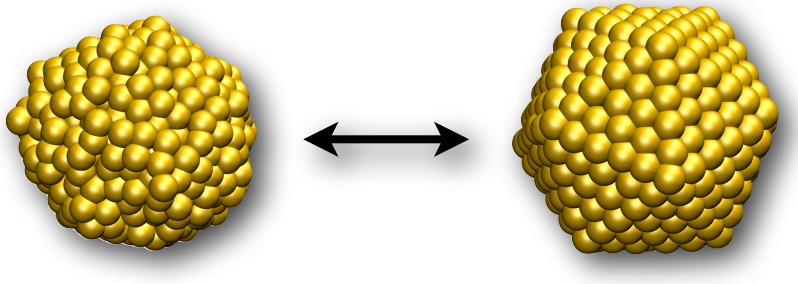
Studying nucleation processes with computer simulations:

Neural networks for force calculation and structure recognition

Christoph Dellago
Faculty of Physics
University of Vienna
Austria

Jörg Behler (U Bochum)
Andreas Singraber (U Vienna)
Philipp Geiger (U Vienna)
Ernesto Borrero (U Vienna)



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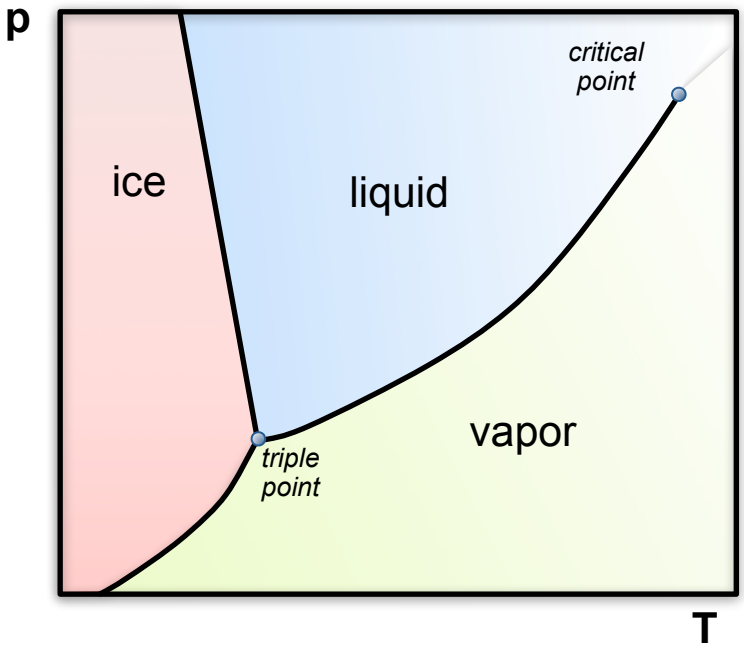
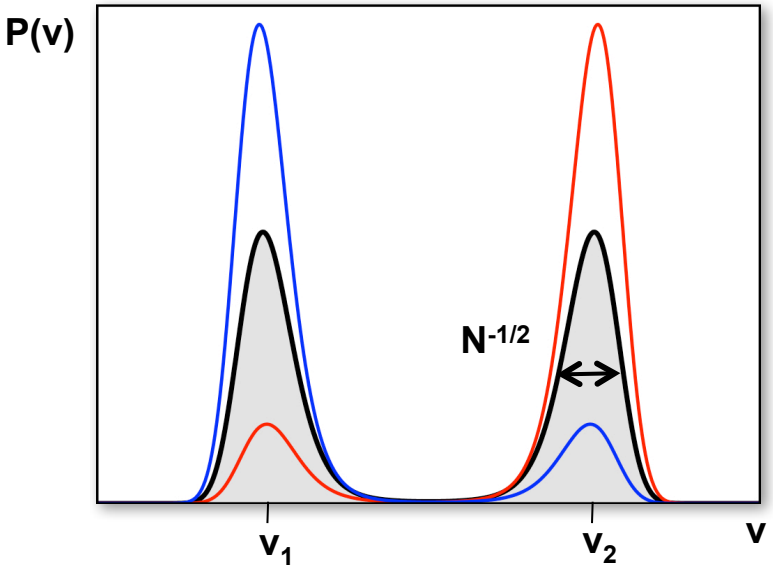
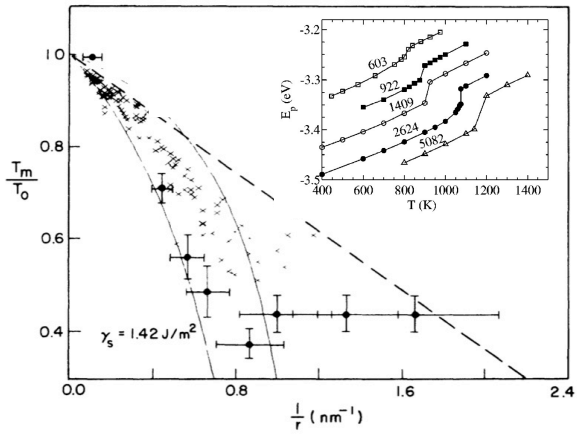
Rounding of phase transition





Phase transitions in small systems

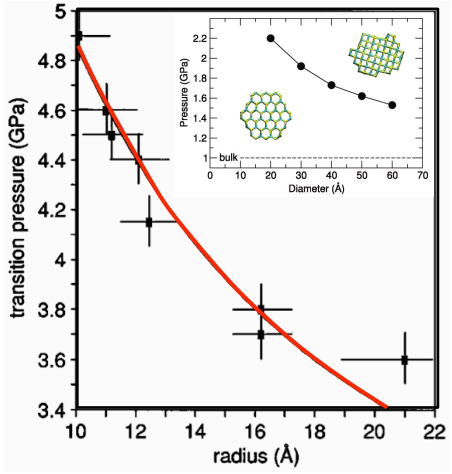
Melting point depression of Au nanoparticles

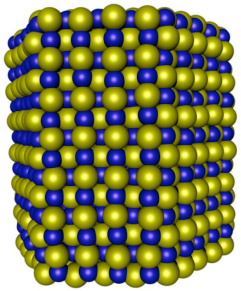


$$\gamma_l < \gamma_s$$

Y. Wang, S. Teitel, and C. Dellago, JCP 122, 214722 (2005)
T. Castro, R. Reifenberger, E. Choi, and R. P. Andres, PRB 42, 8548 (1990)

Transition pressure elevation in CdSe nanocrystals

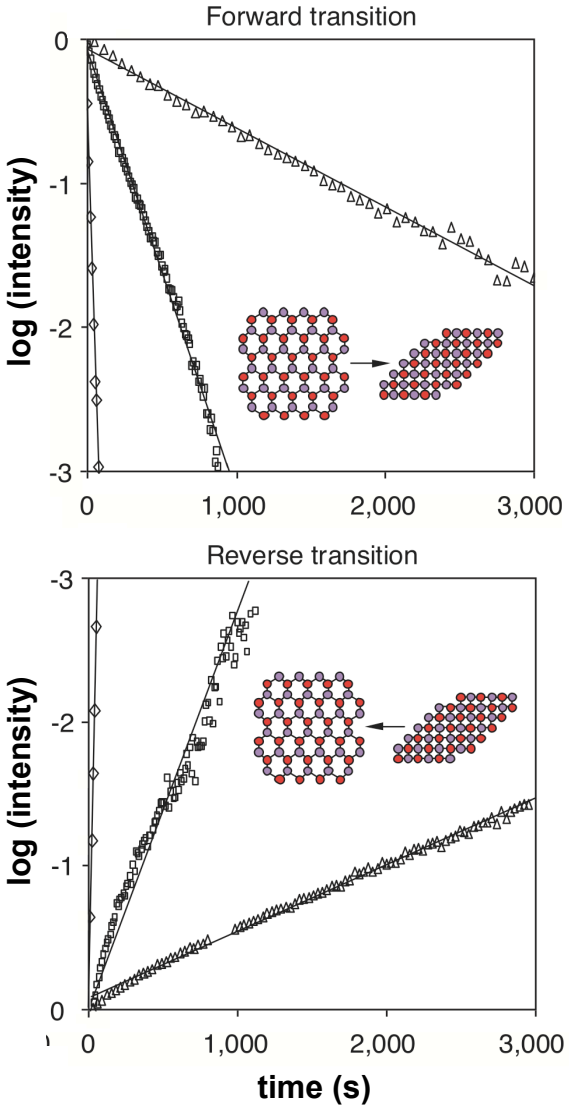


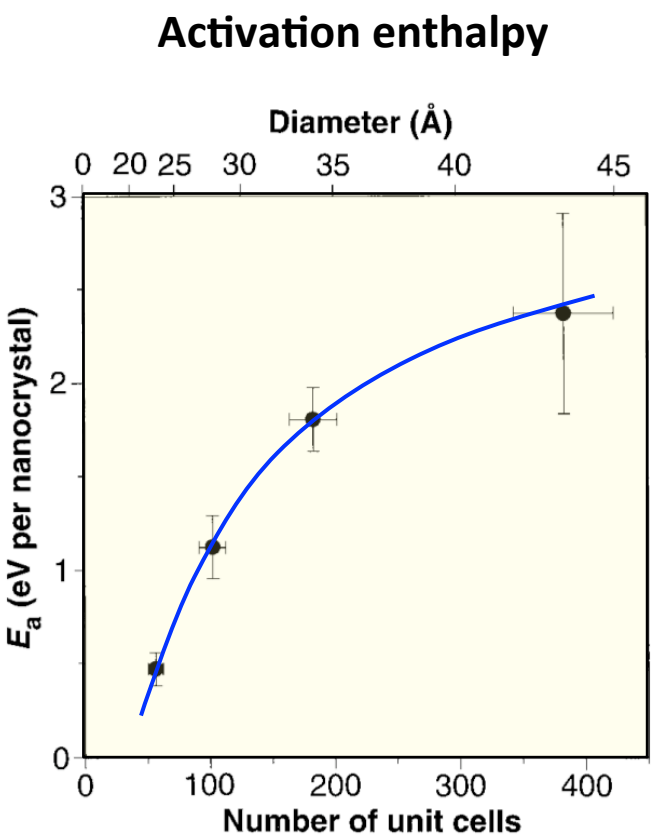


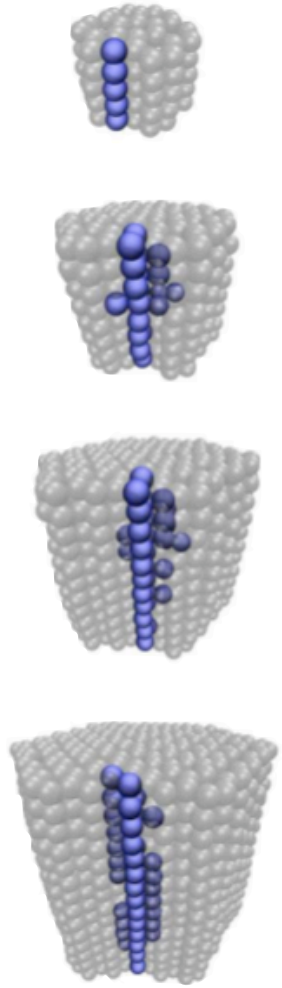
$$\gamma_{\mathrm{WZ}} < \gamma_{\mathrm{RS}}$$

M. Grünwald and C. Dellago, Nano Letters 9, 2099 (2009)
S. H. Tolbert and A. P. Alivisatos, Science 265, 373 (1994)

Transformation kinetics and mechanism

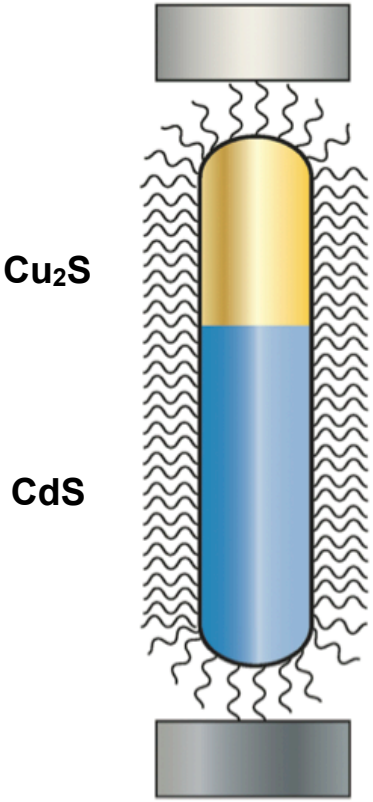


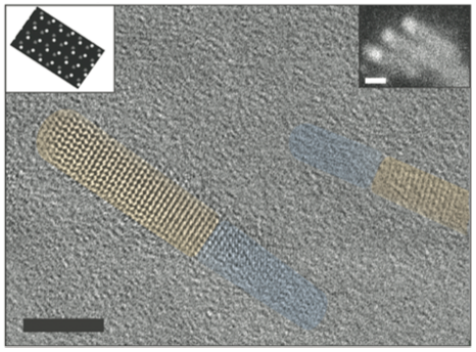


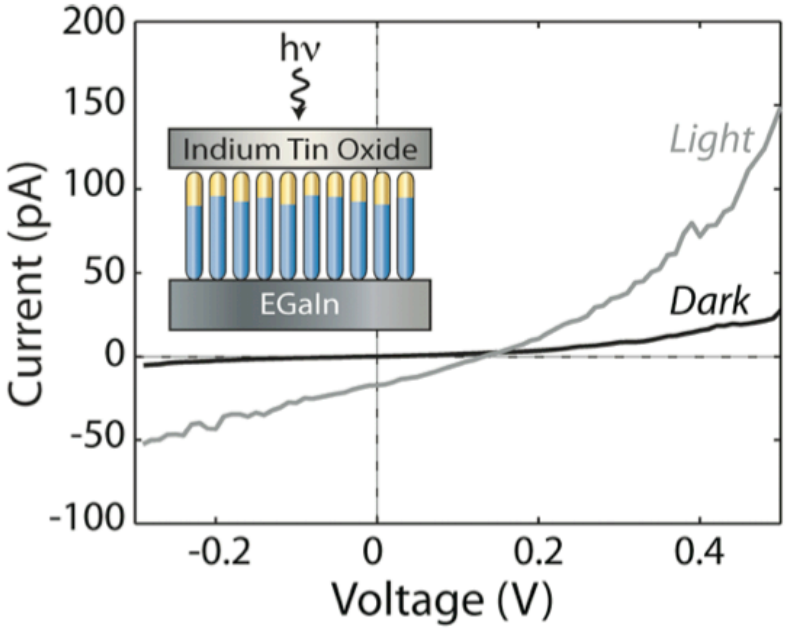


K. Jacobs, D. Zaziski, E. C. Scher, A. B. Herhold, and A. P. Alivisatos, Science 293, 1803 (2001)
M. Grünwald and C. Dellago, Nano Letters 9, 2099 (2009)

Cu_2S nanorods

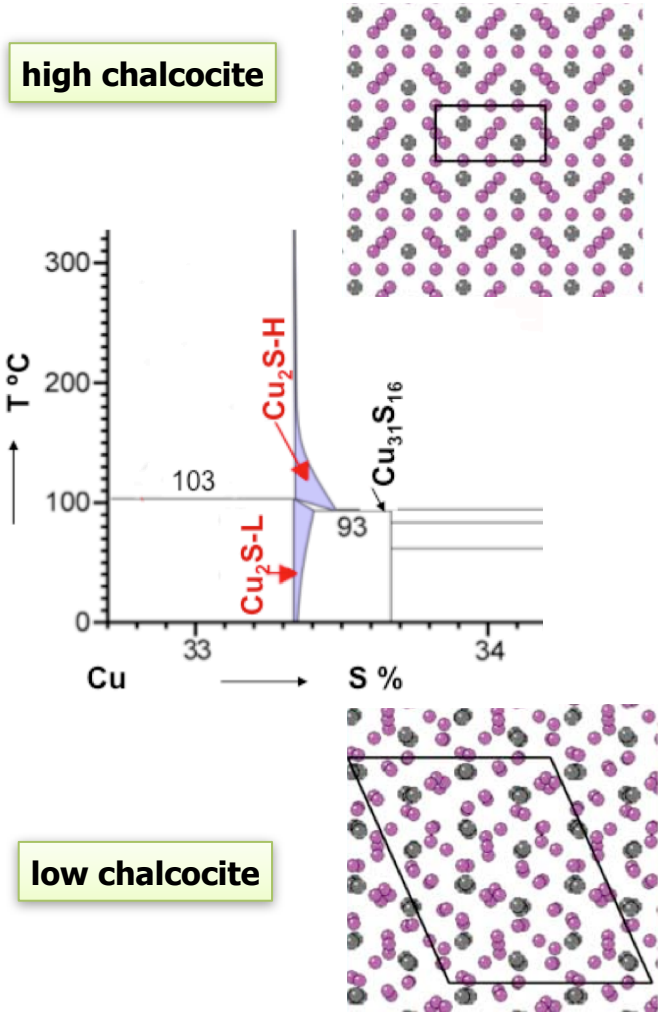


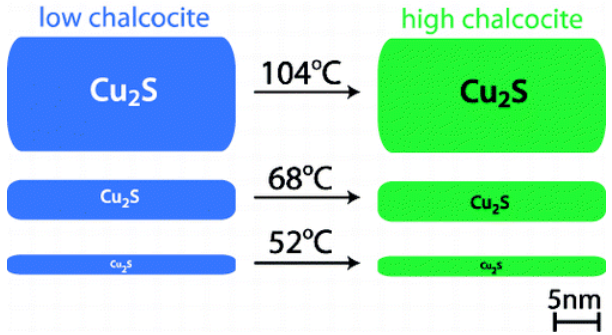


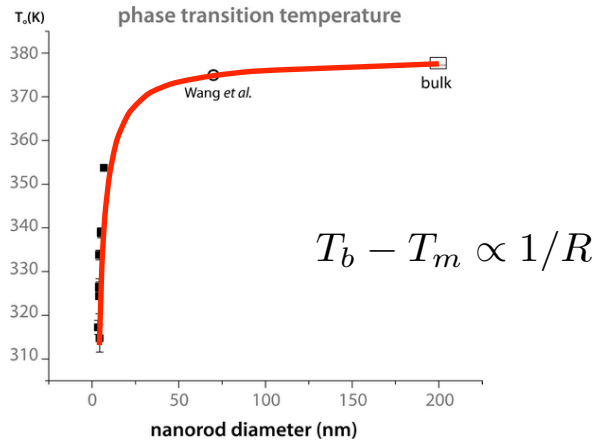


J. B. Rivest et al., ACSNano 5, 3811 (2011)

Low-to-high chalcocite transition in Cu_2S nanorods



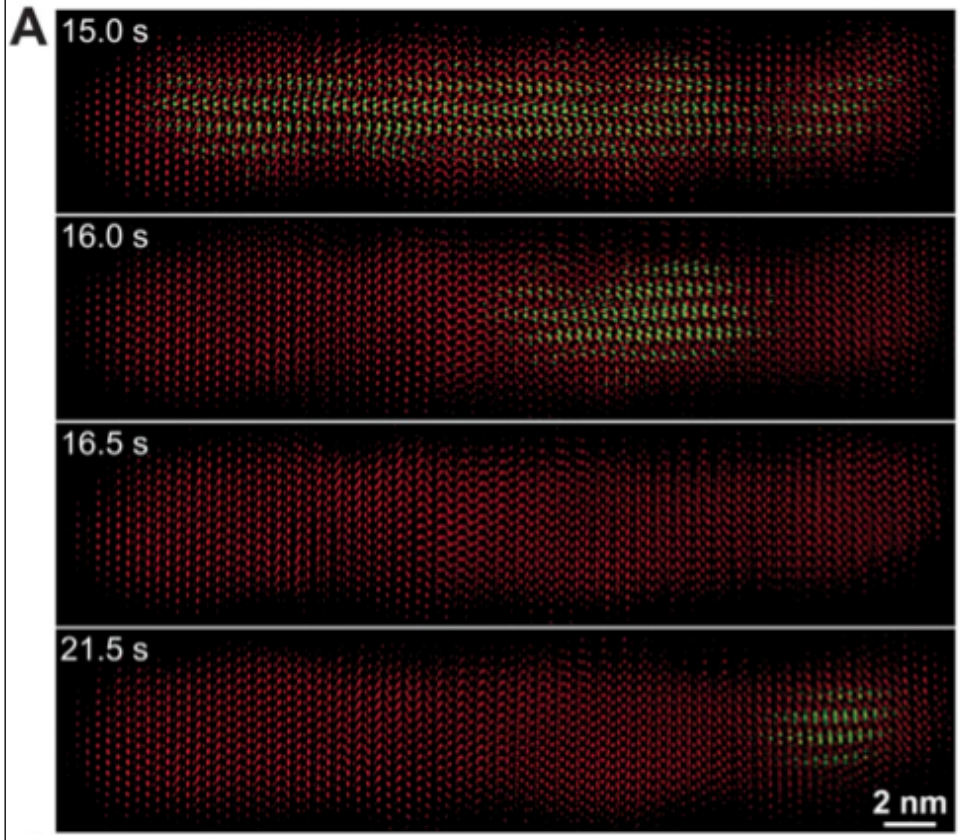


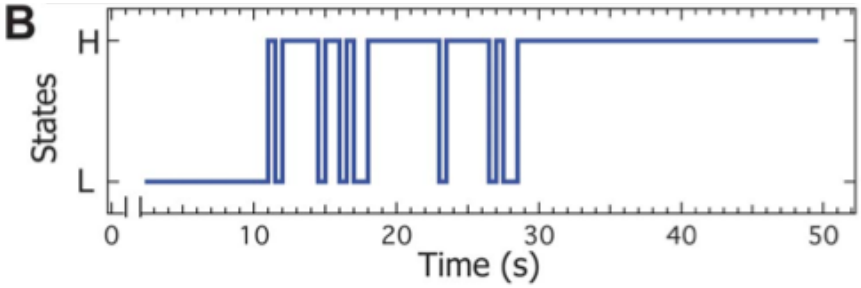


$$T_b - T_m \propto 1/R$$

Zheng, Rivest, Miller, Sadtler, Lindenberg, Toney, Wang, Kisielowski, Alivisatos, Science 333, 207 (2011)

Low- to high-chalcocite transition



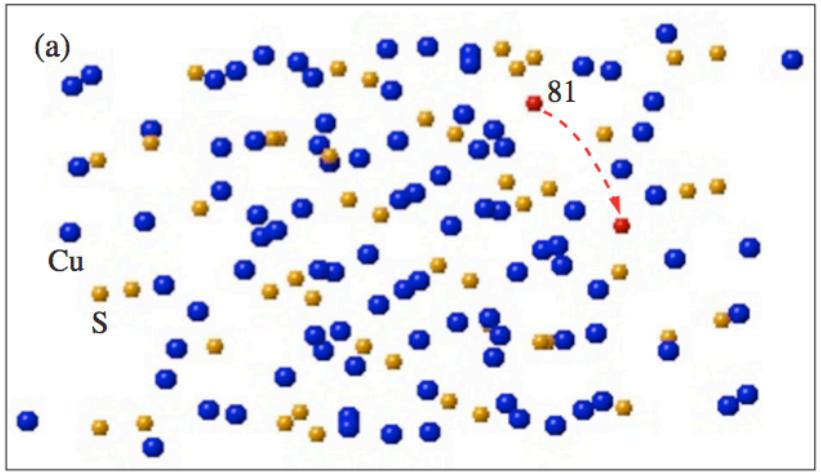


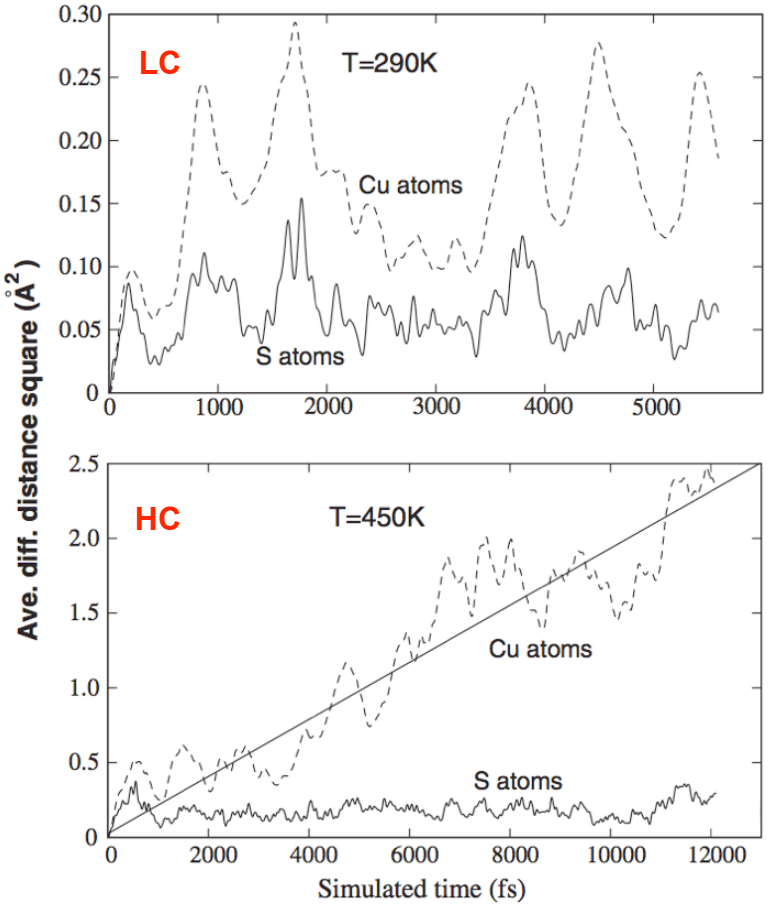
$$P(\mathrm{LC}) = \frac{1}{1 + \exp\left\{\frac{\Delta E}{k_\mathrm{B} T}\frac{(T - T_\mathrm{LH})}{T_\mathrm{LH}}\right\}}$$

$$\Delta T = \frac{4 k_\mathrm{B} T_m^2}{\Delta E} \approx 0.2K$$

Zheng, Rivest, Miller, Sadtler, Lindenberg, Toney, Wang, Kisielowski, Alivisatos, Science 333, 207 (2011)

Cu_2S ab initio simulations





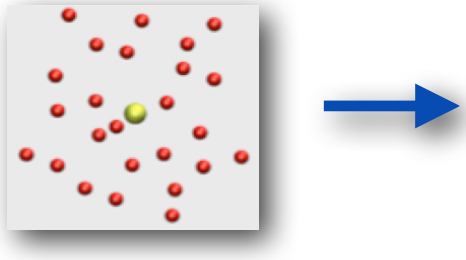
High chalcocite: N=48, 12 ps, T=450 K

Low chalcocite: N=144, 6 ps, T=290 K

Lin-Wang Wang, PRL 108, 085703 (2011)

Representing energy surfaces with neural networks

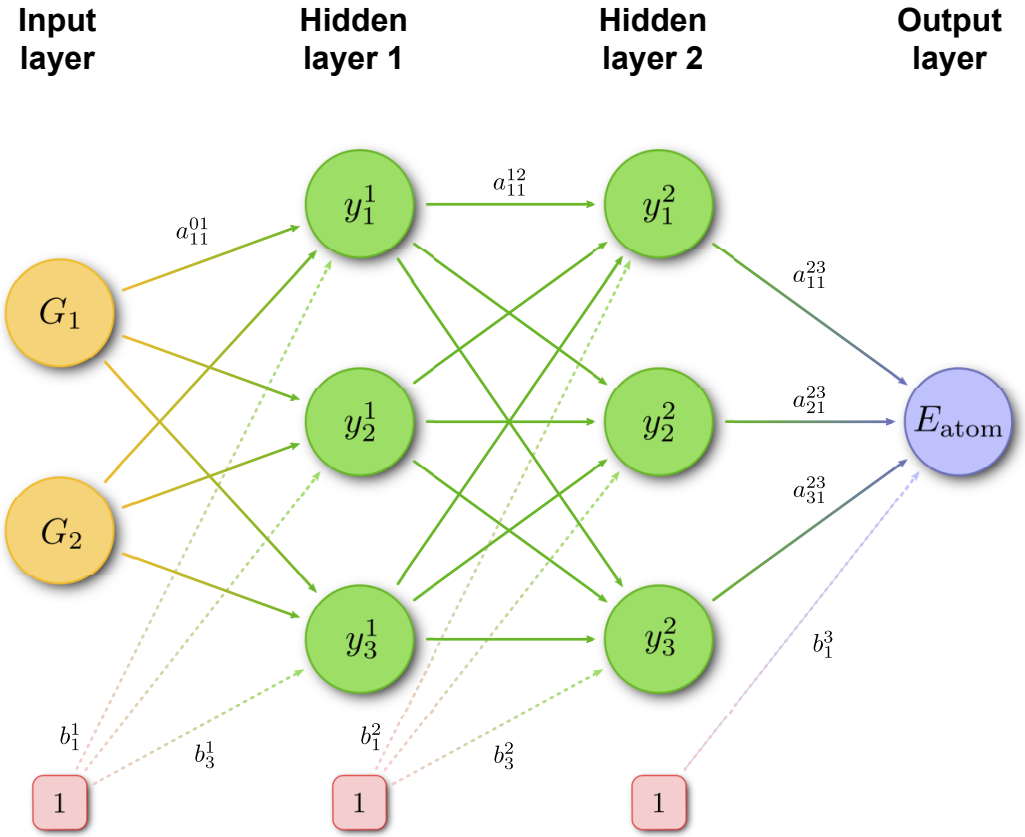
$$E = \sum_i E_i$$



Cartesian coordinates

Symmetry functions

$$\mathbf{R}_i \rightarrow G_j$$

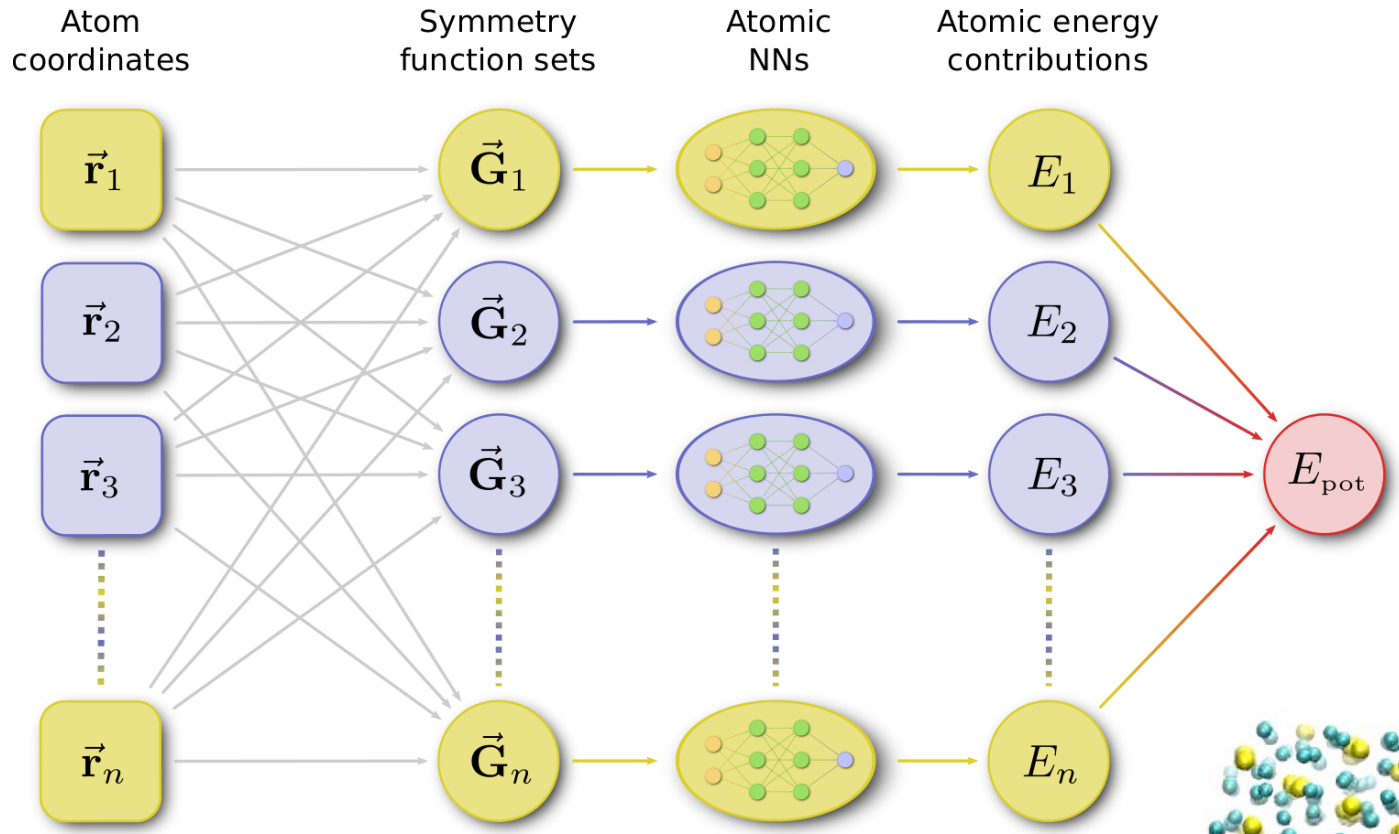


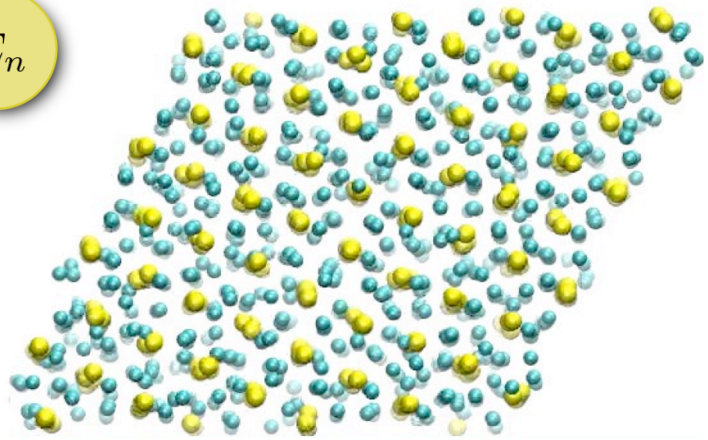
$$E_{\text{atom}} = \tilde{f}\left(b^3 + \sum_n a_n^{23} f\left(b_m^2 + \sum_m a_{mn}^{12} f\left(b_l^1 + \sum_l a_{lm}^{01} G_l\right)\right)\right)$$

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

Al, Si, Na, Cu, ZnO, H_2O

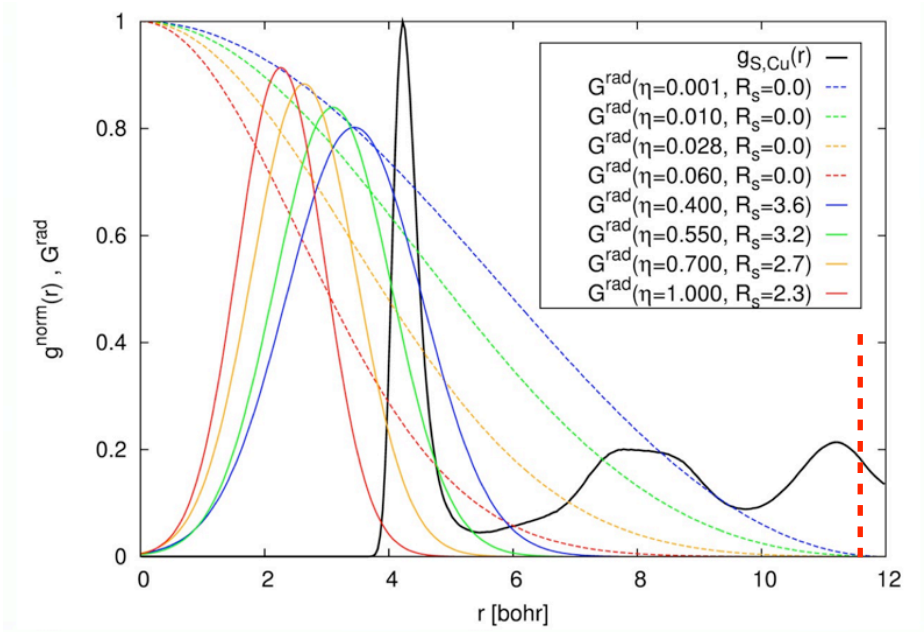
One neural network per atom species





Behler, Parrinello, PRL 98, 146401 (2007)
Behler, PCCP 13, 17930 (2011)

Symmetry functions



cutoff = 6 Angstroem

$$G_i^1 = \sum_{j \neq i} f_c(R_{ij}) \,,$$

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

$$G_i^3 = \sum_{j \neq i} \cos(\kappa R_{ij}) f_c(R_{ij}) \,,$$

$$G_i^4 = 2^{-\zeta} \sum_{j,k \neq i} (1 + \lambda \cos\theta_{ijk})^\zeta \times e^{-\eta(R_{ij}^2+R_{ik}^2+R_{jk}^2)} f_c(R_{ij}) f_c(R_{ik}) f_c(R_{jk}) \,,$$

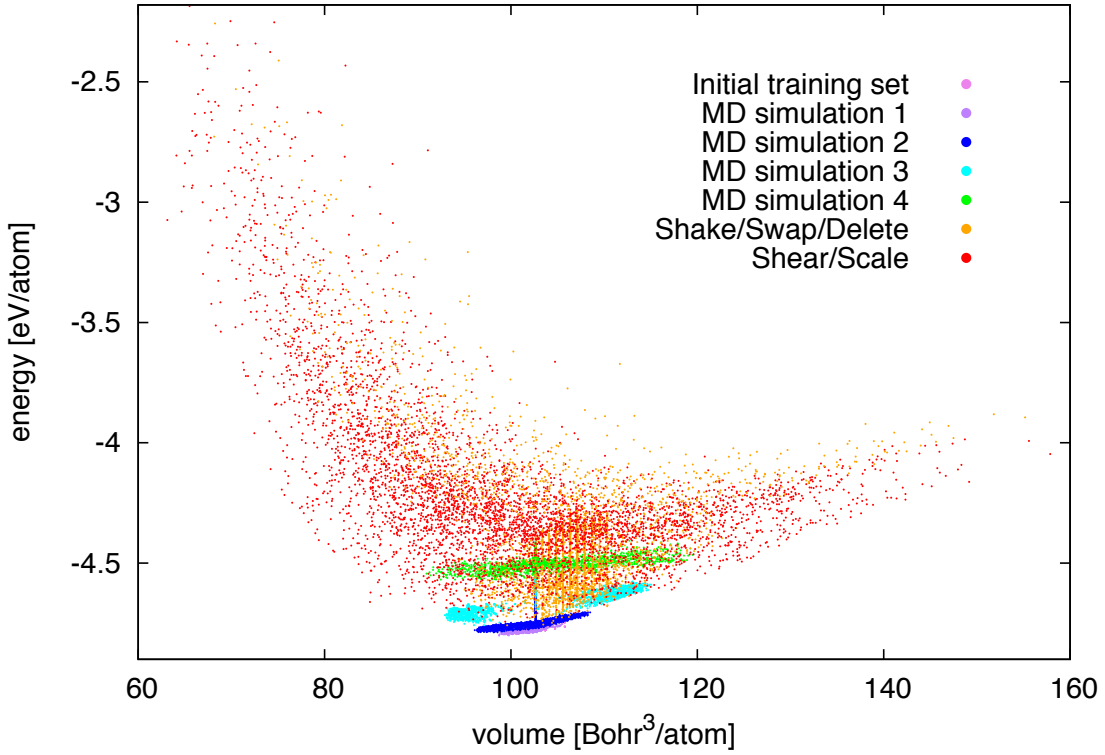
$$G_i^5 = 2^{-\zeta} \sum_{j,k \neq i} (1 + \lambda \cos\theta_{ijk})^\zeta \times e^{-\eta(R_{ij}^2+R_{ik}^2)} f_c(R_{ij}) f_c(R_{ik}) \,,$$

$$G_i^6 = 2^{-\zeta} \sum_{j,k \neq i} (1 + \lambda \cos\theta_{ijk})^\zeta f_a(R_{ij}) f_a(R_{ik}) \,,$$

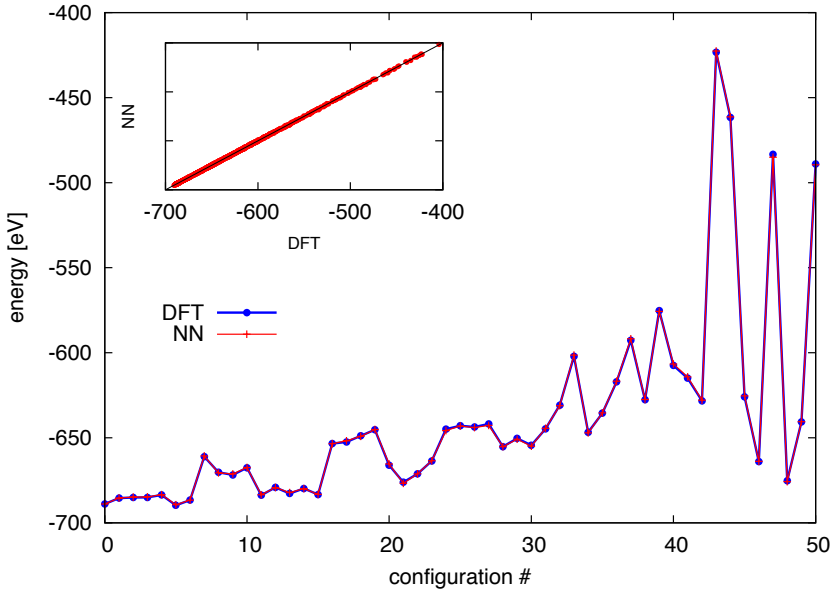
$$G_i^7 = \frac{1}{2} \sum_{j,k \neq i} \sin[(\theta_{ijk} - \alpha)\eta] f_b(R_{ij}) f_b(R_{ik}) \,,$$

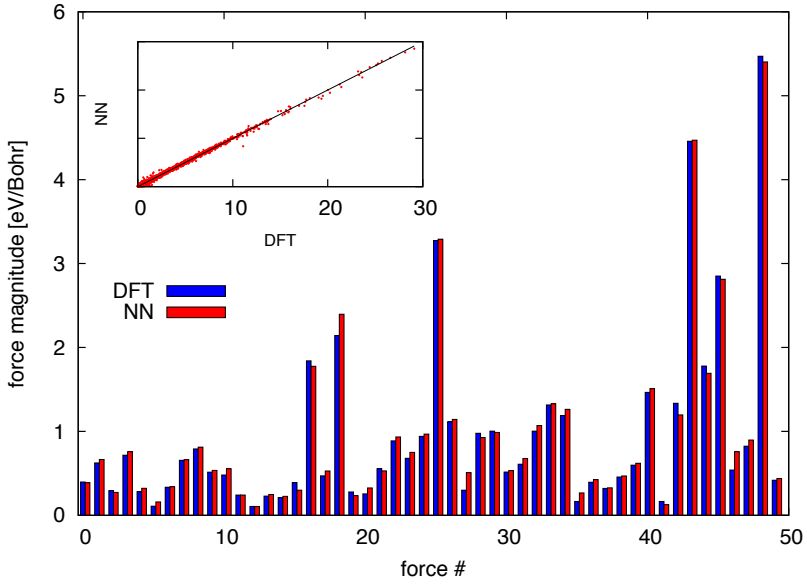
Training set

- Perfect crystals (distorted)
- MD simulations NpT, NVT (different T and p)
- Shear + scale
- Displace + exchange + delete
- Reference energies and forces ab initio
- 21.000 training configurations



Energy and force prediction from NN





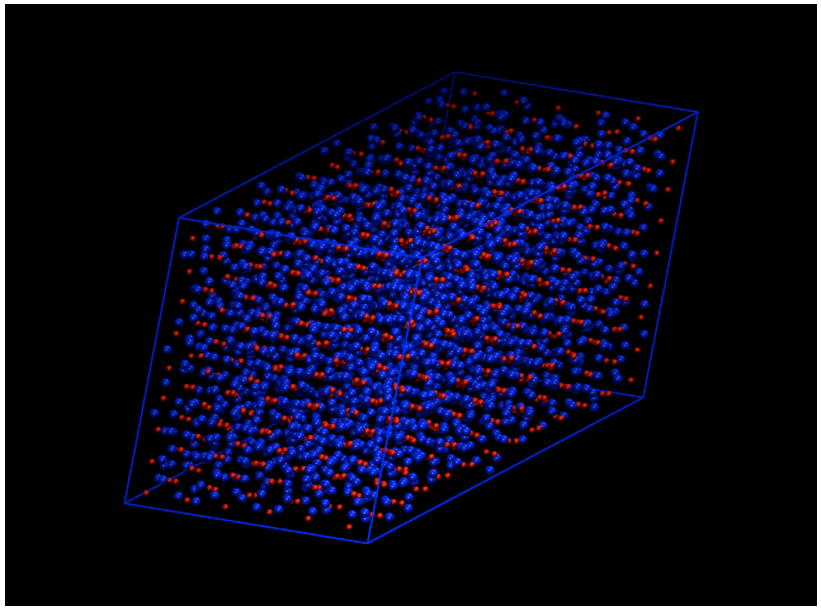
Neural Network

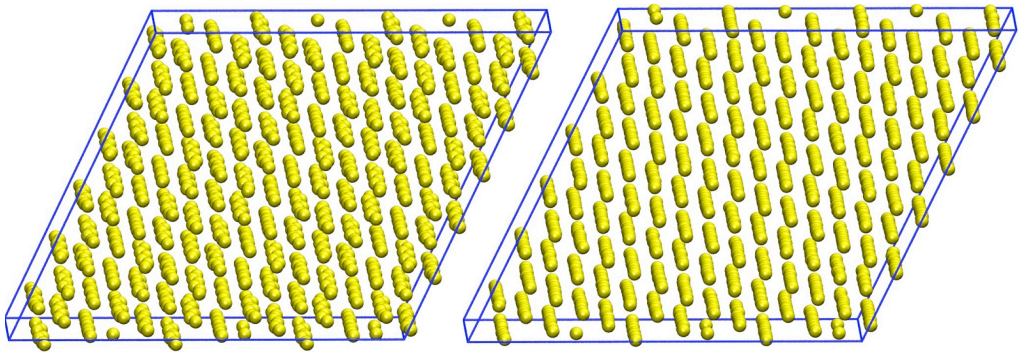
- 50 symmetry functions (Cu, S)
- 2000 weights
- 2 hidden layers 25 nodes
- cutoff: 6 A
- training: Kalman filter
- minimize errors in forces and energies

Errors

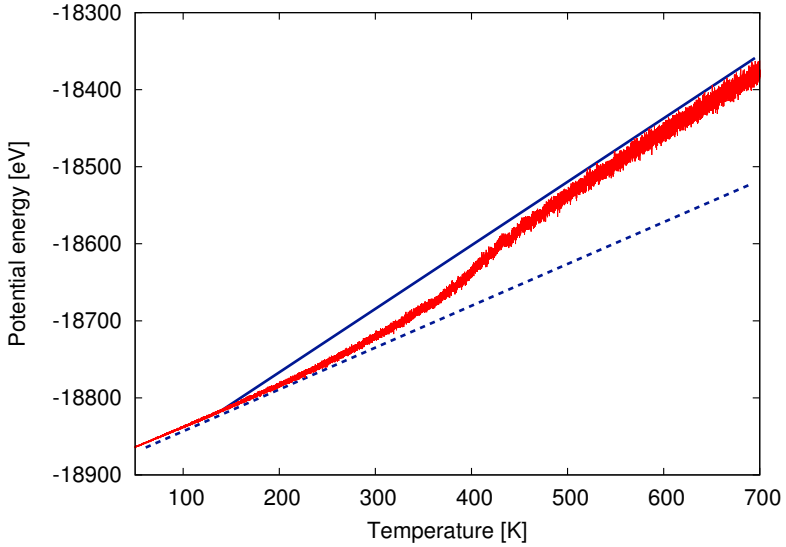
- Energies: 3 meV/atom
- Forces: 80 meV/Bohr

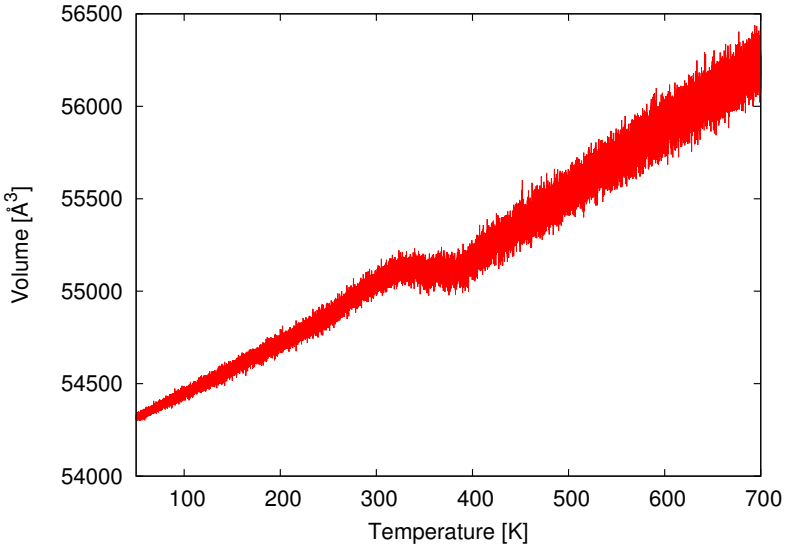
Low- to high-chalocite transition in Cu_2S





low chalcocite high chalcocite

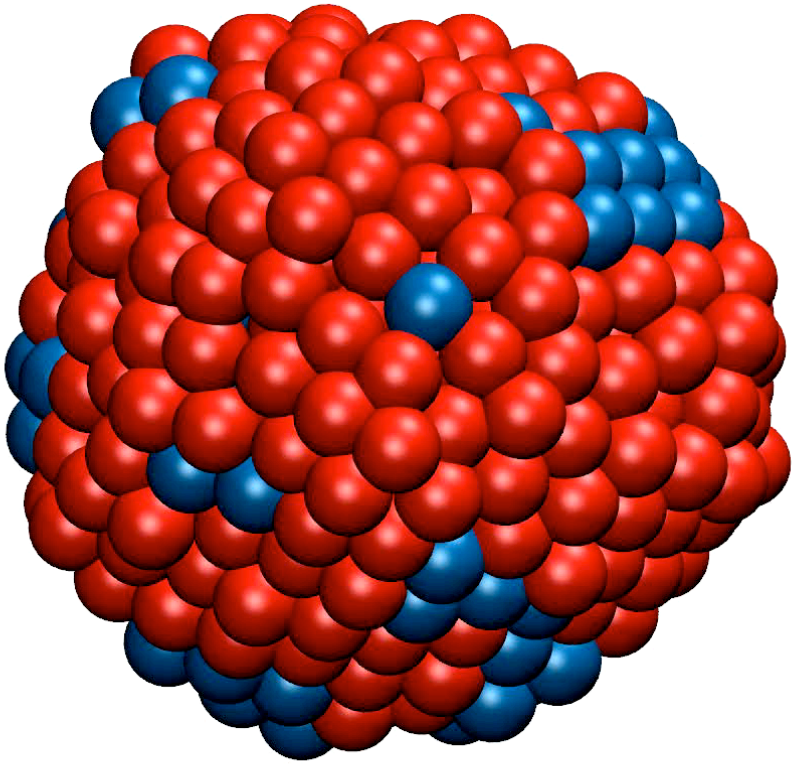




Melting/freezing of Au nanoparticles

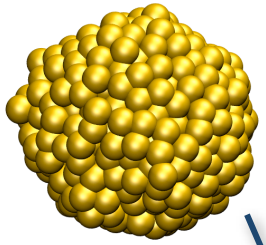
T=760 K, N=561

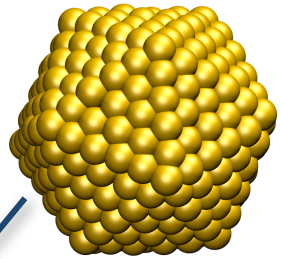
blue = crystalline
red=liquid

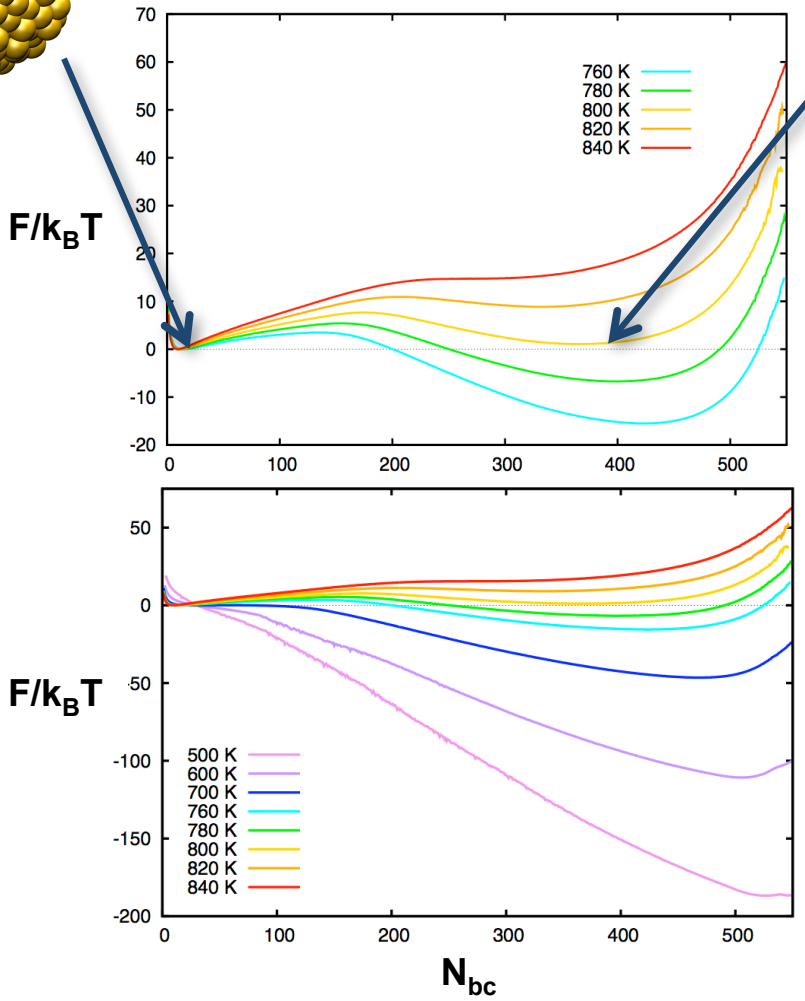


Embedded Atom Potential, S. M. Foiles, M. I. Baskes, and M. S. Daw, PRB 33, 7983–7991 (1986)

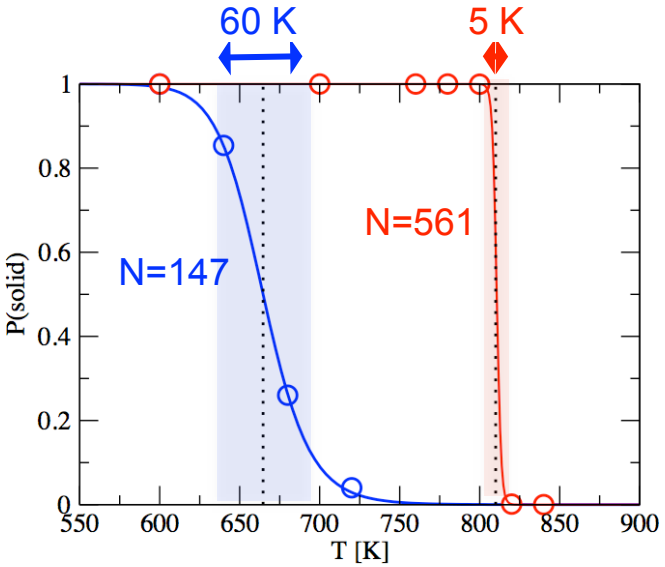
Free energy profiles







$$\Delta T = \frac{4k_{\mathrm{B}}T_{\mathrm{m}}^2}{\Delta E}$$

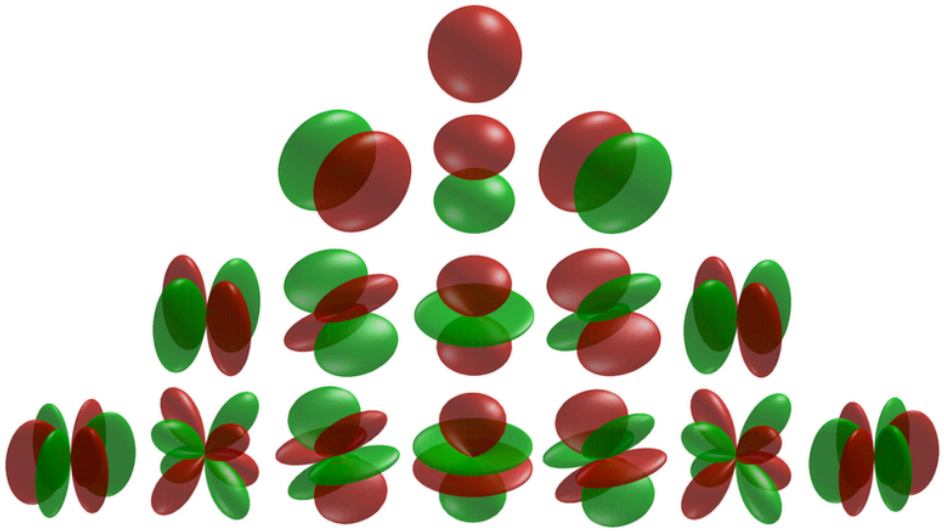


$$P(\mathrm{solid}) = \frac{1}{1+\exp\left\{\frac{\Delta E}{k_{\mathrm{B}}T_{\mathrm{m}}}\frac{(T-T_{\mathrm{m}})}{T}\right\}}$$

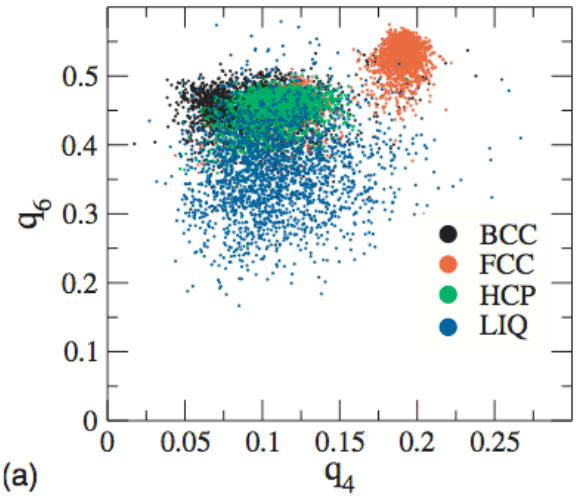
M. S. S. Challa, D.P. Landau, K. Binder, Phys. Rev. B 34, 1841 (1986)

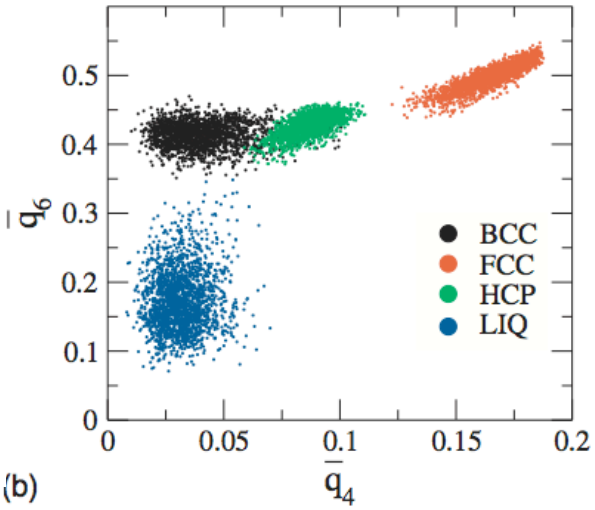
Local structure determination

Steinhardt bond order parameters



Lennard-Jones, 20% undercooling





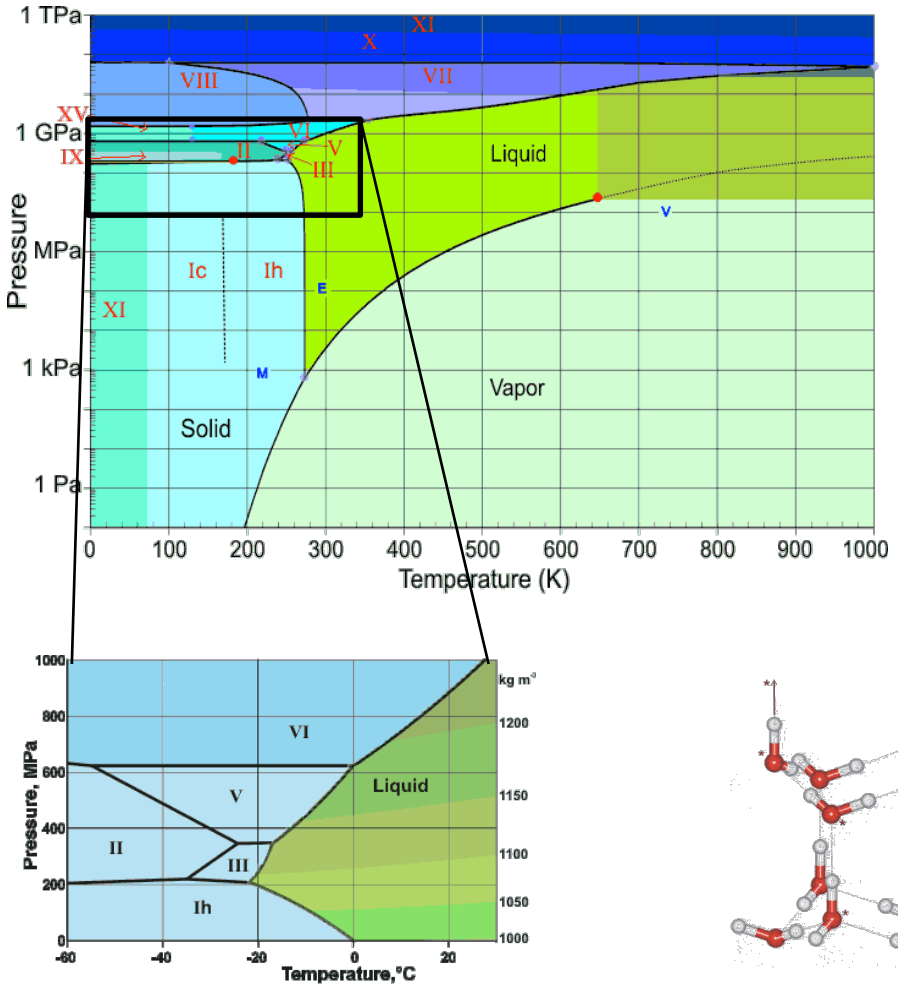
$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\mathbf{r}_{ij}) \qquad q_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}(i)|^2}$$

correlation
sign of crystallinity

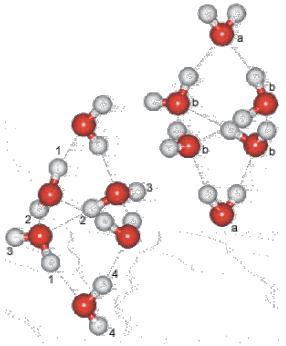
$$S_{ij} = \sum_{m=-6}^{6} q_{6m}(i) q_{6m}^*(j)$$

P. Steinhardt, D. R. Nelson, and M. Ronchetti, PRB 28, 784 (1983)
Ten Wolde, Ruiz-Montero, Frenkel, JCP 110, 1591 (1999)
W. Lechner and C. Dellago, JCP 129, 114707 (2008)

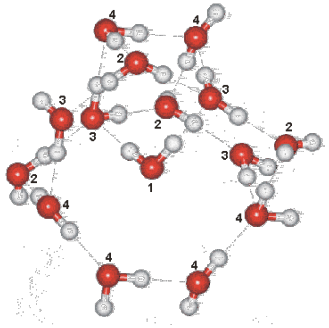
Liquid water and ice



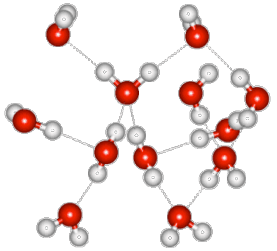
Ih



VI



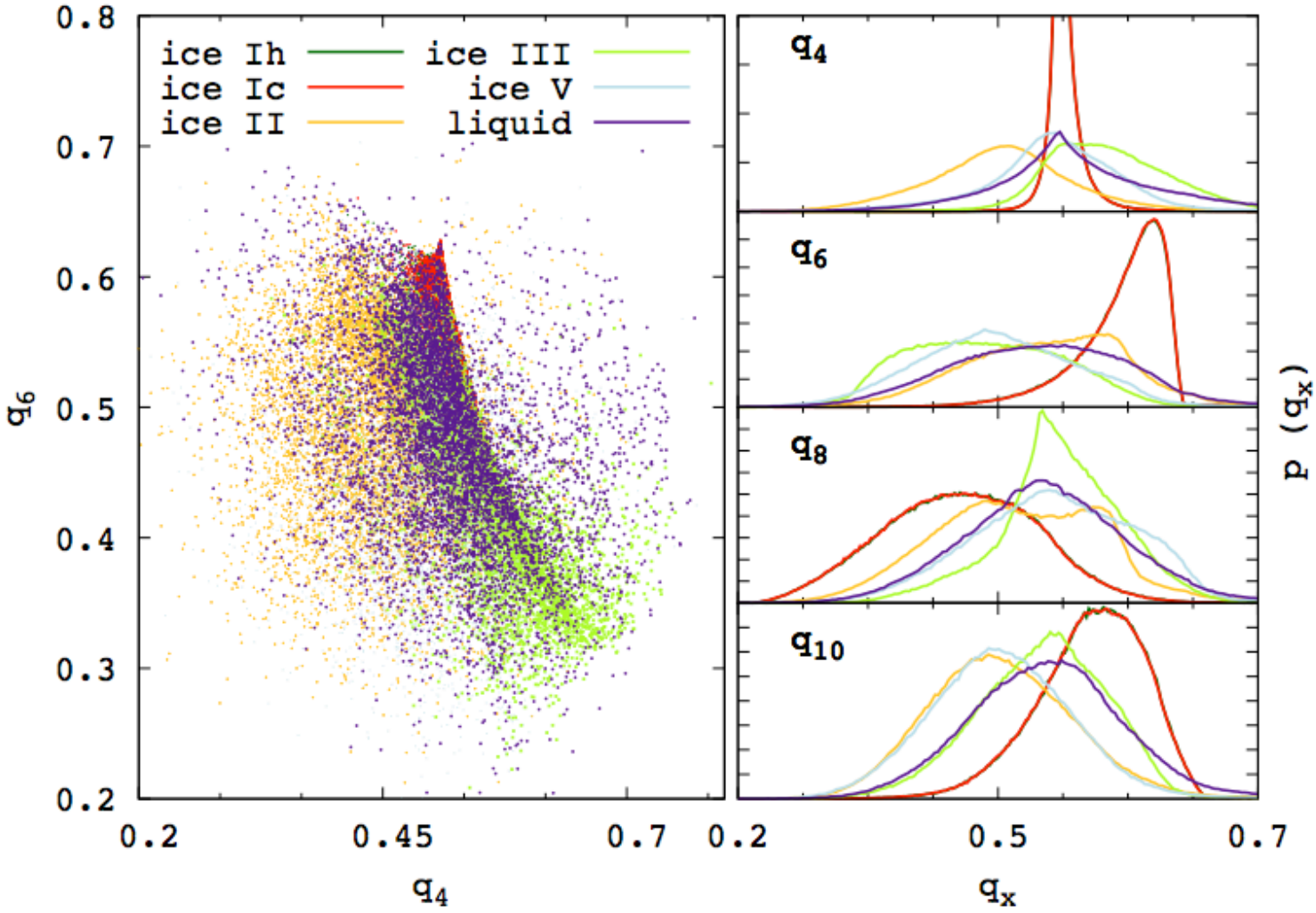
V



III

T. Lörting (Univ. Innsbruck)

Do bond order parameters work for ice?

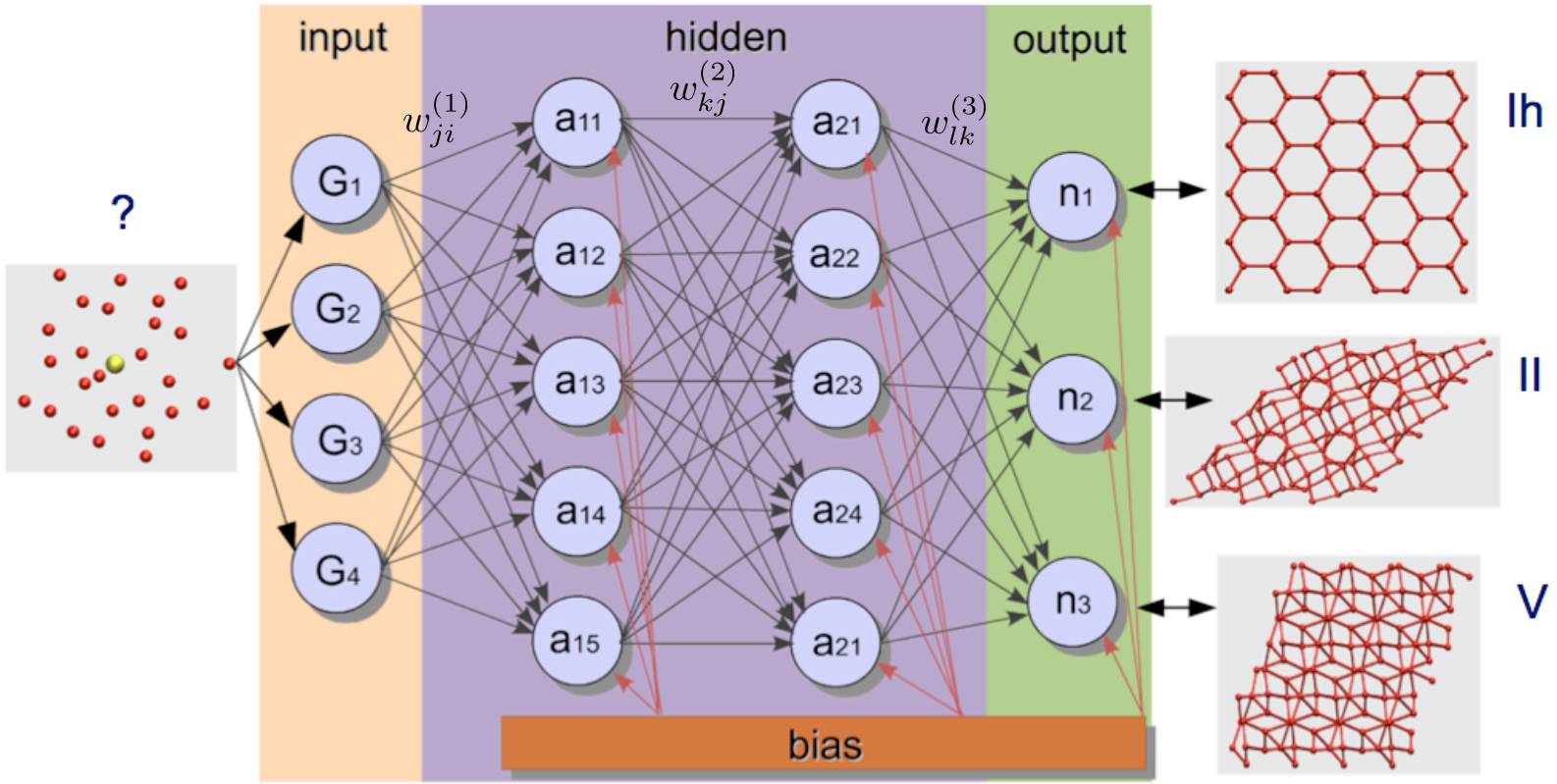


Brukhno, Anwar, Davidchack, and Handel, JPCM 20, 494243 (2008)

Ideal properties of order parameters

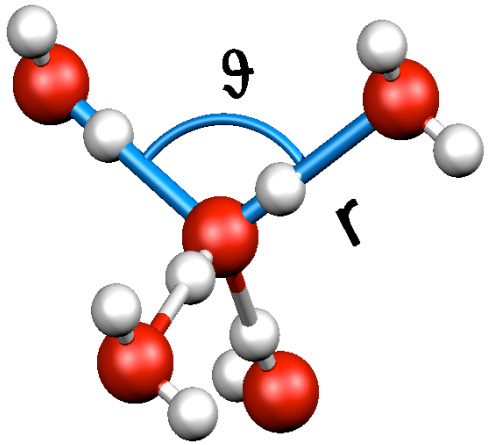
- Accurate assignment of structures
- Invariant with respect to rotations, translations, permutations
- Works over wide range of p & T
- Robust with respect to thermal fluctuations & elastic distortions
- Recognize defects and structures at interfaces
- Flexible
- Computationally inexpensive

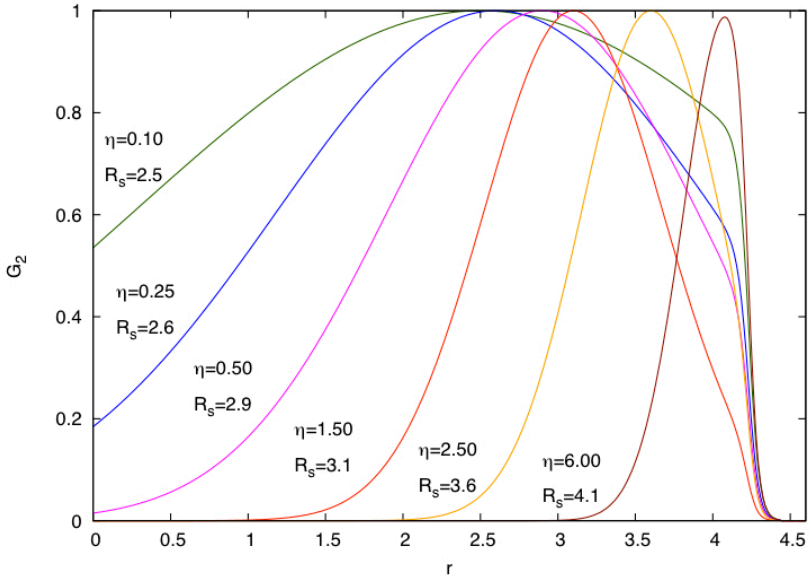
Neural network for structure recognition

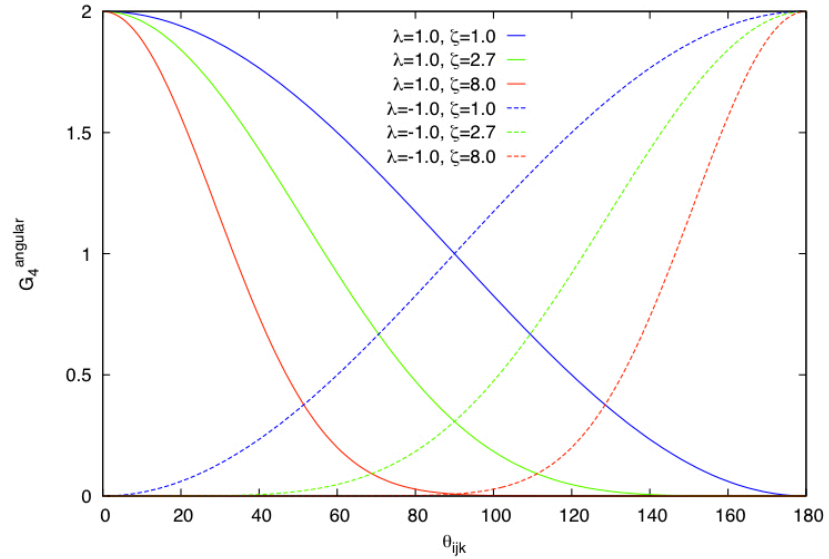


- 30 symmetry functions, 2x30 hidden nodes, 5 output nodes
- ≈ 2000 weights
- Training with global extended Kalman filter to find optimum weights
- Neural network training on GPU (takes a few days)
- Improvement of symmetry functions by sensitivity analysis

Symmetry functions







$$G_i^1 = \sum_{j\neq i} f_c(R_{ij})\,,$$

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

$$G_i^3 = \sum_{j\neq i} \cos(\kappa R_{ij}) f_c(R_{ij})\,,$$

$$G_i^4 = 2^{-\zeta} \sum_{j,k\neq i} (1+\lambda\cos\theta_{ijk})^\zeta \times e^{-\eta(R_{ij}^2+R_{ik}^2+R_{jk}^2)} f_c(R_{ij}) f_c(R_{ik}) f_c(R_{jk})\,,$$

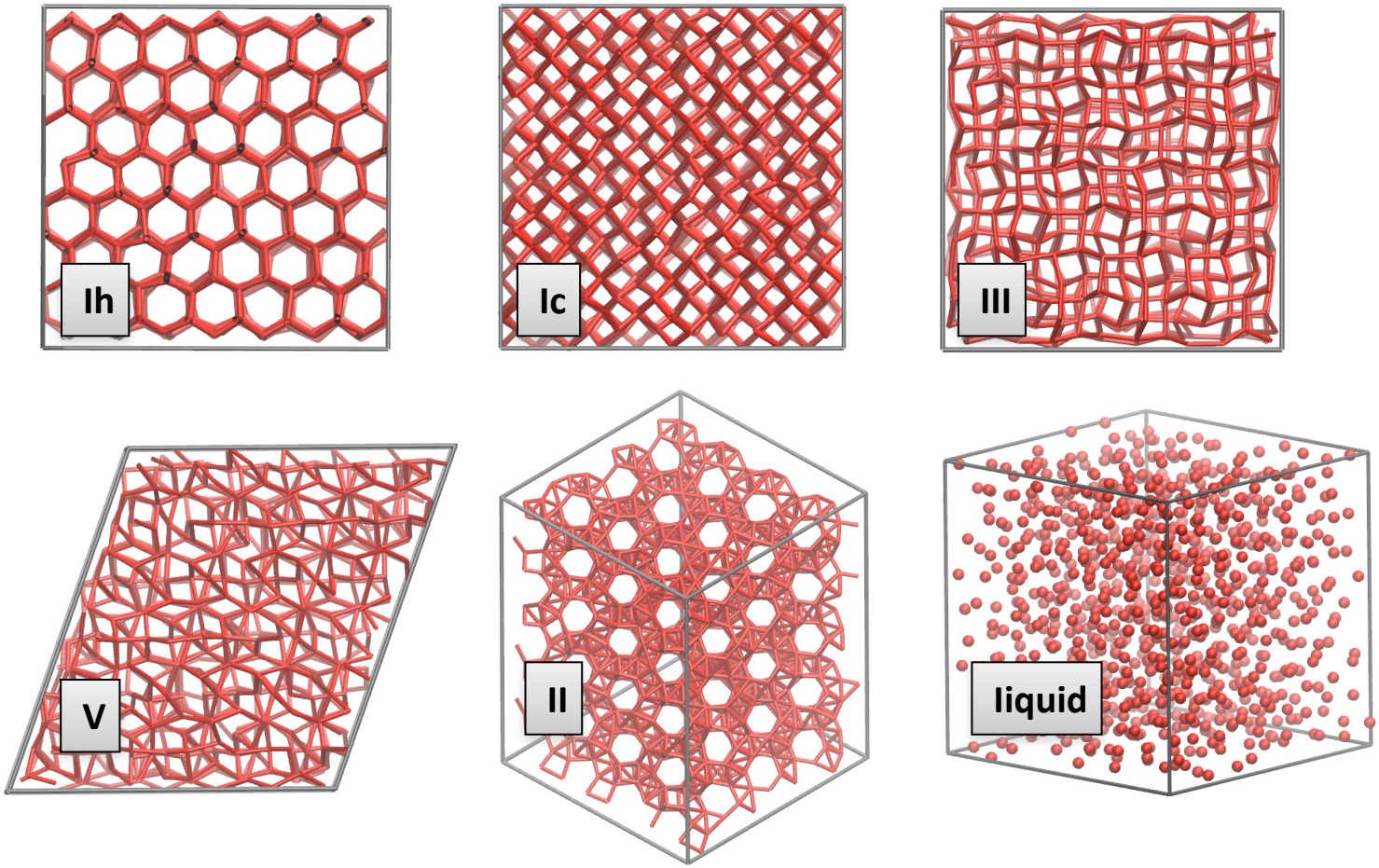
$$G_i^5 = 2^{-\zeta} \sum_{j,k\neq i} (1+\lambda\cos\theta_{ijk})^\zeta \times e^{-\eta(R_{ij}^2+R_{ik}^2)} f_c(R_{ij}) f_c(R_{ik})\,,$$

$$G_i^6 = 2^{-\zeta} \sum_{j,k\neq i} (1+\lambda\cos\theta_{ijk})^\zeta f_a(R_{ij}) f_a(R_{ik})\,,$$

$$G_i^7 = \frac{1}{2} \sum_{j,k\neq i} \sin[(\theta_{ijk}-\alpha)\eta] f_b(R_{ij}) f_b(R_{ik})\,,$$

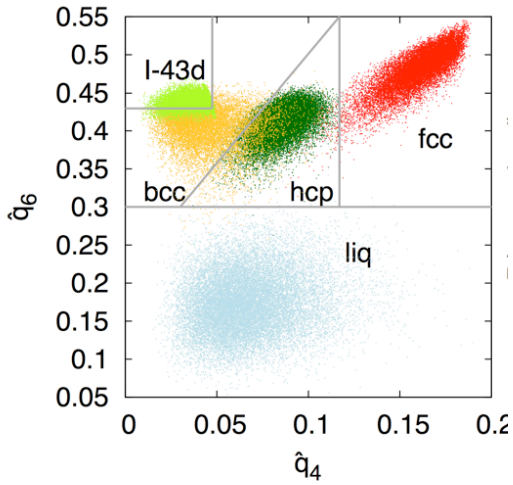
Training set & test set

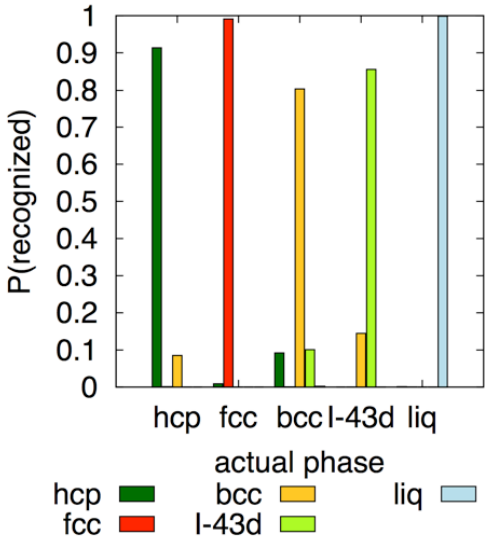
- Run MD simulations at **different p and T** for the **pure phases of H_2O**
- Pick 30.000 **uncorrelated** local environments from MD configurations



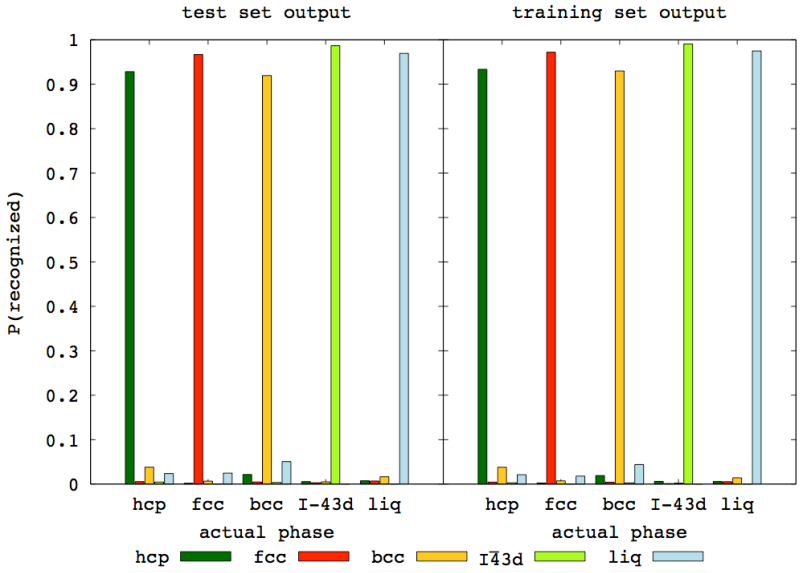
Structure prediction for Lennard-Jonesium

bond order parameters

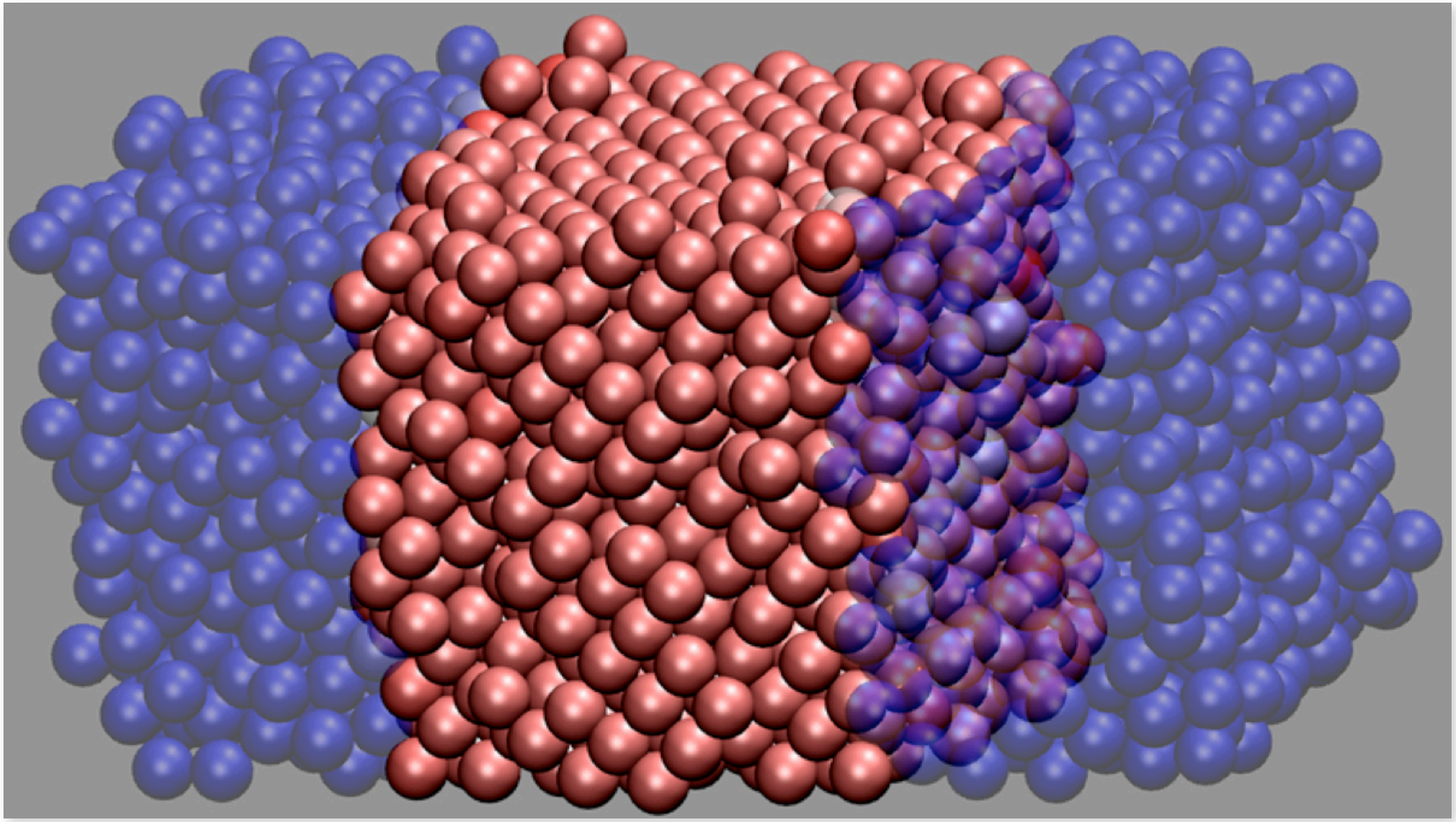




neural network

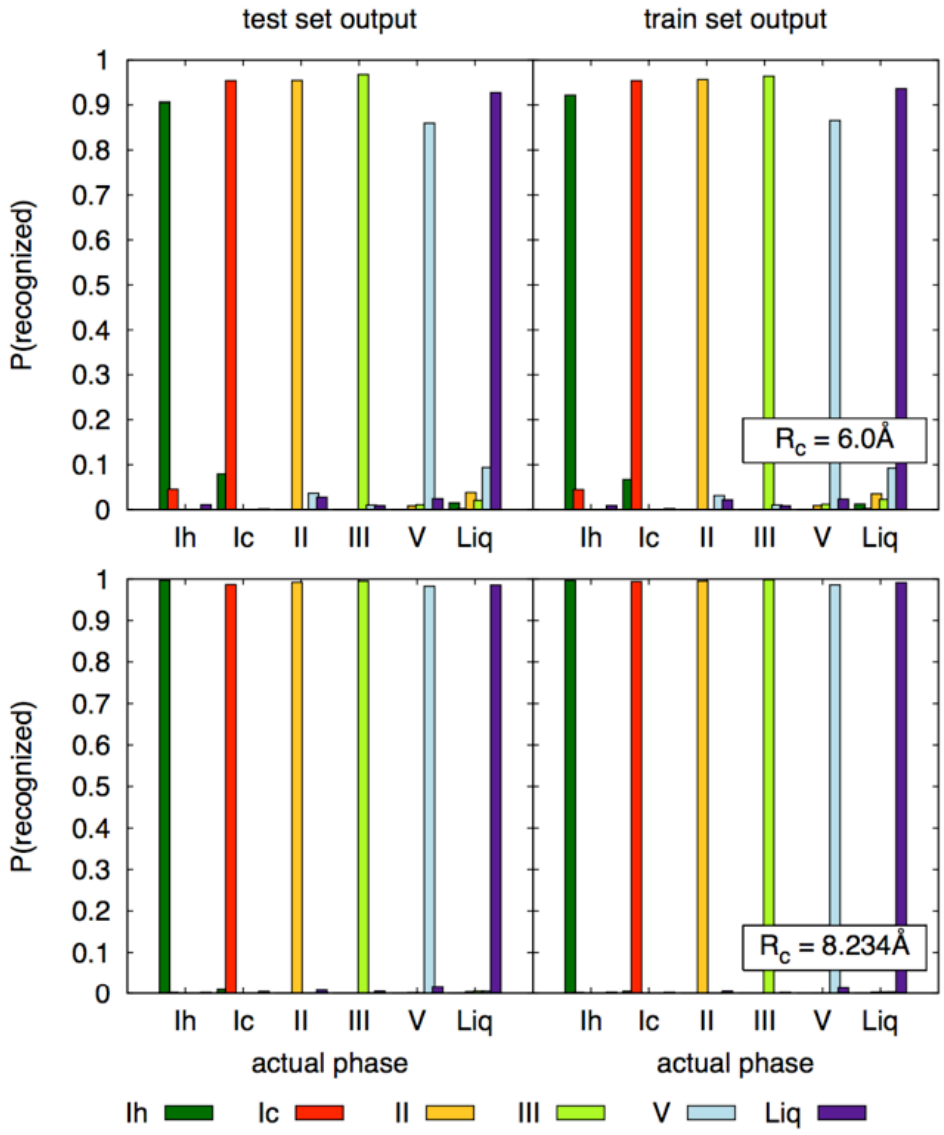


fcc slab in Lennard-Jones liquid



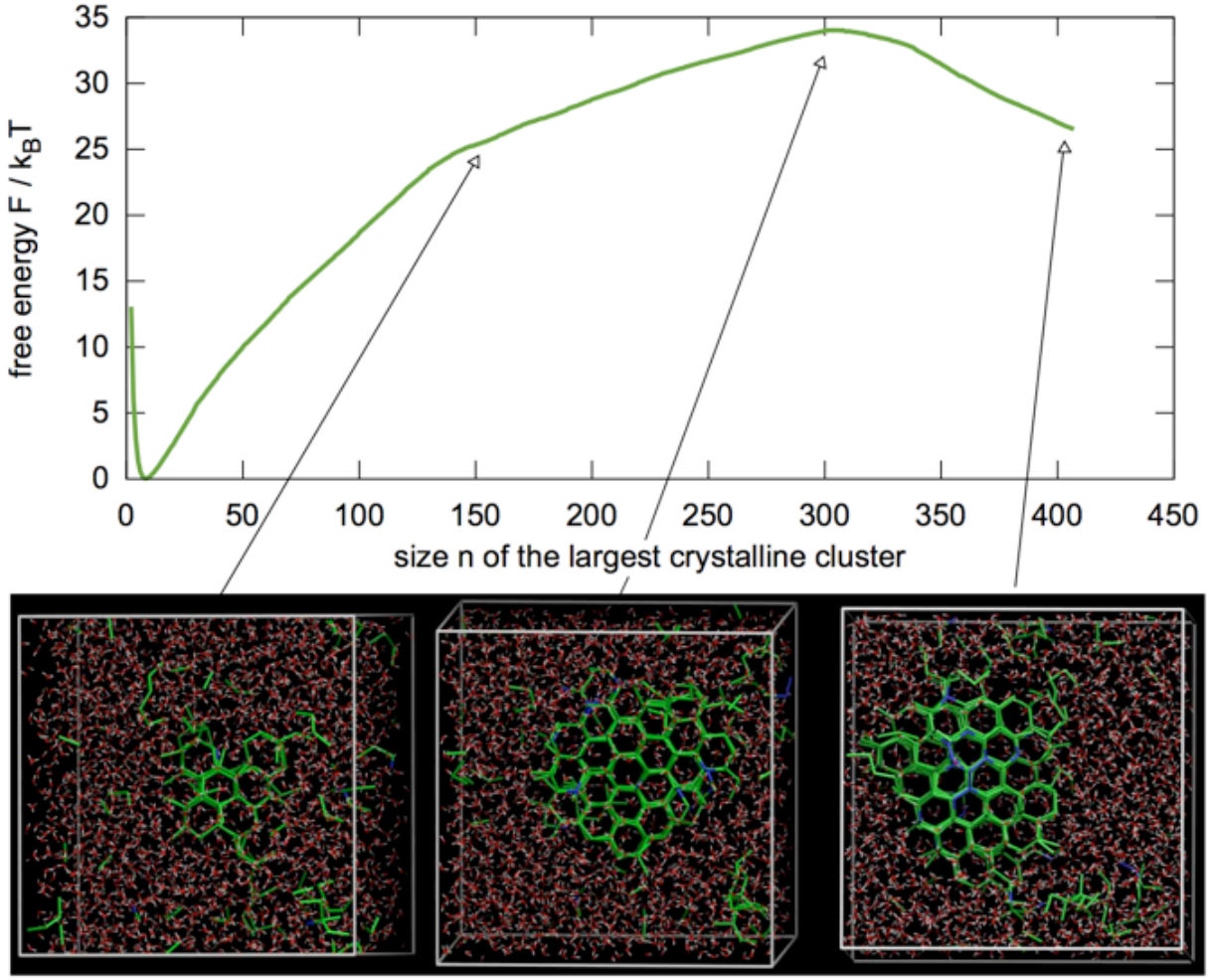
Structure Prediction for Water and Ice

T=270K, various pressures, 30.000 training structures



Nucleation of Ice

TIP4P/ice, T=235K, umbrella sampling + replica exchange



Pro and cons of neural networks

- Flexible, no assumptions
- Accuracy of DFT at fraction of cost
- Accurate structure recognition
- Need new NN for every new material
- Unclear where information resides in NN (black box)