Residual multiparticle entropy for a fractal fluid of hard spheres

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What is the residual multiparticle entropy (RMPE)?

- Consider a fluid system with number density ρ, inverse temperature $\beta = 1/k_B T$, and entropy per particle $s(\rho,\beta)$ (in units of k_B).
- $$s(\rho,\beta) = \underbrace{s_{\mathrm{id}}(\rho,\beta)}_{\text{Ideal gas}} + \underbrace{s_{\mathrm{ex}}(\rho,\beta)}_{\text{Excess entropy (interactions \& correlations)}}$$
- $$s_{\mathrm{ex}}(\rho,\beta) = \underbrace{s_2(\rho,\beta)}_{\text{Pair correlations}} + \underbrace{\Delta s(\rho,\beta)}_{\text{RMPE (cumulated correlations of 3, 4, 5, … particles)}}$$

The residual *two-particle* entropy

$$s_2(\rho, \beta) = -\frac{\rho}{2} \int \mathrm{d}\mathbf{r}\ [g(r) \ln g(r) - g(r) + 1] \leq 0$$

$g(r)$: Radial distribution function (RDF)

$\Rightarrow$ pair correlations

Role of the RDF $g(r)$

$$g(r) \xrightarrow{-\frac{\rho}{2}\int \mathrm{d}\mathbf{r}\,[g(r)\ln g(r) - g(r) + 1]} s_2(\rho,\beta)$$

$$g(r) \xrightarrow{1 - \frac{\rho\beta}{2d}\int \mathrm{d}\mathbf{r}\,\mathbf{r}\cdot\nabla u(r) g(r)} \frac{\beta P}{\rho} \Rightarrow s^{\mathrm{ex}}(\rho,\beta)$$

$$\left.\begin{matrix} s_2(\rho,\beta) \\ s^{\mathrm{ex}}(\rho,\beta) \end{matrix}\right\} \Rightarrow \Delta s(\rho,\beta)$$

Why is the RMPE $\Delta s(\rho,\beta)$ worth studying?

- Even though the interaction potential is *pairwise* additive, there exist *spatial correlations* involving *more than 2 particles*.
- The *net contribution* to entropy of those *non-pair* correlations is represented by the RMPE $\Delta s(\rho,\beta)=s_{\mathrm{ex}}(\rho,\beta)$-$s_2(\rho,\beta)$.
- It can be either *negative* (typically at low densities or high temperatures) or *positive*.
- If $\Delta s(\rho,\beta)>0$, increasingly stronger multiparticle correlations cooperatively concur in increasing the entropy of the system.
- It has been observed that a zero-RMPE criterion, $\Delta s(\rho,\beta)=0$, may signal the onset of *ordering* processes leading to a phase transition (e.g., *freezing*).

Our system:

PRL **115,** 097801 (2015) PHYSICAL REVIEW LETTERS

Classical Liquids in Fractal Dimension

Marco Heinen,[1,*] Simon K. Schnyder,[2] John F. Brady,[1] and Hartmut Löwen[3]

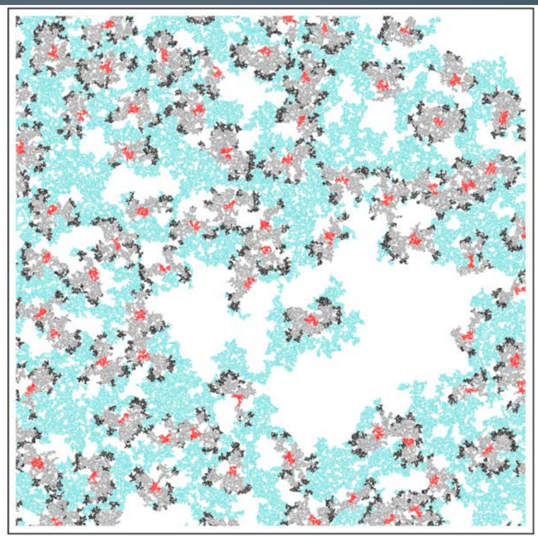

FIG. 1 (color online). Snapshot of a Monte Carlo simulation where 300 fractal particles are located on a percolating cluster, shown in blue. The dimension of each particle and of the cluster is $d_l = 1.67659$, and the chemical distance diameter of each particle is $\sigma = 300a$ (cf. Fig. 2). Red, black, and gray pixels are occupied by particles. (Red) Particle center regions (chemical distance to a particle center is less than 0.1σ). (Black) Particle rim regions (chemical distance to a particle center is more than 0.4σ and less than 0.5σ). (Gray) Regions between particle centers and rims. Every pixel in the figure corresponds to one vertex in the simulation. One quarter of the whole simulation box is shown, containing here 72 particle centers.

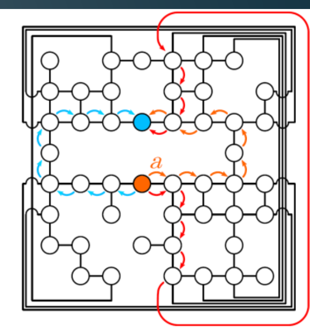

FIG. 2 (color online). Lattice schematic. From an 8×8 square lattice with periodic boundaries, 17 vertices have been removed. Circles are the remaining vertices and black lines are the bonds of length a. The chemical distance between the orange and the blue filled circle is $l = 8a$ along any of the three paths indicated by red, blue, and orange arrows. The corresponding Euclidean distance is $r = 2a$.

ϕ : volume (or packing) fraction

Our approach:

PHYSICAL REVIEW E **93**, 062126 (2016)

Radial distribution function for hard spheres in fractal dimensions: A heuristic approximation

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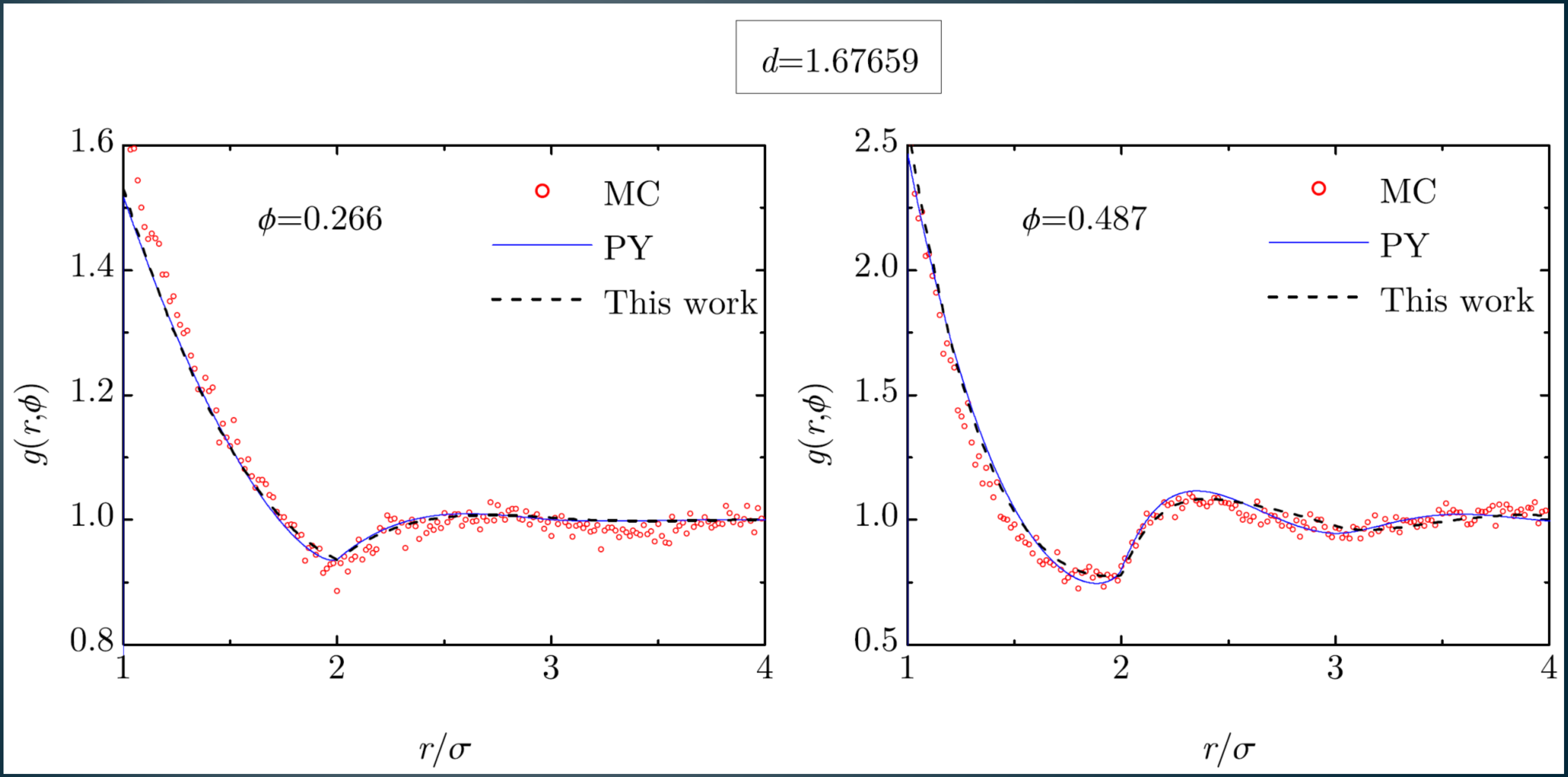
$$g(r;\phi) = \alpha(\phi)\,\underbrace{g_{1\mathrm{D}}(r;\phi_{1\mathrm{D}}^{\mathrm{eff}})}_{\text{Exact}} + [1-\alpha(\phi)]\,\underbrace{g_{3\mathrm{D}}(r;\phi_{1\mathrm{D}}^{\mathrm{eff}})}_{\text{Percus–Yevick}}$$

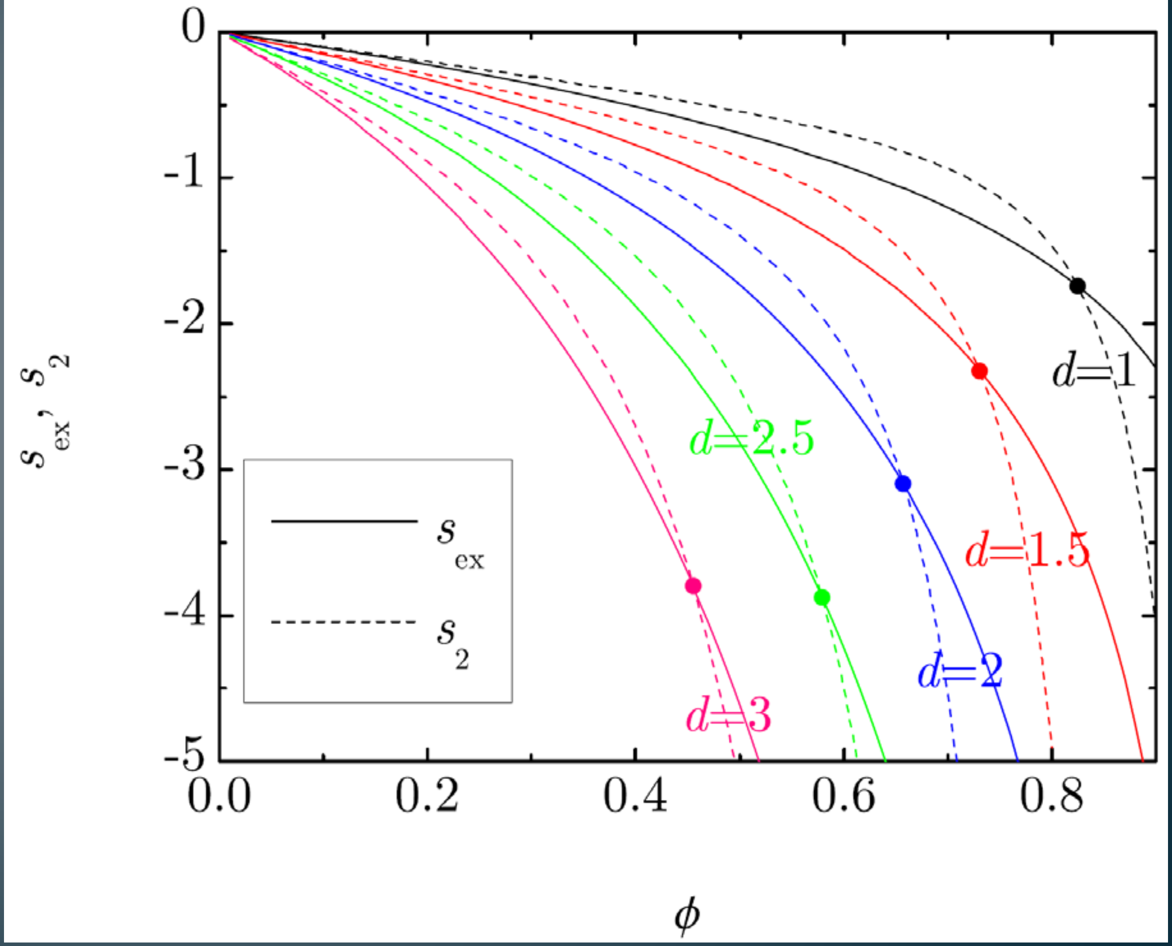
$$= \text{analytic dependence on both } r \text{ and } \phi$$

$$\alpha(\phi), \phi_{1\mathrm{D}}^{\mathrm{eff}}(\phi), \phi_{3\mathrm{D}}^{\mathrm{eff}}(\phi) : \text{determined from consistency conditions}$$

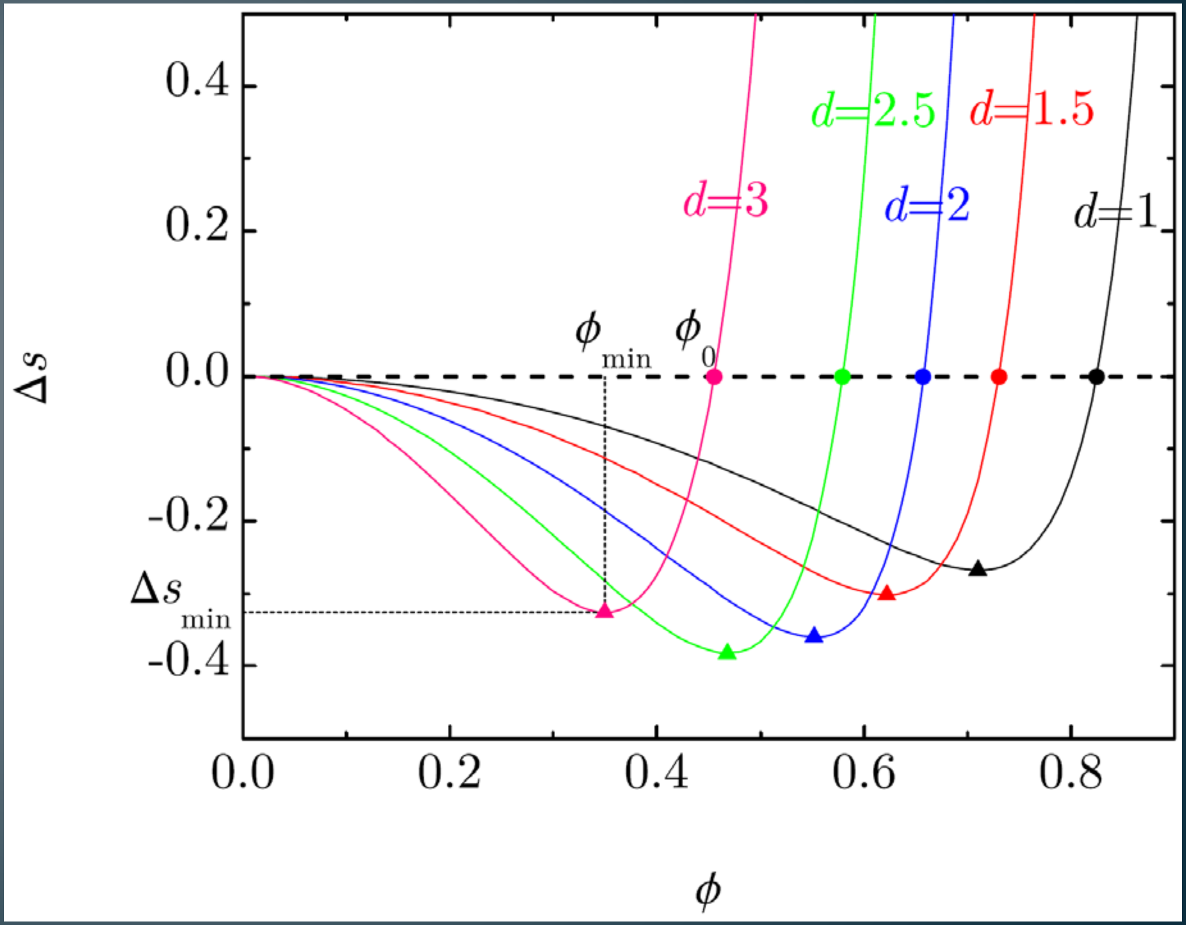
How good is this approximation?



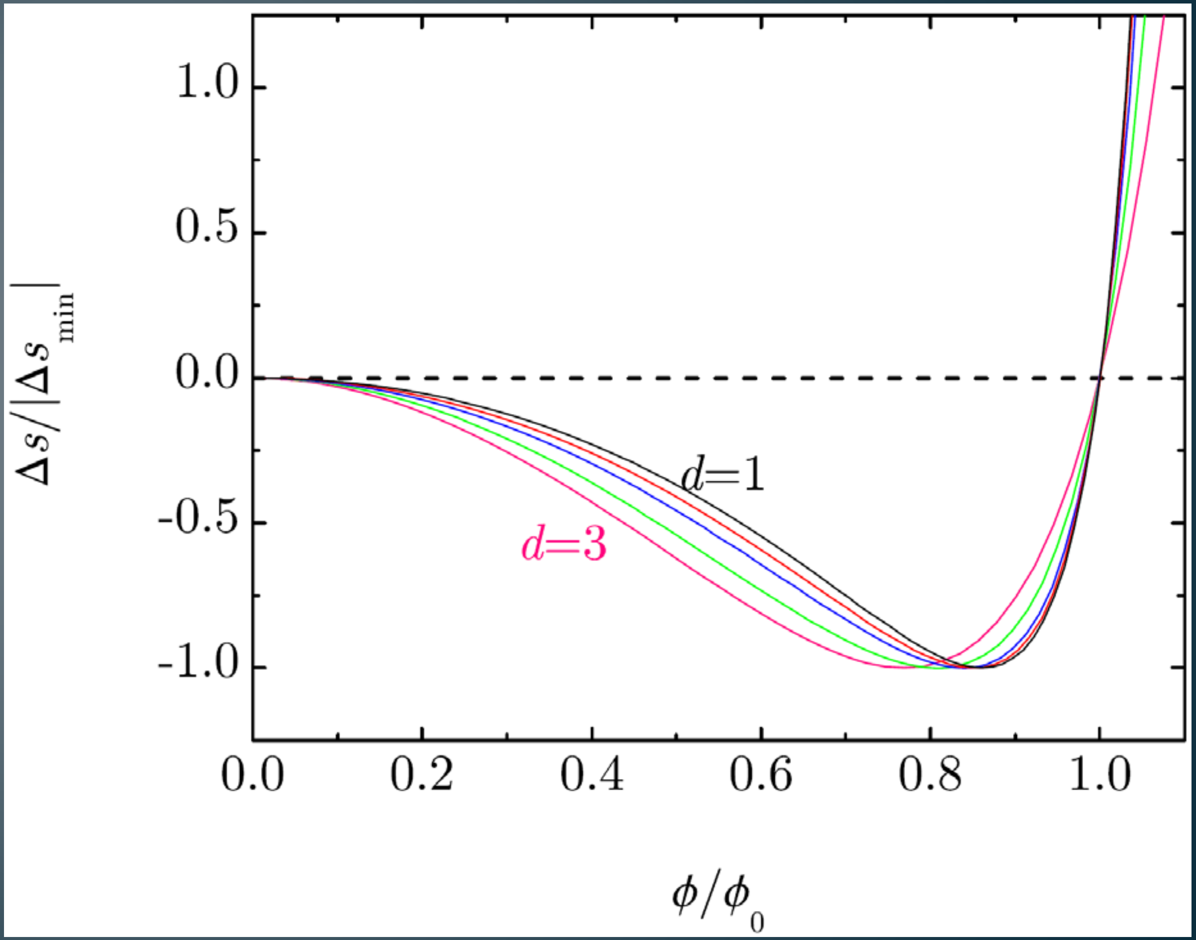
Results:
Excess entropy and its pair contribution



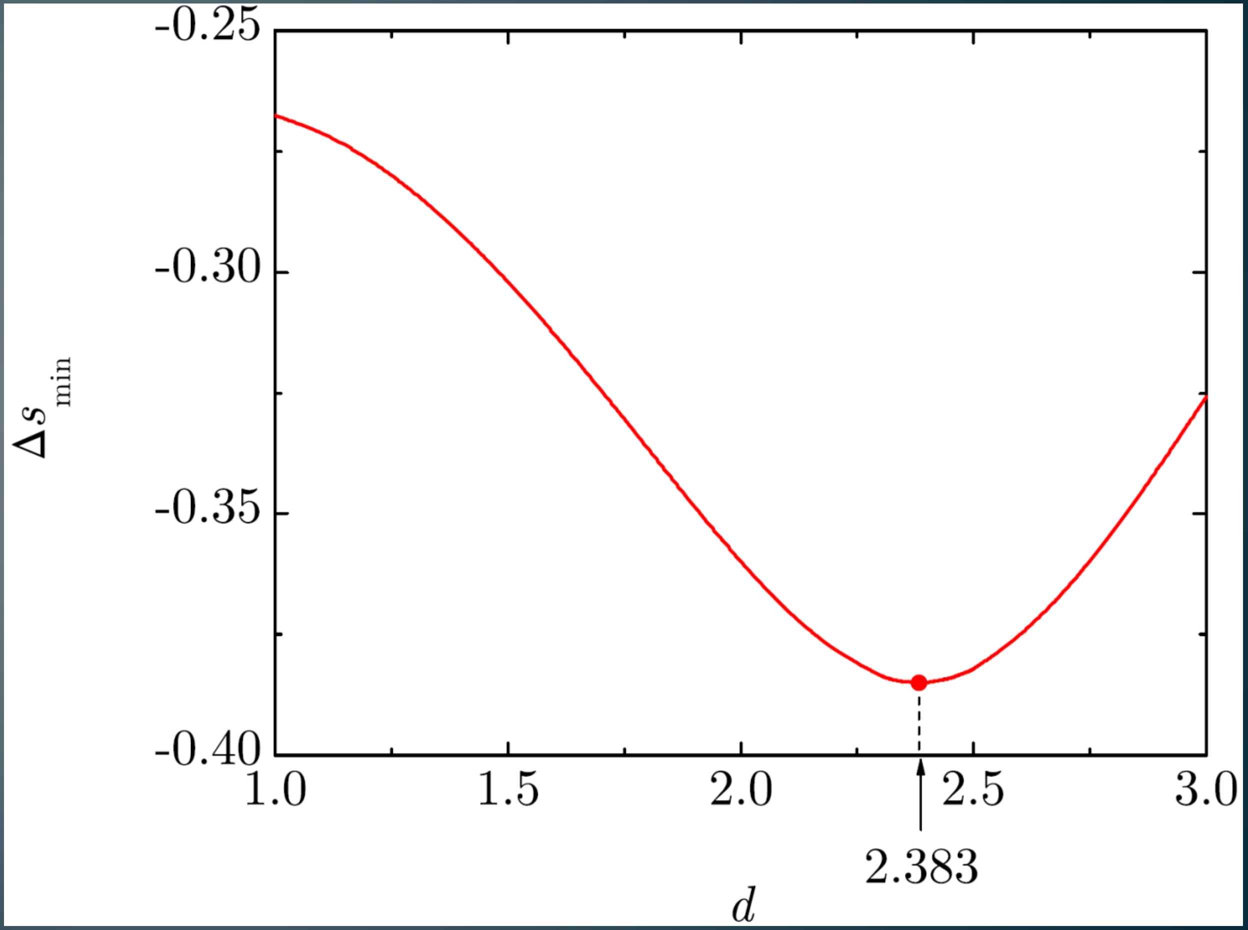
RMPE



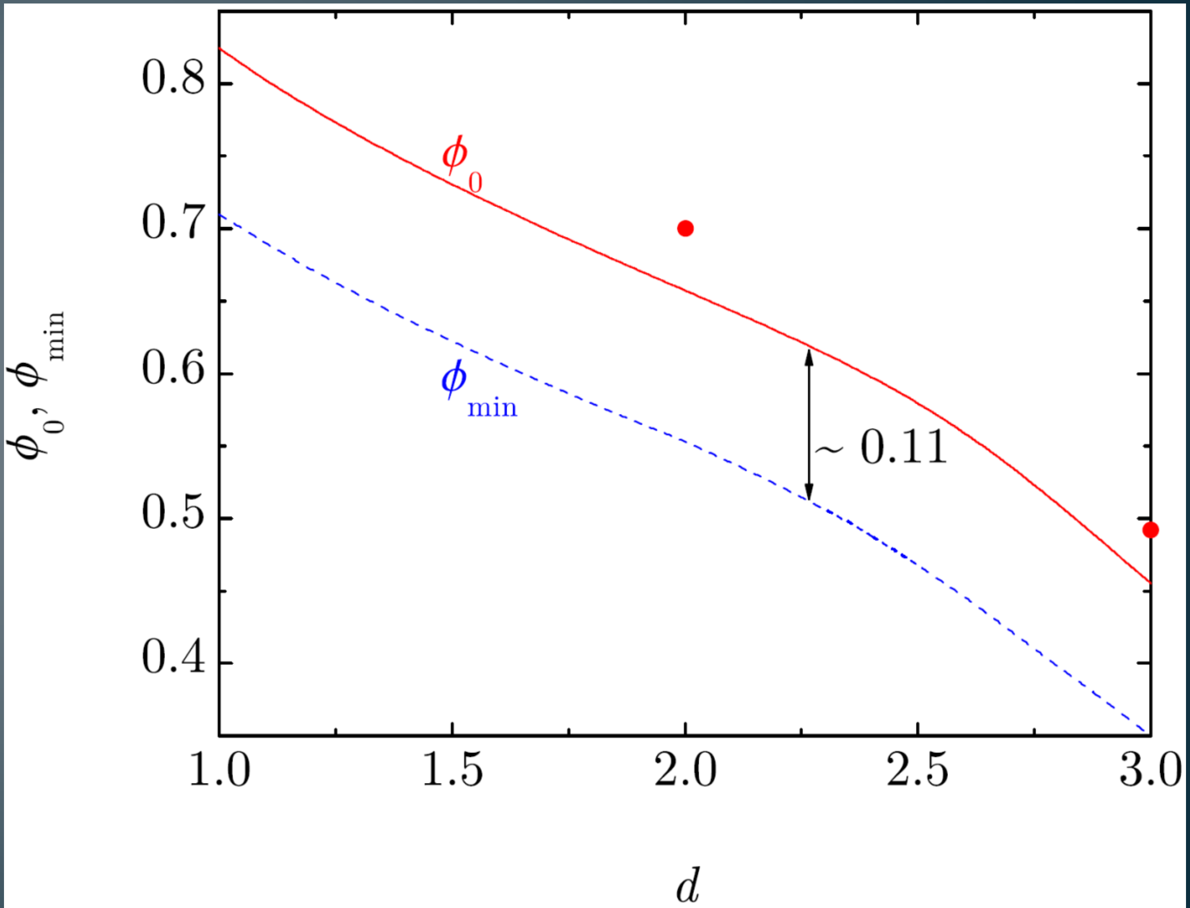
Non-universal behavior



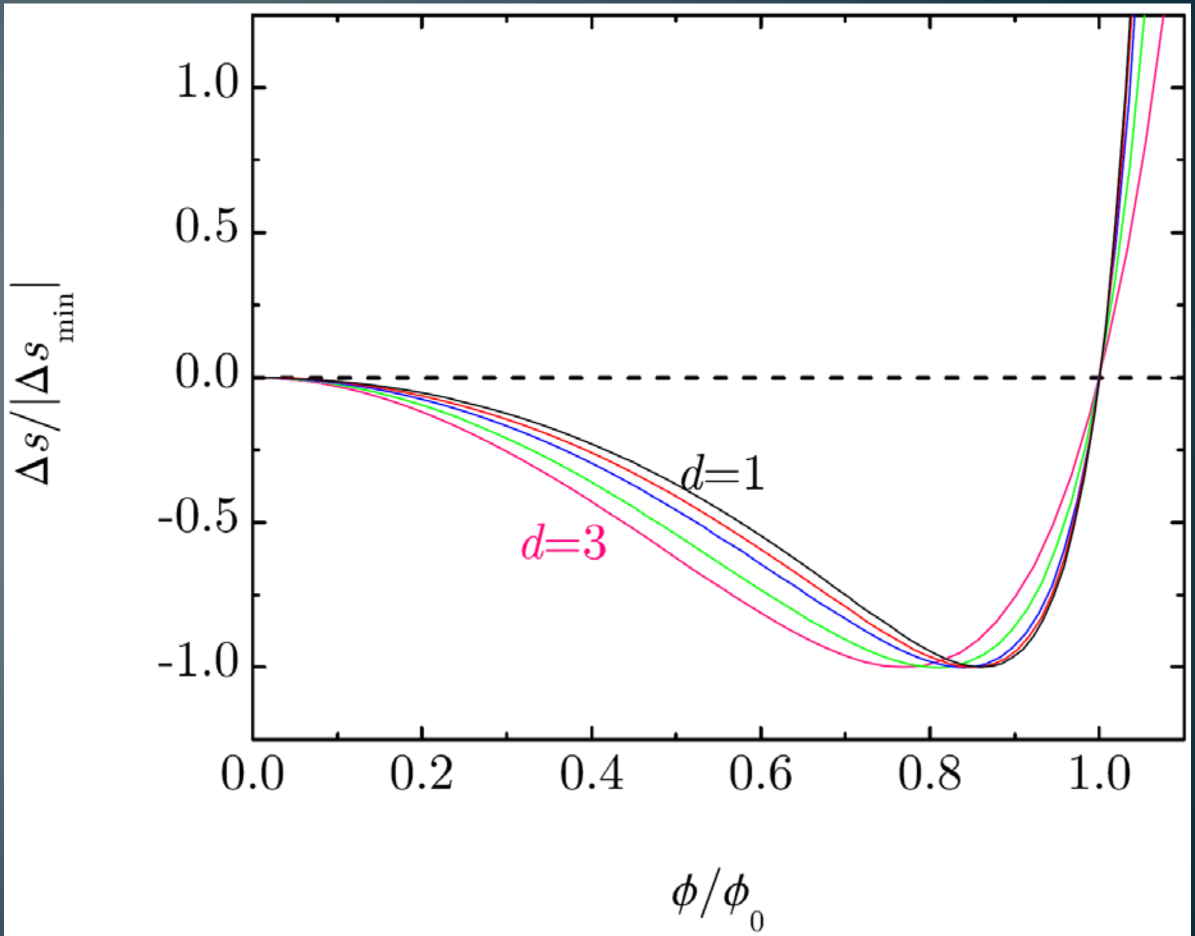
Minimum RMPE



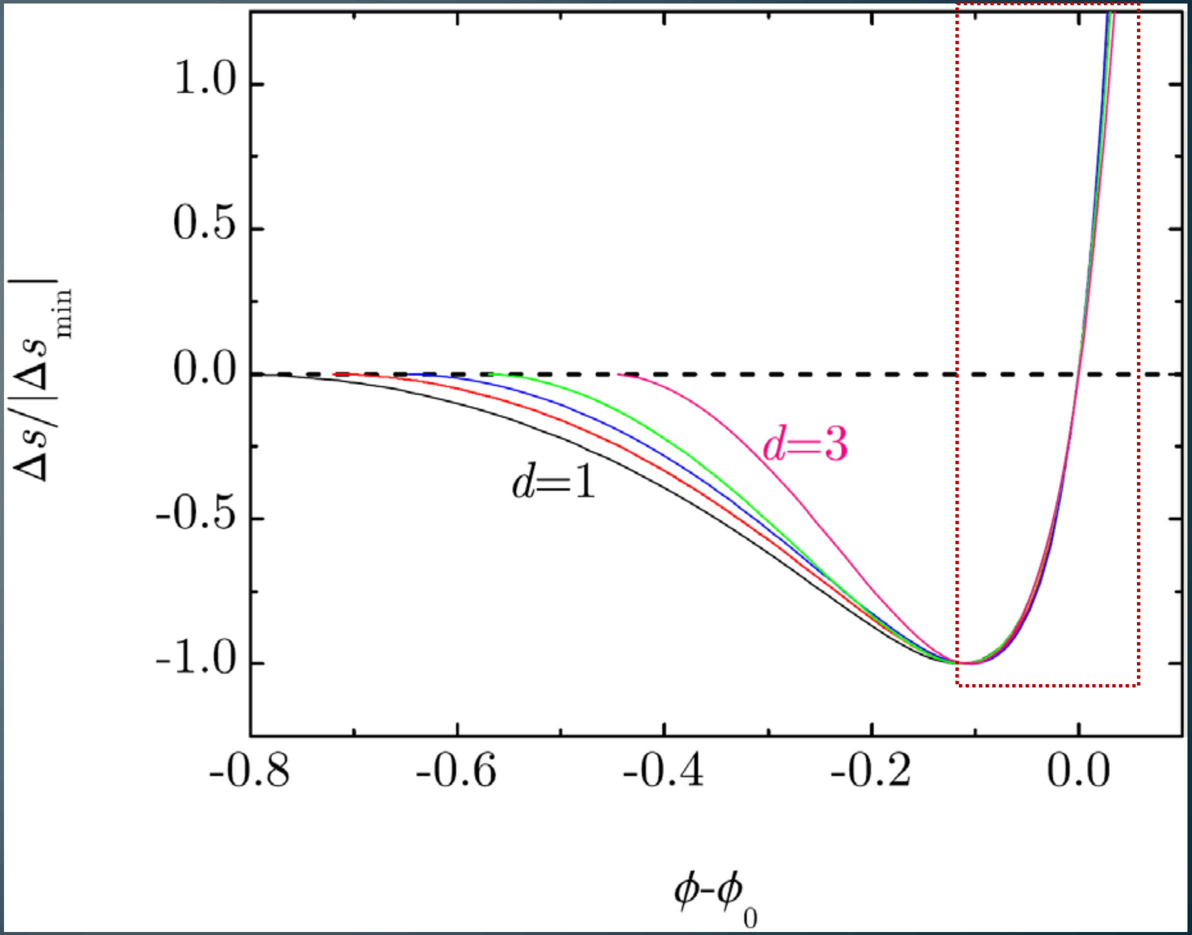
Locations of the minimum and zero RMPE



Non-universal behavior



Non-universal behavior?



Conclusions and outlook

- Simple theory applied to estimate the excess entropy and the RMPE of a *fractal* hard-sphere fluid.
- The minimum value of the RMPE exhibits a nonmonotonic d-dependence, becoming extremal at $d=2.38$.
- Some sort of ordering process is expected beyond the packing fraction ϕ_0 where the RMPE vanishes.
- If a freezing transition in fractal fluids exist, the zero-RMPE criterion would provide a reasonable (lower?) estimate of the freezing density.
- Computer simulations needed!


THANK
YOU!


What people think about
during your conference talk
Hee hee! Animated arrows!
Typo on slide 14, line 3, centre-left. Noted.
Hey! That's what I'm working on!
(RANDOM HAPPY THOUGHTS]
I'm up next I'm up next I'm up next
I'm in the wrong session.
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