Tethered method to approach the equilibrium fluid-solid coexistence of hard spheres

Beatriz Seoane Bartolomé
in collaboration with L. A. Fernández, V. Martín-Mayor and P. Verrocchio

Dipartimento di Fisica La Sapienza Università di Roma

Physics of glassy and granular materials

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Computational problem

Approaching equilibrium in granular systems requires in general a huge amount of time even for very small system sizes, N.

References

V. Martin-Mayor, B. Seoane and D. Yllanes: J. Stat. Phys. **144**, 554 (2011).
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1. We present a general Monte Carlo method (Tethered method) to approach equilibrium in reasonable times.

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1. We present a general Monte Carlo method (Tethered method) to approach equilibrium in reasonable times.
2. Our method boosts the traditional umbrella sampling making practical the study of constrained free energies to several order parameters.
3. We apply the method to a well understood problem, but still extremely hard from the numerical point of view: the crystallization of hard spheres

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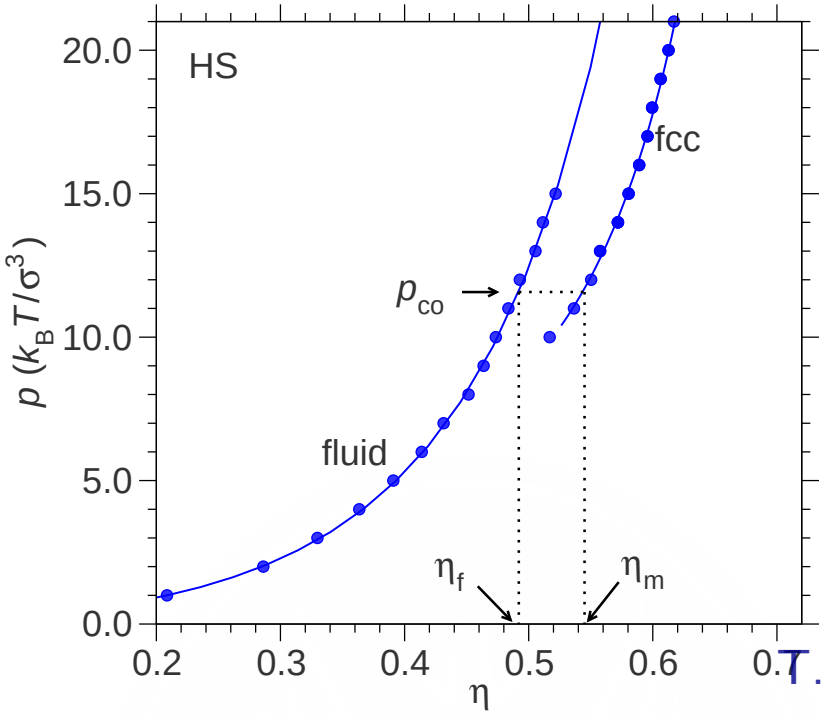
SOLUTION: AVOID THESE METASTABILITIES

Hard Spheres

- Seek the simplest system that suffers crystallization: HS.



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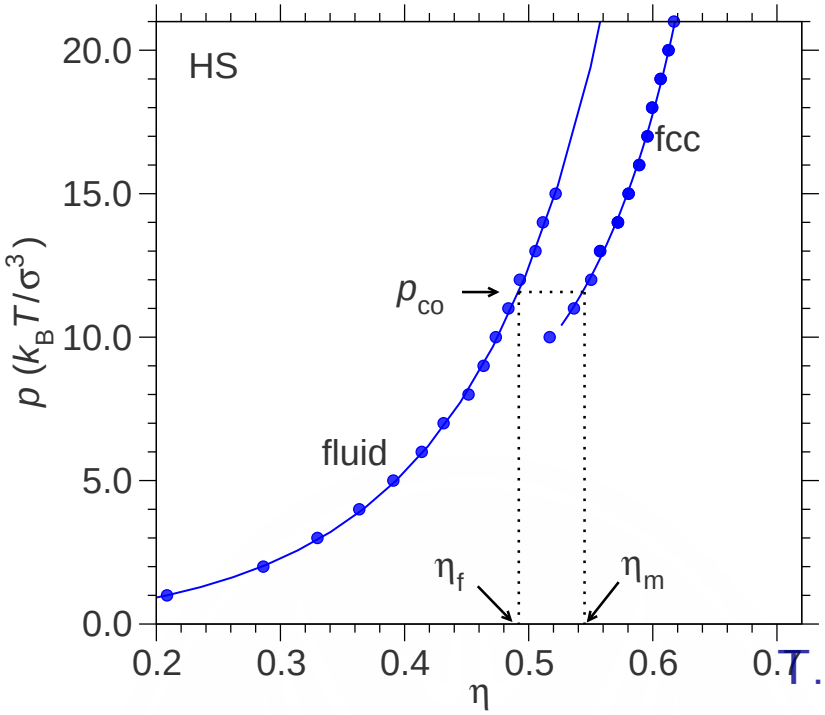

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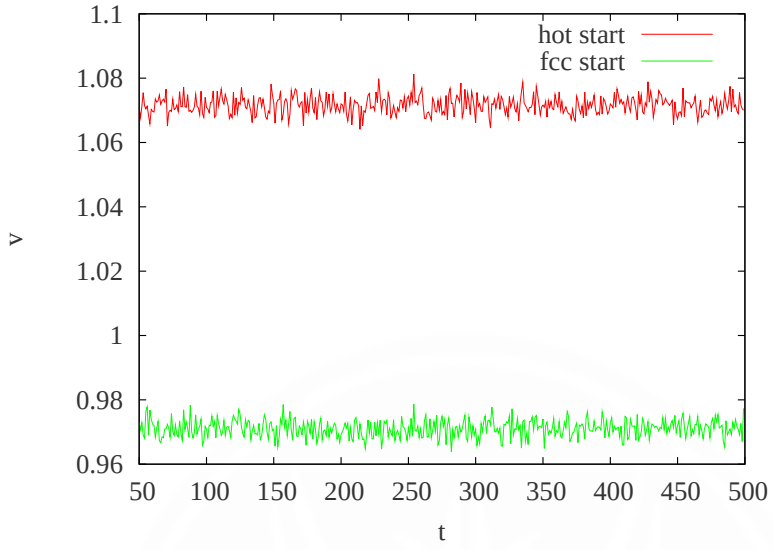

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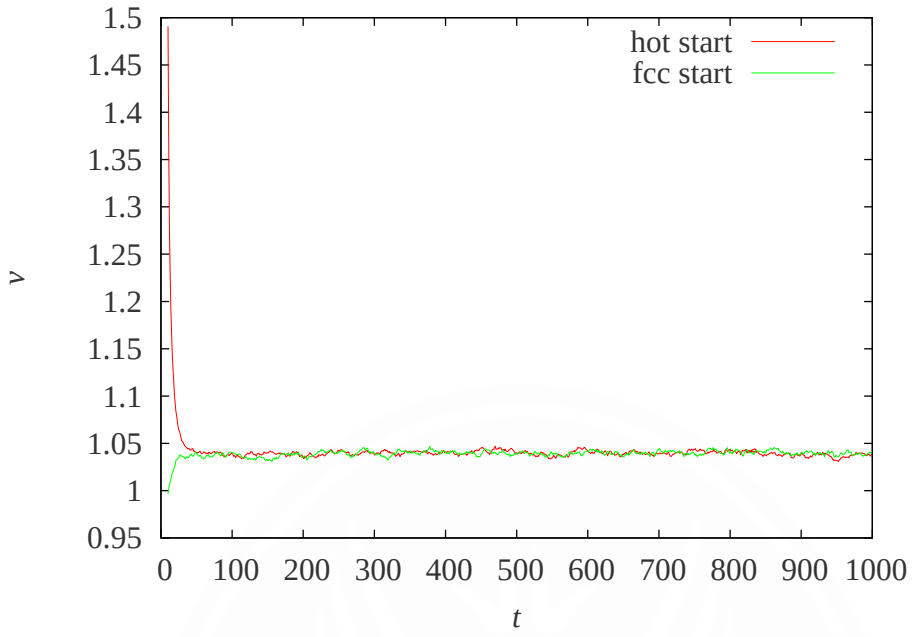

Need observables that label univocally one of the branches: bond order parameters

.

Crystal order parameter Q_6 (rotational symmetry)

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

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

Perfect lattices values

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fluid	**FCC**	**BCC**
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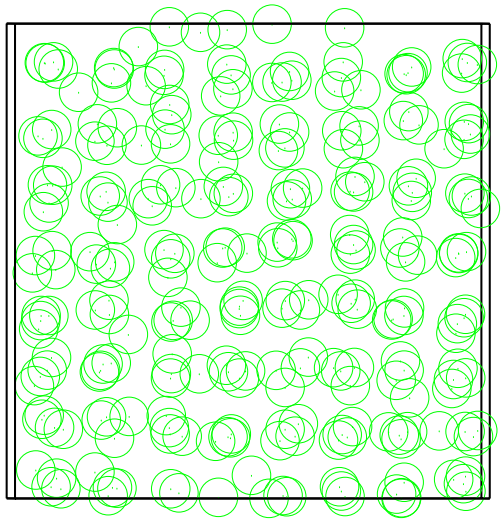

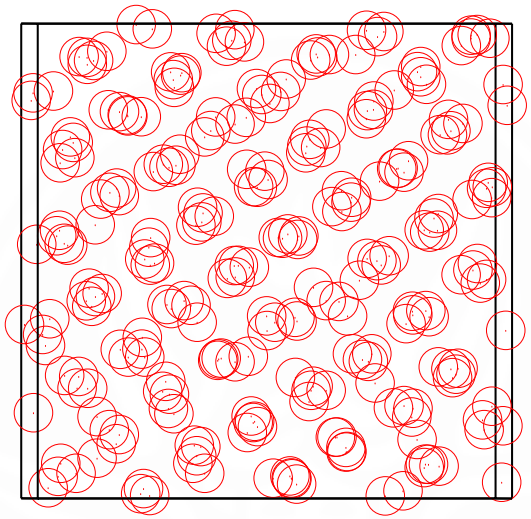

Breaking rotational symmetry...

Second order parameter: C

- Consider a second order parameter with cubic symmetry. (S. Angioletti-Uberti et al., 2010). Replace spherical harmonics by

$$c_\alpha(\hat{r}) = x^4y^4(1-z^4) + x^4z^4(1-y^4) + y^4z^4(1-x^4).$$

$$C = \frac{2288}{79}\frac{\sum_{i=1}^{N}\sum_{j=1}^{N_b(i)} c_\alpha(\hat{\boldsymbol{r}}_{ij})}{\sum_{i=1}^{N} N_b(i)} - \frac{64}{79}$$

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- We need to fix simultaneously C and Q_6 to avoid metastabilities.

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- The probability of finding $(\hat{Q}_6, \hat{C})$ is the convolution of both probabilities. The η_is can be integrated out leading to

$$p(\hat{Q}_6, \hat{C}, p) \propto \mathrm{e}^{-\beta p V}\, \mathrm{e}^{-\beta U(\boldsymbol{R})} \mathrm{e}^{-\frac{\alpha N}{2}\left[\hat{Q}_6 - Q(\boldsymbol{R})\right]^2} \mathrm{e}^{-\frac{\alpha N}{2}\left[\hat{C} - C(\boldsymbol{R})\right]^2}$$

Tethered ensemble (II)

The tethered mean values of an observable $A(\boldsymbol{R})$ at fixed $\hat{Q}_6, \hat{C}$

$$\langle A \rangle_{\hat{Q}_6, \hat{C}} \equiv \frac{\int \mathrm{d}V \int \mathrm{d}\boldsymbol{R}\, A(\boldsymbol{R}) \omega_N(\boldsymbol{R}, p; \hat{Q}_6, \hat{C})}{\int \mathrm{d}V \int \mathrm{d}\boldsymbol{R}\, \omega_N(\boldsymbol{R}, p; \hat{Q}_6, \hat{C})},$$

are obtained with the Metropolis algorithm using this modified weight

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We can define a Helmholtz effective potential

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Saddle point approx. [where $(\hat{Q}_6^*(p), \hat{C}^*(p))$ fulfills $\boldsymbol{\nabla} \Omega_N = 0$] tells us

$$g_N(p, T) = \Omega_N(\hat{Q}_6^*, \hat{C}^*, p) + O(1/N)$$

Tethered ensemble (III)

- Gradients

$$\begin{aligned}\boldsymbol{\nabla}\Omega_N(\hat{Q}_6,\hat{C},p) &= \left(\frac{\partial\Omega_{\boldsymbol{N}}(\hat{Q}_{\boldsymbol{6}},\hat{C})}{\partial\hat{Q}_{\boldsymbol{6}}},\frac{\partial\Omega_{\boldsymbol{N}}(\hat{Q}_{\boldsymbol{6}},\hat{C})}{\partial\hat{C}}\right)\\ &= \left(\left\langle\alpha\left(\hat{Q}_6-Q_6\right)\right\rangle_{\hat{Q}_{\boldsymbol{6}},\hat{C},\boldsymbol{p}},\left\langle\alpha\left(\hat{C}-C\right)\right\rangle_{\hat{Q}_{\boldsymbol{6}},\hat{C},\boldsymbol{p}}\right)\end{aligned}$$

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- Ω_N is recovered using a line integral $\Delta\Omega_N = \int_{\mathcal{C}} \boldsymbol{\nabla}\Omega_N \cdot \mathrm{d}\boldsymbol{l}$

$$g_N^{\mathrm{fluid}}(p_{\mathrm{co}}) = g_N^{\mathrm{FCC}}(p_{\mathrm{co}}) \Leftrightarrow \Delta\Omega_N(p_{\mathrm{co}}) = 0$$

$$\Delta\Omega_N(p) = \Omega_N\left(\hat{Q}_6^{\mathrm{FCC}}(p),\hat{C}^{\mathrm{FCC}}(p),p\right) - \Omega_N\left(\hat{Q}_6^{\mathrm{fluido}}(p),\hat{C}^{\mathrm{fluido}}(p),p\right)$$

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- Reweighting method

$$\langle O\rangle_{\hat{Q}_{\boldsymbol{6}},\hat{C},p+\delta p}=\frac{\langle O\ \mathrm{e}^{-\beta\delta pV}\rangle_{\hat{Q}_{\boldsymbol{6}},\hat{C},p}}{\langle\mathrm{e}^{-\beta\delta pV}\rangle_{\hat{Q}_{\boldsymbol{6}},\hat{C},p}}$$

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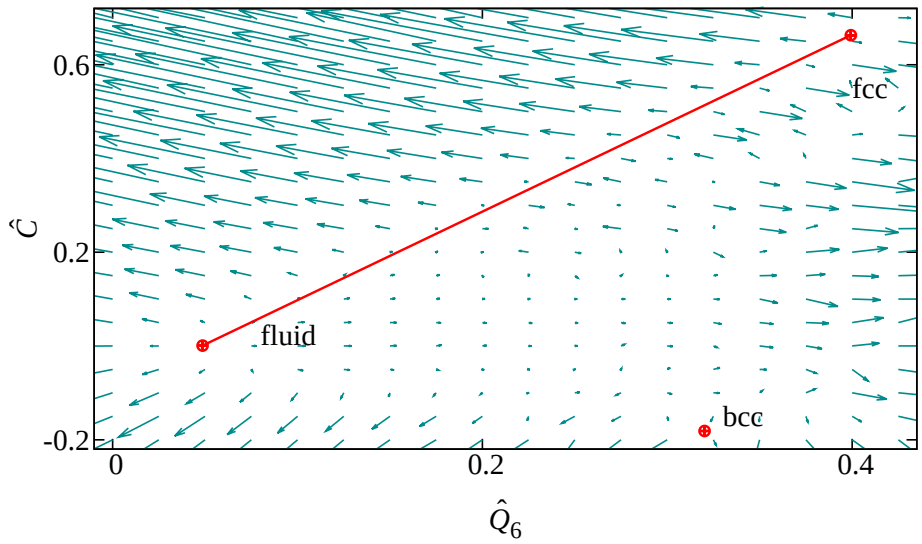
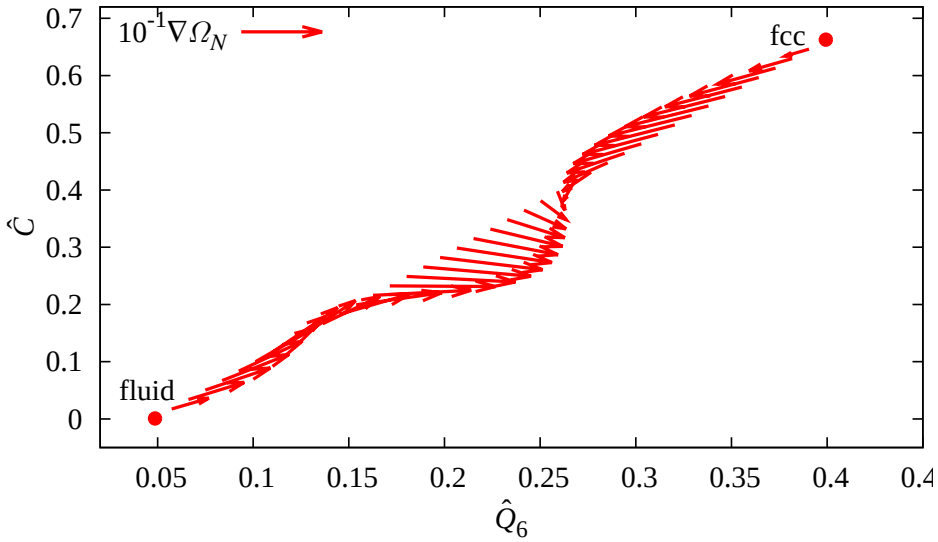
- **Tethered** obtains Ω_N by means of a line integration a MC time average of the conjugated field $\boldsymbol{\nabla}\Omega_N(\hat{Q}_6, \hat{C}, p)$. The number of constrains does not modify the efficiency.

Results


0.6
0.2
-0.2
0
0.2
0.4
$\hat{C}$
$\hat{Q}_6$
fcc
fluid
bcc


$10^{-1}\nabla\Omega_N$
fcc
fluid
0.7
0.6
0.5
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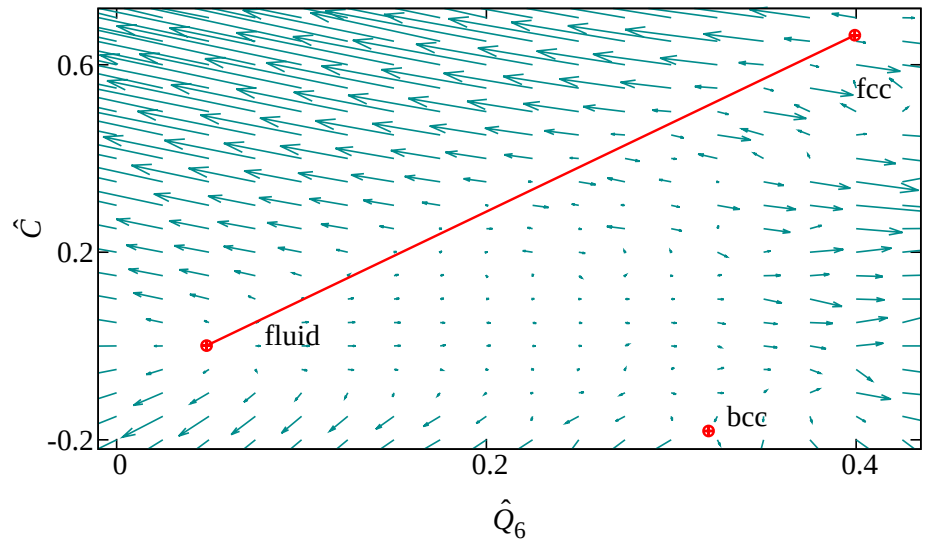
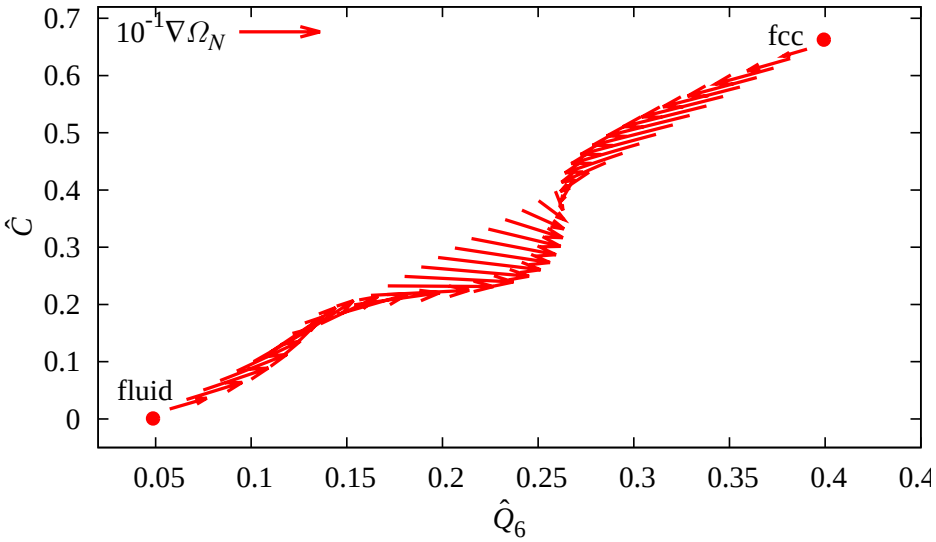
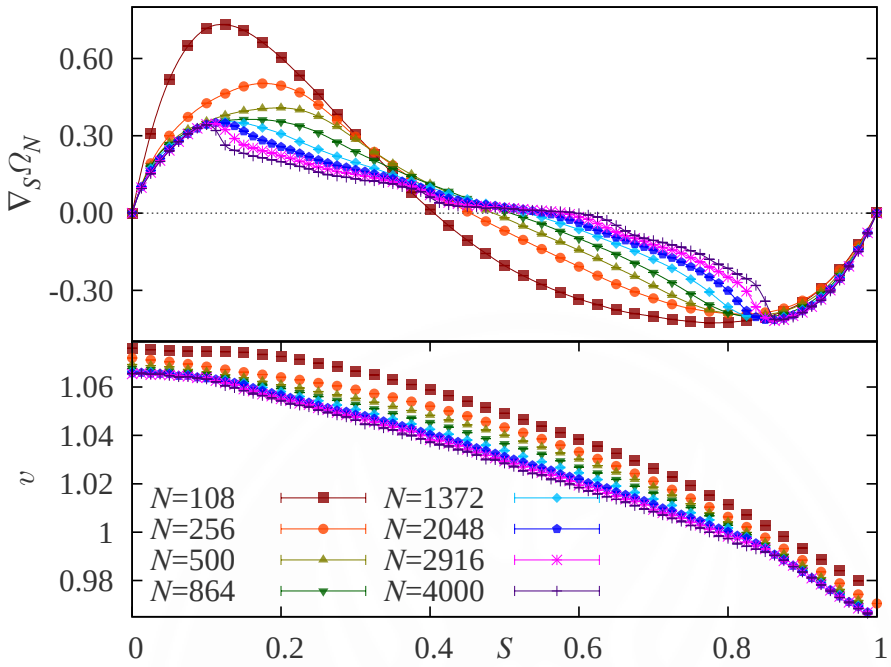




$\nabla_S\Omega_N$, projection $\nabla\Omega_N$ on the line



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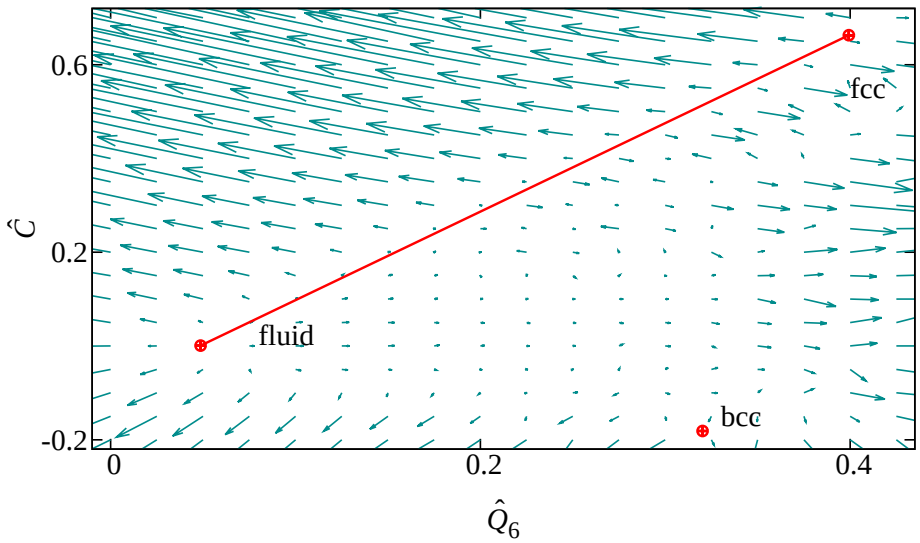
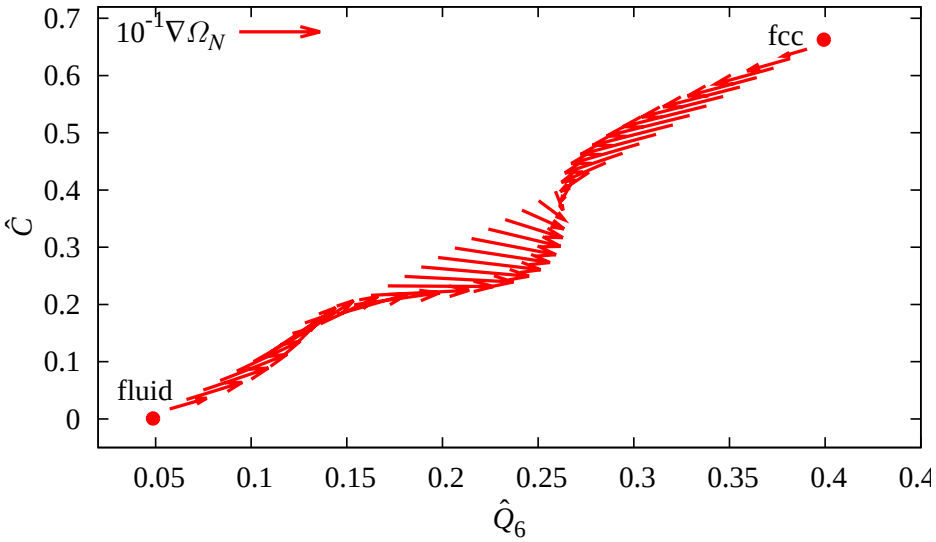
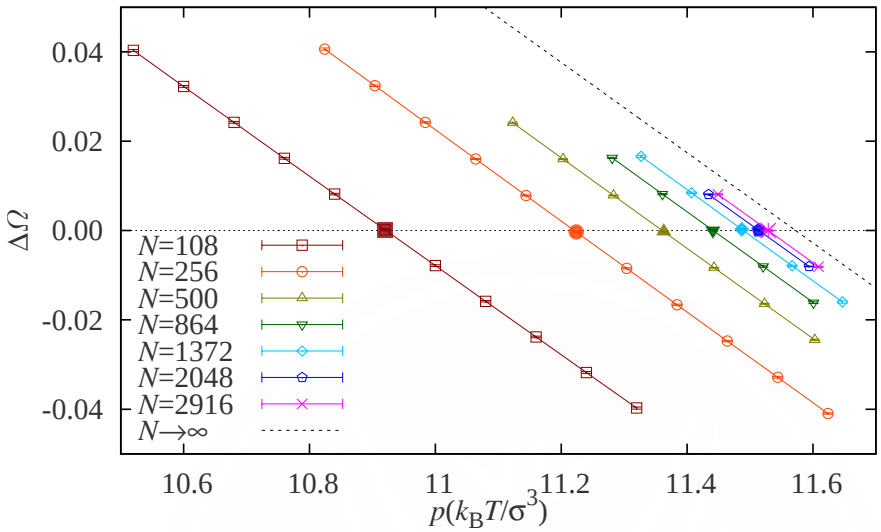
L. A. Fernandez, V. Martin-Mayor, B. Seoane and P. Verrocchio: Phys. Rev. Lett. **108**, 165701 (2012).

Results



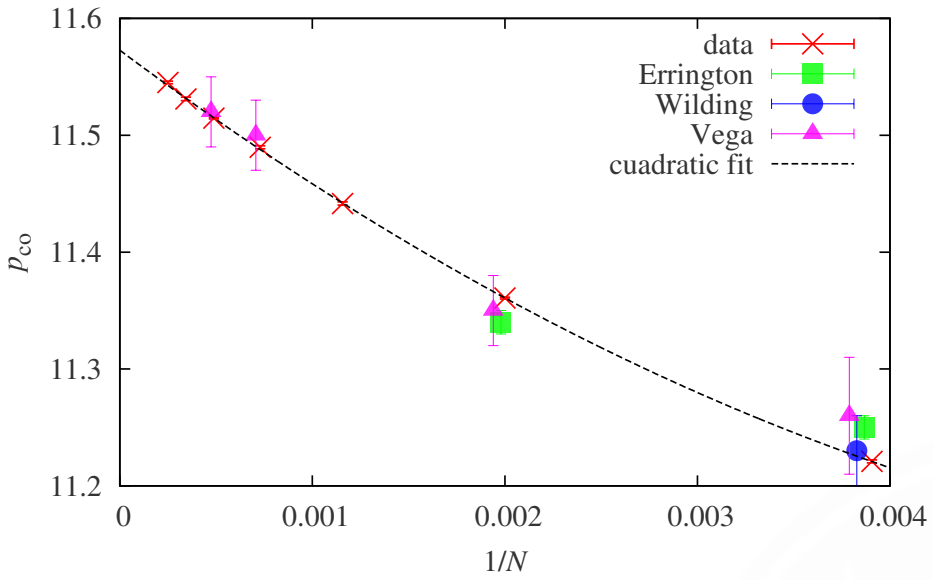


Integrating



V. Martin-Mayor, B. Seoane and D. Yllanes: J. Stat. Phys. **144**, 554 (2011).
L. A. Fernandez, V. Martin-Mayor, B. Seoane and P. Verrocchio: Phys. Rev. Lett. **108**, 165701 (2012).

Coexistence Pressure



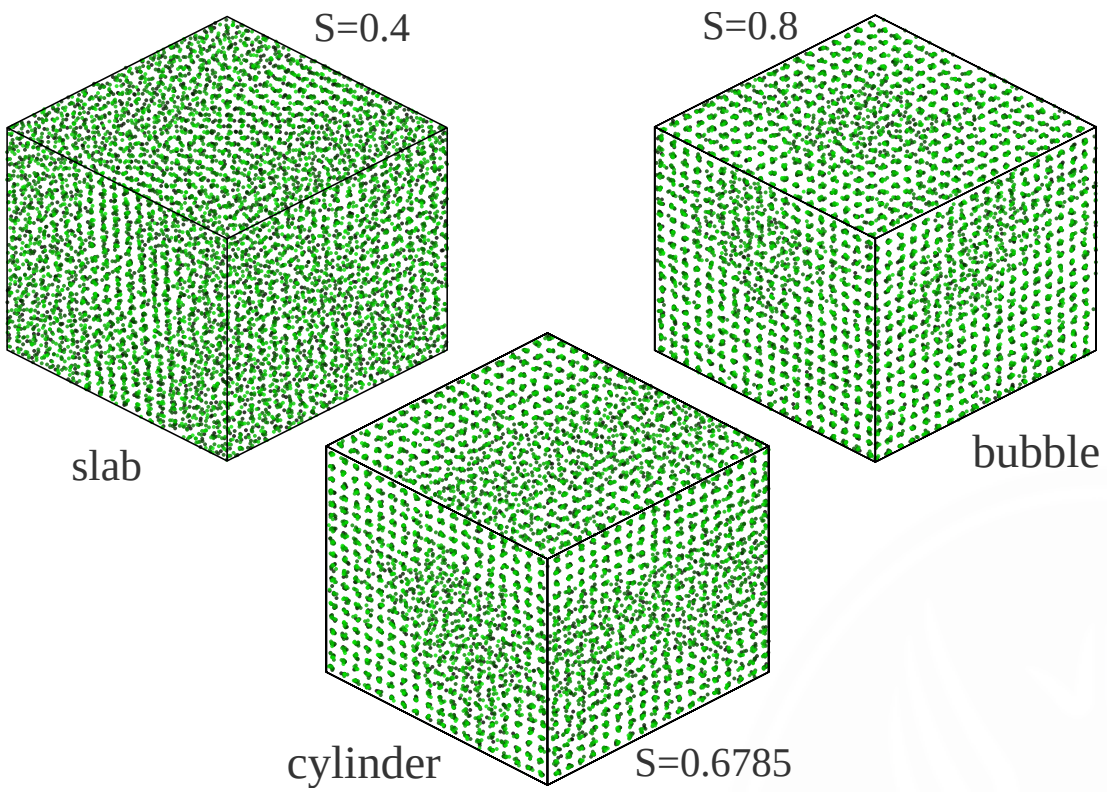
Our estimation in $(k_B T/\sigma^3)$ units $\quad p_{co}^{N=\infty} = 11.5727(10)$

Previous eq. estimation (Wilding & Bruce 2000) $\quad p_{co}^{N=\infty} = 11.50(9)$

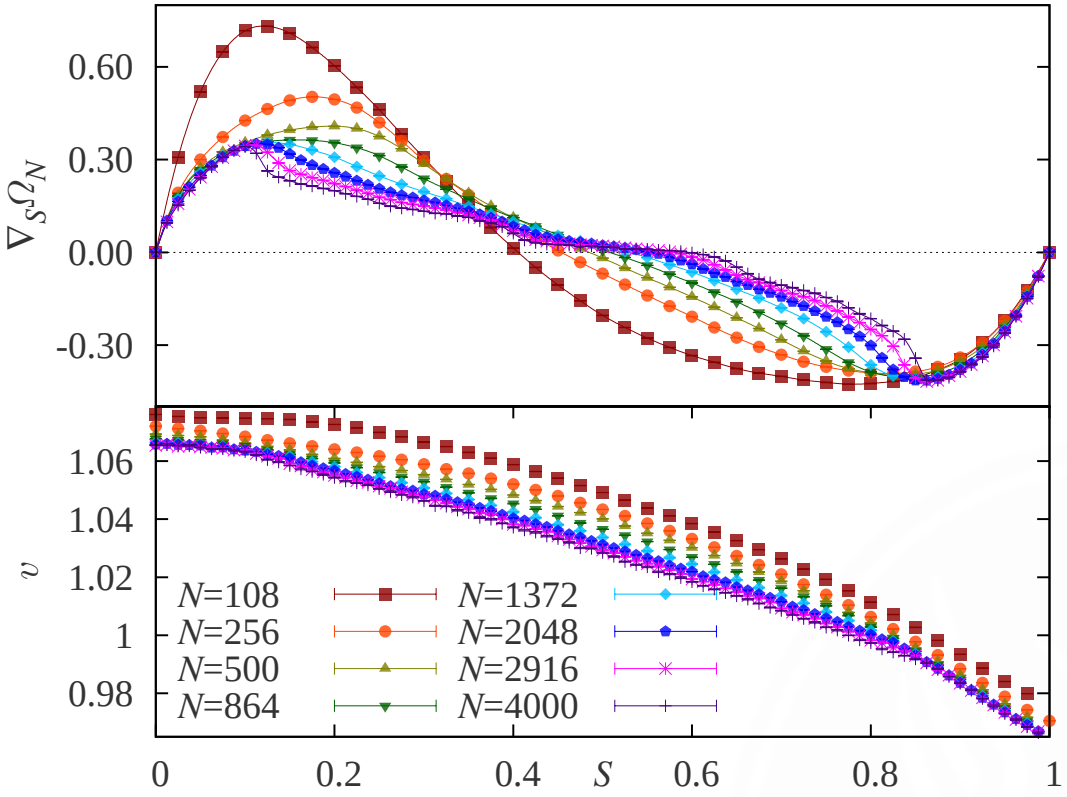
best nonequilibrium $\quad p_{co}^{N=\infty} = 11.576(6)$

($N = 1.6 \times 10^5$, Zykova-Timan *et al.*, 2010)

Geometric transitions and interfacial free energy



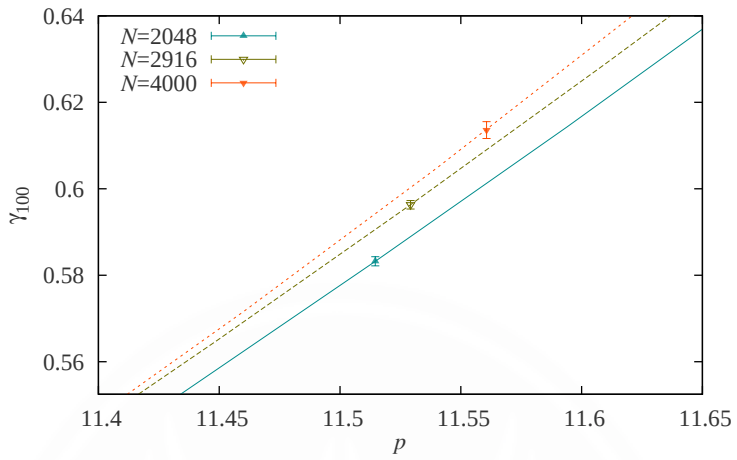
Geometric transitions and interfacial free energy



$$\gamma^{(N)}_{\{100\}} = k_{\mathrm{B}}\, T\, N\, (\Omega_{s^*} - \Omega_{\mathrm{FCC}})\, /(2\, \langle Nv \rangle^{2/3}_{S^*})$$

Geometric transitions and interfacial free energy

- Our estimation $\gamma_{\{100\}} = 0.636(11)$
- Mu *et al.* 2005 $\gamma_{\{100\}} = 0.64(2)$
- Cacciuto *et al.* 2003 $\gamma_{\{100\}} = 0.619(3)$
- Davidchack *et al.* 2010 $\gamma_{\{100\}} = 0.5820(19)$
- Härtel *et al.* 2012 $\gamma_{\{100\}} = 0.639(11)$



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Conclusions

- We have proposed a new method to control crystallization.
- Tethered weight is formally equal than umbrella sampling but allow us to recover the potential by means of a thermodynamic potential.
- Results presented improve previous estimations by several orders of precision with rather short simulations.
- We can track the geometric transitions, giving us a tool to control the interfaces and thus obtain the interfacial free energy.

THANK YOU VERY MUCH