# Disordered Hyperuniform Materials: New States of Amorphous Matter

**Salvatore Torquato** 

**Department of Chemistry**,

**Department of Physics**,

Princeton Institute for the Science and Technology of Materials,

and Program in Applied & Computational Mathematics

**Princeton University** 

## **States (Phases) of Matter**



#### Source: www.nasa.gov

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We now know there are a multitude of distinguishable states of matter, e.g., quasicrystals and liquid crystals, which break the continuous translational and rotational symmetries of a liquid differently from a solid crystal.

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- Disordered hyperuniform many-particle systems can be regarded to be new ideal states of disordered matter in that they

(i) behave more like crystals or quasicrystals in the manner in which they suppress large-scale density fluctuations, and yet are also like liquids and glasses since they are statistically isotropic structures with no Bragg peaks;

- (ii) can exist as both as equilibrium and nonequilibrium phases;
- (iii) come in quantum-mechanical and classical varieties;
- (iv) and, appear to be endowed with unique bulk physical properties.

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- All perfect crystals (periodic systems) and quasicrystals are hyperuniform.
- Thus, hyperuniformity provides a unified means of categorizing and characterizing crystals, quasicrystals and such special disordered systems.

# **SCATTERING AND DENSITY FLUCTUATIONS**



#### **Local Density Fluctuations for General Point Patterns**

**Torquato and Stillinger, PRE (2003)** 

Points can represent molecules of a material, stars in a galaxy, or trees in a forest. Let  $\Omega$  represent a spherical window of radius R in d-dimensional Euclidean space  $\mathbb{R}^d$ .



Average number of points in window of volume  $v_1(R)$ :  $\langle N(R) \rangle = \rho v_1(R) \sim R^d$ Local number variance:  $\sigma^2(R) \equiv \langle N^2(R) \rangle - \langle N(R) \rangle^2$ 

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  - For a Poisson point pattern and many disordered point patterns,  $\sigma^2(R) \sim R^d$ .
  - Solume) We call point patterns whose variance grows more slowly than  $R^d$  (window volume) hyperuniform. This implies that structure factor  $S(k) \to 0$  for  $k \to 0$ .
  - All perfect crystals and perfect quasicrystals are hyperuniform such that  $\sigma^2(R) \sim R^{d-1}$ : number variance grows like window surface area. Hyperuniformity is aka superhomogeneity: Gabrielli, Joyce & Sylos Labini, Phys. Rev. E (2002) - p. 5/33



#### **Pair Statistics in Direct and Fourier Spaces**

. – p. 6/33

#### **Hidden Order on Large Length Scales**



#### Which is the hyperuniform pattern?

#### **Scaled Number Variance for 3D Systems at Unit Density**



#### **Remarks About Equilibrium Systems**

For single-component systems in equilibrium at average number density ho,

$$\rho k_B T \kappa_T = \frac{\langle N^2 \rangle_* - \langle N \rangle_*^2}{\langle N \rangle_*} = S(\mathbf{k} = \mathbf{0}) = 1 + \rho \int_{\mathbb{R}^d} h(\mathbf{r}) d\mathbf{r}$$

where  $\langle \rangle_*$  denotes an average in the grand canonical ensemble.

#### Some observations:

- Any ground state (T = 0) in which the isothermal compressibility  $\kappa_T$  is bounded and positive must be hyperuniform. This includes crystal ground states as well as exotic disordered ground states, described later.
- However, in order to have a hyperuniform system at positive T, the isothermal compressibility must be zero; i.e., the system must be incompressible.

Note that generally 
$$ho kT\kappa_T
eq S({f k}={f 0}).$$

$$X = \frac{S(\mathbf{k} = \mathbf{0})}{\rho k_B T \kappa_T} - 1: \quad \text{Nonequilibrium index}$$

## **GENERAL ENSEMBLE-AVERAGE FORMULATION**

For a translationally invariant point process at number density ho in  $\mathbb{R}^d$  :

$$\sigma^{2}(R) = \langle N(R) \rangle \Big[ 1 + \rho \int_{\mathbb{R}^{d}} h(\mathbf{r}) \alpha(\mathbf{r}; R) d\mathbf{r} \Big]$$

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#### For large R, we can show

$$\sigma^{2}(R) = 2^{d}\phi \Big[ A\left(\frac{R}{D}\right)^{d} + B\left(\frac{R}{D}\right)^{d-1} + o\left(\frac{R}{D}\right)^{d-1} \Big],$$

where A and B are the "volume" and "surface-area" coefficients:

$$A = S(\mathbf{k} = \mathbf{0}) = 1 + \rho \int_{\mathbb{R}^d} h(\mathbf{r}) d\mathbf{r}, \qquad B = -c(d) \int_{\mathbb{R}^d} h(\mathbf{r}) r d\mathbf{r},$$

D: microscopic length scale,  $\phi$ : dimensionless density

• Hyperuniform: 
$$A = 0, B > 0$$

#### **ERTED CRITICAL PHENOMENA: Ornstein-Zernike Formalism**

 ${}$   $h({f r})$  can be divided into direct correlations, via function  $c({f r})$ , and indirect correlations:

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- For any hyperuniform system,  $\tilde{h}(\mathbf{k} = \mathbf{0}) = -1/\rho$ , and thus  $\tilde{c}(\mathbf{k} = \mathbf{0}) = -\infty$ . Therefore, at the "critical" reduced density  $\phi_c$ ,  $h(\mathbf{r})$  is short-ranged and  $c(\mathbf{r})$  is long-ranged.
- This is the inverse of the behavior at liquid-gas (or magnetic) critical points, where  $h(\mathbf{r})$  is long-ranged (compressibility or susceptibility diverges) and  $c(\mathbf{r})$  is short-ranged.

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- This is the inverse of the behavior at liquid-gas (or magnetic) critical points, where  $h(\mathbf{r})$  is long-ranged (compressibility or susceptibility diverges) and  $c(\mathbf{r})$  is short-ranged.
- For sufficiently large d at a disordered hyperuniform state, whether achieved via a nonequilibrium or an equilibrium route,

$$\begin{split} c(\mathbf{r}) &\sim -\frac{1}{r^{d-2+\eta}} & (r \to \infty), \qquad c(\mathbf{k}) \sim -\frac{1}{k^{2-\eta}} & (k \to 0), \\ h(\mathbf{r}) &\sim -\frac{1}{r^{d+2-\eta}} & (r \to \infty), \qquad S(\mathbf{k}) \sim k^{2-\eta} & (k \to 0), \end{split}$$

where  $\eta$  is a new critical exponent.

One can think of a hyperuniform system as one resulting from an effective pair potential v(r) at large r that is a generalized Coulombic interaction between like charges. Why? Because

$$\frac{v(r)}{k_B T} \sim -c(r) \sim \frac{1}{r^{d-2+\eta}} \qquad (r \to \infty)$$

However, long-range interactions are not required to drive a nonequilibrium system to a disordered hyperuniform state.

## **GLE-CONFIGURATION FORMULATION & GROUND STATES**



We showed

$$\sigma^{2}(R) = 2^{d}\phi\left(\frac{R}{D}\right)^{d} \left[1 - 2^{d}\phi\left(\frac{R}{D}\right)^{d} + \frac{1}{N}\sum_{i\neq j}^{N}\alpha(r_{ij};R)\right]$$

where  $\alpha(r;R)$  can be viewed as a repulsive pair potential:



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- Finding global minimum of  $\sigma^2(R)$  equivalent to finding ground states (energy minimizing configurations).
- For large R, in the special case of hyperuniform systems,

$$\sigma^{2}(R) = \Lambda(R) \left(\frac{R}{D}\right)^{d-1} + \mathcal{O}\left(\frac{R}{D}\right)^{d-3}$$

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### **Hyperuniformity and Number Theory**

• Averaging fluctuating quantity  $\Lambda(R)$  gives coefficient of interest:  $\overline{\Lambda} = \lim_{L \to \infty} \frac{1}{L} \int_0^L \Lambda(R) dR$ 

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We showed that for a lattice

$$\sigma^2(R) = \sum_{\mathbf{q}\neq\mathbf{0}} \left(\frac{2\pi R}{q}\right)^d [J_{d/2}(qR)]^2, \qquad \overline{\Lambda} = 2^d \pi^{d-1} \sum_{\mathbf{q}\neq\mathbf{0}} \frac{1}{|\mathbf{q}|^{d+1}}.$$

Epstein zeta function for a lattice is defined by

$$Z_Q(s) = \sum_{\mathbf{q}\neq \mathbf{0}} \frac{1}{|\mathbf{q}|^{2s}}, \qquad \text{Re} \ s > d/2.$$

Summand can be viewed as an inverse power-law potential. For lattices, minimizer of  $Z_Q(d+1)$  is the lattice dual to the minimizer of  $\overline{\Lambda}$ .

Surface-area coefficient  $\overline{\Lambda}$  provides useful way to rank order crystals, quasicrystals and special correlated disordered point patterns.

antifying Suppression of Density Fluctuations at Large Scales: 1D

The surface-area coefficient  $\overline{\Lambda}$  for some crystal, quasicrystal and disordered one-dimensional hyperuniform point patterns.

Pattern	$\overline{\Lambda}$
Integer Lattice	$1/6 \approx 0.166667$
Step+Delta-Function $g_2$	3/16 =0.1875
Fibonacci Chain*	0.2011
Step-Function $g_2$	1/4 = 0.25
Randomized Lattice	$1/3 \approx 0.333333$

\*Zachary & Torquato (2009)

antifying Suppression of Density Fluctuations at Large Scales: 2D

The surface-area coefficient  $\overline{\Lambda}$  for some crystal, quasicrystal and disordered two-dimensional hyperuniform point patterns.

2D Pattern	$\overline{\Lambda}$
Triangular Lattice	0.508347
Square Lattice	0.516401
Honeycomb Lattice	0.567026
Kagomé Lattice	0.586990
Penrose Tiling*	0.597798
Step+Delta-Function $g_2$	0.600211
Step-Function $g_2$	0.848826

\*Zachary & Torquato (2009)

antifying Suppression of Density Fluctuations at Large Scales: 3D

• Contrary to conjecture that lattices associated with the densest sphere packings have smallest variance regardless of d, we have shown that for d = 3, BCC has a smaller variance than FCC.

Pattern	$\overline{\Lambda}$
BCC Lattice	1.24476
FCC Lattice	1.24552
HCP Lattice	1.24569
SC Lattice	1.28920
Diamond Lattice	1.41892
Wurtzite Lattice	1.42184
Damped-Oscillating $g_2$	1.44837
Step+Delta-Function $g_2$	1.52686
Step-Function $g_2$	2.25

Carried out analogous calculations in high d (Zachary & Torquato, 2009), of importance in communications. Disordered point patterns may win in high d (Torquato & Stillinger, 2006).

#### **1D Translationally Invariant Hyperuniform Systems**

An interesting 1D hyperuniform point pattern is the distribution of the nontrivial zeros of the Riemann zeta function (eigenvalues of random Hermitian matrices and bus arrivals in Cuernavaca): Dyson, 1970; Montgomery, 1973; Krbàlek & Šeba, 2000;  $g_2(r) = 1 - \sin^2(\pi r)/(\pi r)^2$ 



1D point process is always negatively correlated, i.e.,  $g_2(r) \le 1$  and pairs of points tend to repel one another, i.e.,  $g_2(r) \to 0$  as r tends to zero.

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Dyson mapped this problem to a 1D log Coulomb gas at positive temperature:  $k_BT = 1/2$ . The total potential energy of the system is given by

$$\Phi_N(\mathbf{r}^N) = \frac{1}{2} \sum_{i=1}^N |\mathbf{r}_i|^2 - \sum_{i \le j}^N \ln(|\mathbf{r}_i - \mathbf{r}_j|).$$

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Constructing and/or identifying homogeneous, isotropic hyperuniform patterns for  $d \ge 2$  is more challenging. We now know of many more examples.

#### **More Recent Examples of Disordered Hyperuniform Systems**

- **Fermionic point processes:**  $S(k) \sim k$  as  $k \to 0$  (ground states and/or positive temperature equilibrium states): Torquato et al. J. Stat. Mech. (2008)
- Maximally random jammed (MRJ) particle packings:  $S(k) \sim k$  as  $k \to 0$ (nonequilibrium states): Donev et al. PRL (2005)
- Ultracold atoms (nonequilibrium states): Lesanovsky et al. PRE (2014)
- Random organization (nonequilibrium states): Hexner et al. PRL (2015); Jack et al. PRL (2015); Weijs et. al. PRL (2015); Tjhung et al. PRL (2015)
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#### **Natural Disordered Hyperuniform Systems**

- Avian Photoreceptors (nonequilibrium states): Jiao et al. PRE (2014)
- Immune-system receptors (nonequilibrium states): Mayer et al. PNAS (2015)
- Neuronal tracts (nonequilibrium states): Burcaw et. al. Neurolmage (2015)

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- Neuronal tracts (nonequilibrium states): Burcaw et. al. NeuroImage (2015)

#### **Nearly Hyperuniform Disordered Systems**

- Amorphous Silicon (nonequilibrium states): Henja et al. PRB (2013)
- Structural Glasses (nonequilibrium states): Marcotte et al. (2013)

## **Hyperuniformity and Jammed Packings**

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- A 3D maximally random jammed (MRJ) packing is a prototypical glass in that it is maximally disordered but perfectly rigid (infinite elastic moduli).
- Such packings of identical spheres have been shown to be hyperuniform with quasi-long-range (QLR) pair correlations in which h(r) decays as  $-1/r^4$  (Donev, Stillinger & Torquato, PRL, 2005).



This is to be contrasted with the hard-sphere fluid with correlations that decay exponentially fast.

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Apparently, hyperuniform QLR correlations with decay  $-1/r^{d+1}$  are a universal feature of general MRJ packings in  $\mathbb{R}^d$ . Zachary, Jiao and Torquato, PRL (2011): ellipsoids, superballs, sphere mixtures

Berthier et al., PRL (2011); Kurita and Weeks, PRE (2011) : sphere mixtures Jiao and Torquato, PRE (2011): polyhedra

#### **Hyperuniformity, Free Fermions & Determinantal Point Processes**

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- Solution One can map random Hermitian matrices (GUE), fermionic gases, and zeros of the Riemann zeta function to a unique hyperuniform point process on  $\mathbb{R}$ .
- Solution We provide exact generalizations of such a point process in d-dimensional Euclidean space  $\mathbb{R}^d$  and the corresponding n-particle correlation functions, which correspond to those of spin-polarized free fermionic systems in  $\mathbb{R}^d$ .



$$g_2(r) = 1 - \frac{2\Gamma(1+d/2)\cos^2\left(rK - \pi(d+1)/4\right)}{K\pi^{d/2+1}r^{d+1}} \qquad (r \to \infty)$$

$$S(k) = \frac{c(d)}{2K}k + \mathcal{O}(k^3) \qquad (k \to 0) \qquad (K: \text{ Fermi sphere radius})$$

Torquato, Zachary & Scardicchio, J. Stat. Mech., 2008 Scardicchio, Zachary & Torquato, Phys. Rev., 2009

#### **Hyperuniformity and One-Component Plasma (OCP)**

- OCP: particles of charge e interacting via the Coulomb potential immersed in a rigid, uniform background of opposite charge.
- By construction, OCPs are hyperuniform. Why? At sufficiently high T, OCPs are disordered.

#### **Hyperuniformity and One-Component Plasma (OCP)**

- OCP: particles of charge e interacting via the Coulomb potential immersed in a rigid, uniform background of opposite charge.
- By construction, OCPs are hyperuniform. Why? At sufficiently high T, OCPs are disordered.
- Solution For d = 2 and a special coupling constant  $\Gamma = e^2/k_BT$  equal to 2, the total correlation function h(r) and S(k) have been ascertained exactly by Jancovici (Phys. Rev. Lett, 1981):

$$h(r) = -\exp\left(-\pi r^2\right)$$

This shows that hyperuniformity is not always accompanied by long-range correlations.

Corresponding structure factor is given by

$$S(k) = 1 - \exp[-k^2/(4\pi)]$$

$$S(k) \sim k^2 \qquad (k \to 0)$$

#### **Out-of-This-World Example**

- Superionic ice is a special group of ice phases at high temperatures and pressures, which may exist in ice-rich planets and exoplanets.
- We reported evidence that from 280 GPa to 1.3 TPa, there are several competing phases within the close-packed oxygen sublattice.

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- At higher pressures, these sublattices become unstable to a new unusual superionic phase in which the oxygen sublattice takes the  $P2_{1/c}$  symmetry.



**•** The diffusive hydrogen in the  $P2_{1/c}^{\text{Pressure (GPa)}}$  superionic phase shows strong

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Superionic ice is nearly hyperuniform.



Sun, Clark, Torquato & Car (2015)

#### In the Eye of a Chicken: Photoreceptors

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Jiao, Corbo & Torquato, PRE (2014).

#### **Avian Cone Photoreceptors**

Disordered mosaics of both total population and individual cone types are effectively hyperuniform, which has been never observed in any system before (biological or not). We term this multi-hyperuniformity.



Jiao, Corbo & Torquato, PRE (2014)

#### **Slow and Rapid Cooling of a Liquid**

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Typically, ground states are periodic with high crystallographic symmetries.

Can classical ground states ever be disordered?

#### **Creation of Disordered Hyperuniform Ground States**

Uche, Stillinger & Torquato, Phys. Rev. E 2004 Batten, Stillinger & Torquato, Phys. Rev. E 2008

**Collective-Coordinate Simulations** 

• Consider a system of N particles with configuration  $\mathbf{r}^N$  in a fundamental region  $\Omega$  under periodic boundary conditions) with a pair potentials  $v(\mathbf{r})$  that is bounded with Fourier transform  $\tilde{v}(\mathbf{k})$ .

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$$\begin{split} \Phi_N(\mathbf{r}^N) &= \sum_{i < j} v(\mathbf{r}_{ij}) \\ &= \frac{N}{2|\Omega|} \sum_{\mathbf{k}} \tilde{v}(\mathbf{k}) S(\mathbf{k}) + \text{ constant} \end{split}$$

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These hyperuniform ground states are called "stealthy" and generally highly degenerate.

#### **Creation of Disordered Hyperuniform Ground States**

Uche, Stillinger & Torquato, Phys. Rev. E 2004 Batten, Stillinger & Torquato, Phys. Rev. E 2008

**Collective-Coordinate Simulations** 

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• Stealthy patterns can be tuned by varying the parameter  $\chi$ : ratio of number of constrained degrees of freedom to the total number of degrees of freedom, d(N-1).

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where n is any whole number. The special case n = 0 is just the simple step function.



In the large-system (thermodynamic) limit with m = 0 and m = 4, we have the following large-r asymptotic behavior, respectively:  $v(r) \sim \frac{\cos(r)}{2}$  (m = 0)

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. – p. 27/33

While the specific forms of these stealthy potentials lead to the same convergent ground-state energies, this may not be the case for the pressure and other thermodynamic quantities.

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**Success rate** to achieve disordered ground states is 100%.



• As  $\chi$  increases, short-range order increases. This suggests new order metric

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For  $\chi > 1/2$ , the system undergoes a transition to a crystal phase and the energy landscape becomes considerably more complex.



#### Animations

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Other applications include new phononic devices.

#### **Ensemble Theory of Disordered Ground States**

Torquato, Zhang & Stillinger, Phys. Rev. X, 2015

- Nontrivial: Dimensionality of the configuration space depends on the number density  $\rho$  (or  $\chi$ ) and there is a multitude of ways of sampling the ground-state manifold, each with its own probability measure Which ensemble? How are entropically favored states determined?
- For some ensemble at fixed density  $\rho$ , the average energy per particle u for radial potentials in the thermodynamic limit is given by

$$u \equiv \langle \frac{\Phi(\mathbf{r}^N)}{N} \rangle = \frac{\rho}{2} \int_{\mathbb{R}^d} v(r) g_2(r) d\mathbf{r}$$
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Remark: Ground-state manifold is generally highly degenerate.

In the thermodynamic limit, parameter  $\chi$  is related to the number density  $\rho$  in any dimension d via  $\rho \, \chi = \frac{V_1(K)}{2d \, (2\pi)^d},$ 

where  $V_1(K)$  is the volume of a *d*-dimensional sphere of radius *K*.

**Remarks:** We see that  $\chi$  and  $\rho$  are inversely proportional to one another. Thus, for fixed K and d, as  $\chi$  tends to zero,  $\rho$  tends to infinity, which corresponds counterintuitively to the uncorrelated ideal-gas limit (Poisson distribution). As  $\chi$  increases from zero, the density  $\rho$  decreases.

#### **Pseudo-Hard Spheres in Fourier Space**

From previous considerations, we see that that an important contribution to S(k) is a simple hard-core step function  $\Theta(k - K)$ , which can be viewed as a disordered hard-sphere system in Fourier space in the limit that  $\chi$  tends to zero, i.e., as the number density  $\rho$  tends to infinity.



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Imagine carrying out a series expansion of S(k) about  $\chi = 0$ . We make the ansatz that for sufficiently small  $\chi$ , S(k) in the canonical ensemble for a stealthy potential can be mapped to  $g_2(r)$  for an effective disordered hard-sphere system for sufficiently small density.

#### **Pseudo-Hard Spheres in Fourier Space**

Let us define

$$\tilde{H}(k) \equiv \rho \tilde{h}(k) = h_{HS}(r=k)$$

There is an Ornstein-Zernike integral eq. that defines FT of appropriate direct correlation function,  $ilde{C}(k)$  :

$$\tilde{H}(k) = \tilde{C}(k) + \eta \,\tilde{H}(k) \otimes \tilde{C}(k),$$

where  $\eta$  is an effective packing fraction. Therefore,

$$H(r) = \frac{C(r)}{1 - (2\pi)^d \eta C(r)}.$$

This mapping enables us to exploit the well-developed accurate theories of standard Gibbsian disordered hard spheres in direct space.



#### **CONCLUSIONS**

- Disordered hyperuniform materials can be regarded to be new ideal states of disordered matter.
- Hyperuniformity provides a unified means of categorizing and characterizing crystals, quasicrystals and special correlated disordered systems.
- The degree of hyperuniformity provides an order metric for the extent to which large-scale density fluctuations are suppressed in such systems.
- Disordered hyperuniform systems appear to be endowed with unusual physical properties that we are only beginning to discover.
- Hyperuniformity has connections to physics and materials science (e.g., ground states, quantum systems, random matrices, novel materials, etc.), mathematics (e.g., geometry and number theory), and biology.
- Halton-type low-discrepancy point sets are hyperuniform but not disordered.

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  Collaborators

Roberto Car (Princeton) Paul Chaikin (NYU) Bryan Clark (U. Illinois) Joseph Corbo (Washington Univ.) Marian Florescu (Surrey) Miroslav Hejna (Princeton) Yang Jiao (Princeton/ASU) Gabrielle Long (NIST) Etienne Marcotte (Princeton) Weining Man (San Francisco State) Sjoerd Roorda (Montreal) Antonello Scardicchio (ICTP) Jiming Sun (Princeton) Paul Steinhardt (Princeton) Frank Stillinger (Princeton) Chase Zachary (Princeton)