Fluctuation Relations and Crystallization

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Motivation

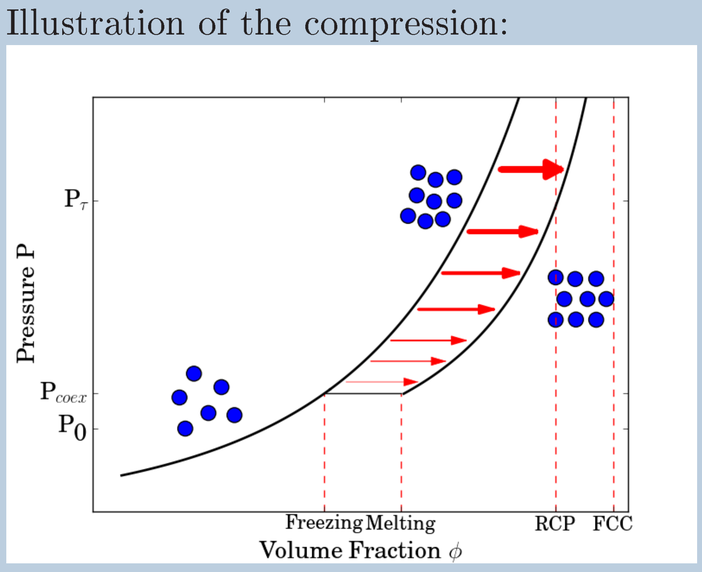
Hard Spheres undergo a fluid to solid phase transition if the packing fraction is approx. > 0.5. The nucleation process itself and structure formation in this transient process are still under investigation. Here a new approach is proposed to correlate forming structure and dissipation directly. Fluctuation relations are the method of choice. Increasing the pressure with time results in thermodynamic work, linked by the first law of thermodynamics to dissipation.
Studying fluctuation relations of structural phase transition and even slow dynamics is important. A new kind of fluctuation enters the dynamics that is macroscopic instead of microscopic based on thermal fluctuations.

Model

Monodisperse Hard Spheres are described by the volume fraction ϕ.
Important facts:

- Very high energy barrier at low over compression, *i.e.* very small nucleation rates.
- Latent heat at the phase transition is purely entropic because of hard potentials.
- Coexistence pressure $P_{\text{coex}} = 11.45$.
- spinodal regime and even glassy dynamics at high packing fractions [1].

Illustration of the compression:



Basic Concepts

The system is compressed by an external time dependent pressure, $P_0 \to P_\tau$
Thermodynamic work (*NPT ensemble*):

$$W = \int_0^\tau dt \dot{P} V(t)$$

The Crooks relation [2]:

$$P_F(W)/P_R(-W) = \exp(-\beta(W - \Delta G))$$

The Jarzynski relation [3]:

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

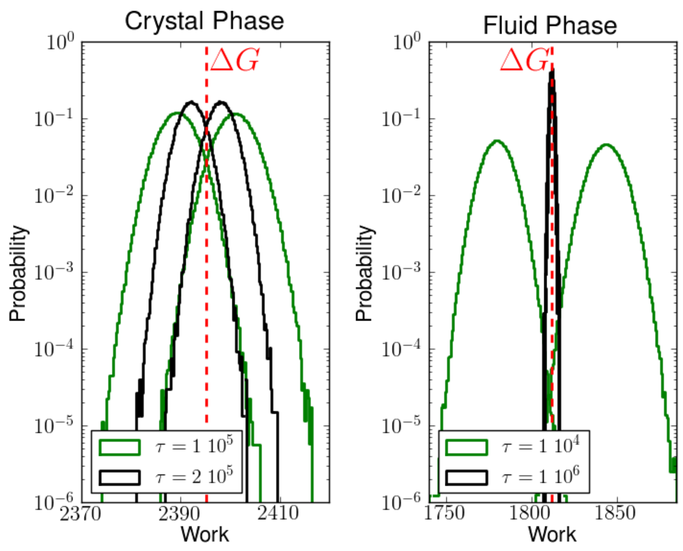
Dissipated Energy: $W_{diss} = \Delta G - W$
Calculate ΔG via the Gibbs–Duhem relations:

$$\left.\frac{\partial \mu}{\partial P}\right|_T = \frac{1}{\rho}$$

The dynamics of the system is based on Monte Carlo simulation. Max step sizes are set constant.

The Single Phase

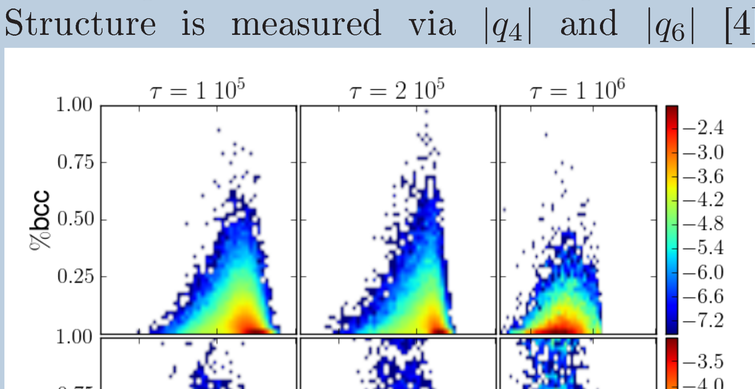
The resulting distribution of work in the fluid resp crystal phase.



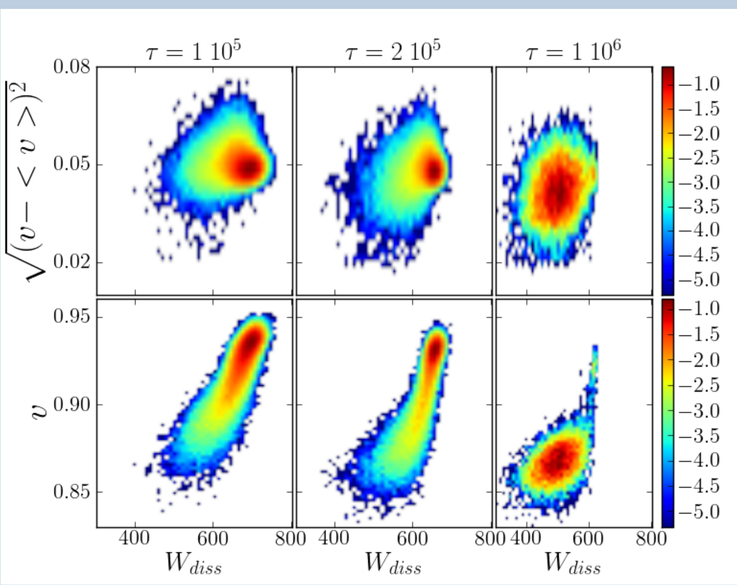
The free energy difference is recovered.
The Crooks relation (NPT ensemble) is verified.
Good definition of thermodynamic work.
The quasistatic limit is recovered for large τ.
For small τ the gaussian approximatian fails, variances are not equal in the forward and reversed process.

Dissipation and Structure

Resulting transient structures on log scale.
Structure is measured via $|q_4|$ and $|q_6|$ [4].



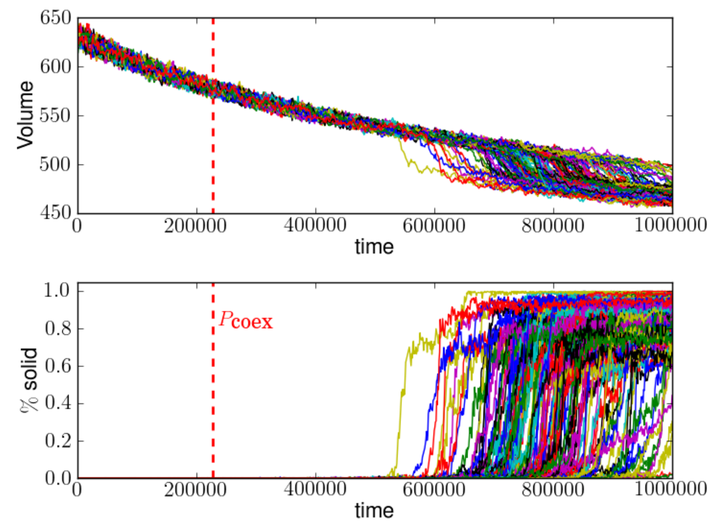
Particles are considered
fcc, if $|q_6| > 0.35$ and $|q_4| > 0.125$
bcc, if $|q_6| > 0.35$ and $|q_4| < 0.06$.



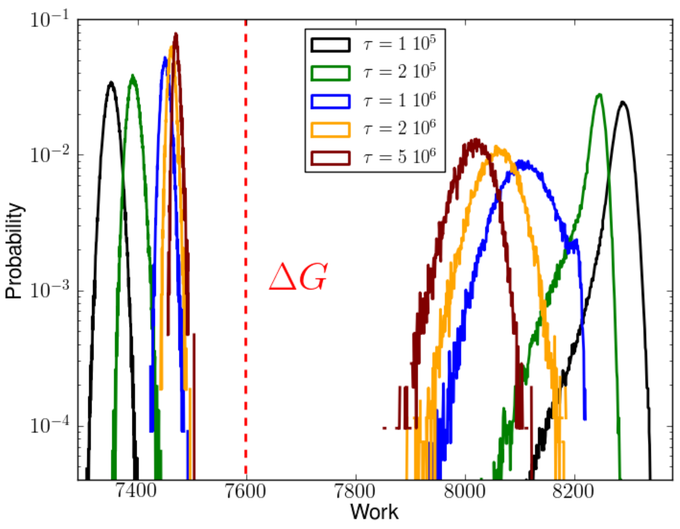
Single particle volume v [5] information is directly linked to dissipation.

The Phase Transformation

Single runs ($n = 40$)

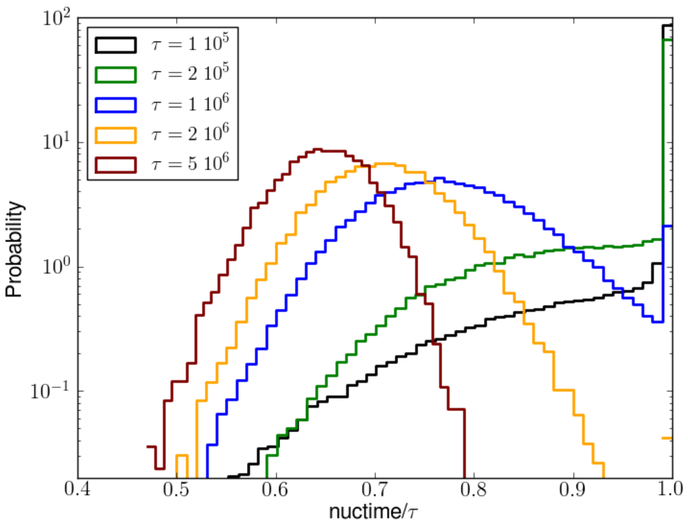


The distribution of work



⇒ Large assymetry in the transition crystallization–melting.
⇒ Exponential contribution - Poisson process.

The distribution of nucleation times



Conclusion and Outlook

The crystallization process is characterized by a macroscopic fluctuation. Fluctuation theorems capture this effect. Dissipation can be calculated during this transient process and allows one to study correlations to the emerging structures. Work distributions are not Gaussian in this case. An additional Poisson process is present.
This phenomena here studied for the most simple liquid, should be extended to dynamic arrest, anisotropy, and interactions exhibiting latent heat.

References

[1] P. N. Pusey et al, Phil. Trans. R. Soc. A 367 (2009)
[2] G. E. Crooks, Phys. Rev. E 60 2721 (1999)
[3] C. Jarzynski, Phys. Rev. Lett. 78 2690 (1997)
[4] W. Lechner et al, J. Chem. Phys. 129, 114707 (2008)
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Acknowledgements

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