

Modeling crystallization pathways of polymorphic materials: enhanced sampling techniques and method development

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Introduction

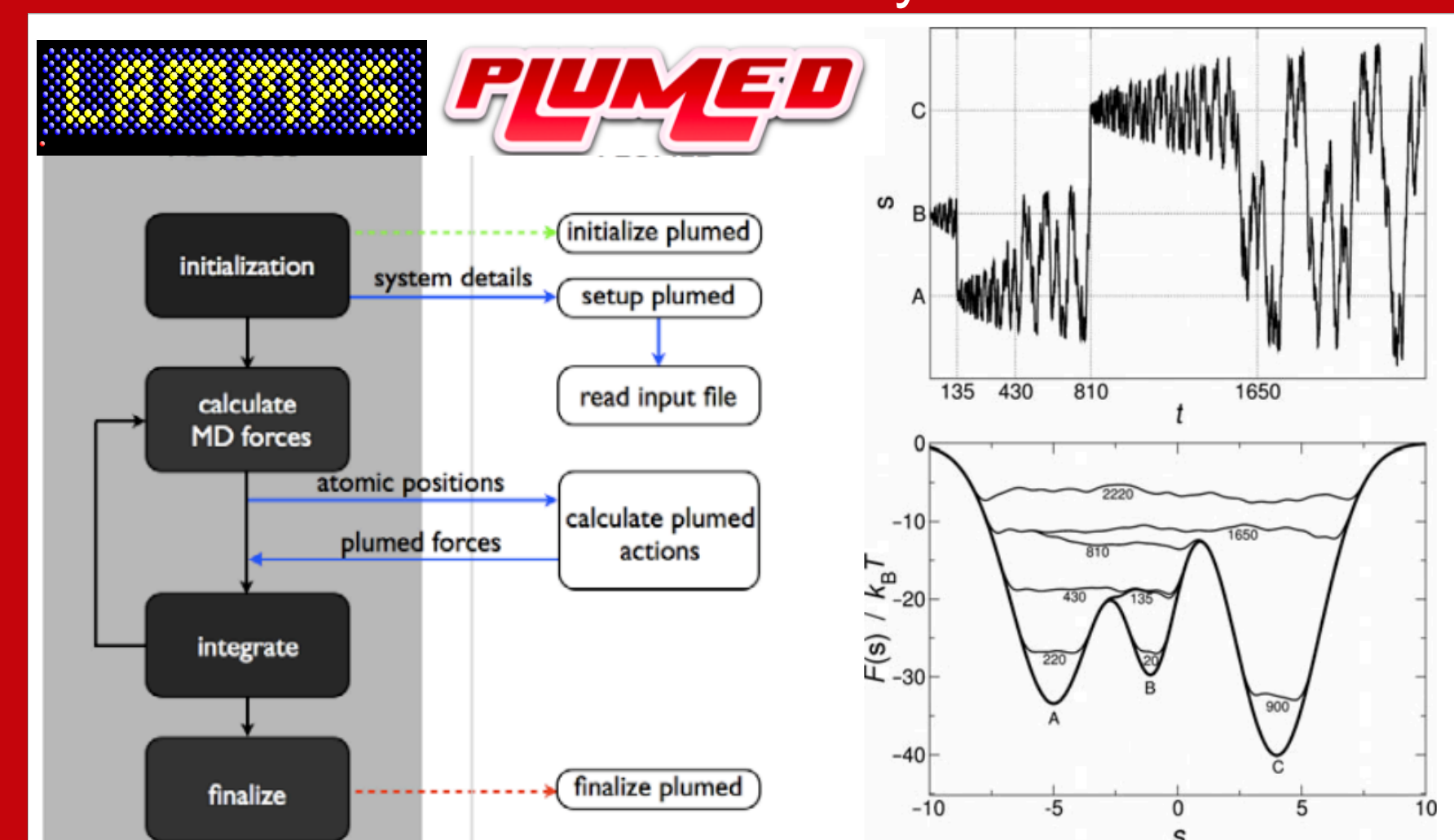
The **long-term goal** is to develop a model for solid-phase epitaxy (SPE) of complex metal oxides at the atomic scale.

Molecular dynamics (MD) studies are inhibited by the timescales necessary for crystallization.

- MD has been applied to model SPE growth of silicon and other simple systems [1].
- Complex metal oxides are too viscous and remain inaccessible to traditional MD.

Biasing techniques facilitate crystallization by enhancing sampling the free energy landscape.

- Well-Tempered Metadynamics (WT-MetaD) [2,3] is a popular approach to calculate free energy differences between kinetically isolated states.



Here, we take **WT-MetaD** a step further to determine whether a metadynamics yields information regarding the mechanism and pathways of crystallization.

Methods

Molecular dynamics simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [4].

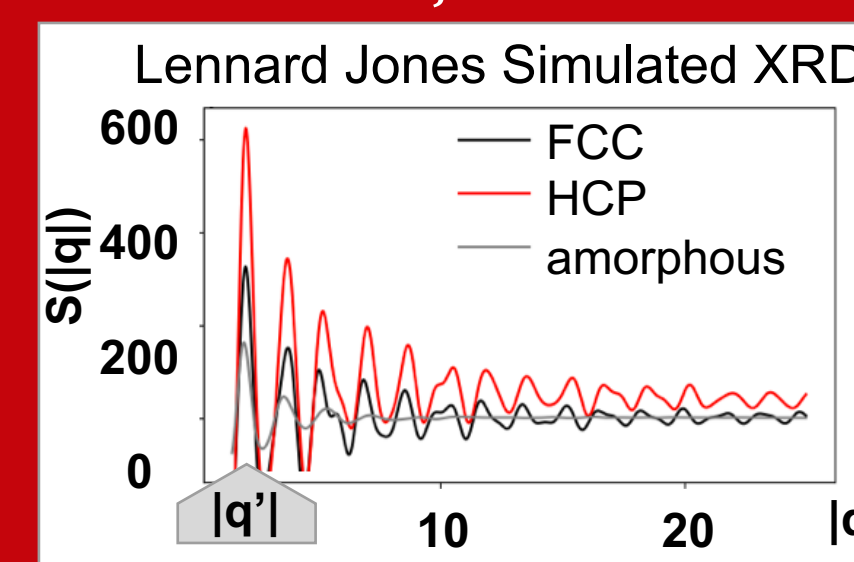
- Lennard Jones is chosen as a model which is well understood, obeys classical nucleation theory, and possesses polymorphic metastable states.
- Vashishta and Matsui potentials or alumina (Al_2O_3) were compared to assess accuracy and utility to crystallization studies.

Metadynamics was incorporated with PLUMED2 and LAMMPS [5].

- The collective variable, $S(|q'|)$, used for bias was the value of the Debye-scattering function, modelling x-ray diffraction (XRD) intensity [6]:

$$S(|q'|) = \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N f_i(q') f_j(q') \frac{\sin(q' \cdot R_{ij})}{q' \cdot R_{ij}} W(R_{ij})$$

- q' is a characteristic reciprocal lattice vector used to direct crystallization via $S(|q'|)$.



Mechanistic insight from metadynamics

To determine whether metadynamics yields information regarding the mechanism/pathways of crystallization, we start with the simple case of Lennard Jones. The presence of a metastable HCP structure permits investigation of transitions among different polymorphs.

Order from disorder

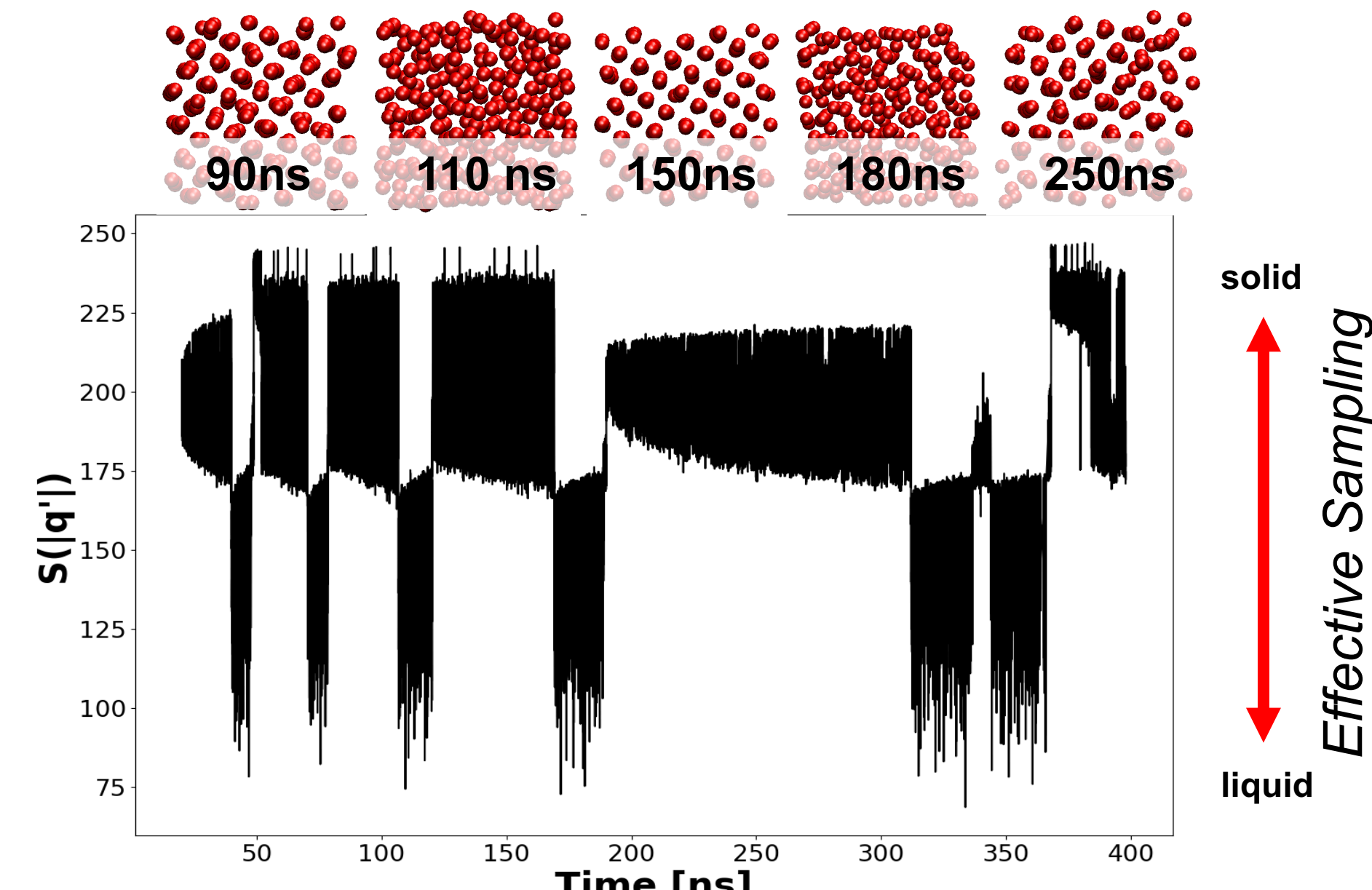


Figure 1: Oscillations in $S(|q'|)$ during the simulation correspond with transitions between phases.

Quantifying local order

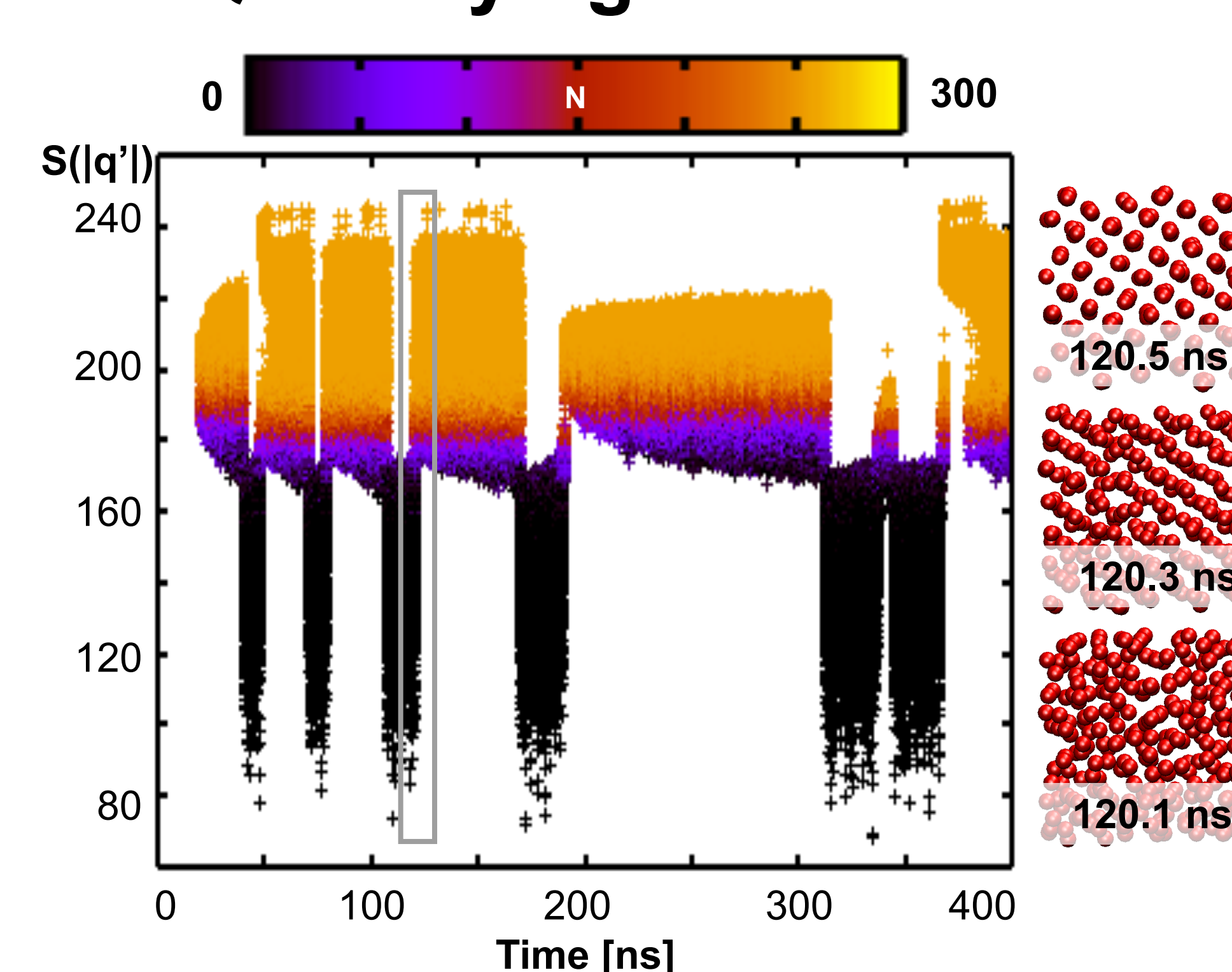
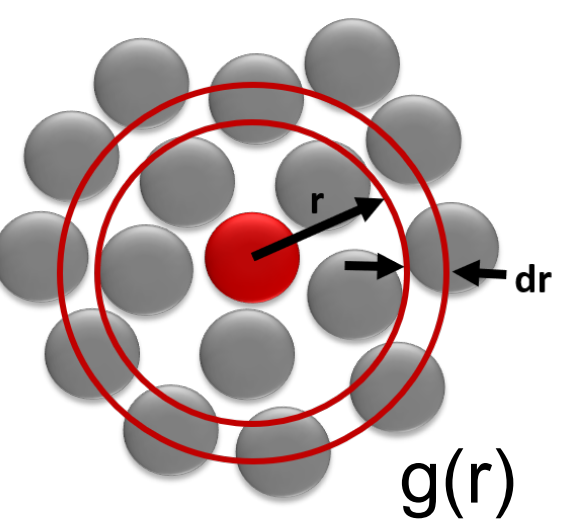


Figure 2. Collective variable during simulation time and extent of crystallization. The consistent correlation between cluster size (N) and the collective variable ($S(|q'|)$) is visually apparent and implies the presence of a preferred kinetic pathway between amorphous and crystal states.

The crystal cluster size (N) is determined from an average “local entropy,” a function of the radial distribution function, $g(r)$ [7,8]:



$$s_S^i = -\rho k_B \int_0^{r_m} [g_m^i(r) \ln g_m^i(r) - g_m^i(r) + 1] r^2 dr$$

Crystallization pathways

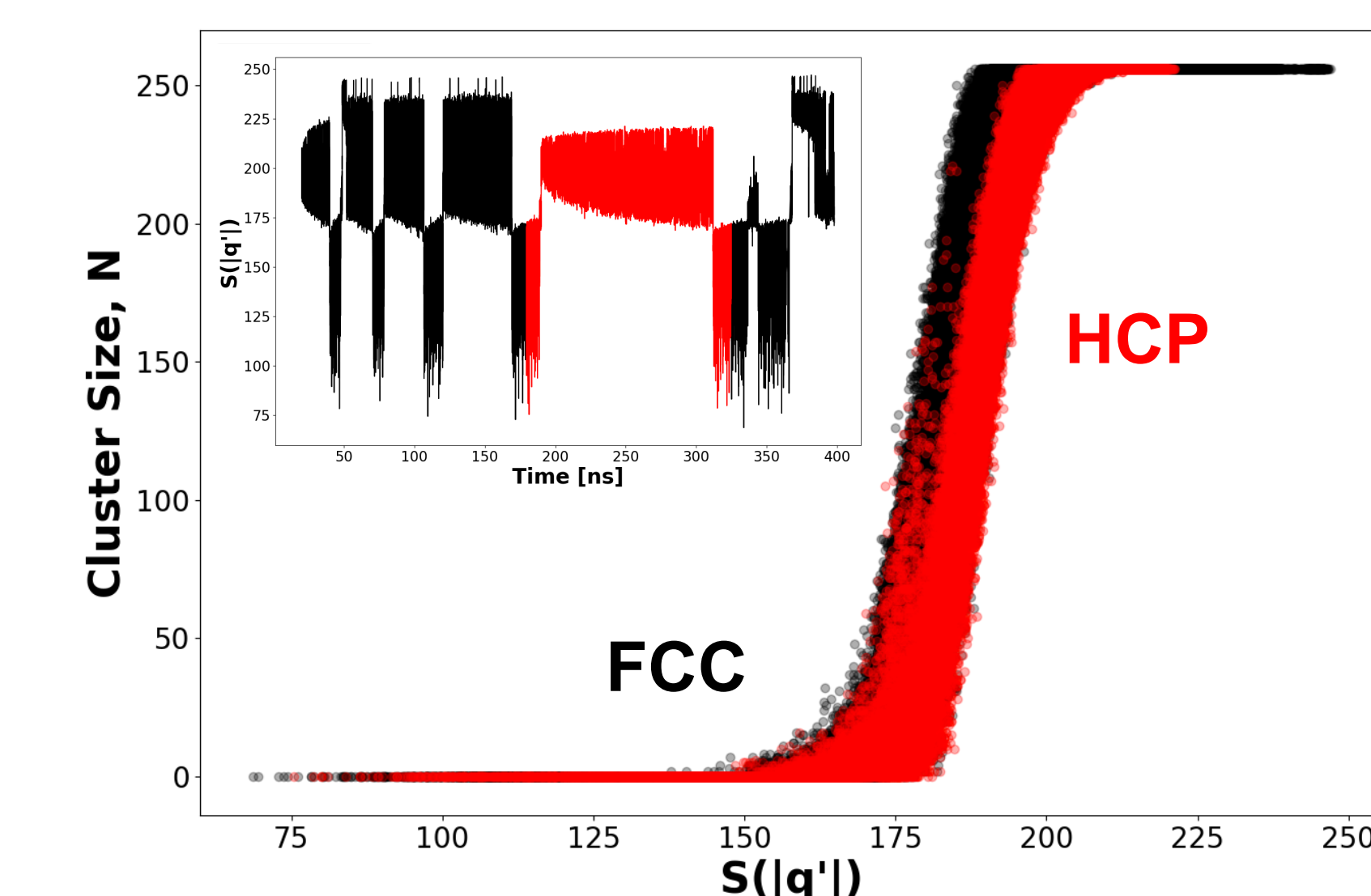


Figure 3: The strong correlation between cluster size and $S(|q'|)$ is shown. Pathways for different polymorphic states may be distinguished.

Determining free energy

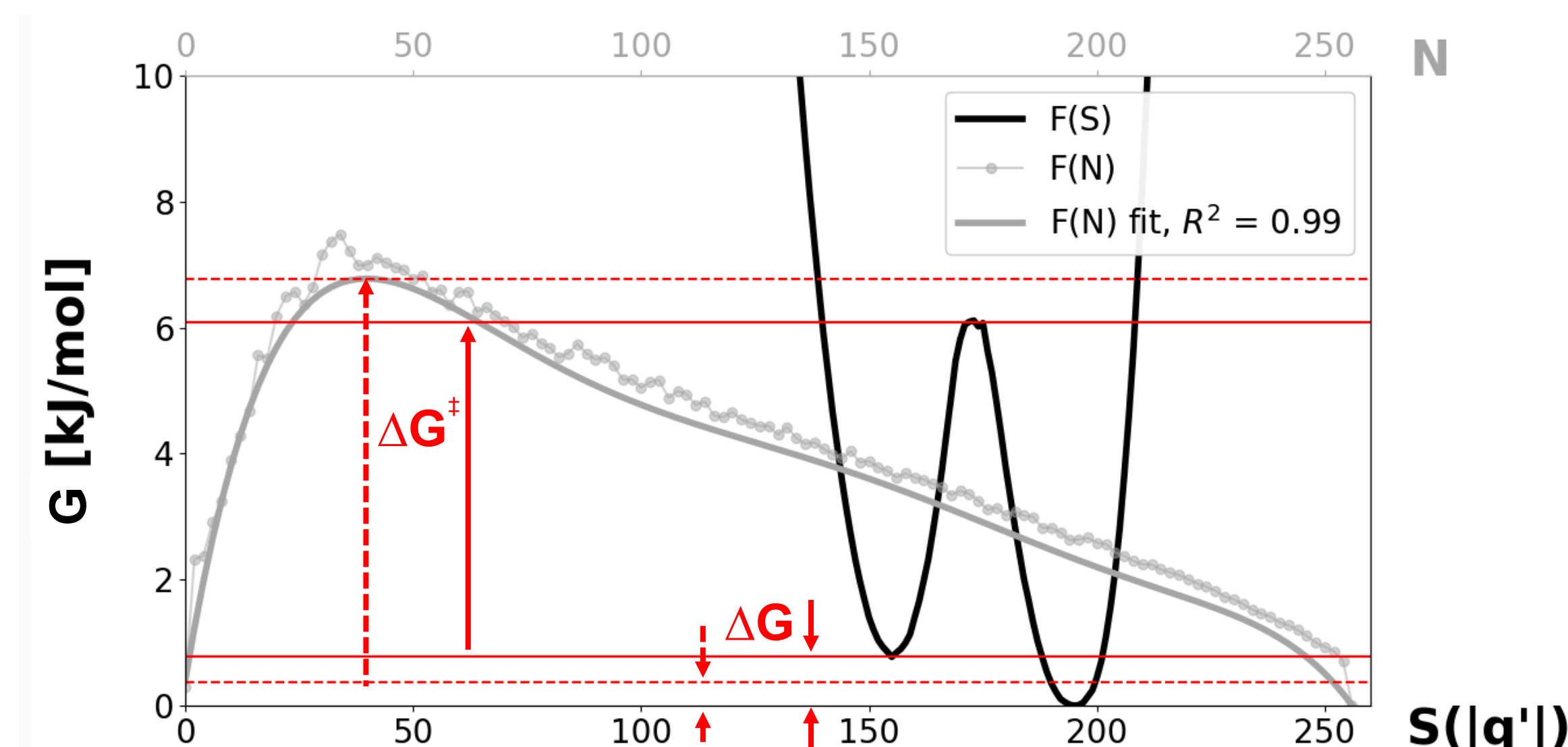


Figure 4: Free energies (G) are obtained by reweighting the histogram of sampled states by the added bias. Recalculated as a function of cluster size, energy differences and barrier heights match within 1 kJ/mol.

Conclusions

Summary

- Metadynamics provides an effective tool to study the crystallization pathways and barriers in complex materials.
- This method can be extended to SPE systems using a suitable interfacial collective variable.

Ongoing and Future Tasks

- Apply this technique for metal oxides such as Al_2O_3 .

Interfacial growth and complex systems

An interface-dependent collective variable will enable SPE modeling. Alumina is a future application for this method due to readily available force fields.

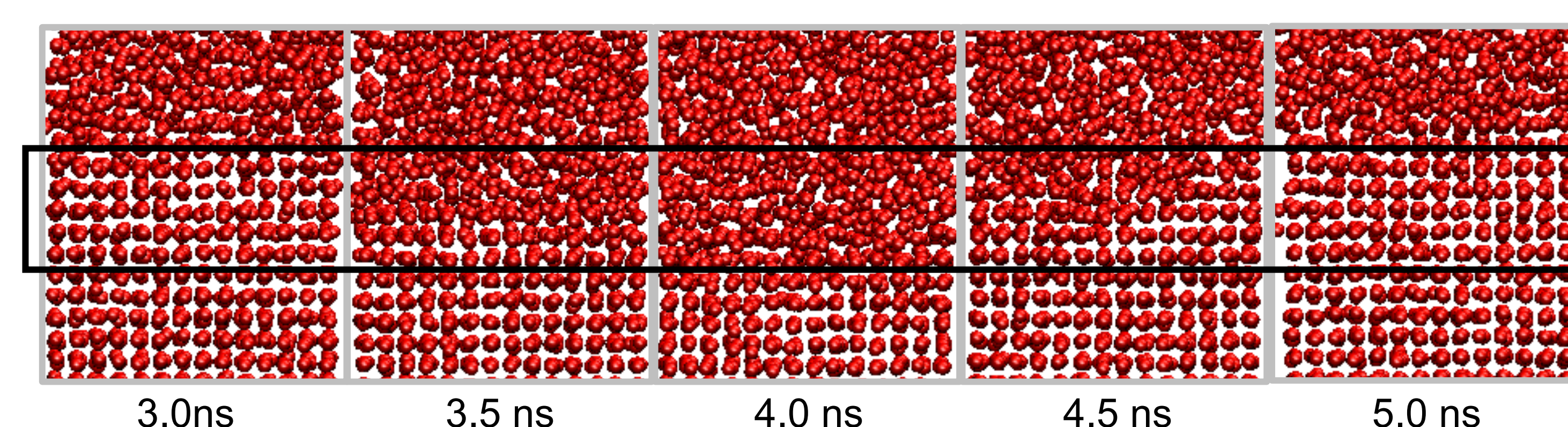


Figure 5: SPE growth may be characterized by targeting select atoms about the interface and adding bias as a function of this region's order.

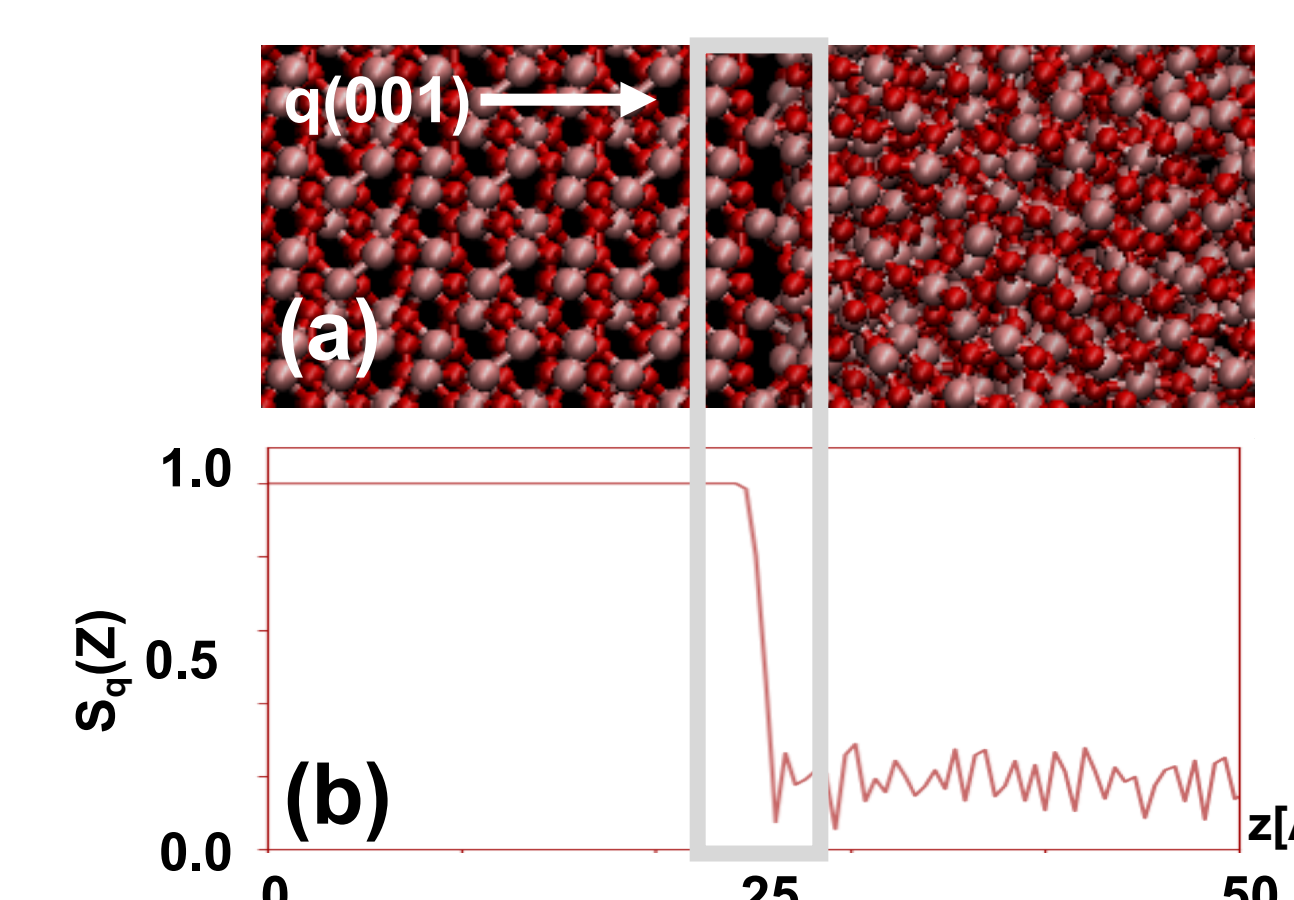


Figure 6: Interface identification of (a) α -alumina via (b) $S_q(z) = \left| \frac{1}{N(z)} \sum_{z_i \in [z, z+dz]} \exp(j\vec{q} \cdot \vec{r}_i) \right|$

References

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