Cavity averages for hard spheres in the presence of polydispersity and incomplete data

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Motivation

Recent confocal experiments on colloidal solids – crystals as well as jammed and disordered materials – generate large numbers of snapshots which contain positions and sizes of particles. We present a method how to extract the pressure and the chemical potentials from such snapshots. Both together present a consistent set of **thermodynamic information** and give direct access to free energies. The presented methods are based on the paradigma of statistical mechanics: Counting all possible configurations and averaging over them.

Reference:

M. Schindler and A. C. Maggs: *Cavity averages for hard spheres in the presence of polydispersity and incomplete data.* arxiv 1506.05007.

Counting configurations

$\Omega(N)$ are all different configurations to place N spheres in a box of volume V. For example, the total number of configurations is

$$|\Omega(N)| = \frac{1}{N!\,\omega^N} \prod_{n=0}^{N-1} \langle V_0 \rangle_{\Omega(n)},$$

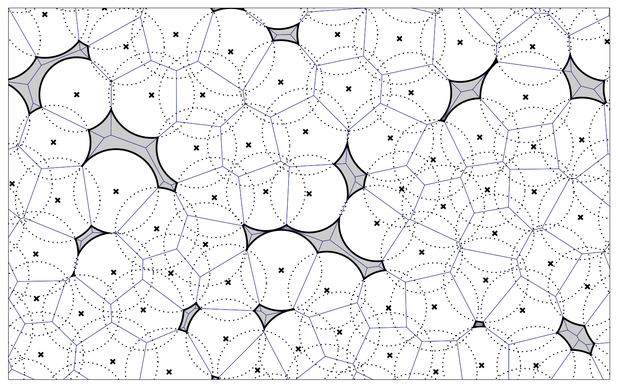
because

$$\langle V_0 \rangle_{\Omega(n)} := \frac{1}{|\Omega(n)|} \sum_{k \in \Omega(n)} V_0(k),$$

$$|\Omega(n)| = \frac{1}{\omega n} \sum_{k \in \Omega(n-1)} V_0(k) = |\Omega(n-1)| \frac{\langle V_0 \rangle_{\Omega(n-1)}}{\omega n}$$

Radical-plane tesselation

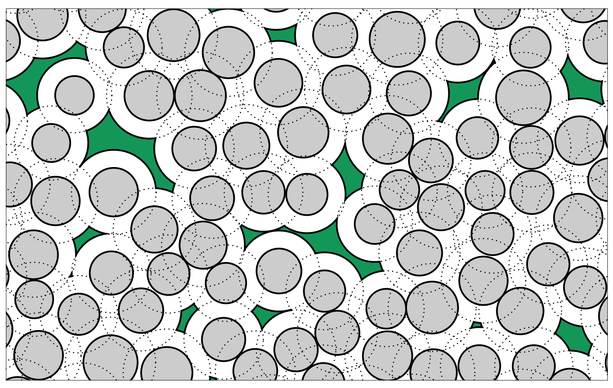
allows to measure the cavity volume and its surface



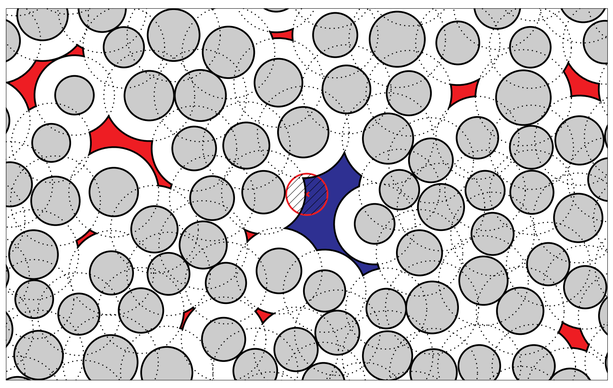
Cavities:

$k = \{\mathbf{r}_1, \ldots \mathbf{r}_N\}$ is one configuration.

Available volume of N particles: $V_0(k)$
Try to insert another particle $(N{+}1)$



Free volume of one particle: $V_f(k,i)$
Move particle i in its cage, the others are fixed!



Available volume after take-out of one particle: $V_0(k\backslash\mathbf{r}_i)$
Remove particle i and reinsert it, the others are fixed!

Pressure

Polydisperse system, particle types α.
From the available volume:

$$\frac{pV}{N\,kT} - 1 = \frac{1}{2dN} \sum_{\alpha=A,B} N_\alpha \sigma_\alpha \frac{\langle S_0^\alpha \rangle_{\Omega(N_\alpha - 1, N.)}}{\langle V_0^\alpha \rangle_{\Omega(N_\alpha - 1, N.)}}. \quad (\mu\text{AV})$$

From the free volume:

$$\frac{pV}{N\,kT} - 1 = \frac{1}{2dN} \sum_{\alpha=A,B} N_\alpha \sigma_\alpha \left\langle \frac{S_f^\alpha}{V_f^\alpha} \right\rangle_{\mathcal{F}^\alpha(N_A,N_B)} \quad (\mu\text{FV})$$

From the available-volume-after-takeout:

$$\frac{pV}{NkT} - 1 = \frac{1}{2dN} \sum_{i=1}^{N} \sigma_i \left\langle \frac{S_0^{\alpha_i}(k\backslash\mathbf{r}_i)}{V_0^{\alpha_i}(k\backslash\mathbf{r}_i)} \right\rangle_{k \in \Omega(N_A,N_B)} \quad (\mu\text{AVATO})$$

Chemical potentials

From the available volume:

$$\frac{\mu_A}{kT} - \ln \lambda_A^d = \ln \frac{N_A}{\left\langle V_0^A(k) \right\rangle_{k \in \Omega(N_A - 1, N_B)}} \quad (\mu\text{AV})$$

From the free volume:

$$\frac{\mu_A}{kT} - \ln \lambda_A^d = \ln \frac{N_A \left\langle 1/V_f^A \right\rangle_{\mathcal{F}^A(N_A,N_B)}}{\left\langle N_c^A(k) \right\rangle_{k \in \Omega(N_A - 1, N_B)}} \quad (\mu\text{FV})$$

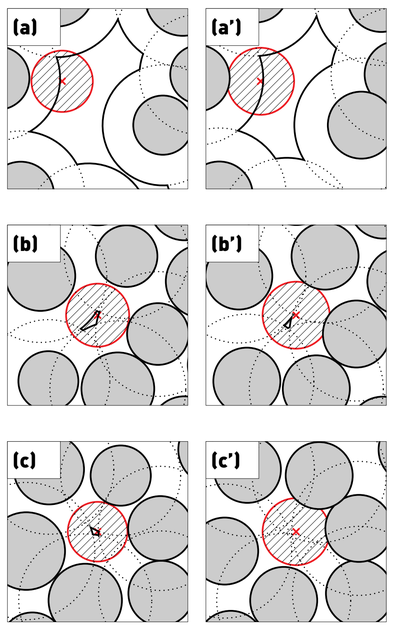
From the available-volume-after-takeout:

$$\frac{\mu_A}{kT} - \ln \lambda_A^d = \ln N_A \gamma_A \left\langle \frac{1}{V_0^A} \right\rangle_{\mathcal{T}^A(N_A,N_B)} \quad (\mu\text{AVATO-A})$$

$$\frac{\mu_A}{kT} - \ln \lambda_A^d = \ln \frac{N_A \left\langle N_c^A / V_0^A \right\rangle_{\mathcal{T}^A(N_A,N_B)}}{\left\langle N_c^A \right\rangle_{\Omega(N_A - 1, N_B)}} \quad (\mu\text{AVATO-B})$$

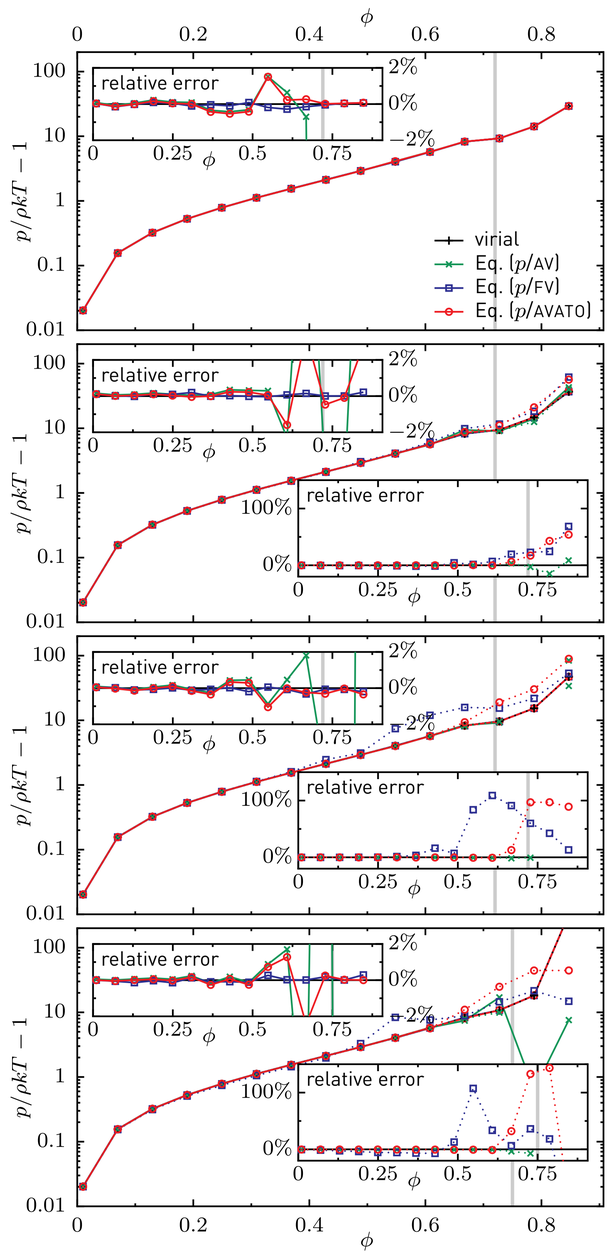
Missing radius information:

Take the particles to be monodisperse, although they are not:



Are the cavity averages robust against this?

Data from molecular dynamics: Pressure



Data from molecular dynamics: Chemical potentials