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
Consider a system of $N$ particles in a volume $V$ (for an average number density $\rho = N/V$) and at a temperature $T$ ($\beta = 1/kT$). The particle coordinates are $r_i$, with $i = 1, \ldots, N$. The potential energy due to the interaction between particles is $U_N(r_1 \ldots, r_N)$.

The ensemble averages are taken in the canonical ensemble $(N, V, T)$, with

$$Z_N = \int \cdots \int e^{-\beta U_N} \, dr_1 \cdots dr_N$$  \hspace{1cm} (1)

taken over all possible combinations of particle positions. The probability of an elementary configuration, namely finding particle 1 in $dr_1$, particle 2 in $dr_2$, etc. is given by

$$P_{(N)}(r_1, \ldots, r_N) \, dr_1 \cdots dr_N = \frac{e^{-\beta U_N}}{Z_N} \, dr_1 \cdots dr_N.$$  \hspace{1cm} (2)
Correlation Functions

- The probability of a reduced configuration, where the positions of only $n < N$ particles are fixed, in $r_1 \ldots, r_n$, with no constraints on the remaining $N - n$ particles:

$$P(n)(r_1, \ldots, r_n) = \frac{1}{Z_N} \int \cdots \int e^{-\beta U_N} \, dr_{n+1} \cdots dr_N$$

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

$$\rho(n)(r_1, \ldots, r_n) = \frac{N!}{(N-n)!} P(n)(r_1, \ldots, r_n)$$

- These can be written as

$$\rho(1)(r) = \langle \sum_i \delta(r - r_i) \rangle$$

$$\rho(2)(r, r') = \langle \sum_i \sum_{j \neq i} \delta(r - r_i) \delta(r' - r_j) \rangle$$

$$\vdots$$

(5)
Correlation Functions

- We then have

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

- 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 \( \rho^n \) and therefore \( g(n) \) corrects for the correlation between particles.

- It then follows that

\[
g(n)(\mathbf{r}_1, \ldots, \mathbf{r}_n) = \frac{V^n N!}{N^n(N - n)!} \cdot \frac{1}{Z_N} \int \cdots \int e^{-\beta U_N} \, d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N \quad (8)
\]
“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.”

Grand Canonical Ensemble

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

\[
\Xi = \sum_N z^N Z_N \quad \text{with} \quad p(N) = \frac{z^N Z_N}{N! \Xi}
\]  

- The \(n\)-particle densities can then be defined as

\[
\rho_n(r_1, \ldots, r_N) = \sum_{N \geq n} p(N) \rho_{(n)}^N(r_1, \ldots r_N)
\]  

- The normalization then becomes

\[
\int \cdots \int \rho_n(r_1, \ldots, r_N) dr_1 \cdots dr_N = \left\langle \frac{N!}{(N-n)!} \right\rangle
\]
\[
\int \rho_1(r_1) dr_1 = \langle N \rangle
\]
\[
\int \int \rho_2(r_1, r_2) dr_1 dr_2 = \langle N^2 \rangle - \langle N \rangle
\]
Correlations in the Grand Canonical Ensemble

- Using these normalizations we have

\[
\int \int [\rho(2)(\mathbf{r}_1, \mathbf{r}_2) - \rho(1)(\mathbf{r}_1)\rho(1)(\mathbf{r}_2)]
\, d\mathbf{r}_1 \, d\mathbf{r}_2 = \langle N^2 \rangle - \langle N \rangle - \langle N \rangle^2
\]  

(12)

- We then have precisely

\[
g(n)(\mathbf{r}_1, \ldots, \mathbf{r}_N) \rightarrow 1 \quad \text{as all} \quad \mathbf{r}_i - \mathbf{r}_j \rightarrow \infty
\]  

(13)

- We next define a *pair correlation function*

\[
h(2)(\mathbf{r}_1, \mathbf{r}_2) = g(2)(\mathbf{r}_1, \mathbf{r}_2) - 1
\]  

(14)

- We then have

\[
h(2)(\mathbf{r}_1, \mathbf{r}_2) \rightarrow 0 \quad \text{as} \quad \mathbf{r}_1 - \mathbf{r}_2 \rightarrow \infty
\]  

(15)
In the grand canonical ensemble the average particle number is

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

Similarly

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

$$\chi_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T$$

in the Canonical ensemble \hspace{1cm} (18)

We also have

$$\ln z = \mu = \left( \frac{\partial F}{\partial N} \right)_{T,V}$$

in the Grand Canonical Ensemble \hspace{1cm} (19)

Using ensemble equivalence, we have (skipping steps)

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \rho k_B T \chi_T$$ \hspace{1cm} (20)
Correlations and Compressibility

- For *homogeneous* systems

\[ 1 + \rho \int [g_{(2)}(r) - 1] \, dr = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \]  

(21)

- Therefore the compressibility of the system is

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

(22)

- Alternatively

\[ \rho k T \chi_T = 1 + \rho \int_V d\mathbf{r} \, h_{(2)}(r). \]  

(23)
Fourier Transforms

- The Fourier transform is defined as
  \[
  f(k) = \int f(r) e^{-i k \cdot r} dr \equiv \frac{1}{\sqrt{N}} \sum f(r) e^{-i k \cdot r},
  \]
  and the associated inverse operation is defined by
  \[
  f(r) = \frac{1}{(2\pi)^d} \int f(k) e^{i k \cdot r} dk \equiv \frac{1}{\sqrt{N}} \sum f(k) e^{i k \cdot r},
  \]
  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.,
  \[
  S(k) \geq 0 \quad \forall k.
  \]
Structure Factor

- We have

\[
S(k) := \frac{1}{N} \left\langle \sum_i \sum_j e^{-ik(r_i-r_j)} \right\rangle
= 1 + \frac{1}{N} \left\langle \sum_i \sum_{j \neq i} e^{-ik(r_i-r_j)} \right\rangle
= 1 + \frac{1}{N} \left\langle \int_V d\mathbf{r} e^{-ik\mathbf{r}} \sum_i \sum_{j \neq i} \delta[\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_j)] \right\rangle
= 1 + \frac{1}{N} \int_V d\mathbf{r} e^{-ik\mathbf{r}} \left\langle \sum_i \sum_{j \neq i} \delta[\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_j)] \right\rangle
\]

(27)

- Therefore

\[
S(k) = 1 + \rho \int_V d\mathbf{r} e^{-ik\mathbf{r}} g_2(\mathbf{r})
\]

(28)
This is only valid for distributions, since $g_2(r)$ is not normalized:

$$\lim_{r \to \infty} g_2(r) = 1, \quad \lim_{k \to 0} S(k) = \rho \delta(k)$$  \hspace{1cm} (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:

$$S(k) \equiv S(k) - \rho \delta(k) = 1 + \rho \int_V d\mathbf{r} e^{-i\mathbf{k}\mathbf{r}} [g_2(r) - 1].$$  \hspace{1cm} (30)

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

$$S(k) = 1 + \rho h_2(k).$$  \hspace{1cm} (31)
Structure Factor and Compressibility

- If the system is isotropic (usually for liquids)

\[ S(k) = 1 + 4\pi \rho \frac{1}{q} \int dr \, r \sin(qr)[g_2(r) - 1] \]  \hspace{1cm} (32)

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

\[ S(k \to 0) = 1 + \rho \int_V dr [g_2(r) - 1] = \rho kT \chi_T \]  \hspace{1cm} (33)

- If the system is incompressible then

\[ S(k \to 0) \to 0 \]

\[ g_2(r \to \infty) \to 1. \]  \hspace{1cm} (34)
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**


**Figure:** Schematics indicating a regular domain or window $\Omega$ and its centroid $x_0$ for two different point patterns. Left panel: A periodic point pattern. Right panel: An irregular point pattern. The statistics of the points contained within $\Omega$ 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
  \[ \langle N^2_\Omega \rangle - \langle N_\Omega \rangle^2 = \langle \Delta N^2_\Omega \rangle, \]  
  (35)
  where angular brackets denote an ensemble average.
- For a large class of irregular point patterns (including Poisson):
  \[ \langle N^2_\Omega \rangle - \langle N_\Omega \rangle^2 \propto R^d. \]  
  (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. \[ J. \text{ Beck, } \textit{Acta Mathematica} 159, 1 (1987). \]
- What about as the surface area?
  \[ \langle N^2_\Omega \rangle - \langle N_\Omega \rangle^2 \sim R^{d-1}. \]  
  (37)
These are defined as “hyperuniform” systems because such systems do not possess infinite-wavelength fluctuations.
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

$$\left(n_1 - a_1\right)^2 + \left(n_2 - a_2\right)^2 \leq R^2,$$

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 $\pi R^2$ 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

\[
\langle N^2(R) \rangle - \langle N(R) \rangle^2 = \langle N(R) \rangle \left[ 1 + \rho \int_{\mathbb{R}^d} h(r) \alpha(r; R) \, dr \right],
\]

(39)

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

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

(40)

where \(D\) is a characteristic microscopic length scale and \(A\) and \(B\) are the asymptotic constants and \(\phi\) is a dimensionless density.
Direct Correlation Function

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

$$h(r) = c(r) + \rho \int_{\mathbb{R}^d} h(r - r')c(r)dr'.$$

(41)

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

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

(42)

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

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

(43)
For a hyperuniform system, $h(0) = -1/\rho$ by definition. Therefore $h(r)$ is a short-ranged function that decays to zero faster than $|r|^{-d}$.

Interestingly, this means that the denominator on the right side of (42) vanishes at $k = 0$ and therefore $c(k = 0)$ diverges to $-\infty$.

Therefore the direct correlation function $c(r)$ is long-ranged, i.e., decays slower than $|r|^{-d}$.

$c(r)$ thus behaves similarly to the total correlation function $h(r)$ for an equilibrium system near its critical point.

One expects the following asymptotic behavior for large $r \equiv |r|$ and sufficiently large $d$:

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

(44)

where $(2 - d) < \eta \leq 2$ is a new “critical” exponent associated with $c(r)$ for hyperuniform systems.
Critical Exponents

- For noninteger values of $\eta$, $h(k)$ is a nonanalytic function of $k \equiv |k|$.

- The fourier transform of the direct correlation function behaves as

$$c(k) \sim -\frac{1}{k^{2-\eta}} \quad (k \to 0),$$

(45)

- This implies

$$S(k) \sim k^{2-\eta} \quad (k \to 0).$$

(46)

- The specific asymptotic form of $S(k)$ for small $k$ contributes to determining the “universality” class of the hyperuniform system.
“Let us now consider a point pattern with a reduced density $\phi$ that is nearly hyperuniform and which can be made hyperuniform by increasing and/or decreasing the density. We denote by $\phi_c$ the reduced density at the hyperuniform state. The reduced densities $\phi$ and $\phi_c$ 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 $k = 0$, $\xi$ is the correlation length, and $c(r)$ is the direct correlation function.

<table>
<thead>
<tr>
<th>Exponent</th>
<th>Asymptotic behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$</td>
<td>$S^{-1}(0) \sim (1 - \frac{\phi}{\phi_c})^{-\gamma}$ (\phi \to \phi_c^-)</td>
</tr>
<tr>
<td>$\gamma'$</td>
<td>$S^{-1}(0) \sim \left(\frac{\phi}{\phi_c} - 1\right)^{-\gamma'}$ (\phi \to \phi_c^+)</td>
</tr>
<tr>
<td>$\nu$</td>
<td>$\xi \sim (1 - \frac{\phi}{\phi_c})^{-\nu}$ (\phi \to \phi_c^-)</td>
</tr>
<tr>
<td>$\nu'$</td>
<td>$\xi \sim \left(\frac{\phi}{\phi_c} - 1\right)^{-\nu'}$ (\phi \to \phi_c^+)</td>
</tr>
<tr>
<td>$\eta$</td>
<td>$c(r) \sim r^{2-d-\eta}$ (\phi = \phi_c)</td>
</tr>
</tbody>
</table>
**Example: Hard Sphere Packings**

**Figure:** The variance $\sigma^2$ 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. $\phi$ is 0.632. Source: S. Torquato, F. H. Stillinger, *Phys. Rev. E* **68**, 041113 (2003).
**Example: Hard Sphere Packings**

![Graph](image)

**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.