Crystal Nucleation in Supercooled Silicon

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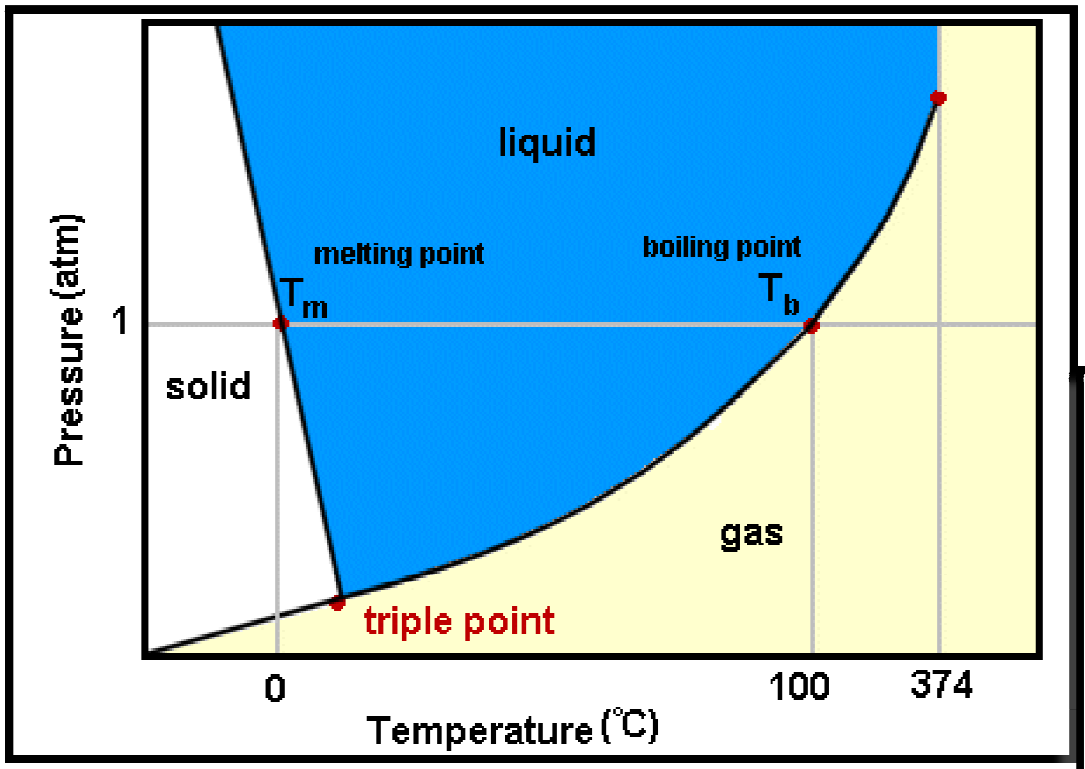
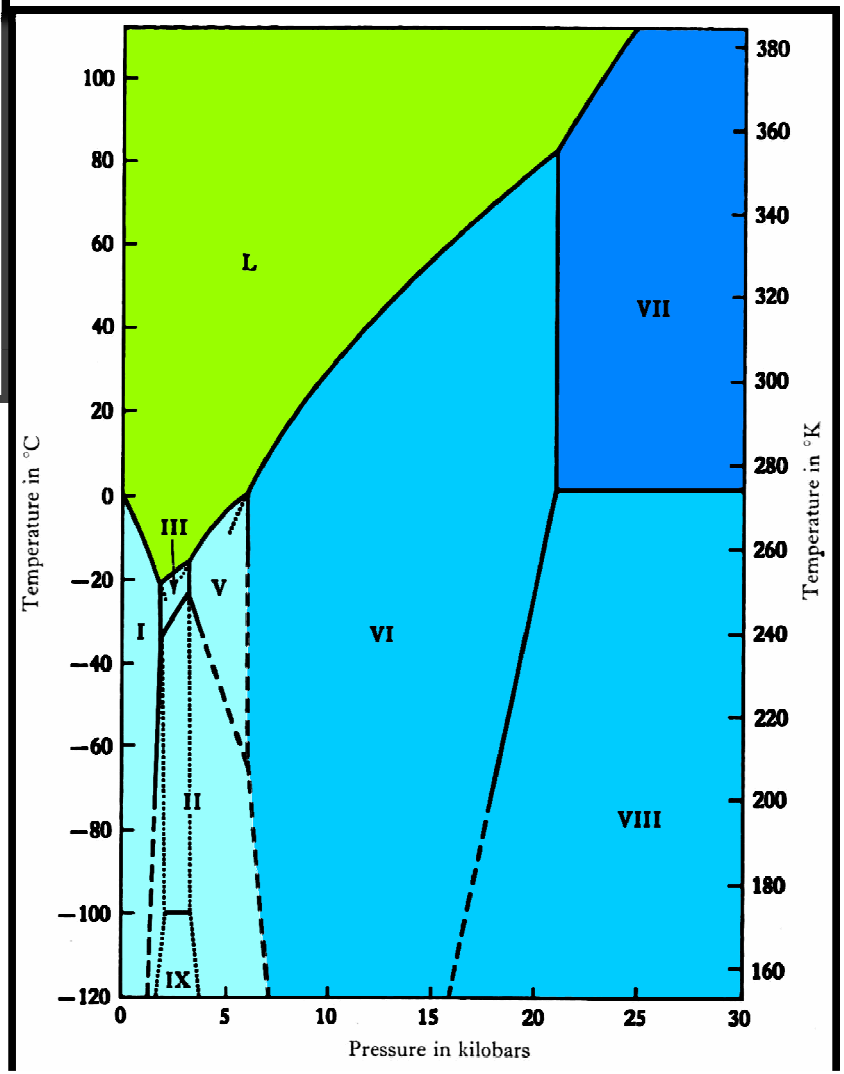
Solids, liquids, gases, glasses..

Sunset in the Antarctic, showing all three phases of water

- Materials exist in many phases -- commonly known are solid (crystal), liquid, gas.
- What distinguishes these are density, microscopic structure, and mechanical response…



The phase behavior an essential part of understanding a material, and can be complex:
e. g., Polymorphism in water.



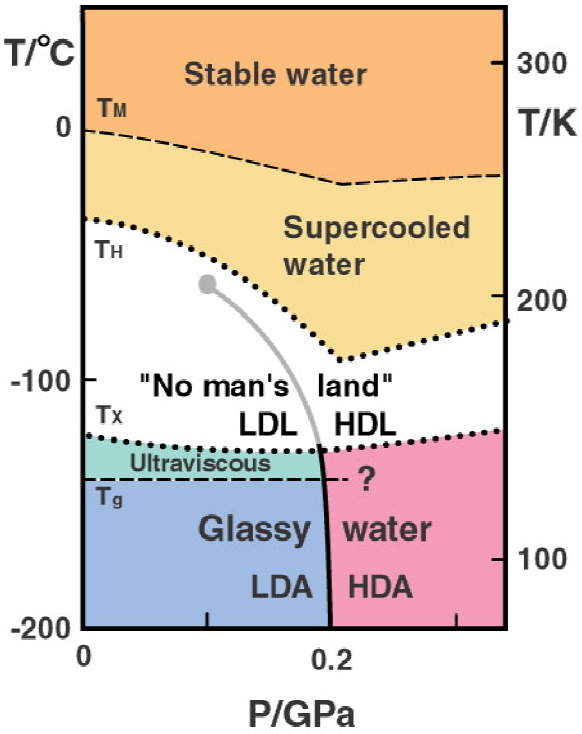
Consderation of metastable states and arrested states (e.g.,glass) makes phase behavior much richer.

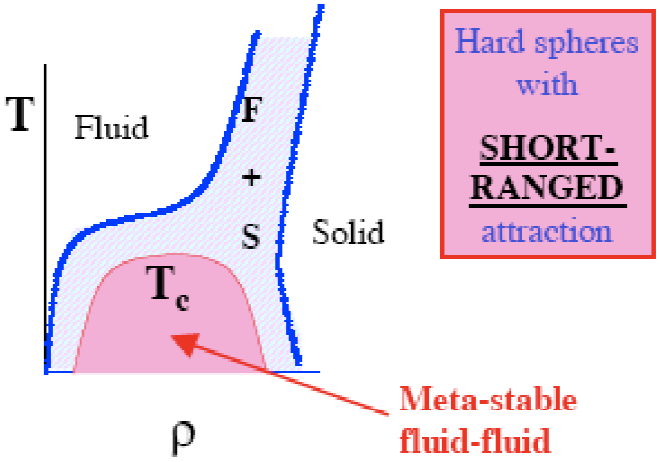
Phase transitions in metastable conditions – a very interesting special case.

Consequences of many phenonmena of interest.

A novel liquid-liquid transition has been proposed as one of possible explanations for the anomalous behavior of water.

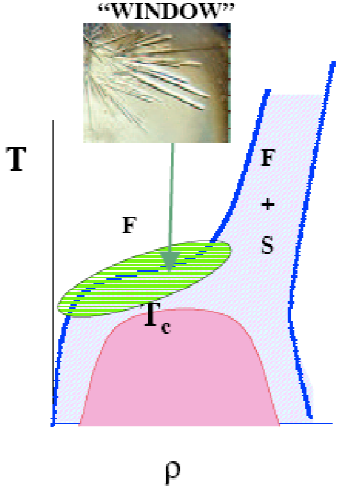
Also proposed/studied for other materials with local tetrahedral geometry – silica, carbon, phosphorous, silicon…

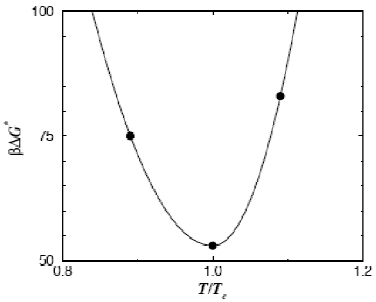




Hard spheres with **SHORT-RANGED** attraction

RELATION BETWEEN PHASE DIAGRAM AND PROTEIN-CRYSTALLIZATION "WINDOW"

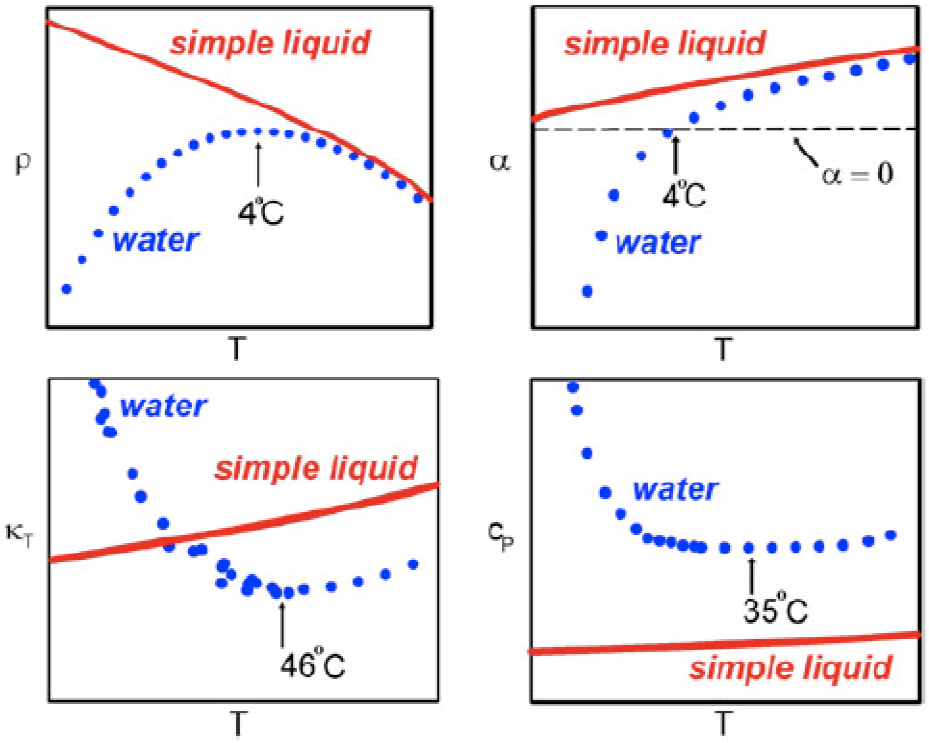




Metastable FF critical point affect crystallization rates.

Liquid Liquid Transition

A possible explanation for the anomalous properties of water:

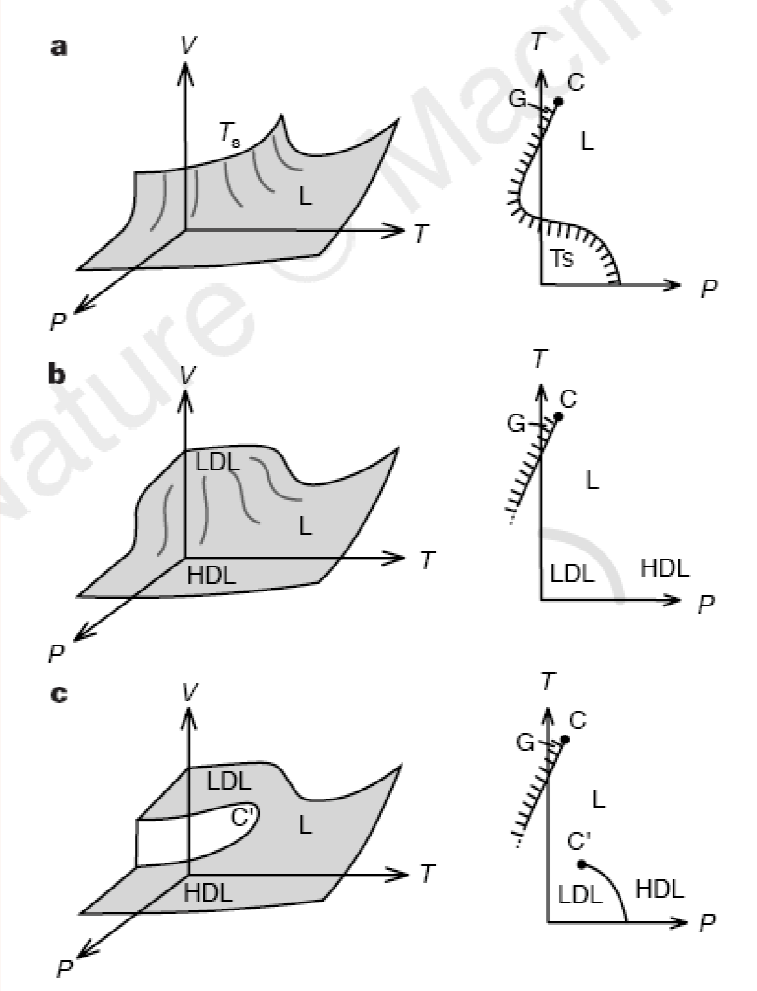


Density, coefficient of thermal expansion, compressibility, specific heat, and many dynamic properties show marked deviations from “normal” behavior at low T.

Can we understand this in terms of features of the phase diagram?

Three scenarios..

Thermodynamic arguments, model calculations, and simulation results have suggested three possible behaviors:

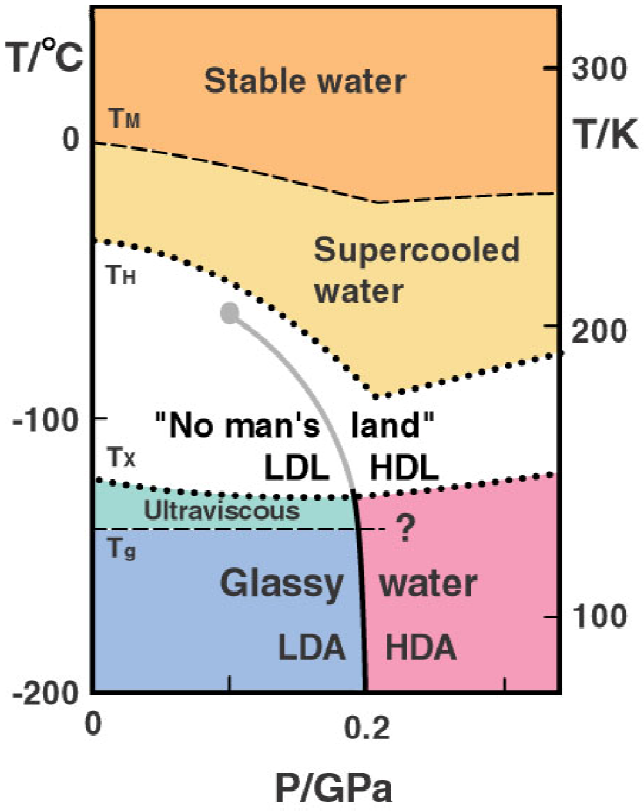


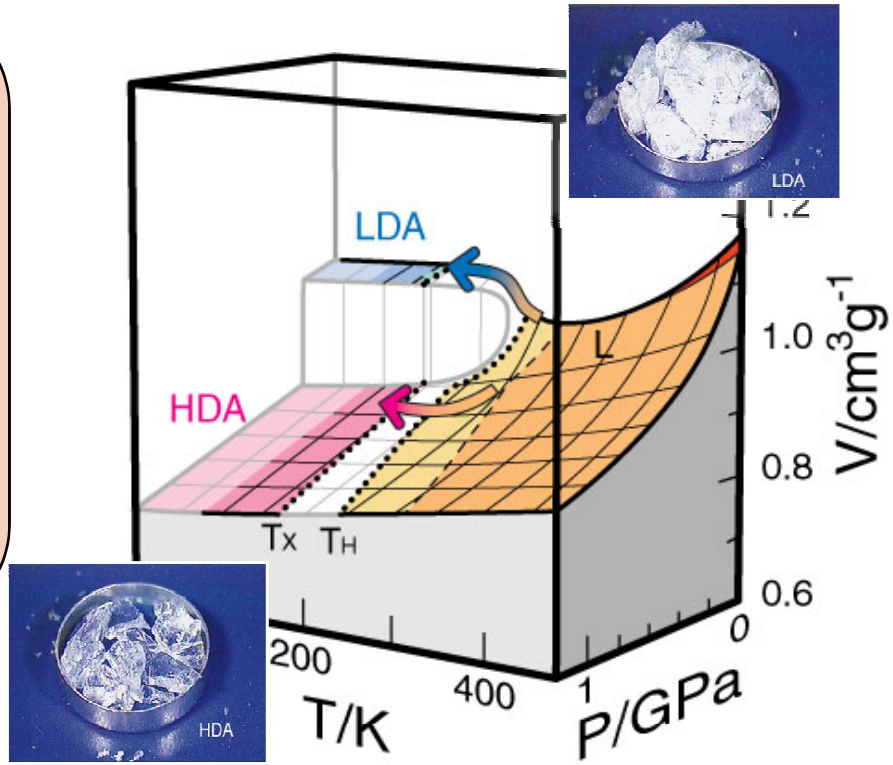
Reentrant spinodal scenario
(Speedy and Angell 1976)

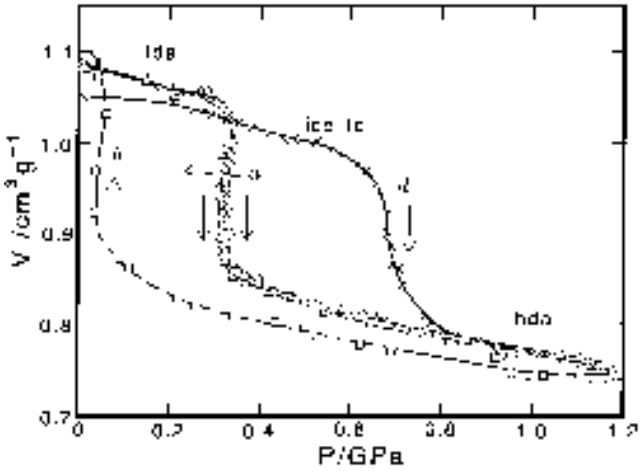
Singularity free scenario
Sastry et al 1996

Two critical point scenario
Poole et al 1992

The two critical point scenario consistent with experimental observations, including transformations among amorphous ices, but difficult to probe directly (“no man’s land”). However, much indirect evidence gives weight to the possibility.
Proposed for many other substances: Silicon, Silica, carbon, phosphorous..







From O. Mishima, J. Chem. Phys. **100**, 5910 (1994)

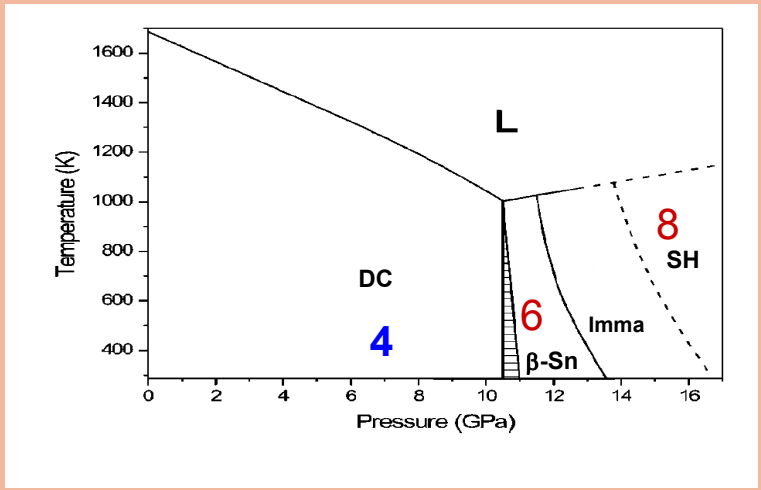
Liquid Liquid transition in Silicon

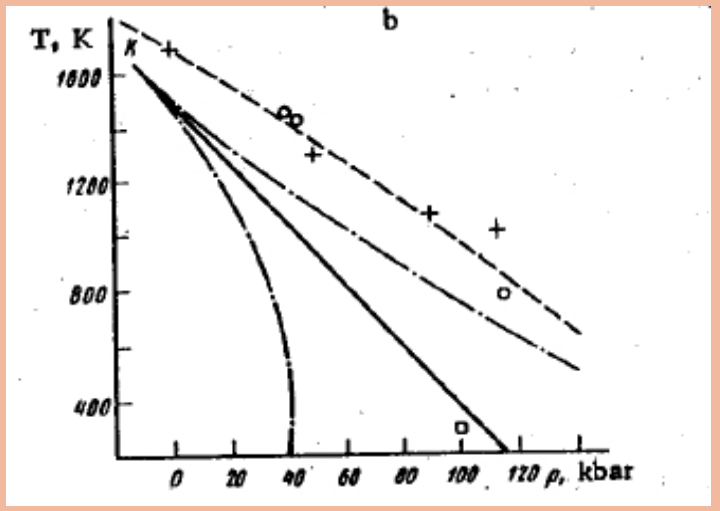
For silicon, previous evidence for amorphous-liquid phase transition (~ 1450 K; below freezing T of ~ 1700 K) has been reinterpreted as a LL transition.

Consistent with suggestion by Aptekar (1979).

Evidence molecular dynamics from simulations using the Stillinger Weber potential. Supported by recent experiments.

Metal – non-metal transition accompanies LL transition [Ashwin et al 2004]





Aptekar, Dokl. Akad. Nauk. SSSR1979

Liquid Liquid transition in Silicon

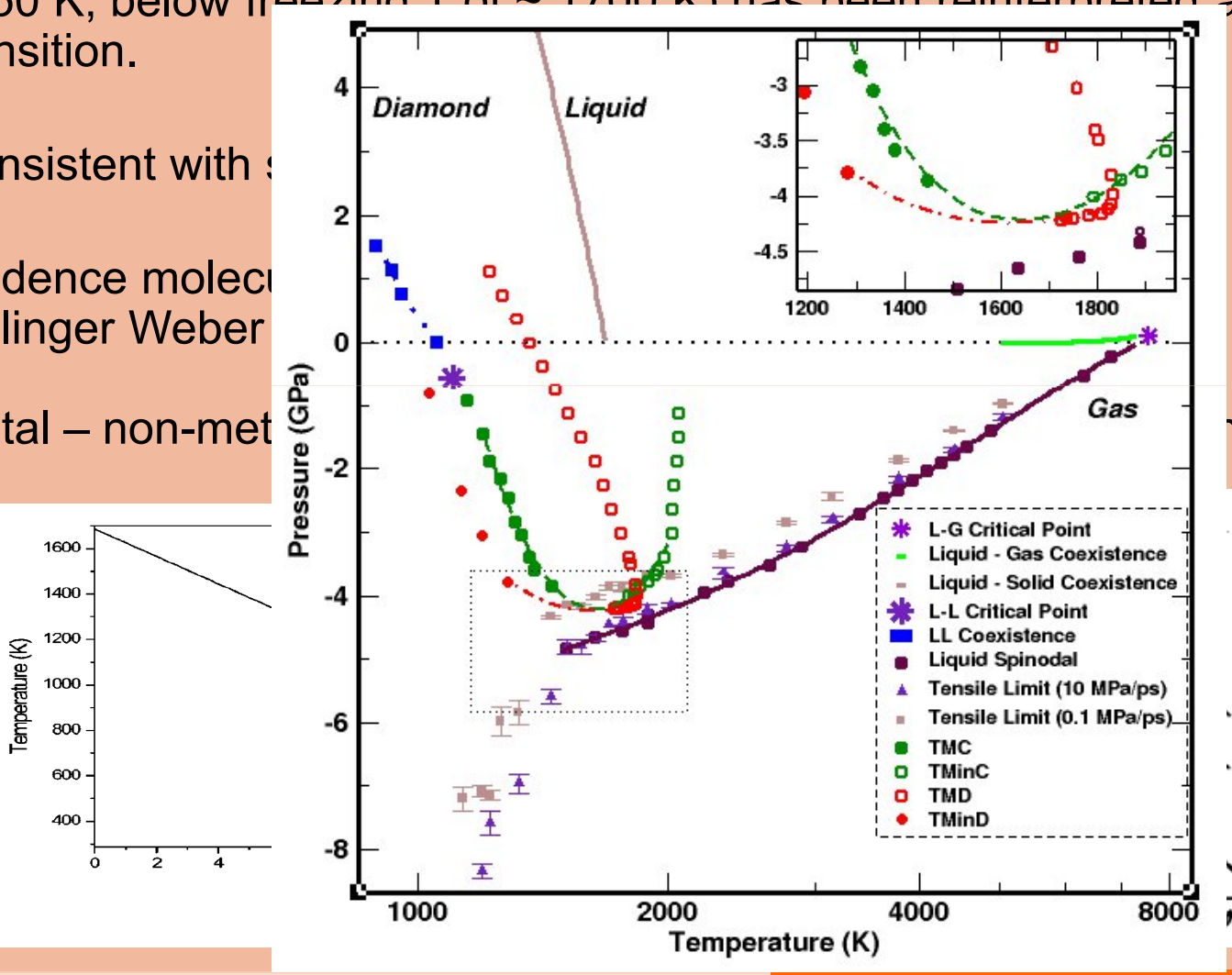
Our simulations

For silicon, previous evidence [illegible] quid phase transition (~ 1450 K; below freezing T of ~ 1700 K) has been reinterpreted as a LL transition.

Consistent with [illegible]

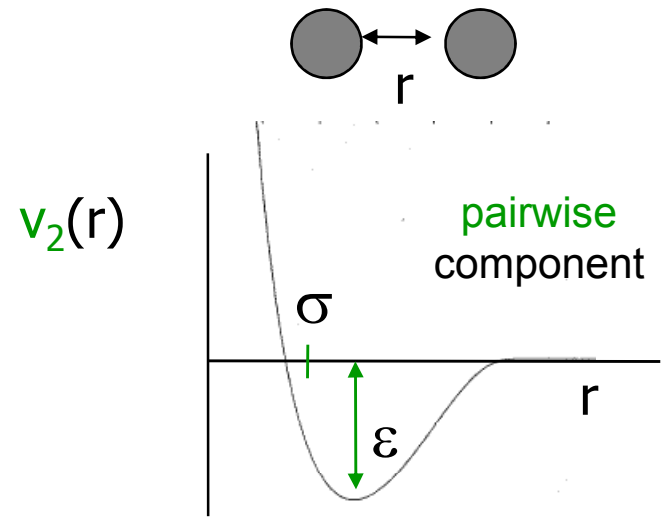
Evidence molecu[illegible]
Stillinger Weber [illegible]

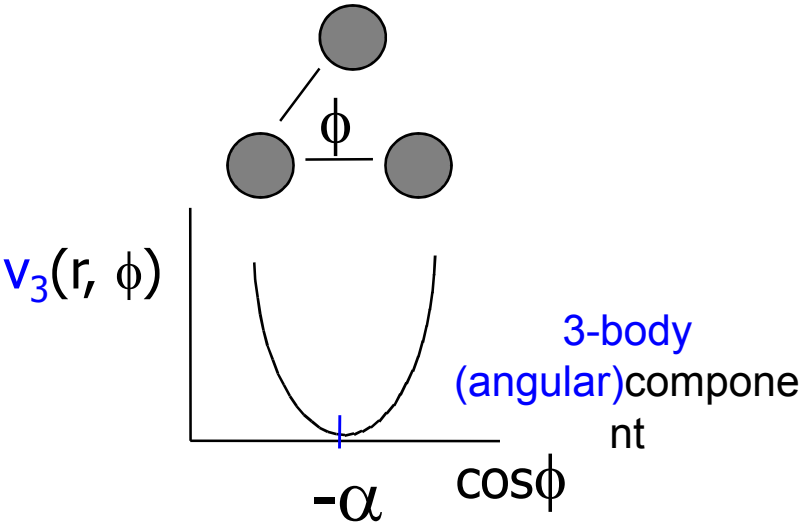
Metal – non-met[illegible] et al 2004]



Aptekar, Dokl. Akad. Nauk. SSSR1979

Molecular Dynamics Simulation Study of LL transition in Silicon using the Stillinger-Weber potential





Stilinger-Weber potential:

Sum of two and theree body terms.

$$v_2(r) + \lambda v_3(\alpha, r, \phi)$$

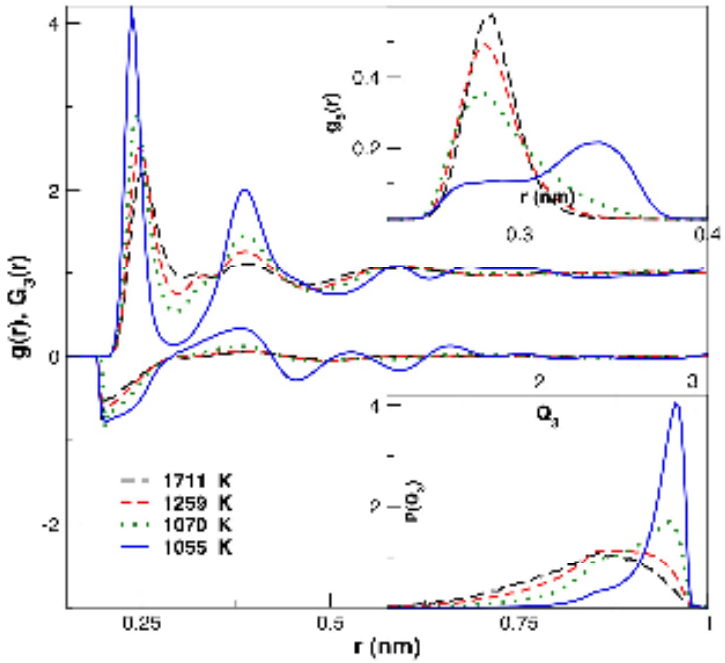
λ determines the strength of the three body interaction – "tetrahedrality"

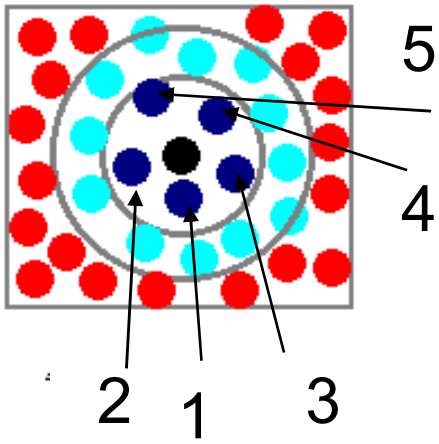
Silicon: $\lambda=21$, $\alpha = 1/3$

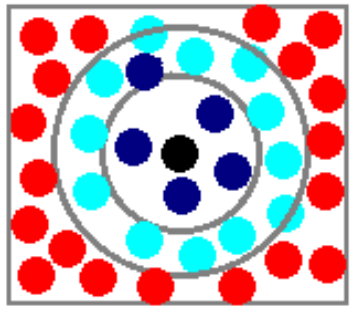
(Stillinger& Weber, 1985)

Study at zero pressure shows first order transition
(Sastry & Angell Nature Materials 2003)

LL transition in SW Si for P = 0: structure

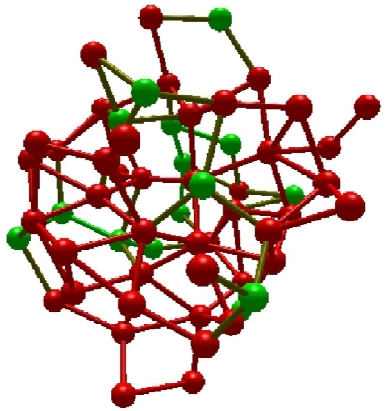




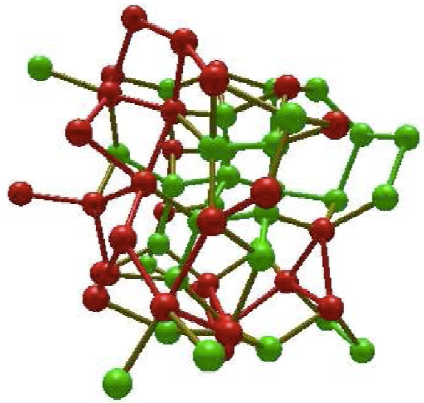


Structure evolves towards four coordinated tetrahedral structure.

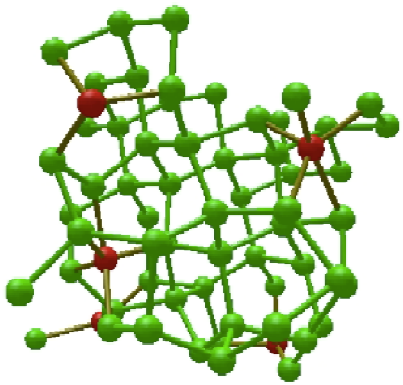
T = 1711 K



T = 1070 K



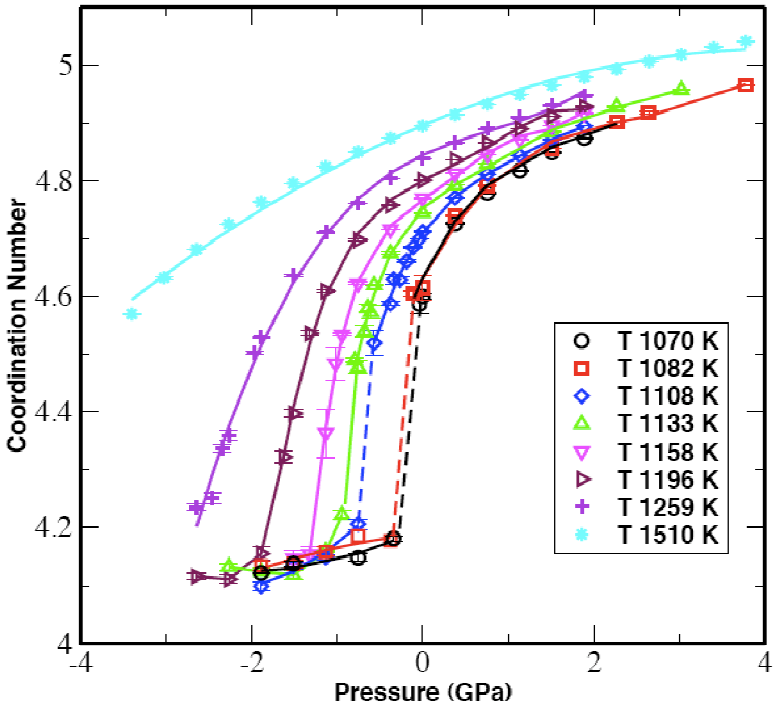
T = 1055 K



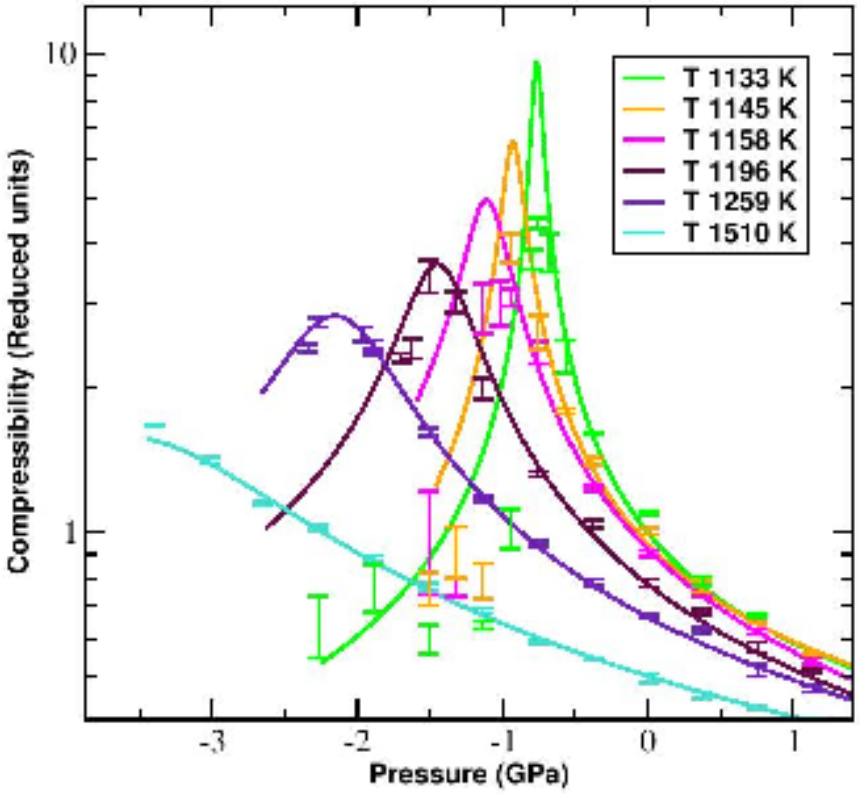
Red: Coordination other than 4.
Green: Coordination = 4

Sharp change towards tetrahedral coordination at first order transition.

Local Structure, Density fluctuations



Local structure changes towards tetrahedral coordination as pressure decreases.



Increased density fluctuations (compressibility) as T =1100 K is approached.

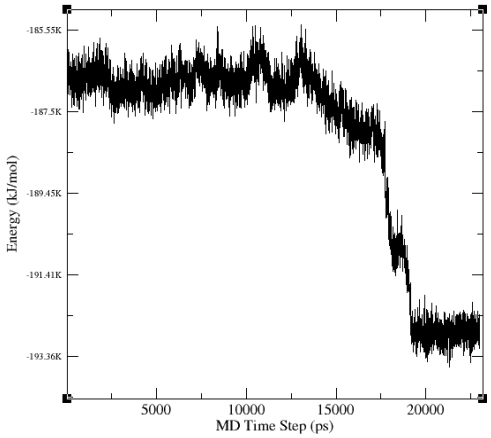
LL Critical point in SW Si

Molecular dynamics simulations at negative pressures (NPT, NVT)

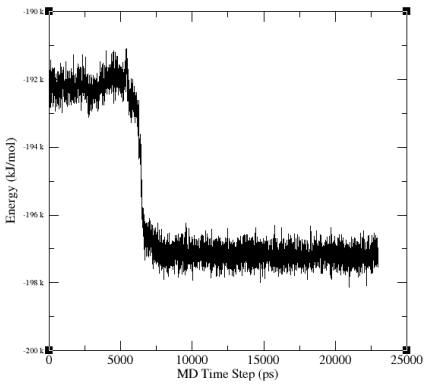
Issues:

- Dramatically reduced mobility at low pressures.
- Rapid crystallization at low temperatures and negative pressures.
- Critical fluctuations, as well as change in local structure contribute to crystal nucleation (Frenkel & co. 1997, 2007)
- Seen in SW Si for the low T liquid, and near critical point.

T = 1082 K, P = -0.75 GPa



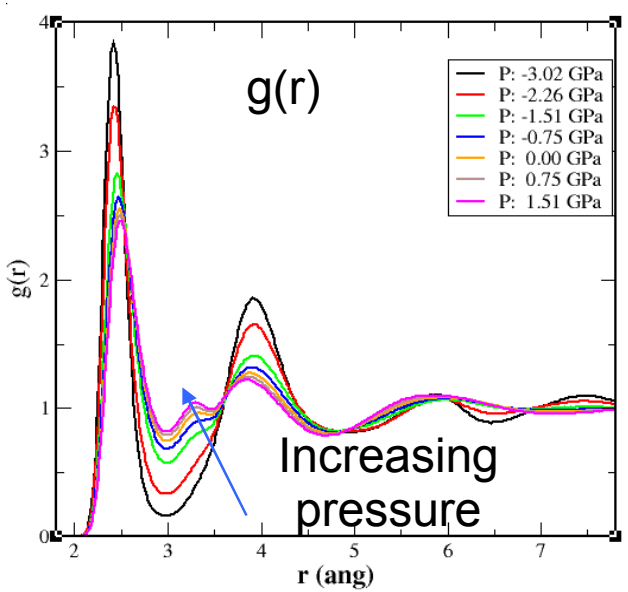
T = 1039 K, P = 0



Energy change due to crystallization

Crystallization on nanosecond time scales

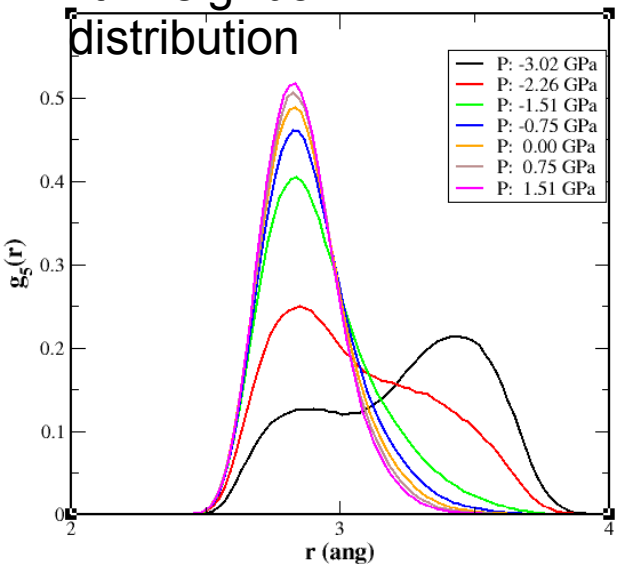
Radial Distribution Function and Fifth Neighbour Distribution



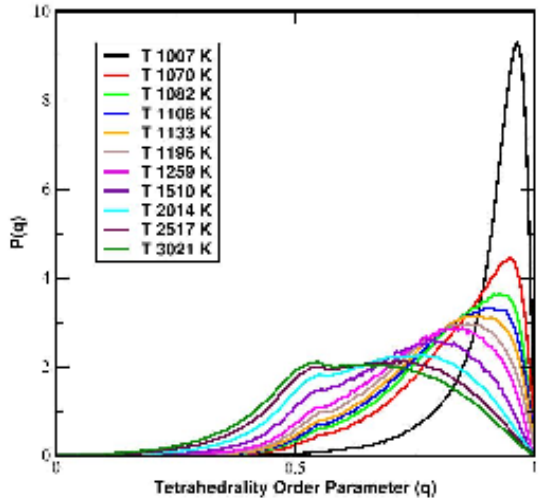
T = 1258 K (0.050)

With decreasing pressure, temperature local structure becomes closer to four coordinated.

Fifth neighbor distribution



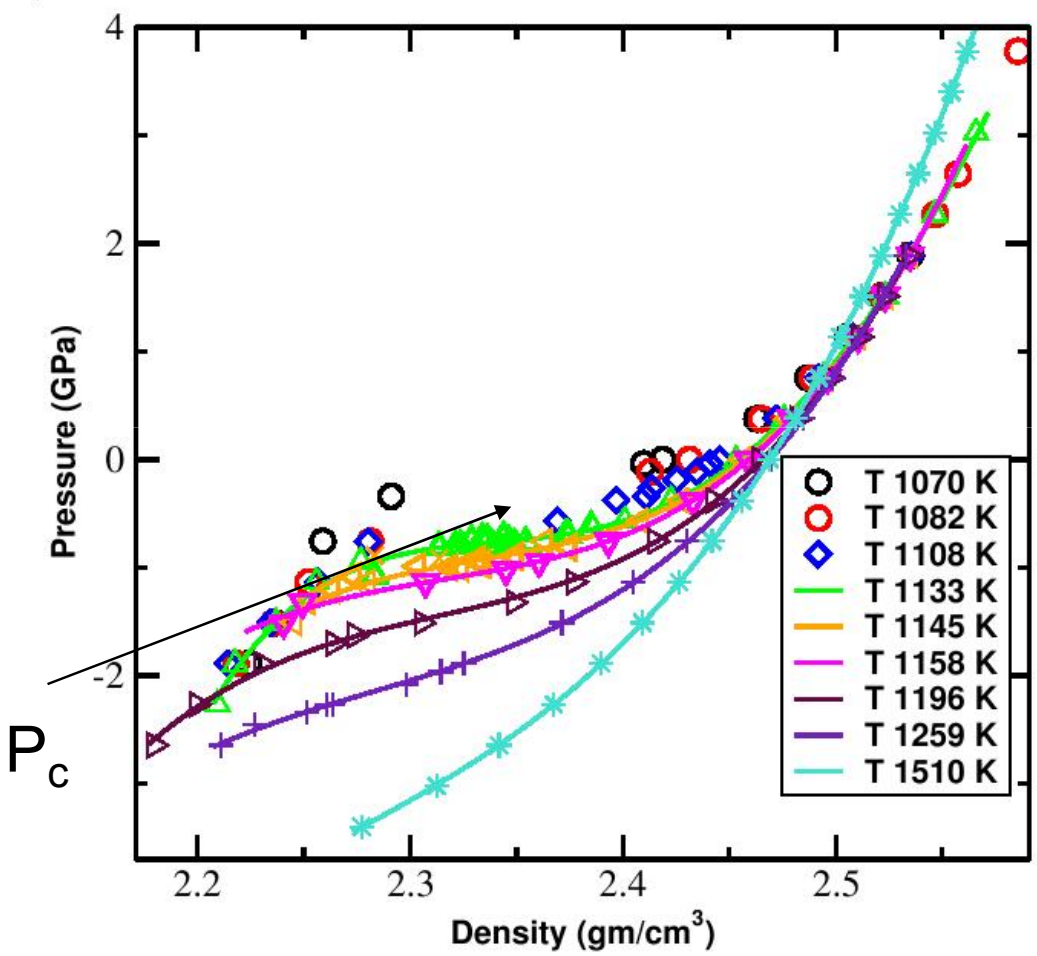
Tetrahedrality Order Parameter



Zero Pressure

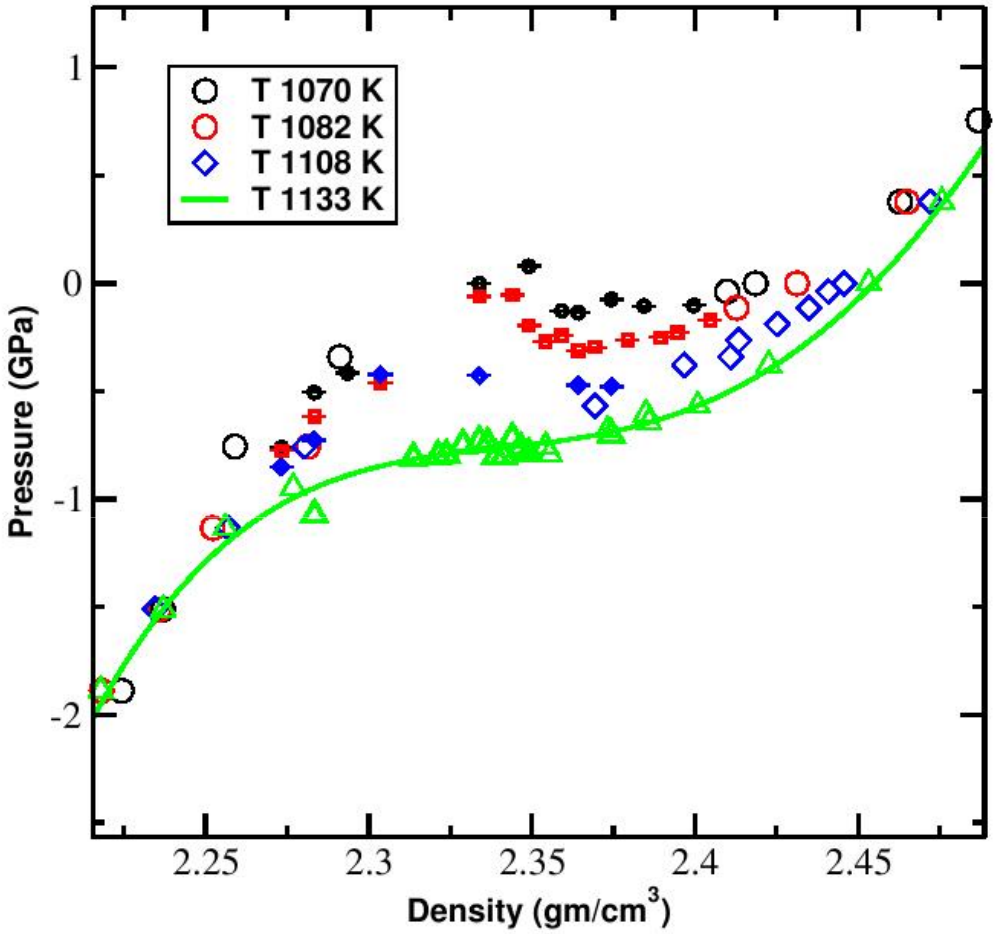
$$q = 1 - \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(cos(\psi_{jk}) + \frac{1}{3}\right)^2$$

Equation of State



- Isotherms between 1510 K and 1133 K are monotonic and continuous
- Low temperature isotherms starting from 1196 K exhibit inflection in the region of 2.3gcm^{-3} density.
- Below 1133 K we observe jumps in the density in NPT simulations.
- Isotherms cross at many pressure values – An indication of density maxima.

Equation of State



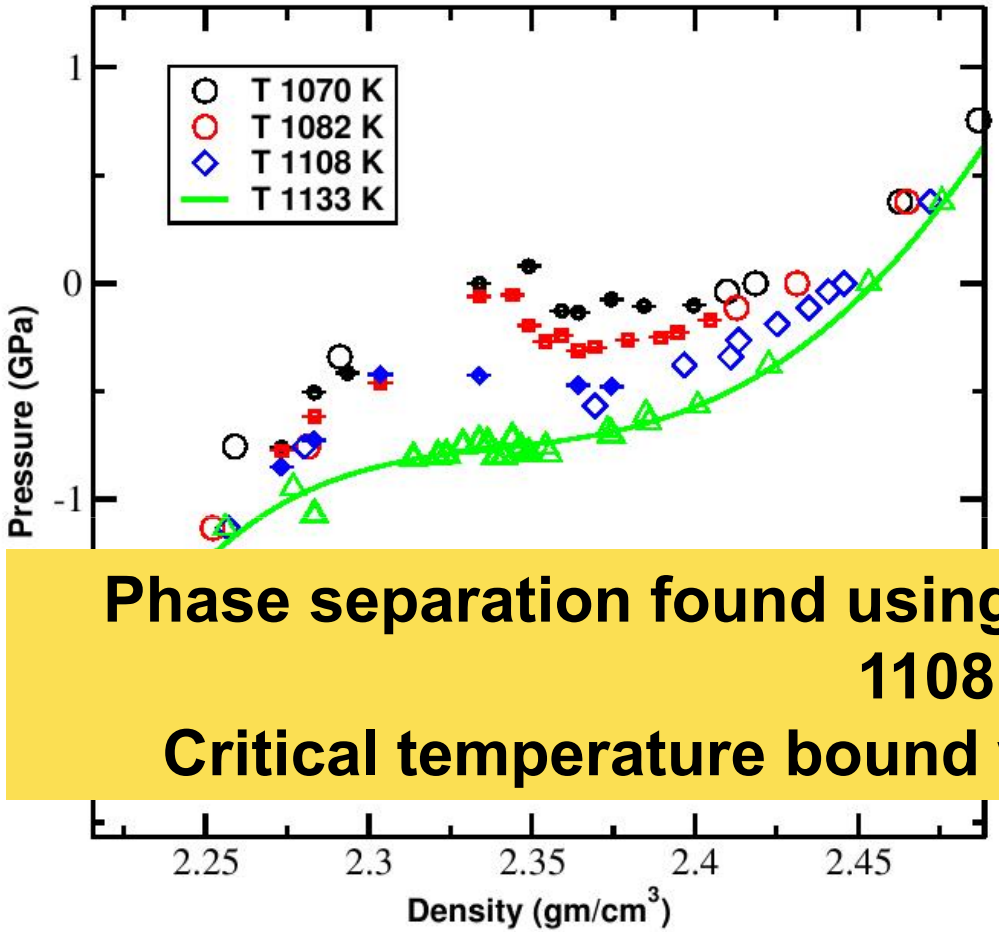
Symbols denote data from NVT simulation

Dark green symbols for T 1133 decreases monotonically with density

Points to note

- When a region of positive slope interrupts a negative slope of PV isotherm – van der Waals loop.
- Positive slope corresponds to negative compressibility, which implies unstable region or phase separation.
- van der Waals loops observed at temperatures a and below 1108 K
- Calculation of compressibility from NVT simulations being carried out.

Equation of State



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Points to note

- When a region of positive slope interrupts a negative slope of PV isotherm – van der Waals loop.
- Positive slope corresponds to negative compressibility, which implies unstable

Phase separation found using van der Waals loop below 1108 K

Critical temperature bound within 1133 K and 1108 K

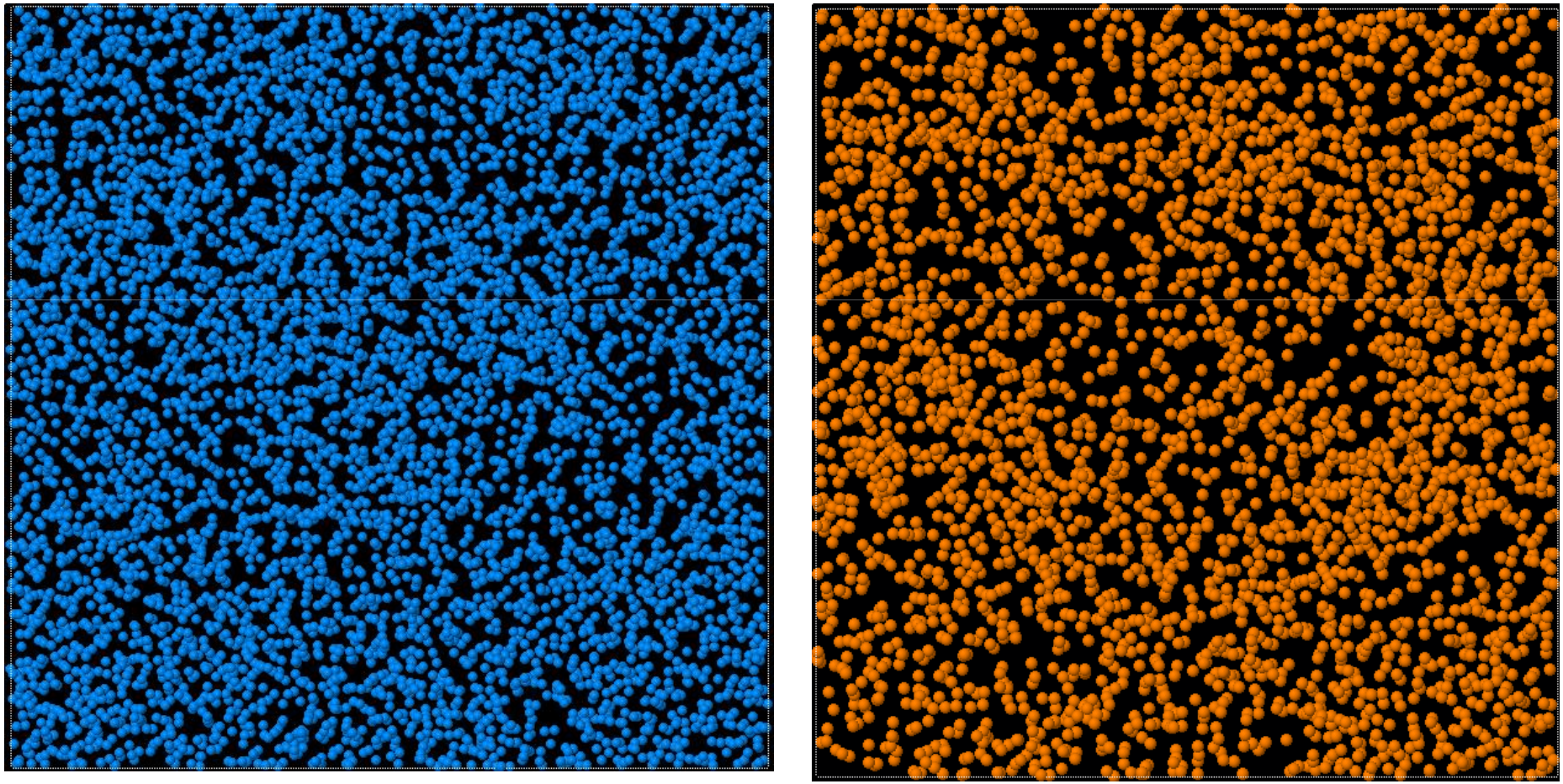
and below 1108 K

- Calculation of compressibility from NVT simulations being carried out.

Fluctuations

Bounding the critical point from below by observing phae separation (preliminary)

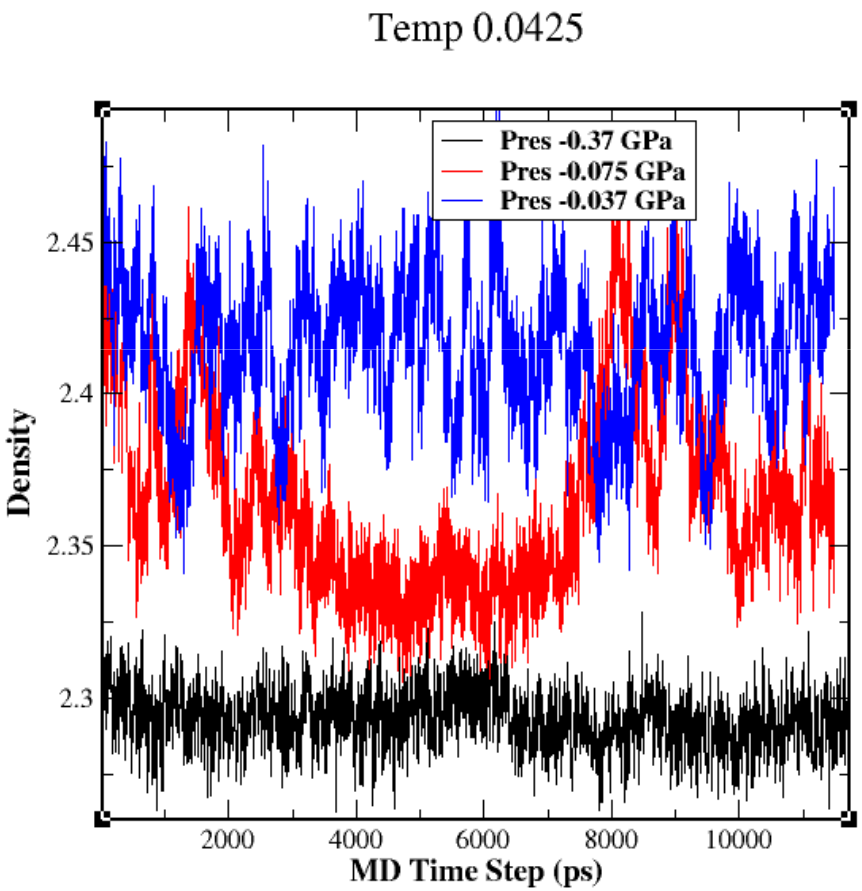
Snapshot of Four (blue) Coordinated and Five (Orange) Coordinated Particles



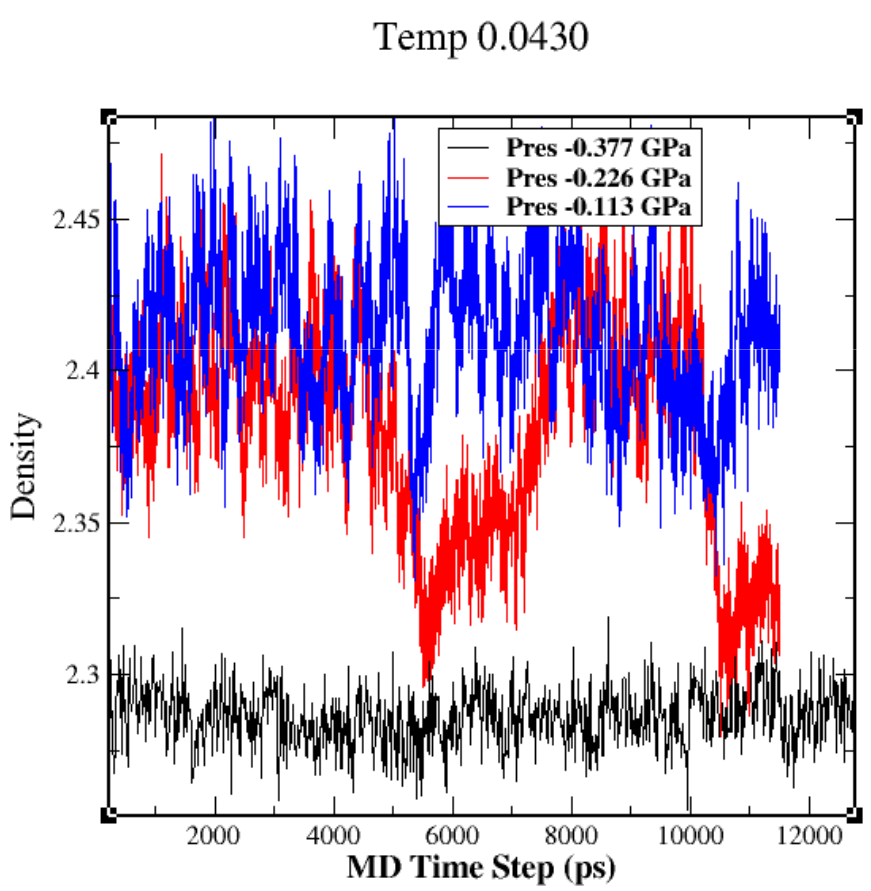
T 1082 K (0.0430) Density 2.35 gm/cm^3 (0.465)
Particles 10000, Run length 10 Million

Density fluctuations at temperatures below T_c

T = 1070K



T = 1082 K



Nucleation

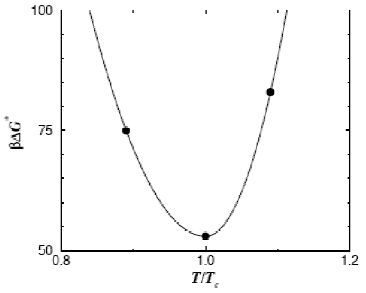
Previous work suggests that both critical fluctuations, as well as change in local structure contribute to crystal nucleation (Frenkel & co. 1997, 2007)

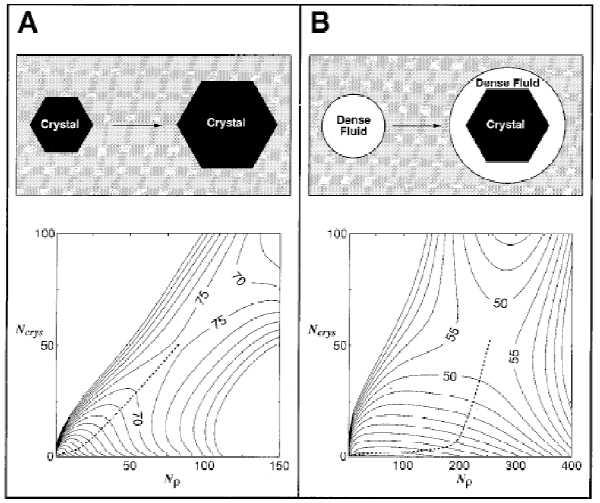
Crystal nucleation enhancement in proteins by critical density fluctuation[1]

- Away from critical temperature, the path of lowest free energy is one where increase in N_ρ is proportional to N_{crys}. Here N_{crys} is the number of solid-like particles belonging to a given crystal nucleus and N_ρ is number of connected particles that have high density environment.

- Around Tc, the route to the critical nucleus leads through a region where N_ρ increases while N_{crys} is zero, suggesting that the first step towards the critical nucleus is the formation of a liquid like droplet.

- Nucleation barrier is lowest at Tc





[1]Enhancement of protein crystal nucleation by critical density fluctuations, ten Wolde et. al., Science **277,** 1975 (1997)

Nucleation

Diamond nucleation enhancement in carbon controlled by the local structure [2]

- Nucleation rate increases when the local coordination of the liquid changes from threefold to fourfold.

- The free-energy cost to create a diamond-liquid interface is lower in the fourfold than in the threefold liquid.

In Silicon, near the LL critical point, one has both critical fluctuations (which displays a maximum along the compressibility maximum line) and a monotonic approach of local coordination to the crystalline value of 4.

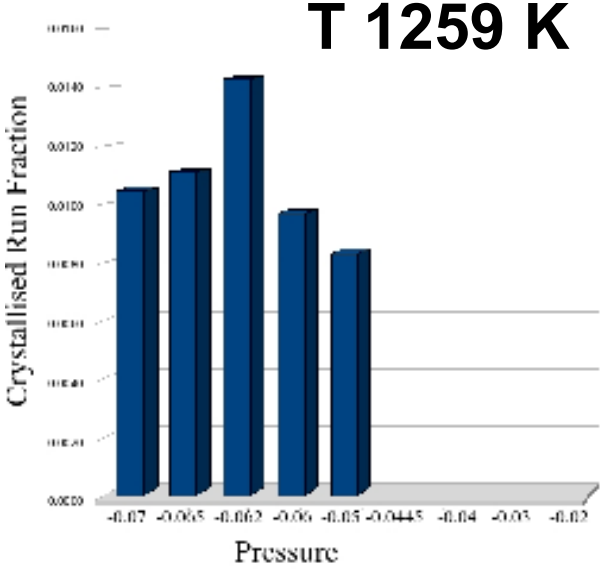
Interesting to study the competition between the two.

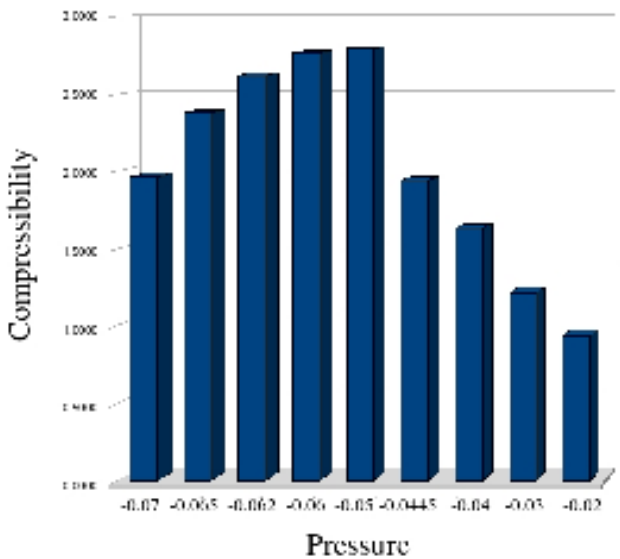
Statistics of crystallization events and free energy barrier calculations done to analyze this.

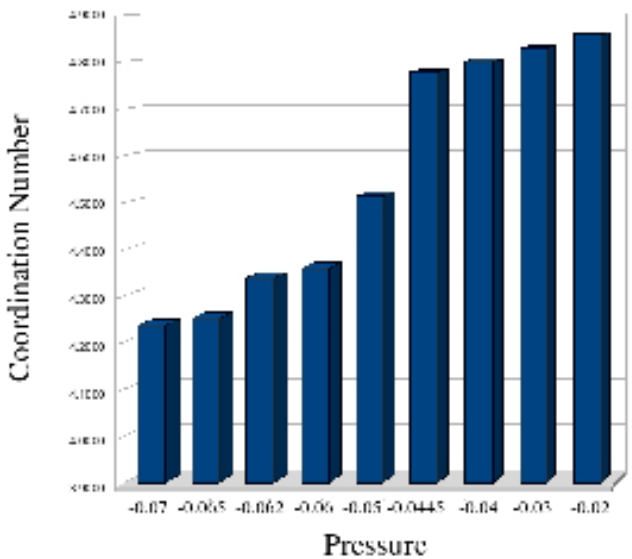
[2] Local structure of liquid carbon controls diamond nucleation, Ghiringhelli et. al. PRL. **99,** 055702 (2007)

Nucleation Statistics

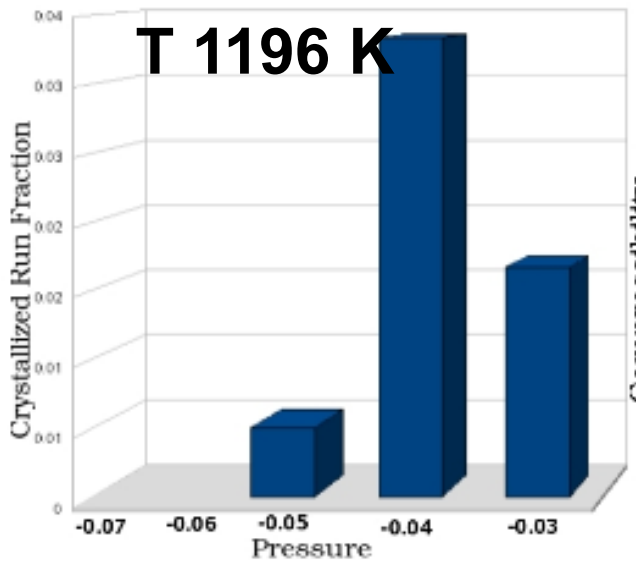
T 1259 K

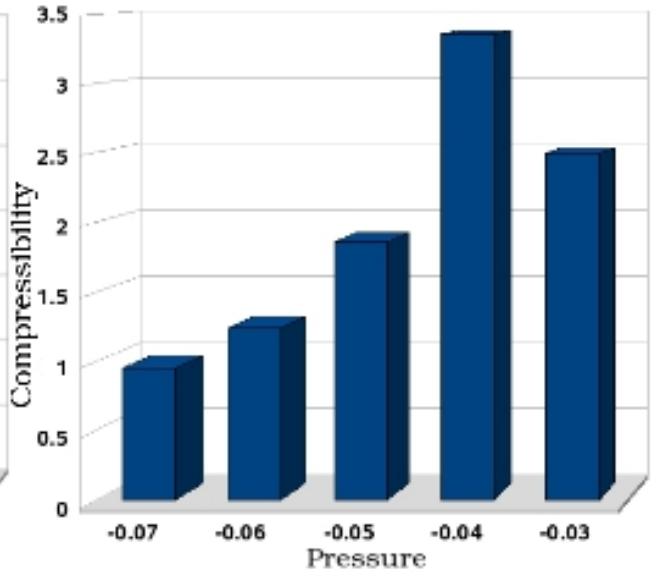


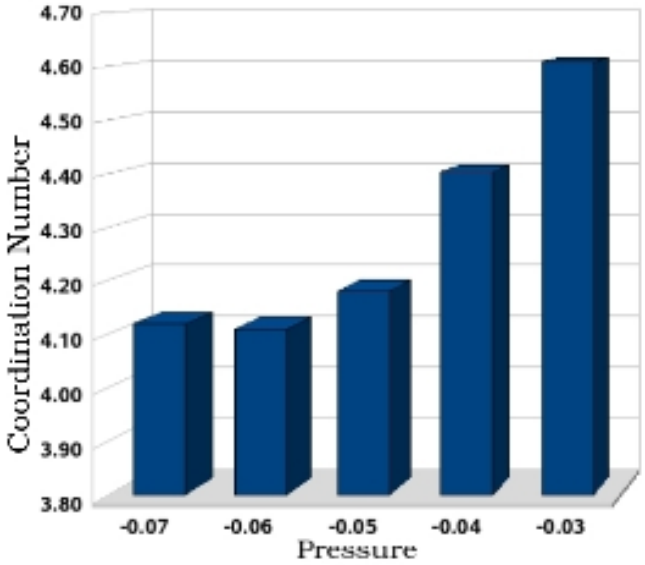




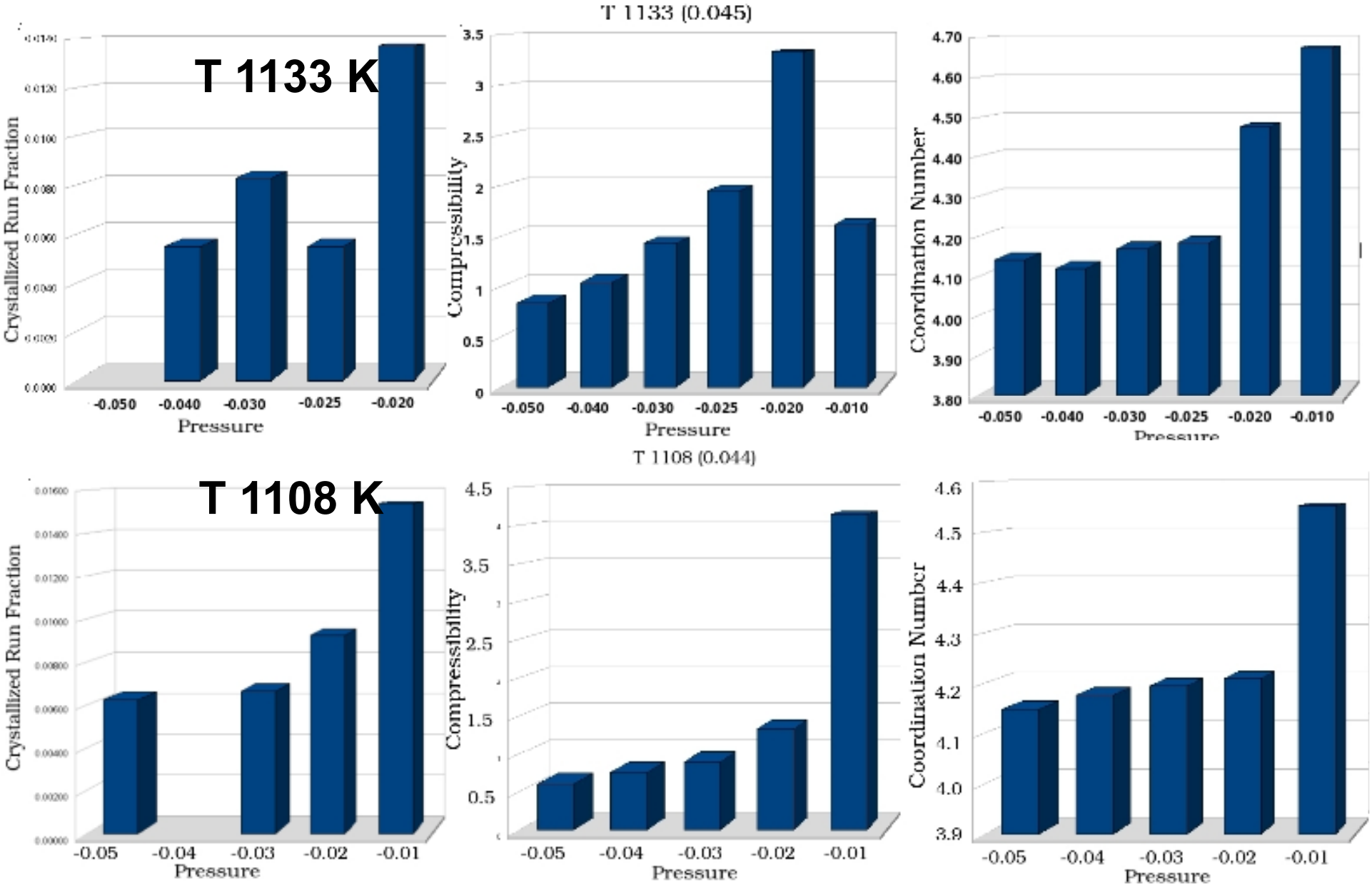
T 1196 K



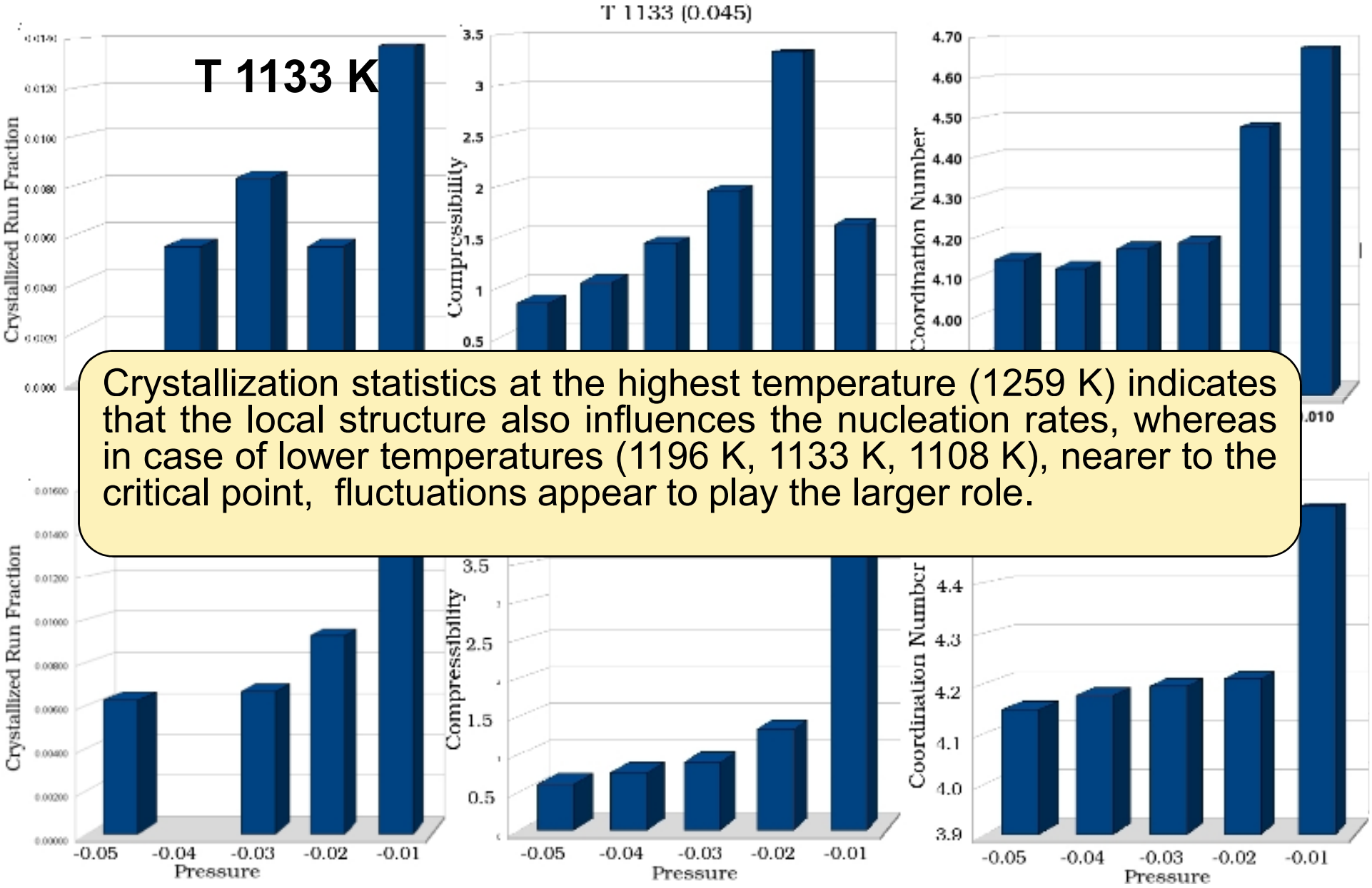




Nucleation Statistics



Nucleation Statistics



Crystallization statistics at the highest temperature (1259 K) indicates that the local structure also influences the nucleation rates, whereas in case of lower temperatures (1196 K, 1133 K, 1108 K), nearer to the critical point, fluctuations appear to play the larger role.

Free energy barrier calculation

Probability of formation of a critical nucleus is given

$$P_{crit} \propto \exp(-\Delta G_{crit}/k_B T)$$

where ΔG_{crit} is the height of the nucleation barrier

To compute the free energy barrier umbrella sampling Monte Carlo scheme is being used, which makes it possible to concentrate the sampling region of the free energy barrier by applying a bias.

Bias potential is a harmonic function of the size of the largest cluster in the system

$$w = \frac{1}{2}k(n_1 - n_0)^2$$

where, k is a constant, n1 is the largest cluster in the system and n0 is the chosen cluster size for biasing

Order parameter

To compute the free energy barrier as a function of cluster size and to measure the degree of crystallinity of the system.

Orientational order parameter

$$q_l(i) = \left(\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}(i)|^2 \right)^{1/2}$$

where

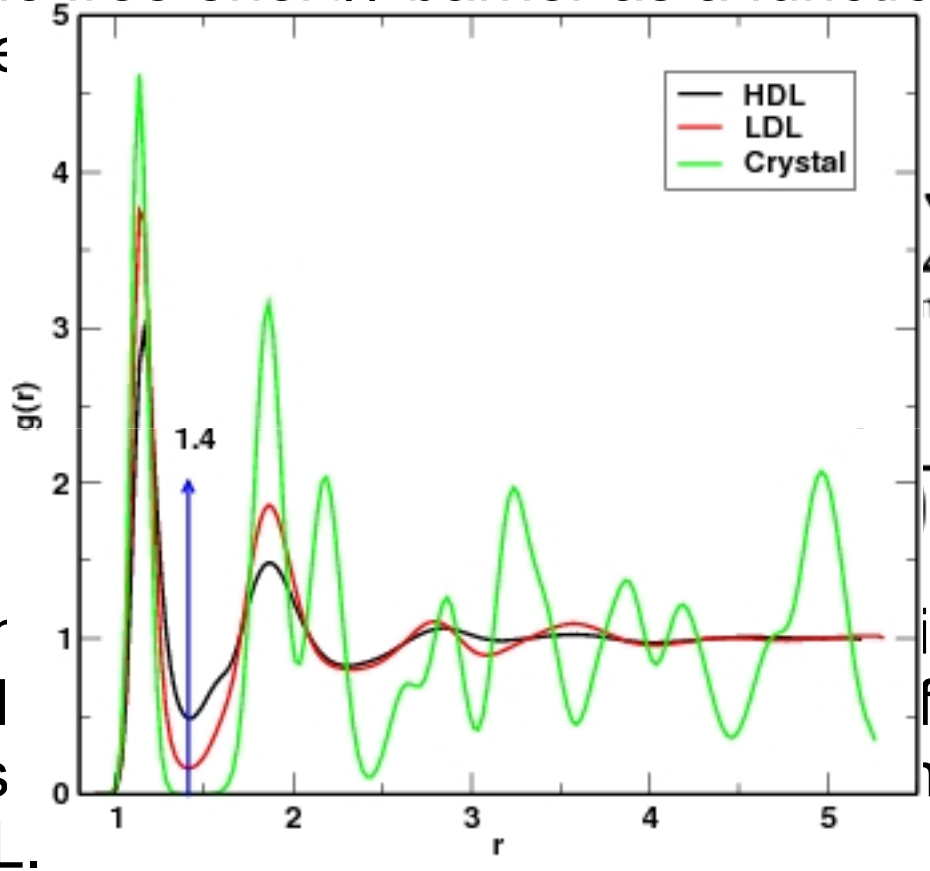
$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{\mathbf{r}}_{ij})$$

N_b is the number of neighbours within a certain cutoff radius, found from the first minima distance of g(r).
In silicon, first coordination shell radius is same for crystal, HDL and LDL.

q_3 is used for our calculations of free energy

Order parameter

To compute the free energy barrier as a function of cluster size and to me of the system.



Orientational parameter

$$\left(\sum_{i=-l}^{l} |q_{lm}(i)|^2 \right)^{1/2}$$

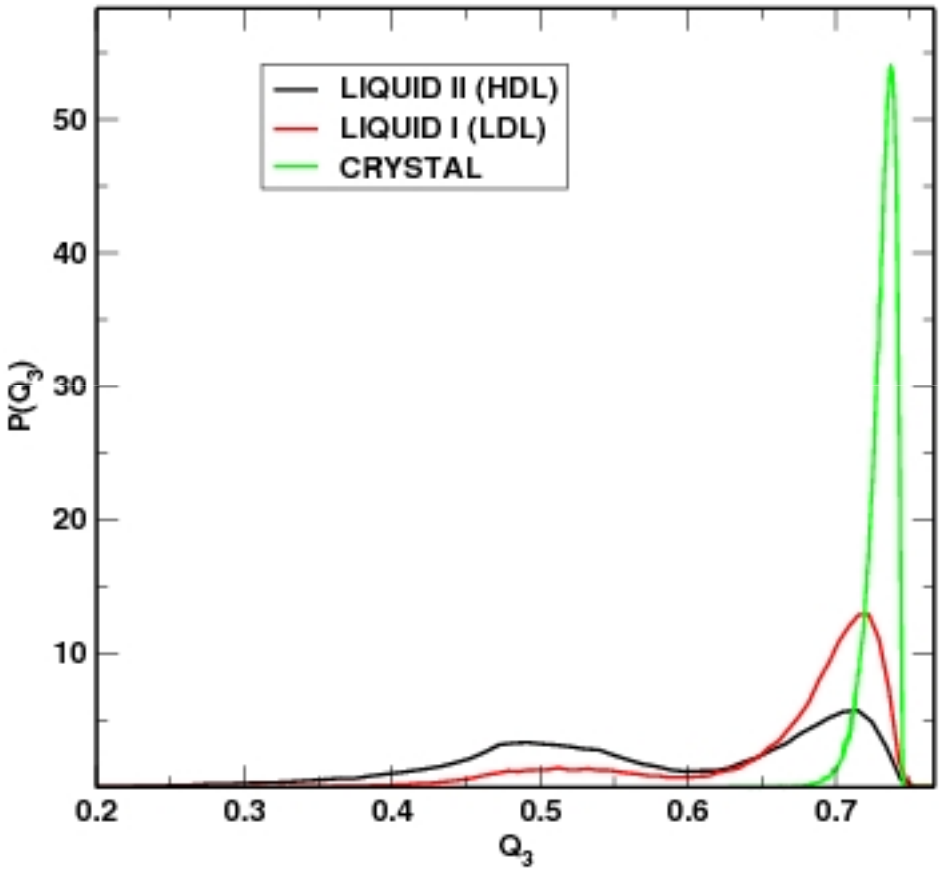
$$\frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{\mathbf{r}}_{ij})$$

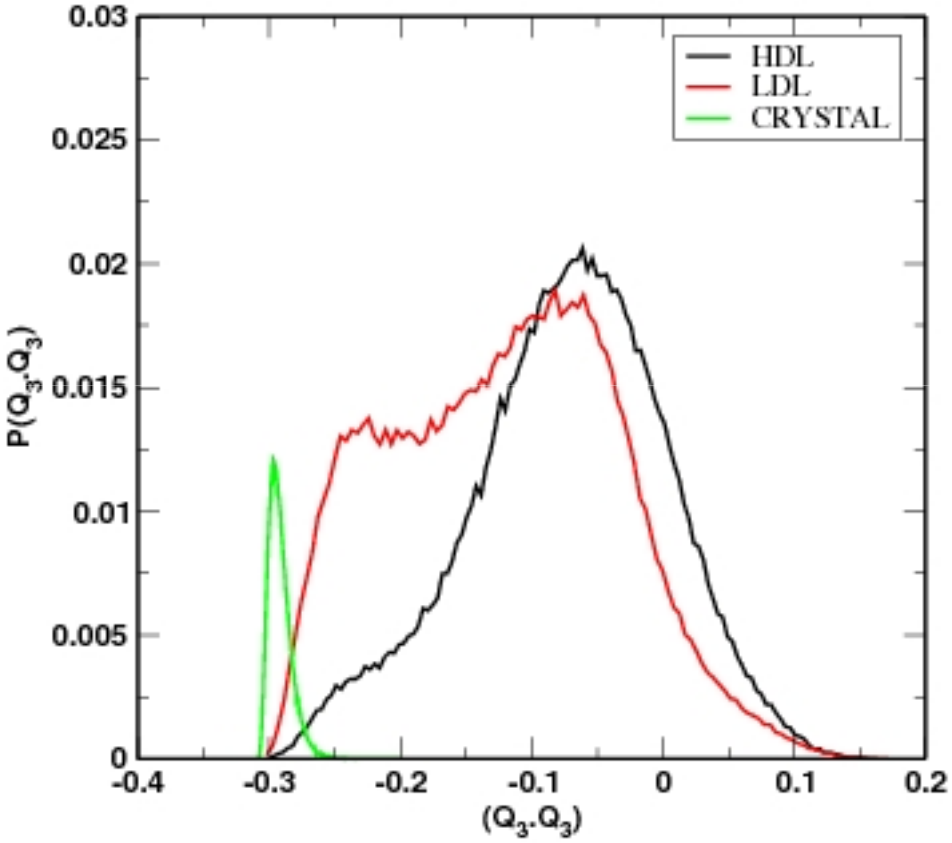
N_b is the num in cutoff radius, found f g(r). In silicon, firs ne for crystal, HDL and LDL.

q_3 is used for our calculations of free energy

Order parameter

q_3 and $q_3.q_3$ in case of a pure crystal, HDL and LDL

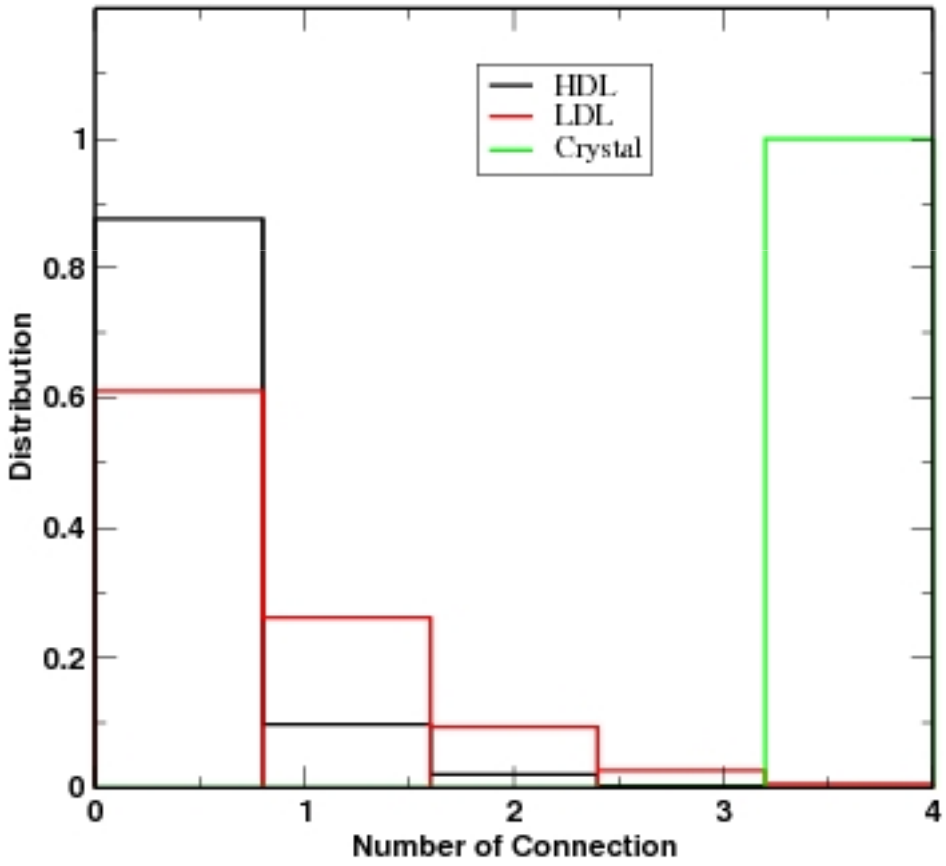




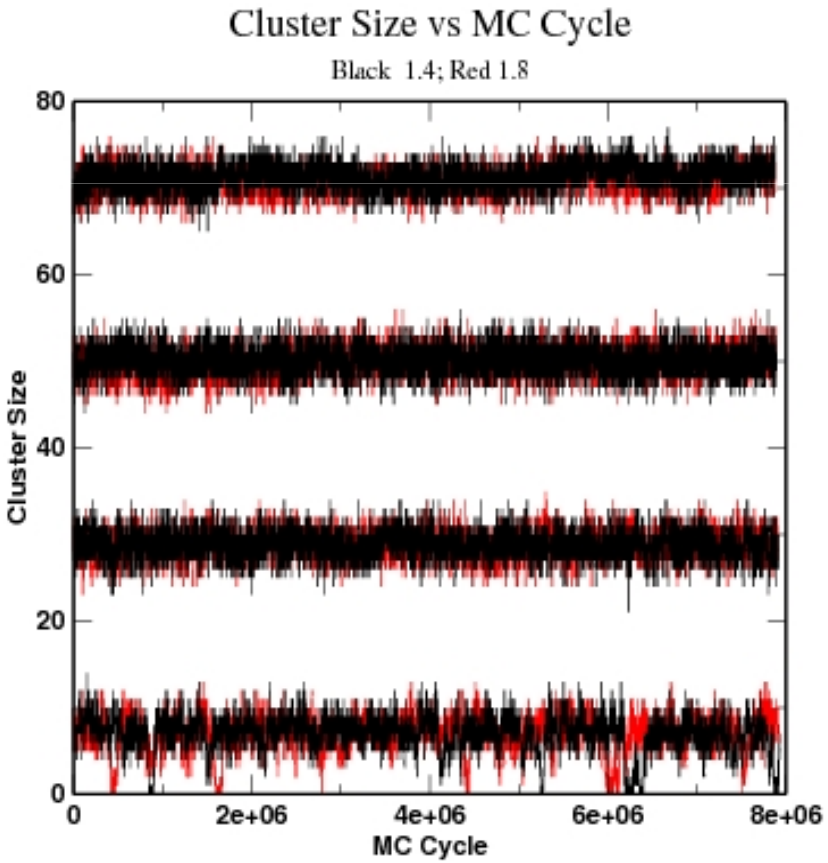
Criteria I: A particle 'i' is in a solid-like environment if $q_3(i).q_3(j)$ is < -0.23

Order parameter

Criteria II: Threshold number of connection greater than three



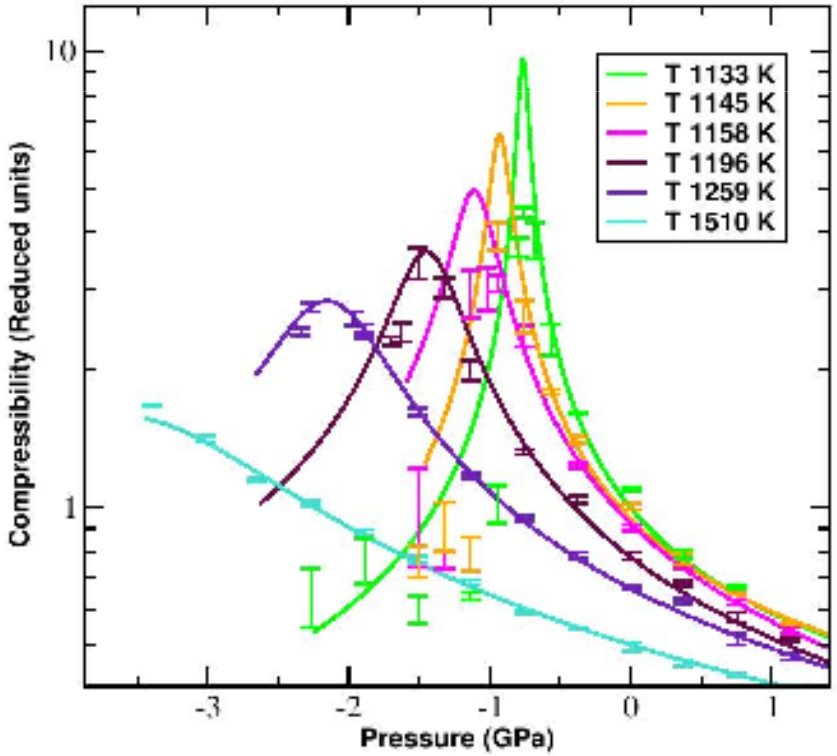
Cluster Criteria: Two solid-like particles with a certain cutoff radius. Chosen value is 1.8σ

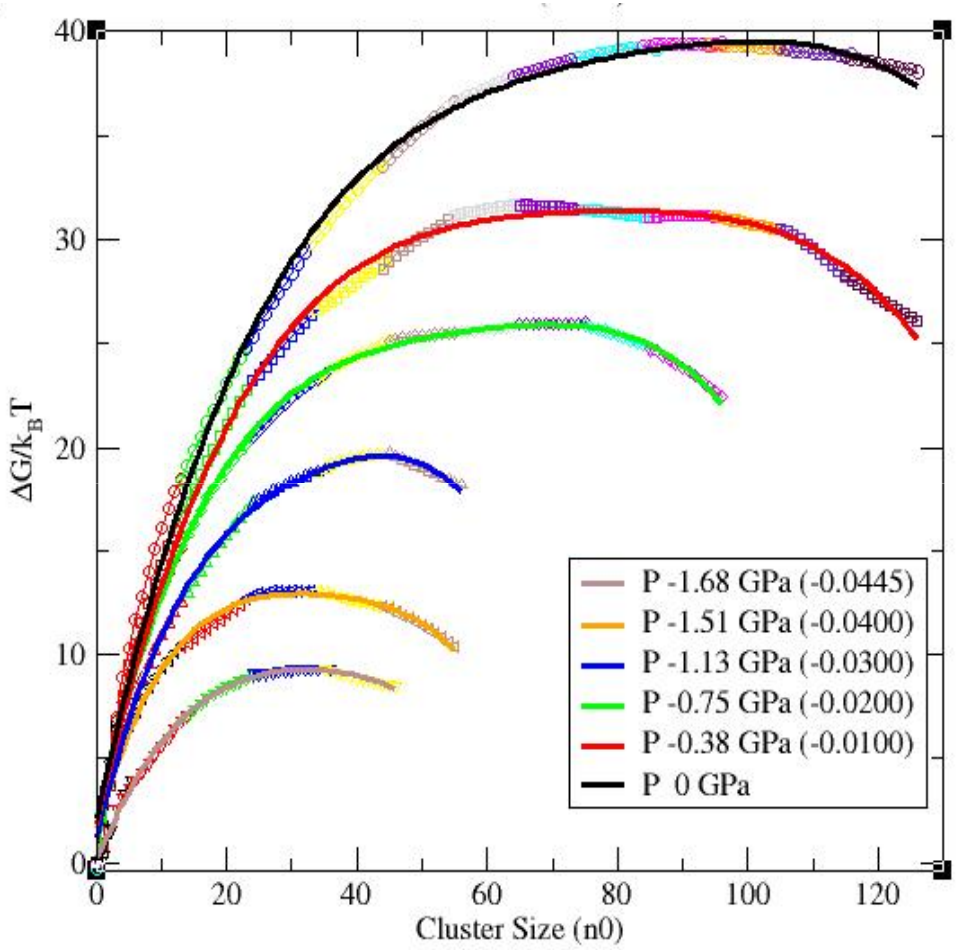


Nucleation rates

Do nucleation free energies capture observed behavior?

Estimated free energy barriers decrease with increasing compressibility at T = 1259 K.

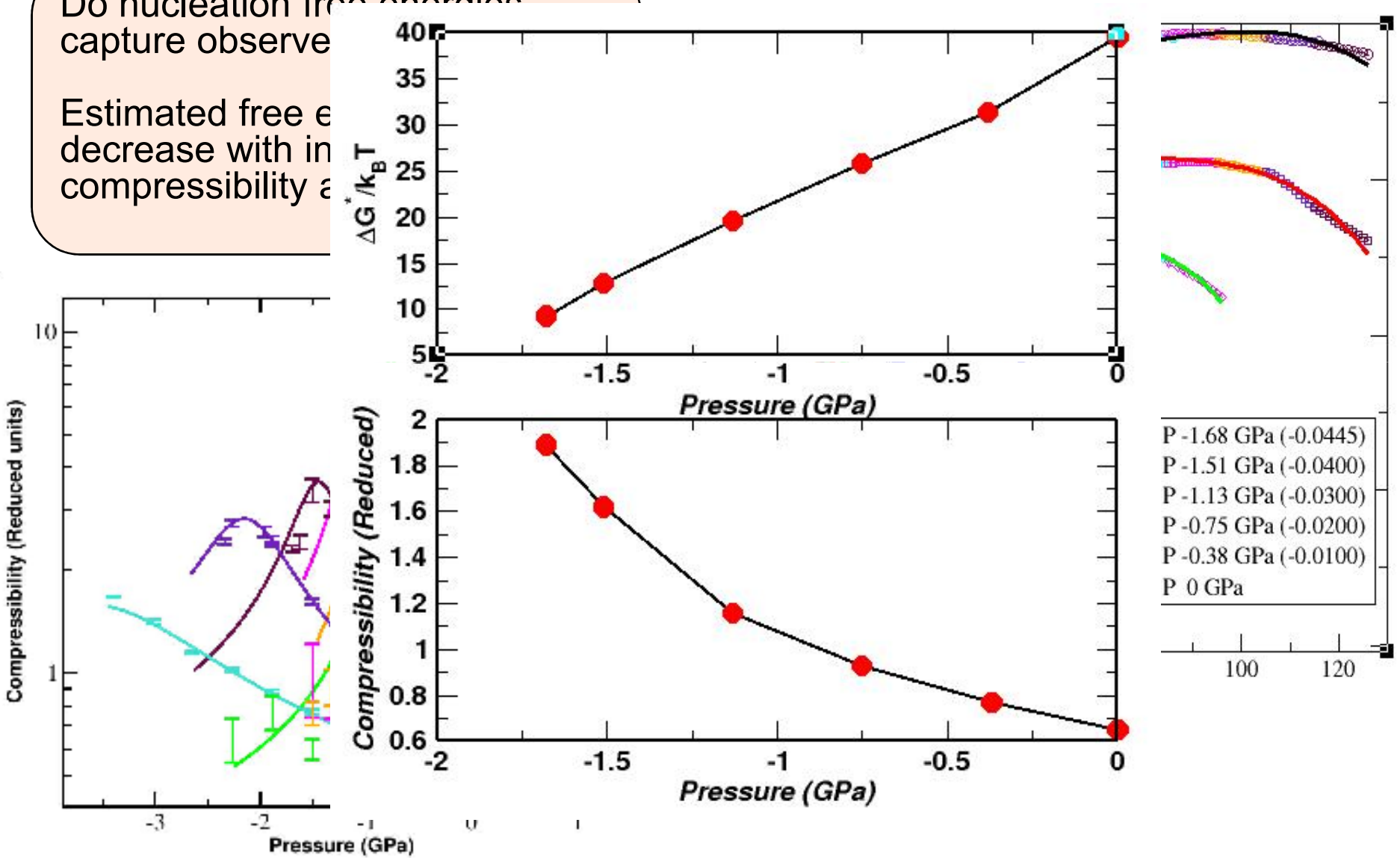




Nucleation rates

Do nucleation free energies
capture observe

Estimated free e
decrease with in
compressibility a



Low T : Equilibrium and Methodological Issues

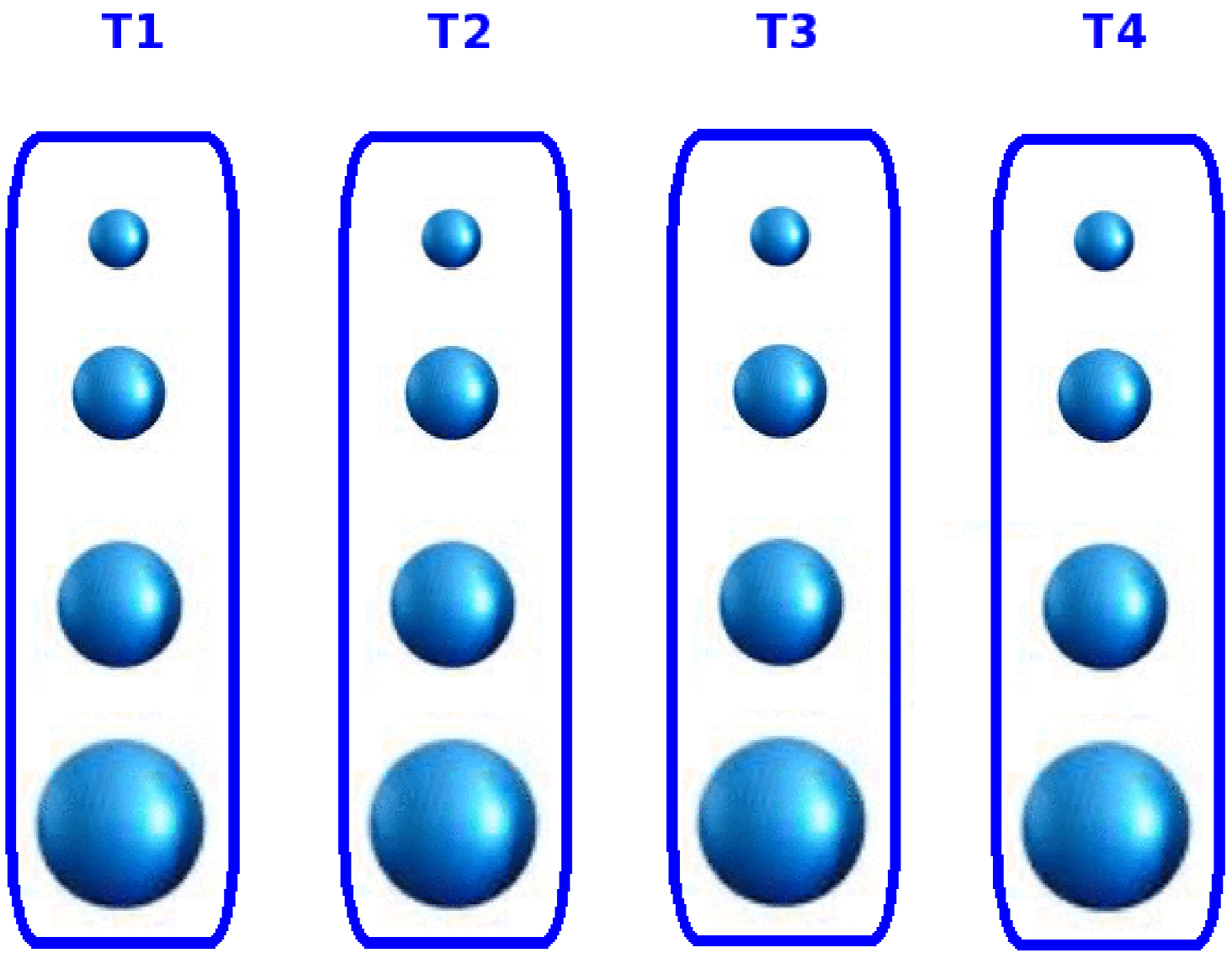
- Relaxation time increases from ps to ns upon crossing "Widom line" -***Larger equilibration time***
- Very small critical nucleus - **Hence $P(n_{max}) \neq N(n)$**

Parallel Tempering Simulation – *Facilitates faster equilibrium*

Parallel tempering carried out in both n0 and T

1. Choose a set of T's - Slower to faster equilibrium state point – which swaps
2. Each T has a set n0 which swaps

Parallel tempering in n0 and T

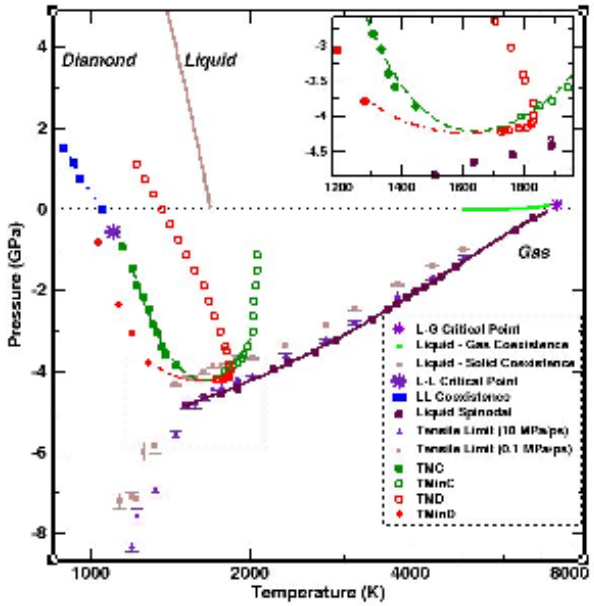


Methodical Issues

- **$P(n_{max})$** - Largest cluster size distribution as calculated in Umbrella sampling
- **N(n)** – Equilibrium cluster size distribution or number of clusters containing n particles

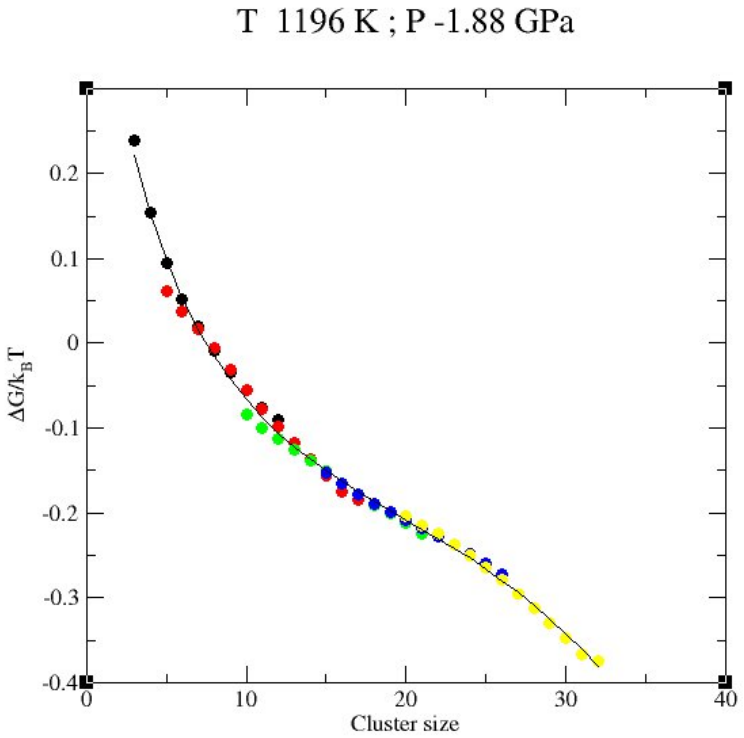
- At P = -1.88 GPa, T > 1196 K **$P(n_{max}) = N(n)$**
  - *Only one cluster of size ~* **n_{max}** *in a configuration*
  - *Critical cluster size - 15 to 100 particles*

- For P = -1.88 GPa, T < 1196 K Critical cluster size < 10
  - *Many clusters in a configuration of size ~* **n_{ma}**
  - *Hence* ***$P(n_{max}) \neq N(n)$***

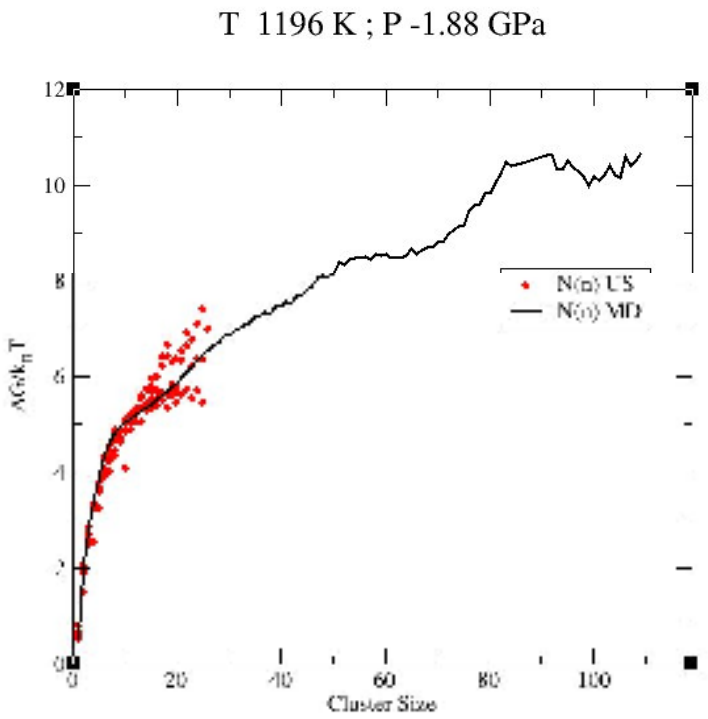


Free energy from Umbrella Sampling and MD runs

Free energy from $\mathbf{P(n_{max})}$



Free energy from $\mathbf{N(n)}$



$\boldsymbol{P(n_{max}) \neq N(n)}$

More analysis needed to extract N(n) at low temperatures as a result.

Ref: Bagchi, Bowles talks

Summary and Outlook

- Liquid-liquid transition between high density, high coordination liquid to low density, low coordination liquid in Si
- Critical point lies at negative pressures
- Enhanced crystal nucleation due to density fluctuations, and development of local structure similar to crystal.
- Density fluctuations appear to play a larger role than structure based on preliminary results.
- Evaluation of free energy barrier to the nucleation indicates as the density fluctuations increase the free energy barrier decreases.
- More analysis needed to extract free energy barriers at low temperatures.