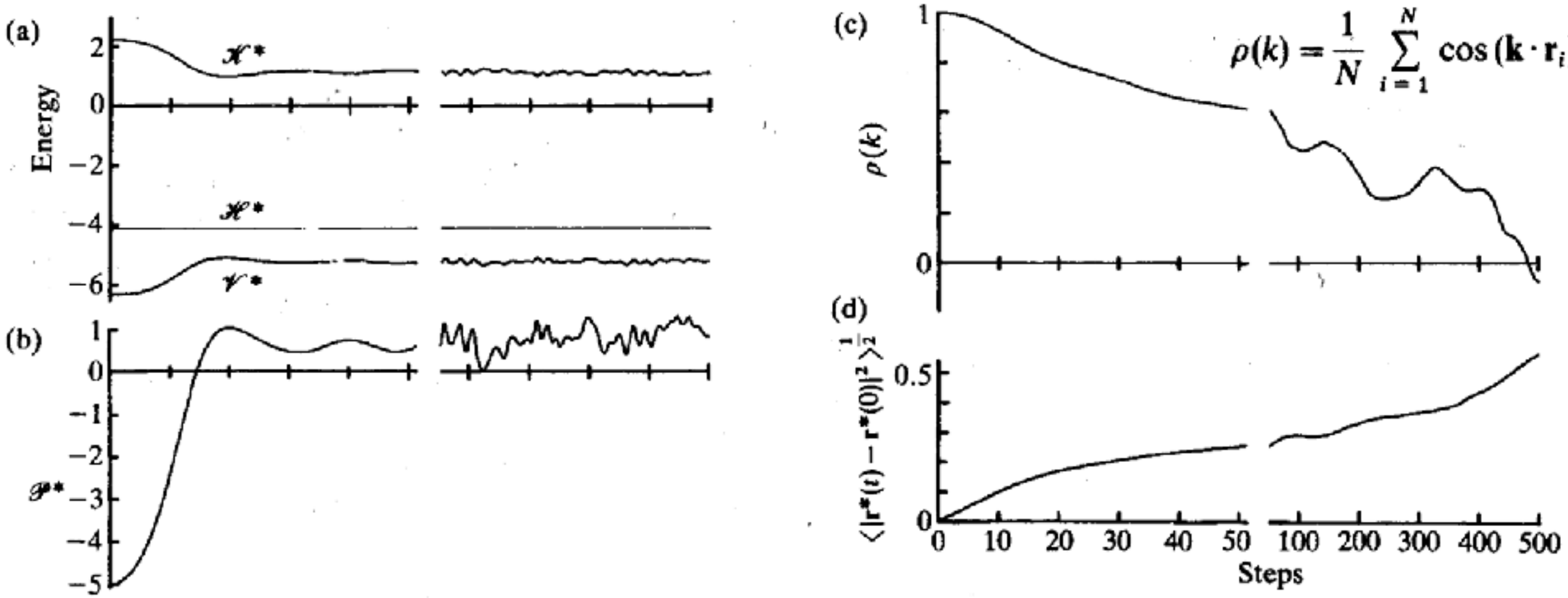

- To speed equilibration from lattice, can often increase **T** to "melt" the lattice, then later decrease to desired **T**

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?

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- 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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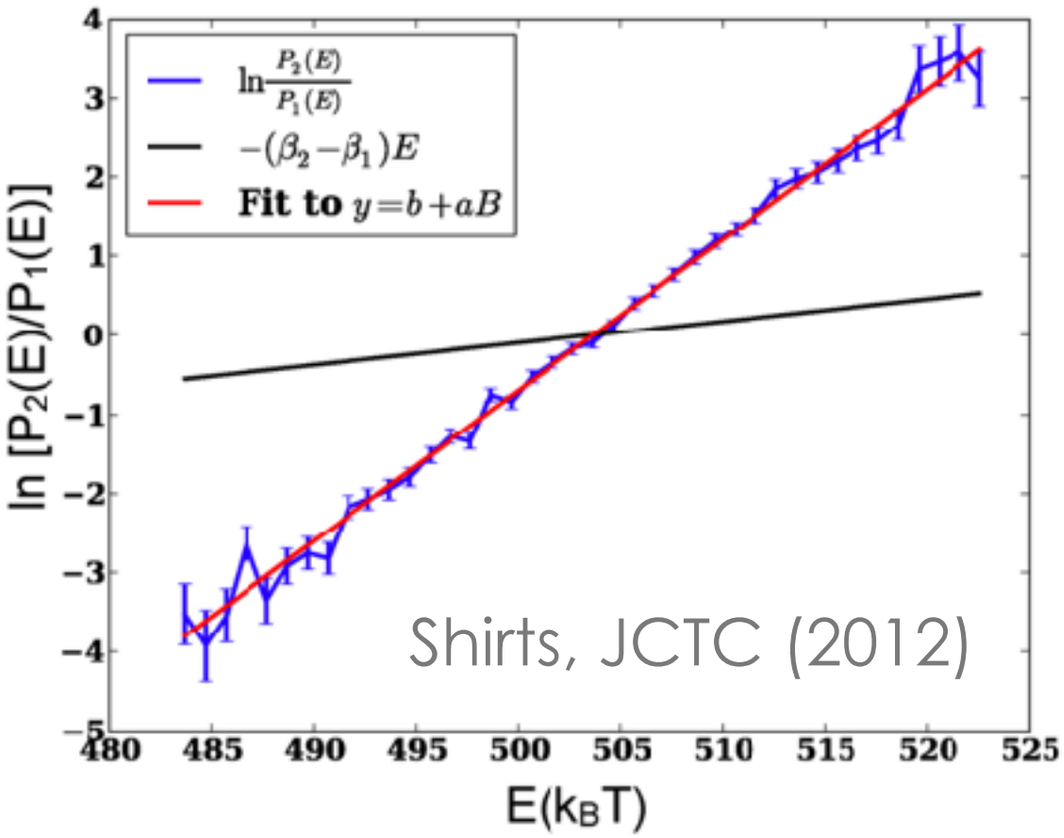

- **Berendsen does not preserve canonical distribution** (incorrect fluctuations in KE)

- 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

Nosé-Hoover Thermostat

- **Nosé (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***

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

Nosé-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…

Nosé-Hoover Thermostat

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

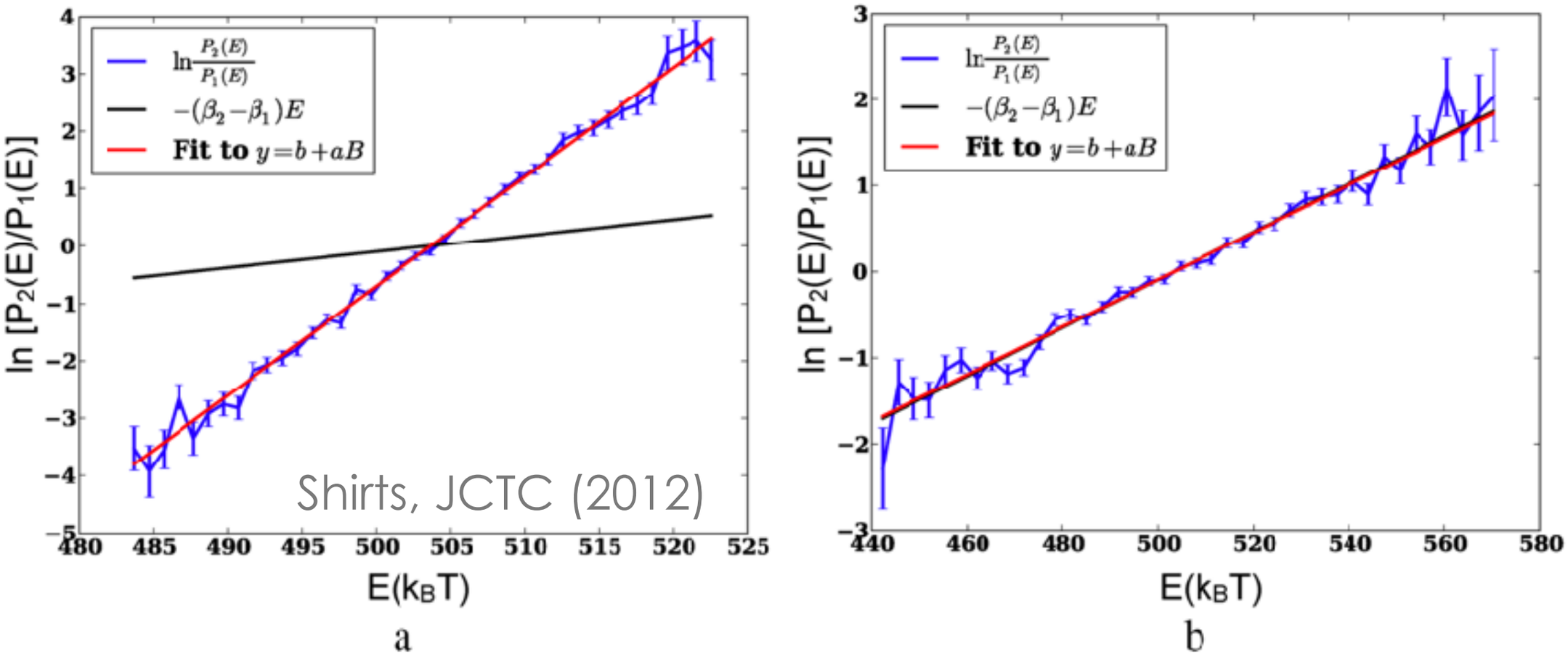


Figure 5. Differences in validation of Berendsen and Nosé–Hoover thermostats. (a) Berendsen temperature control produces simulations deviating greatly from the true distribution; in this case, the slope $\beta_2 - \beta_1$ of the kinetic energy log ratio is 7 times higher than it should be, 68 standard 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.

- **Nosé-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

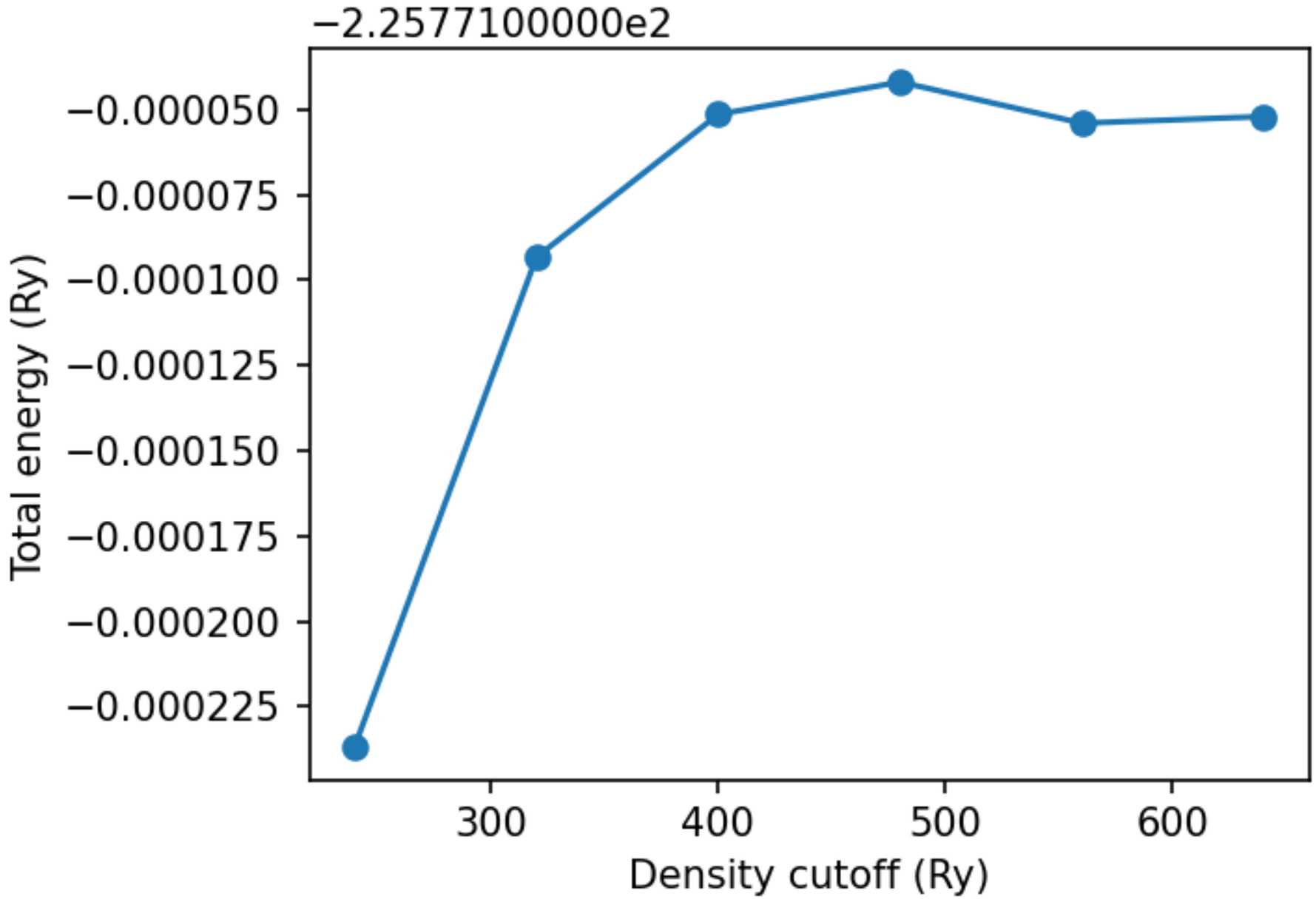
- Can readily extend thermostatting approaches
- Consider coupling to "pressure bath" instead of "temperature bath"

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,…

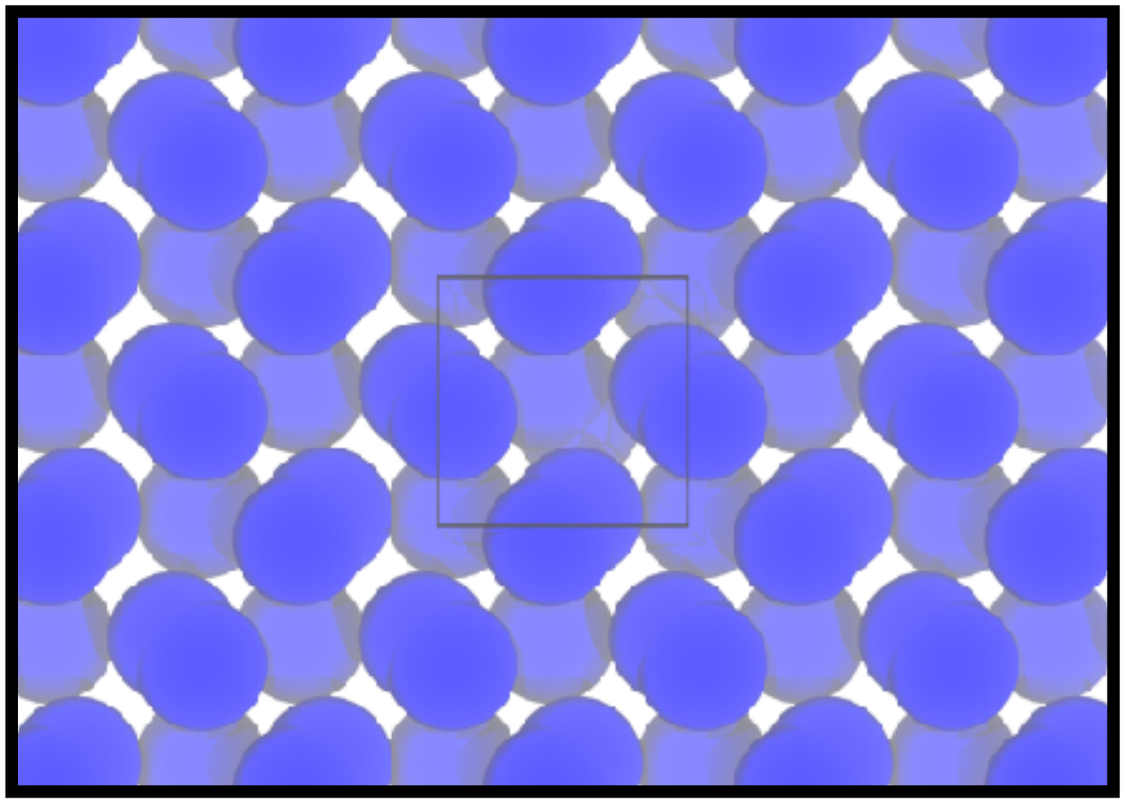
Preview of the tutorials

Tutorial 1: Convergence

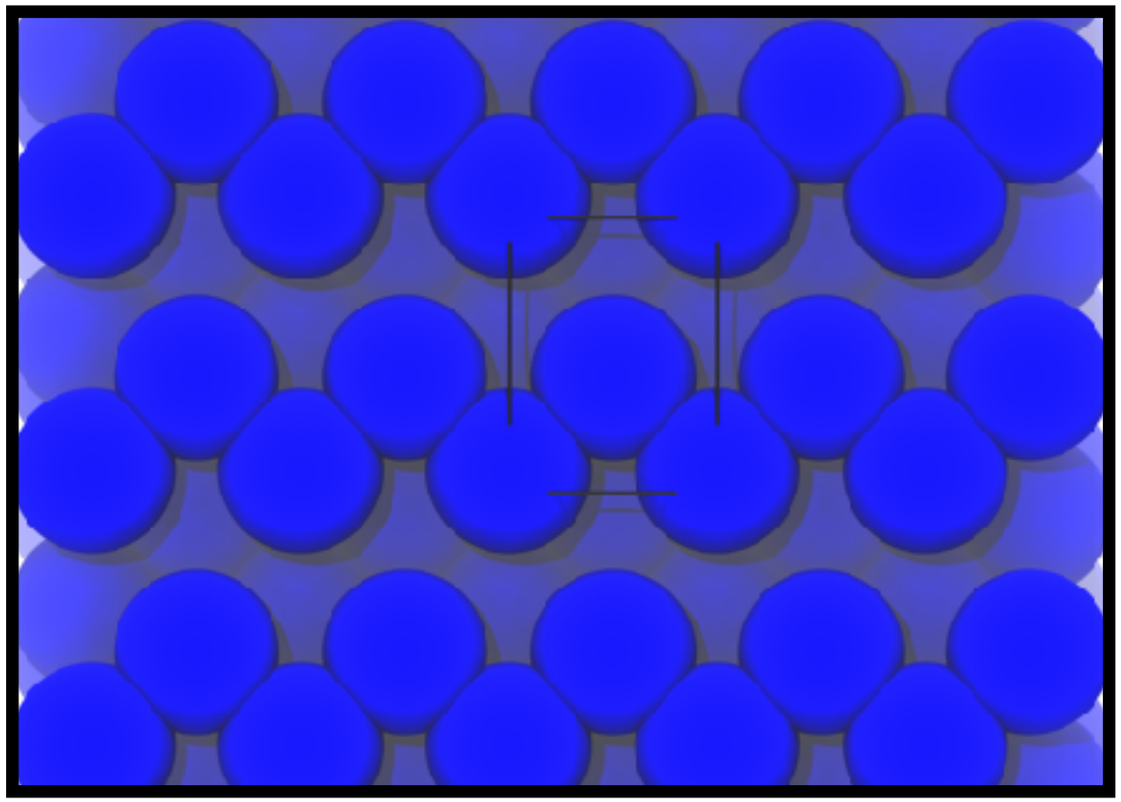


- Systematically vary parameters in calculation until energy (and other quantities) converge within desired tolerance

Tutorial 2: Equations of State



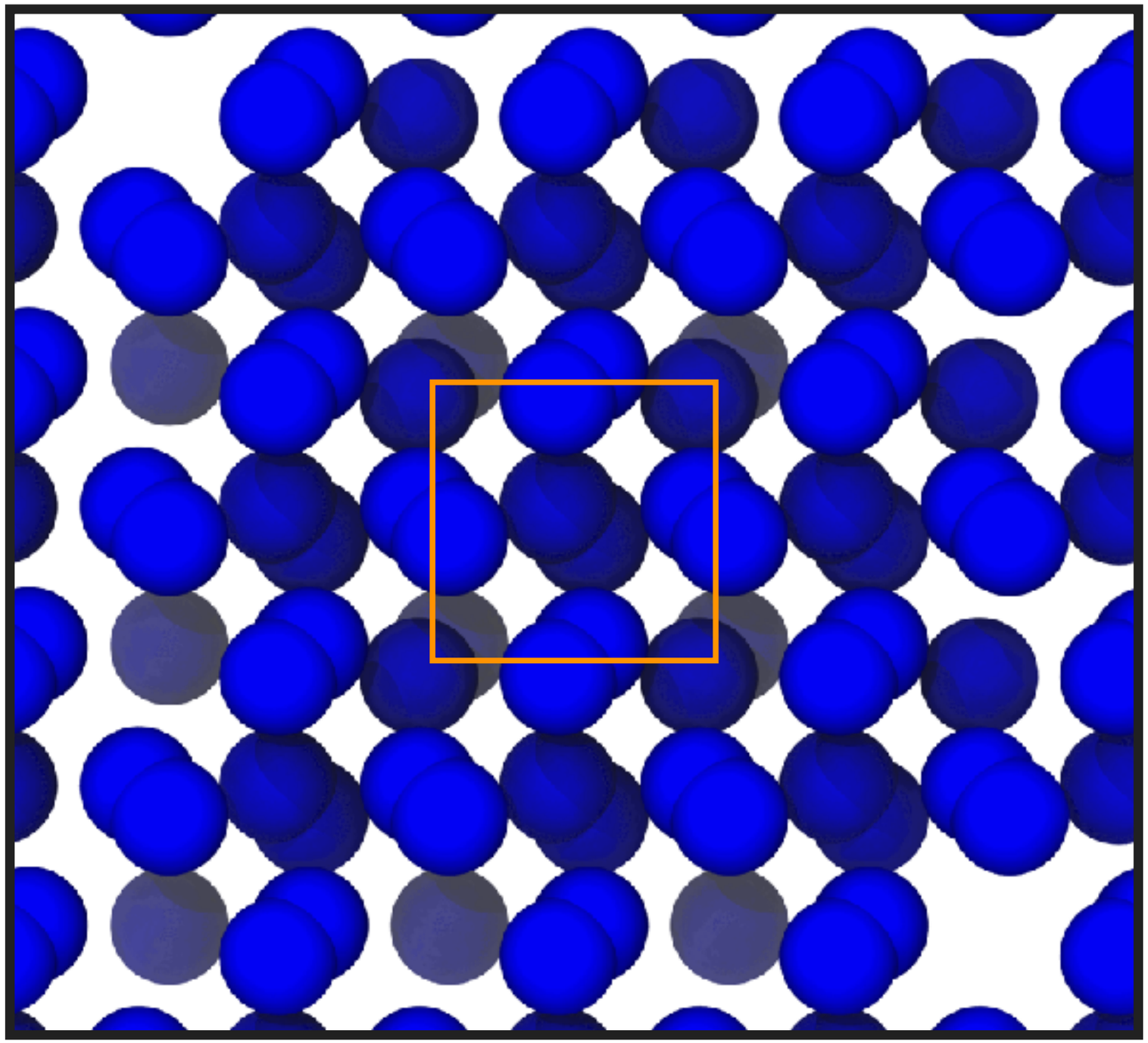
- α-N_2: cubic crystal formed at low T and low P



- BP-N_2: black phosphorus structure formed at high P

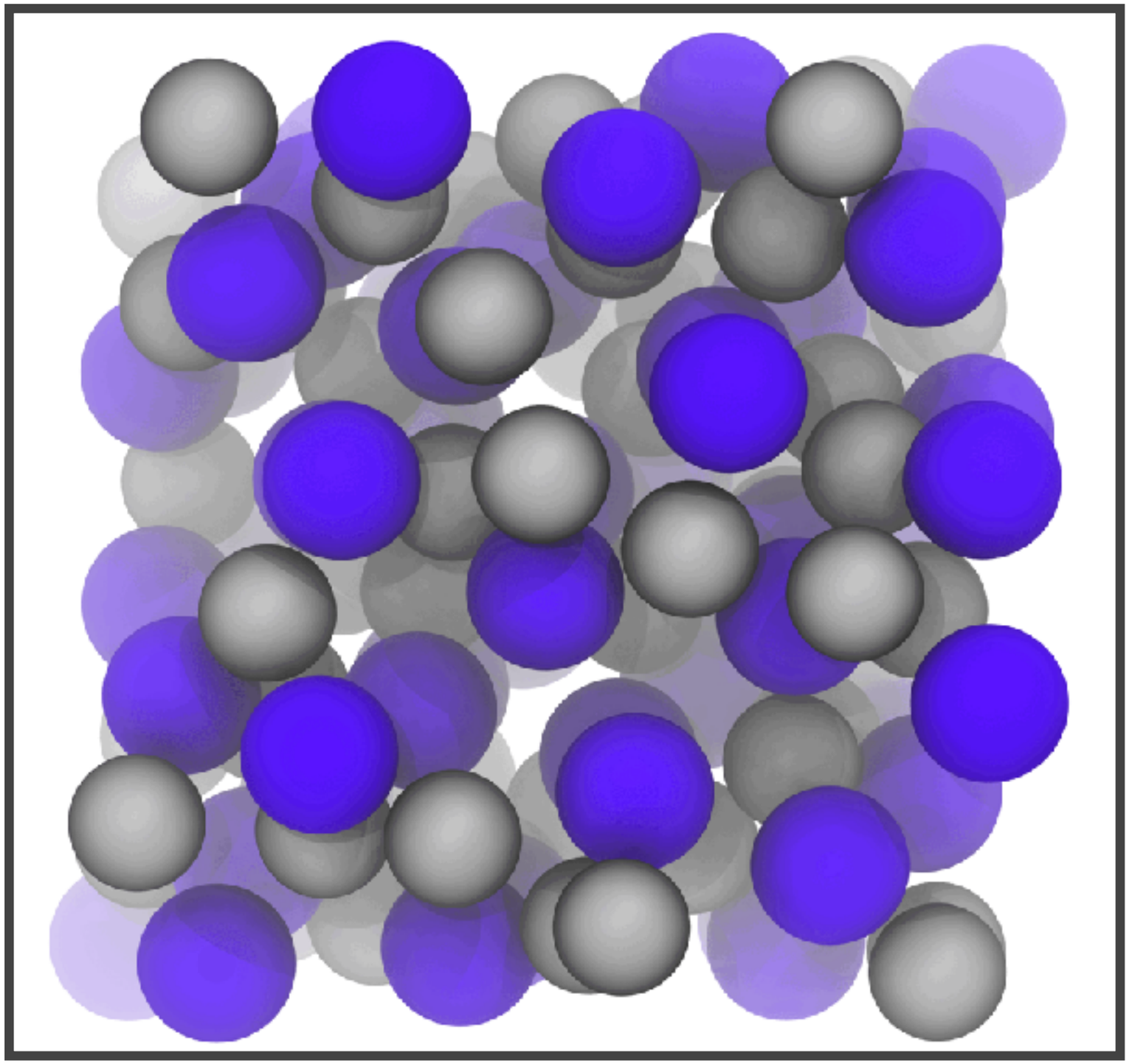
- Fit energies to determine EoS and extract minimum energy volume and bulk modulus

Tutorial 3: Molecular Dynamics Simulations



- Choose a proper timestep
- Run simulations and compute properties
- …small systems and short timescales (*we have limited time*)

Advanced: MD Simulations of AgI



- AIMD simulations of more complex system
- Machine learning potential for fast simulations (*long timescales!*)