

Thermodynamic integration

Localizing liquid-solid phase transitions

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Overview

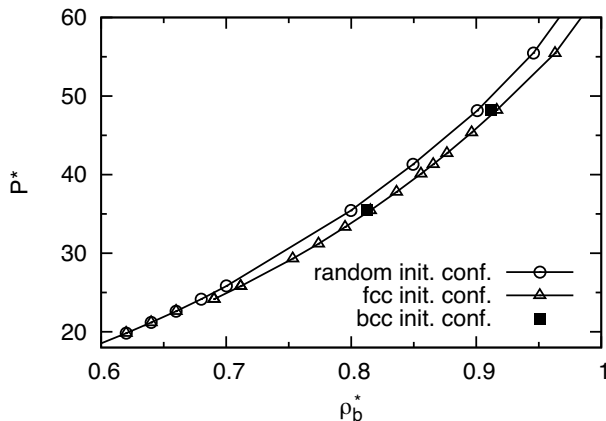
Problem

Theoretical basics

Thermodynamic integration

Localization of phase equilibria

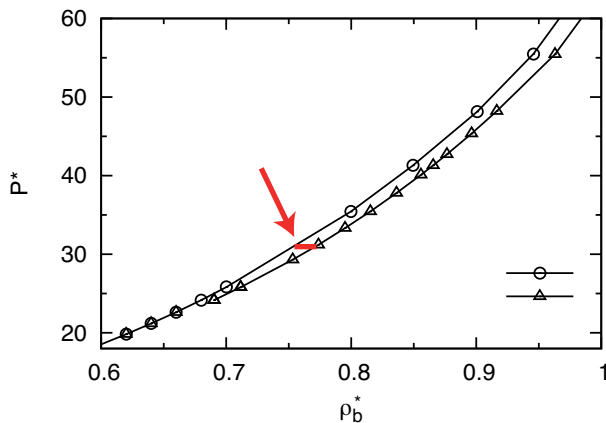
Problem



S. Grandner and S. H. L. Klapp: *Freezing of charged colloids in slit pores*. J. Chem. Phys., **129**, 244703 (2008).

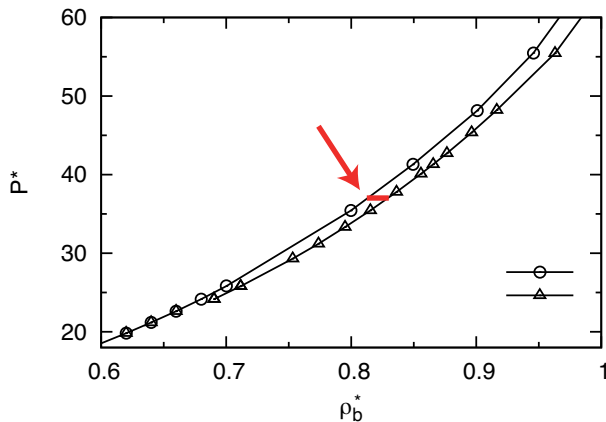
- Simulations predict solid *and* fluid phase
- Metastable density range

Problem



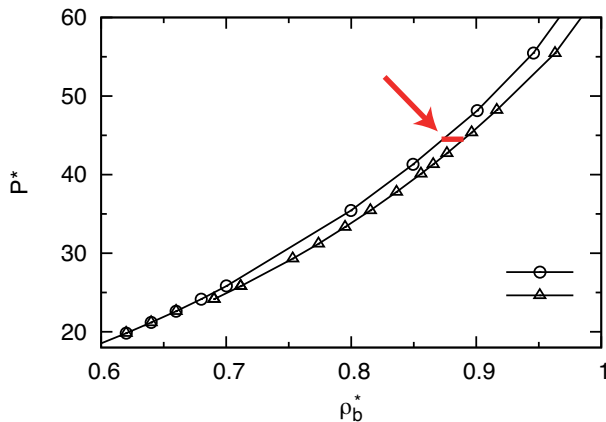
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Thermodynamics of phase equilibria

- Condition for equilibrium between solid (s) and liquid (l) phase:

$$\mu_s(P, T) = \mu_l(P, T)$$

- With chemical potential

$$\mu = g = \frac{G}{N}$$

- and Gibbs free energy

$$G = F - PV$$

- and Helmholtz free energy F .

Thermodynamics of phase equilibria

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$$F(N, V, T) = -\frac{1}{\beta} \ln Z(N, V, T)$$

$$Z(N, V, T) = \frac{1}{\Lambda^{3N} N!} \int \exp[-\beta U(\mathbf{r})] d^{3N}r$$

with $\Lambda = h \sqrt{\beta/2\pi m}$ and $\beta = 1/k_B T$.

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- In general impossible to evaluate directly

Observation: Derivatives of F

- Derivatives of the thermodynamic potentials are easy to calculate:

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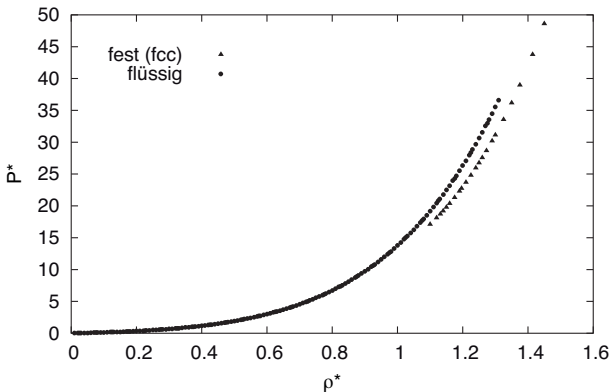
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- For solid phase: Phase transitions break the reversibility of the integration path
- But thermodynamic integration is still possible

Thermodynamic integration: solid phase

- Define effective interaction potential:

$$\tilde{U}(\lambda) = (1 - \lambda)U + \lambda U_{\text{Ref}} \quad \lambda \in [0,1]$$

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$$\begin{aligned} \left(\frac{\partial F(\lambda)}{\partial \lambda} \right)_{NVT} &= -\frac{1}{\beta} \frac{\partial}{\partial \lambda} \ln Z(N, V, T, \lambda) \\ &= -\frac{1}{\beta Z} \frac{\partial Z}{\partial \lambda} \end{aligned}$$

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Thermodynamic integration: solid phase

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$$\tilde{U}(\lambda) = (1 - \lambda)U + \lambda U_{\text{Ref}} \quad \lambda \in [0,1]$$

- Thermodynamic integration:

$$F = F_{\text{Ref}} - \int_0^1 \langle U_{\text{Ref}} - U \rangle_{\lambda} d\lambda$$

- Choose reference system with known free energy F_{Ref} .

Einstein crystal

- Potential:

$$U_{\text{Ein}}(\mathbf{r}) = \sum_{i=1}^N \frac{\alpha}{2} (\mathbf{r}_i - \mathbf{r}_{i,0})^2$$

- Free energy:

$$F_{\text{Ein}} = -\frac{3N}{2\beta} \ln\left(\frac{2\pi}{\alpha\beta\Lambda^2}\right)$$

Einstein crystal: choice of α

- Choose α such that fluctuations in the integrand become minimal:

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- Condition:

$$\alpha = \frac{3k_B T}{\langle r^2 \rangle_{\lambda=0}}$$

Constrained center of mass

- For $\lambda \rightarrow 0$ the particles are no longer bound to their lattice sites. The integrand in

$$F = F_{\text{Ein}} - \underbrace{\int_0^1 \langle U_{\text{Ein}} - U \rangle_\lambda d\lambda}_{\Delta F}$$

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- \Rightarrow Constrain the center of mass movement.
- Free energy changes:

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$$\beta (F_{\text{Ein}} - F_{\text{Ein}}^{\text{CM}}) = \frac{3}{2} \ln \left(\frac{\beta^2 \alpha}{4\pi^2 m} \right)$$

- and for arbitrary interacting crystals:

$$\beta (F - F^{\text{CM}}) = \ln(\rho) + \frac{3}{2} \ln \left(\frac{\beta}{2\pi N m} \right)$$

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- Excess free energy $F^{\text{ex}} \equiv F - F_{\text{id}}$ of the unconstrained crystal:

$$\frac{\beta F^{\text{ex}}}{N} \approx -\frac{3}{2} \ln\left(\frac{2\pi}{\alpha\beta}\right) - \frac{\beta\Delta F^{\text{CM}}}{N} + \frac{3}{2N} \ln\left(\frac{2\pi}{\alpha\beta}\right) - 2\frac{\ln N}{N} + \frac{\ln \rho}{N} - \ln \rho + 1 - \frac{\ln(2\pi)}{2N}.$$

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- System size dependence:

$$\frac{\beta\Delta F^{\text{CM}}}{N} = \text{const.} - \frac{\ln N}{N} + \mathcal{O}(N^{-1})$$

Constrained center of mass

- Excess free energy $F^{\text{ex}} \equiv F - F_{\text{id}}$ of the unconstrained crystal:

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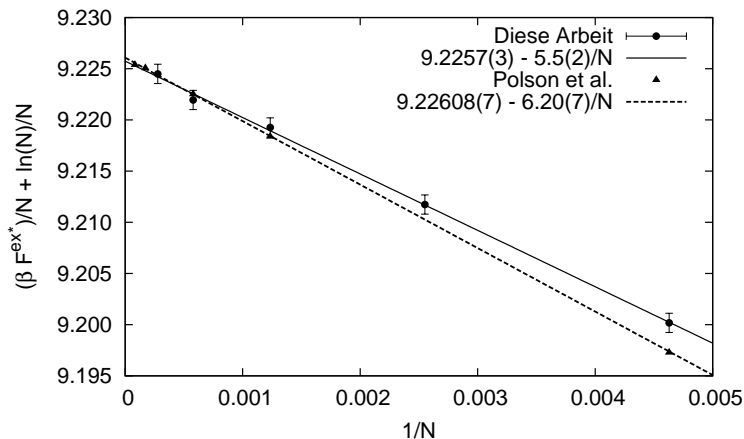
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$$\frac{\beta \Delta F^{\text{CM}}}{N} = \text{const.} - \frac{\ln N}{N} + \mathcal{O}(N^{-1})$$

- So $\beta F^{\text{ex}}/N + \ln N/N$ depends linear on $1/N$.

System size dependence

- Soft sphere fcc-crystal at $\rho = 1.1964$, using $\alpha = 132$ and $N = 216, 392, 810, 1728, 3600$



Summary

- Thermodynamic integration for fluid phase:

$$\frac{\beta F^{\text{ex}}}{N} = \beta \int_0^{\rho} \frac{P(\tilde{\rho}, T) - \tilde{\rho}/\beta}{\tilde{\rho}^2} d\tilde{\rho}$$

Summary

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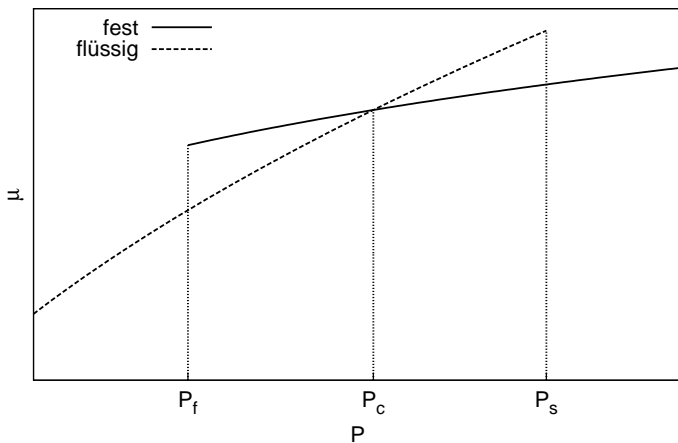
$$\frac{\beta F^{\text{ex}}}{N} = \beta \int_0^{\rho} \frac{P(\tilde{\rho}, T) - \tilde{\rho}/\beta}{\tilde{\rho}^2} d\tilde{\rho}$$

- Thermodynamic integration for solid phase:

$$\begin{aligned} \frac{\beta F^{\text{ex}}}{N} = & -\frac{3}{2} \ln\left(\frac{2\pi}{\alpha\beta}\right) - \frac{\beta}{N} \int_0^1 \langle U_{\text{Ein}} - U \rangle_{\lambda} d\lambda + \frac{3}{2N} \ln\left(\frac{2\pi}{\alpha\beta}\right) \\ & - 2\frac{\ln N}{N} + \frac{\ln \rho}{N} - \ln \rho + 1 - \frac{\ln(2\pi)}{2N} \end{aligned}$$

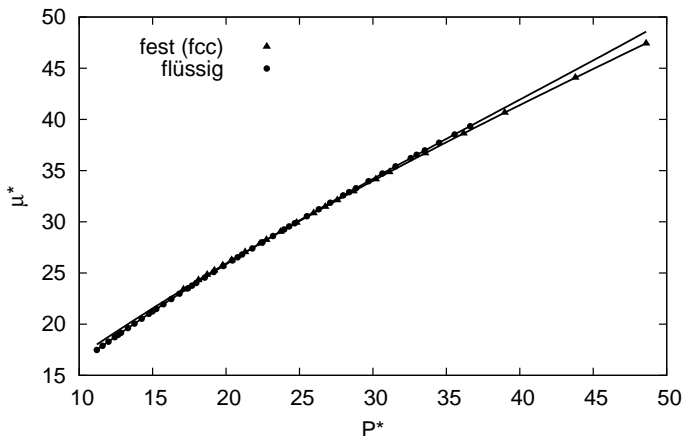
Can we now find phase-equilibria?

- Theoretically expected form of the chemical potential vs. pressure:



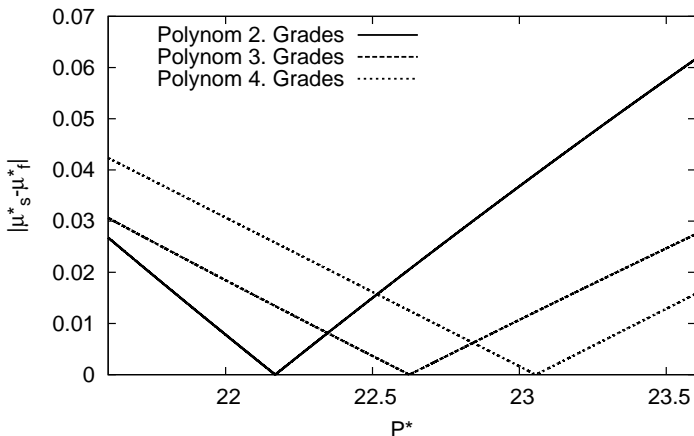
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- Computer simulation results for $U(r) = \varepsilon(r^*)^{-12}$ soft spheres at $T^* = 1$:



Can we now find phase-equilibria?

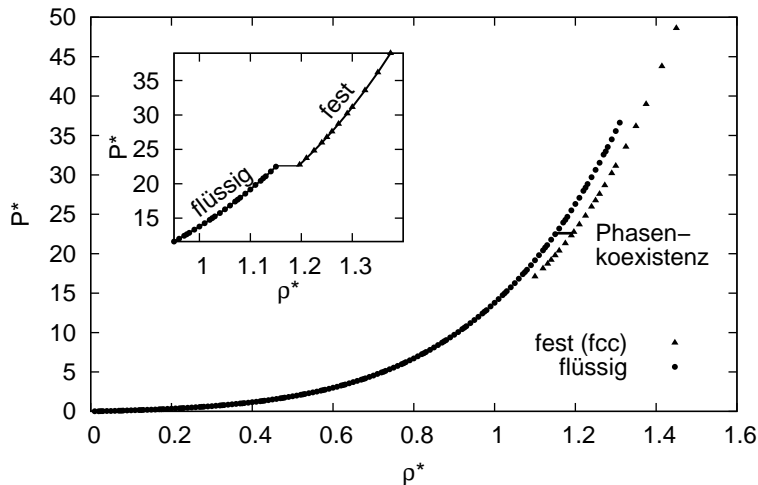
- Difference between the previously shown curves:



- Phase coexistence at $P^* = 22.6(5)$

Equation of state for soft spheres

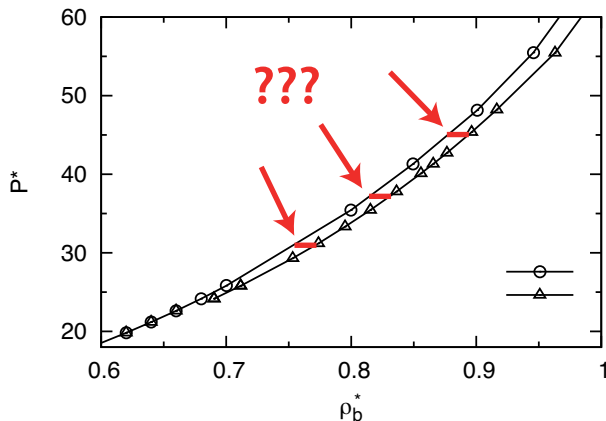
- Coexistence at $P^* = 22.6(5)$, $\rho_f^* = 1.152(7)$, $\rho_s^* = 1.194(7)$



Summary

- Thermodynamic integration for liquid and solid phase.
- Allows calculation of Helmholtz free energy in NVT -Ensemble.
- Gibbs free energy follows directly.
- Phase coexistence can be found.
- Equation of state can be drawn.

What about the charged colloids?



- Coexistence pressure still to be found...
- Effects due to walls?