# Effective potential study of hard-spheres crystallization

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http://teorica.fis.ucm.es/grupos/grupo-TEC.html

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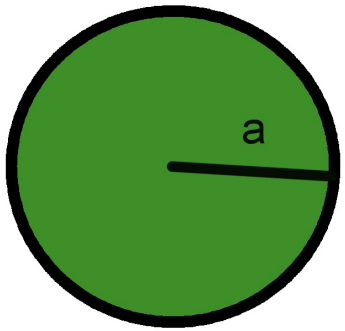
## Hard Spheres

$$V(r) = \begin{cases} \infty & r < a \\ 0 & r > a \end{cases} \qquad (1)$$



## NpT ensemble

Partition function for $N$ particles

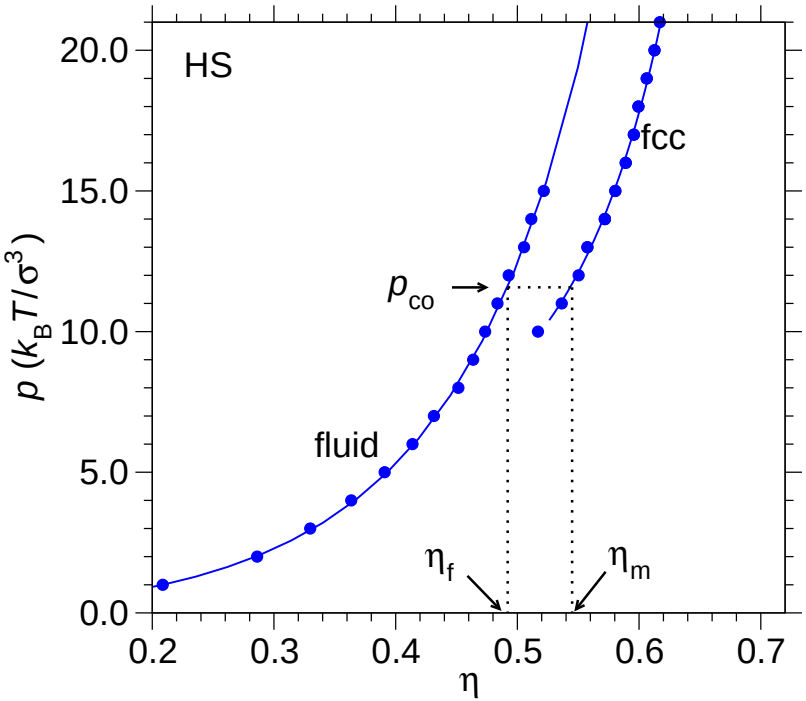
$$Y_{NpT} = \int dV \; e^{-pV} Z_{NVT}$$

with

$$Z_{NVT} = \int \prod_{i=1}^{N} d\boldsymbol{r}_i e^{-\beta \sum_{i,j} V(|\boldsymbol{r}_i - \boldsymbol{r}_j|)}$$

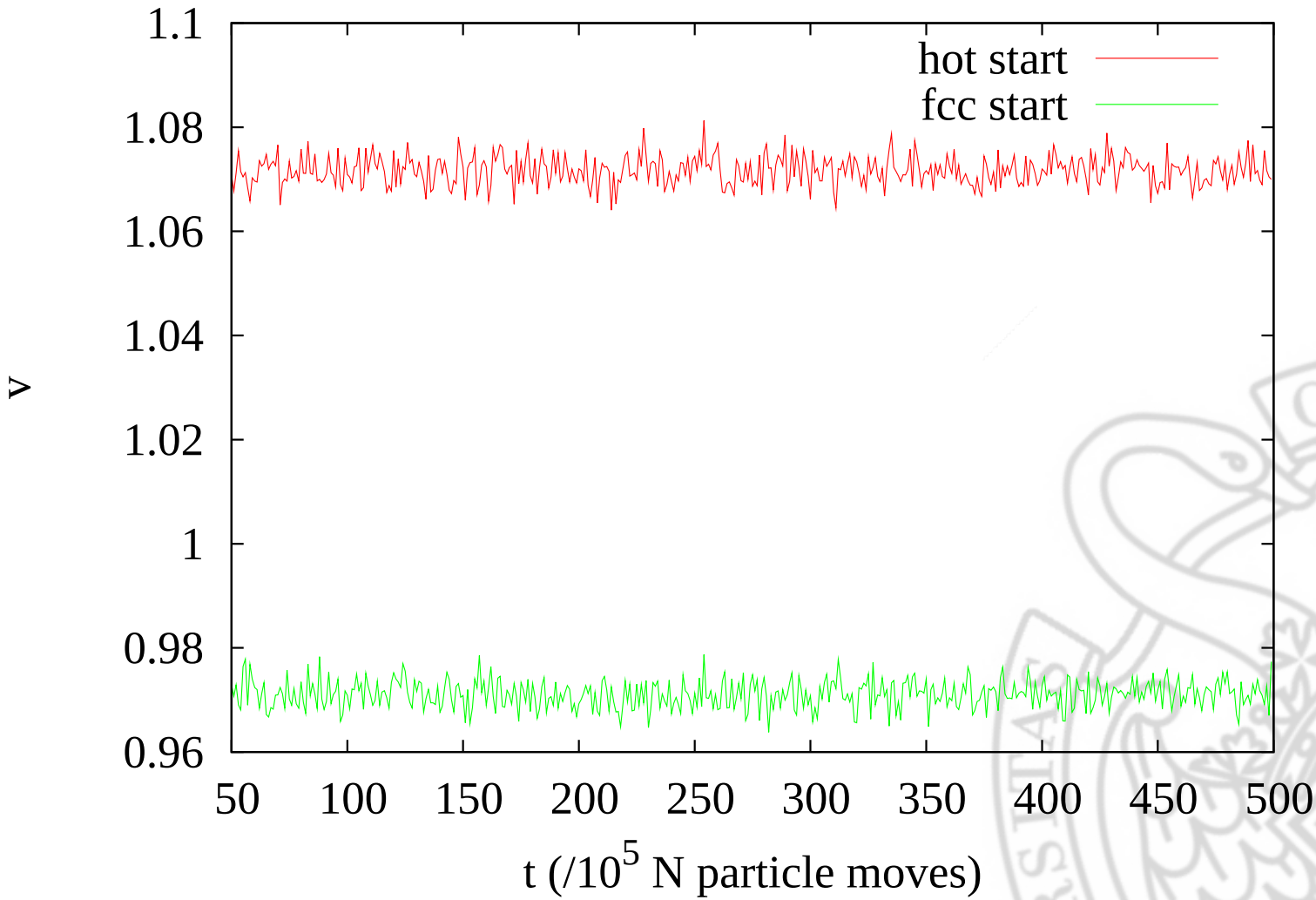
The Gibbs free-energy density (equal to the chemical potential) is thus defined as

$$\mu(p) = g_{NpT} = -\frac{1}{N} \log Y_{NpT}$$




T. Zykova-Timan, J. Horbach and K. Binder, J. Chem. Phys. **133**, 014705 (2010)

# NpT simulations forever in the same phase!!



## More sophisticated algorithms are necessary

- Direct coexistence simulation methods (big systems, nonequilibrium dynamical method)
- Phase Switch Monte Carlo (equilibrium method but suffers *exponential critical slowing-down*, $N_{\max} = 500$) (Wilding & Bruce, 2000)

## Our choice: Tethered MC with Crystal Parameters

### Rotationally invariant

$$Q_l \equiv \left( \frac{4\pi}{2l+1} \sum_{m=-l}^{l} |Q_{lm}|^2 \right)^{1/2}$$

$$Q_{lm} \equiv \frac{\sum_{i=1}^{N} q_{lm}(i)}{\sum_{i=1}^{N} N_b(i)}, q_{lm}(i) \equiv \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{r}_{ij})$$

### Perfect lattice values

| $Q_6$ | | |
|---|---|---|
| **liquid** | **FCC** | **BCC** |
| 0 | 0.574 | 0.510 |

## Tethered algorithm (see V. Martin-Mayor's talk)

We would like to simulate the system in a way that $\langle Q_6 \rangle$ is conserved. With this aim we introduce a new variable

$$\hat{Q}_6 = Q_6 + \frac{1}{N_\alpha} \sum_{i=1}^{N_\alpha} \eta_i$$

where $\eta_i$ are normal gaussian daemons, and then, $\langle Q_6 \rangle = \hat{Q}_6$.
The tethered mean values for $O$, given $\hat{Q}_6$ and $p$, are thus defined as

$$\langle O \rangle_{\hat{Q}_6, p} = \frac{\int_0^V dV \sum_{\boldsymbol{R}} O(\hat{Q}_6, p; V, \boldsymbol{R})\, \omega(p, \hat{Q}_6, N; V, \boldsymbol{R})}{\int_0^V dV \sum_{\boldsymbol{R}(V)} \omega(p, \hat{Q}_6, N; V, \boldsymbol{R})},$$

with

$$\omega(p, \hat{Q}_6, N; V, \boldsymbol{R}) = e^{-pV - \frac{N_\alpha}{2}\left[\hat{Q}_6 - Q_6(\boldsymbol{R}(v), p)\right]^2}$$

## Tethered algorithm

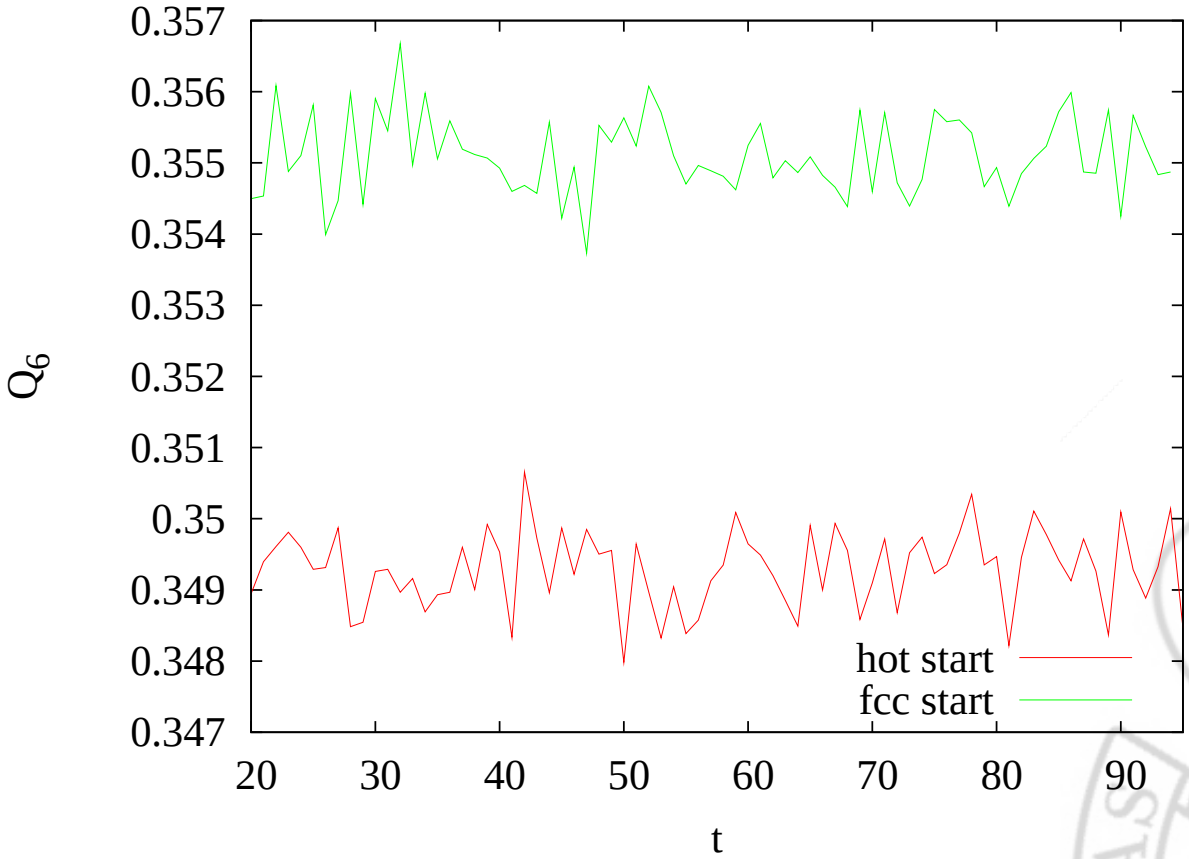
The *effective potential* $\Omega_N(\hat{Q}_6, p)$

$$\exp\left[N\Omega_N(\hat{Q}_6, p)\right] = \frac{1}{Z}\int_0^\infty \mathrm{d}V\ e^{-pV} \sum_{\boldsymbol{R}(v)} e^{-\frac{N_\alpha}{2}\left[\hat{Q}_6 - Q_6(\boldsymbol{R}(v), p)\right]^2}$$

can be recovered by measuring $h(\hat{Q}_6, p; v, \boldsymbol{R}) = -\alpha(\hat{Q}_6 - Q_6)$ during the simulation, since

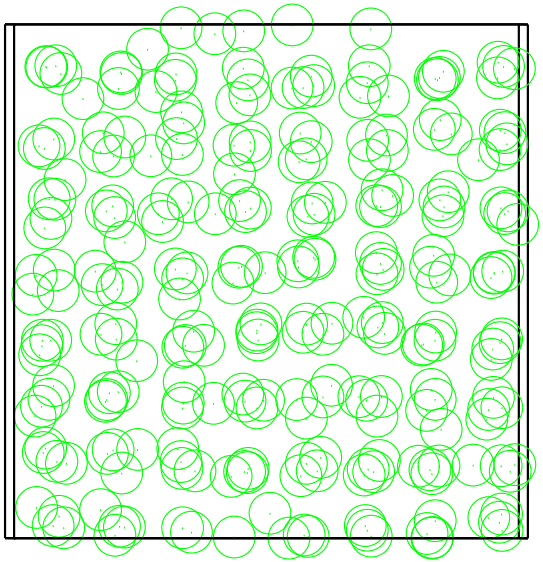
$$\langle h \rangle_{\hat{Q}_6, p} = \frac{\partial \Omega_N(\hat{Q}_6, p)}{\partial \hat{Q}_6}. \tag{2}$$

# When we fix $\hat{Q}_6$

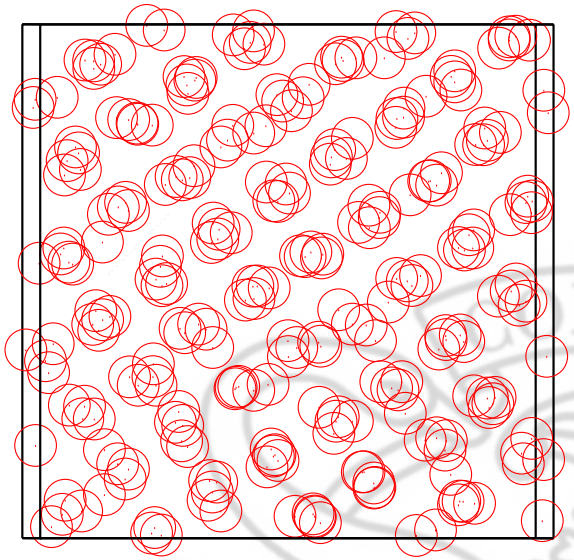



Strong metaestability: it does not thermalize

FCC start



hot start

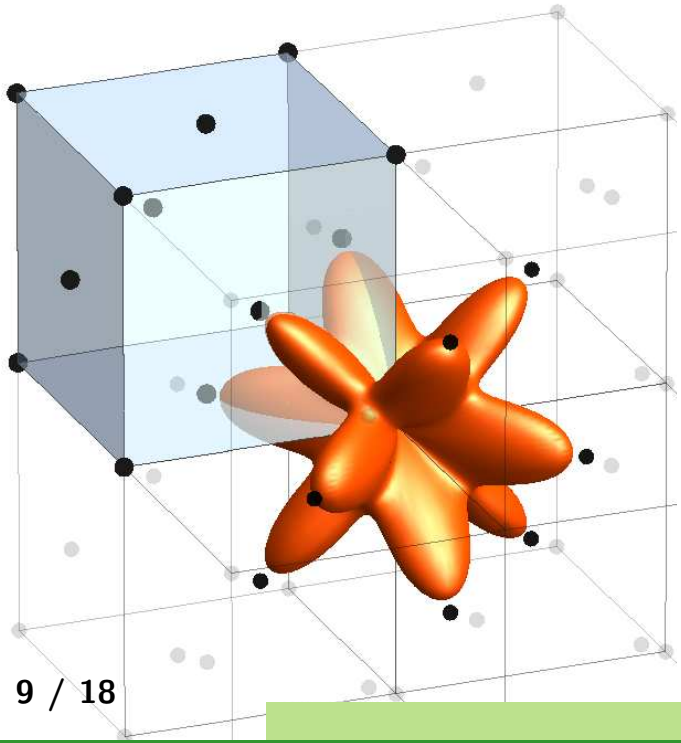


# Crystal Parameters

## Cubic parameter

$$c_\alpha(\boldsymbol{r}) = \frac{1}{r^8}\left[x^4y^4\left(1-z^4/r^4\right)+y^4z^4\left(1-x^4/r^4\right)+z^4x^4\left(1-y^4/r^4\right)\right]$$

$$C = \frac{2288}{79}\phi - \frac{64}{79},\quad \phi = \frac{\sum_{i=1}^{N}\phi(\boldsymbol{r}_i)}{\sum_{i=1}^{N}N_b(i)},\quad \phi(\boldsymbol{r}_i) = \sum_{j=1}^{N_b(i)} c_\alpha(\boldsymbol{r}_j-\boldsymbol{r}_i)$$

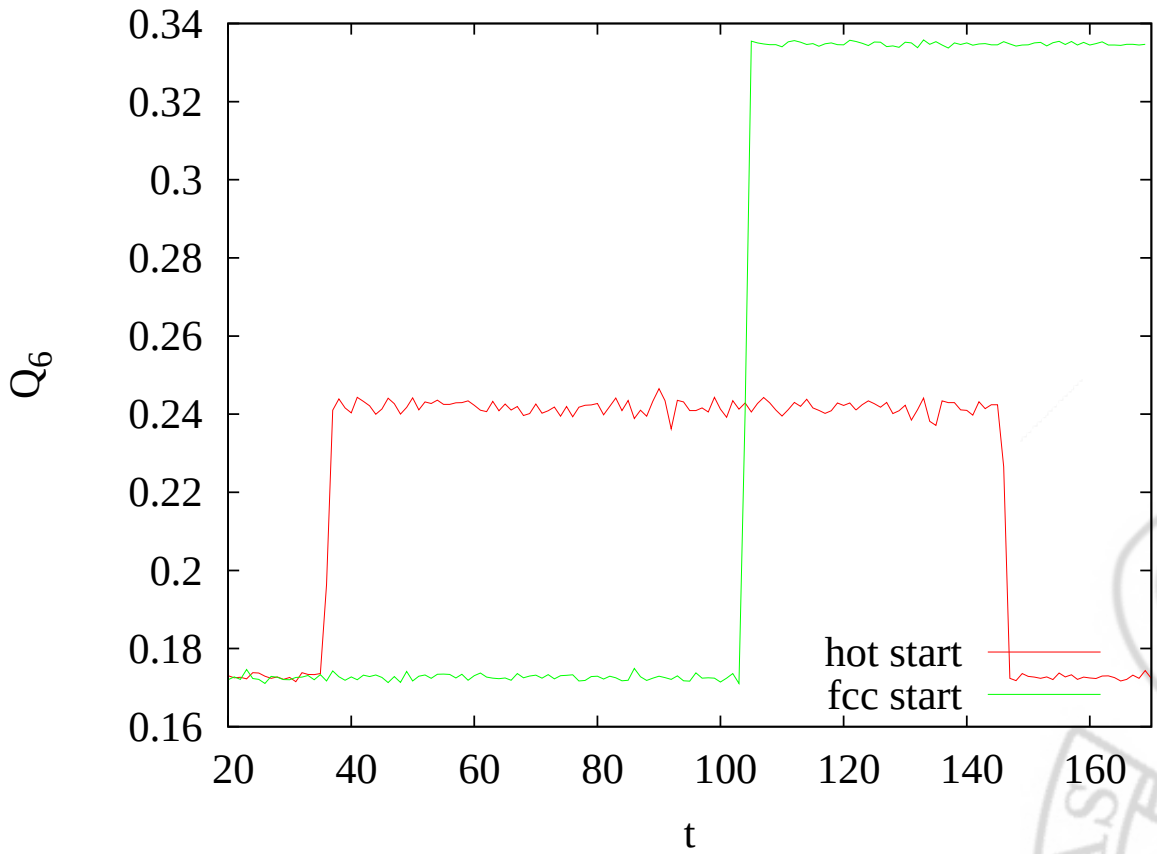


Perfect lattice values

| C | | |
|---|---|---|
| **liquid** | **FCC** | **BCC** |
| 0 | 1 | -0.26 |

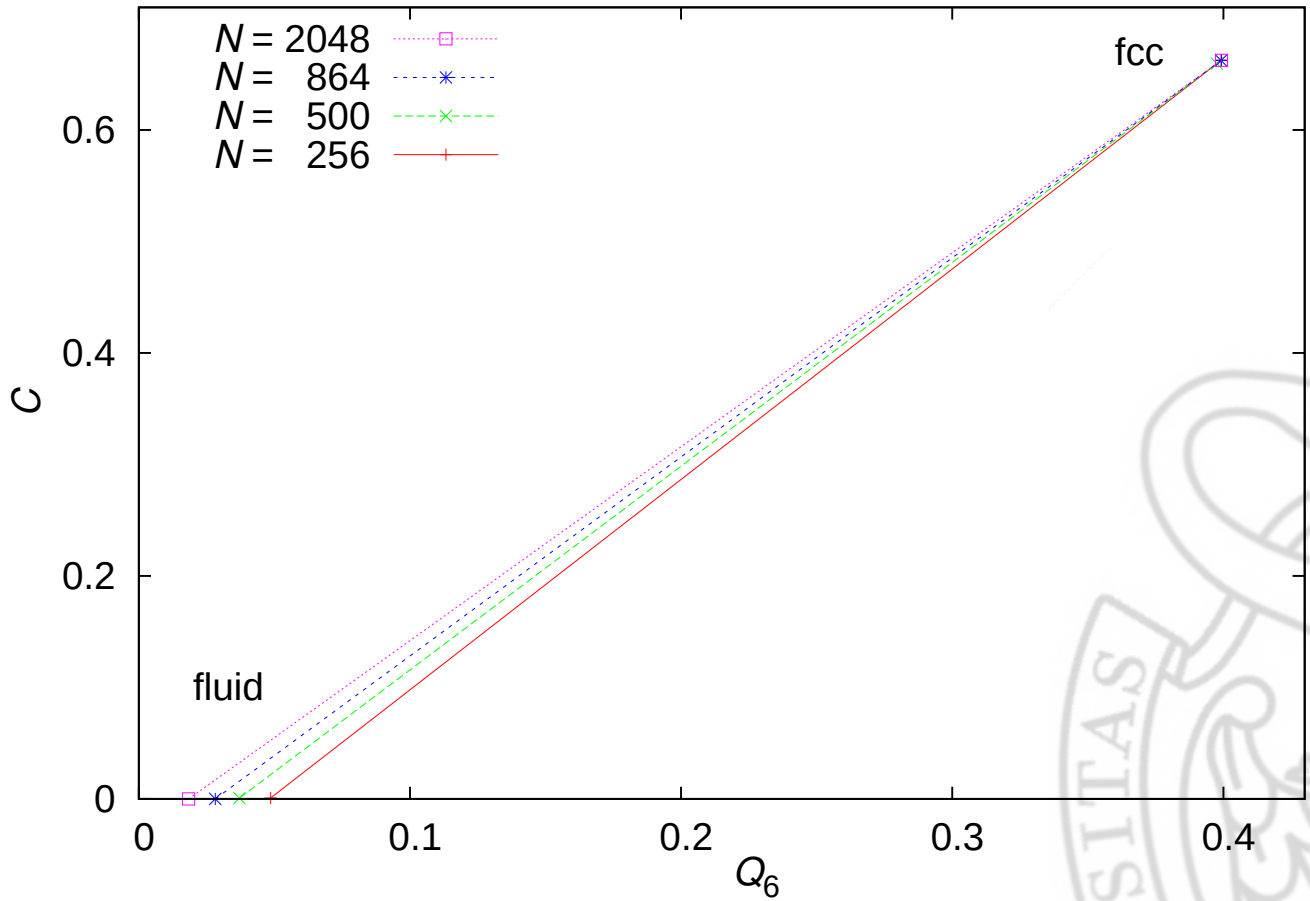
S. Angioletti-Uberti, M. Ceriotti, P. D. Lee, and M. W. Finnis, Phys. Rev. B 81, 125416 (2010)

# When we fix the cubic parameter $C$

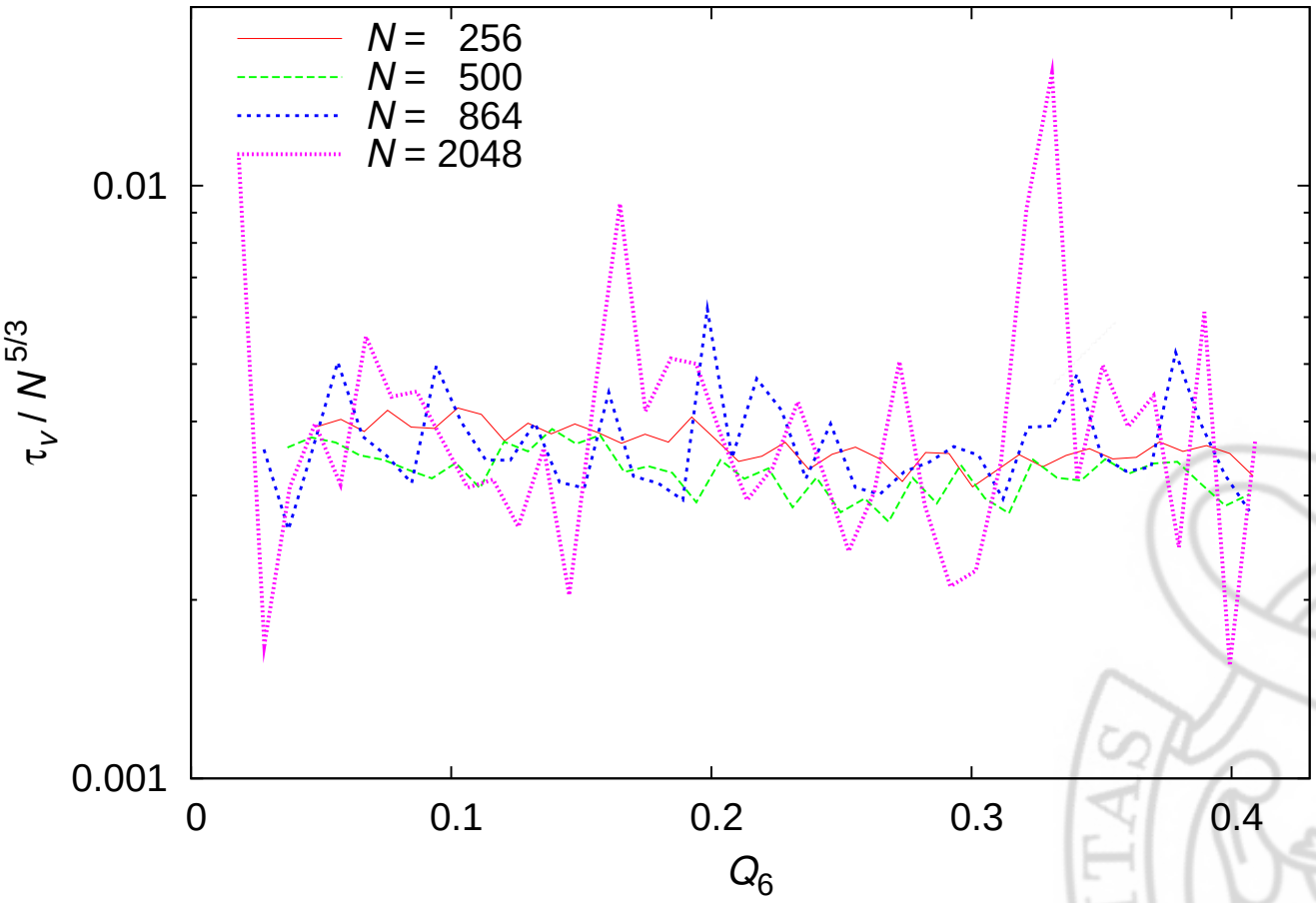



We need to fix both $C$ and $Q_6$!!

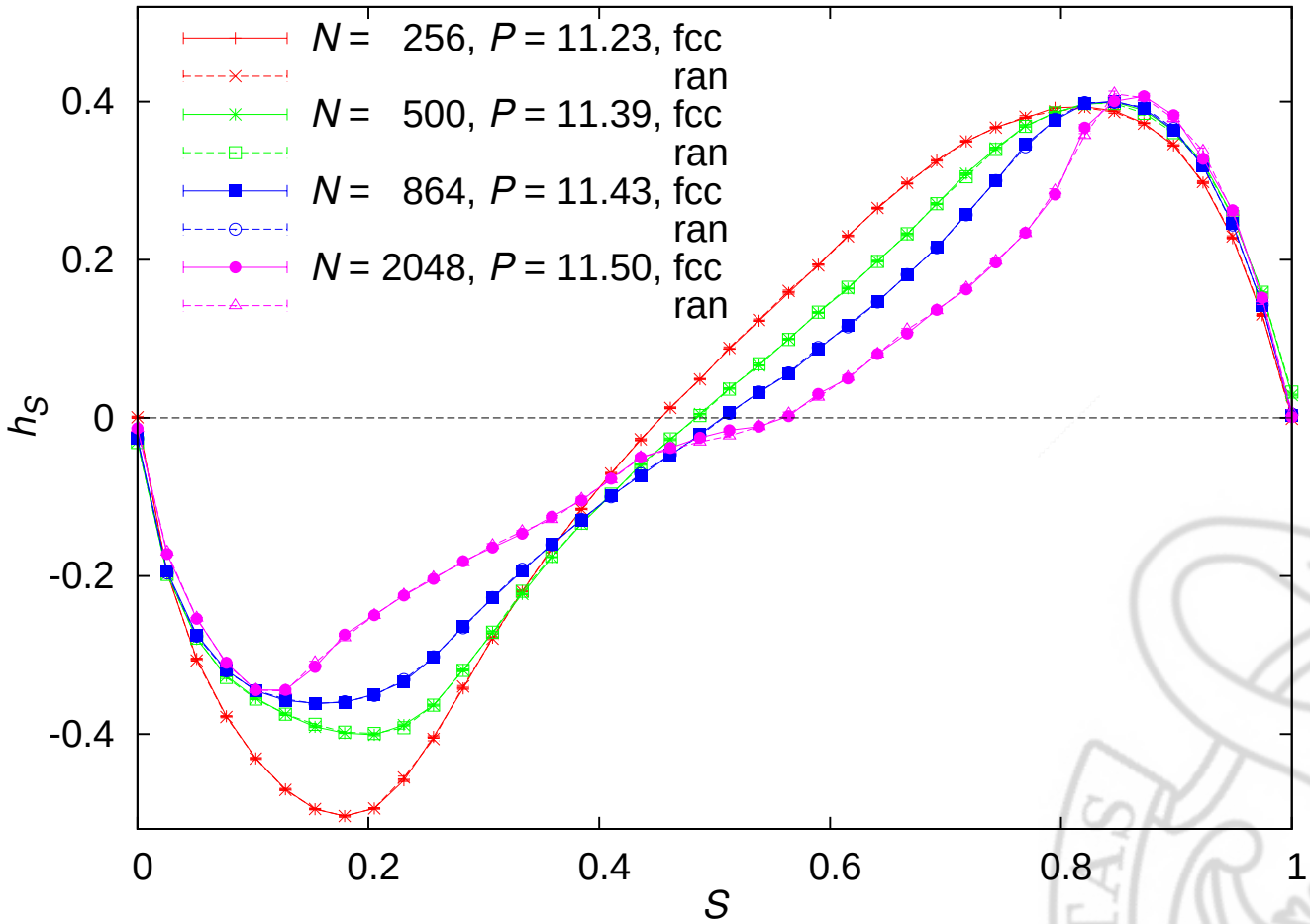
We want to obtain $\Delta\Omega = \Omega_{\mathrm{FCC}} - \Omega_{\mathrm{liq}}$, but $\Omega$ is a potential field, then $\Delta\Omega$ does not depend on the path $(Q_6(s), C(s))$ covered to join $(Q_6^{\mathrm{FCC},N}, C^{\mathrm{FCC},N})$ and $(Q_6^{\mathrm{liq},N}, C^{\mathrm{liq},N})$. We choose a path that allow us to thermalize easily the system, the straight line in between.



# No exponential critical slowing down



# $\Omega_{FCC} - \Omega_{fluid}$: integrate $\nabla\Omega$ projected along the path



$$Y(p) = e^{-Ng(p)} = \int dC \; dQ_6 \; e^{-N\Omega(Q_6, C)} \Rightarrow$$

$$g(p) = \Omega(Q_6^*, C^*) + O(1/N)$$

Phase transition occurs at the pressure when the Gibbs potential is equal in the two phases $g_{\mathrm{FCC}}(p_c) = g_{\mathrm{liq}}(p_c)$, then

$$\Delta g(p_c) = \Omega(Q^*_{6,\mathrm{FCC}}, C^*_{\mathrm{FCC}}) - \Omega(Q^*_{6,\mathrm{liq}}, C^*_{\mathrm{liq}}) + O(1/N) = 0$$

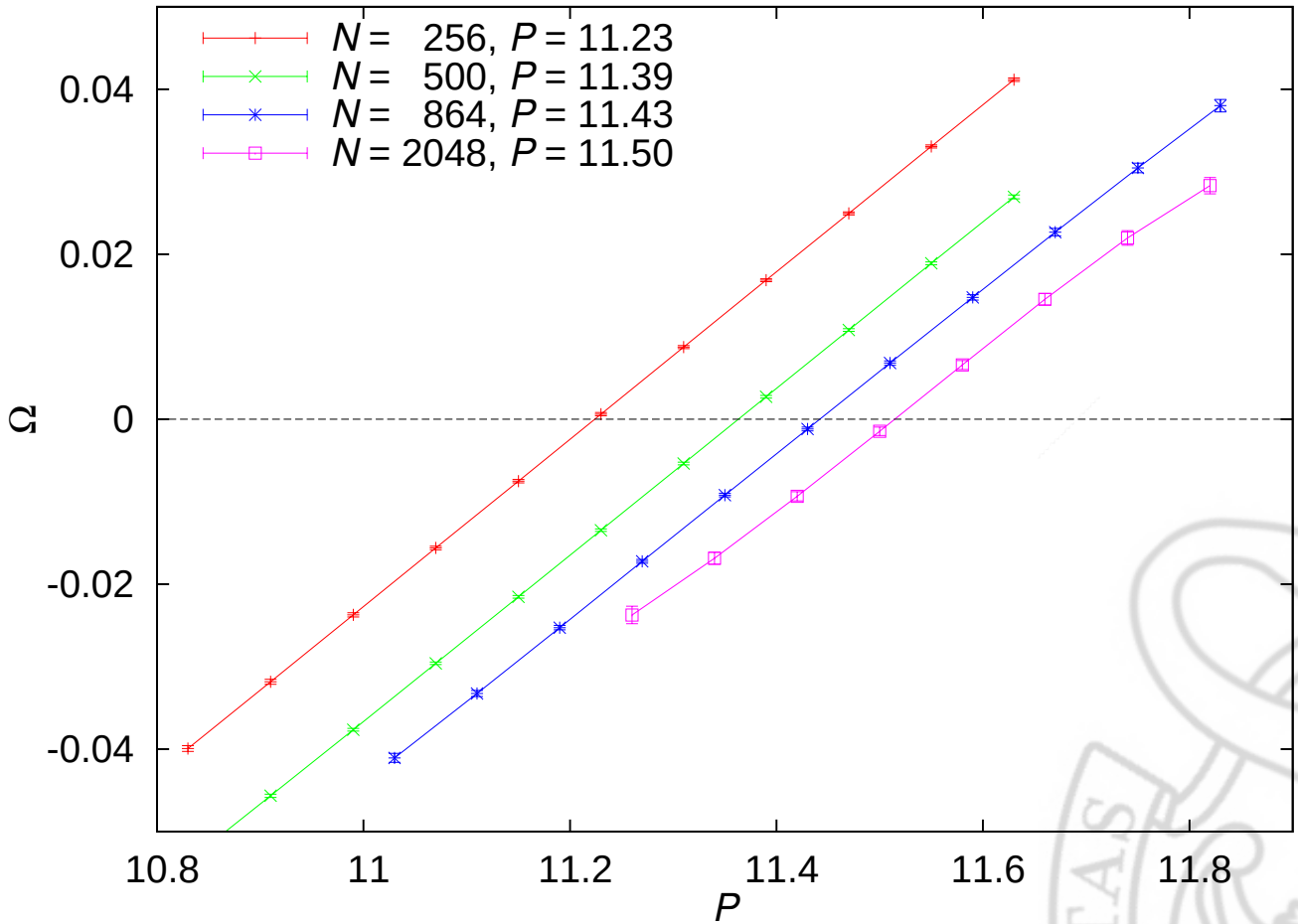
Then, we seek the pressure that satisfy $\Delta\Omega = 0$

## Reweighting Method

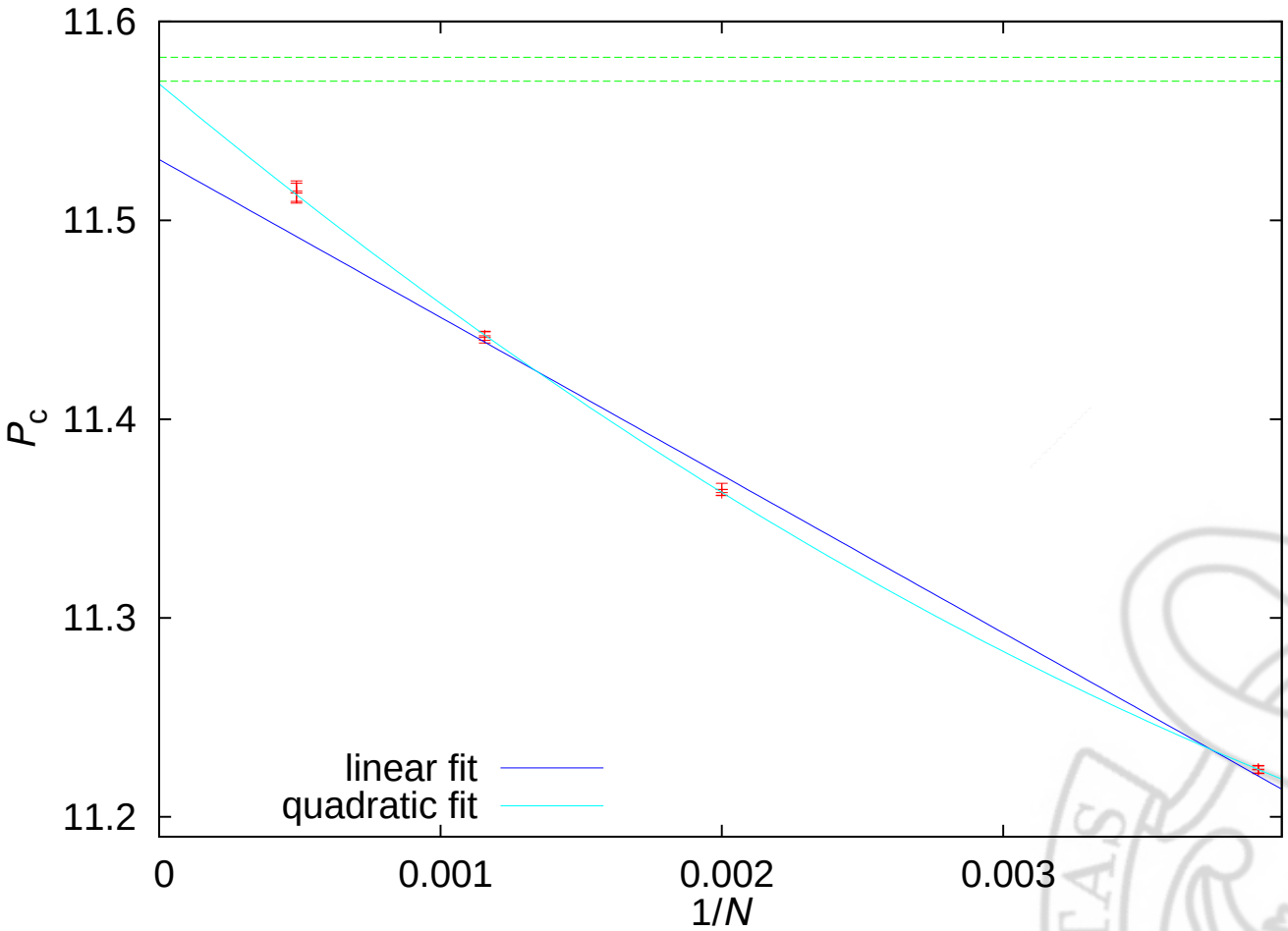
We do not need to simulate every pressure. Notice that we can obtain the mean values at pressure $p' = p + \delta p$ by means of simulations at $p$

$$\langle O \rangle_{p', \hat{Q}_6} = \frac{\langle O \, e^{-\delta p V} \rangle_{p, \hat{Q}_6}}{\langle e^{-\delta p V} \rangle_{p, \hat{Q}_6}}$$

We integrate $h_S$ along the curve and obtain $\Delta\Omega$



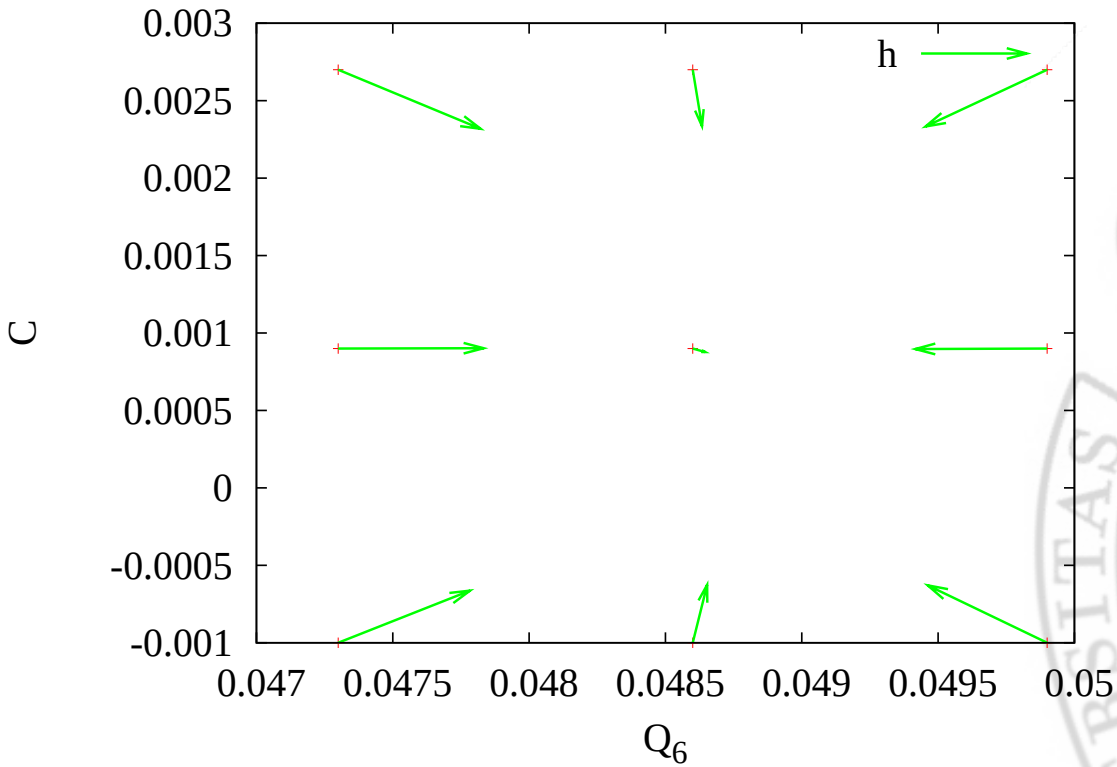
# Extrapolation



# Corrections due to integration-path end-points

Near local maxima, the effective potential $\Omega$ is approximately quadratic, i.e.

$$\Omega(Q_6, C) - \Omega(Q_6^*, C^*) \approx$$
$$A_{QQ}(Q_6 - Q_6^*)^2 + 2A_{QC}(Q_6 - Q_6^*)(C - C^*) + A_{CC}(C - C^*)^2$$



## Conclusions

- We have applied *tethered algorithm* for the first time to colloid's crystallisation.
- We have thermalized very large systems, avoiding exponential critical slowing down.
- We obtain $P_c^\infty$ improving error by a factor of 20, as compared with previous equilibrium studies.
- Our determination of $P_c^\infty$ is compatible (and of similar accuracy) with the very best non-equilibrium determination (Binder et al. 2010).
- Total simulation time: 40 independent simulations of 3.5 days each.