UNIVERSITY OF CAMBRIDGE

Relating Microstructure with Rheology in Glassy Colloids

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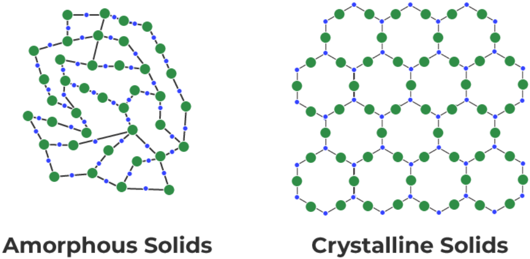
Outline

- Glasses and colloids
- The correlation function
- Excess entropy
- Expansion of excess entropy in correlation functions
- Relate correlation functions with dynamics via excess entropy

Glasses and colloids

Glasses are like if a liquid was solid.

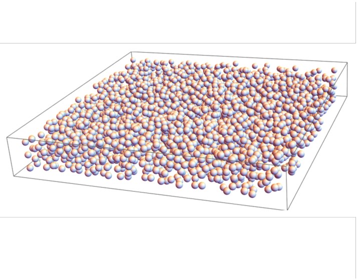
- I.e., they are rigid but isotropic.
- Their dynamics involve long-timescale *relaxations*.

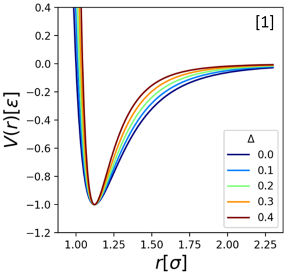


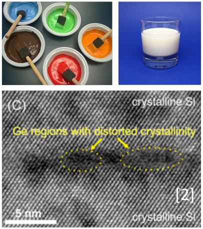
Glasses and colloids

Colloids are suspensions of particles.

- They are often spherical.
- They have interactions.
- They often form glasses and other disordered states.

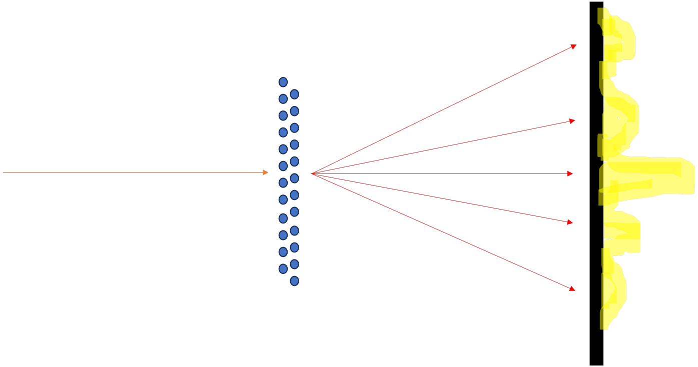




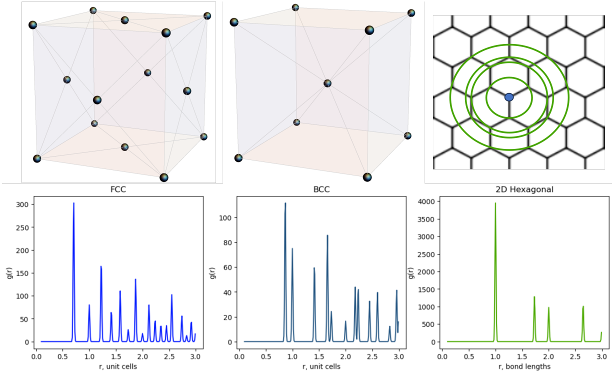


The correlation function *g(r)*

- *g(r)* is the expected (relative) density of particles given that you are a distance *r* away from some particle.
- It can be calculated from scattering experiments.



g(r) contains information about structure



g(r) is calculated experimentally using a **histogram**.

Recall: g(r) *is the expected (relative) density of particles given that you are a distance* r *away from some particle.*

What if the lattice has disorder?

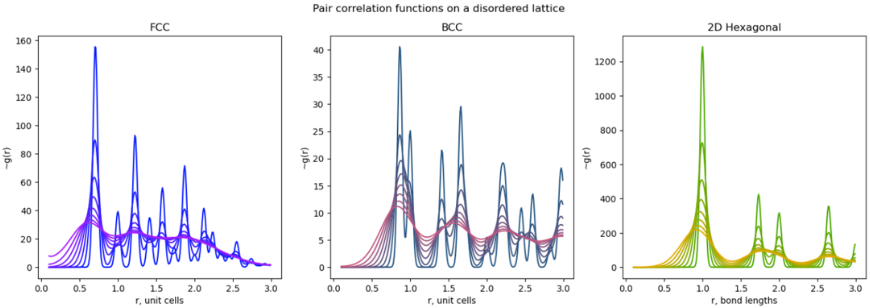
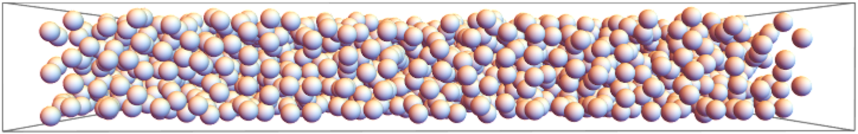
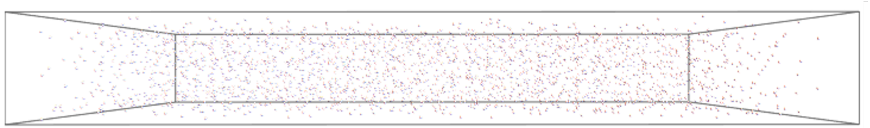


Figure: *g(r)* on lattice with gaussian fluctuations, which increase in length scale from 0.03 (less red) to 0.19 (more red) units.

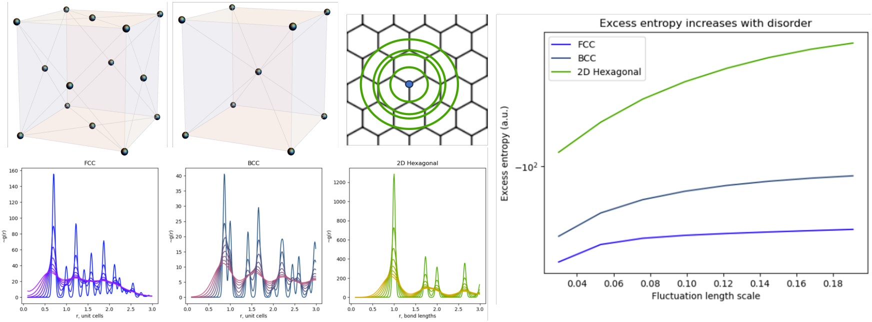
Configurational entropy

- The ideal gas has maximal configurational entropy.
- In terms of entropy, colloidal spheres and an equivalent ideal gas differ principally in the number of available (spatial) configurations.
- This difference is called **excess entropy**.





Excess entropy measures disorder



Excess entropy in terms of correlation functions

- We can write the entropy of a colloid in terms of correlation functions.
- The bulk of the **excess** entropy is accounted for by a term involving only $g_2(r) = g(r)$.

[3]

$$S_N = -\frac{k_B}{h^{3N}N!}\int\cdots\int P_N \ln P_N \, d\mathbf{r}_1 \, d\mathbf{p}_1 \cdots d\mathbf{r}_N \, d\mathbf{p}_N$$

$$= -\frac{k_B}{N!}\int\cdots\int f_N^{(N)} \ln h^{3N} f_N^{(N)} d\mathbf{r}_1 \, d\mathbf{p}_1 \cdots d\mathbf{r}_N \, d\mathbf{p}_N$$

$$H_N = \sum_{\kappa=1}^{N} \frac{\mathbf{p}_\kappa^2}{2m} + \Phi_N$$

$$f_N^{(N)}(\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_N, \mathbf{p}_N) = \frac{e^{-\beta H_N}}{h^{3N} Z_N}$$

$$= f_N^{(1)}(\mathbf{p}_1)\cdots f_N^{(1)}(\mathbf{p}_N) g_N^{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

$$f_N^{(1)}(\mathbf{p}) = \rho_N (\beta/2\pi m)^{3/2} \exp(-\beta \mathbf{p}^2/2m)$$

$$g_N^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \frac{\rho_N^{N-n}}{(N-n)!}\int\cdots\int g_N^{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N) d\mathbf{r}_{n+1}\cdots d\mathbf{r}_N$$

$$f_N^{(n)}(\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_n, \mathbf{p}_n) = \frac{1}{(N-n)!}\int\cdots\int f_N^{(N)}(\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_N, \mathbf{p}_N) \times d\mathbf{r}_{n+1} \, d\mathbf{p}_{n+1}\cdots d\mathbf{r}_N \, d\mathbf{p}_N .$$

$$g_N^{(N)}(1, \ldots, N) = g_N^{(2)}(1,2)\cdots g_N^{(2)}(N-1,N) \times \delta g_N^{(3)}(1,2,3)\cdots \delta g_N^{(3)}(N-2,N-1,N) \times\cdots\times \delta g_N^{(N)}(1,\ldots,N) .$$

$$f_N^{(n)}(\mathbf{r}_1, \mathbf{p}_1, \ldots, \mathbf{r}_n, \mathbf{p}_n) = f_N^{(1)}(\mathbf{p}_1)\cdots f_N^{(1)}(\mathbf{p}_n) g_N^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n)$$

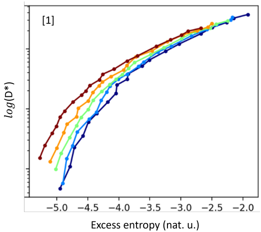
$$S_2 = -2\pi\rho \int_0^\infty \{g(r)\ln[g(r)] - [g(r) - 1]\} r^2 \mathrm{d}r$$ [4]

Connecting entropy with dynamics

Recall that the dynamics of glassy states consist of long-timescale rearrangements.

- Idea: The frequency of rearrangements is proportional to the number of available microstates [5].
- This holds at the ensemble level [1], and is predicted to hold at the **single-particle level**.

$$D^* \propto e^S \tag{1}$$



Summary

- *g(r)* is the expected (relative) density of particles given that you are a distance *r* away from some particle. It characterizes the structure in a system.
- Excess entropy is the entropy minus that of an equivalent ideal gas. It characterizes the degree of disorder in a system.
- Intuitively, systems with higher structure will change less over time.
  - Excess entropy quantifies the connection between *g(r)* and particle dynamics.

Citations

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2. Grydlik, M. *et al.* (2016) 'Lasing from glassy ge quantum dots in Crystalline Si', *ACS Photonics*, 3(2), pp. 298–303. doi:10.1021/acsphotonics.5b00671.
3. Wallace, D.C. (1987) 'On the role of density fluctuations in the entropy of a fluid', *The Journal of Chemical Physics*, 87(4), pp. 2282–2284. doi:10.1063/1.453158.
4. Baranyai, A. and Evans, D.J. (1989) 'Direct entropy calculation from computer simulation of liquids', *Physical Review A*, 40(7), pp. 3817–3822. doi:10.1103/physreva.40.3817.
5. Dzugutov, M. (1996) 'A universal scaling law for atomic diffusion in condensed matter', *Nature*, 381(6578), pp. 137–139. doi:10.1038/381137a0.