ATOMIC FORCES

An object that is at rest will tend to remain at rest. An object that is in motion will tend to remain in motion unless acted upon by an outside force.

-Isaac Newton

THIS LECTURE

- Atomic motion and *ab initio* computation of forces
- *Ab initio* molecular dynamics (AIMD)
- Equilibrium structures and phases

ATOMIC MOTIONS

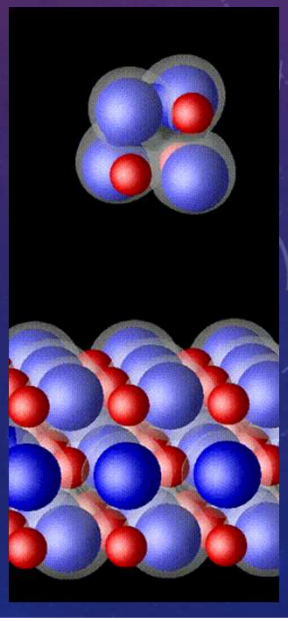
- Born-Oppenheimer: e^-'s adjust instantaneously to atomic locations
  $\Rightarrow E_0(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N)$

- Atoms sufficiently heavy to be treated classically (most cases)

  $\lambda_{\text{th}} = \frac{h}{\sqrt{2\pi M k_B T}} \approx$ 0.19 Å (Si), 0.29 Å (C) 🤓 1.01 Å (H) 😐

  $ZPE = \frac{1}{2}\hbar\sqrt{\frac{k}{m}} \approx$ 0.027 eV (Si), 0.041 eV (C) 🤓 0.140 eV (H) 😐

- Classical phsyics $\Rightarrow \vec{F}_I = M_I \frac{d^2}{dt^2}\vec{R}_I$



HELLMANN-FEYNMAN THEOREM

Definition of force: $\vec{\mathrm{F}}_I = -\frac{d}{d\vec{R}_I} E_0(\{\vec{R}_I\})$

- For us: $E_0(\vec{R}_I) = \min_{\psi_{n\vec{k}}} E_0(\vec{R}_I, \psi_{n\vec{k}})$
- Trick: Define $\psi^{(0)}_{n\vec{k}}(\vec{R}_I) = \arg\min_{\psi_{n\vec{k}}} E_0(\vec{R}_I, \psi_{n\vec{k}})$

$$\Rightarrow E_0(\vec{R}_I) \equiv E_0(\vec{R}_I, \psi^{(0)}_{n\vec{k}}(\vec{R}_I))$$

- Then, $\vec{\mathrm{F}}_I = -\frac{d}{d\vec{R}_I} E_0(\vec{R}_I, \psi^{(0)}_{n\vec{k}}(\vec{R}_I))$

$$= -\frac{\partial}{\partial\vec{R}_I} E_0(\vec{R}_I, \psi^{(0)}_{n\vec{k}}(\vec{R}_I)) - \sum_{n\vec{k}} \frac{\partial}{\partial\psi_{n\vec{k}}} E_0(\vec{R}_I, \psi^{(0)}_{n\vec{k}}(\vec{R}_I)) \frac{d}{d\vec{R}_I} \psi^{(0)}_{n\vec{k}}(\vec{R}_I)$$

- But $\frac{\partial}{\partial\psi_{n\vec{k}}} E_0(\vec{R}_I, \psi^{(0)}_{n\vec{k}}(\vec{R}_I)) = 0$ (minimum!), so $\vec{\mathrm{F}}_I = -\frac{\partial}{\partial\vec{R}_I} E_0(\vec{R}_I, \psi^{(0)}_{n\vec{k}}(\vec{R}_I))$
- Fixed-$\psi_{n\vec{k}}$ derivative $\frac{\partial E_0}{\partial\vec{R}_I} = \frac{\partial}{\partial\vec{R}_I}(T_e + V_{ee} + V_{NN} + V_{eN}) = \frac{\partial V_{NN}}{\partial\vec{R}_I} + \frac{\partial V_{eN}}{\partial\vec{R}_I}$ are "easy" —

only issue: need to know $\psi^{(0)}_{n\vec{k}}$ from E_0 calculation ! (🤓)

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- ***Ab initio* molecular dynamics (AIMD)**
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AB INITIO MOLECULAR DYNAMICS (AIMD)

$$\vec{F}_I = M_I \frac{d^2 \vec{R}_I}{dt^2}$$

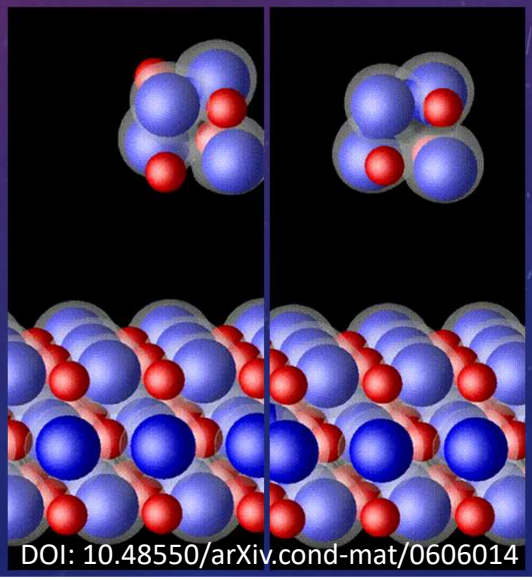
- Verlet algorithm (time reversible, conserves energy)

$$\vec{F}_I\left(\vec{R}_I(t_n)\right) = M_I \frac{\frac{\vec{R}_I(t_{n+1}) - \vec{R}_I(t_n)}{\Delta t} - \frac{\vec{R}_I(t_n) - \vec{R}_I(t_{n-1})}{\Delta t}}{\Delta t} = M_I \frac{\vec{R}_I(t_{n+1}) - 2\vec{R}_I(t_n) + \vec{R}_I(t_{n-1})}{\Delta t^2}$$

$\Rightarrow$

$$\circlearrowright \vec{R}_I(t_{n+1}) = 2\vec{R}_I(t_n) - \vec{R}_I(t_{n-1}) + \frac{\Delta t^2}{M_I} \vec{F}_I(\vec{R}_I(t_n))$$

- Study of impact of cluster temperatures on PLD of MgO
  $\Rightarrow$ "Hot" incoming MgO PLD clusters have higher sticking coefficient that "cold" clusters (*Freedman and Arias*)



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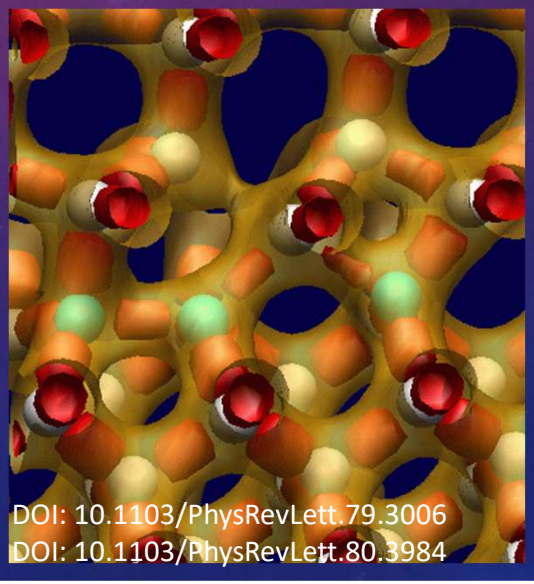
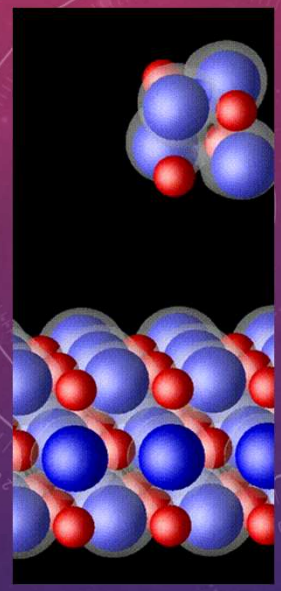
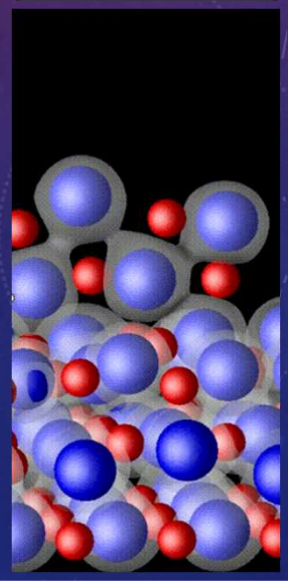
EQUILIBRIUM STRUCTURES

- Over time, $\vec{R}_I$'s settle into lowest energy configuration (simulated annealing)
- Short cut:
  $\circlearrowleft \vec{R}_I \leftarrow \vec{R}_I + \epsilon \vec{F}_I(\vec{R}_I)$
  (gradient descent: $\vec{F}_I = -\nabla_{\vec{R}_I} E_0$)
- Led to discovery of paramagnetically active, 5-fold coordinated Si atom in core of 30° partial dislocation (*Engeness, Csanyi, Arias*)
- Always verify your iterative convergence! (😠)



DOI: 10.1103/PhysRevLett.79.3006
DOI: 10.1103/PhysRevLett.80.3984





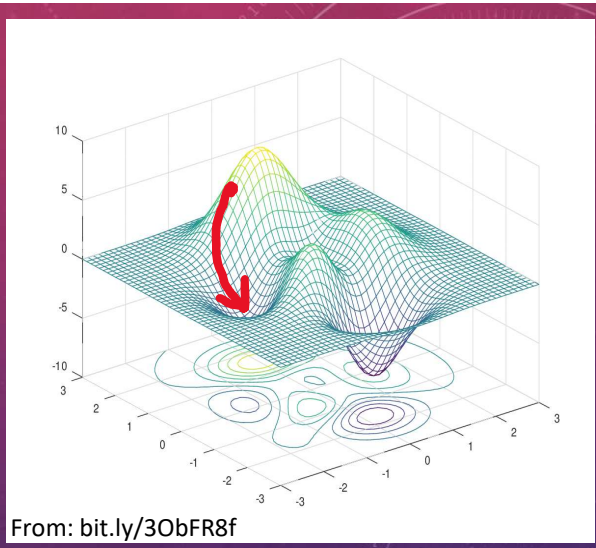
MULTIPLE MINIMA PROBLEM

- Gradient descent finds “nearest” local minimum
  (e^- minimization is convex*, has only 1 minimum 🤓!)
  *Except magnetic systems (multiple magnetic orderings)

- Global minimum problem is unsolved
  - Subject of ML approaches
  - Simulated annealing
  - Chemical intuition

- All approaches descend from set of reasonable starting locations

- Nature often exhibits multiple structure/phases



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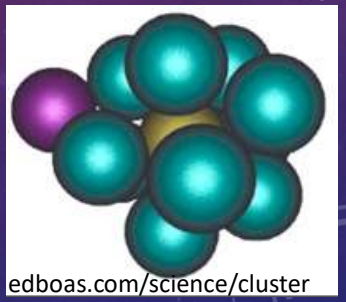
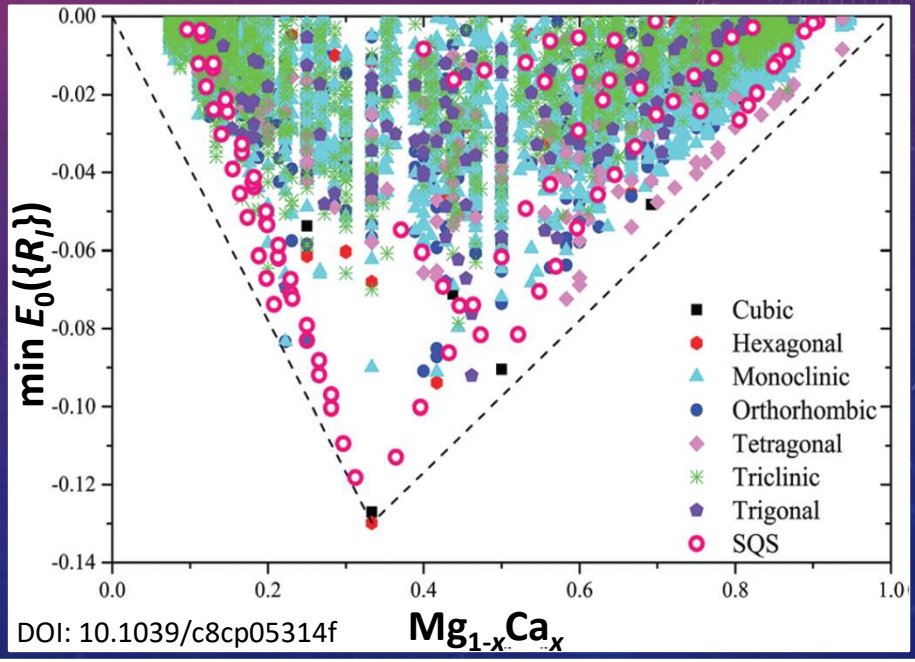

edboas.com/science/cluster

DETERMINATION OF STABLE PHASES

Thermodynamic construction

- Compute min $E_0(R_i)$ for "exhaustive" list of minima
- Construct convex hull diagram
- Stable, realizable phases occur at vertices



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THANK YOU!

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