Transforming Matter at Extreme Conditions: Crystallization and Self-Assembly for New Materials

NVidia GTC, Session S9235
San Jose, CA

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Jonathan L. Belof[1] and Edward W. Lowe, Jr.[2]
[1]Group Leader, Material Dynamics and Kinetics
Lawrence Livermore National Laboratory
[2]Director of Lose It! Labs, FitNow, Inc.

Lawrence Livermore National Laboratory

LLNL-PRES-764280

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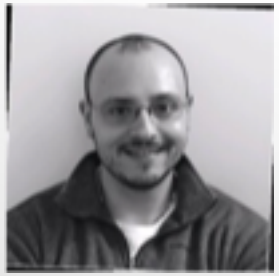
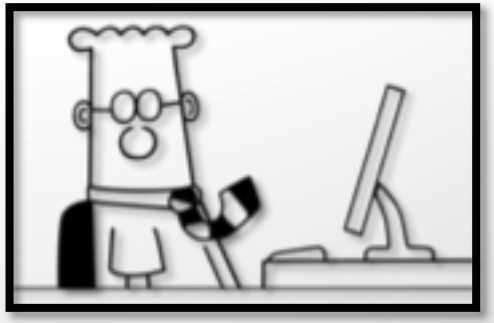
Kinetics at Extreme Conditions Team



Will Lowe (Lose It!)

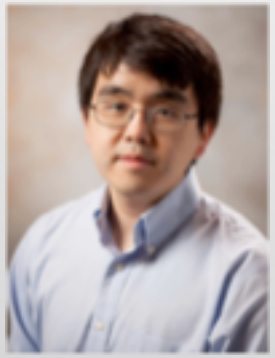
Lorin Benedict

Alex Chernov



Burl Hall

Sebastien Hamel



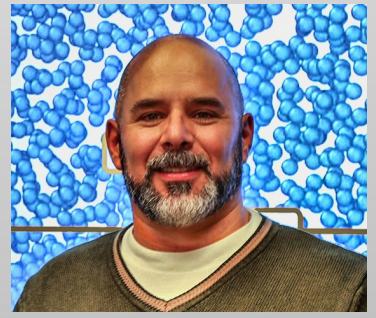
Philip Myint

Tomas Oppelstrup

Babak Sadigh

Dane Sterbentz

Amit Samanta



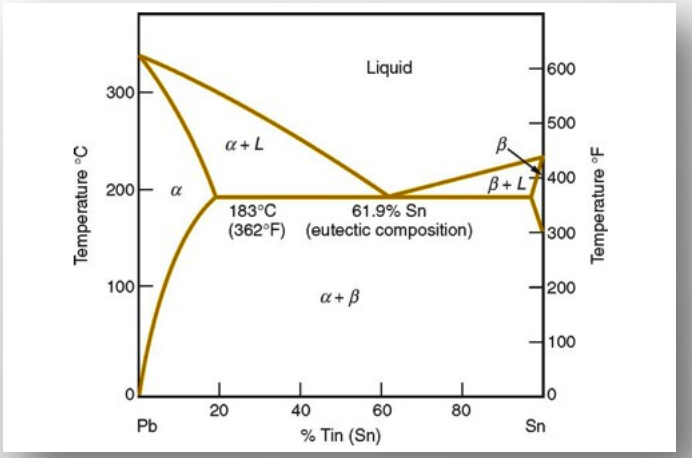
Luis Zepeda-Ruiz

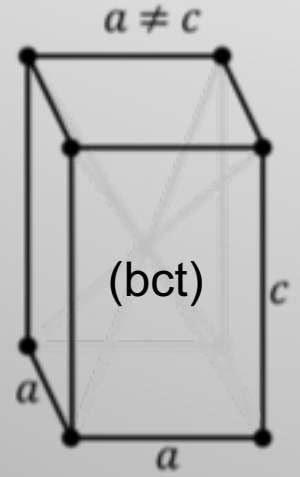
Tianshu Li (GWU)

Summary

- Scientific and technological impact to understanding phase transformations far from equilibrium
- The role of solidification in exoplanets and the search for extrasolar life
  - Liquid/ice states of water
  - Nucleation kinetics
- Nucleation theory and the role of simulation
- Multiscale nucleation modelling and acceleration with *GPU supercomputing*
- New approach to nucleation kinetics based on coarse-graining and GLE
- Path forward toward concurrent simulations methods

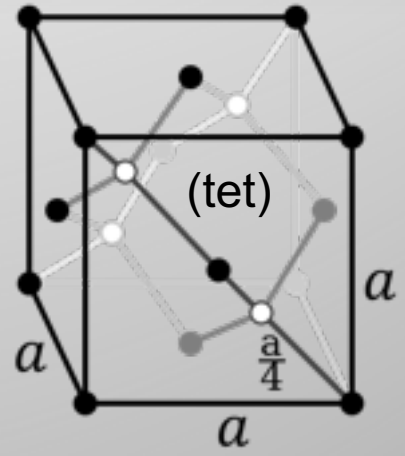
Phase transformations have real-world consequences





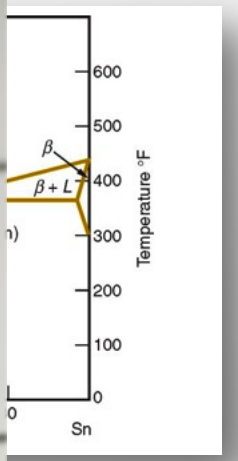
β-Sn

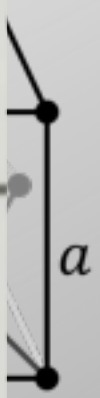
"Napoleon's Army May Have Suffered From the Greatest Wardrobe Malfunction in History", *Smithsonian News* (2012)



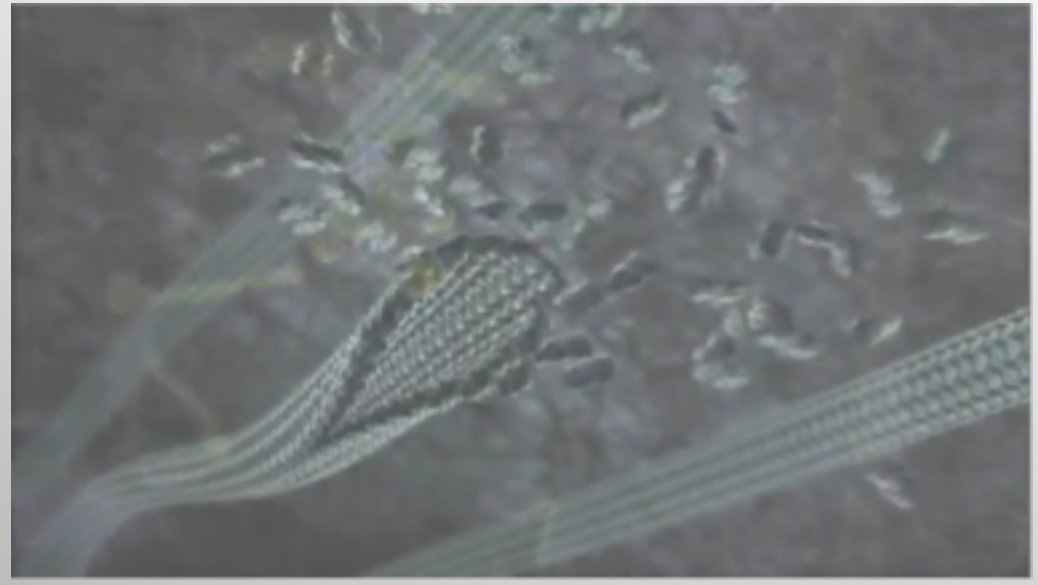
α-Sn

Phase transformations have real-world consequences



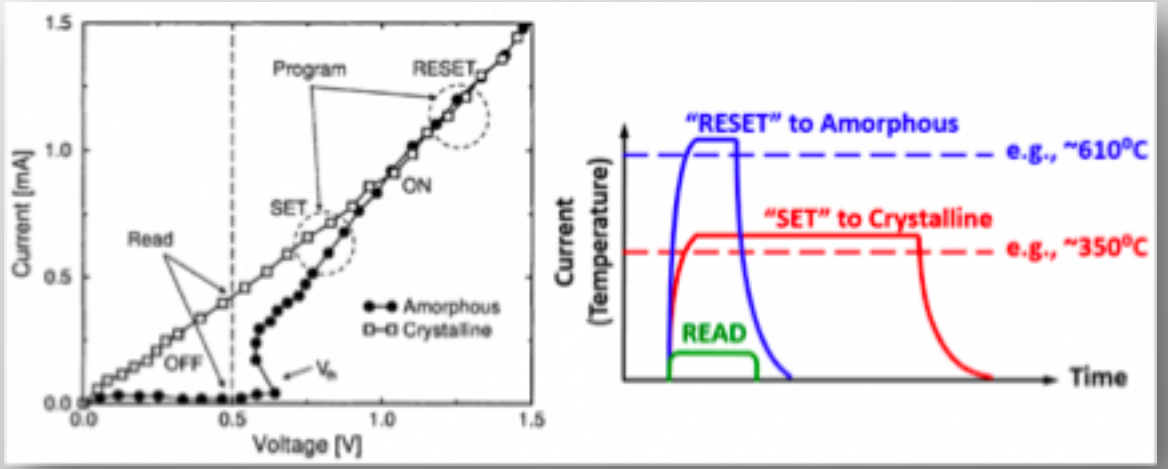


Self-assembly processes are ubiquitous in nature, yet poorly understood



microtubulin assembly / disassembly

nucleation of the initial state? dynamic stability?

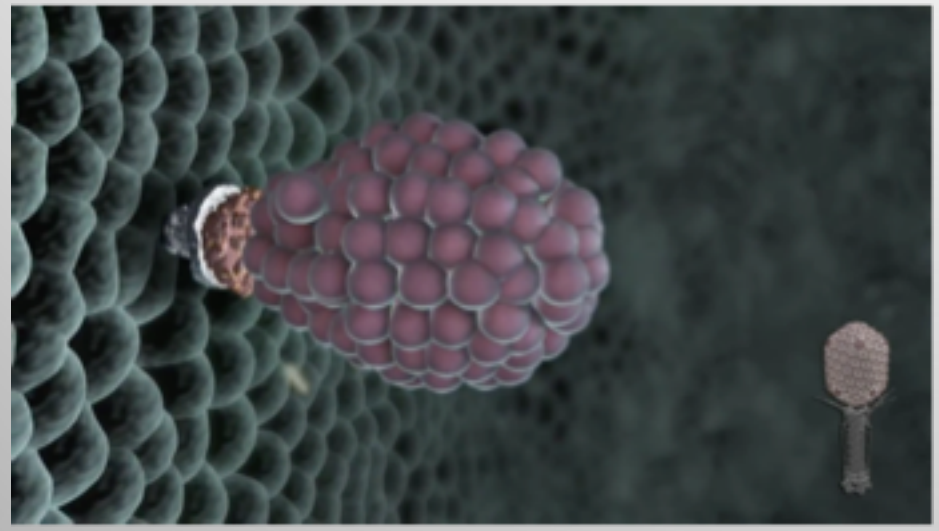


phase change memory technology

need new materials with fast nucleation kinetics to achieve ns read/write

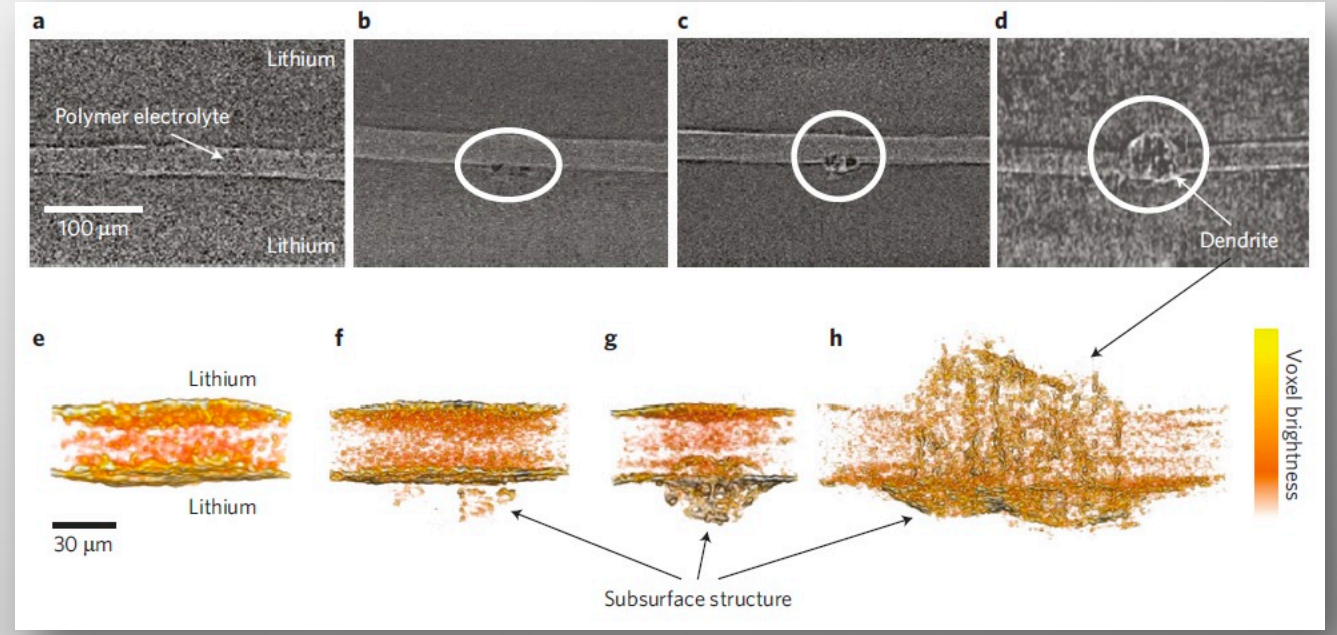
Self-assembly processes are ubiquitous in nature, yet poorly understood

Rossman lab, Purdue Univ.



virus capsid dynamic assembly

Harry *et. al*., "detection of subsurface structures underneath dendrites formed on cycled lithium metal electrodes", *Nature Mat.* (2014)



dendrite formation in Li ion batteries

Work presented today

ice VII-specific work:

P.C. Myint, A.A. Chernov, B. Sadigh, L.X. Benedict, B.M. Hall, S. Hamel and J.L. Belof, “Nanosecond Freezing of Water at High Pressures: Nucleation and Growth near the Metastability Limit”, *Phys. Rev. Lett*., 121:155701 (2018)

P.C. Myint and J.L. Belof, "Rapid freezing of water under dynamic compression”, *J. Phys. Condens. Matter*, 30:233002 (2018)

P.C. Myint, L.X. Benedict and J.L. Belof. "Free energy models for ice VII and liquid water derived from pressure, entropy, and heat capacity relations”, *J. Chem. Phys.*, 147:084505 (2017)

atomistic techniques of simulating liquid/solid interfaces:

Samanta and J.L. Belof, "The thermodynamics of a liquid-solid interface at extreme conditions: A model close-packed system up to 100 GPa”, *J. Chem. Phys*., 149:124703 (2018)

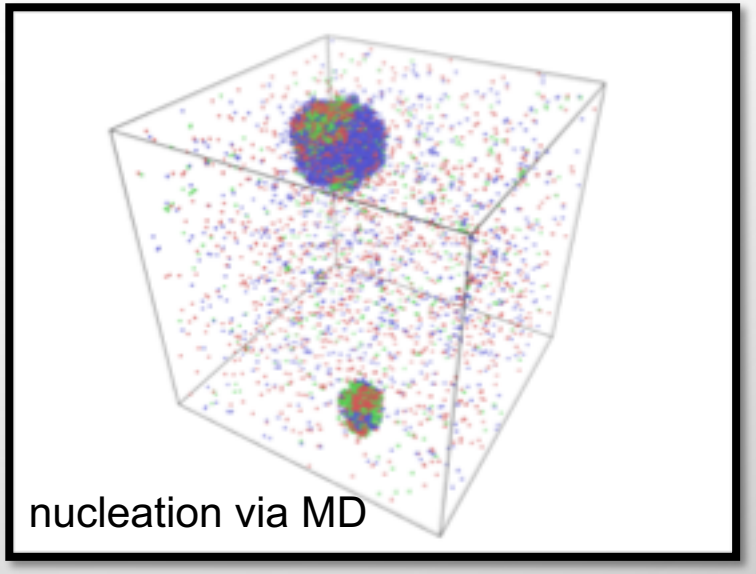
L.A. Zepeda-Ruiz, *et. al., “*Extraction of effective solid-liquid interfacial free energies for full 3D solid crystallites from equilibrium MD simulations”, *J. Chem. Phys*., 147:194704 (2017)

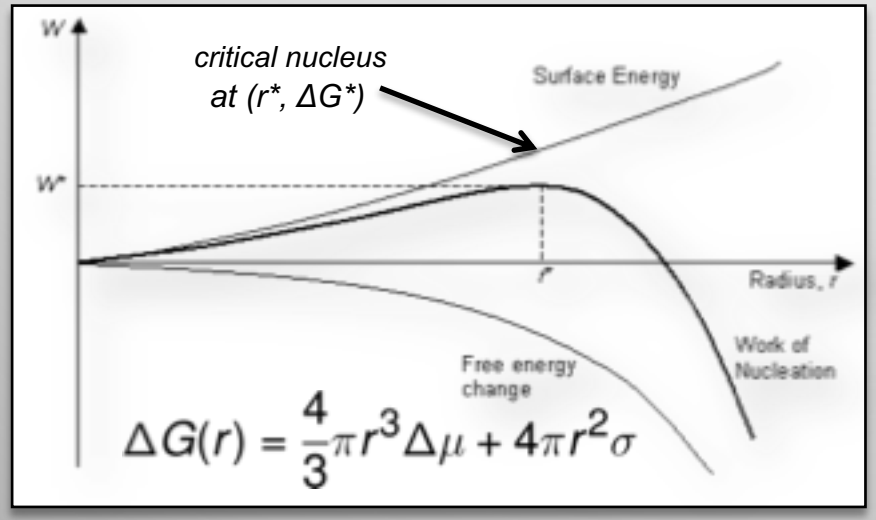
coarse-graining and generalized langevin equation for nucleation

J.L. Belof and E.W. Lowe, ”Coarse-grained nucleation model from projection operators”, *Phys. Rev. E*., (in prep)

Statistics of the atomic configurations makes it extremely likely for phase transition to occur through a process of nucleation

- Fluctuations in the (metastable, undercooled) liquid result in an atomic configuration that resembles the solid
- Forming this small solid in the liquid creates an interface which has an entropic penalty (interfacial free energy), opposing the thermodynamic (bulk) driving force





barrier height:

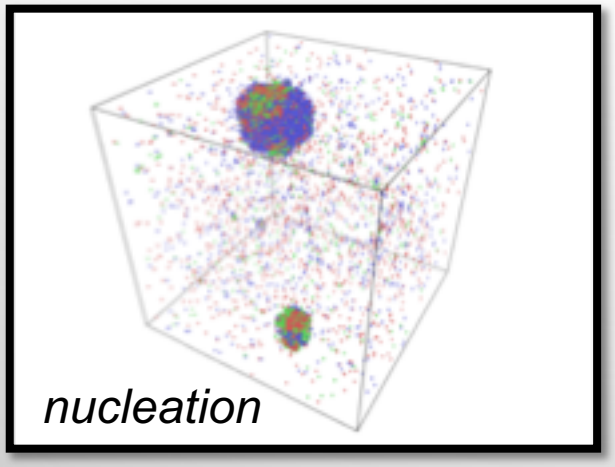
$$\Delta G^* = \frac{16\pi}{3}\frac{\sigma^3}{(\rho\Delta\mu^2)}$$

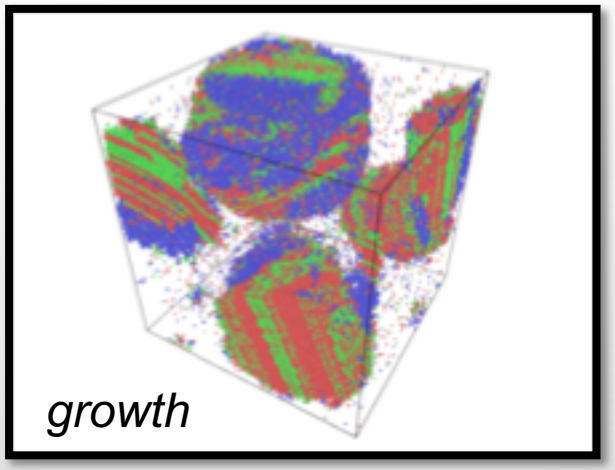
the nucleation rate goes like

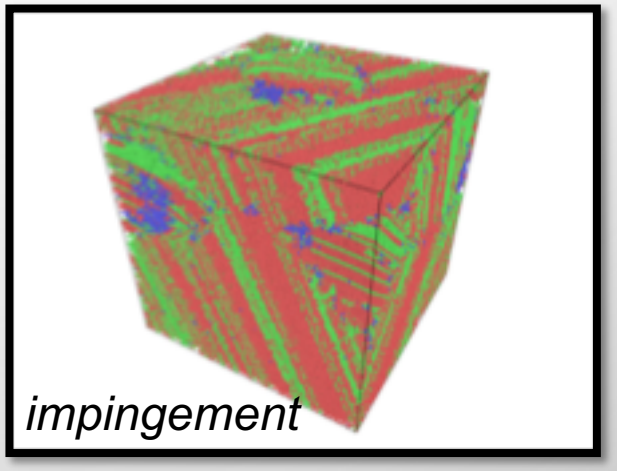
$$J \propto \exp(\sigma^3)$$

The free energy barrier to nucleation is most dependent upon interfacial free energy

The overall volume of transformed material is a function of both nucleation and growth rates







A.N. Kolmogorov, "On The Statistical Theory of Metal Crystallization", *Izv. Akad. Nauk SSSR Ser. Mat.* 3:355 (1937)

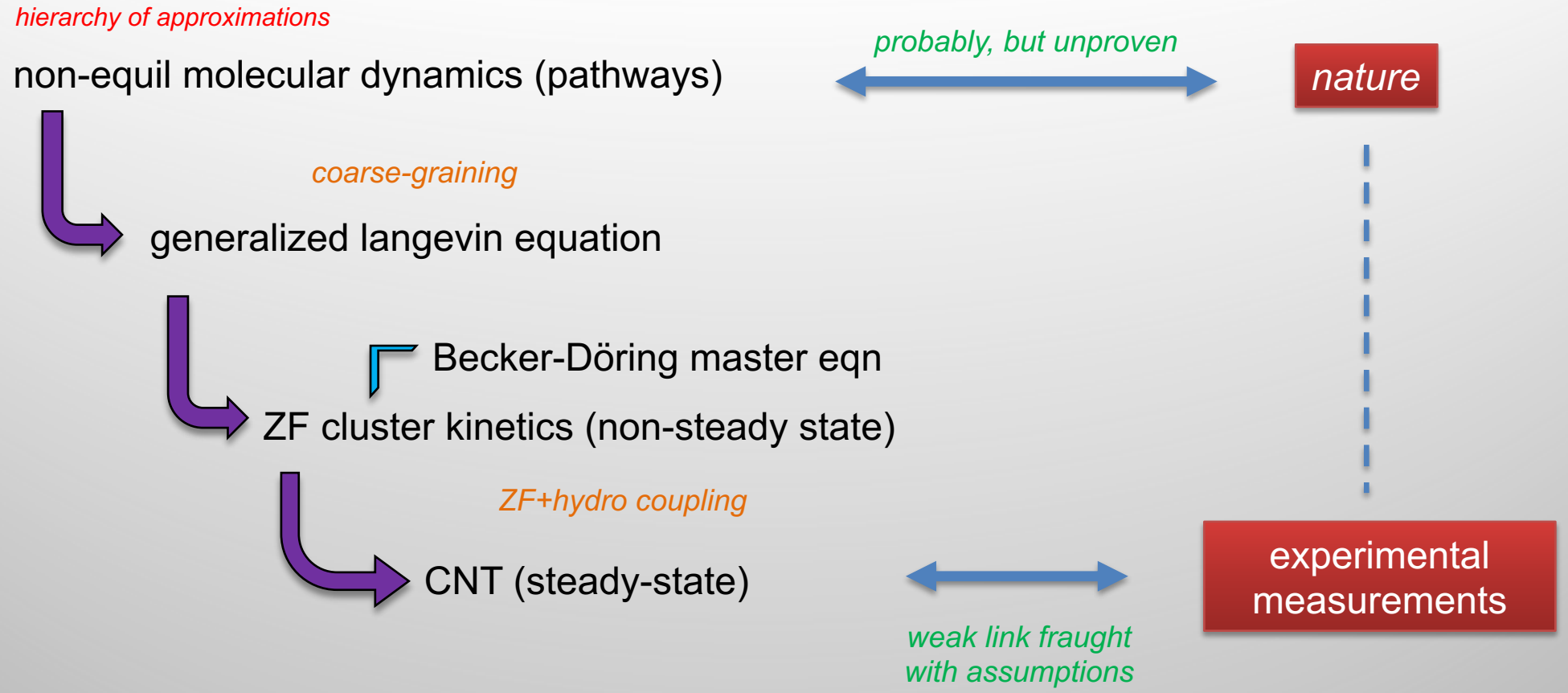
Assumptions:
- Shapes have same orientation
- Nucleation occurs in infinite medium
- Liquid and solid have same volume and temperature

$$\frac{\partial \phi}{\partial t} = \frac{4\pi}{3}(1-\phi)\left\{3\gamma(t)\int_0^t dt' J(t')\left[\int_{t'}^t dt'' \gamma(t'')\right]^2\right\}$$

ϕ – volume fraction of product phase
J – nucleation rate
γ – growth rate

The Kolmogorov approach allows us to calculation the phase fraction from nucleation/growth rates

The theoretical description of nucleation can be expressed as a hierarchy of theory based on level of approximation

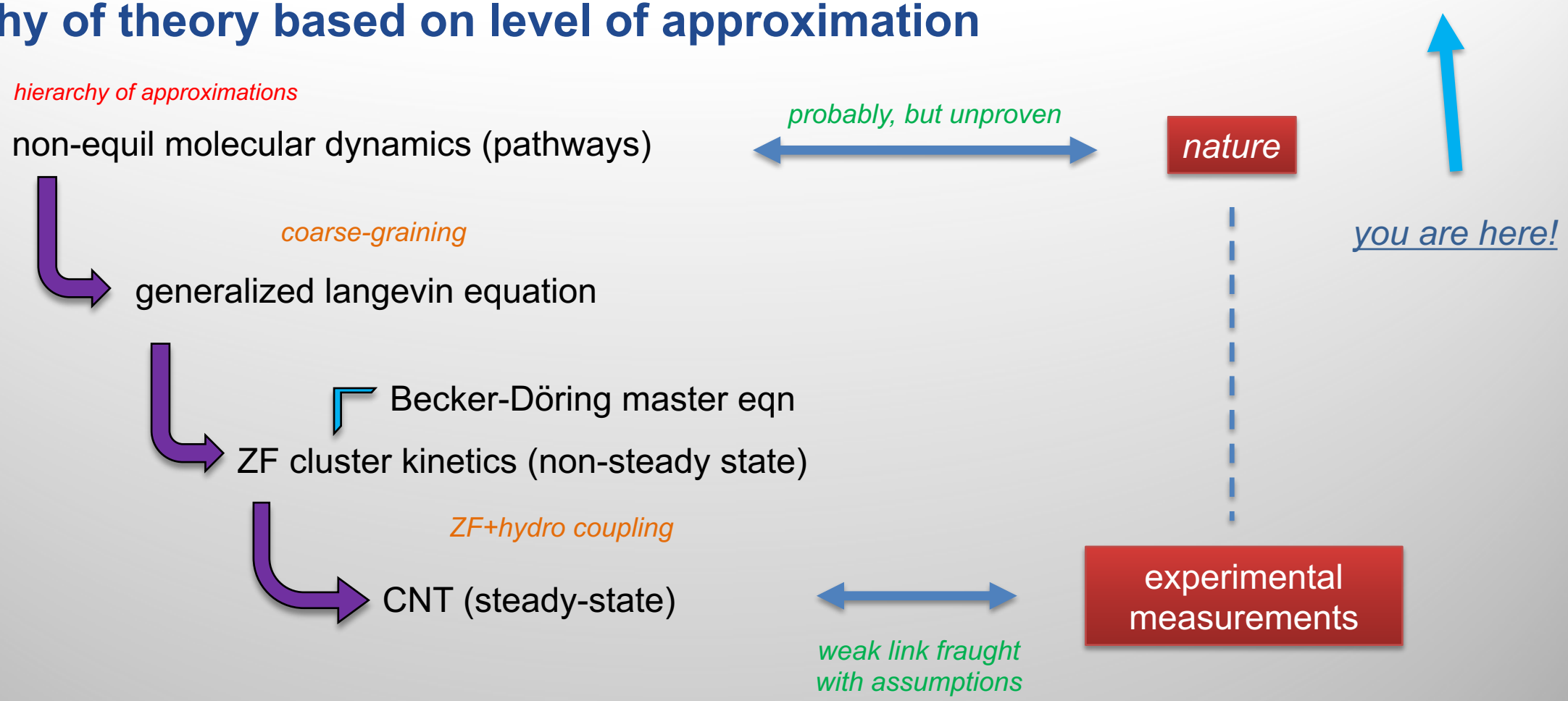


Still active debate on whether atomistic corrections (pathways, intermediates) to CNT are sufficient:
Lupi *et. al.* Nature 551:218 (2017), Bi *et. al.*, Nature 8:15372 (2017)

Developing predictive models of nucleation, from first principles, remains a very active area of research

The theoretical description of nucleation can be expressed as a hierarchy of theory based on level of approximation

MD ⇒ *GLE* ⇒ *ZF* ⇒ *CNT*



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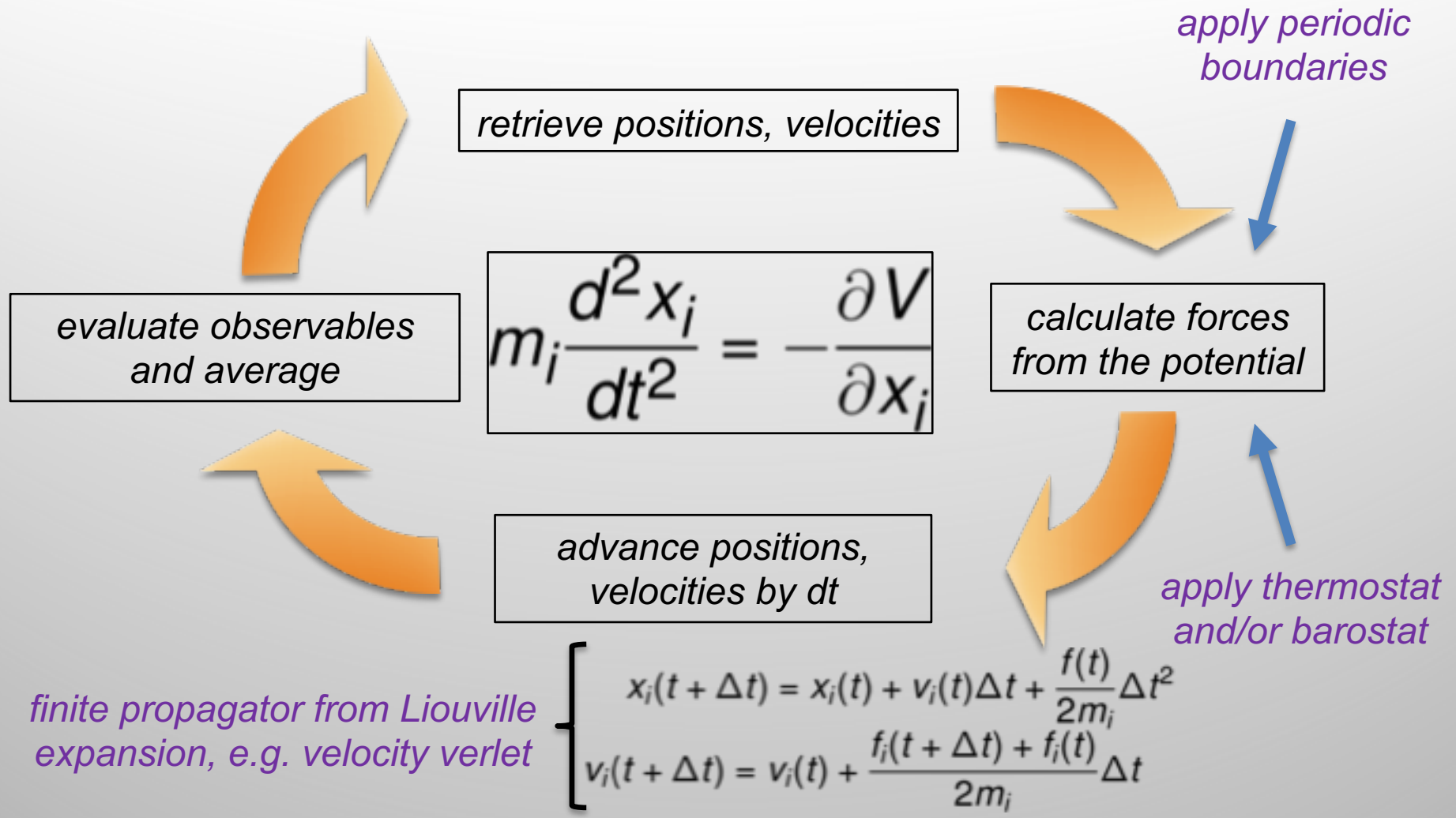
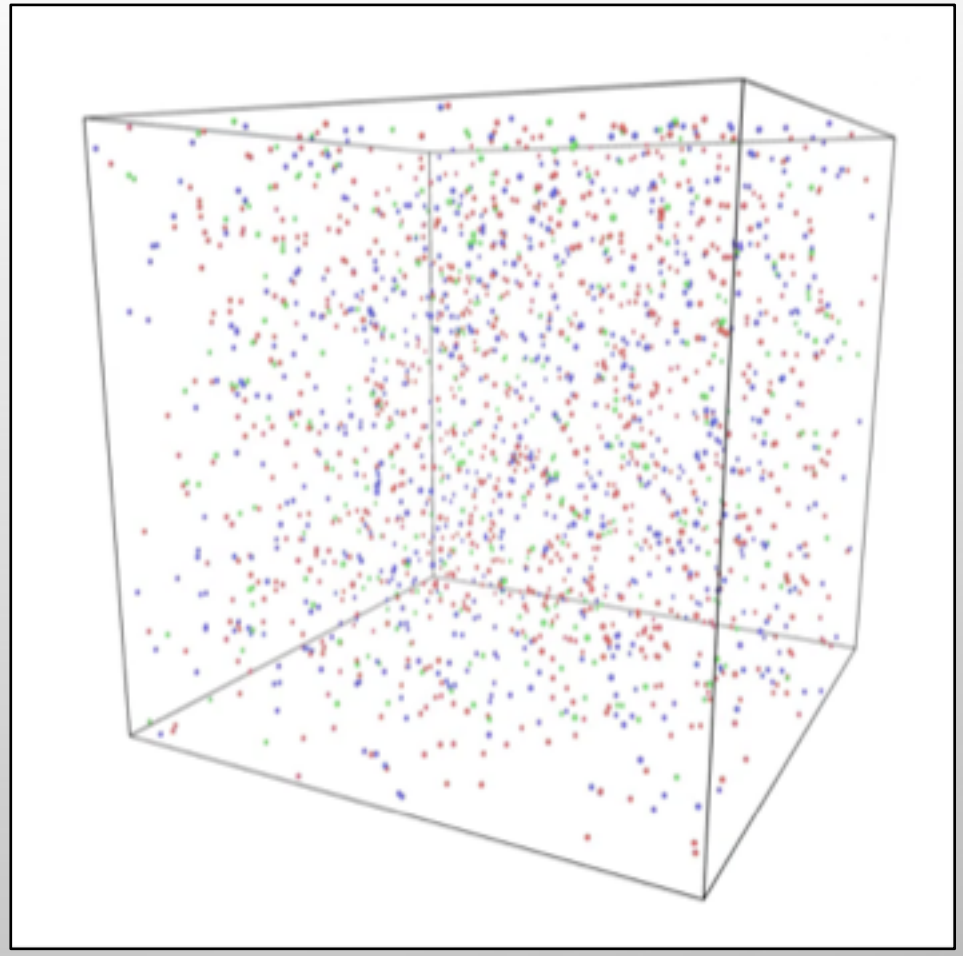
Developing predictive models of nucleation, from first principles, remains a very active area of research

What is molecular dynamics (MD)?

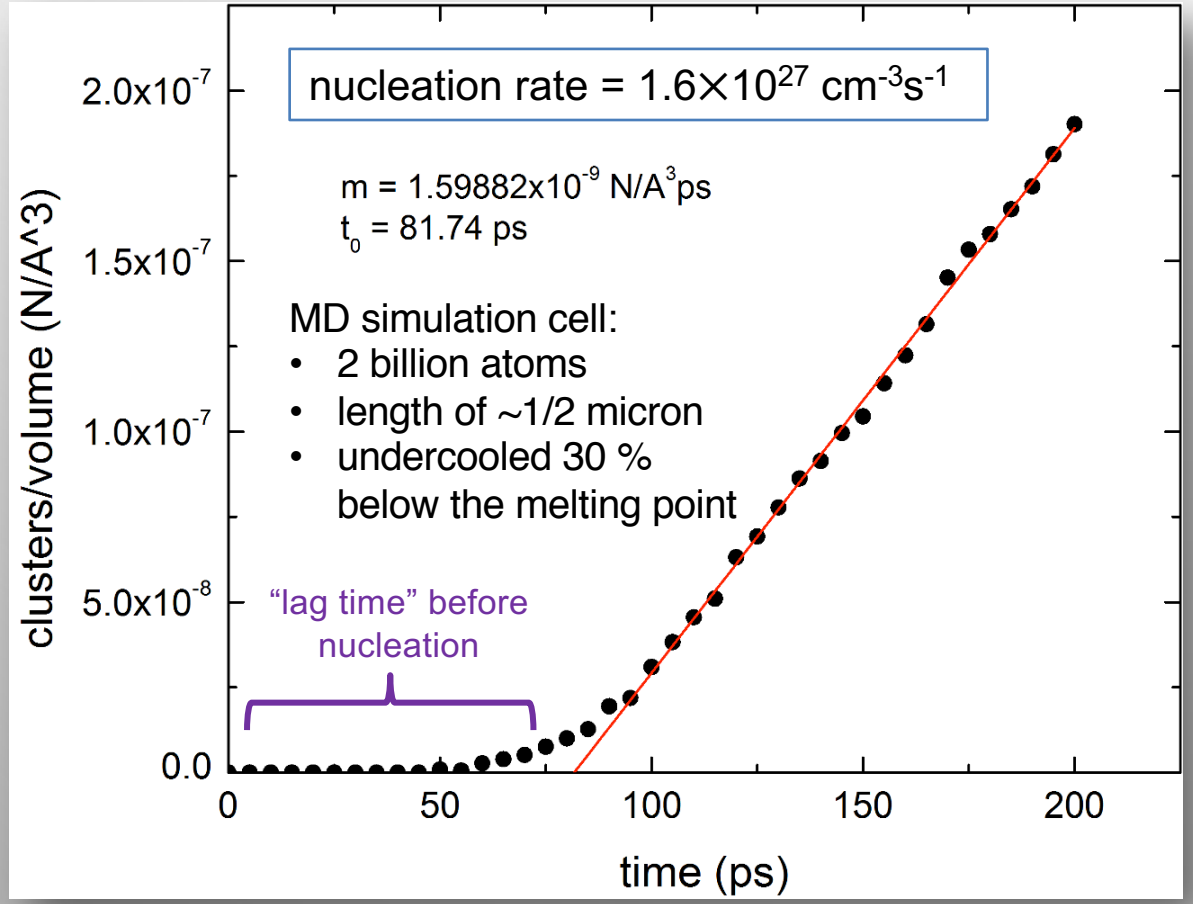


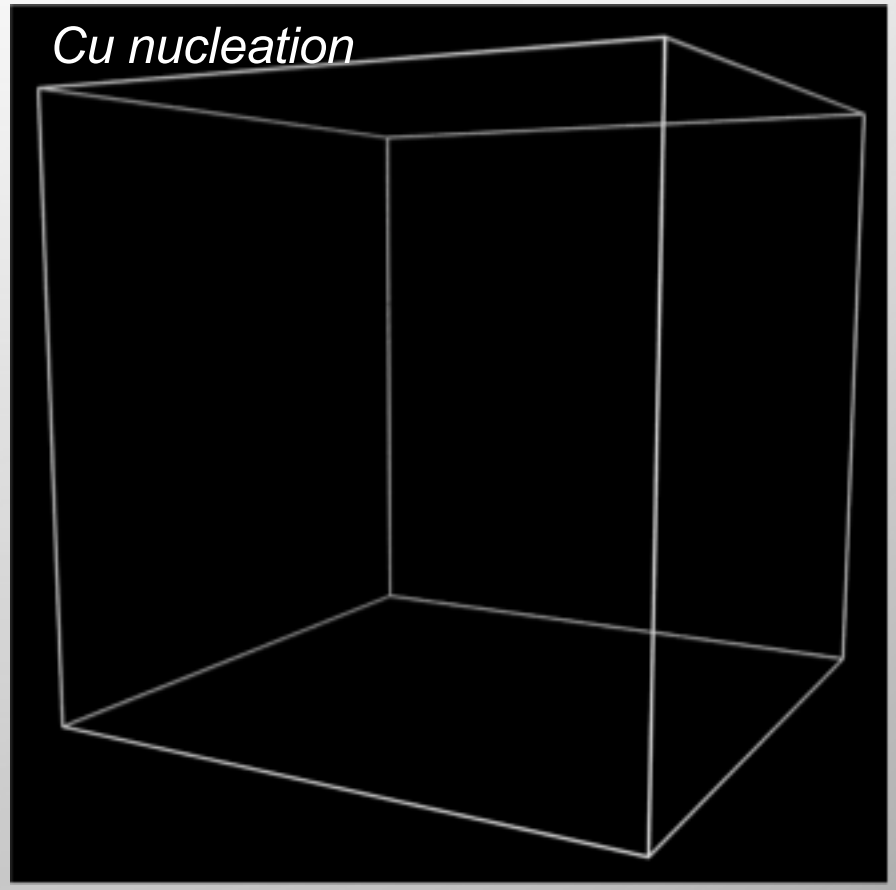
MD simulation provides a tool for investigating nucleation and growth processes

- 64 million atoms
- Cu EAM potential (Mishin et al., PRB, 2001)
- Temperature quench at constant pressure
- Several ns dynamics
- Common neighbor analysis for phase detection:
  - liquid = transparent
  - fcc = green
  - hcp = red
  - bcc = blue



Molecular dynamics simulations, utilizing GPU-driven HPC, are allowing us to calculate the nucleation rate for solidification directly

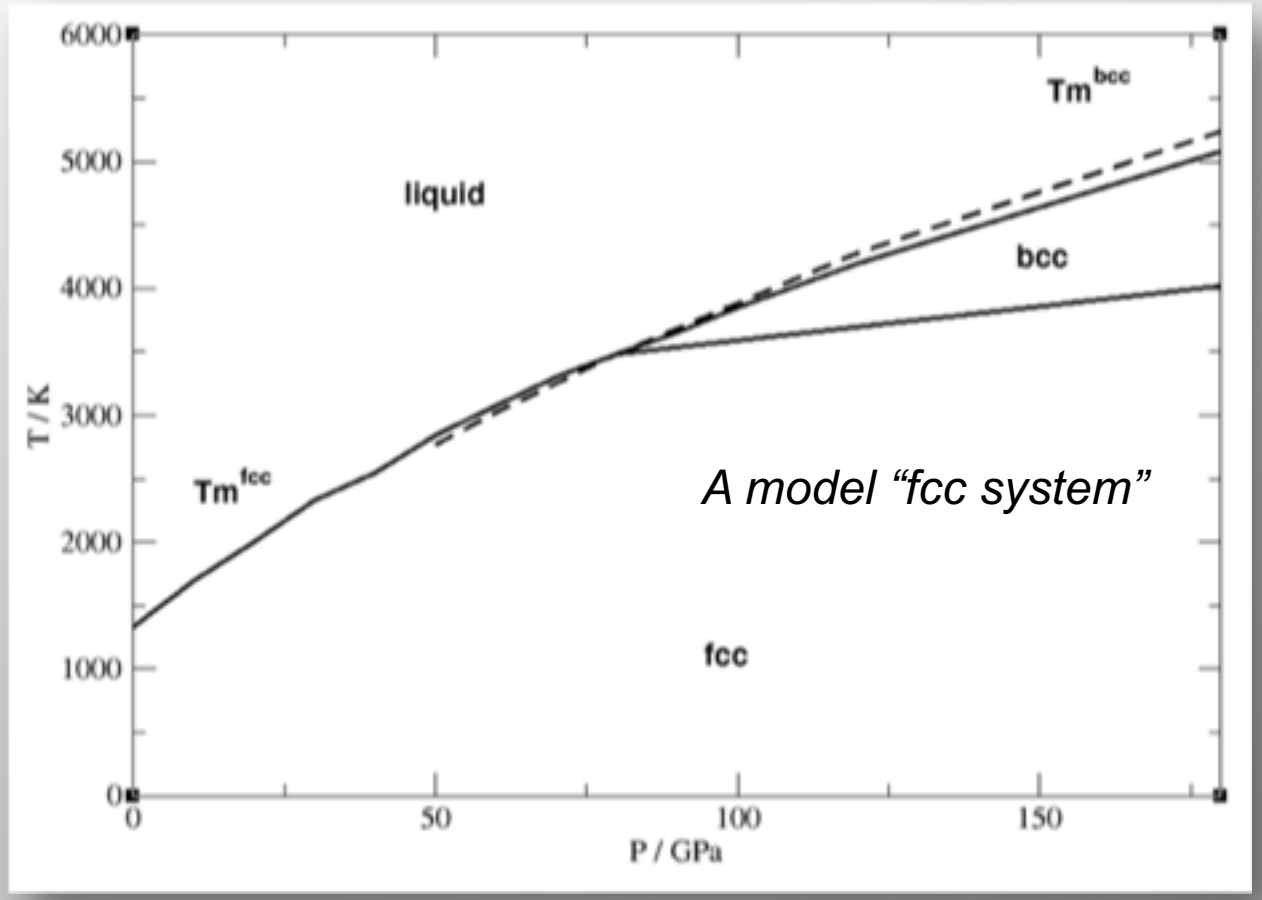




This approach allows us to directly examine the applicability of nucleation theory

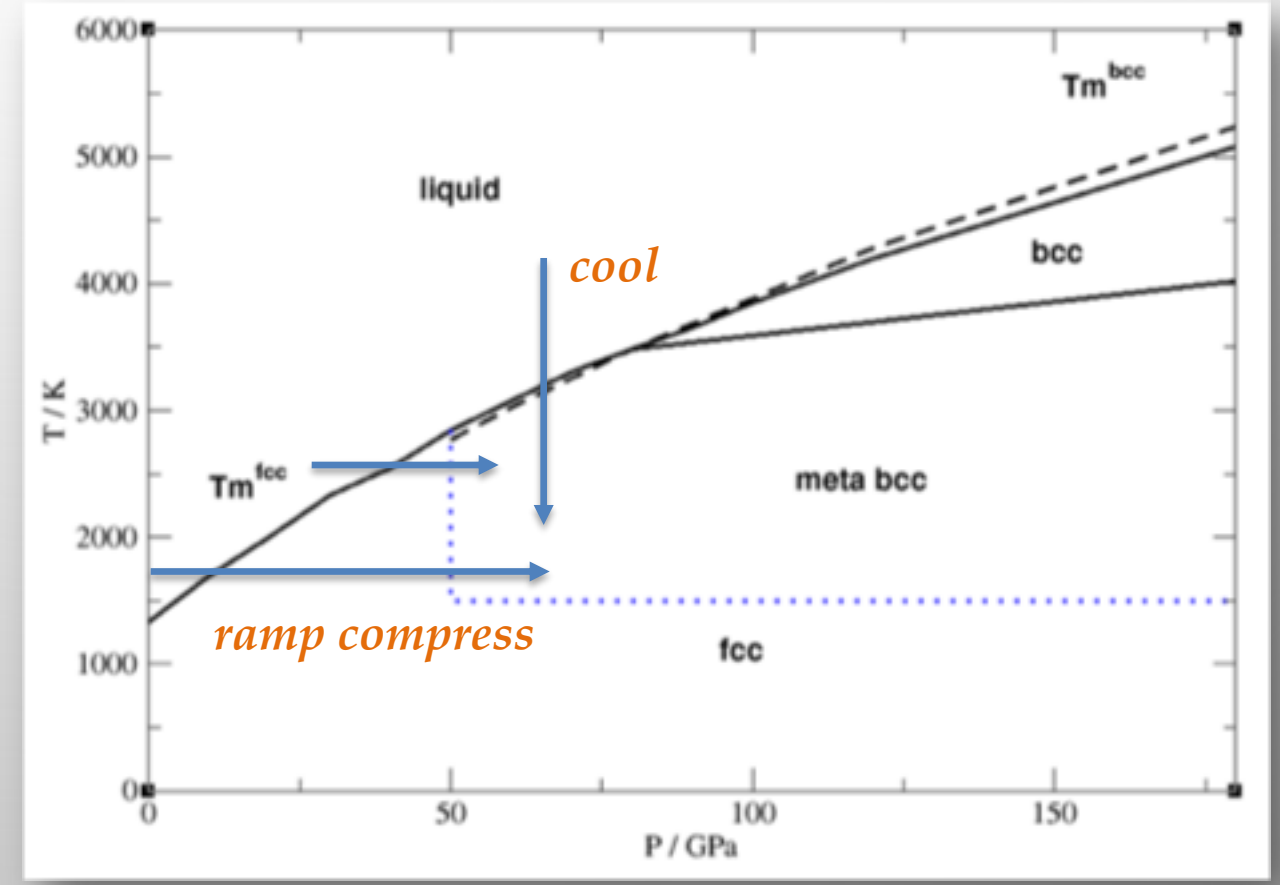
Atomistic simulation can provide a "proving ground" for the testing or development of new theories

- Mishin EAM potential
- Liq-fcc and liq-bcc melting curves calculated from 2-phase coexistence MD
- fcc-bcc phase boundary calculated *via* Clausius-Claperyon
- liq-bcc-fcc triple point at P = 80 GPa and T = 3200 K



Under rapid cooling or compression, metastable bcc nucleates!

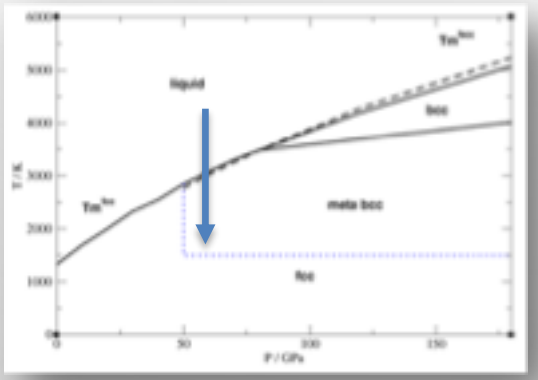
- A rapid temp quench or compression will nucleate bcc
- There's nothing special about this system, generally any fcc system will do, including without thermodynamically stable bcc phase* [Rein ten Wolde *et. al.*, PRL 75:2714 (1995)]
- Occurs at a pressure *lower* than stable bcc



*see also [Alexander, McTague, PRL 41:702 (1978)]

MD temperature quench at P = 50 GPa

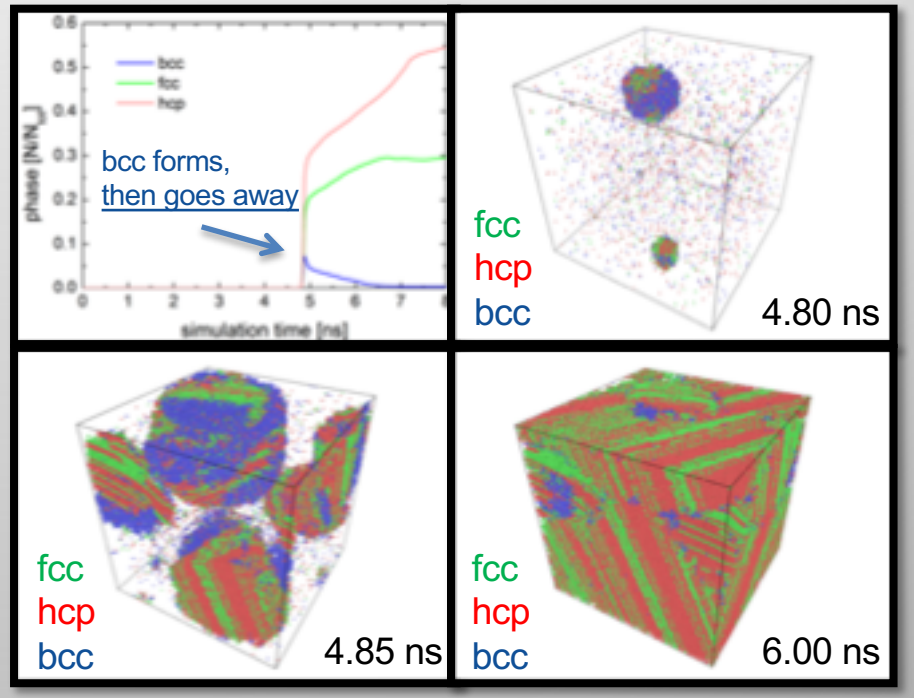
0.1 K ps^{-1} cooling rate



4 million atoms, NPT

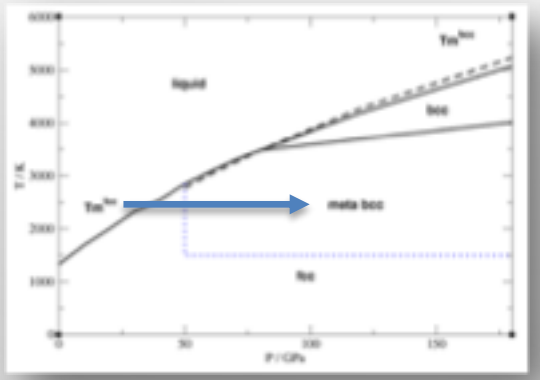
- Most bcc is gone by the time all of the liquid is consumed
- We are at the edge of the metastability field
- What about compression?

- Nucleus that forms is bcc
- Inside of nucleus converts to fcc
- fcc/hcp stacking faults present
- Highlights the need for large simulation cells to study nucleation!



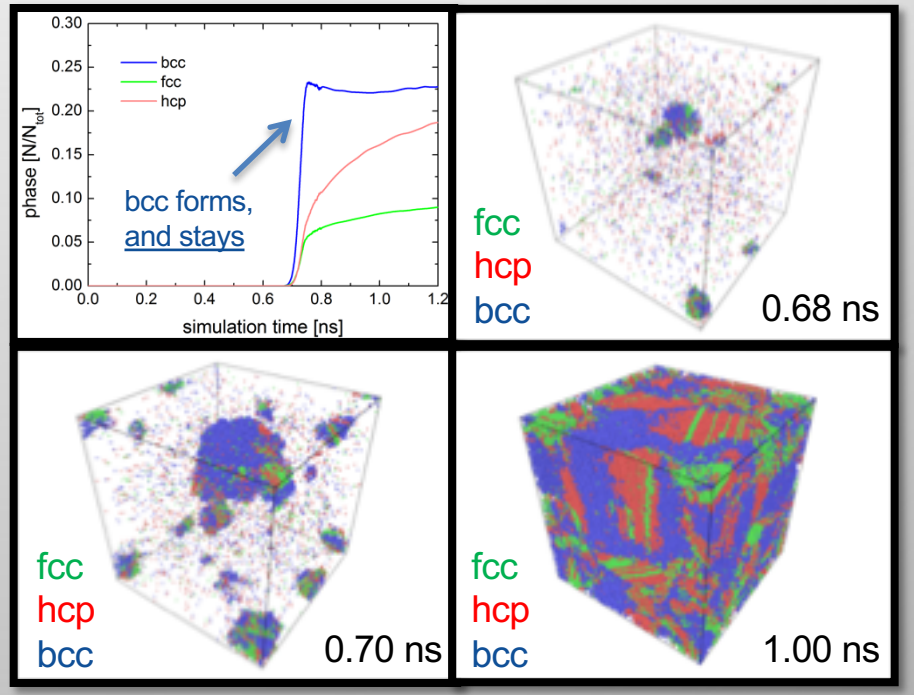
MD isothermal (T = 2500 K) compression to P = 100 GPa

10^6 s^{-1} strain rate



- Not only is bcc retained, but the dominant phase!
- We are deep in the bcc metastability field
- "Effective cooling rate" was also higher here, larger driving force – but didn't favor fcc

- Nucleus that forms is bcc
- Some of the inside converts to fcc
- fcc/hcp stacking faults present



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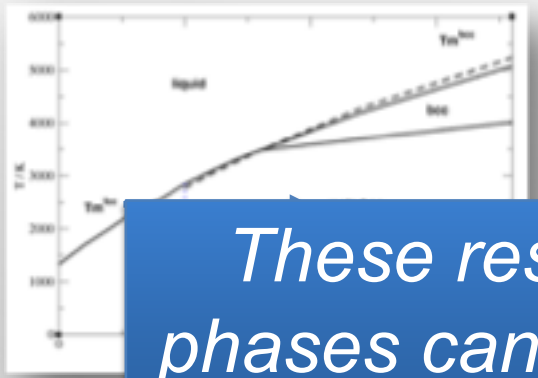
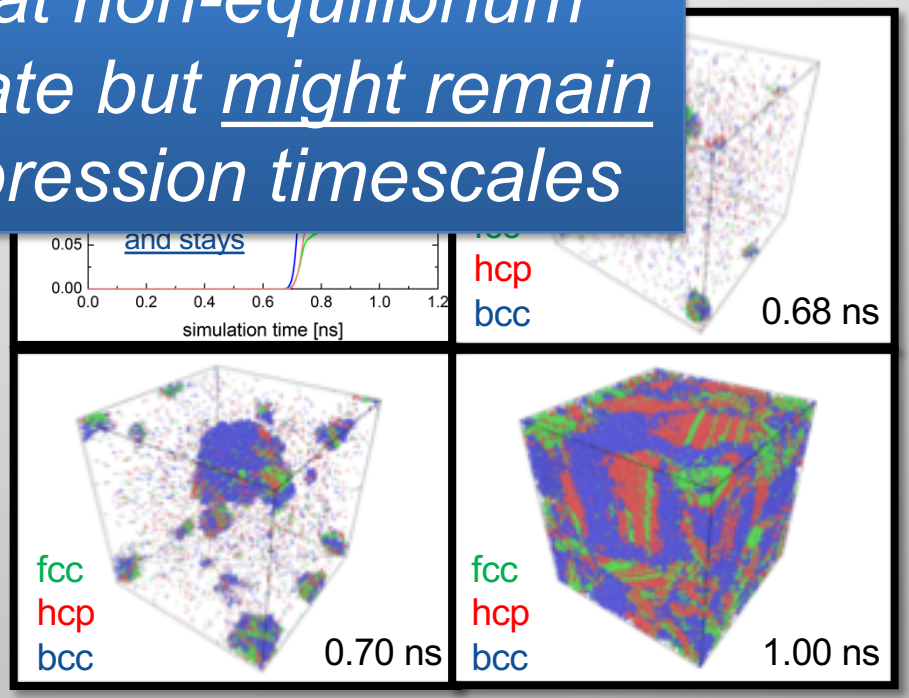


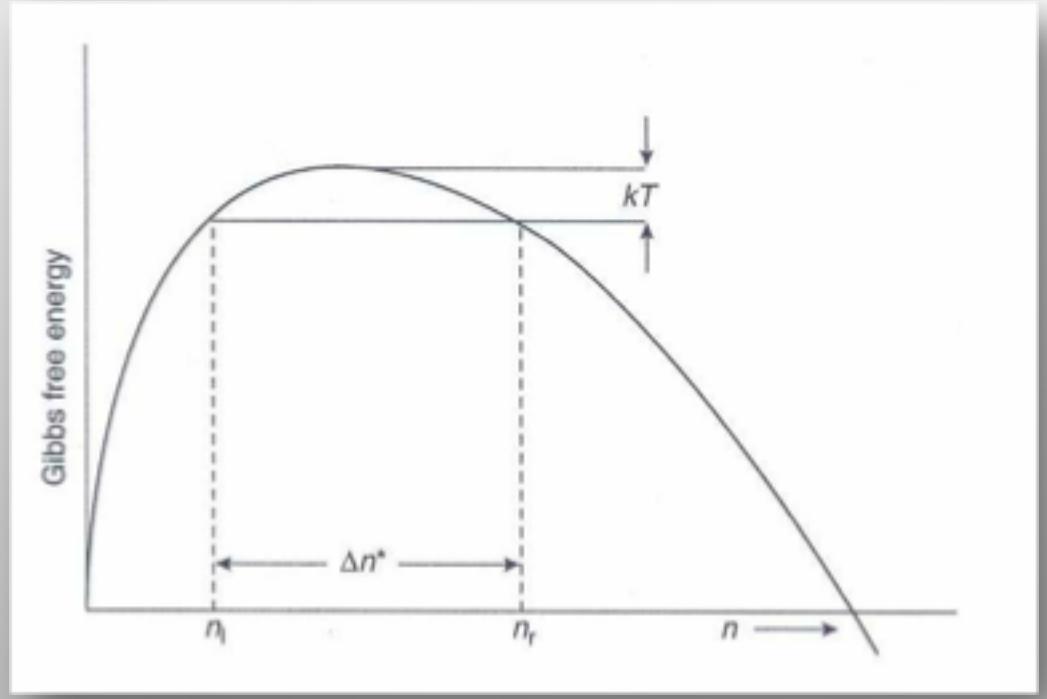
- Nucleus that forms is bcc
- Some of the inside converts to fcc
- fcc/hcp stacking faults present

These results suggest that non-equilibrium phases can not only nucleate but <u>might remain stable</u> over dynamic compression timescales

- Not only is bcc retained, but the dominant phase!
- We are deep in the bcc metastability field
- "Effective cooling rate" was also higher here, larger driving force – but didn't favor fcc



Nucleation is a stochastic process – getting to the top of the hill is not enough



Y. Zel'doivich

$$Z \approx \sqrt{-\frac{1}{2\pi kT}\frac{\partial^2 \Delta G(n=n^*)}{\partial n^2}}$$

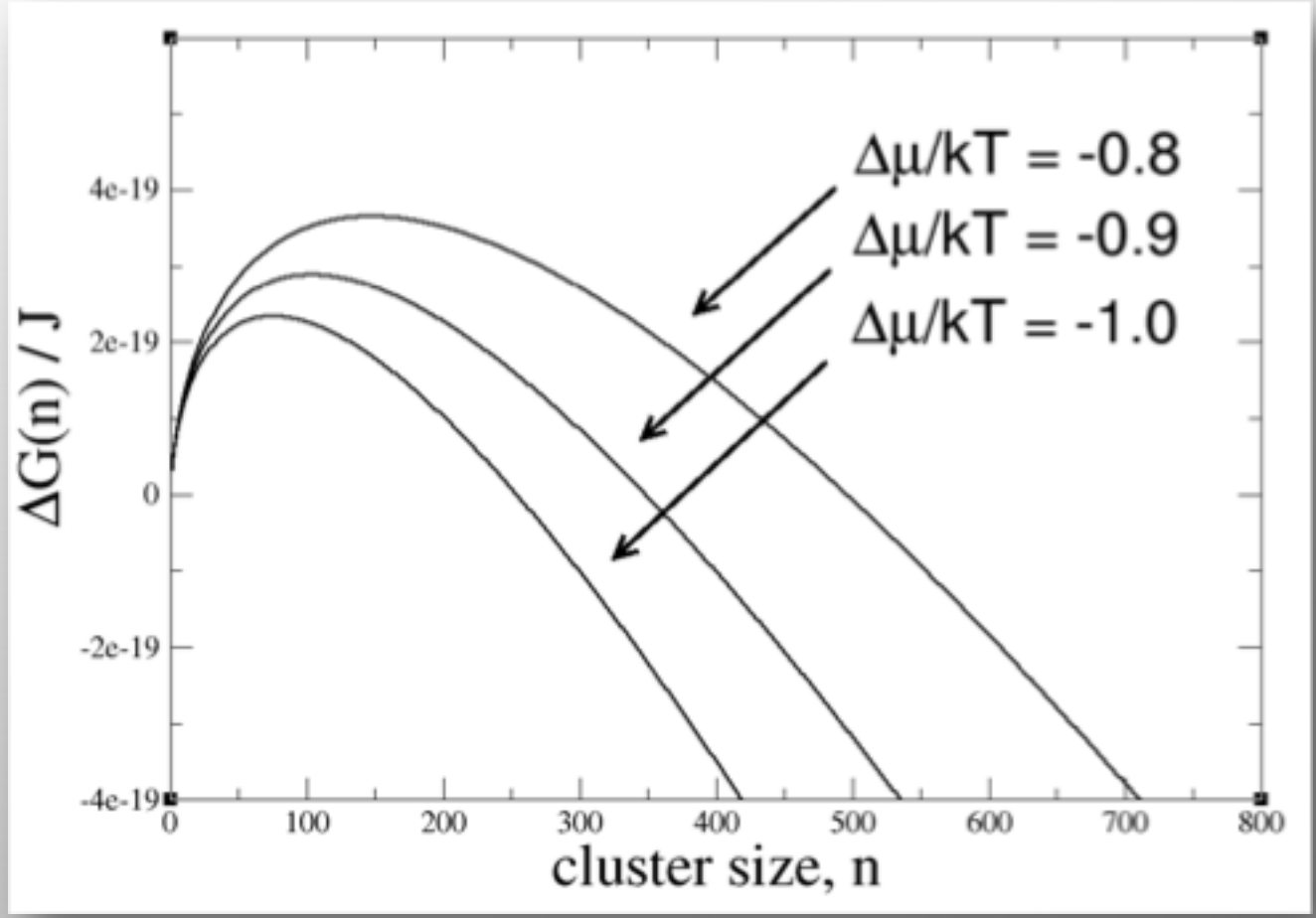
Zel'dovich factor "Z" provides a correction to the nucleation rate, on the order of 10^3-10^5 !

- Zel'dovich considered that attachment is a stochastic process and that the cluster will do a random walk about the barrier

$$J = D^* Z \rho e^{-\Delta G^*/kT}$$

Zel'dovich factor is an approximation – good in one limit, but suspect in another

- Zel'dovich correction reasonable when the curvature of the barrier is small (corresponding to small undercooling / low driving force)
- But for strongly driven system, the cluster doing the random walk will "feel" the potential, creating a more complex response
- Atomistic MD is expensive and probably overkill



Projection operators acting on the atomistic dynamics can provide coarse-grained equations of motion: generalized Langevin equation (GLE)

- Lump atoms together into a cluster of size n, which follows it's own stochastic dynamics
- Starting from initial condition

$$n_i = n^* - \tfrac{1}{2}\,\Delta n$$

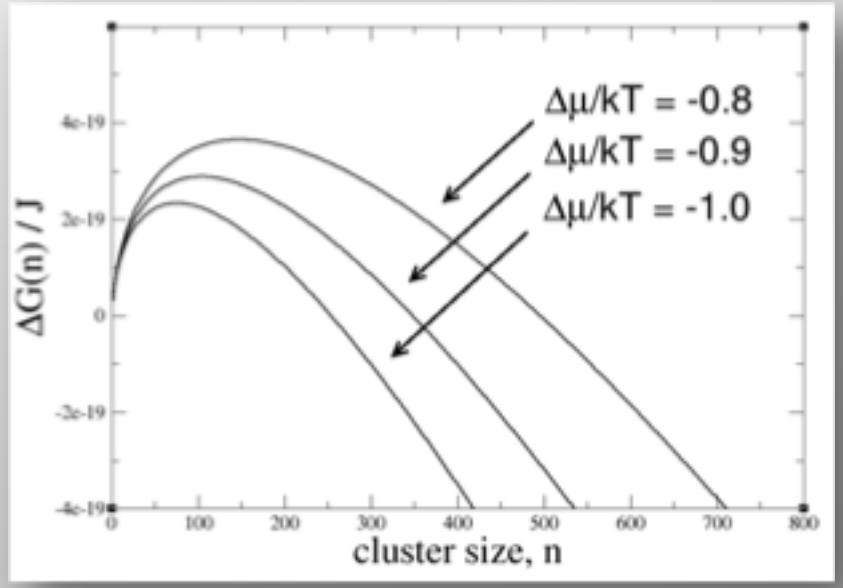
How many random walkers make it to the final condition

$$n_f = n^* + \tfrac{1}{2}\,\Delta n$$

?

Let $\pi(n_i \rightarrow n_f)$ be the probability of a supercritical cluster

$$\frac{dn}{dt} = -\frac{D(n)}{kT}\frac{\partial \Delta G(n)}{\partial n} + \eta(D; kT)$$



Numerical implementation of the GLE

seed RNG

set initial cluster size

Loop over instantiations

Loop over timesteps until cluster is outside of Zel'dovich interval

calculate determistic "force" (based on thermodynamics) and D

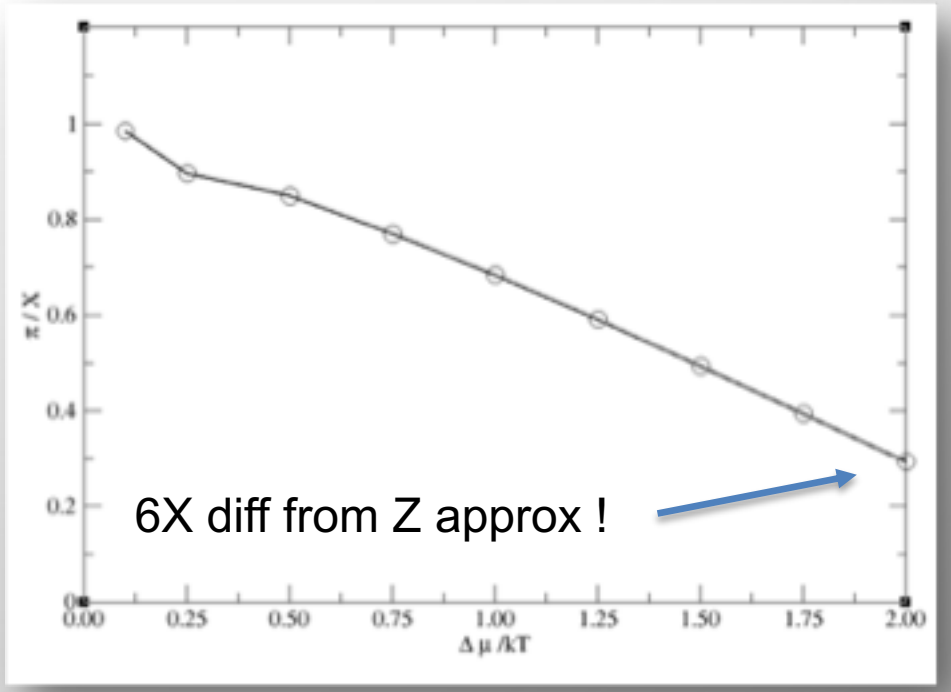
calculate randomly sampled gaussian for the thermal fluctuations

1st order (Euler) or 2nd order (Gunsteren-Berendsen) time integration

update thermodynamics

But there is a problem: in order to reduce the error bars enough for useful correction to the theory, extremely large number of timesteps is required…for the small undercooling limit, CPU cannot give better than 20 % error or so!

Multi-GPU numerical implementation of the GLE



seed RNG

set initial cluster size

Loop over GPUs

Kernel assignment: loop over instantiations

Loop over timesteps until cluster is outside of Zel'dovich interval

calculate determistic "force" (based on thermodynamics) and D

calculate randomly sampled gaussian for the thermal fluctuations

1st order (Euler) or 2nd order (Gunsteren-Berendsen) time integration

update thermodynamics

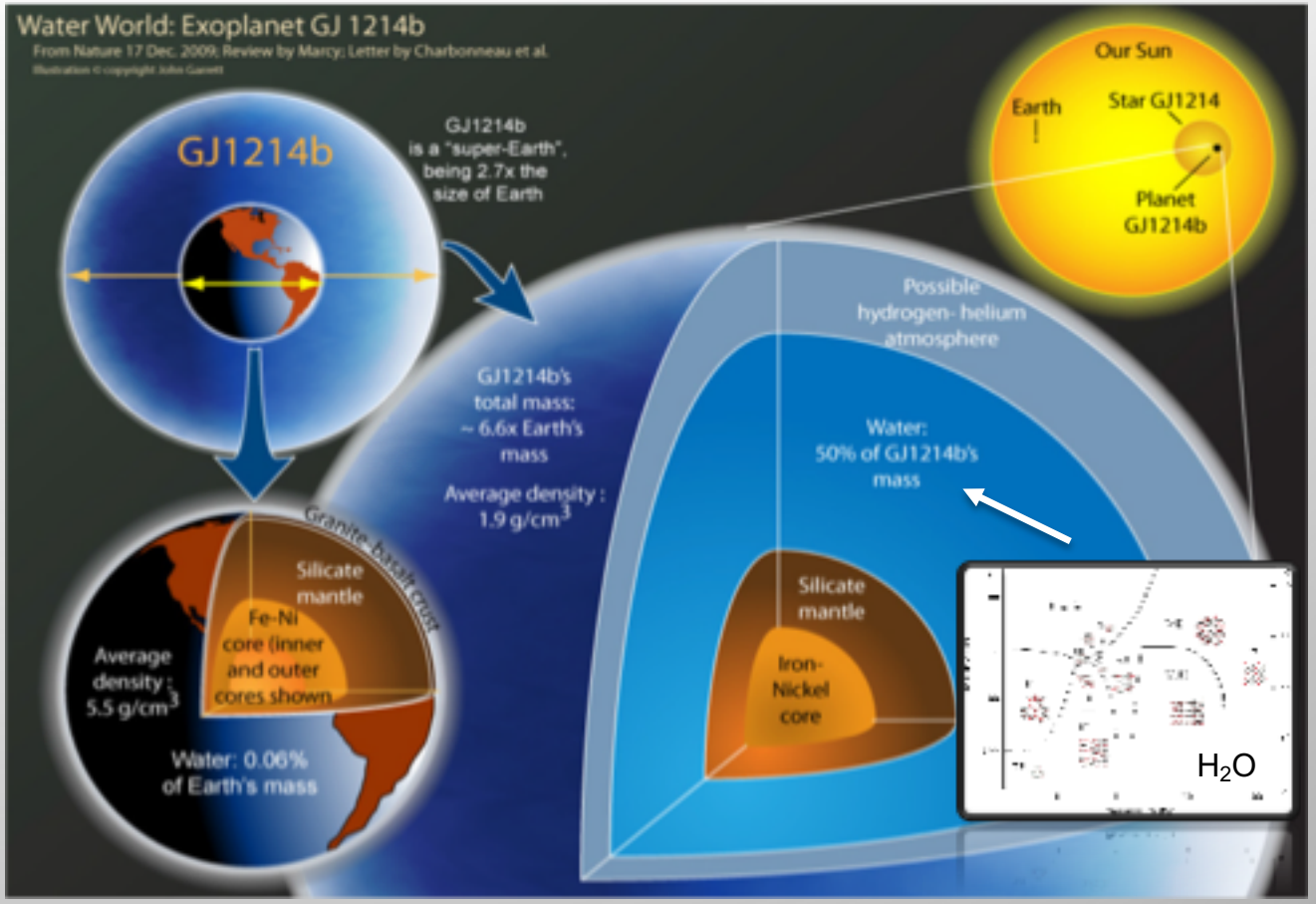
Accumulate and reduce averages

~100X speedup on V100 compared with a single Power9 core

A new age of discovery for extrasolar planetary formation, enabled by observation…

- Estimates of the number of habitable planets greatly exceed predictions [Petigura *et. al*, PNAS 110:19273 (2013], **>40 billion earth-sized in HZ** within MW galaxy alone
- ”Requisite” of water for life, what are it’s bounds?
- Water under “super-earth” conditions invariably at high pressure, liquid-solid boundary from internal heat

Charbonneau *et. al*., Nature 462:891 (2009)

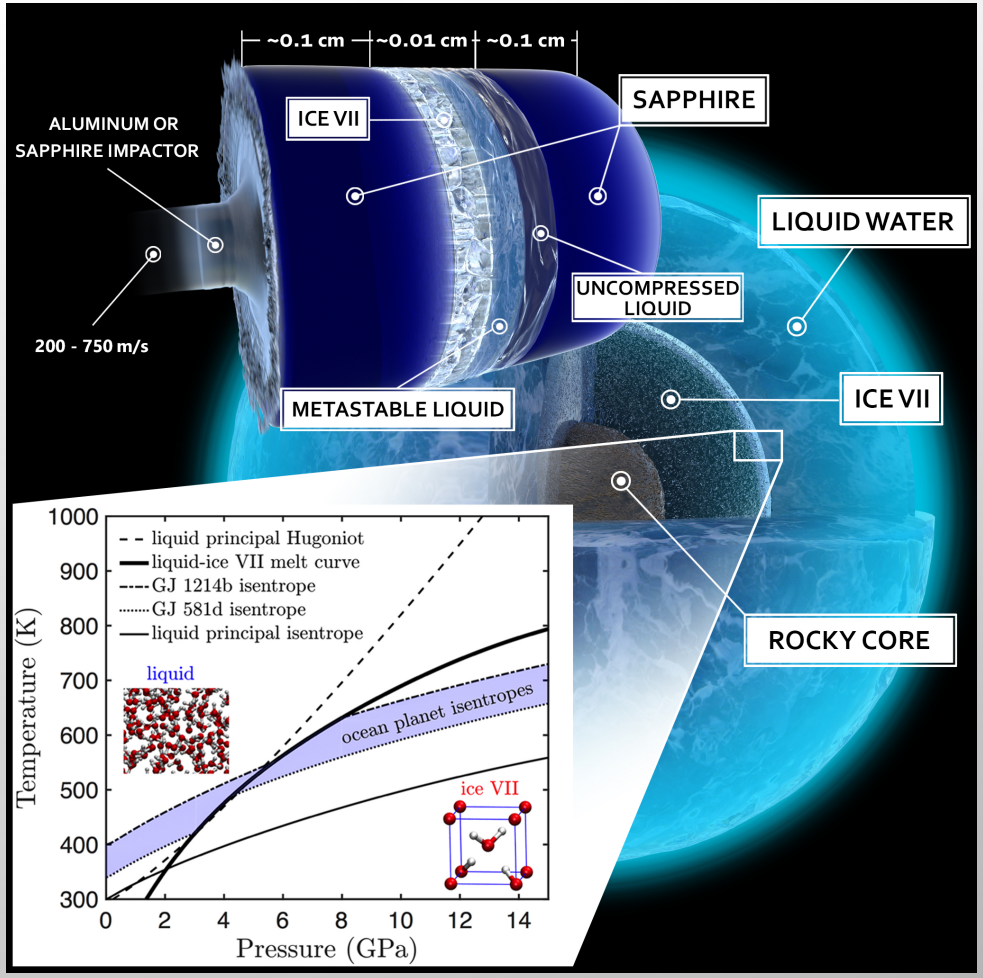


Cleeves *et. al*., “The ancient heritage of water ice in the solar system”, Science 345:1590 (2014)

…Life, quite literally, hangs in the balance of the liquid/ice phase transition

High-pressure/shock experiments to constrain the water EOS

- Laboratory experiments have yielded multiple insights into the nature of high pressure water
- Through quasi-isentrope compression, we can access specific states along the geotherm
- The solidification process takes time – *how can we extract phase boundaries accurately when a phase transition is time-dependent?*



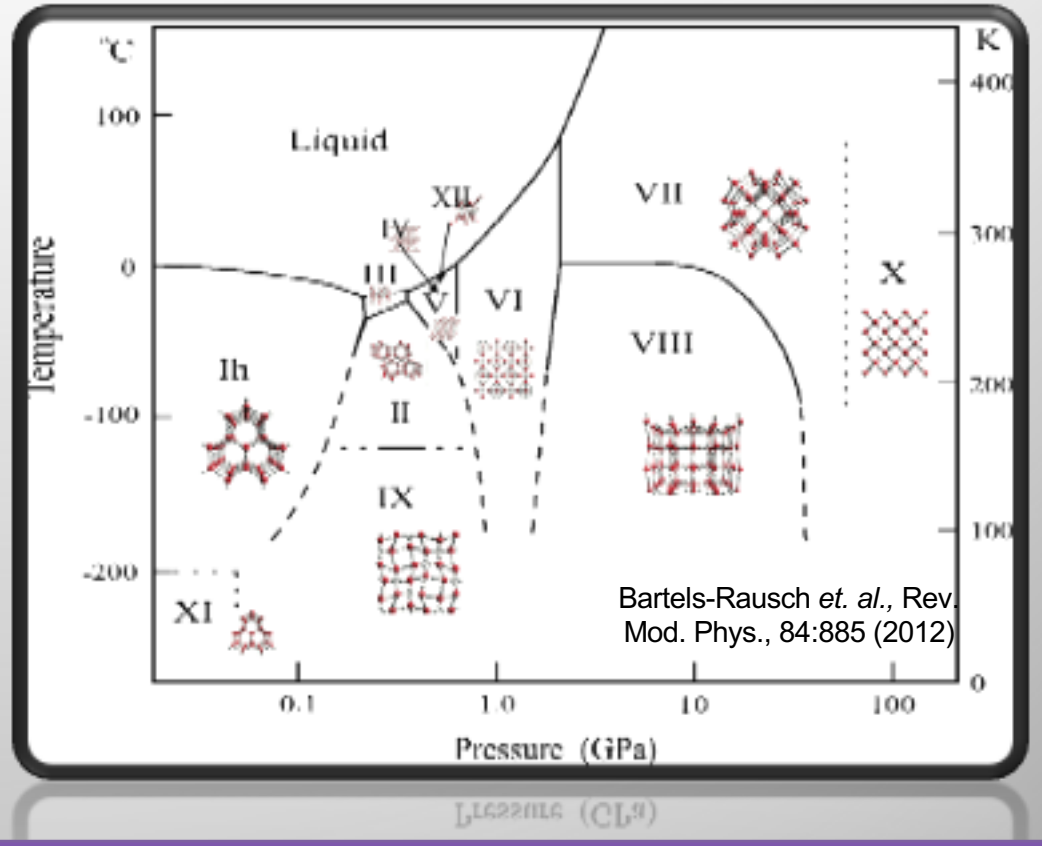
The goal is to untangle equilibrium (relevant for planets) vs. non-equilibrium (what we are stuck with when we do experiments)

H_2O is extremely polymorphic, having over 17 distinct ice phases* (probably even more undiscovered)

*18 now with superionic fcc! Millot *et. al.*

- Highly anharmonic OH vibration
- Vibrational states are in the quantum limit (θ_{vib} > 5,000 K)
- Induced dipole-dipole interactions influence the hydrogen bond network in both liquid and solid phases
- Non-negligible zero point motion of the proton contributes greatly to the heat capacity

"near cancellation" of free energy contributions result in a rich phase diagram



The equilibrium states of water, let alone non-equilibrium transitions, present considerable complexity

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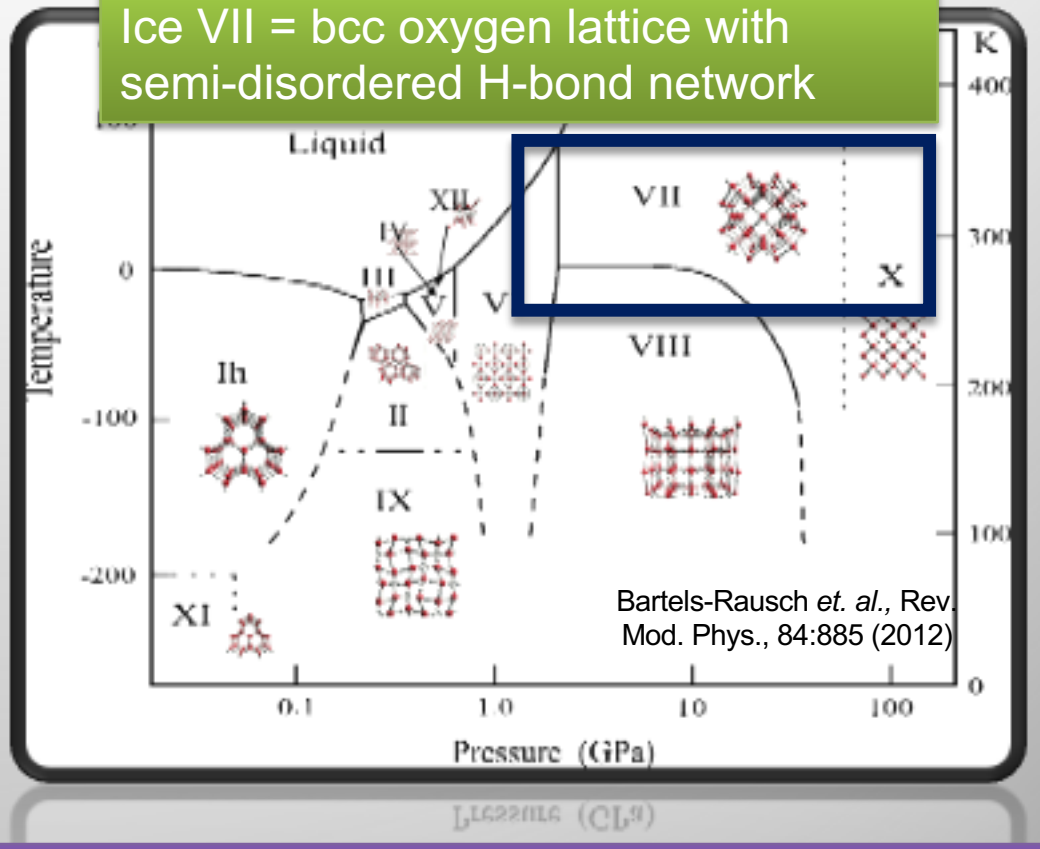
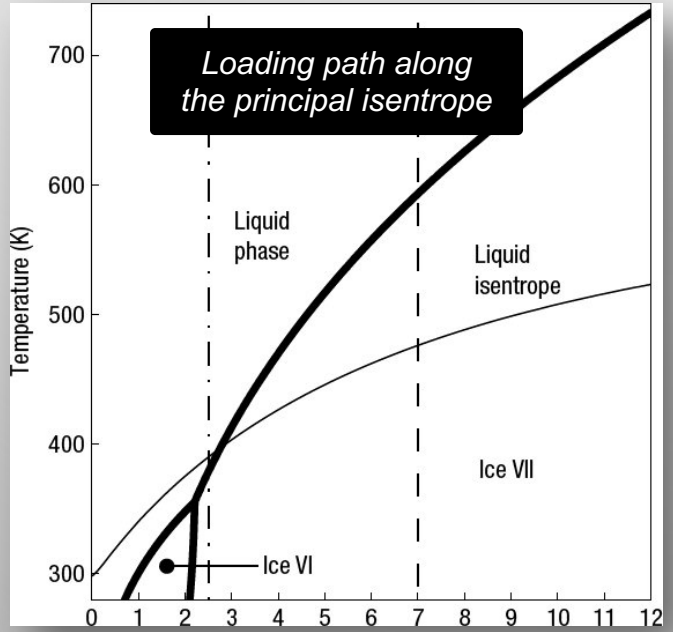
Ice VII = bcc oxygen lattice with semi-disordered H-bond network

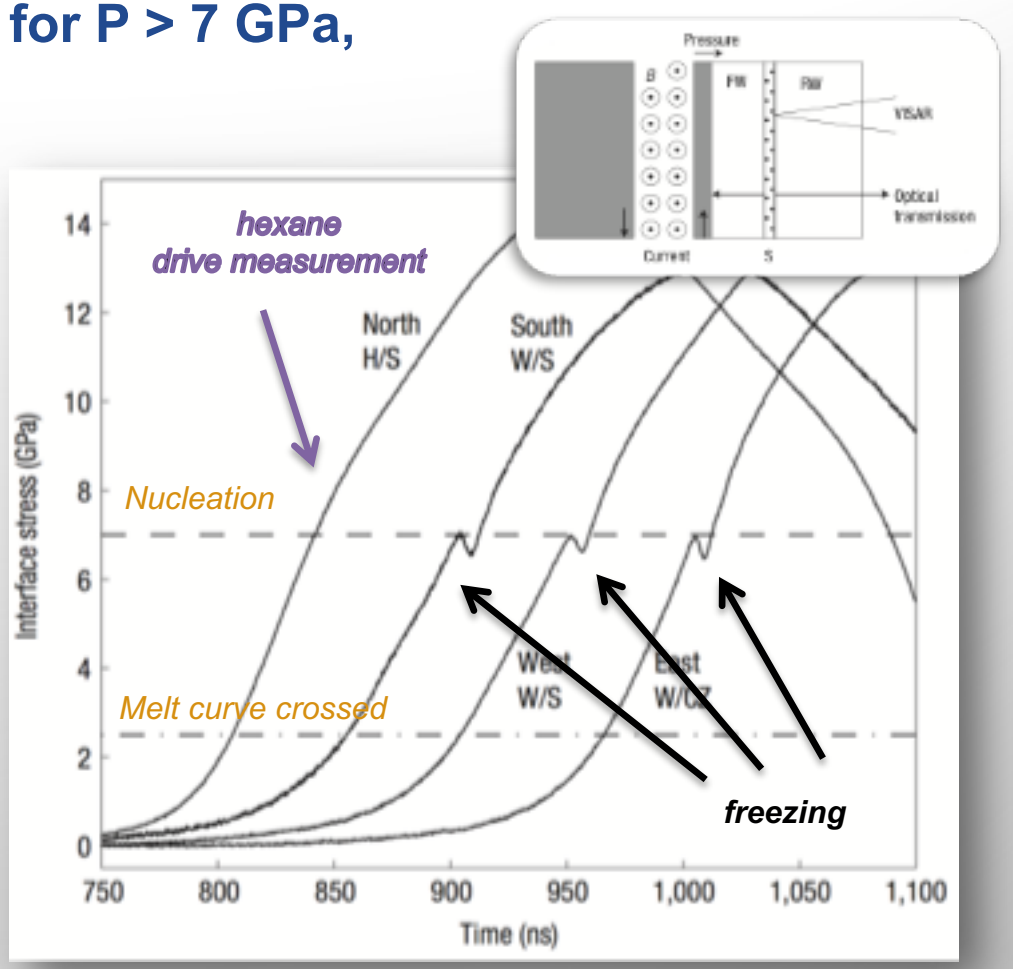


The equilibrium states of water, let alone non-equilibrium transitions, present considerable complexity

Compressive freezing of water occurs with sapphire for P > 7 GPa, Dolan *et. al.*, Nature Lett. 3:339 (2007)

- Thin (25 μm) water sample ramp loaded using a magnetic field (Z machine)
- Ramp compression up to 15 GPa, into ice VII



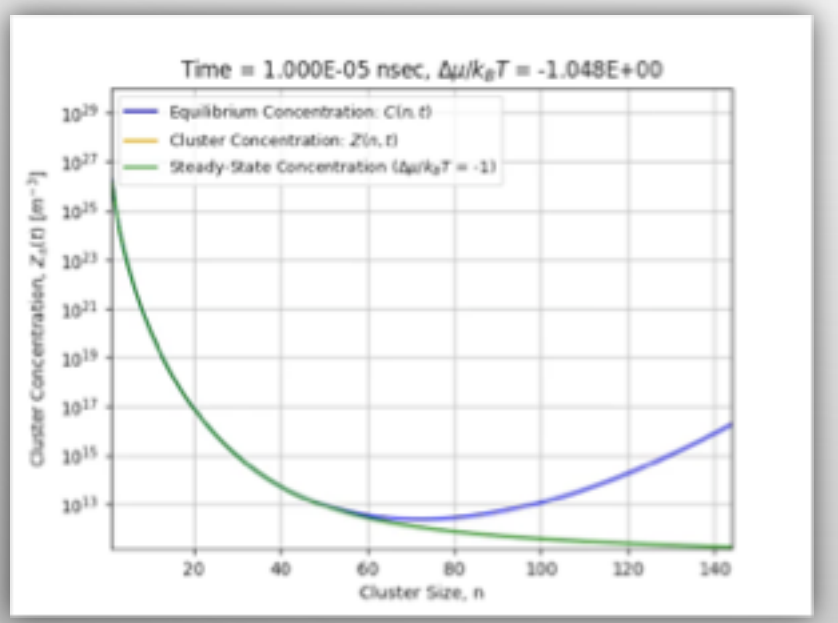


- Wave profiles indicate a freezing transition at pressure well beyond the liquid stability field

These ramp compression results, under more rapid drive to higher pressure, indicate that water is nucleating homogeneously

For a very rapid application of the driving force, there is additional time lag due to developing the cluster distribution

D. Kaschiev, "Nucleation: Basic theory with applications", (2000);
I. Toschev, *J. Cryst. Growth*, **3**:436 (1968);
D. Kashchiev, *Surf. Sci.*, **18**:389 (1969);



Kinetic response toward a steady-state

Zel'dovich-Frenkel eqn provides the *general solution:*

$$\frac{\partial}{\partial t} f(n,t) = -\frac{\partial}{\partial n} F$$

$$F(n,t) = -D(n) f_{eq}(n) \frac{\partial}{\partial n} \left\{ \frac{f(n,t)}{f_{eq}(n,t)} \right\}$$

e.g., under assumption of steady state: $J = F(n^*, t)$ for all t

$$J = J_0 \left\{ 1 + 2 \sum_{k=1}^{\infty} (-1)^k \exp\left(-k^2 \frac{t}{\tau} \right) \right\}$$

$$\tau = \frac{8kT}{\pi \lambda D^*} \qquad \lambda = \frac{\partial^2 G}{\partial n^2}\Big|_{N^*}$$

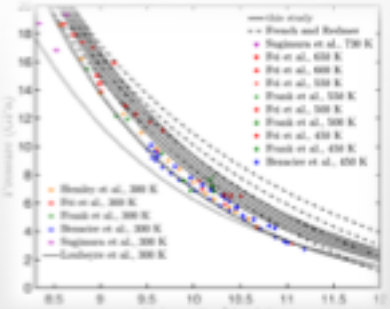
This extension to CNT is critically important for very rapid cooling or compression rates

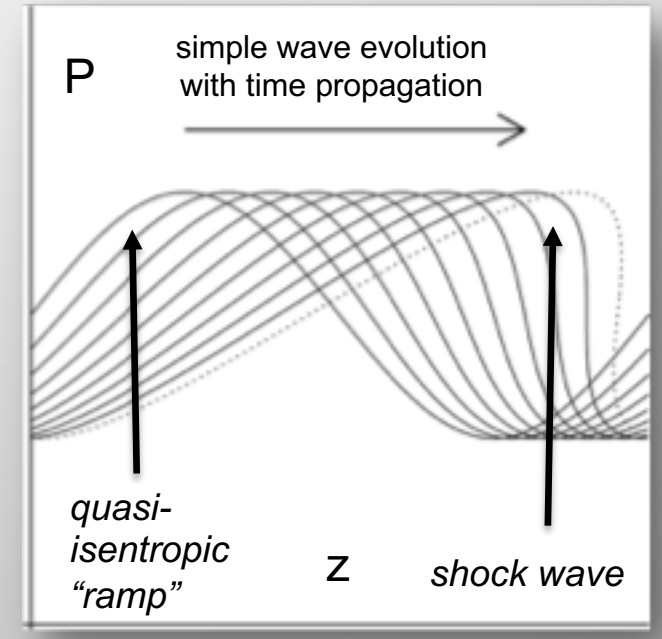
The hydrodynamic equations lead to singular behavior – the "shock wave"

For simplicity, let's assume the Euler form for the hydrodynamic equations (in Lagrangian frame, covariant derivative)

$$\left.\begin{aligned} \frac{\partial \rho}{\partial t} &= -\rho \nabla \cdot u \\ \rho \frac{\partial u}{\partial t} &= -\nabla P(\phi) \\ \rho \frac{\partial E}{\partial t} &= -P(\phi) \nabla \cdot u \end{aligned}\right\} =$$

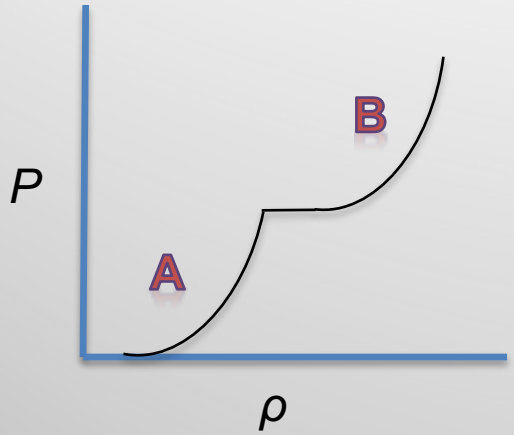
+



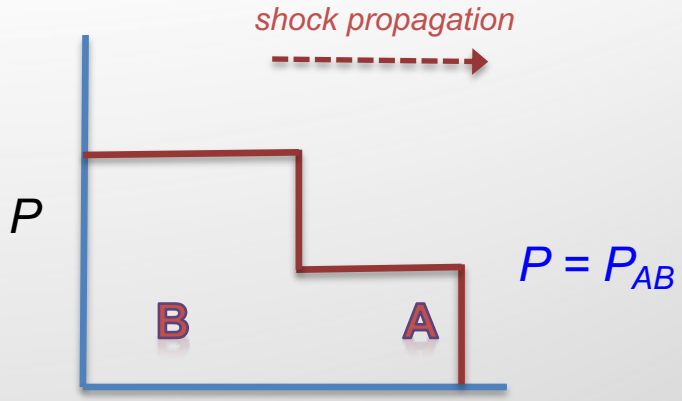


Subject to lack of dissipation, any simple wave (if allowed enough space/time to propagate) will evolve into a shock wave

How does a first-order phase transition affect the propagation of a shock-wave?

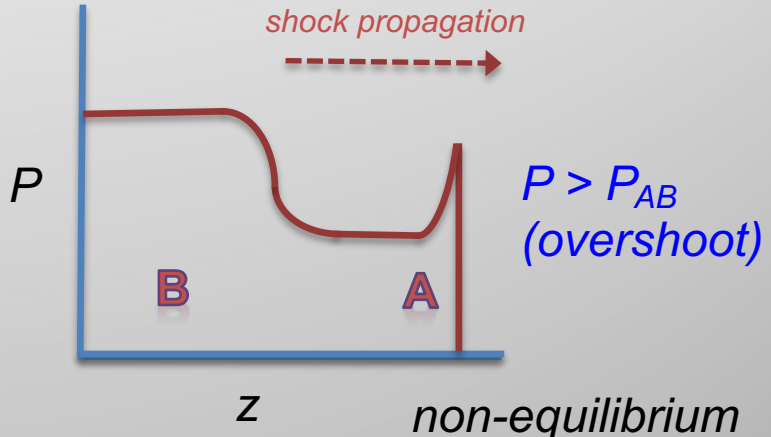


Transition
from phase A
to phase B



$P = P_{AB}$

equilibrium



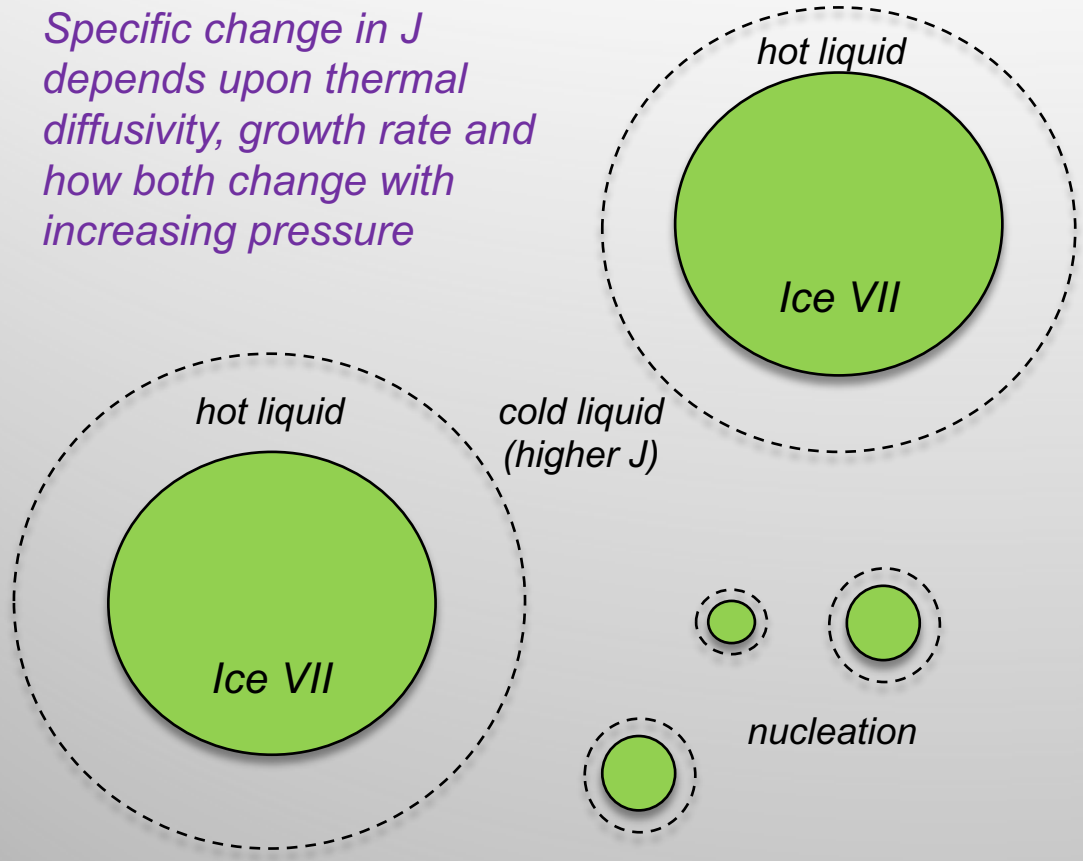
$P > P_{AB}$
(overshoot)

non-equilibrium

Information about the kinetics processes can sometimes be encoded in the time-dependent material response/observables, with (sometimes) simple interpretation

Under the HED conditions, the driving force of water is so high that heat transport plays no active role

Specific change in J depends upon thermal diffusivity, growth rate and how both change with increasing pressure



$$T_{liquid} = T_m - \frac{\Delta H}{C_p}$$

(latent heat propagation)

$$P_{solid} = P_{liquid} + \frac{2\sigma}{r}$$

(Laplace pressure)

- Growth rate goes like $\Delta\mu$/kT and can exceed the thermal velocity
- Increasing the loading rate will reduce thermal boundary layer and increase nucleation
- On the other hand, faster loading means additional lag time and larger overshoot and reduced wave dispersion (XRD mitigates), not to mention potential shock heating

At 7 GPa, the extreme temperature disequilibrium and competition between attachment vs. thermal transport kinetics eliminates the role of a thermal boundary layer

Hydrodynamic coupling to the phase transition order parameter field

Derivatives are covariant, in Lagrangian frame

$$\frac{\partial \rho}{\partial t} = -\rho \nabla \cdot u$$

$$\rho \frac{\partial u}{\partial t} = -\nabla P(\phi)$$

$$\rho \frac{\partial E}{\partial t} = -P(\phi) \nabla \cdot u$$

- Order parameter field evolution with ALE hydrodynamics
- Pressure flux accounts for mixed phase
- 4th equation for phase evolution relies on sub-grid model
- Inline EOS solution for P, T
- Timestep controls, t-integration, *etc.*

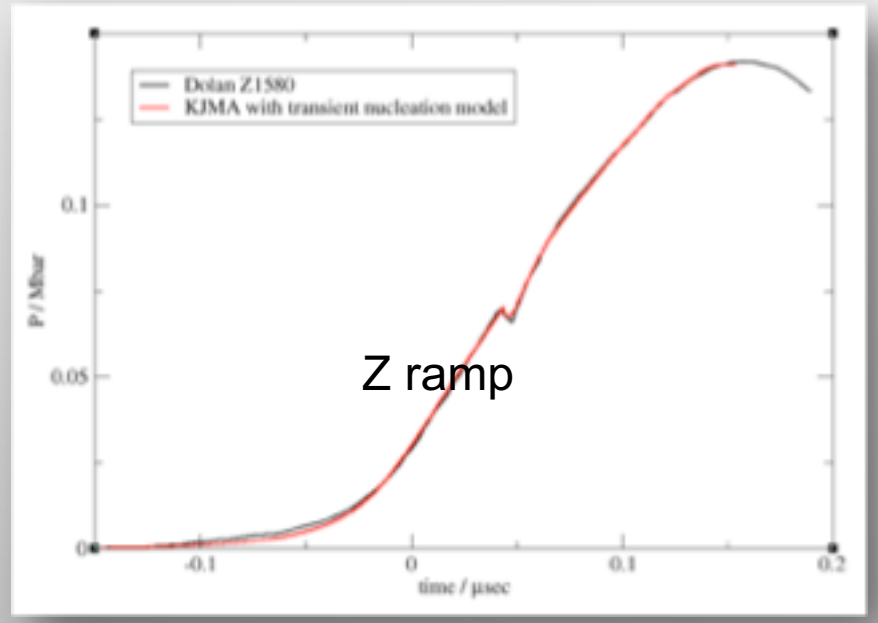
Model implemented in the LLNL kinetics code ***SAMSA***

$$\frac{\partial \phi}{\partial t} = \frac{4\pi}{3}(1-\phi)\left\{3\gamma(t)\int_0^t dt' \, J(t')\left[\int_{t'}^t dt'' \, \gamma(t'')\right]^2\right\}$$

Including all of the previous theory, let's simulate the experiments…

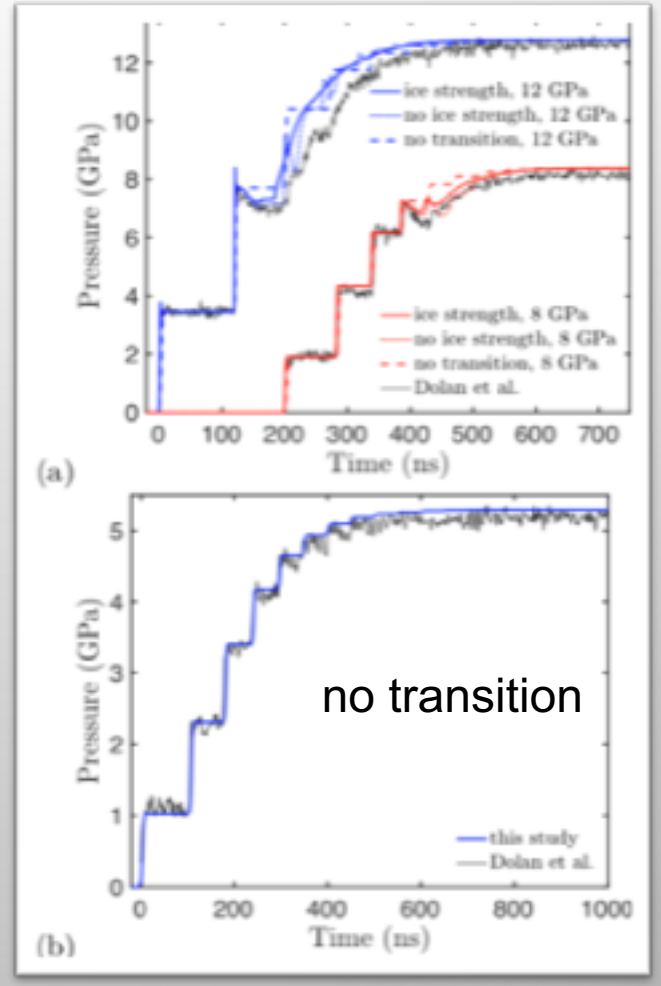
SAMSA simulations quantitative match all higher pressure dynamic experiments

- Ring-up experiments indicate development of strength in ice after solidification



- Physic-based kinetics model appears to work well, once transient and thermal effects accounted for

gas-gun ring-up



Summary

- Scientific and technological impact to understanding phase transformations far from equilibrium
- The role of solidification in exoplanets and the search for extrasolar life
  - Liquid/ice states of water
  - Nucleation kinetics
- Nucleation theory and the role of simulation
- Multiscale nucleation modelling and acceleration with *GPU supercomputing*
- New approach to nucleation kinetics based on coarse-graining and GLE
- Path forward toward concurrent simulations methods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