The Glass Forming Ability of a Binary Mixture:The Role of Entropy

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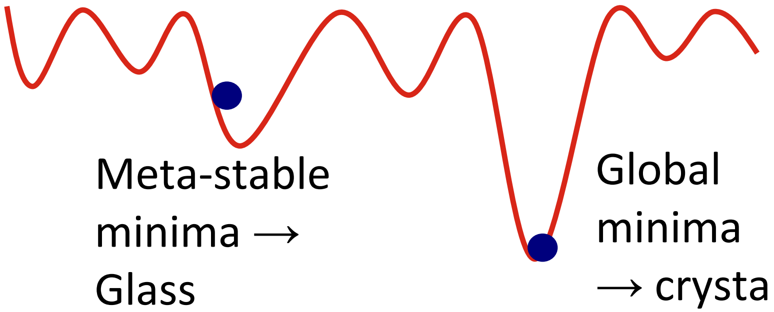
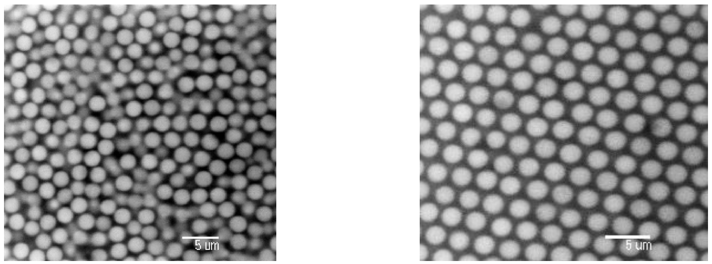
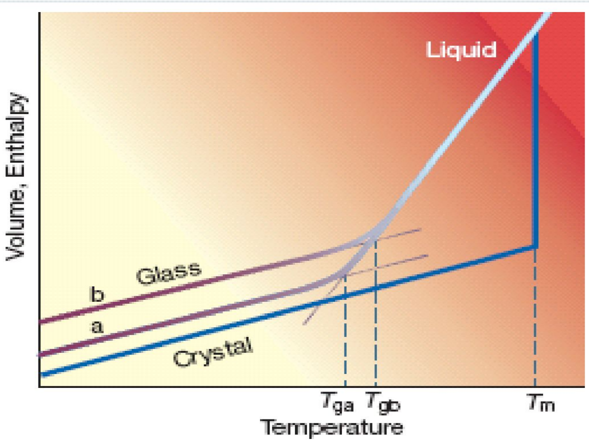
What is glass forming ability?



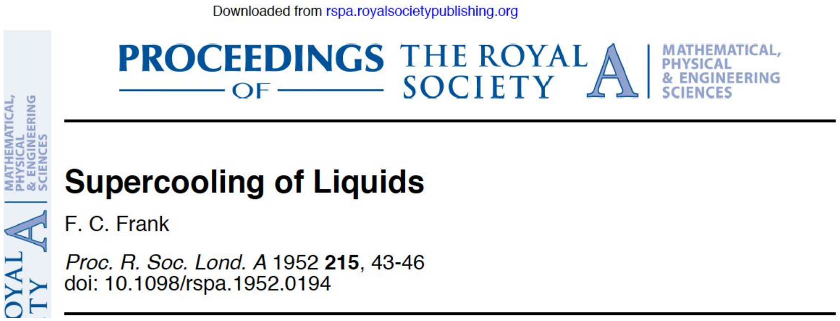




Debenadatti, Nature 410, 259-267 (2001)

Role of frustration

C. Frank→



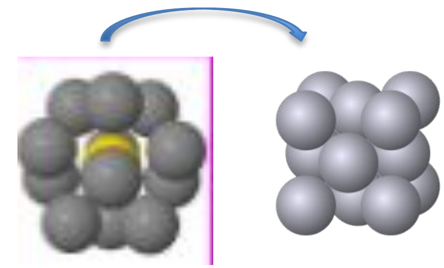
PROCEEDINGS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Supercooling of Liquids

F. C. Frank

Proc. R. Soc. Lond. A 1952 **215**, 43-46
doi: 10.1098/rspa.1952.0194

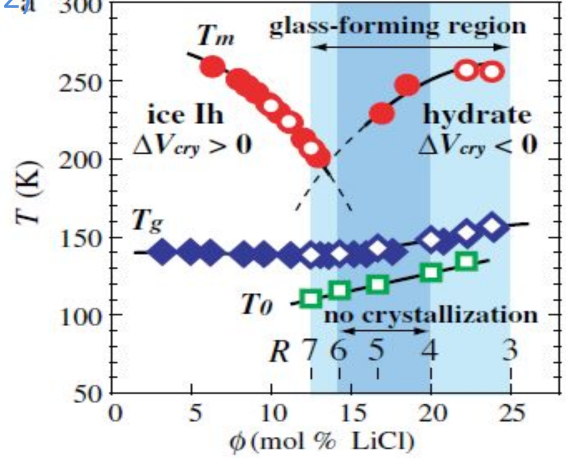
J. Non-Crys. Solids **407** 34 (2015)



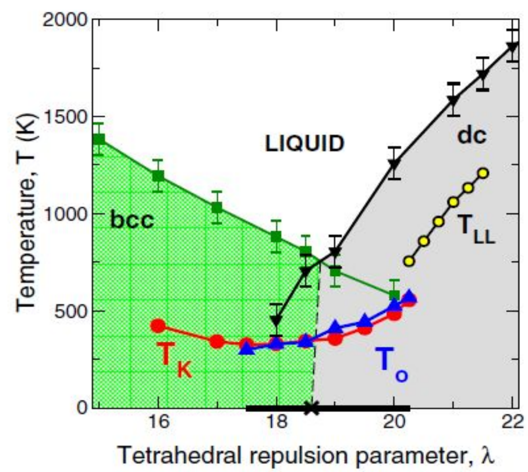
Stability of supercooled liquid: Icosahedral ordering locally stable . Crystal ordering globally stable. Costly local rearrangement of molecules slows down crystallization, promotes supercooling.

V shaped phase diagram and frustration

Tanaka Eur. Phys. J. E, **35**:113, (2012)

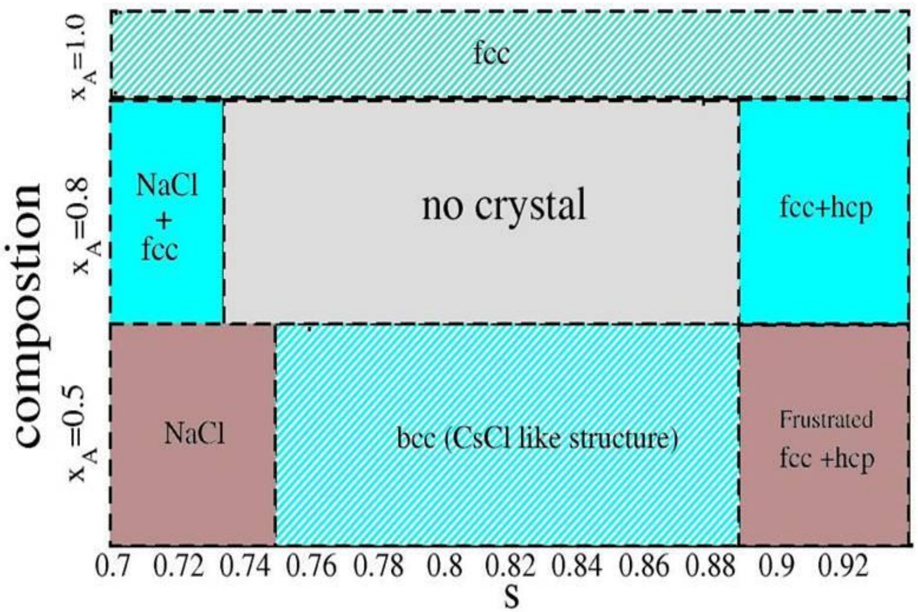


Molinero et al PRL., **97**:075701 (2006)



➢Frustration between two different crystal structures

Crystallization vs.Glass transtion



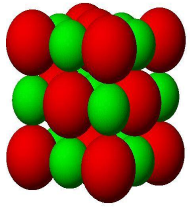
Binary Lennard- Jones mixtures

σ_{AA}=1.0 σ_{BB}=0.88

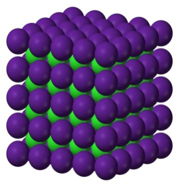
$S=\sigma_{AB}/\sigma_{AA}$

ε_{AA}=1.0 ε_{BB}=0.5

ε_{AB}=1.5



NaCl crystal

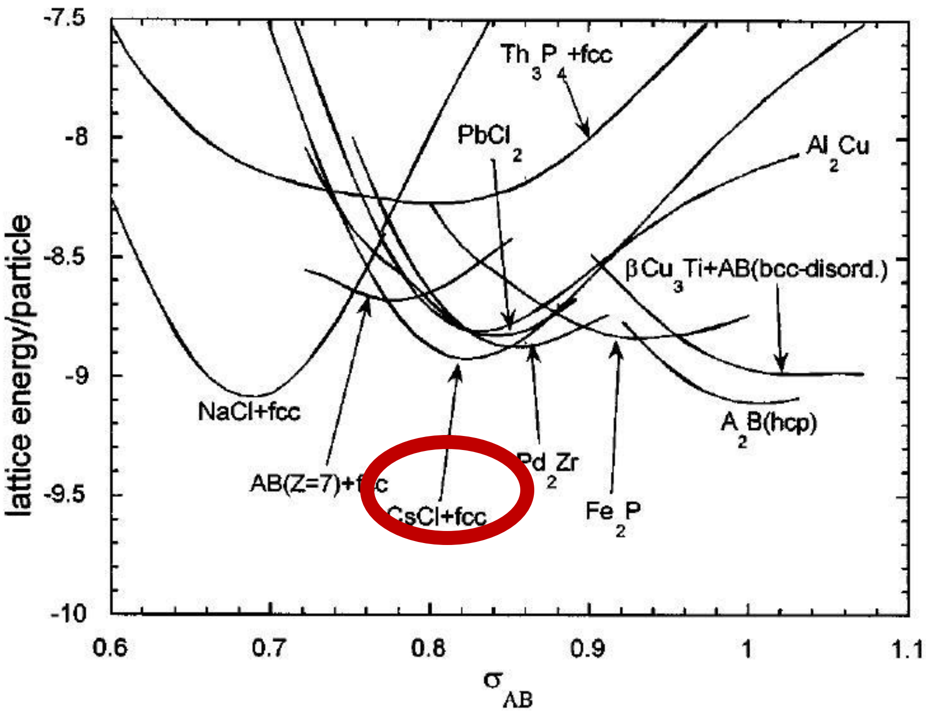


CsCl (bcc) crystal

Overlap between bcc (CsCl) zone and no crystal zone

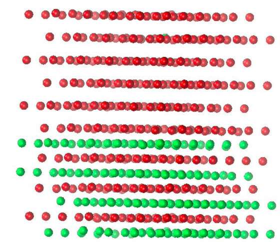
Banerjee,Chakrabarty,Bhattachryya,JCP,**139**.104501(2013)

Global Structure of the no crystal zone

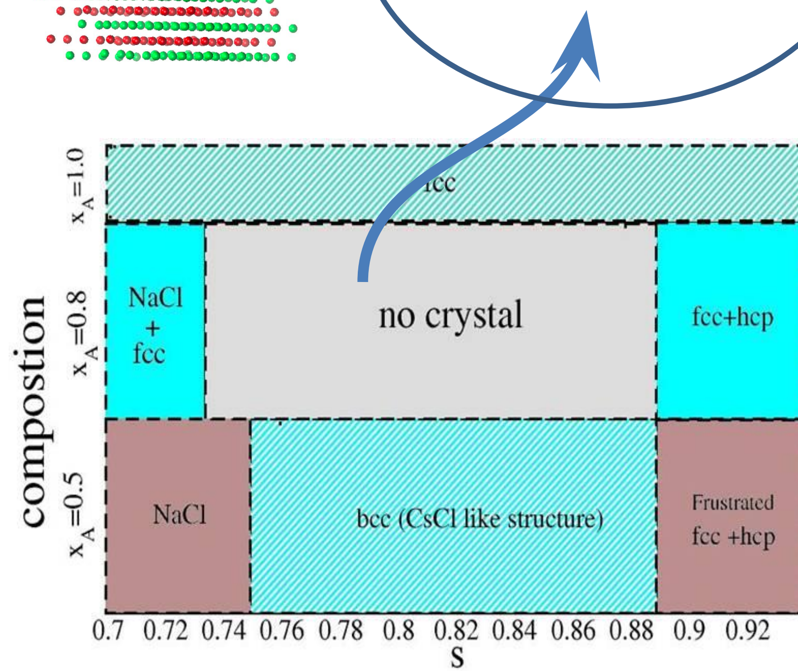


Fernandez & Harrowell JCP,120,9222(2004)

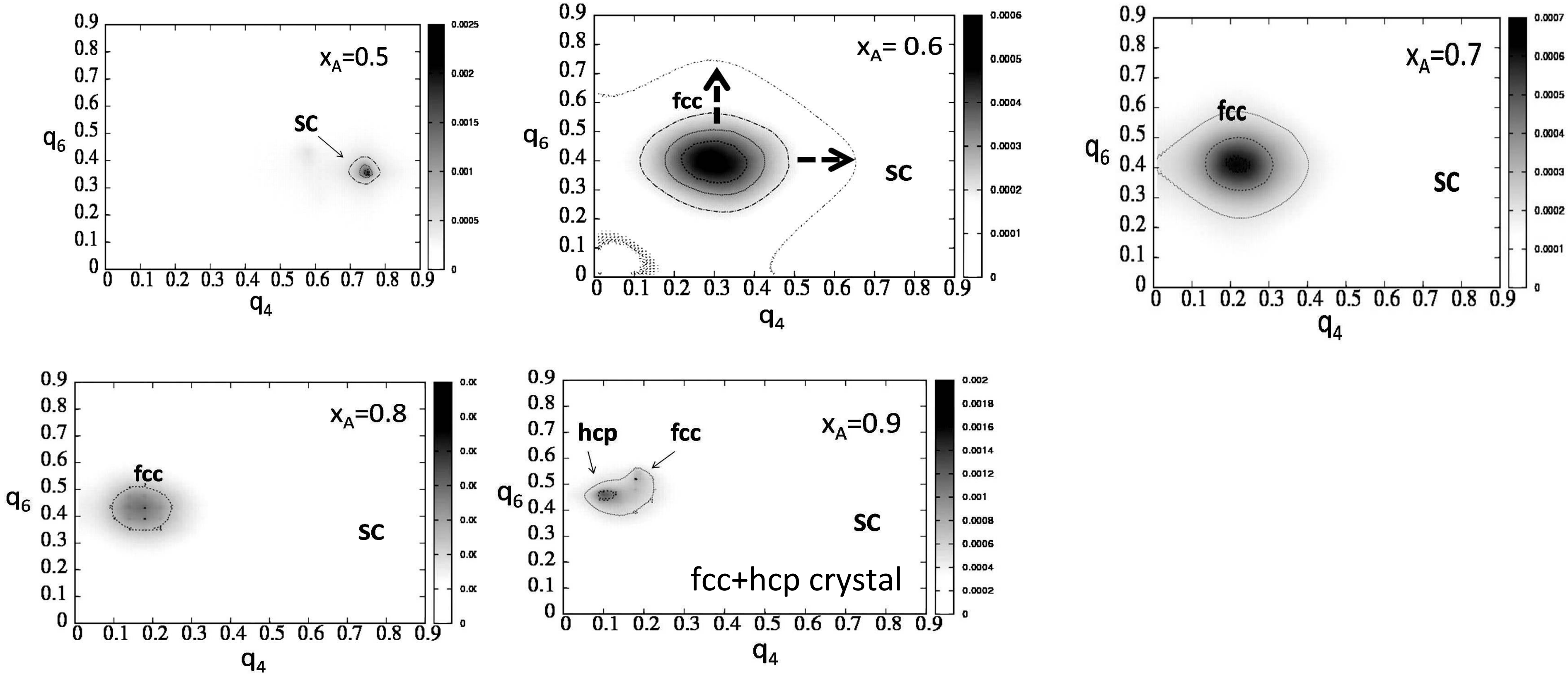
AB particles form CsCl crystal
Remaining A particles form pure fcc structure



Global Structure CsCl+fcc



Transition from sc to fcc with increasing x_A

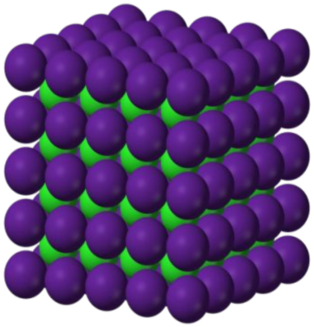


No sc (bcc) formation tendency at x_A=0.8

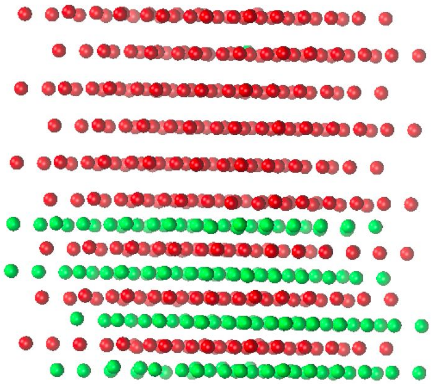
➔ Nucleation barrier for bcc formation increases with x_A

Banerjee,Chakrabarty,Bhattachryya,JCP,**139**.104501(2013)

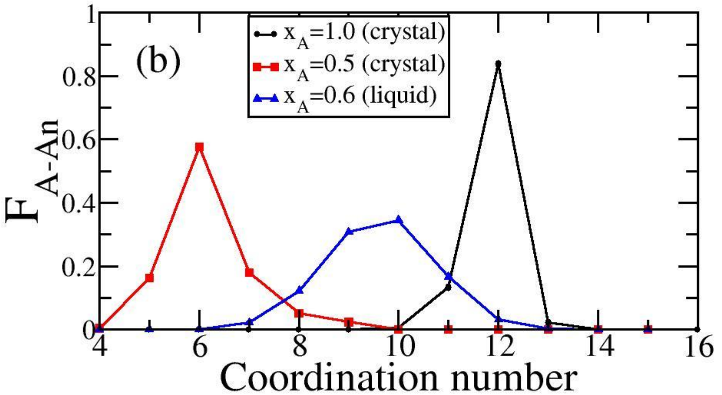
CsCl vs. CsCl+fcc



CsCl → interpenetrating sc's
A-A→ sc (6 nn)



CsCl +fcc
A-A→ sc and fcc (6 and 12 nn)



fcc and sc → large difference in nearest neighbours

Criteria for stability against Crystallization

Global structure has two different crystalline forms (NaCl+ fcc, CsCl+fcc)

&

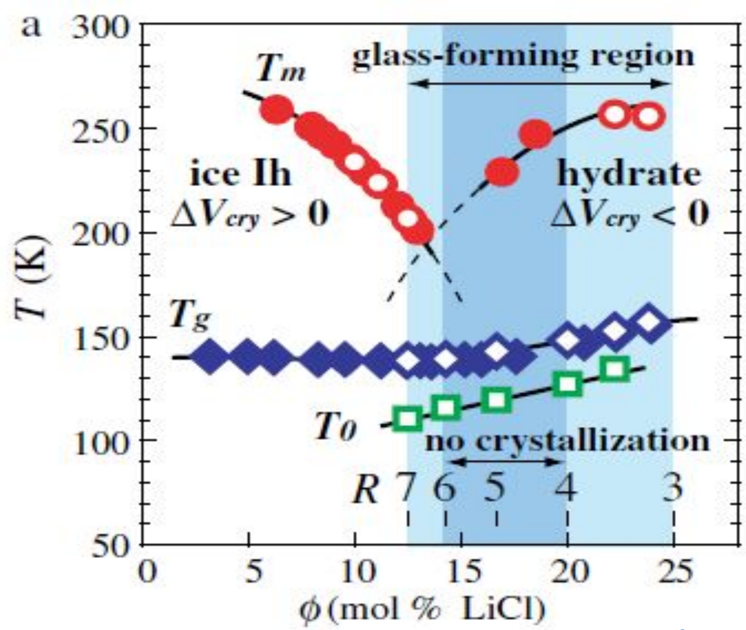
A single species contribute to both crystal forms (A in NaCl, fcc or in CsCl, fcc)

&

A large difference in its order parameter (CN or local BOO or any other order parameter like A in CsCl and fcc)

Frustration between the LPS and the global structure

V Shaped zone → Kinetics Vs. Thermodynamics



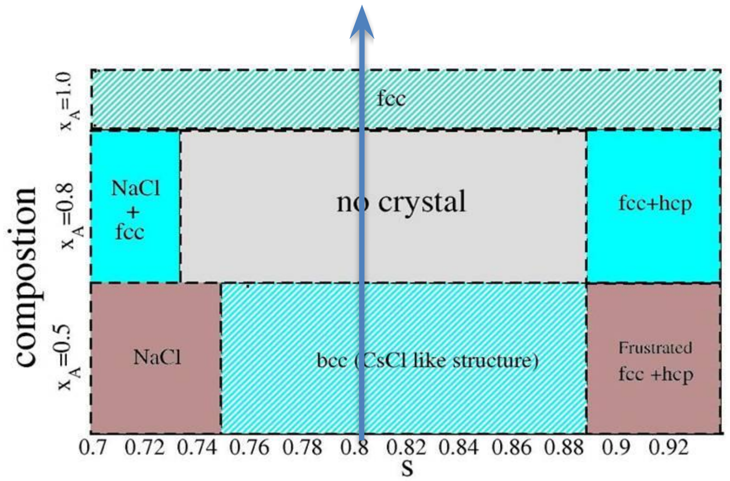
Tanaka Eur. Phys. J. E, **35**:113, (2012)

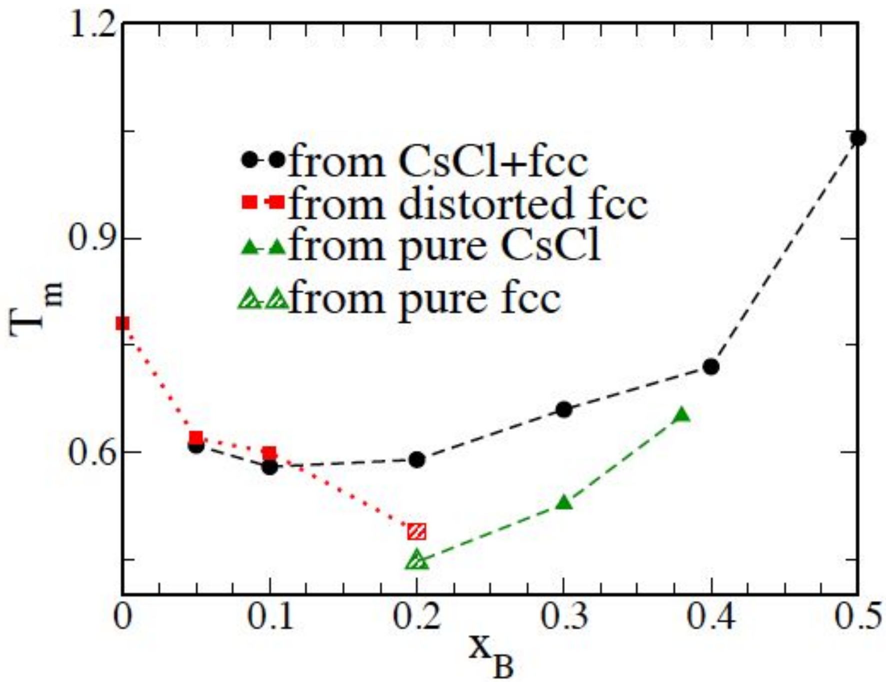
Overlap of glass forming region and eutectic point.

Eutectic point → Slow dynamics → Suppression of nucleation

Kinetic or Thermodynamics ????

Thermodynamics vs. Kinetics

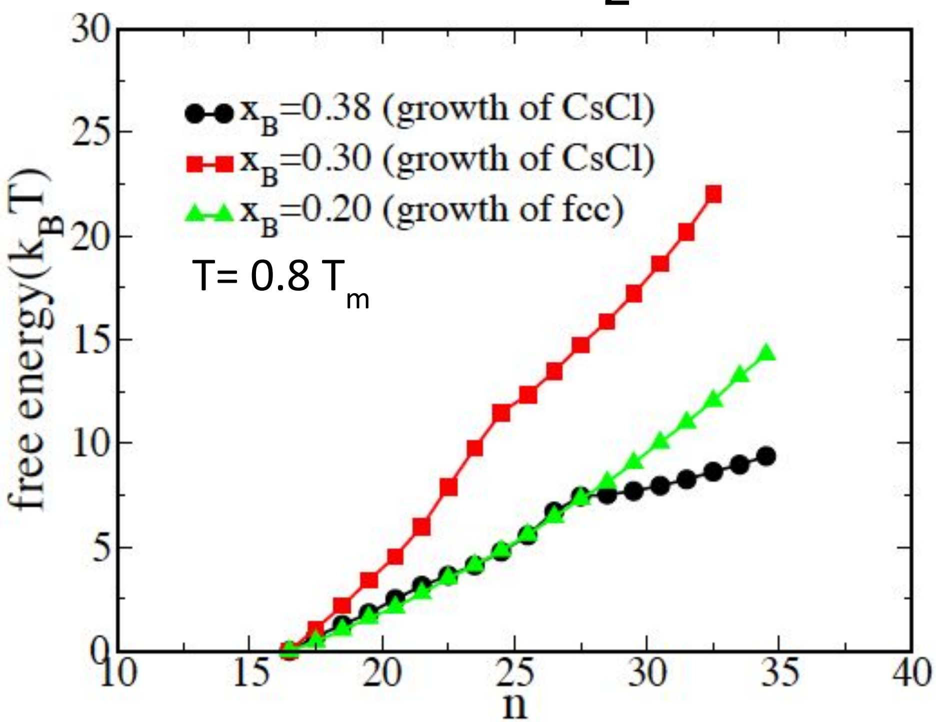




Free energy cost of nucleation

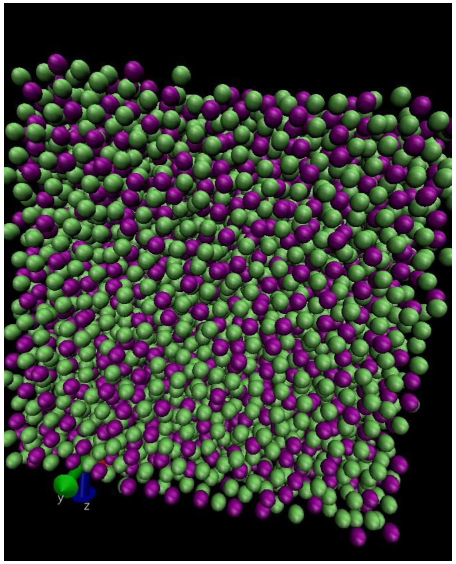
Biased MC

External potential -- $\frac{1}{2}k(n - n_c)^2$



- Free energy cost is high
- B particles ↓ → free energy cost of growth of CsCl ↑

Unbiased simulation with a seed of 432 particles



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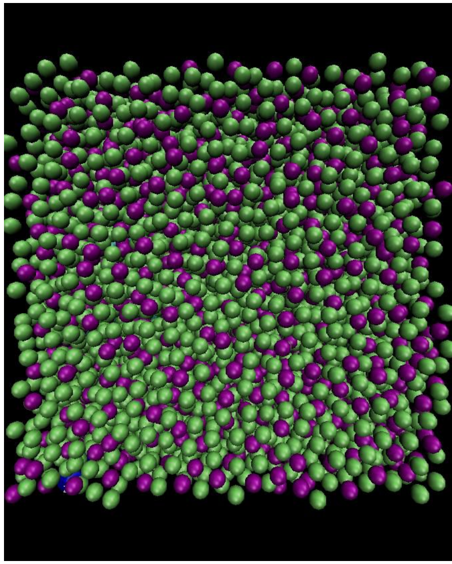


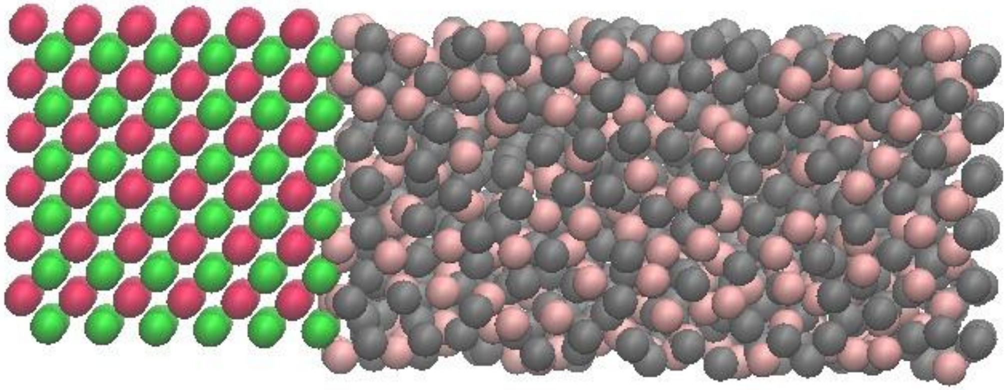
70:30

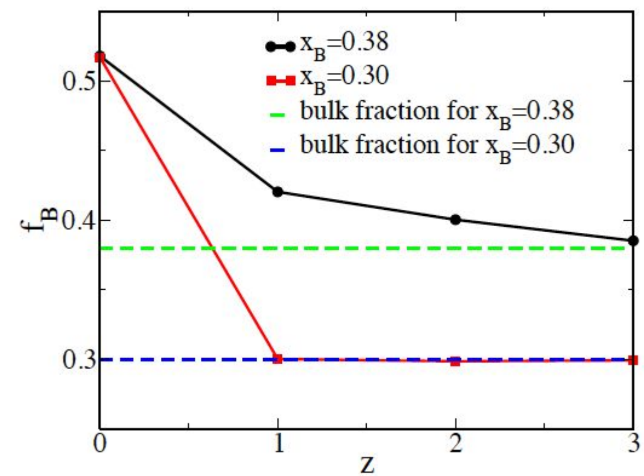
Nandi, Banerjee, Chakrabarty and Bhattachryya, JCP **145,** 034503 (2016)

Is the demixing an effect of crystallization or a cause of it ???

Role of demixing

T= 1.2 T_m





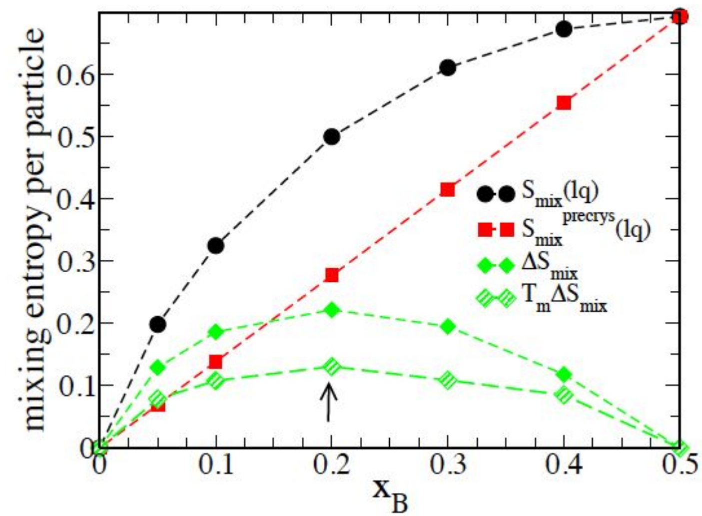
❖Pre crystalline demixing in liquid

Liquid Entropy $s_{mix}(lq) = -\sum x_i \ln x_i$

Demixed liquid entropy $s_{mix}^{precrys}(lq) = -2x_B \times 0.5\ln 0.5$

$$\Delta S = s_{mix}(lq) - s_{mix}^{precrys}(lq)$$

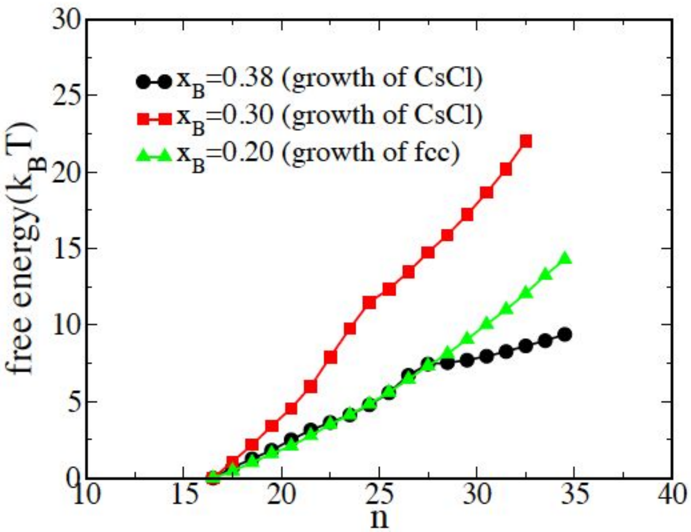
$$= -\sum x_i \ln x_i + 2x_B \times 0.5\ln 0.5$$



❖Non monotonic composition dependence of demixing entropy

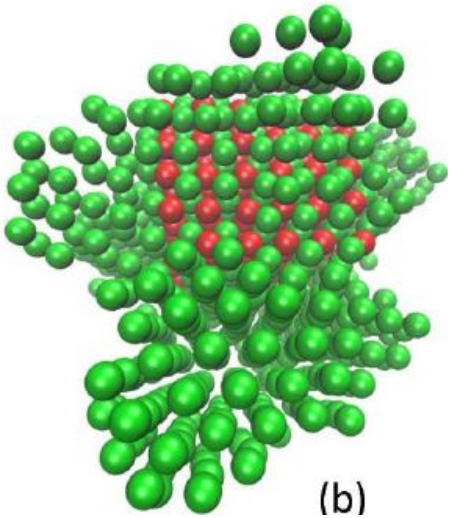
Nandi, Banerjee, Chakrabarty and Bhattachryya, JCP **145,** 034503 (2016)

Tendency of fcc formation in 80:20 mixture ??



- Free energy cost for fcc formation less than CsCl formation

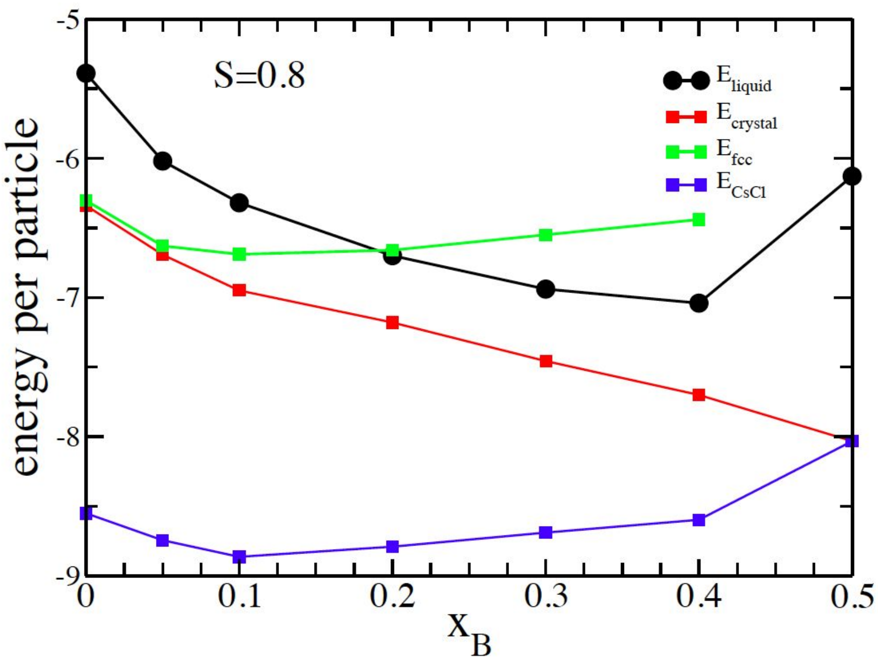
- Growth of fcc around CsCl

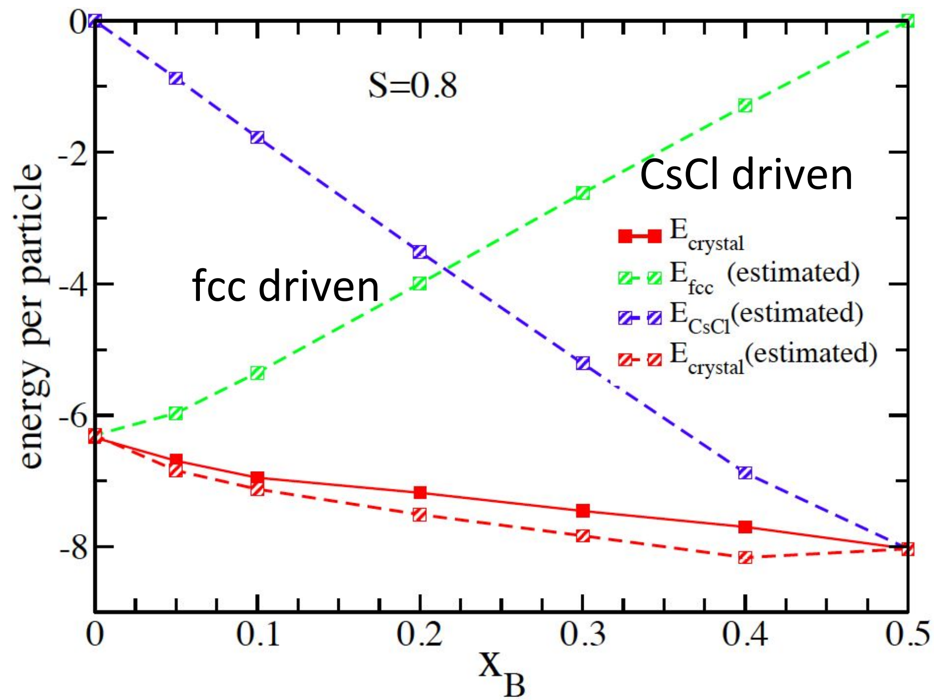


Driving force for crystallization

$$E_{crystal}(estimated) \square E_{CsCl}(estimated) \square E_{fcc}(estimated)$$

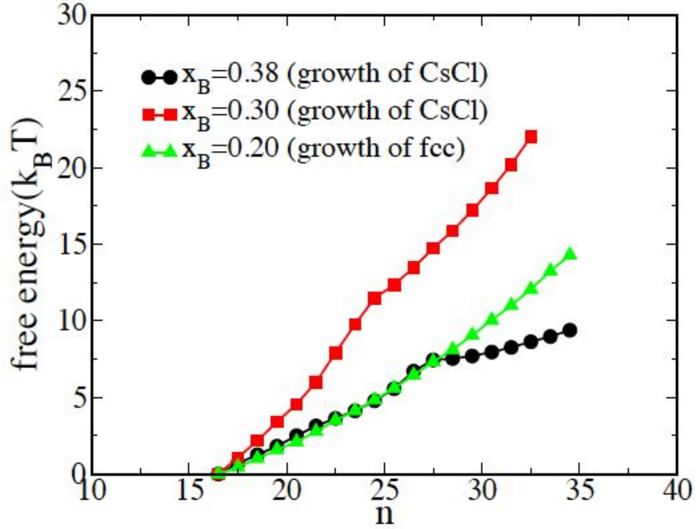
$$\square\ 2x_B E_{CsCl} \square (x_A \square x_B) E_{fcc}$$

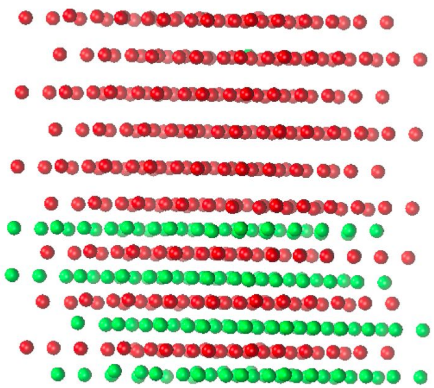




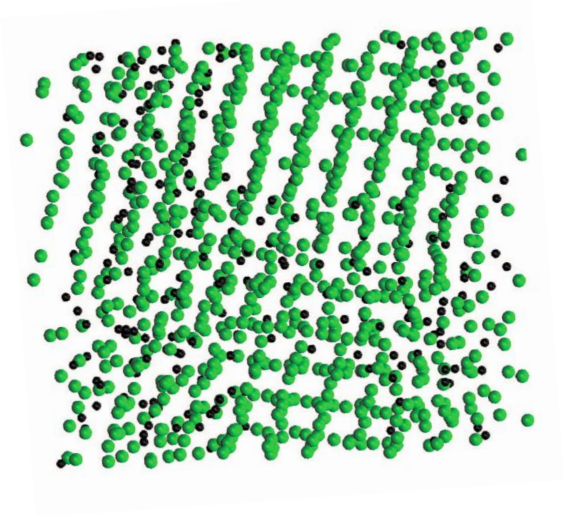
$x_B < 0.2 \longrightarrow$ crystallization dominated by fcc formation

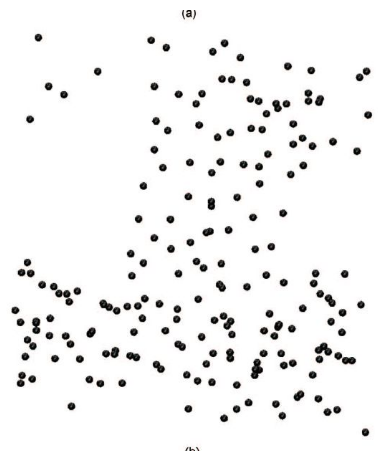
Why fcc has a lower barrier ??

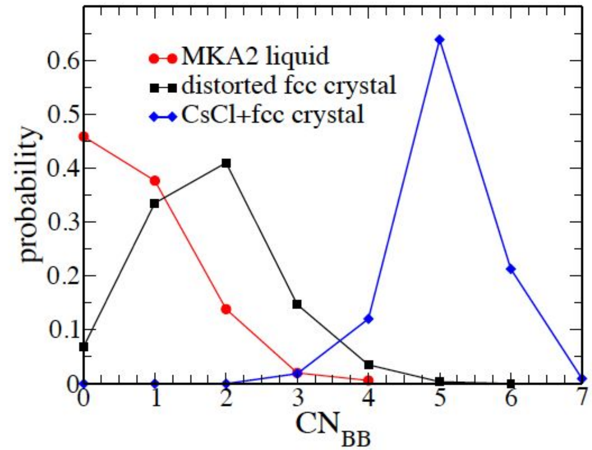




MKA2 model → reduces AB interaction → Lowers the viscosity of the system

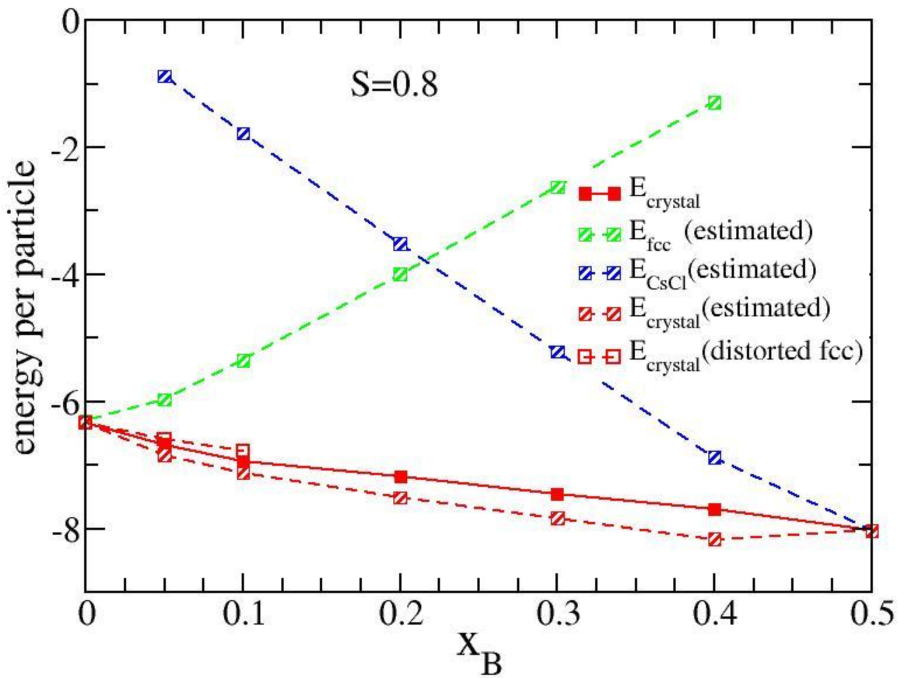






Toxvaerd, Pedersen, Schrøder, & Dyre JCP **130**, 224501 (2009)

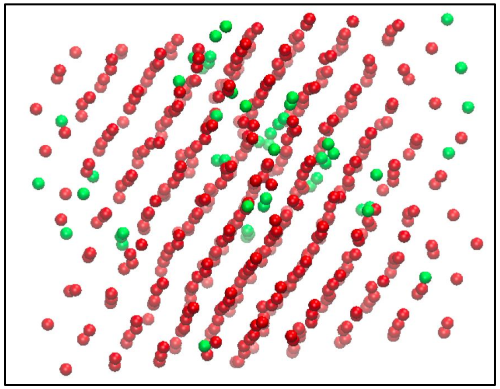
Mixed vs. Demixed crystal



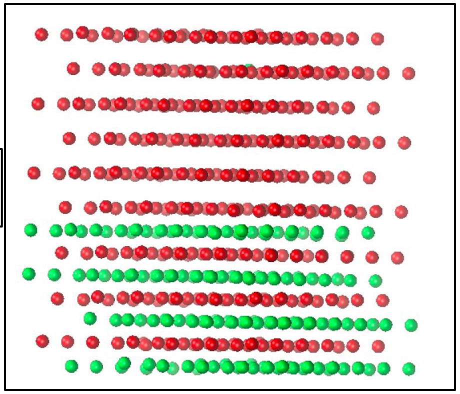
x_B=0.1

x_B=0.3

fcc → less demixing

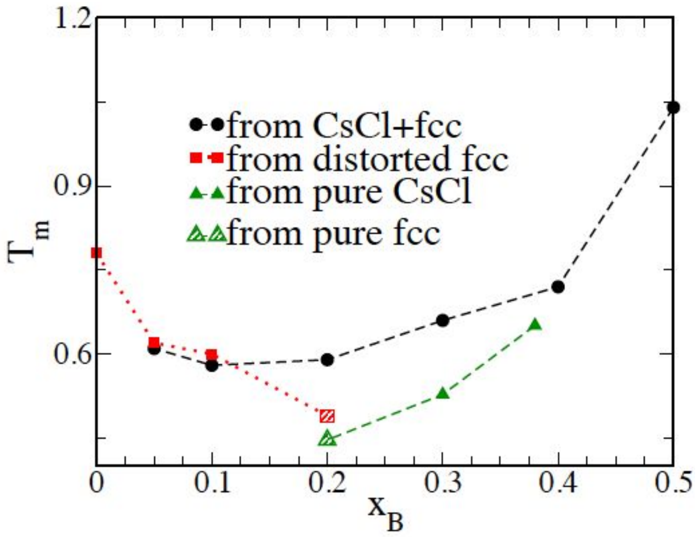


CsCl +fcc → Demixing



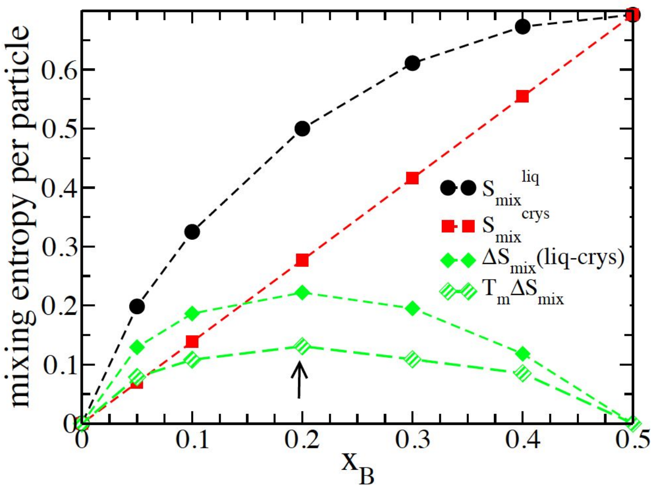
$\text{Entropy}_{\text{distorted fcc}} > \text{Entropy}_{\text{CsCl+ fcc}}$

Factors working for 80:20 mixture

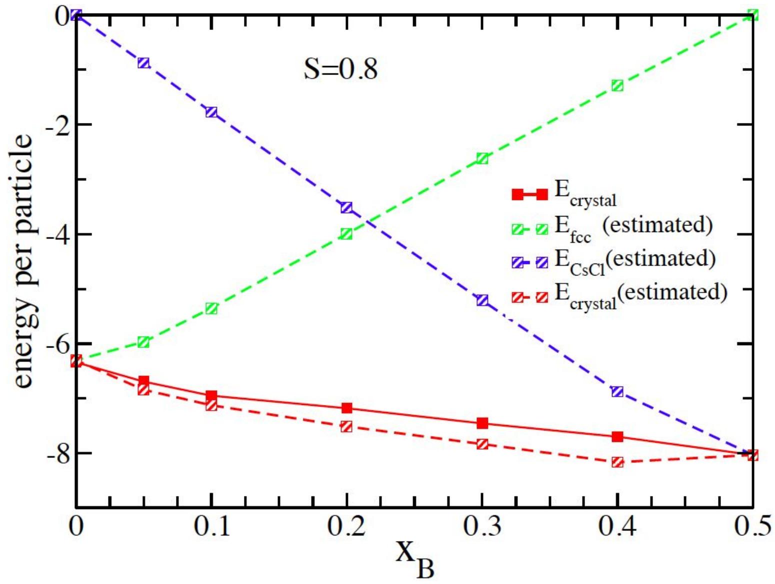


Sitting at the deep eutectic point
→ Kinetically favoured

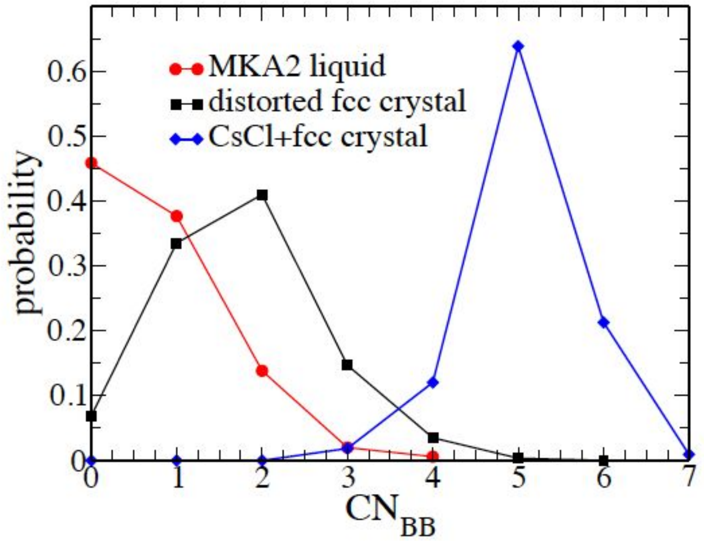
Maximum loss of mixing entropy → largest barrier



Factors working against 80:20 mixture



Sitting at the edge of fcc formation tendency



Distorted fcc → less demixing

Summary

- *Frustration between locally favoured structure and Global structure*

- *Loss of demixing entropy*

- *Thermodynamics plays a greater role → GFA*

Acknowledgement

Funding

- DST
- DPCP
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Thank
You