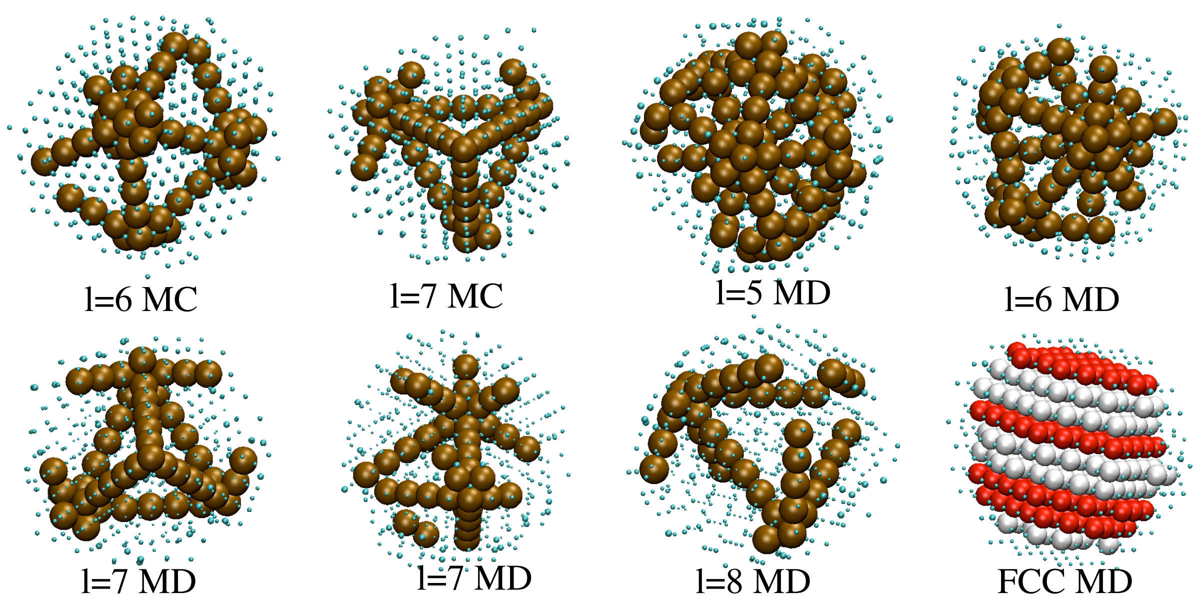
Competitive nucleation in nanoparticle clusters.

NAG, Bengaluru, July 2010



Eduardo Mendez-Villuendas, Ivan Saika-Voivod
Louis Poon, Cletus Asuquo,
Richard Bowles
University of Saskatchewan

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Overview

Background

Simulation Techniques

Surface Freezing in Gold Nanoparticles

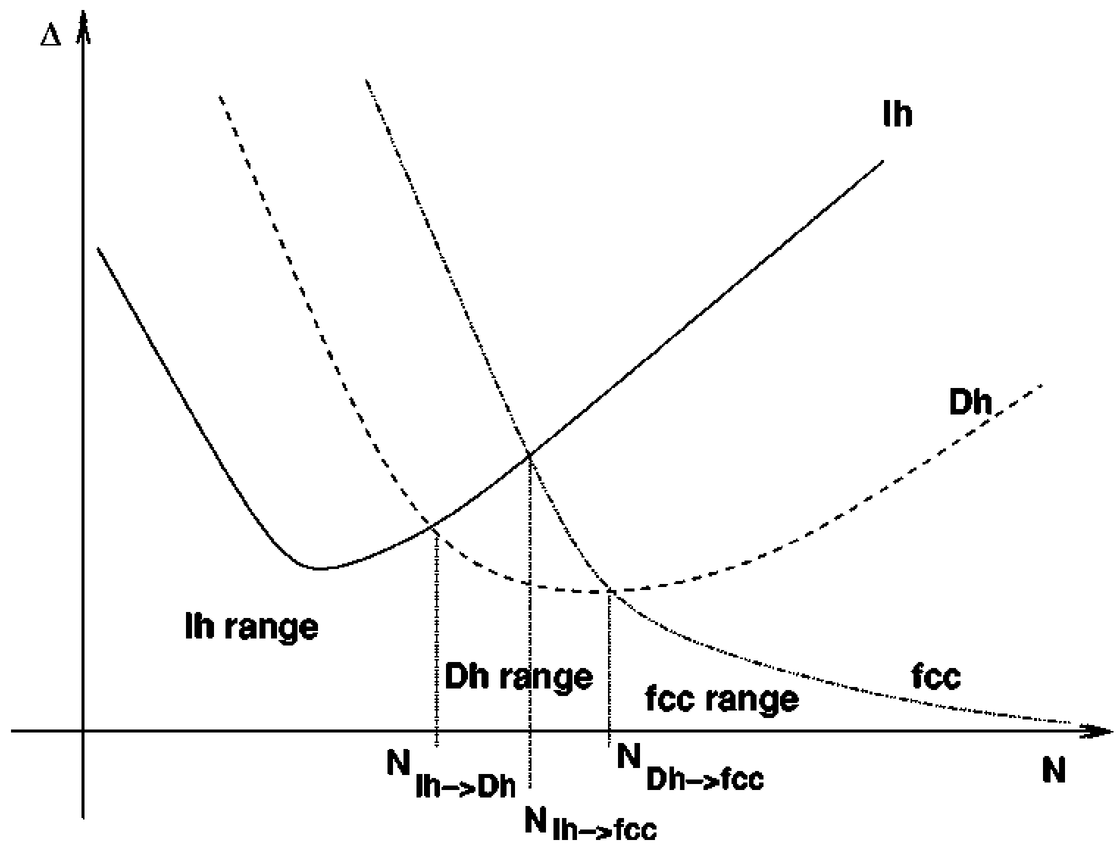
Freezing in Medium Sized Lennard Jones

Another look at gold

Summary

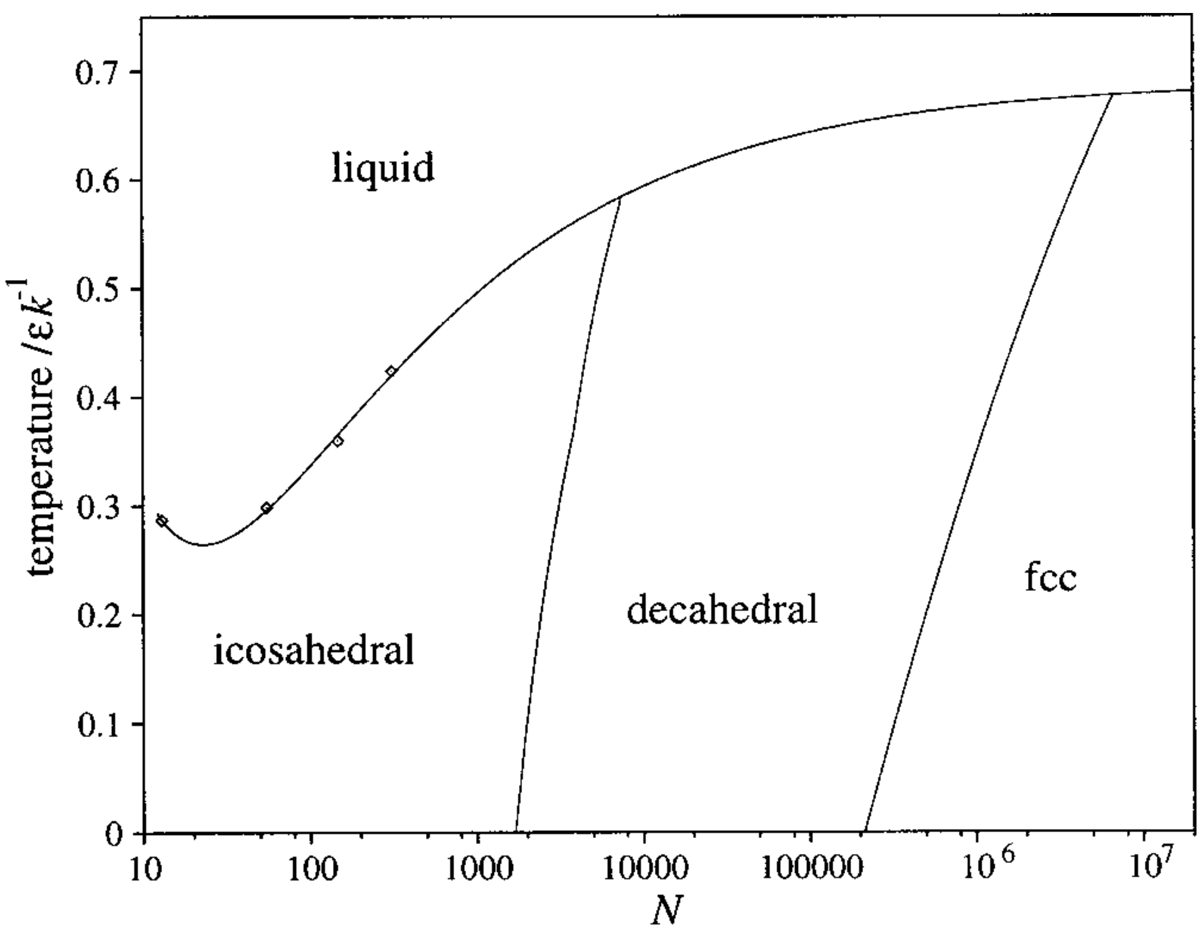
Phase Behaviour of Clusters

$$\Delta(N) = \frac{E_b(N) - N\epsilon_{coh}}{N^{2/3}}$$

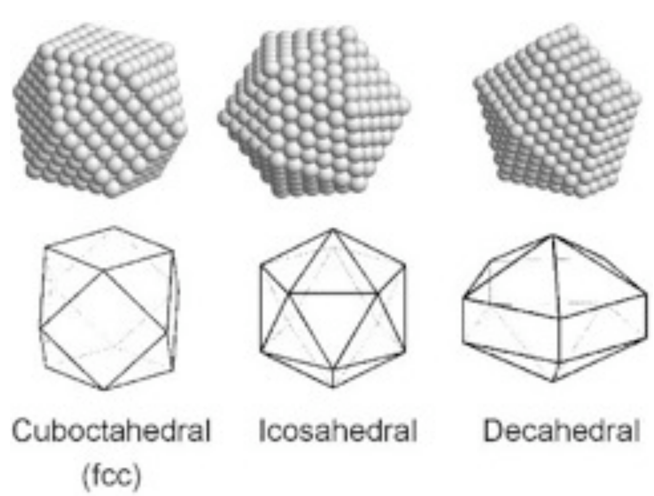


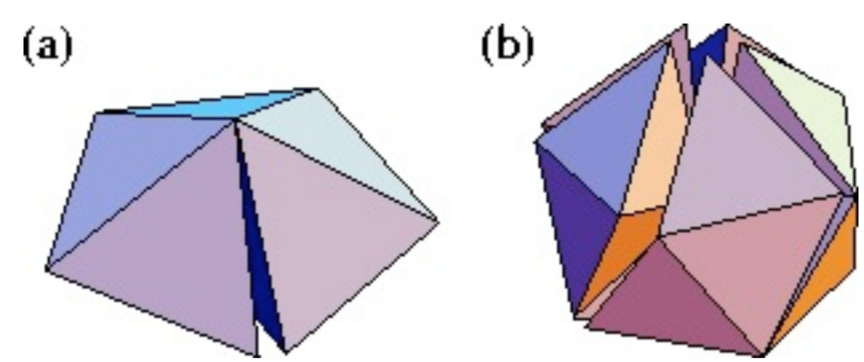
F. Baletto, R. Ferrando, Rev. Mod. Phys., 77, 371 (2005).

Lennard Jones Clusters



J. P. K. Doye, F. Calvo,J. Chem. Phys., 116, 8307 (2002).





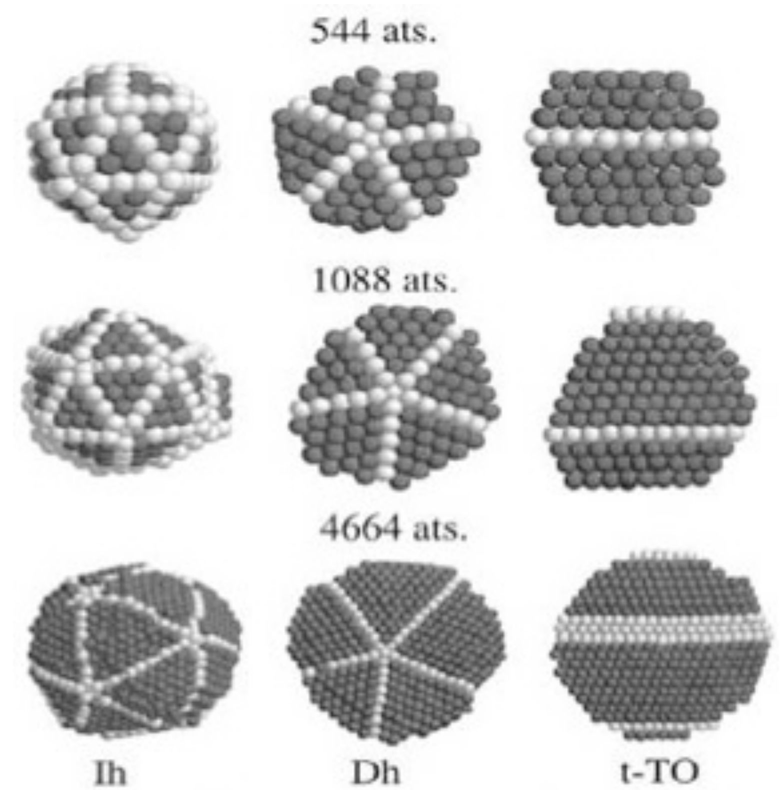
J. P. K. Doye, webpage

Which structure is nucleated?

Gold: FCC is the most stable structure n > 300

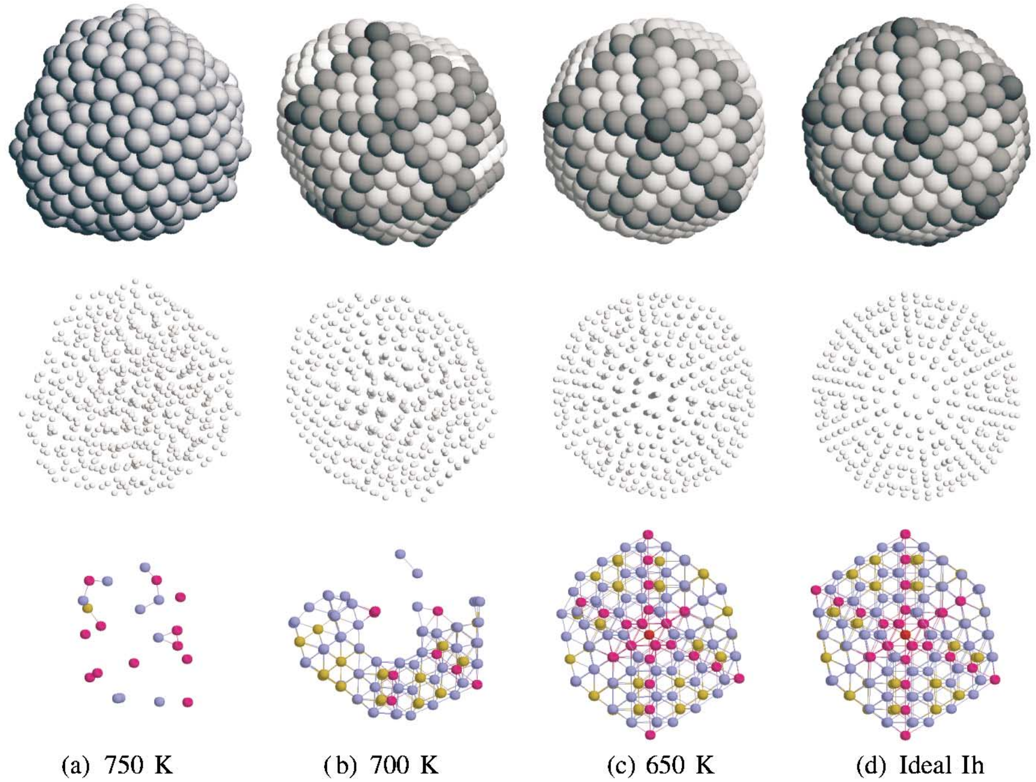
TABLE 3: Distributions of Final Configurations Materializing Spontaneously during the Freezing of Gold Nanoclusters

	459-atom clusters		1157-atom clusters			3943-atom clusters	
structure	700 K	720 K	700 K	720 K	740 K	720 K	740 K
Ih	18	19	12	13	12	7	7
Dh	1	1	2	1	4	1	4
TO	1		6	4	3	2	1
HCP				2		1	
???						1	
total	20	20	20	20	19	12	12

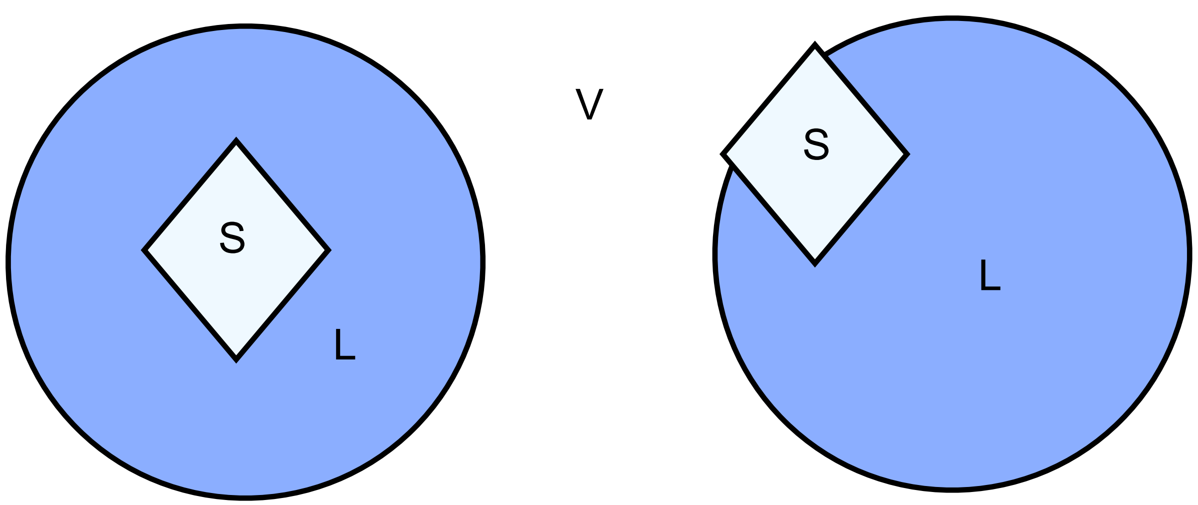


Y. G. Chushak, L. S. Bartell, J. Phys. Chem. B, 105, 11605 (2001)

Surface Nucleation



H. S. Nam et al., Phys. Rev. Lett, 89, 275502 (2002)



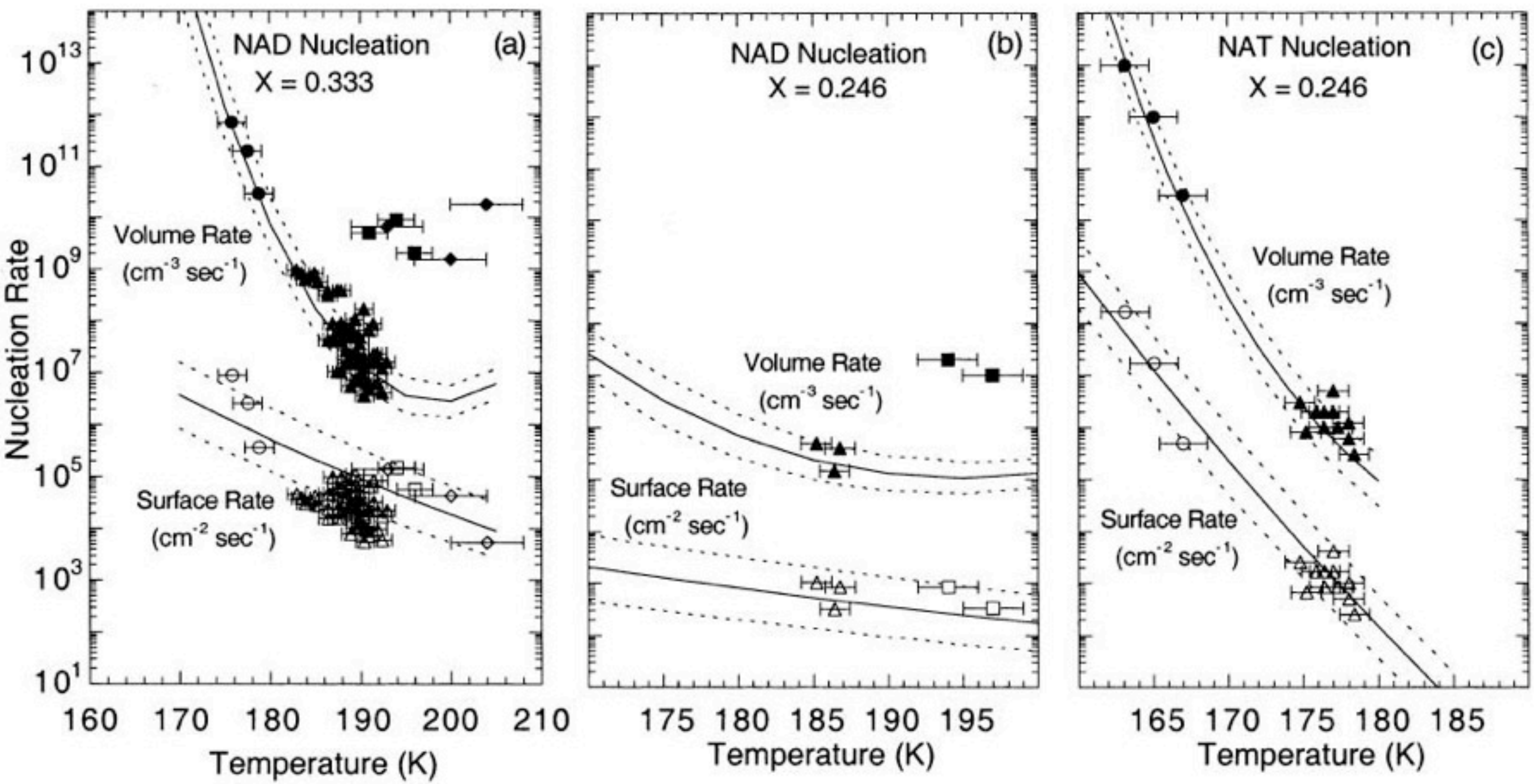
$$\sigma_{vs} - \sigma_{vl} < \sigma_{ls}$$

condition for partial wetting of crystal by melt

Y. S. Djikaev et al., J. Phys. Chem. A, 106, 10247 (2002)

Surface Effects

Surface Nucleation of Stratospheric Cloud Particles *J. Phys. Chem. A, Vol. 106, No. 43, 2002* **10243**



Some Questions

Which structures can nucleate from a liquid nanopartcle?

Icosahedra, decahedra, FCC based, but are there others?

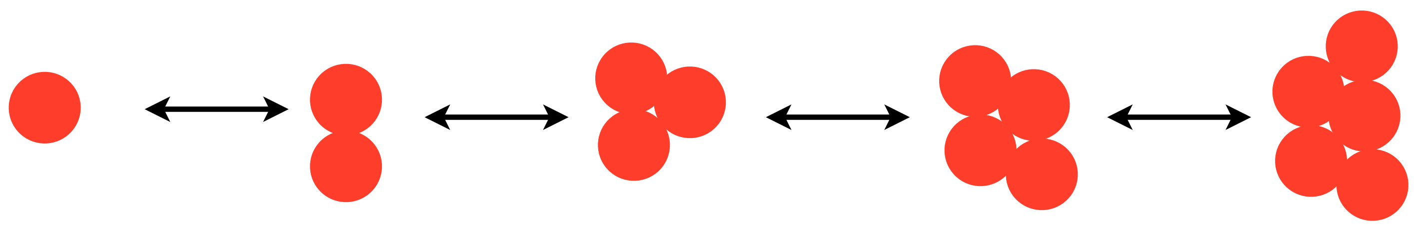
How are the different structures formed?

What reaction coordinate describes the reaction?
How do non-crystalline structures form?

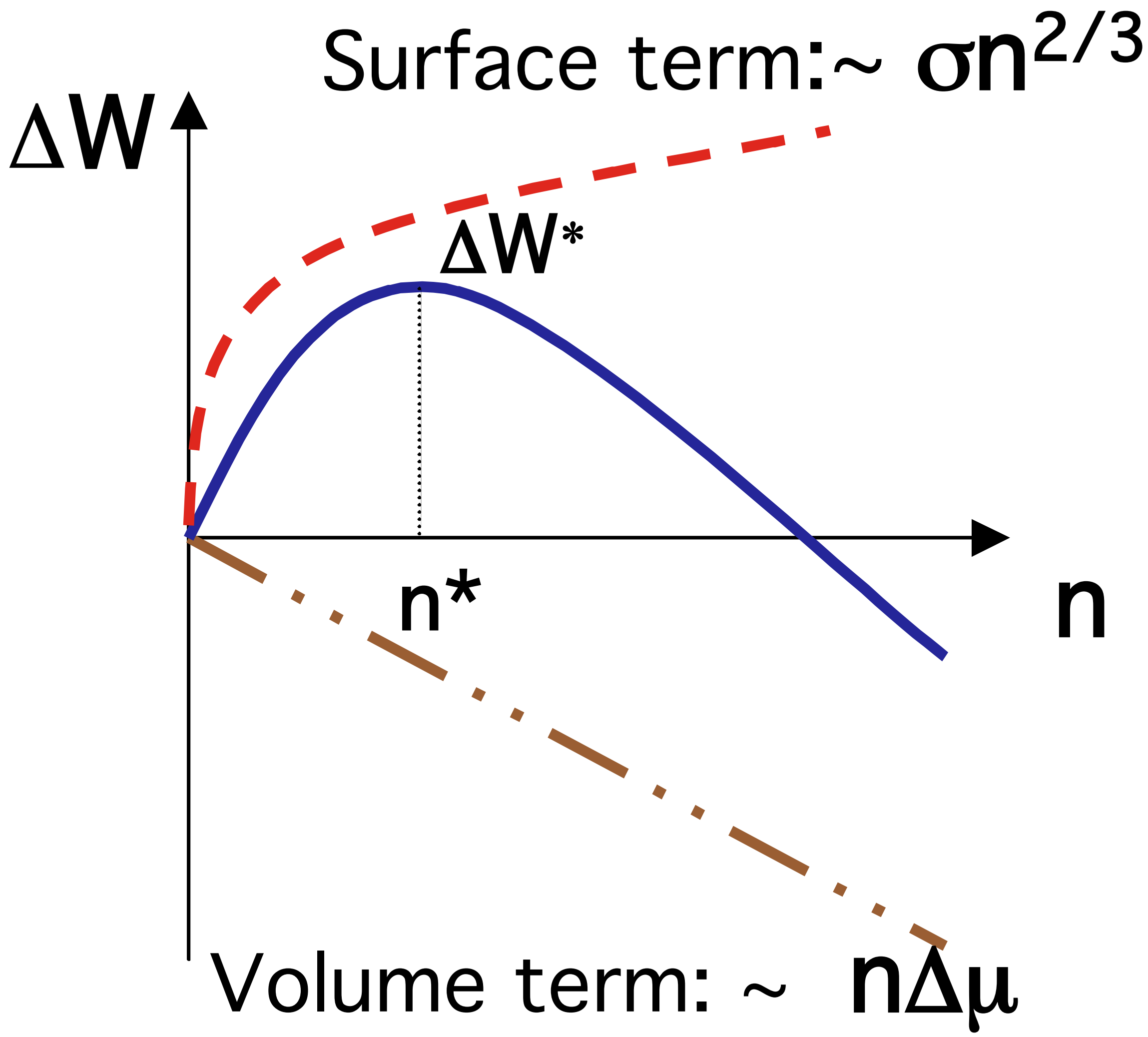
What is the role of surface phenomena in the freezing process?

Gold clusters freezes from the surface, LJ clusters freeze from the core yet they form similar structures!

Classical Nucleation



$$J = j(n^*) Z N_n(n^*) \qquad W = n\Delta\mu + a\sigma n^{2/3}$$



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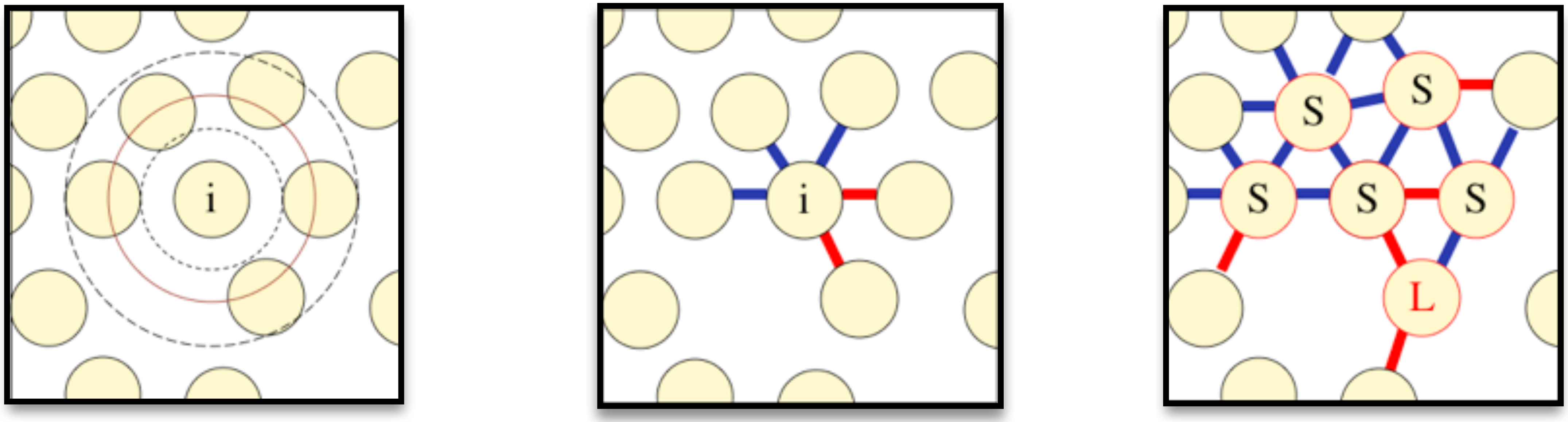
Molecular Approach

Embryo Criteria

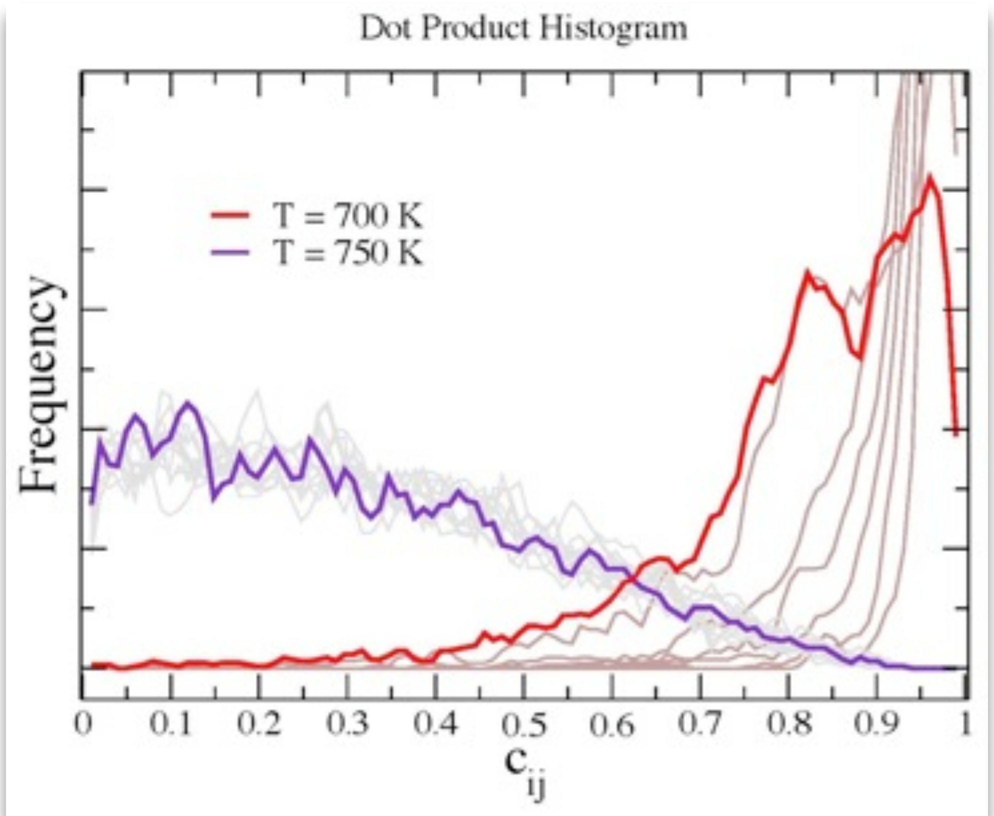


n-sized embryo as reaction coordinate

Local Order

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

$$\mathbf{q}_6(i) \cdot \mathbf{q}_6(j) = \sum_{m=-6}^{m=6} q_{6m}(i) \cdot q_{6m}(j)$$



Free Energy Barrier Calculations

Rare Embryo-Low/Moderate Supercooling

$$J = j(n^*) Z N_n(n^*)$$

$$\langle N_n \rangle = P_n(1) + 2P_n(2) + 3P_n(3) + \cdots +$$

$$P_n = P_n(1) + P_n(2) + P_n(3) + \cdots +$$

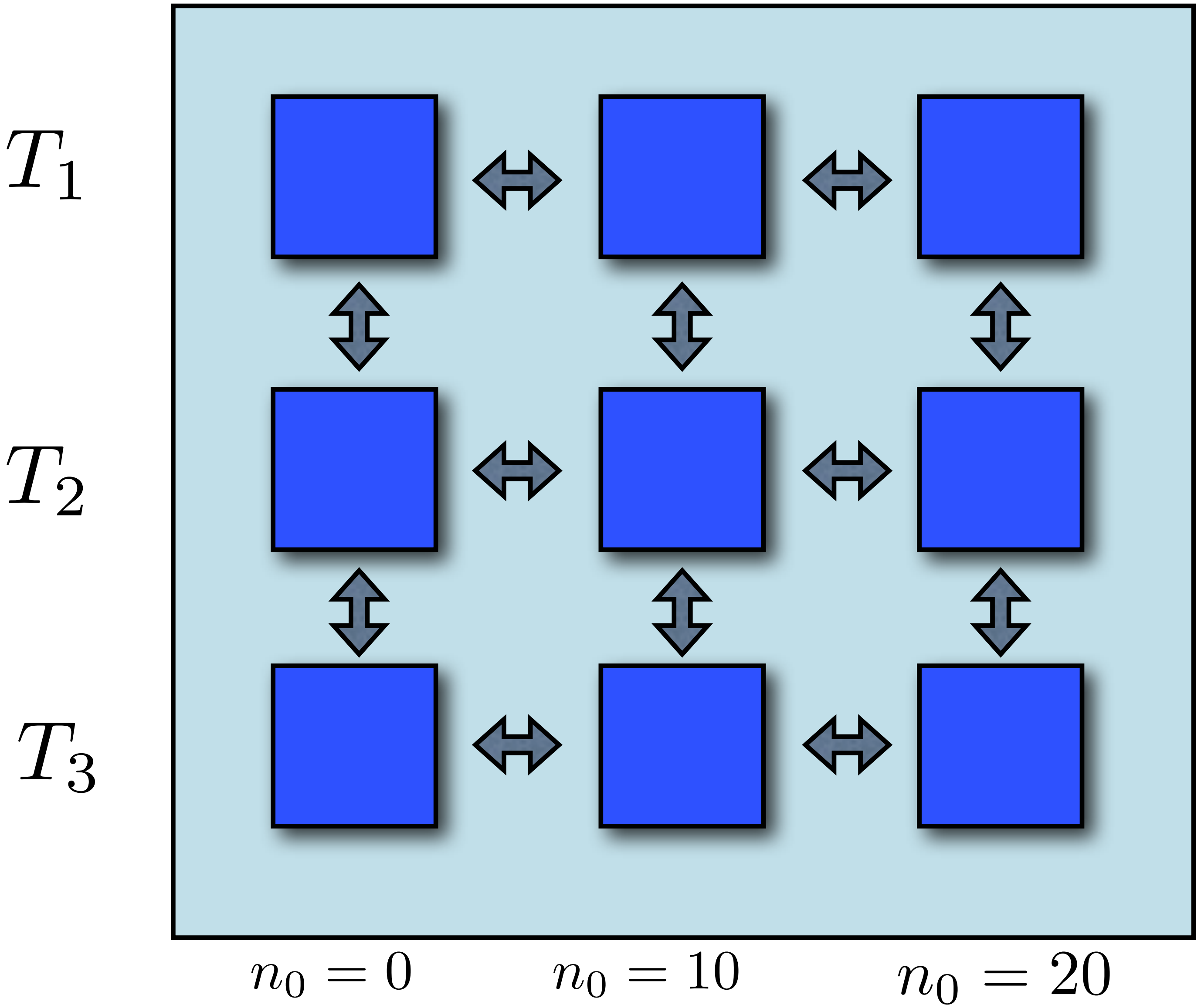
$$N_n \approx P_n = \exp[-W(n)]$$

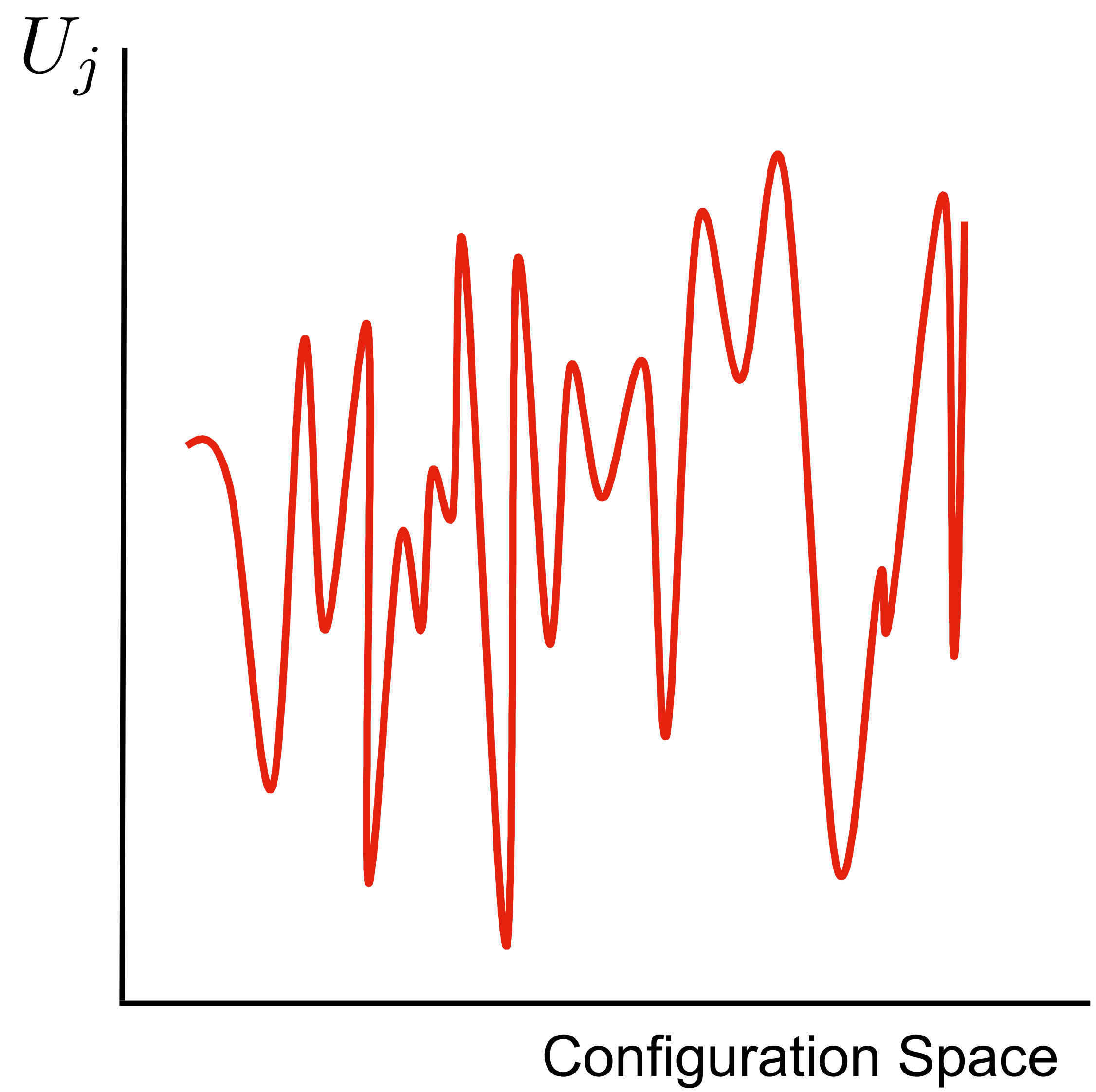
Work of forming an embryo within the metastable fluid phase

Simulation Techniques

Parallel Tempering

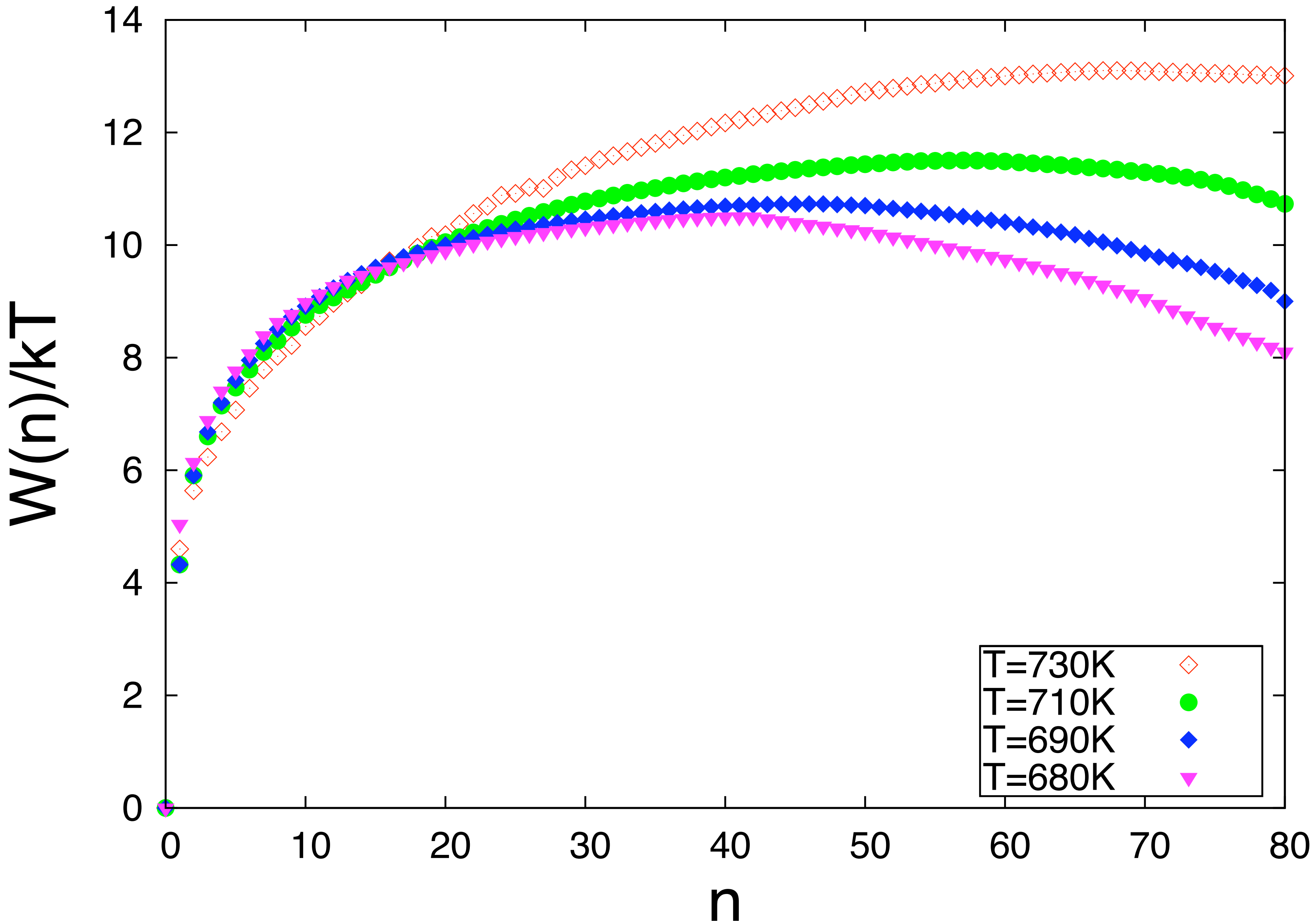
Overcoming kinetic barriers in the formation of complex structures





$$Q_{extended} = \prod_i \prod_j Q(N, V, T_i, U_j)$$

Free Energy Barrier
Gold Nanoparticle N=456 atoms



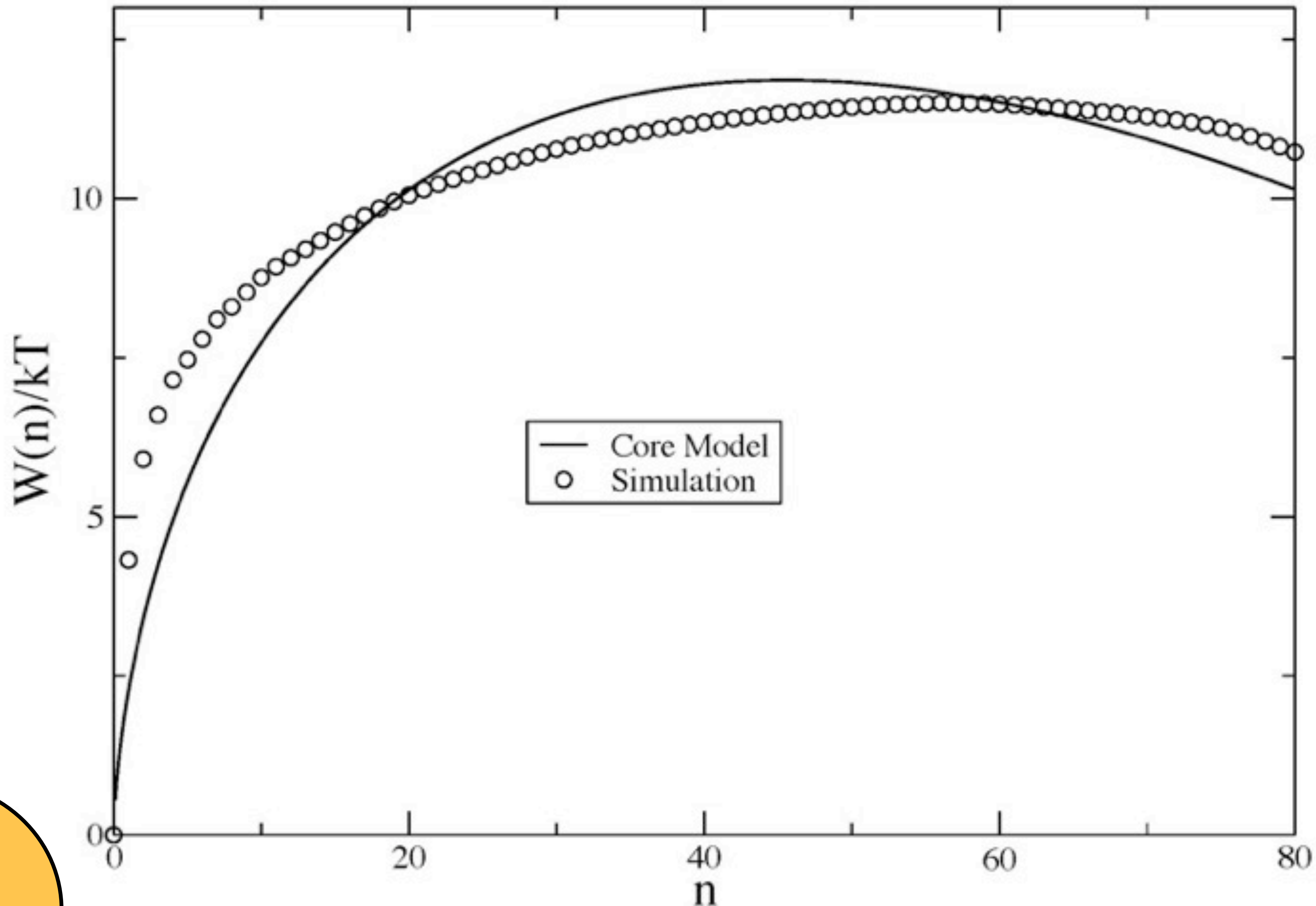
$$N_n \approx P_n = \exp(-W/kT)$$

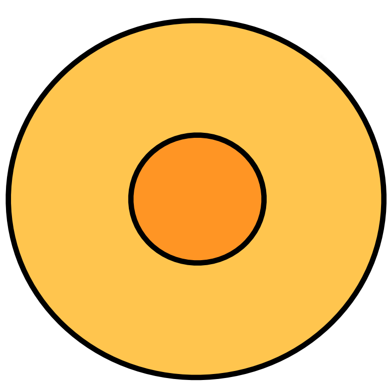
Umbrella Sampling and Parallel Tempering

E. Mendez-Villuendas and R.K.B, PRL, 98 185503 (2007).

Core Nucleation

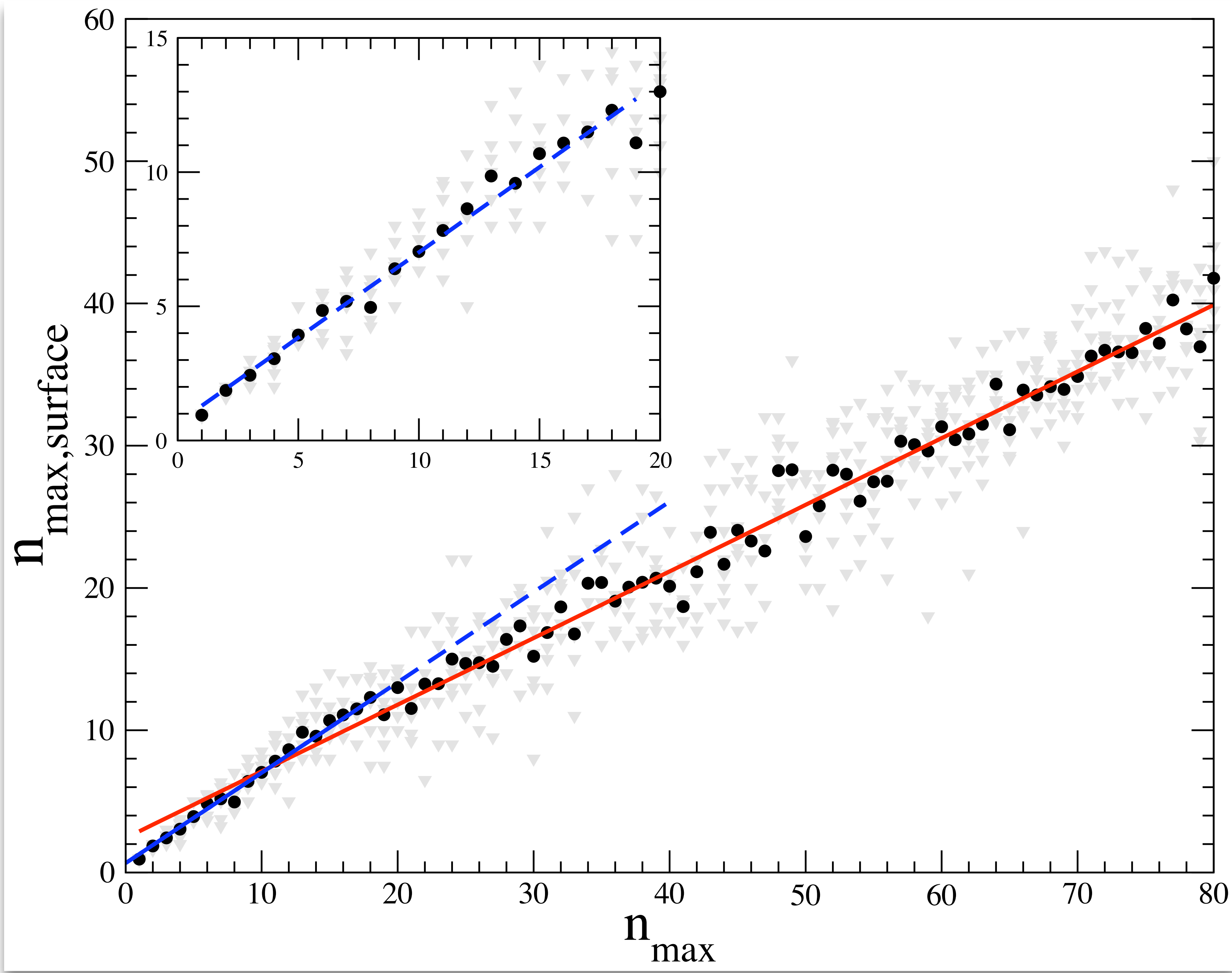
Gold Nanoparticle N=456 atoms

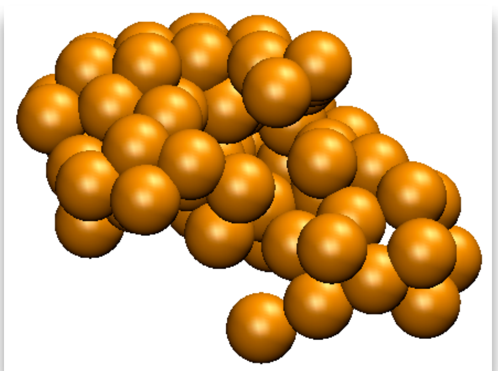


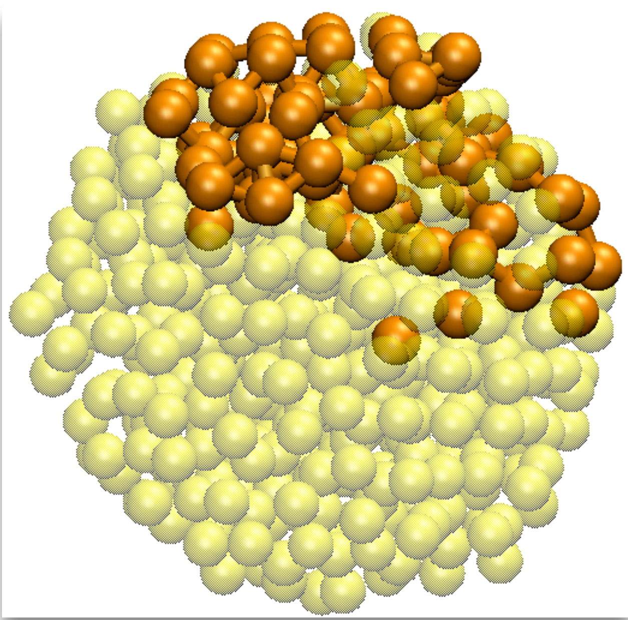


Core Nucleation

Gold Nanoparticle N=456 atoms

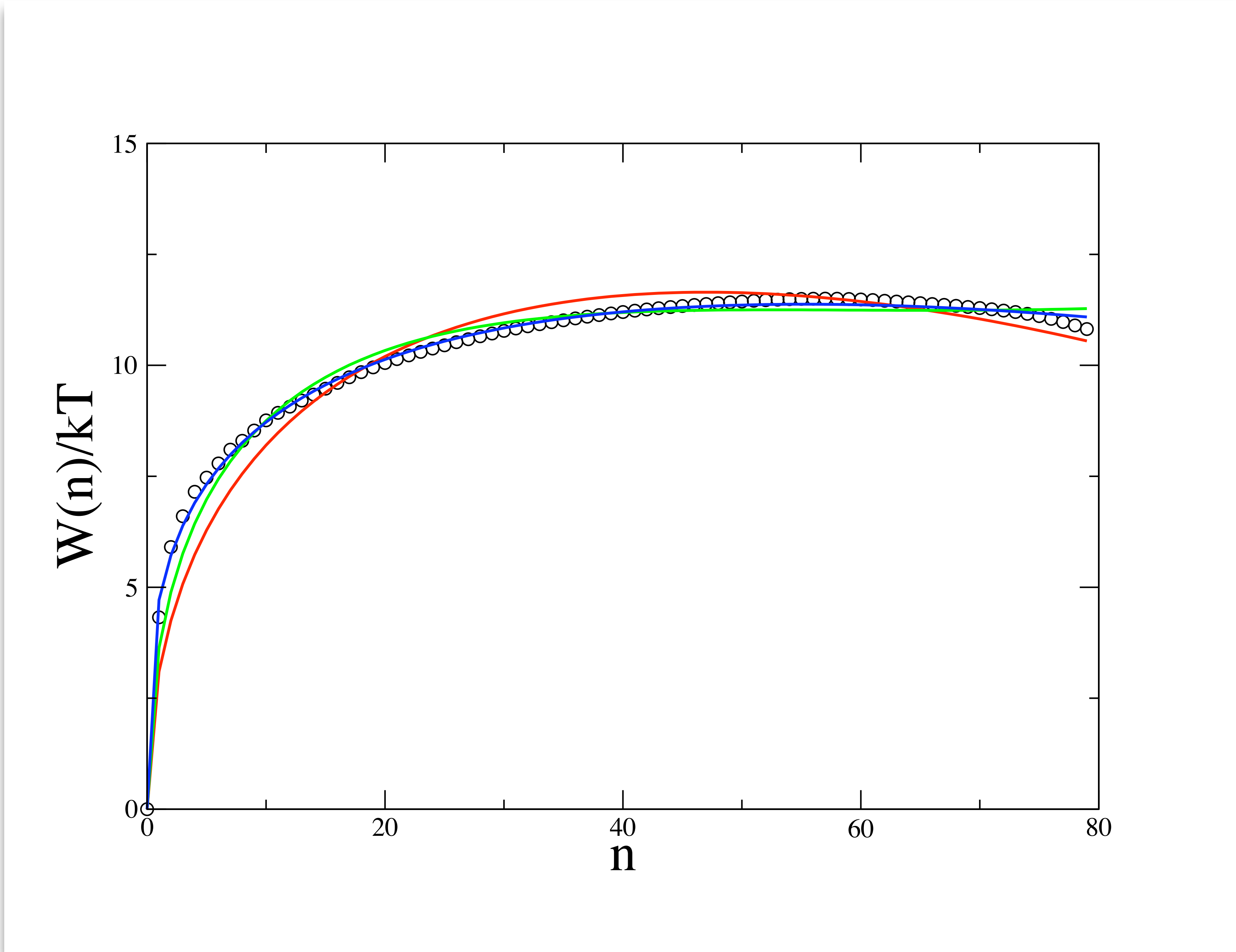


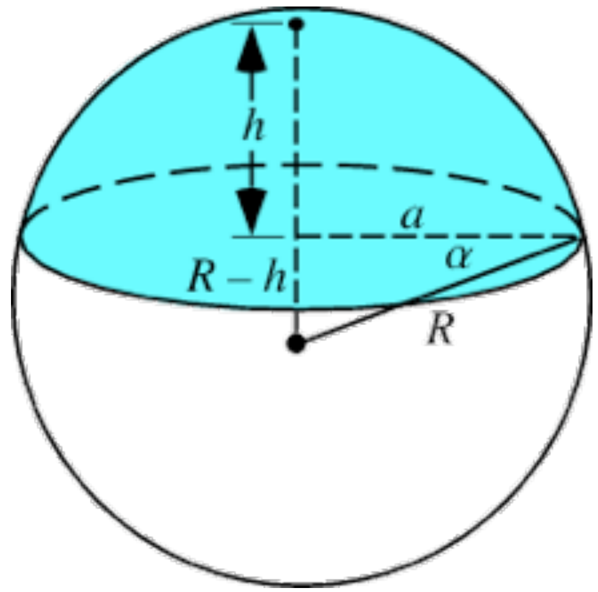


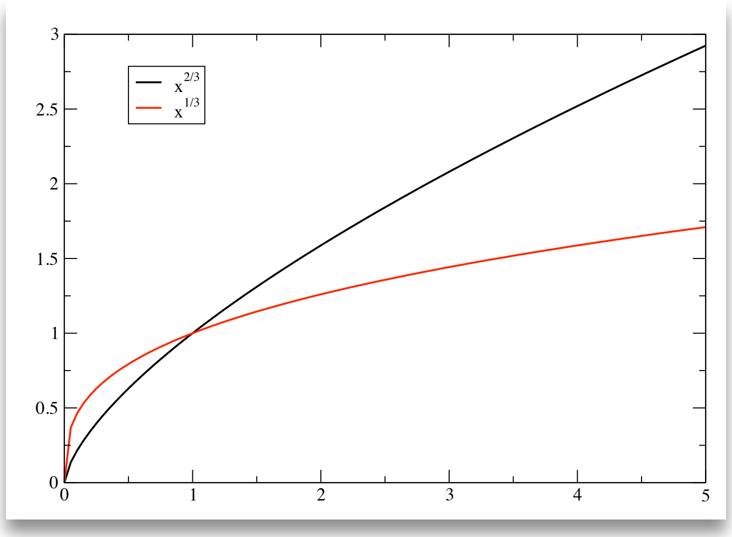


Surface Nucleation

Spherical cap model



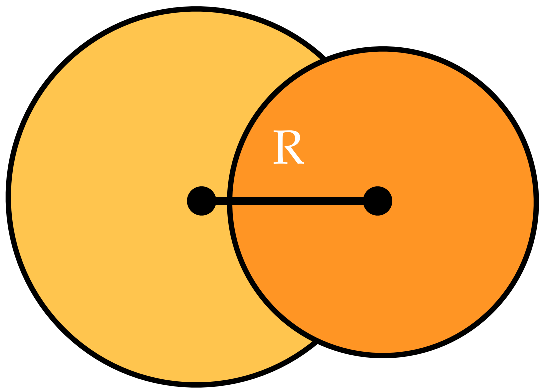


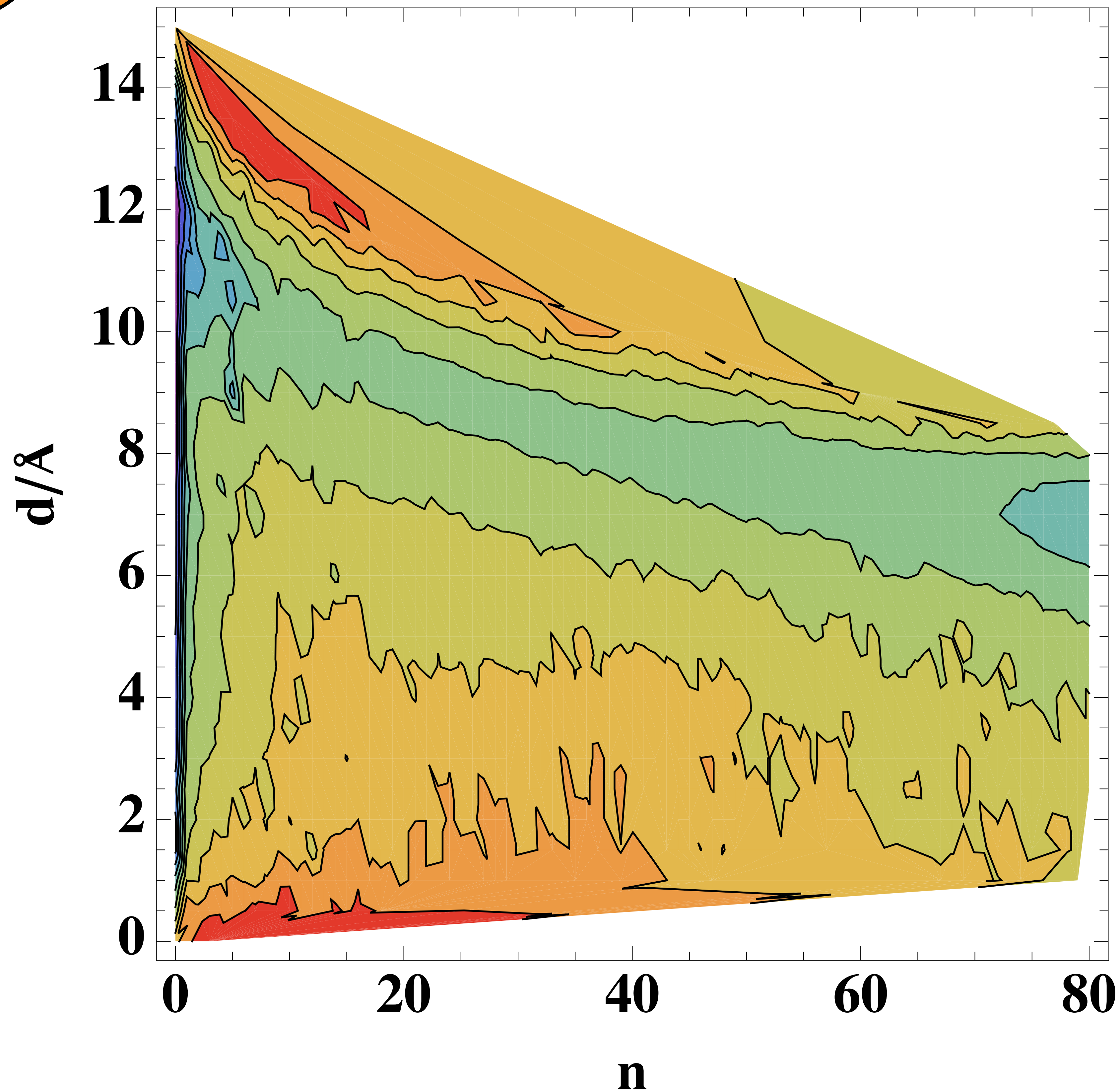


$$W(n)/kT = n\Delta\mu + A_{lv}\sigma_{lv} + A_{sv}\sigma_{sv} + A_{ls}\sigma_{ls} + l_{slv}\tau$$

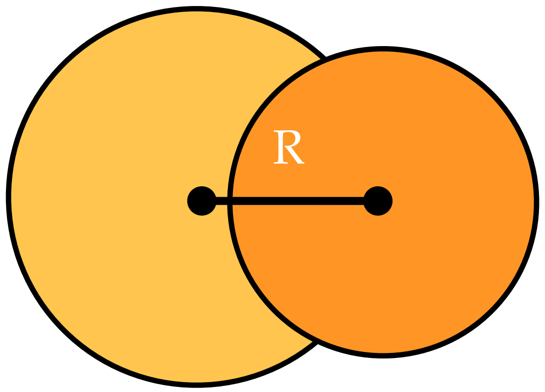
Surface Nucleation

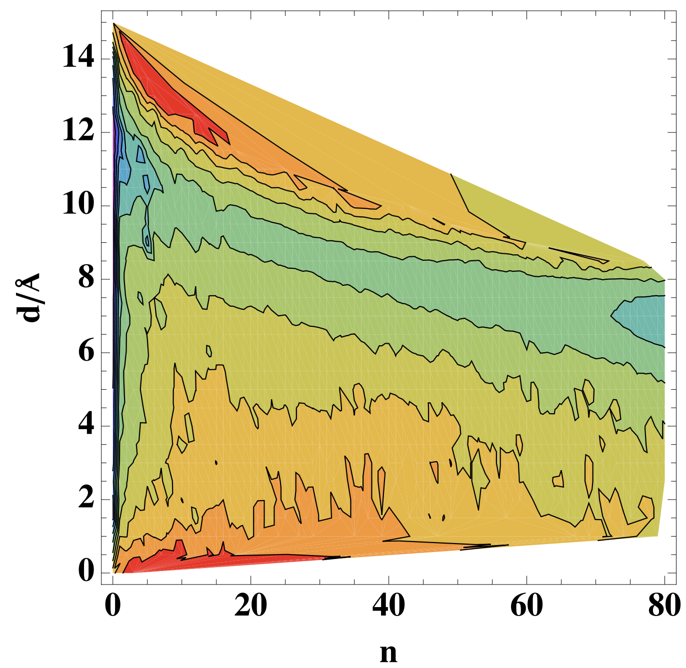
Sphere-in-Sphere model

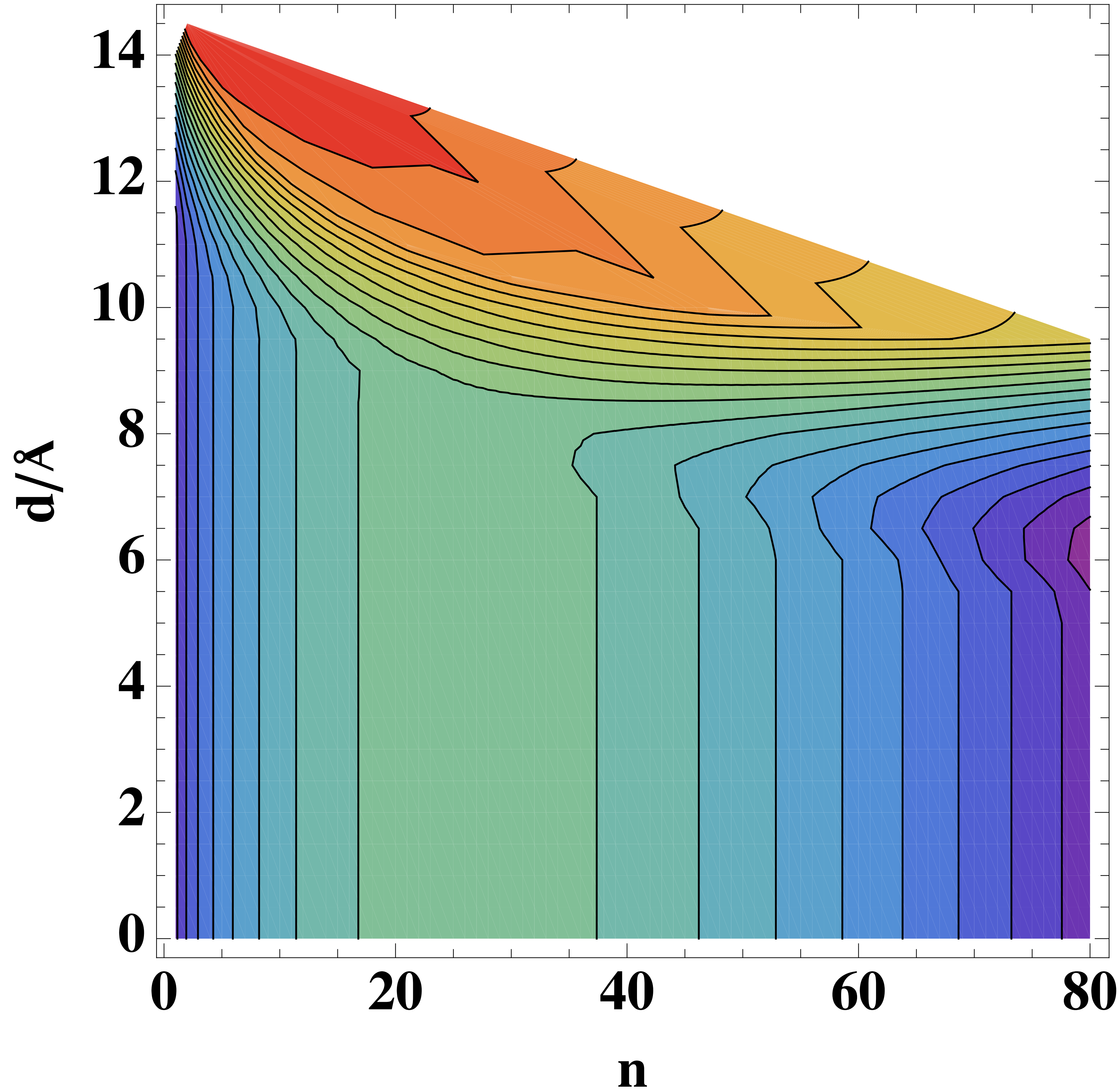




Surface Nucleation
Sphere-in-Sphere model

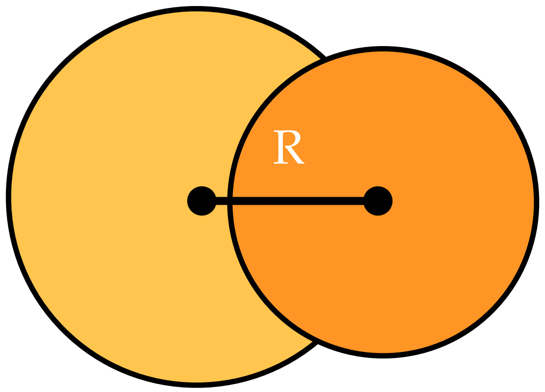


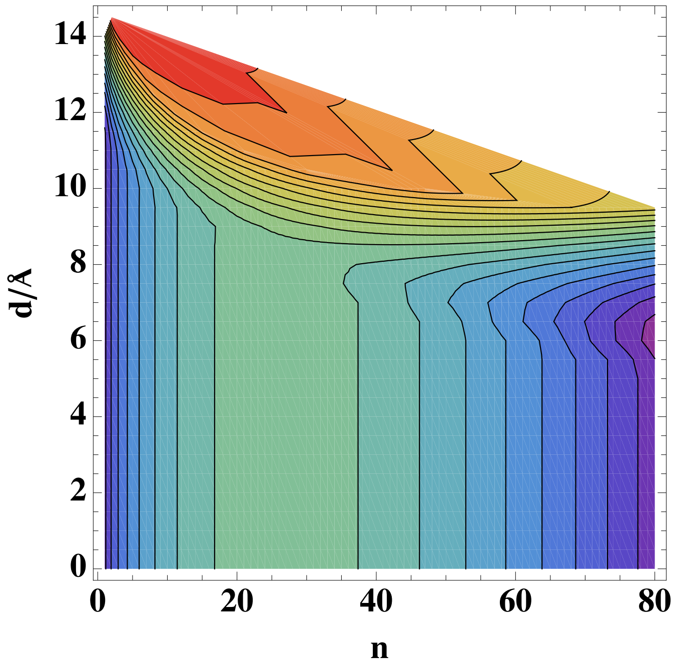


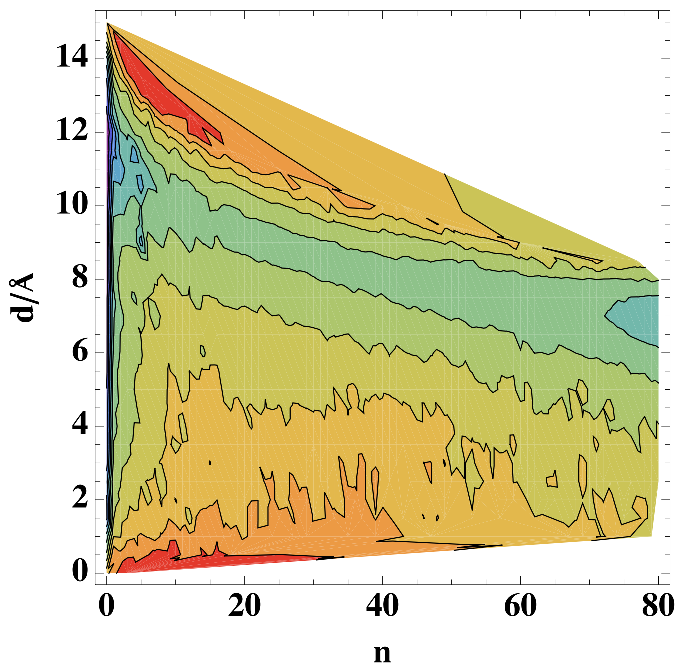


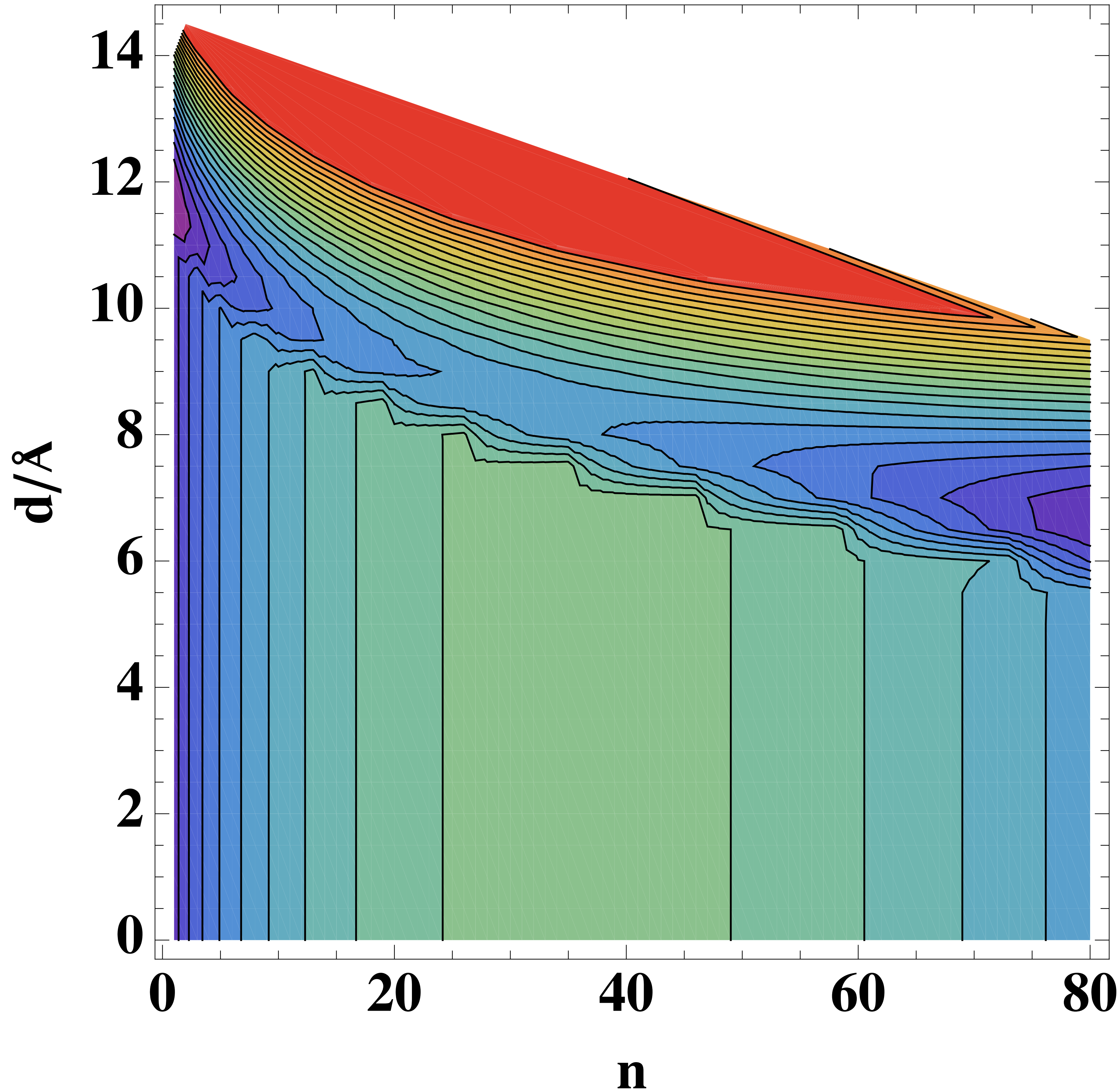
Surface Nucleation

Sphere-in-Sphere model









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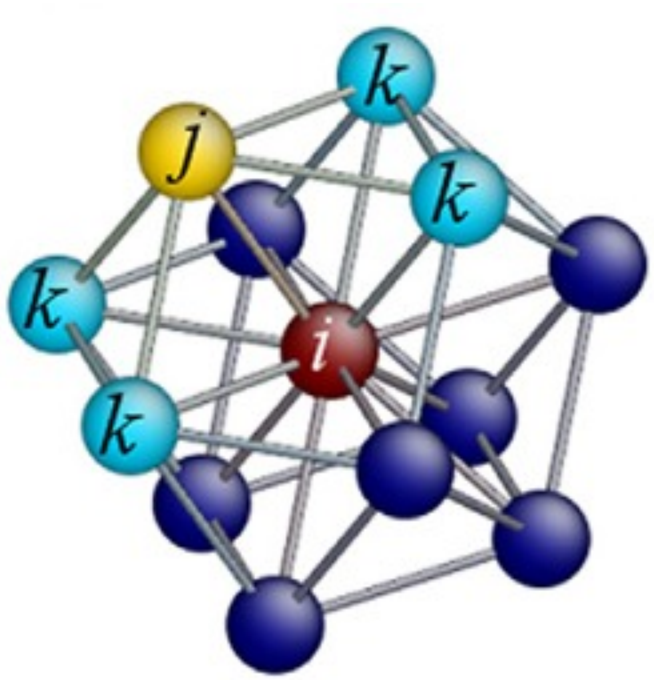
Medium sized Lennard Jones Clusters

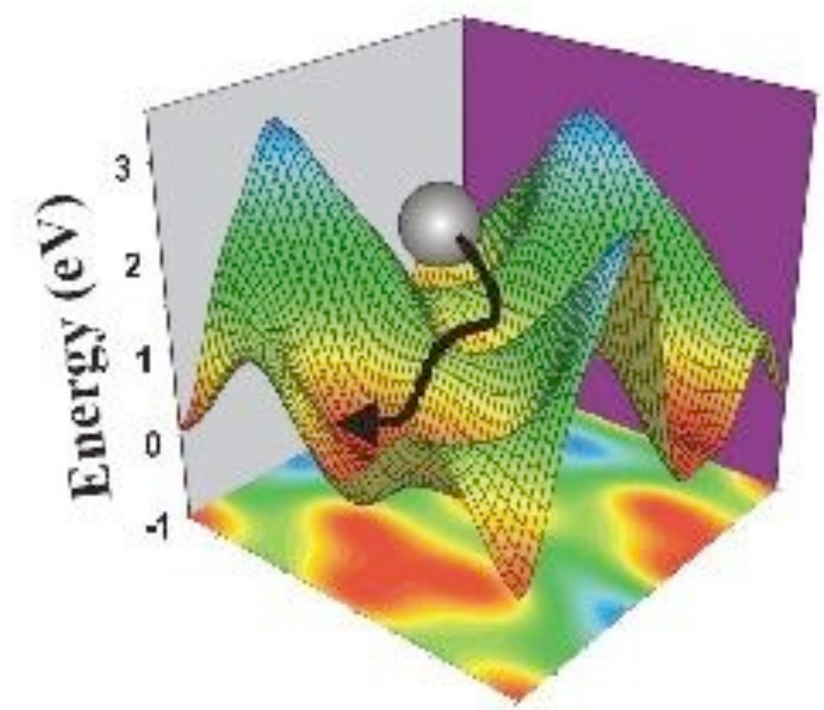
Identifying Different Structures

Common neighbour Analysis



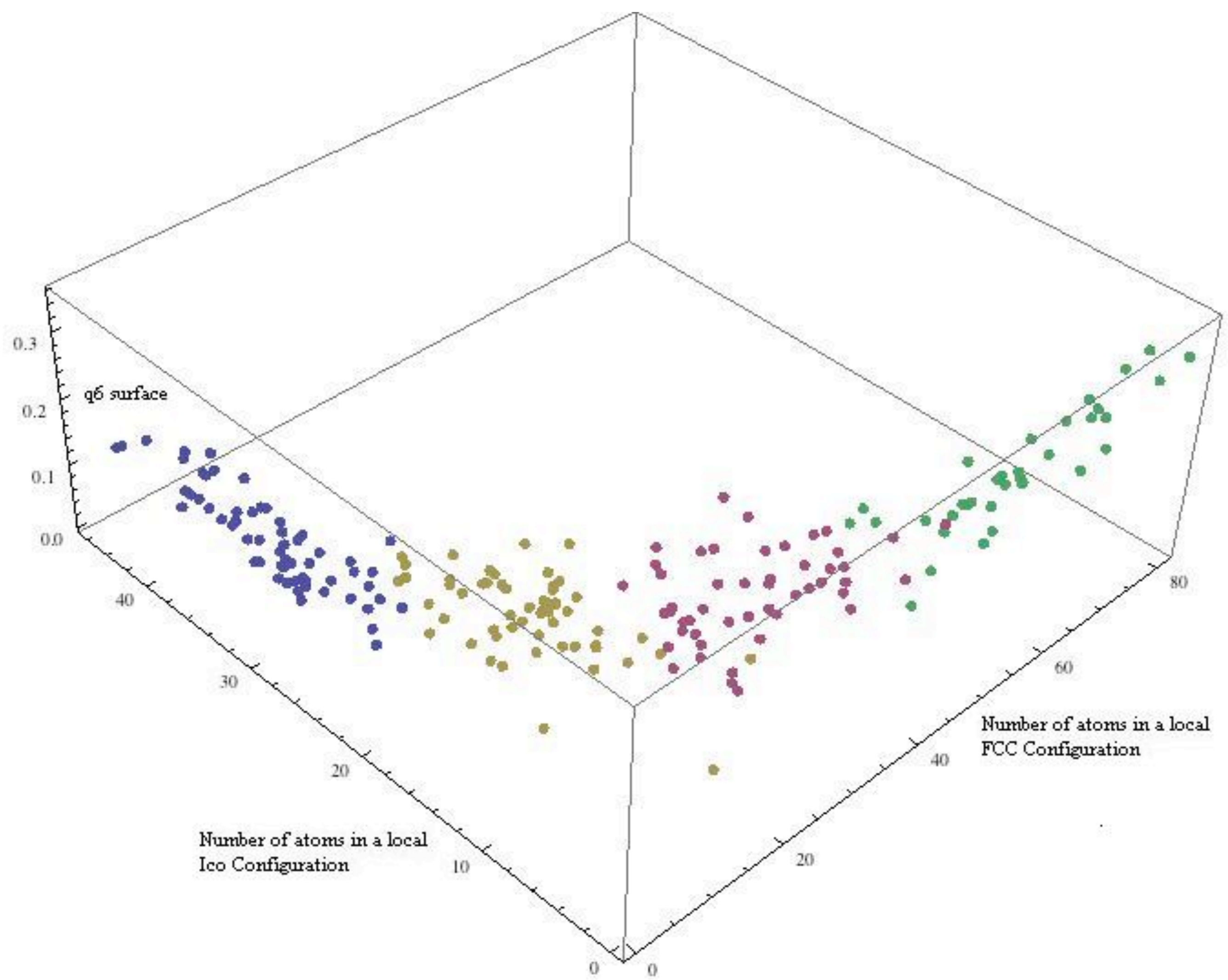
H. Tsuzuki et al., *Comp. Phys. Comm.,* **2007**, 177 518–523

Inherent structure quench

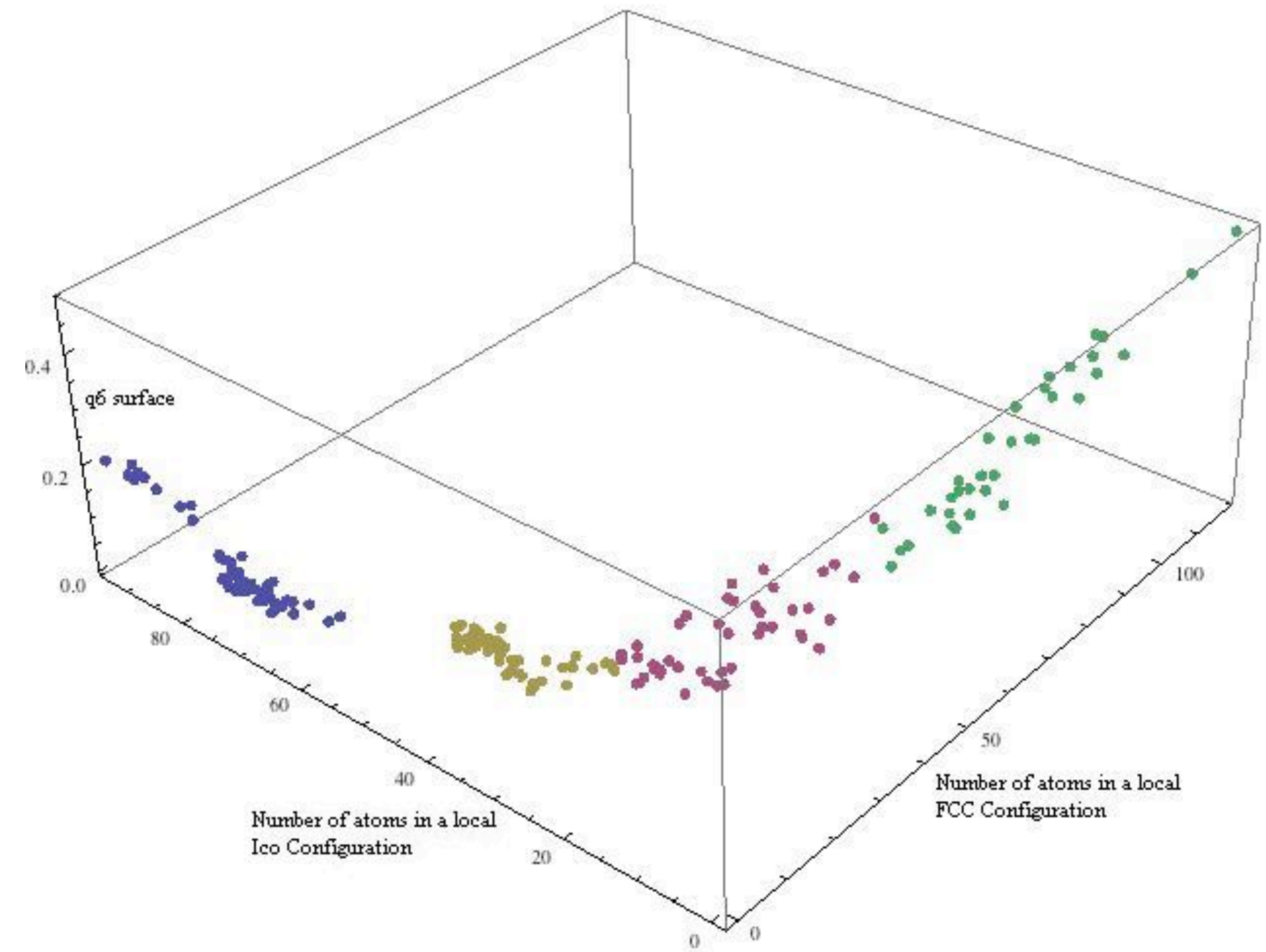


Medium sized Lennard Jones Clusters

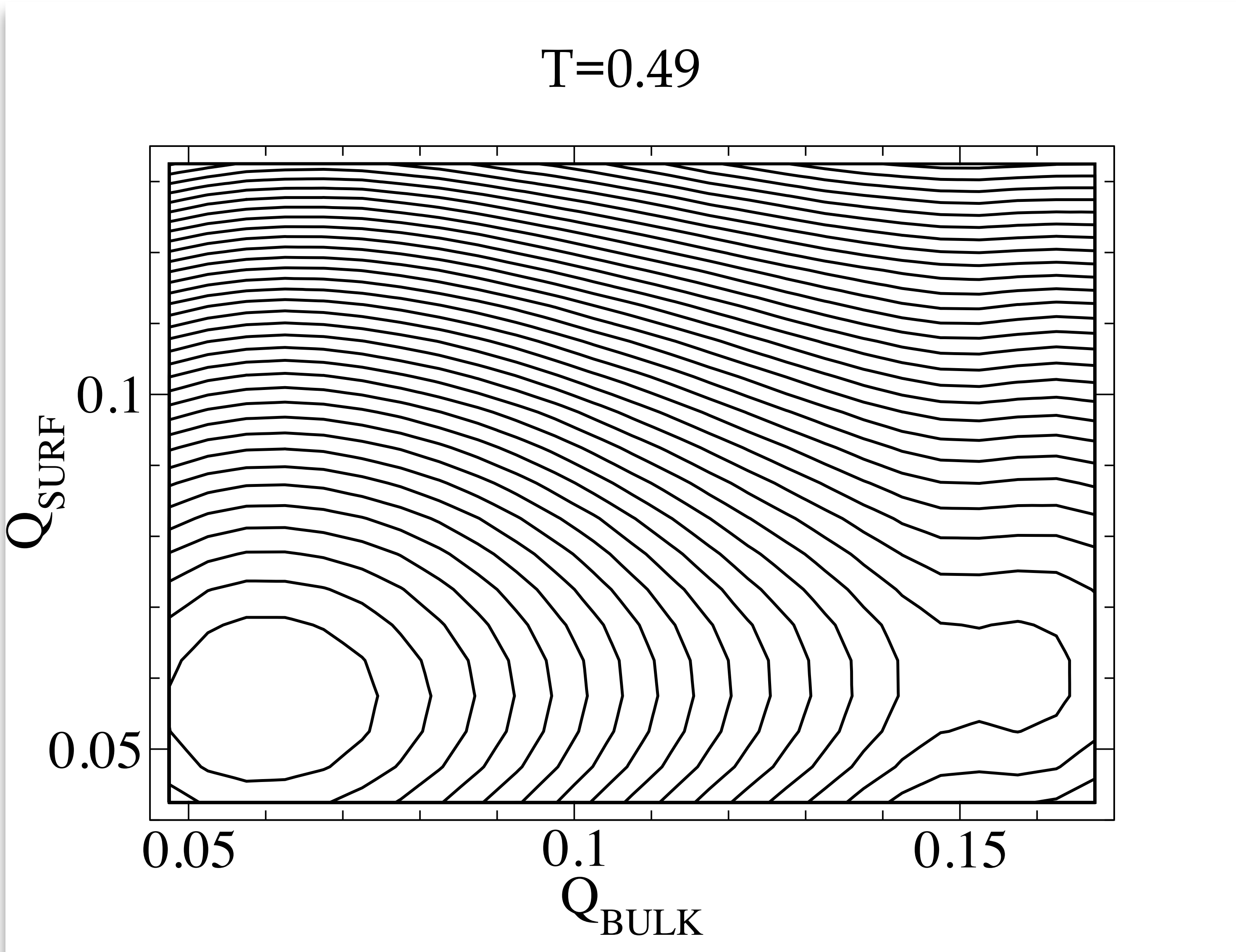
Before IS Quench



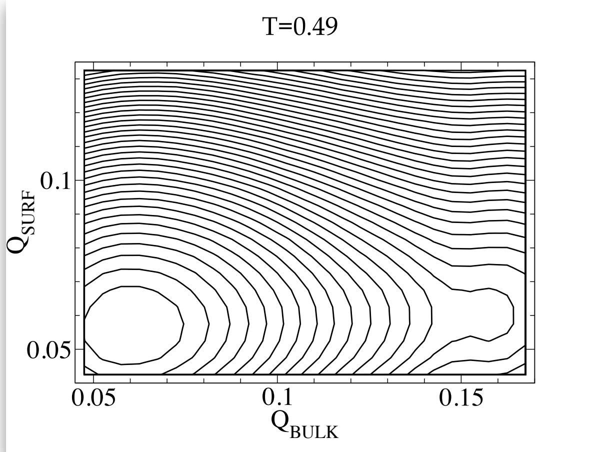
After IS Quench

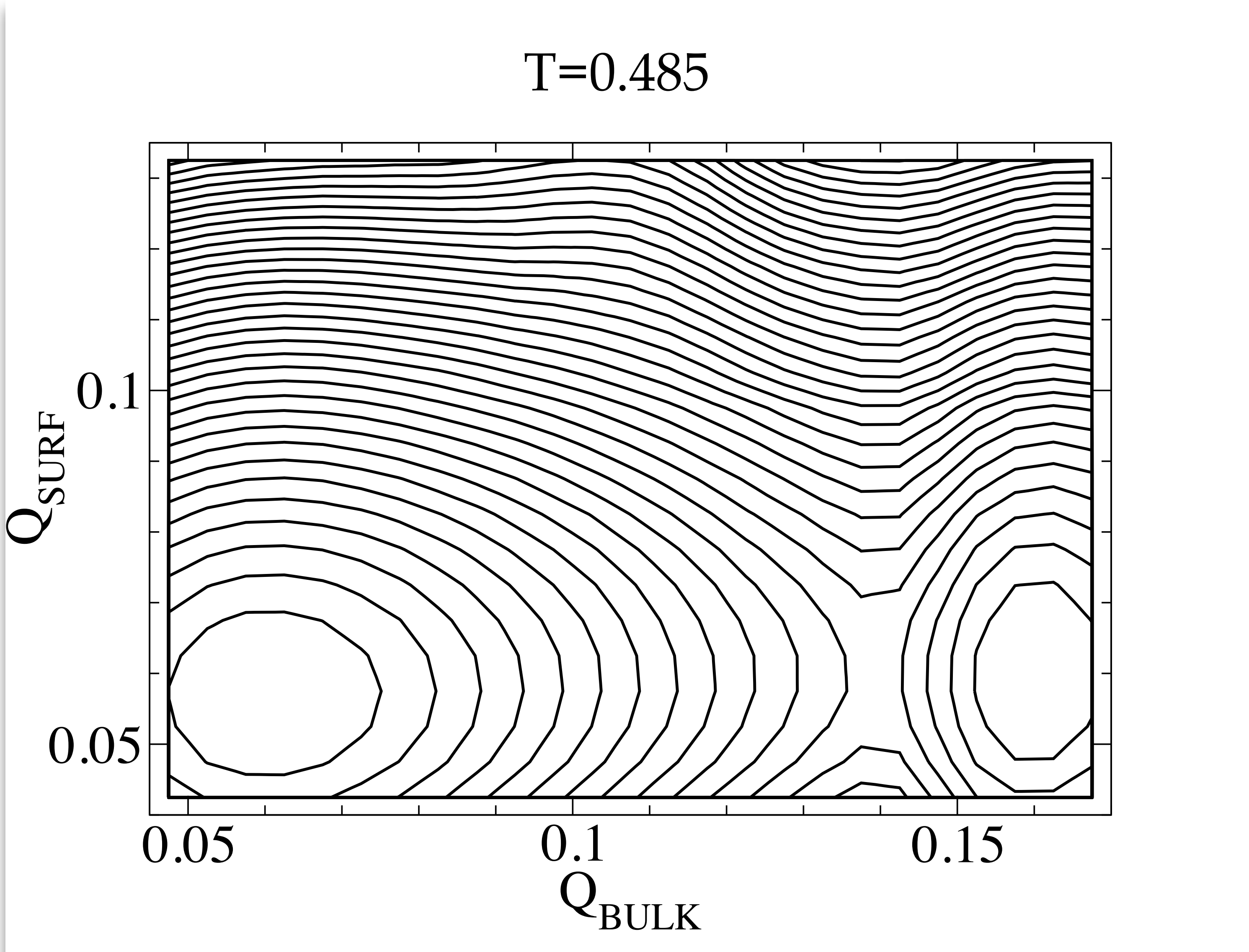


Free Energy Surface LJ N=600



Free Energy Surface LJ N=600





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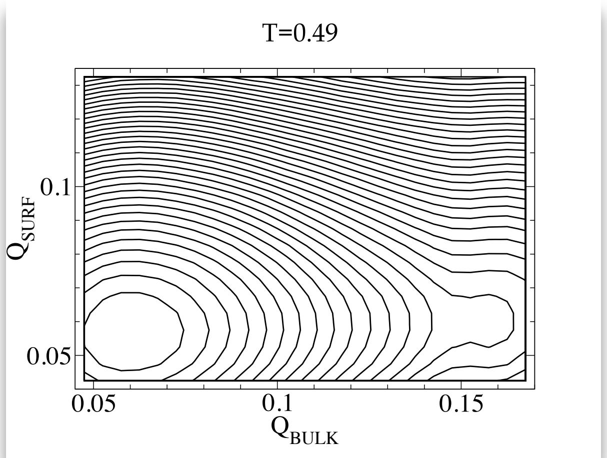

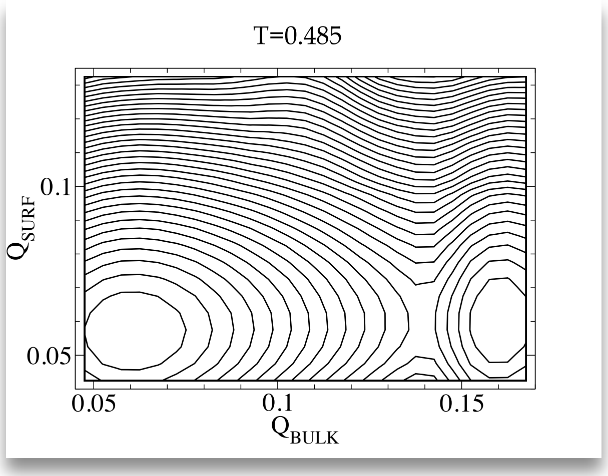

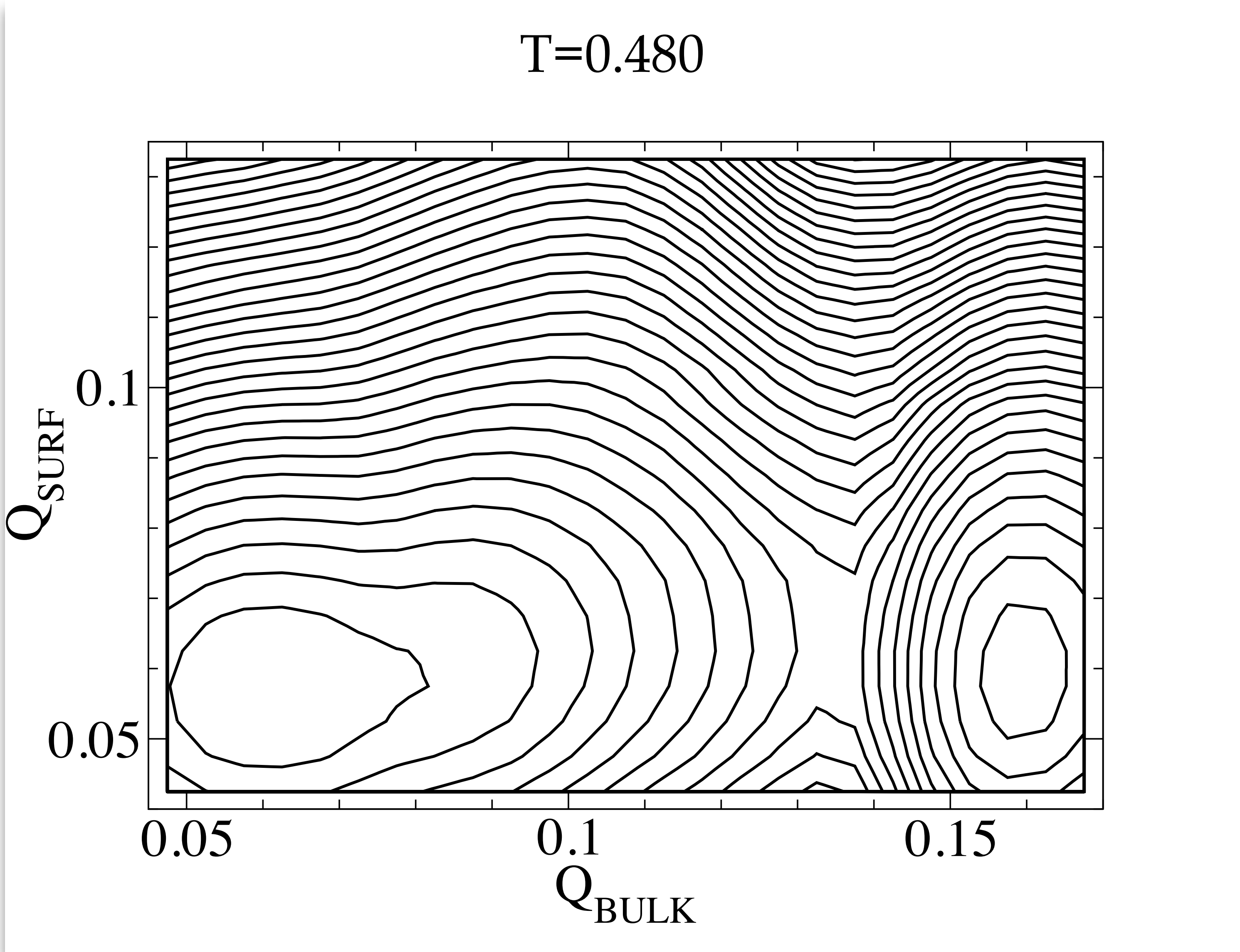

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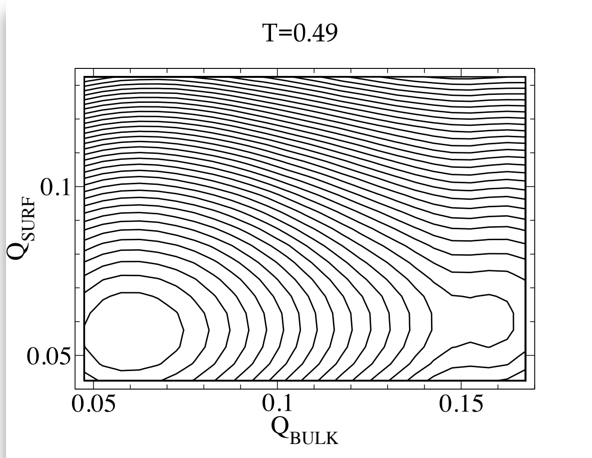
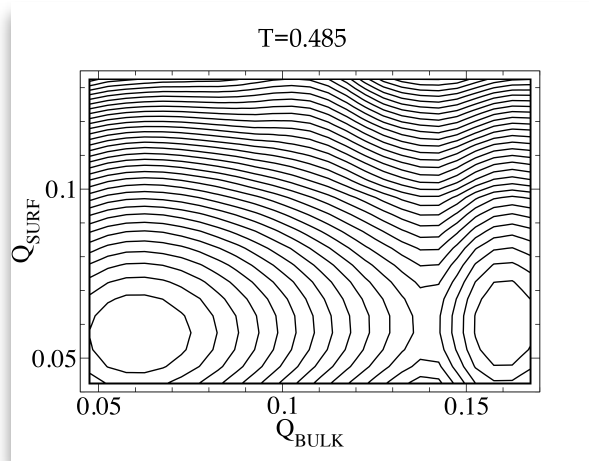
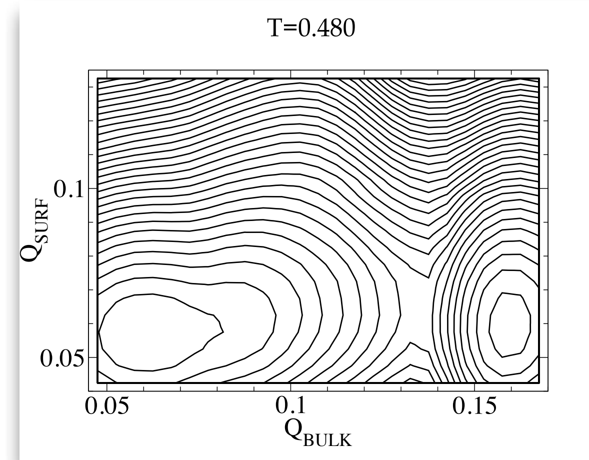
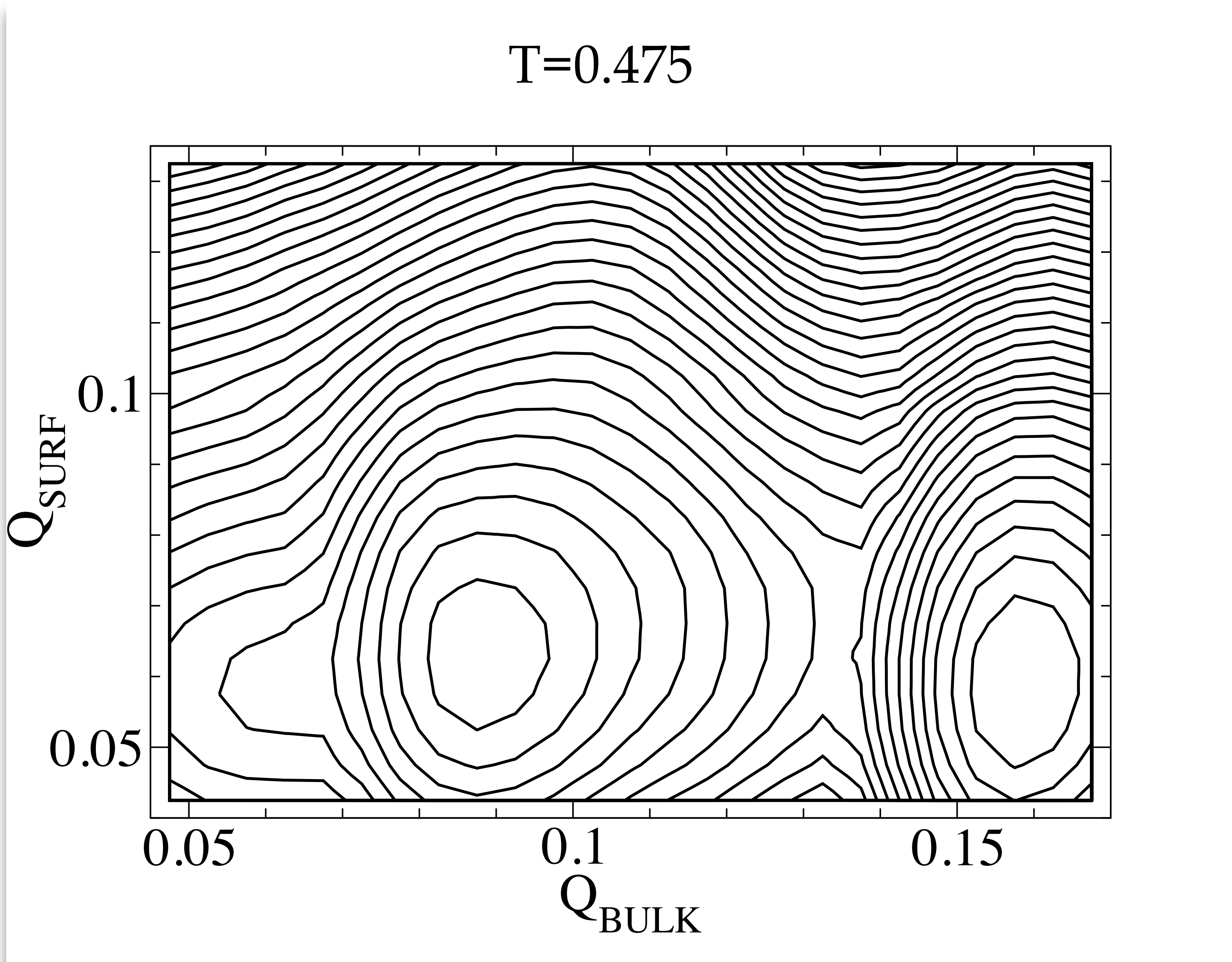
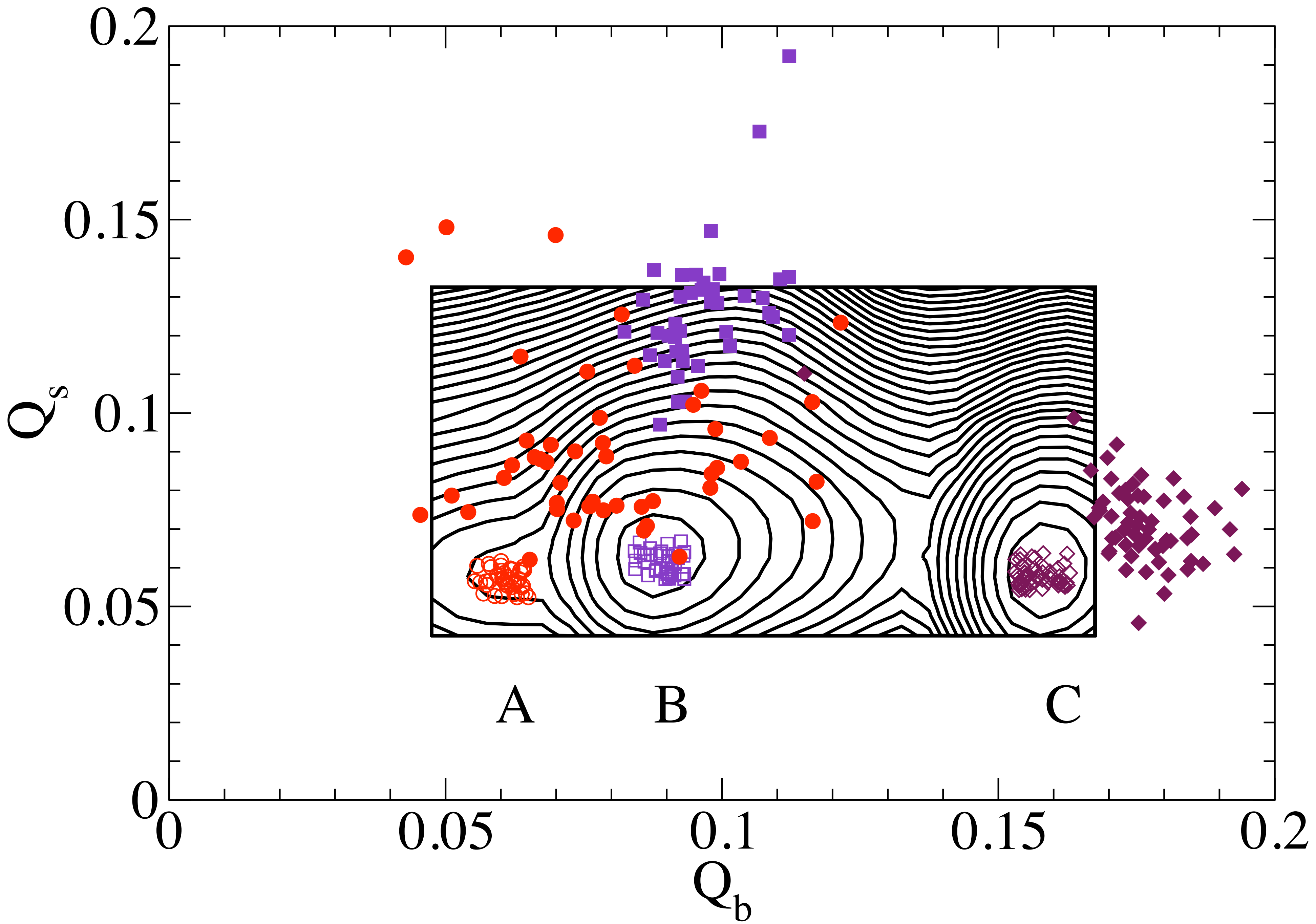








Quenched Configurations



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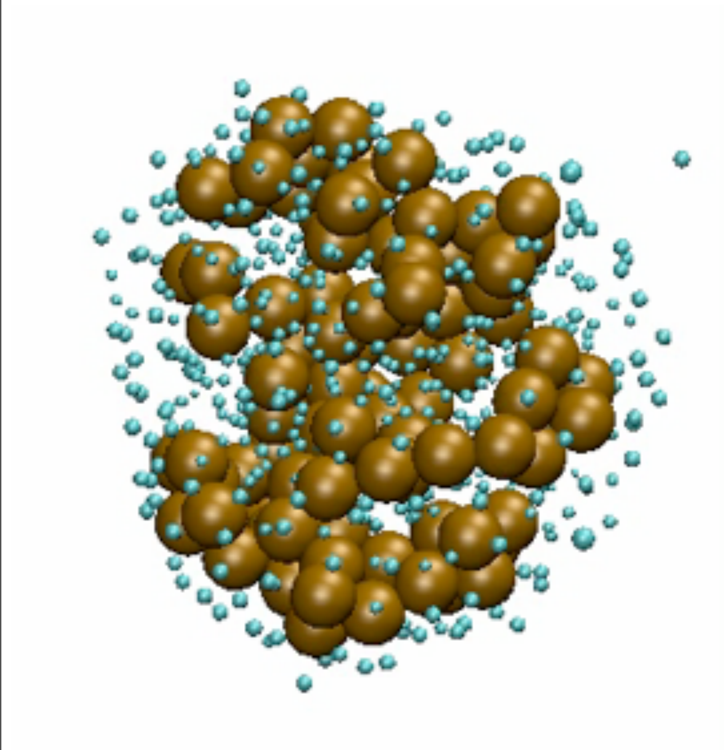

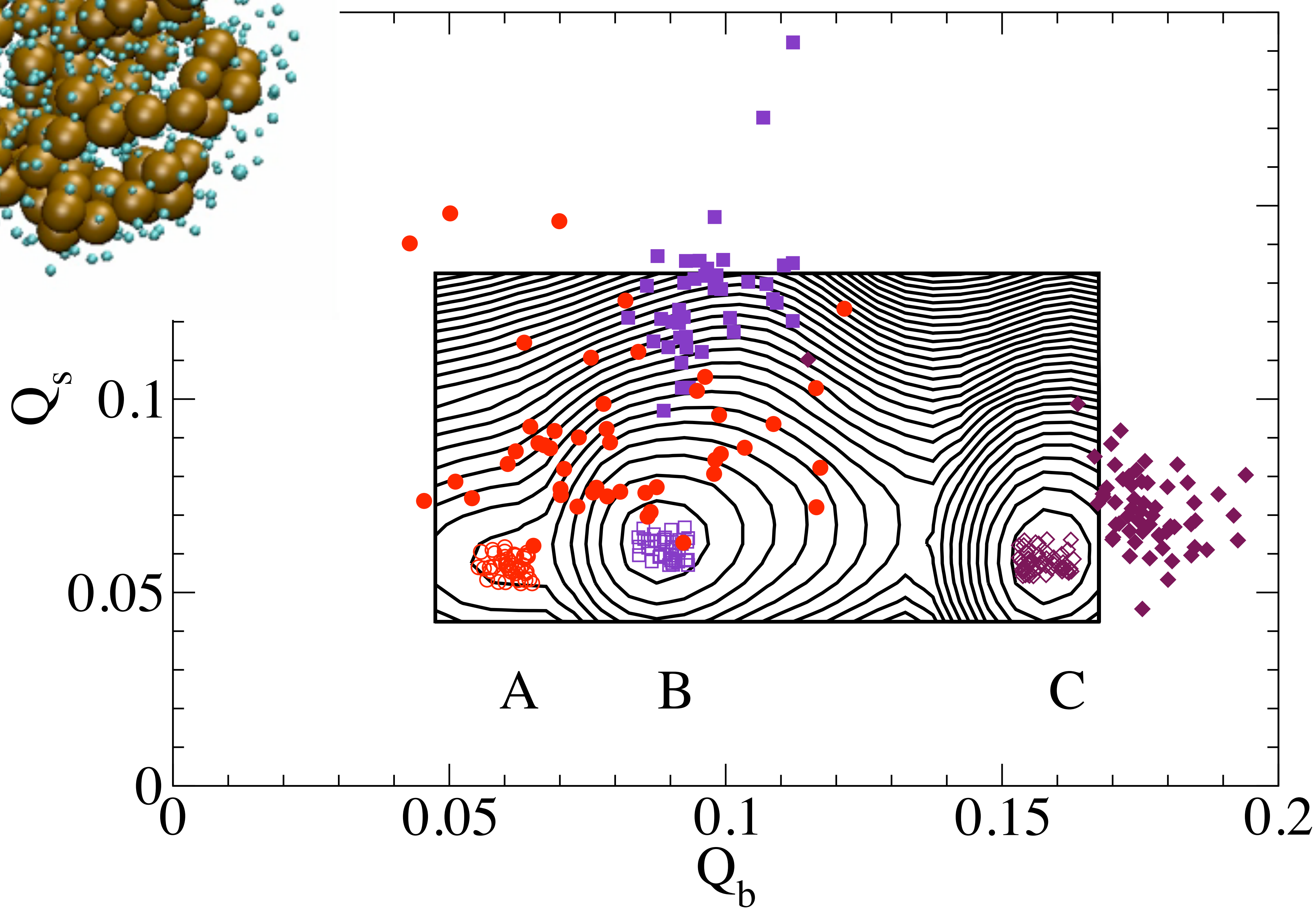

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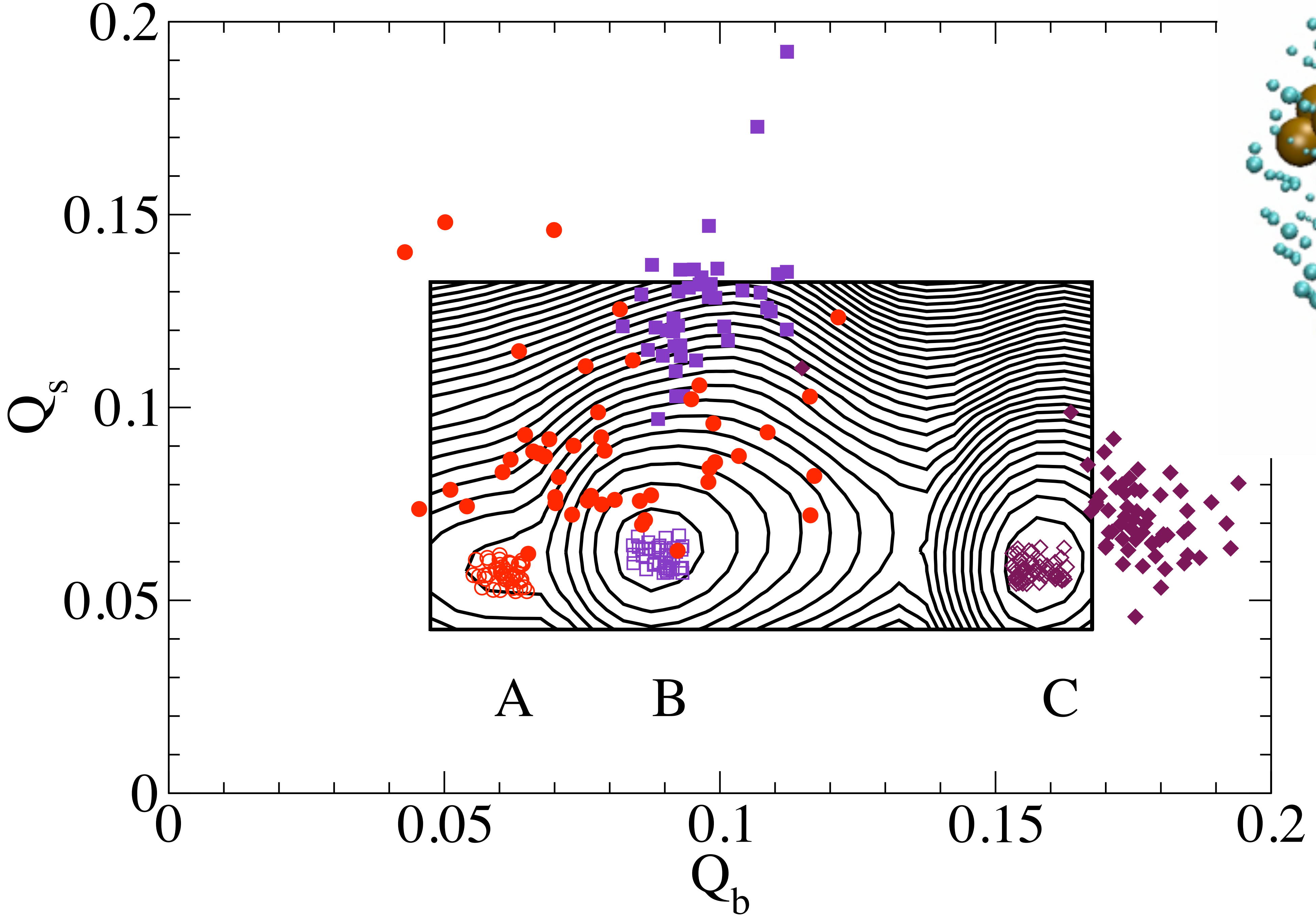

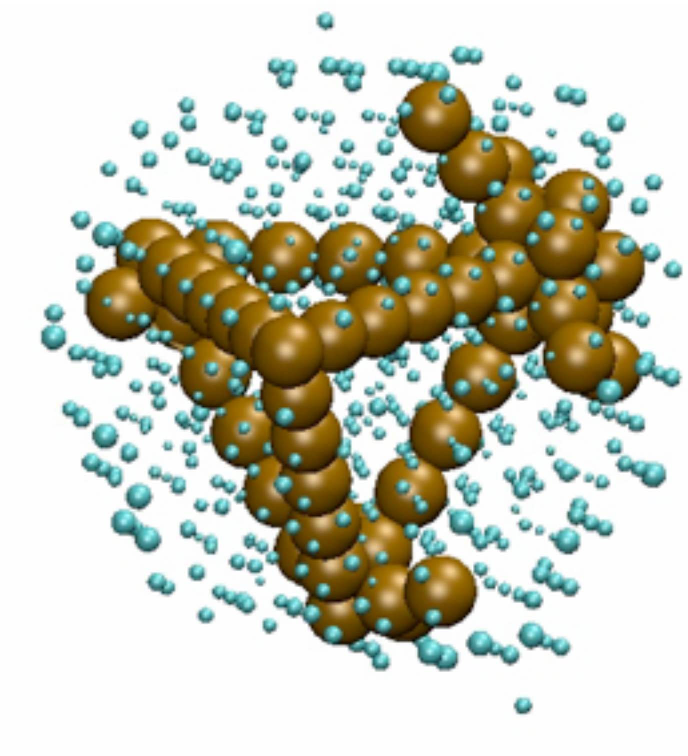

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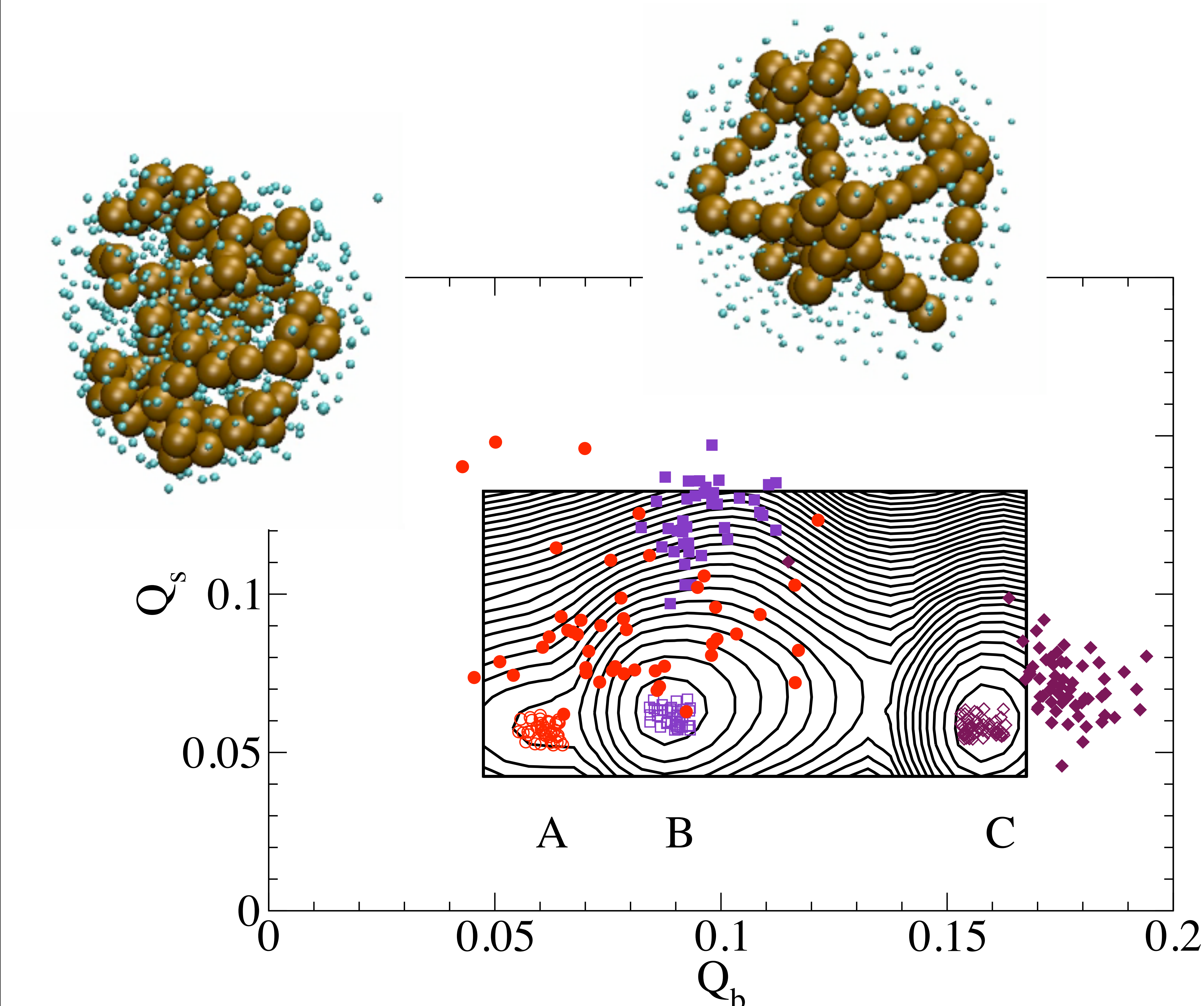
Quenched Configurations

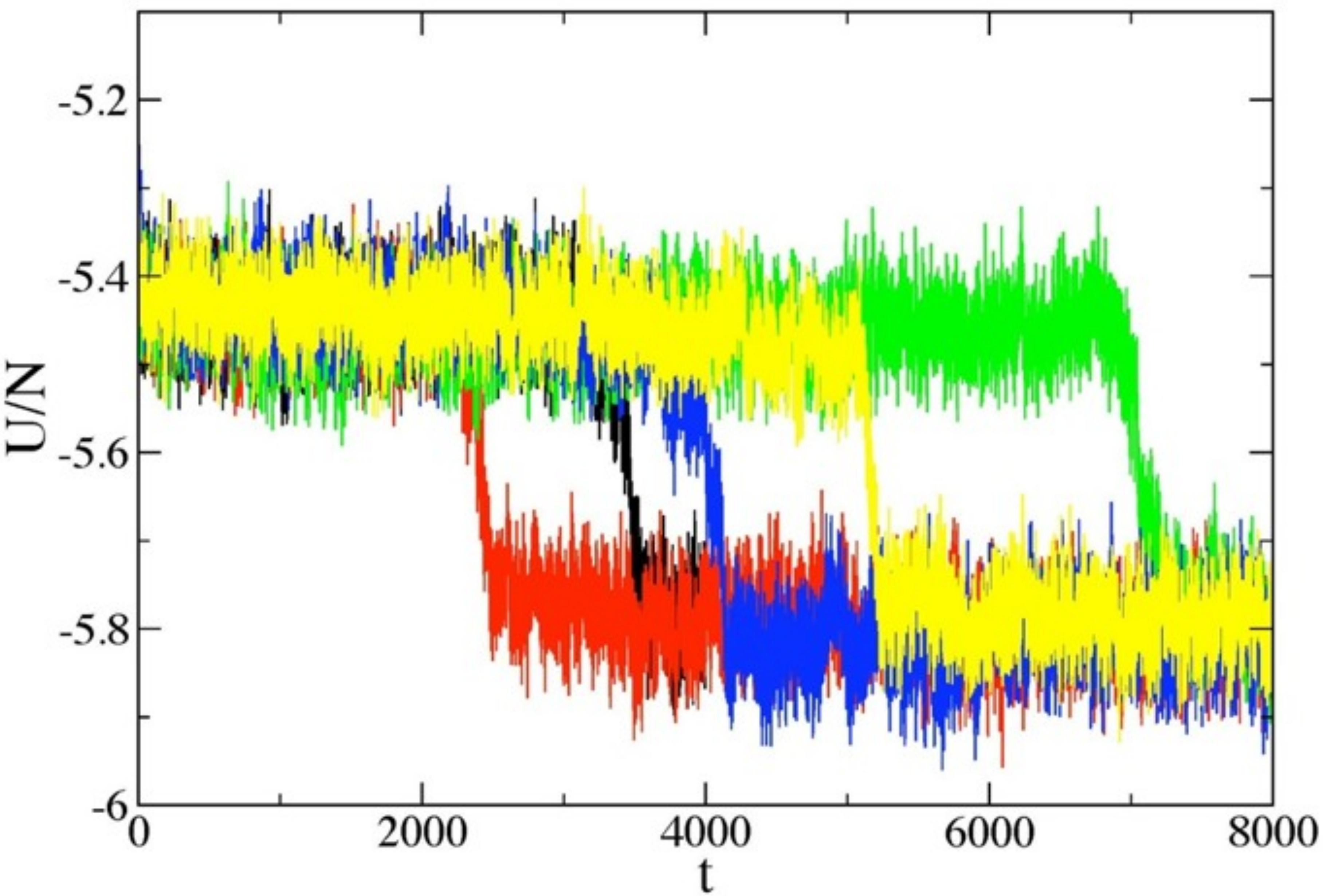


Molecular Dynamics Simulations

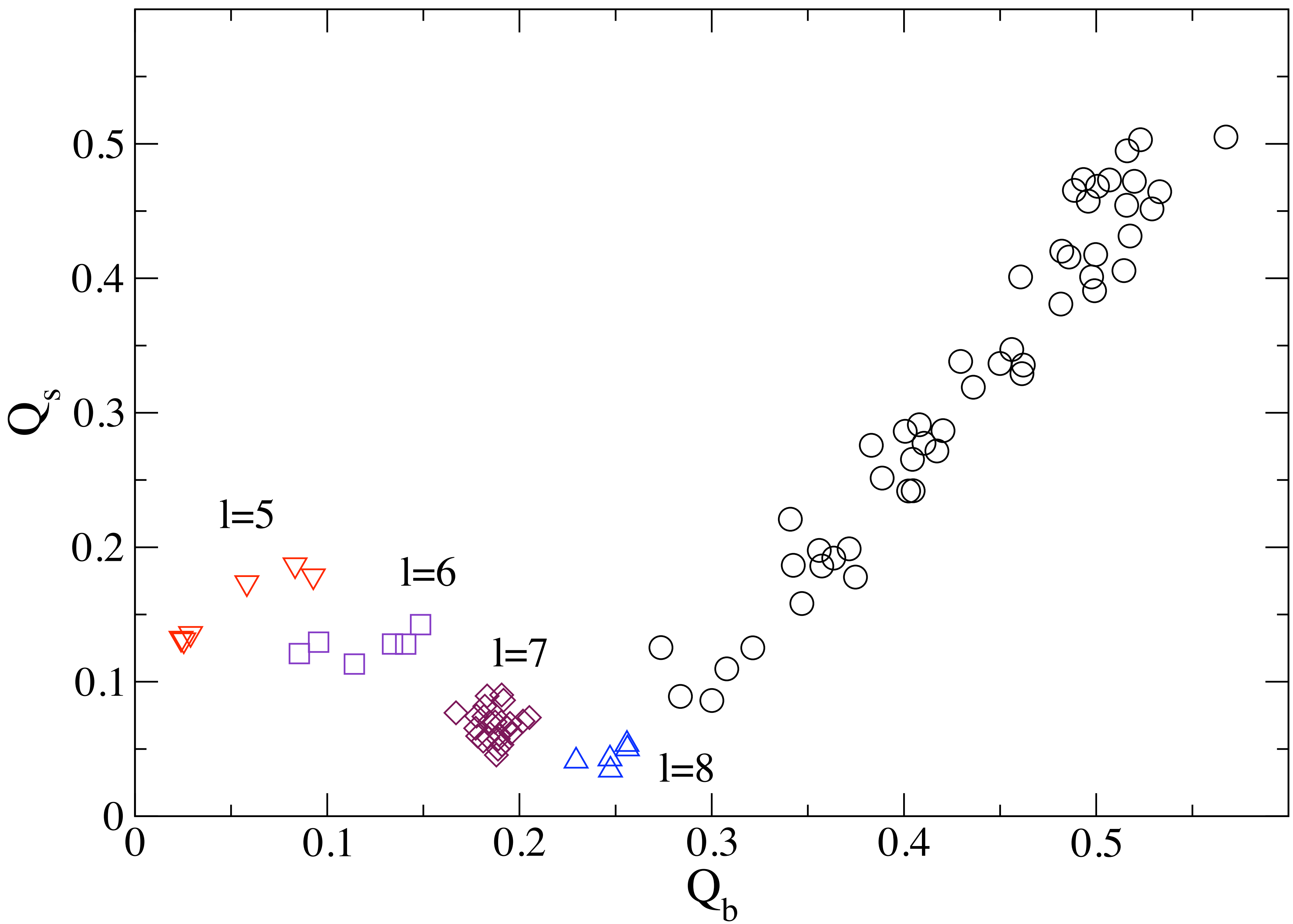
Equilibrium liquid
T*=0.53

→

Instantaneous T decrease
T*=0.44



Molecular Dynamics Simulations



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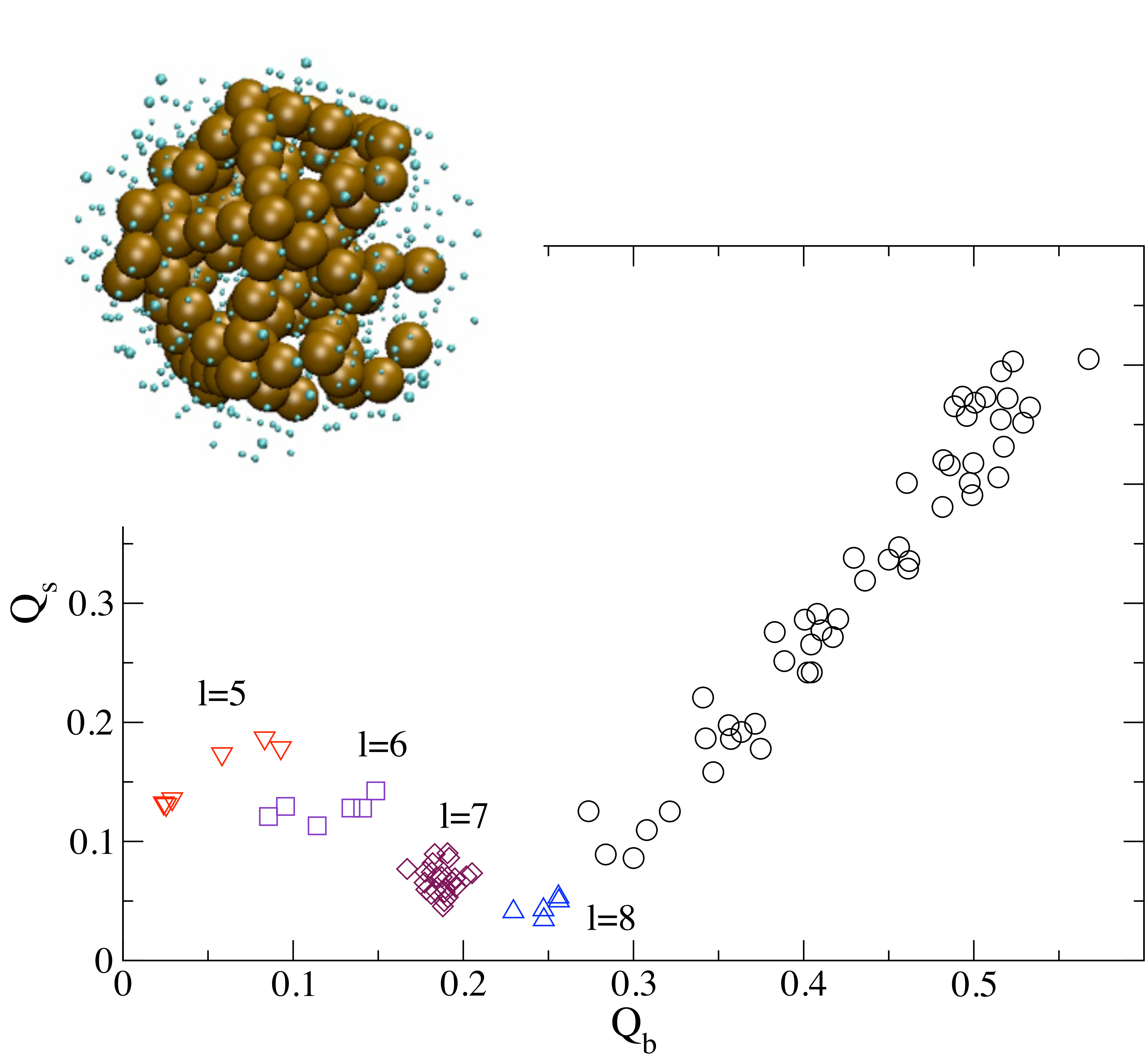

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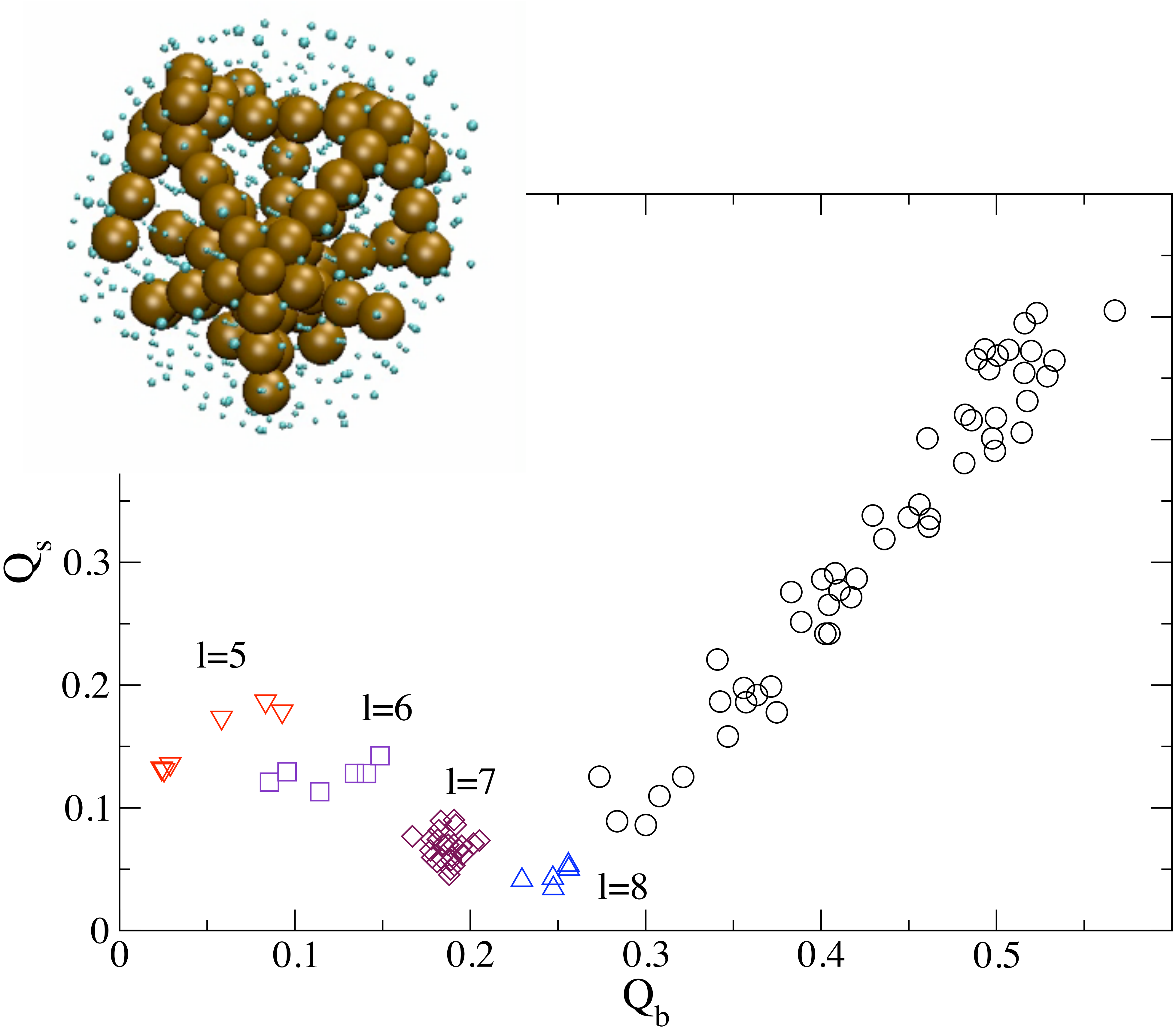

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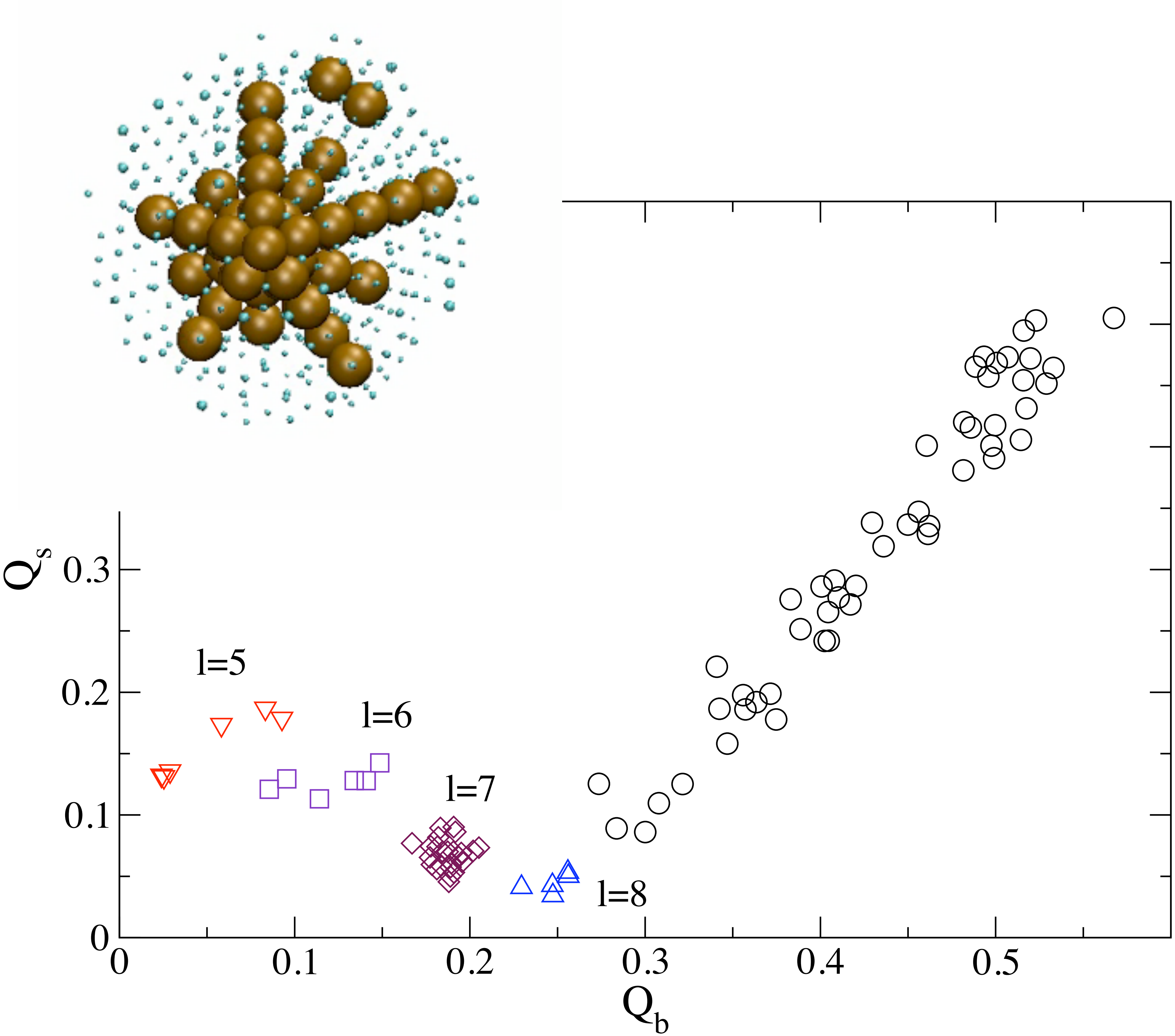
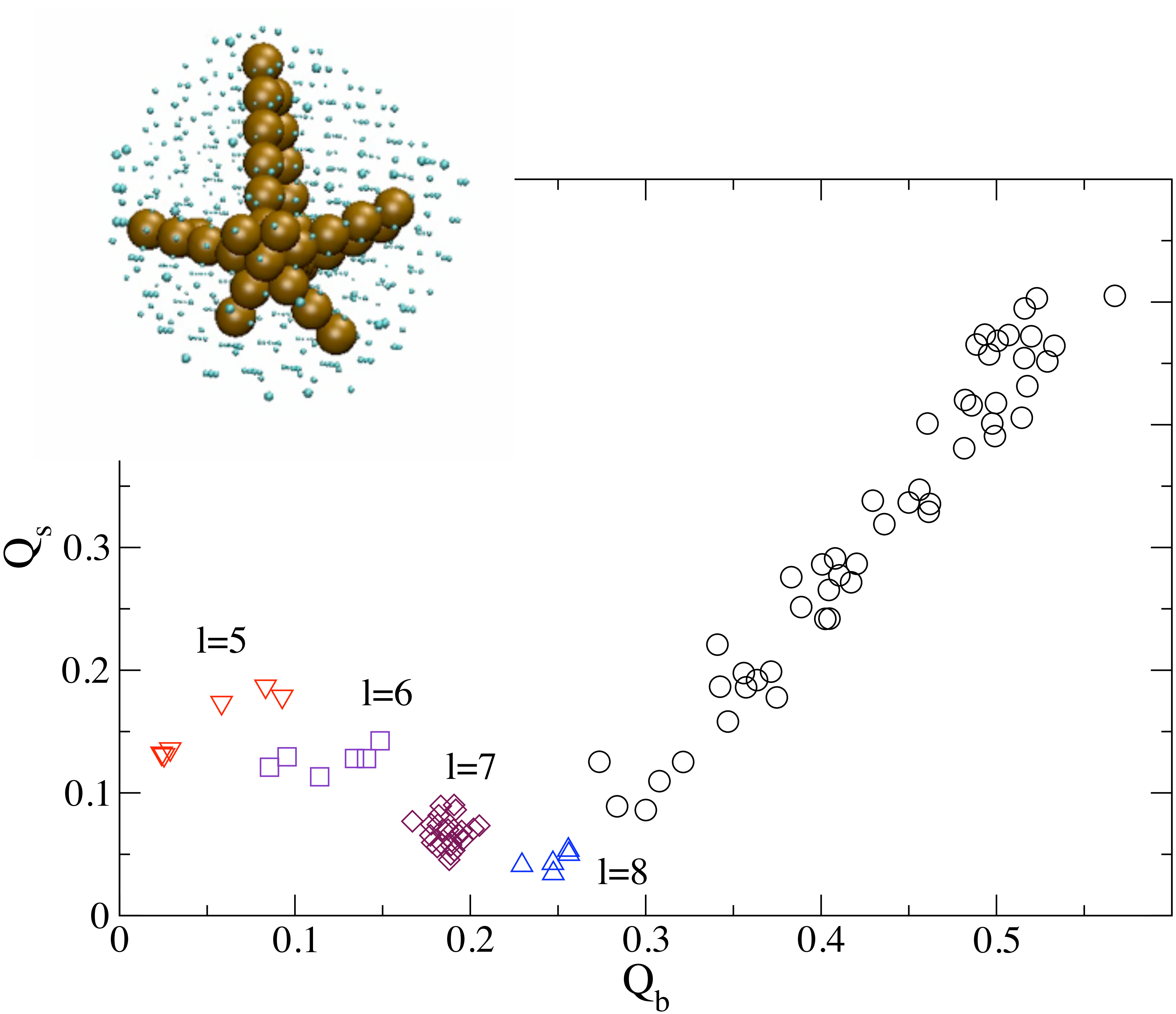
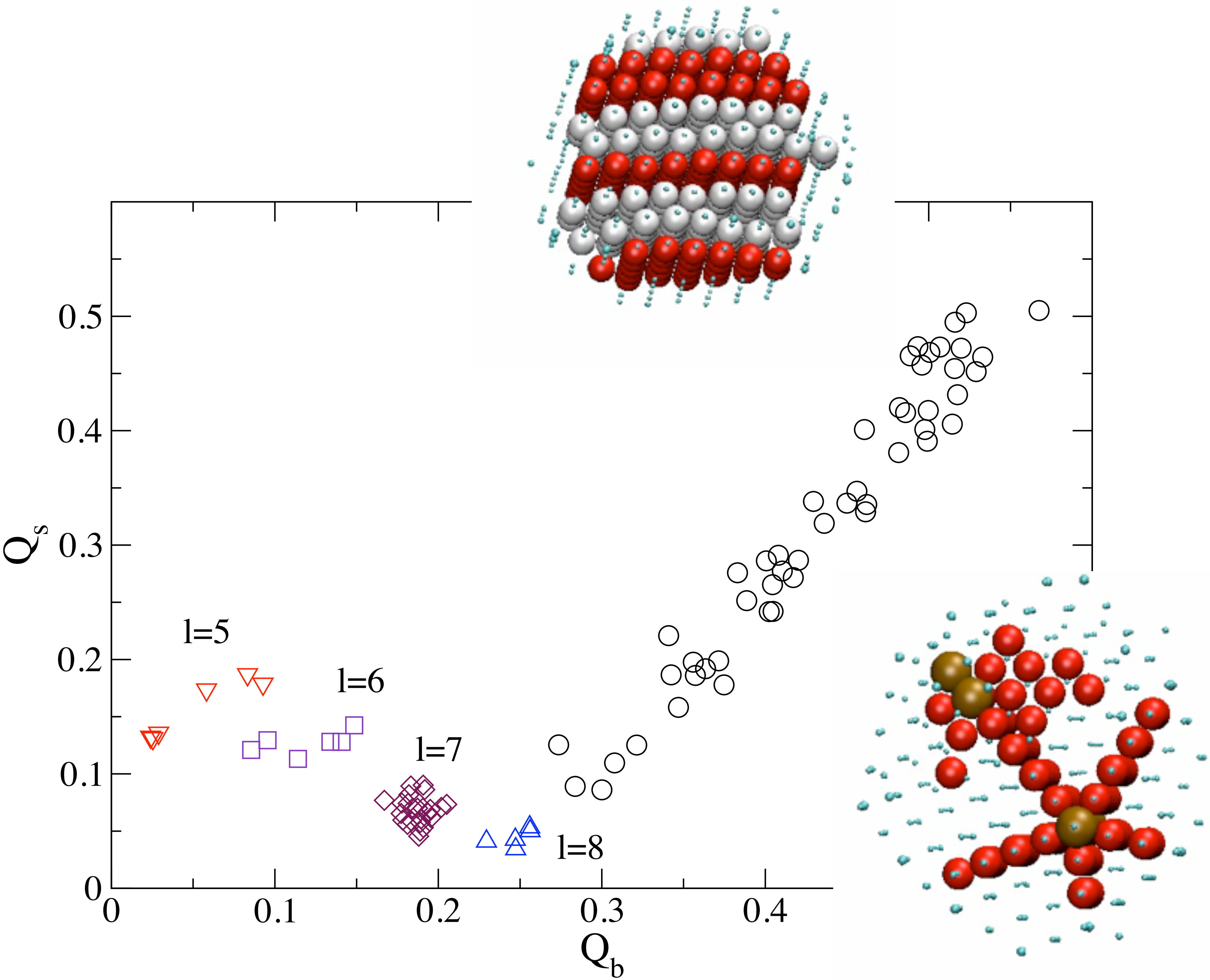


Molecular Dynamics Simulations



Molecular Dynamics Simulations



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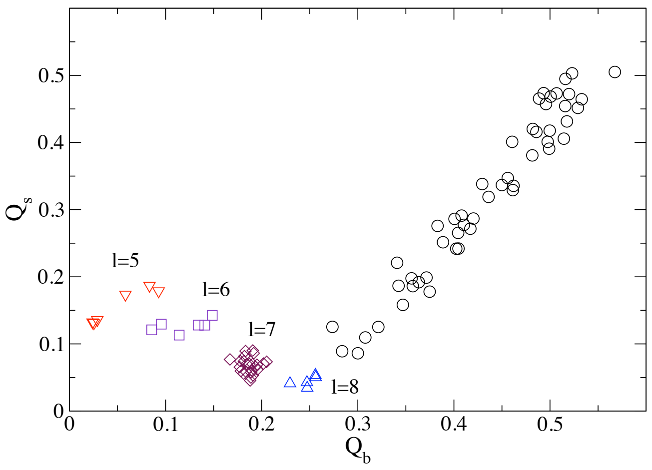
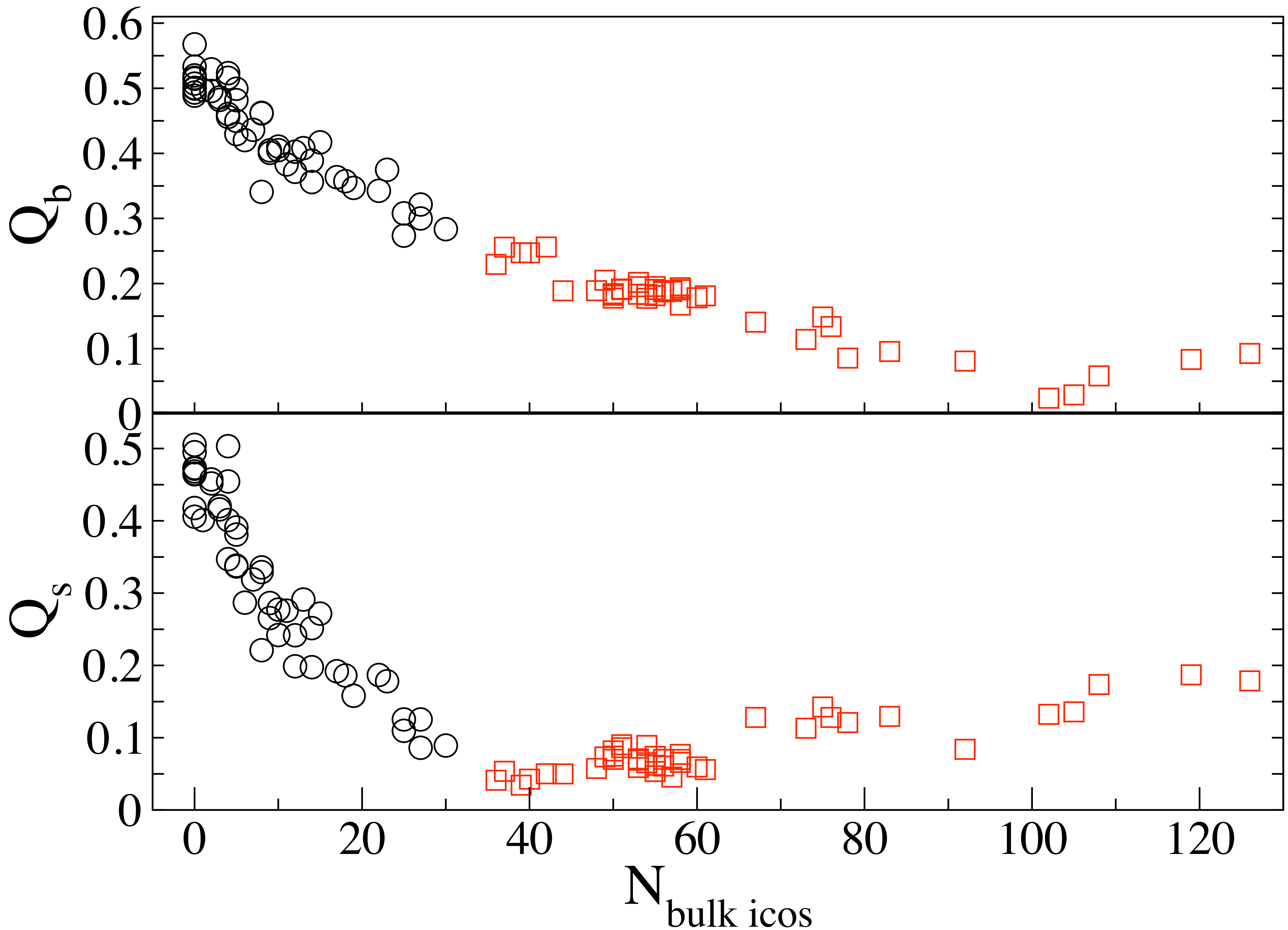
Qs and Qb Correlations





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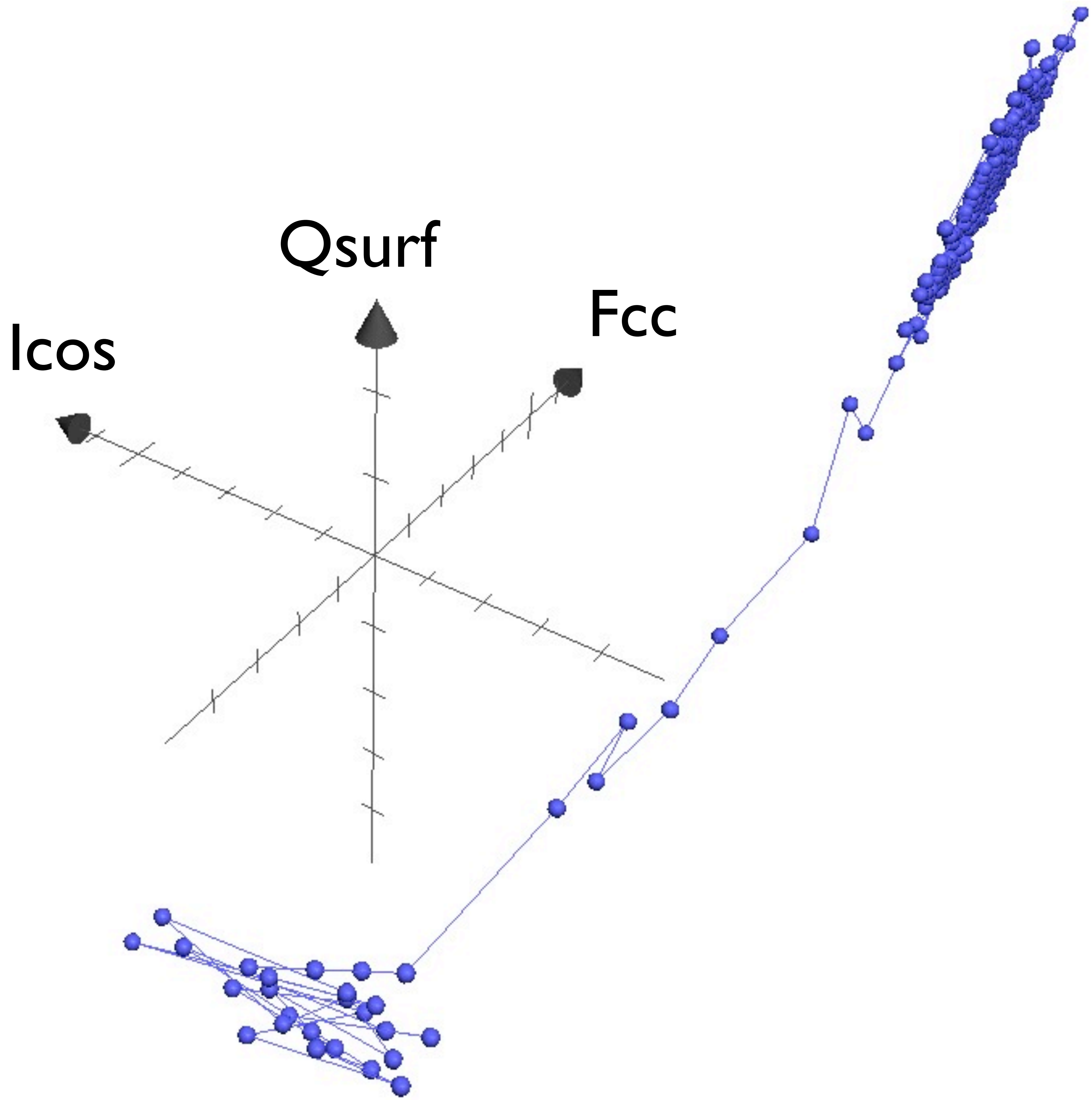
Trajectories



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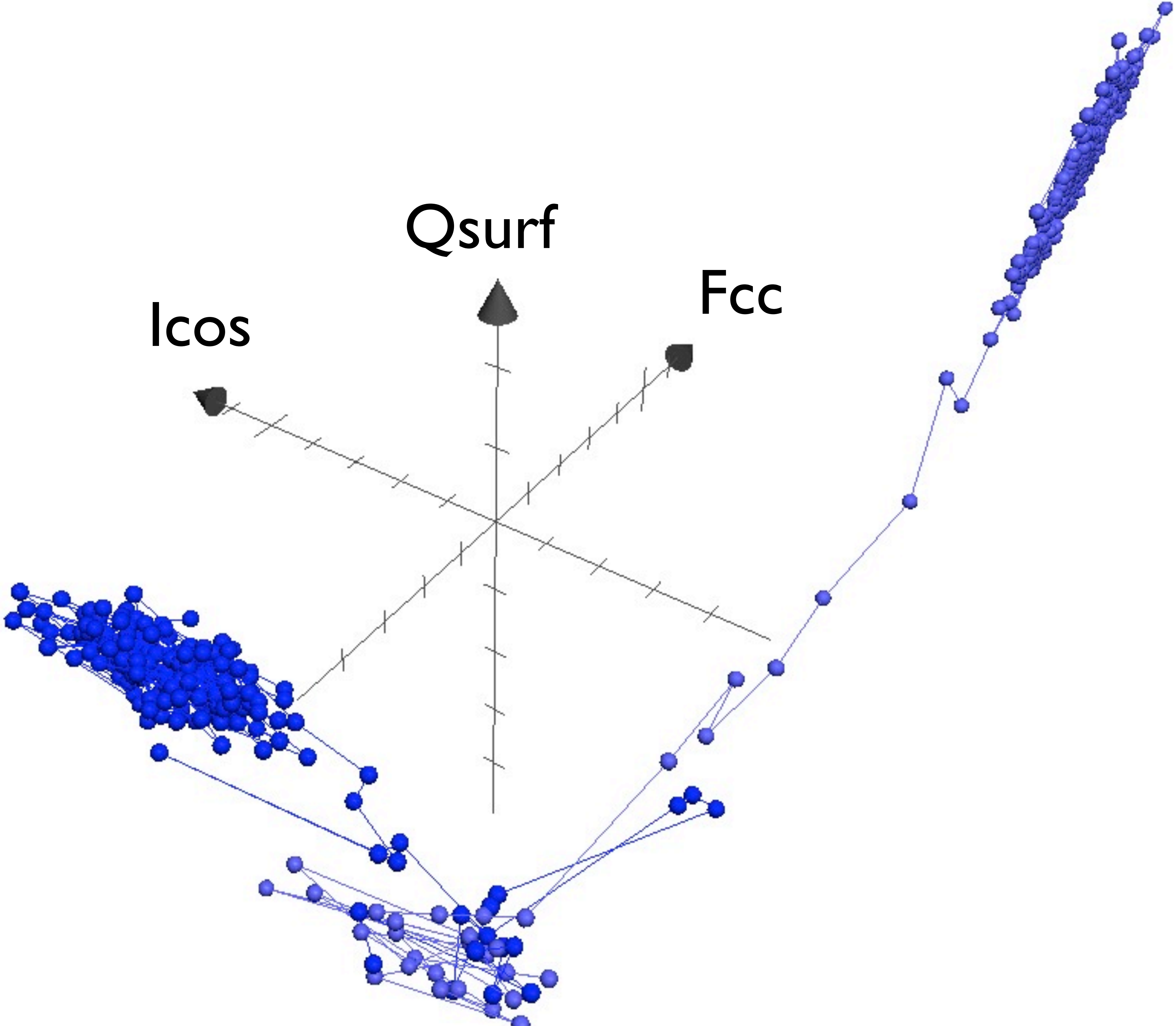
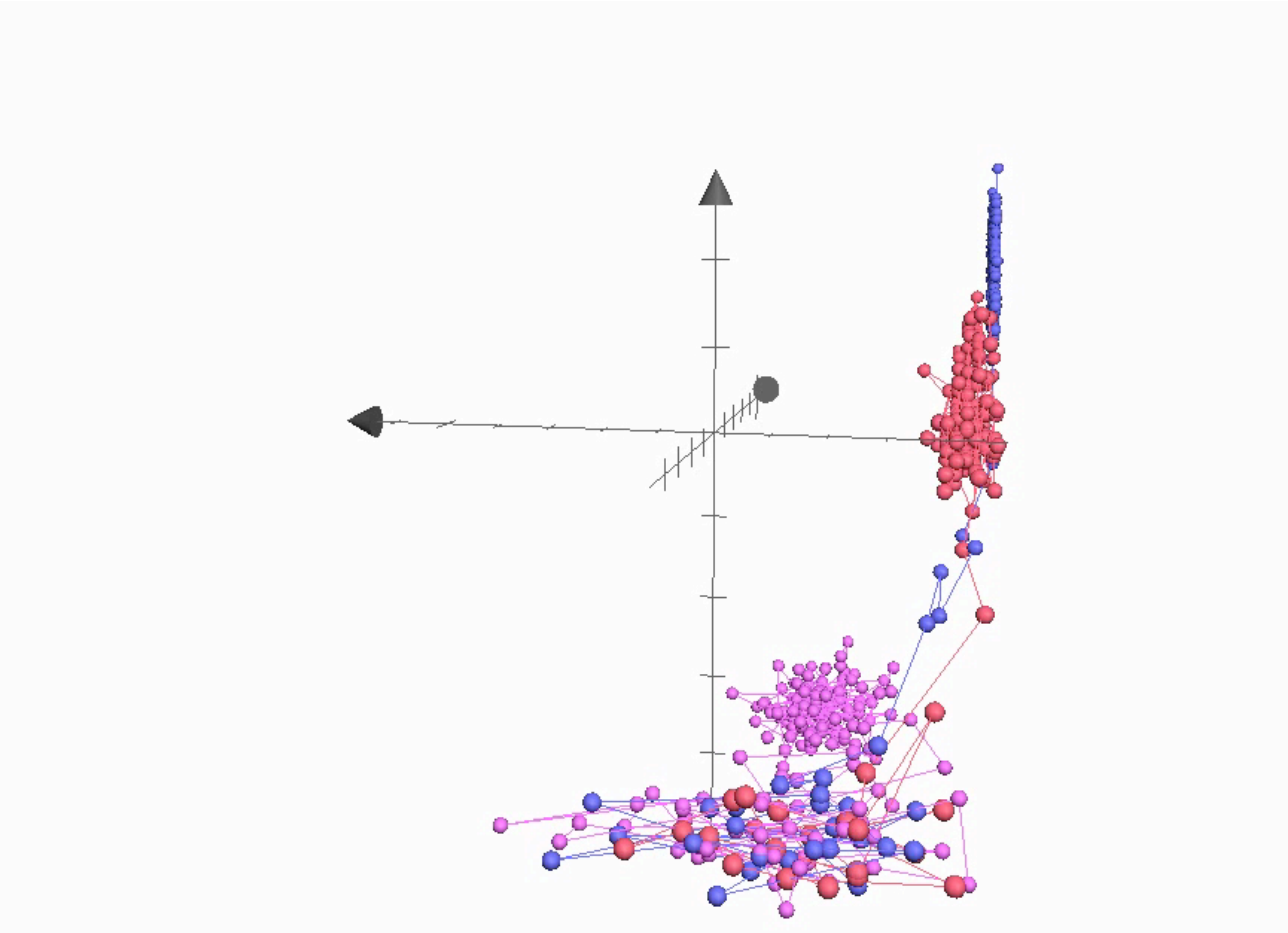
Trajectories



Trajectories

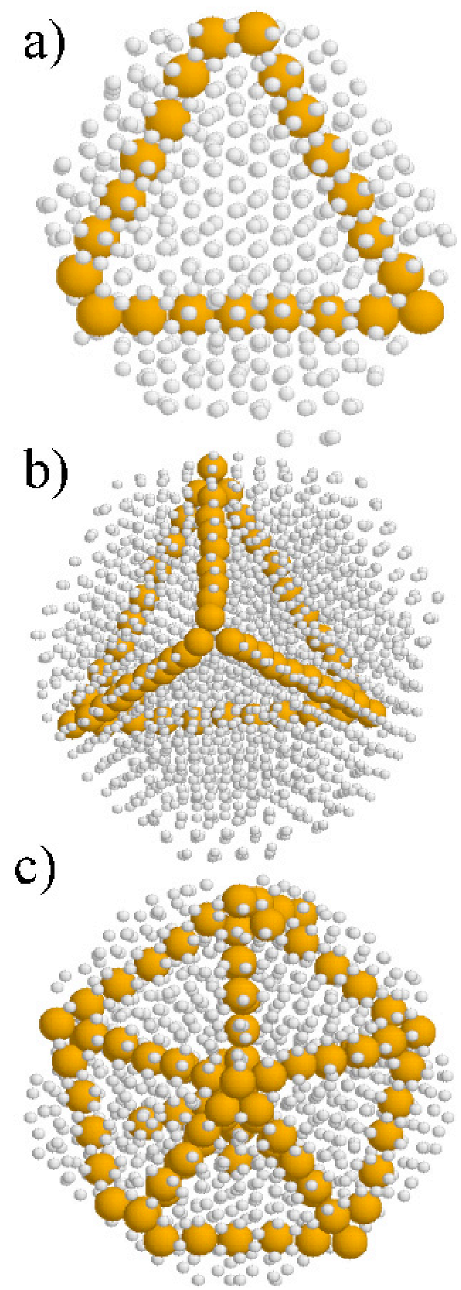
Trajectories



Gold Clusters

Poly Decahedral

Au$_{586}$	Ih	Dh	p-Dh	fcc
2 K ns^{-1}	6	9	3	6
10 K ns^{-1}	8	5	5	6
50 K ns^{-1}	15	2	3	4
Au$_{976}$				
1K ns^{-1}	7	8	2	7
10 K ns^{-1}	10	0	4	10
50 K ns^{-1}	11	2	6	5
100 K ns^{-1}	11	—	9	4
Au$_{2075}$				
2 K ns^{-1}	4	3	10	7
10 K ns^{-1}	9	1	5	9
50 K ns^{-1}	7	0	9	7
100 K ns^{-1}	5	5	11	3

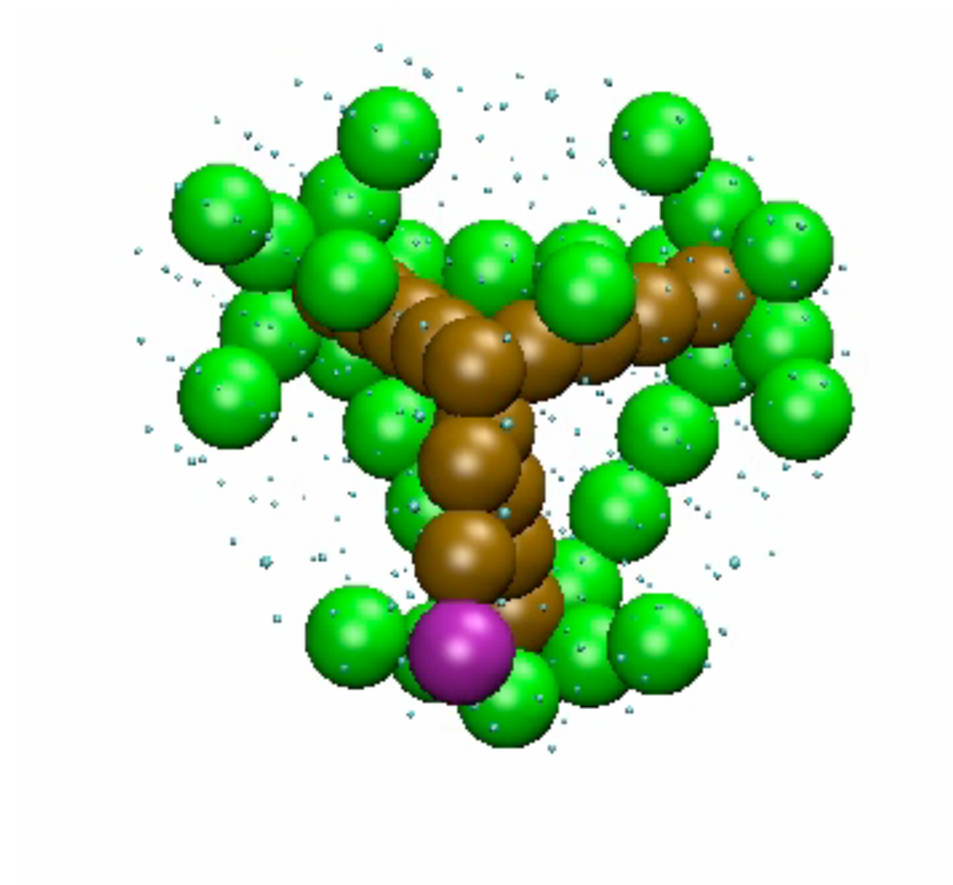


586

2075

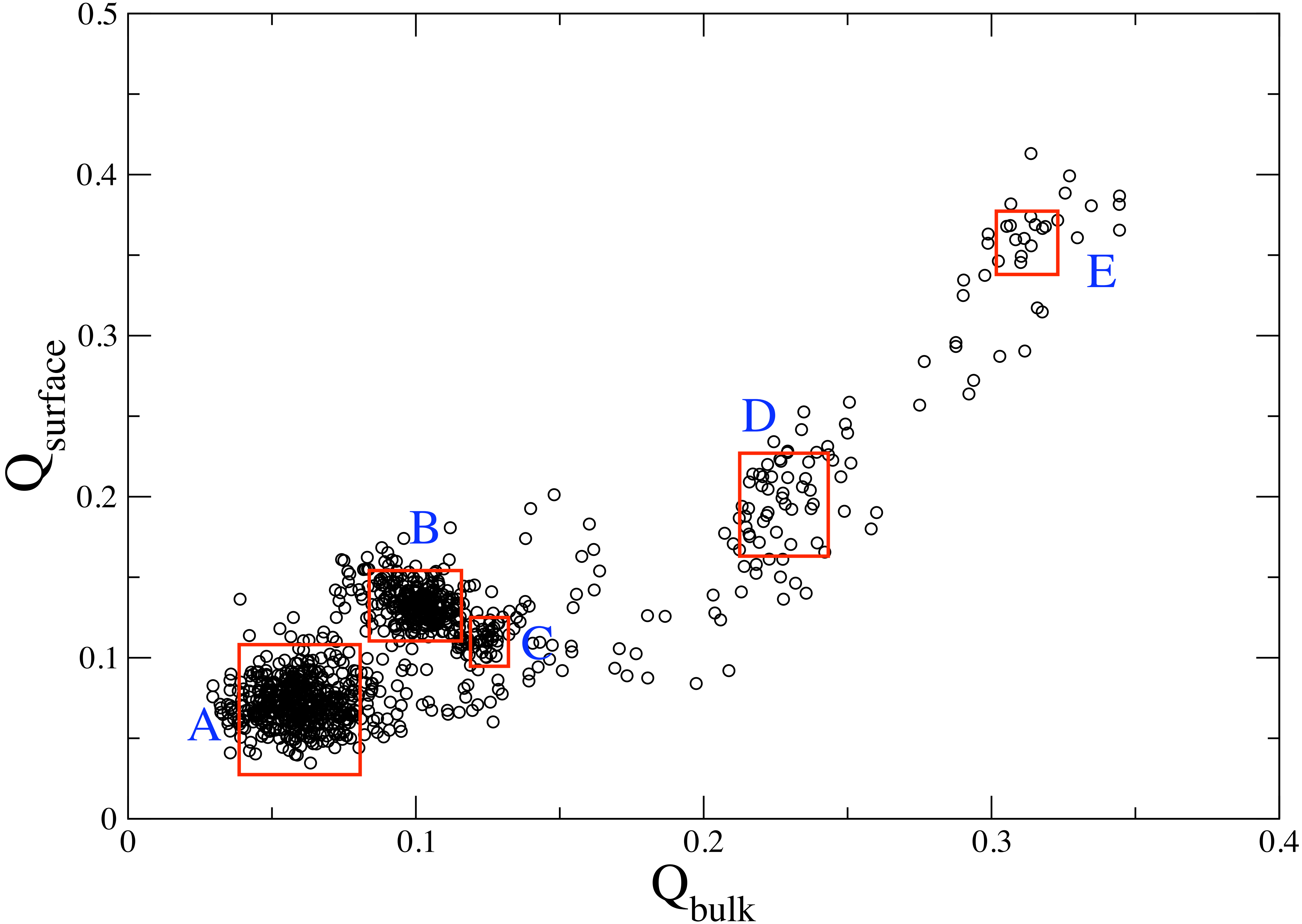
975

309



G. Rossi, R. Ferrando,Nanotec. 18, 225706 (2007).

Gold Clusters N=459



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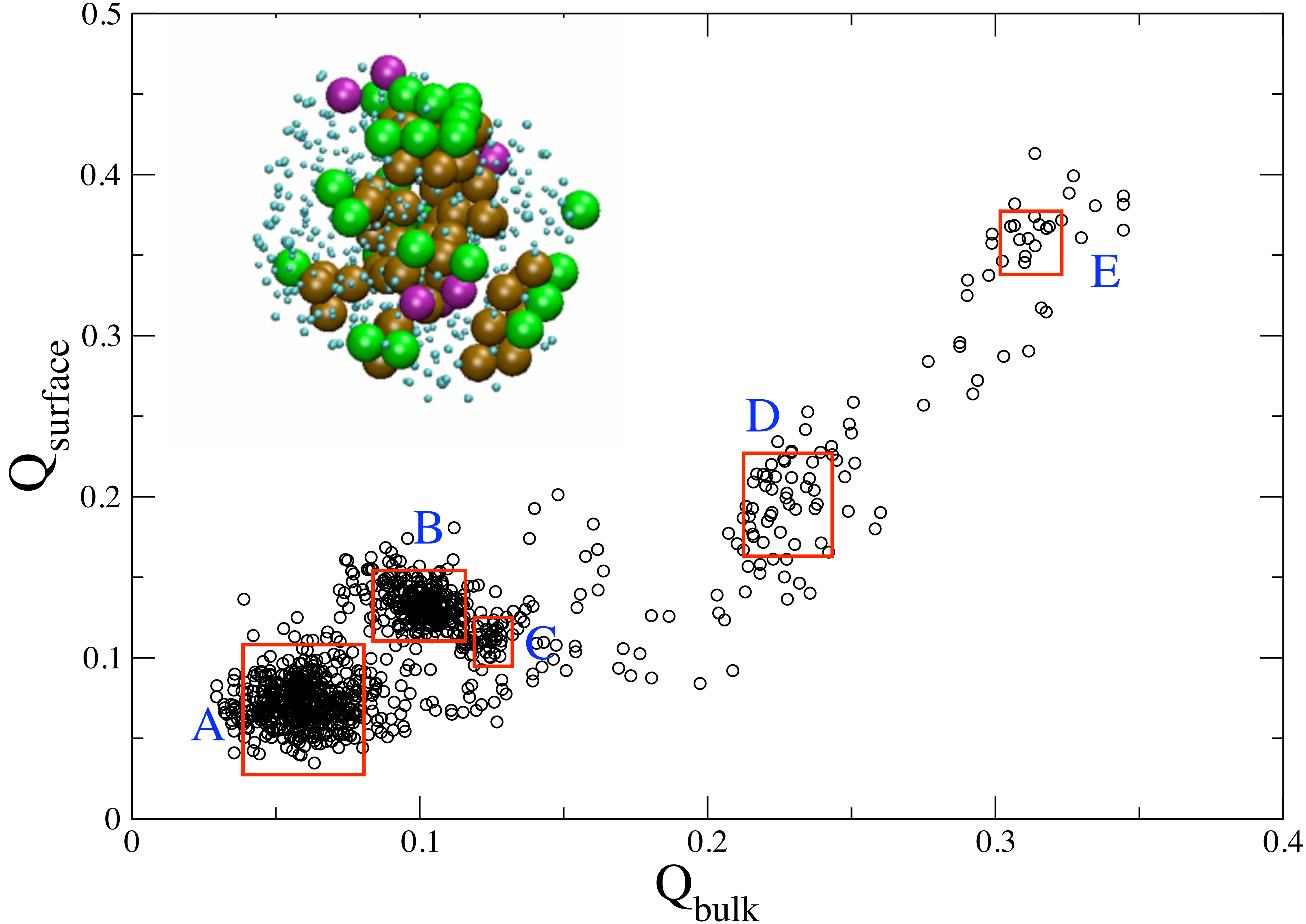
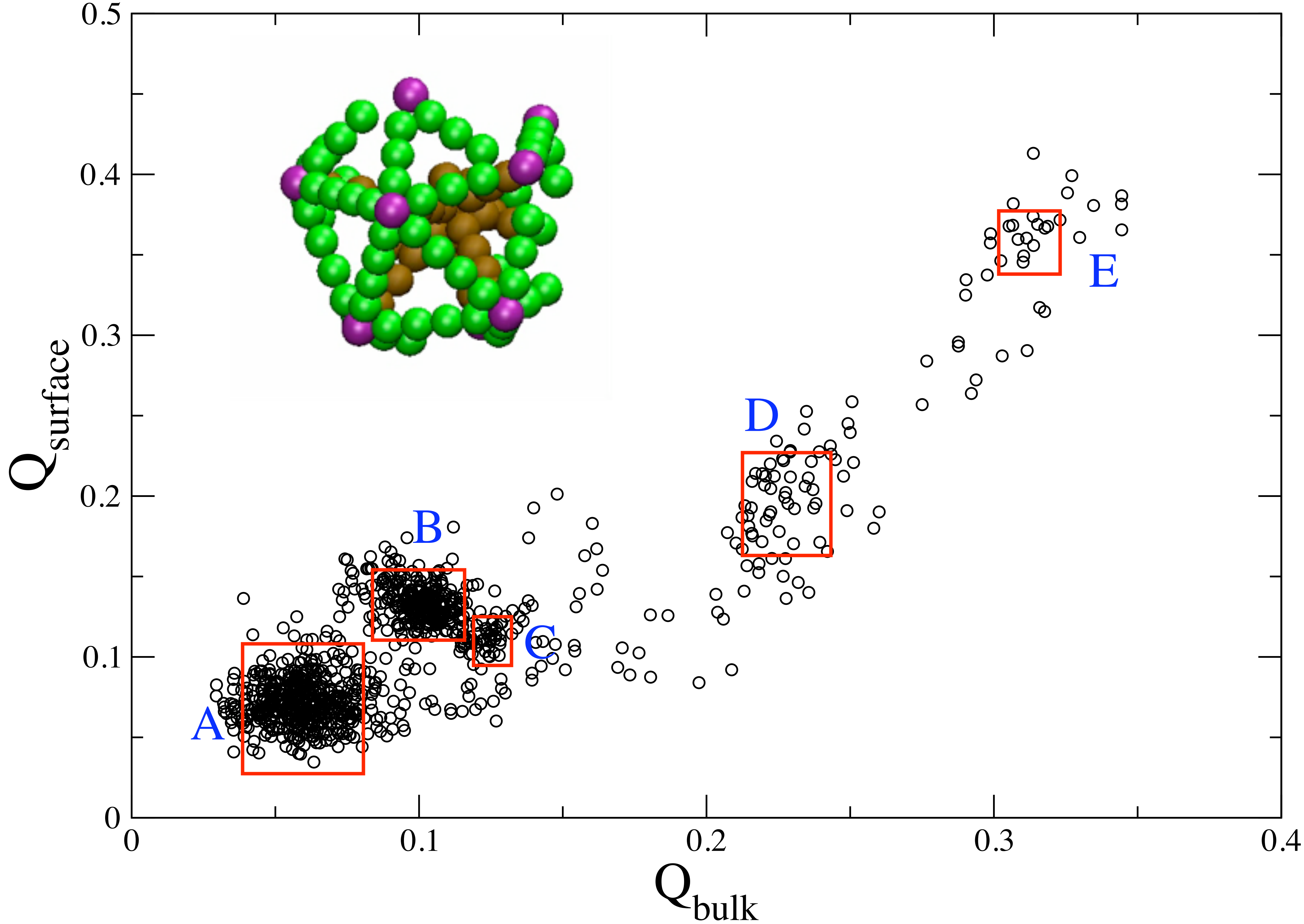
Gold Clusters N=459



Gold Clusters N=459



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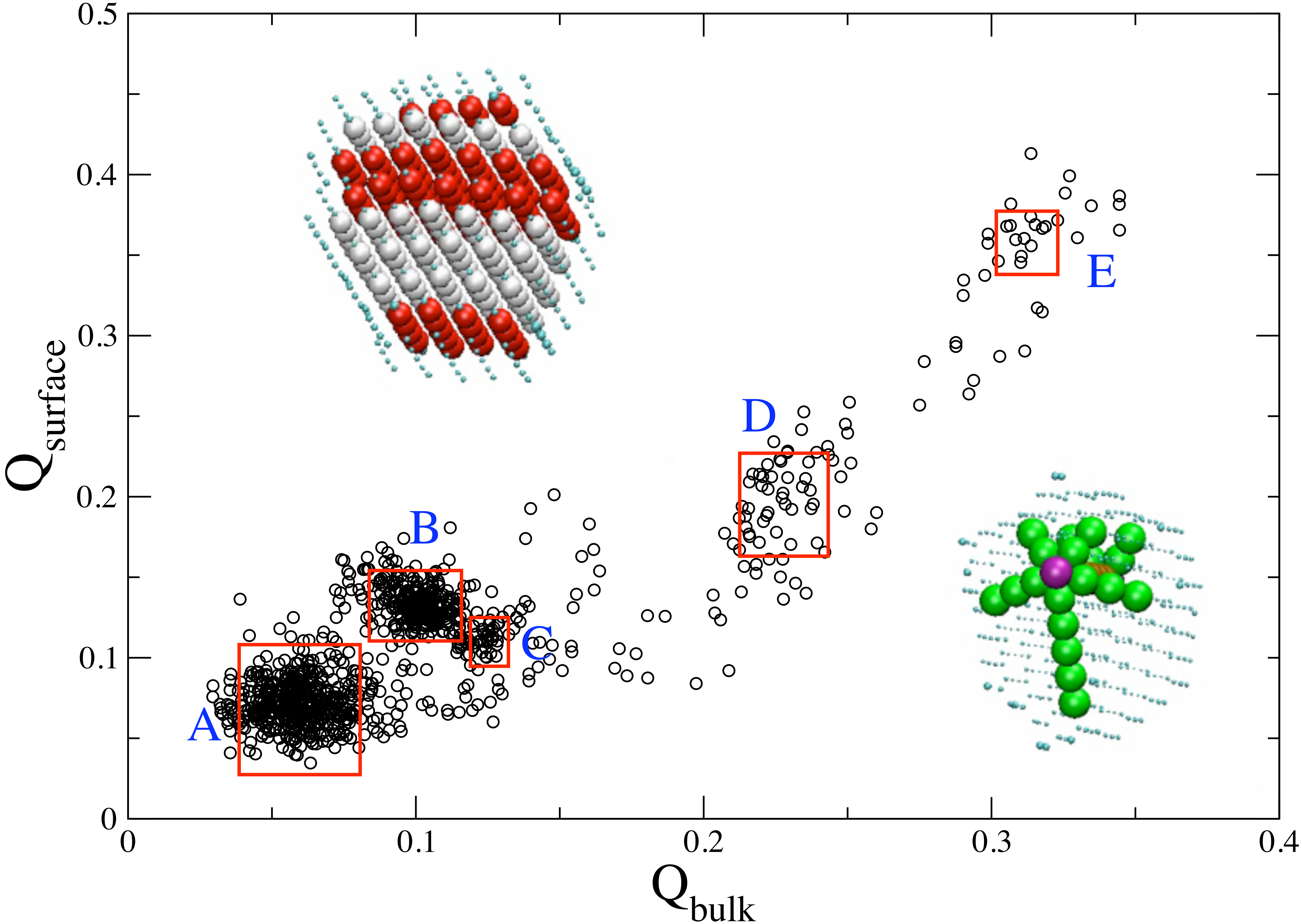
Gold Clusters N=459



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Summary

Medium Sized Clusters Exhibit New Phases

Tetrahedra formation

Important for phase behaviour

Important for nucleation of non-crystalline structures?

Still looking for reaction coordinates

Transition states ensembles and Trajectories

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