

Crystal nucleation in the Gaussian Core Model



Wolfgang Lechner, Elisabeth Schöll-Paschinger, and Christoph Dellago

Faculty of Physics, University of Vienna

Crystal Nucleation

Using NPT simulations we investigate the nucleation process during the fluid solid transition in the Gaussian-core model[1]. The free energy barrier is determined as a function of the size of the largest nucleus using umbrella sampling in combination with parallel tempering. We find that subcritical clusters display a pronounced deviation from the spherical shape.

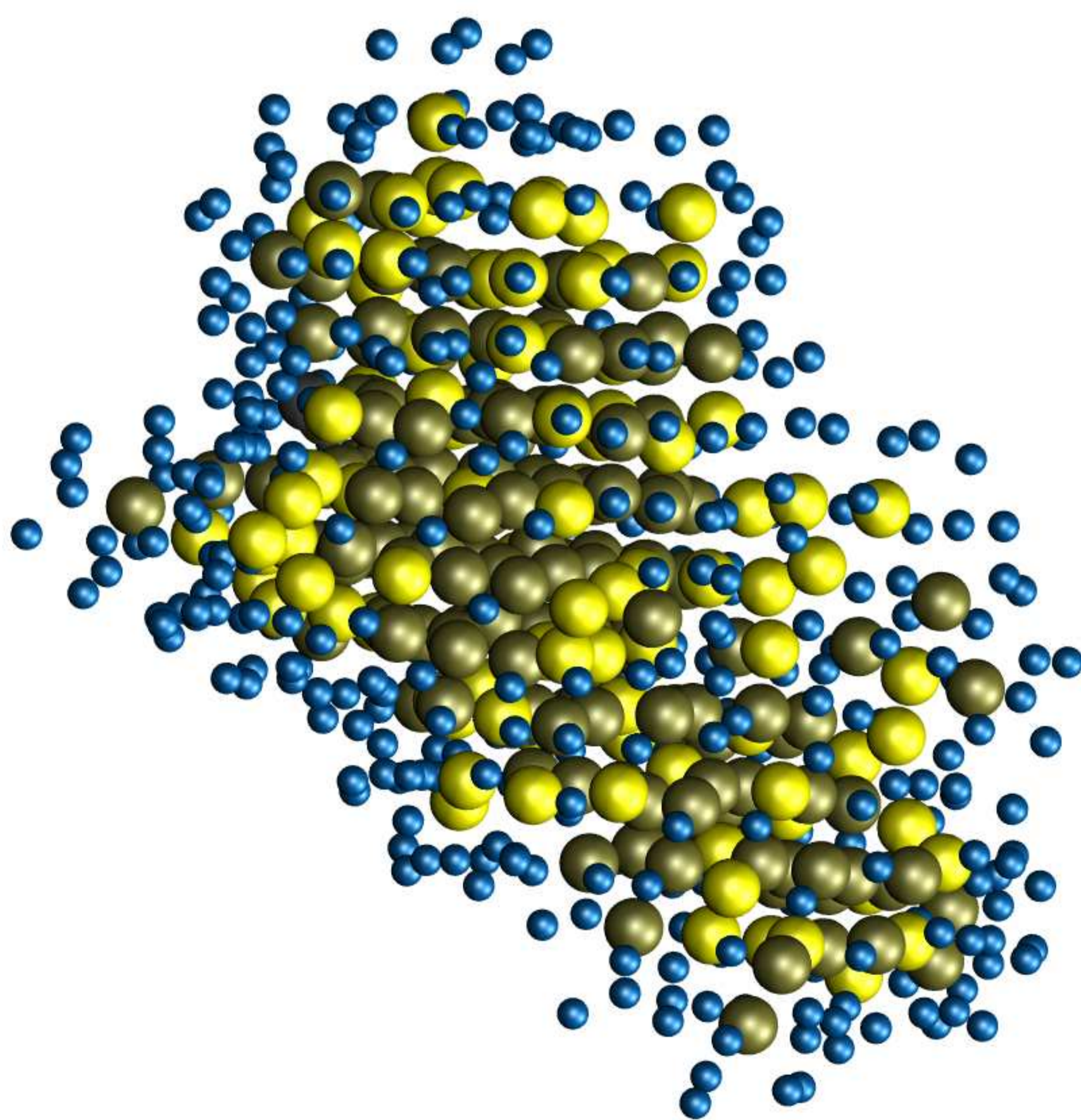
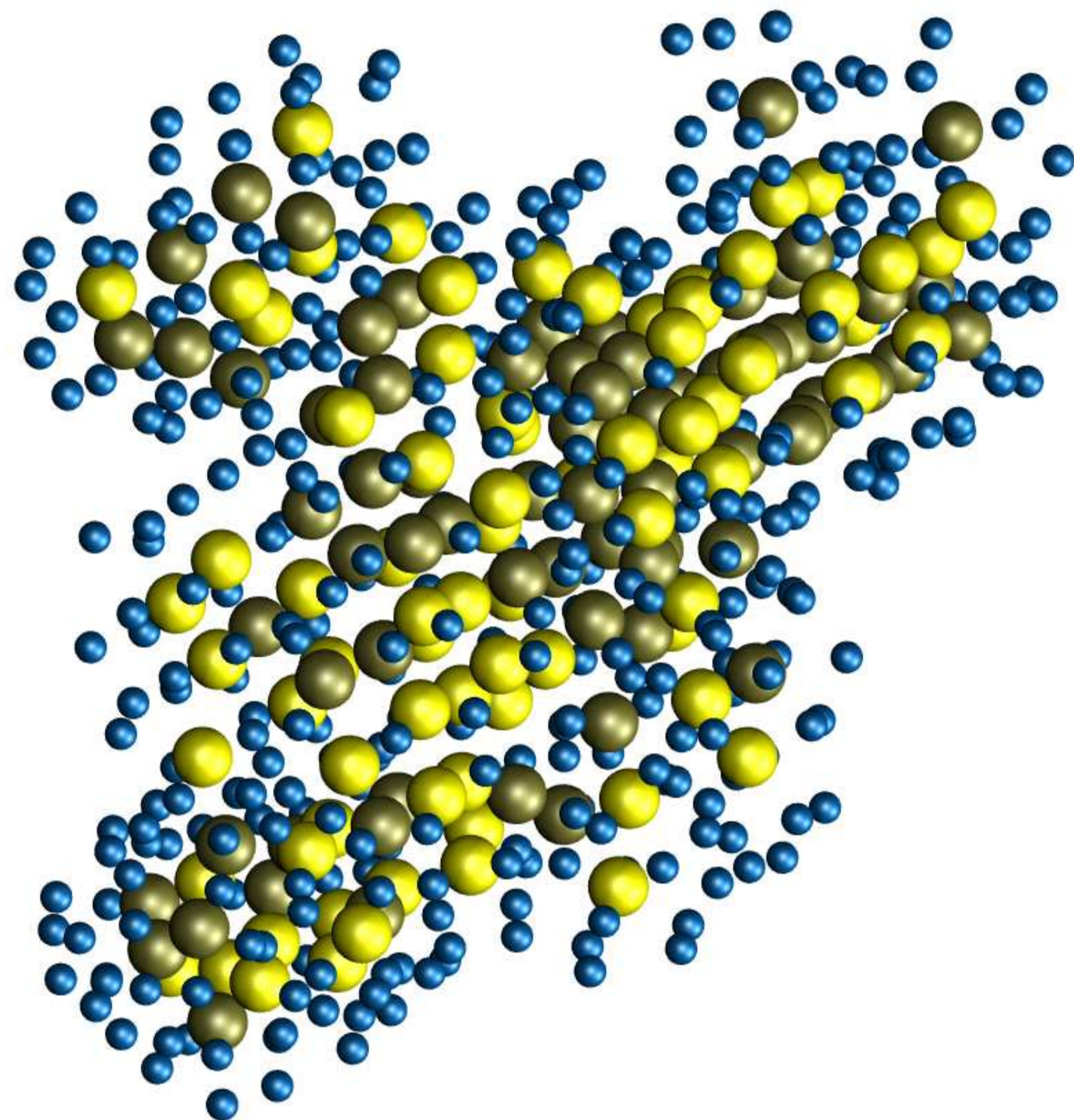
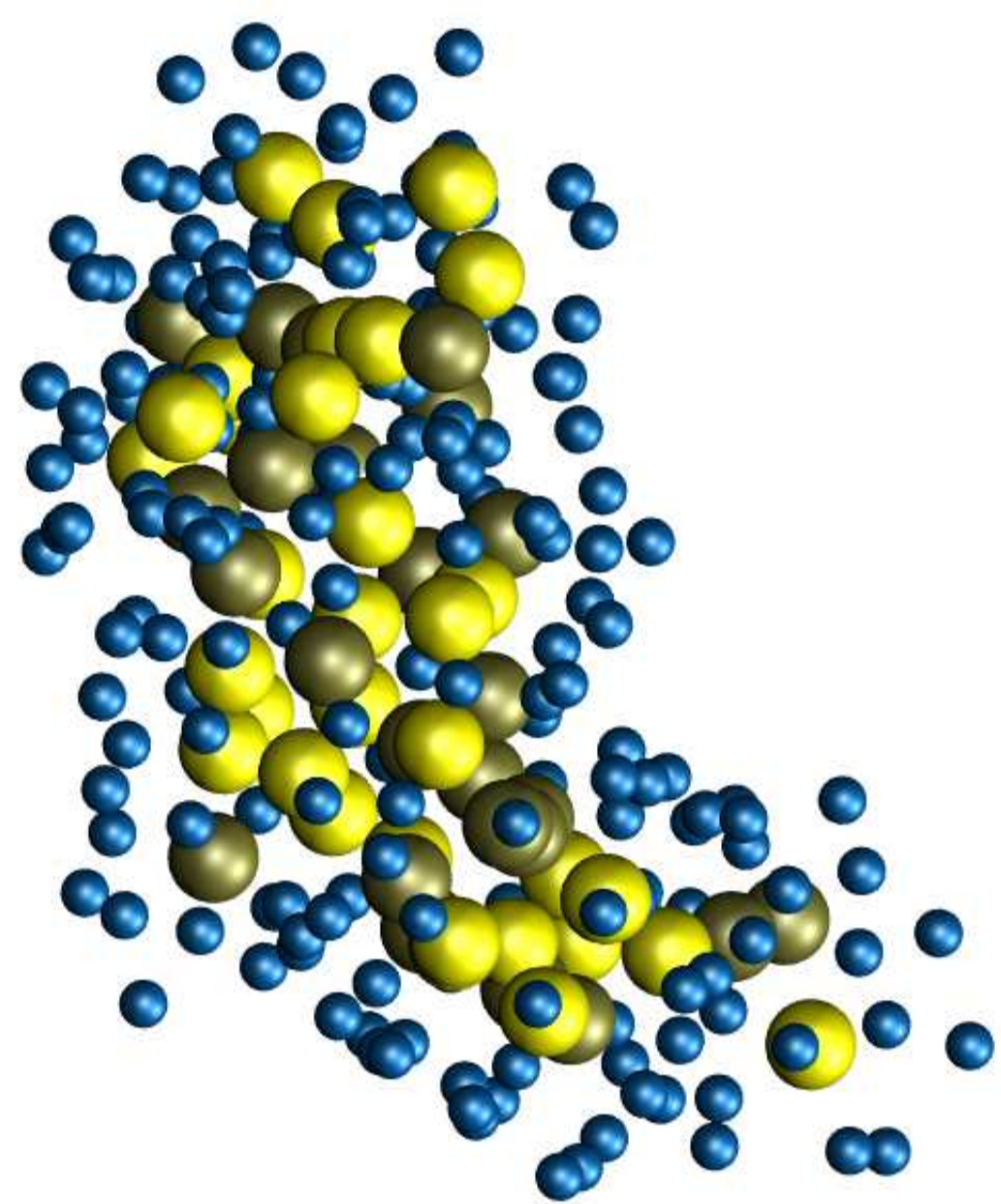


Figure 1: Snapshots of clusters of various sizes. Gold particles: solid particles in the HCP structure, yellow particles: solid particles in the FCC structure and blue particles: surface particles. Cluster size from top to bottom: 50, 150, and 300. The latter case corresponds to the size of the critical cluster.

Free energy barrier

Classical nucleation theory predicts a free energy barrier of the form $\Delta G(N) \propto aN^{2/3} - bN$ where N is the size of the largest cluster of the system. The simulation results predict a quantitative different curve. We calculate the free energy $\Delta G(N) = -k_B T \ln[P(N)]$ where k_B is Boltzmann's constant, T is the temperature and $P(N)$ is the probability to find a crystal cluster of size N .

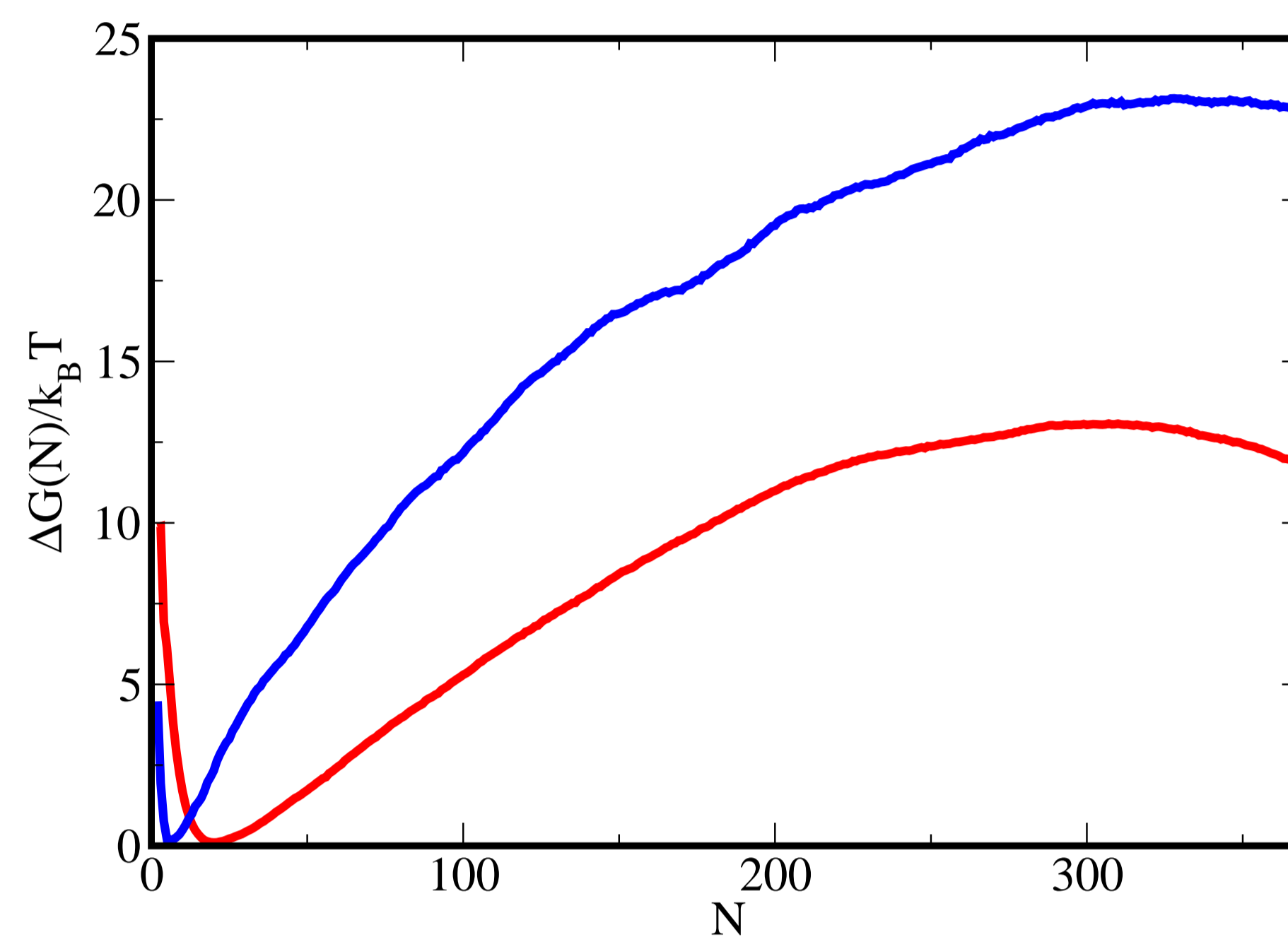


Figure 2: Free energy profile for the Gaussian-core model as a function of the size of the largest cluster for temperature $T = 0.0030$ and pressure $P = 0.1$.

To distinguish between fluid and solid particles we use the local bond order parameter q_6 . We calculate the correlation function of q_6 between two neighboring particles and define this bond as solid if the correlation is larger than 0.5. If a particle has more than 7 solid bonds the particle is defined as solid [2].

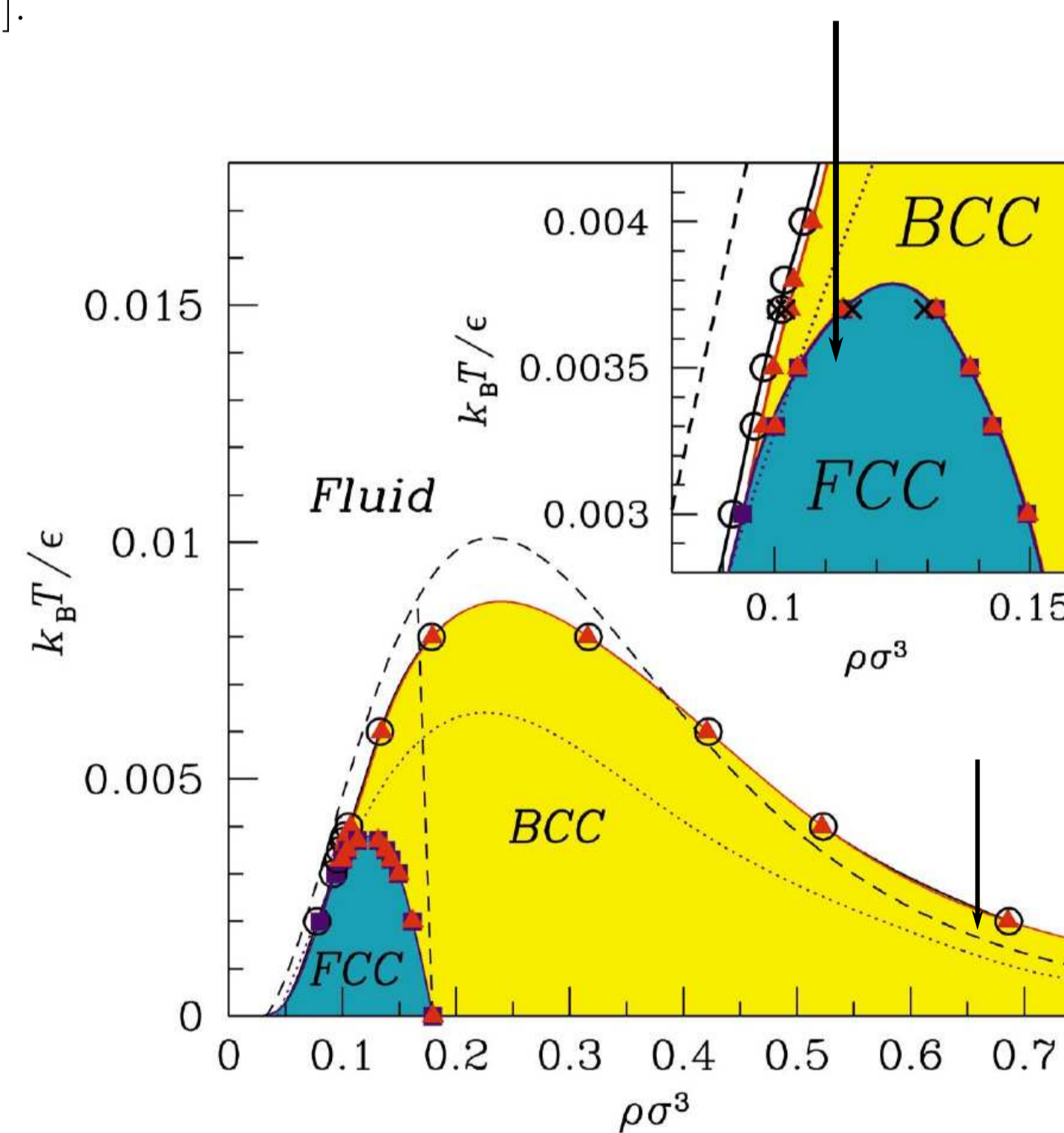


Figure 3: Phase Diagram of the Gaussian-core model from [3]. The system was undercooled to the points in the phase diagram indicated by the arrows.

The free energy calculation was performed in the NPT ensemble using the multiple histogram method combined with parallel tempering where we exchange the center of the harmonic windows. The results from the specific windows are then combined using the self-consistent histogram method [4].

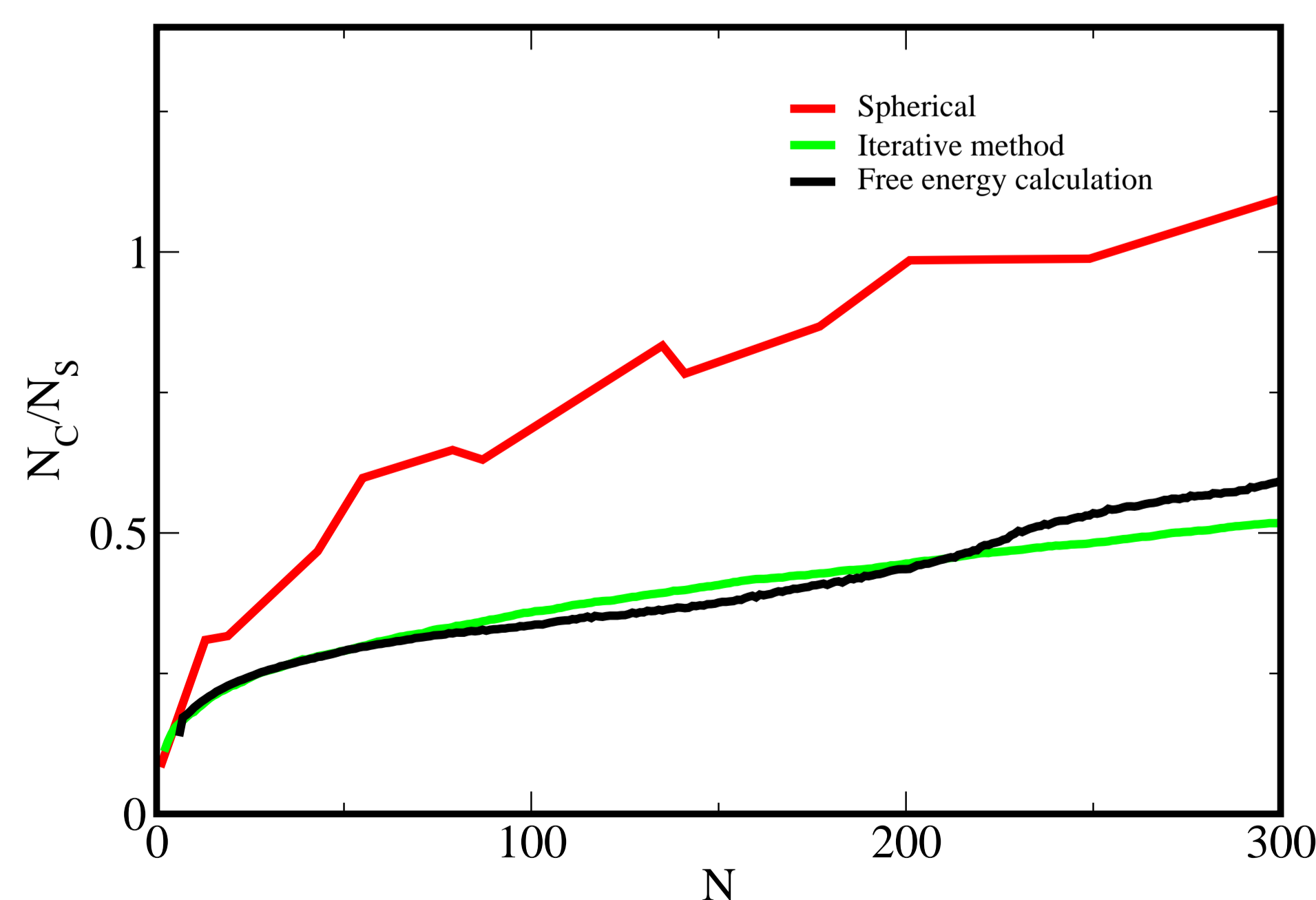


Figure 4: The ratio of volume particles to surface particles N_c/N_s as a function of the clustersize. We find large deviation from the perfect spherical shape and good agreement with the iterative method for small clusters. For larger clustersizes the ratio becomes linear.

Cluster analysis

We analyze the shape and the structure of the crystal cluster as a function of the clustersize. The ratio between volume particles to surface particles give us insight about the shape of the cluster. The crystal structure of the particles is determined using the local bond order parameters q_4 and q_6 averaged over all neighboring particles. In the $q_4 q_6$ plane the different structures overlap to a large extent while in the averaged version they are separated.

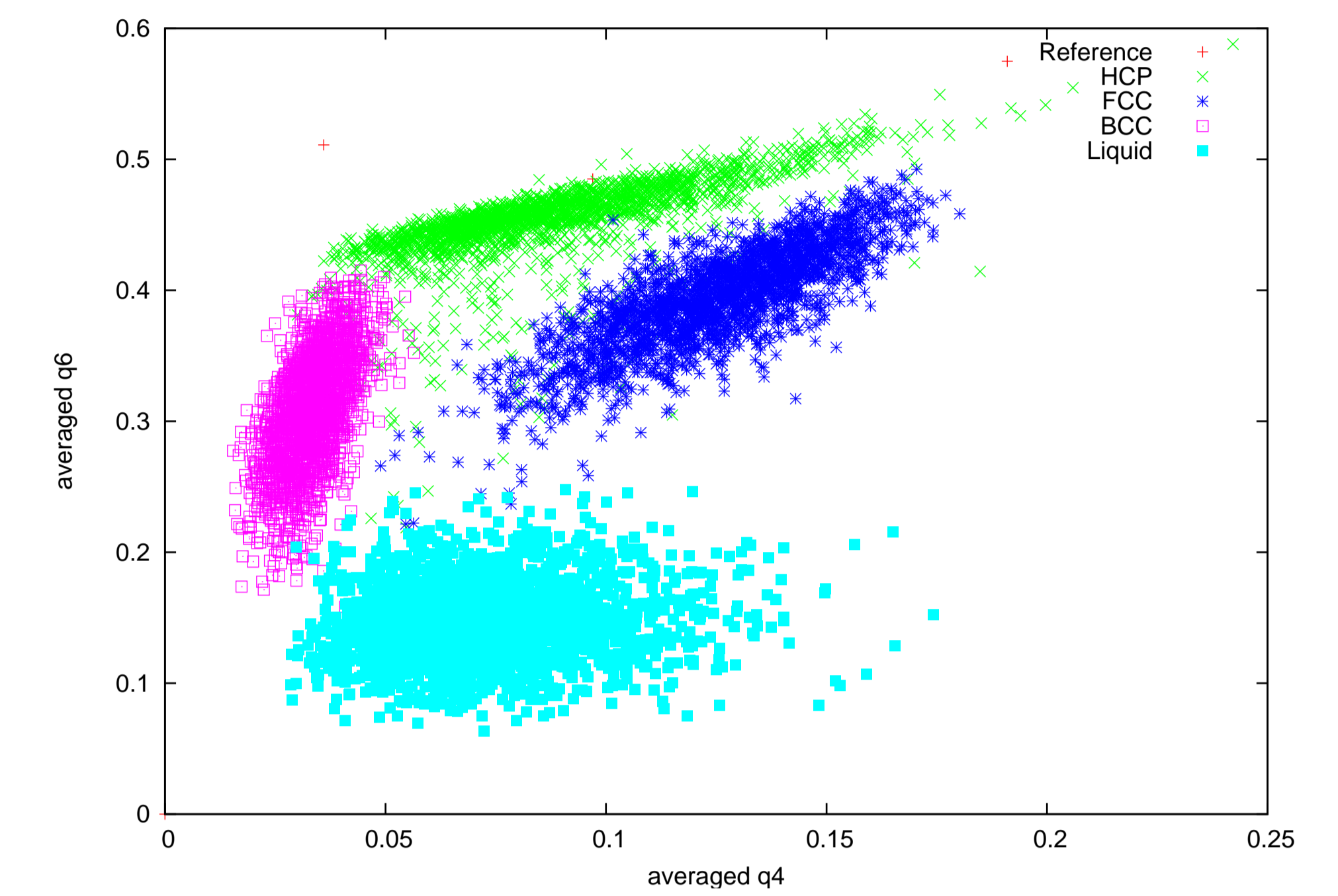


Figure 5: 2d Plot of the order parameters q_4 and q_6 averaged over all neighbors.

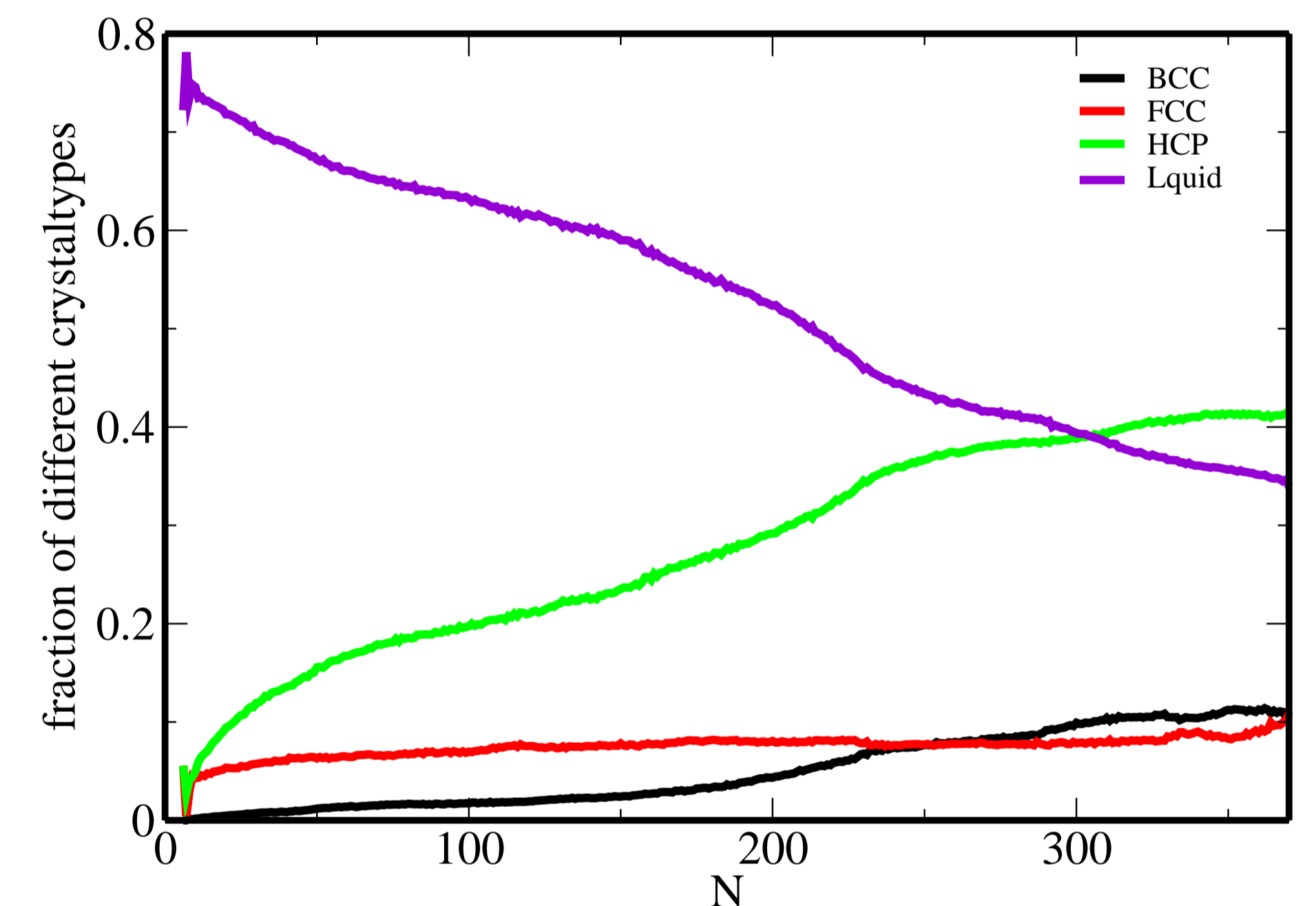


Figure 6: Composition of the cluster as function of its size.

Committer

In order to test whether N is an accurate reaction coordinate we calculate the committor distribution for various clustersizes. We find that the function is not strongly peaked but very flat. This indicates that the clustersize alone is not a sufficient order parameter in the Gaussian-core model.

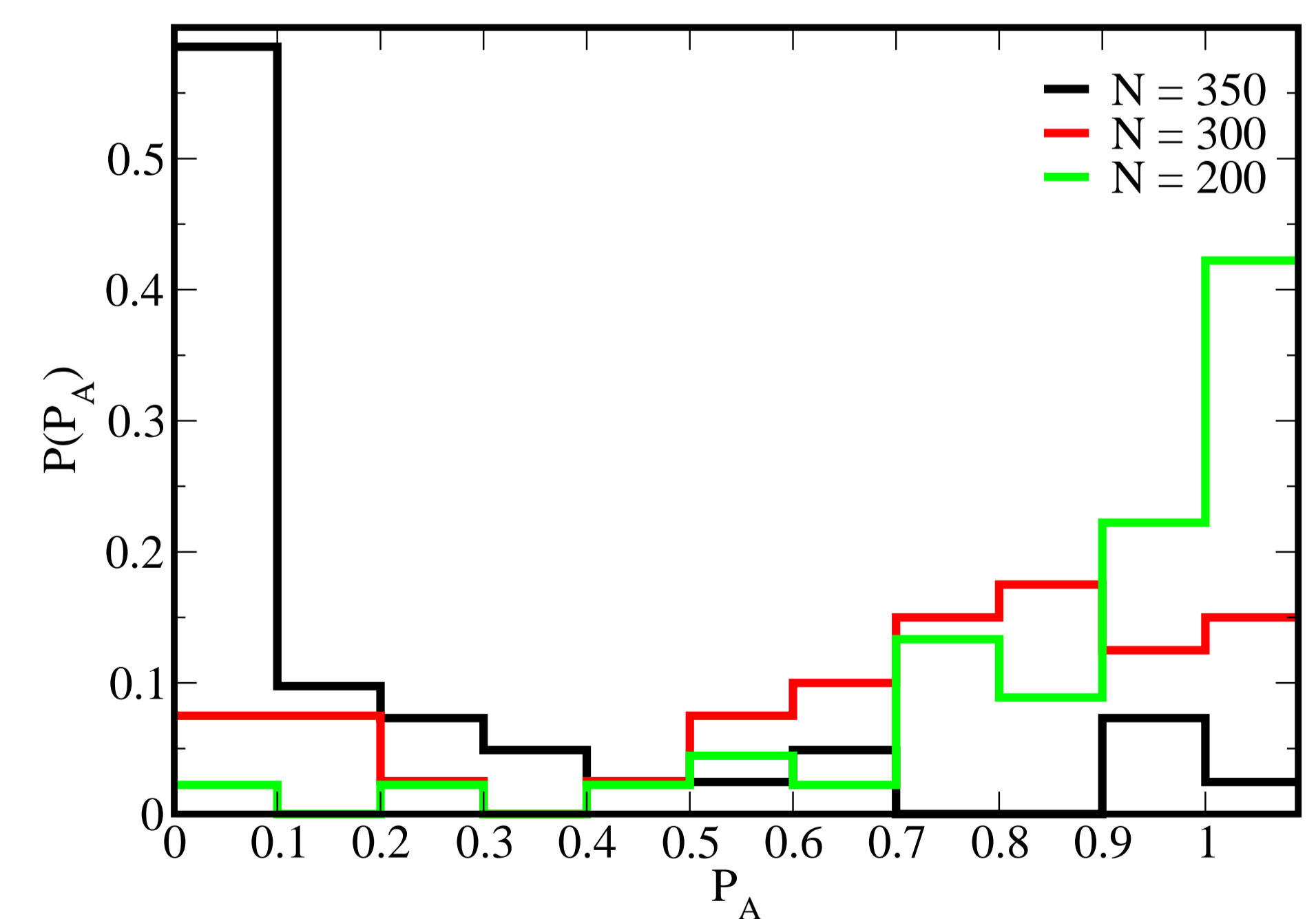


Figure 7: Committor distribution for clustersizes $N = 205$, $N = 300$ and $N = 350$ with 40 independent configurations averaged over 100 trajectories.

References

- [1] F. H. Stillinger, J. Chem. Phys. **63**, 3968 (1976).
- [2] S. Auer and D. Frenkel, Adv. Polym. Sci. **173**, 149 (2005).
- [3] F. S. S. Prestipino and P. V. Giaquinta, Phys. Rev. E **71**, 050102 (2005).
- [4] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic Press, Orlando FL, 2001).