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Calculations of high pressure melt boundaries

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Crux of the problem is entropy

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- DFT based QMD calculations are naturally and routinely used for calculating pressure (P) and energy (E) at finite temperature
- At low temperatures, information about the forces on the atoms can be used to derive a low energy Hamiltonian for the ion thermal free energy (Harmonic approximation)
- For melting, no such approximation has proven useful
- Several approaches are used
  - Thermodynamic Integration
  - Z-Method
  - Coexistence
  - Direct Calculation of Entropy

Thermodynamic Integration

- Methods exist to relate the free energy at a given density and temperature from one Hamiltonian to another

$$\Delta F = \int_0^1 d\lambda \langle \Delta U \rangle_\lambda \approx \langle \Delta U \rangle_{\lambda=0} - \frac{1}{2k_B T} \left\langle (\Delta U - \langle \Delta U \rangle_{\lambda=0})^2 \right\rangle_{\lambda=0}$$

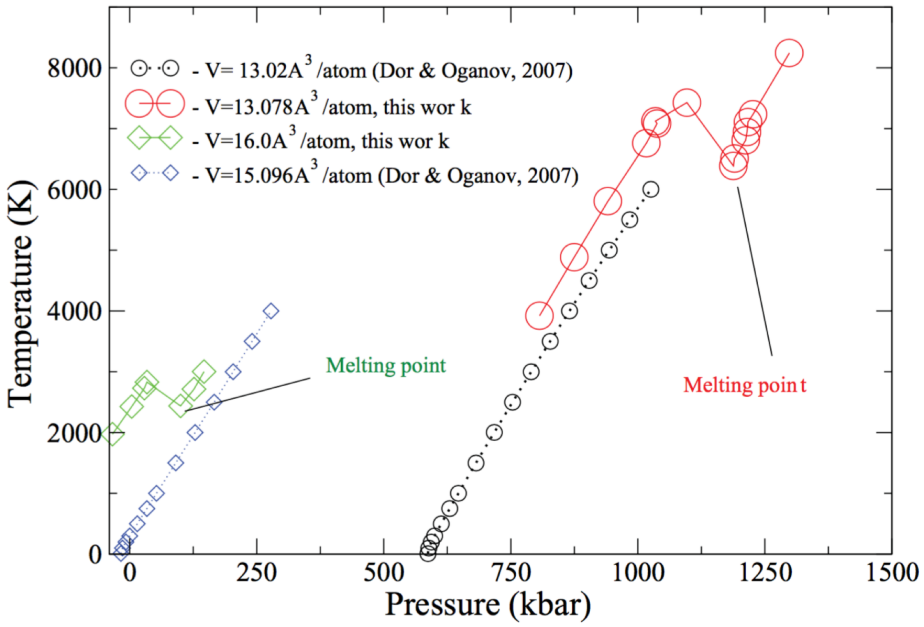
- Procedure
  - Start from classical Hamiltonian where free energy (and hence entropy) is known
  - Run long MD trajectories where the Hamiltonian is replaced by:

$$H = (1-\lambda) H_{ref} + \lambda H_{DFT}$$

  - Perform integration above for each phase
- Drawbacks
  - Requires many different calculations
  - Integrand may not be smooth
  - Ergodic assumption may not be satisfied in practice

”Z method” to dynamically determine melt point

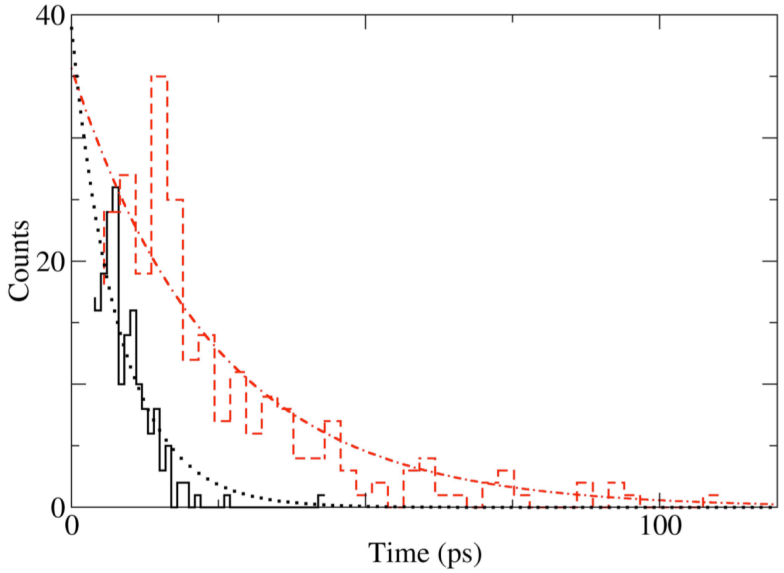
- Ideal: use QMD while manipulating the thermostat
  - Mimic experiment by heating until melting or cooling until freezing
  - Hope phase will change when free energies swap magnitude
  - Problem is short time scales (ps) and small system sizes (nm) guarantee superheating or supercooling
    - Cooling may also find a glassy phase instead of the most stable solid
- The “Z method” performs NVE calculations at successively higher energies monitoring the resulting temperature and pressure
  - Eventually the superheated solid melts, absorbing the latent heat
  - This point is on the melt curve



Belonoshko and Rosengren, PRB **85**, 174104 (2012)

Subtleties of the Z method

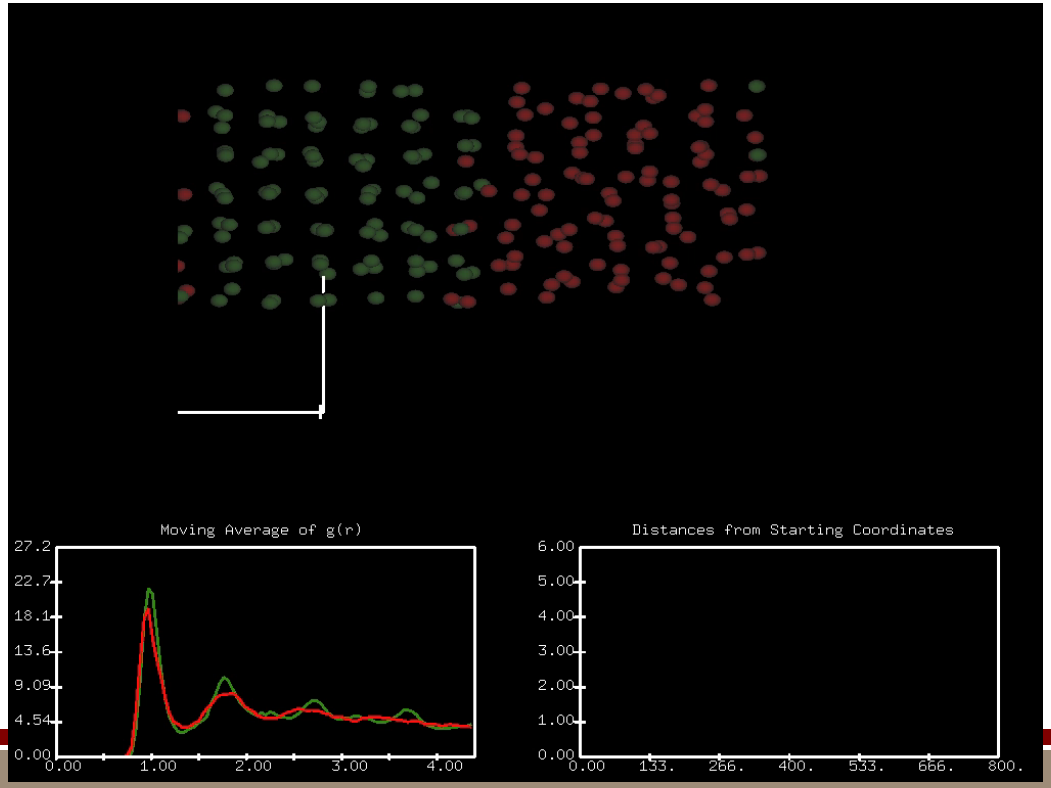
- The Z method rests on an ergodicity assumption
- Near the melt boundary, homogeneous melting may not be quick
- Repeated simulations for melting of Fe often required very long run times
  - Meaning Z method calculations have a tendency to overestimate melt temperature and pressure



Alfe, Cazorla and Price. J. Chem. Phys. **135**, 024102 (2011)

Resorting to Brute Force: Coexistence

- Run at different temperatures or starting energies and watch phase boundary
- Relative heat capacities and enthalpy of melting determine range of phase coexistence



- NVE simulations allow for a range of values on the melt curve to be found
- NVT simulations can bracket melt

Coexistence subtleties

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- Phase coexistence simulations allow a very direct comparison of free energy between phases

- The $O(N^3)$ scaling of DFT means calculations with cells containing 2x the number of atoms cost 8x computer power
- Constraints on system size and cell shape can easily introduce non-hydrostatic stress
- Even very large classical MD calculations have been shown to have significant finite size effects

Direct entropy calculation

- Using long MD calculations, it is possible to calculate the entropy directly
- Method presented in Desjarlais PRE, **88**, 062145 (2013)
  - Extension of 2PT model that divides motion into phonon-like and diffuse-like
  - Change the original hard sphere model for the diffuse component into soft sphere contribution
  - In cases where data is available, it is possible to determine the entropy to within a couple of percent of experiment

Entropy Calculation Subtleties

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- Requires long QMD calculations to obtain accurate velocity autocorrelation function
- Calculations of melting require solid entropy as well as liquid
  - Anharmonic content is treated as an approximate renormalized phonon model
  - Even with a direct application, melt P/T determined to within ~5% for Al at high pressure
- Must take care to add back in other degrees of freedom (electronic or magnetic for instance)
- Extension to multi-component systems is ongoing
  - Most difficult scenario is a fluid with incomplete bonding

Summary

- Several methods exist for calculating high pressure melting curves
- These methods (thermodynamic integration, z-method, coexistence and entropy) work by establishing relative (or direct) free energies
- This can provide a direct check for possible multi-phase EOS construction methods