The State Of The Hard-Sphere Solid

A journal-club-style-type seminar outlining these two papers:

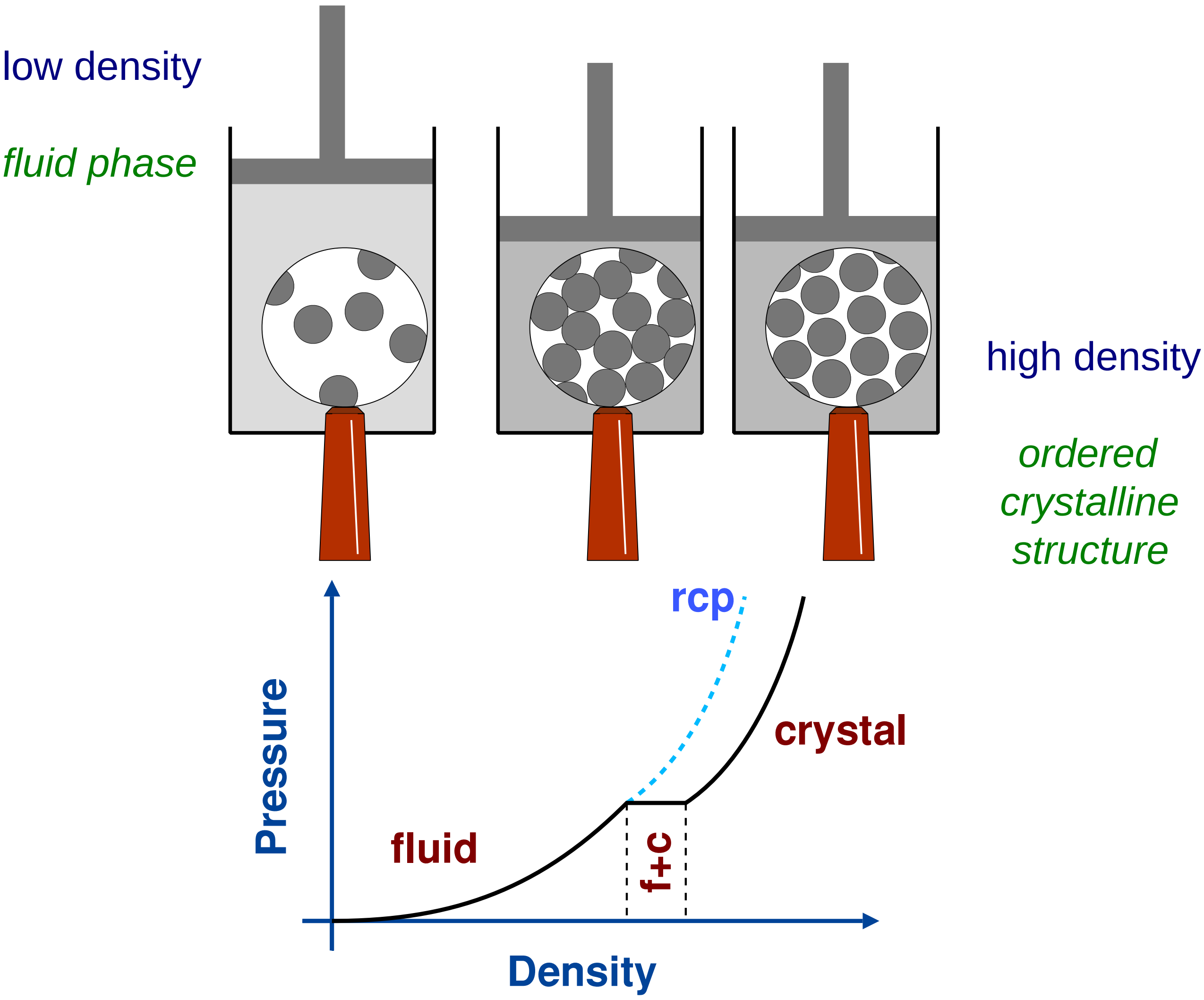
Stacking entropy of hard-sphere solids
Siun-Chuon Mau & David A. Huse
April 1999: Physical Review E,
Vol. 59, No. 4, pp. 4396-4401.

Can stacking faults in hard-sphere crystals anneal out spontaneously?
Sander Pronk & Daan Frenkel
March 1999: Journal of Chemical Physics,
Vol. 110, No. 9, pp. 4589-4592.

With a bit of the stuff I'm doing as well.

Don't Let It Phase You

The phase transition of hard-spheres is driven by entropy alone.

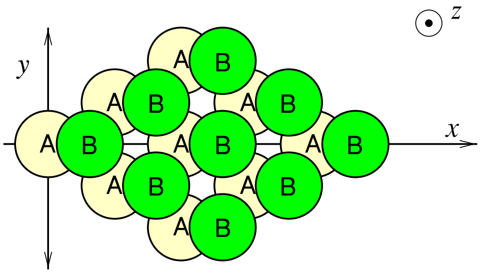


So, What Precisely Is My Problem?

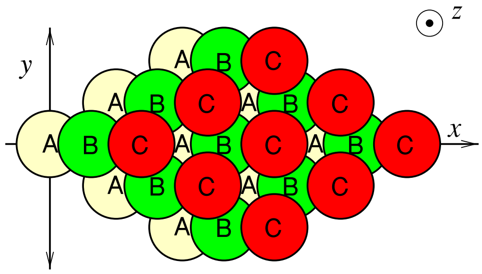
What is the structure of the solid phase?

The close-packed structures lead to highest entropy...

Hexagonal Close-Packed

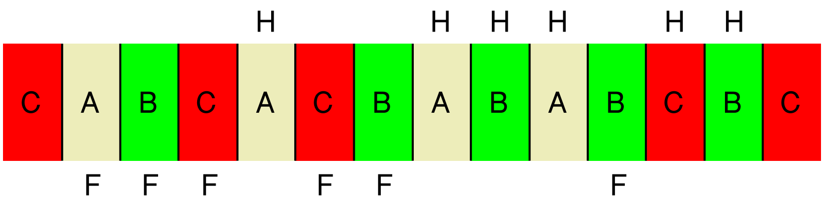


Face-Centred Cubic



Or some combination

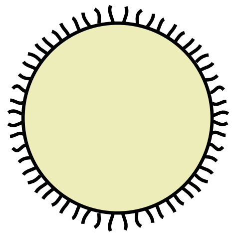
e.g. random hexagonal close-packed?



We define:

$$\alpha = \frac{V_{fcc}}{V_{total}} \quad \begin{array}{l} = 0.0 \text{ for HCP} \\ = 0.5 \text{ for RHCP} \\ = 1.0 \text{ for FCC} \end{array}$$

Real-Life Experience



Sterically-stabilised PMMA colloid suspension,
i.e. lots of hairy spheres (radius ~ 200nm).

Polymer hair provides short range repulsion.
Good approximation to hard-spheres.

Structure of crystals (usually) investigated via light-scattering.

Most get RHCP:
Implying it doesn't care which stacking pattern it's in.

Some get FCC:
Implying it does care, and that FCC is preferred.

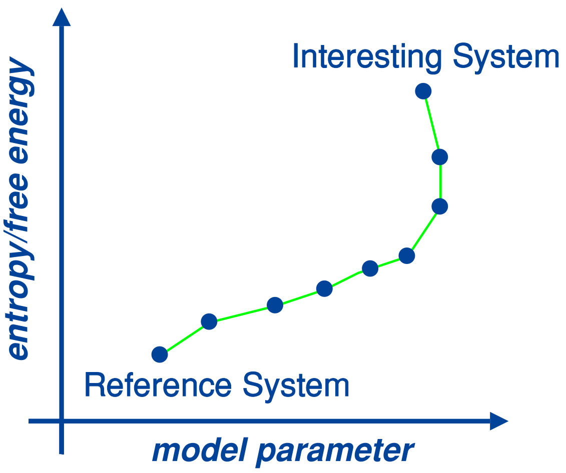
FCC has been seen in:
Samples grown slowly (weeks to months) via sedimentation.
Slow annealing RHCP to FCC.
Density matched (no gravitational effects) samples.
Gently sheared samples.

So, what does theory tell us...

Theory: Summing It Up

We have a classical many-body problem.
There is no reliable pen-and-paper theory.

Monte Carlo techniques cannot calculate free-energies directly.
So, use integration methods:



e.g. integrate

$$\left(\frac{dS}{dV}\right)_U = \frac{P}{T}$$

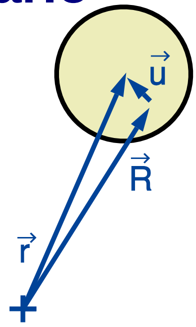
from ideal gas ($V = \infty$)
to crystal (low V)

using pressure data from
simulations in between.

Used to estimate the entropy difference between FCC and HCP.
Typical results were ~ 0.0005 ± 0.0015 Nk.

Monte Carlo CAN evaluate this entropy difference,
IF the simulation can visit BOTH phases.

Simulation: Lattice-Switch Monte Carlo

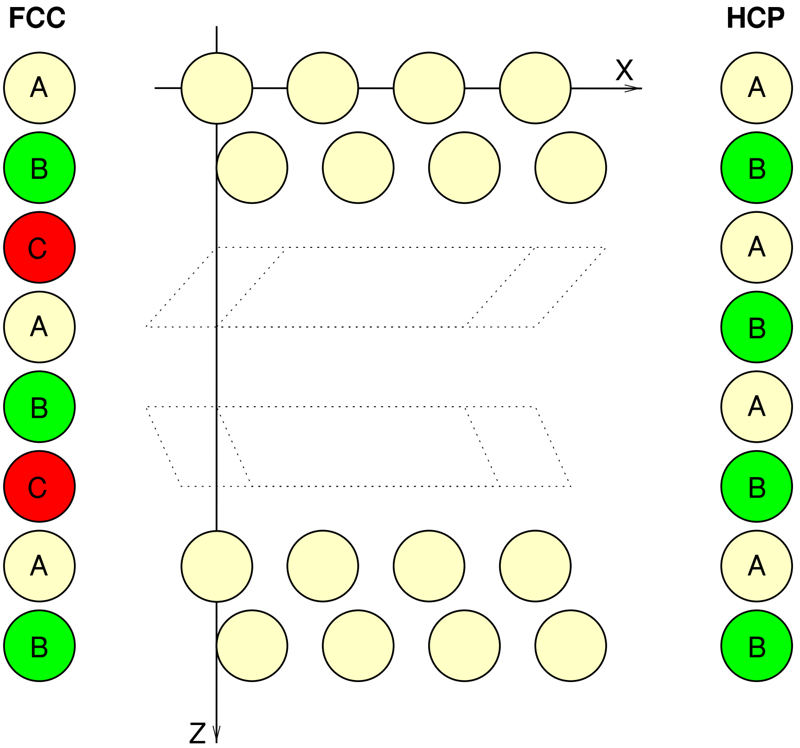


Decompose sphere positions into

$$\vec{r} = \vec{R} + \vec{u}$$

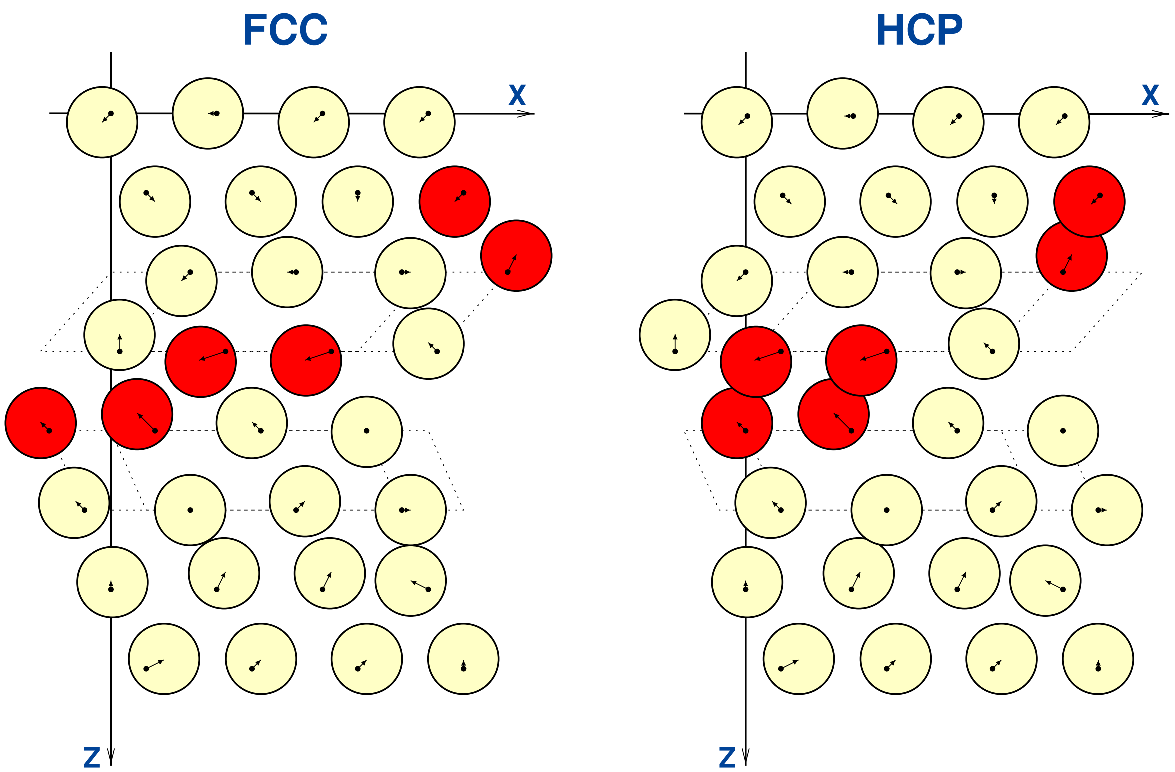
Lattice sites $\{R\}$ and displacements $\{u\}$

One can attempt to switch between two lattices, e.g. $R_{HCP} \leftrightarrow R_{FCC}$ while holding the displacements {u} constant.



Simulation: Lattice-Switch Monte Carlo (2)

However, the switch is rather unlikely.



So some nifty sampling is required (multi-canonical Monte Carlo).

See Phys. Rev. Lett. & forthcoming paper (or just ask me).

Mau & Huse: Overview

Stacking entropy of hard-sphere solids

April 1999: Physical Review E,
Vol. 59, No. 4, pp. 4396-4401.

Simulations used to evaluate entropy differences between various stacking patterns.

Uses Lattice-Switch Monte Carlo and a related shear technique.

Simulation of the close-packed (infinite pressure) limit directly by simulating a system of hard-dodecahedra.

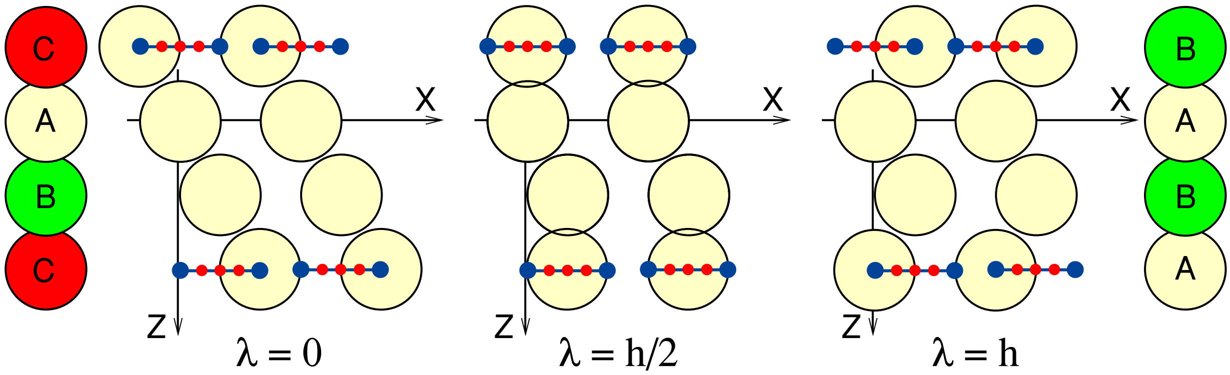
Fitting the results from different stacking patterns to a 'spin-model'. This allows the evaluation of the strength of correlations across 3, 4 and 5 layers.

Use their results to prove that FCC has the highest entropy compared to all other possible stackings, and for all densities from close-packed to melting.

Mau & Huse: By Shear Chance

Define $\lambda = 0...h$ lattices $\{R_\lambda\}$ to linearly interpolate between two lattices.

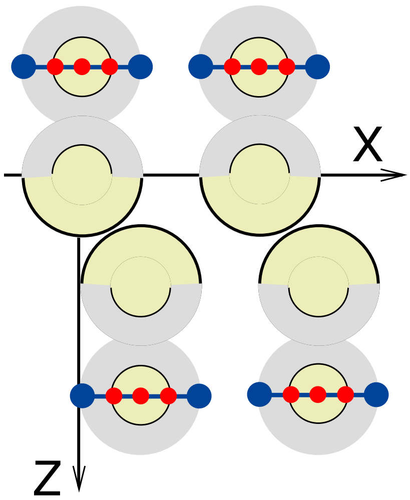
$$\vec{R}_\lambda = \frac{\lambda}{h} . \vec{R}_{HCP} + \frac{(h-\lambda)}{h} . \vec{R}_{FCC}$$



Between $\lambda = 0$ and $\lambda = h$, the pair-wise interactions $d_{ij}(\lambda)$ (the diameters) are altered so that all λ are visited.

That's ~ $6(h-1)N$ numbers to twiddle!

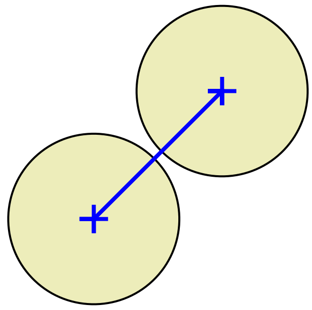
OK for small systems (up to $N = 8^3$). Bottlenecks form in larger systems, where λ very rarely changes.



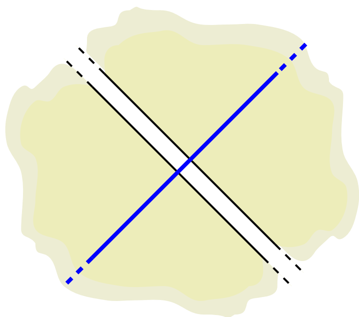
Thus, most results taken via our lattice-switch overlap technique.

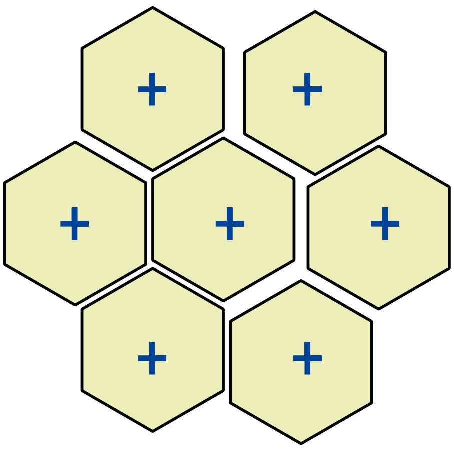
Mau & Huse: Taking It To The Limit

As the pressure tends to infinity,
the density tends to the close-packed limit,
and the distance between the surfaces of
adjacent spheres tends to zero.



In this limit, the curvature of the spheres
becomes negligible...



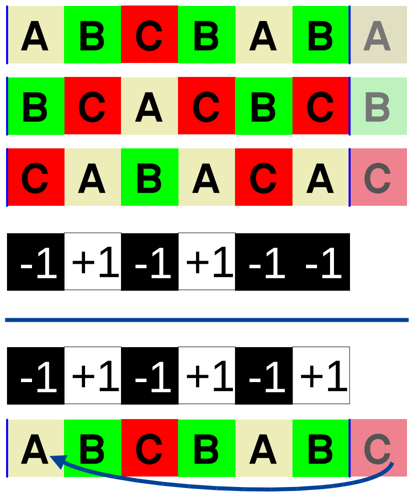


...and the system is formally equivalent[†]
to a system of hard-dodecahedra
(which cannot rotate).

In this way, we can simulate the
close-packed limit directly.

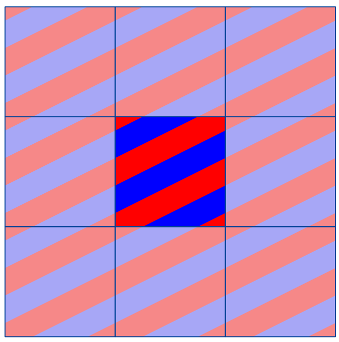
[†] See Alder et al, Journal Of Computational Physics, vol. 7, pp. 361-366 (1971).

Mau & Huse: Different Stackings

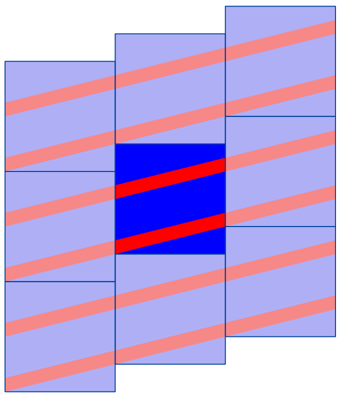


Distinct stacking patterns can be identified with and Ising-like spin-model:
σ = +1 for FCC, -1 for HCP.

But, not all spin patterns will fit into normal periodic boundary conditions.



So, use shifted periodic boundary conditions.



Also, the spin-model allows the entropy to be expressed as:

$$S = \overbrace{N s_0}^{\text{local}} + \overbrace{N_L h \sum_i \sigma_i}^{\text{3 layer}} + \overbrace{N_L J \sum_i \sigma_i \sigma_{i+1}}^{\text{4 layer}} + \underbrace{N_L h' \sum_i \sigma_i \sigma_{i+1} \sigma_{i+2} + N_L J' \sum_i \sigma_i \sigma_{i+2}}_{\text{5 layer}}$$

So, we can estimate the range of correlations across layers.

Mau & Huse: Results

$S_{FCC} - S_{HCP} = 2h + 2h'$: at melting = 0.00090(4) Nk (per sphere), and at close-packing = 0.00115(4) Nk (per sphere).

Analysis of various different stackings:
At close-packing, correlations extend over 4 layers.
Near melting, correlations fall off more slowly.
All values of h, J, h' & J' indicate that FCC is preferred.

Finite size effects only observed for $N < 8^3$.

No anisotropy detected in HCP phase.
*(*c/a *within* ±0.002 *of isotropic value)*

Collisions with 2nd nearest neighbours found to contribute very little to the entropy (~0.00008 Nk at melting).
No significant difference in the 2nd NN interactions between the two structures.

We (currently) find $S_{FCC} - S_{HCP}$ at close-packing = 0.00132(4) Nk.
Also, we find 2nd NN entropy ~ $6 \cdot 10^{-6}$ Nk at melting.
Our simulations (for this data) have only been at $N = 6^3$.

Pronk & Frenkel: Overview

Can stacking faults in hard-sphere crystals anneal out spontaneously?

March 1999: Journal of Chemical Physics, Vol. 110, No. 9, pp. 4589-4592.

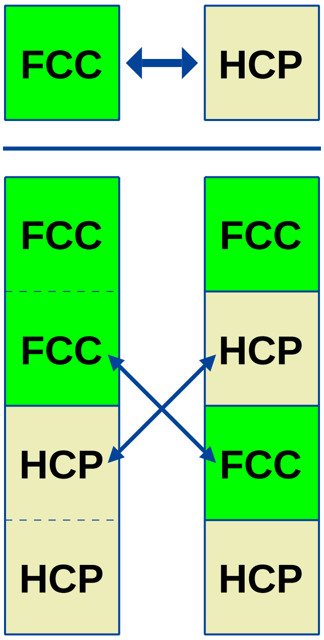
Lattice-Switch Monte Carlo used to evaluate the bulk and interfacial entropy difference between FCC and HCP.

This information is then used to construct an estimate of the entropy difference between FCC and RHCP.

Determination of the range of stability of RHCP and FCC, which is dependent on crystallite size.

A version of the Wilson-Frenkel Law is used to estimate the rate at which a RHCP crystal will convert to FCC.

Pronk & Frenkel: Nifty Calculations



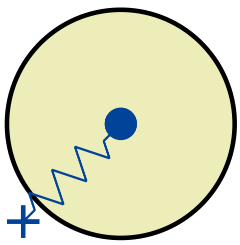
Simple lattice-switch used to get FCC-HCP bulk entropy difference.

Also, lattice-switch simulation used to evaluate the difference between two systems at the same α (0.5), but where one has twice the interfacial area of the other.

Results are checked using an integration method:

Spheres are attached to their sites by springs, all with the same spring constant λ.

$\delta S / \delta \lambda$ is integrated from a system with very strong springs (ie an Einstein crystal) to one with very weak/non-existant springs (normal crystal).



Pronk & Frenkel: Results

$S_{FCC} - S_{HCP}$ near melting (77.78% of the close-packed density):
L-S, $N = 6^3$: $132(4) \cdot 10^{-5}$ Nk
L-S, $N = 12^3$: $112(4) \cdot 10^{-5}$ Nk
IM, $N = 12^3$: $113(4) \cdot 10^{-5}$ Nk

Speculates that $N = 12^3$ is effectively equivalent to the thermodynamic limit ($N \rightarrow \infty$).

Our new lattice-switch results (at the same density):
$N = 6^3$: $133(3) \cdot 10^{-5}$ Nk
$N = 12^3$: $113(3) \cdot 10^{-5}$ Nk
$N = 18^3$: $110(3) \cdot 10^{-5}$ Nk

So $N = 12^3$ is indeed statistically indistinguishable from the thermodynamic limit.

Interfacial entropy difference estimated (from $N = 12 \cdot 12 \cdot 24$) to be $\gamma_{fcc\text{-}hcp} = 26(6) \cdot 10^{-5}$ Nk.

Mau & Huse: $\gamma_{fcc\text{-}hcp} = 2J + 2J' = 12(4)...41(10) \cdot 10^{-5}$ Nk.

Pronk & Frenkel: Random Stackage

The entropy difference (per sphere) between FCC and RHCP is:

$$\Delta S_{fcc-rhcp} = 0.5\,\Delta S_{fcc-hcp} + 0.5\,\gamma_{fcc-hcp} - \frac{ln\,2}{N_{layer}}$$

1st term: As RHCP is half and half FCC and HCP.
2nd term: On average there is a stacking fault every 2 layers.
3rd term: Each layer has a choice of 2 stackings.
This term disappears in the thermodynamic limit.

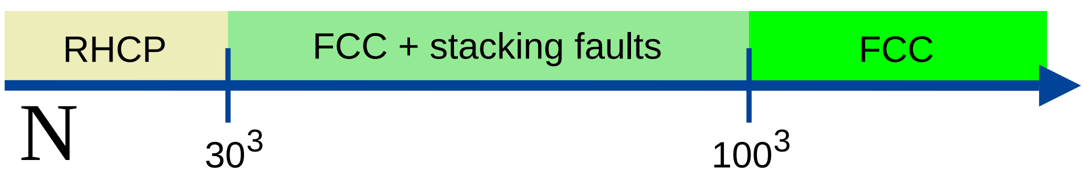
Using their results for the thermodynamic limit:

$$\Delta S_{fcc-rhcp} = 69\,(5) \times 10^{-5} - \frac{ln\,2}{N_{layer}}$$

Mau & Huse find 1st term = $63(4)...66(11)\cdot 10^{-5}$ Nk.

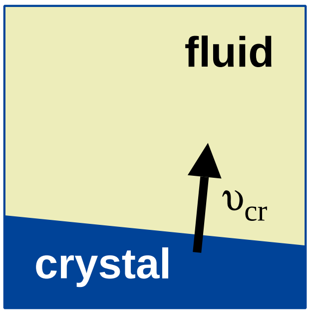
Pronk & Frenkel assume that stacking faults do not interact.
Corrections are probably smaller than statistical uncertainty.

Equilibrium behaviour depends on crystallite size.



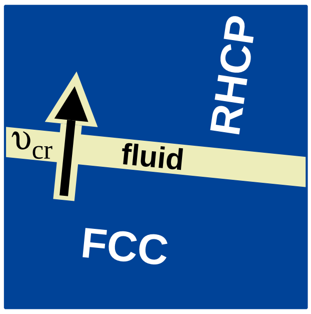
Pronk & Frenkel: Estimating Growth

Assumption that conversion occurs only at the grain boundaries.
Apply the Wilson-Frenkel law:



$$\upsilon_{cr} \approx \frac{D}{\Lambda}\left(e^{\Delta\mu/k_B T} - 1\right)$$

D =(short-time) self-diffusion rate.
Λ is how far a particle must travel to become part of the crystal.

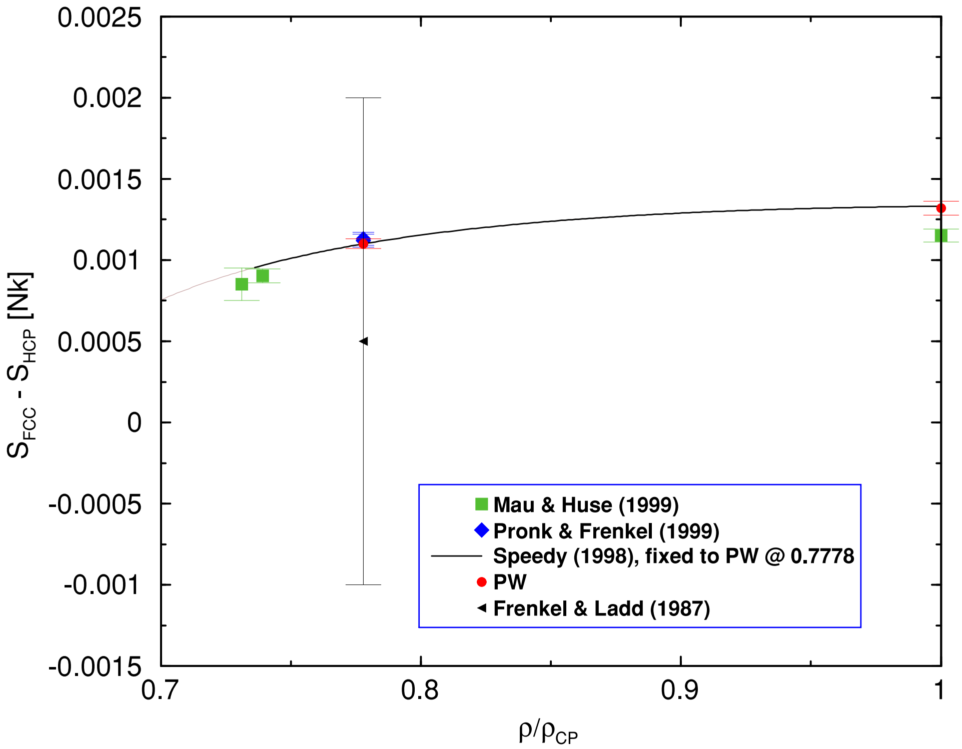


We assume grain boundaries are fluid-like,
take Λ ~ sphere radius ≈ 200nm,
we replace $\Delta\mu$ by $\Delta S_{FCC\text{-}RHCP}$ and take $D \sim 2{\cdot}10^{-10}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$.
$\therefore\ \upsilon_{cr} \sim 7{\cdot}10^{-9}\,\mathrm{cm\,s}^{-1}$.
ie several months to convert a 1mm RHCP crystallite to FCC.

Can determine a rate function:
$\Gamma(\mathcal{L}) = \upsilon_{cr}(\mathcal{L})/\mathcal{L}$ = time taken for crystallite of linear dimension $\mathcal{L}$ to change from RHCP to FCC.

Maximum occurs at $N \sim 60^3$ ($\mathcal{L} \sim 12\mu\mathrm{m}$).
Crystals of this size should be the first to become FCC.

The Grand Finale



For RHCP, we get $S_{FCC} - S_{RHCP} \sim 6{\cdot}10^{-4}$ Nk (per sphere).
Size dependence and RHCP to FCC conversion may explain most of the experimental results.

We need to know (from experiment) the size-distribution of crystallites to test this speculation rigorously.

Work so far cannot (directly) explain the effect gravity has on crystallisation, but size-distribution data may help.