Disordered Hyperuniformity: Liquid-like Behaviour in Structural Solids, A New Phase of Matter?

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States of Matter

- Solid
- Liquid
- Gas
- Plasma
- No others?

States of Matter: Properties

Characteristics of a Solid

- Permanent Density Modulations
- For crystals: Long Range Correlations
- Global Rigidity

Characteristics of a Liquid

- Short Range Correlations
- Zero Shear Modulus

Characteristics of a Gas

- Short Range Correlations
- Zero Shear Modulus
- Large Bulk Compressibility

Preliminaries from Statistical Mechanics

Reference: J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, Academic Press, New York, (1986).

- Consider a system of N particles in a volume V (for an average number density $\rho = N/V$) and at a temperature T ($\beta = \frac{1}{kT}$). The particle coordinates are $\mathbf{r}_i$, with $i = 1, \ldots, N$. The potential energy due to the interaction between particles is $U_N(\mathbf{r}_1 \ldots, \mathbf{r}_N)$.
- The ensemble averages are taken in the *canonical ensemble* (N, V, T), with

$$Z_N = \int \cdots \int \mathrm{e}^{-\beta U_N} \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_N \tag{1}$$

taken over all possible combinations of particle positions. The probability of an elementary configuration, namely finding particle 1 in $\mathrm{d}\mathbf{r}_1$, particle 2 in $\mathrm{d}\mathbf{r}_2$, etc. is given by

$$P_{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N)\, \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_N = \frac{\mathrm{e}^{-\beta U_N}}{Z_N} \mathrm{d}\mathbf{r}_1 \cdots \mathrm{d}\mathbf{r}_N. \tag{2}$$

Correlation Functions

- The probability of a reduced configuration, where the positions of only $n < N$ particles are fixed, in $\mathbf{r}_1 \ldots, \mathbf{r}_n$, with no constraints on the remaining $N - n$ particles:

$$P_{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \frac{1}{Z_N} \int \cdots \int \mathrm{e}^{-\beta U_N} \, \mathrm{d}\mathbf{r}_{n+1} \cdots \mathrm{d}\mathbf{r}_N \tag{3}$$

- For identical particles, consider the *n-particle density*

$$\rho_{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \frac{N!}{(N-n)!} P^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n) \tag{4}$$

- These can be written as

$$\begin{aligned} \rho_{(1)}(\mathbf{r}) &= \langle \sum_i \delta(\mathbf{r} - \mathbf{r_i}) \rangle \\ \rho_{(2)}(\mathbf{r}, \mathbf{r}') &= \langle \sum_{j \neq i} \sum_i \delta(\mathbf{r} - \mathbf{r_i}) \delta(\mathbf{r}' - \mathbf{r_j}) \rangle \\ &\vdots \end{aligned} \tag{5}$$

Correlation Functions

- We then have

$$\frac{1}{V}\int \rho_{(1)}(\mathbf{r})\,\mathrm{d}\mathbf{r} = \frac{N}{V} = \rho, \qquad \int\int \rho_{(2)}(\mathbf{r},\mathbf{r}')\,\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' = N(N-1) \quad (6)$$

- We introduce a correlation function $g_{(n)}$ by

$$g_{(n)}(\mathbf{r}_1\ \ldots,\ \mathbf{r}_n) = \frac{1}{\rho^n}\rho_{(n)}(\mathbf{r}_1\ \ldots,\ \mathbf{r}_n), \quad (7)$$

- $g_{(n)}$ is called a correlation function, since if the particles are independent from each other $\rho_{(n)}$ would simply equal ρ^n and therefore $g_{(n)}$ corrects for the correlation between particles.
- It then follows that

$$g_{(n)}(\mathbf{r}_1\ \ldots,\ \mathbf{r}_n) = \frac{V^n N!}{N^n(N-n)!}\cdot\frac{1}{Z_N}\int\cdots\int \mathrm{e}^{-\beta U_N}\,\mathrm{d}\mathbf{r}_{n+1}\cdots\mathrm{d}\mathbf{r}_N \quad (8)$$

Grand Canonical Ensemble

- “The fact that in the canonical ensemble the pair distribution function behaves asymptotically as $(1 - 1/N)$ rather than tending strictly to unity is often irrelevant since the term of order $N - 1$ vanishes in the thermodynamic limit. On the other hand, if a term of that order is integrated over the volume of the system, a result of order V/N is obtained, which usually cannot be ignored. The difficulties that this situation sometimes creates can be avoided by working in the grand canonical ensemble.”

  - J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, Academic Press, New York, (1986).

Grand Canonical Ensemble

- We now allow for the fluctuations of the number of particles ($z = e^{\mu}$).

$$\Xi = \sum_N z^N Z_N \qquad \text{with} \qquad p(N) = \frac{z^N}{N!}\frac{Z_N}{\Xi} \tag{9}$$

- The n-particle densities can then be defined as

$$\rho_{(n)}(\mathbf{r}_1, ..., \mathbf{r}_N) = \sum_{N \geq n}^{\infty} p(N) \rho^N_{(n)}(\mathbf{r}_1, ...\mathbf{r}_N) \tag{10}$$

- The normalization then becomes

$$\begin{aligned} \int .. \int \rho_{(n)}(\mathbf{r}_1, ..., \mathbf{r}_N) d\mathbf{r}_1..d\mathbf{r}_N &= \left\langle \frac{N!}{(N-n)!} \right\rangle \\ \int \rho_{(1)}(\mathbf{r}_1) d\mathbf{r}_1 &= \langle N \rangle \\ \int \int \rho_{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 &= \langle N^2 \rangle - \langle N \rangle \end{aligned} \tag{11}$$

Correlations in the Grand Canonical Ensemble

- Using these normalizations we have

$$\int\int \left[\rho_{(2)}(\mathbf{r}_1,\mathbf{r}_2) - \rho_{(1)}(\mathbf{r}_1)\rho_{(1)}(\mathbf{r}_2)\right] d\mathbf{r}_1 d\mathbf{r}_2 = \langle N^2\rangle - \langle N\rangle - \langle N\rangle^2 \tag{12}$$

- We then have precisely

$$g_{(n)}(\mathbf{r}_1,..,\mathbf{r}_N) \to 1 \quad \text{as all} \quad \mathbf{r}_i - \mathbf{r}_j \to \infty \tag{13}$$

- We next define a *pair correlation function*

$$h_{(2)}(\mathbf{r}_1,\mathbf{r}_2) = g_{(2)}(\mathbf{r}_1,\mathbf{r}_2) - 1 \tag{14}$$

- We then have

$$h_{(2)}(\mathbf{r}_1,\mathbf{r}_2) \to 0 \quad \text{as} \quad \mathbf{r}_1 - \mathbf{r}_2 \to \infty \tag{15}$$

Number Fluctuations in the Grand Canonical Ensemble

- In the grand canonical ensemble the average particle number is

$$\langle N \rangle = \sum N p(N) = \frac{1}{\Xi} \sum N \frac{z^N}{N!} Z_N = \frac{\partial \ln \Xi}{\partial \ln z} \tag{16}$$

- Similarly

$$\frac{\partial \langle N \rangle}{\partial \ln z} = z \frac{\partial}{\partial z} \left(\frac{1}{\Xi} \sum N \frac{z^N}{N!} Z_N \right) = \langle N^2 \rangle - \langle N \rangle^2 \tag{17}$$

Number Fluctuations and Compressibility

- In the thermodynamic limit, i.e. the limit $\langle N \rangle \to \infty$, $V \to \infty$ with $\rho = \langle N \rangle / V$ held constant, the number of particles in the system of interest (the thermodynamic variable N) may be identified with the grand canonical average, $\langle N \rangle$. In the same limit thermodynamic properties calculated in different ensembles become identical.
- The isothermal compressibility of the system is defined as

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{in the Canonical ensemble} \tag{18}$$

- We also have

$$\ln z = \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \quad \text{in the Grand Canonical Ensemble} \tag{19}$$

- Using ensemble equivalence, we have (skipping steps)

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \rho k_B T \chi_T \tag{20}$$

Correlations and Compressibility

- For *homogeneous* systems

$$1 + \rho \int \left[g_{(2)}(r) - 1 \right] dr = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \tag{21}$$

- Therefore the compressibility of the system is

$$\rho k T \chi_T = 1 + \rho \int_V \mathrm{d}\mathbf{r}\, [g_{(2)}(r) - 1]. \tag{22}$$

- Alternatively

$$\rho k T \chi_T = 1 + \rho \int_V \mathrm{d}\mathbf{r}\, h_{(2)}(r). \tag{23}$$

Fourier Transforms

- The Fourier transform is defined as

$$f(\mathbf{k}) = \int f(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r} \equiv \frac{1}{\sqrt{N}} \sum f(\mathbf{r}) \mathbf{e}^{-\mathbf{ik}\cdot\mathbf{r}}, \tag{24}$$

  and the associated inverse operation is defined by

$$f(\mathbf{r}) = \frac{1}{(2\pi)^d} \int f(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}}\, d\mathbf{k} \equiv \frac{1}{\sqrt{N}} \sum f(\mathbf{k}) \mathbf{e}^{\mathbf{ik}\cdot\mathbf{r}}, \tag{25}$$

  where **k** is the wave vector.
- The structure factor is proportional to the scattered intensity of radiation from a system of points and thus is obtainable from a scattering experiment.
- An important property of the structure factor is that it must be nonnegative for all **k**, i.e.,

$$S(\mathbf{k}) \geq 0 \qquad \forall \mathbf{k}. \tag{26}$$

Structure Factor

- We have

$$\begin{aligned} S(\mathbf{k}) &:= \frac{1}{N}\langle\sum_i\sum_j \mathrm{e}^{-i\mathbf{k}(\mathbf{r}_i-\mathbf{r}_j)}\rangle \\ &= 1+\frac{1}{N}\langle\sum_i\sum_{j\neq i} \mathrm{e}^{-i\mathbf{k}(\mathbf{r}_i-\mathbf{r}_j)}\rangle \\ &= 1+\frac{1}{N}\left\langle\int_V \mathrm{d}\mathbf{r}\,\mathrm{e}^{-i\mathbf{k}\mathbf{r}}\sum_i\sum_{j\neq i}\delta\left[\mathbf{r}-(\mathbf{r}_i-\mathbf{r}_j)\right]\right\rangle \\ &= 1+\frac{1}{N}\int_V \mathrm{d}\mathbf{r}\,\mathrm{e}^{-i\mathbf{k}\mathbf{r}}\underbrace{\left\langle\sum_i\sum_{j\neq i}\delta[\mathbf{r}-(\mathbf{r}_i-\mathbf{r}_j)]\right\rangle}_{V\rho^2 g_{(2)}(\mathbf{r})} \qquad (27) \end{aligned}$$

- Therefore

$$S(\mathbf{k}) = 1+\rho\int_V \mathrm{d}\mathbf{r}\,\mathrm{e}^{-i\mathbf{k}\mathbf{r}} g_{(2)}(\mathbf{r}) \qquad (28)$$

Structure Factor and Correlations

- This is only valid for *distributions*, since $g_{(2)}(\mathbf{r})$ is not normalized:

$$\lim_{r\to\infty} g_{(2)}(\mathbf{r}) = 1, \qquad \lim_{k\to 0} S(\mathbf{k}) = \rho\delta(\mathbf{k}) \tag{29}$$

- Experimentally the term corresponds to radiation that passes through the sample unscattered. We subtract it and redefine the structure factor as a regular function:

$$S(\mathbf{k}) \equiv S(\mathbf{k}) - \rho\delta(\mathbf{k}) = 1 + \rho \int_V \mathrm{d}\mathbf{r}\, \mathrm{e}^{-i\mathbf{kr}} [g_{(2)}(\mathbf{r}) - 1]. \tag{30}$$

- The structure factor $S(\mathbf{k})$ is related to the Fourier transform of $h_2(\mathbf{r})$, denoted by $h_2(\mathbf{k})$, via the expression

$$S(\mathbf{k}) = 1 + \rho h_2(\mathbf{k}). \tag{31}$$

Structure Factor and Compressibility

- If the system is *isotropic* (usually for liquids)

$$S(k) = 1 + 4\pi\rho\frac{1}{q}\int \mathrm{d}r\, r\sin(qr)[g_{(2)}(r) - 1] \tag{32}$$

- We can then derive the isothermal compressibility from the structure factor

$$S(k \to 0) = 1 + \rho\int_V \mathrm{d}\mathbf{r}[g_{(2)}(\mathbf{r}) - 1] = \rho k T \chi_T \tag{33}$$

- **If the system is incompressible then**

$$\begin{aligned} S(k \to 0) &\to 0 \\ g_{(2)}(r \to \infty) &\to 1. \end{aligned} \tag{34}$$

Disordered Hyperuniform Materials

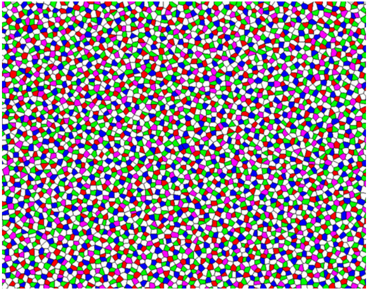

Figure: Spatial distribution of the five types of light-sensitive cells known as cones in the chicken retina. The unusual arrangement display “disordered hyperuniformity”. These states have a “hidden order” that allows them to behave like crystal and liquid states of matter. They exhibit order over large distances and disorder over small distances.(Figure Courtesy: Joseph Corbo and Timothy Lau, Washington University in St. Louis).

Definition of Hyperuniformity S. Torquato, F. H. Stillinger, *Phys. Rev. E* **68**, 041113 (2003).

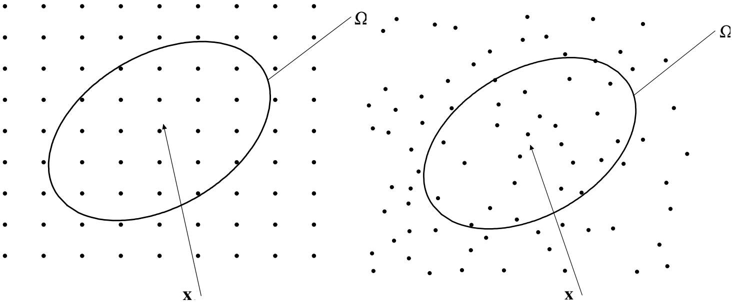

Figure: Schematics indicating a regular domain or window Ω and its centroid $\mathbf{x_0}$ for two different point patterns. Left panel: A periodic point pattern. Right panel: An irregular point pattern. The statistics of the points contained within Ω for these two types of patterns are fundamentally different from one another.

Definition of Hyperuniformity

- The number variance for a point pattern is given by

$$\langle N_\Omega^2 \rangle - \langle N_\Omega \rangle^2 = \langle \Delta N_\Omega^2 \rangle, \tag{35}$$

where angular brackets denote an ensemble average.

- For a large class of irregular point patterns (including Poisson):

$$\langle N_\Omega^2 \rangle - \langle N_\Omega \rangle^2 \propto R^d. \tag{36}$$

- Mathematical Proof: For any statistically homogeneous and isotropic point pattern, the variance **cannot grow more slowly than the surface area** of a strictly convex domain. J. Beck, *Acta Mathematica* **159**, 1 (1987).
- What about **as** the surface area?

$$\langle N_\Omega^2 \rangle - \langle N_\Omega \rangle^2 \sim R^{d-1}. \tag{37}$$

These are **defined as "hyperuniform" systems** because such systems do not possess infinite-wavelength fluctuations.

Hyperuniformity on the Square Lattice

- What about points arranged on a regular (periodic) lattice? Consider the **square lattice for simplicity**. How many points in a circular window of radius R with the center at (a_1, a_2) in the unit square?
- This amounts to finding all of the integer solutions of

$$(n_1 - a_1)^2 + (n_2 - a_2)^2 \leq R^2, \tag{38}$$

  a problem of interest in number theory.
- This problem is directly related to the **determination of the number of energy levels** less than some fixed energy in integrable quantum systems. It is clear that $N(R)$ asymptotically approaches the window area πR^2 and unit density, for large R.

Hyperuniformity on the Square Lattice

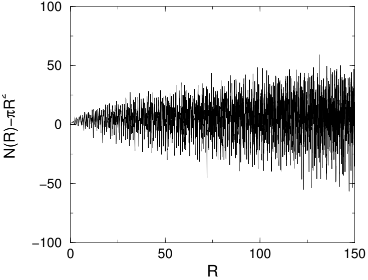

Figure: The function $N(R) - \pi R^2$ versus R for the unit-spacing square lattice, using a circular window of radius R centered on a lattice point. This illustrates the apparent “random” nature of $N(R)$ which grows with R. Source: S. Torquato, F. H. Stillinger, *Phys. Rev. E* **68**, 041113 (2003).

Non-Periodic Point Patterns

- It is considerably more challenging to identify non-periodic point patterns, such as **disordered and quasiperiodic** ones, that are hyperuniform.
- These must obey the counterintuitive property of a **long-ranged "direct" correlation function**, are determined from a general formula for the number variance of such systems.
- This is reminiscent of the behavior of the pair correlation function of a thermal system near its **critical point**.
- It can be shown that the hyperuniform state is at a "critical-point" of a type with appropriate scaling laws and critical exponents.

Ensembles and Point Patterns

- The ensemble analysis can easily be generalized to ensembles of point patterns, and also to **single realizations**.
- For arbitrary convex shaped windows we can generalize

$$\langle N^2(\mathbf{R})\rangle - \langle N(\mathbf{R})\rangle^2 = \langle N(\mathbf{R})\rangle \left[1 + \rho \int_{\Re^d} h(\mathbf{r})\alpha(\mathbf{r};\mathbf{R}) d\mathbf{r}\right], \tag{39}$$

- $\alpha(\mathbf{r};\mathbf{R})$ corrects for the intersection volume between the window and the point pattern. For infinite sized windows $R \to \infty$ as $\alpha(\mathbf{r};\mathbf{R}) \to 1$.
- The variance formula for large R is given by

$$\langle N^2(R)\rangle - \langle N(R)\rangle^2 = 2^d \phi \left[A\left(\frac{R}{D}\right)^d + B\left(\frac{R}{D}\right)^{d-1} + \ell\left(\frac{R}{D}\right)^{d-1}\right], \tag{40}$$

  where D is a characteristic microscopic length scale and A and B are the asymptotic constants and ϕ is a dimensionless density.

Direct Correlation Function

- The *direct* correlation function $c(\mathbf{r})$ of a hyperuniform system behaves in an unconventional manner.
- In real space, this function is defined by the Ornstein-Zernike equation

$$h(\mathbf{r}) = c(\mathbf{r}) + \rho \int_{\Re^d} h(\mathbf{r} - \mathbf{r}')c(\mathbf{r})d\mathbf{r}'. \tag{41}$$

- This is a convolution integral and therefore Fourier transforming leads to

$$c(\mathbf{k}) = \frac{h(\mathbf{k})}{1 + \rho h(\mathbf{k})}, \tag{42}$$

- We can express the number variance for a window of arbitrary shape:

$$\langle N^2(\mathbf{R})\rangle - \langle N(\mathbf{R})\rangle^2 = \langle N(\mathbf{R})\rangle \left[\frac{1}{(2\pi)^d} \int \frac{\alpha(\mathbf{k};\mathbf{R})}{1 - \rho c(\mathbf{k})} d\mathbf{k}\right]. \tag{43}$$

Inverted Critical Phenomenon?

- For a hyperuniform system, $h(0) = -1/\rho$ by definition. Therefore $h(\mathbf{r})$ is a short-ranged function that decays to zero faster than $|\mathbf{r}|^{-d}$.
- Interestingly, this means that the denominator on the right side of (42) vanishes at $\mathbf{k} = \mathbf{0}$ and therefore $c(\mathbf{k} = \mathbf{0})$ diverges to $-\infty$.
- Therefore the direct correlation function $c(\mathbf{r})$ is long-ranged, i.e., decays slower than $|\mathbf{r}|^{-d}$.
- $c(\mathbf{r})$ thus behaves similarly to the total correlation function $h(\mathbf{r})$ for an equilibrium system near its critical point.
- One expects the following asymptotic behavior for large $r \equiv |\mathbf{r}|$ and sufficiently large d:

$$c(\mathbf{r}) \sim -\frac{1}{r^{d-2+\eta}} \qquad (r \to \infty), \tag{44}$$

where $(2-d) < \eta \leq 2$ is a new "critical" exponent associated with $c(\mathbf{r})$ for hyperuniform systems.

Critical Exponents

- For noninteger values of η, $h(\mathbf{k})$ is a nonanalytic function of $k \equiv |\mathbf{k}|$.
- The fourier transform of the direct correlation function behaves as

$$c(\mathbf{k}) \sim -\frac{1}{k^{2-\eta}} \qquad (k \to 0), \tag{45}$$

- This implies

$$S(\mathbf{k}) \sim k^{2-\eta} \qquad (k \to 0). \tag{46}$$

- The specific asymptotic form of $S(\mathbf{k})$ for small k contributes to determining the **"universality" class** of the hyperuniform system.

Critical Exponents (cont.)

- "Let us now consider a point pattern with a reduced density ϕ that is nearly hyperuniform and which can be made hyperuniform by increasing and/or decreasing the density. We denote by ϕ_c the reduced density at the hyperuniform state. The reduced densities ϕ and ϕ_c play the same role as temperature T and critical temperature T_c, respectively, in the analogous thermal problem in the vicinity of a critical point." - S. Torquato, F. H. Stillinger, *Phys. Rev. E* **68**, 041113 (2003).

Critical Exponents (cont.)

Table: Definitions of the critical exponents in the vicinity of or at the hyperuniform state. Here $S^{-1}(0)$ is the inverse of the structure factor at $k = 0$, ξ is the correlation length, and $c(r)$ is the direct correlation function.

Exponent	Asymptotic behavior
γ	$S^{-1}(0) \sim (1 - \frac{\phi}{\phi_c})^{-\gamma} \quad (\phi \to \phi_c^-)$
$\gamma\,'$	$S^{-1}(0) \sim (\frac{\phi}{\phi_c} - 1)^{-\gamma'} \quad (\phi \to \phi_c^+)$
ν	$\xi \sim (1 - \frac{\phi}{\phi_c})^{-\nu} \quad (\phi \to \phi_c^-)$
$\nu\,'$	$\xi \sim (\frac{\phi}{\phi_c} - 1)^{-\nu'} \quad (\phi \to \phi_c^+)$
η	$c(r) \sim r^{2-d-\eta} \quad (\phi = \phi_c)$

Example: Hard Sphere Packings

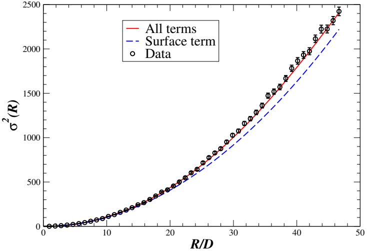

Figure: The variance σ^2 as a function of the window radius for a 10^6-particle packing. The uncertainty in the variance, as shown with error bars, is estimated to be of the order of $\sigma^2/\sqrt{M}$, where $M = 10^4$ is the number of windows used for a given window. Also shown is the theoretically predicted dependence of the form $AX^3 + CX^2 \ln X + B_0X^2$, along with just the surface term B_0X^2, which dominates the density fluctuations. Source: A. Donev, S. Torquato and F. H. Stillinger, *Phys. Rev. Lett.* **95**, 090604 (2005).

Example: Hard Sphere Packings

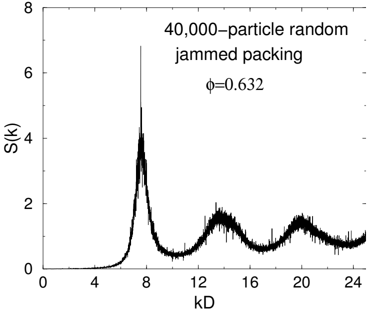

Figure: The structure factor for a random packing of three-dimensional identical hard spheres of diameter D near the MRJ state. as computed from a single realization consisting of 40,000 particles in a cubical box with periodic boundary conditions. ϕ is 0.632. Source: S. Torquato, F. H. Stillinger, *Phys. Rev. E* **68**, 041113 (2003).

Example: Hard Sphere Packings

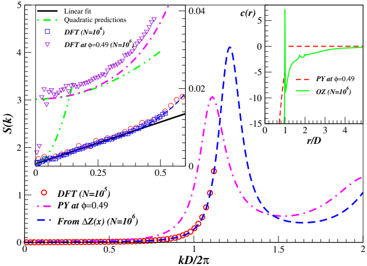

Figure: Structure factor for a 10^6-particle packing ($\phi = 0.642$) and for a hard-sphere liquid near the freezing point ($\phi = 0.49$), as obtained via two alternative numerical methods and also from the Percus-Yevick (PY) theory for the liquid. DFT results are also shown over a larger range of K for a 10^5-particle packing ($\phi = 0.643$). Source: A. Donev, S. Torquato and F. H. Stillinger, *Phys. Rev. Lett.* **95**, 090604 (2005).

Is this Hyperuniform?

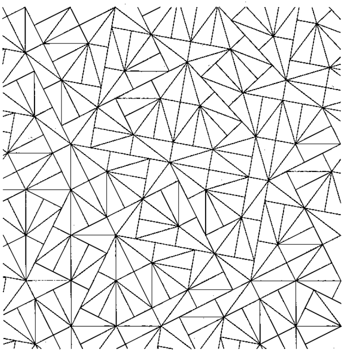

Figure: Portion of a pinwheel tiling.

Conclusions

- **Number fluctuations** calculated for variable window geometries offer a **powerful tool to characterize and to classify point-particle media**.
- This allows for characterization of both spatially periodic (crystalline) particle patterns, as well as those that are **globally disordered (amorphous)**.
- "Hyperuniform" point patterns are those for which volume fluctuations vanish identically; equivalently these are systems for which the structure factor $S(k)$ vanishes at $k = 0$.
- All infinitely extended perfectly periodic structures are hyperuniform.
- Geometrically **less regular cases of hyperuniformity also exist**, including those that are spatially uniform and isotropic.

Thank You.