Fluctuation Relations of Phase Transitions - Externally Driven Crystallization

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Core Junior Project (FNR Luxembourg)
Theory of Soft Condensed Matter
University of Luxembourg

Three Parts

- I : Compressing the system into the solid phase
- II : Periodically compressing/ decompressing across the coexistence pressure
- III : Studying active particles

Three Parts

- I : Driving the system away from an equilibrium state
- II : Driving the system in a non equilibrium steady state
- III : Driving the system away from a non equilibrium steady state

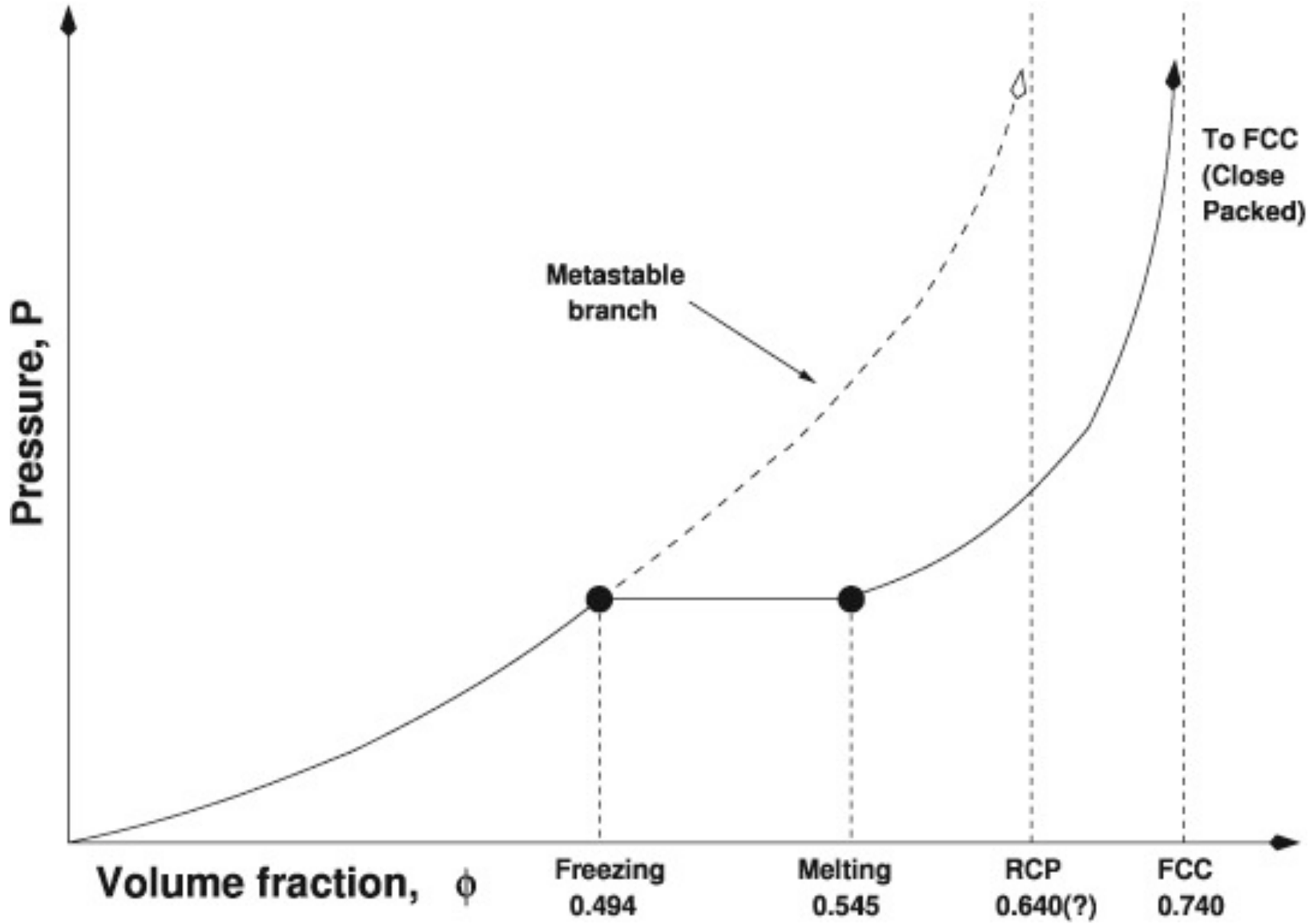
Main Research Goal

- Study the disspation in colloidal systems
- Connect structures to disspation locally
- Advance the formalism of phase transition and fluctuation relations
- Bridge the two fields of research

Main Idea

- Work is defined, i.e. dissipated energy can be calculated.
- Study macroscopic fluctuations instead of microscopic thermal fluctuations (FT)
- This will also work in experiments

Suspensions of Hard Spheres

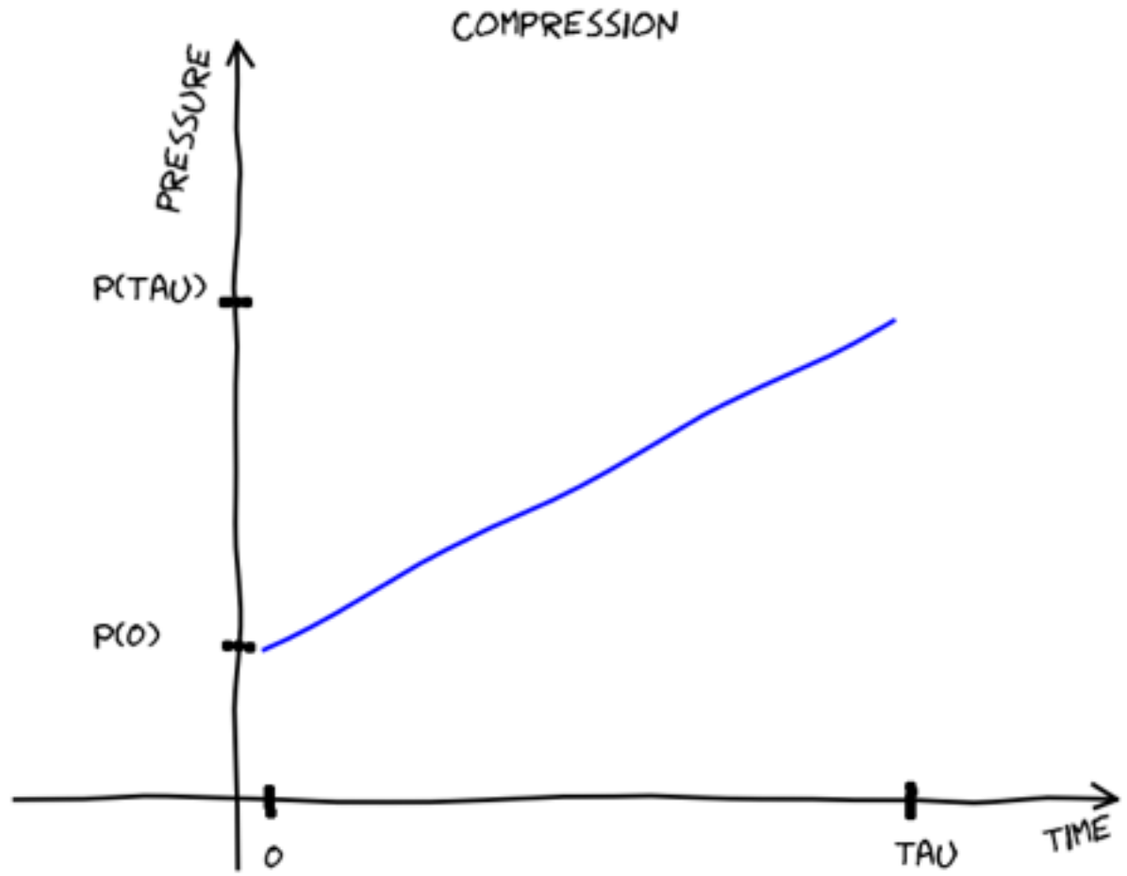


Jarzynski and Crooks Relation

in the NPT ensemble

$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta G)$

G: Gibbs Free Energy



with the underlying symmetry

$P(W) = P^{\dagger}(-W) \exp(\beta(W - \Delta G))$

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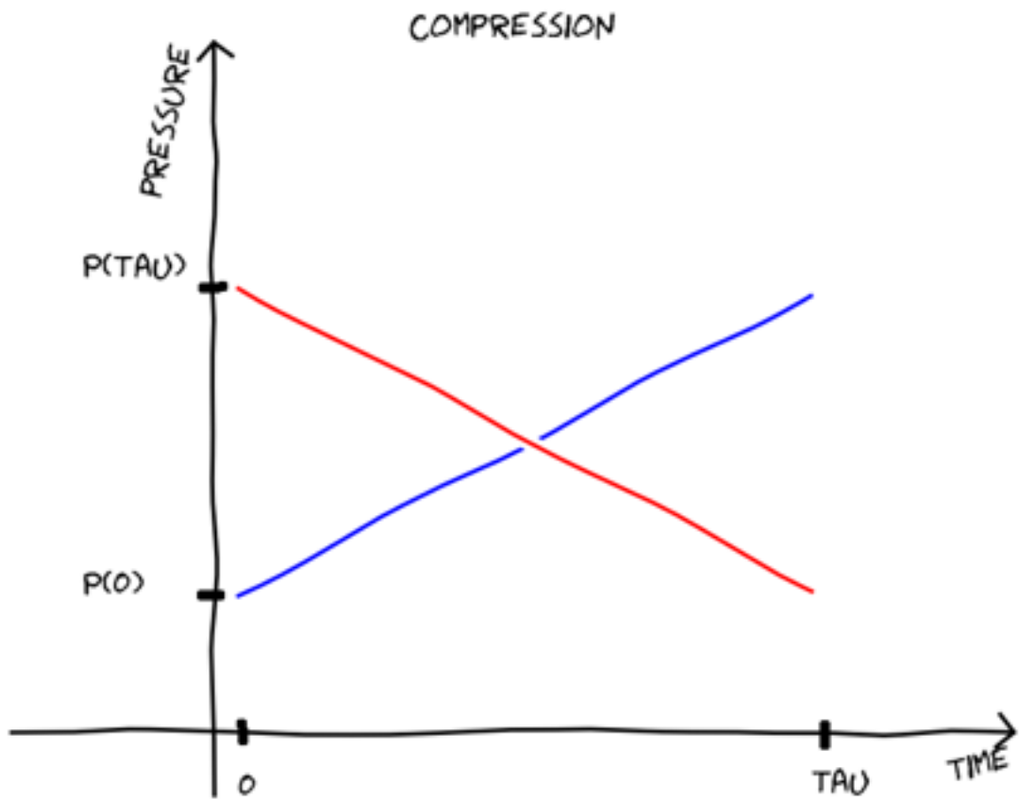

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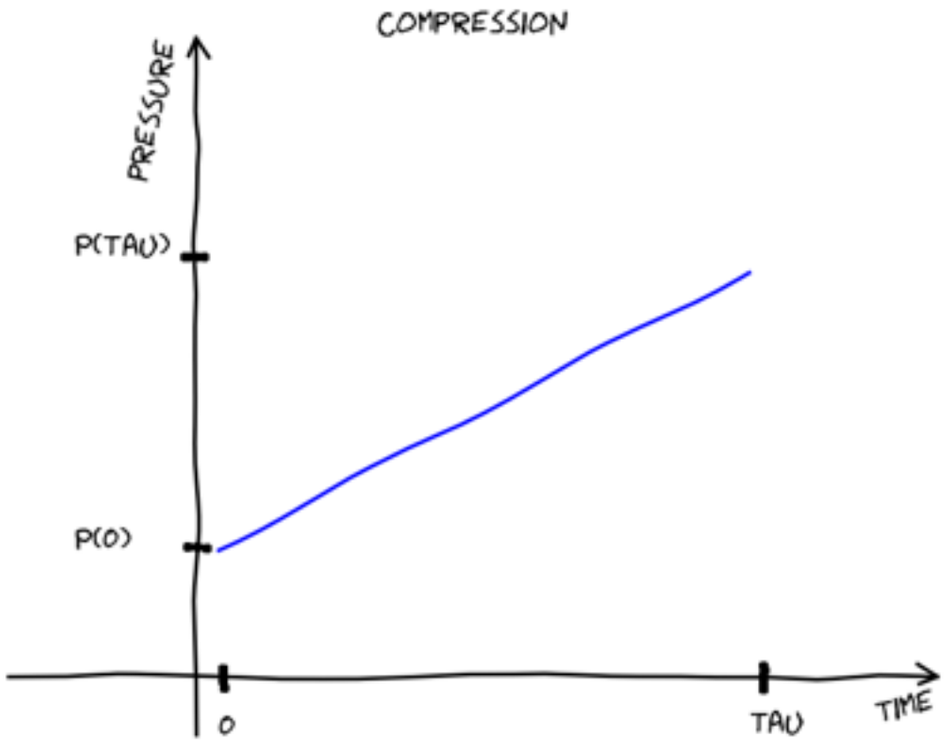
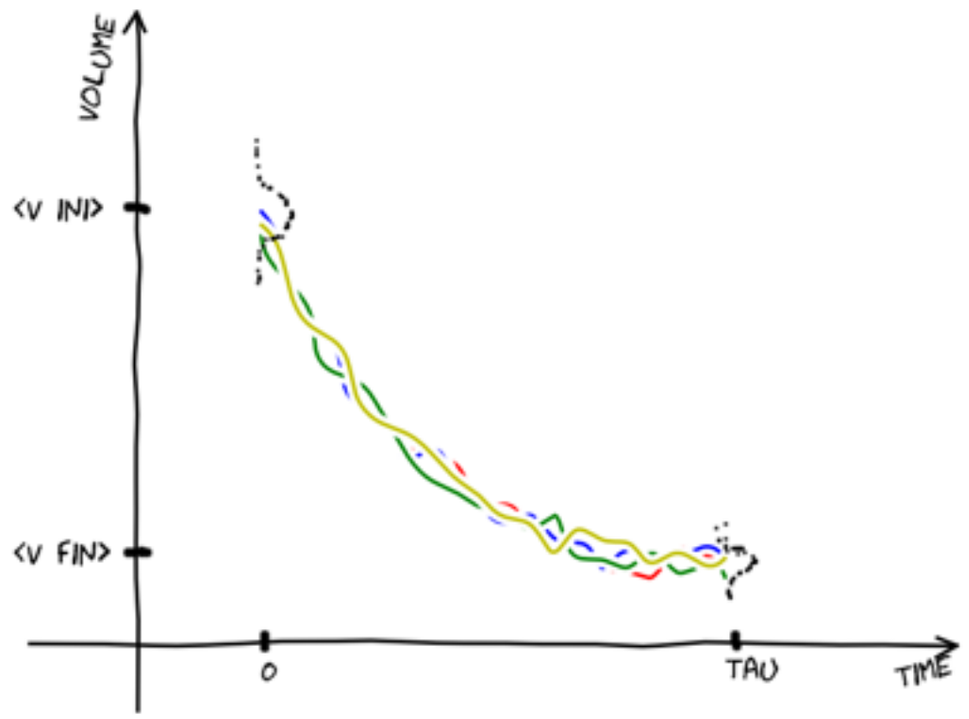
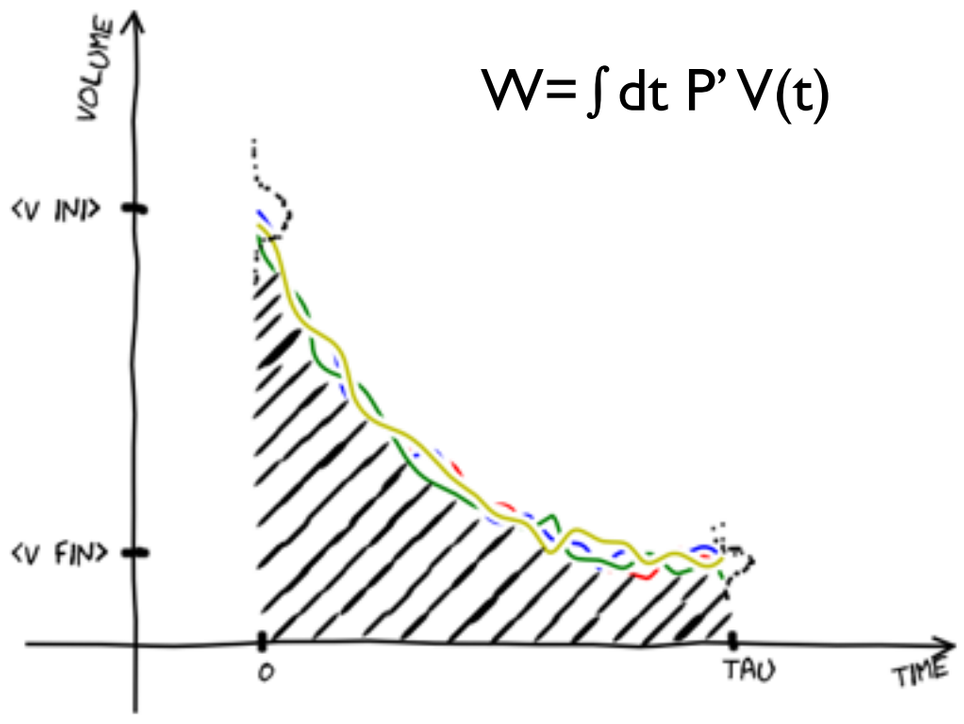
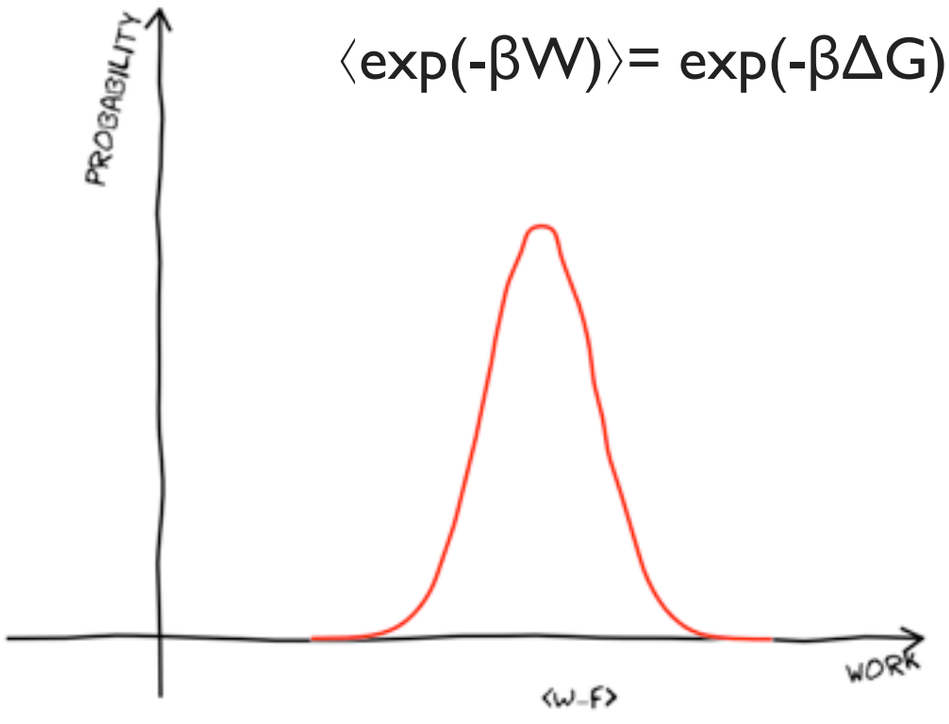






$$W = \int dt\, P' V(t)$$

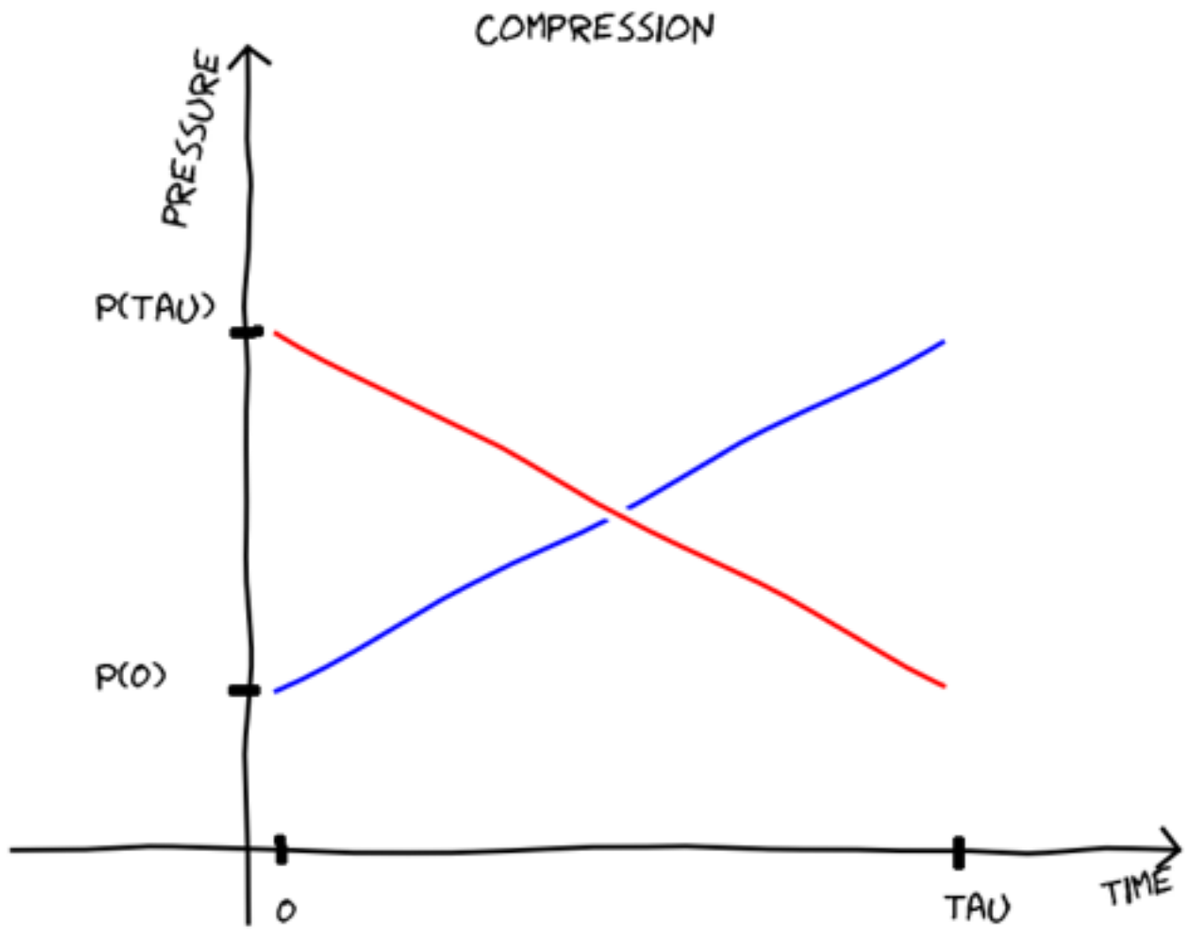


$$\langle \exp(-\beta W) \rangle = \exp(-\beta \Delta G)$$

Work Distribution
Compression in the fluid phase

Numerical study:
N=540 spheres,
initial pressure
P=8, pressure
increase ΔP=3

distributions for
different tau



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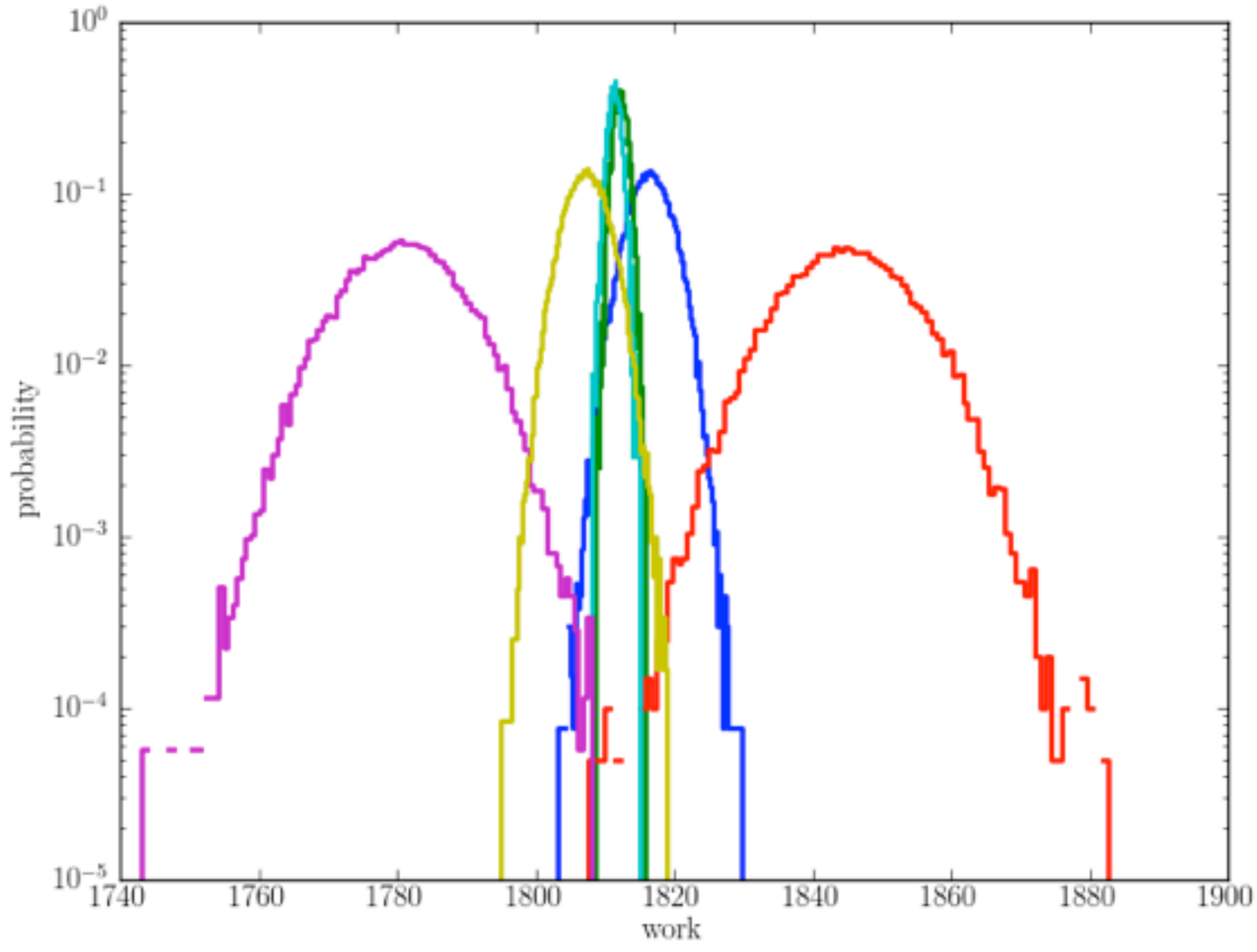

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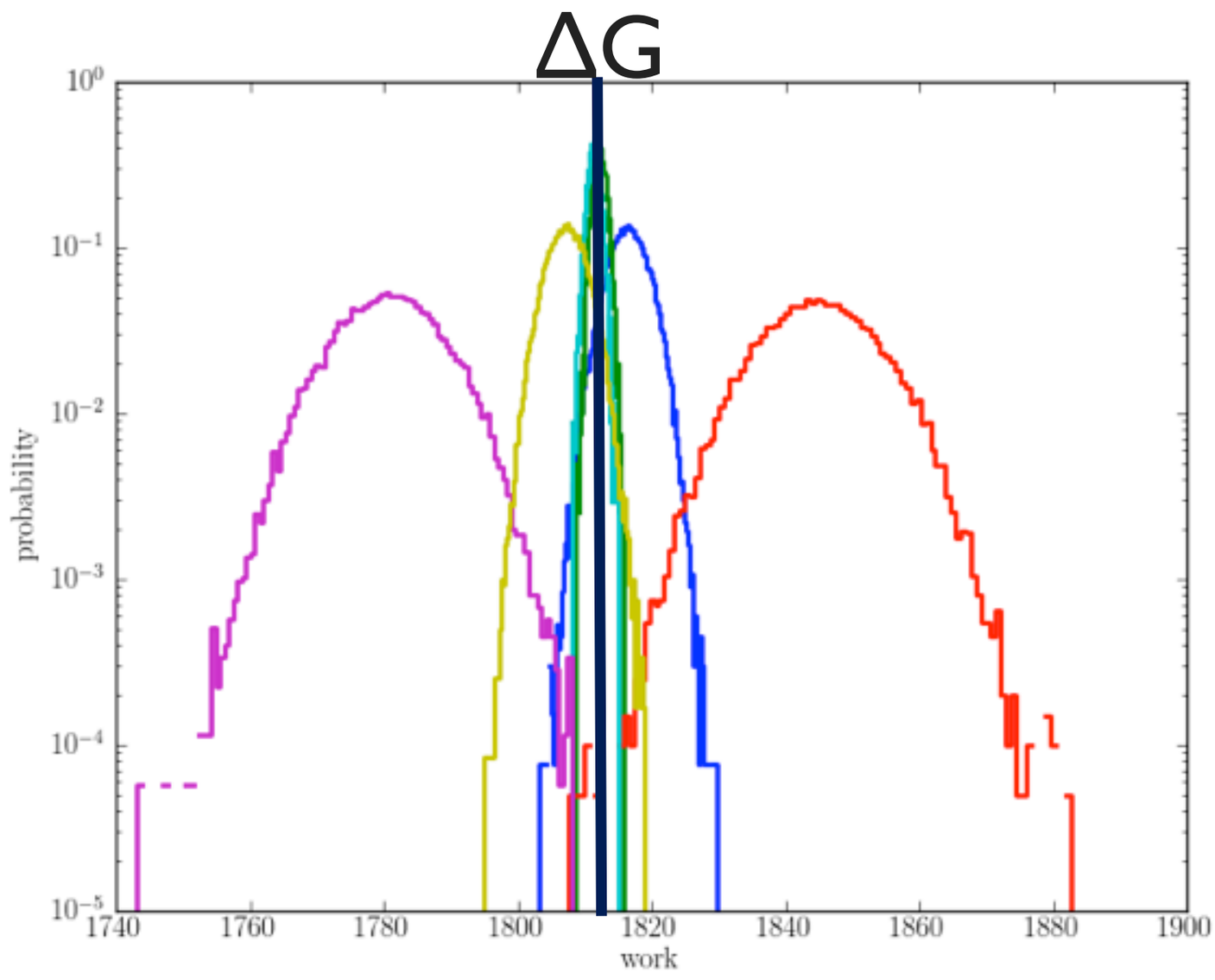

distributions for
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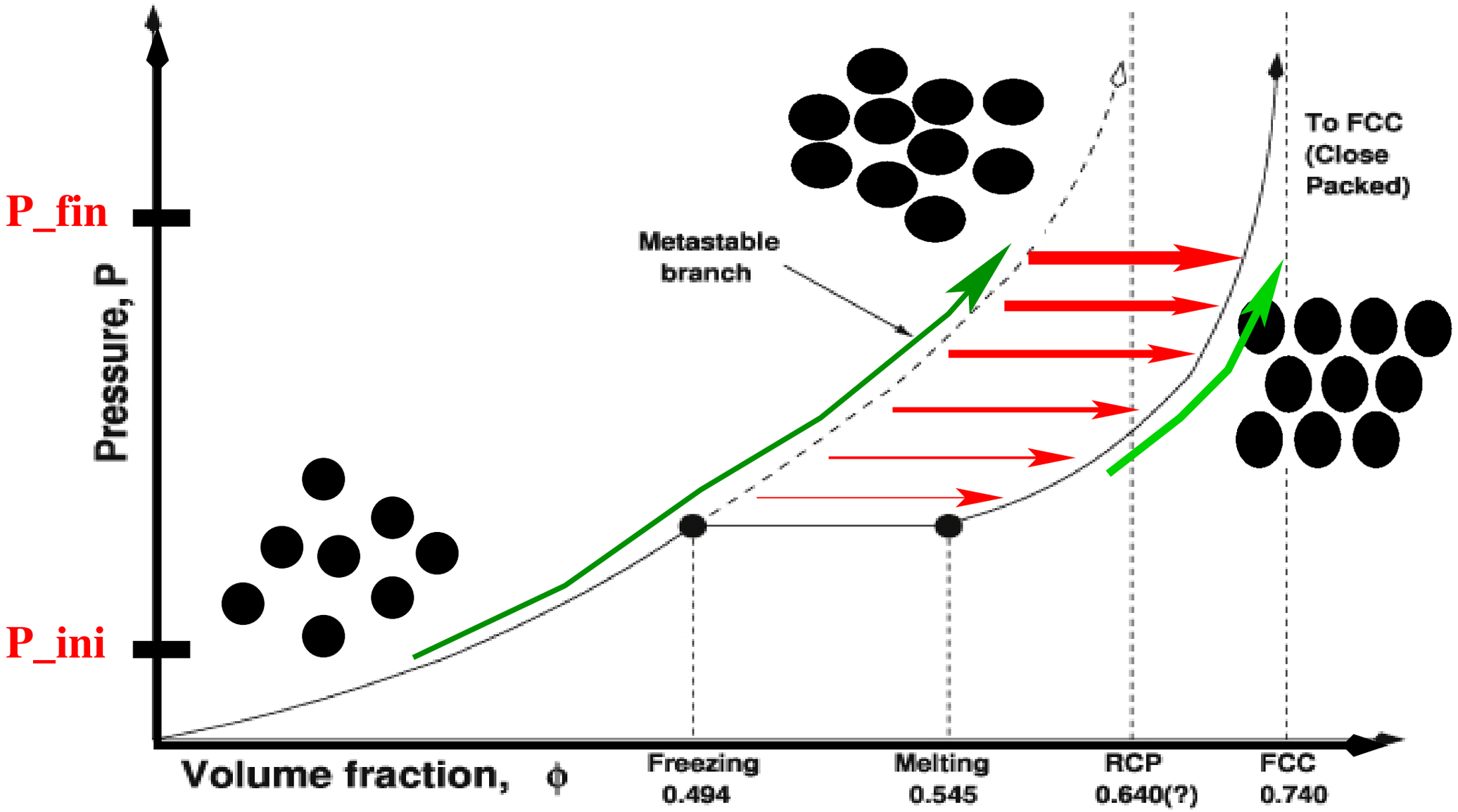
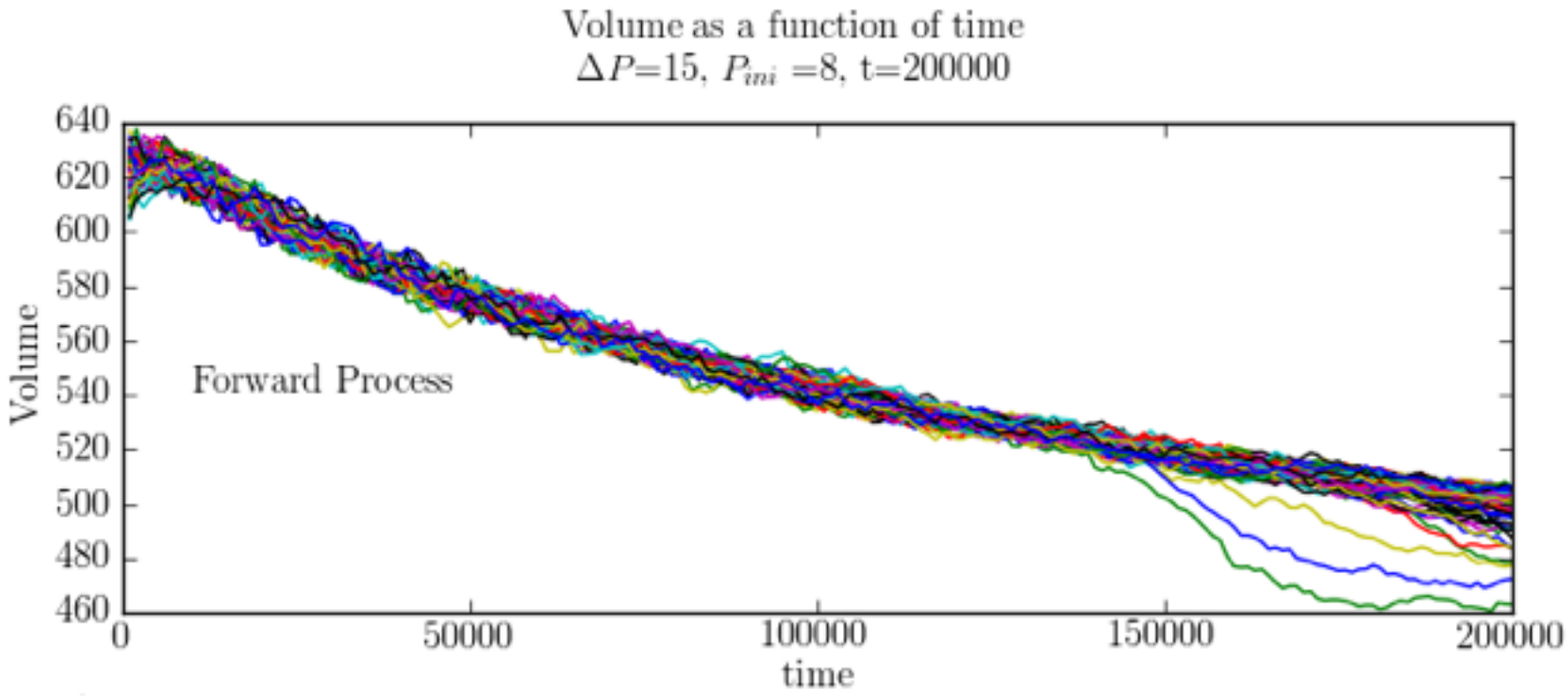
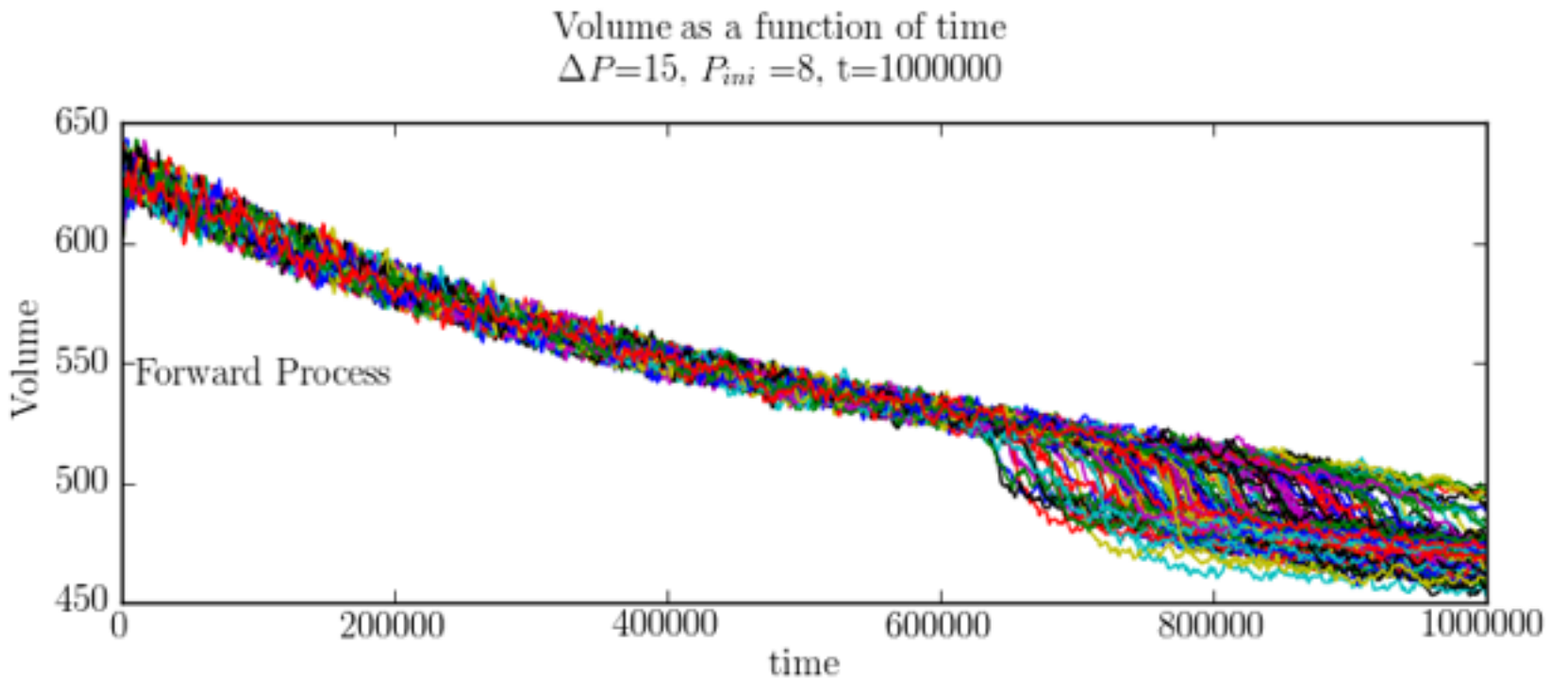
Crystallization Event - Compressing into the solid phase

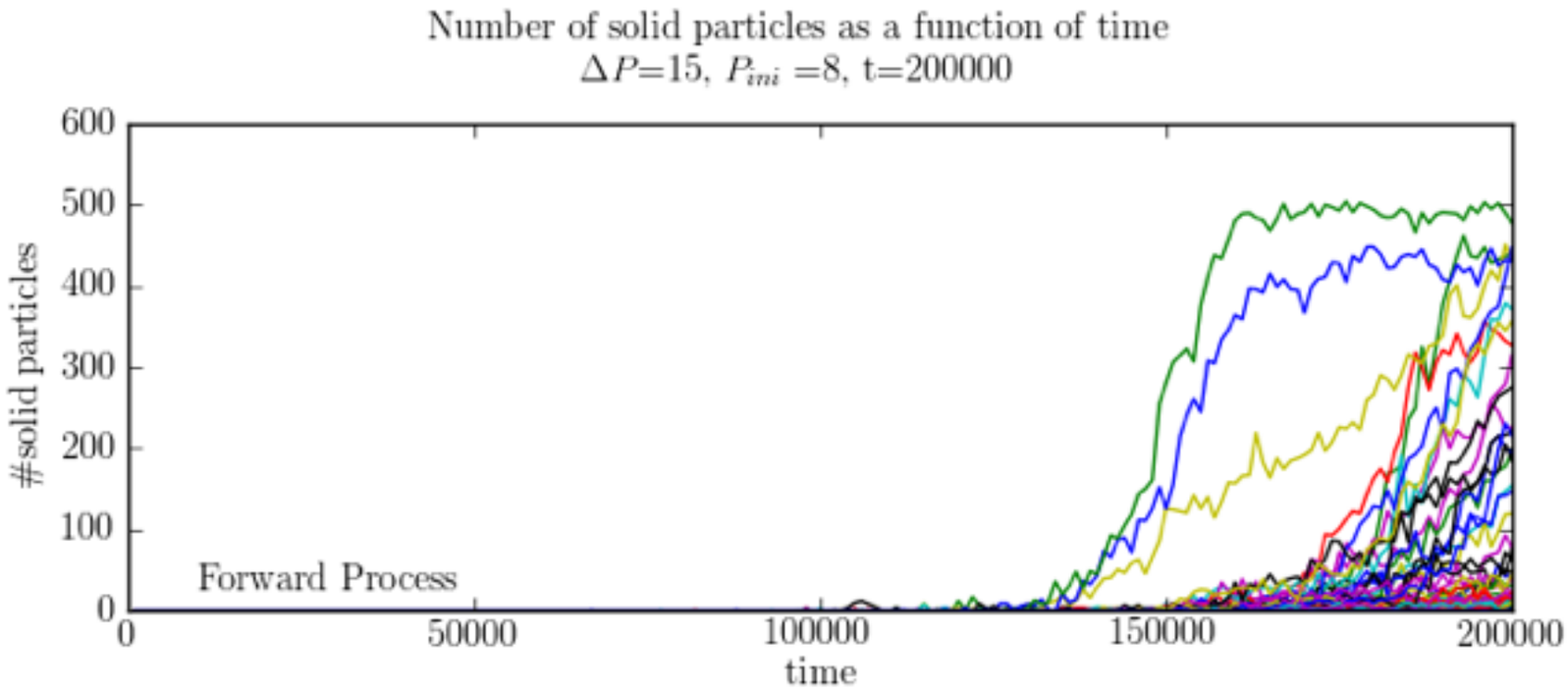


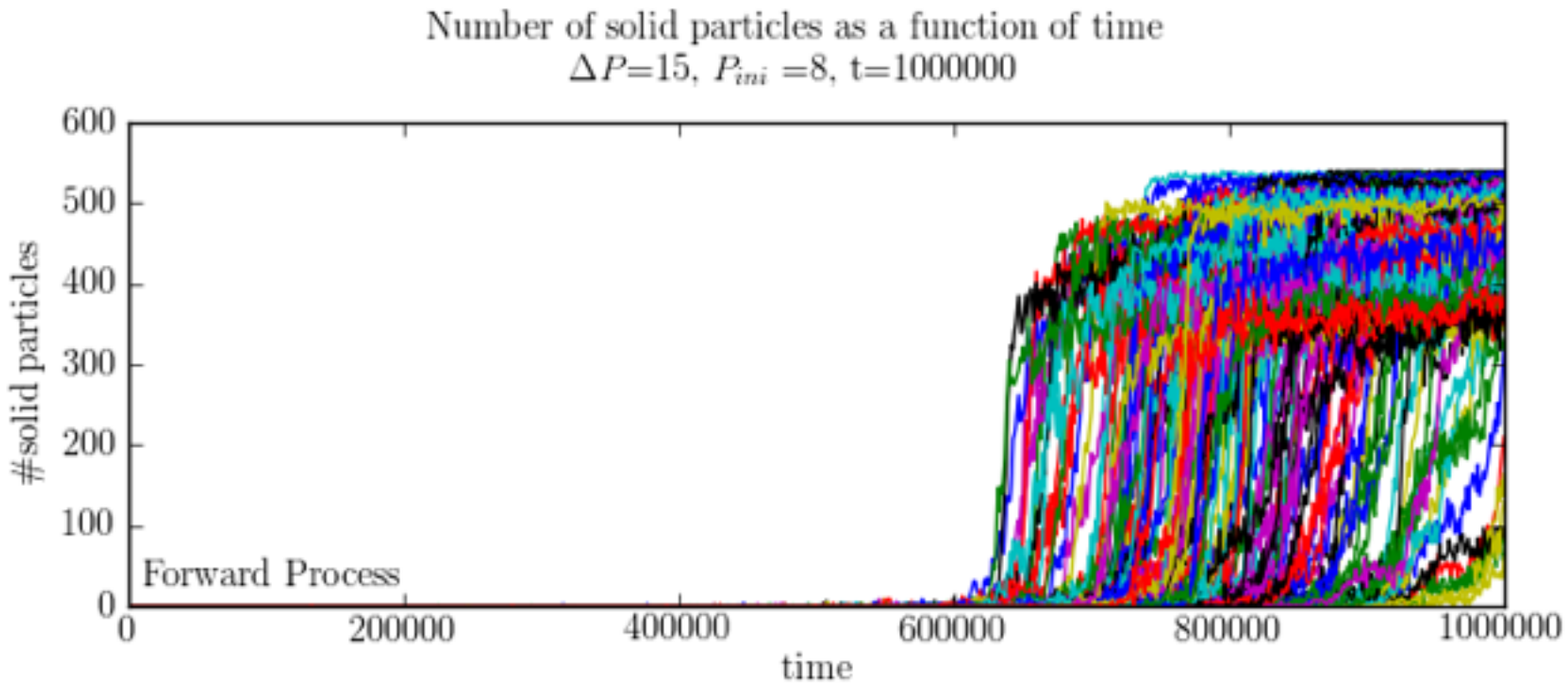
Jump in the Volume



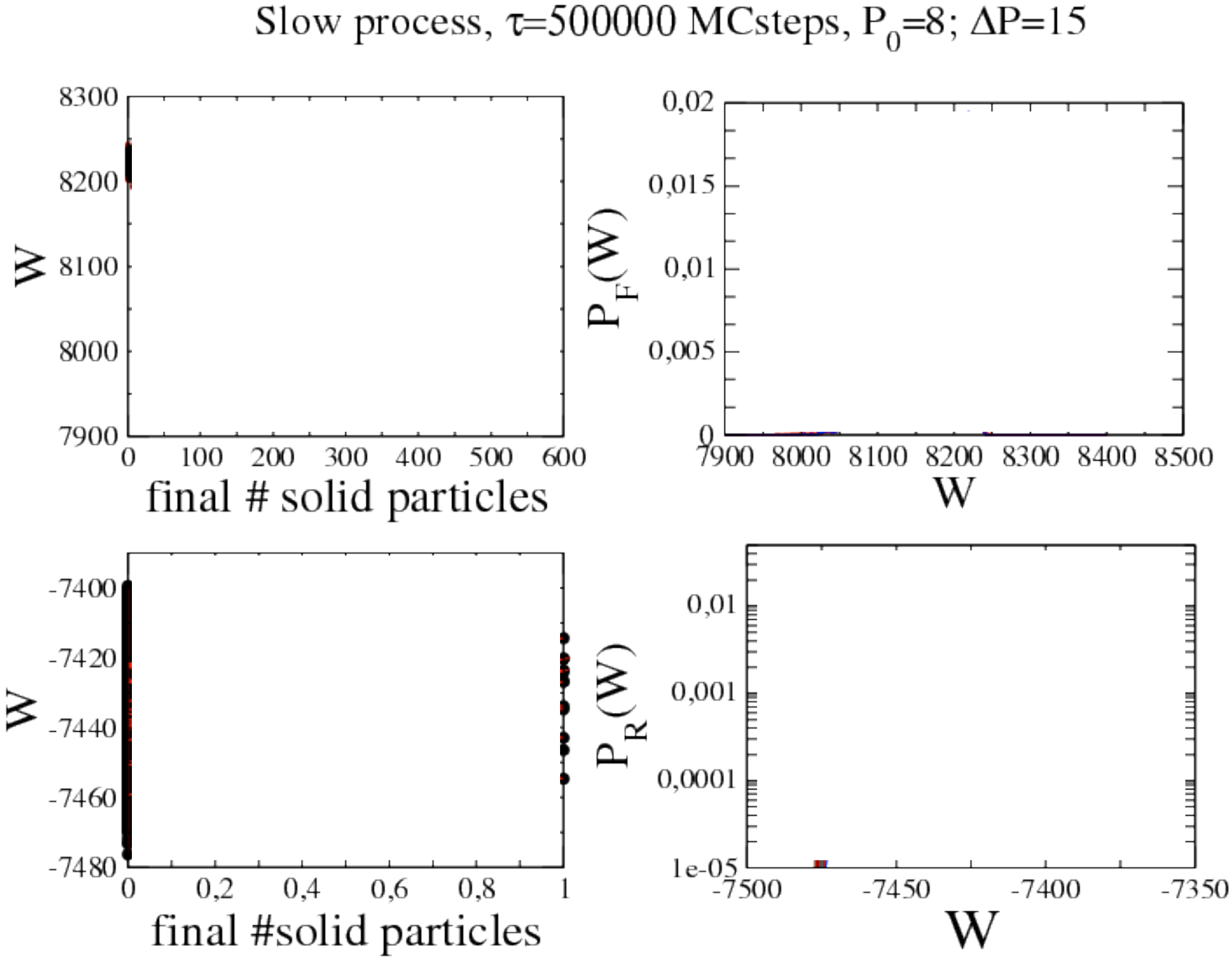


Appearance of crystal structures





Work distribution



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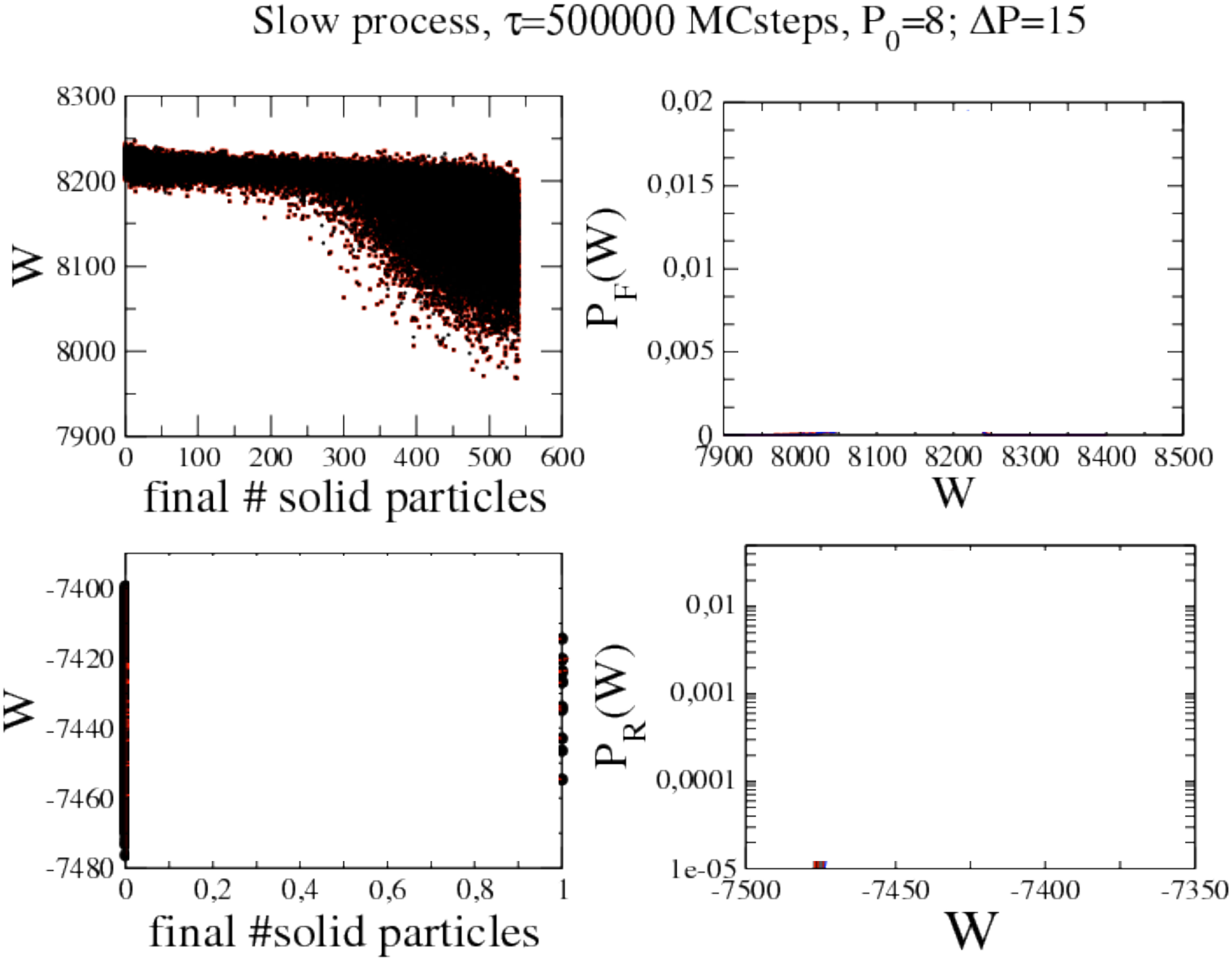

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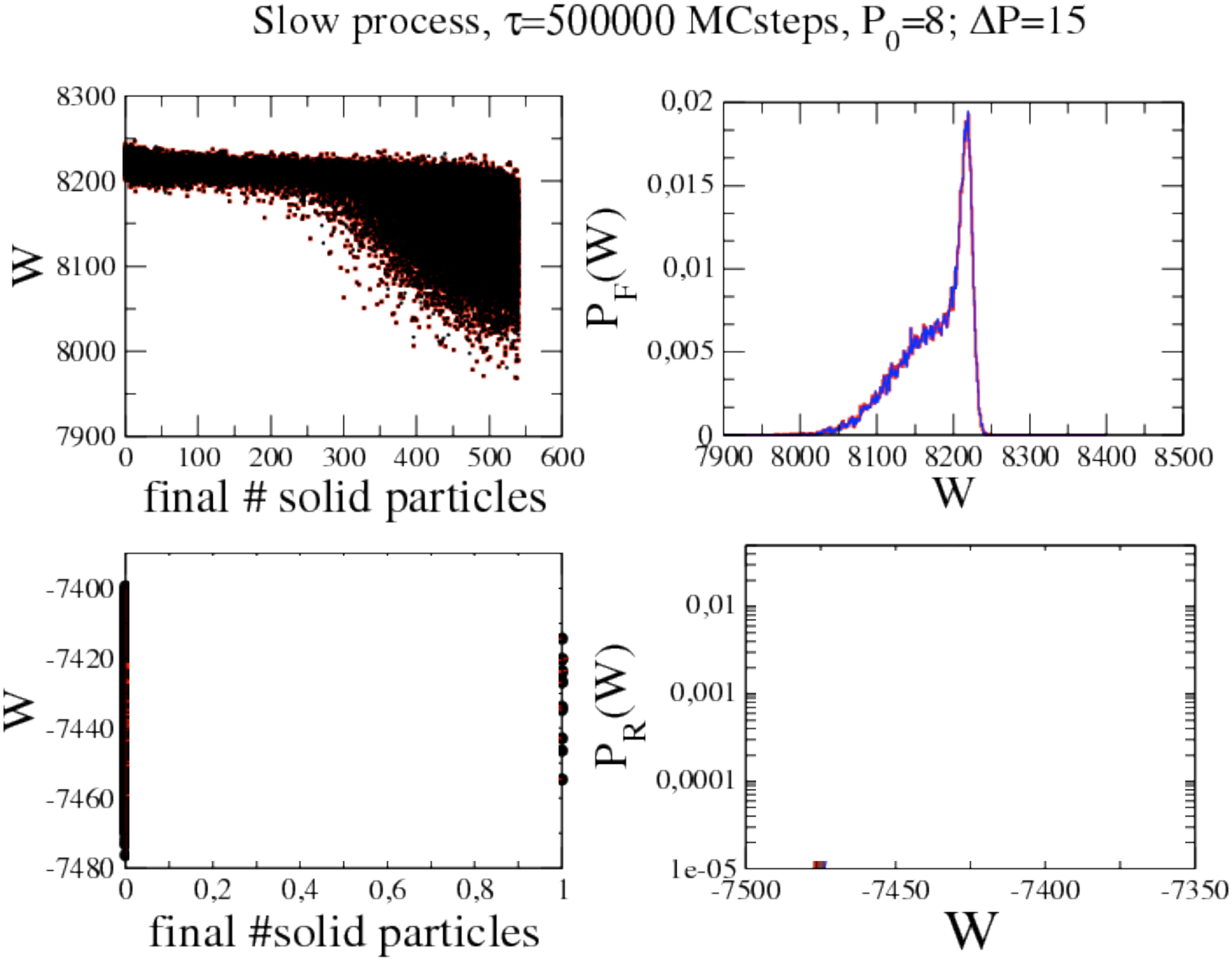

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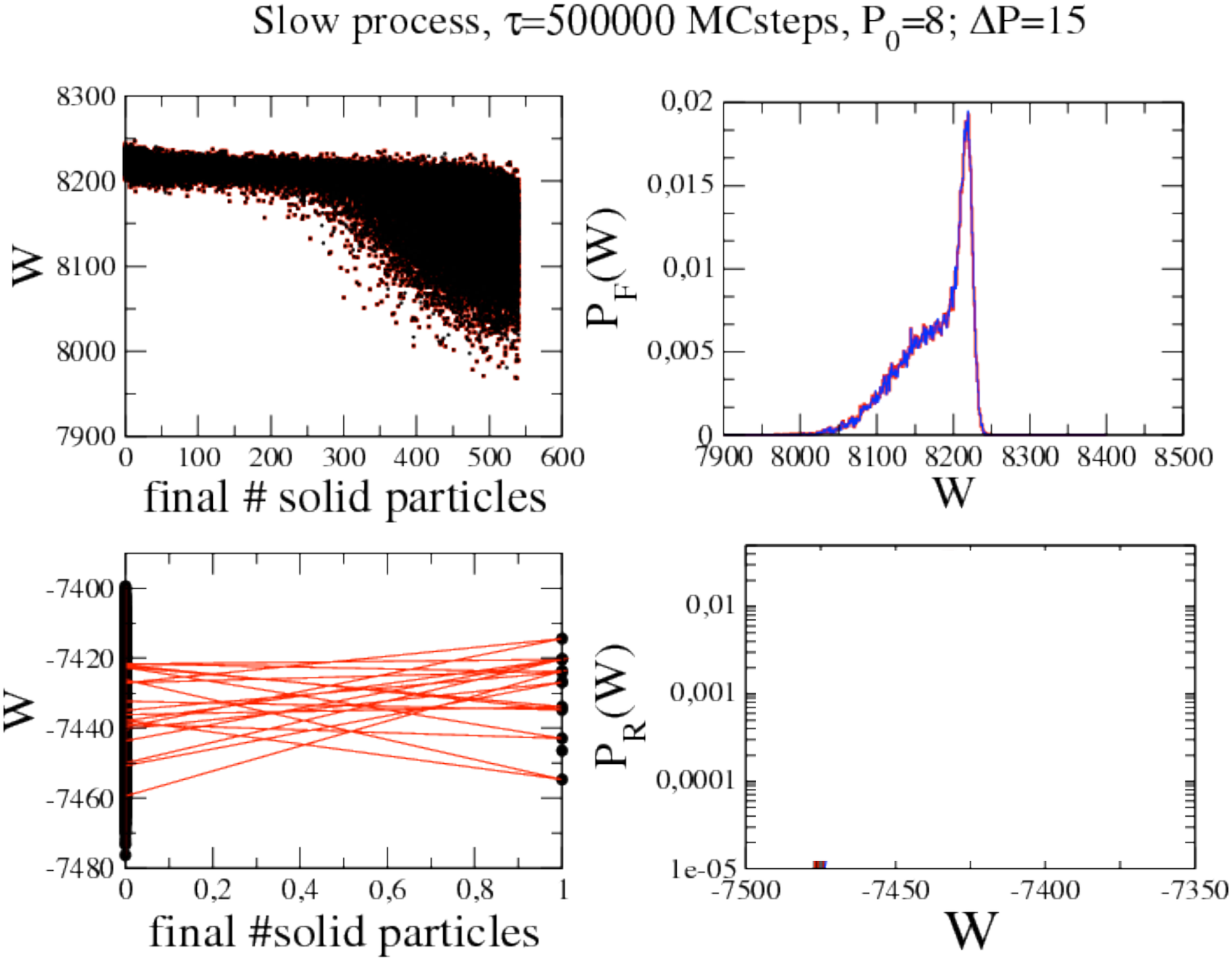

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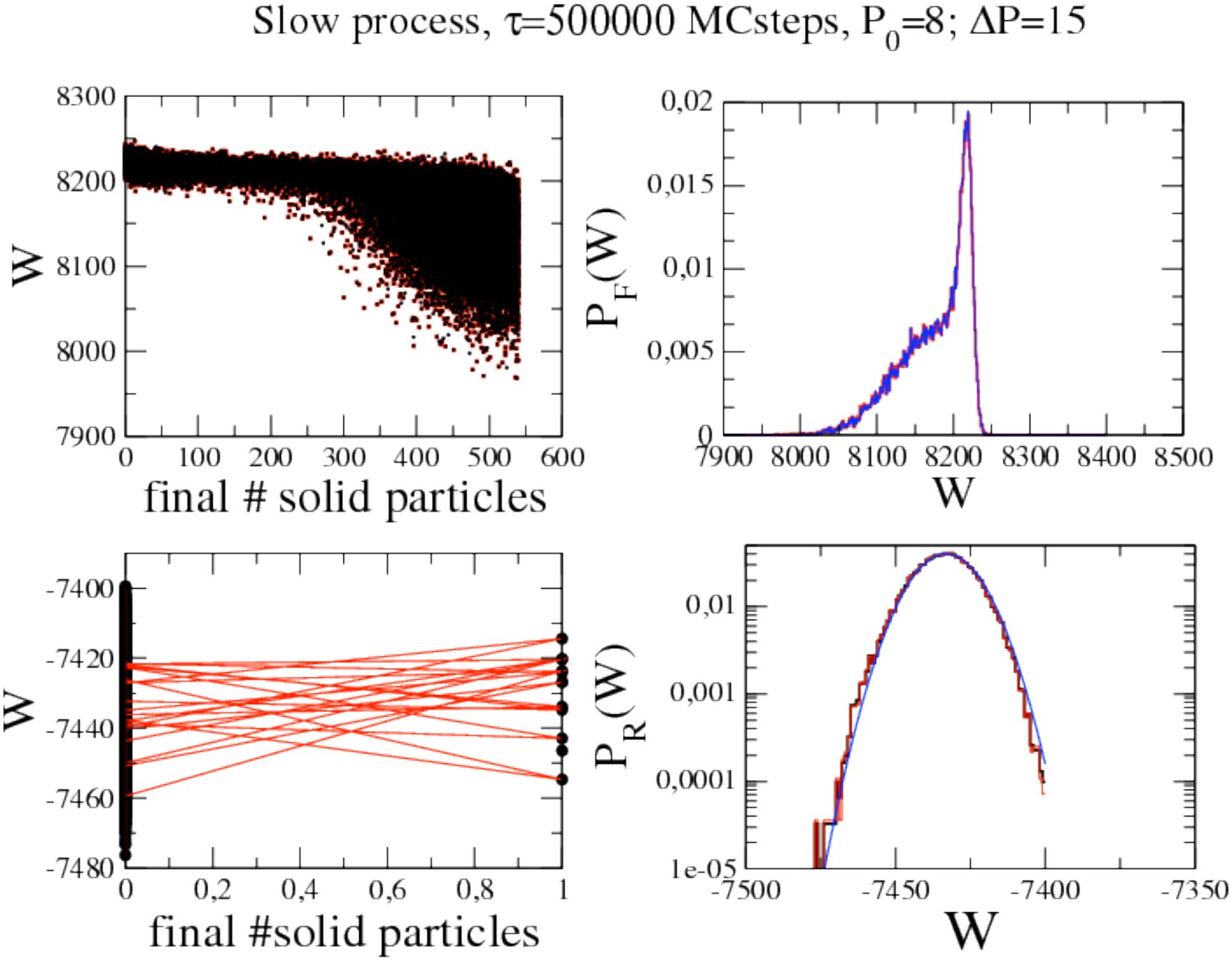

Where am I in this project?

- simulations are running- unbiased.
- rare event sampling not setup yet- needs to be done.
- delta G needs to be obtained to compare to results via Jarzynski relation. forward and reversed process separately.
- no long ellipsoids considered yet ... (consider fluid nematic transition)

Modeling of the process

- Input of all the equilibrium properties at fixed pressure
- Input of the nucleation rates
- obtain work distributions ⟶ Compare to MC simulation
- supervision of Master student (next three months)

Where am I in this project ?

- Again, I need to calculate the free energy difference to compare to simulation results.
- check the relation deltaG=<W>-<Wdiss^2>/k_b T (Gaussian approximation)
- reversed process not realized yet.
- i need to obtain melting rates...

Other ongoing projects

- Compression in centrifuge > Work distribution measurement (project with INM Saarbruecken and T.Platini Coventry University) (open questions: Thermostat EDMD algorithm, determine local pressure inside the suspension.)

- Structure factor measurements for ellispoid suspensions (Martschenko Lundt University) (open questions: too many parameters to play with)

- Charged ellipsoids + Derjaguin approxiamtion (project with Tanja, Martin Oettel)

- Crystallization in system of hard spheres including random pinning. Frustration causes changes in energy barriers.

Further Goals of the Project

- organize workshop in Luxembourg, fix the list of speakers
- visit schools and organize stand at the researchers night for students.
- Lecturing.
- habilitation at the end of the three years.
- think about plans for after the project (Spring 2016).