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University of BRISTOL

Local structure in clusters and crystallisation of ‘hard spheres’ in experiments and simulation

All is not as it seems: beware of electrostatics

Nucleation Aggregation and Growth 2010
JNCASR Bengaluru

29-Jul-2010

Paddy Royall

Collaborators

Bristol
Monica Moreno, Jade Taffs and Alex Malins

Canberra
Stephen Williams (TCC)

Tokyo
Hajime Tanaka
(early experiments)

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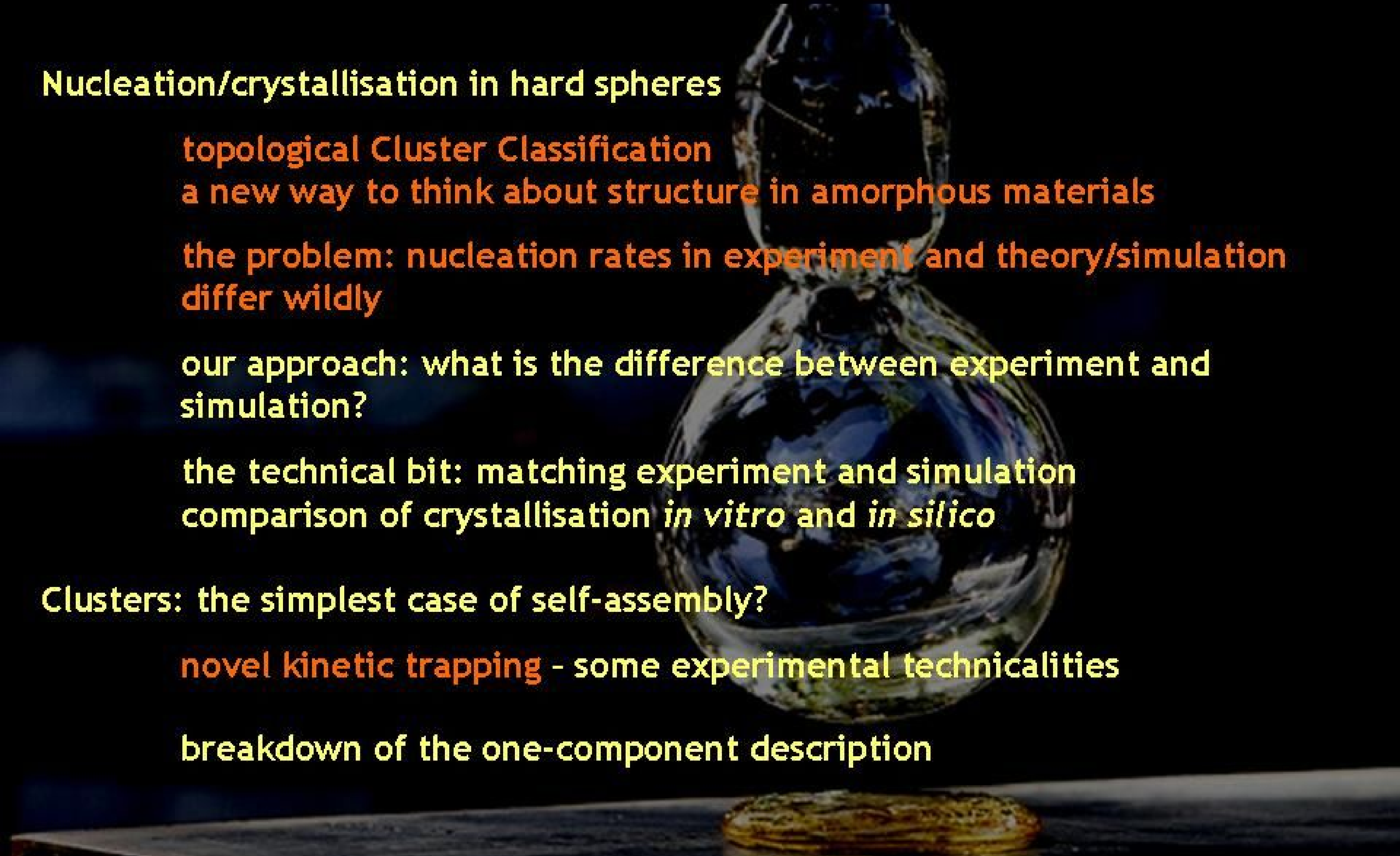
EPSRC
IOP Institute of Physics

Outline: hard spheres - crystallisation and clusters



Nucleation/crystallisation in hard spheres

topological Cluster Classification
a new way to think about structure in amorphous materials

the problem: nucleation rates in experiment and theory/simulation differ wildly

our approach: what is the difference between experiment and simulation?

the technical bit: matching experiment and simulation
comparison of crystallisation *in vitro* and *in silico*

Clusters: the simplest case of self-assembly?

novel kinetic trapping - some experimental technicalities

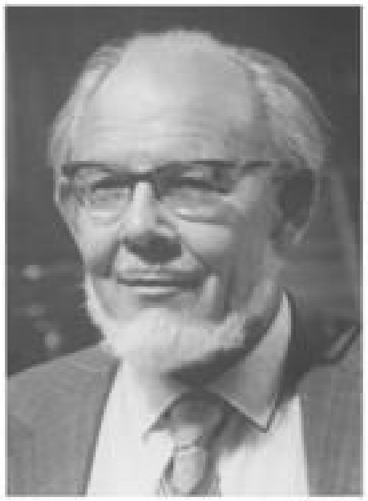
breakdown of the one-component description

Local structure?

Supercooling of liquids

By F. C. Frank

H. H. Wills Physics Laboratory, Bristol University



The theoretical argument is misleading also. Consider the question: 'In how many different ways can one put twelve billiard balls in simultaneous contact with one, counting as different the arrangements which cannot be transformed into each other without breaking contact with the centre ball?' The answer is *three*. Two which come to the mind of any crystallographer occur in the face-centred cubic and hexagonal close-packed lattices. The third comes to the mind of any good schoolboy, and is to put one at the centre of each face of a regular dodecahedron. That body has five-fold axes, which are abhorrent to crystal symmetry: unlike the other two packings, this one cannot be continuously extended in three dimensions. You will find that the outer twelve in this packing do not touch each other. If we have mutually attracting deformable spheres, like atoms, they will be a little closer to the centre in this third type of packing; and if one assumes they are argon atoms (interacting in pairs with attractive and repulsive energy terms proportional to r^{-6} and r^{-12}) one may calculate that the binding energy of the group of thirteen is 8·4 % greater than for the other two packings. This is 40 % of the lattice energy per atom in the crystal. I infer that this will be a very common grouping in liquids, that most of the groups of twelve atoms around one will be in this form, that freezing involves a substantial rearrangement, and not merely an extension of the same kind of order from short distances to long ones; a rearrangement which is quite costly of energy in small localities, and only becomes economical when extended over a considerable volume, because unlike the other packing it can be so extended without discontinuities.

Frank, *Proc. R. Soc.* (1952)

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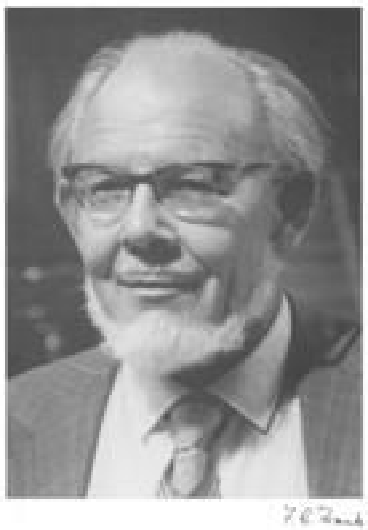

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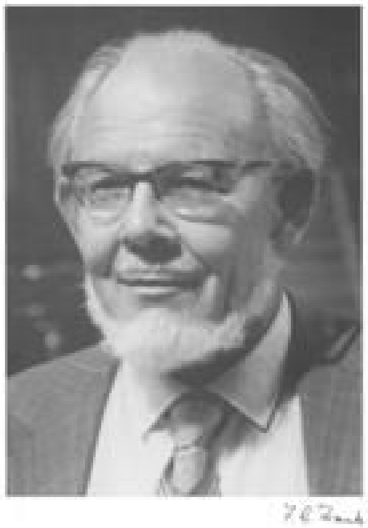
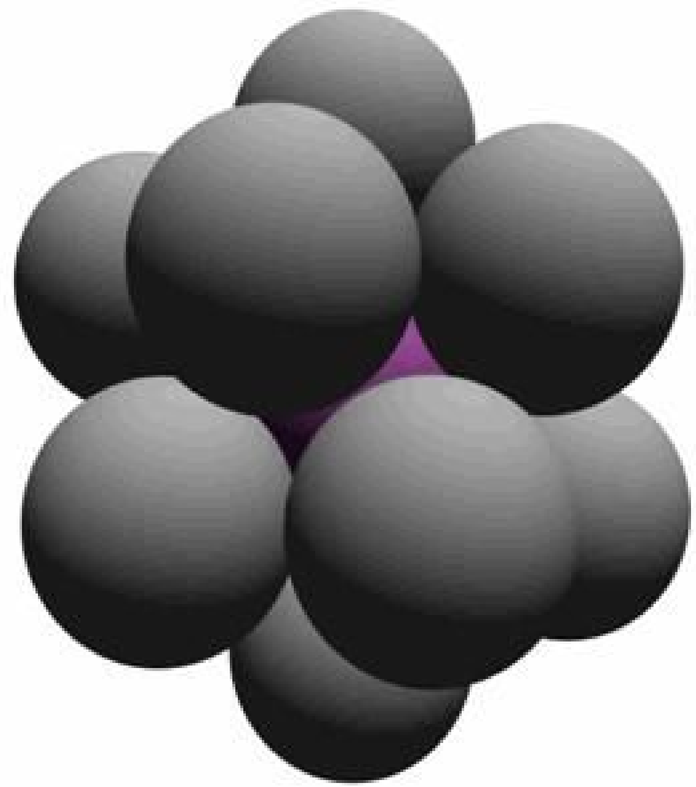
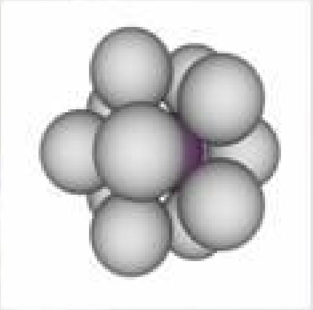




Frank, *Proc. R. Soc.* (1952)

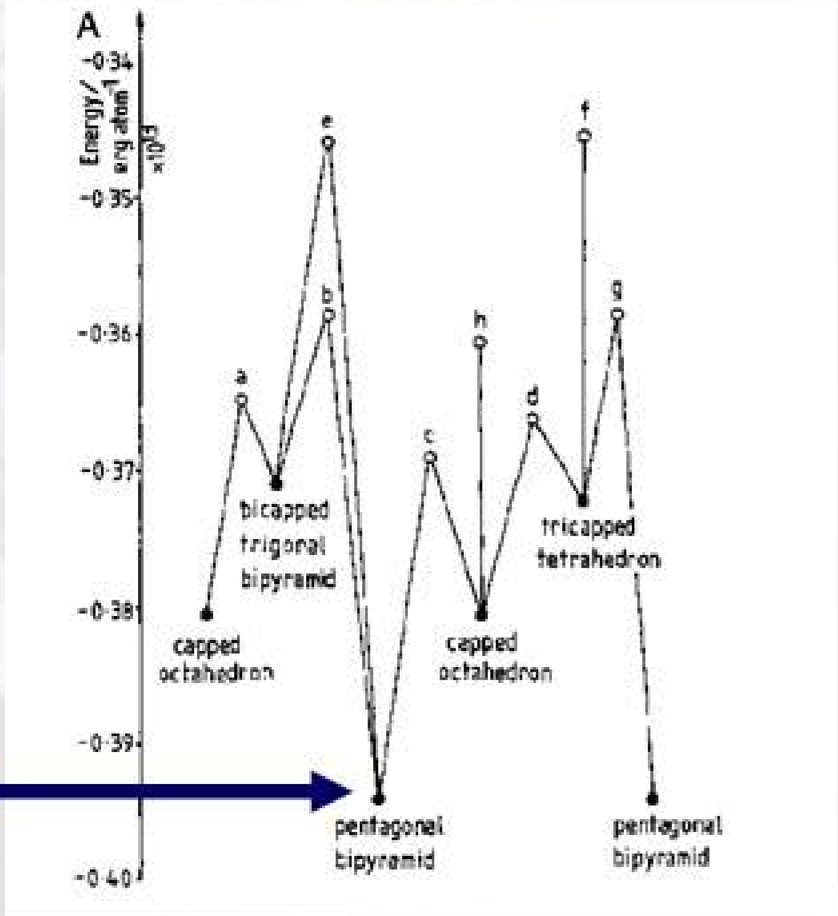
Using the energy landscape: make N small

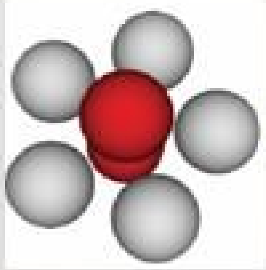
Frank-> m=13 Lennard-Jones, icosahedron



is there anything special about m=13?

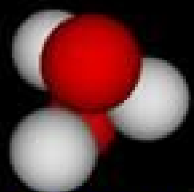
but we know that for m=7, global minimum is the pentagonal bipyramid



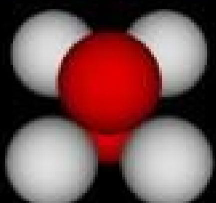


Berry *JCP* 1988

Locally favoured structures for colloids

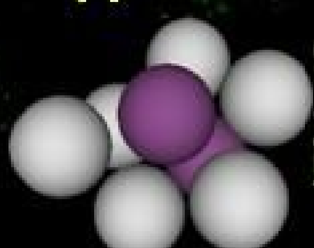


5A triangular bipyramid

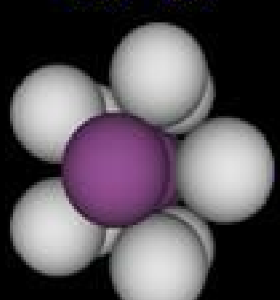


6A octahedron

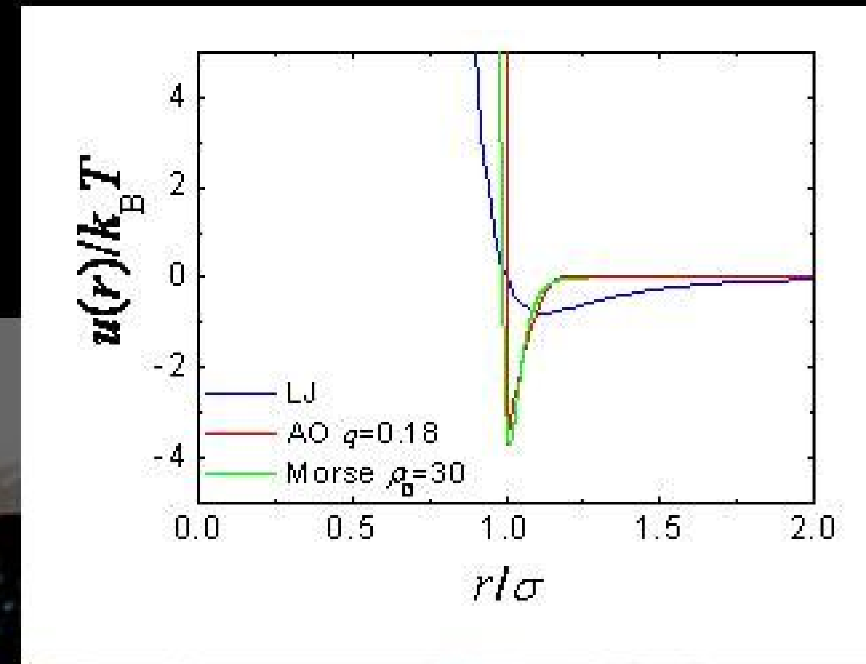
7A pentagonal bipyramid



8B Cs



13B D5h

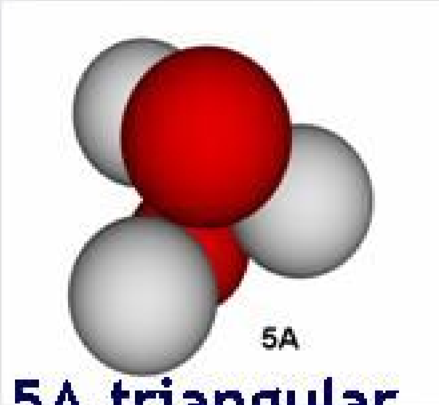


	Point group	n_{nn}	E_{strain}	$\rho_0=3.0$	$\rho_0=6.0$	$\rho_0=10.0$	$\rho_0=14.0$	ρ_{min}	ρ_{max}
5A	D_{3h}	**9**	**0.000**	**−9.299 500**	**−9.044 930**	**−9.003 565**	**−9.000 283**		
6A	O_h	**12**	**0.000**	**−13.544 229**	**−12.487 810**	**−12.094 943**	**−12.018 170**		
7A	D_{5h}	**16**	**0.062**	**−17.552 961**	**−16.207 580**	**−15.956 512**	**−15.883 113**		
8A	D_{2d}	18	0.006	−22.042 901	−19.161 862	−18.275 118	−18.076 248		5.28
8B	C_s	**19**	**0.062**		**−19.327 420**	**−18.964 638**	**−18.883 688**	**5.28**	
9A	D_{3h}	21	0.002	−26.778 449	−22.330 837	−21.213 531	−21.037 957		5.50
9B	C_{2v}	**22**	**0.062**	**−26.037 771**	**−22.488 044**	**−21.975 747**	**−21.884 483**	**5.50**	
10A	D_{4d}	24	0.002	−31.519 768	−25.503 904	−24.204 958	−24.031 994		2.26
10B	C_{3v}	**27**	**0.694**	**−31.888 630**	**−27.473 283**	**−26.583 857**	**−26.132 735**	**2.26**	
11A	D_{4d}	34	10.374	−37.930 817	−28.795 153[4]	−23.666 072[5]			3.40
11B	C_{2v}	32		−37.891 674[1]				3.40	3.67
11C	C_{2v}	31	0.792		−31.521 880	−30.265 230	−29.588 130[1]	3.67	13.57
11D	C_s	30					−29.596 054	13.57	15.29
11E	C_2	30	0.248	−36.613 190[1]	−30.698 890	−29.808 994	−29.524 398	15.29	20.59
11F	C_{2v}	**29**	**0.001**	**−36.697 760**	**−30.431 713**	**−29.215 51**	**−29.037 941**	**20.59**	
12A	C_{2v}	38		−43.971 339[1]	−35.199 881[1]				2.67
12B	C_{5v}	36	1.704	−44.097 880	−36.400 278	−34.366 755	−33.115 942[1]	2.67	12.15
12C	C_s	34					−33.199 505	12.15	13.03
12D	D_{2d}	34	0.346	−41.816 393	−34.838 761	−33.724 155	−33.332 305	13.03	17.08
12E	D_{3h}	**33**	**0.001**	**−42.121 440**	**−34.568 002**	**−33.222 331**	**−33.038 298**	**17.08**	
13A	I_h	42	2.425	−51.737 046	−42.439 863	−39.662 975	−37.258 877		14.76
13B	D_{5h}	**37**	**0.141**	**−49.998 058[1]**	**−39.360 710[1]**	**−37.208 019[1]**	**−36.790 507**	**14.76**	

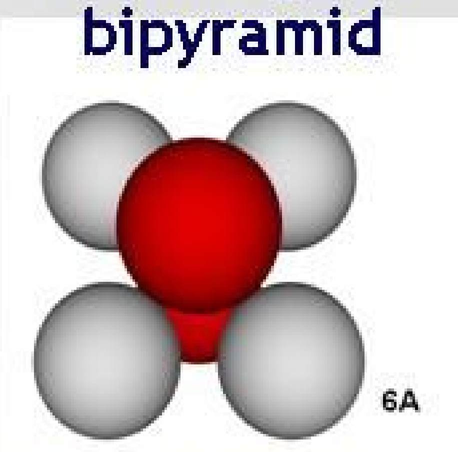
Doye, *J.Chem.Phys.* 1995

Locally Favoured Structures for hard spheres (no attraction)

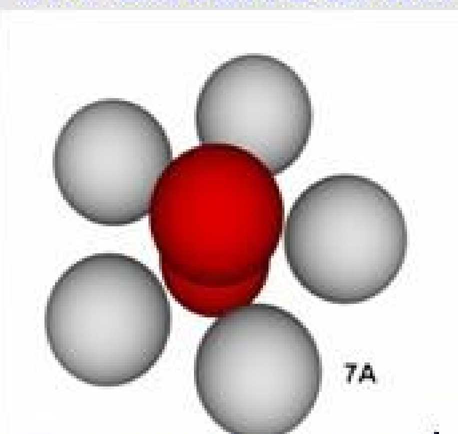
Minimise second moment (radius of gyration)



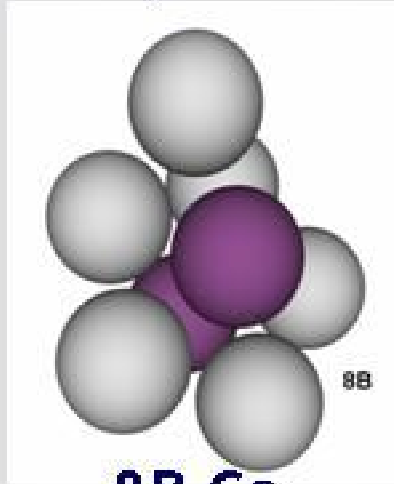
5A triangular bipyramid



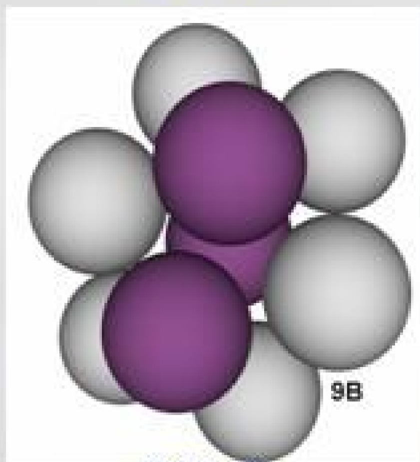
6A octahedron



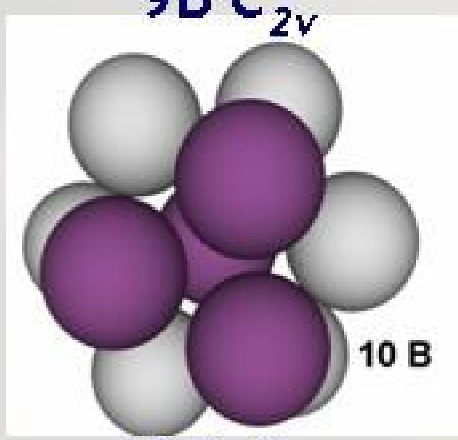
7A pentagonal bipyramid



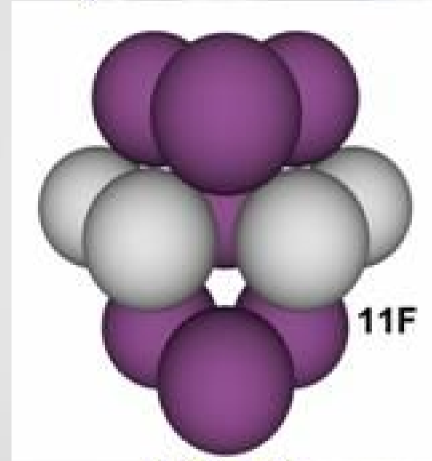
8B *Cs*



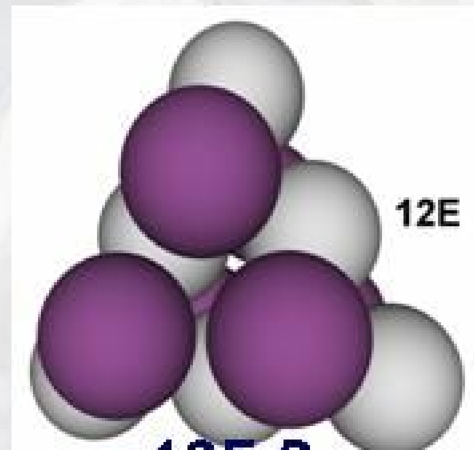
9B C_{2v}



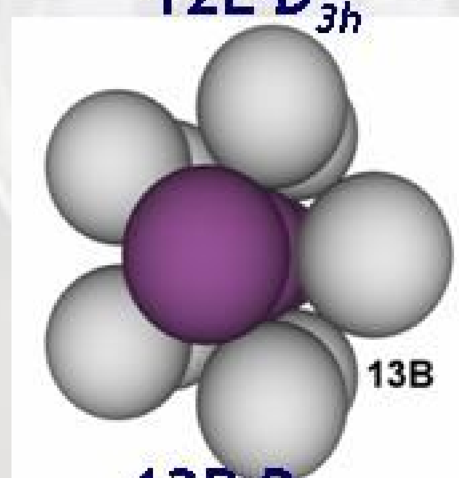
10B C_{2v}



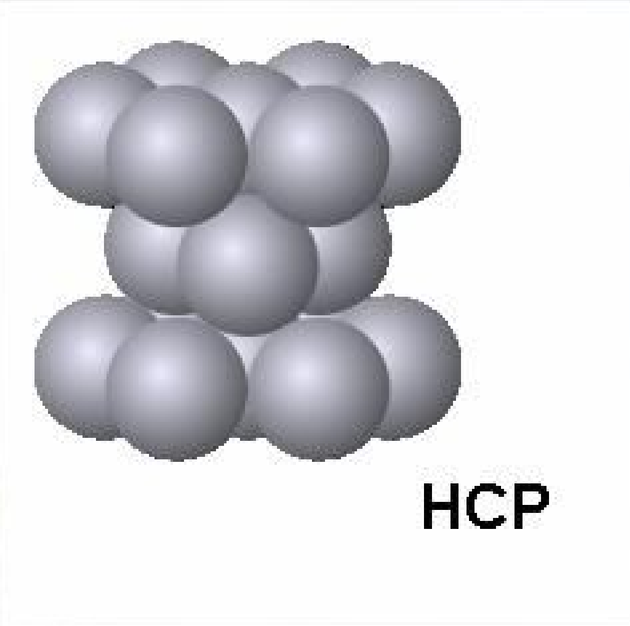
11F C_{3v}

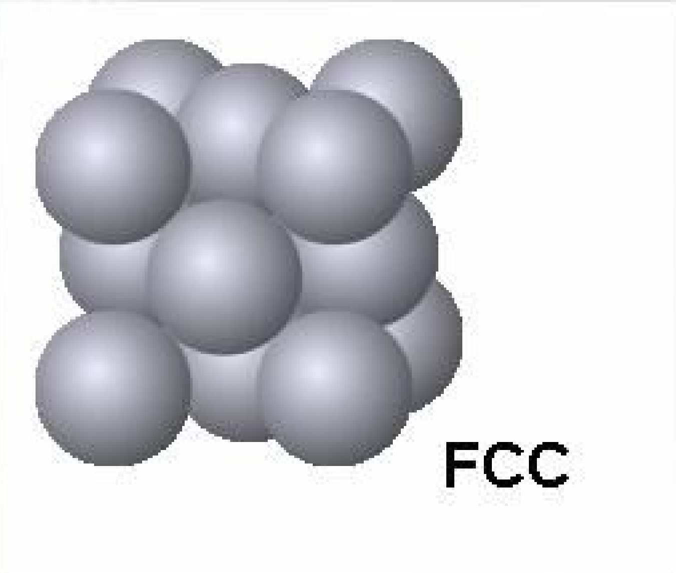


12E D_{3h}



13B D_{5h}





Sloane, N.J.A, Hardin, R.H. & Conway, J.H. *Discrete Comput. Geom.* **14**, 237-259, (1995)
Manoharan, Elesser and Pine, *Science* **301**, 483-487 2003

Locally Favoured Structures for hard spheres

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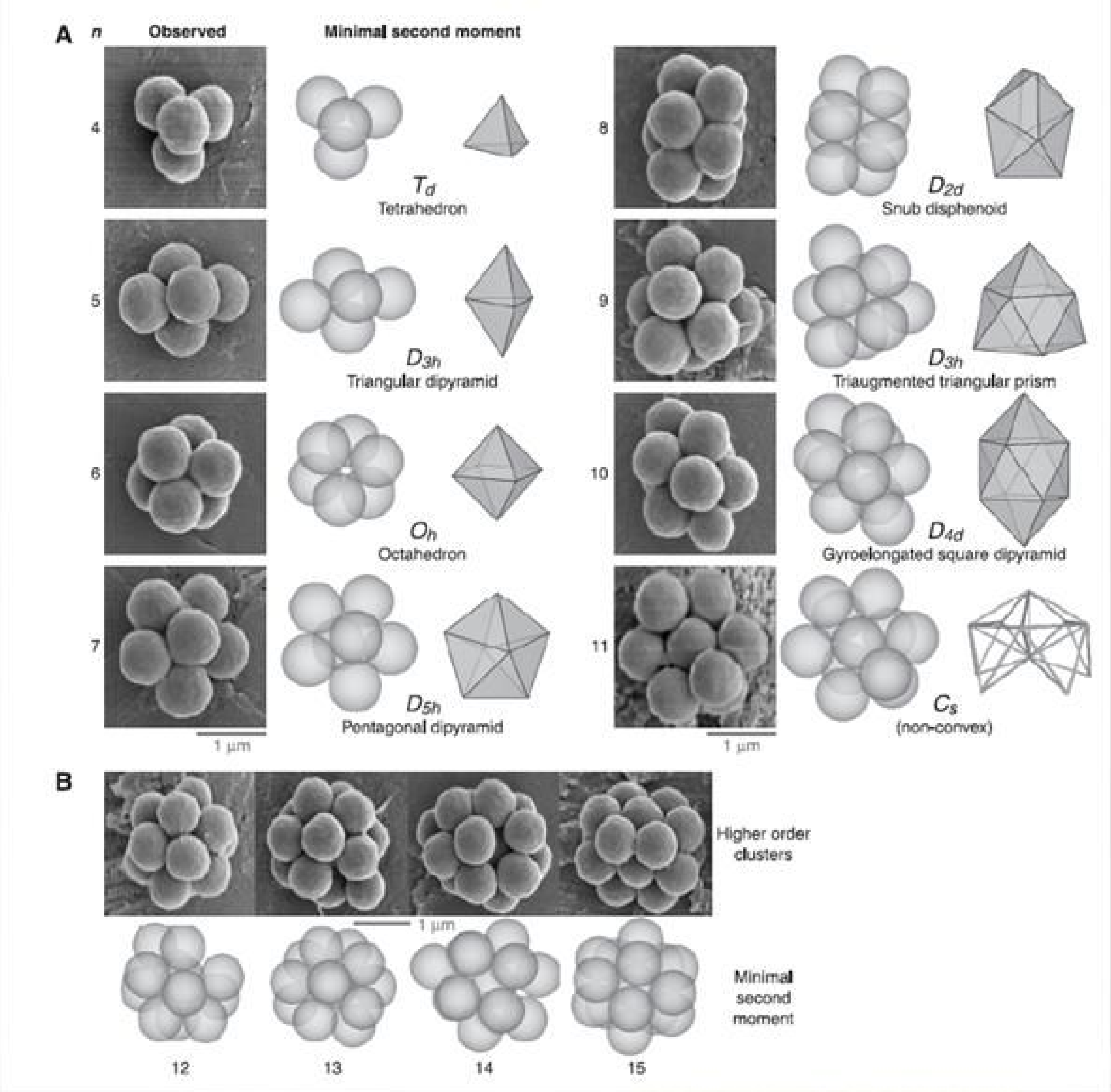


Manoharan, Elesser and Pine, *Science* **301**, 483-487 2003

Topological Cluster Classification

2D picture of the TCC

efficiently identifies clusters in terms of their bond networks

bond network via Voronoi (dense) and simple bond length (dilute)

Topological Cluster Classification

2D picture of the TCC

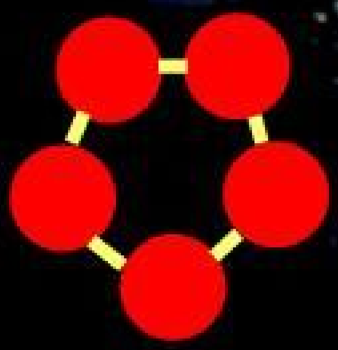
5-membered ring LFS
Shintani and Tanaka Nature Physics 2006

How to identify five-member rings in bulk?

efficiently identifies clusters in terms of their bond networks
bond network via Voronoi (dense) and simple bond length (dilute)

Topological Cluster Classification

2D picture of the TCC



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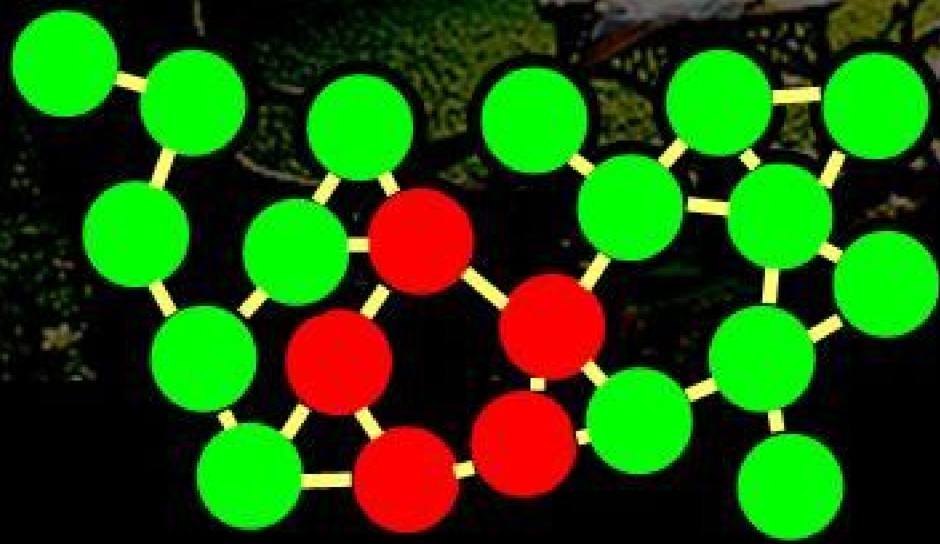

topological approach:
use the bond network

efficiently identifies clusters in terms of their bond networks
bond network via Voronoi (dense) and simple bond length (dilute)

Topological Cluster Classification

2D picture of the TCC

efficiently identifies clusters in terms of their bond networks
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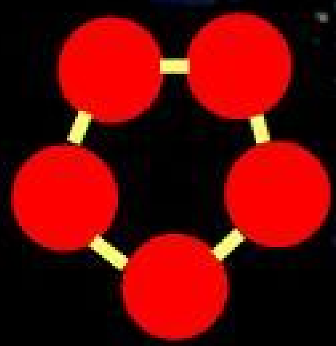

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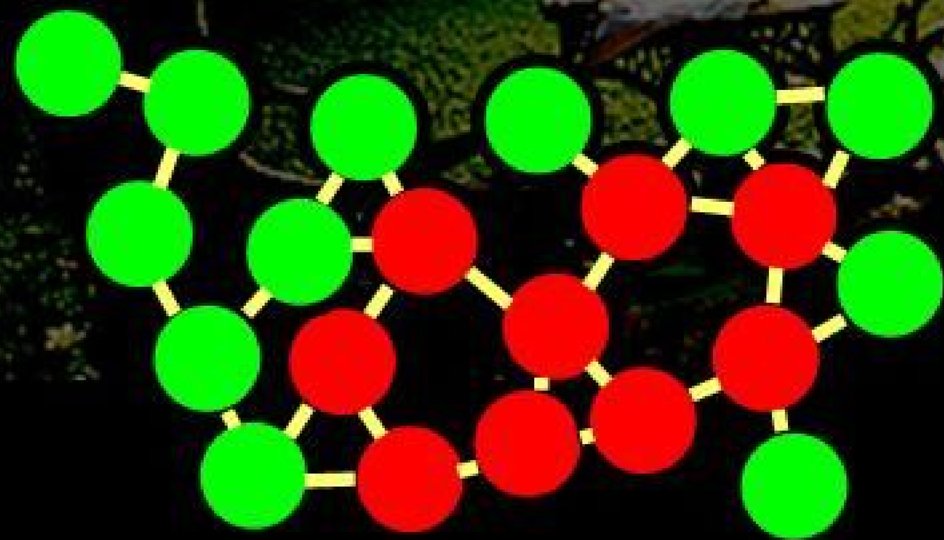
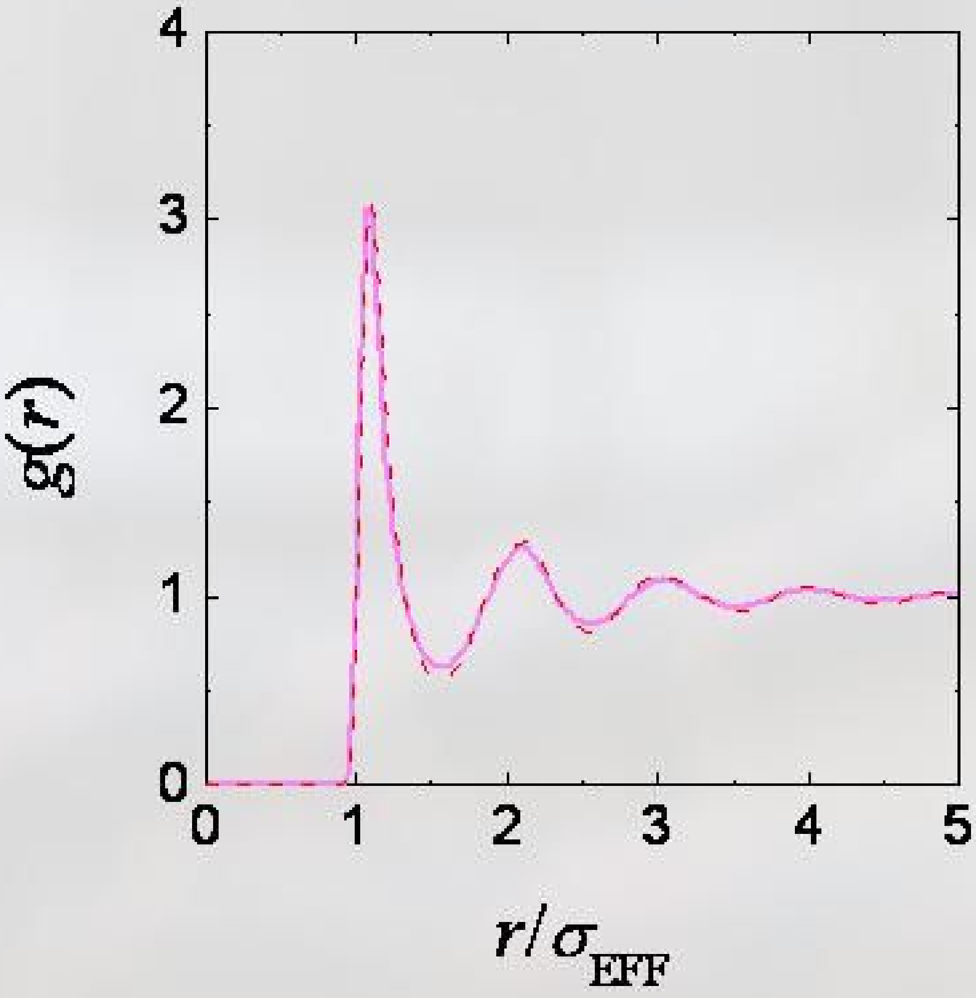


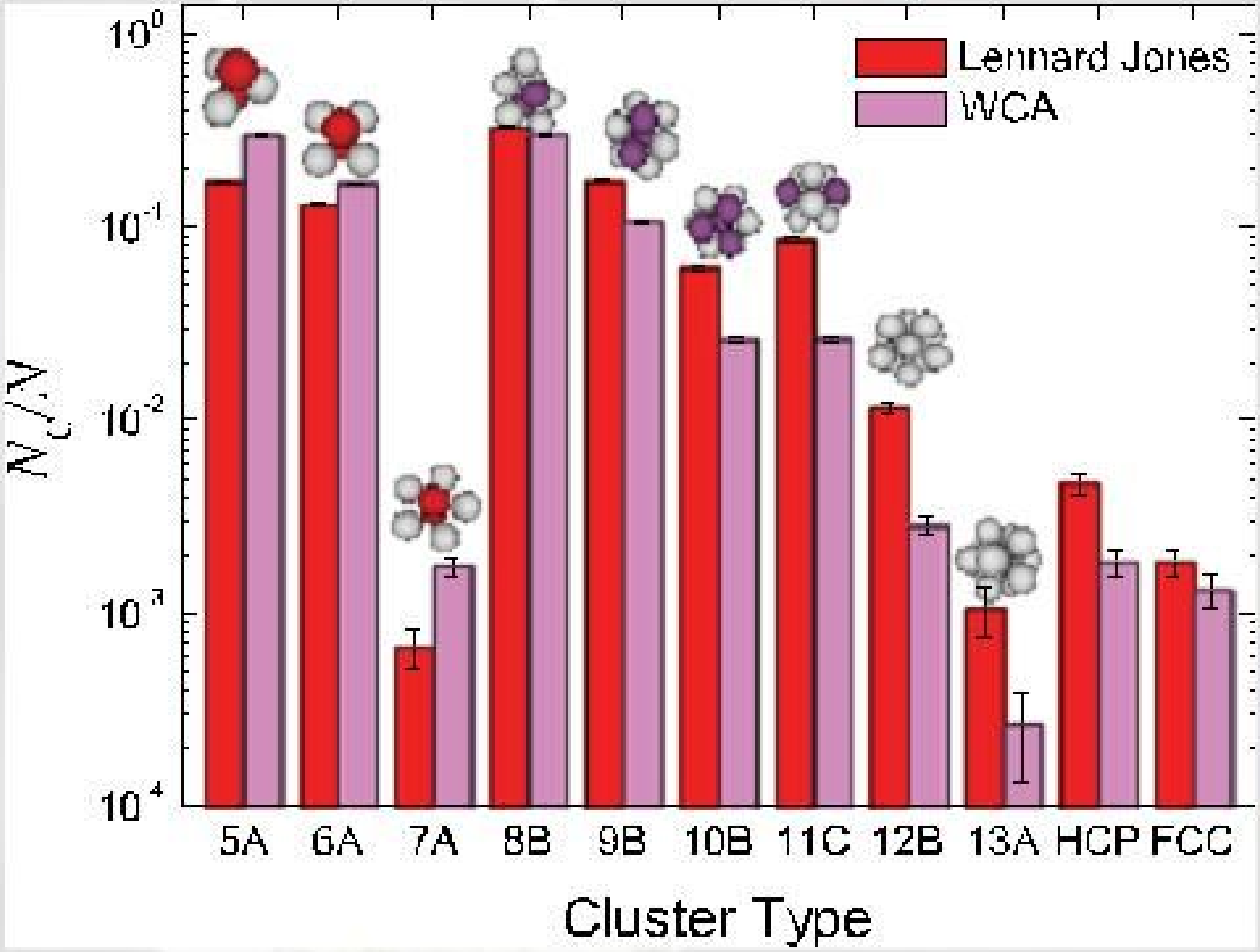
Strategy:
Search for LFS in bulk, for m<14.
If small LFS contained within larger, only consider larger
Also identify FCC and HCP

efficiently identifies clusters in terms of their bond networks
bond network via Voronoi (dense) and simple bond length (dilute)

Testing the TCC

can we detect changes in structure when g(r) can't?





Lennard-Jones (red) vs Weeks-Chandler-Andersen (pink LJ without attractions) at the LJ triple point

Taffs et al submitted to *JCP*

Testing the TCC

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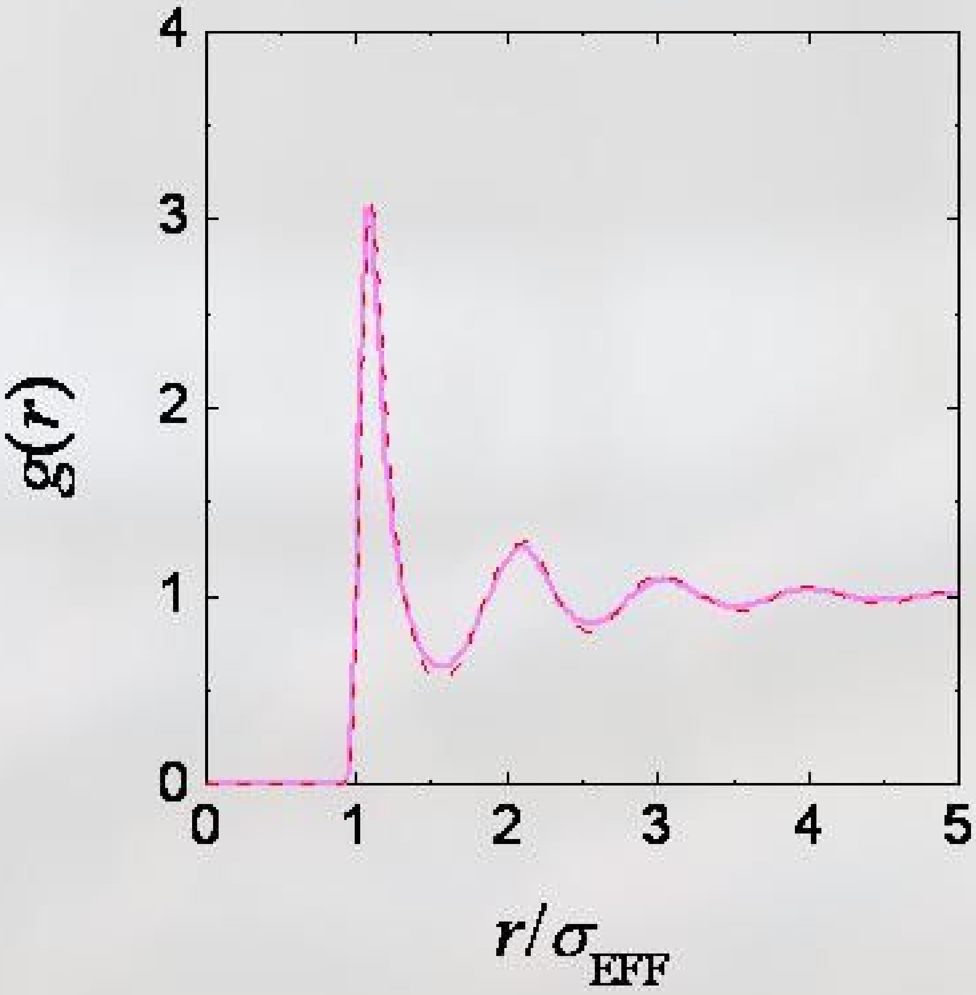
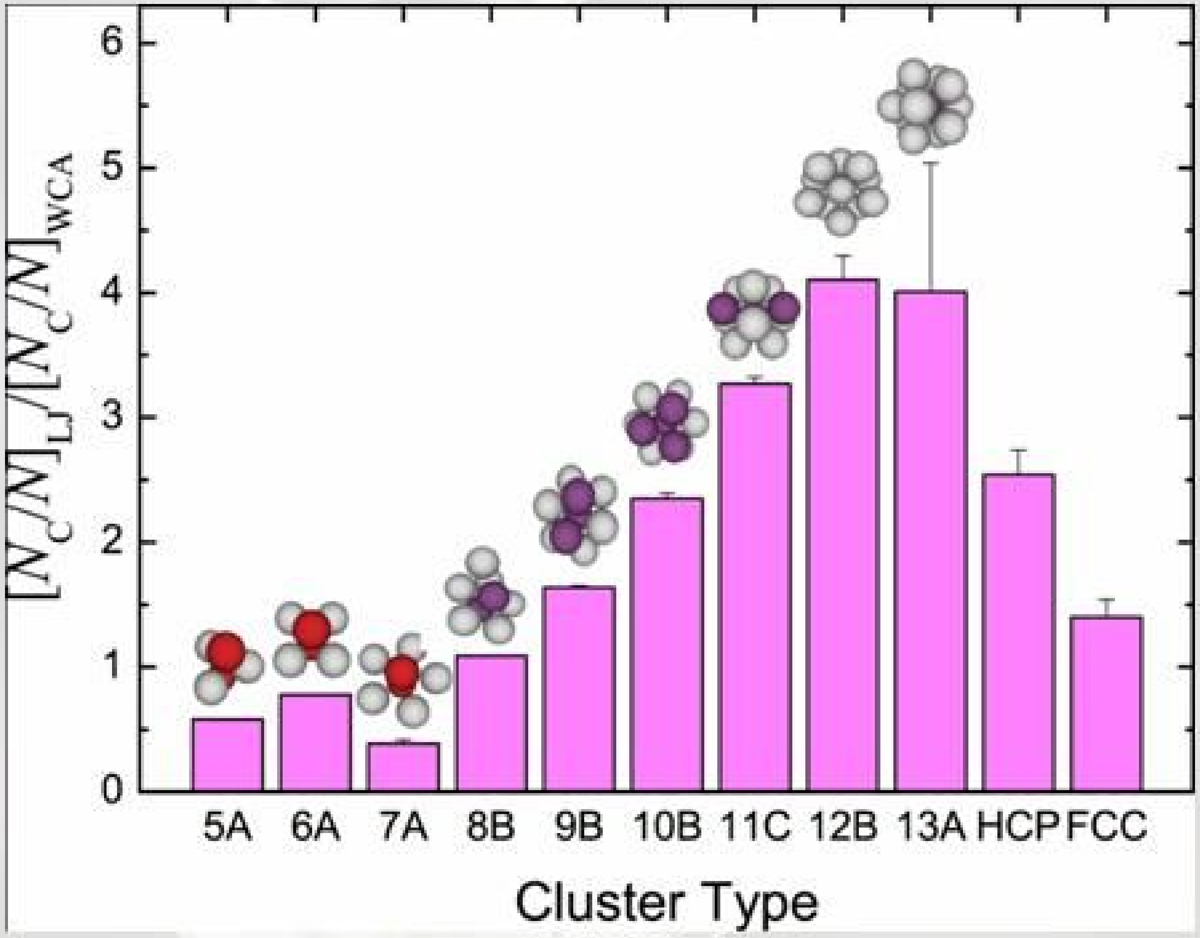




Lennard-Jones (red) vs Weeks-Chandler-Andersen (pink LJ without attractions) at the LJ triple point

Taffs et al submitted to *JCP*

What can colloids tell us?

PMMA Colloids 2-3 μm
polydispersity 4%

CyclohexylBromide-cis Decalin RI,
density match

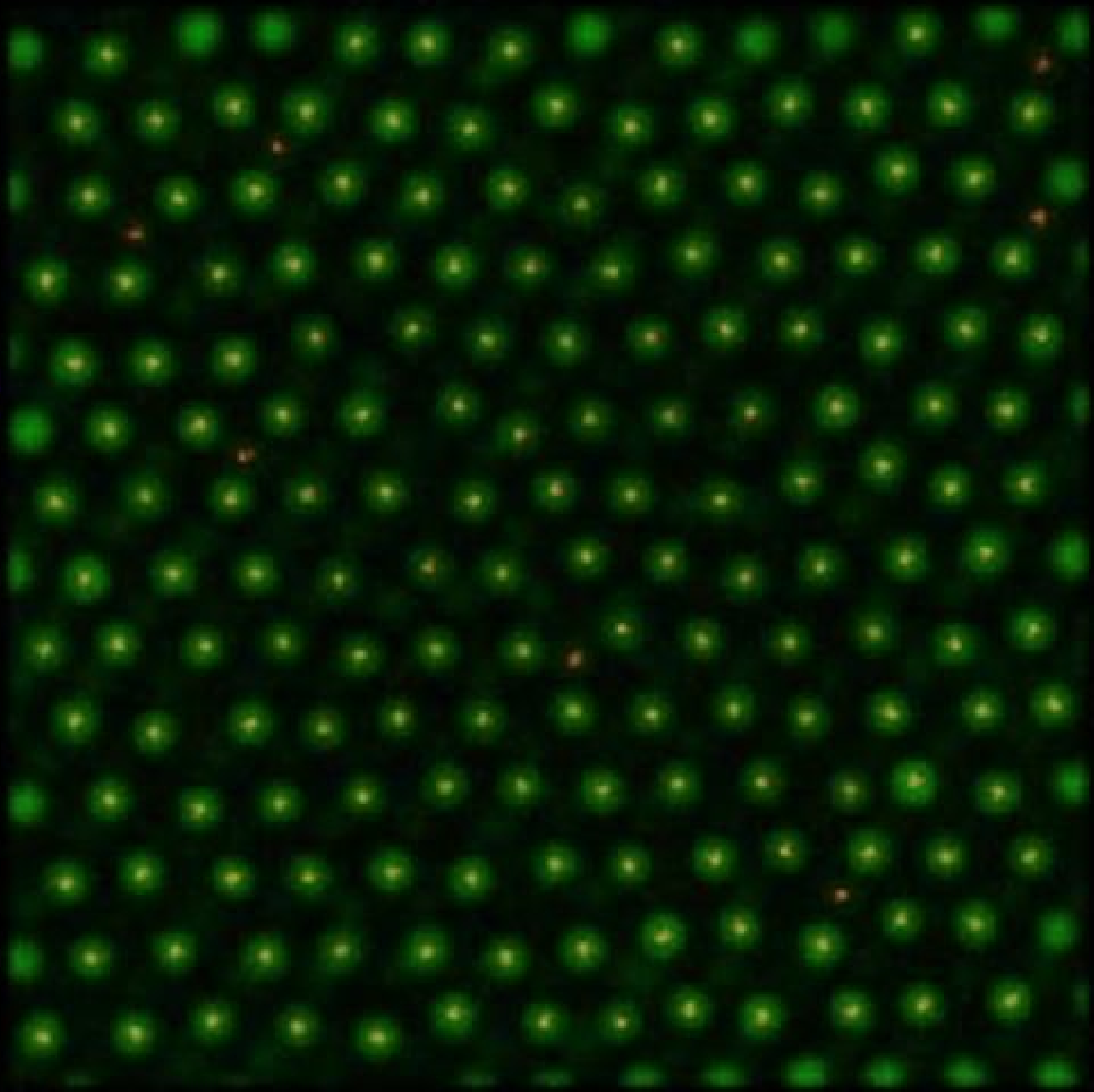
TetraButylAmmoniumBromide salt
to screen electrostatics

Tune electrostatics with solvent
dielectric constant CHB ε_R~8,
TetraChloroEthylene ε_R~2

Dynamically accessible
(τ_B~30s)
τ_B is a characteristic diffusion
time in the dilute limit

$\tau_B = 3\pi\eta\sigma^3/4k_BT$

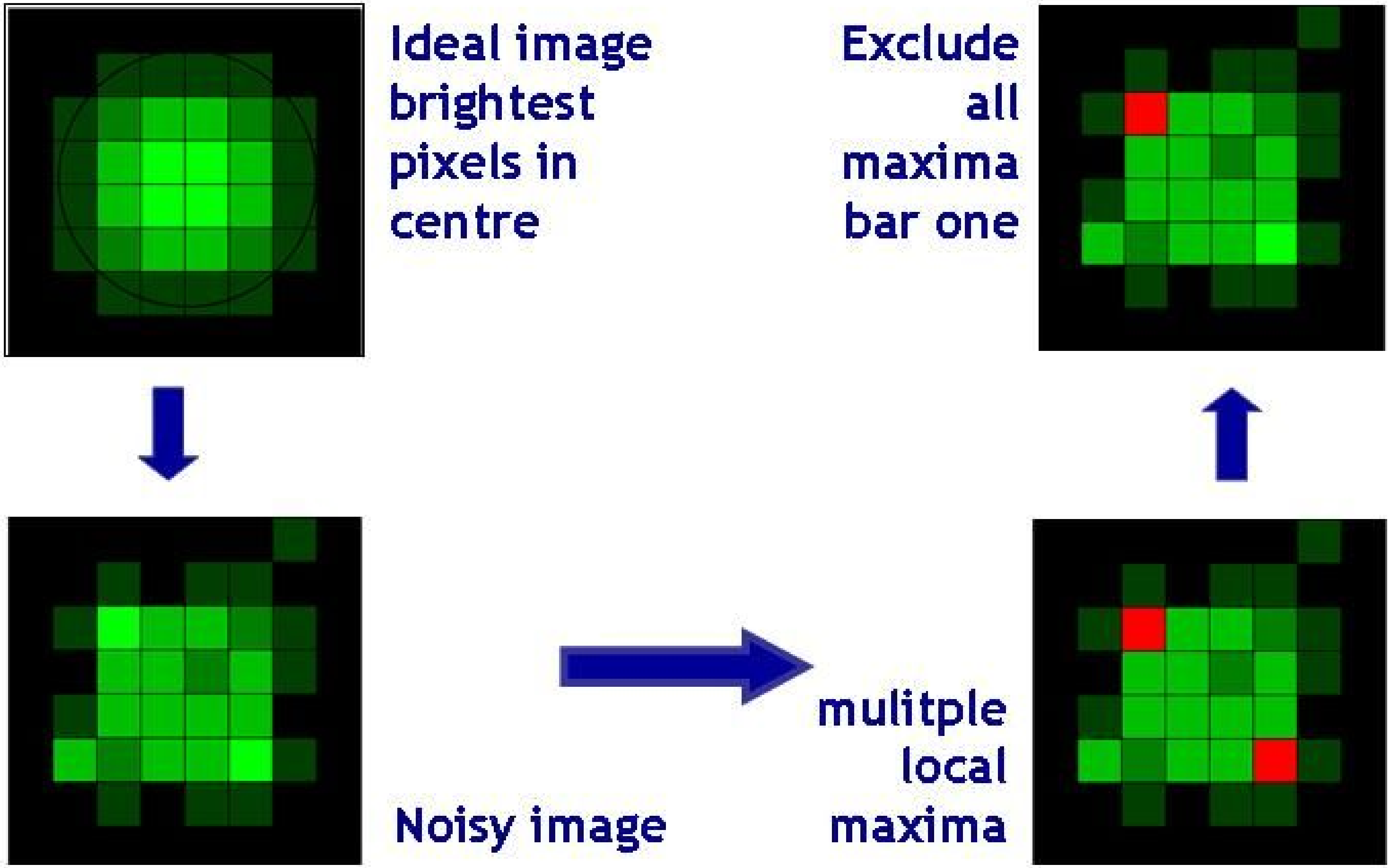
can directly SEE
Thermal motion: Big Atoms



confocal microscopy: track centres of
2μm colloidal particles to ~ 30 nm
accuracy in 3D

CPR et al, *J. Phys. Condens. Matter.* 15 S3581 (2003)

Particle tracking



CPR et al, J. Phys. Cond. Matter. 15 S3581 (2003)

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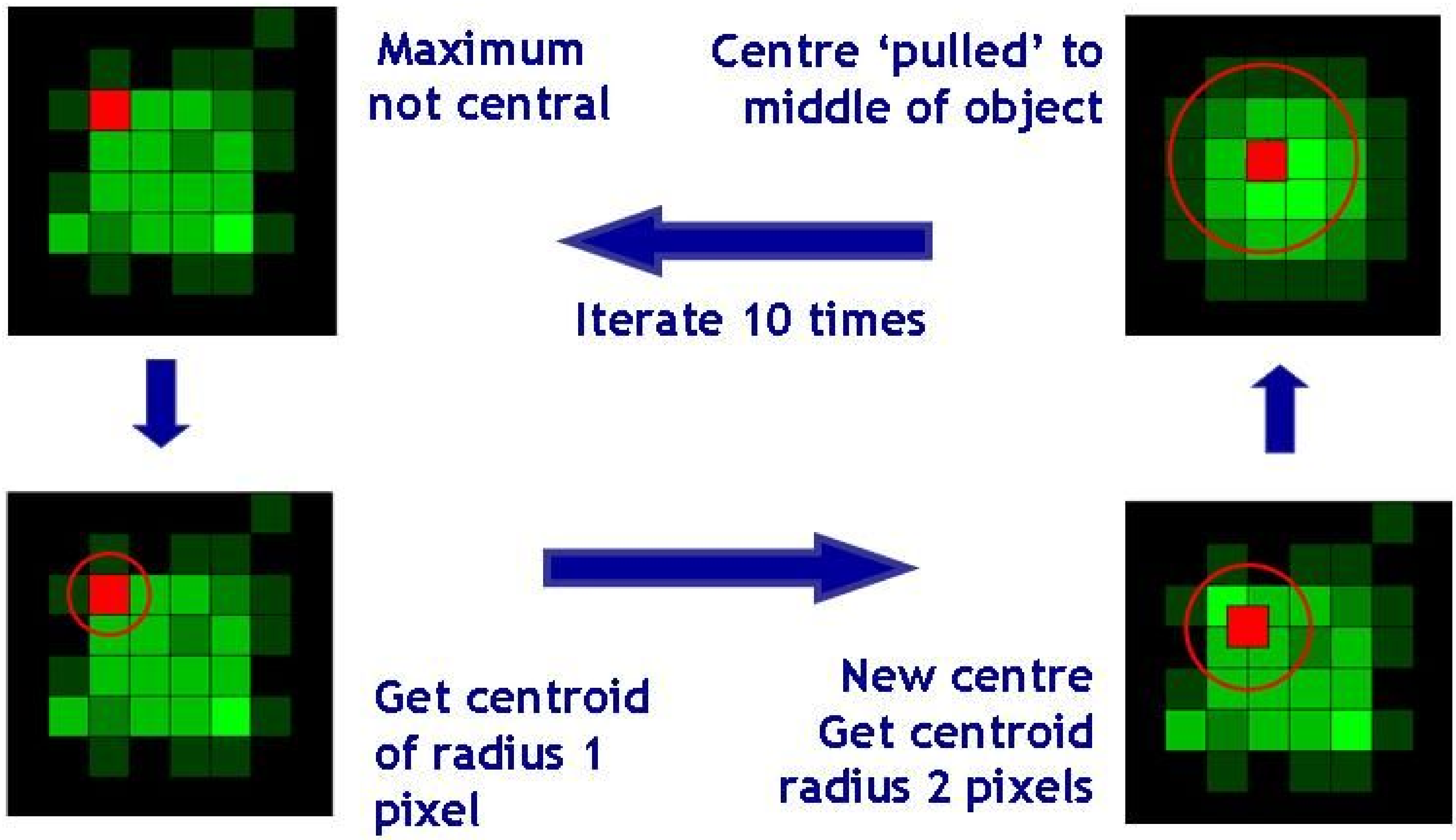


CPR et al, J. Phys. Cond. Matter. 15 S3581 (2003)


crystallisation

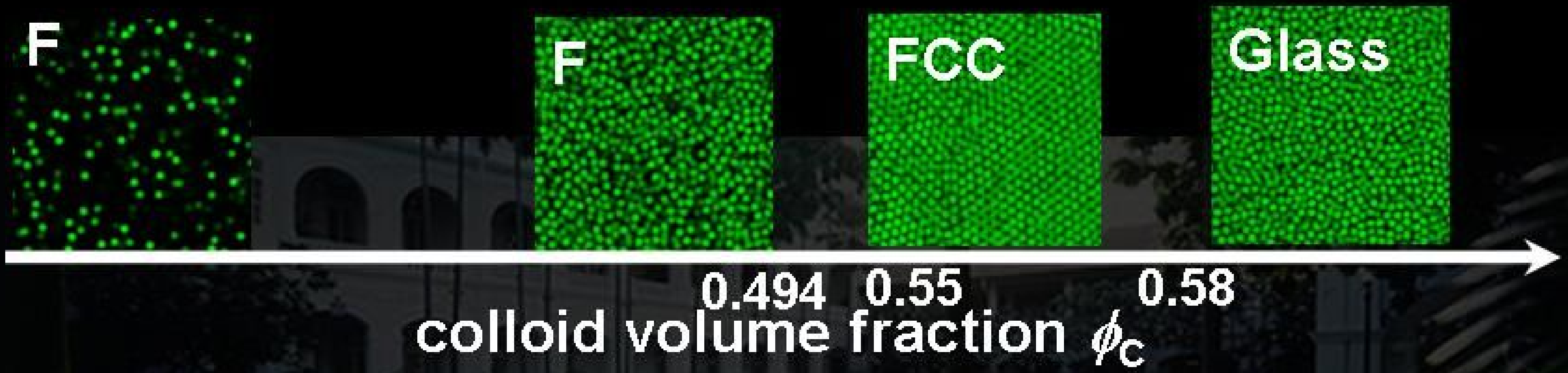
PMMA-experimental 'hard' spheres

University of BRISTOL

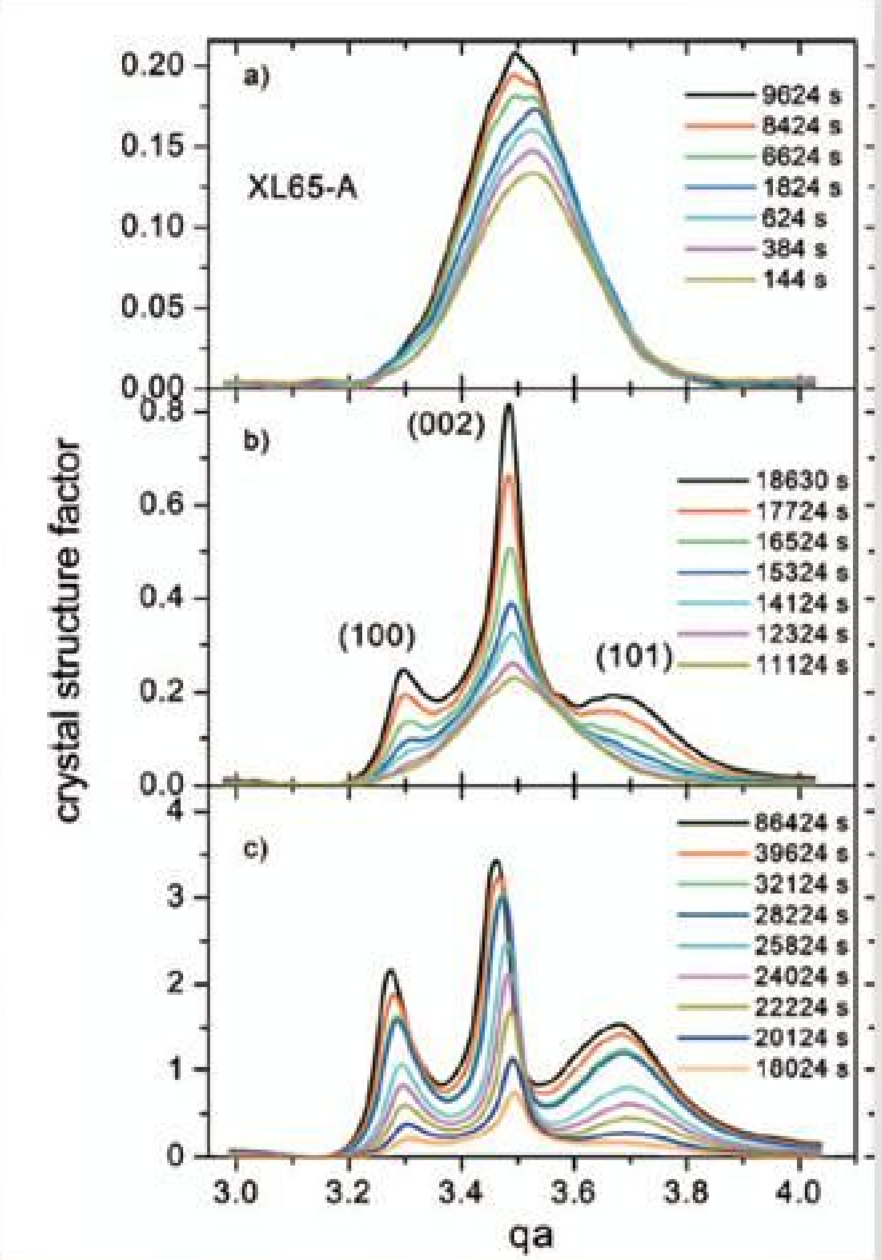
Ron Ottewill
PMMA
synthesis

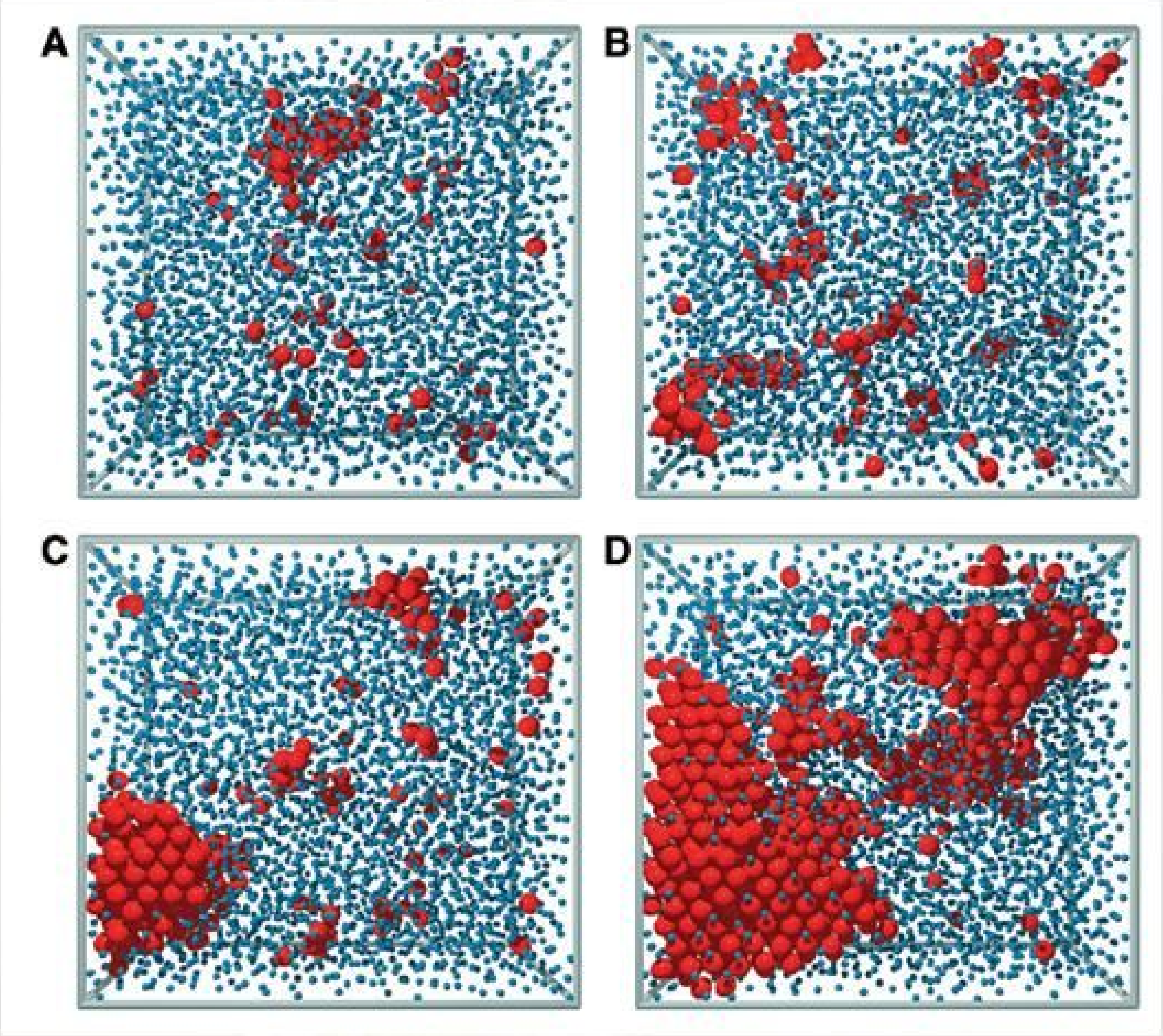
Pusey and van Megen Nature 1986

Experimental 'hard' sphere phase diagram



Measuring crystallisation





static light scattering
small colloids: many τ_B

$\tau_B \sim \sigma^3$

Schope et al *JCP* **127** 084505 (2007)

real space analysis
large colloids: fewer τ_B

Gasser et al *Science* **292** 258 (2001)

Don't we know everything already?

classical nucleation theory (CNT)

$$\Delta G = 4\pi r^2 \gamma - \frac{4\pi}{3} r^3 \Delta\mu n$$

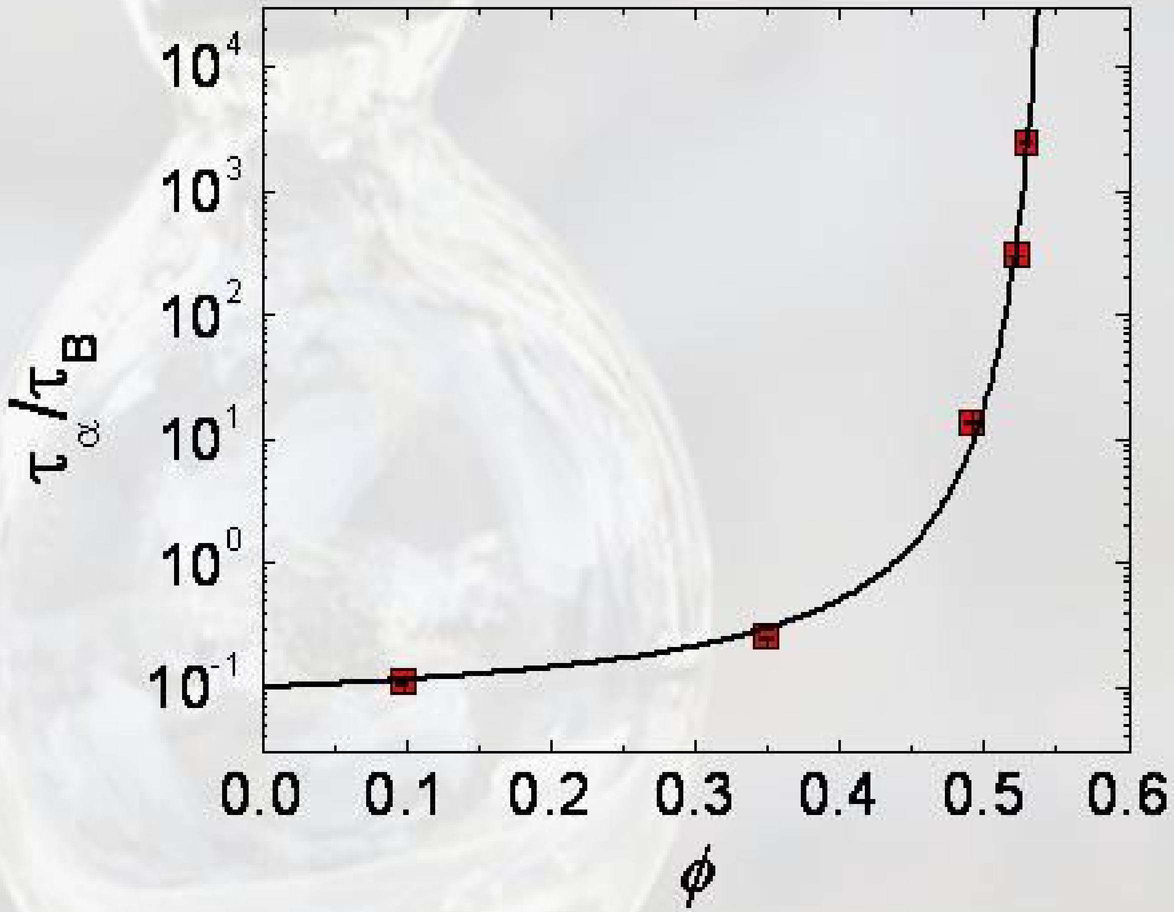
surface tension term r^2 (cost)
free energy gain r^2 (gain)

deeper quenching larger $\delta\upsilon$

smaller critical nucleus (more likely)

faster nucleation

but....



hard spheres have a glass transition so at very ϕ everything slows

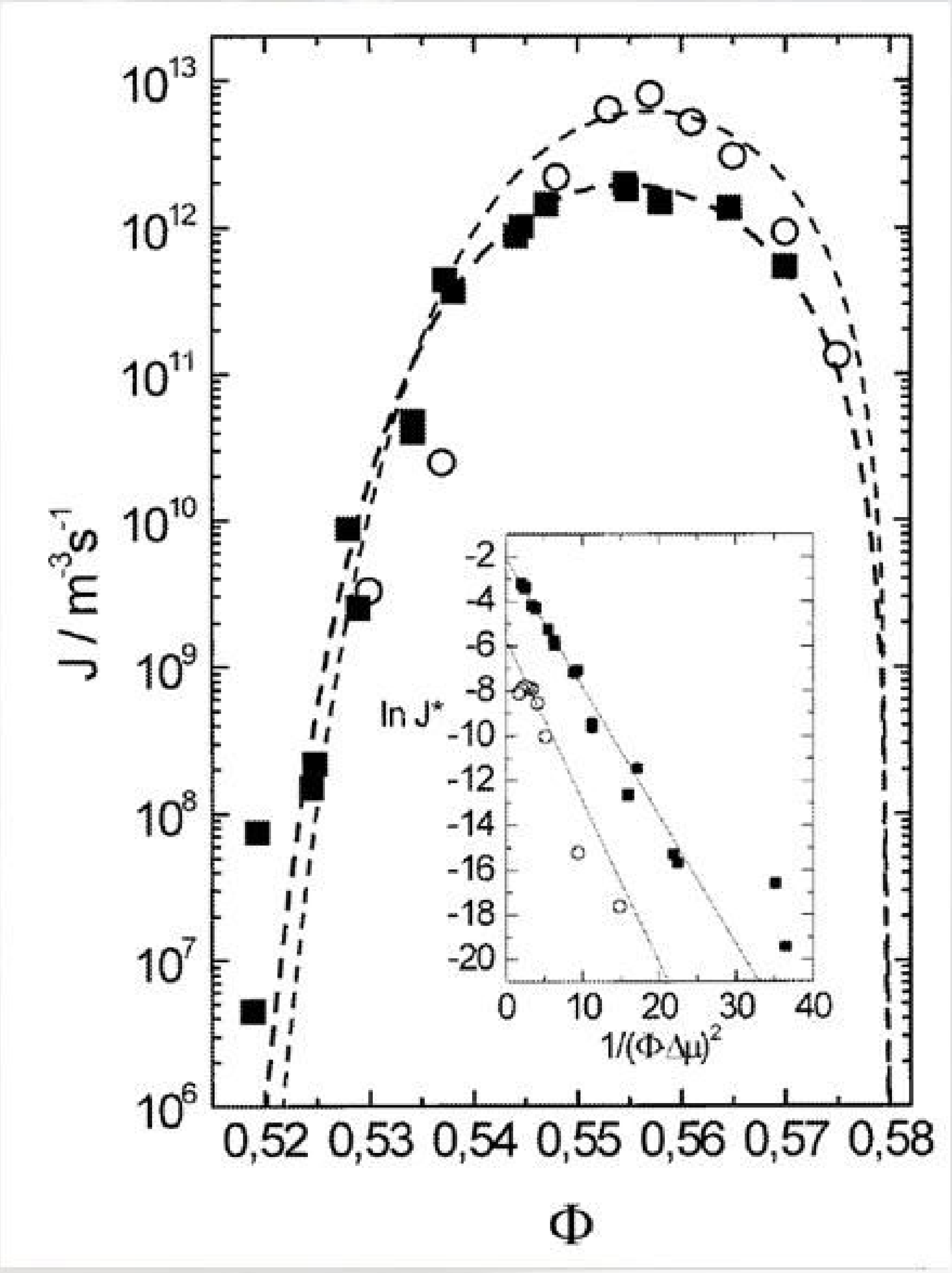
Don't we know everything already?

so at first nucleation should increase with ϕ J up

...then slow dynamics take over J down

Zaccarelli *et al PRL* (2009)

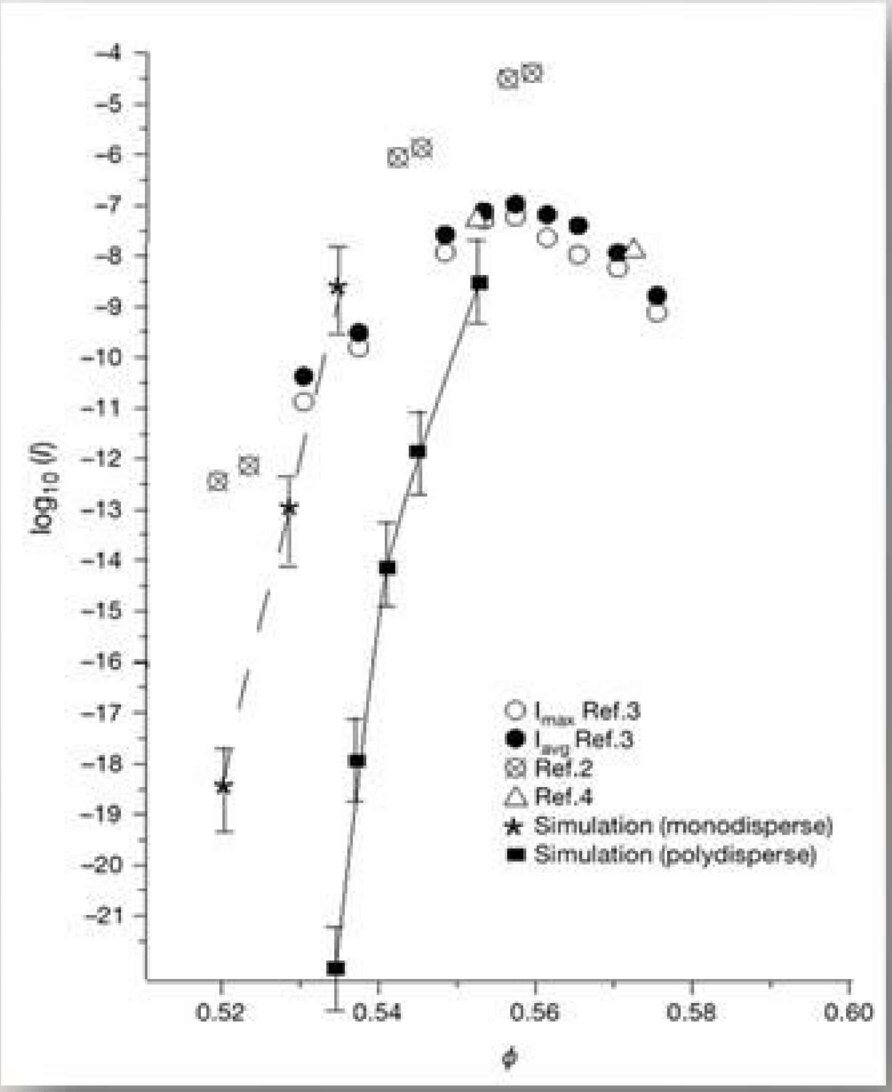
This CNT picture assumes nucleus can be treated as bulk thermodynamic object



Palberg *J. Phys: Condens. Matter*. **11** R323 (1999)

Frenkel and Auer: simulation of nucleation rate

Weitz new experiment



Computer simulations and experimental systems crystallise at extremely different rates why is this?

Can we learn anything from the locally favoured structures?

A tiny change in parameters - huge change in J

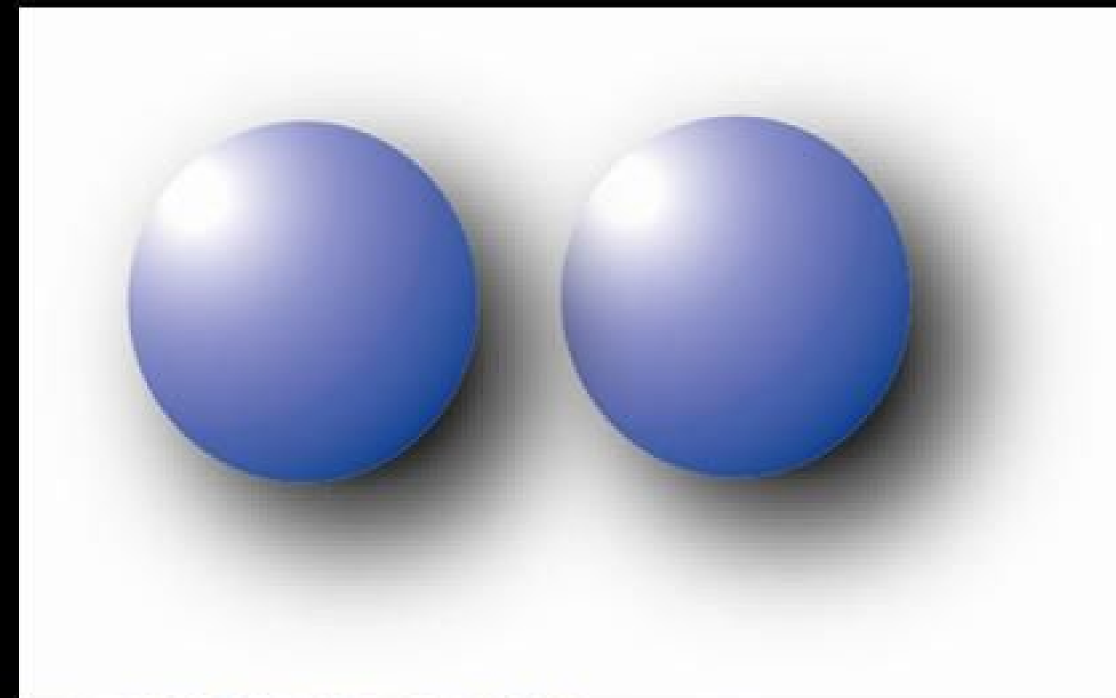
Auer, S. & Frenkel, D., *Nature*, **409**, 1020 (2001)

Differences between 'model' colloidal 'hard' spheres and 'real' in-silico hard spheres

Pusey and van Megen Nature 1986

What have the Easter Bunny and uncharged colloids in common?

Easter bunny



Uncharged colloids

What have the Easter Bunny and uncharged colloids in common?

Easter bunny

rged colloids

Neither exists!
There is no such thing as a hard sphere (except in our computers and minds)
All colloids carry charge

DLVO pair potential

Coarse grain out small ions: Poisson-Boltzmann

Linearise (valid for 'small charge density')

$\beta\varepsilon_Y$

$$\beta u_{DLVO}(r) = \begin{cases} \infty & r < \sigma \quad \text{hard core} \\ \dfrac{(Z)^2 l_B}{(1+\kappa\sigma/2)^2} \dfrac{\exp(-\kappa(r-\sigma))}{r} & r \geq \sigma \end{cases}$$

where Z is the effective colloid charge, l_B the Bjerrum length

κ inverse Debye length

$u_{DLVO}(r)$

Simple analytical expression for $u(r)$

Repulsive Yukawa form (VdW attractions are *Very* short ranged)

$l_B = e^2/(kT\varepsilon)$

$\kappa^2 = 8\pi l_B \rho_i$

Differences between 'model' colloidal 'hard' spheres and 'real' in-silico hard spheres

Charge? considered by Auer and Frenkel, but slope of J similar (but if rates are to match, must include) JPCM 14 S9053 (2002)

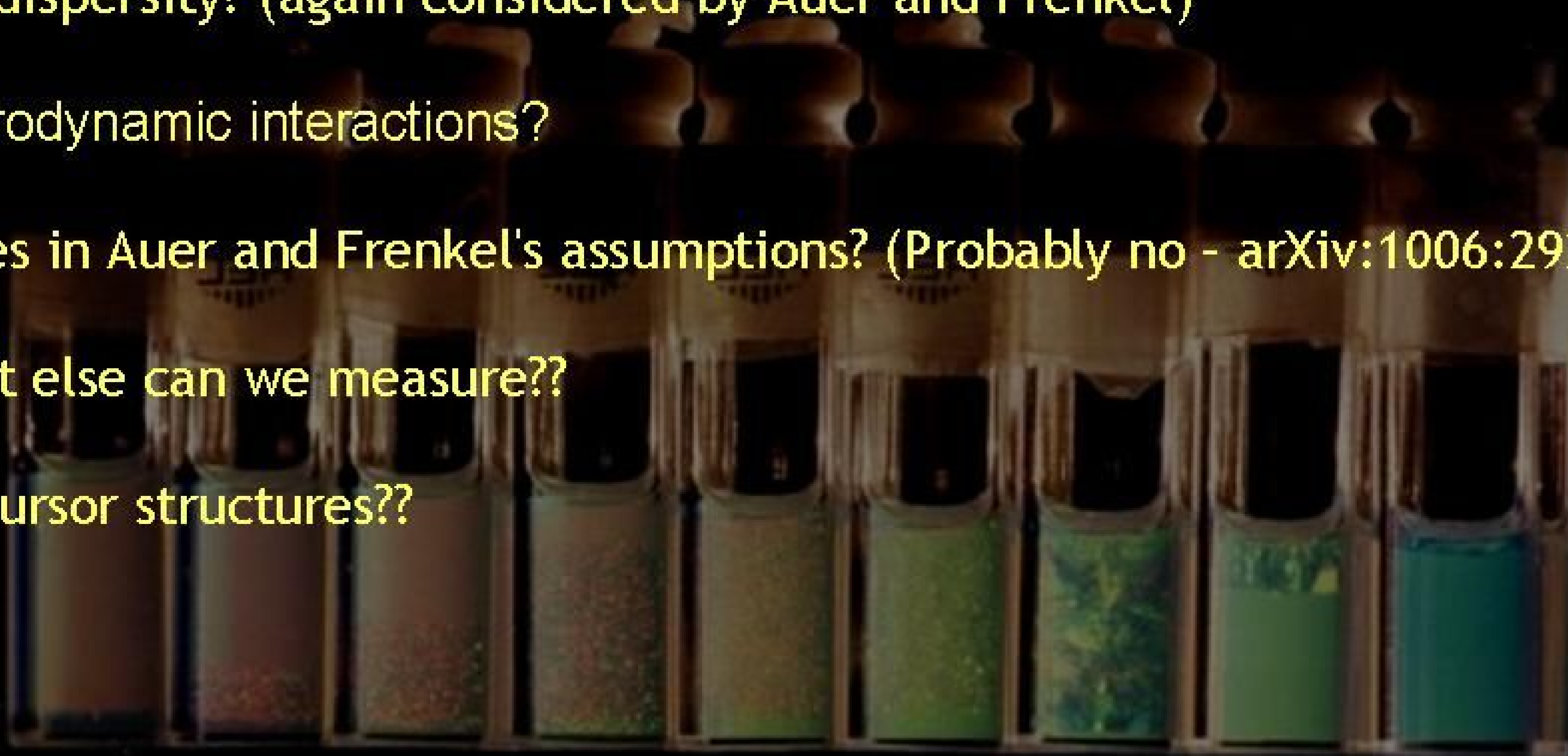
Polydispersity? (again considered by Auer and Frenkel)

Hydrodynamic interactions?

Issues in Auer and Frenkel's assumptions? (Probably no - arXiv:1006:2925v1)

What else can we measure??

Precursor structures??



Pusey and van Megen Nature 1986

Differences between 'model' colloidal 'hard' spheres and 'real' in-silico hard spheres

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Polydispersity?

Hydrodynamic

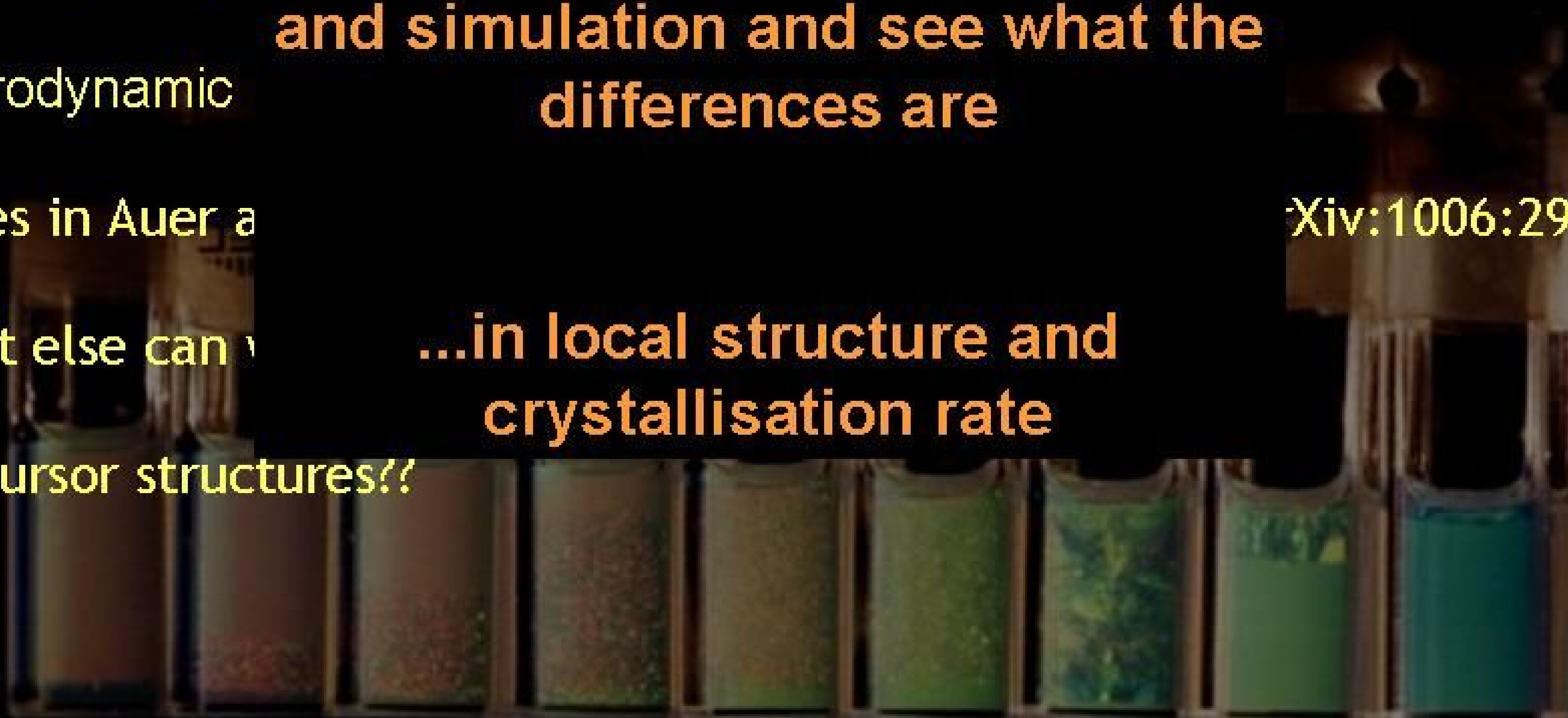
Issues in Auer a ... Xiv:1006:2925v1)

What else can ...

Precursor structures??

carefully compare experiment and simulation and see what the differences are

...in local structure and crystallisation rate



Pusey and van Megen Nature 1986

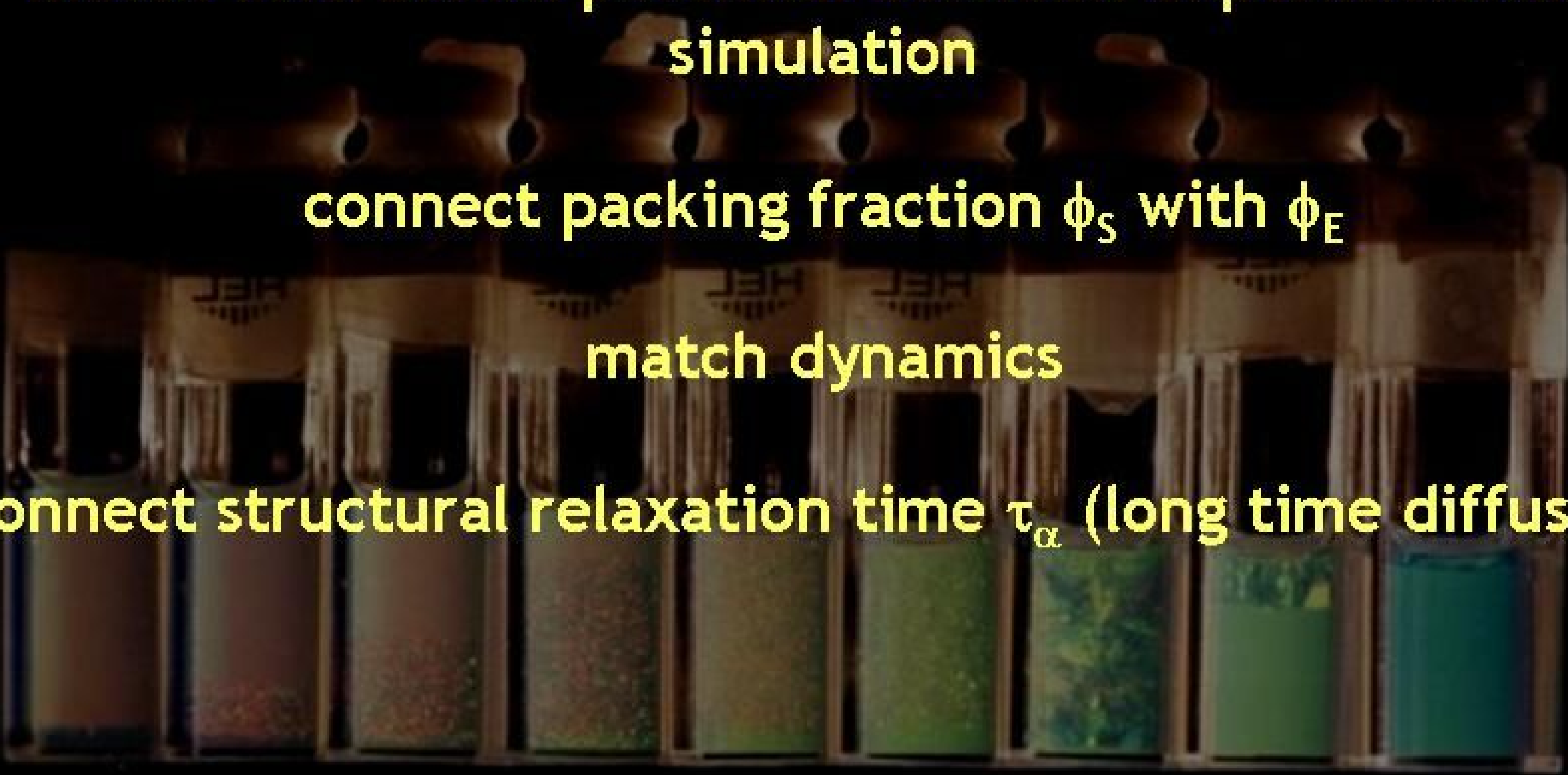
Strategy

match interaction potential between experiment and simulation

connect packing fraction ϕ_S with ϕ_E

match dynamics

connect structural relaxation time τ_α (long time diffusion)



Mapping simulation to experiment

Can calculate radial distribution function $g(r)$

Cornerstone of liquid state physics
Ornstein-Zernike equation

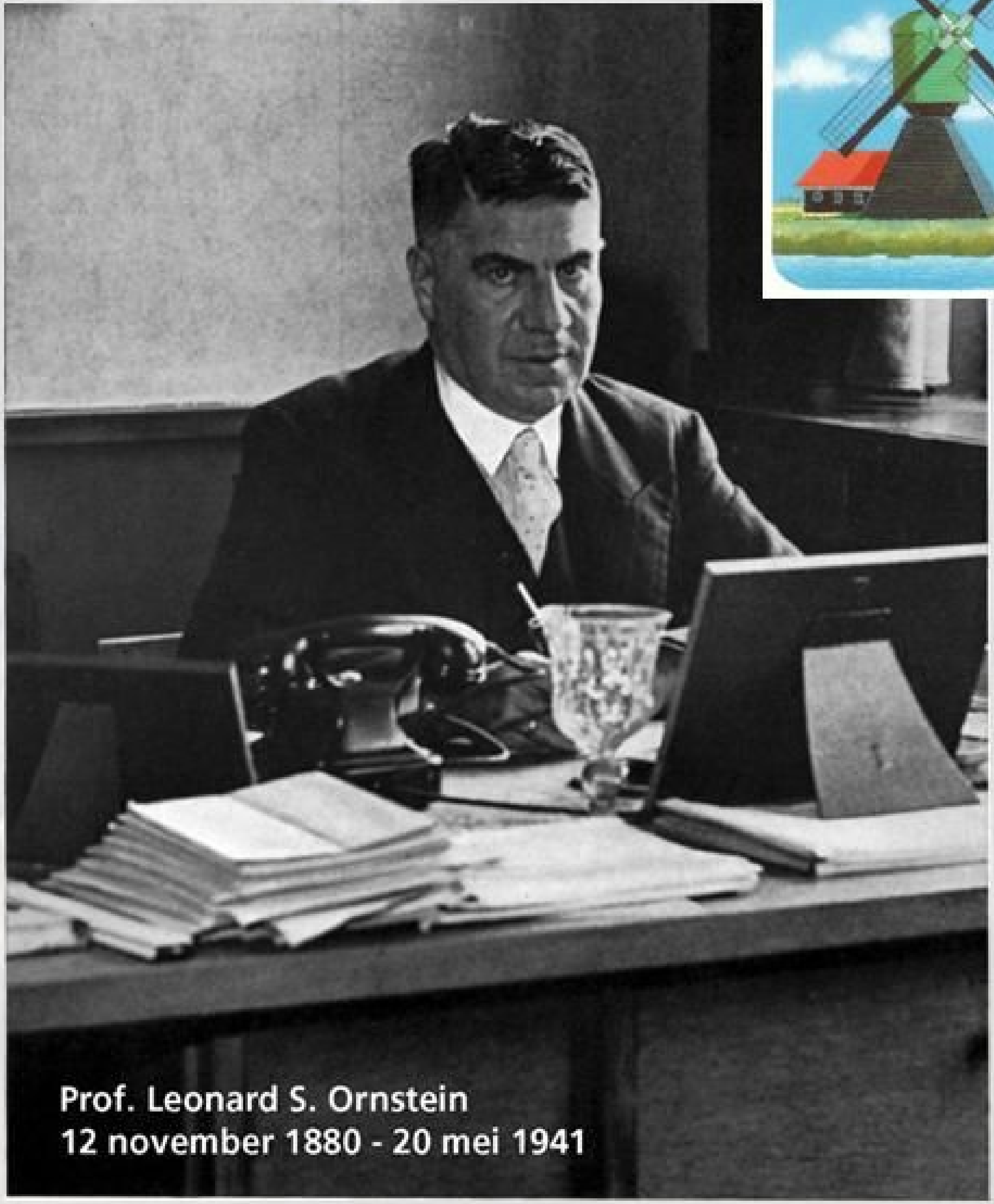
$$h(r) = c(r) + \rho \int c\left(\left|\underline{r} - \underline{r}'\right|\right) h(r')\, d\underline{r}'$$

$g(r)$ uniquely defined by $u(r)$ (pairwise additive homogenous fluid)

dilute limit $\quad g(r)_{\lim \rho \to 0} = \exp[-\beta u(r)]$

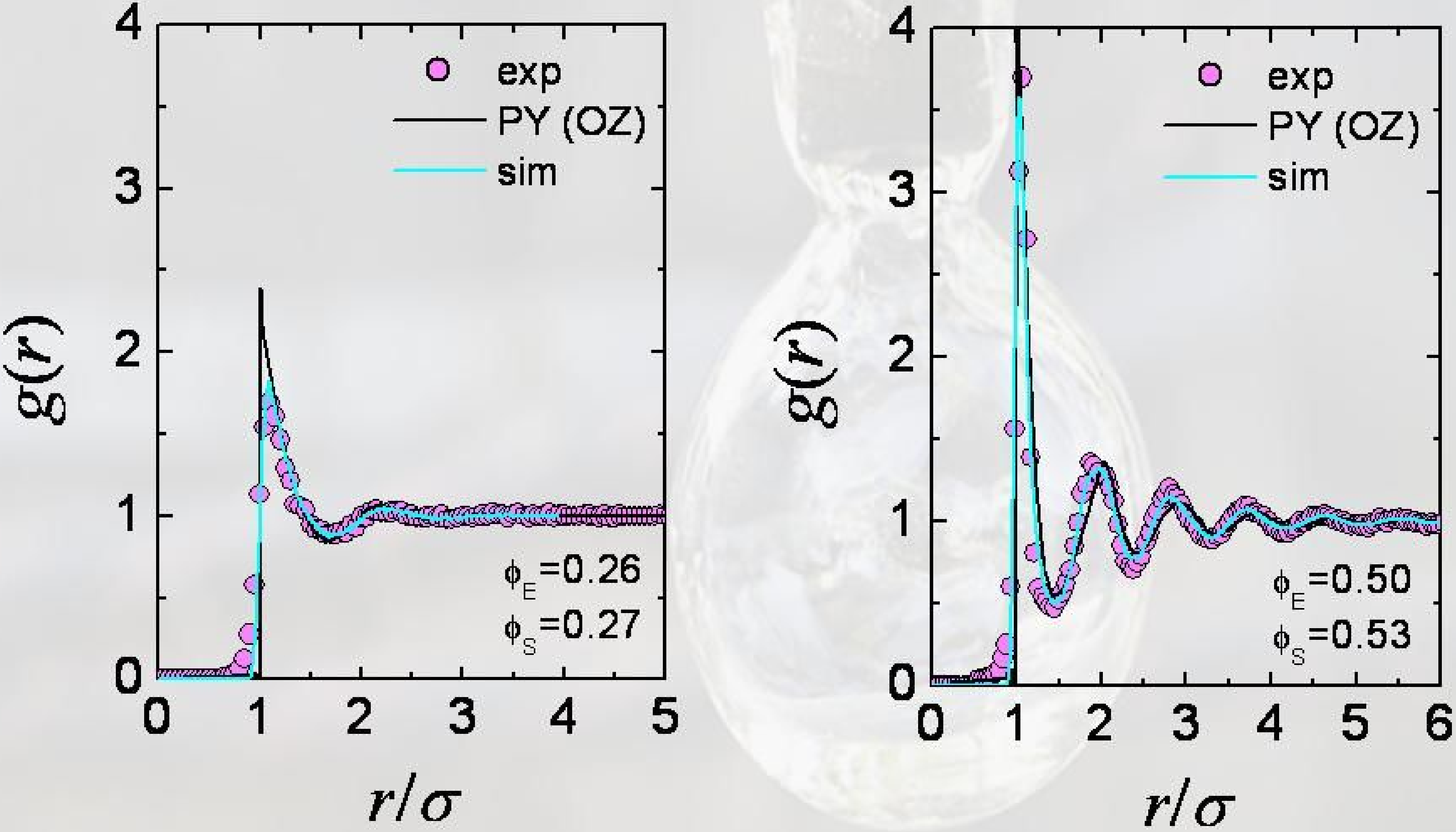
Hard Spheres

$$g(r) = \begin{cases} 0 & r < \sigma \\ 1 & r < \sigma \end{cases}$$



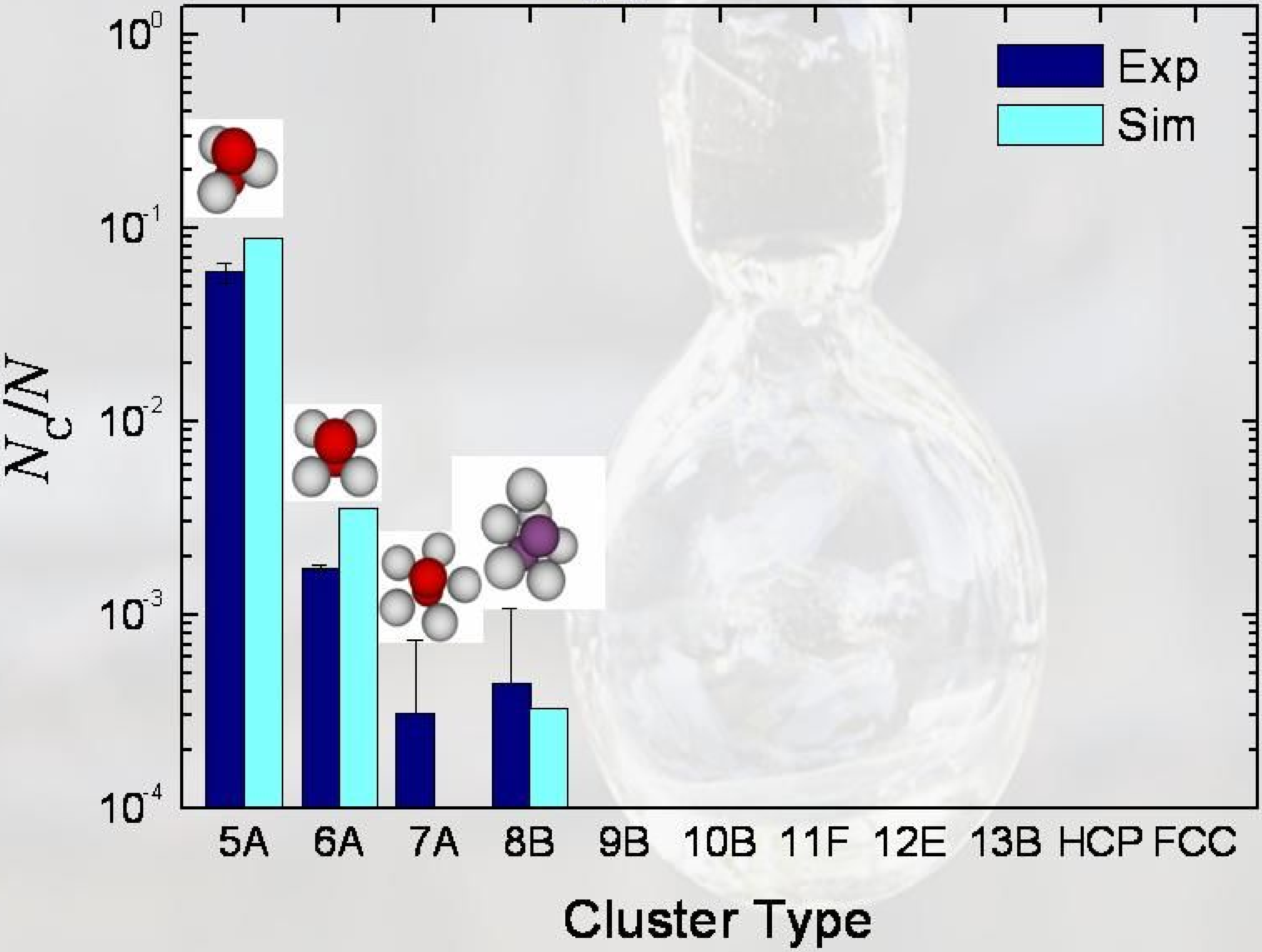
$h(r)=g(r)-1$ $\beta=1/k_B T$ $c(r)$ direct correlation function CPR *et al*, *J. Chem. Phys.* **127** 044507 (2007)

Same g(r) implies same interaction potential



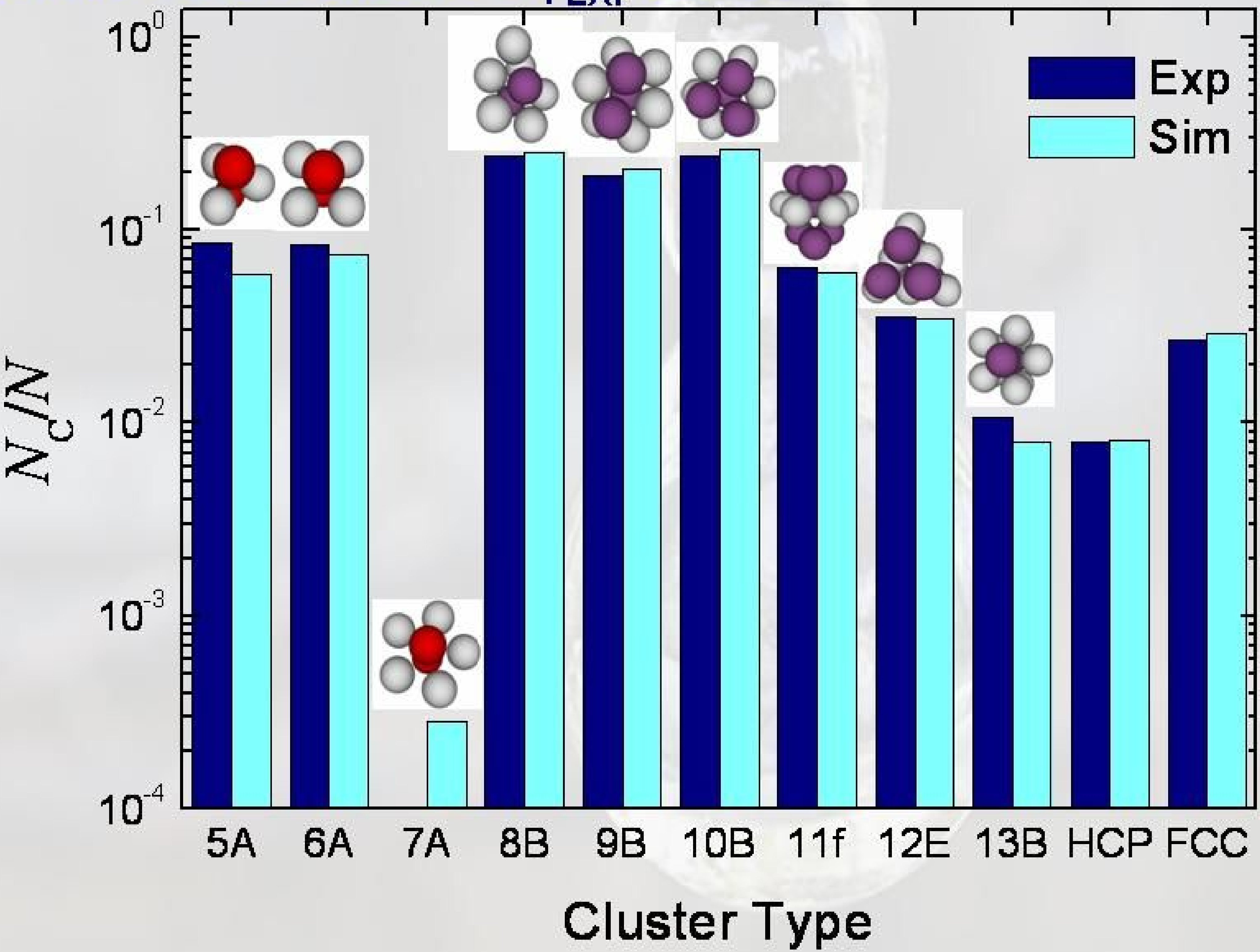
Yukawa parameters $\beta\varepsilon_Y=1$ $\kappa\sigma=30$ ϕ_E experimental packing fraction ϕ_S packing fraction in simulation polydispersity 4%

TCC cluster distribution ϕ_{EXP}=0.26



Yukawa parameters $\beta\varepsilon_Y$=1 $\kappa\sigma$=30 ϕ_E experimental packing fraction ϕ_S packing fraction in simulation polydispersity 4%

TCC cluster distribution $\phi_{EXP}=0.50$



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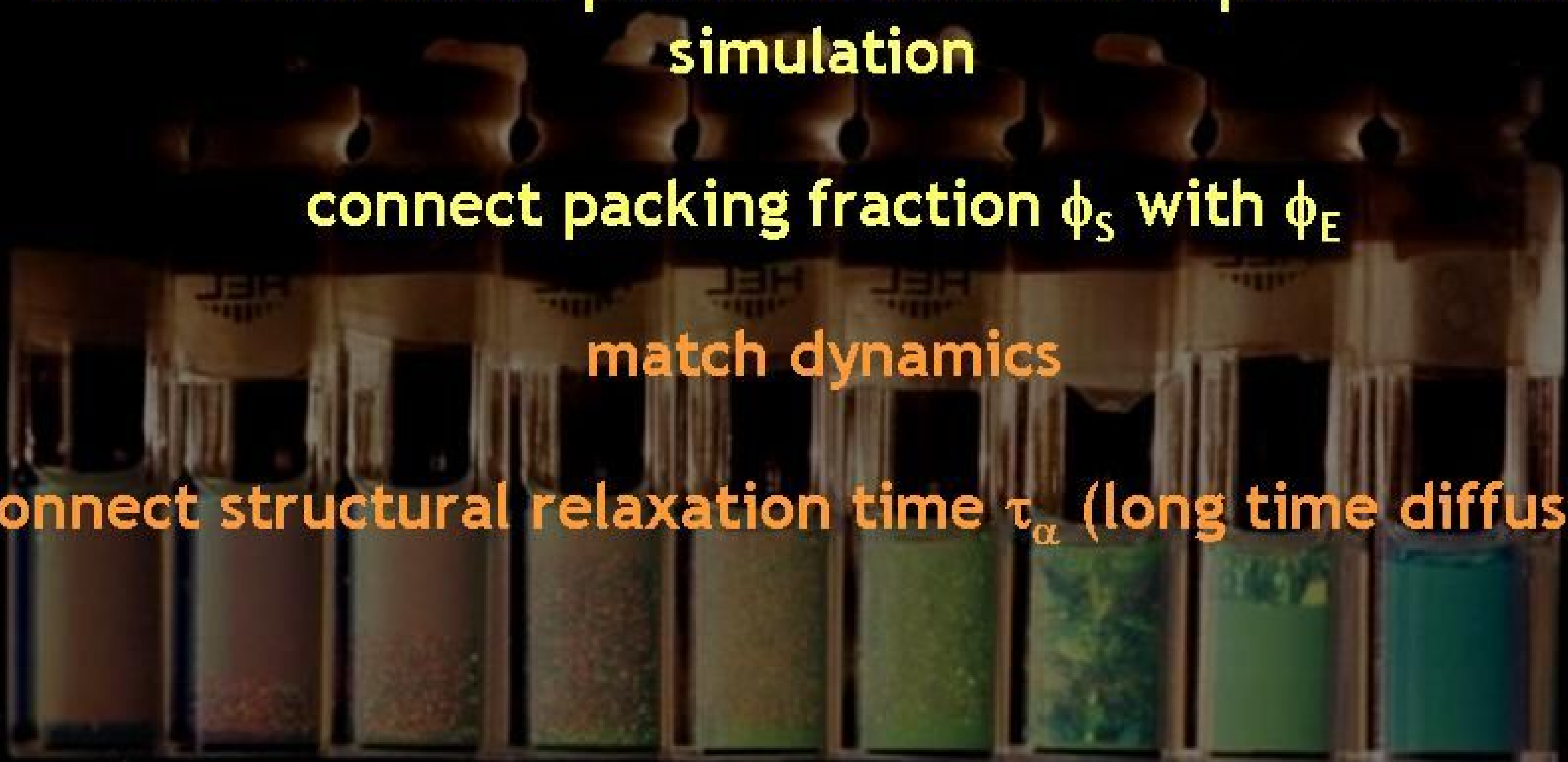
match dynamics

connect structural relaxation time τ_α (long time diffusion)



Matching dynamics: intermediate scattering function

experiment: hydrodynamic interactions.

Brownian dynamics simulation

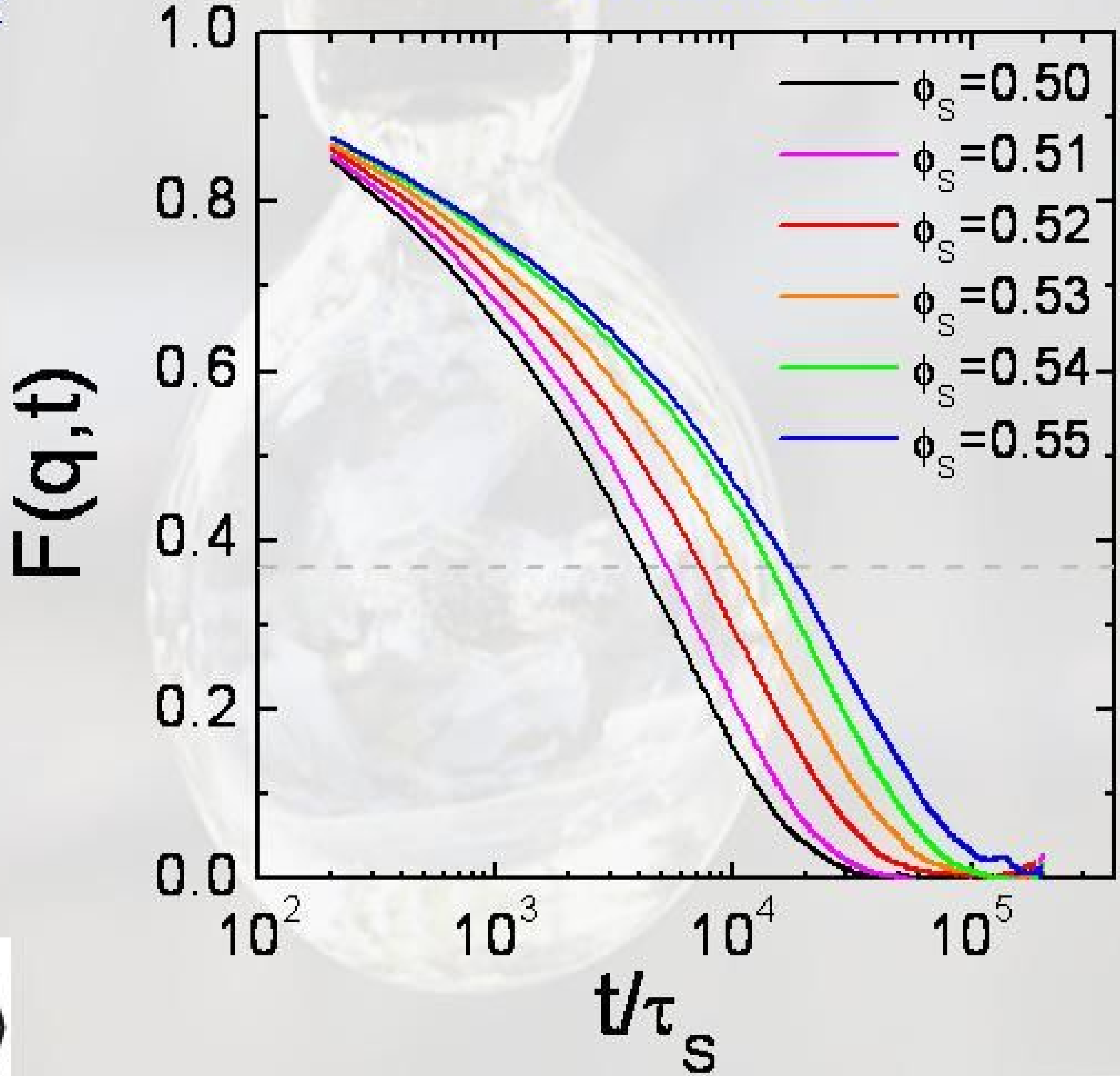
assume if long-time self diffusion matched then dynamics matched

intermediate scattering function

$$F_s(q,t) = \left\langle \frac{1}{N} \sum_{j=1}^{N} e^{i\mathbf{q}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]} \right\rangle$$

τ_α time at which $F(q,\tau_\alpha)=1/e$

simulation



set τ_α for highest ϕ_S which doesn't crystallise

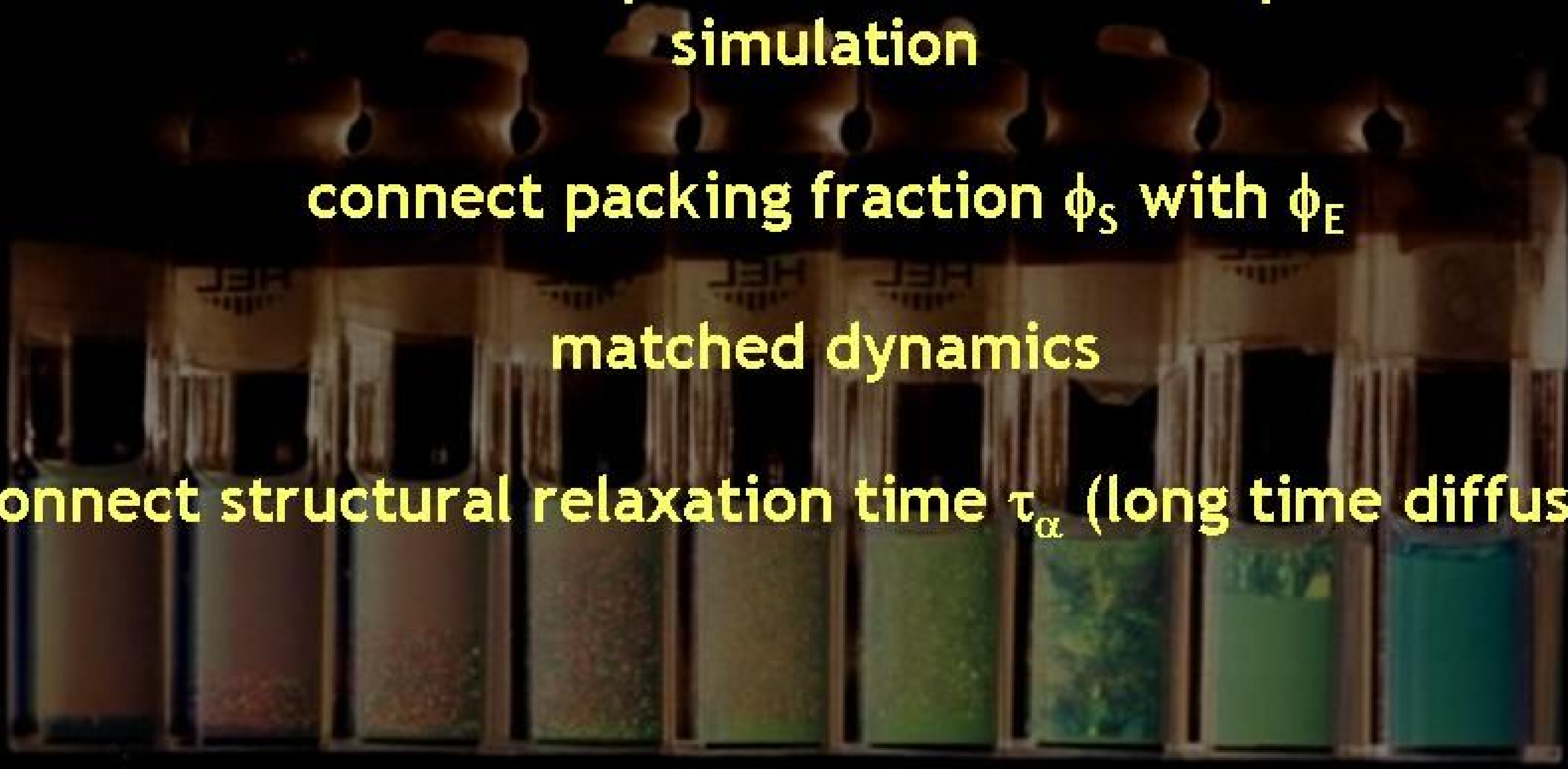
Set parameters to compare

matched interaction potential between experiment and simulation

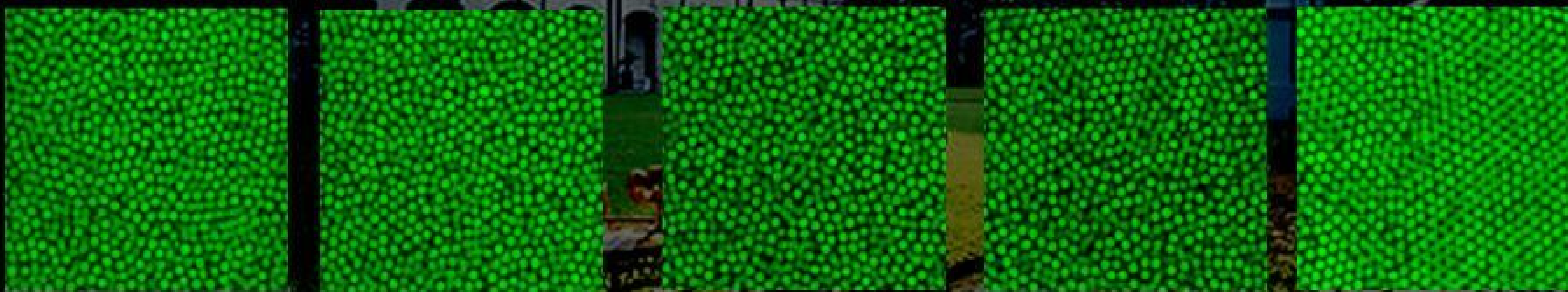
connect packing fraction ϕ_S with ϕ_E

matched dynamics

connect structural relaxation time τ_α (long time diffusion)



Typical experimental results



t=0 $t=481\ \tau_B$ $t=3176\ \tau_B$ $t=7796\ \tau_B$ $t=12032\ \tau_B$

Topological cluster classification: crystallisation in experiment ϕ_E=0.51

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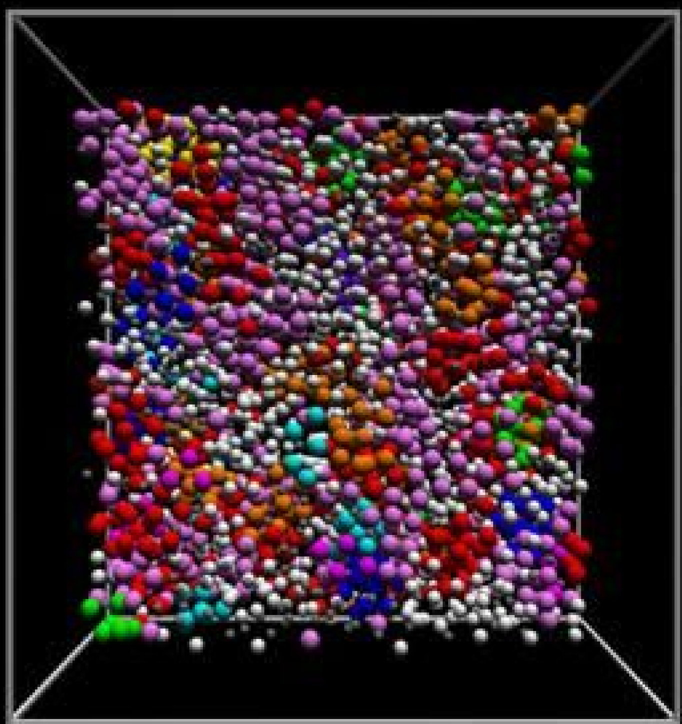
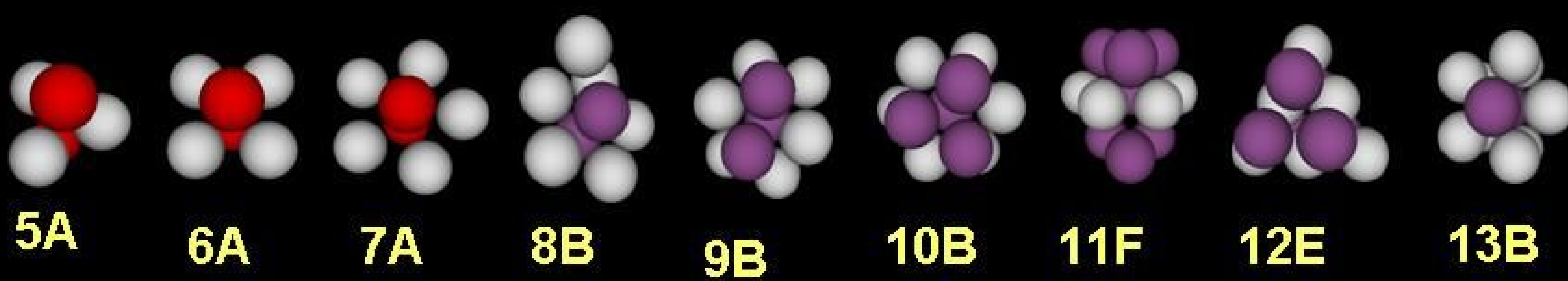


$t=10\ \tau_B$



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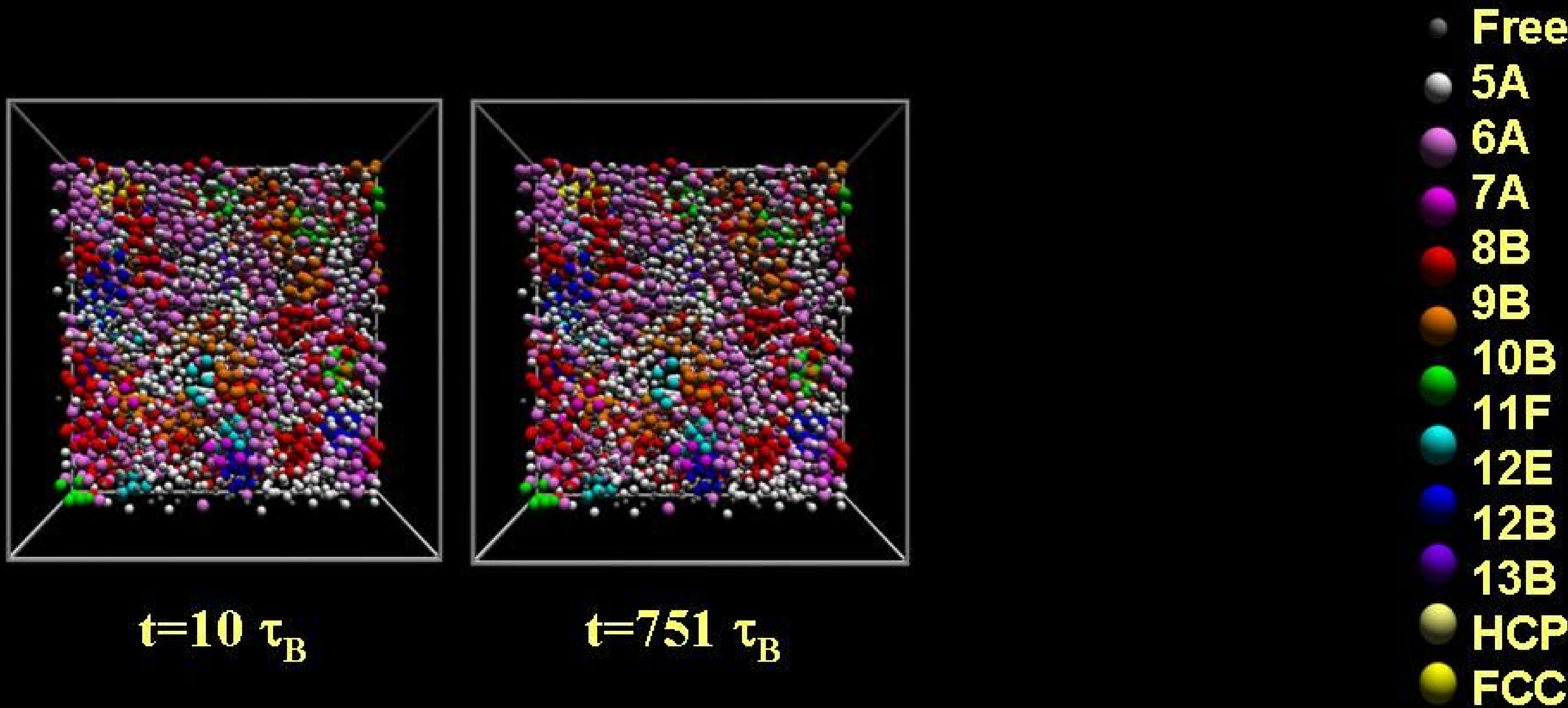

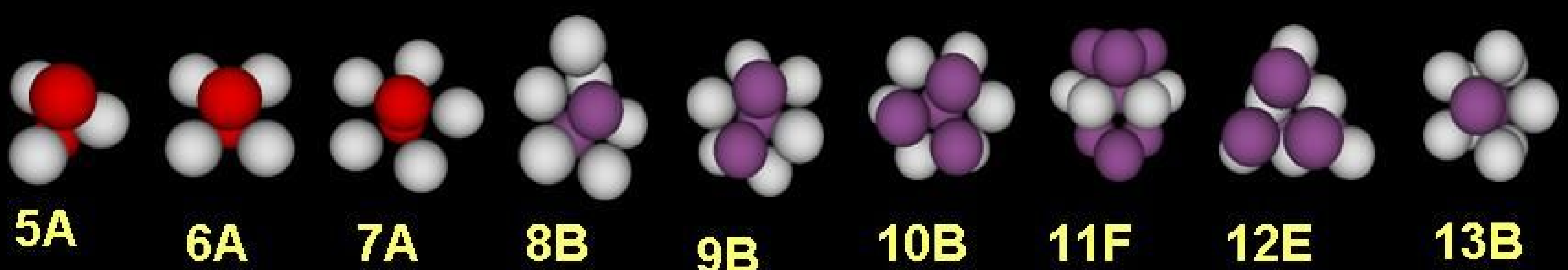

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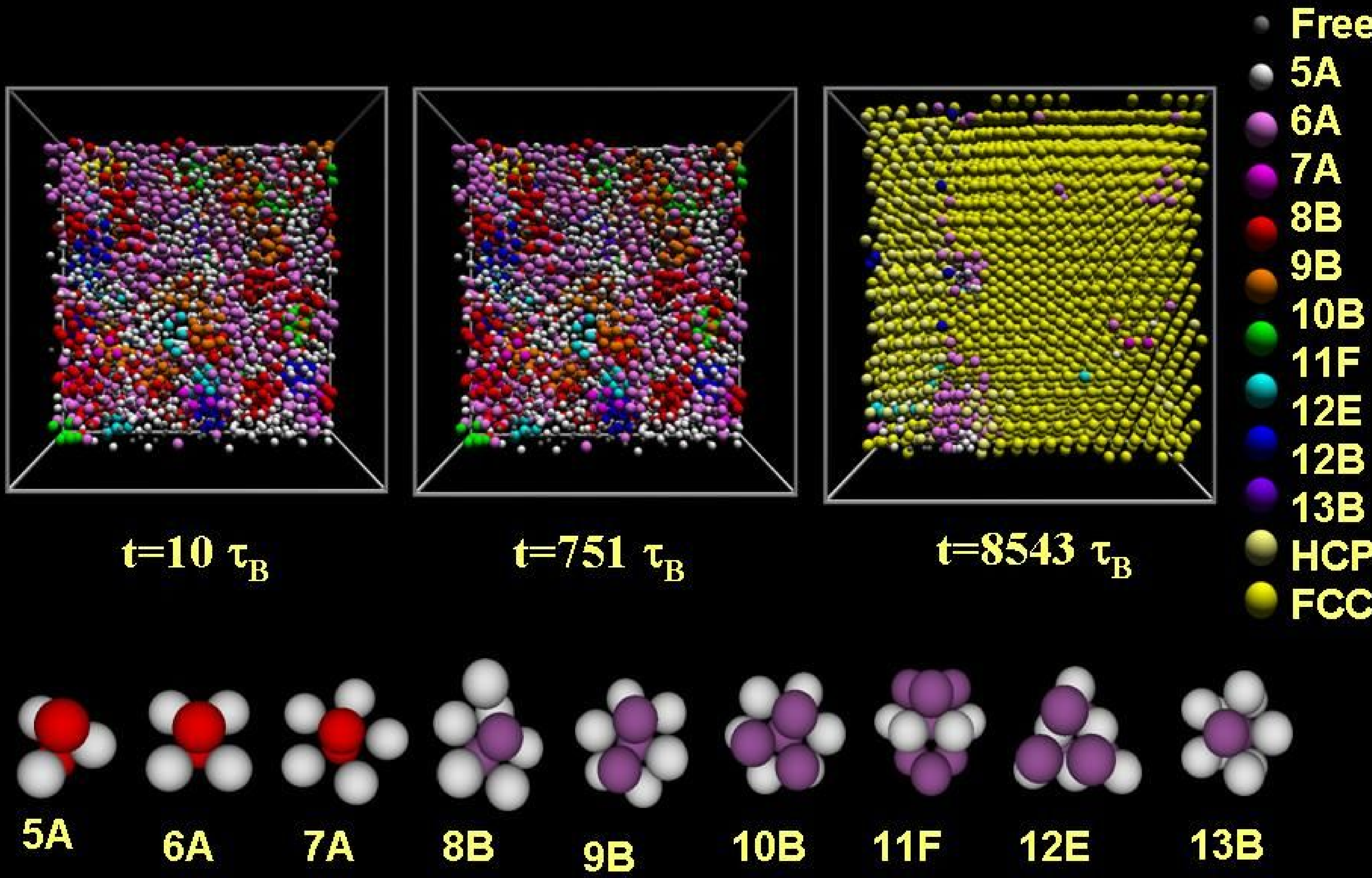
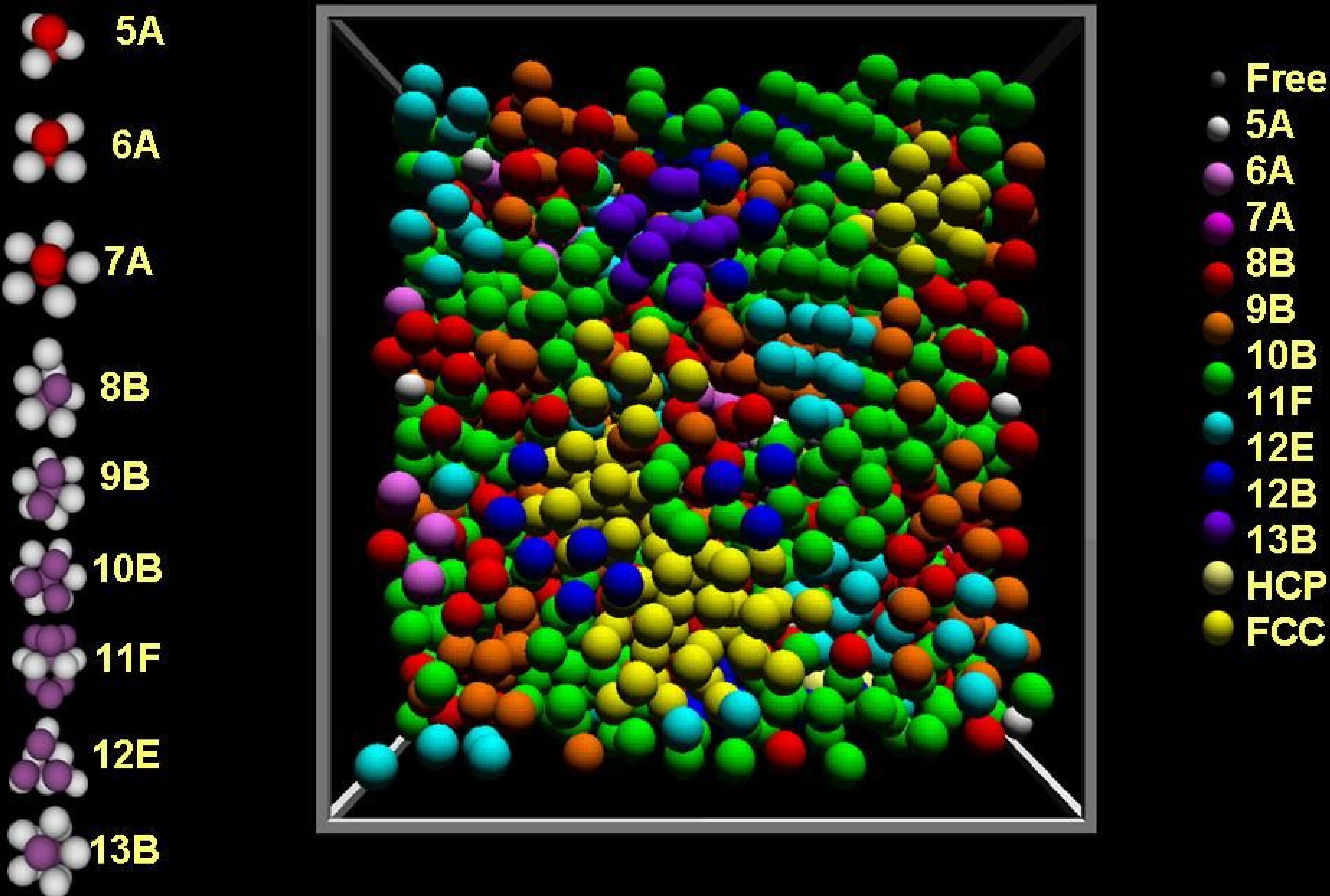


Topological cluster classification: crystallisation in simulation ϕ_S=0.56



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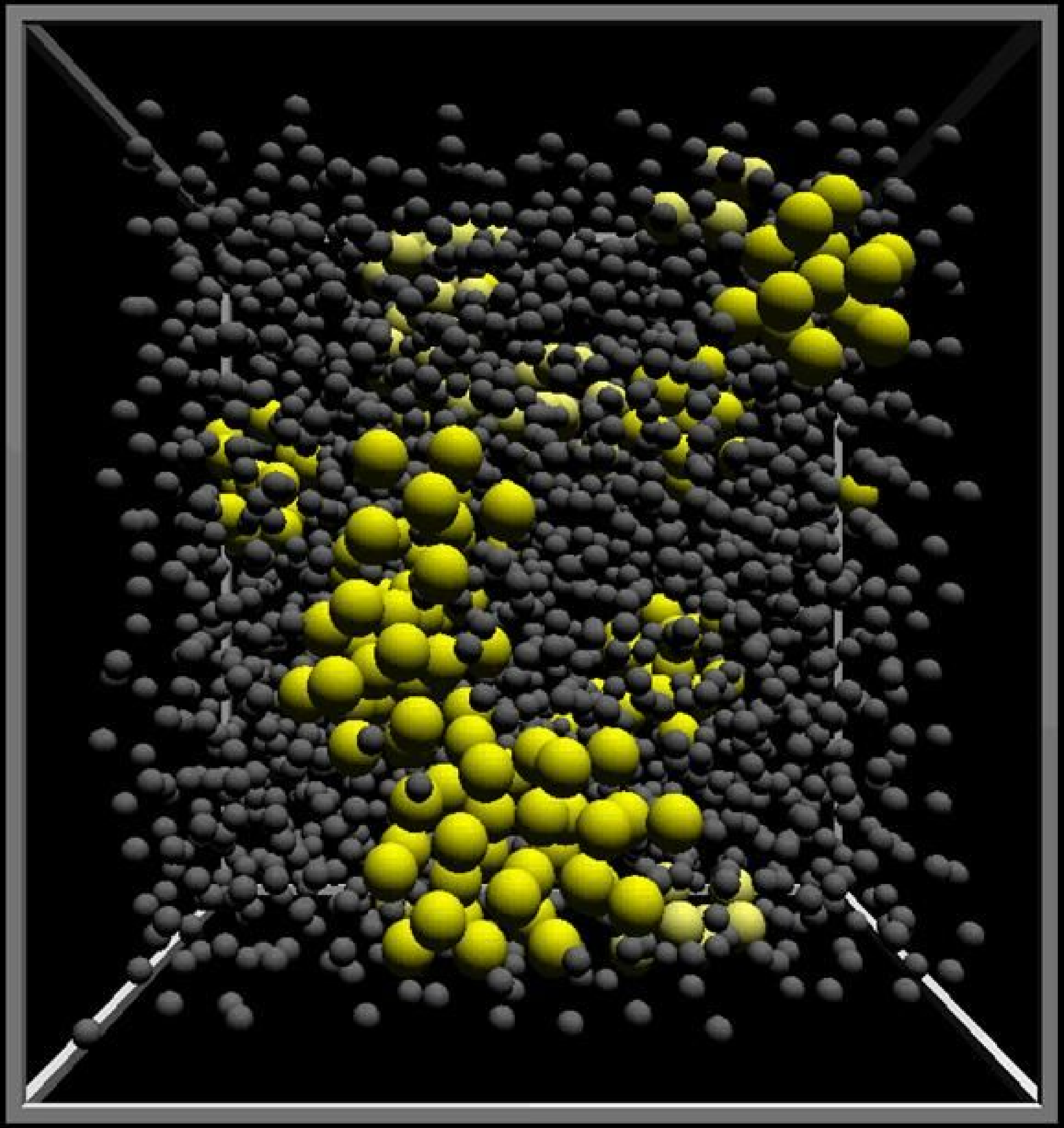
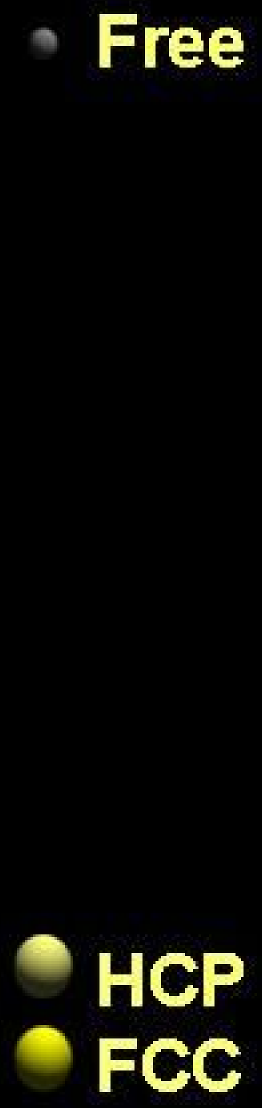
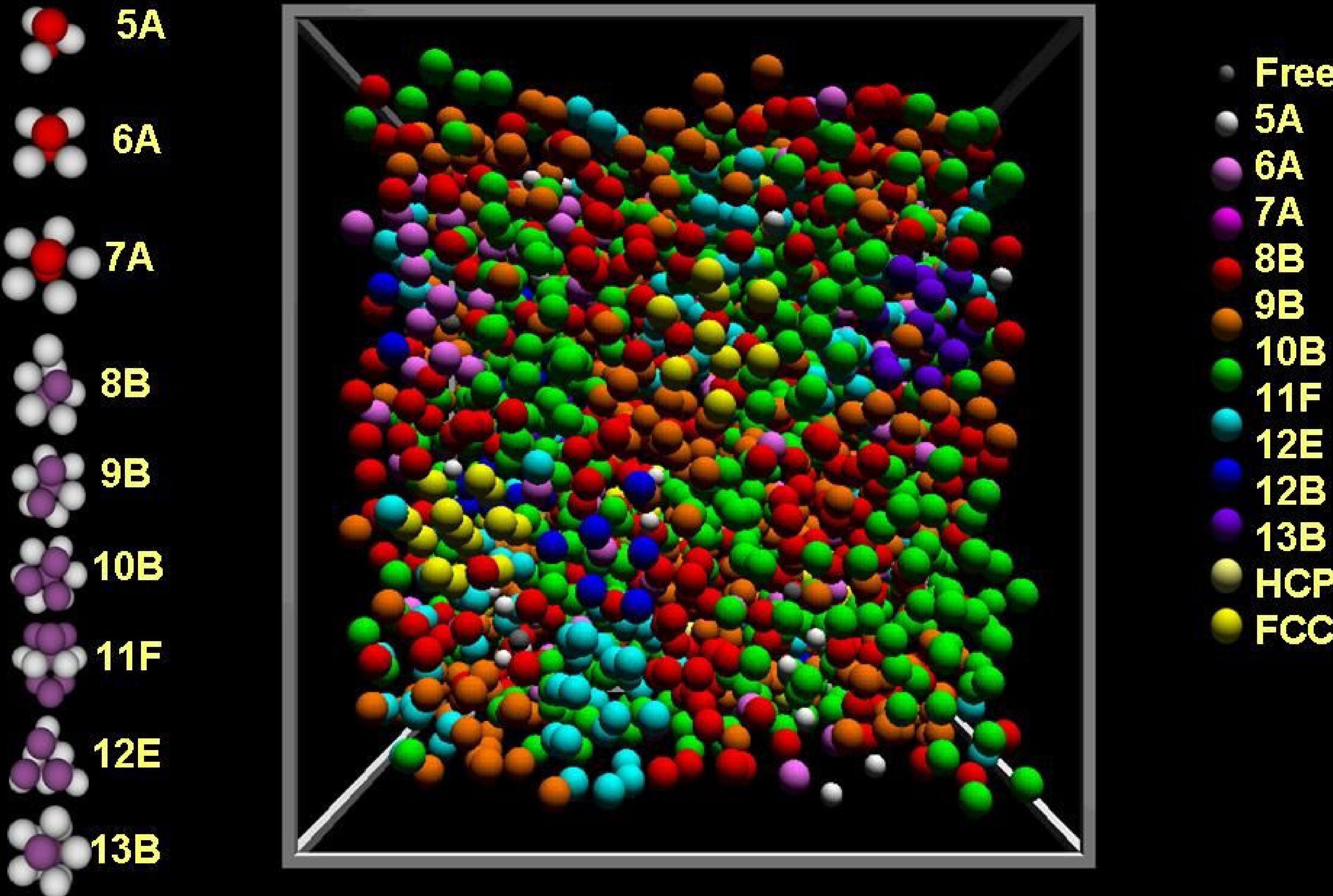




Topological cluster classification: metastable liquid in simulation ϕ_S=0.55



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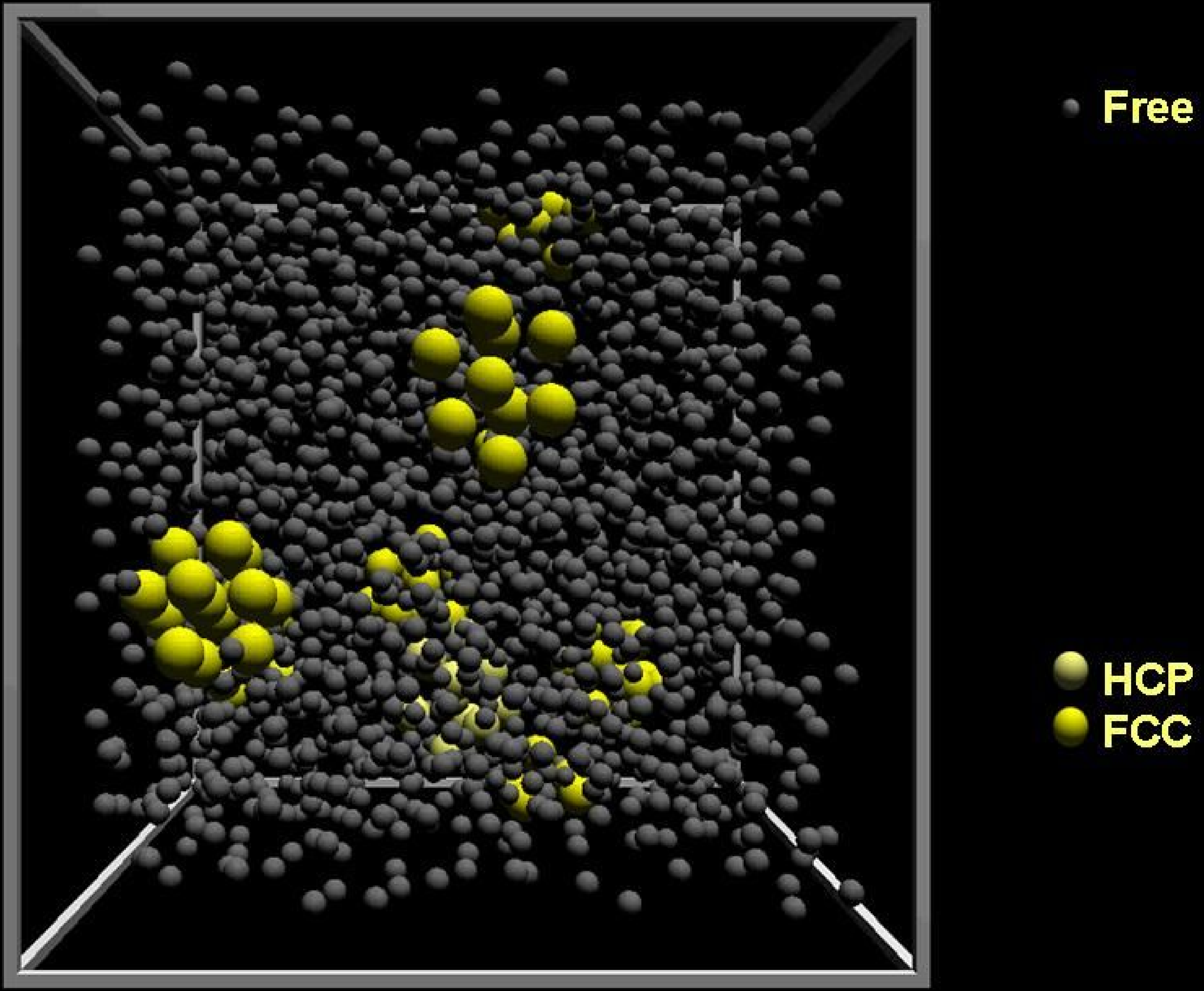
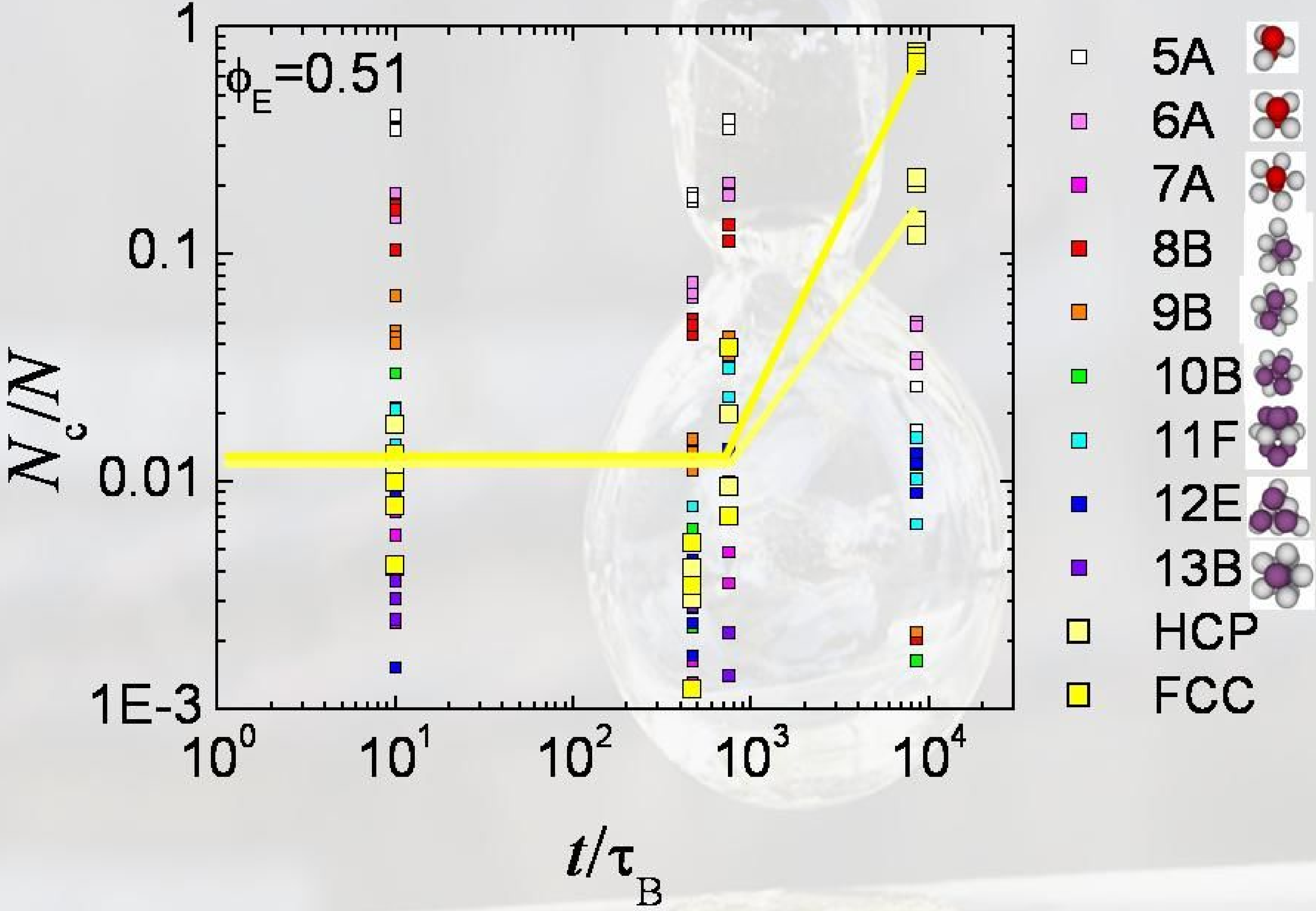
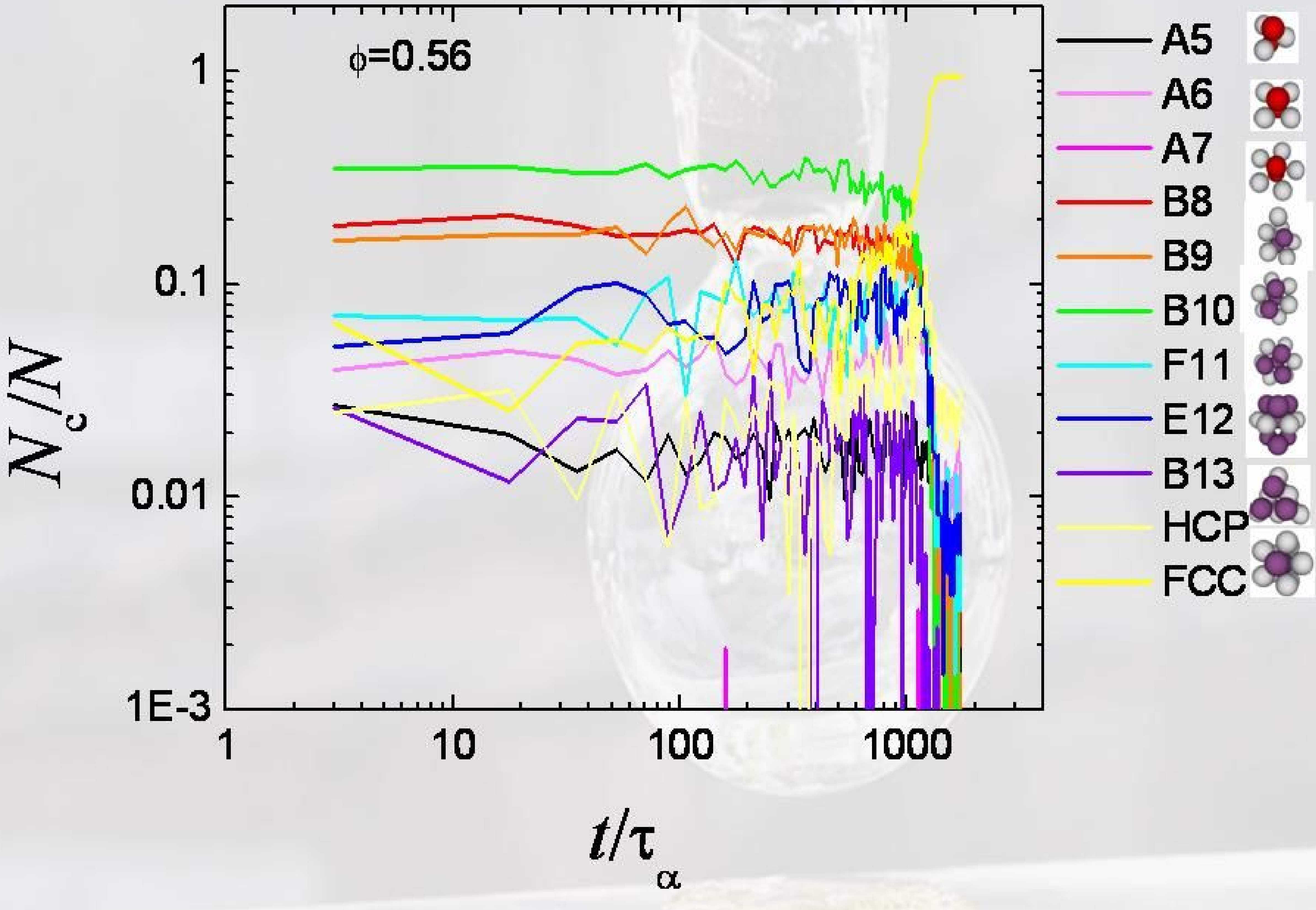


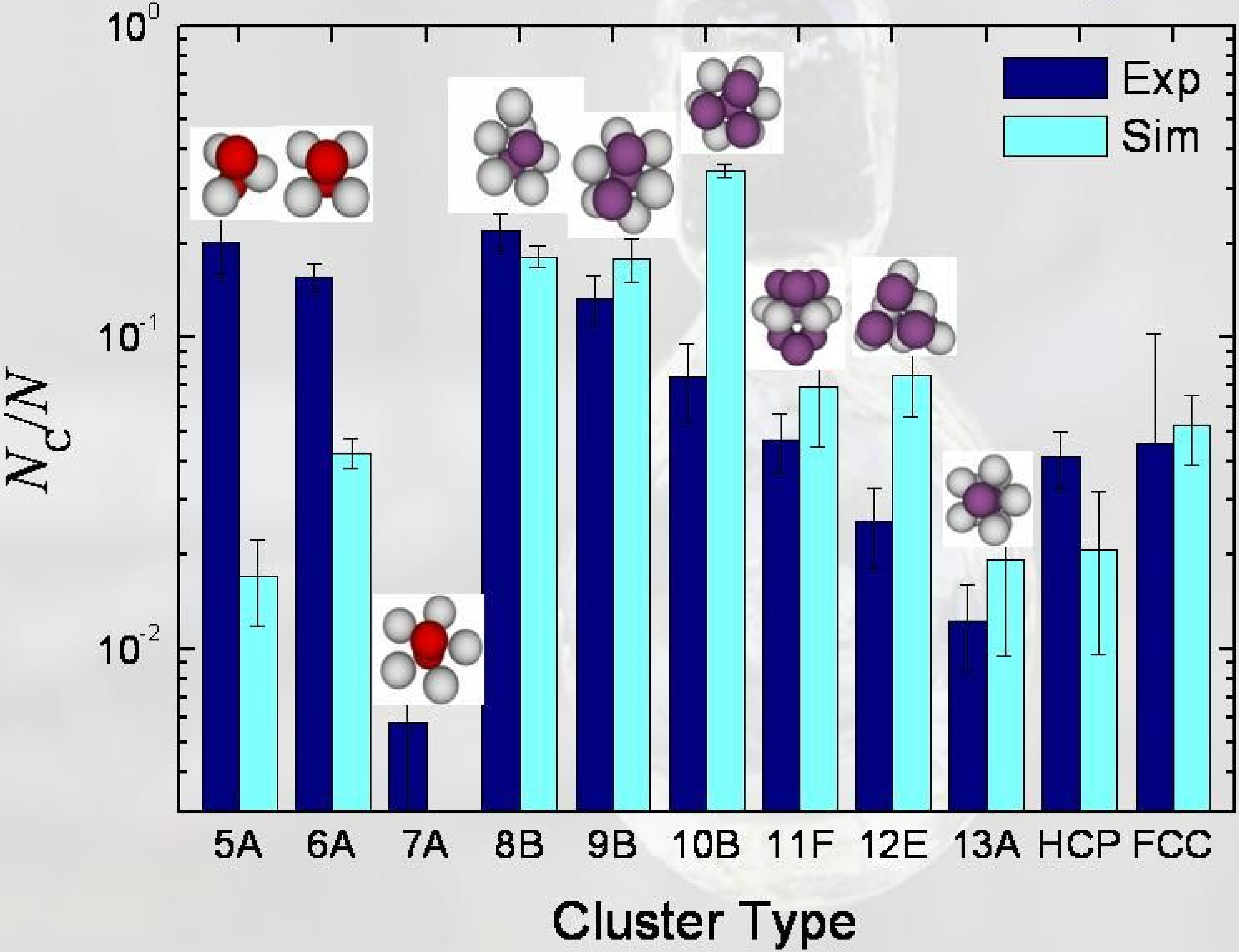
Crystallisation in experimental system - TCC



Crystallisation in simulation- TCC



TCC cluster distribution metastable fluid $\phi_{EXP}=0.52$



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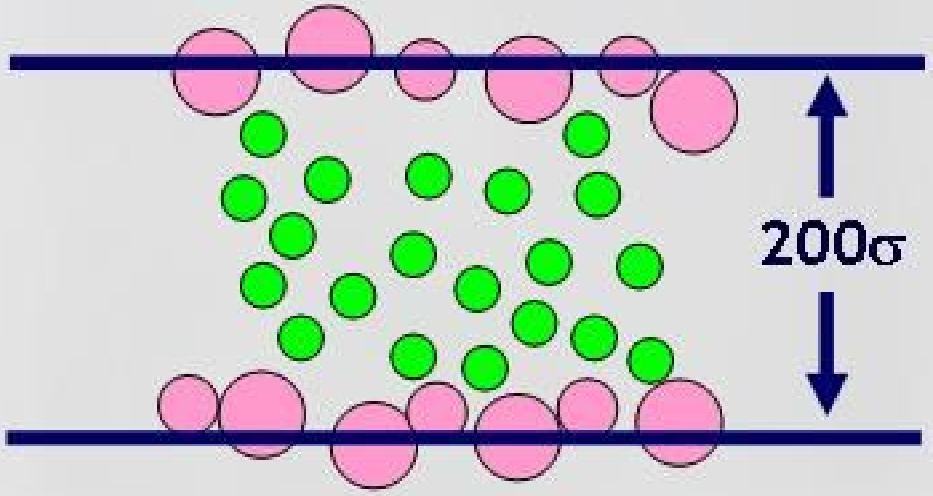
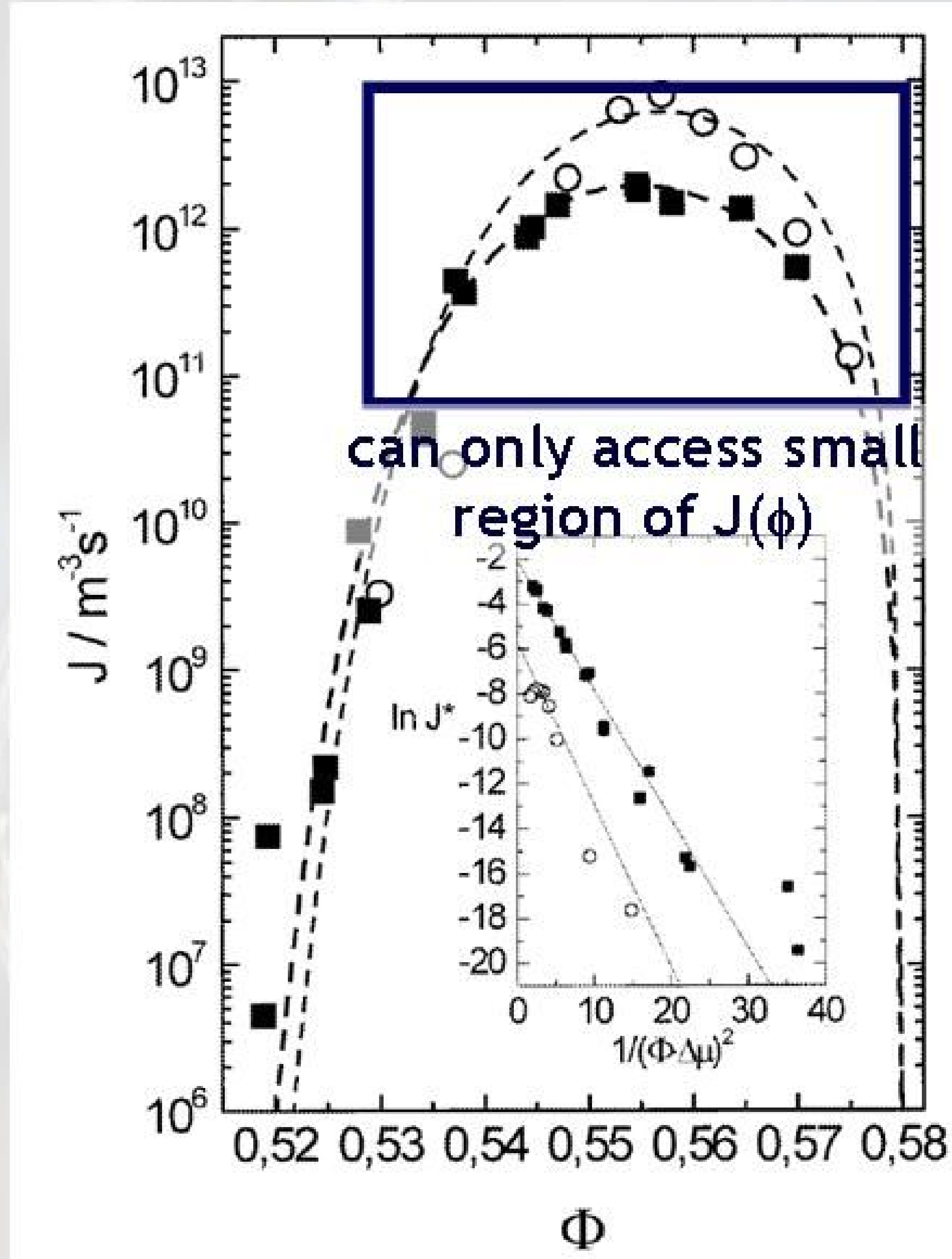
Real space analysis: a few big slow colloids



exp: suppress nucleation at wall with adsorbed polydisperse larger colloids

Exp: 200σ
Sim: 20σ
naively:
$J_{EXP} \sim 10^3 J_{SIM}$

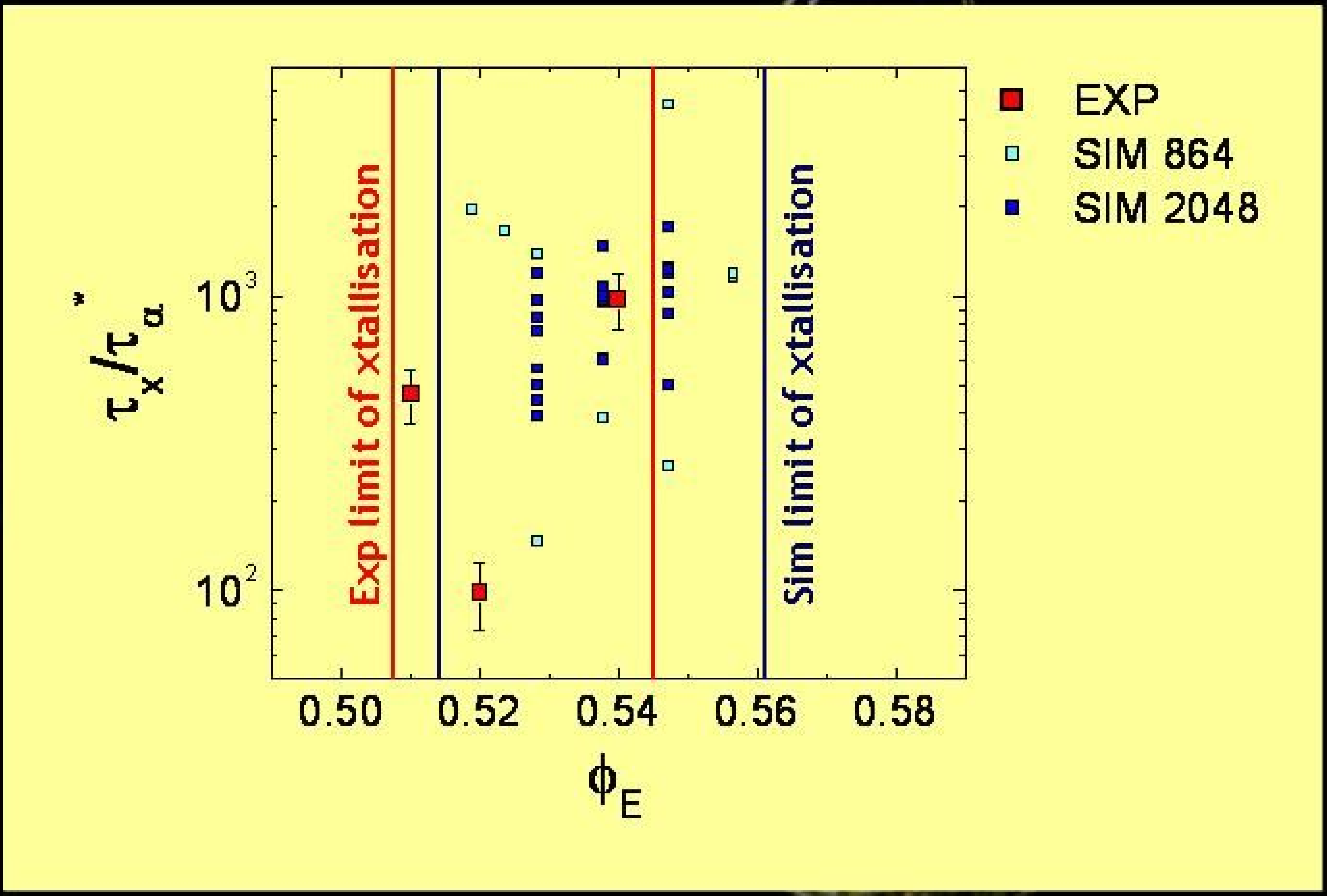
$\tau_B \sim \sigma^3$ so 200nm to 2000nm
3 orders slower and sedimentation



Palberg *J. Phys: Condens. Matter*. **11** R323 (1999)


define 'crystallisation time'
where >50% are HCP or FCC

Crystallisation times in experiment and simulations
Scaled parameters

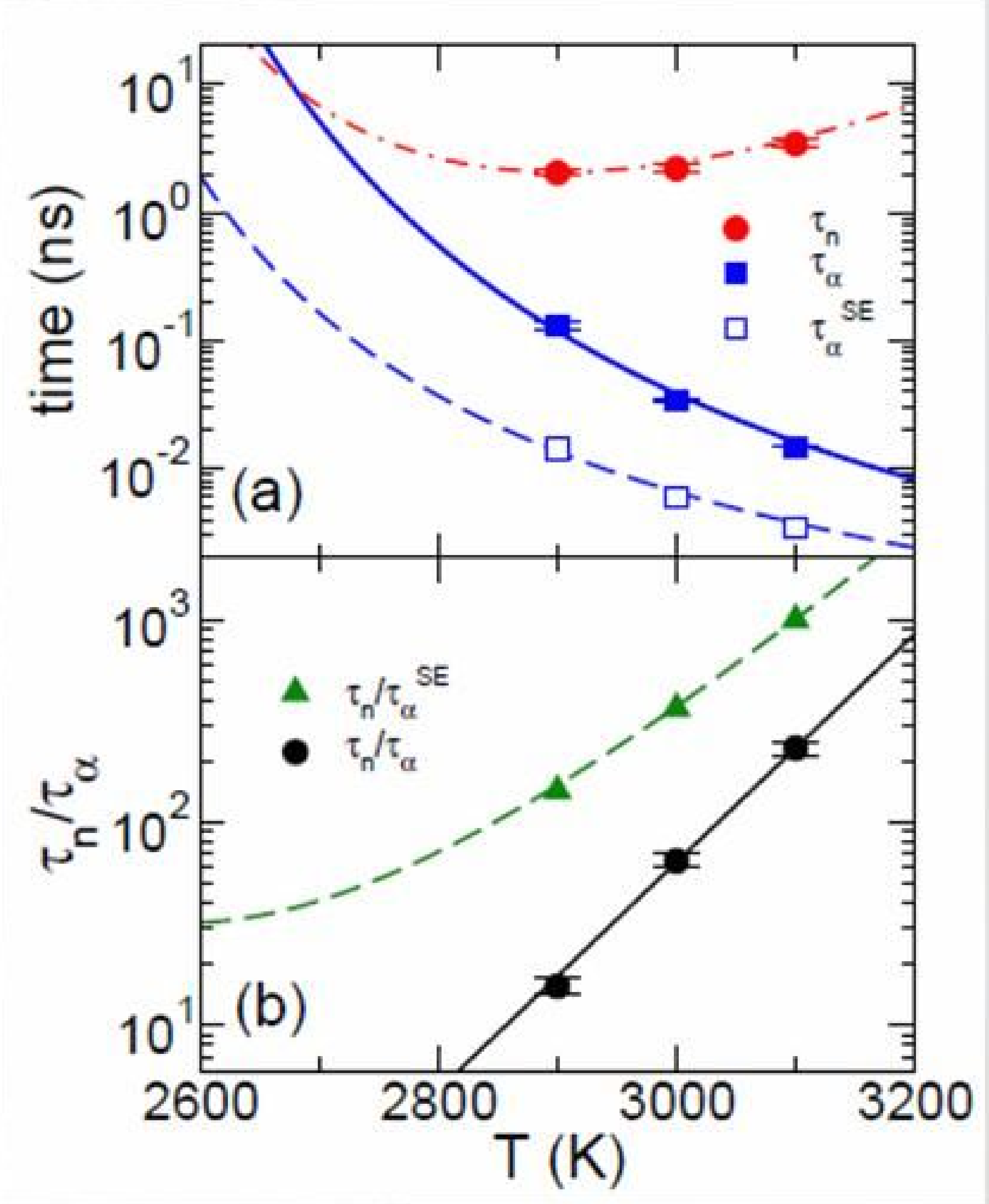


What about spinodal nucleation?

Why is τ_X so insensitive to ϕ?

Zaccarelli et al: PRL 2009
spinodal nucleation:
but there msd < ~ σ^2
here ~100-1000τ_α polydispersity=4%

Saika-Voivod, Bowles and Poole: PRL 2010
Spinodal nucleation of BKS silica->
The numbers look V similar
τ_n last time for no non-xtal particles



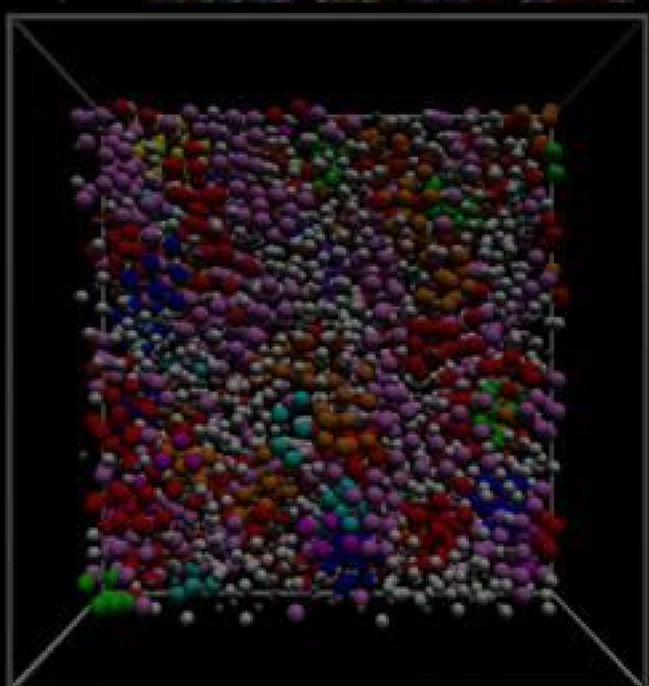
Crystallisation in 'hard spheres'

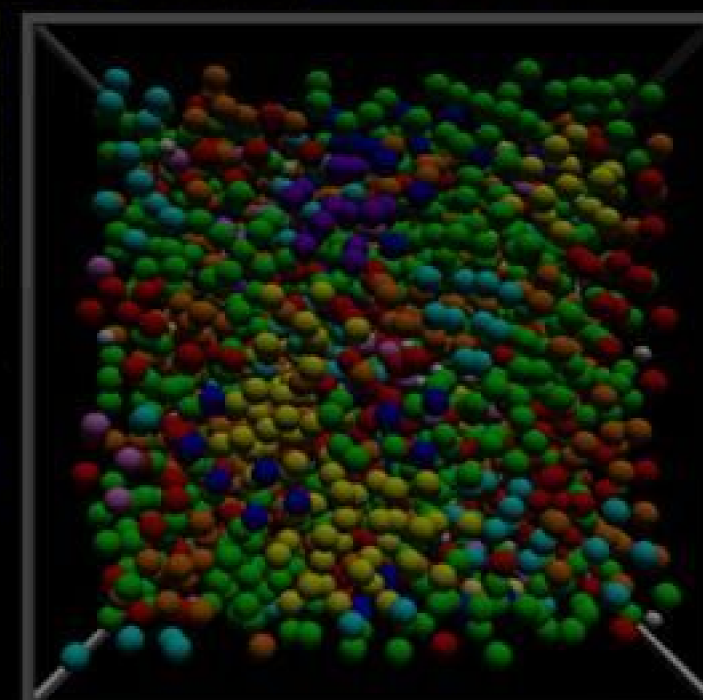
Much slower than HS 'spinodal' crystallisation - but like silica

τ_X ~ indep of ϕ : non-classical nucleation : nuclei small

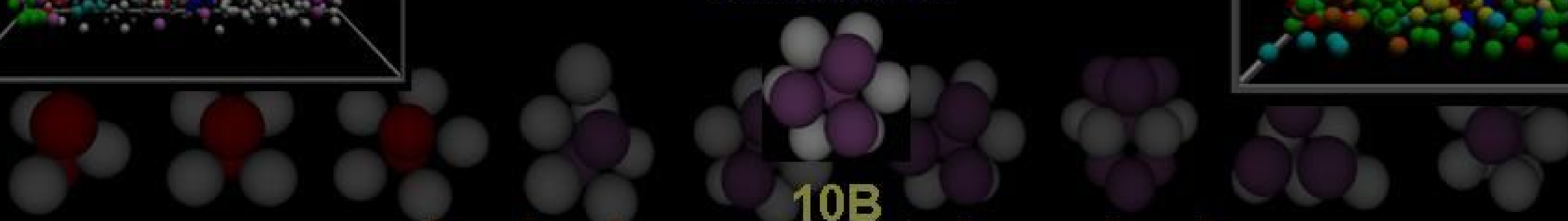
Semi-quantitative agreement between experiment and simulation although exp <1000 times bigger

Structural differences: 5, 6 and 8 membered clusters dominate exp





10 membered clusters dominate simulation



hard spheres are not always hard

and this can be important!

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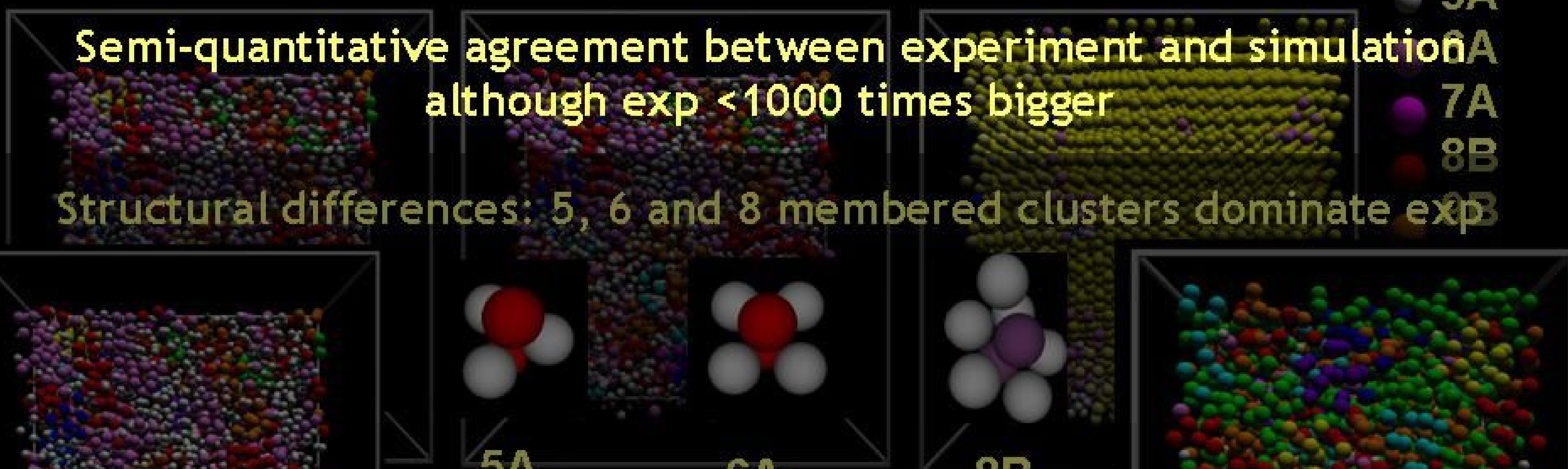

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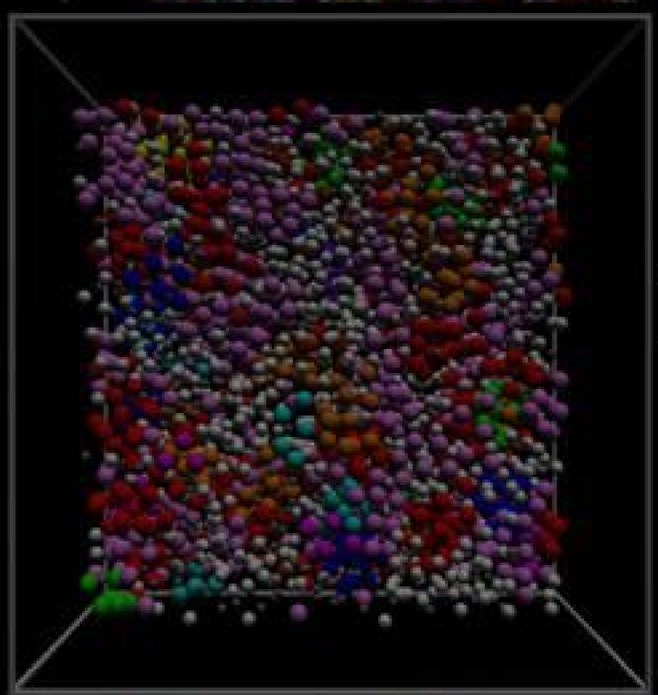

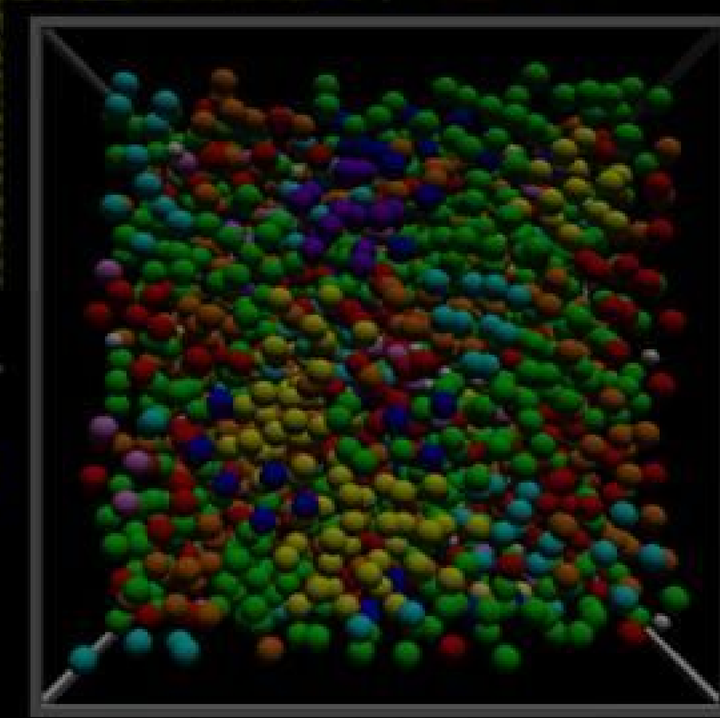

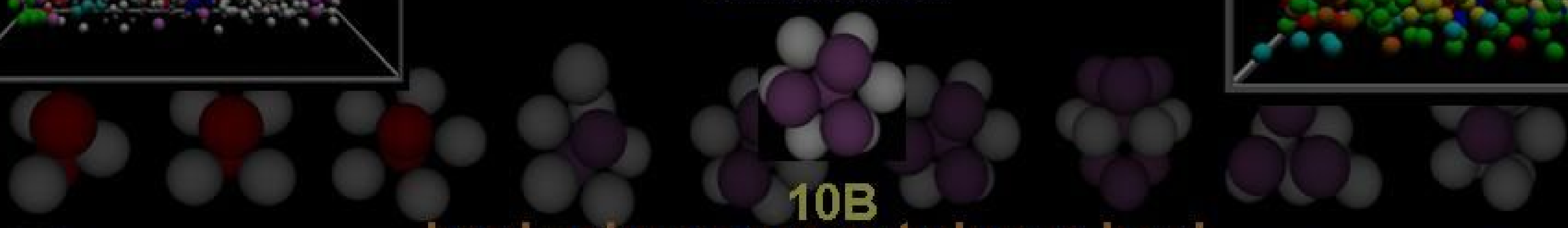

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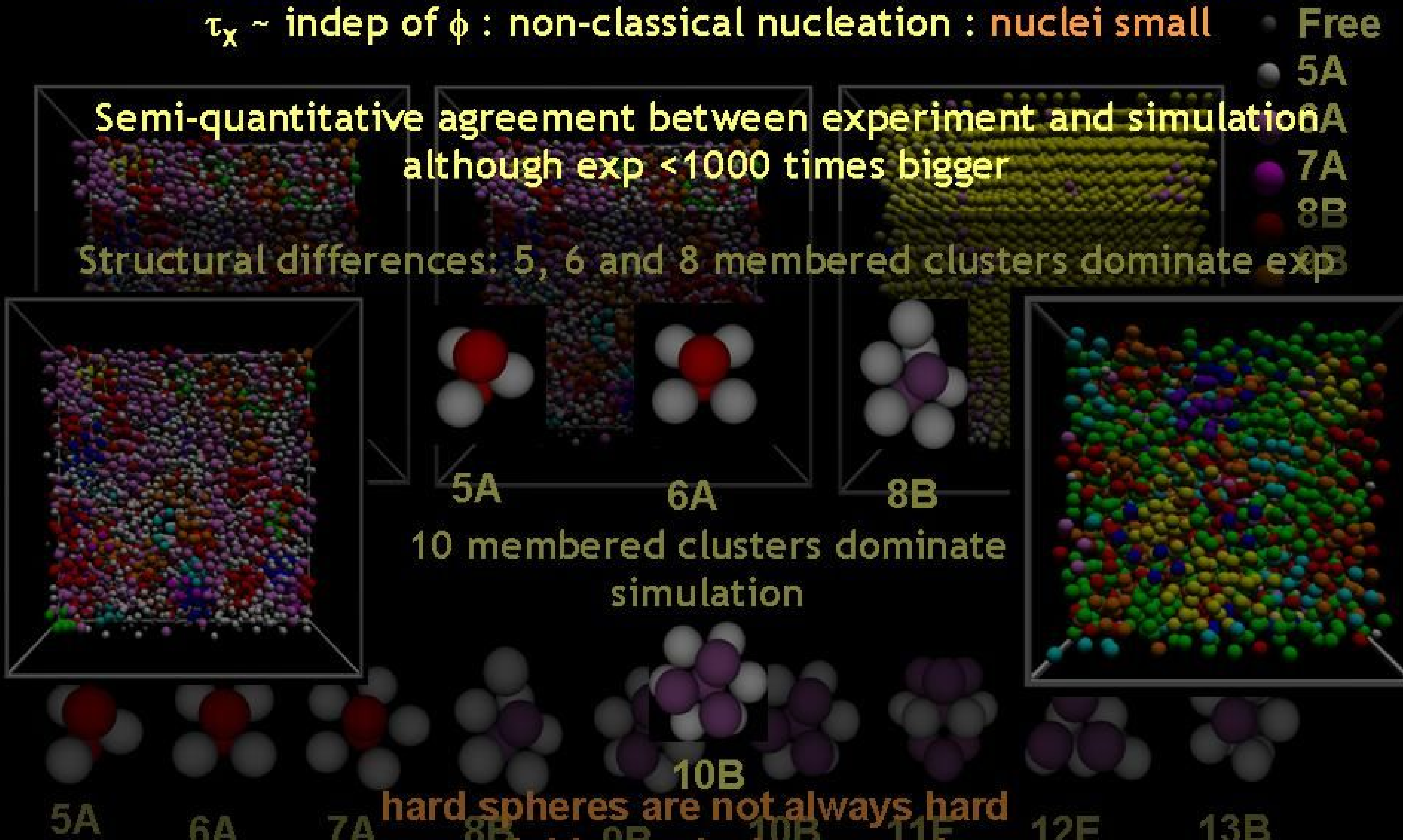

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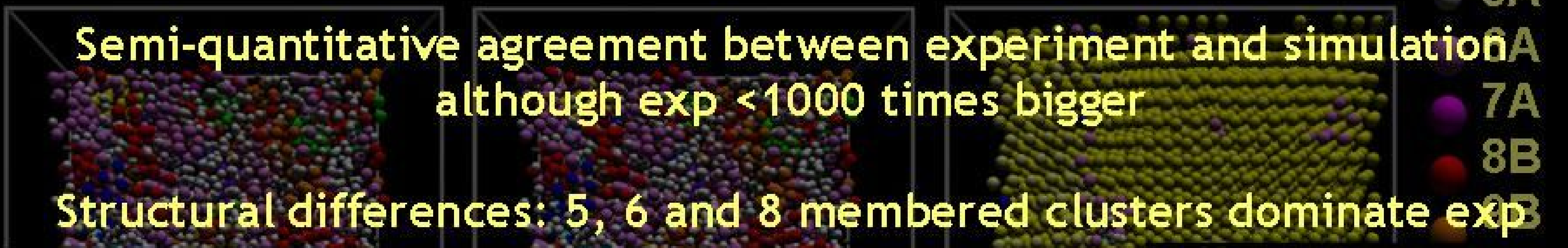

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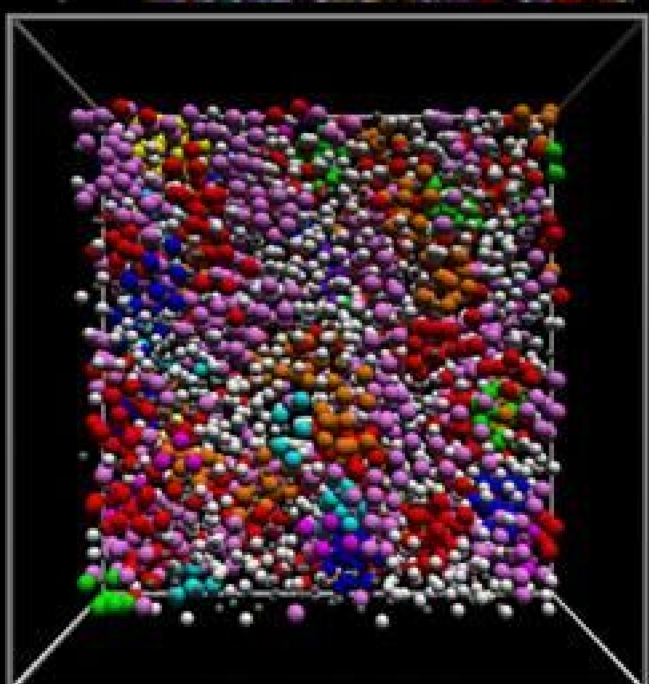
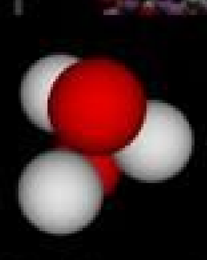
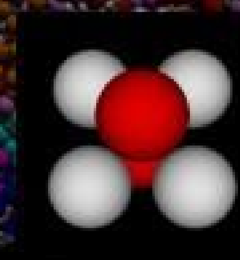
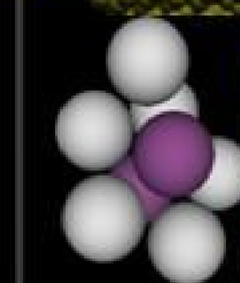
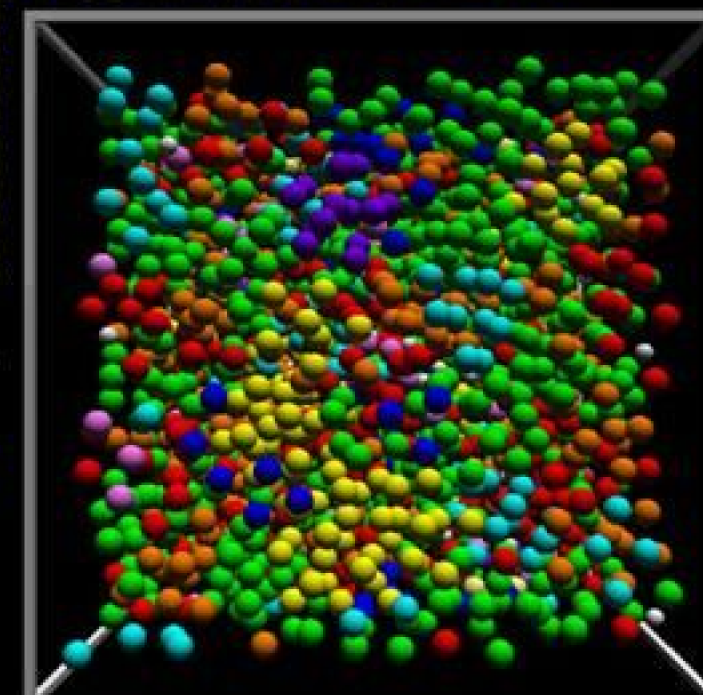



5A


6A


8B



10 membered clusters dominate simulation

10B

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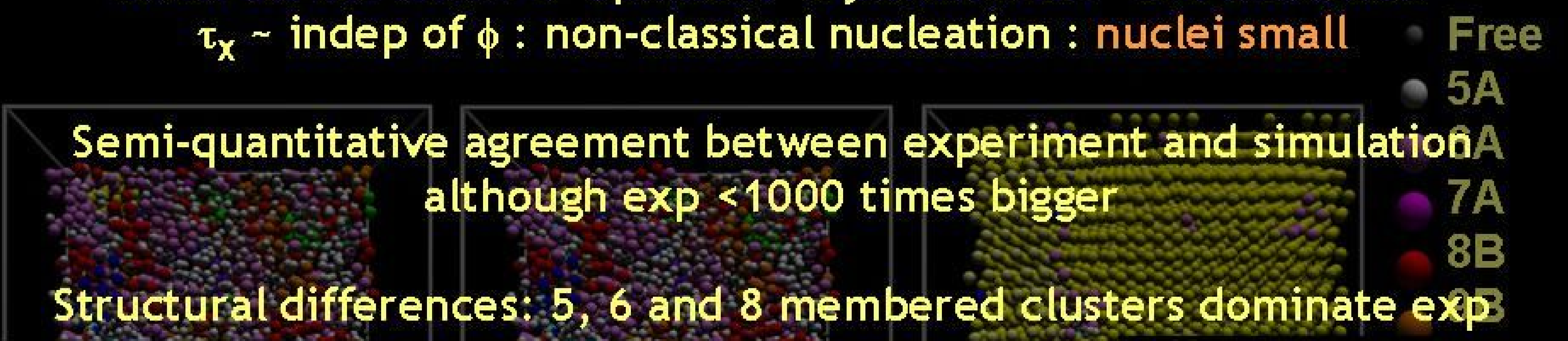

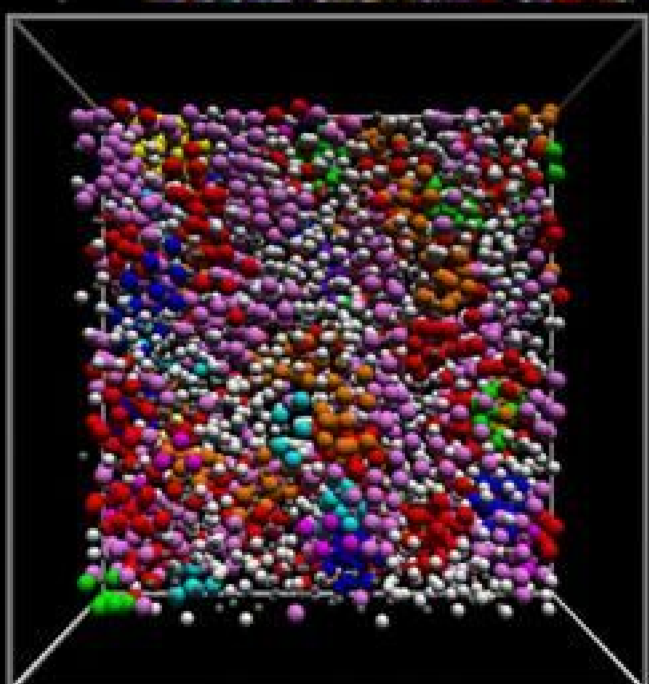

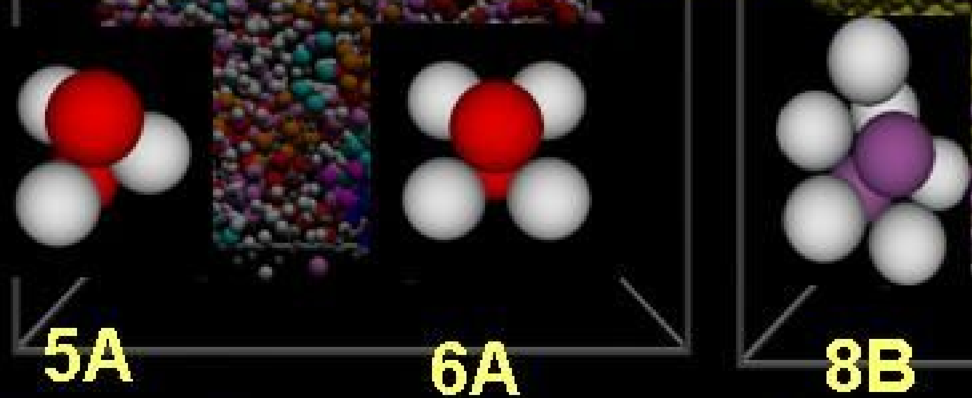

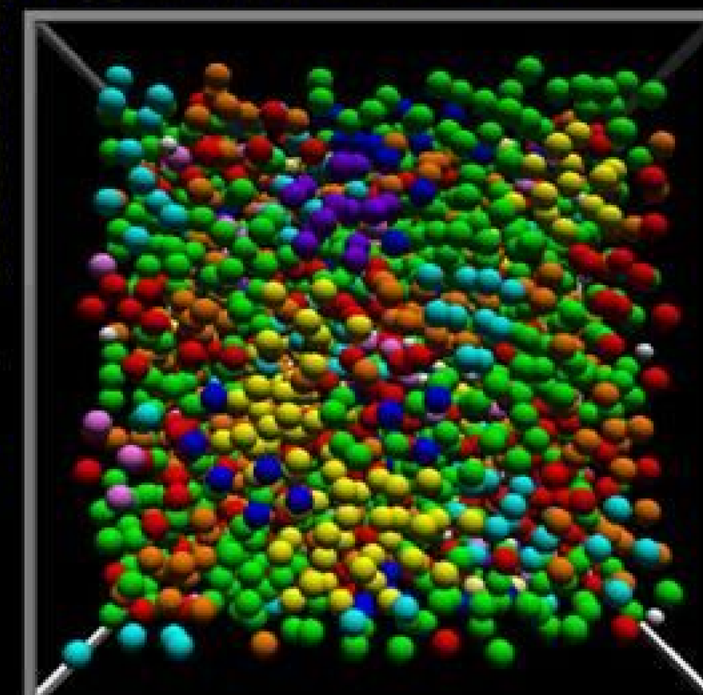

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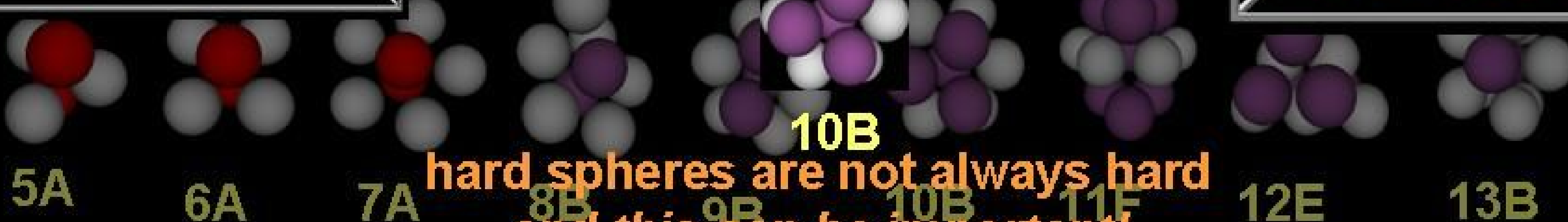

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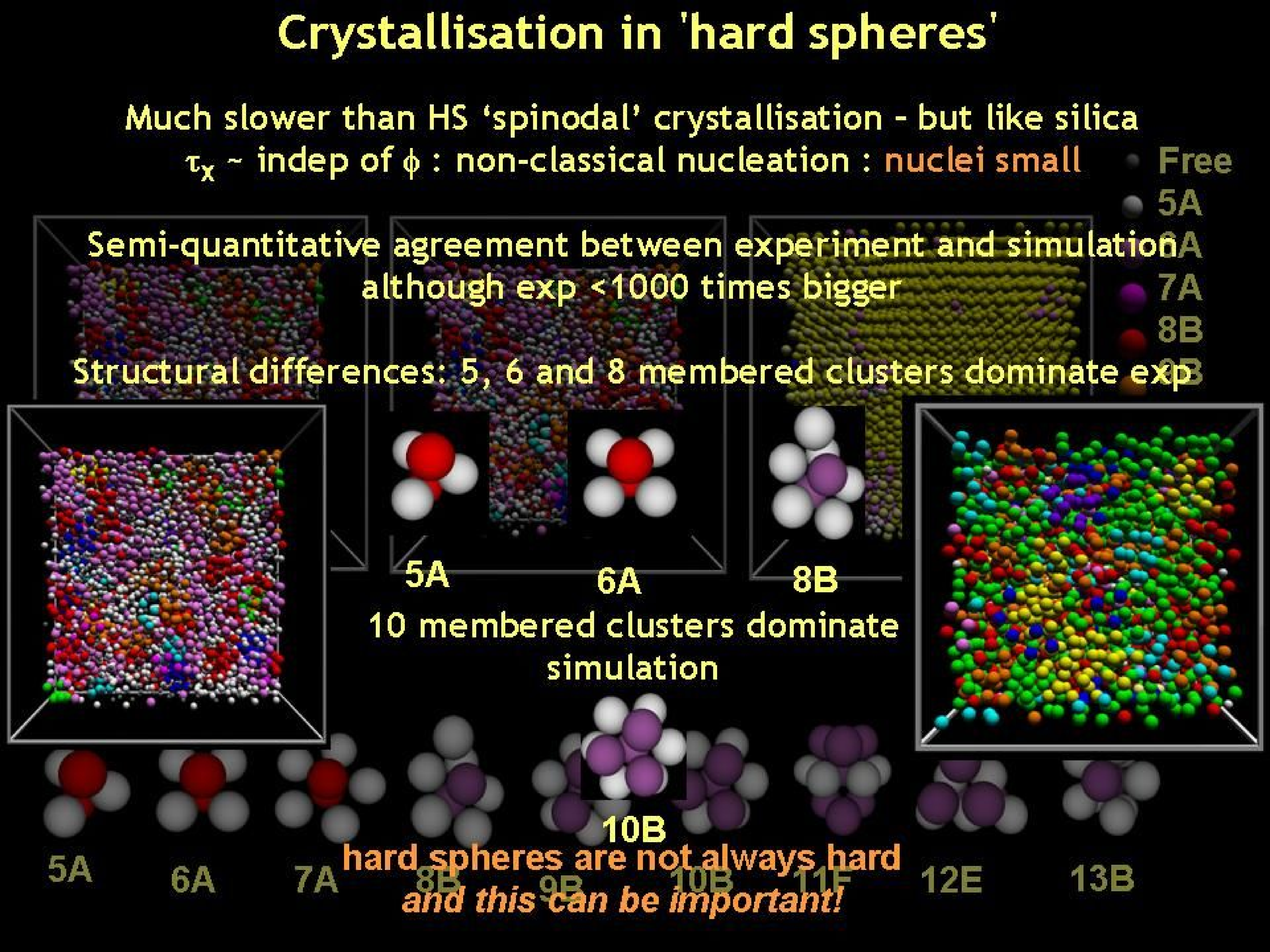
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5A
6A
8B
10 membered clusters dominate simulation
10B
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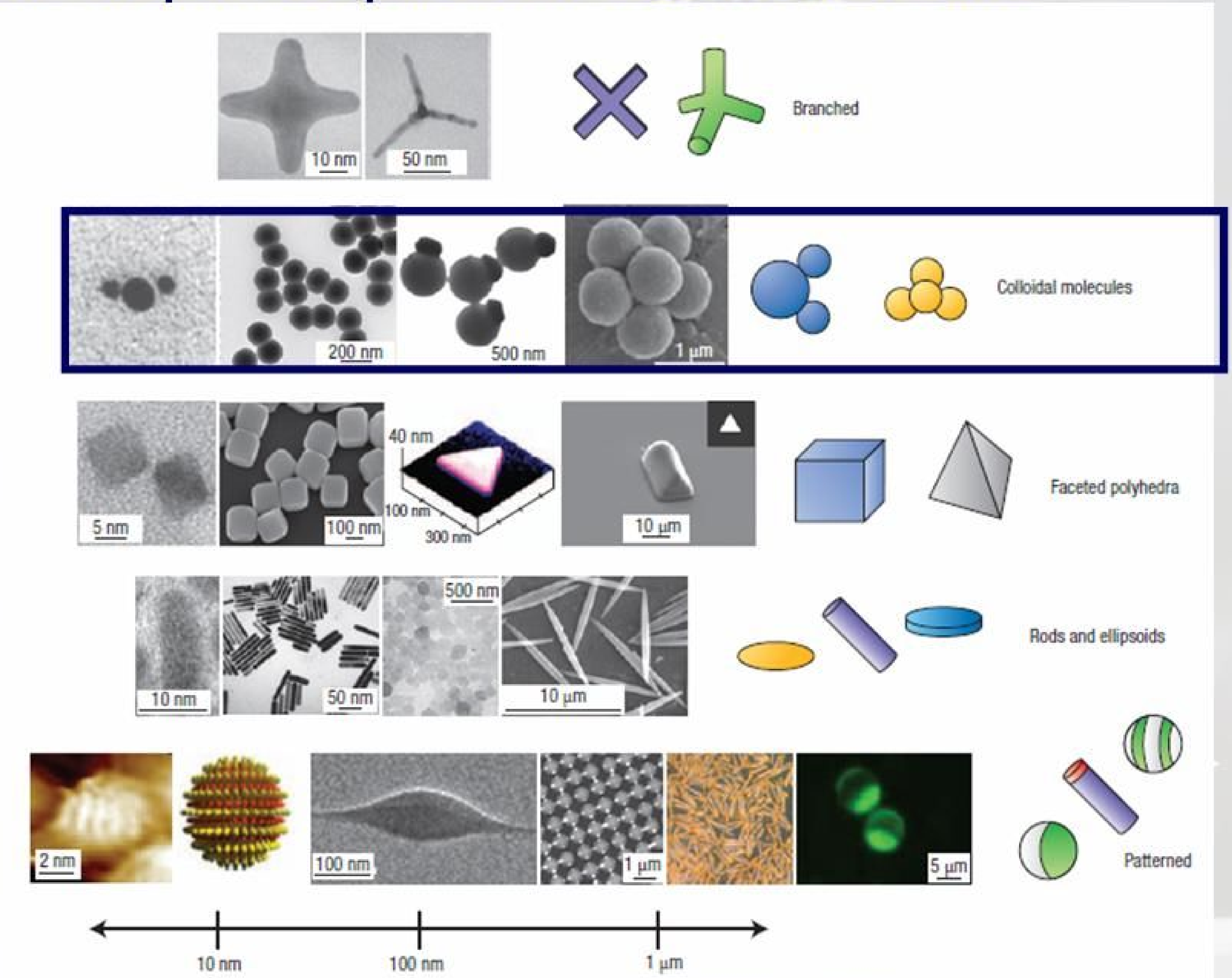
5A
6A
7A
8B
9B
10B
11F
12E
13B

The strange world of charging in apolar systems: a new way forward?

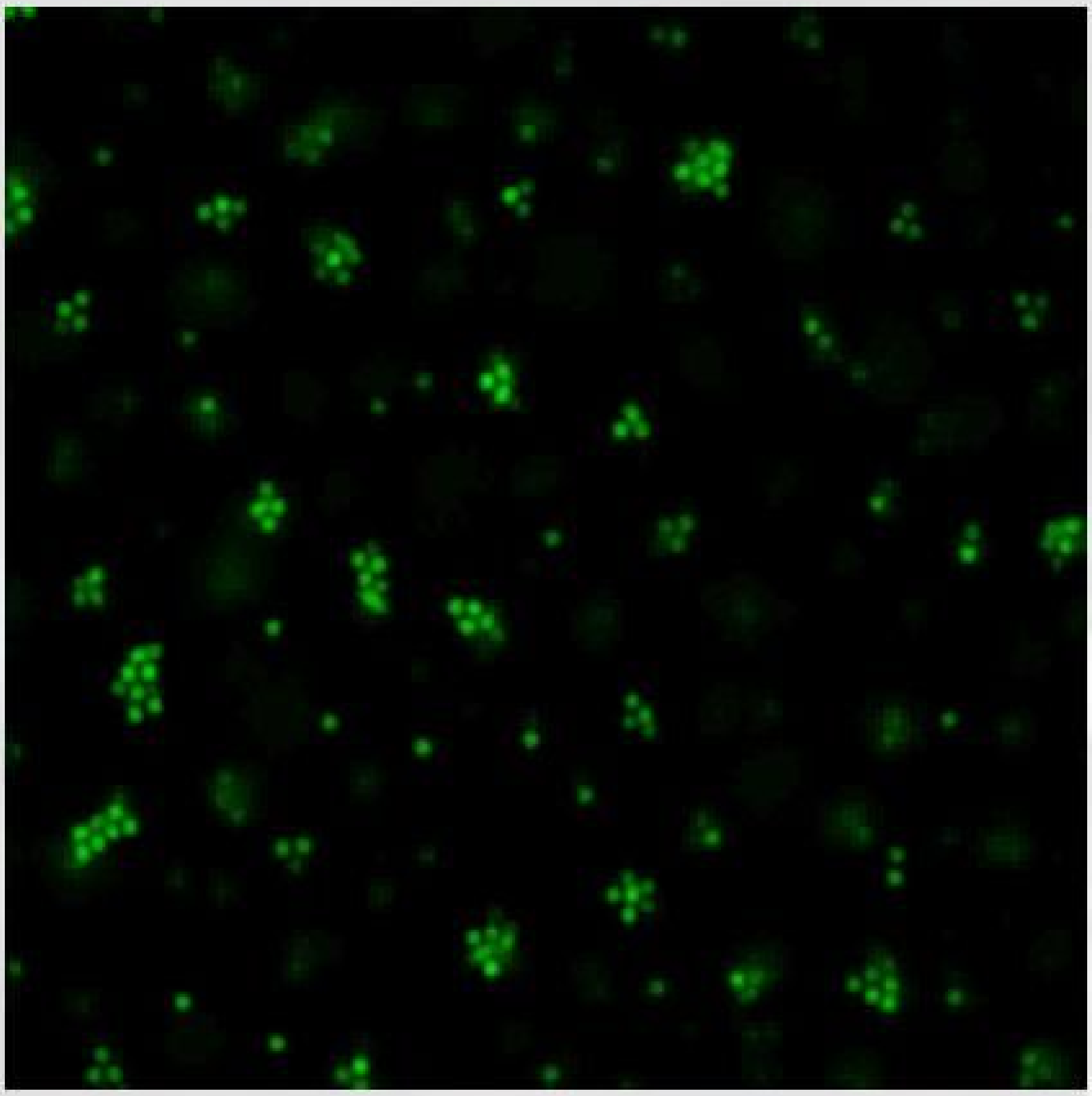
Clusters of spherical particles: colloidal molecules



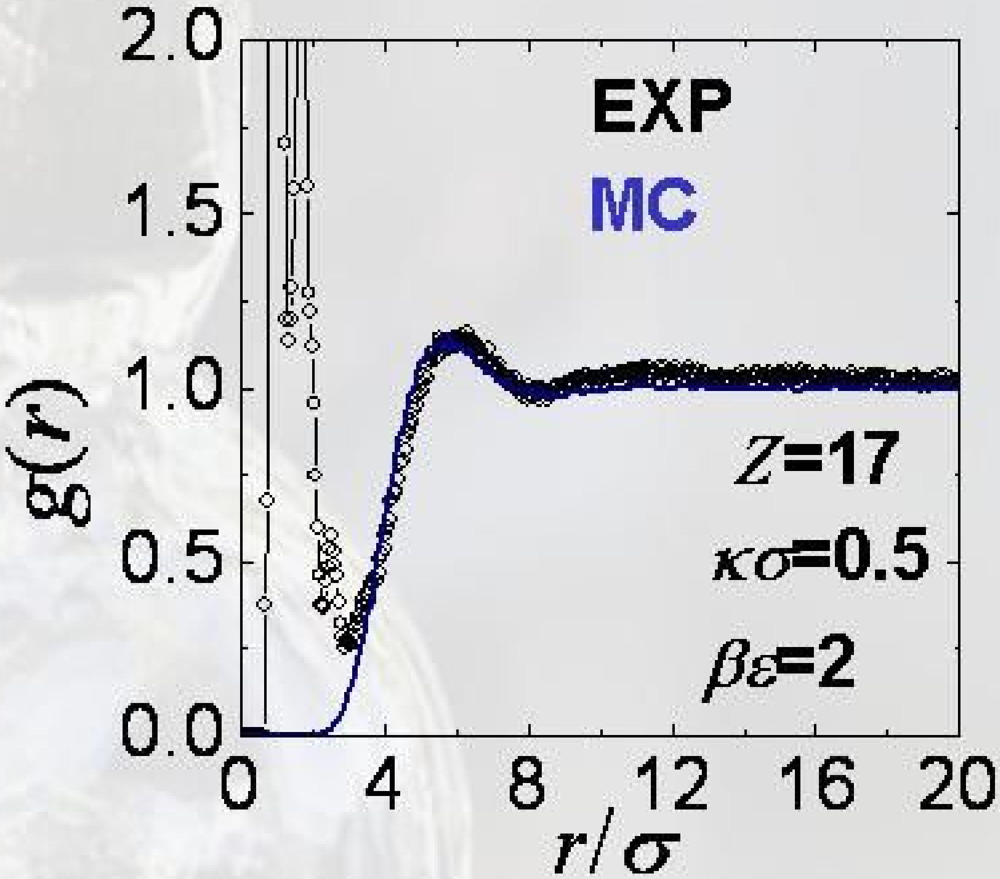
Glotzer and Solomon, *Nature Materials.* (2007)

Designing the system

Suppress aggregation/phase separation with electrostatics



Tune solvent dielectric constant : ε~2.9 : ultra-weak repulsion



Cluster-cluster correlations fit with MC simulation

colloid charge Z = cluster charge $Z_{\mathrm{CLUS}}/\langle m\rangle$ = 17

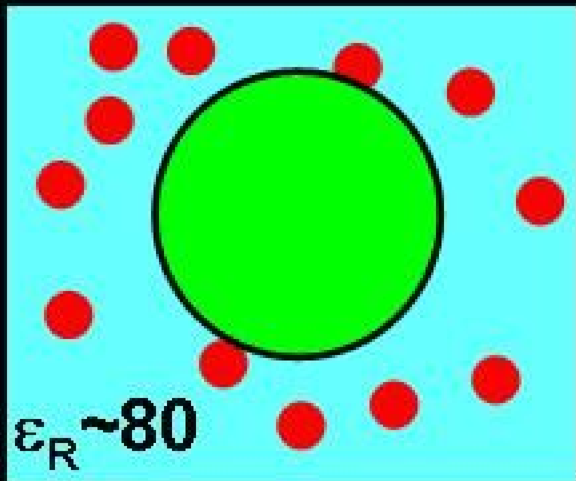
Sciortino et. al., *PRL*, 055701 (2004)

Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

Charging regimes

$$u_{Coul} = \frac{e^2}{4\pi\varepsilon_0\varepsilon_R d}$$

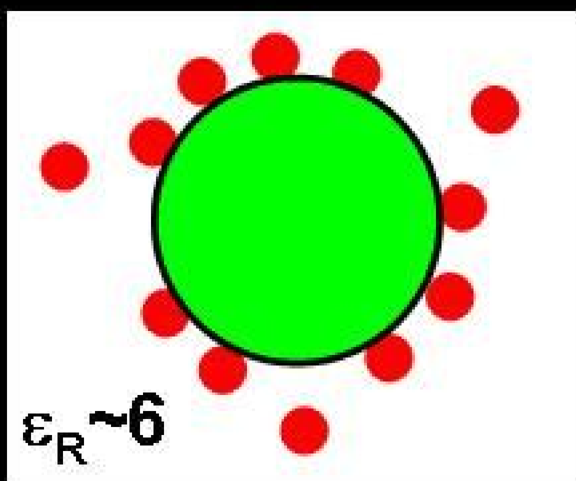
Typical ion size:d~ nm



water

u_{Coul}~kT:

strong charging



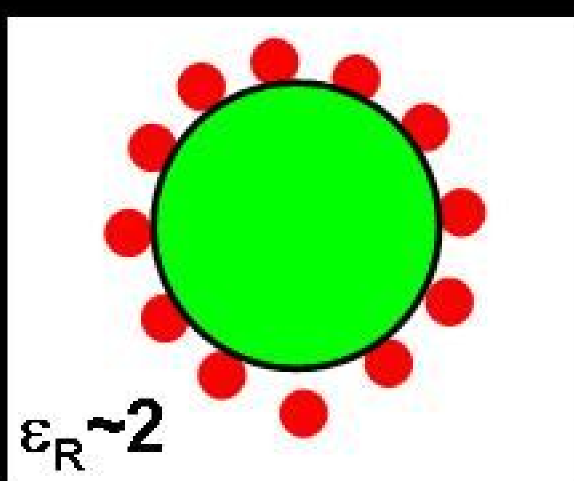
CHB-cis-decalin

u_{Coul}~10kT:

weak charging

Yethiraj and van Blaaderen Nature 2003

Phase behaviour strongly perturbed



TCE-cis-decalin

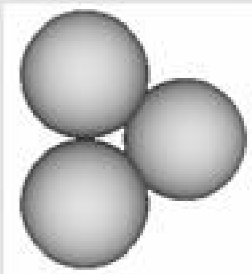
u_{Coul}~40kT:

ultra-weak charging

(same ε_R as Pusey and van Megen Nature 1986)

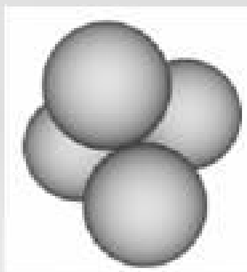
What clusters will this system form?

m=3



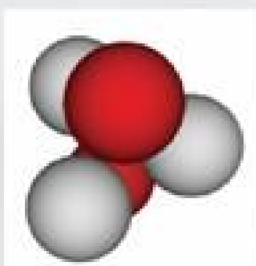
3A triangle

m=4



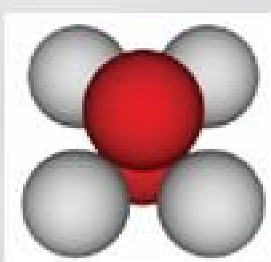
4A tetrahedron

m=5



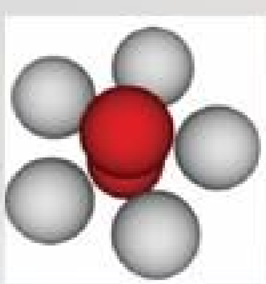
5A triangular bypyramid

m=6

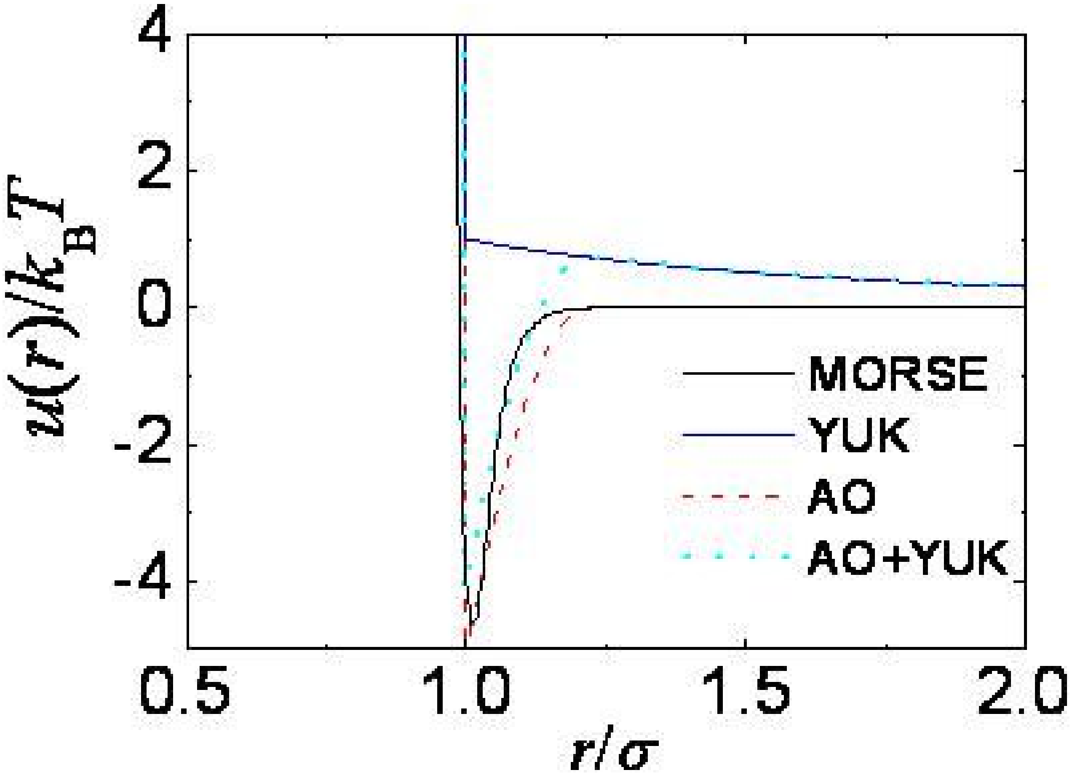


6A octahedron

m=7



7A pentagonal bipyramid



$$V_{\mathrm{M}} = \epsilon \sum_{i<j} e^{\beta(r_0 - r_{ij})}\left(e^{\beta(r_0 - r_{ij})} - 2\right)$$

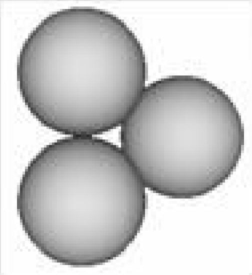
$$\equiv \sum_{i<j} e^{\rho_0(1 - r'_{ij})}\left(e^{\rho_0(1 - r'_{ij})} - 2\right),$$

Mossa et.al. *Langmuir* 20 10756 (2004)

Doye *et. al.*, *JCP*, 103 4234 (1995)

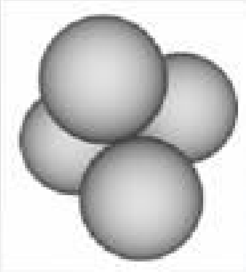
What clusters will this system form?

m=3



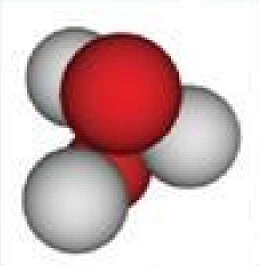
3A triangle

m=4



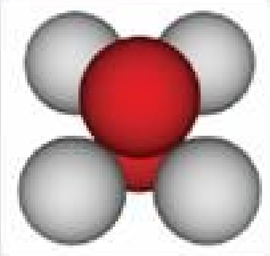
4A tetrahedron

m=5

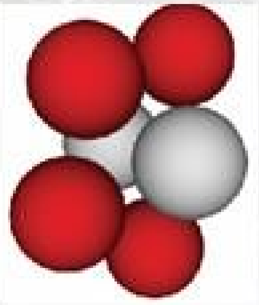


5A triangular bypyramid

m=6

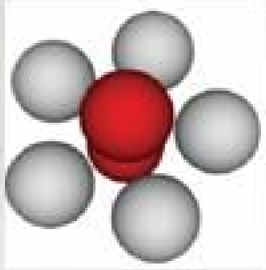


6A octahedron

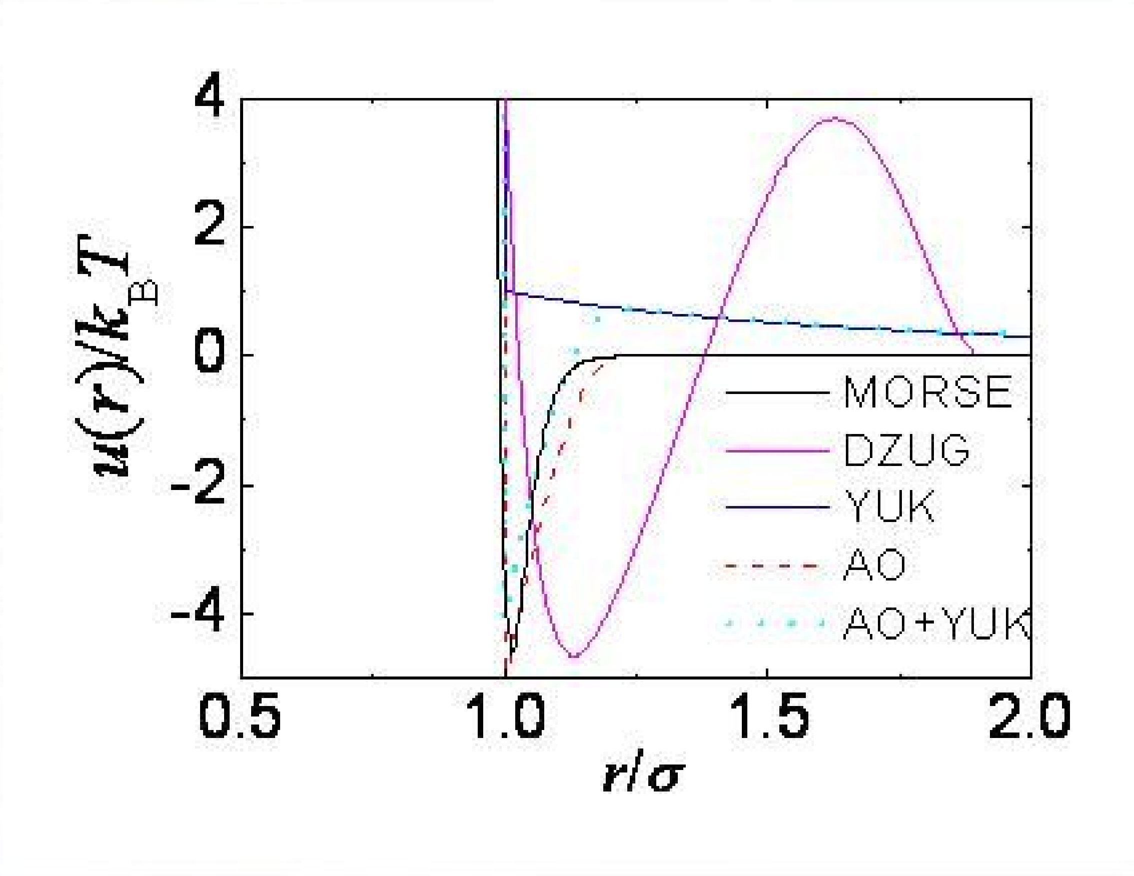


6Z

m=7



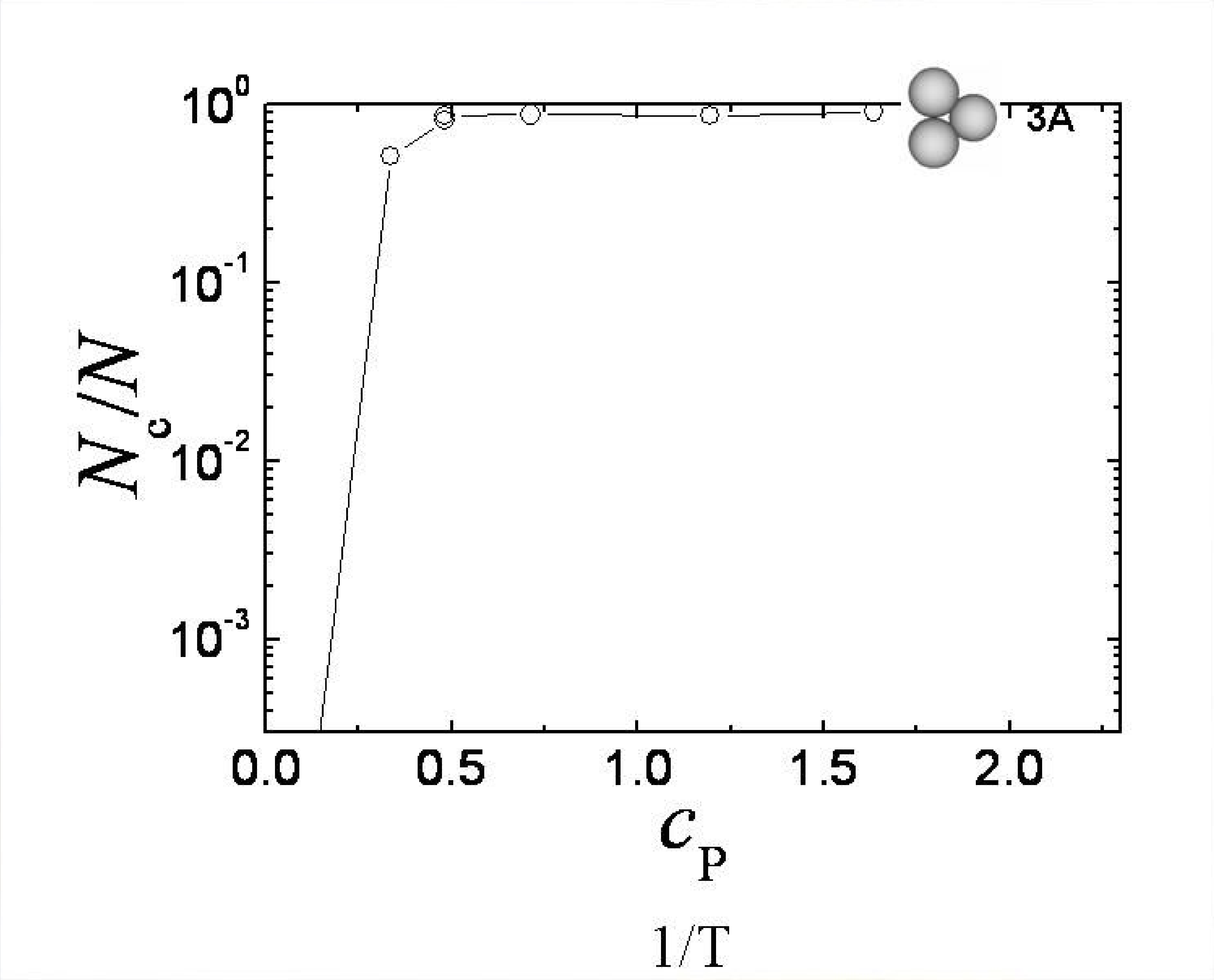
7A pentagonal bipyramid



Mossa et.al.Langmuir 20 10756 (2004)

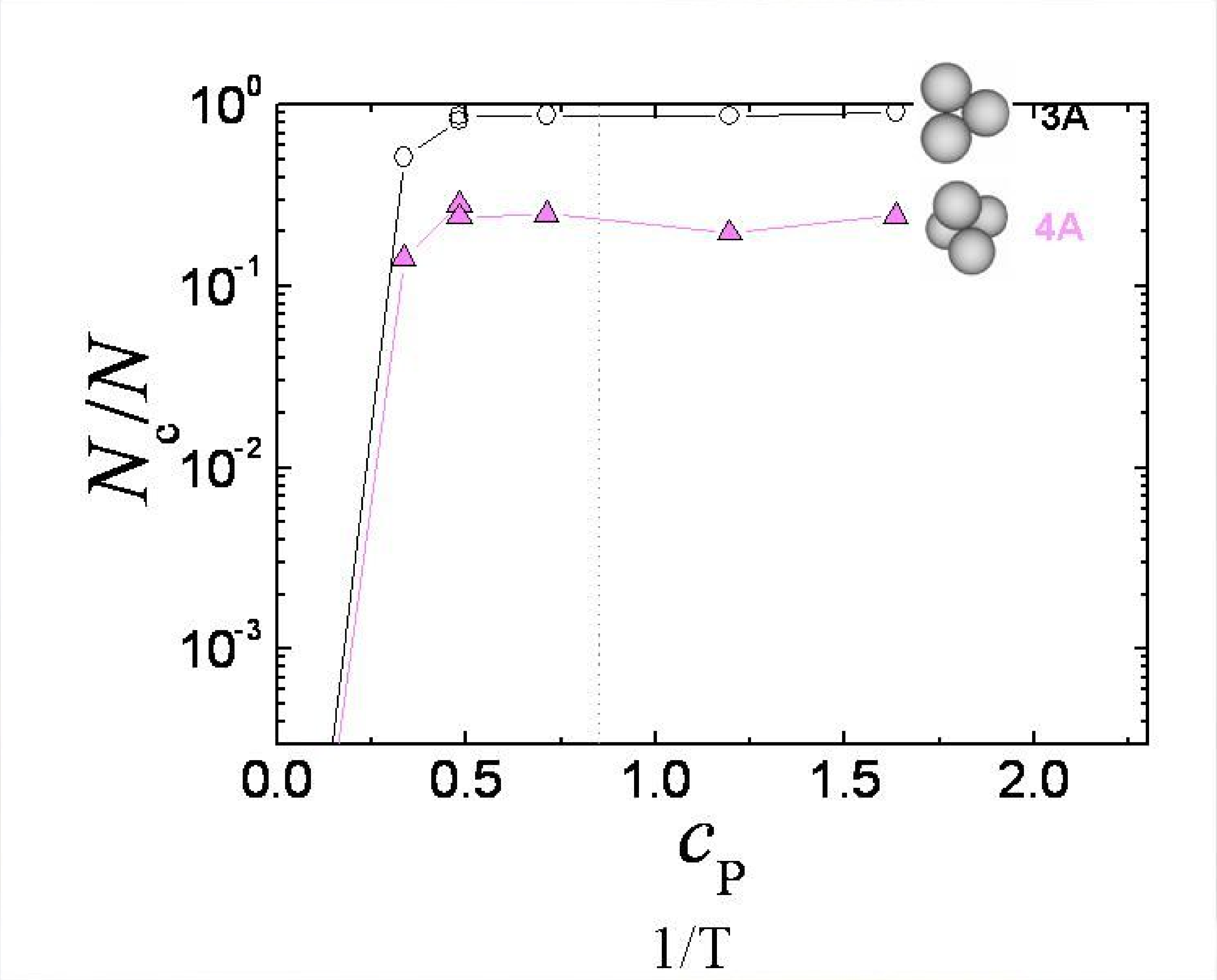
Doye *et. al.*, *JCP*, 103 4234 (1995)

What happens?



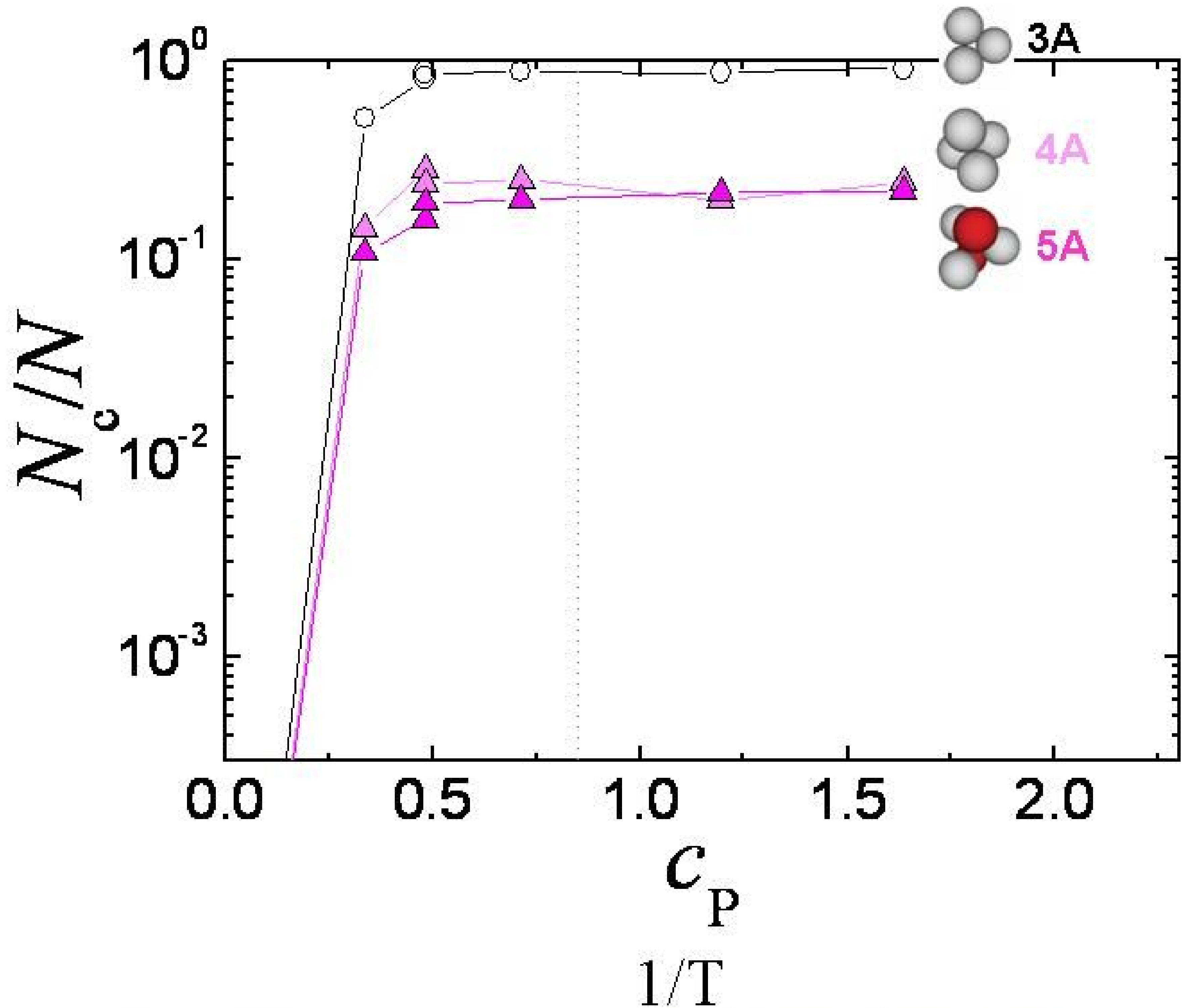
Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

What happens?



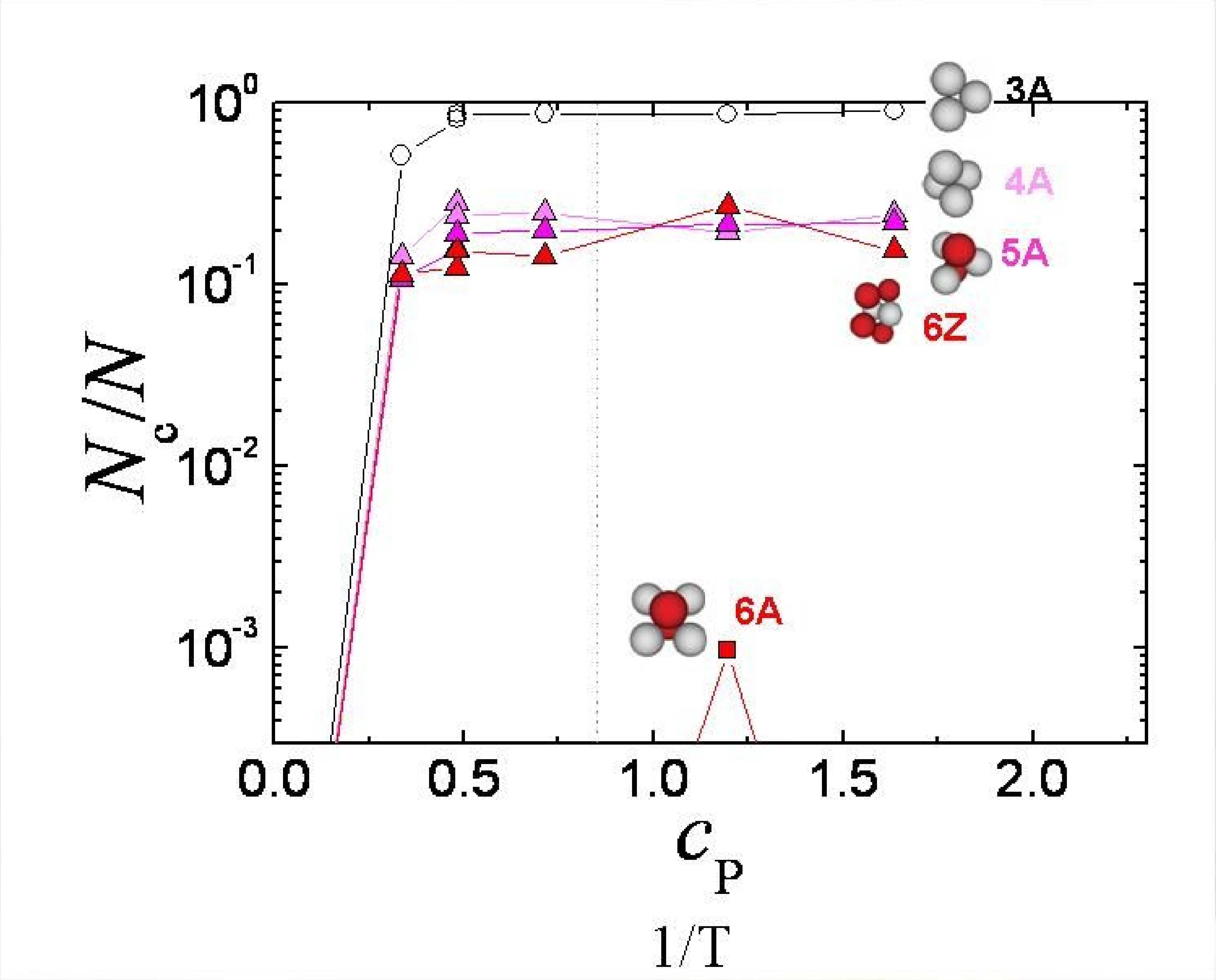
Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

What happens?



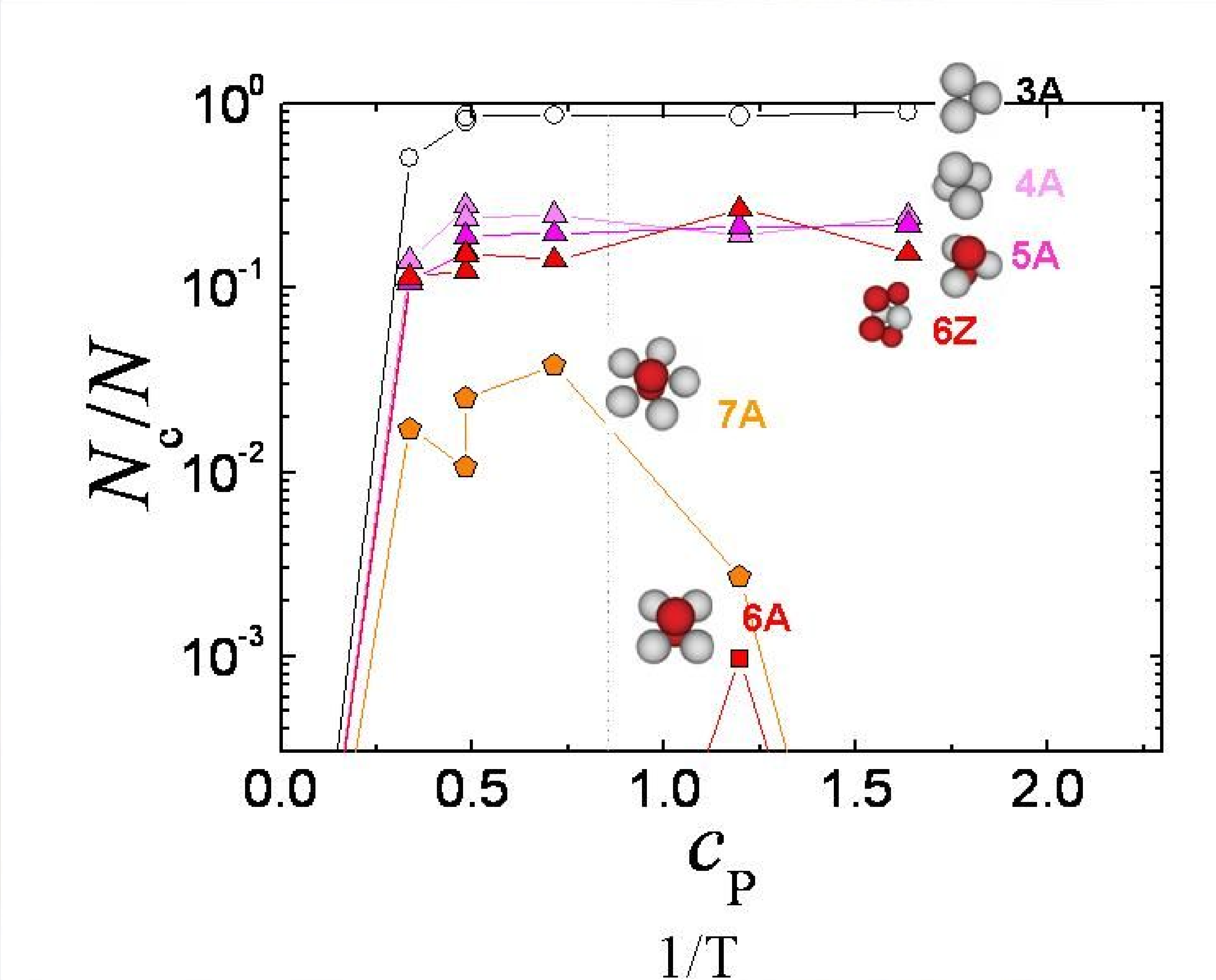
Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

What happens?



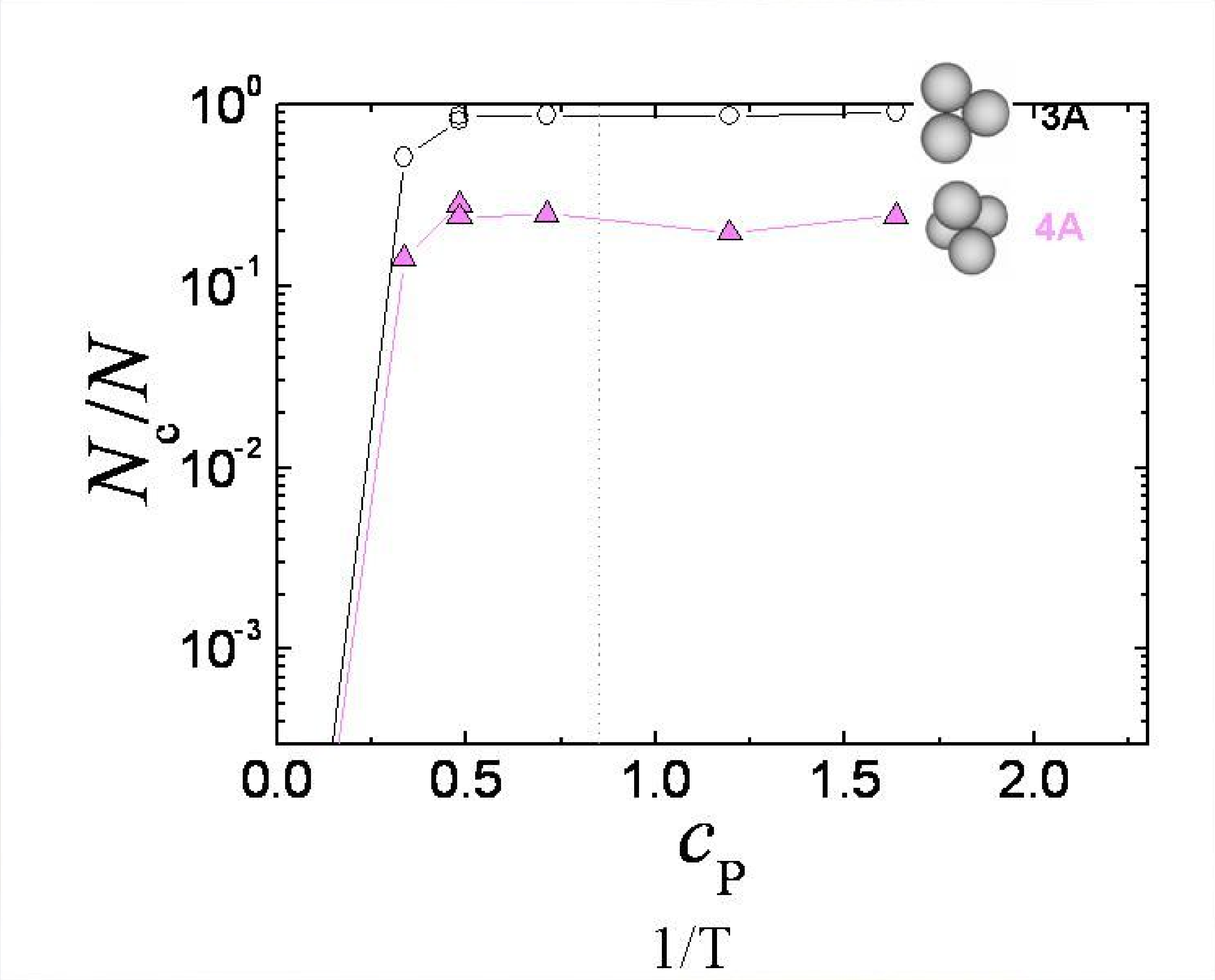
Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

What happens?



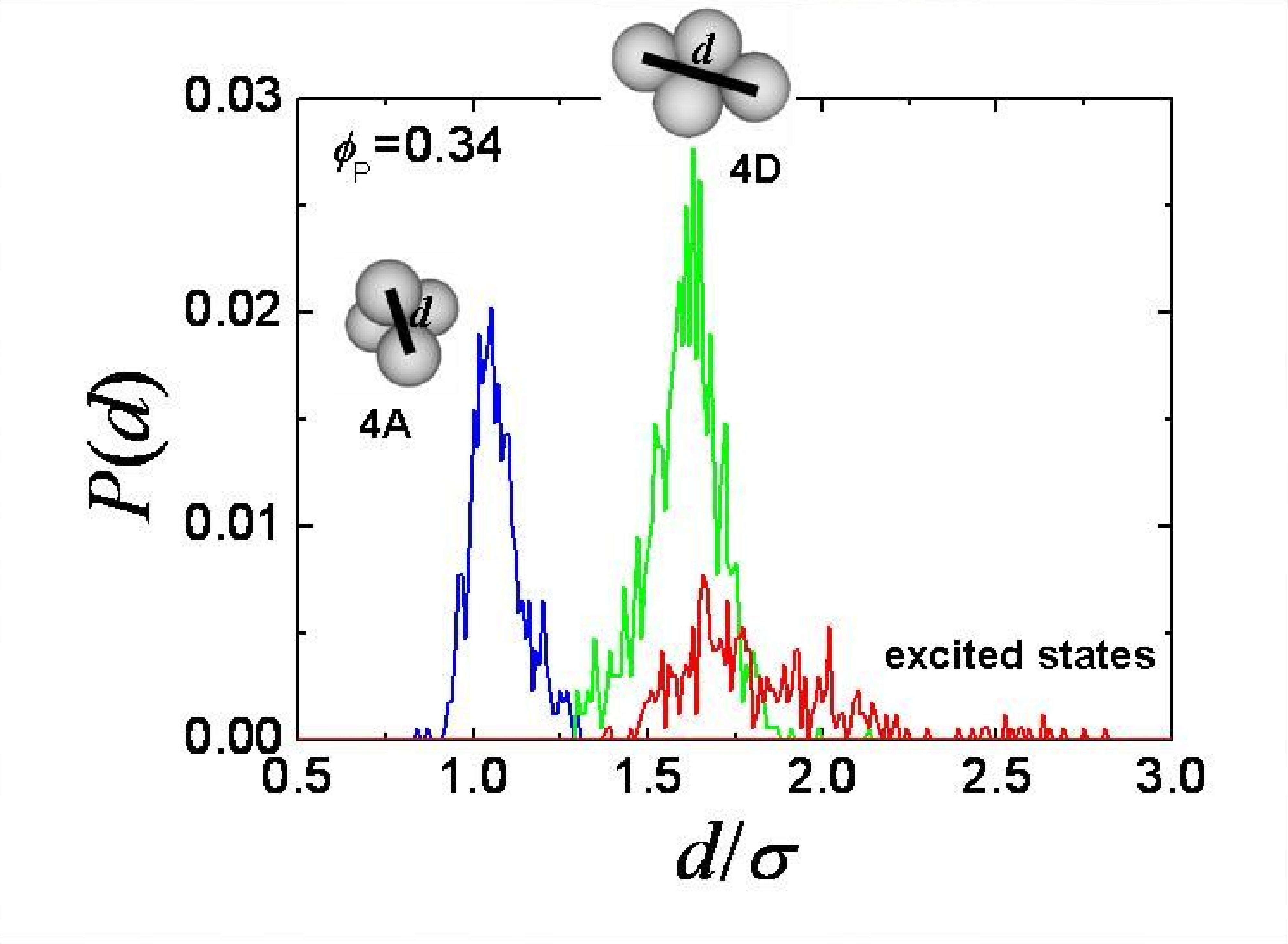
Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

A closer look at m=4



Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

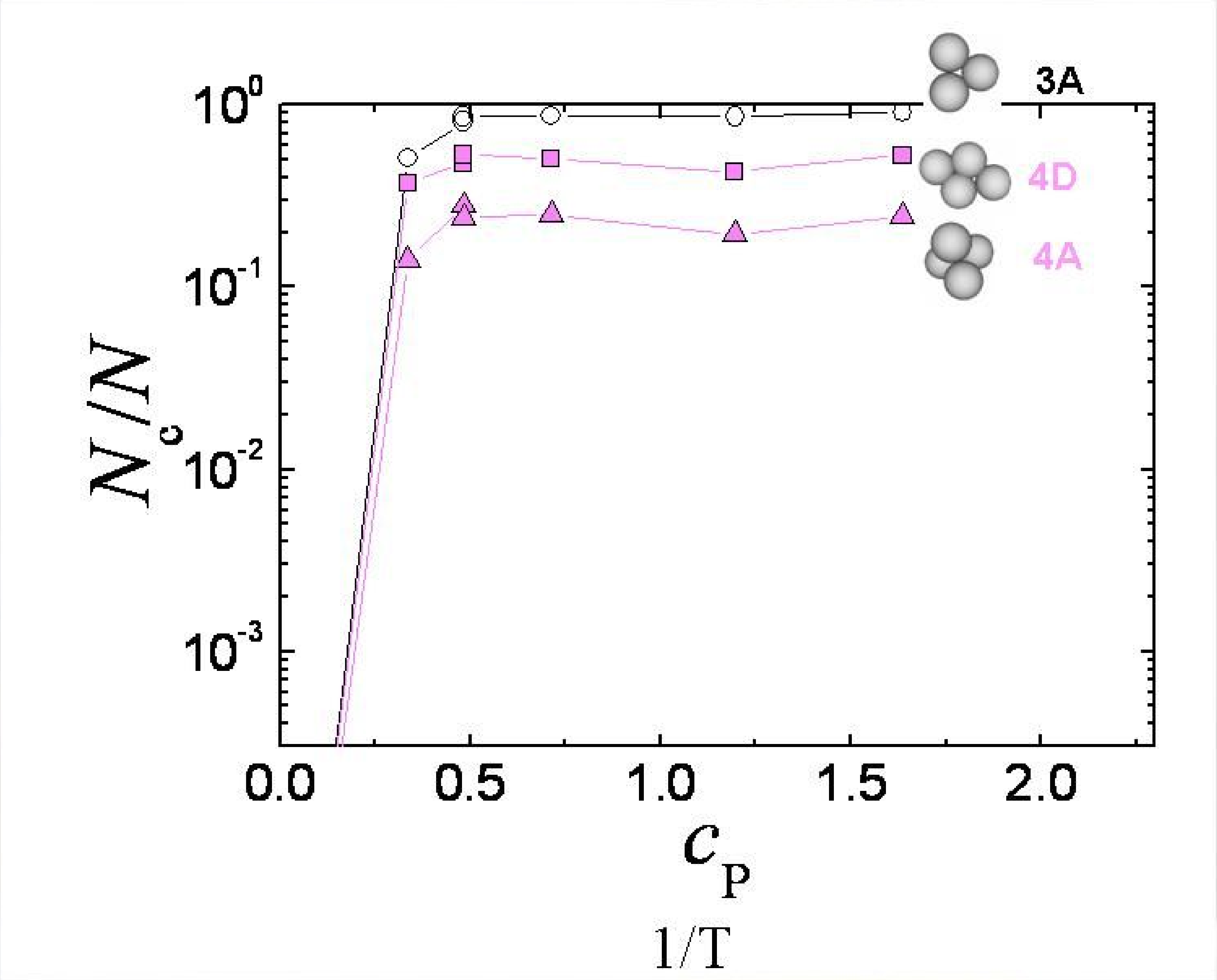
What happens for m=4?



order parameter d max centre-centre separation $\sigma<d<3\sigma$

Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

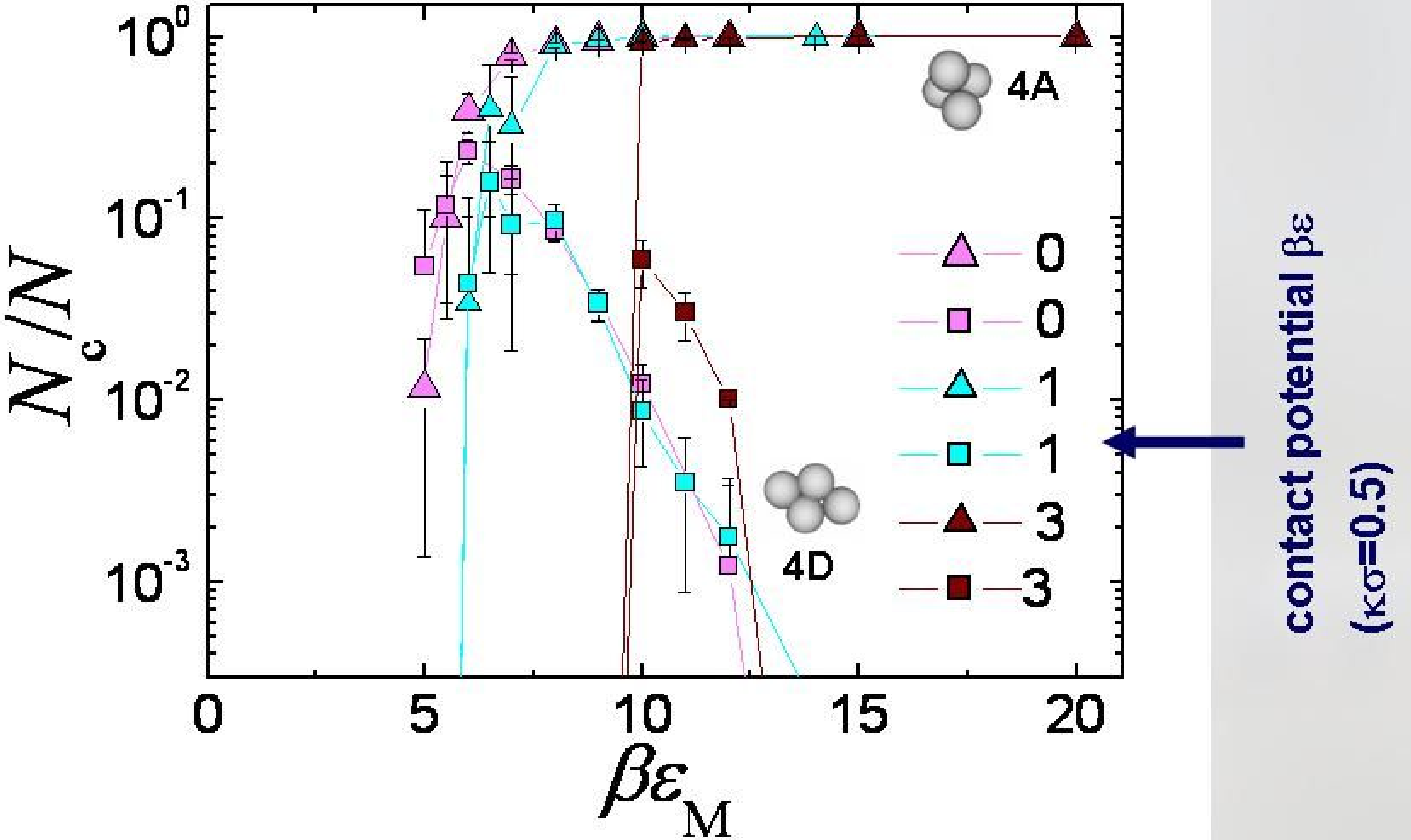
How popular is 4D?



Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

Reality check: Brownian dynamics

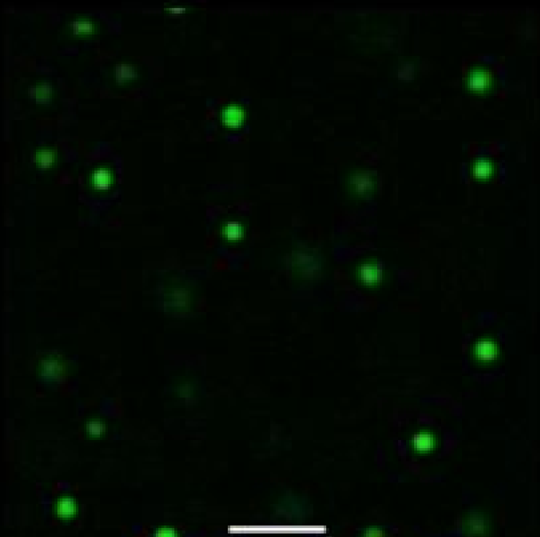
Discrepancy with experiment: spherically symmetric description breaks down



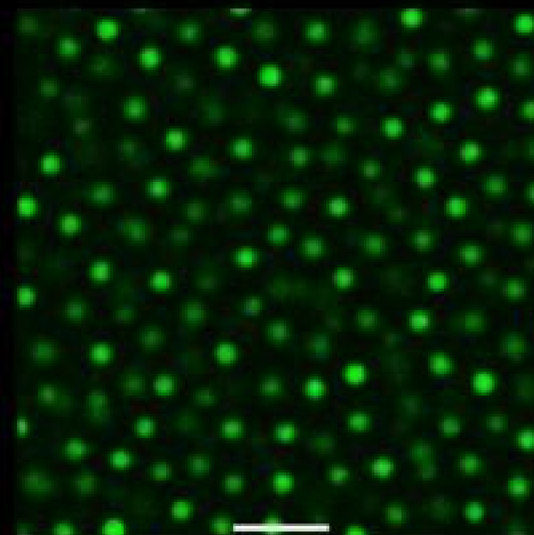
Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

A brief foray into the weak charging regime (ε_r~6)

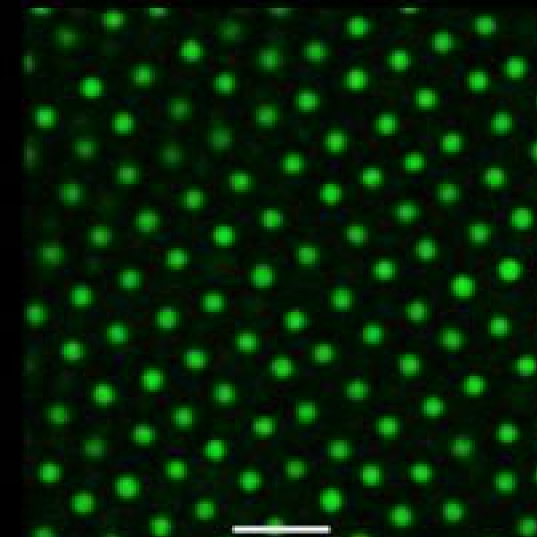
PMMA in CHB-cis decalin



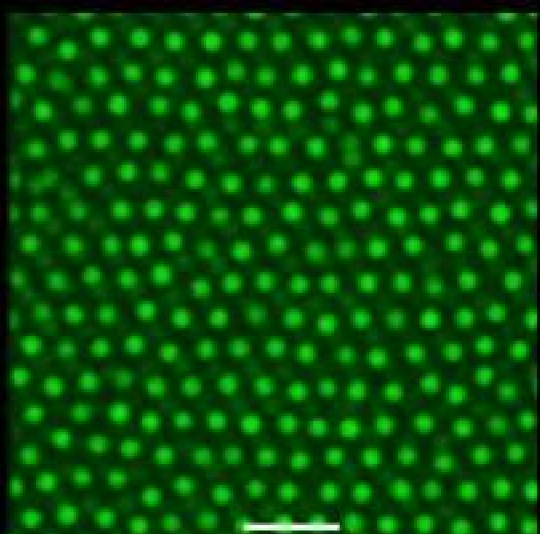
ϕ=0.0037



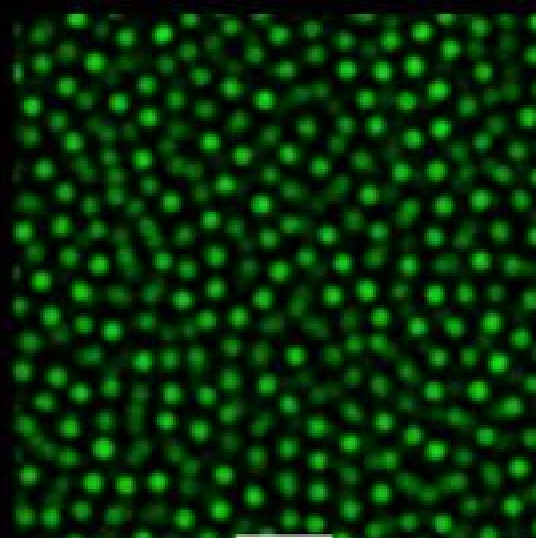
ϕ=0.041



ϕ=0.042
BCC

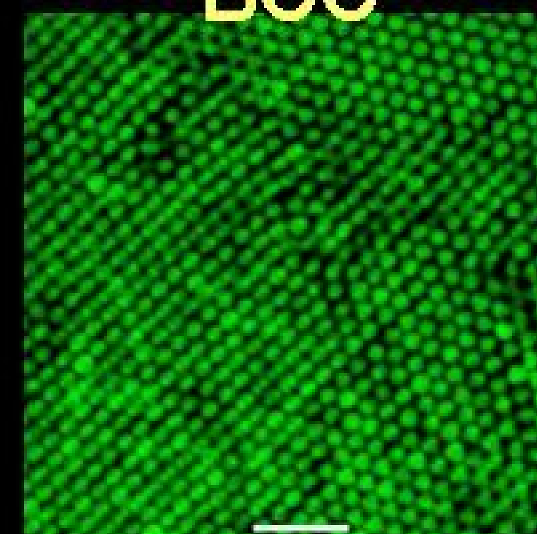


ϕ=0.115



ϕ=0.118

re-entrant fluid

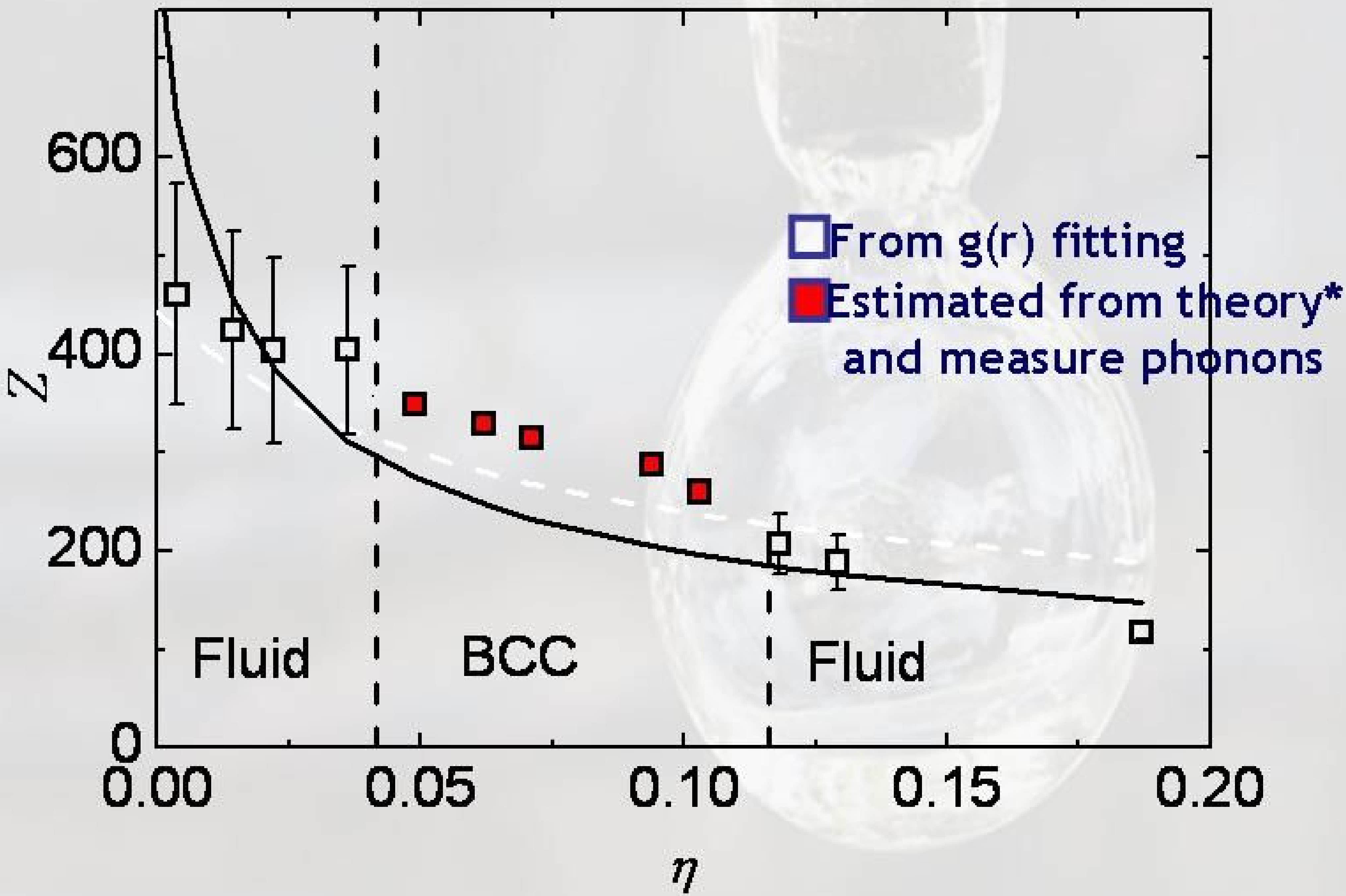


ϕ=0.5
FCC

Bars=10 μm

CPR et al, *J. Chem. Phys.* 124 1 (2006)

Falling colloid charge with ϕ

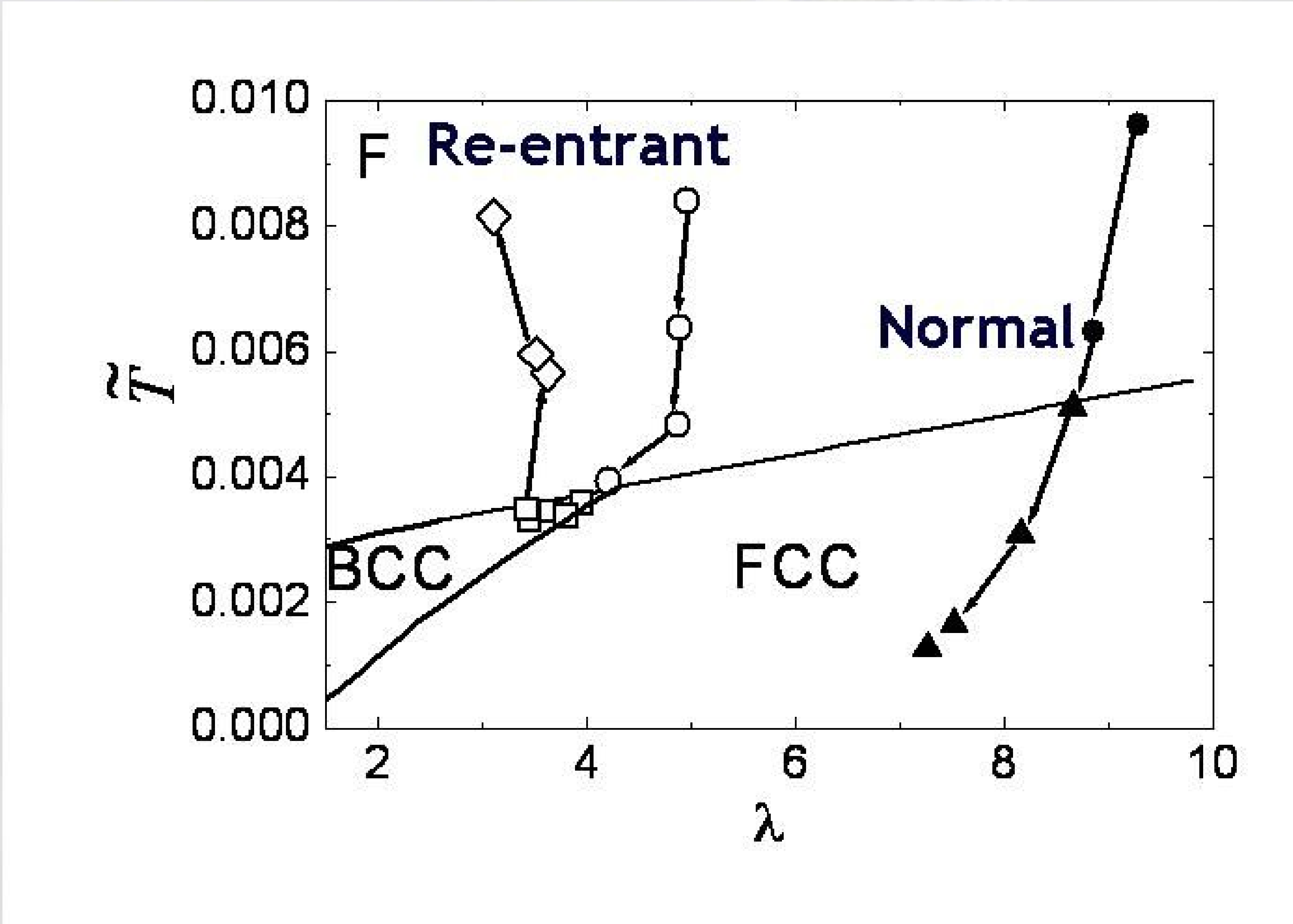


*Hamaguchi *Phys Rev E* 56, 4671, (1997)

CPR et al, *J. Chem. Phys.* 124 1 (2006)

Yukawa phase diagram

colloid charge Z~500 spherically symmetric Yukawa works



$$\tilde{T}_0 = \left[\frac{2}{3}\lambda^2 \beta u_M(\lambda)\right]^{-1}$$

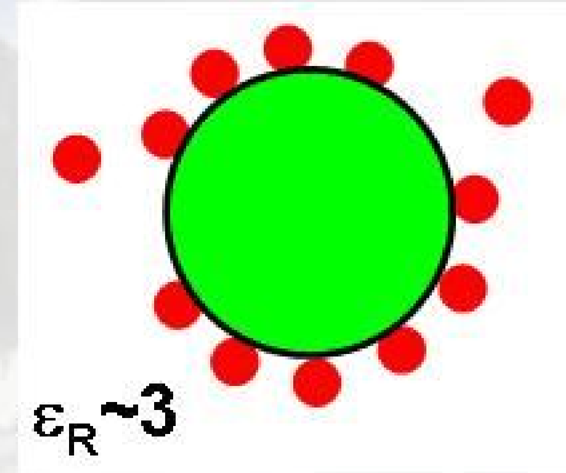
$$\lambda = \kappa\sigma(6\phi/\pi)^{-1/3}$$

u_M Madelung energy of ground state FCC CPR et al, *J. Chem. Phys.* 124 1 (2006)

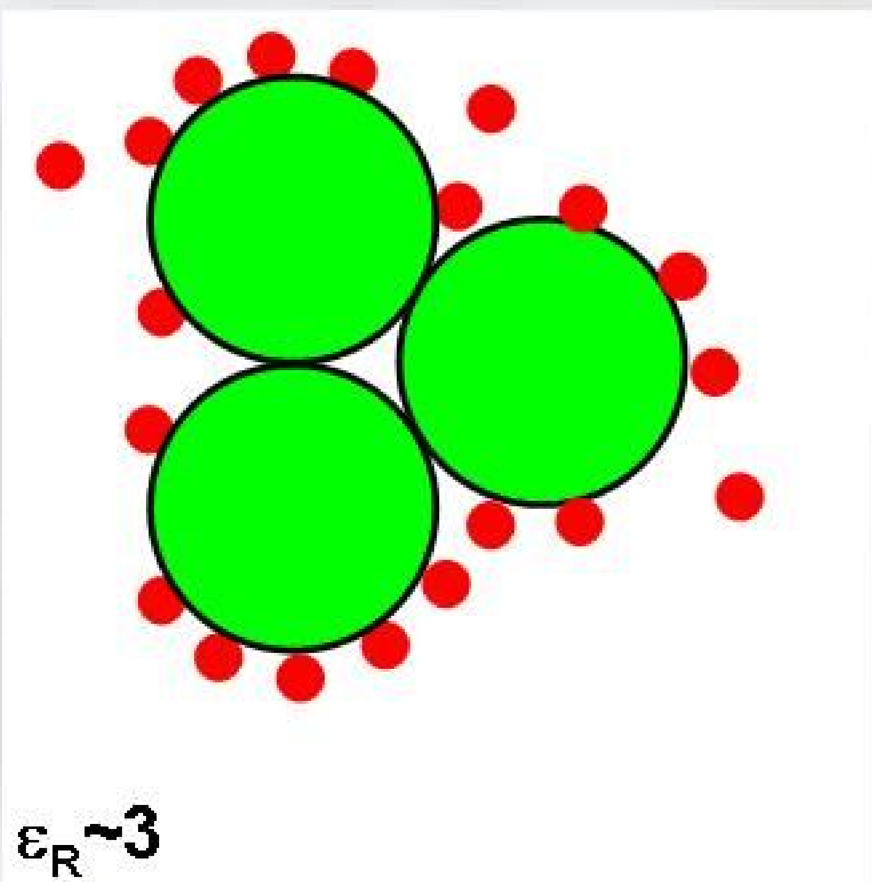
Back to ultra-weak charging (ε_r~2-3)

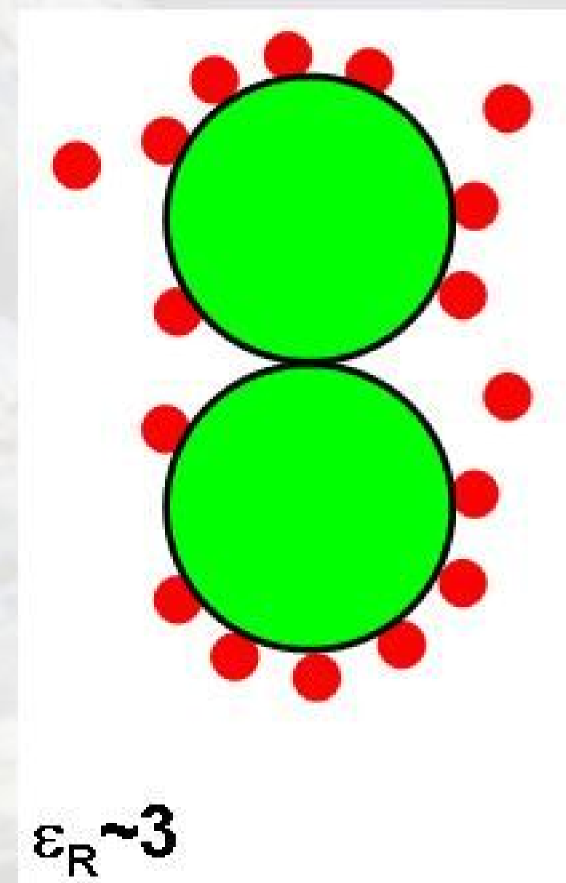
What does this mean for clusters?

Z falls with ϕ: effect of neighbouring colloids



what about clustering?
clustering->neighbours at contract



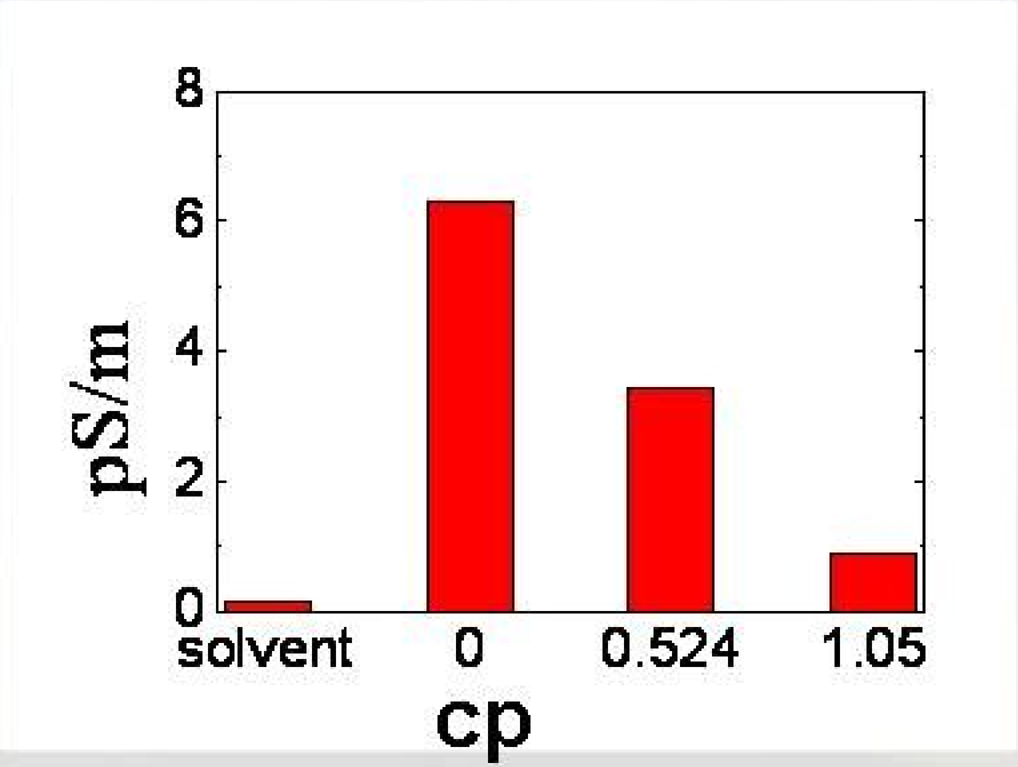


Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

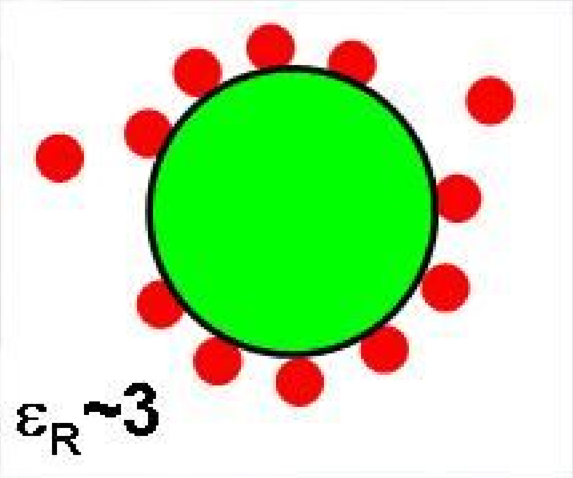
What does this mean for clusters?

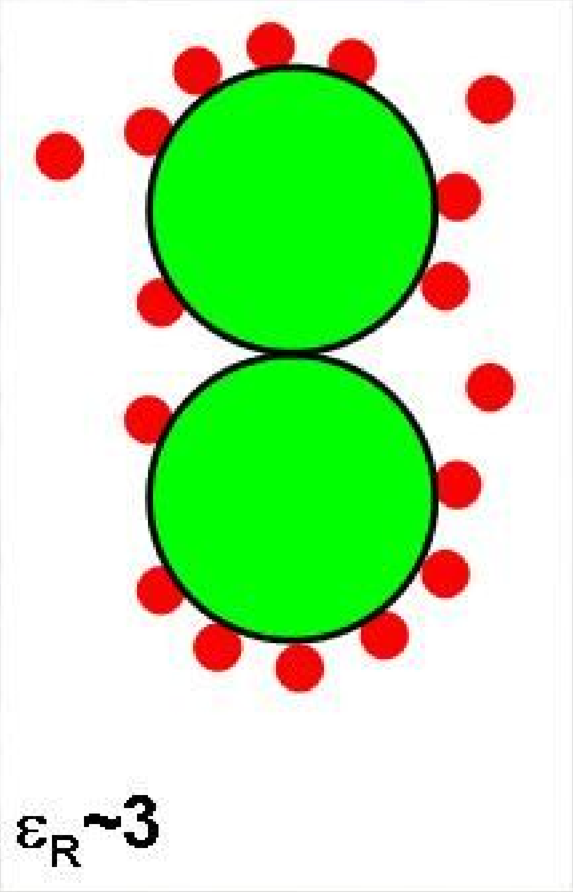
Z falls with ϕ: effect of neighbouring colloids

what about clustering?
clustering->neighbours at contract



experimental evidence - conductivity drops with increasing polymer concentration

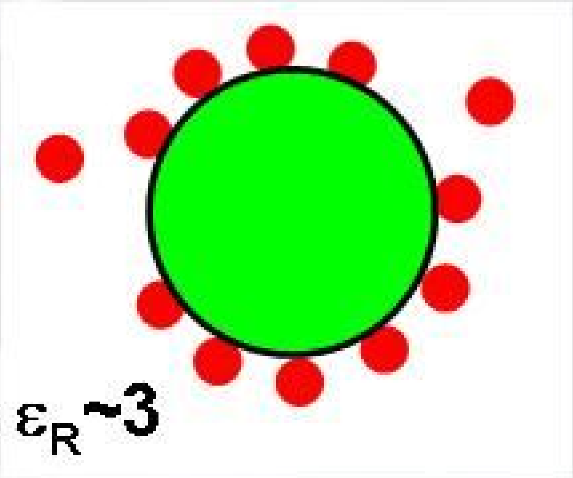




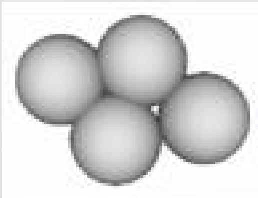
Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

What does this mean for clusters?

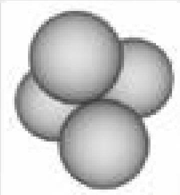
Z falls with ϕ: effect of neighbouring colloids



what about clustering?
clustering->neighbours at contract

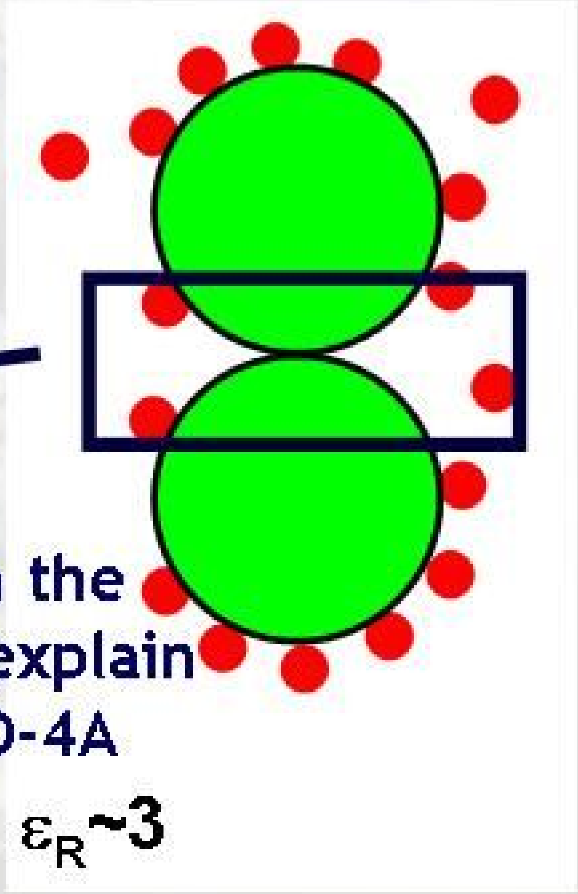


4D



4A

Can anisotropy in the charge distribution explain the suppressed 4D-4A transition?



How does the anisotropy arise?
Explicit site primitive model

Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

The primitive model

3-component system

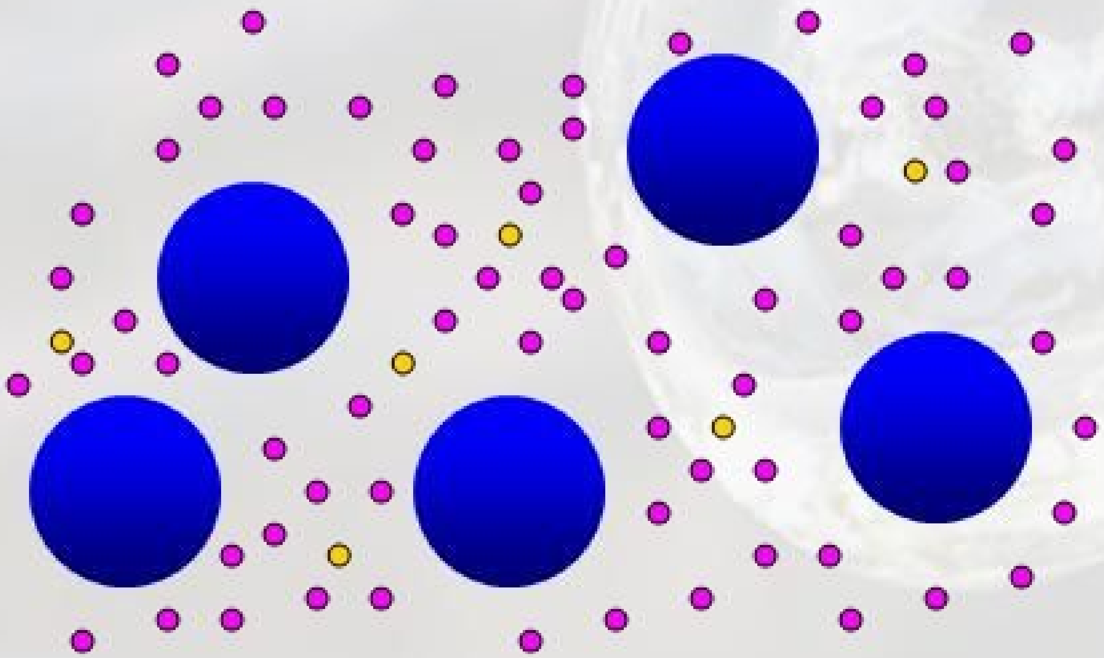
$+Ze$ macro-ions (colloids)

$-e$ counter-ions

$+e$ like-charged micro-ions

Coulomb interactions

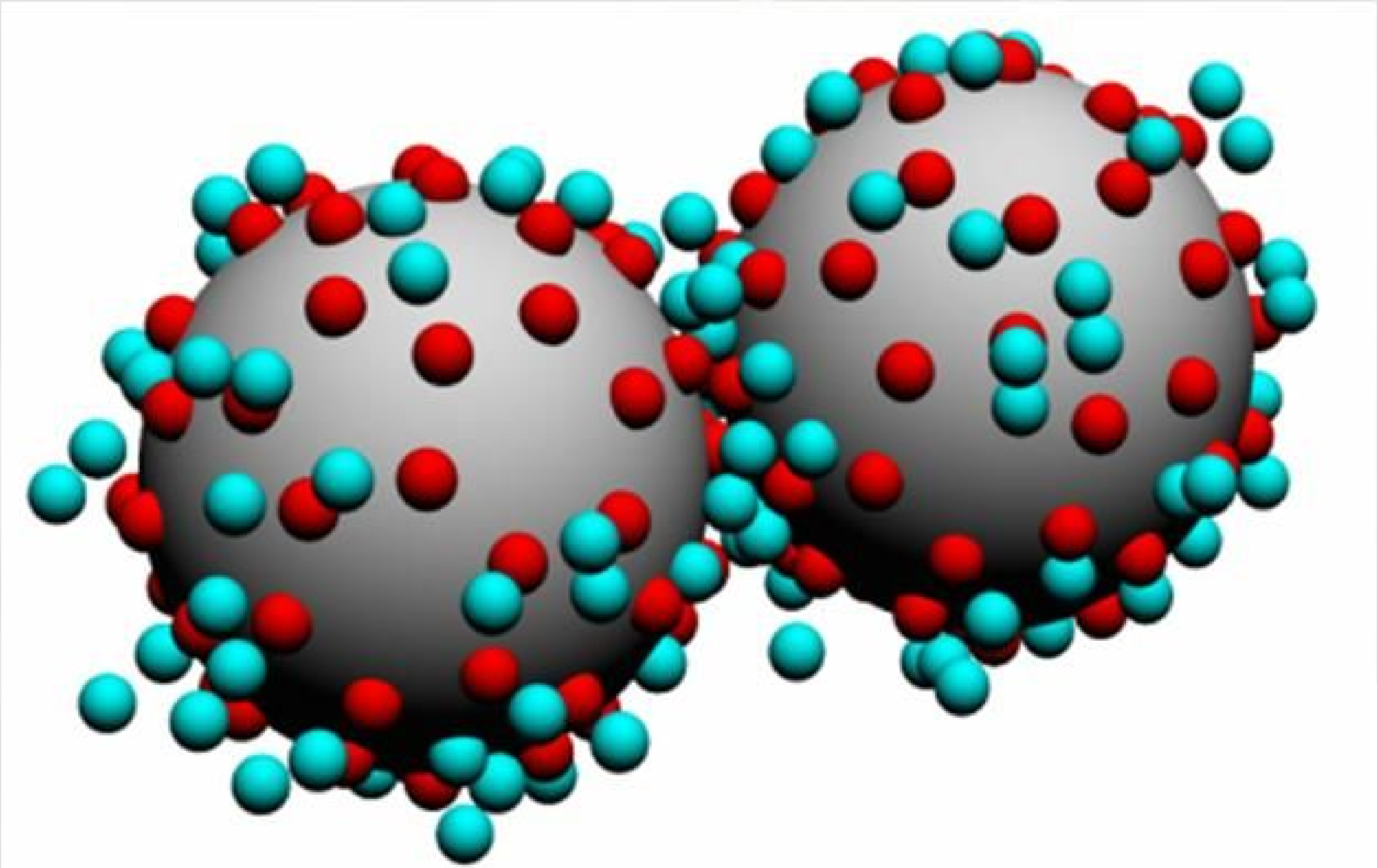
$$u_{ij}(r_{ij}) = \frac{1}{4\pi\varepsilon}\frac{q_i q_j}{r_{ij}}$$



still isotropic:
in reality colloids and proteins have discrete sites.

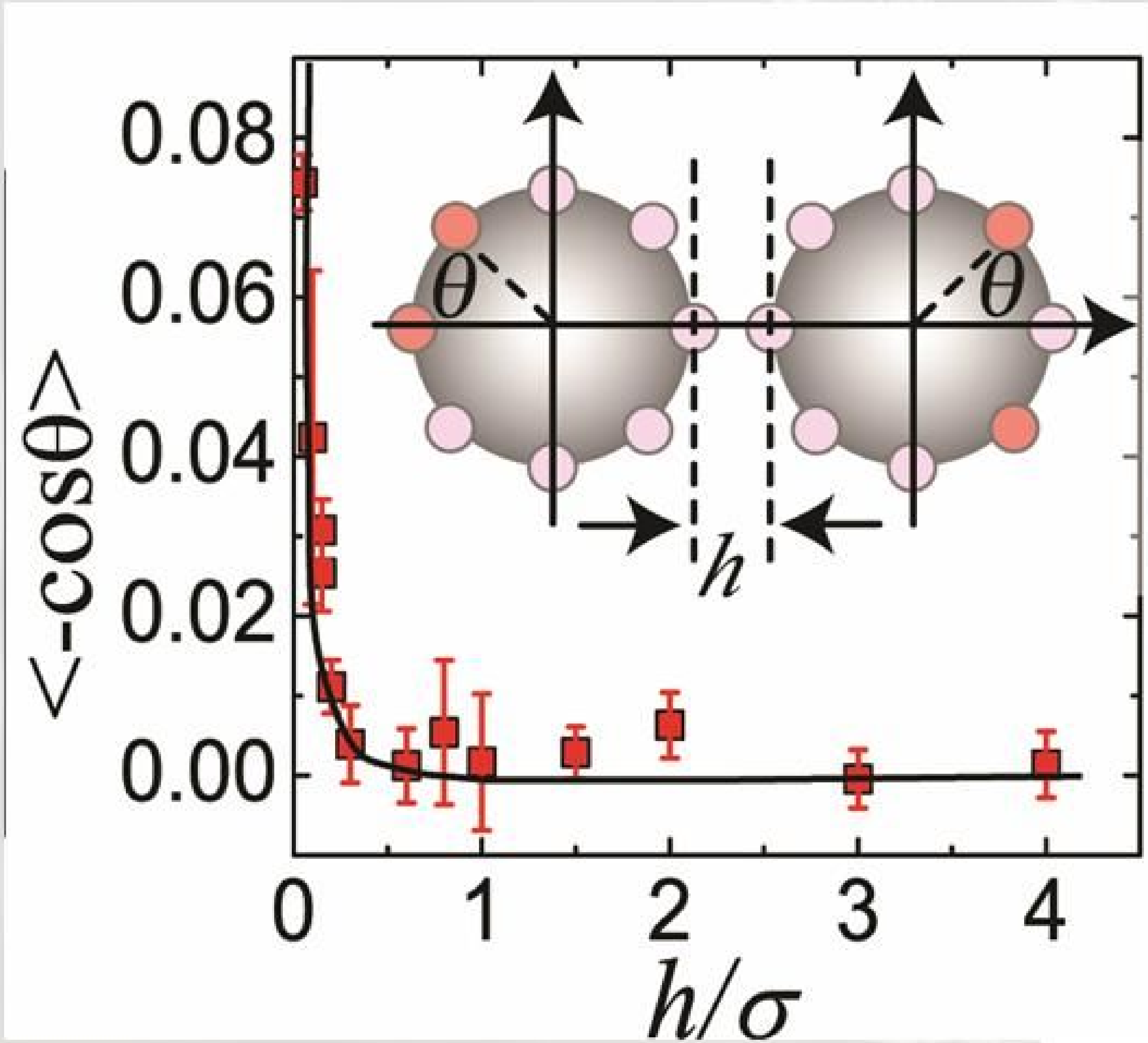
explicit site primitive model: each of Z charging sites Coulombic. 2Z counterions, 2 colloids

Explicit site primitive model introduces anisotropy



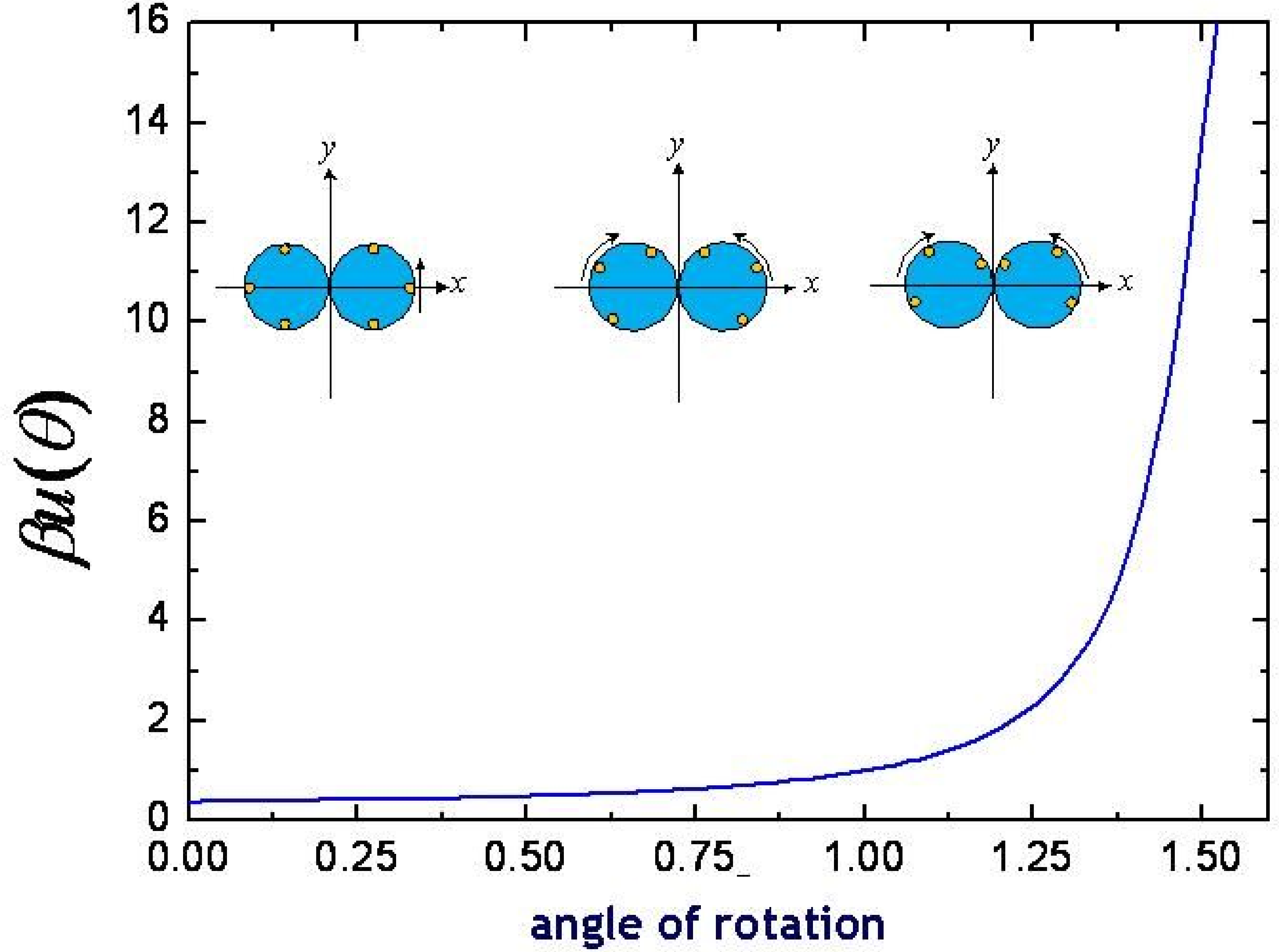
Explicit site primitive model: sites and ions

Explicit site primitive model introduces anisotropy



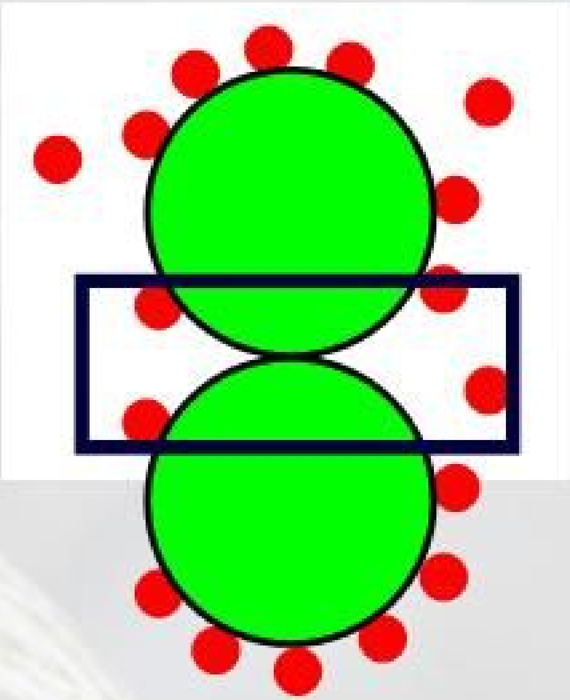
Explicit site primitive model: h surface separation θ angle of bound sites to axis Z=60

Experimental parameters for same <-cosθ>



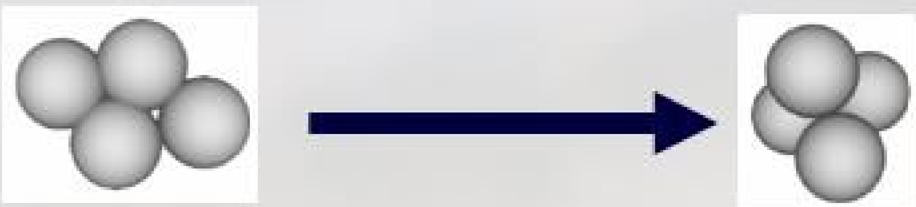
Klix *et. al.*, *ArXiV*, 0903.3393v1(2009)

Finally…



The explicit site primitive model predicts an anisotropic charge distribution when two colloids approach

The anisotropy order parameter $\langle \cos\theta \rangle$ predicts an energy barrier ~20kT to colloid rotation



4D 4A

We believe this is the origin of the suppressed 4D-4A transition

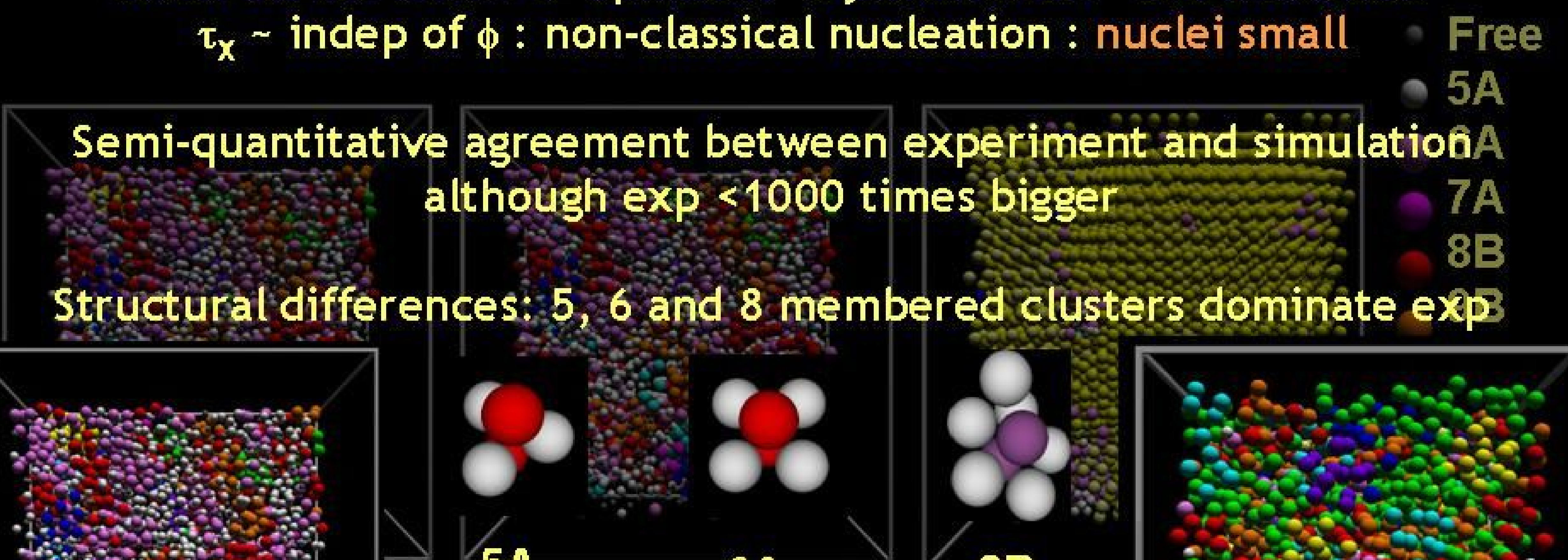
Crystallisation in 'hard spheres'

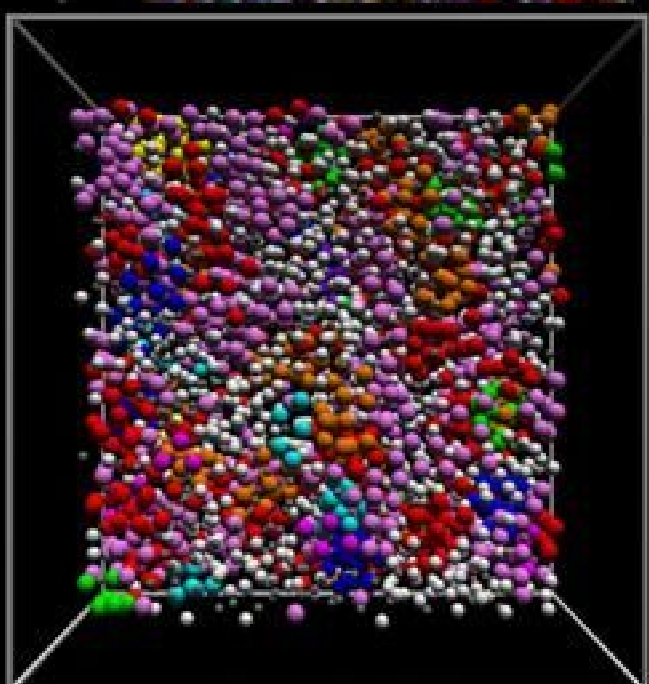
Much slower than HS 'spinodal' crystallisation - but like silica

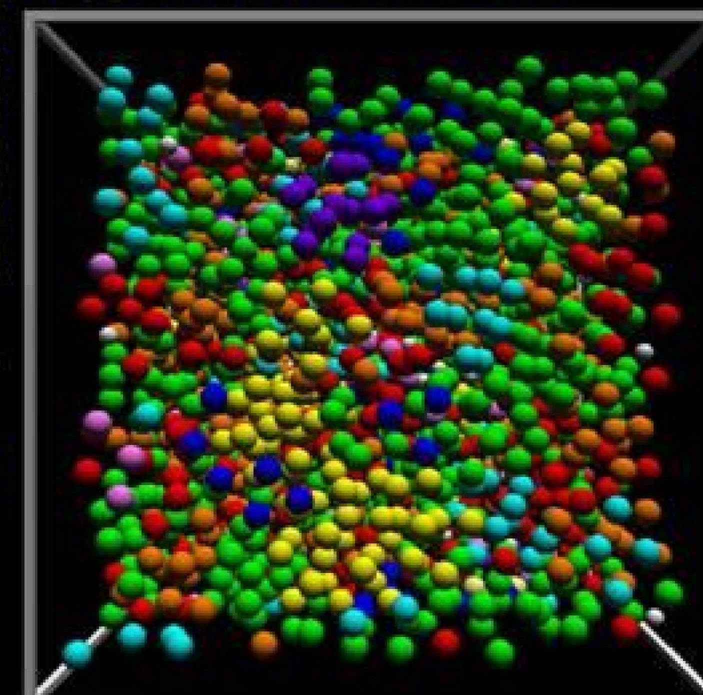
τ_X ~ indep of ϕ : non-classical nucleation : nuclei small

Semi-quantitative agreement between experiment and simulation although exp <1000 times bigger

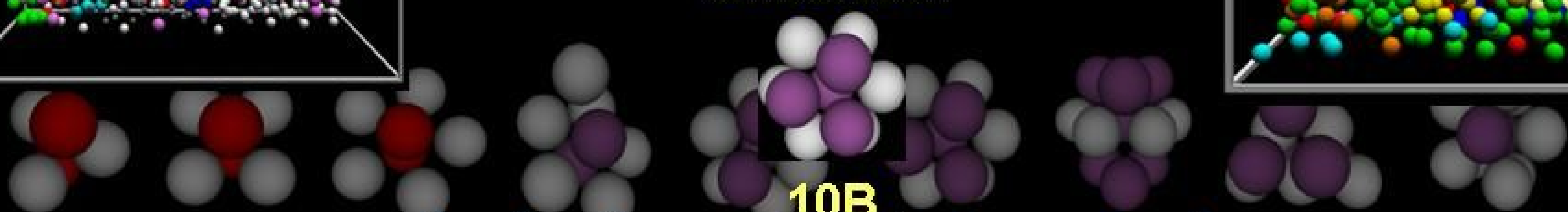
Structural differences: 5, 6 and 8 membered clusters dominate exp







10 membered clusters dominate simulation



hard spheres are not always hard

and this can be important!

Acknowledgements - you for your attention

Bristol

Monica Moreno, Jade Taffs and Alex Malins

Canberra

Stephen Williams (TCC)

Tokyo

Hajime Tanaka

(early experiments)

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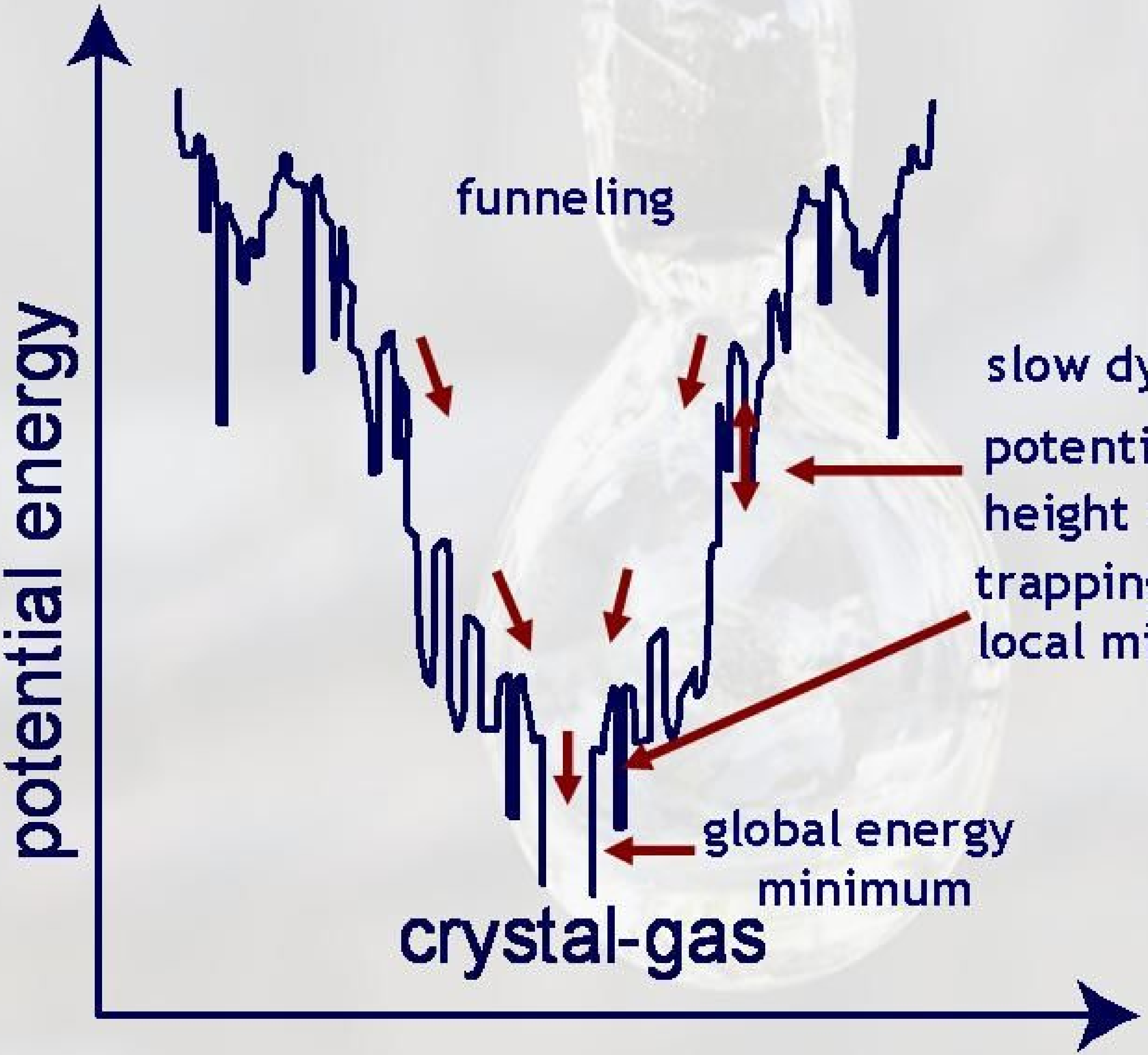
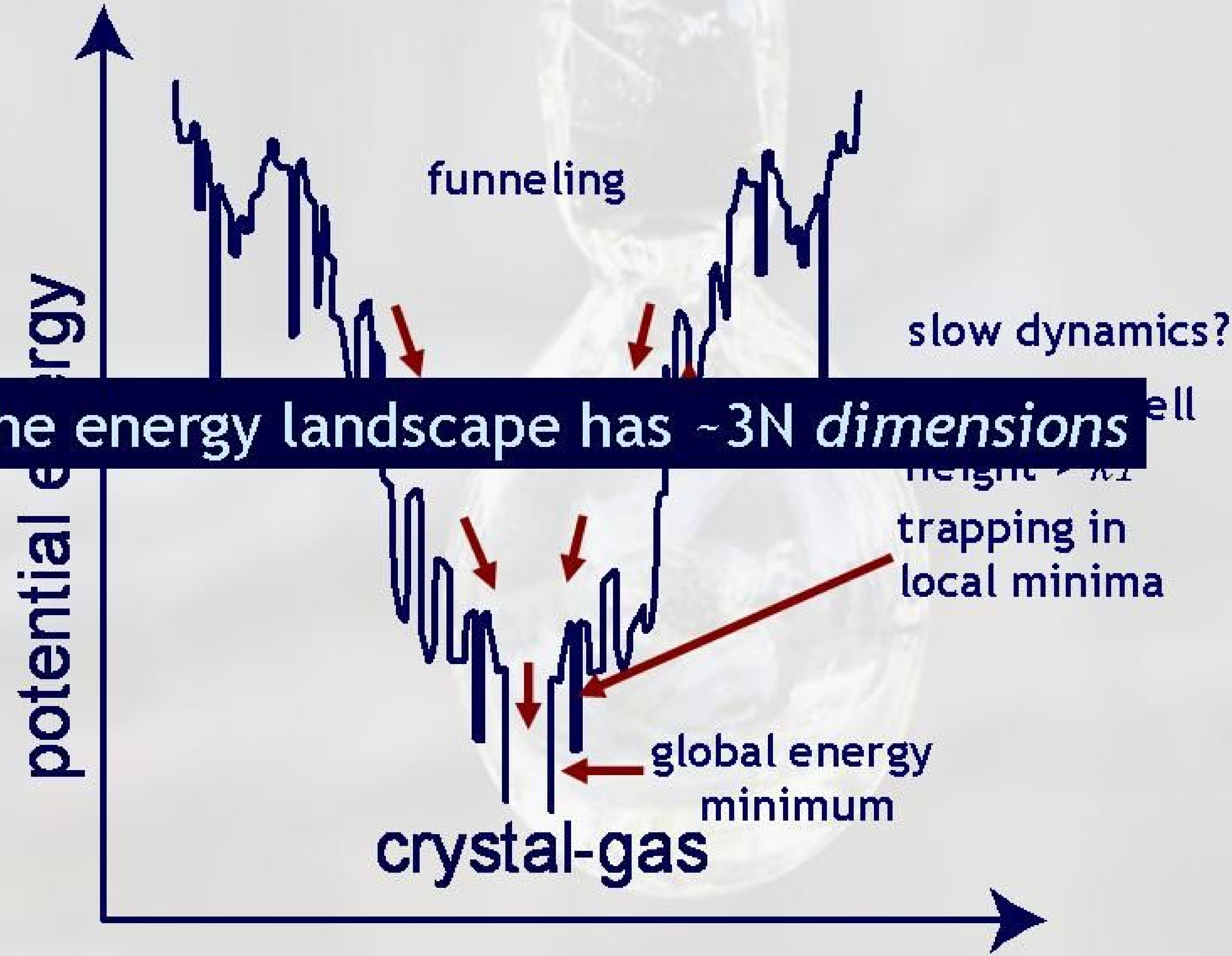
IOP Institute of Physics

The energy landscape



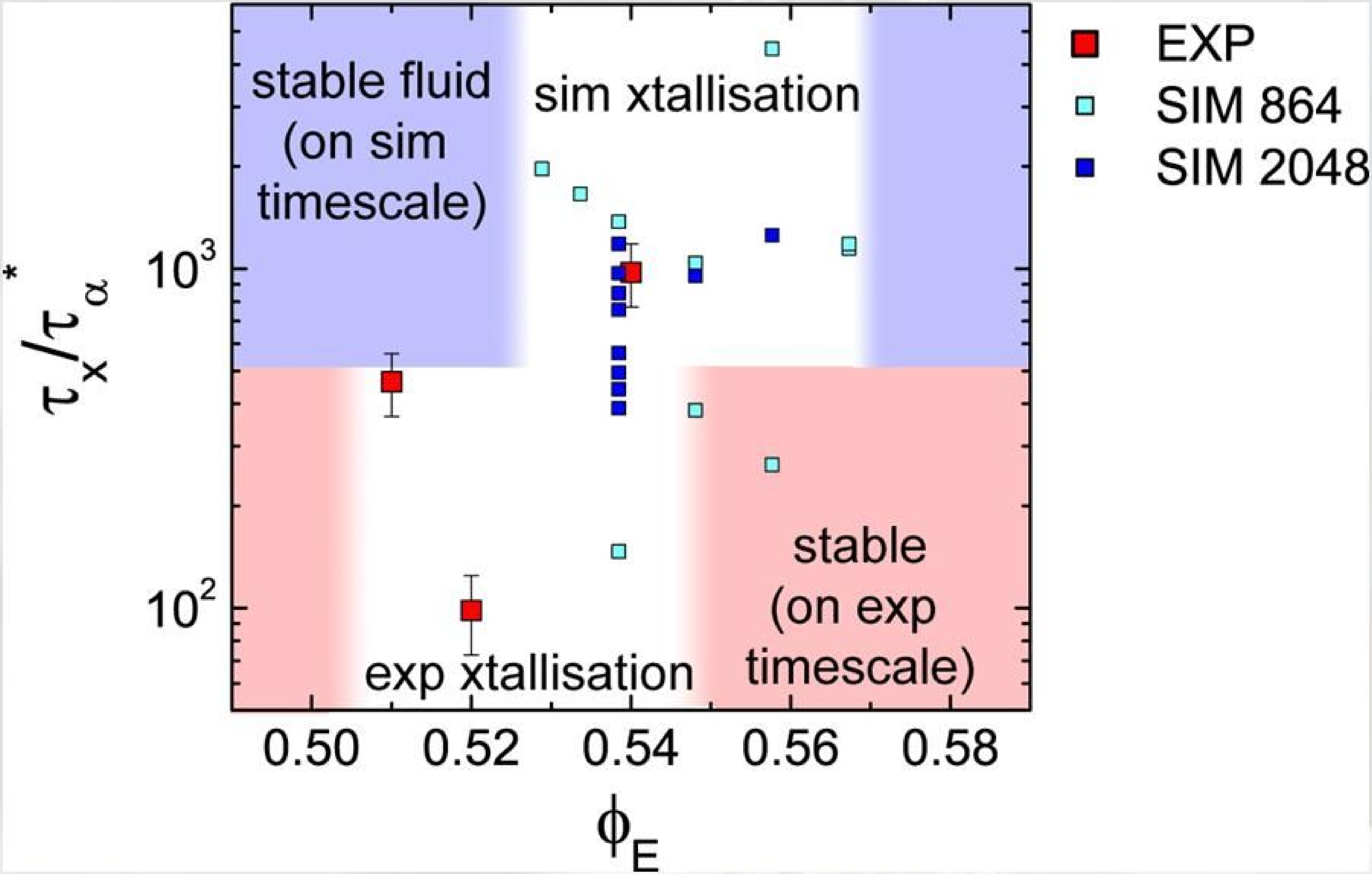
The energy landscape



…but the energy landscape has ~3N *dimensions*

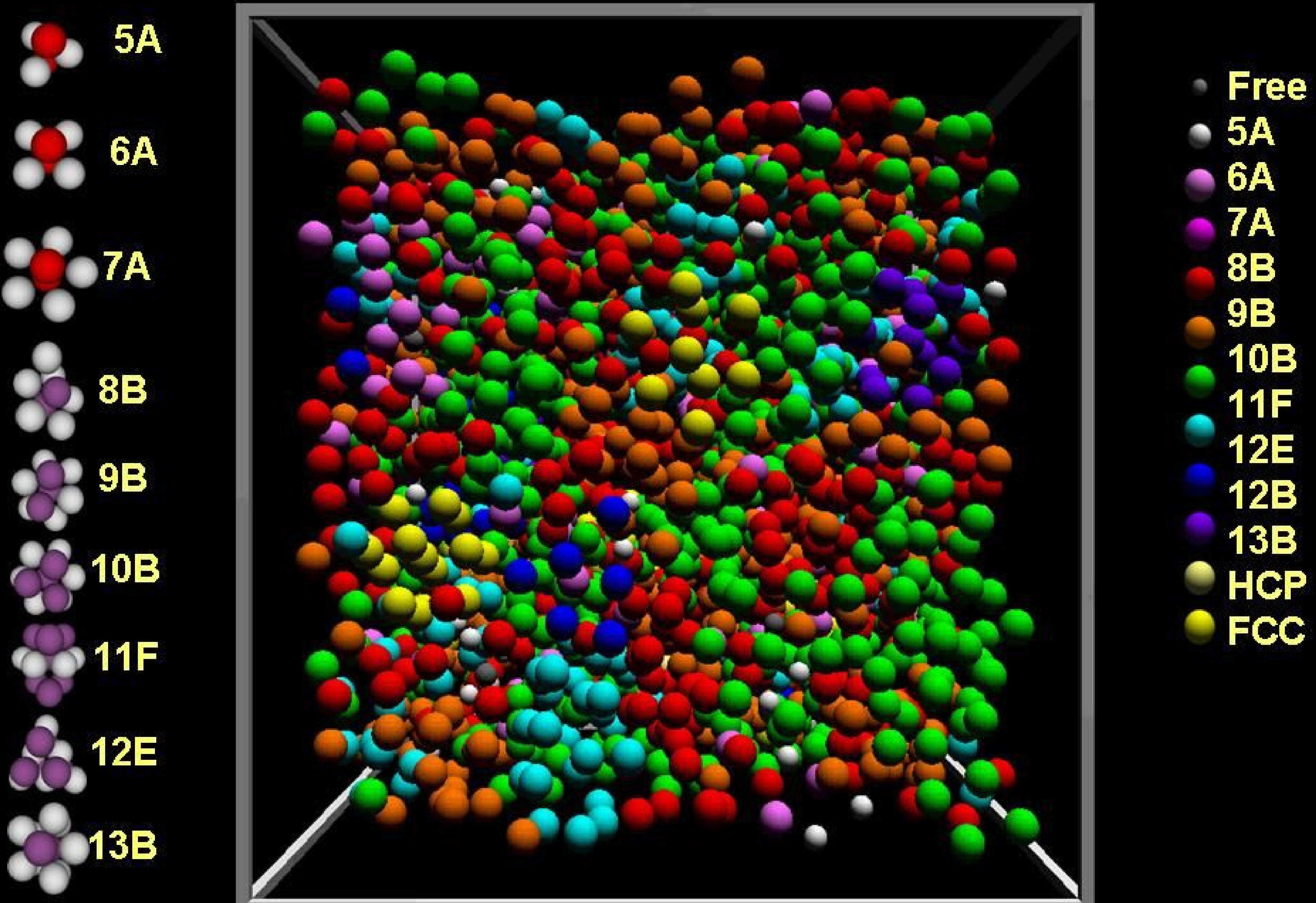
Crystallisation times in experiment and simulations

Scaled parameters

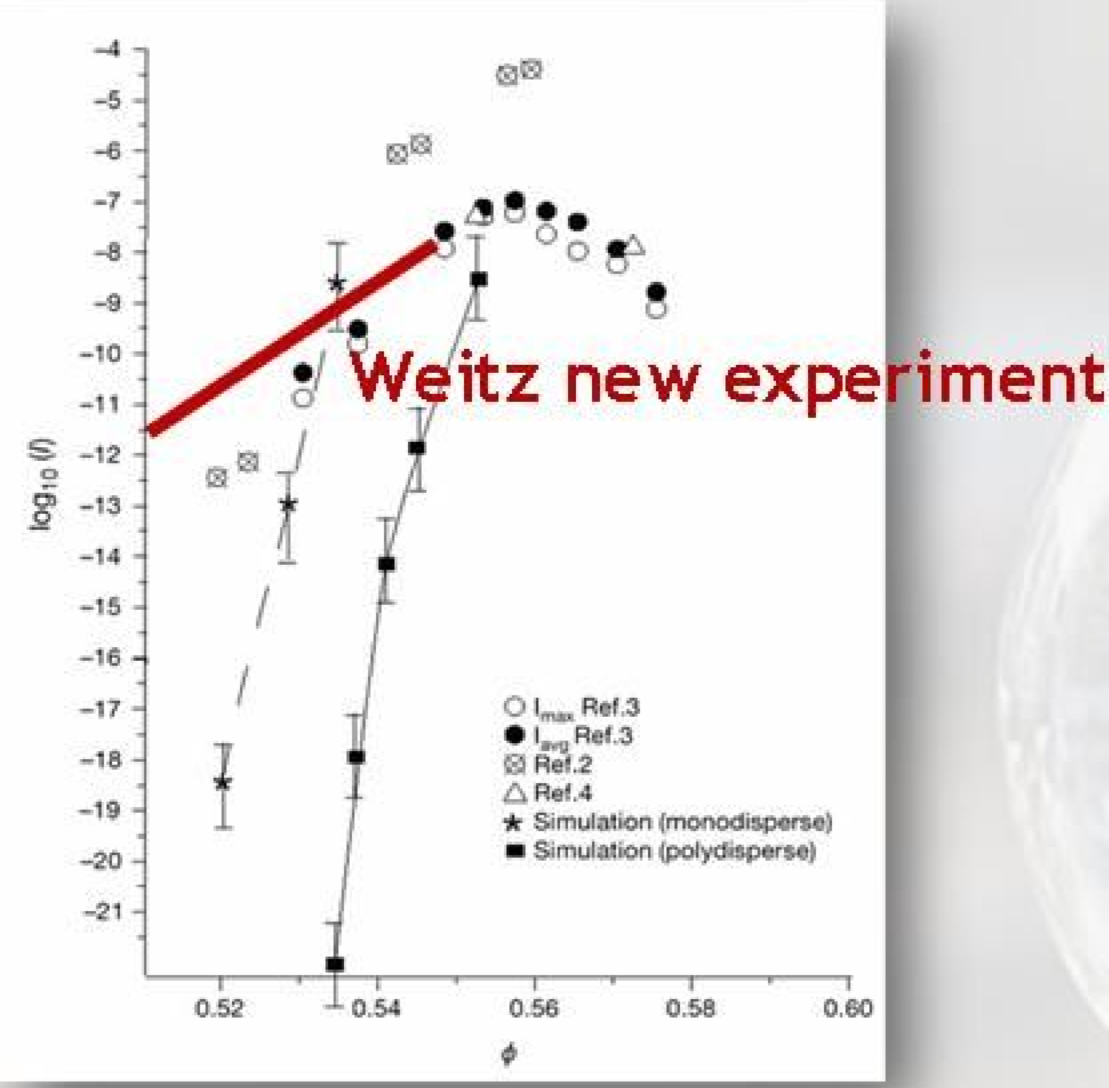


what happened to $J_{EXP} \sim 10^3 J_{SIM}$?

Topological cluster classification: fluid stable for simulation ϕ_S=0.55



Frenkel and Auer: simulation of nucleation rate



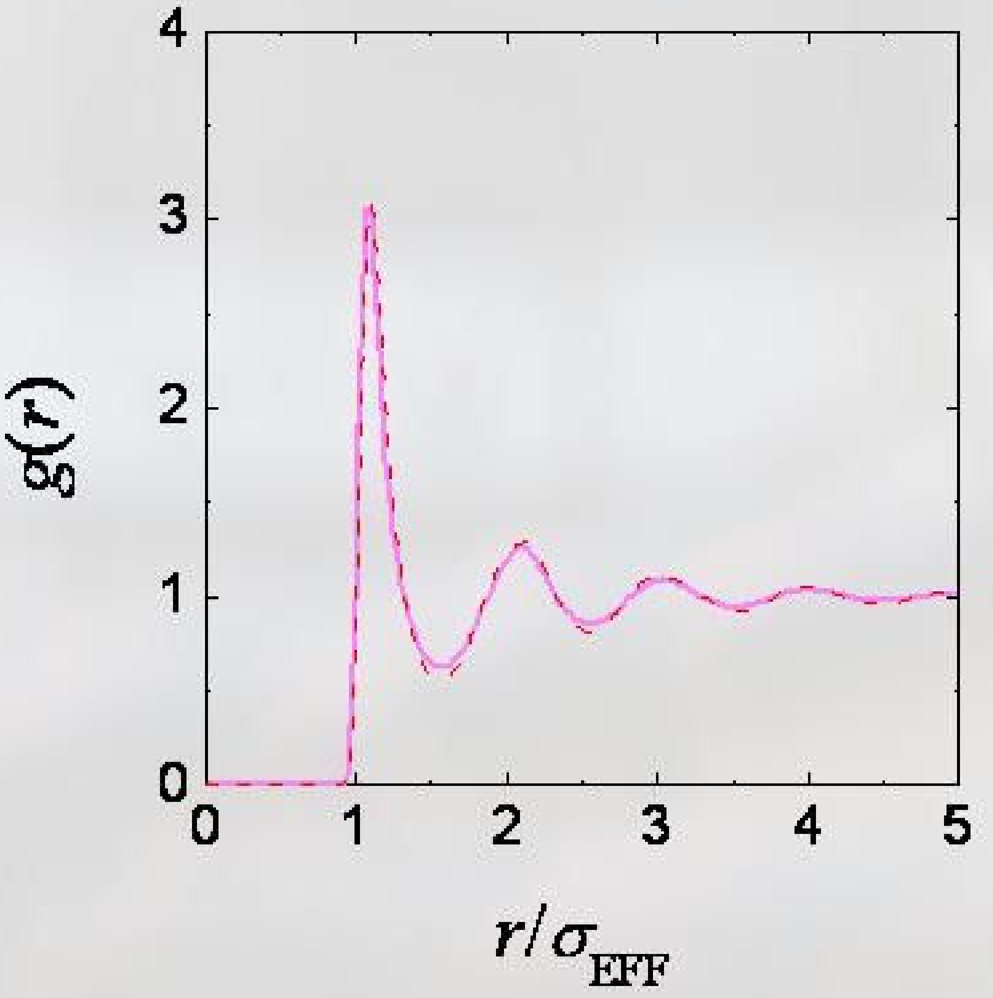
Computer simulations and experimental systems crystallise at extremely different rates why is this?

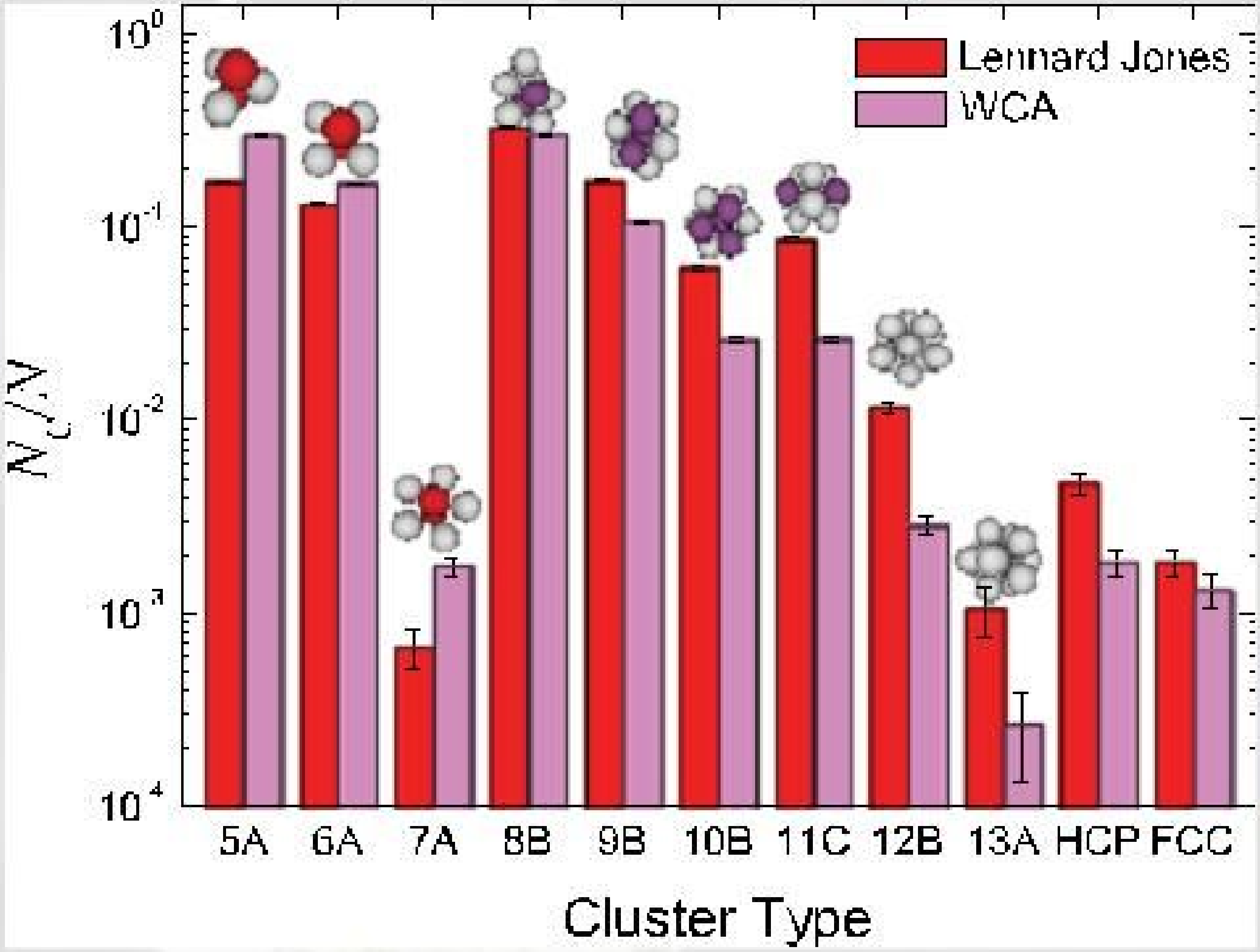
Can we learn anything from the locally favoured structures?

Auer, S. & Frenkel, D., *Nature*, **409**, 1020 (2001)

Testing the TCC

can we detect changes in structure when g(r) can't?

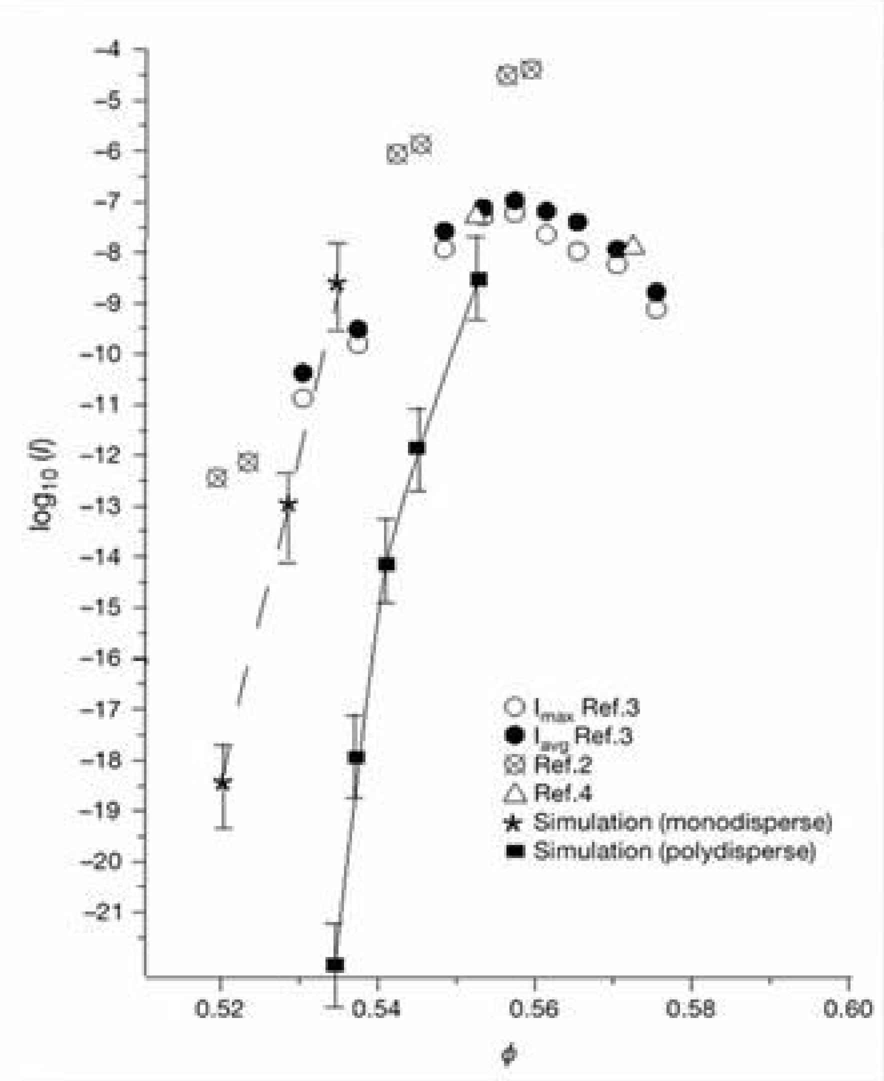




Lennard-Jones (red) vs Weeks-Chandler-Andersen (pink LJ without attractions) at the LJ triple point

Taffs et al submitted to *JCP*

Frenkel and Auer: simulation of nucleation rate



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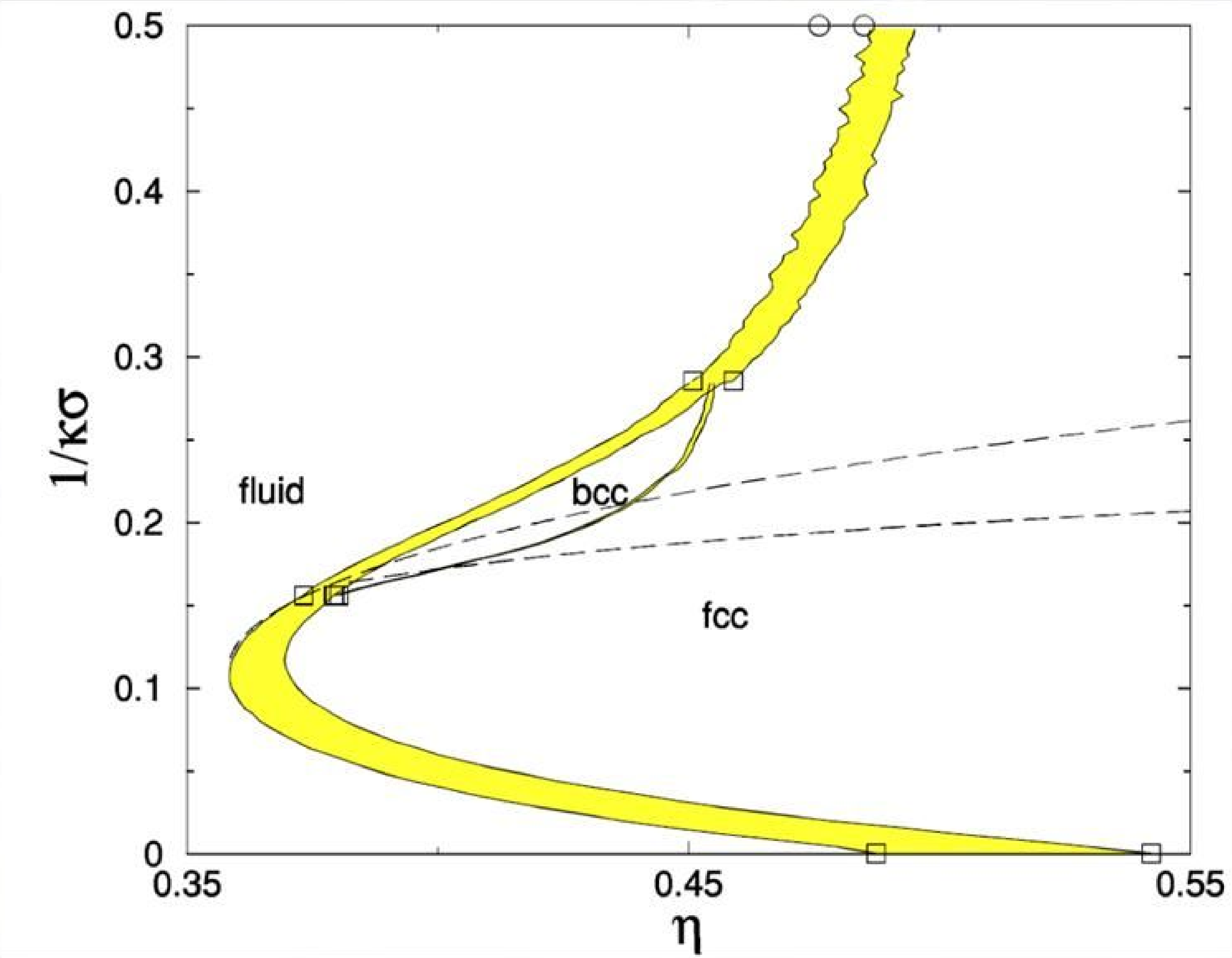
Consequences for the phase diagram of weak charging

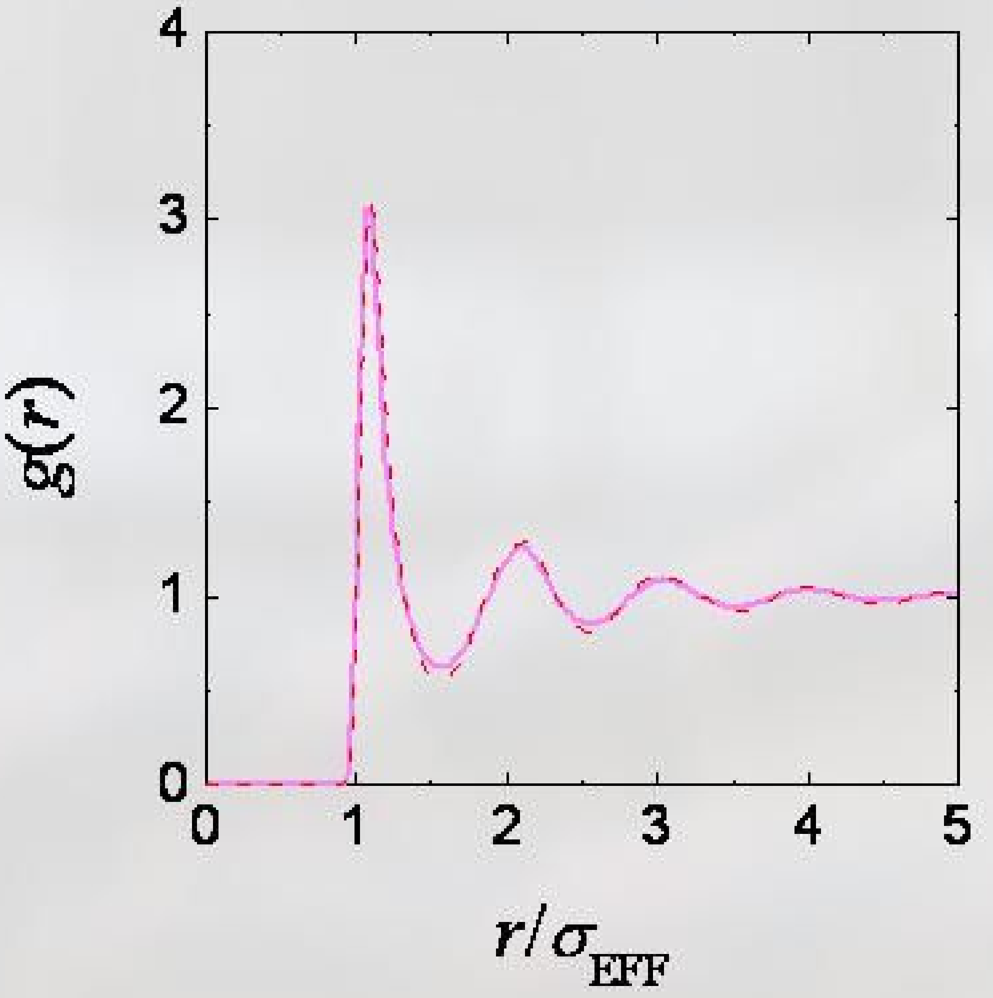


contact potential $\beta\varepsilon_\gamma$=8

Hynninen and Dijkstra PRE 2002

Testing the TCC

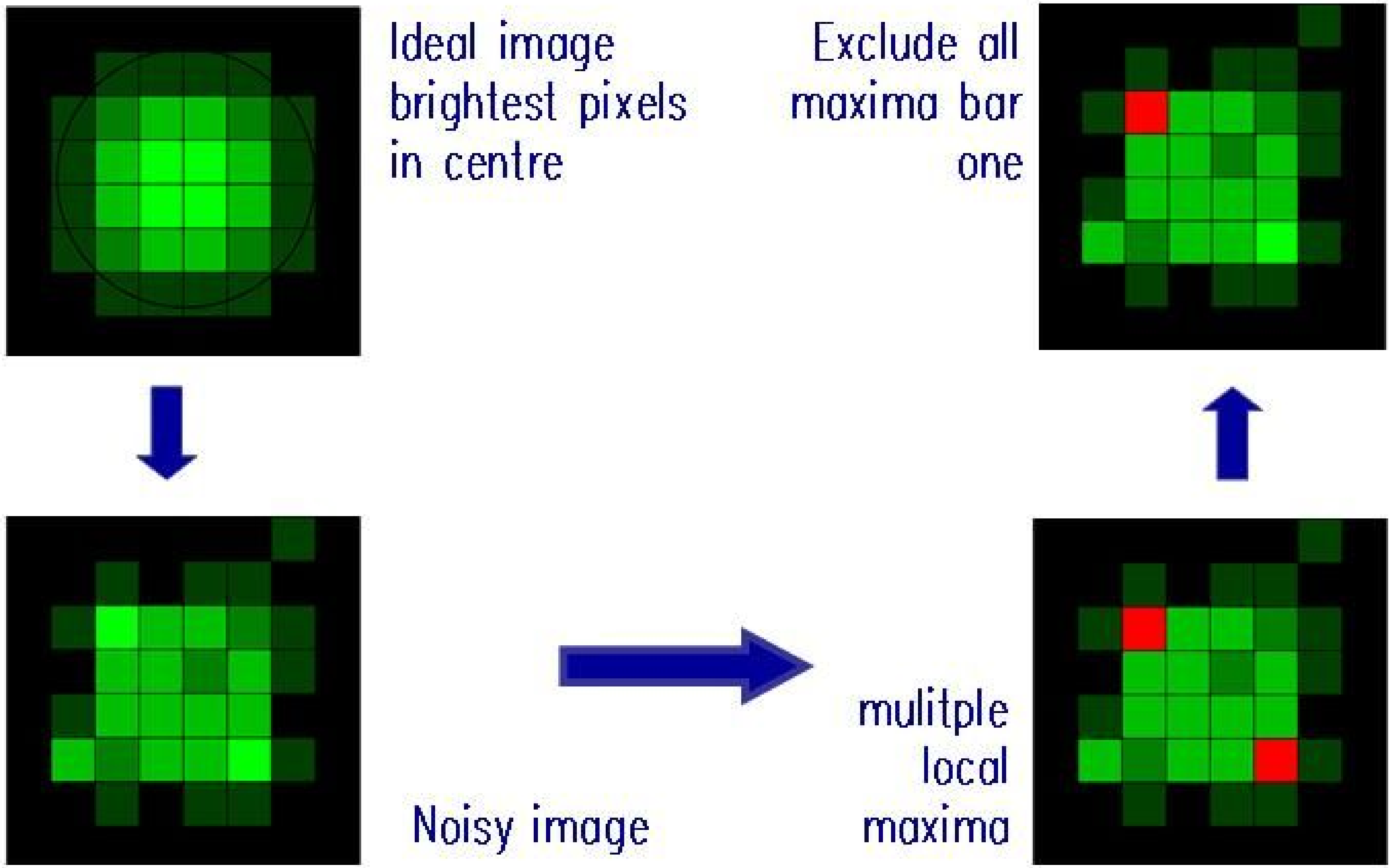
can we detect changes in structure when g(r) can't?



Lennard-Jones (red) vs Weeks-Chandler-Andersen (pink LJ without attractions) at the LJ triple point

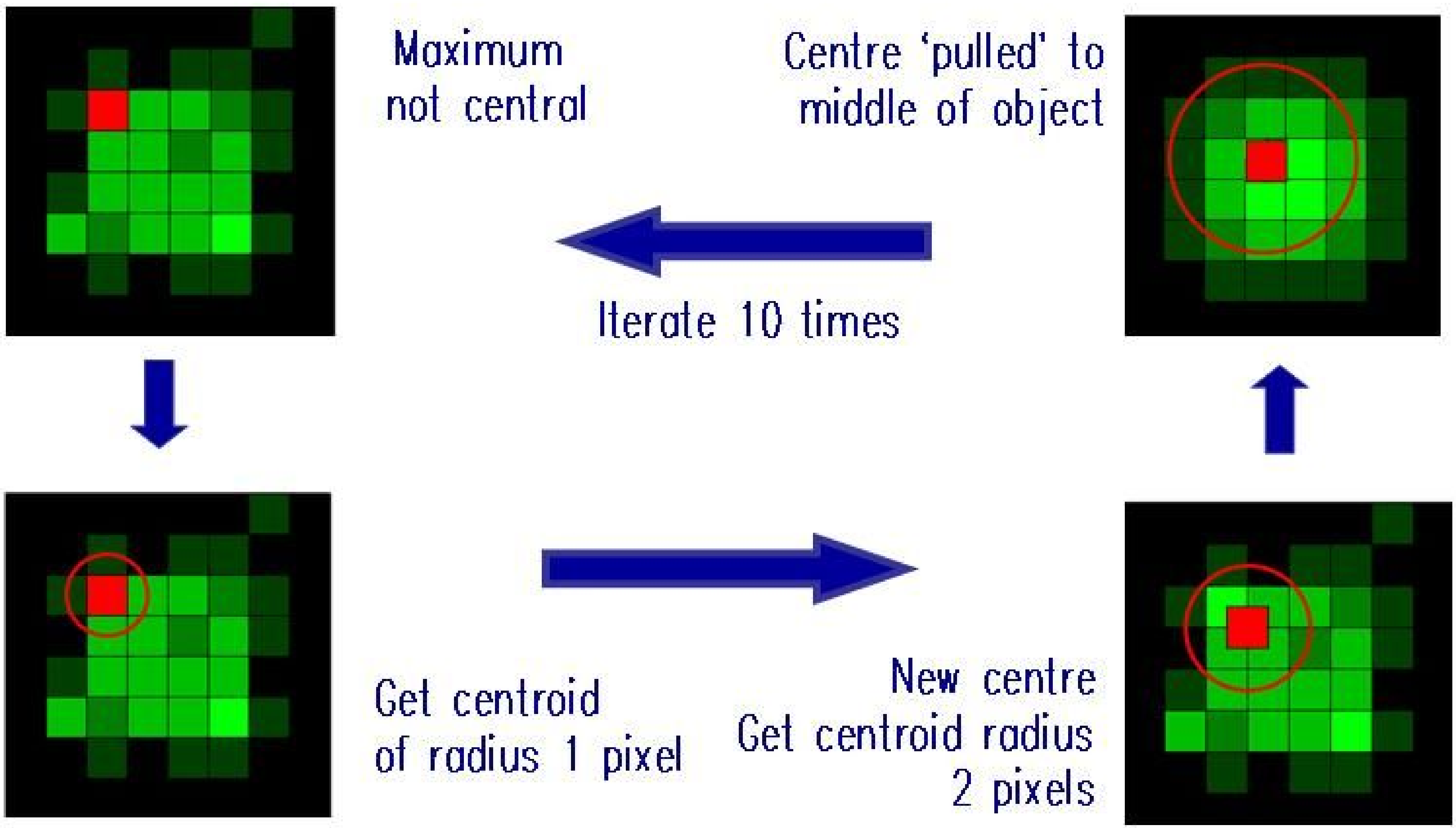
Weeks-Chandler-Andersen JCP 1971

Particle tracking



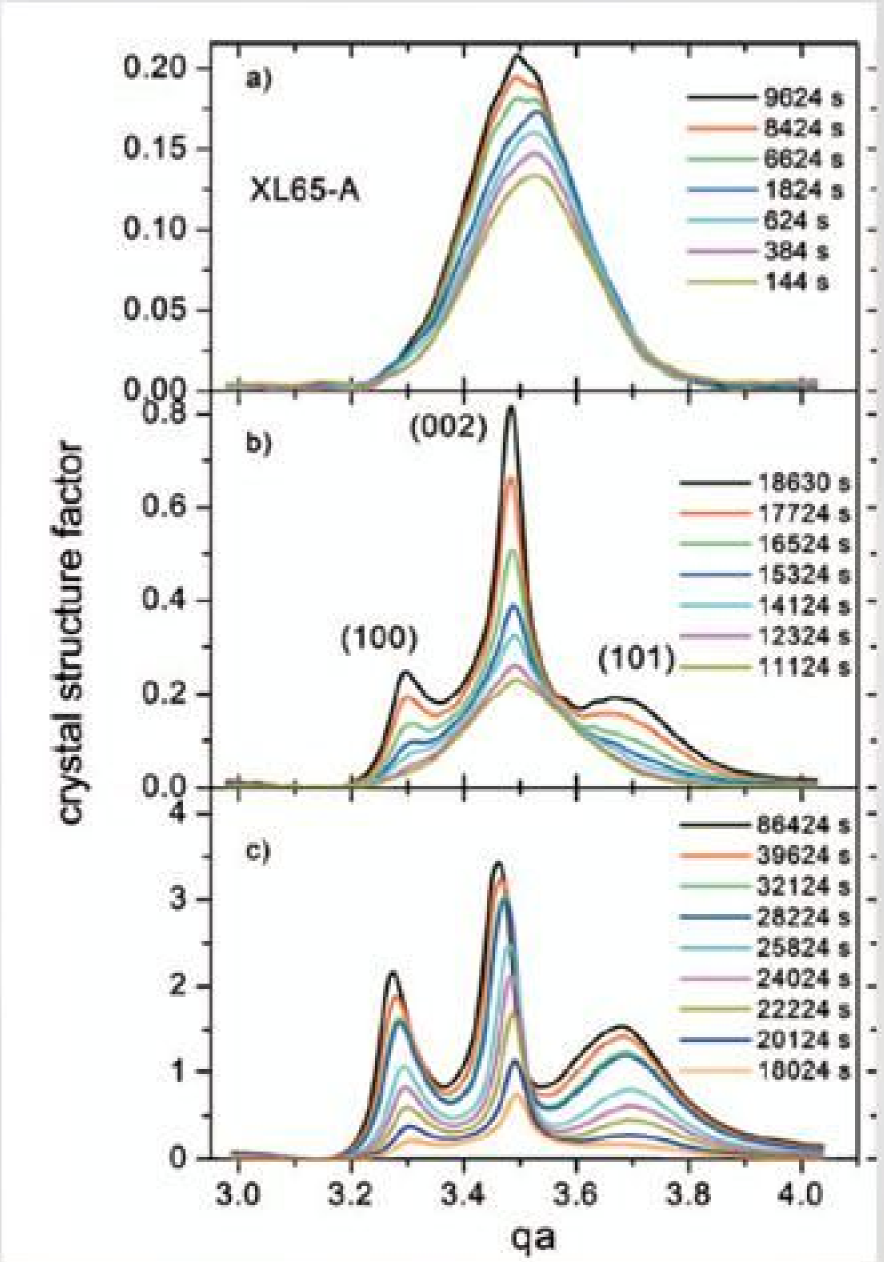
CPR et al, *J. Phys. Cond. Matter*. **15** S3581 (2003)

Particle tracking



CPR et al, *J. Phys. Cond. Matter*. **15** S3581 (2003)

Measuring crystallisation



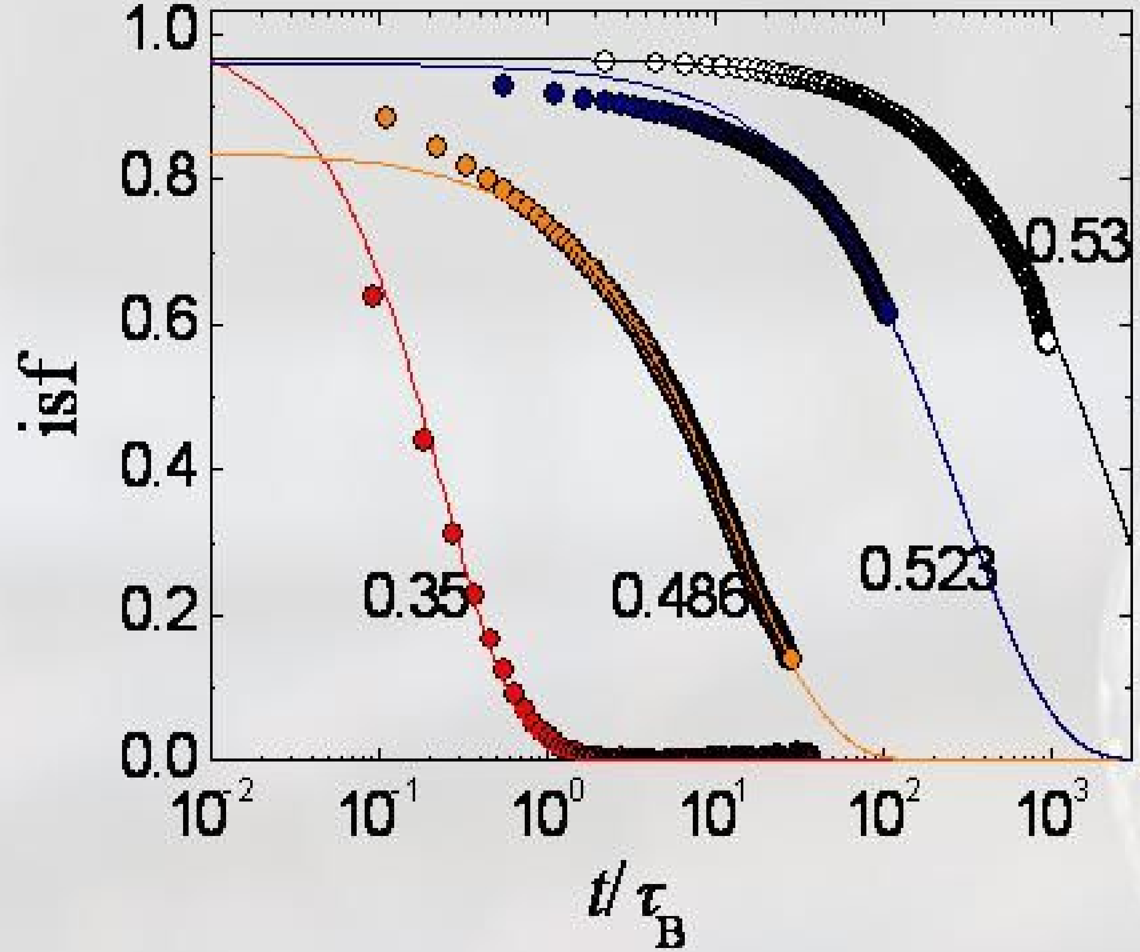
static light scattering

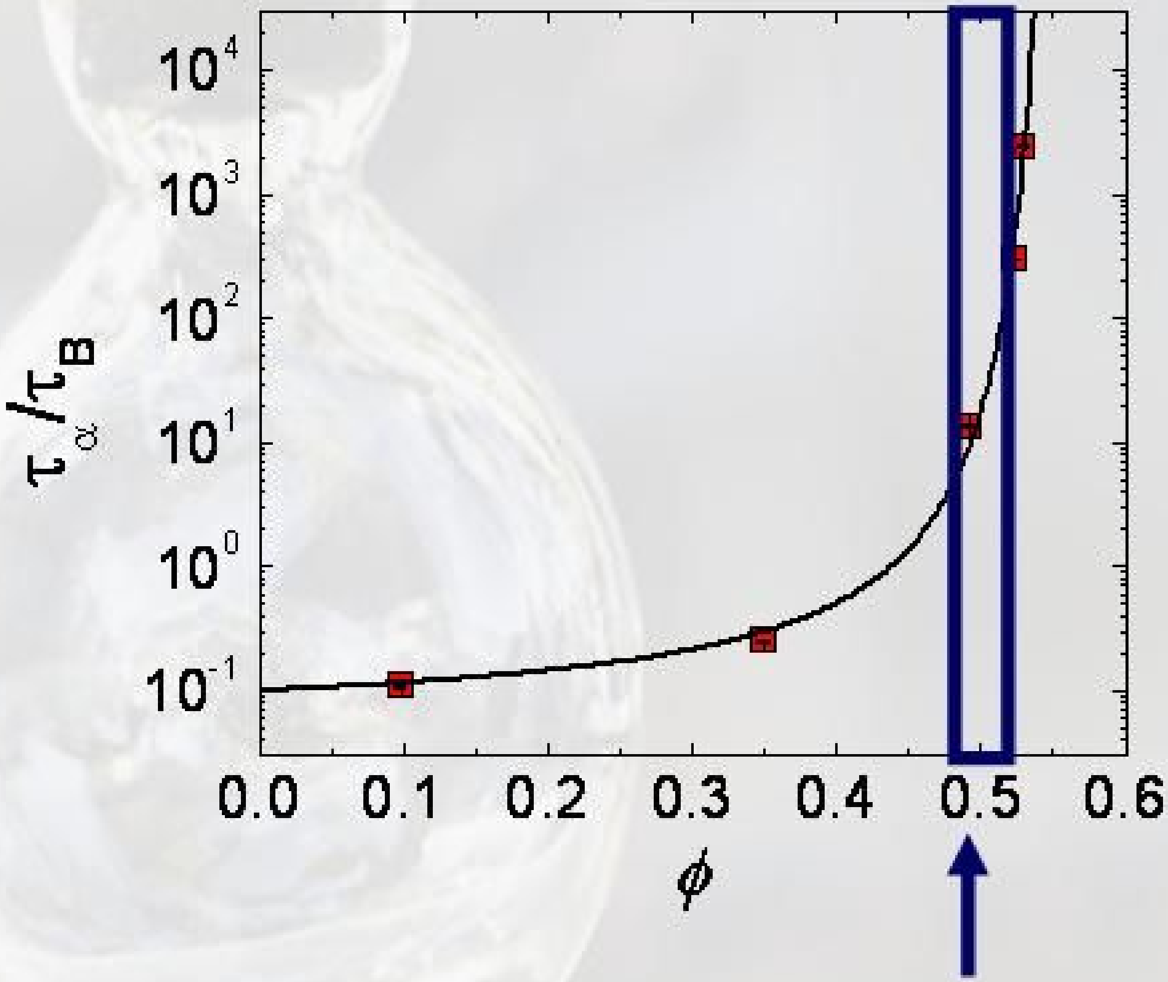
small colloids: many τ_B

$\tau_B \sim \sigma^3$

Schope et al *JCP* **127** 084505 (2007)

Experimental ISF - similar approach





set τ_α for highest ϕ_E which doesn't crystallise

$\tau_\alpha(\phi_E)$ changes strongly around 10x in regime of interest

NB - slightly different exp system, here gives rough order of τ_α

Don't we know everything already?

classical nucleation theory (CNT)

$$\Delta G = 4\pi r^2 \gamma - \frac{4\pi}{3} r^3 \Delta\mu n$$

surface tension term r^2 (cost)
free energy gain r^2 (gain)

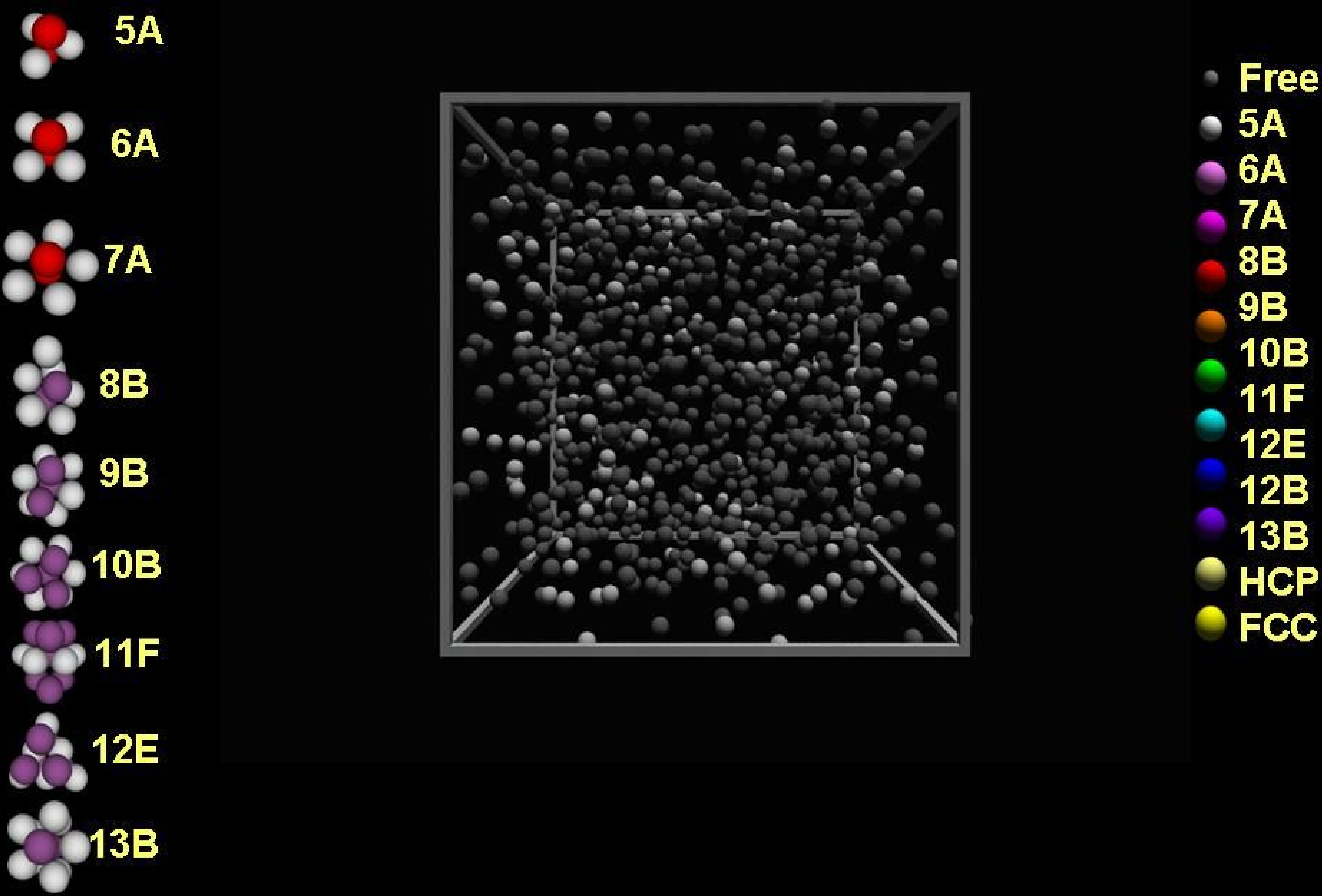
deeper quenching larger $\Delta\mu$

smaller critical nucleus (more likely)

faster nucleation

but....

Topological cluster classification locally favours structures in a fluid



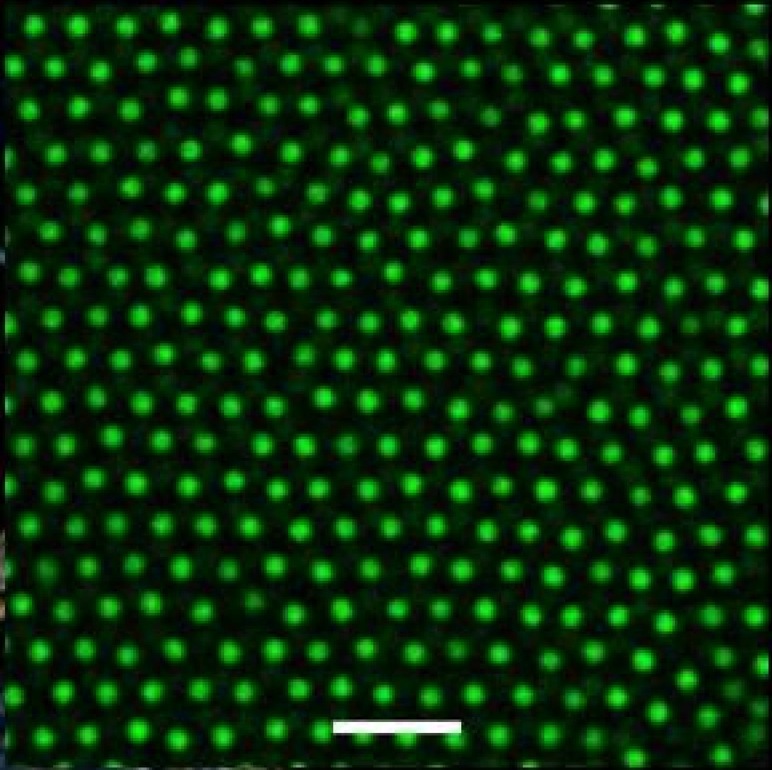
'Hard sphere' colloids for confocal microscopy

PMMA - decalin: not density matched

Confocal colloids are big->sediment

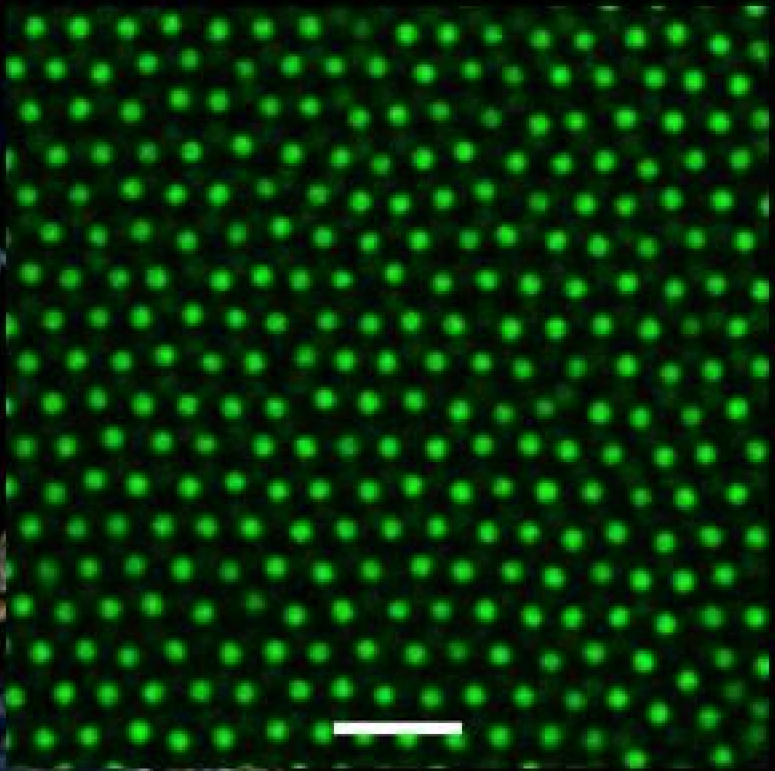
Density match: Cylohexylbromide $C_6H_{11}Br$

Charged! but nobody knows why or how

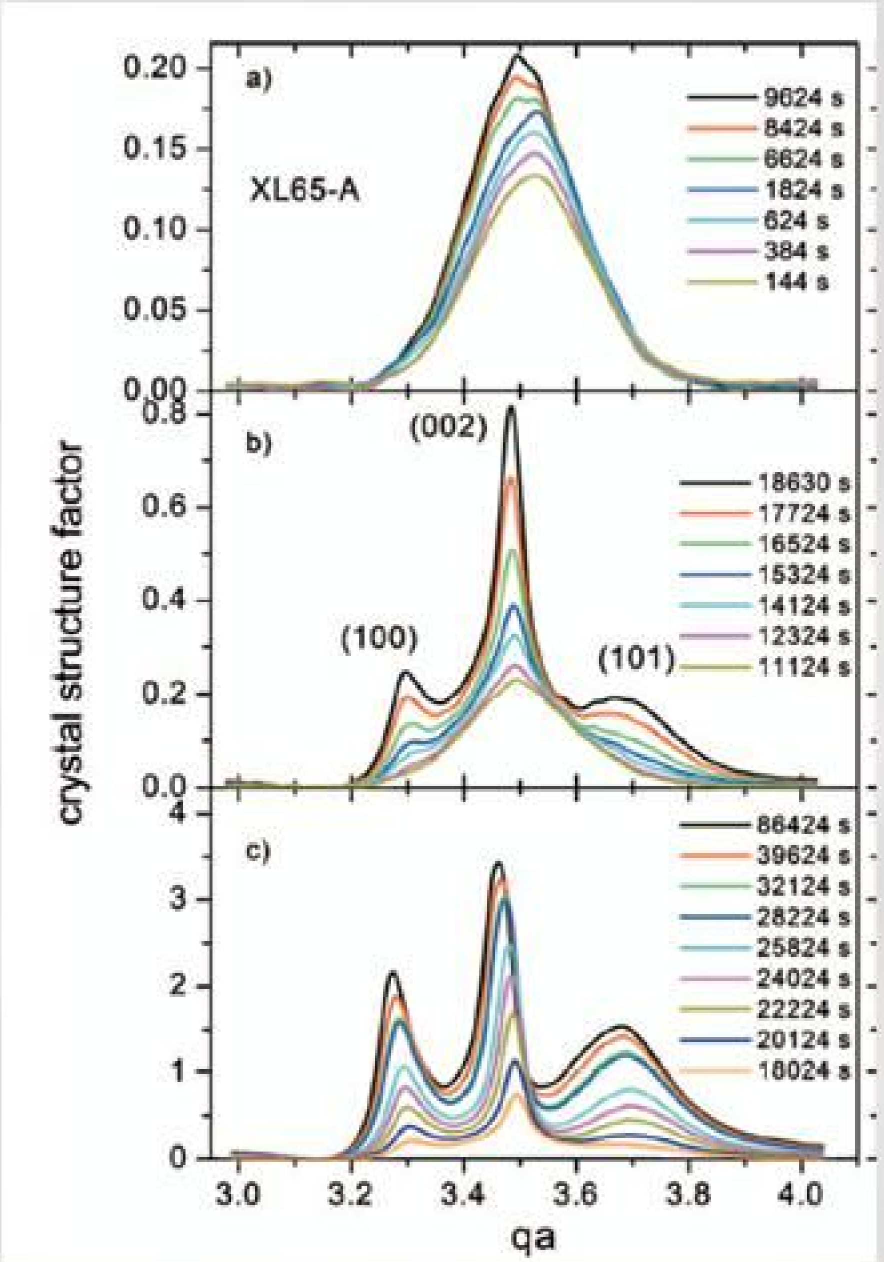


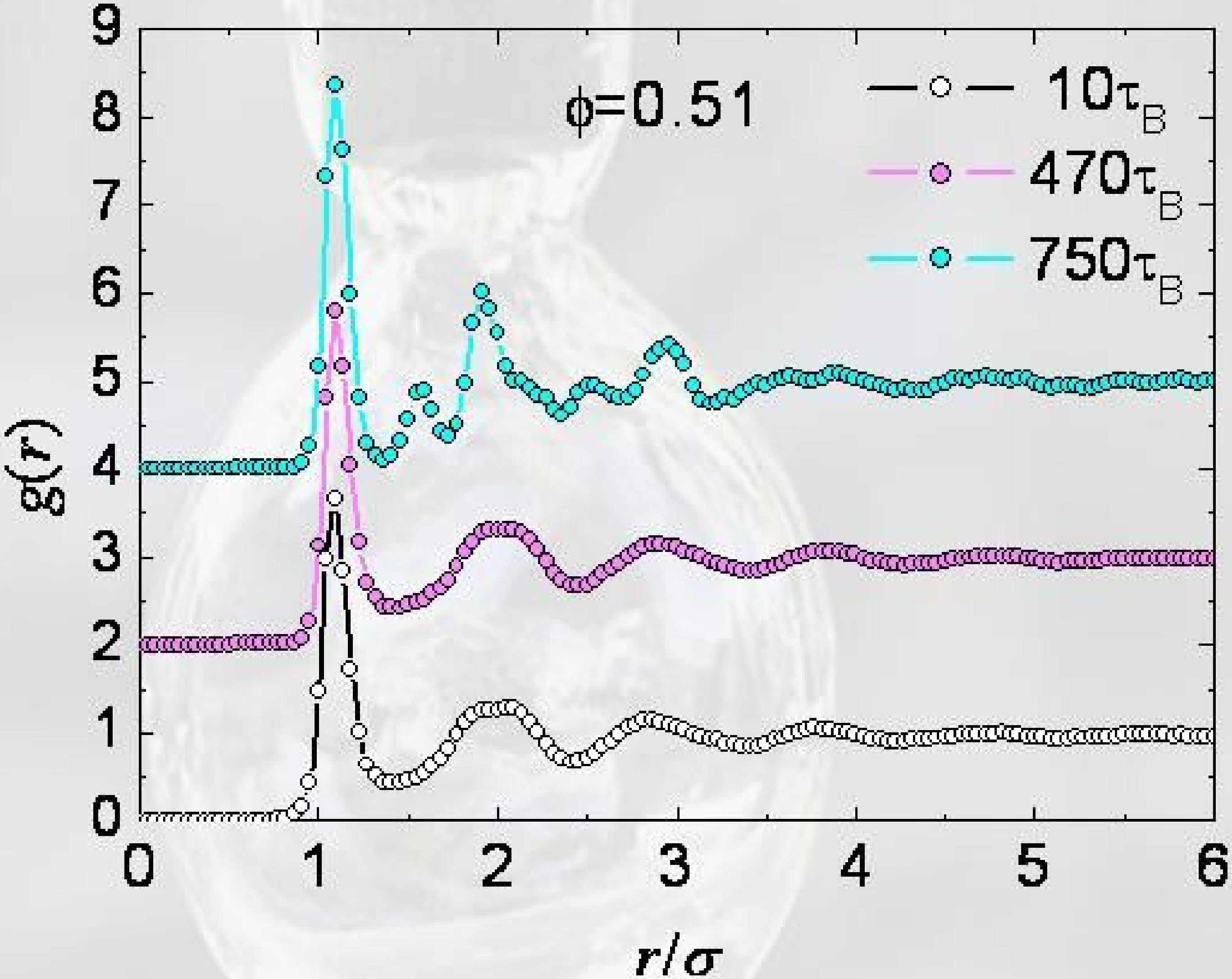
Cyclohexyl Bromide vs Water

	Water	CHB
dielectric constant	78	~8
Bjerrum length	0.7nm	~10nm
energy to separate ions	few kT	tens kT
	dissociation	~little dissociation



Connect to reciprocal space data
(but note difference in timescales)





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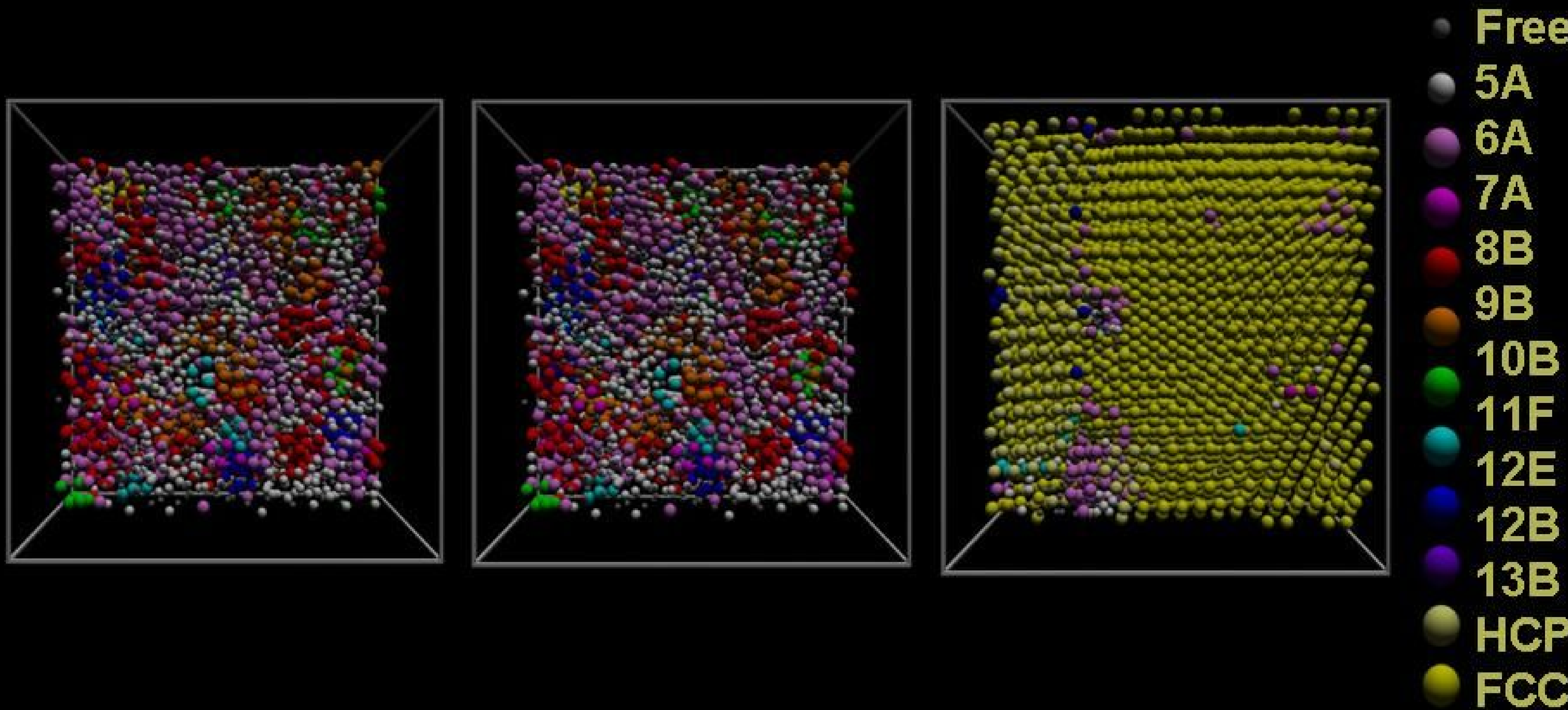
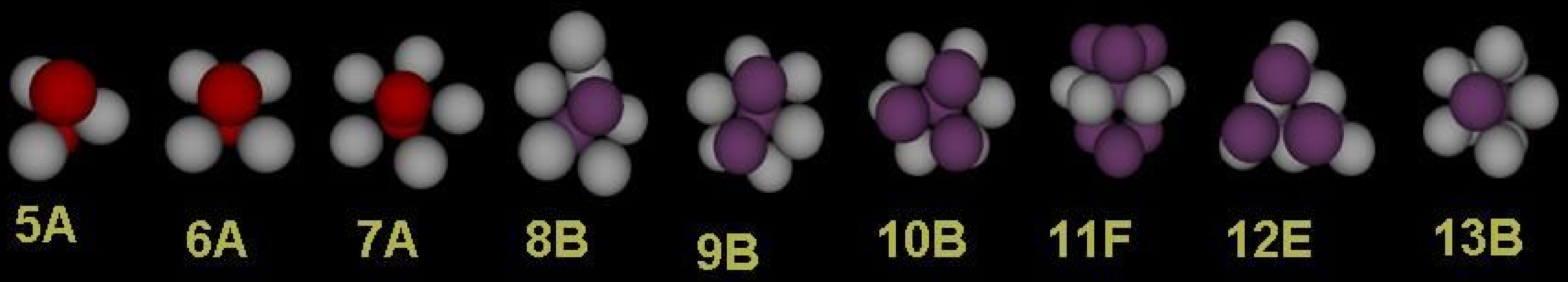
$\tau_B \sim \sigma^3$

Schope et al *JCP* **127** 084505 (2007)

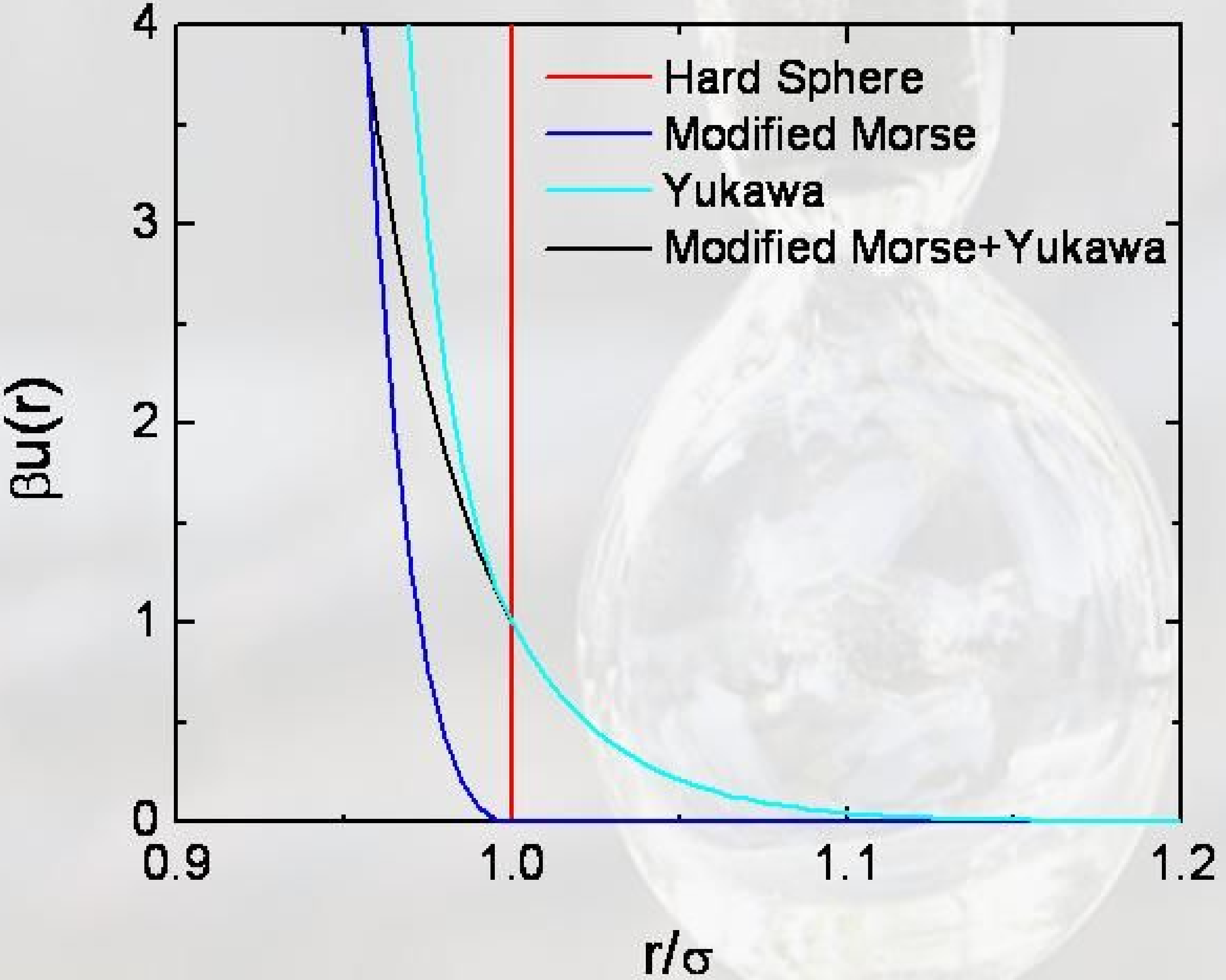
Acknowledgements - you for your attention





Simulation pair potential

$\beta\varepsilon=1$ $\kappa\sigma=30$

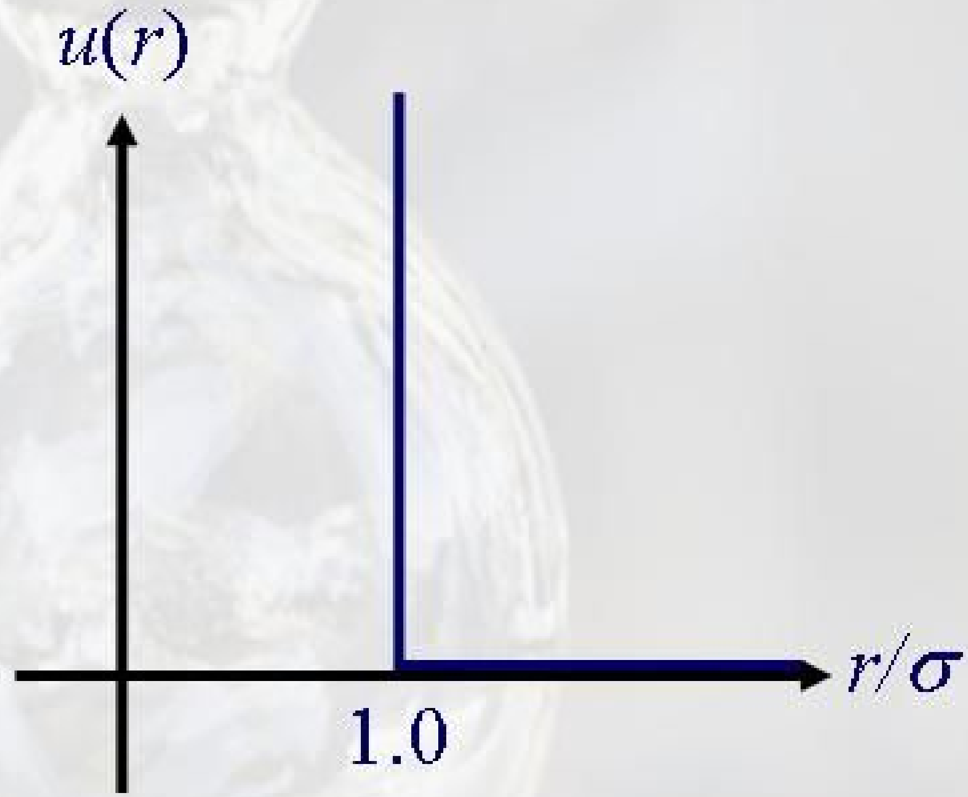


What's useful about knowing the coordinates?

Can calculate radial distribution function $g(r)$

Cornerstone of liquid state physics
Ornstein-Zernike equation

$$h(r) = c(r) + \rho \int c\left(\left|\underline{r} - \underline{r}'\right|\right) h(r')\,d\underline{r}'$$



$g(r)$ uniquely defined by $u(r)$ (pairwise additive homogenous fluid)

dilute limit $$g(r)_{\lim \rho \to 0} = \exp[-\beta u(r)]$$

Hard Spheres

$$g(r) = \begin{cases} 0 & r < \sigma \\ 1 & r < \sigma \end{cases}$$

$h(r) = g(r) - 1$ $\beta = 1/k_B T$ $c(r)$ direct correlation function CPR *et al*, *J. Chem. Phys.* **127** 044507 (2007)

Approximating the Hard Sphere Potential

- Using a modified Morse potential

The Morse potential:

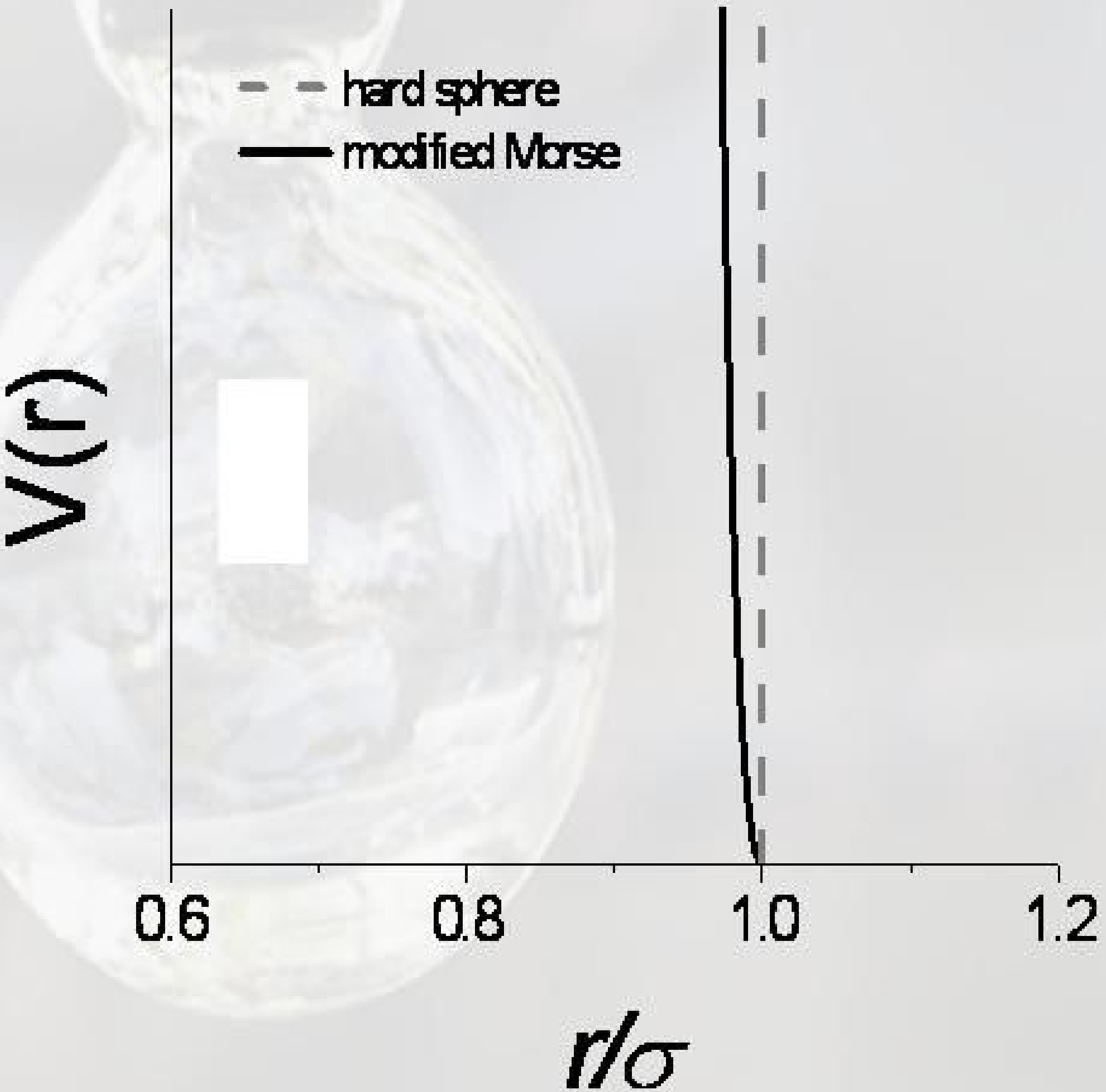
$$\beta V(r) = \varepsilon e^{\rho_0 (r_e - r)}\left(e^{\rho_0 (r_e - r)} - 2\right)$$

Where: $\beta = 1/kT$

$\varepsilon = 1$ well depth

$\rho_0 = 25$ parameter which controls the steepness and the range

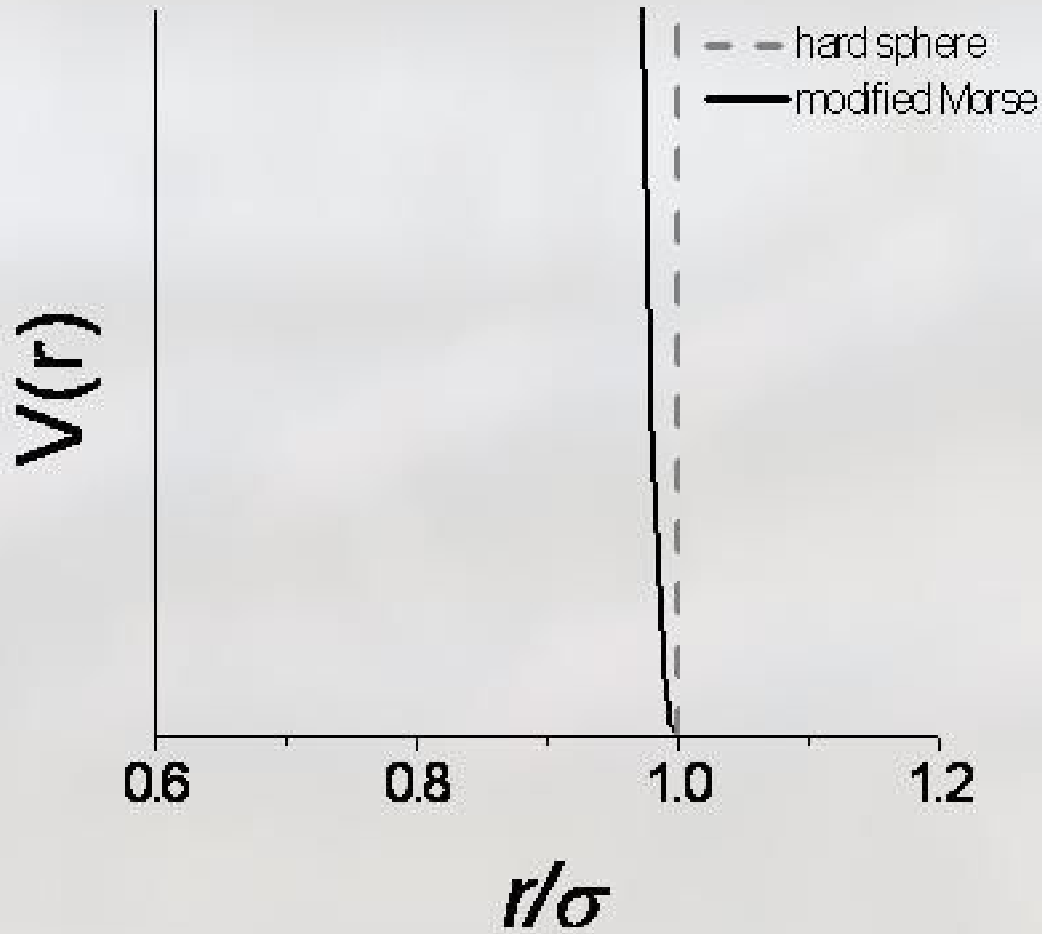
By truncating and shifting the Morse potential we get a good approximation of the hard sphere potential



The Effective Hard Sphere Diameter

- Accounting for the softness in the new potential

No longer using true hard spheres - what would the particle diameter be if it were a hard sphere?



- **Effective hard sphere diameter, σ_{eff}:**

$$\sigma_{eff} = \int_0^\infty dr\left[1 - e^{-\frac{V_{rep(r)}}{kT}}\right]$$

- **Need to adjust value of volume fraction to account for new, smaller radius**

$$\phi_{eff} = \phi\left(\frac{\sigma_{eff}}{\sigma}\right)^3$$

Barker and Henderson, ***Rev. Mod. Phys.*, 48,** 587, (1976)

Where does that leave us?

The Primitive Model

3-component system

+Ze macro-ions (colloids)

-e counter-ions

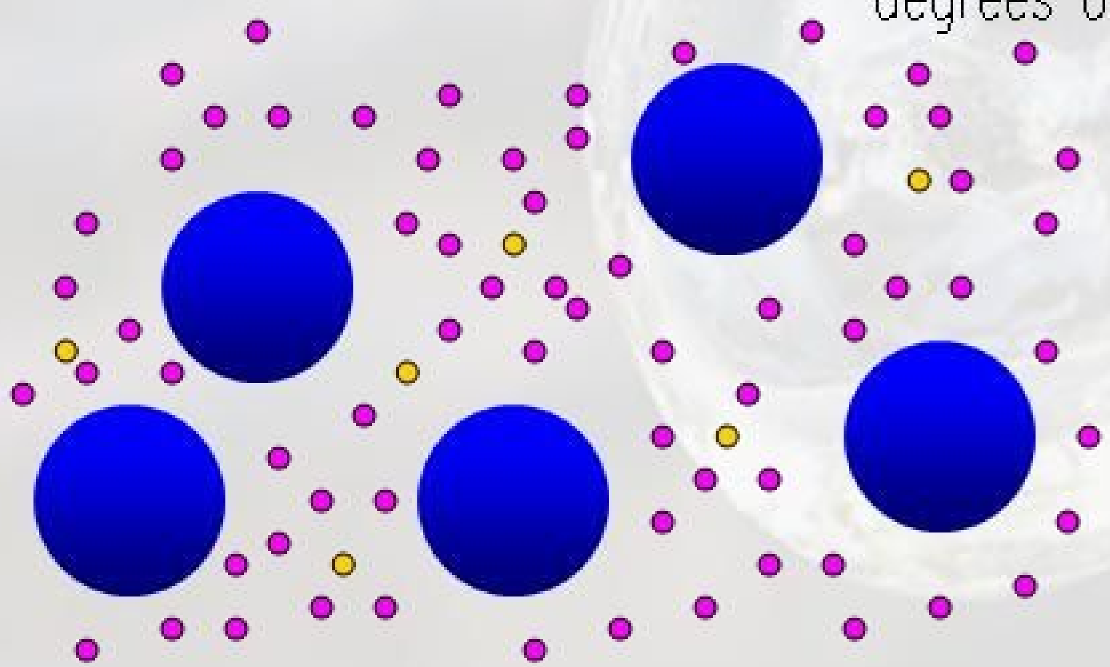
+e like-charged micro-ions

Coulomb interactions

$$u_{ij}(r_{ij}) = \frac{1}{4\pi\varepsilon}\frac{q_i q_j}{r_{ij}}$$

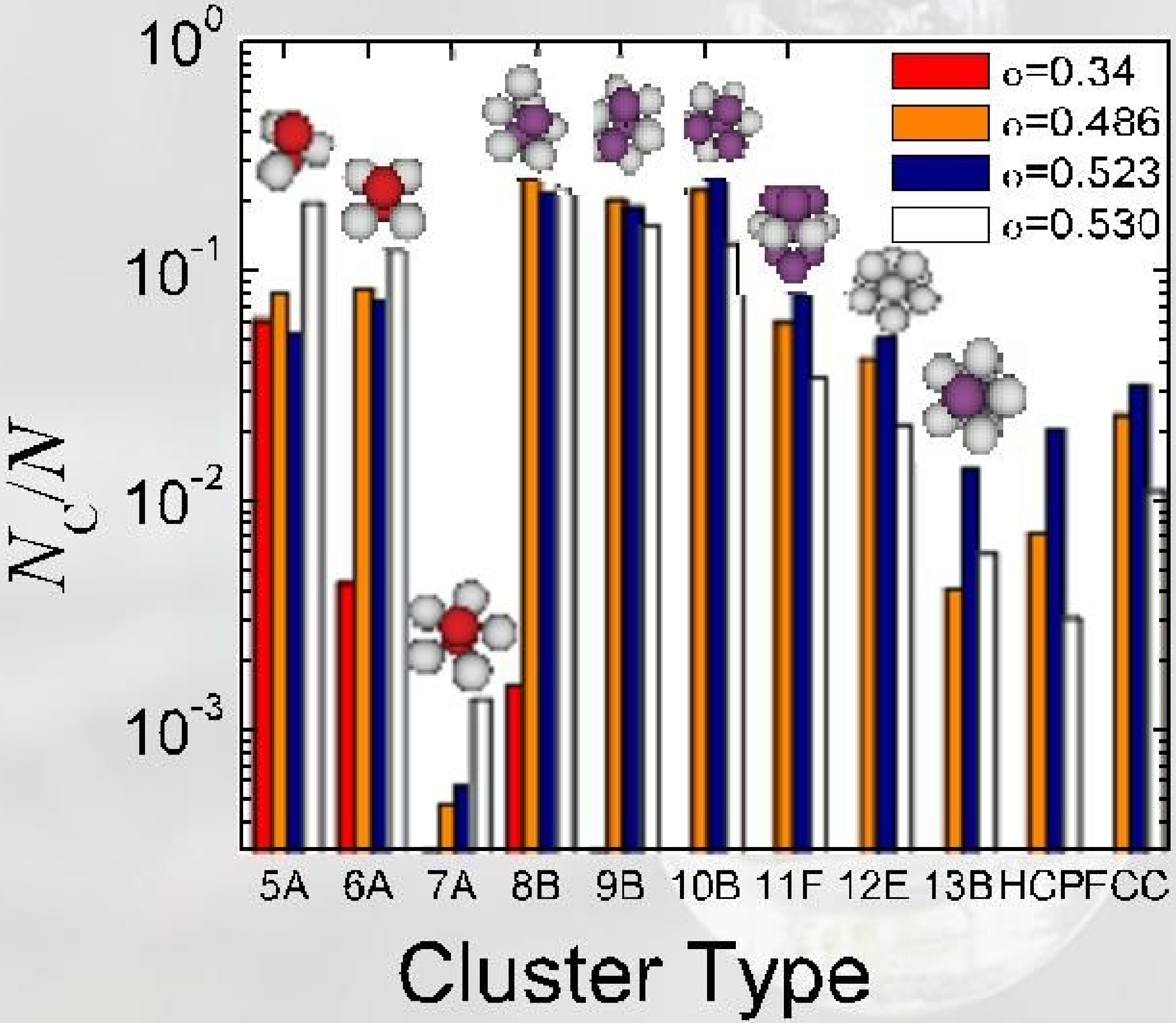
..but have too many particles to deal with

want to coarse-grain out microscopic degrees of freedom



solvent as dielectric medium ε

Locally favoured structure population approaching the hard sphere glass



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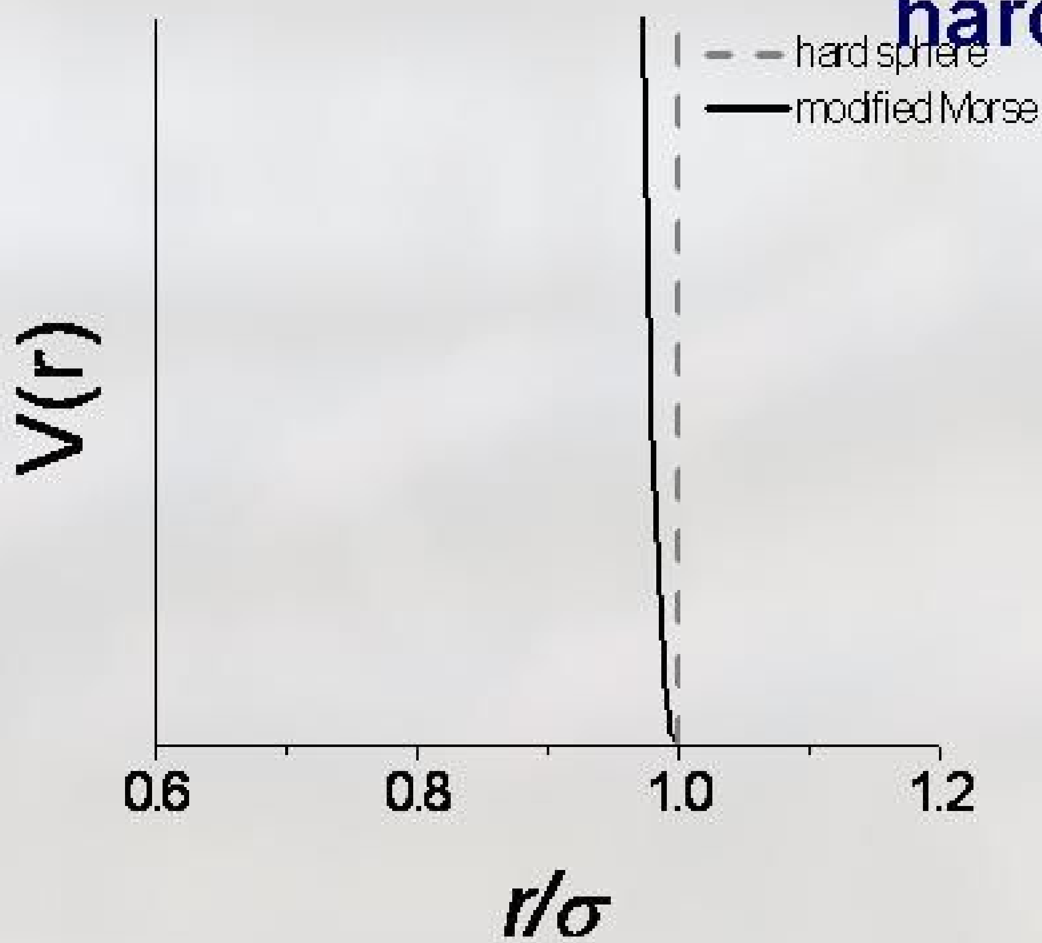


- **Effective hard sphere diameter, σ**

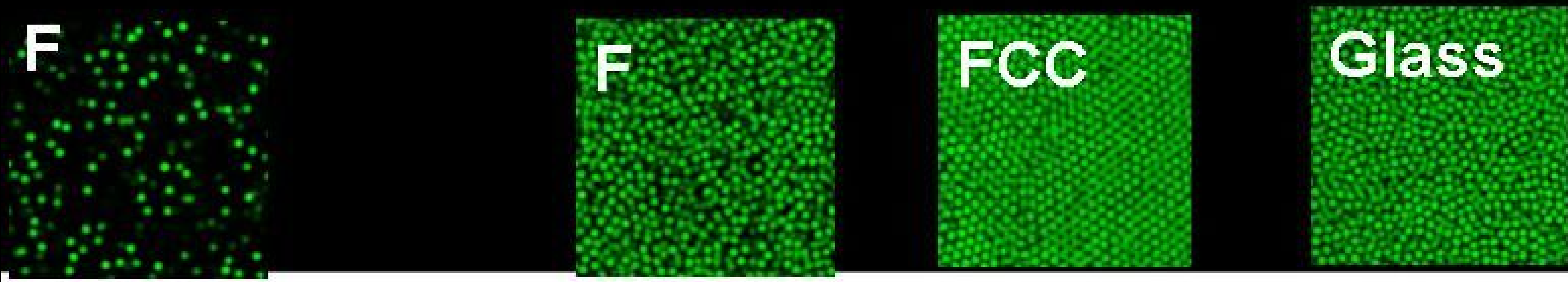
$$\sigma_{eff} = \int_0^{\infty} dr\left[1 - e^{-\frac{V_{rep(r)}}{kT}}\right]$$

- **Nee... lue of volum... ccount for new, smaller radius**

$$\phi_{eff} = \phi\left(\frac{\sigma_{eff}}{\sigma}\right)^3$$

*Barker and Henderson, Rev. Mod. Phys., 48, 587, 1976

Experimental 'hard' sphere phase diagram



0.494 0.55 0.58

colloid volume fraction ϕ_C

Truncated Morse (assuming $\sigma_{EFF} = 0.978\sigma_{HS}$)

0.528 0.587

colloid volume fraction ϕ_C

Truncated Morse+Yukawa (assuming $\sigma_{EFF} = 1.022\sigma_{HS}$)

0.461 0.513 0.58

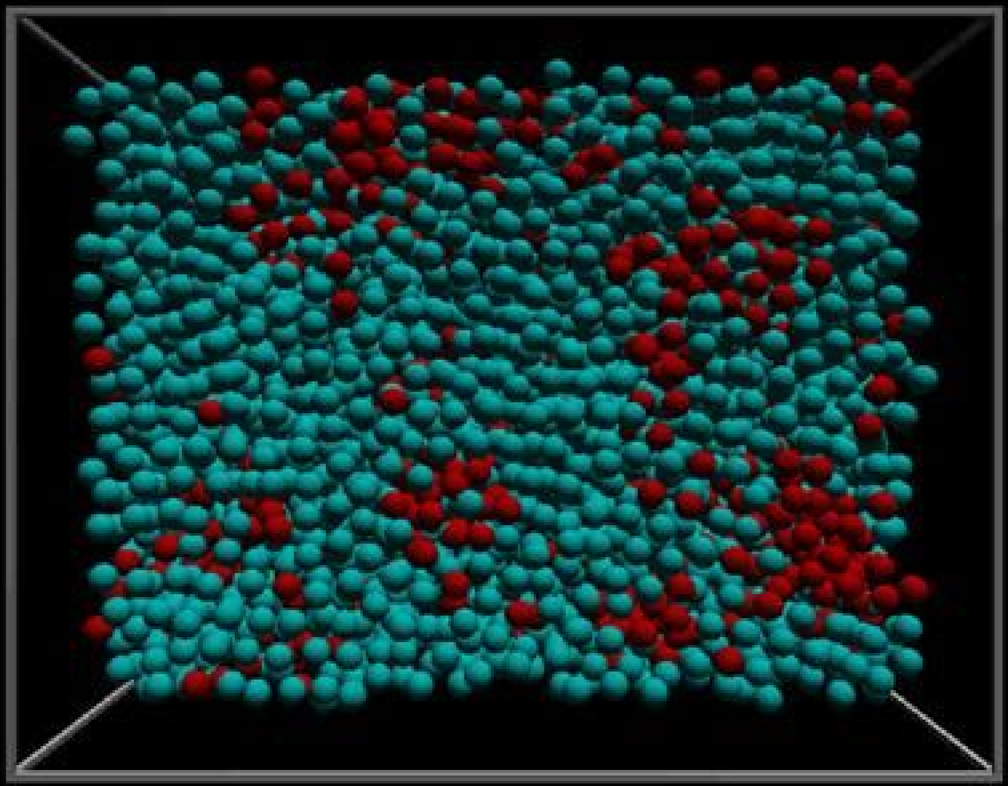
colloid volume fraction ϕ_C

Truncated Morse+Yukawa (assuming interpolating from Hynninen and Dijkstra)

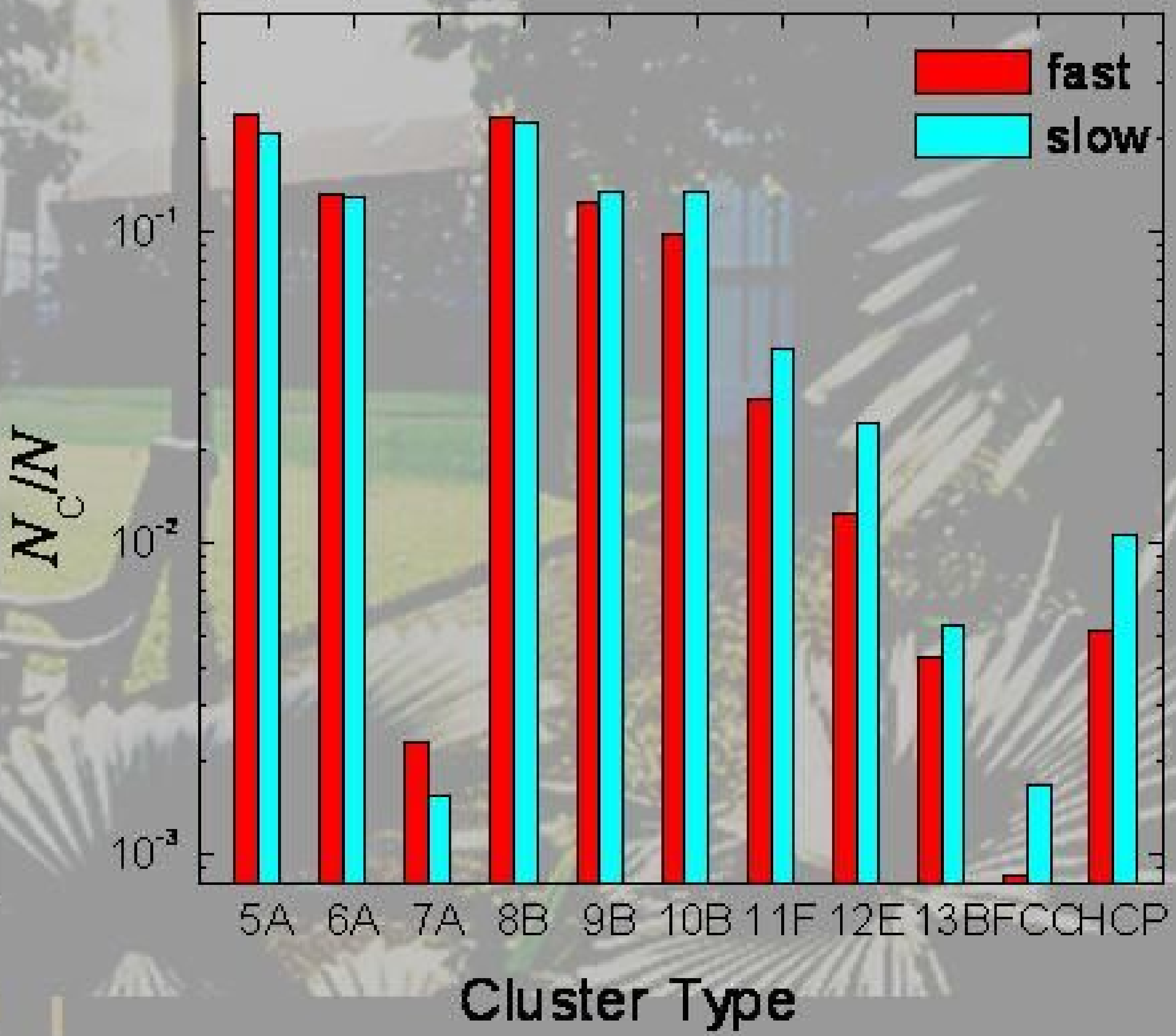
0.517 0.573 0.58

colloid volume fraction ϕ_C

Locally favoured structures / dynamical heterogeneities



fastest 10% : red



LFS populations

cf Weeks *Science* 2001

The New York Times

The nature of glass remains anything but clear

"Many people tell me this is very contentious.
I disagree violently with them."
Peter Wolynes, UCSD ✓

"The arrangement of atoms and molecules in glass is indistinguishable from that of a liquid." ✗

New York Times July 2008

Acknowledgements - you for your attention

Bristol
Alex Malins, Jens Eggers (gels, liquids)
Ian Williams, Isla Zhang, Adam Irwin
Rebecca Rice, Anais Marquis (liquid-liquid transition)
Monica Moreno, Jade Taffs (nucleation)
Paul Hopkins (binary Yukawa)

Utrecht
Alfons van Blaaderen

Stuttgart
Roland Roth (anisotropic particles)

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Pietro Cicuta, David Snoswell, 2D systems
Daan Frenkel (polymorphism)

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Richard Sear (nucleation)

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Stephen Williams (TCC)

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Hajime Tanaka
Takehiro Ohtsuka (W_6)
Mathieu Leocmach (particle tracking)
Chris Klix (clusters)
Kenichiro Murata

Duesseldorf
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Adam Wysocki (Rayleigh-Taylor)
Martin Rex (Laning)

Oxford
Dirk Aarts (criticality)
Ard Louis (liquid state theory)

Nagoya
Junpei Yamanaka (binary charged)

Paris/Osaka
Didi Derks (interfaces)

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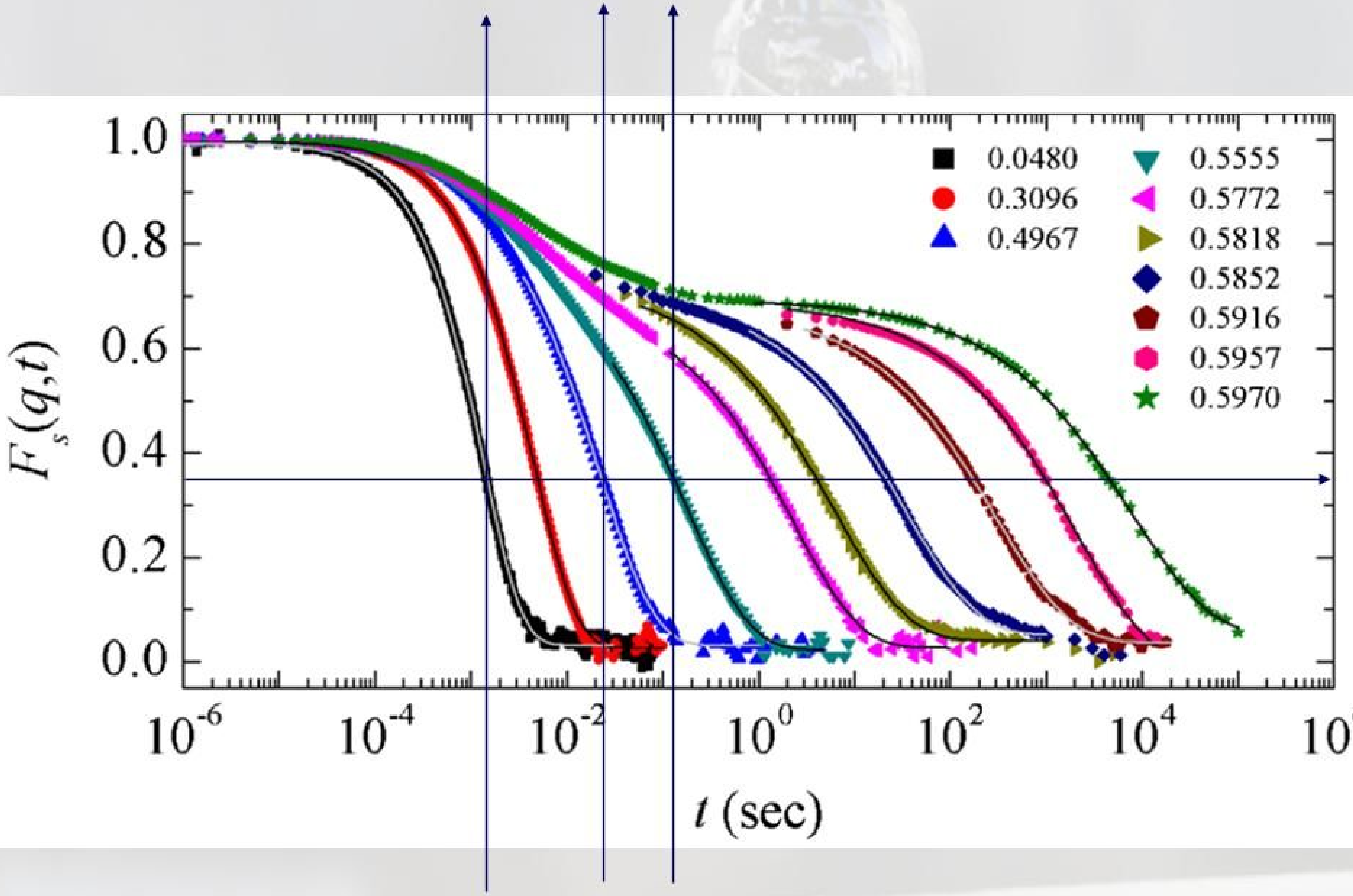

El Masri et al *J. Stat. Mech. P07015* (2009)