First principles simulations of supercooled liquids and glasses

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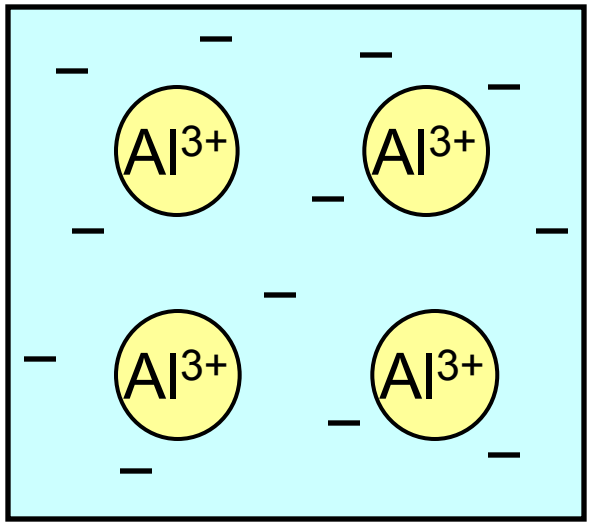
Outline:

- First principles calculation: what? why?
- Metallic glass: structure, formation and optimization
- Supercooled silicon: a liquid-liquid phase transition

Electronic Density Functional Theory



FCC Aluminum, one unit cell

- Born-Oppenheimer approximation
- Wavefunction $\Psi^{(N)}(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)$
- Schrödinger: $\mathbf{H}\Psi^{(N)} = E\,\Psi^{(N)}$

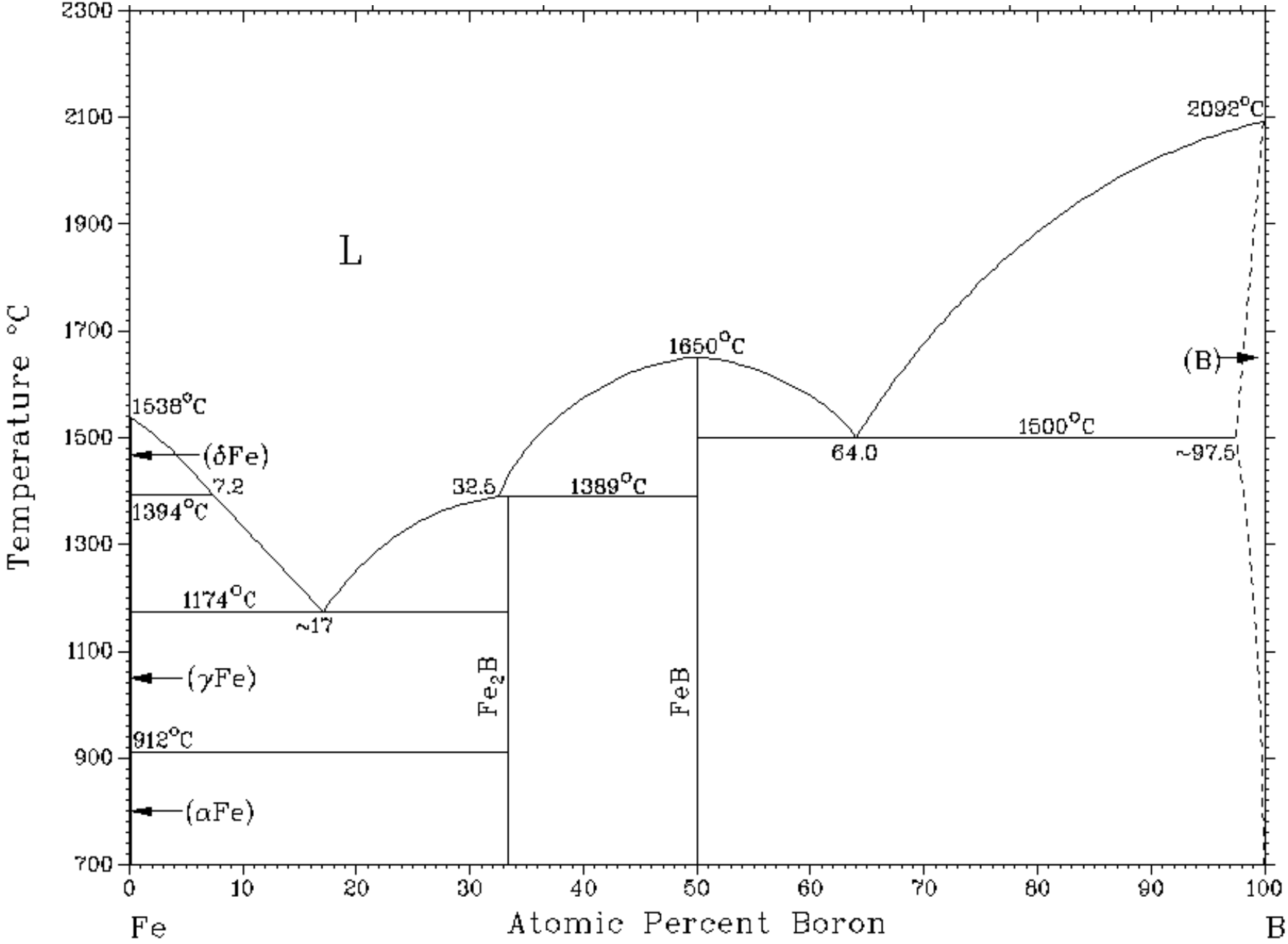
Hohenberg-Kohn/Kohn-Sham:

Transform $\Psi^{(N)}$ to *N* coupled 1-body problems for $\psi(\mathbf{r})$

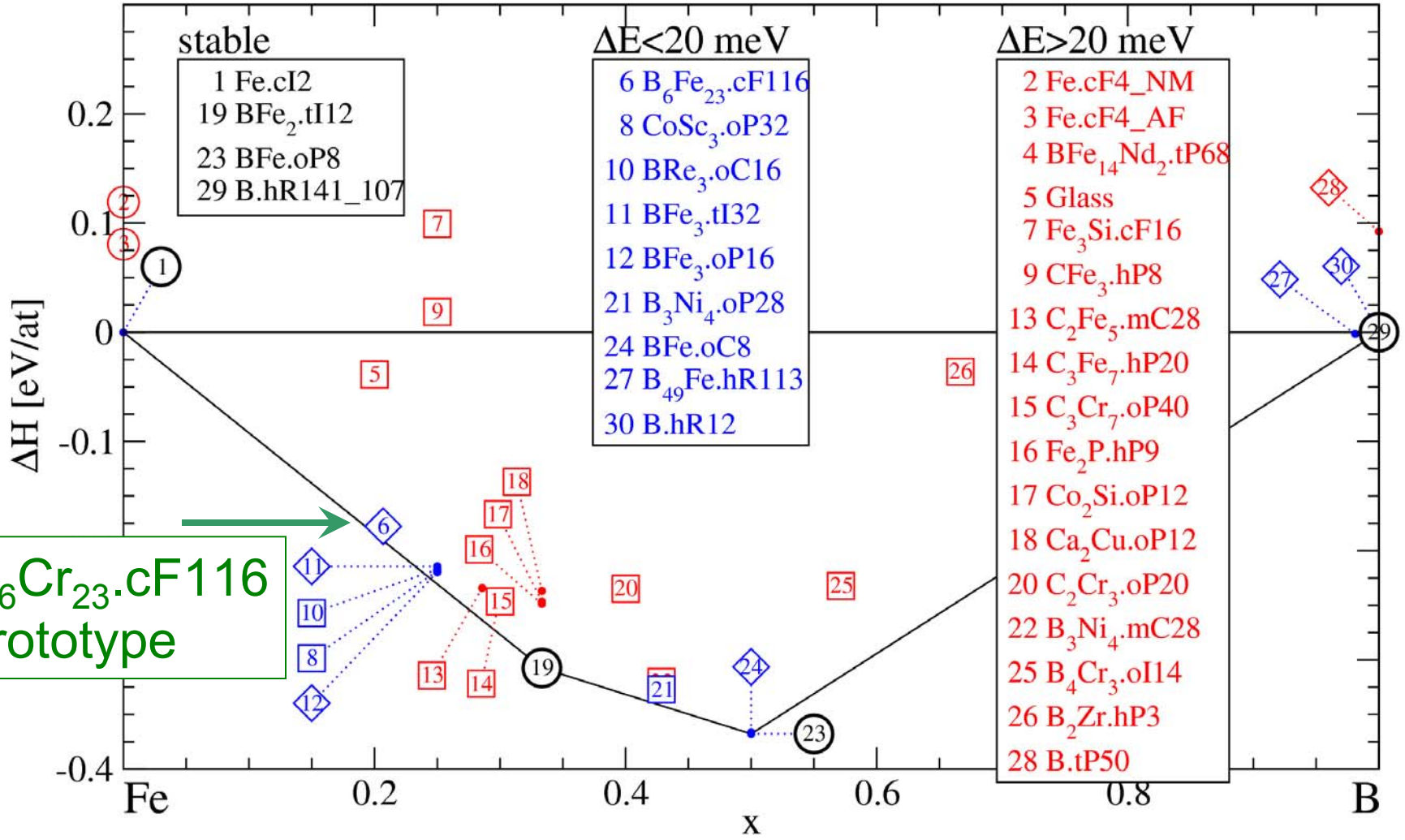
$$\left(-\frac{1}{2}\nabla_i^2 + V_{eff}(\mathbf{r}) - \varepsilon_i\right)\psi_i = 0 \qquad E = \sum_{i=1}^{N} \varepsilon_i$$ - *(double counting)*

- $V_{eff} = V_{eff}[\rho(\mathbf{r})]$ ... but $\rho(\mathbf{r}) = \Sigma_i |\psi_i(\mathbf{r})|^2$
- Evaluate $V_{eff}[\rho(\mathbf{r})]$ in LDA or GGA

Iron-Boron Phase Diagram



Enthalpy of formation

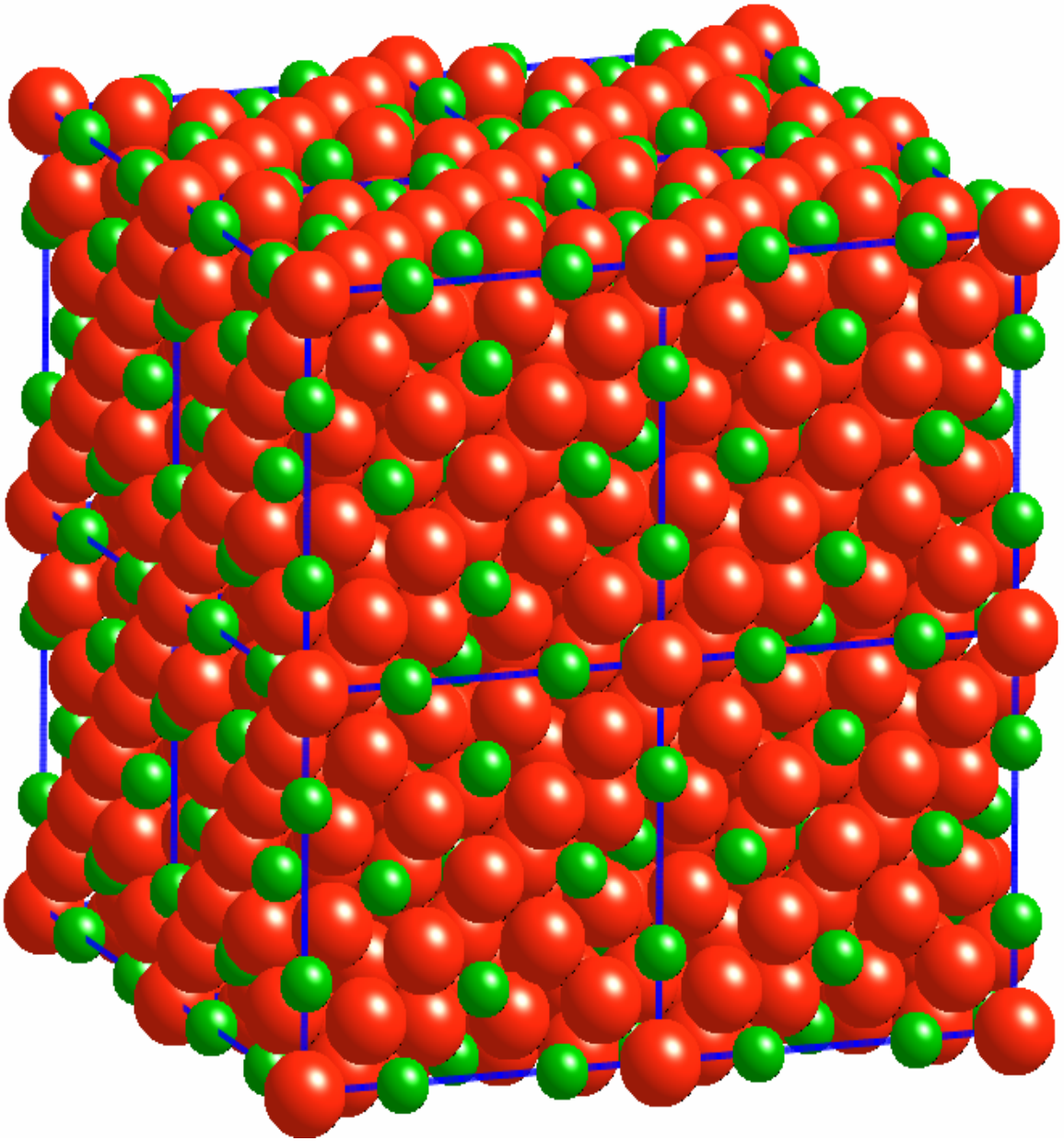


C_6Cr_{23}.cF116 prototype

○ Known LT stable ◇ Known metastable

○ Known HT stable □ Unknown/hypothetical http://alloy.phys.cmu.edu

B_6Fe_{23} in C_6Cr_{23} prototype, Pearson notation cF116



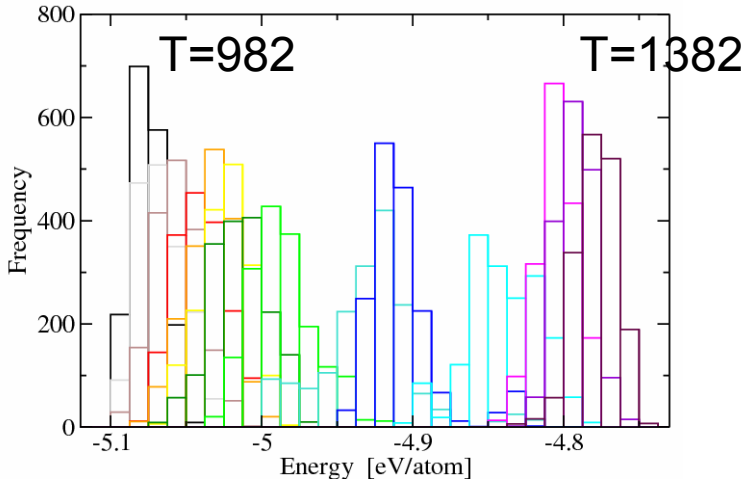
Fe

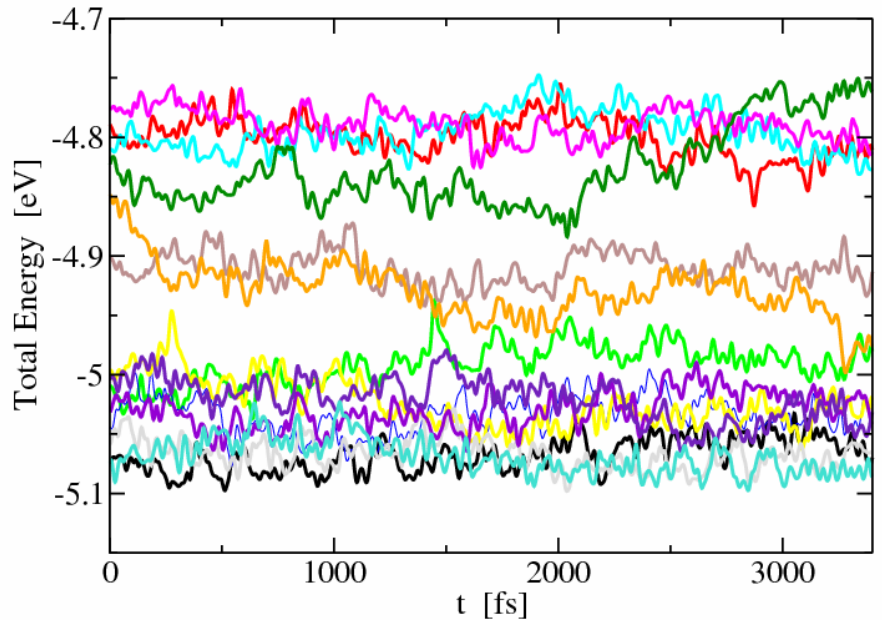
B

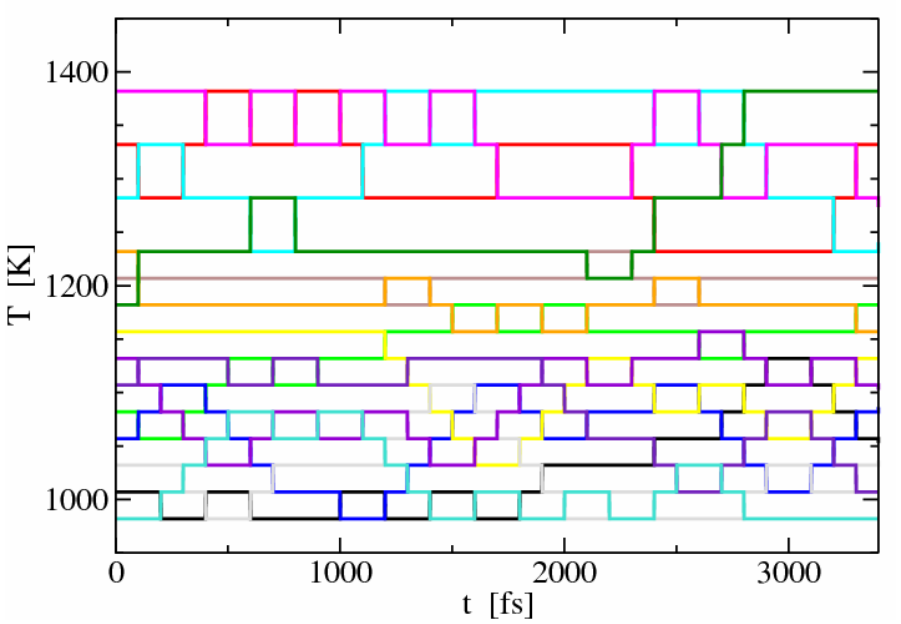
Tempering Molecular Dynamics

run:1 at $\beta_1=1/k_BT_1$ with energy E_1
run:2 at $\beta_2=1/k_BT_2$ with energy E_2

Swap Probability ~ $\exp(\Delta\beta\Delta E)$







(Multiple) Histogram Method

Ferrenberg & Swendsen (1989)

- Energy histogram at temperature T: $H_T(E)$
- Configurational density of states: $\Omega(E) \sim H_T(E)\, e^{+E/k_BT}$
- Partition function: $Z(T) = \int \Omega(E) e^{-E/k_BT}\, dE$
- Free energy (Helmholtz): $F(T) = -k_BT \ln Z(T)$
- Combine multiple temperatures:

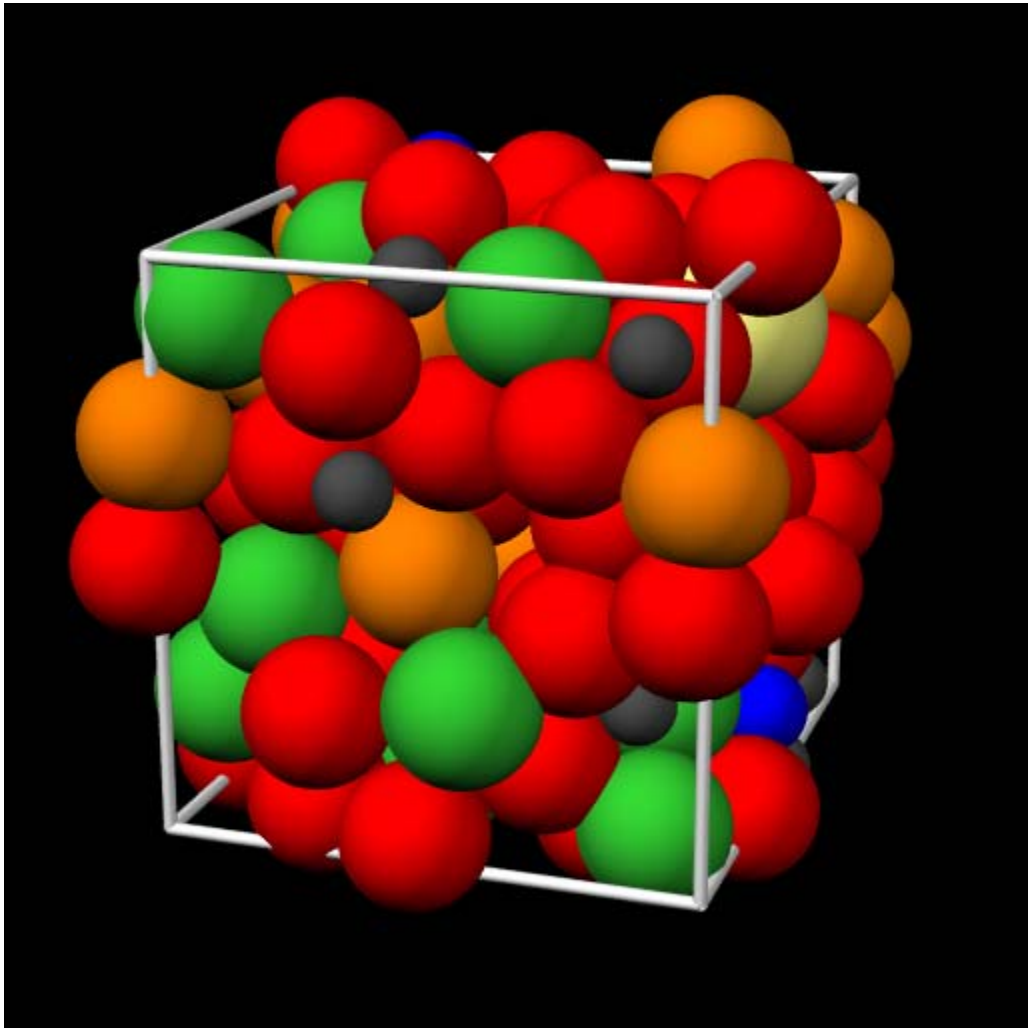
$$\Omega(E) = \{\Sigma_T\, H_T(E)\} / \{\Sigma_T\, e^{(F(T)-E)/k_BT}\}$$

- Averages:

$$U(T) = \int E\Omega(E) e^{-E/k_BT}\, dE, \qquad P(T) = \int \langle P \rangle (E) \Omega(E) e^{-E/k_BT}\, dE$$

Simulated Glassy Structure

$Fe_{48}B_6C_{15}Er_2Mo_{14}Cr_{15}$



Iron

Boron

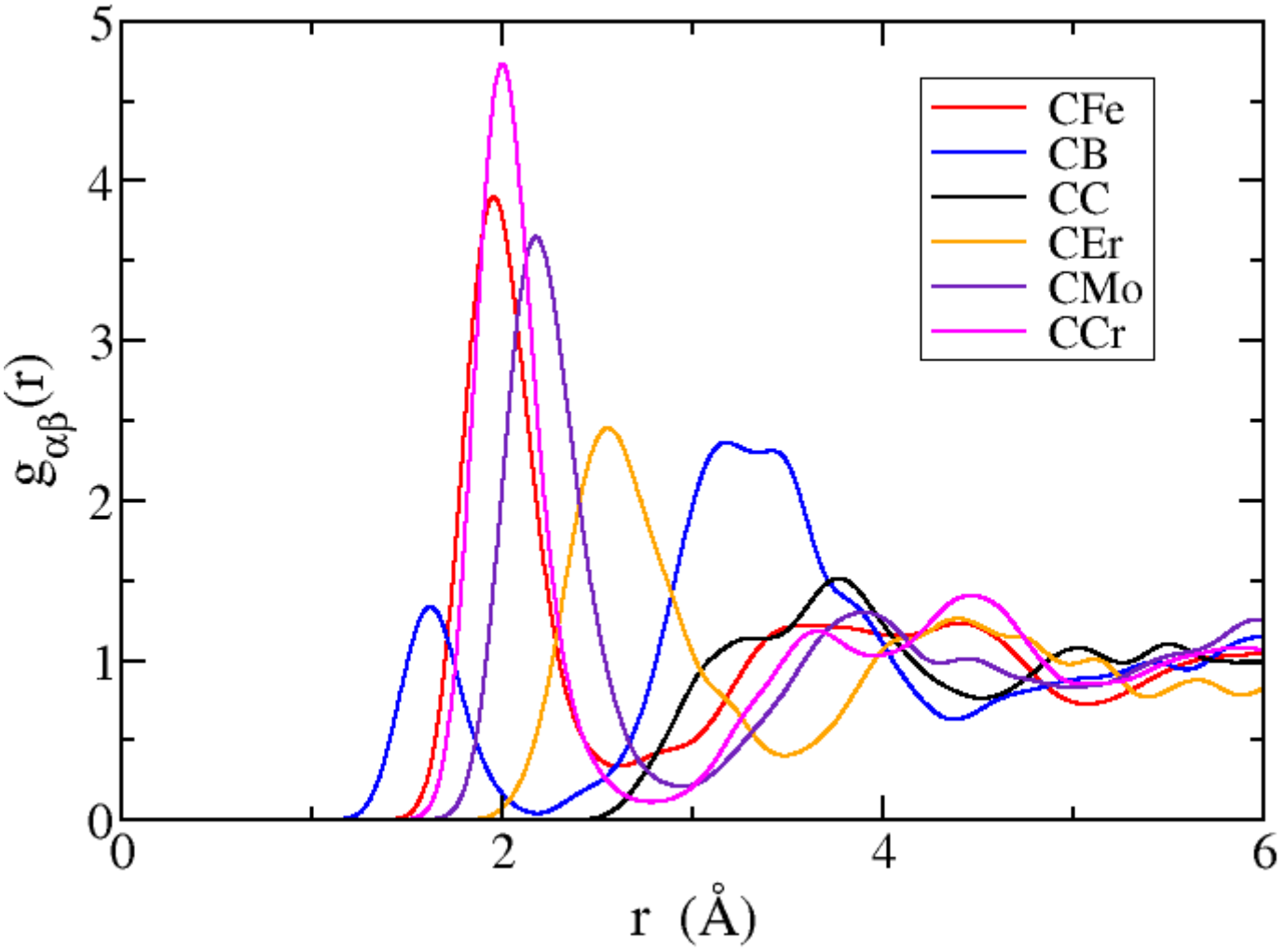
Carbon

Erbium

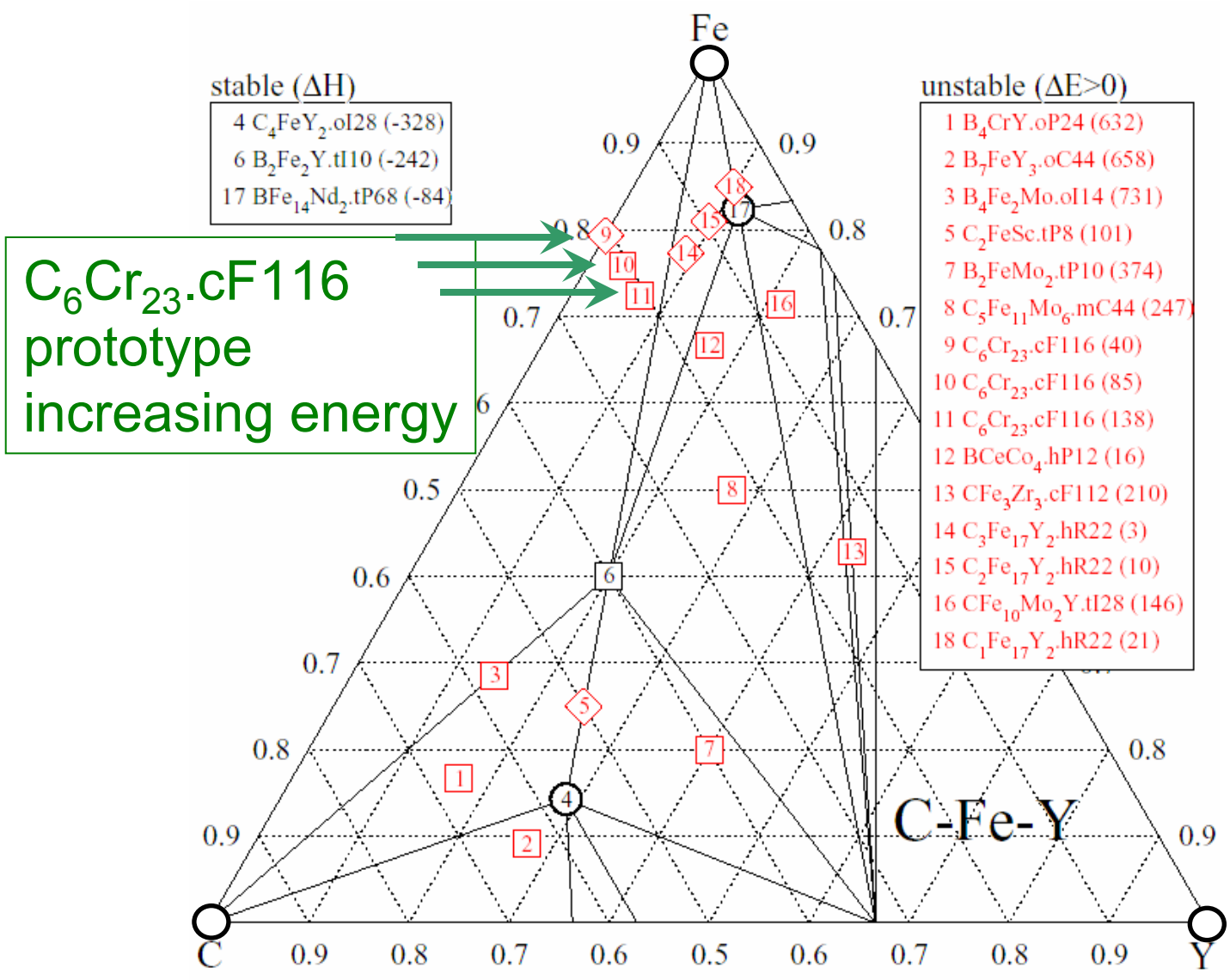
Chromium

Molybdenum

Carbon Pair Correlation Functions
Liquid $Fe_{48}B_6C_{15}Er_2Mo_{14}Cr_{15}$ T=1000K (VASP-TMD)

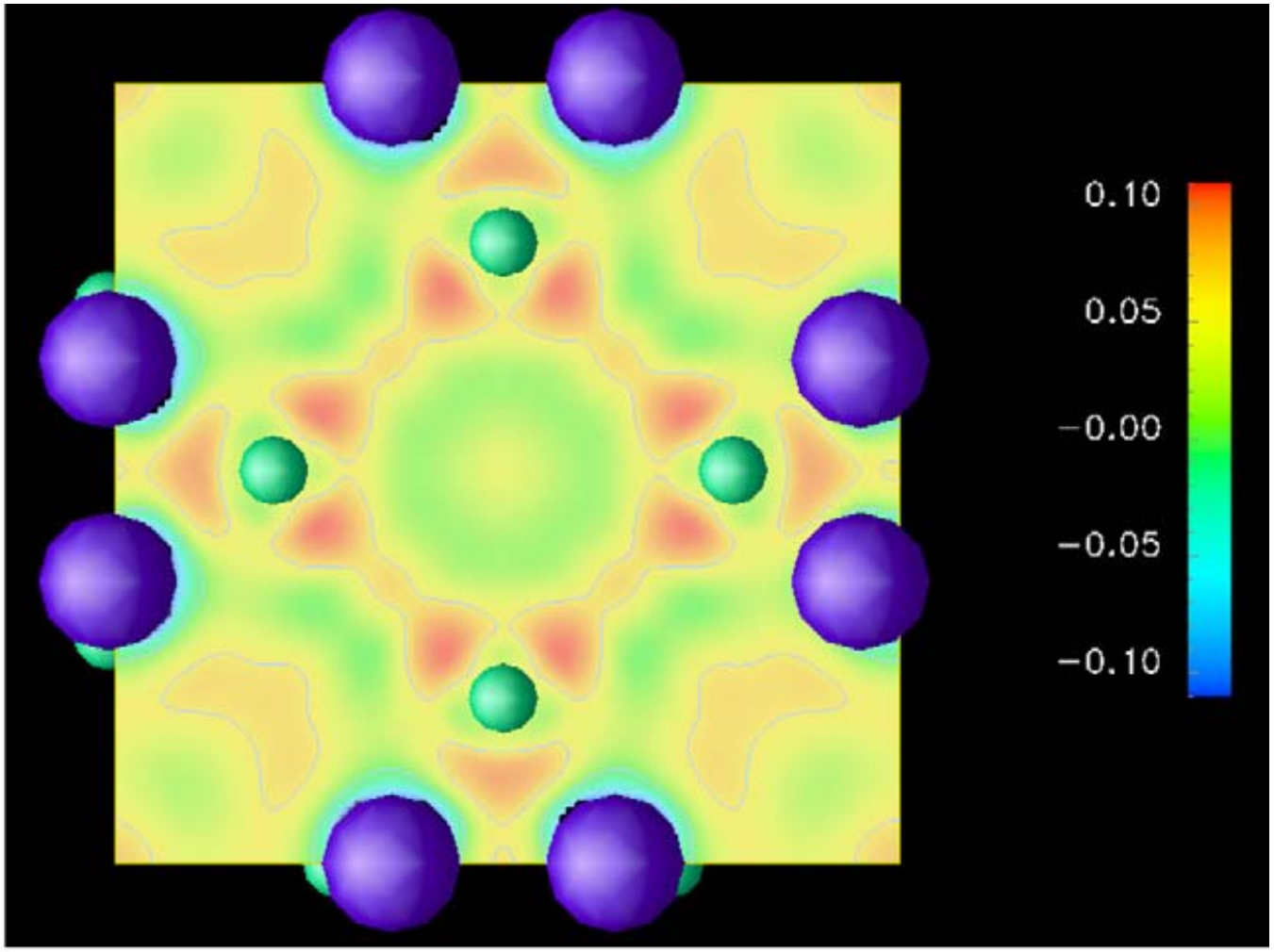


Ternary Enthalpy Diagram ==>> Glass Formability



Bonding Analysis

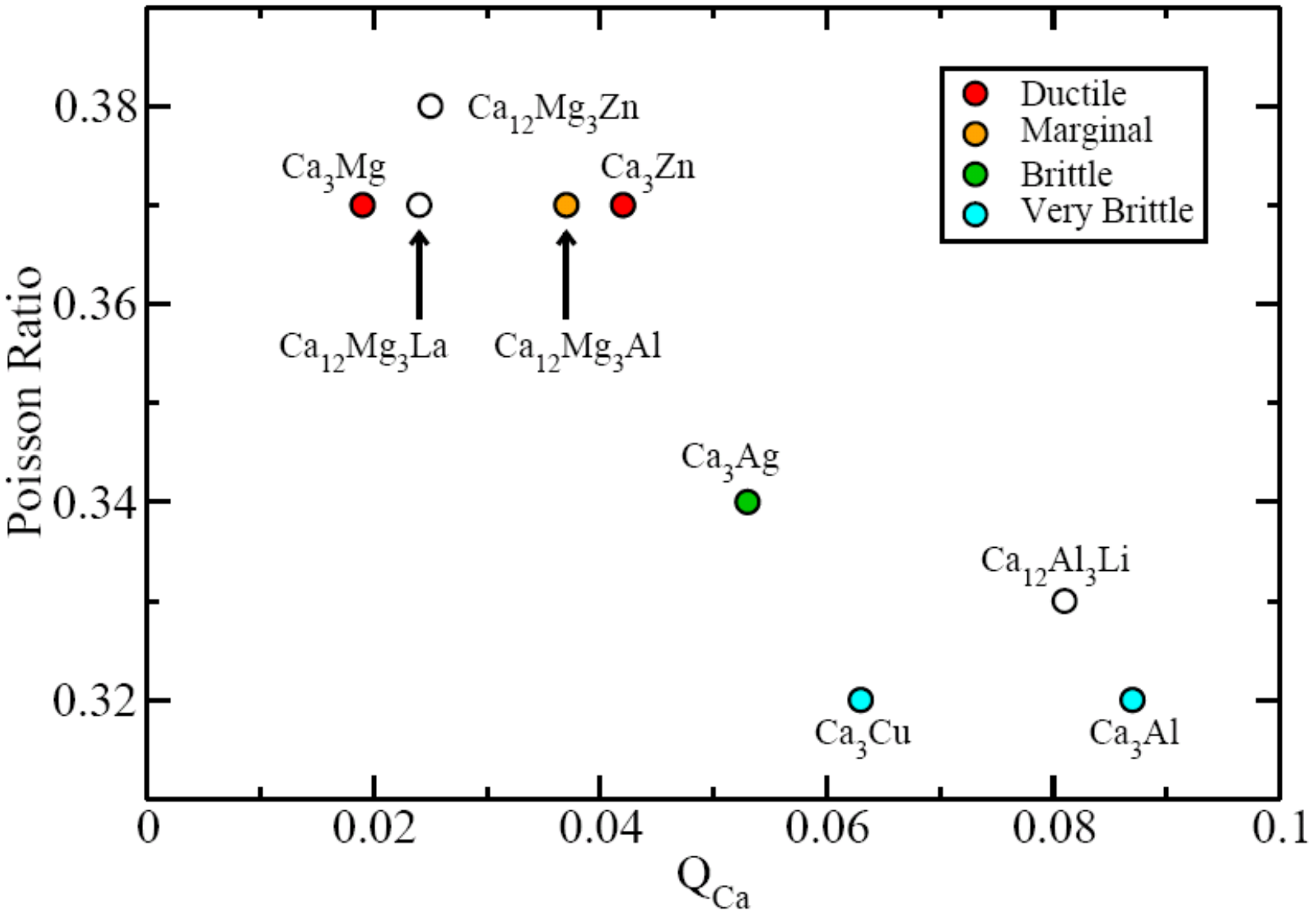
Charge transfer ΔQ COHP $\langle \chi_\alpha(R_i)|H_{dft}|\chi_\beta(R_j)\rangle$



Iron

Carbon

Engineering ductility of Ca-based glass



Conclusions (Metallic Glass)

- First-principles total energy, band structure and molecular dynamics

Method of high realism, but computationally intensive

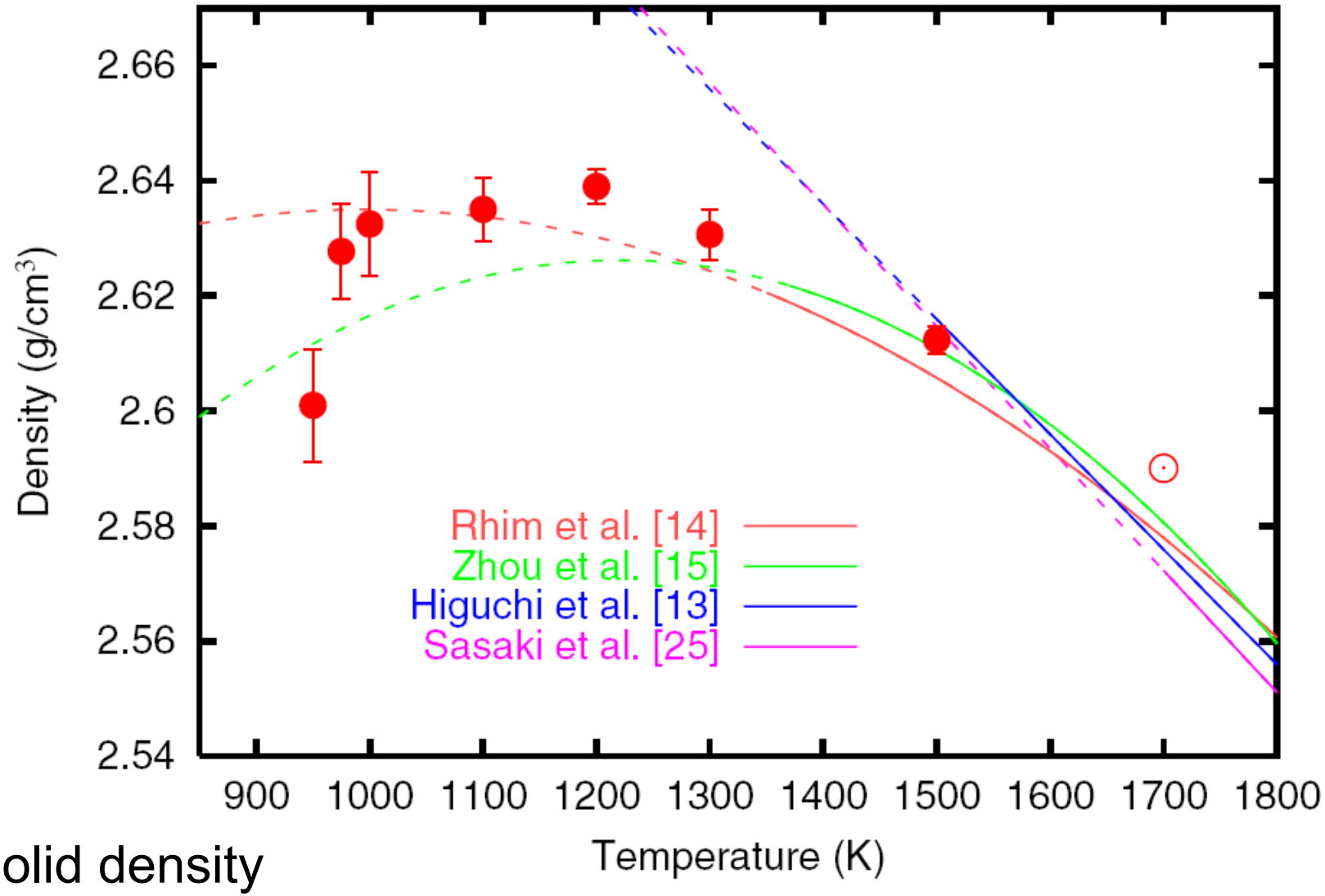
- Enthalpy (relative cohesive energy)

Predicts phase stability relevant to glass formation

- Interatomic bonding (ΔQ and COHP)

Can assist in predicting mechanical properties including ductility

Density of silicon

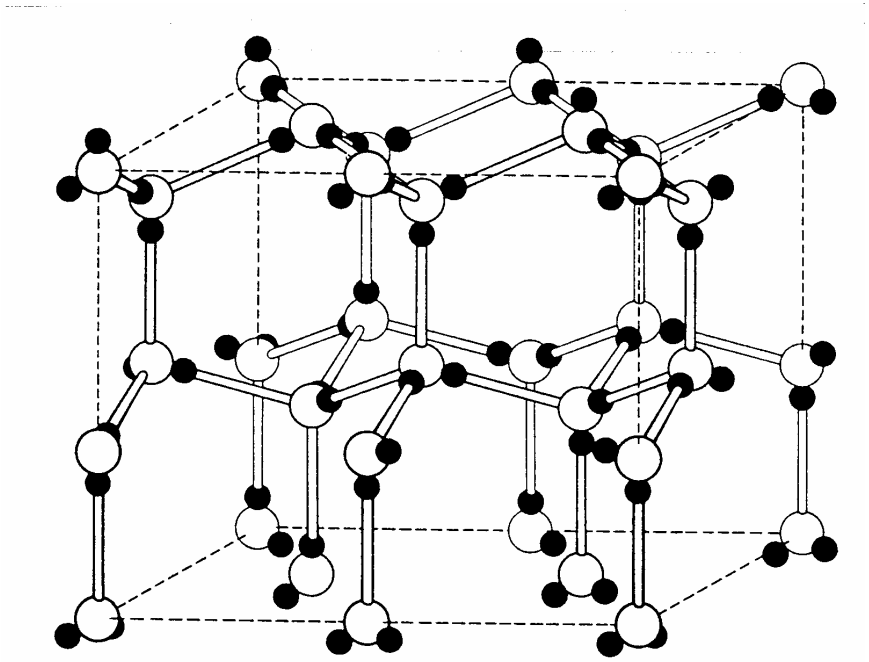


solid density
2.33 g/cm3

Morishita (2006), FPMD, N=64 atoms

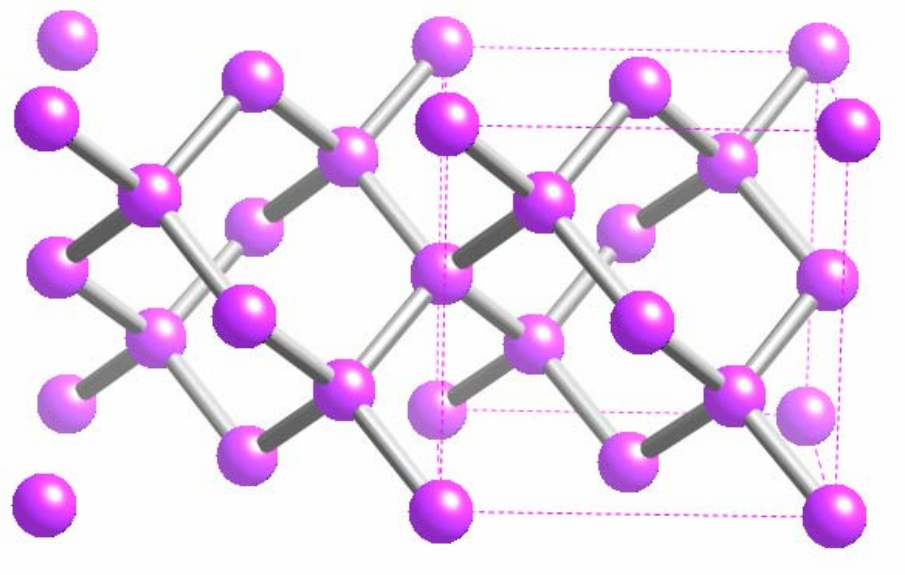
Crystal Structures

open tetra-coordinated networks



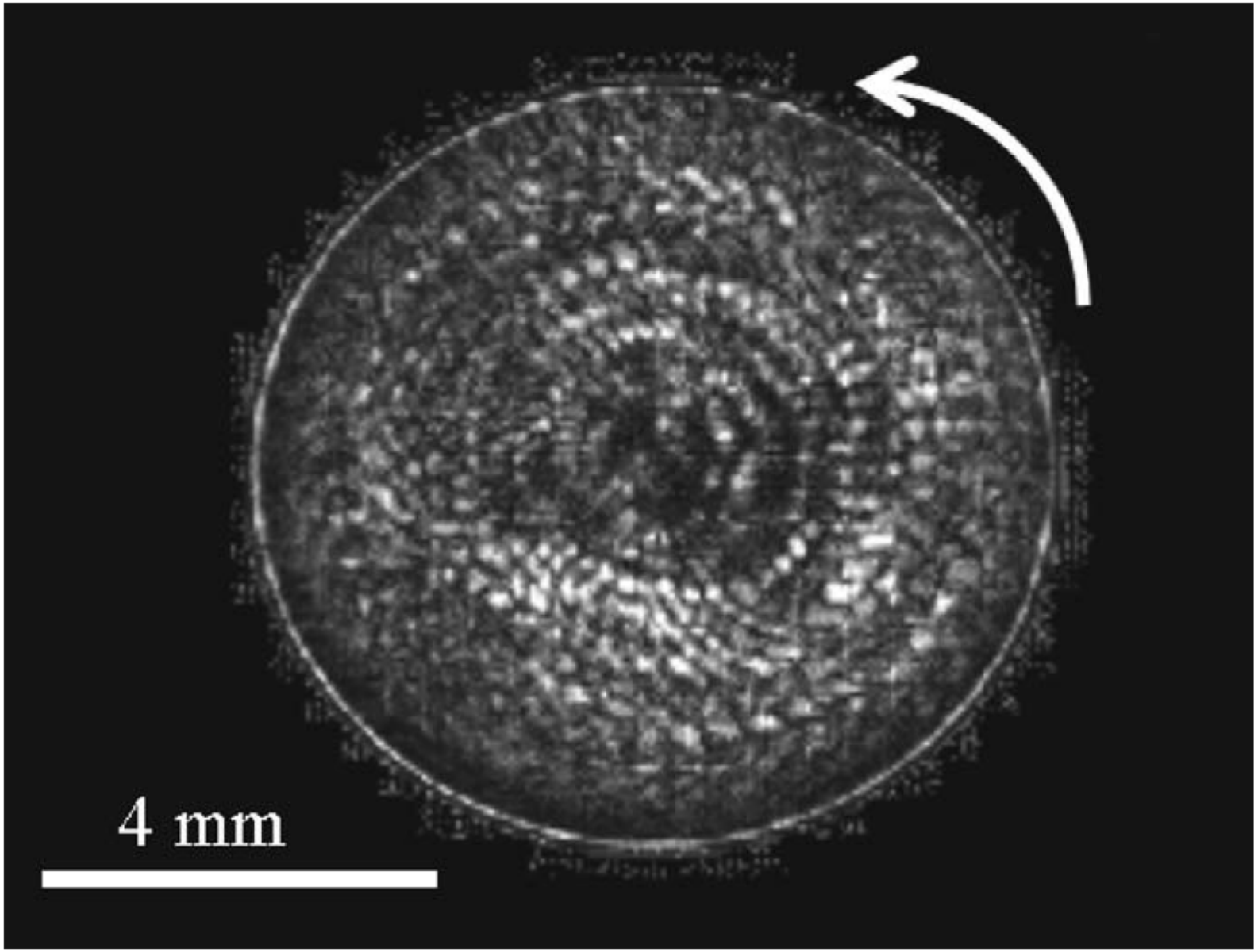
Oxygen (-2)

Hydrogen (+1)



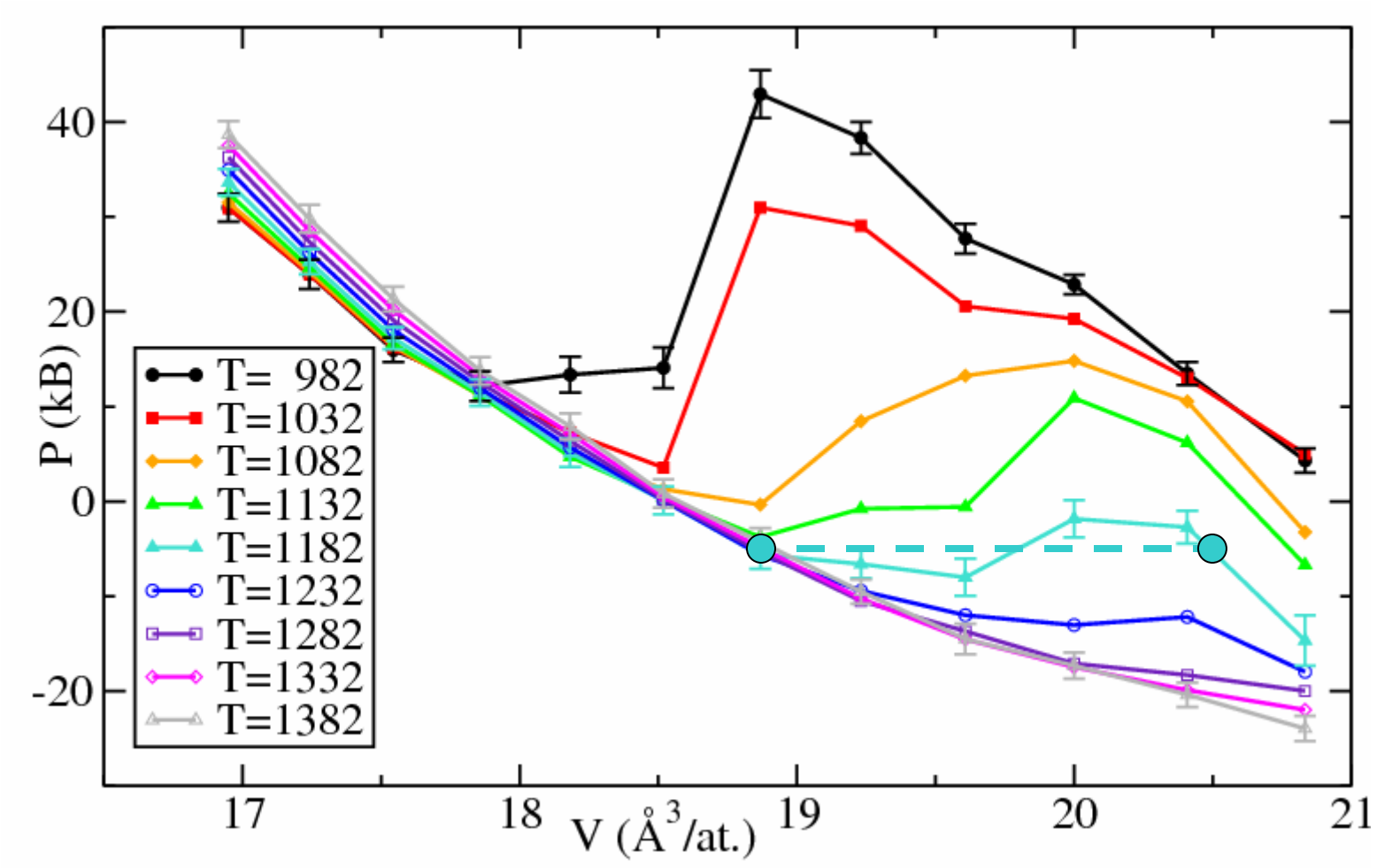
Silicon

Angell&Sastry (Stillinger-Webber)



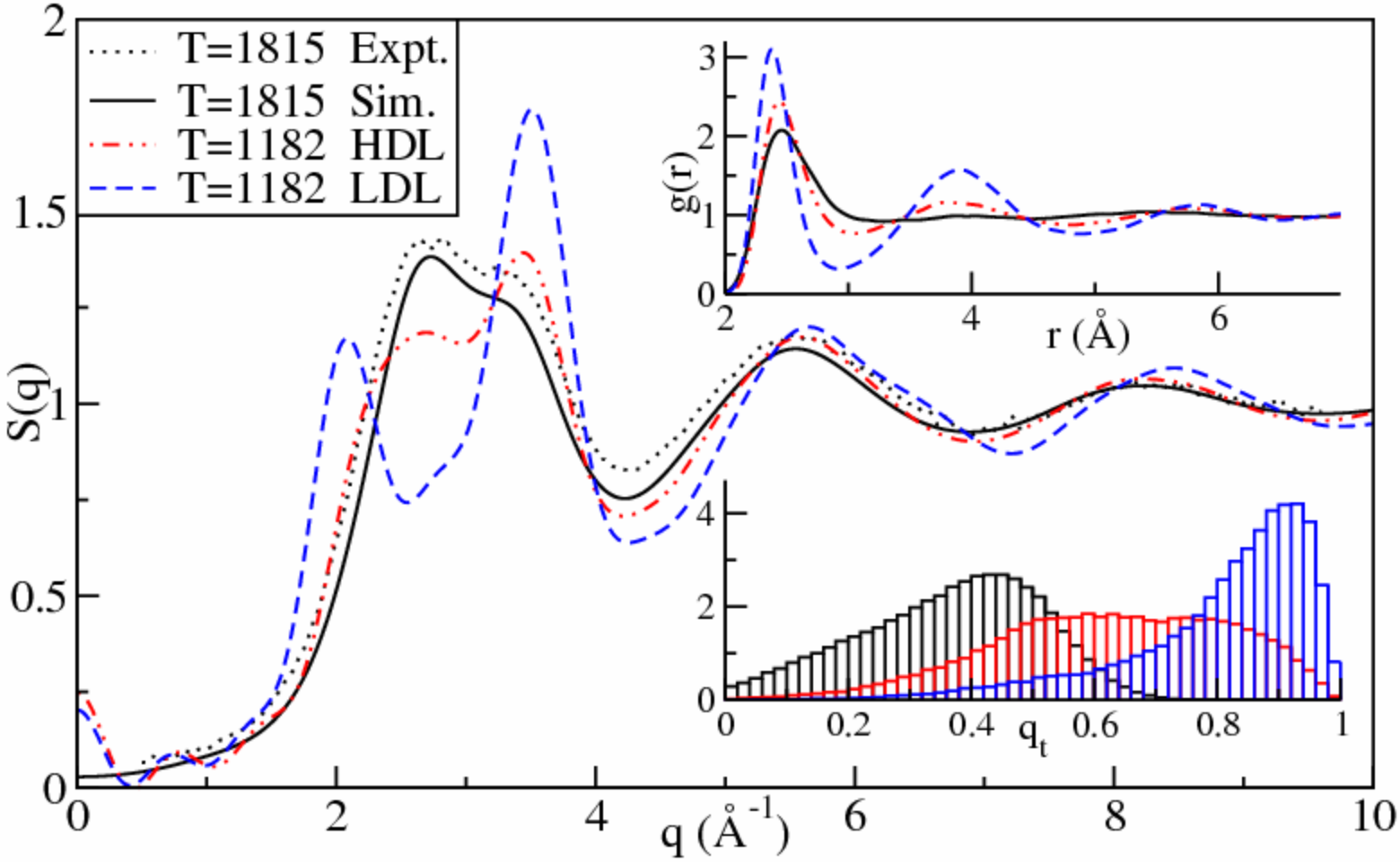
Kobatake, et al. (2007) Motion of silicon grains floating on the surface of liquid silicon (top view)

Pressure-Volume Isotherms



Maxwell Equal Area Construction

Structure Comparison

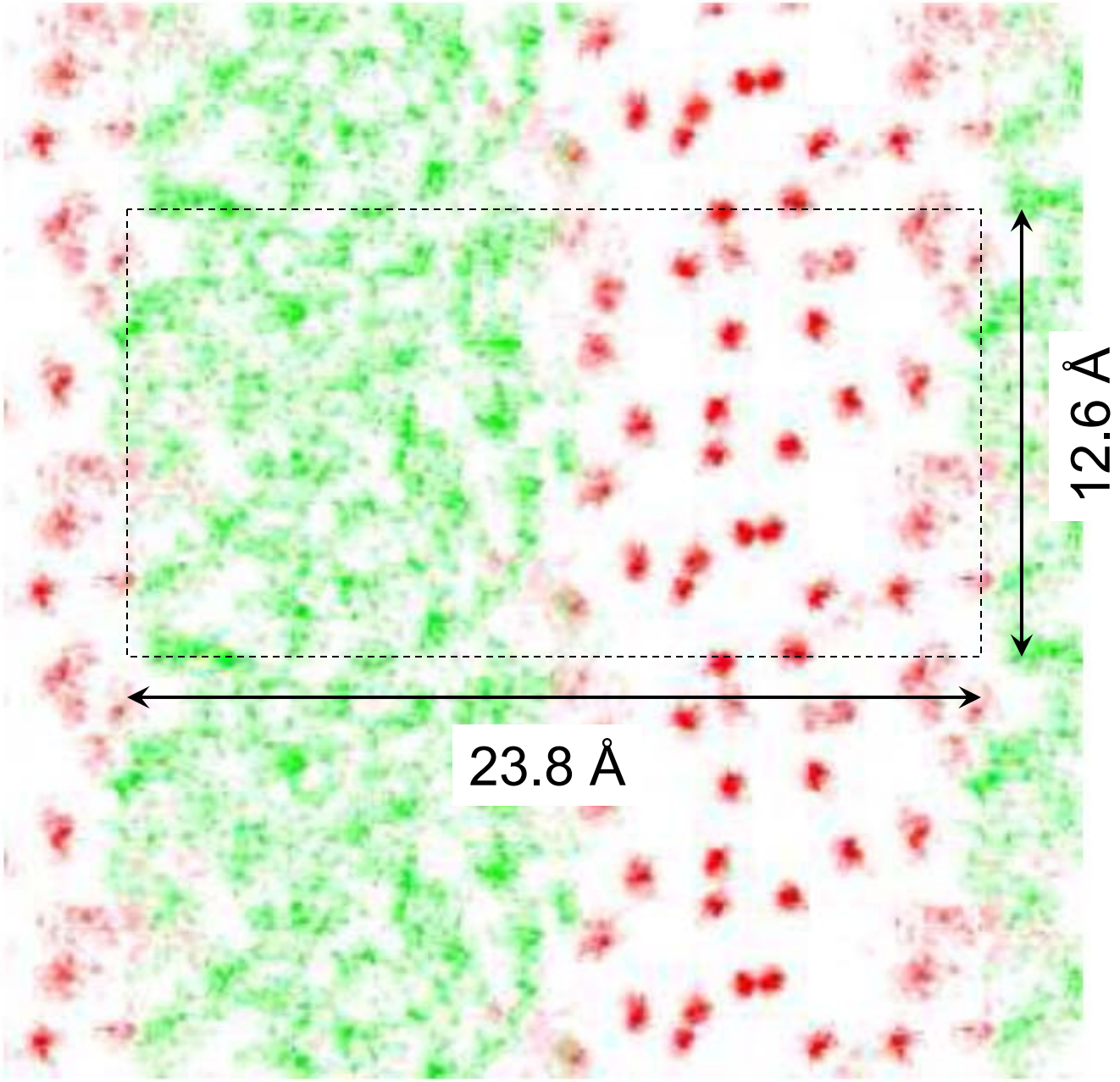


Coexistence Simulation

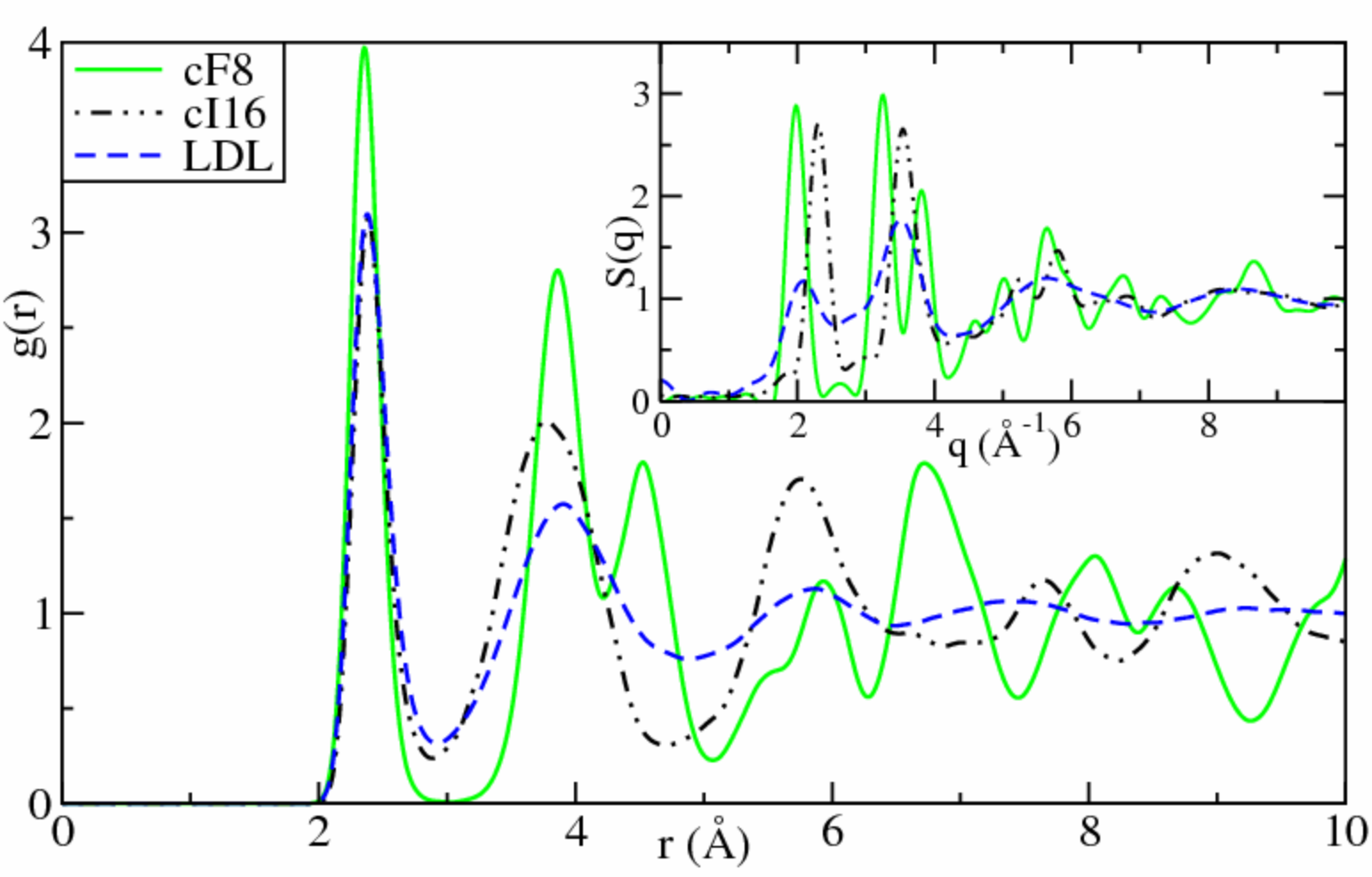
T = 1032 K
V = 19.8 Å^3/atom
P = –0.8 kBar

N = 200 atoms
5 picoseconds

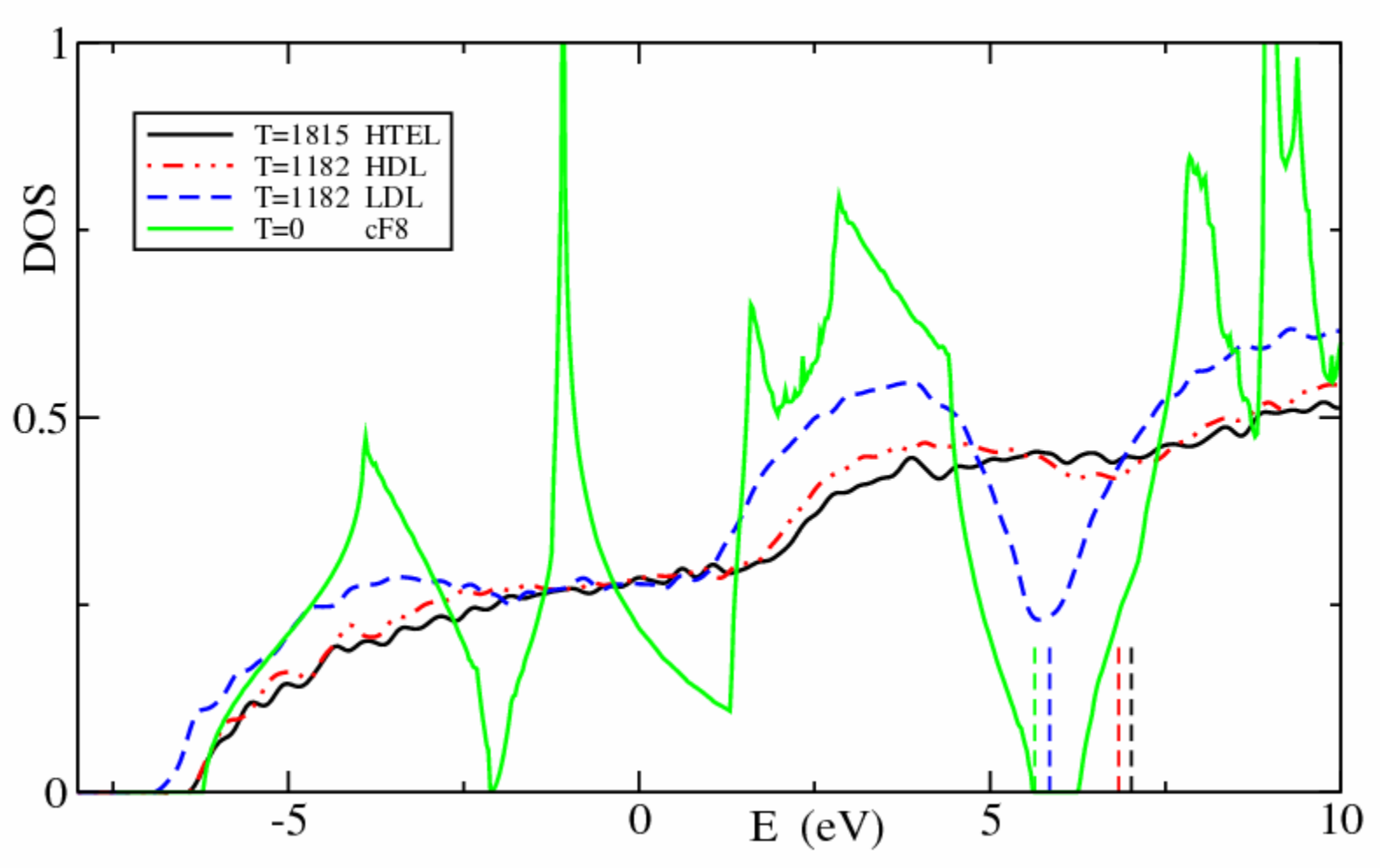
Initial state:
HDL (green)
LDL (red)
100 atoms each



LDL is non-crystalline



HDL is metallic, LDL has pseudogap



Conclusions (Supercooled Silicon)

- Liquid silicon has two metastable phases in the supercooled regime

Experiments are lacking but two amorphous states are known to exist

- Transition is between dense metallic structure and open structure with pseudogap

Is the low density liquid semiconducting?

- Future work

Switch to constant pressure ensemble