Entropy, free-volume distributions and the disorder parameter in hard particle fluids

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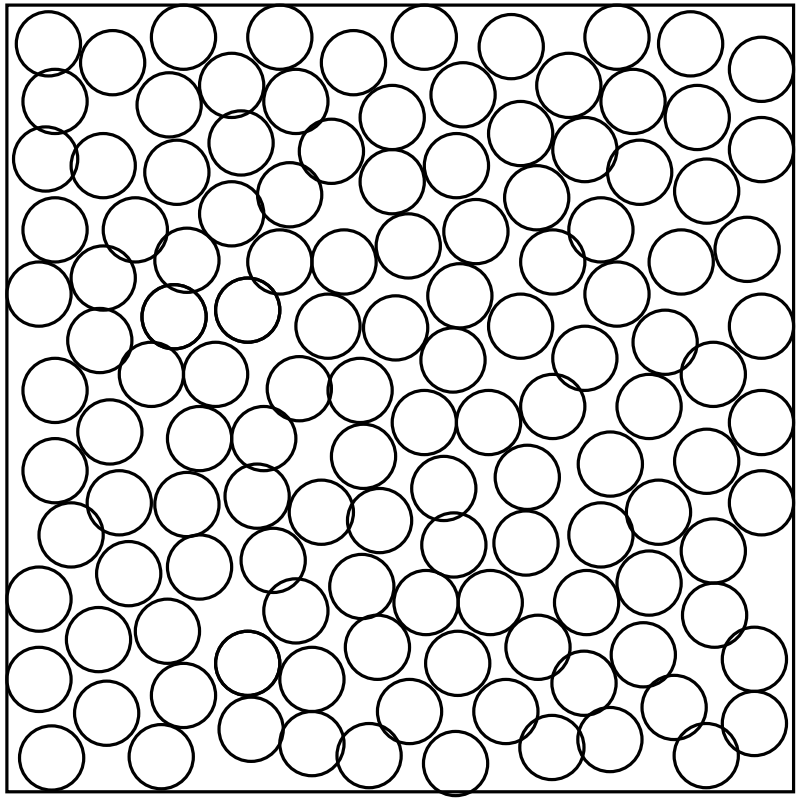
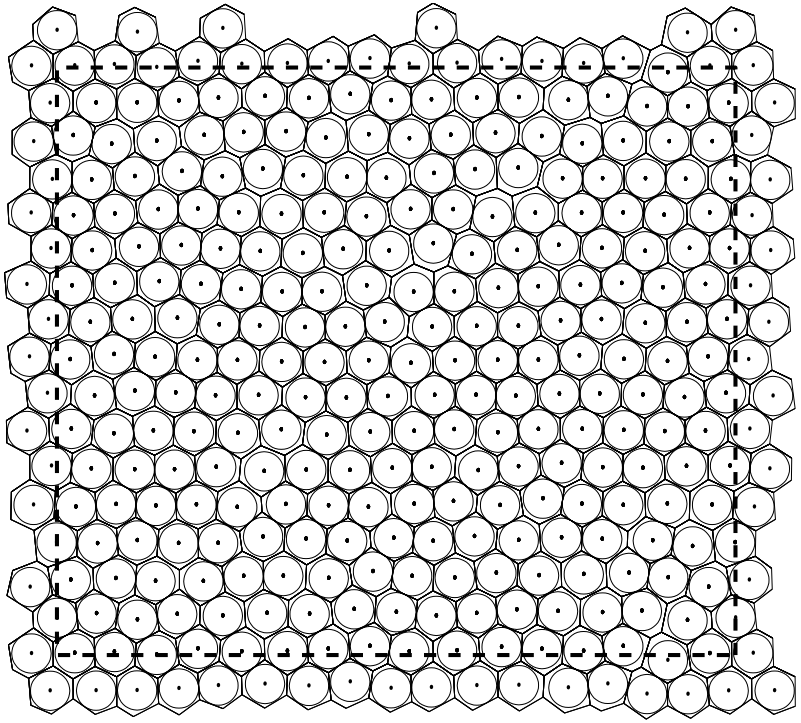
Disordered states:

- Density $\sim$ crystalline state.
- Created by rapid quenching.
- *Thermodynamic or dynamical phenomenon?*
- Free volume theories — structural arrest when *free volume* vanishes.
- *Statistical theory of structural geometry.*
- *Relation to thermodynamic measures.*

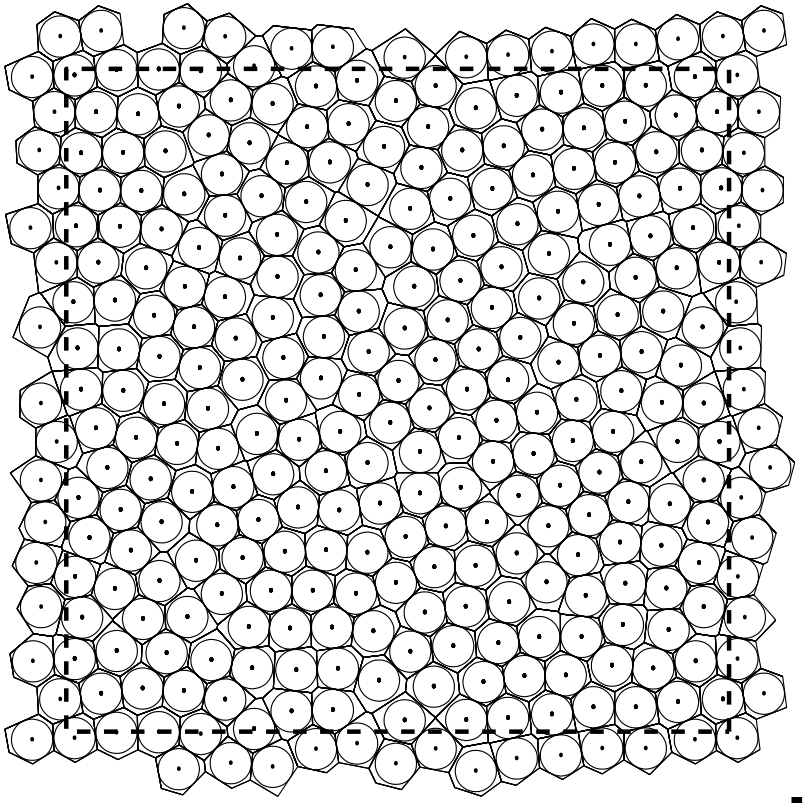


Structural characteristics of dense hard particle assemblies.

Ordered state $\nu = 0.78$:



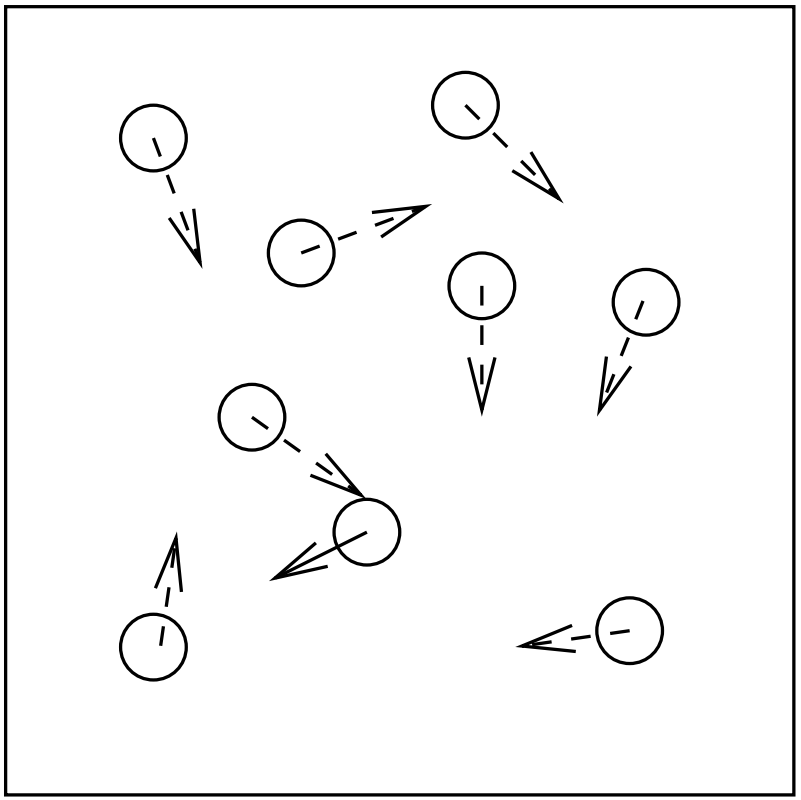
Disordered state $\nu = 0.78$:



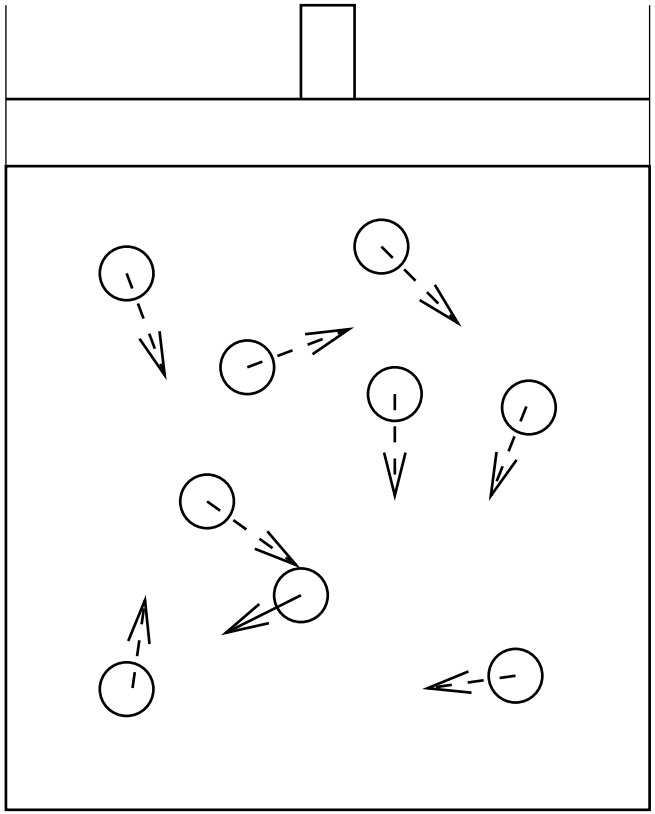
Relation to thermodynamics.

Simulation techniques

Monte Carlo NVE



Monte Carlo NPT



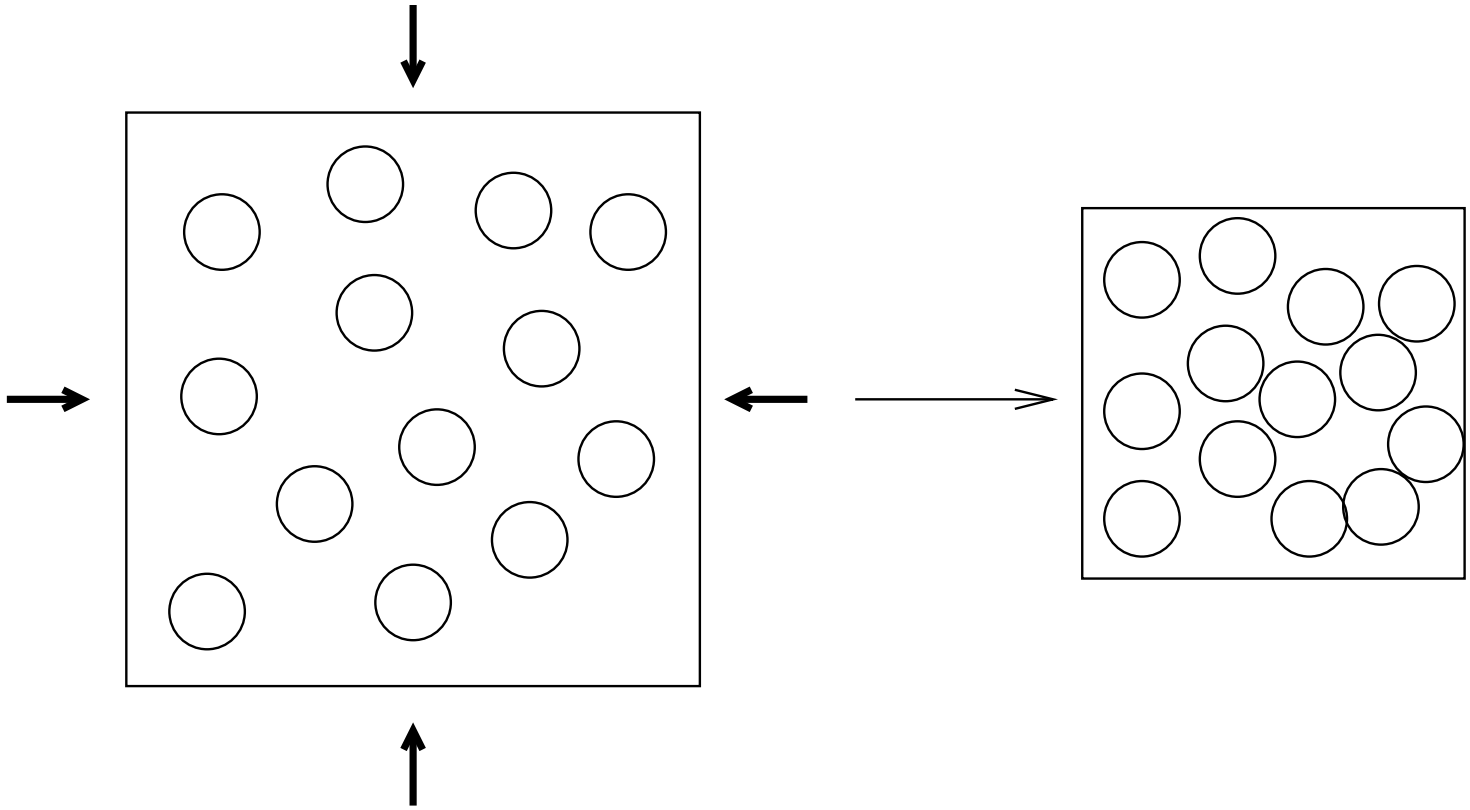
Creation of disordered solids:

Soft particle fluids:

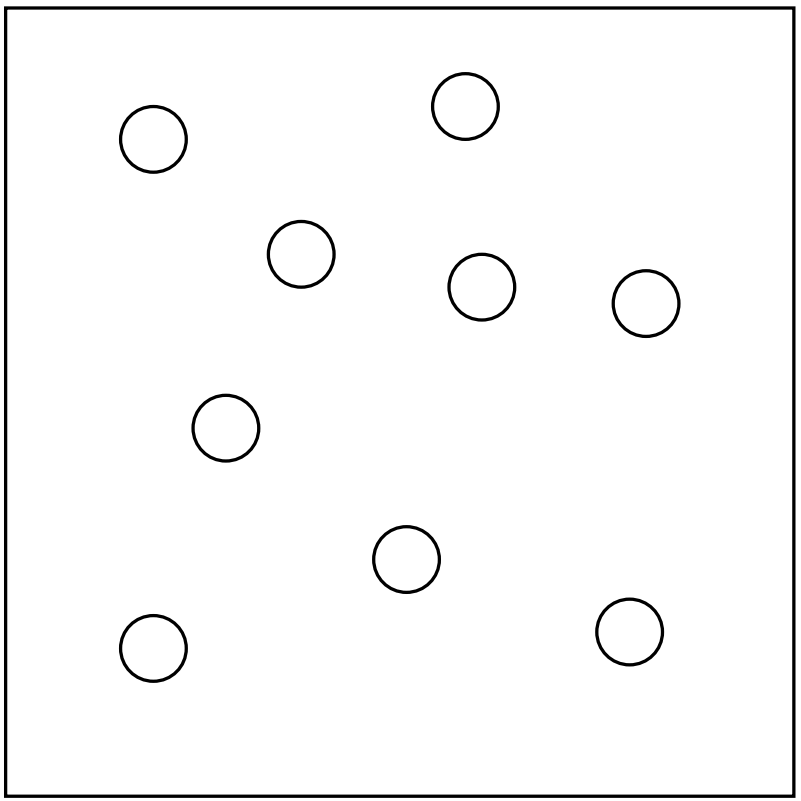
Quench (lower temperature) without permitting system to equilibrate to a crystal.

Hard particle fluids:

Compress (reduce volume) without permitting system to equilibrate to a crystal.

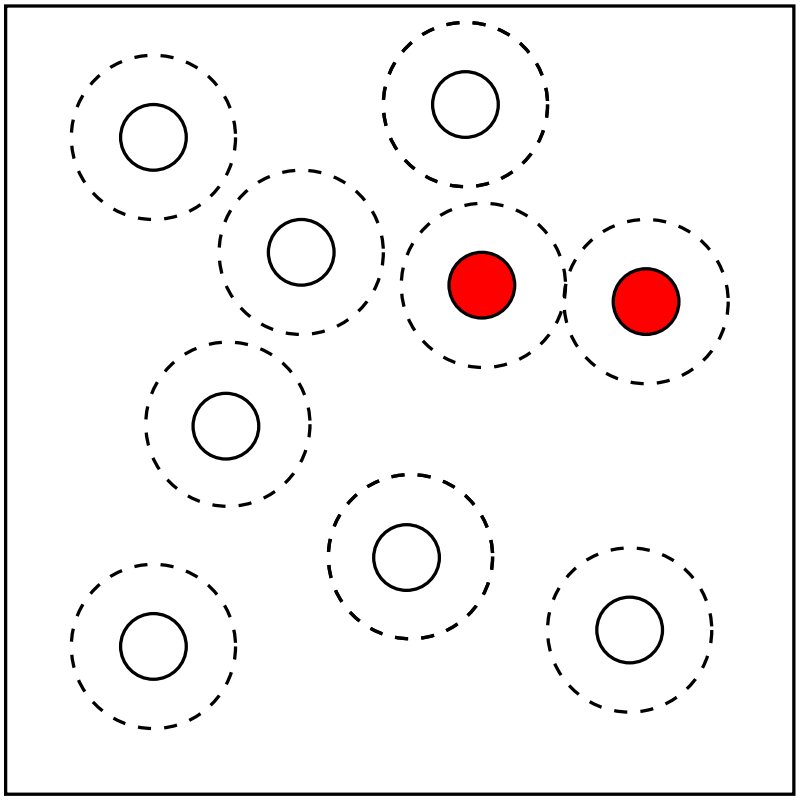


Swelling algorithm



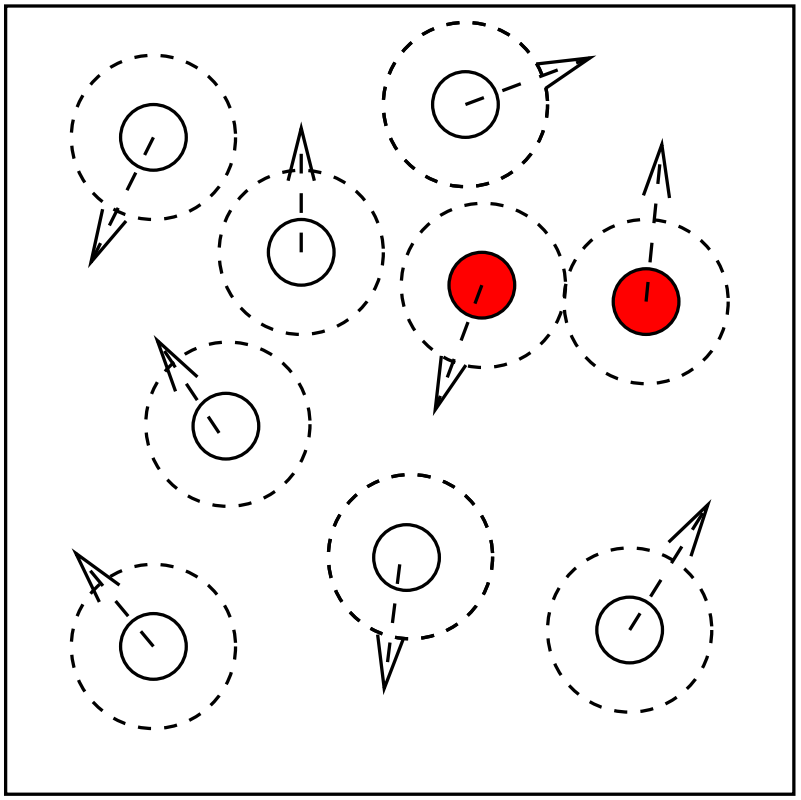
Initial configuration

Swelling algorithm



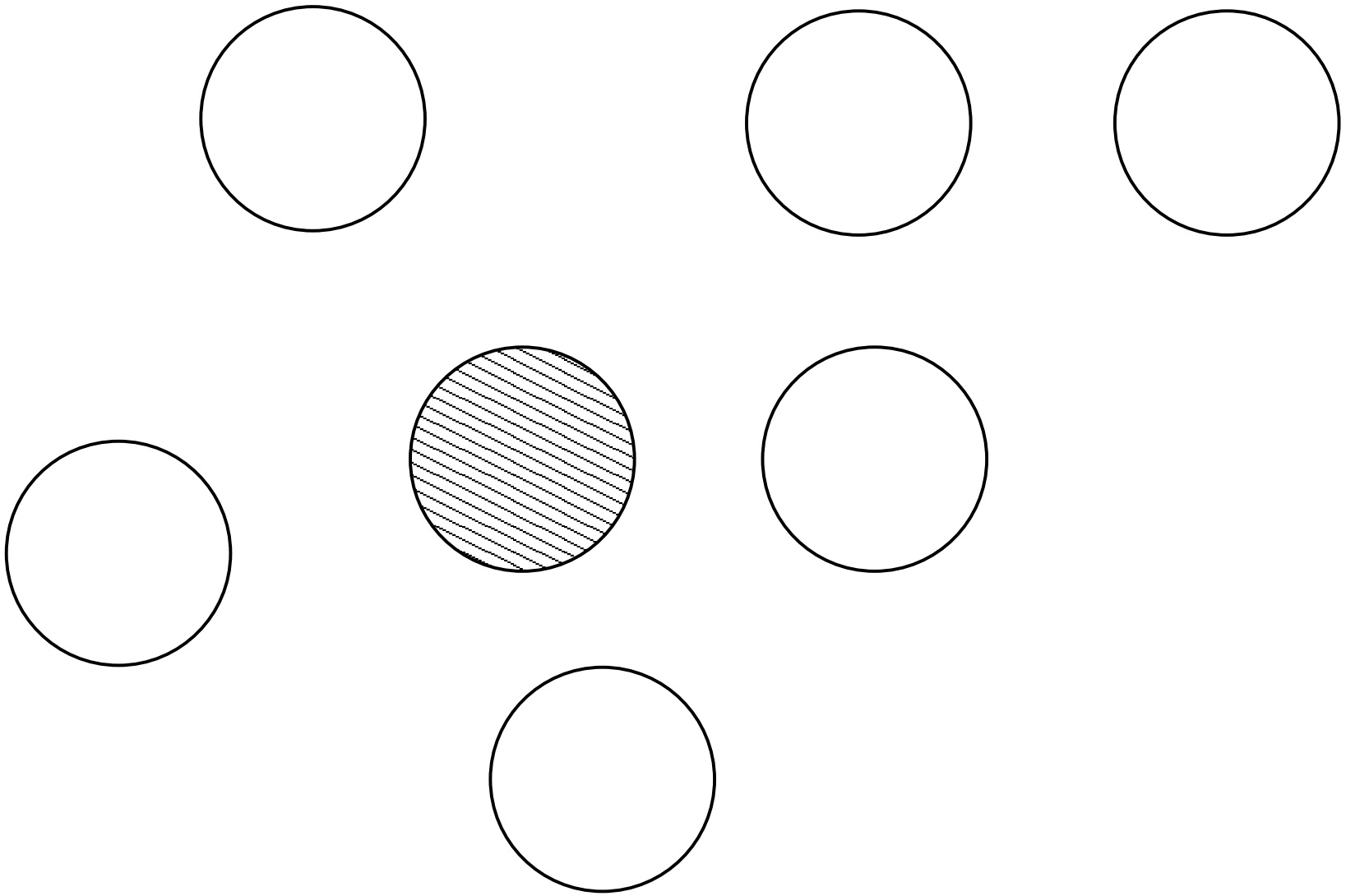
Swell all particles till the surfaces of two particles touch.

Swelling algorithm

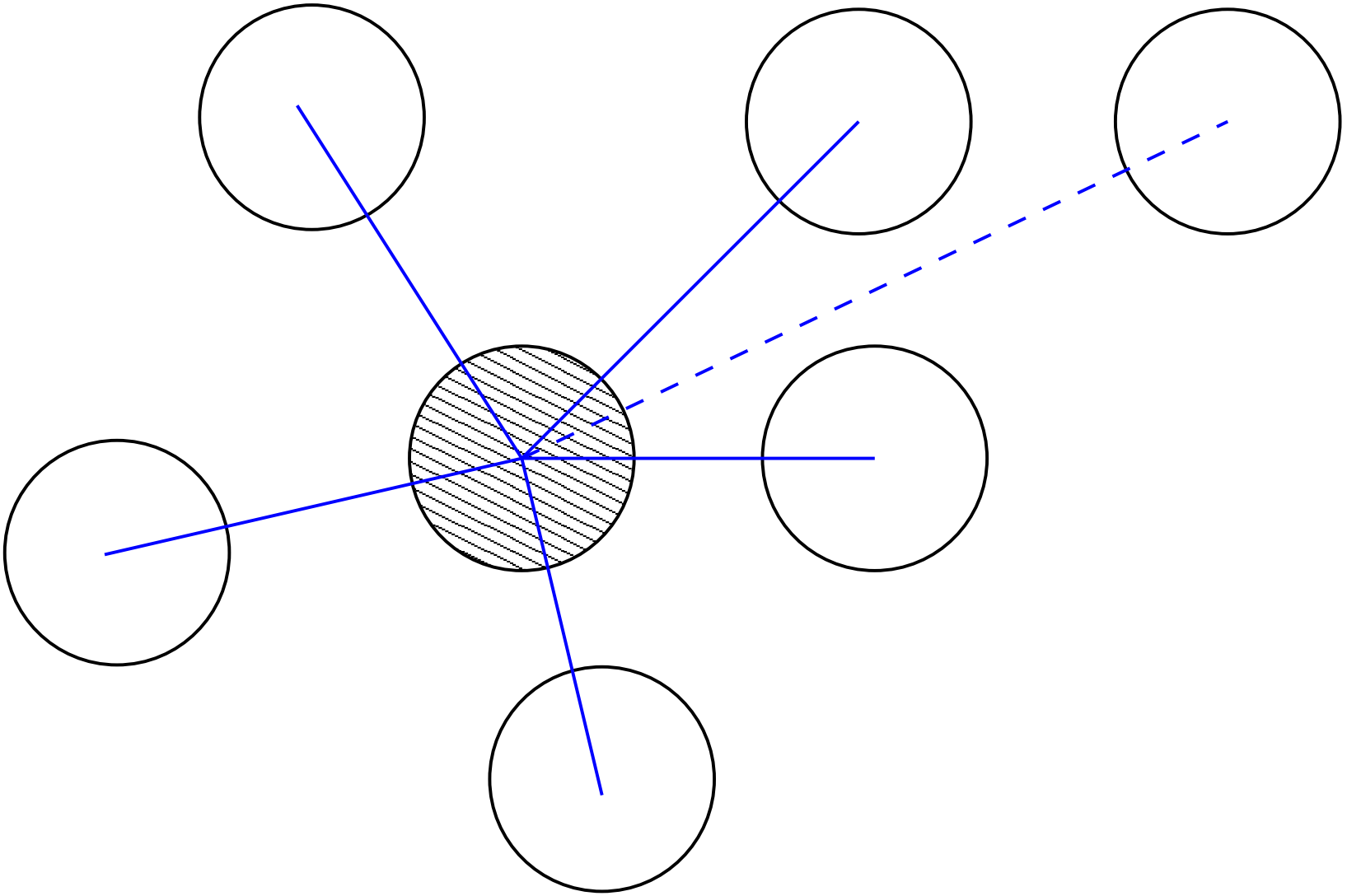


Effect a random Monte-Carlo move to attain a pre-specified acceptance rate.

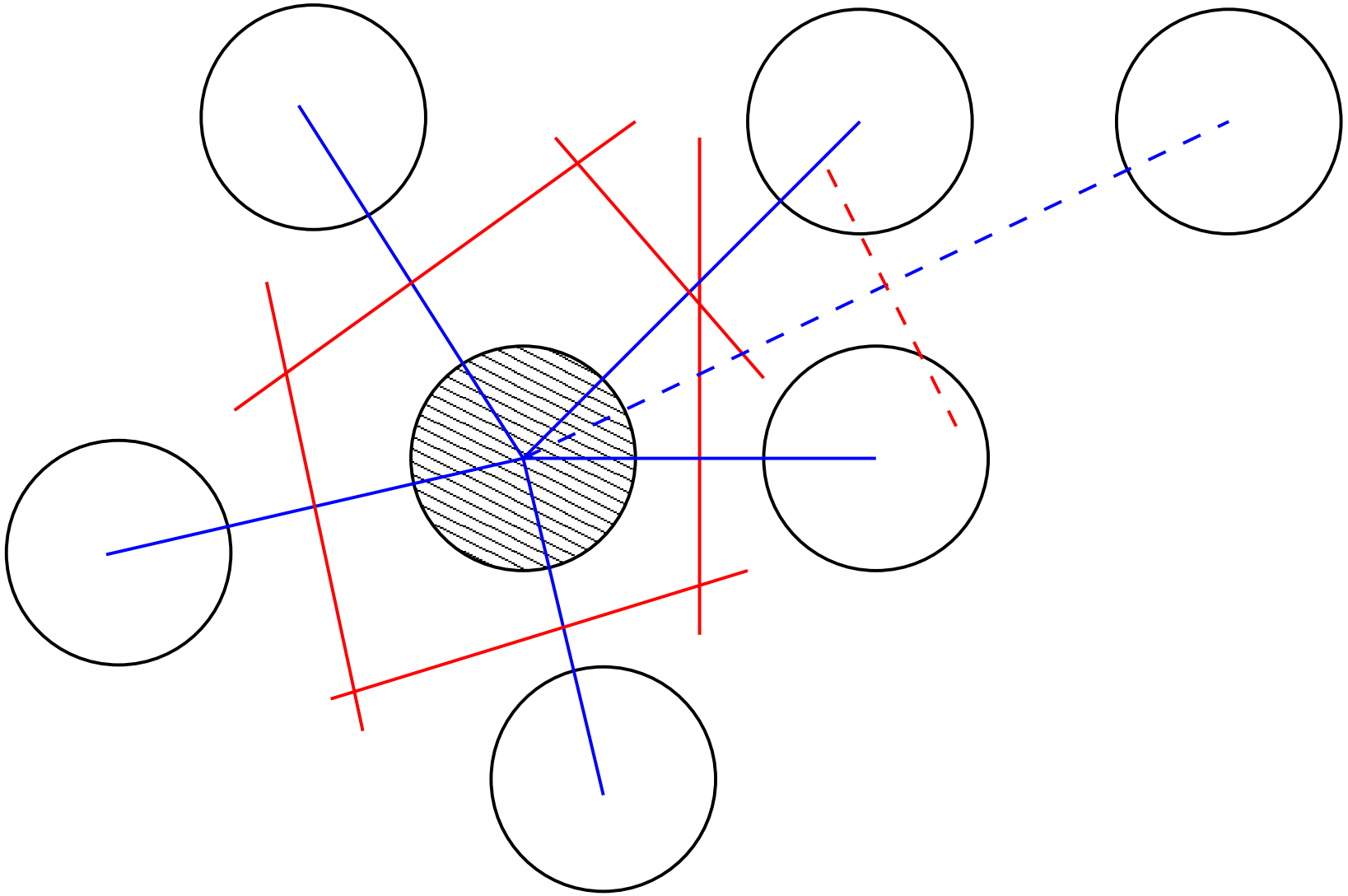
Voronoi volume construction



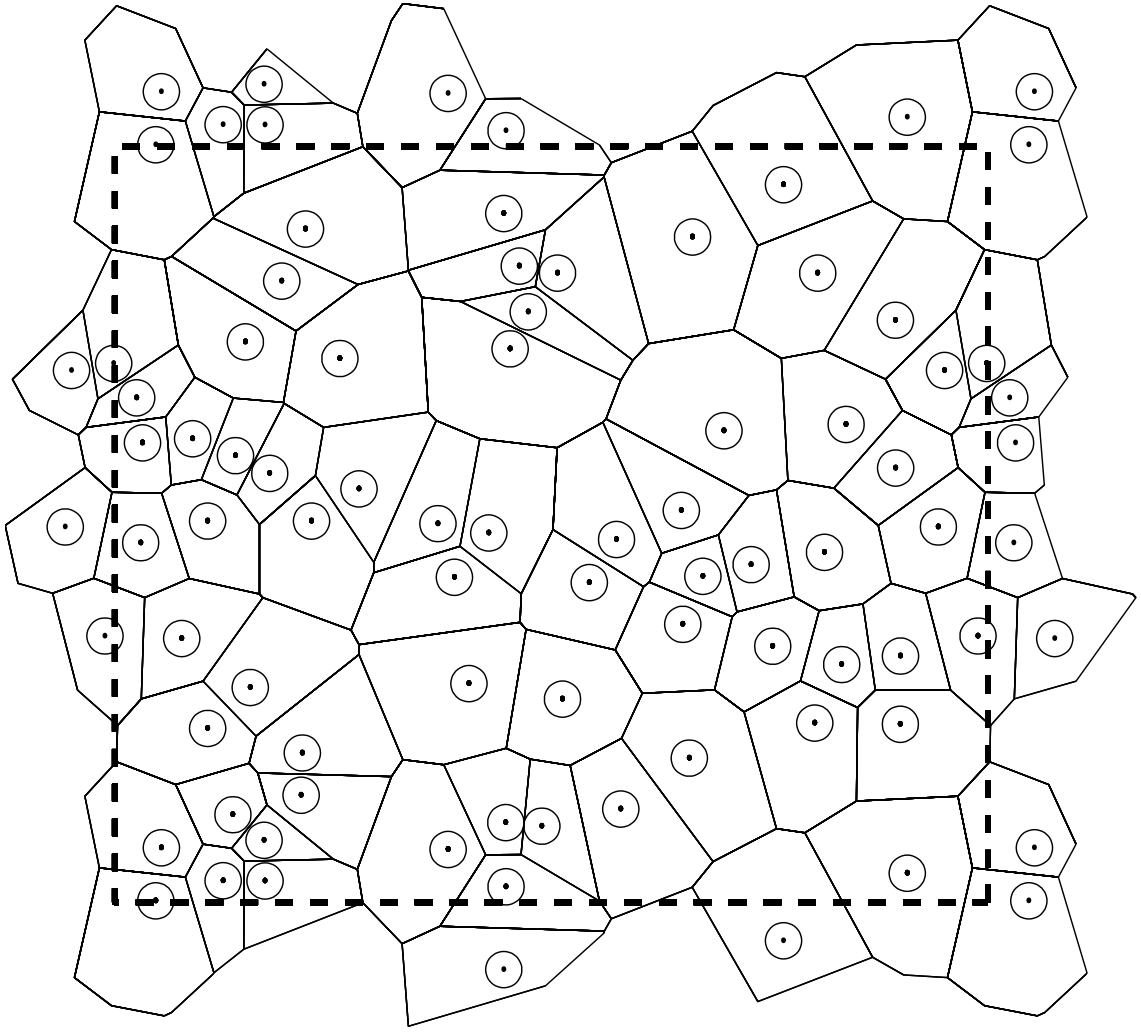
Voronoi volume construction



Voronoi volume construction

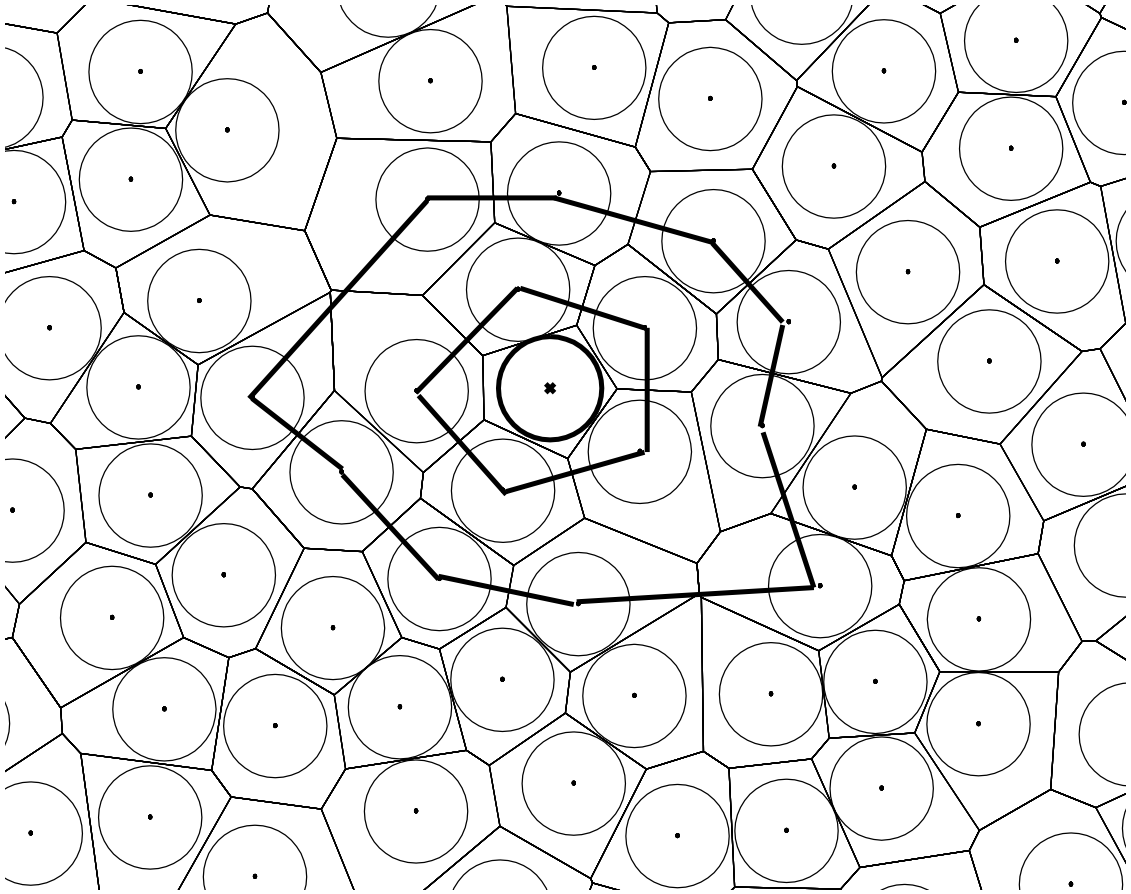


Voronoi tessellation



Precise definition of n^{th} neighbour coordination number C_n

Precise definition of probability of finding n first neighbours P_n.

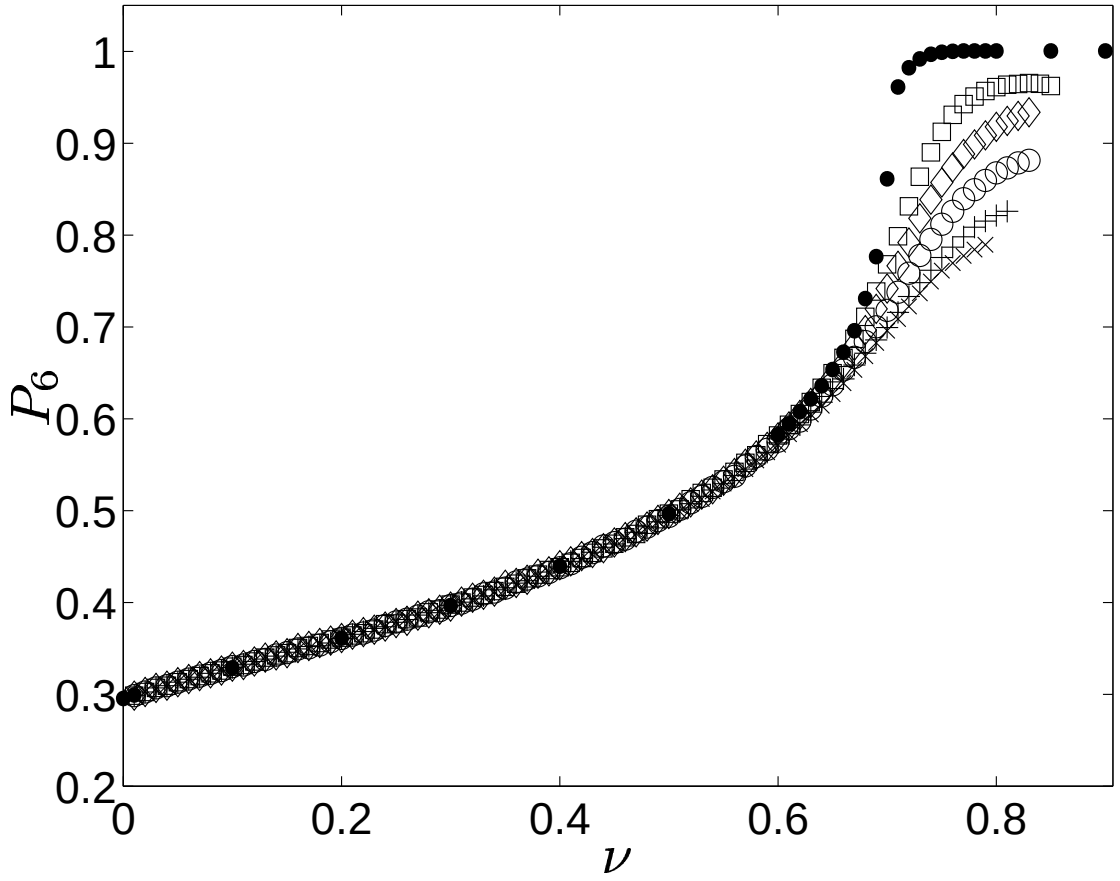


Results

1. Neighbour distributions.
2. Free volume distributions.
3. Free volume entropy & thermodynamic entropy.

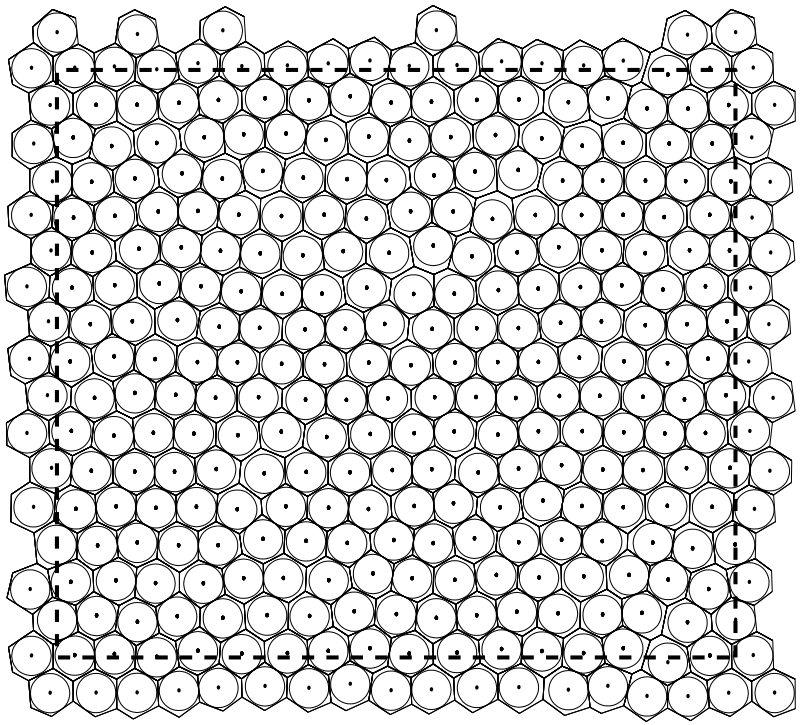
Neighbour statistics 2D

P_6 Probability of 6 faces.

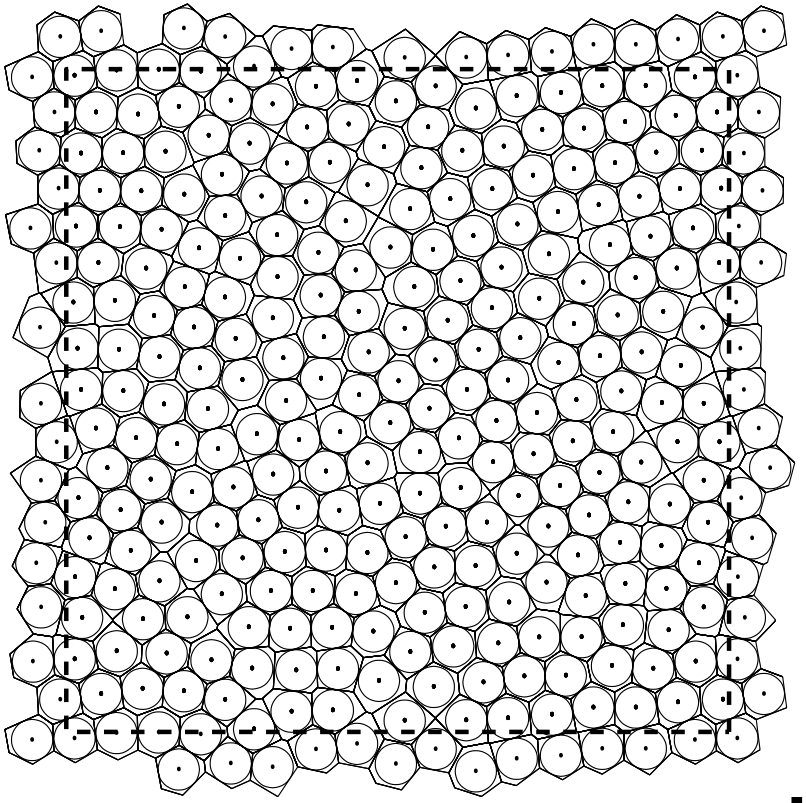


Equilibrium (●).
Swelled random configurations.
10% ().
30% (◇).
50% (○).
70% (+).
90% (×).

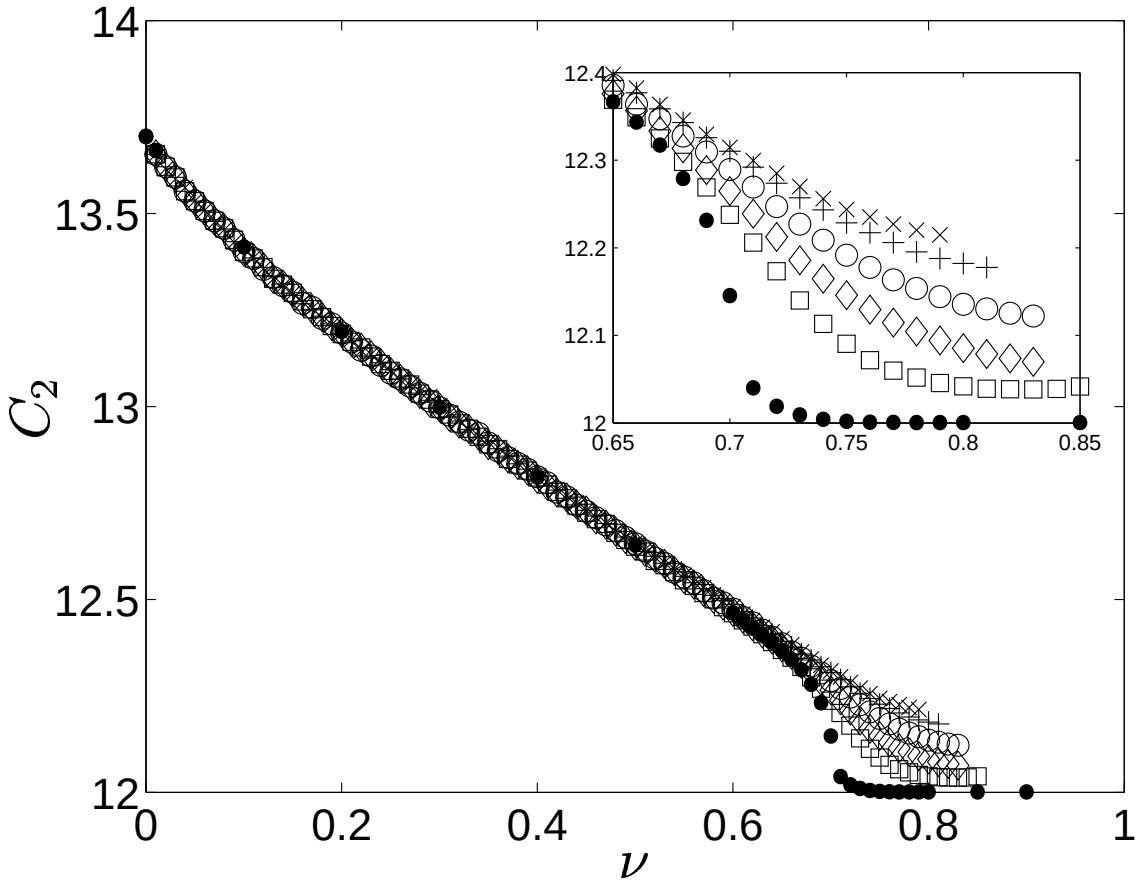
Ordered state $\nu = 0.78$:



Swelled random 50% $\nu = 0.78$:

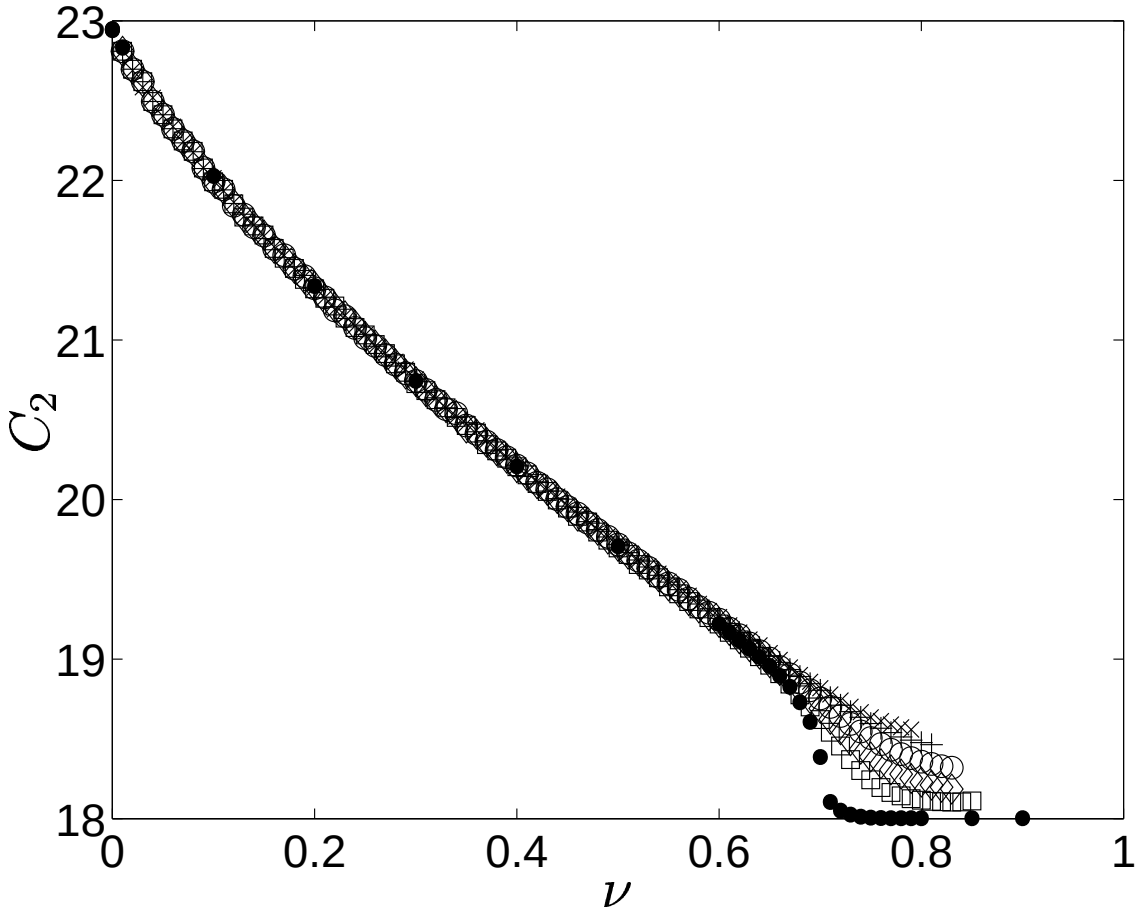


Second neighbour coordination number C_2 (2D):



Equilibrium (●).
Swelled random configurations.
10% ().
30% (◇).
50% (○).
70% (+).
90% (×).

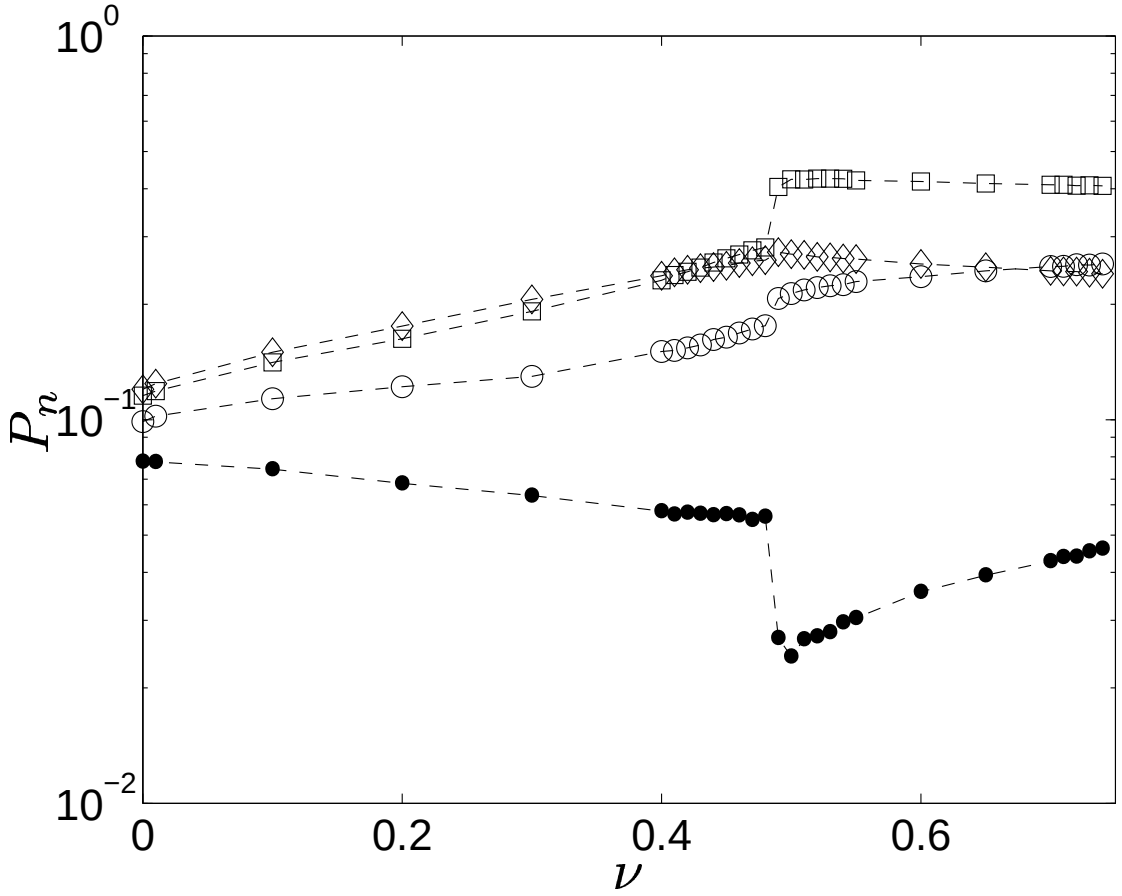
Third neighbour coordination number C_3 2D:



Equilibrium (●).
Swelled random configurations.
10% ().
30% (◇).
50% (○).
70% (+).
90% (×).

Neighbour statistics 3D

P_n Probability of n faces.



Equilibrium:

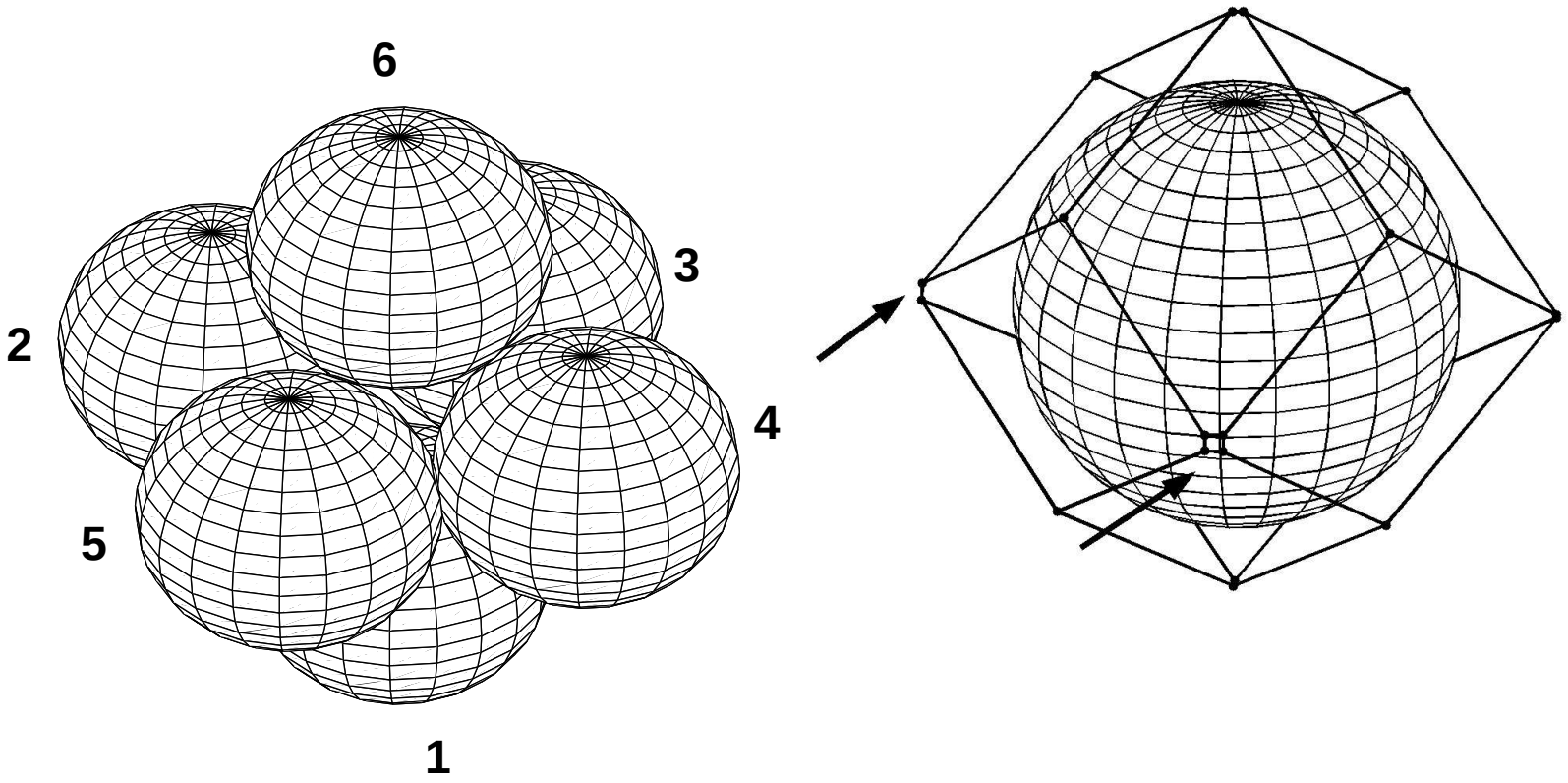
n =12 (●)

n =13 (○)

n =14 ()

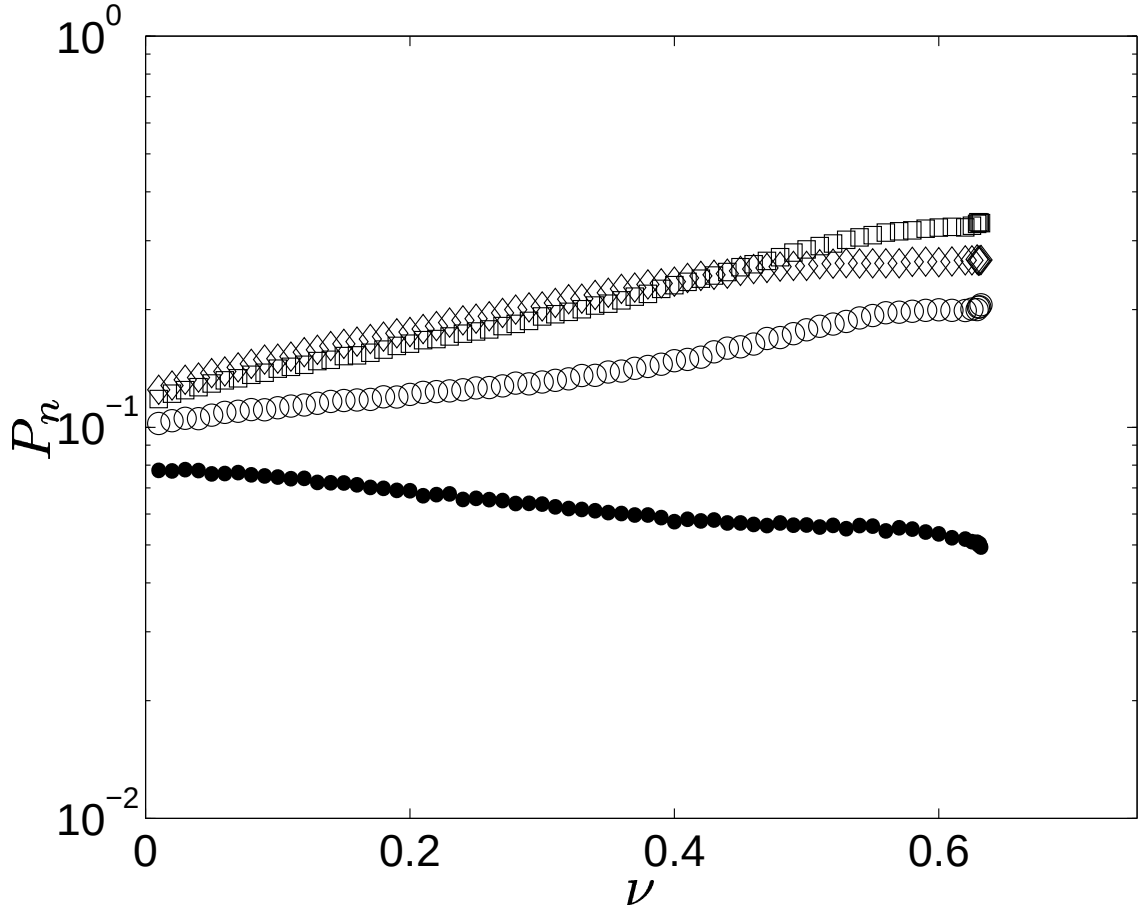
n =15 (◇)

Topological instability of FCC lattice:



Neighbour statistics 3D

P_n Probability of n faces.



Swollen random 50%:

n =12 (●)

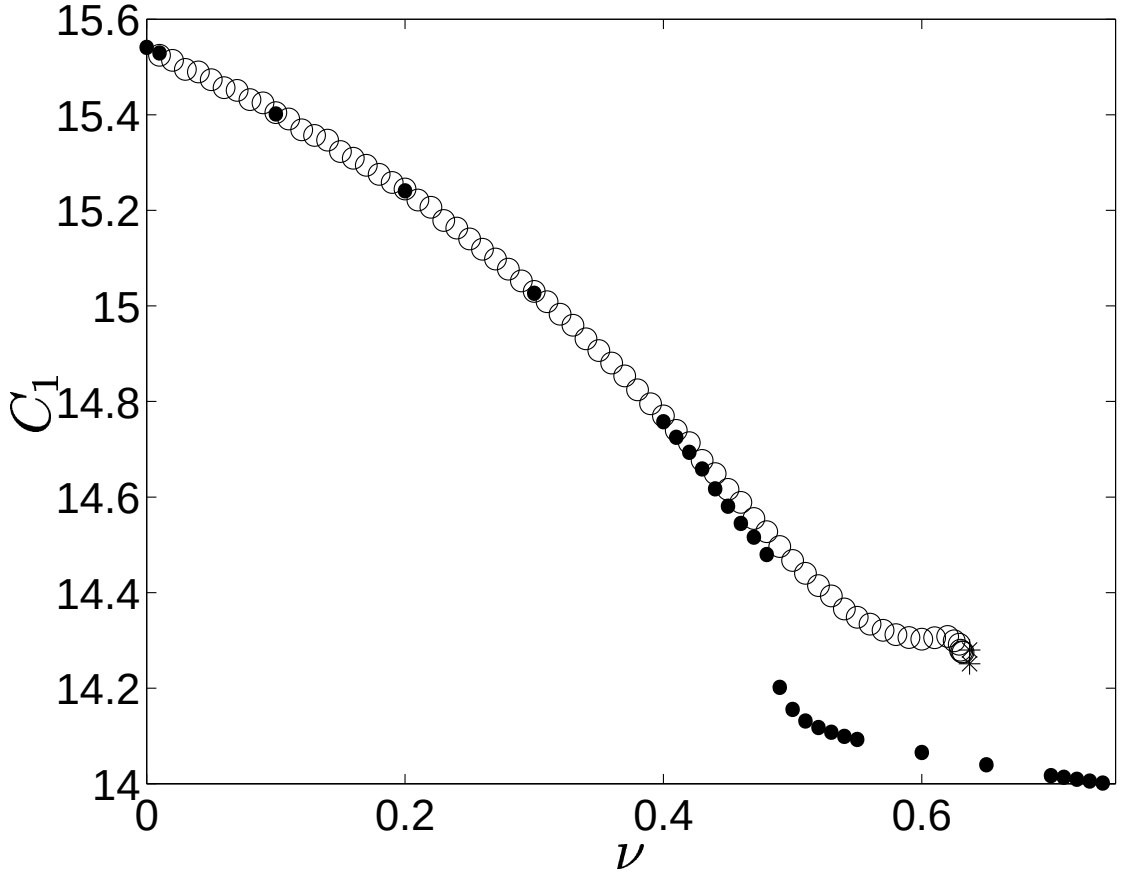
n =13 (○)

n =14 ()

n =15 (◇)

Neighbour statistics 3D

C_1 Nearest neighbour coordination number.

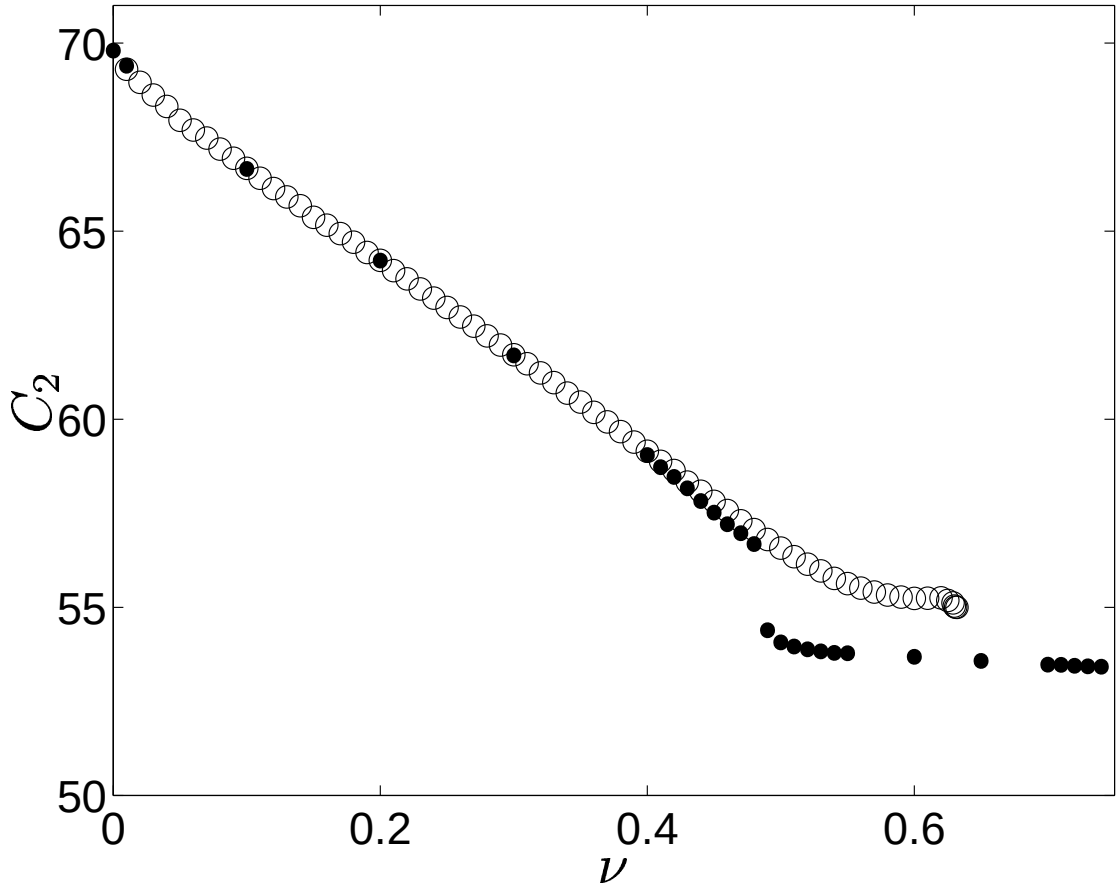


(•) Equilibrium

(○) Swelled random 50%

Neighbour statistics 3D

C_2 Second nearest neighbour coordination number.



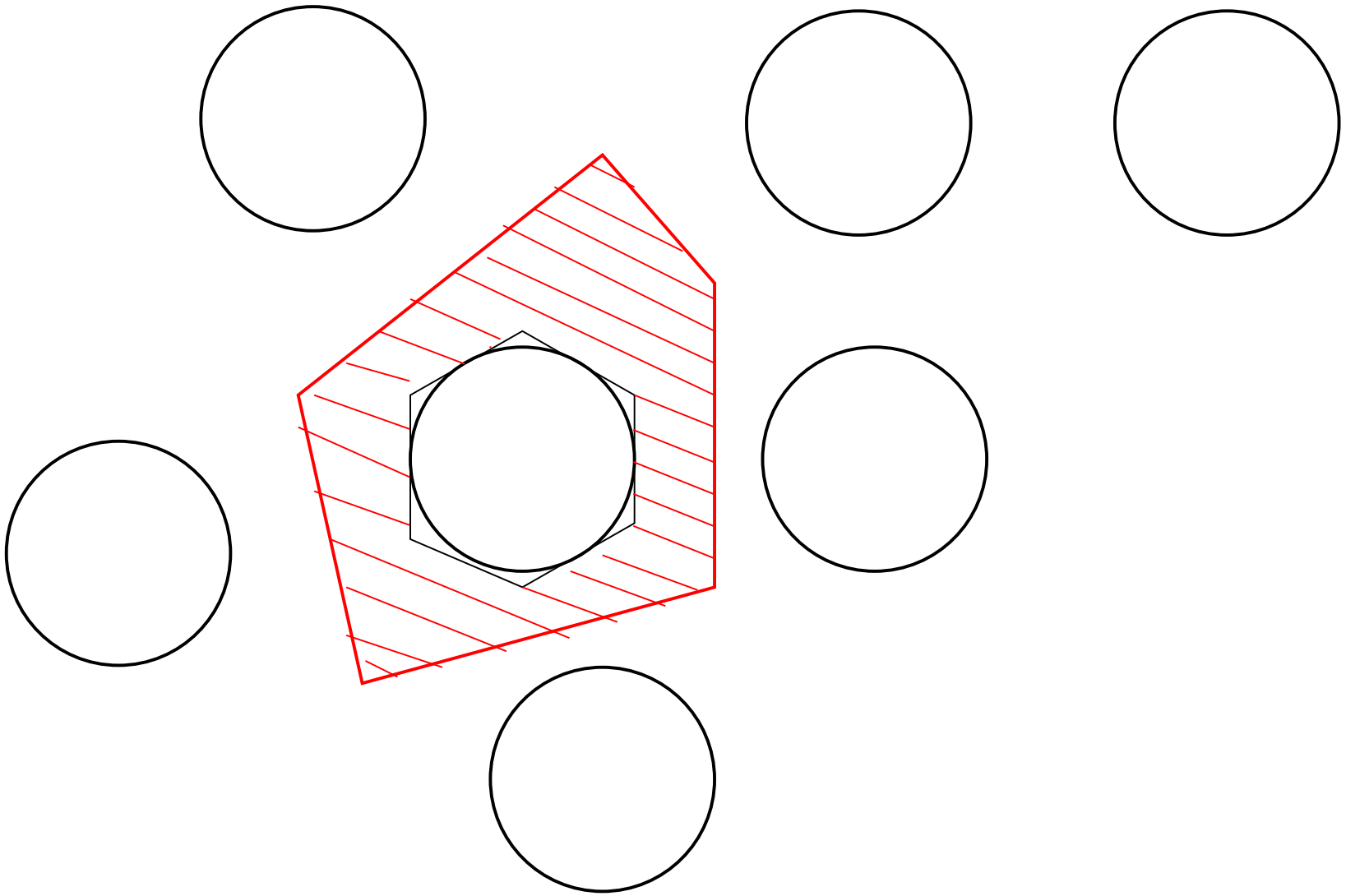
(•) Equilibrium

(○) Swelled random 50%

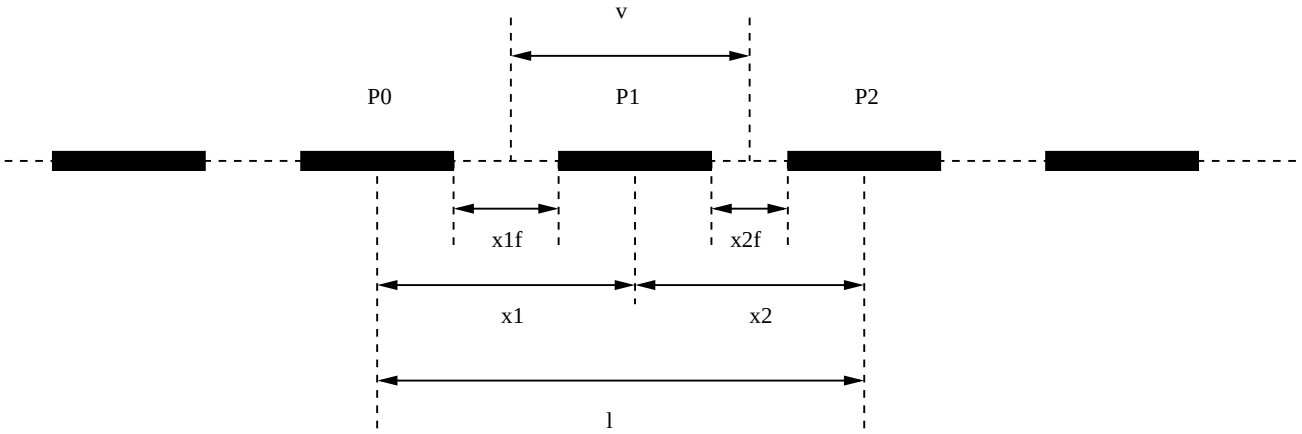
Conclusions:

- Neighbour coordination number sensitive to structure.
- 'Crystallisation' at finite volume fraction in two dimensions for equilibrium simulations.
- Topological instability in three dimensions in equilibrium simulations.
- Random structures have coordination numbers very different from equilibrium structures.

Free volume v^* computation



Free volume distribution in 1D:



Nearest neighbor distance distribution function $f(x)$ (Fisher 1964):

$$f(x) = \begin{cases} 0 & \text{if } x < \sigma; \\ \frac{1}{(\overline{v}-\sigma)} \exp\left[-\frac{(x-\sigma)}{(\overline{v}-\sigma)}\right] & \text{if } x \geq \sigma. \end{cases} \quad (1)$$

Can derive length distribution:

$$f(l) = a^2 l \exp(-a\, l). \quad (2)$$

Gamma function with $m = 2$.

Free volume distribution

- Two parameter Gamma

$$f(v^*) = \frac{\alpha^m}{\Gamma(m)} v^{*(m-1)} e^{(-\alpha v^*)}$$

- One parameter α fixed by the density,

$$\overline{v^*} = (\alpha/m)$$

- 'Regularity' parameter m

$$m = \left(\frac{\overline{[(v^* - \overline{v^*})^2]}}{\overline{v^*}^2} \right)^{-1}$$

- Three parameter Gamma

$$f(v^*) = \frac{\delta \alpha^{\frac{m}{\delta}}}{\Gamma(\frac{m}{\delta})} \, v^{*(m-1)} \, e^{-\alpha v^{*\delta}}$$

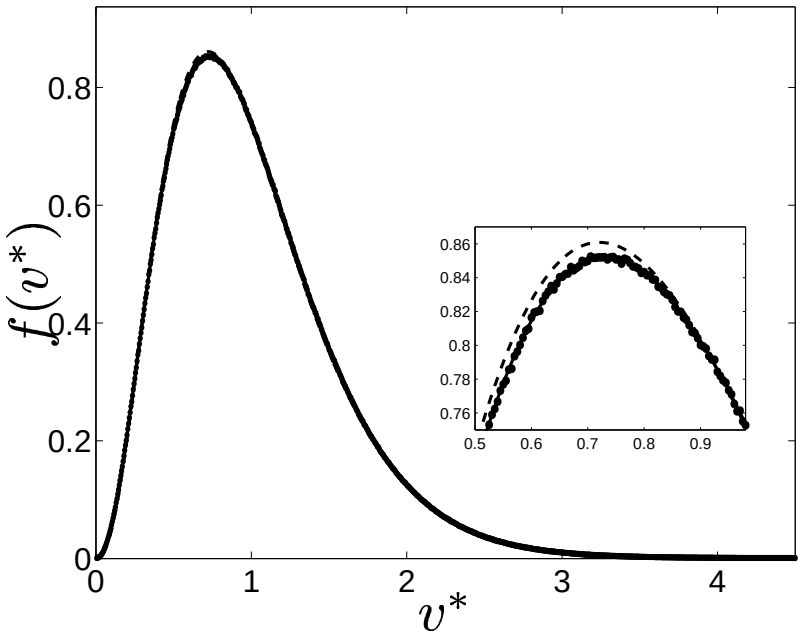
- One parameter fixed by

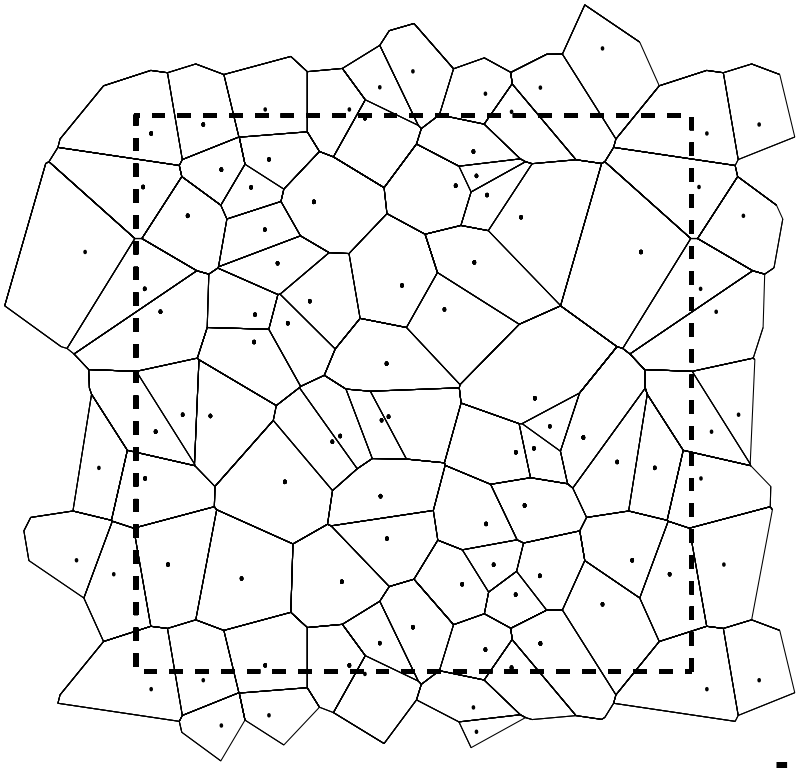
$$\overline{v^*} = \frac{\Gamma\left(\frac{m+1}{\delta}\right)}{\Gamma\left(\frac{m}{\delta}\right) \alpha^{\frac{1}{\delta}}}$$

- Regularity parameter

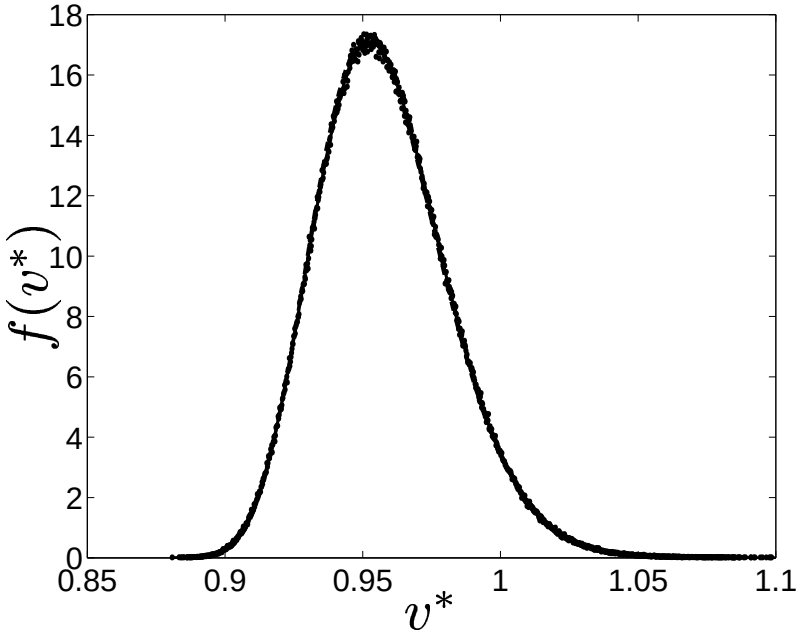
$$\delta m \approx \left(\frac{\overline{[(v^* - \overline{v^*})^2]}}{\overline{v^*}^2} \right)^{-1}$$

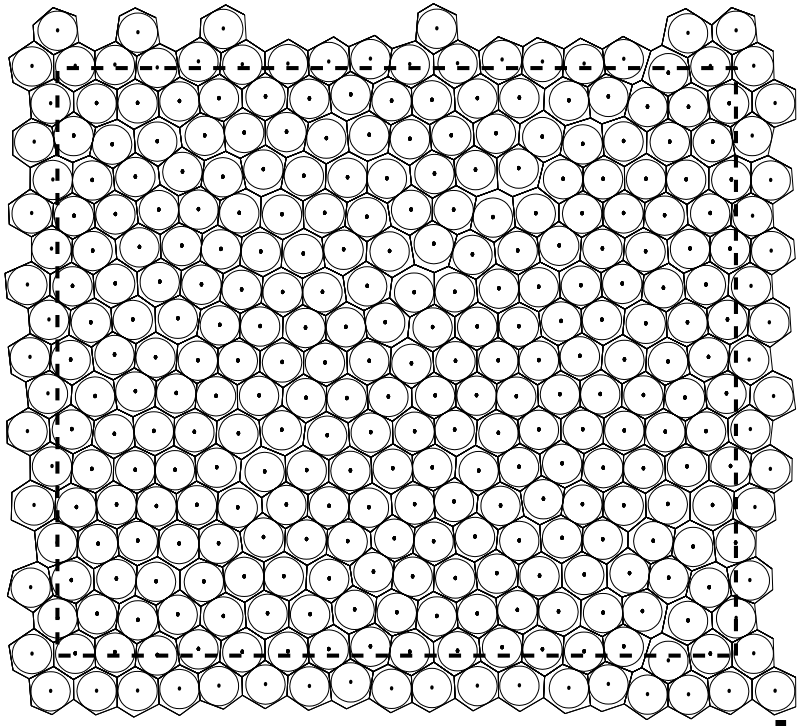
Dilute limit:



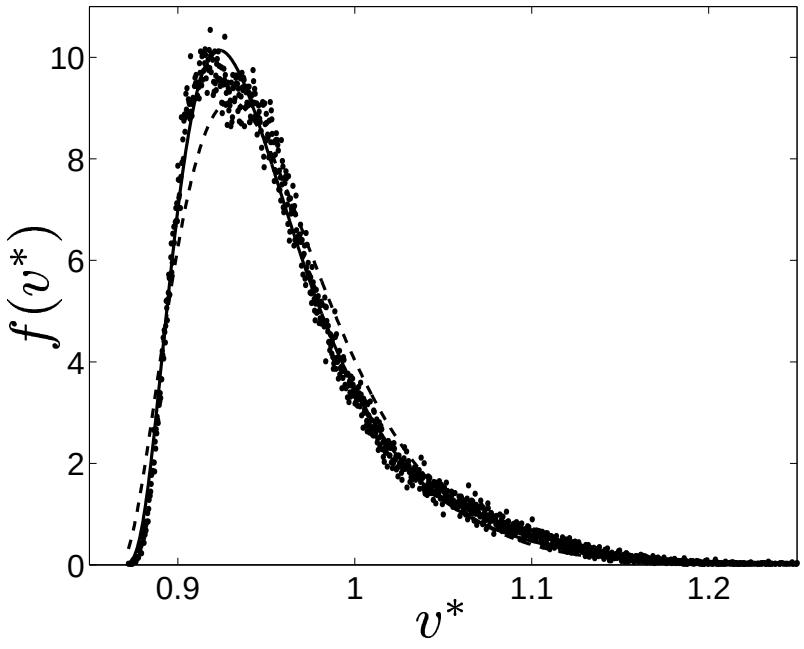


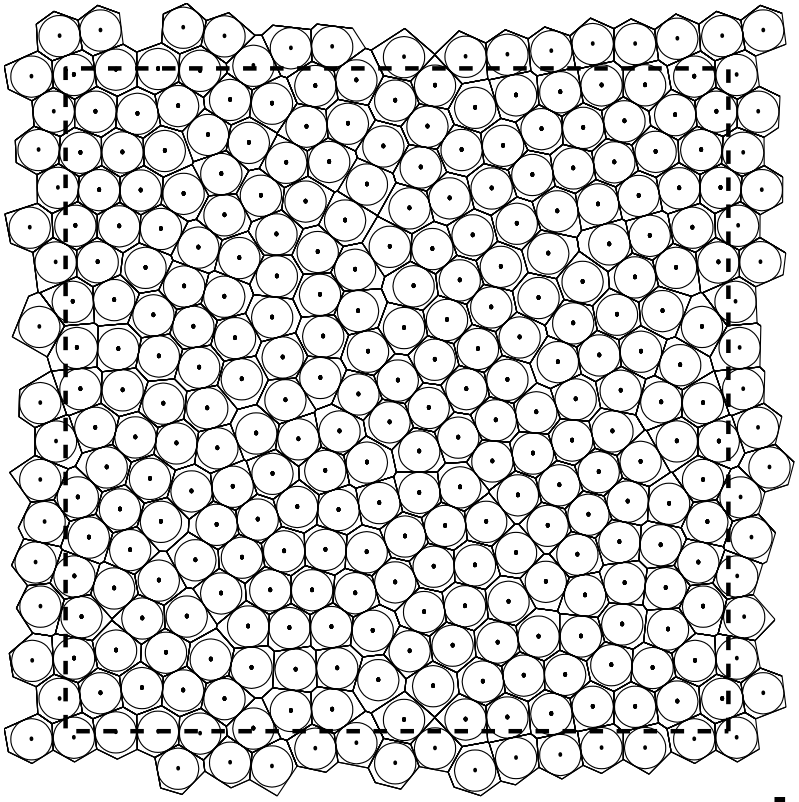
Dense equilibrium structures (Area fraction 0.78):





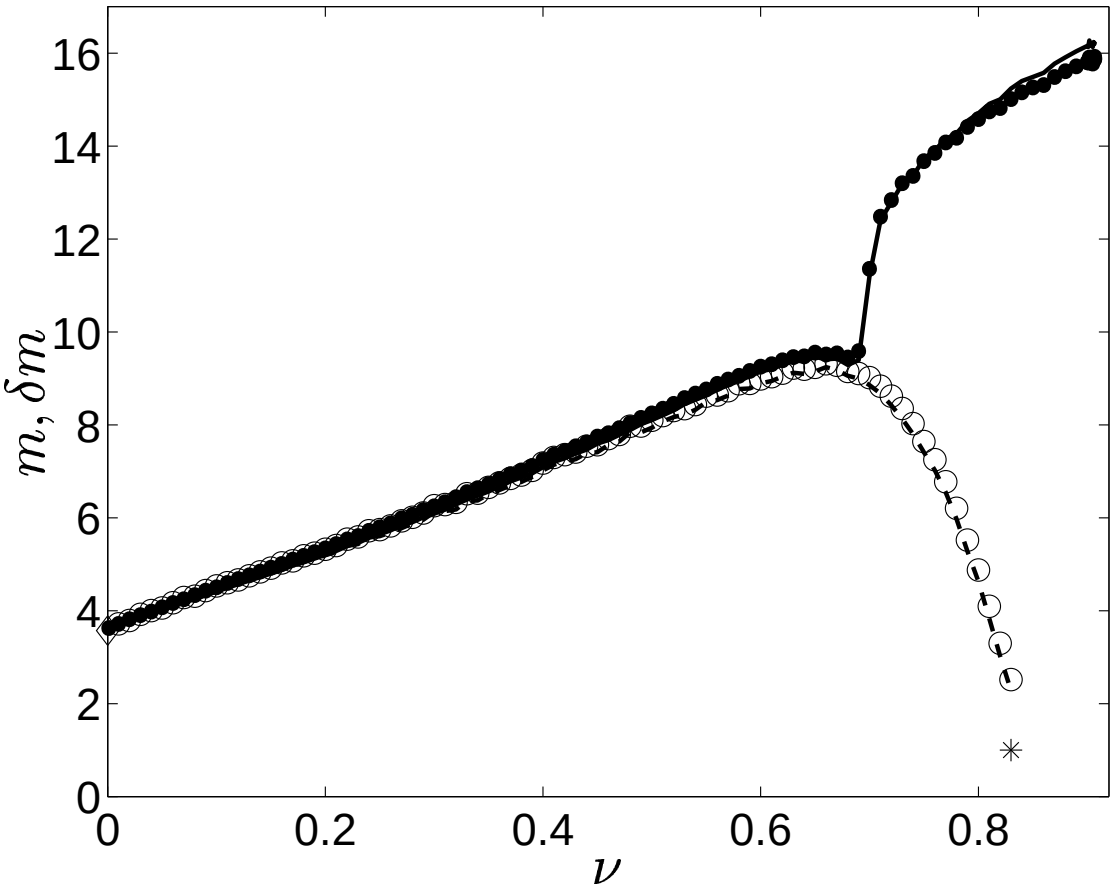
Dense random structures (Area fraction 0.78):





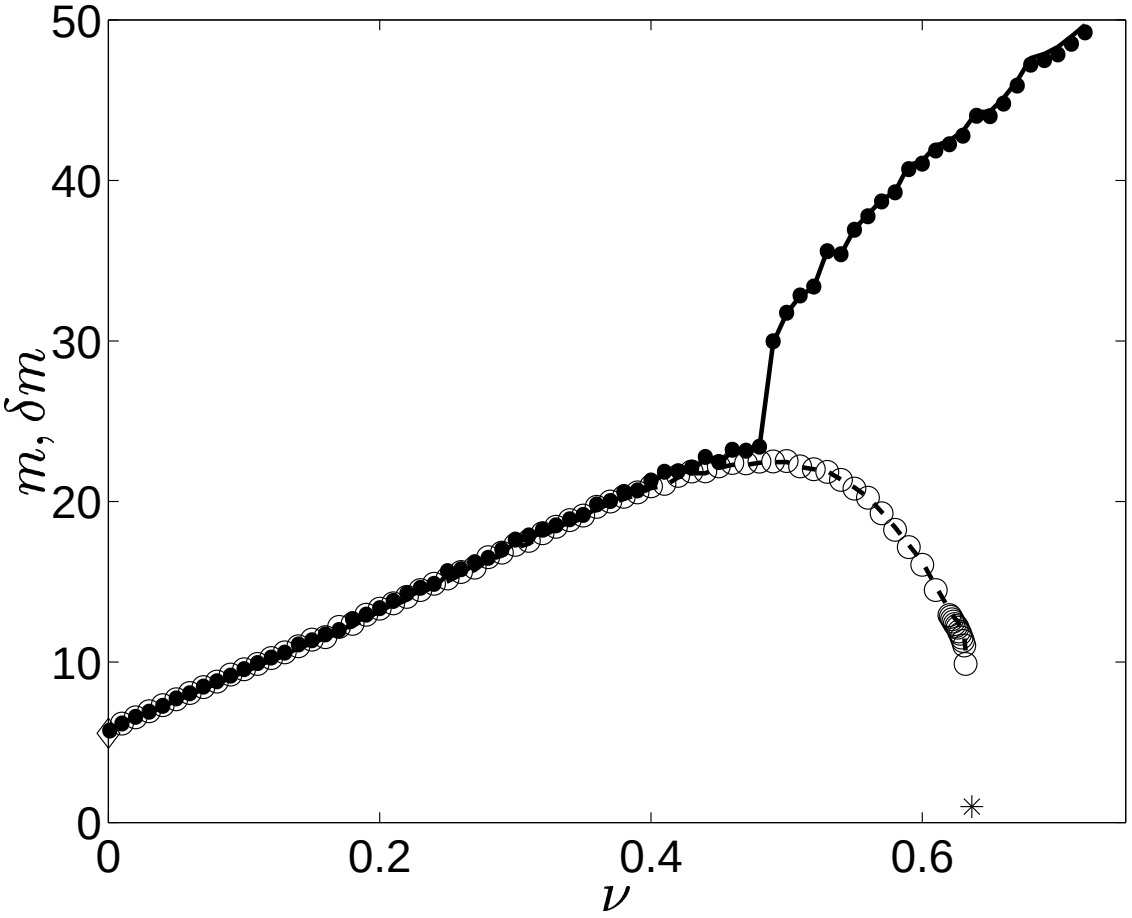
Variation of regularity factor with density

2 Dimensions, 256 particles, 1000 configurations for each point.



Variation of regularity factor with density

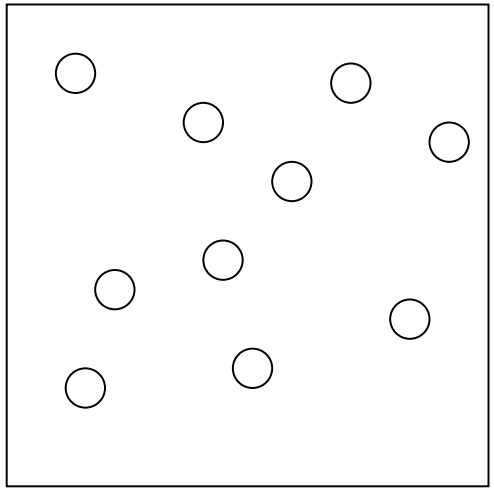
3 Dimensions, 256 particles, 1000 configurations for each point.



Free-volume entropy:

- Conf. entropy (Kirkwood 1950)

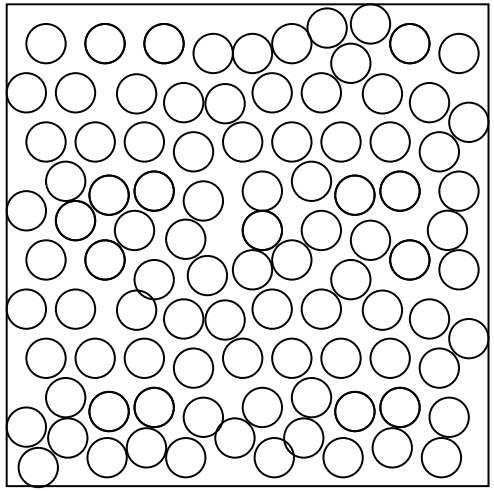
$$s_c = s_{fv} + s_{com}$$



- Free volume entropy:

$$s_{fv} = -k_B \int dv^* f(v^*) \log\left(f(v^*)\right)$$

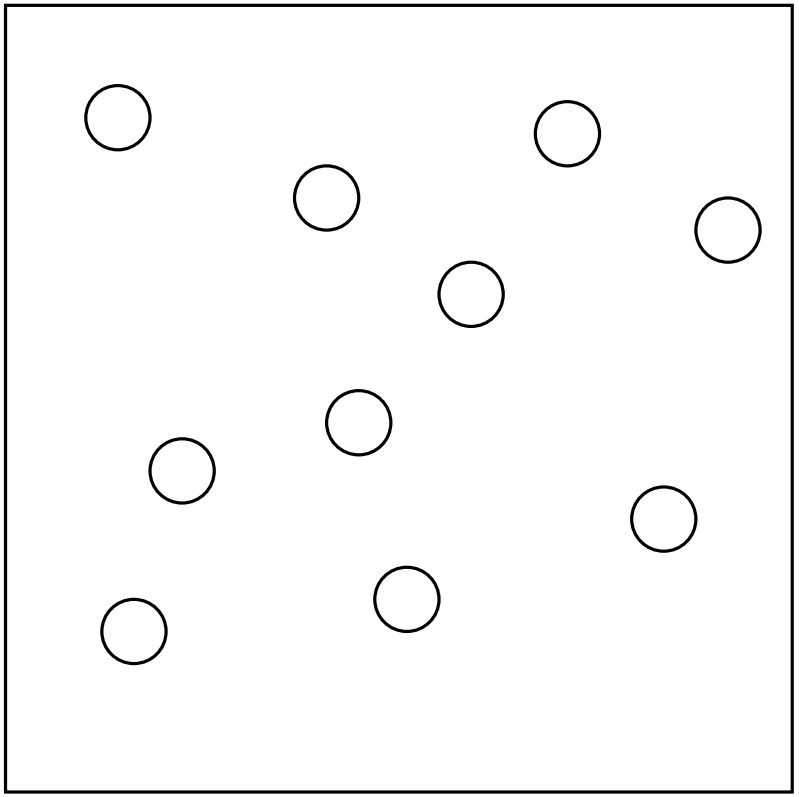
- Communal entropy:
  Motion of particle within liquid clusters.



- Dense limit $s_{com} \to 0$; $s_c = s_{fv}$.
- Excess specific entropy

$$s_c^{ex} = s_c - s_c^{id}$$

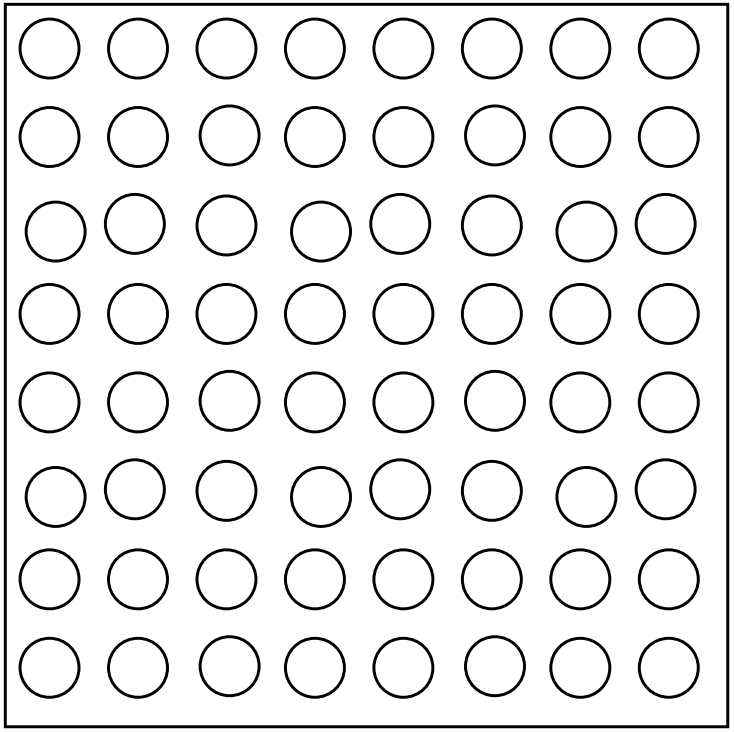
Communal Entropy



N particles, total volume V

Conf integral $Z_N = \frac{V^N}{N!}$

$S_{conf} = Nk_B \log(V/N) + Nk_B$



N particles, specific volume v

Conf integral $Z_N = (V/N)^N$

$S_{conf} = Nk_B \log(V/N)$

Free volume & Thermodynamic entropy

- Free volume entropy

$$s_{fv} = -\lambda k_B \int dv^* f(v^*) \log\left(f(v^*)\right)$$

- Free volume excess entropy

$$s_{fv}^{ex} = s_{fv} - s_{fv}^{id}$$

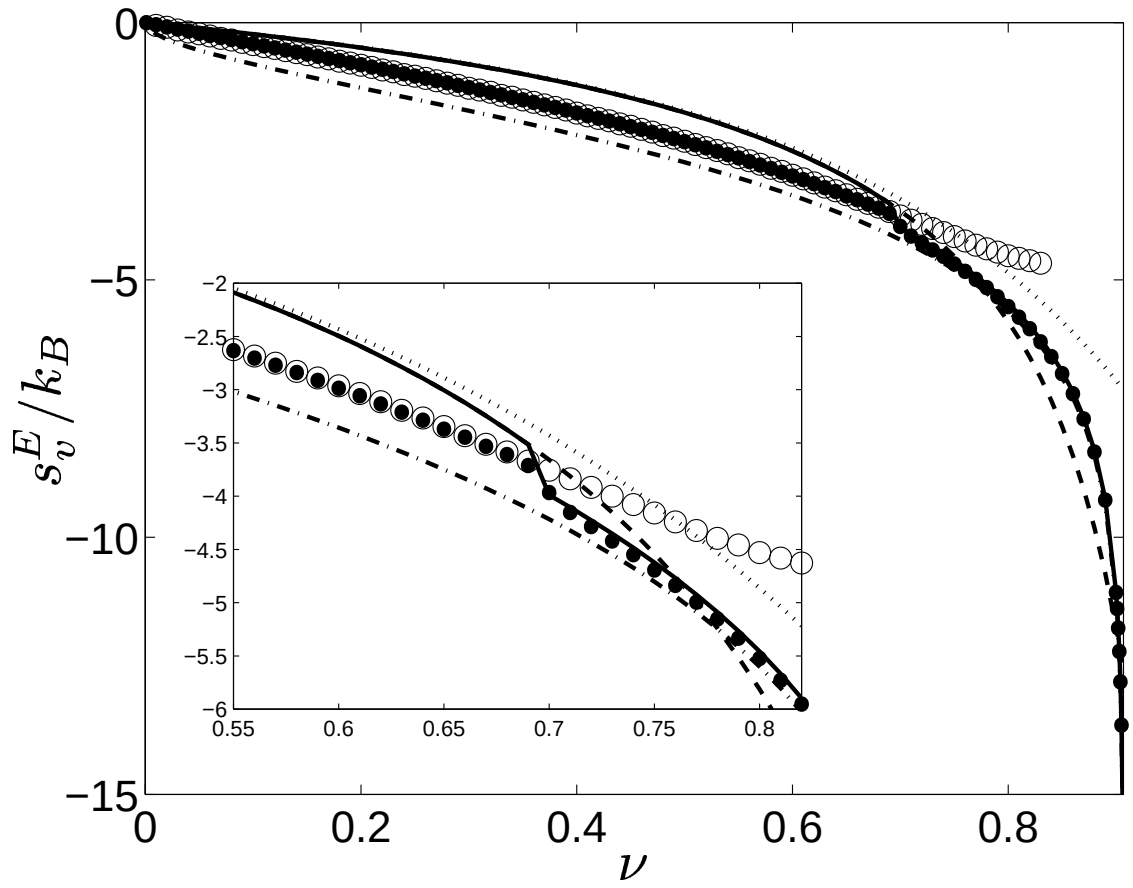
Thermodynamic entropy

- Volume fraction $y = (v_c/\overline{v})$.
- Excess entropy

$$\frac{s^{ex}}{k_B} = -\int_0^y \frac{Z-1}{y} dy.$$

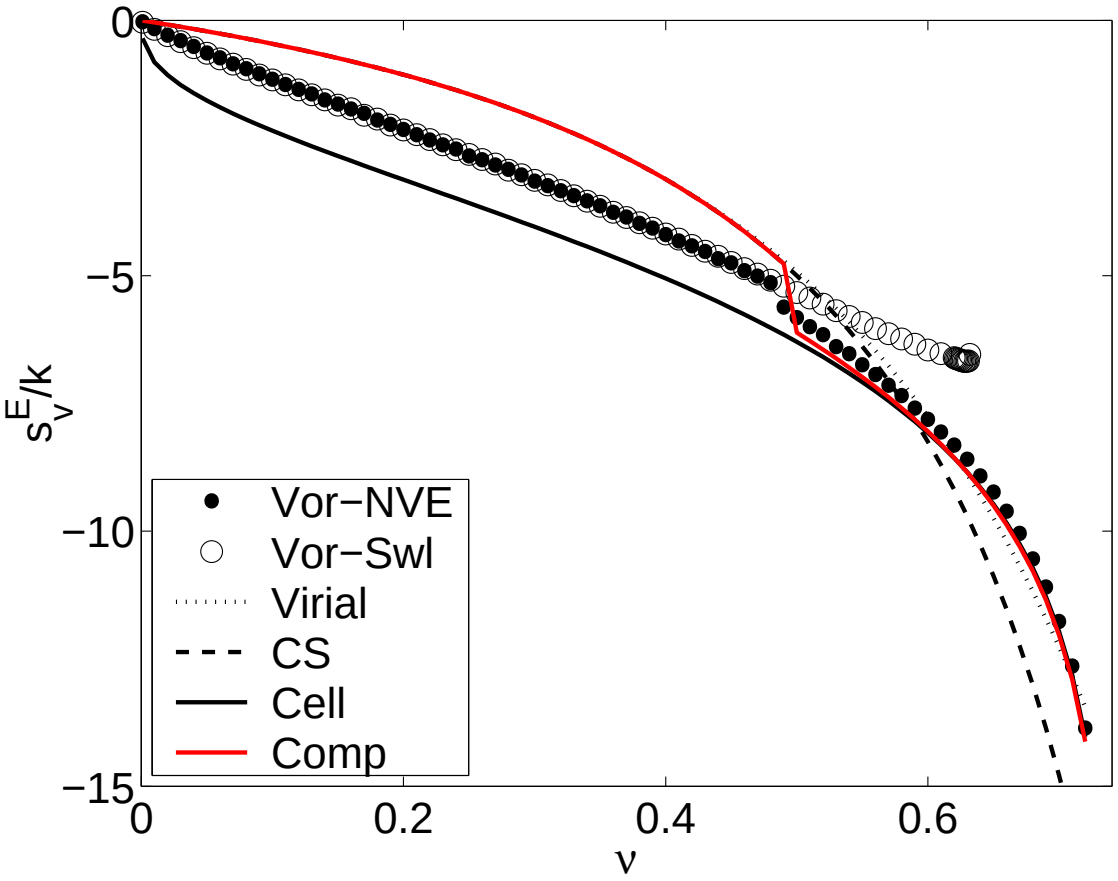
- Configuration integral Z determined from equation of state.

Thermodynamic & Free volume entropy (2D)



Free volume entropy $s_{fv} = -2k_B \int dv^* f(v^*) \log\left(f(v^*)\right)$

Thermodynamic & Free volume entropy (3D)



Free volume entropy $s_{fv} = -3k_B \int dv^* f(v^*) \log\left(f(v^*)\right)$

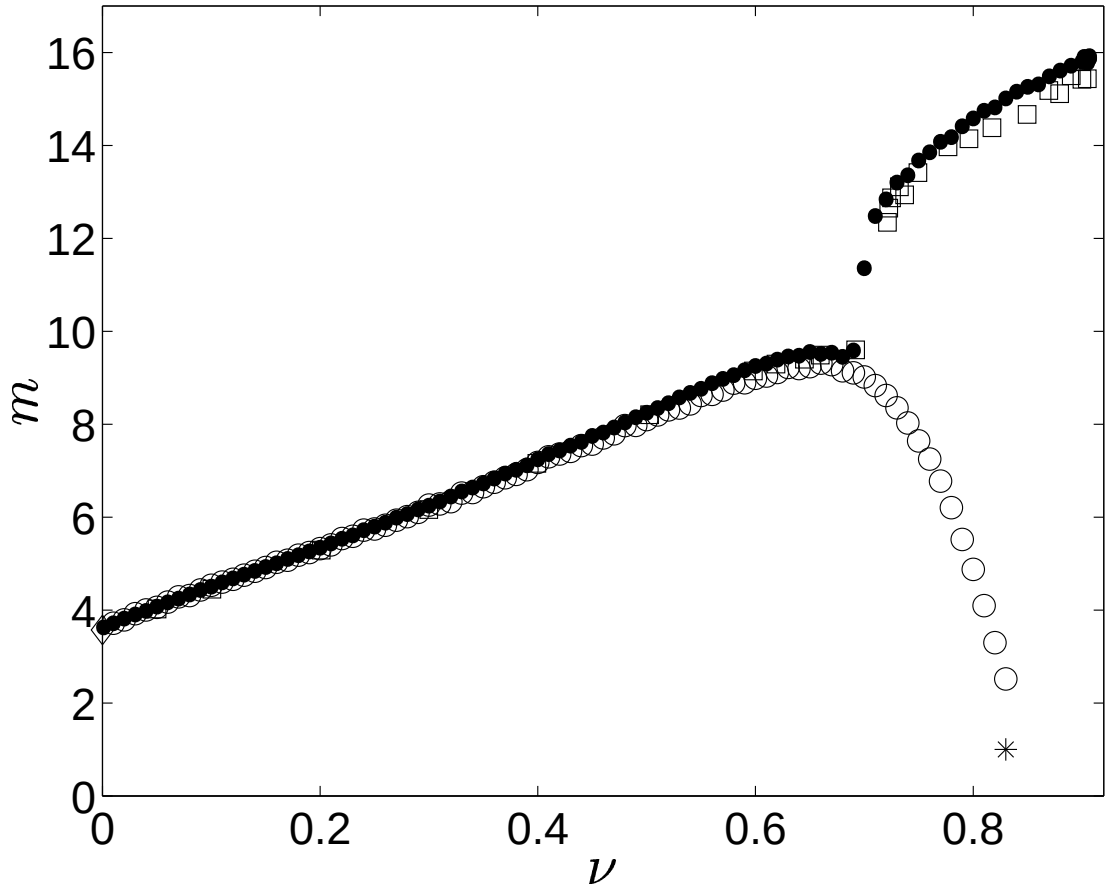
Thermodynamic entropy

$$s = s_{fv} + s_{com}$$

Exact expression for free volume entropy

$$s_{fv} = -Dk_B \int dv^* f(v^*) \log\left(f(v^*)\right)$$

Disordered states (2D):



Regularity parameter *decreases* for swelling algorithm.

Regularity parameter approaches 1 at *dense random packing*.

Extremisation of free volume entropy:

Entropy functional (of free volume distribution):

$$\mathcal{S}[f] = -Dk_B \int_0^\infty v^* f(v^*) \log\left(f(v^*)\right) dv^*$$

Subject to:

- Normalisation condition

$$\int dv^*\ f(v^*) = 1$$

- Total volume constraint:

$$\int dv^*\ v^* f(v^*) = \overline{v^*}$$

Extremise functional

$$\mathcal{S}[f] - \alpha \int dv^*\ f(v^*) - \beta \int dv^*\ v^* f(v^*)$$

Result:

$$f(v^*) = N^{-1} \exp\left(-\beta v^*\right)$$

Exponential distribution; Gamma distribution with $m = 1$.

Thus, the maximally disordered state maximes the free volume entropy.

Conclusions

- Unambiguous specification of concept of free volume.
- Relationship between free-volume entropy and thermodynamic entropy.
- Extremisation of free-volume entropy in maximally disordered states.