Challenges in the simulation of nucleation processes: from transition pathways to reaction coordinates

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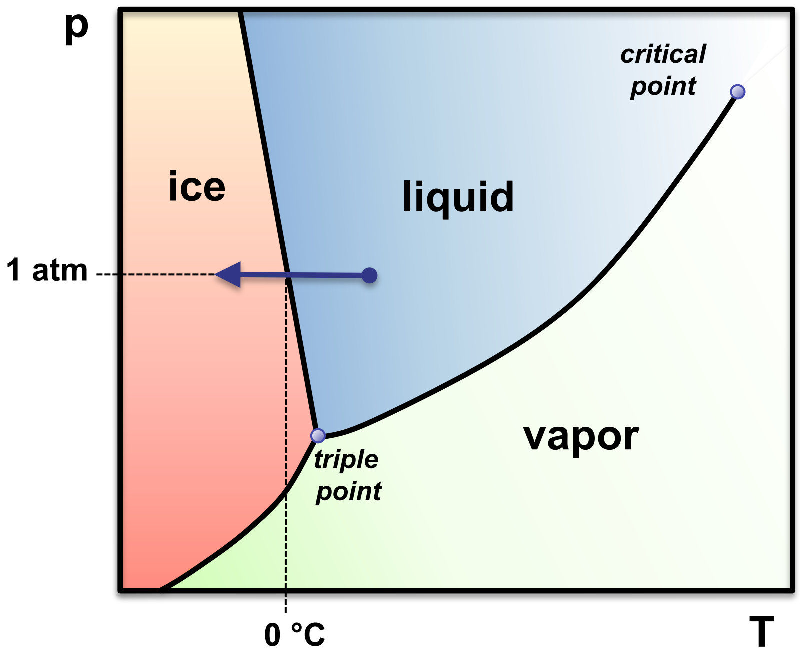
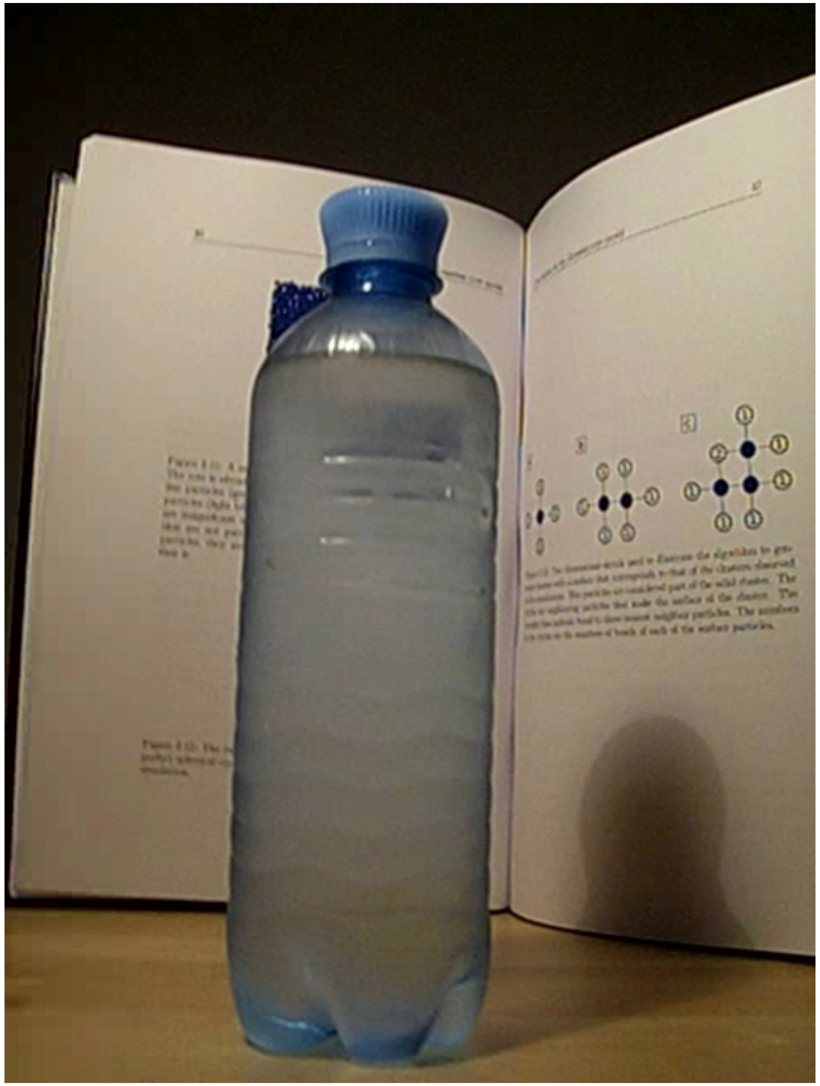
A kitchen experiment





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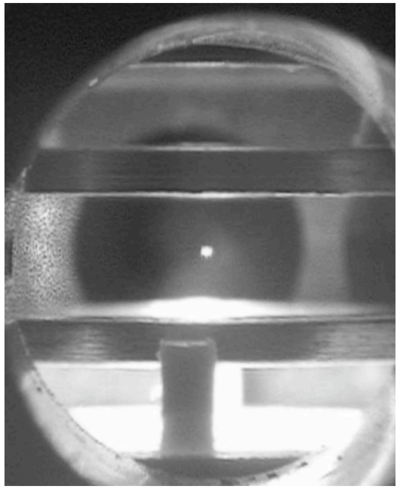
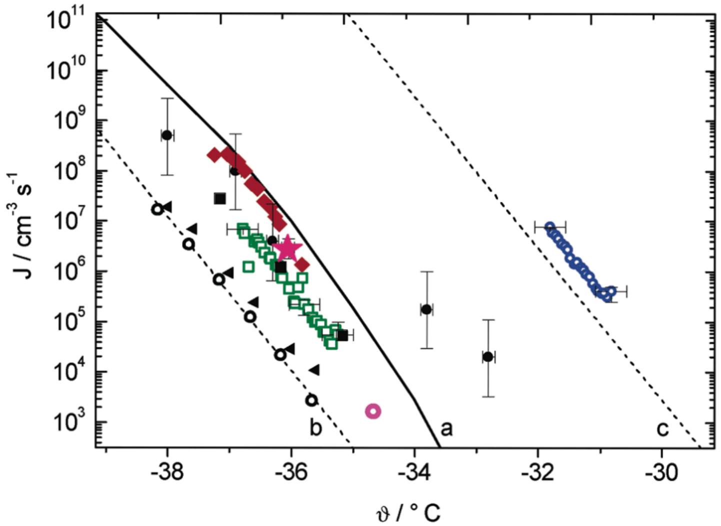
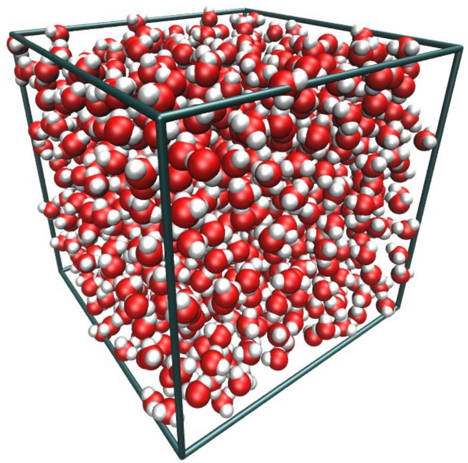
Freezing of supercooled water







J = nucleation rate = events / time and volume

N = 1000

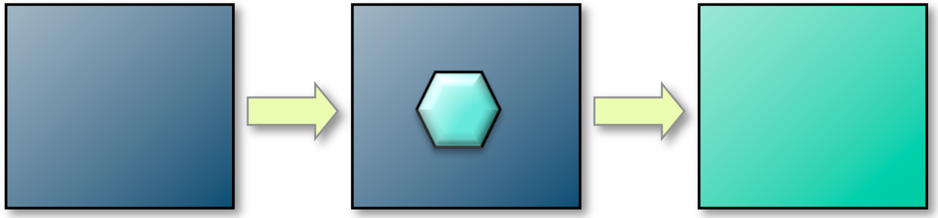
V = 3 x 10^{-20} cm^3

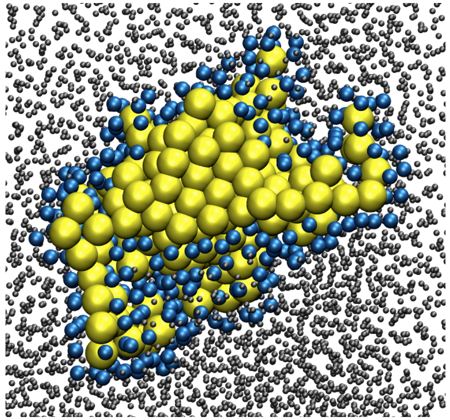
1 event per 10^{10}-10^{15} sec

10^{25}-10^{30} MD steps

Stöckel, Weidinger, Baumgärtel, Leisner, J. Phys. Chem. A 109, 2540 (2005)

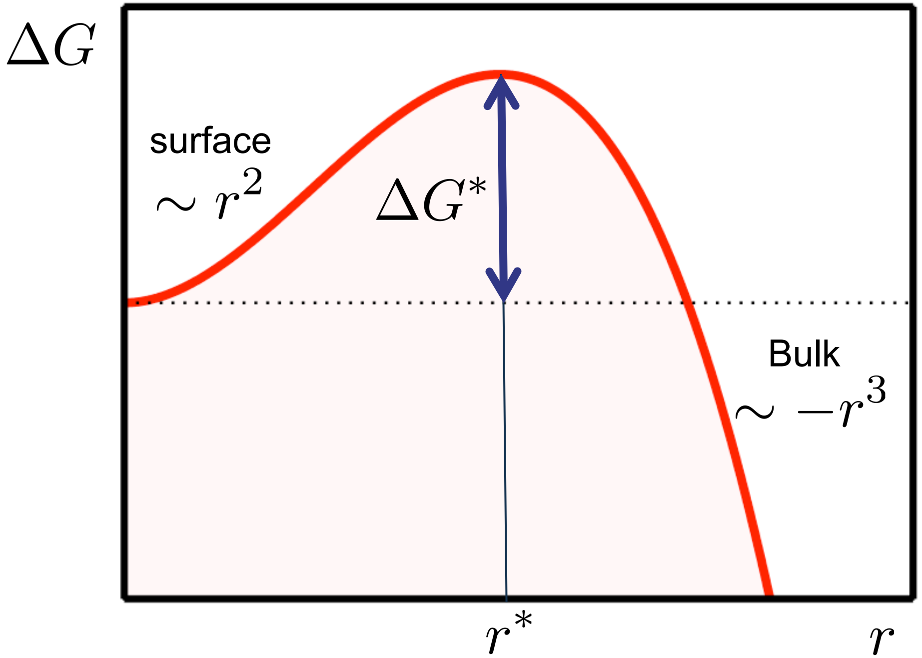
Classical nucleation theory



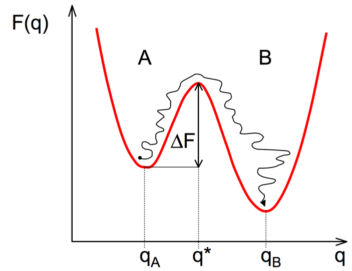


$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3}\pi r^3 \rho_s \Delta\mu$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3\rho_s \Delta\mu^2}$$

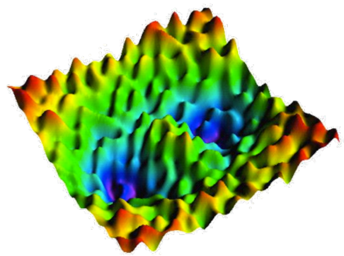


Computational Challenges of Nucleation



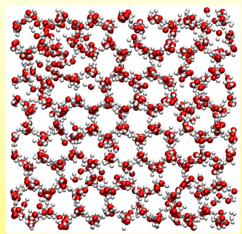
Rare events: large time scale gap

- Biased Monte Carlo
- Blue Moon Sampling
- Metadynamics
- Adiabatic Free Dynamics, TAMD
- **Transition Path Sampling**



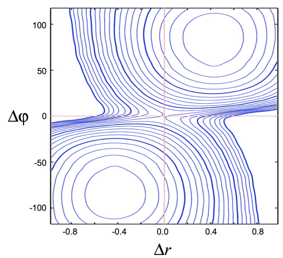
Ergodic sampling of trajectories

- Parallel Replica
- Wang Landau
- TPS + Metadynamics



Local structure recognition

- Bond order parameters
- **Neural Networks**



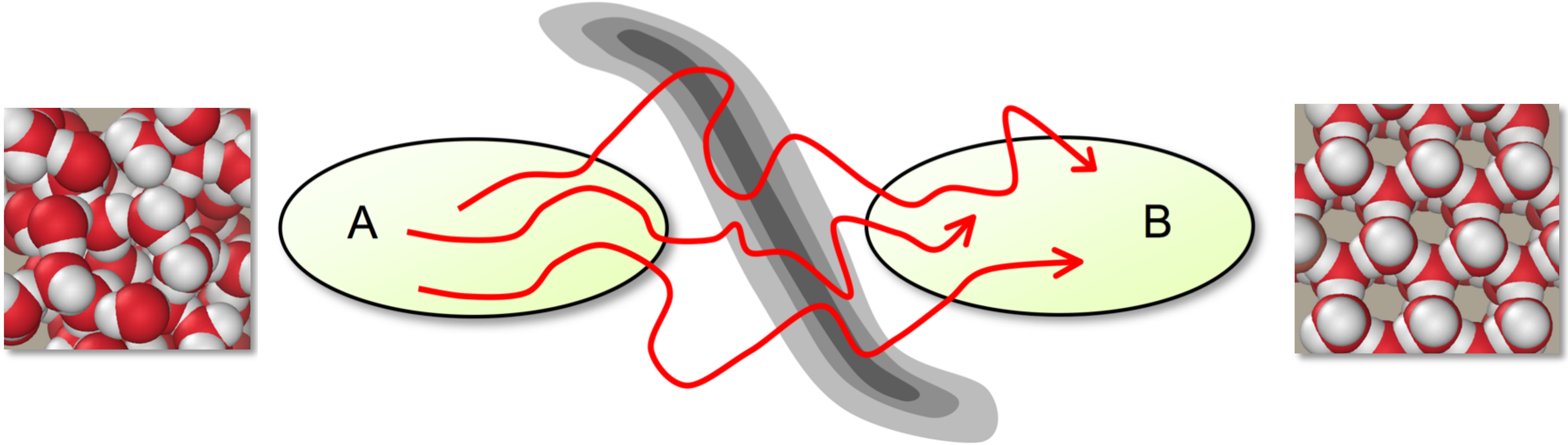
Reaction coordinate analysis

- String method
- Neural network analysis
- Likelihood Maximization

Transition path sampling

Transition path ensemble

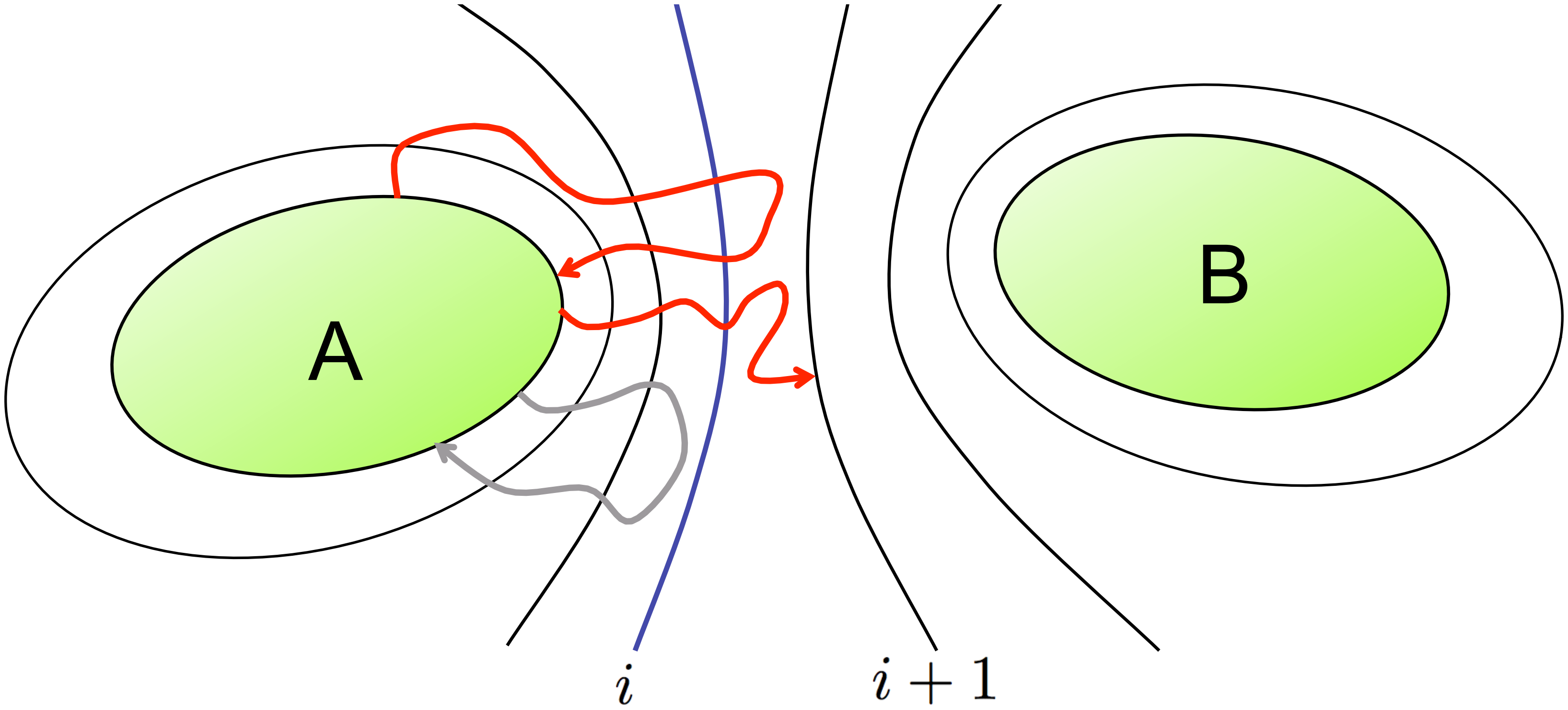
$$\mathcal{P}[x(t)] \propto h_A(x_0)\rho(x_0)\prod_{i=0}^{L-1} p(x_i \rightarrow x_{i+1})h_B(x_L)$$



Sample TPE with Monte Carlo

C. Dellago, P. G. Bolhuis, F. S. Csajka, D. Chandler, JCP 108, 1964 (1998)
C. Dellago, P. L. Geissler, P. G. Bolhuis, Adv. Chem. Phys. 123, 1 (2002)

Transition interface sampling

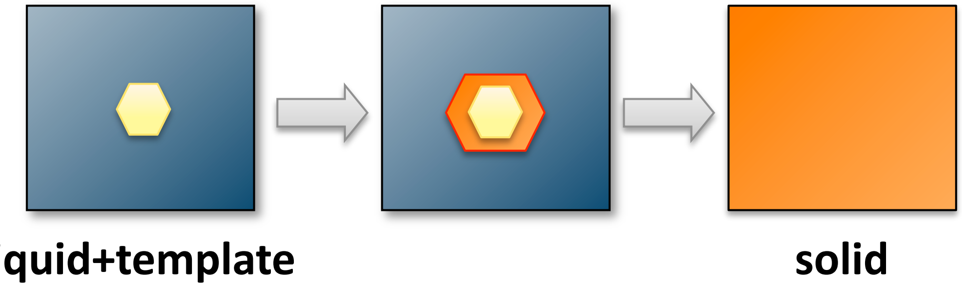


$\mathcal{P}_A(i+1|i)$ = probability that path crossing i for first time after leaving A reaches i+1 before A

$$k_{AB} = \frac{\langle \phi_{AB} \rangle}{\langle h_\mathcal{A} \rangle} = \frac{\langle \phi_{A1} \rangle}{\langle h_\mathcal{A} \rangle} \prod_{i=1}^{n-1} \mathcal{P}_A(i+1|i)$$

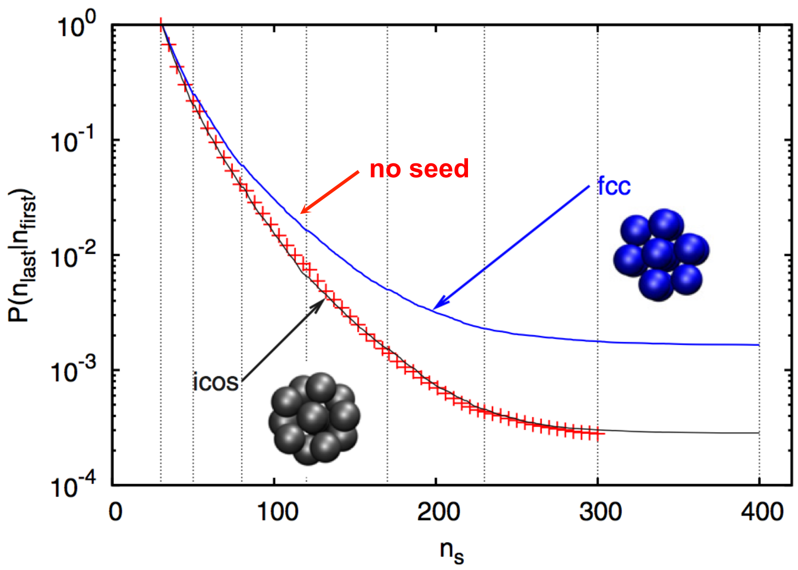
T. S. van Erp, D. Moroni and P. G. Bolhuis, J. Chem. Phys. 118 , 7762 (2003)
T. S. van Erp and P. G. Bolhuis, J. Comp. Phys. 205, 157 (2005)

Crystallization on tiny templates



crossing probability $P_A(\lambda_j|\lambda_1) = \prod_{i=1}^{j-1} P_A(\lambda_{i+1}|\lambda_i)$

- 28% undercooling
- Lennard-Jones particles
- N=6600 particles
- Seed size n=13
- NpH-ensemble



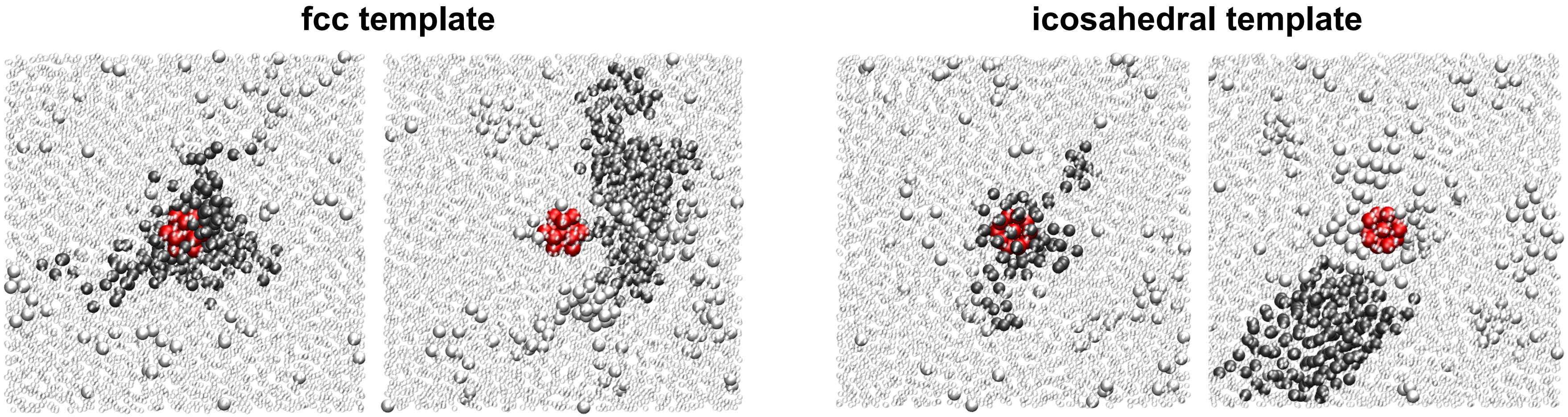
J_{fcc}=1.7x10^{-7}

J_{ico}=3.1x10^{-8}

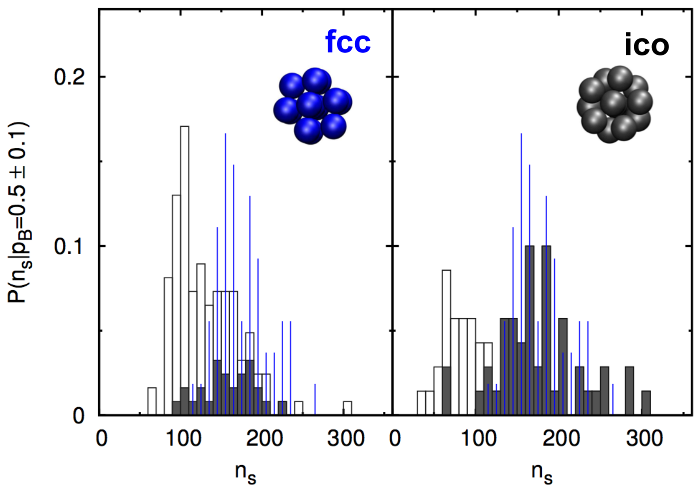
J_{hom}=3.0x10^{-8}

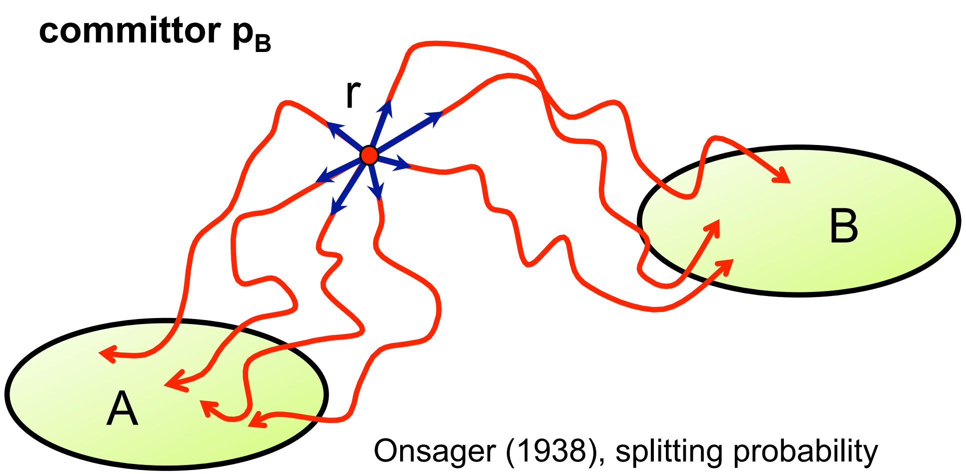
S. Jungblut and C. Dellago, Europhys. Lett. 96, 56006 (2011)

Crystallization Pathways



Cluster size distributions
in transition state ensemble

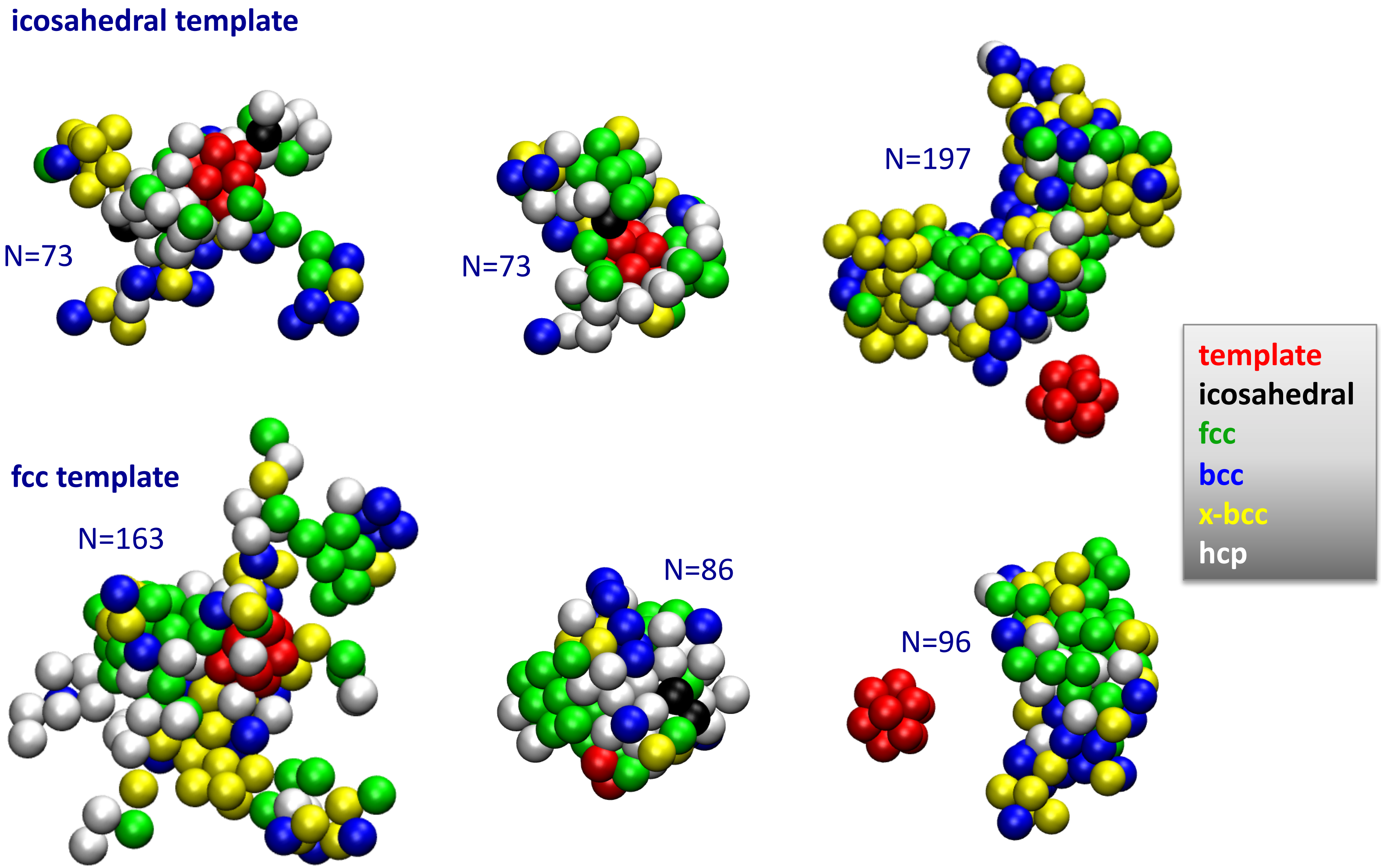




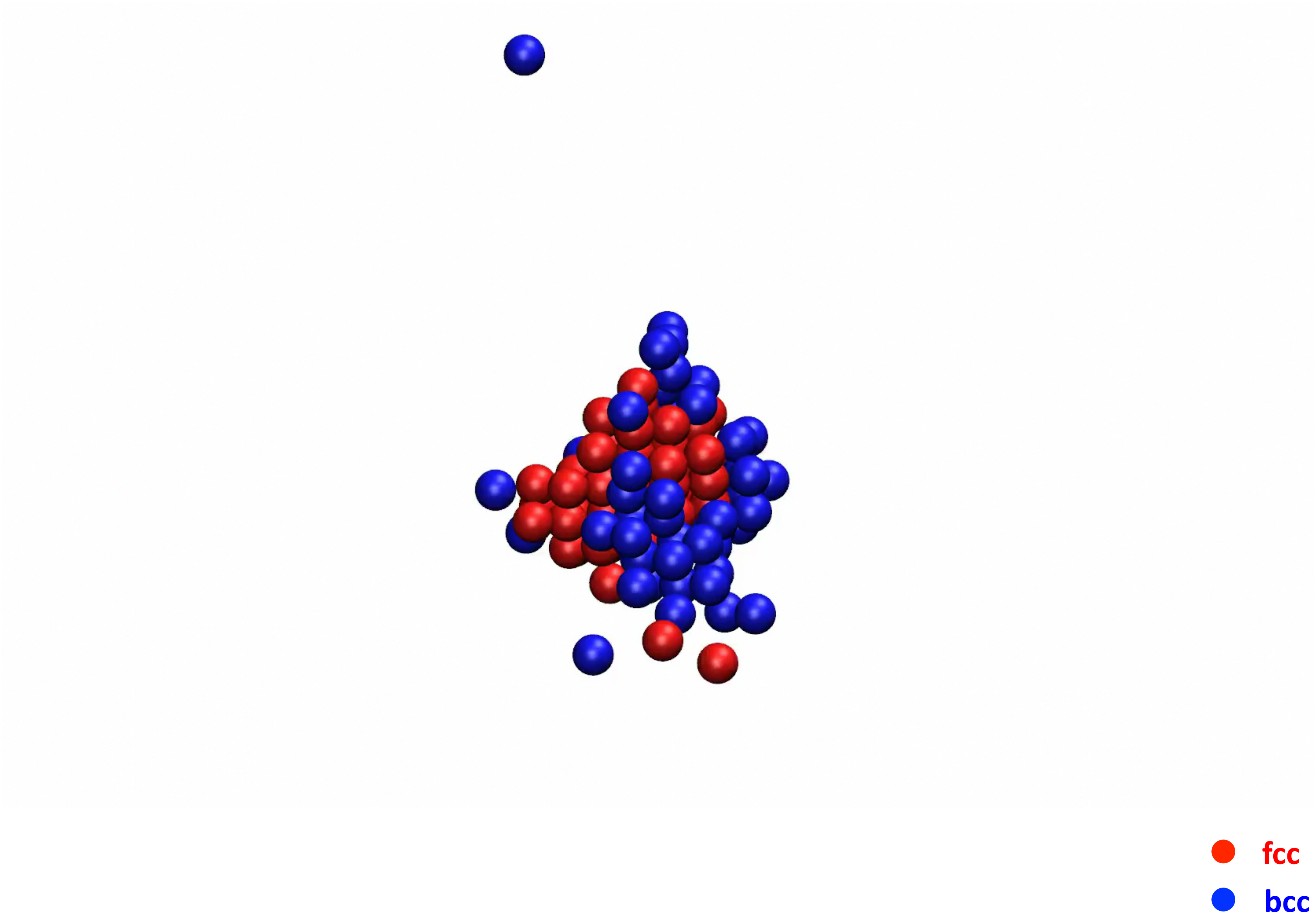
Onsager (1938), splitting probability
Klosek, Matkowsky, Schuss (1991)
Pande, Grosberg, Tanaka, Shaknovich (1998)

J. D. Honeycutt and H. C. Andersen, CPL 108, 535 (1984); JPC 90, 1585 (1986)

Structure of Critical Clusters

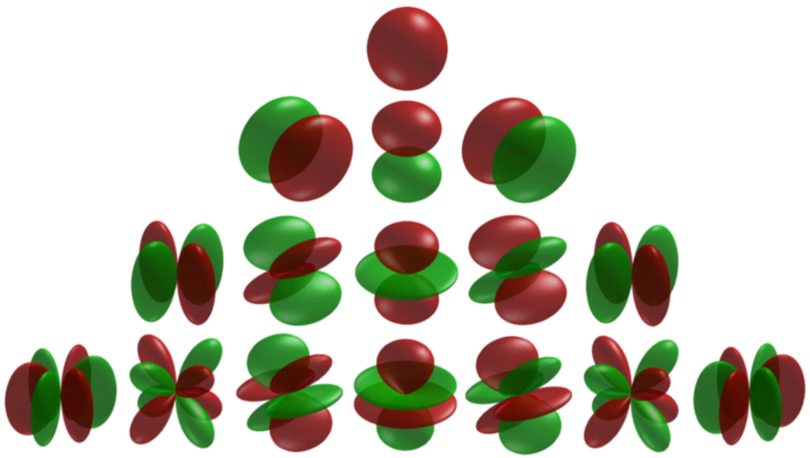


Generalized exponential model GEM4



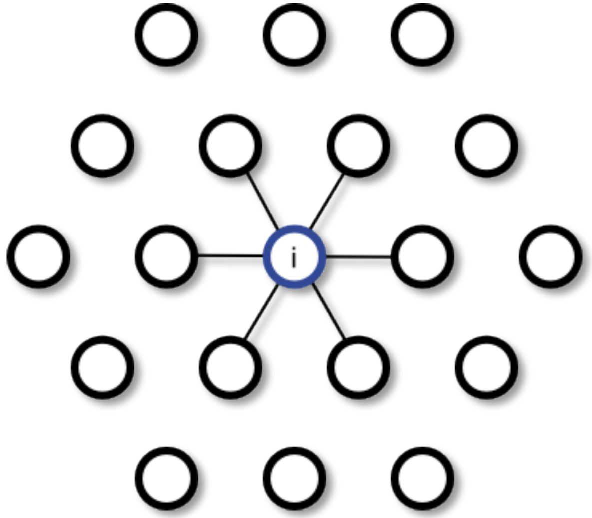
Detecting local order

Steinhardt bond order parameters



spherical harmonics

$$Y_{lm}(\vartheta,\varphi)$$



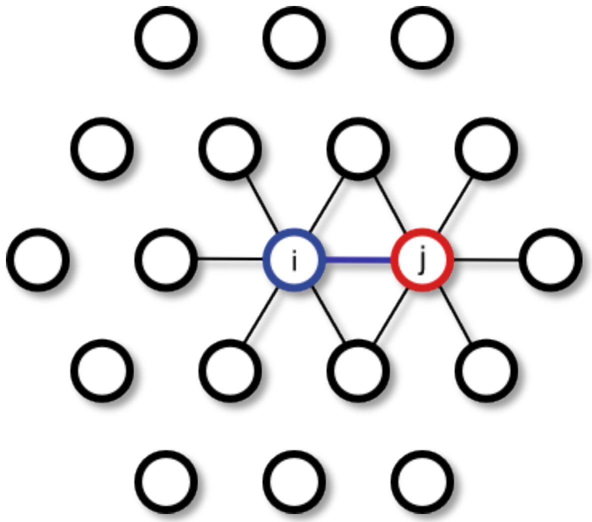
$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(r_{ij})$$

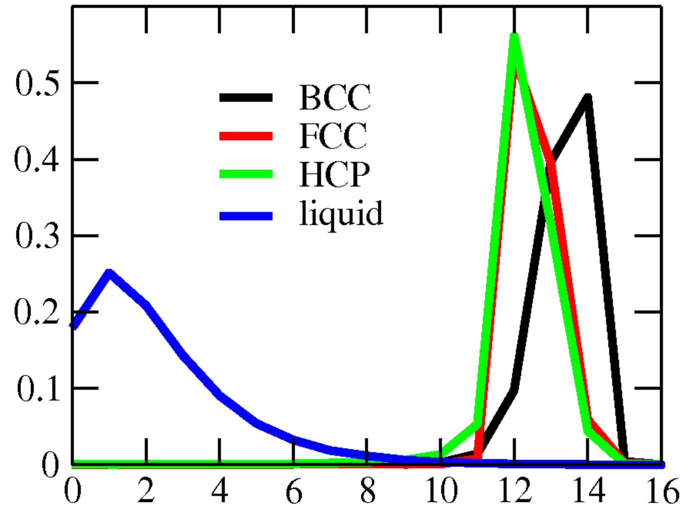
rotationally invariant

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

P. Steinhardt, D. R. Nelson, and M. Ronchetti, PRB 28, 784 (1983)

Distinguishing liquid from solid



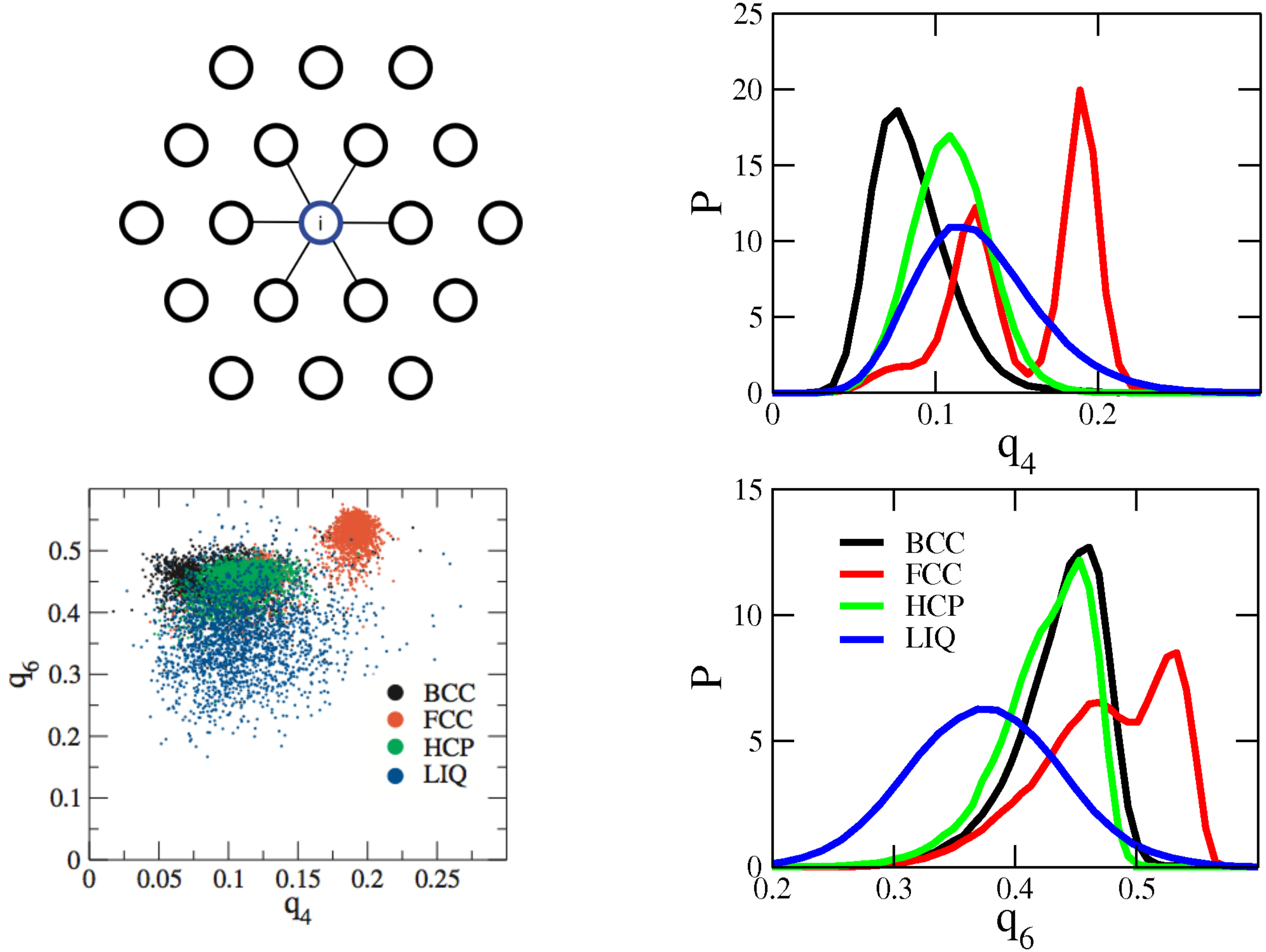


structural correlations

$$s_{ij} = \frac{4\pi}{2l+1} \frac{\sum_{m=-l}^{l} q_{lm}(i) q_{lm}^*(j)}{q_l(i) q_l(j)}$$

$$N_{bonds} = \sum_{N_b} \Theta(s_{ij} - 0.5)$$

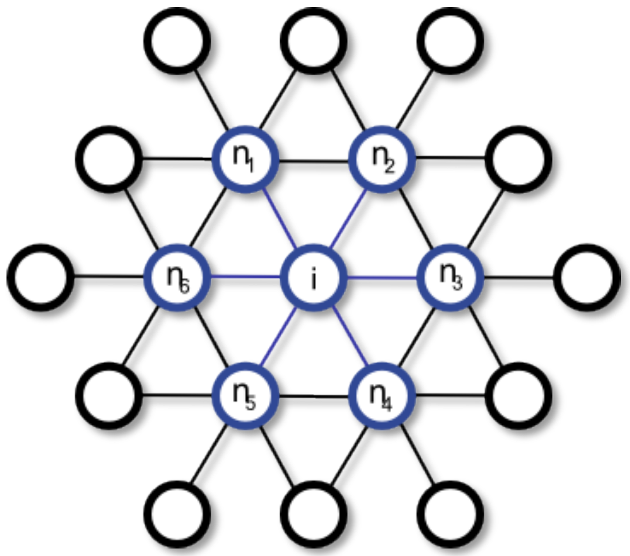
Distinguishing solid structures



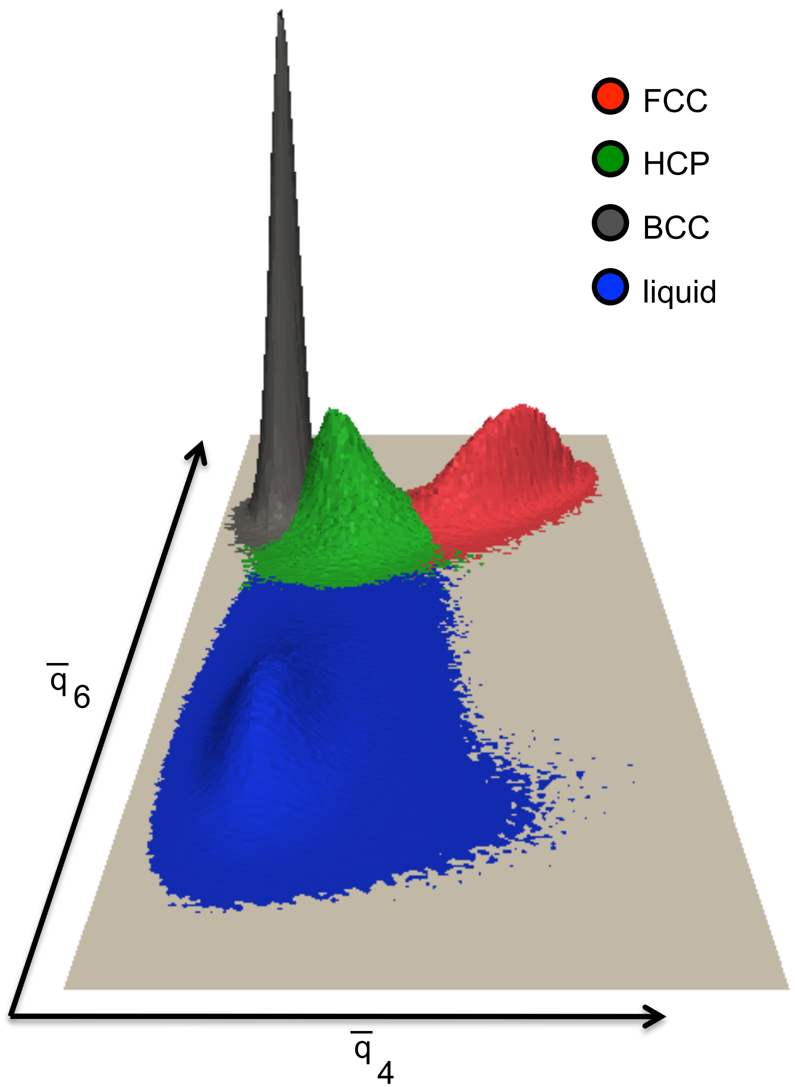
Ten Wolde, Ruiz-Montero, Frenkel, JCP 110, 1591 (1999)

Averaged local order parameters

$$\bar{q}_{lm}(i) = \frac{q_{lm}(i) + \sum_{k=0}^{N_b} q_{lm}(k)}{N_b + 1}$$

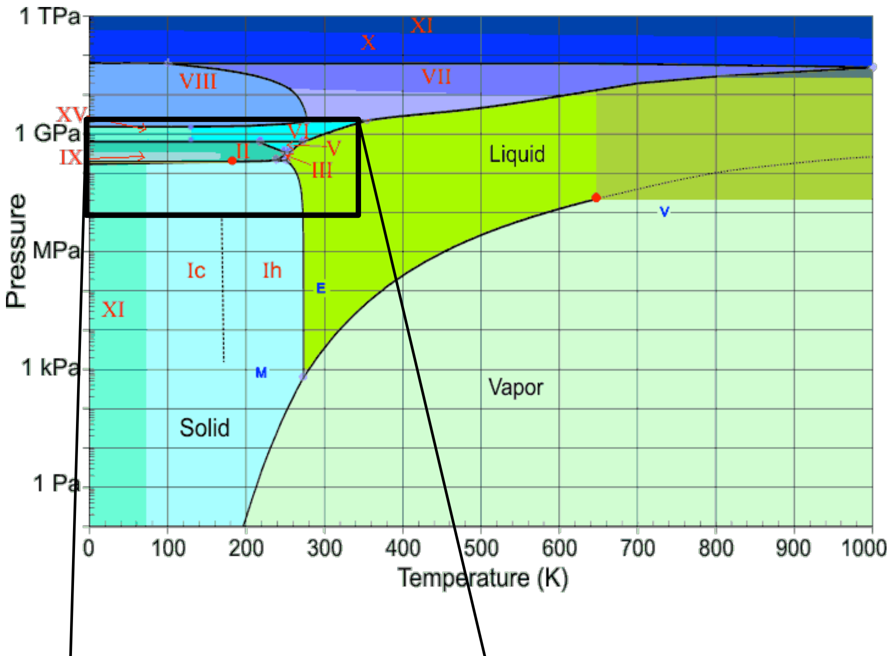


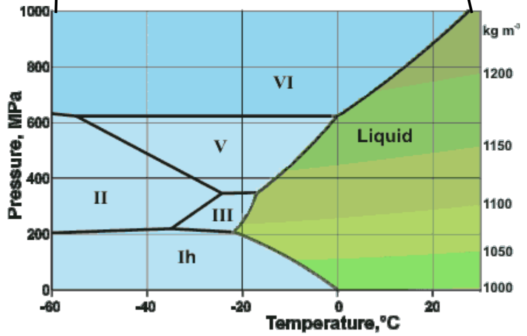
$$\bar{q}_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} \left| \bar{q}_{lm}(i) \right|^2}$$

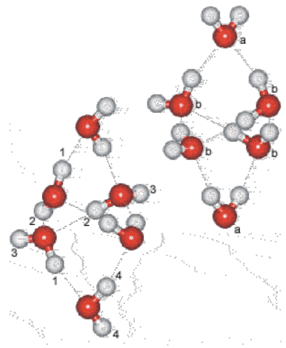


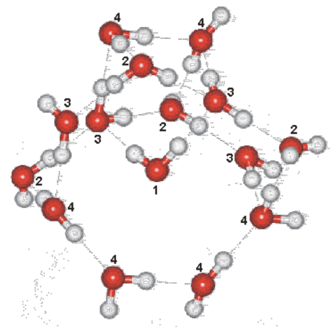
W. Lechner and C. Dellago, JCP 129, 114707 (2008)

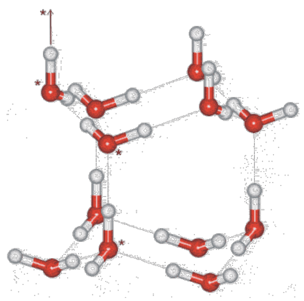
Liquid water and ice

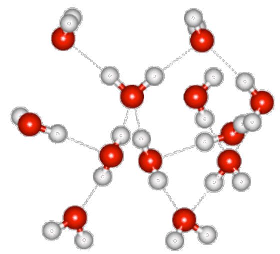






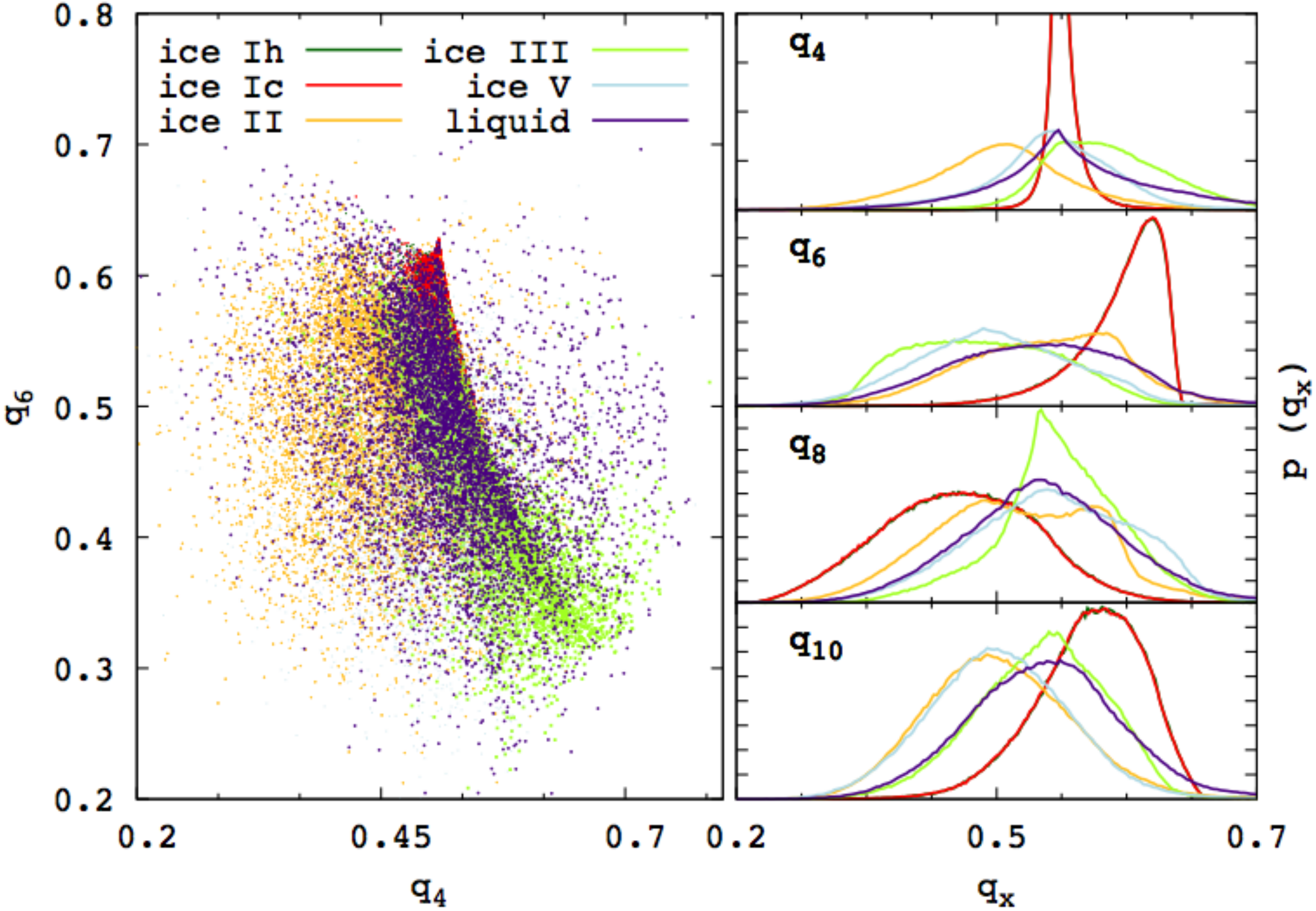






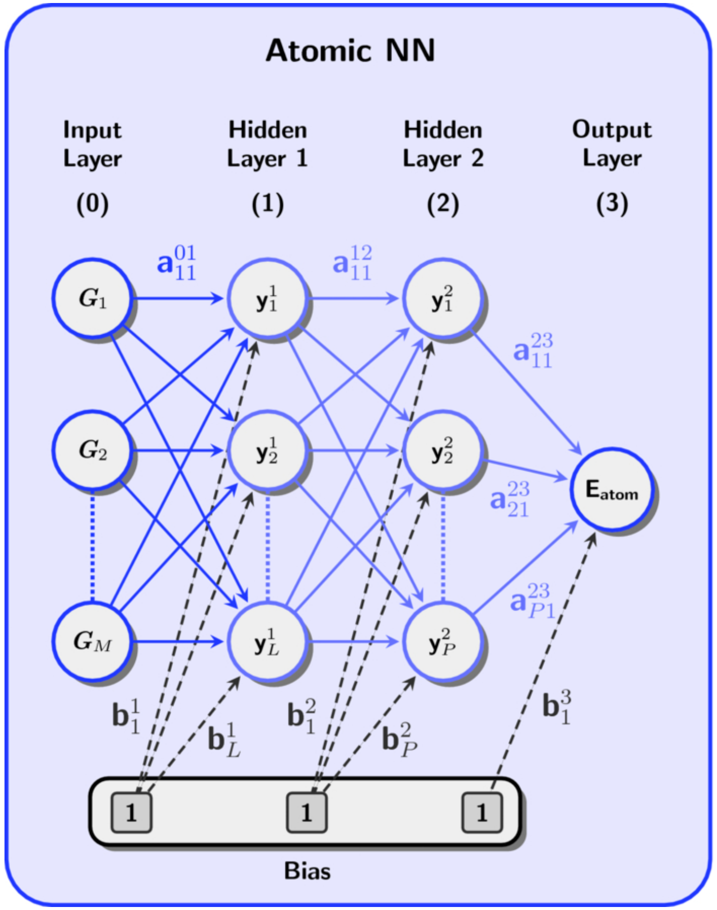
T. Lörting (Univ. Innsbruck)

Do bond order parameters work for ice?



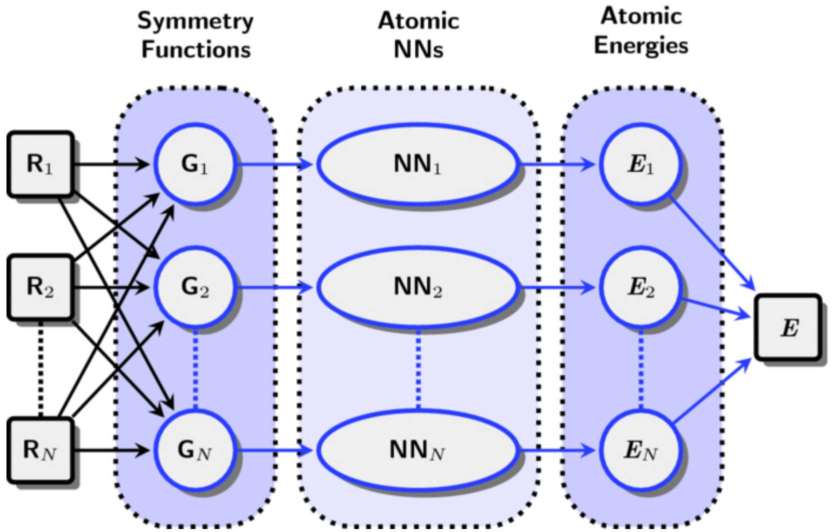
Brukhno, Anwar, Davidchack, and Handel, JPCM 20, 494243 (2008)

Representing energy surfaces with neural networks



$$E_i = f_a^2\left[w_{01}^2 + \sum_{j=1}^{3} w_{j1}^2 f_a^1\left(w_{0j}^1 + \sum_{\mu=1}^{2} w_{\mu j}^1 G_i^\mu \right)\right]$$

Behler, Parrinello, PRL 98, 146401 (2007)
Behler, Lorenz, Reuter, JCP 127, 014705 (2007)
Behler, PPCP 13, 17930 (2011)



Al, Si, Na, Cu, ZnO, H_2O

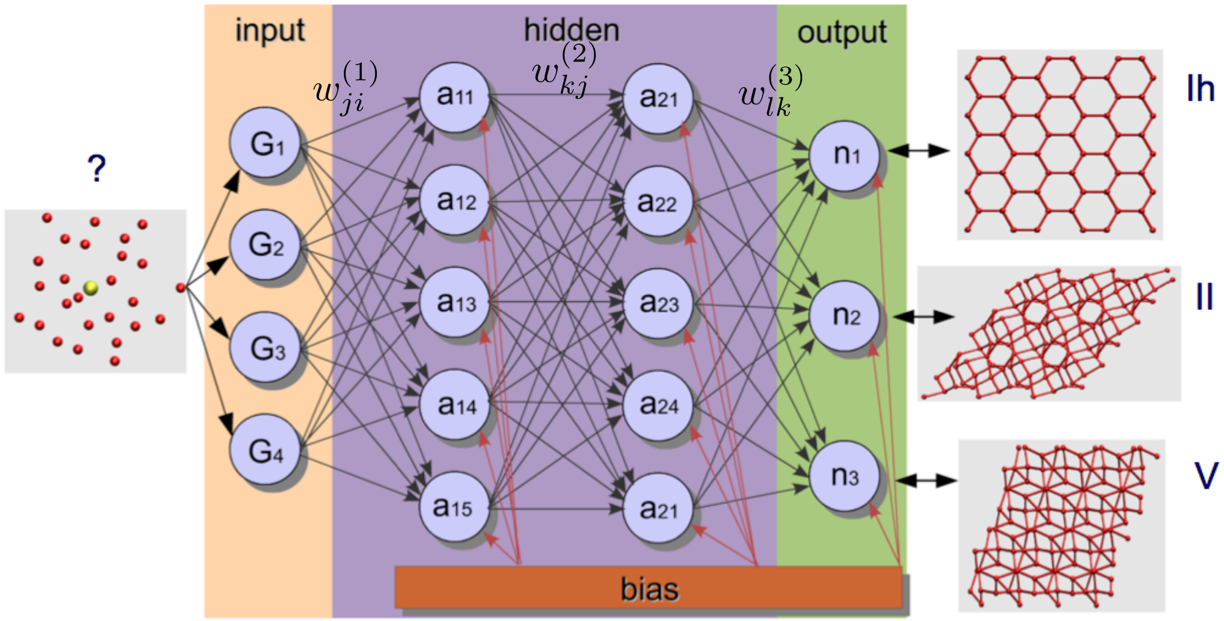
Symmetry functions

$$f_c(R_{ij}) = \begin{cases} 0.5 \times \left[\cos\left(\frac{\pi R_{ij}}{R_c}\right) + 1\right] & \text{for } R_{ij} \le R_c \\ 0 & \text{for } R_{ij} > R_c. \end{cases}$$

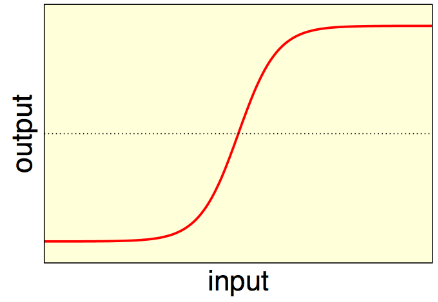
$$G_i^1 = \sum_{j \neq i}^{\text{all}} e^{-\eta (R_{ij} - R_s)^2} f_c(R_{ij}).$$

$$G_i^2 = 2^{1-\zeta} \sum_{j,k \neq i}^{\text{all}} (1 + \lambda \cos\theta_{ijk})^\zeta \times e^{-\eta (R_{ij}^2 + R_{ik}^2 + R_{jk}^2)} f_c(R_{ij}) f_c(R_{ik}) f_c(R_{jk})$$

Neural network for structure recognition



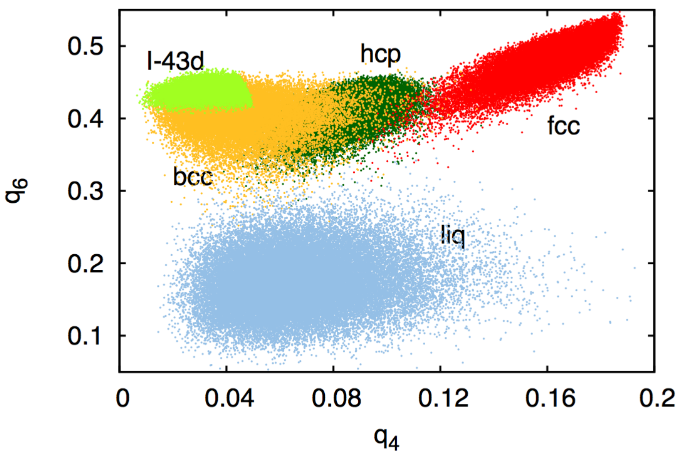
activation function

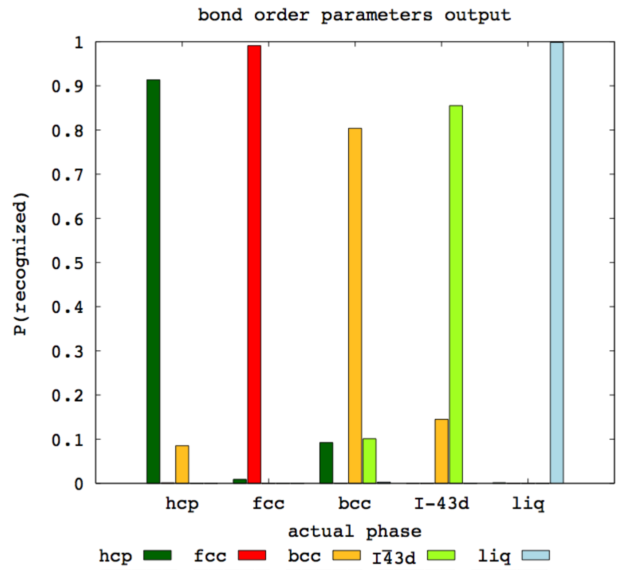


- Training with glocal extended Kalman filter to find optimum weights
- Training set: 30.000 uncorrelated configurations from MD (different densities)
- NN training on GPU (takes a few days)

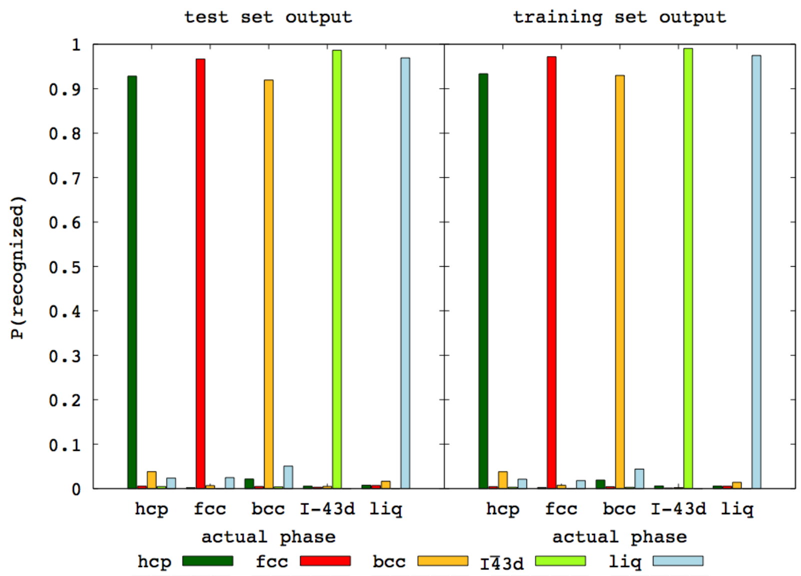
Structure prediction for Lennard-Jonesium

bond order parameters



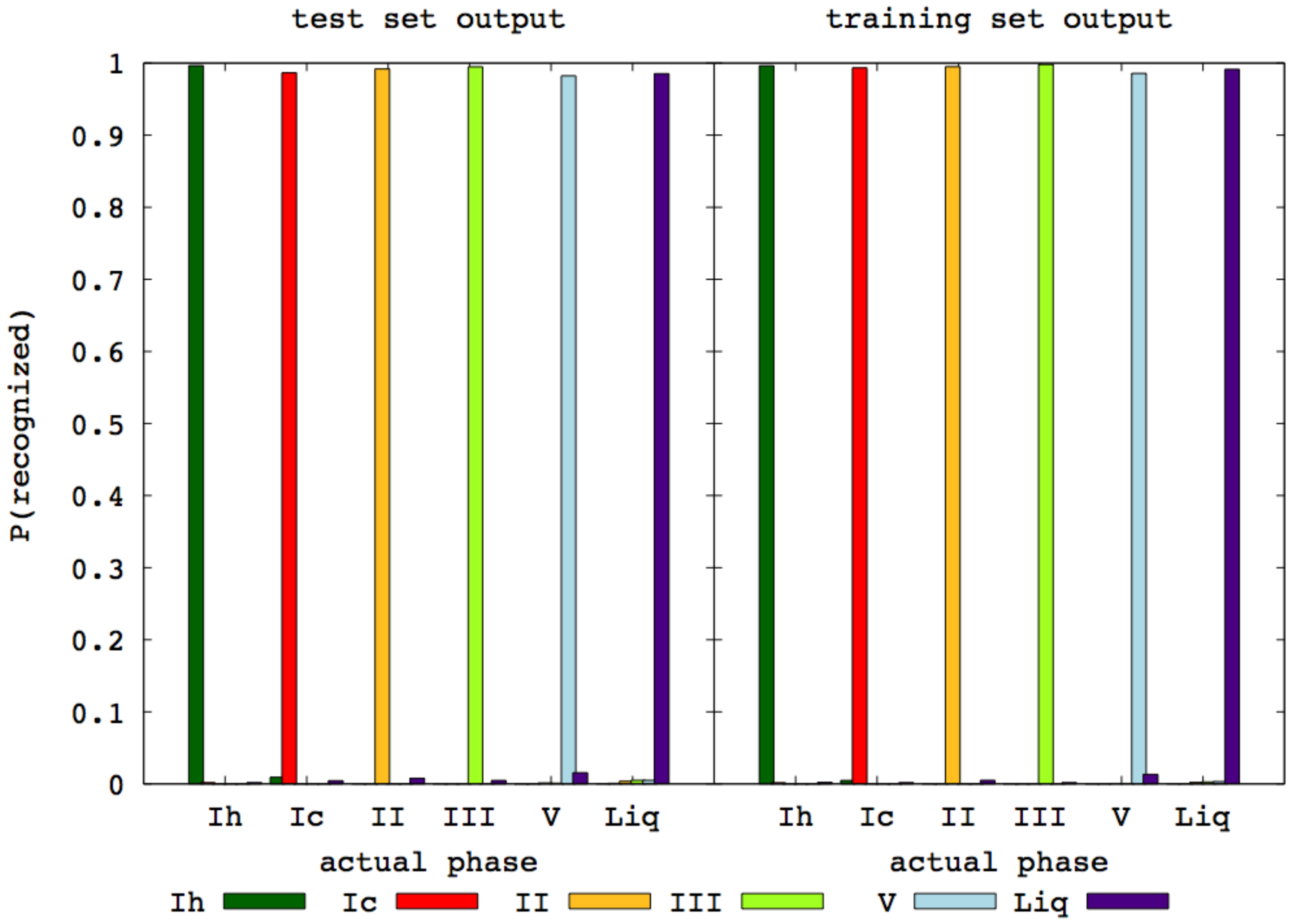


neural network



Structure Prediction for Water and Ice

T=270K, various pressures, 30.000 training structures



Nucleation of Ice Ih and Ice III