Motivation

Hard Spheres undergo a fluid to solid phase transition if the packing fraction is above 0.5. The nucleation process itself and developing structures in this transient process are still matter of current research. Here a new approach is proposed to correlate forming structure and dissipation directly. The system driven externally by a time varying pressure is compressed in a finite time. Thermo dynamic work measured and directly correlated to structural information recorded during the process. Fluctuation theorems set the framework of this analysis that still hold at the first order process. 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 \( \tau \). For small \( \tau \) the gaussian approximation fails, variances are not equal in the forward and reversed process.

Model

Monodisperse Hard Spheres are described by the volume fraction \( \phi \).

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 \( P_{coex} = 11.45 \).
- Spinodal regime and even glassy dynamics at high packing fractions [1].

Basic Concepts

The system is compressed by an external time dependent pressure, \( P_0 \to P_0 \).

Thermo dynamic work (NPT ensemble):

\[
W = \int_0^\infty dt PV(t)
\]

The Crooks relation [2]:

\[
P_T(W)/P_R(-W) = \exp(-\beta(W - \Delta G))
\]

The Jarzynski relation [3]:

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

Dissipated Energy: \( W_{diss} = \Delta G - W \)

Calculate \( \Delta G \) via the Gibbs-Duhem relations:

\[
\frac{\partial \mu}{\partial P}|_T = \frac{1}{\rho}
\]

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.

\begin{align*}
\text{Crystal Phase} & \quad \Delta G \\
\text{Fluid Phase} & \quad \Delta G
\end{align*}

Dissipation and Structure

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

Particles are considered for, if \( |q_4| > 0.35 \) and \( |q_6| > 0.125 \)

bec, if \( |q_4| > 0.35 \) and \( |q_6| < 0.06 \).

Conclusion and Outlook

The crystallization process is characterised 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.

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