Unexpected Density Fluctuations in Jammed Disordered Sphere Packings

Aleksandar Donev,1,2 Frank H. Stillinger,3 and Salvatore Torquato1,2,3,*
1Program in Applied and Computational Mathematics, Princeton University, Princeton, New Jersey 08544, USA
2PRISM, Princeton University, Princeton, New Jersey 08544, USA
3Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA
(Received 15 April 2005; published 26 August 2005)

We computationally study jammed disordered hard-sphere packings as large as a million particles. We show that the packings are saturated and hyperuniform, i.e., that local density fluctuations grow only as a logarithmically augmented surface area rather than the volume of the window. The structure factor shows an unusual nonanalytic linear dependence near the origin, $S(k) \sim |k|$. In addition to exponentially damped oscillations seen in liquids, this implies a weak power-law tail in the total correlation function, $h(r) \sim -r^{-4}$, and a long-ranged direct correlation function $c(r)$.

DOI: 10.1103/PhysRevLett.95.090604 PACS numbers: 05.20.-y, 61.20.-p

The characterization of local density fluctuations in many-particle systems is a problem of great fundamental interest in the study of condensed matter, including atomic, molecular, and granular materials. In particular, long-wavelength density fluctuations are important to such diverse fields as statistical mechanics, granular flow, and even cosmology [see Ref. [1] and references therein]. Previous work by some of us [1] considered the quantitative characterization of local density fluctuations in point patterns, and, in particular, those in which infinite-wavelength fluctuations are completely suppressed, i.e., the structure factor $S(k)$ vanishes at the origin. In these so-called hyperuniform [or superhomogeneous [2]] systems, the variance in the number of points inside a large window grows slower than the volume of the window, typically like the window surface area. Known examples include ordered lattices and quasicrystals [1,2], but it is important to identify statistically homogeneous and isotropic systems (e.g., glasses) that are hyperuniform.

For equilibrium liquids and crystals, $S(k = 0)$ is proportional to the isothermal compressibility and is thus positive. Strictly jammed sphere packings [3] are rigorously incompressible (and nonshearable), but they are also non-equilibrium systems. In Ref. [1], it was conjectured that all saturated [4] strictly jammed packings are hyperuniform. Of particular importance are disordered jammed packings, especially the maximally random jammed (MRJ) state [5]. The MRJ state is the most disordered among all strictly jammed packings and is related to the view of jamming as a rigidity transition and/or dynamic arrest in both granular [6] and glassy materials [7]. Hyperuniformity involves an “inverted critical phenomenon” in which the range of the direct correlation function $c(r)$ diverges [1]. It is hence of great interest to test whether disordered jammed sphere packings are hyperuniform. In this Letter, we demonstrate that MRJ packings are indeed hyperuniform and saturated. Moreover, we observe an unusual nonanalytic structure factor $S(k) \sim |k|$ for $k \rightarrow 0$, or equivalently, a quasi-long-ranged negative tail of the total pair correlation function $h(r) \sim -r^{-4}$, just as found in diverse systems such as the early Universe [2] and in liquid helium [8].

We prepare jammed packings of hard spheres under periodic boundary conditions using a modified Lubachevsky-Stillinger (LS) packing algorithm [see Ref. [9]]. The generated disordered sphere packings typically have volume fractions in the range $\phi = 0.64-0.65$, and to a good approximation the packings should be representative of the MRJ state. For this study, we have generated a dozen packings of $N = 10^3$ and $N = 10^5$ particles jammed up to a reduced pressure of $10^{12}$ using an expansion rate of $10^{-3}$ [9] with $\phi \approx 0.644$. Generating such unprecedented one-million-particle packings was necessary in order to study large-scale density fluctuations without relying on dubious extrapolations.

The packings generated by the LS and other algorithms have a significant fraction (~2.5%) of rattling particles that are not truly jammed but can rattle inside a small cage formed by their jammed neighbors [9]. Assuming that the rattlers are more or less randomly distributed among all particles, a hyperuniform packing from which the rattlers are then removed would have $S(0) = 0.025 > 0$. Similarly, the hyperuniformity could be destroyed by randomly filling large-enough voids with additional rattlers. It is therefore important to verify that the jammed packings are saturated, i.e., that there are no voids large enough to insert additional rattlers. Figure 1 shows the complementary cumulative pore-size distribution [10] $F(\delta)$, which gives the probability that a sphere of diameter $\delta$ could be inserted into the void space, with and without the rattlers. Clearly there is no room to insert any additional rattlers; the largest observed voids are around $\delta_{\text{max}} = 0.08D$. The algorithm used to produce the packings appears to fill all void cages with particles; i.e., the packings are saturated.

When periodic boundary conditions apply with a periodic box of length $L$, particle correlations can only be studied up to a distance $L/2$, and there are large finite-size corrections for distances comparable to $L$. Additionally, as we show later, strong statistical fluctuations appear due to

0031-9007/05/95(9)/090604(4)$23.00 090604-1 © 2005 The American Physical Society
finite system size, making it necessary to use even larger systems to measure pair correlations at large distances. In reciprocal space, \( S(k) \) can only be measured for \( k \geq 2\pi/L \), with large discretization errors for the smallest wave vectors. To overcome these finite-size effects, it was necessary to generate packings of one million particles.

Consider a large isotropic three-dimensional packing of \( N \) hard spheres of diameter \( D \), with average number density \( \rho = N/V \) and average volume fraction \( \phi = \pi\rho D^3/6 \).

We employ the usual pair correlation function \( g_2(x = r/D) \) or the total correlation function \( h(x) = g_2(x) - 1 \) in real space, or the equivalent Fourier representation given by the structure factor

\[
S(K = kD) = 1 + 24\phi \int_0^\infty \frac{\sin(Kx)}{Kx} x^2 h(x)dx.
\]

Of particular interest are the moments of \( h(x) \), \( \langle x^n \rangle = \int_0^\infty x^n h(x)dx \). Computer-generated packings are always finite, and thus binning techniques must be used to obtain probability densities like \( h \). Accordingly, we prefer to use the more readily measurable excess coordination

\[
\Delta Z(x) = 1 + 24\phi \int_0^x w^2 h(w)dw.
\]

This is the average excess number of points inside a spherical window of radius \( xD \) centered at a particle, compared to the ideal-gas expectation \( 8\phi x^3 \). Any integral containing \( h(x) \) can easily be represented in terms of \( \Delta Z(x) \) using integration by parts. For the structure factor we get

\[
S(K, R) = \lim_{R \to \infty} S(K, R) = \frac{\Delta Z(R) \sin(KR)}{KR} - \int_0^R \Delta Z(x) \frac{d \sin(Kx)}{dx} \frac{dx}{Kx}.
\]

This has quadratic behavior near \( k = 0 \) when expanded in a Taylor series,

\[
S(K) = S(0) + \frac{K^2}{3} \int_0^\infty x[\Delta Z(x) - S(0)]dx,
\]

where \( S(0) = \Delta Z(x \to \infty) \) vanishes for a hyperuniform system. For large \( x \), an explicit finite-size correction of order \( 1/N \) needs to be applied to the infinite-system excess coordination, \( \Delta Z(x) = S(0)[1 - 8\phi x^3/N] \) [11], as it is clear that the excess coordination must vanish for windows as large as the whole system.

Figure 2 shows \( S(k) \) for the simulated packings as obtained via a direct Fourier transform (DFT) of the particle positions, \( S(k) = N^{-1} \sum_{i=1}^N \exp(i \vec{k} \cdot \vec{r}_i)^2 \), where \( \vec{k} \) is a reciprocal lattice vector for the periodic unit cell [12]. To obtain an approximation to the radially symmetric infinite-system \( S(k) \), we average over the reciprocal lattice vectors inside a spherical shell of thickness \( 2\pi/L \). Using Eq. (1) together with a numerical (truncated) \( \Delta Z(x) \) quickly gives \( S(k) \) over a wide range of wavelengths. However, the behavior near the origin is not reliable since it depends on the analytic extension for the tail of \( \Delta Z(x) \). The results of the DFT calculations are shown in Fig. 2, and they closely match the one obtained from \( \Delta Z(x) \) for wavelengths smaller than about 20 diameters.

Figure 2 reveals that the saturated packing is indeed hyperuniform [as conjectured in Ref. [1]] to within \( S(0) < 10^{-3} \). The behavior of \( S(k) \) near the origin is very surprising. The observed \( S(k) \) follows closely a nonanalytic linear
relationship [13] well fitted by $S(K) = 6.1 \times 10^{-4} + 3.4 \times 10^{-3} K$ over the whole range $K/2\pi < 0.4$. By contrast, analytic quadratic behavior is observed for a liquid sample at $\phi = 0.49$, as shown in the figure. Theoretical finite-size corrections to the small-$k$ behavior of $S(k)$ have only been considered for relatively low-density liquid systems with relatively small $N$ [11], and are not useful for our purposes. Although estimating the corrections to the DFT data analytically is certainly desirable, such corrections appear to be rather small at least for the well-understood liquid at $\phi = 0.49$. Comparison among the different $N = 10^6$ samples shows that statistical fluctuations in $S(k)$ near the origin are very small.

Equation (2) shows that if $h$ is truly short ranged, the structure factor must be analytic (i.e., an even power of $k$, usually quadratic) near the origin. Our numerical observations point strongly to a linear $S(k)$ for small $K$. This observation $S(k) \sim |k|$ implies a negative algebraic power-law tail $b(x) \sim -x^{-4}$ uncharacteristic of liquid systems and typically only seen in systems with long-range interactions. Such nonanalytic behavior is assumed in the so-called Harrison-Zeldovich power spectrum of the density fluctuations in the early Universe [2] and is also seen in the ground state of liquid helium [8]. A long-ranged tail must appear in the direct correlation function $c(r)$ for a strictly hyperuniform system due to the divergence of $\bar{c}(0)$, in a kind of “inverted critical phenomenon” [1]. Such a tail is uncharacteristic of liquids where the range of $c(r)$ is substantially limited to the range of the interaction potential. The direct correlation function can numerically be obtained from its Fourier transform via the Ornstein-Zernike (OZ) equation, $\tilde{c}(k) = (\pi/6\phi)[S(k) - 1]/S(k)$, and we have shown it in the inset in Fig. 2, along with the corresponding Percus-Yevick (PY) ansatz [14] for $c(r)$ at $\phi = 0.49$ which makes the approximation that $c(r)$ vanishes outside the core. Two unusual features relative to the liquid are observed for our jammed packing. First, there is a positive $\delta$ function at contact corresponding to the $Z = 6$ average touching neighbors around each jammed particle [9]. Second, there is a relatively long tail outside the core, the exact form of which depends on the behavior of $S(k)$ around the origin [15].

The numerical coefficient in the power-law tail in $h(x)$ is very small, $\Delta Z(x) \approx 4.4 \times 10^{-3} x^{-1}$, and cannot be directly observed, as we will show shortly. It is, however, possible to observe its effect on large-scale density fluctuations. For monodisperse hard-sphere systems it suffices to focus only on the positions of the sphere centers and consider density fluctuations in point patterns. Following Ref. [1], consider moving a spherical window of radius $R = XD$ through a point pattern and recording the number of points inside the window $N(X)$. The number variance is exactly [1]

$$\sigma^2(X) = \langle X^2(X) \rangle - \langle N(X) \rangle^2$$

$$= \frac{3}{2} \phi \left[ (2X)^2 (\Delta Z_0(2X) - \Delta Z_2(2X)) \right],$$

where $\Delta Z_0(x) = \int_0^x w^2 \Delta Z(w) dw$ denotes a running moment of $\Delta Z$. Asymptotically, for large windows, in an infinite system with analytic $S(k)$, $\sigma^2(X) \approx AX^3 + BX^2$, where $A = 8\phi(1 + 24\phi(\pi^2)) = 8\phi S(0)$ is the volume fluctuation coefficient, and $B = -144\phi^2(\pi^2) = 6\phi \Delta Z_0(\infty)$ is the surface fluctuation coefficient. When a nonintegrable power-law tail exists in $\Delta Z(x)$, asymptotically the “surface” fluctuation coefficient contains an additional logarithmic term, $B(X) = B_0 + C \ln X$. Such a logarithmic correction does not appear for any of the examples studied in Ref. [1]. Explicit finite-size effects for nonhyperuniform systems yield a correction $A(X) = 8\phi S(0)[1 - 8\phi X^2/N]$ [16]. Figure 3 shows numerical results for the number variance as a function of window size, along with the predicted asymptotic dependence, including both the logarithmic and $N^{-1}$ corrections [17]. Both corrections need to be included in order to observe this close a match between the data and theory. The constants $S(0)$ and $C$ were obtained from the linear fit to $S(k)$, while $B_0 = 1.02$ was obtained by numerically integrating $\Delta Z(x)$, as explained shortly [18].

![FIG. 3 (color online). The variance $\sigma^2$ vs window radius for a jammed $10^6$-particle packing. The uncertainty in the variance (shown with error bars) is estimated to be $\sigma^2/\sqrt{M}$, where $M = 10^6$ is the number of windows used for a given window size. Also shown is the theoretically predicted dependence of the form $AX^3 + CX^2 \ln X + B_0 X^2$, along with just the surface term $B_0 X^2$, which dominates the density fluctuations.](https://example.com/fig3.png)
increase with increasing order: it approaches infinity for ordered lattices, is two for perturbed lattices, and is one for MRJ. In this sense, the MRJ packings are markedly more disordered: they have macroscopic density fluctuations which are much larger than crystalline packings. Quantitative understanding of this aspect of disorder and its relation to local density fluctuations remains an intriguing open problem.

This work was supported in part by the National Science Foundation under Grant No. DMS-0312067.

*Electronic address: torquato@electron.princeton.edu

[4] A saturated packing is one in which no additional particles can be added.
[12] This calculation potentially involves many reciprocal lattice points and cannot easily and accurately be made faster using fast Fourier transforms (FFT).
[13] Since $S(k)$ is an even function, its derivative must vanish at the origin for it to be analytic.
[15] We used the linear fit to $S(k)$ when producing the figure, implying $c(r) \sim r^{-2}$.
[17] Additional implicit finite-size effects due to the periodicity of the system have been found to be significantly smaller in Ref. [16].
[18] The surface coefficient $B_0$ cannot be determined from just the linear part of $S(k)$ near the origin.
[21] Compare this fit to $\xi \approx 1.4$ and $K_0 \approx 7.9$ as measured in R. Jullien, P. Jung, D. Caprion, and D. Quittmann, Phys. Rev. E 54, 6035 (1996).