Statistical geometry

How to measure thermodynamics in hard-sphere configurations

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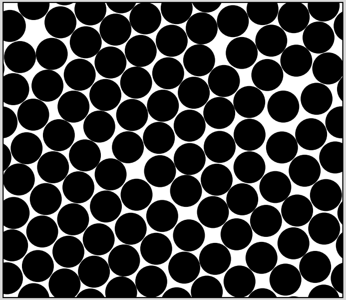
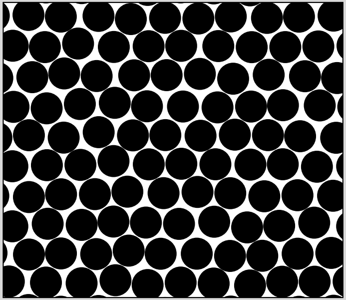
Target: Get free energy





$$\left.\begin{array}{l} T \text{ fixed} \\ V \text{ fixed} \\ N \text{ fixed} \end{array}\right\} \Longrightarrow \begin{array}{l} \text{Helmholtz' Free Energy } F(N,V,T) \\ \text{is minimized at equilibrium} \end{array}$$

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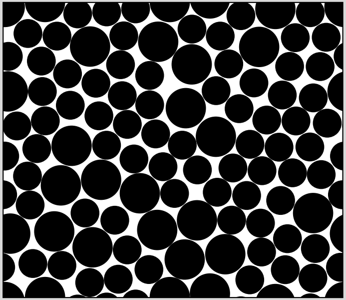
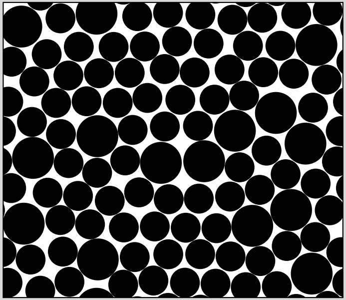




$$\left.\begin{array}{l} T \text{ fixed} \\ V \text{ fixed} \\ N \text{ fixed} \end{array}\right\} \Longrightarrow \begin{array}{l} \text{Helmholtz' Free Energy } F(N,V,T) \\ \text{is minimized at equilibrium} \end{array}$$

Where is geometry in all this?

The model: hard spheres with elastic collisions

Spatial geometry:

Periodic, flat space

Phase space:

Curved by constraints

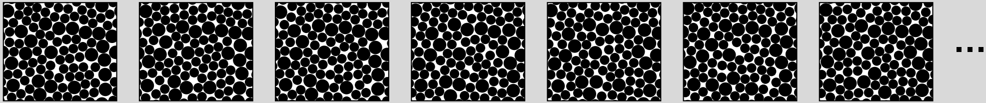
Conserved total energy $\frac{1}{2}\sum_i m_i \mathbf{v}_i^2$

Conserved total momentum $\sum_i m_i \mathbf{v}_i$

Non-overlapping particles $\|\mathbf{r}_i - \mathbf{r}_j\|^2 \geq (R_i + R_j)^2$ for all $i \neq j$

Configurations

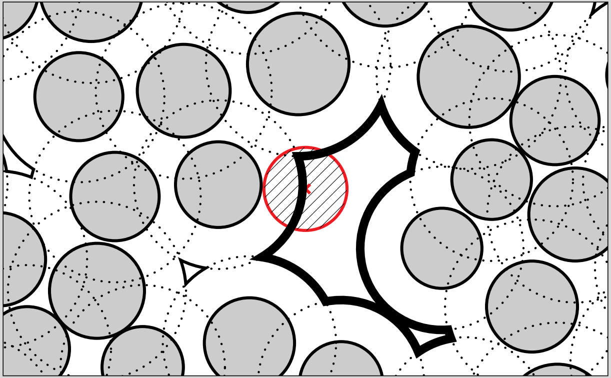
Molecular dynamics **samples** phase space uniformly. . .



Partition function separates into configuration and dynamical parts

Analyse only configurations!

Pressure



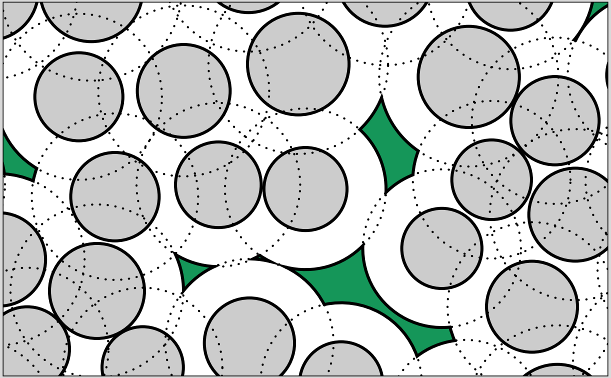
$$p = -\frac{\partial F}{\partial V} \quad \sim \frac{\partial F}{\partial R}$$

$$p = kT\frac{N}{V}\left(1 + \frac{\sigma}{2d}\left\langle\frac{S_f}{V_f}\right\rangle\right)$$

Chemical potentials: "Widom insertion"

$$\mu = \frac{\partial F}{\partial N} \quad \text{or rather:} \quad F(N,V,T) - F(N-1,V,T)$$

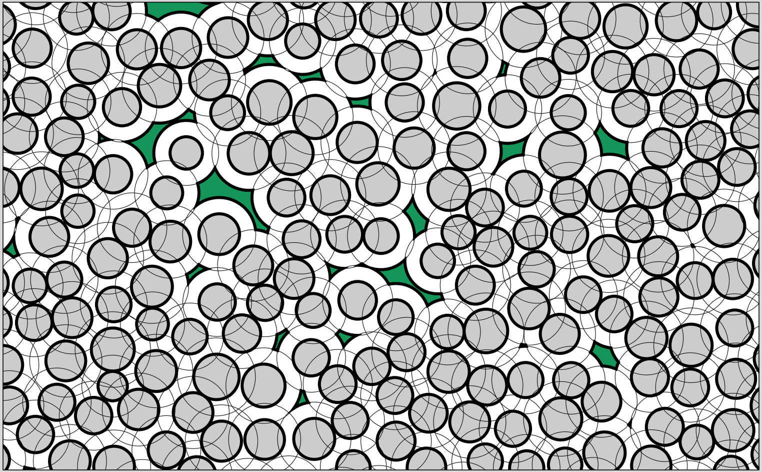
$$\mu = kT \ln \frac{\lambda^d N}{\langle V_0 \rangle}$$



Three different geometrical protocols

Available volume

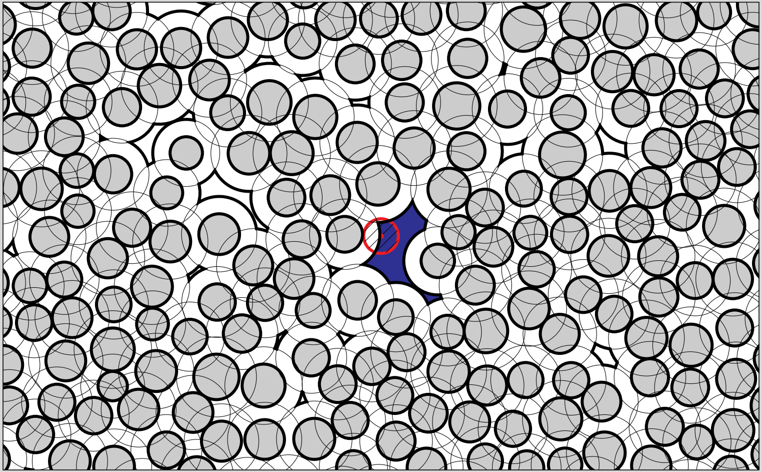
Calculate volumes and surfaces of all cavities, using N-particle config:



Three different geometrical protocols

Free volume

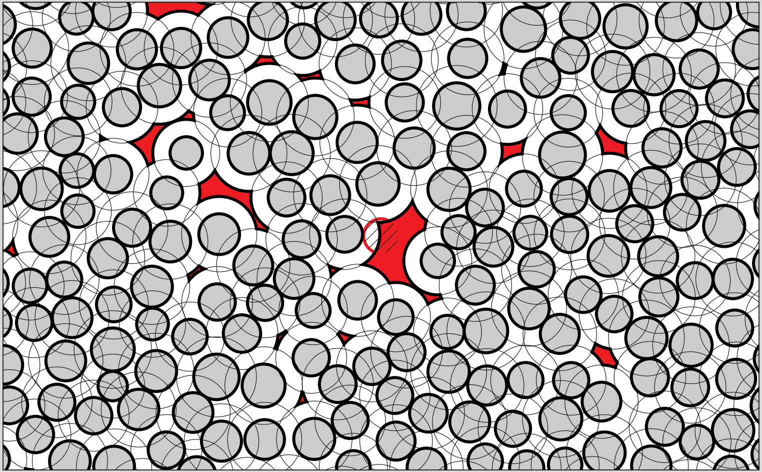
Calculate volume and surface of one cavity, using $(N-1)$-particle config:



Three different geometrical protocols

Available volume after take-out (AVATO)

Calculate volumes and surfaces of all cavities, using $(N-1)$-particle config:



Three different geometrical protocols

...here $\Omega(N)$ is the set of all configurations of N particles...

$$\frac{pV}{kT\,N} - 1 = \frac{\sigma}{2d}\frac{\langle S_0(k)\rangle_{k\in\Omega(N-1)}}{\langle V_0(k)\rangle_{k\in\Omega(N-1)}}$$

$$= \frac{\sigma}{2dN}\sum_{i=1}^{N}\left\langle \frac{S_f(k\backslash \mathbf{r}_i)}{V_f(k\backslash \mathbf{r}_i)}\right\rangle_{k\in\Omega(N)}$$

$$= \frac{\sigma}{2dN}\sum_{i=1}^{N}\left\langle \frac{S_0(k\backslash \mathbf{r}_i)}{V_0(k\backslash \mathbf{r}_i)}\right\rangle_{k\in\Omega(N)}$$

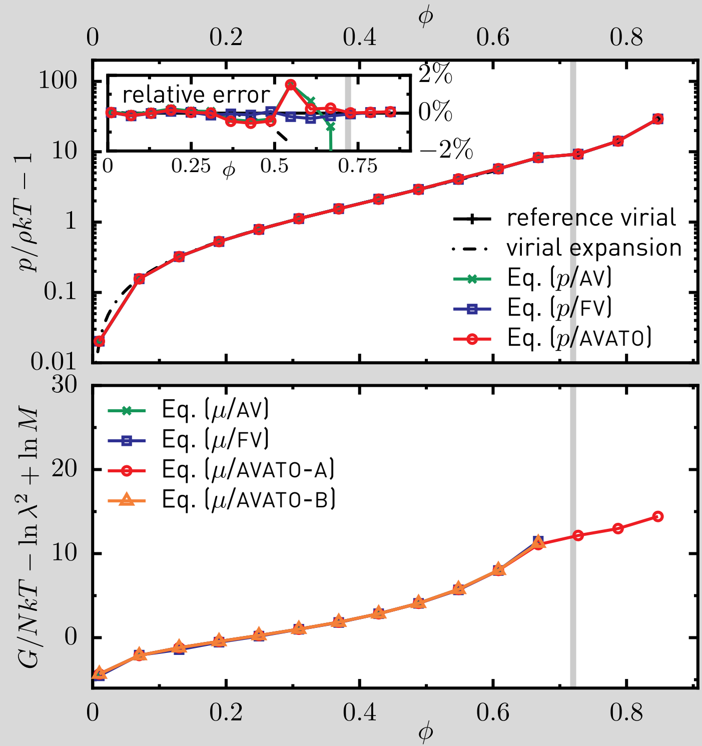
$$\frac{\mu}{kT} - \ln\lambda^d = \ln\frac{N}{\langle V_0(k)\rangle_{k\in\Omega(N-1)}}$$

$$= \ln\frac{\sum_{i=1}^{N}\left\langle \frac{1}{V_f(k\backslash \mathbf{r}_i)}\right\rangle_{k\in\Omega(N)}}{\langle N_c(k)\rangle_{k\in\Omega(N-1)}}$$

$$= \ln\frac{\sum_{i=1}^{N}\left\langle \frac{N_c(k\backslash \mathbf{r}_i)}{V_0(k\backslash \mathbf{r}_i)}\right\rangle_{k\in\Omega(N)}}{\langle N_c(k)\rangle_{k\in\Omega(N-1)}}$$

$$\gtrsim \ln\sum_{i=1}^{N}\left\langle \frac{1}{V_0(k\backslash \mathbf{r}_i)}\right\rangle_{k\in\Omega(N)}$$

Results in 2D: monodisperse



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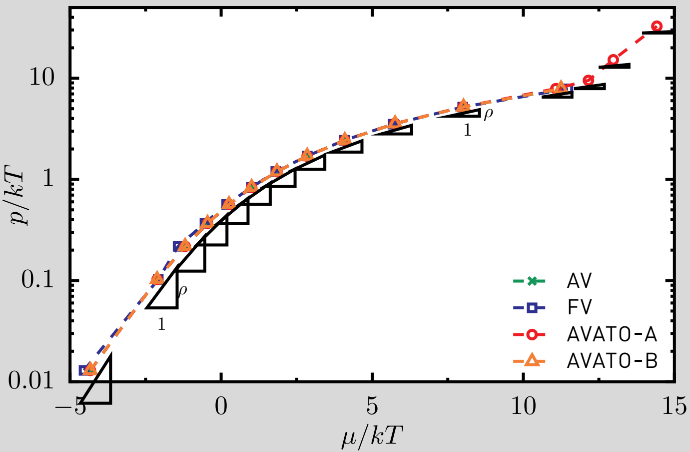
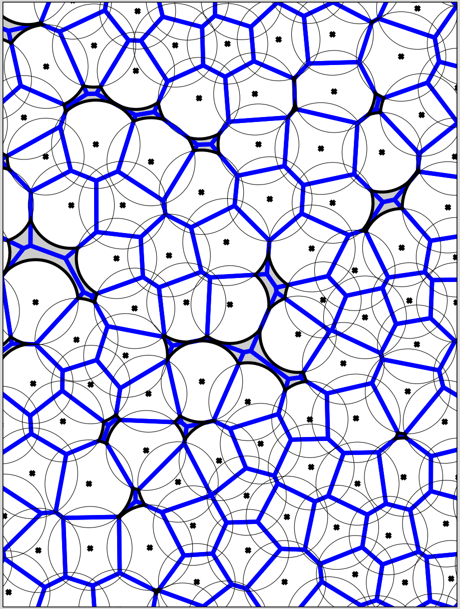
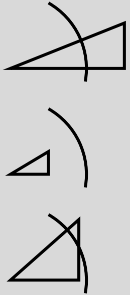


This is where CGAL comes in . . .



Decompose every Voronoi cell into little triangles:

Three solvable standard problems:



What would be different in curved space?

Things to check:

- Is the distribution of states still uniform?
- Weighted Delaunay/Voronoi tesselations?
- Are the standard problems analytically solvable?

... thank you for your attention (and for CGAL) ...