

Observable Microscopic Density Fluctuations and the Gauss Circle Problem

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In discrete systems the number density, defined as the number of particles per unit volume, is subject to fluctuations depending on the size and location of the sampling volume. Experimentally, fluctuations in the pair distribution function die out quickly in disordered materials but persist in crystals. Counter intuitively, we show that for a single atom at the origin, fluctuations should persist even in the case of a random system, only disappearing after ensemble averaging. We demonstrate a useful connection to the classic unsolved problem in mathematics known as the Gauss circle problem, which leads to new insights.

Measurements of the density of materials have been an important characterization method since the time of Archimedes. The atomic pair distribution function (PDF) has been used to study the local density in disordered materials since the 1930's.^{1,2} The PDF is experimentally accessible by Fourier transforming X-ray or neutron diffraction data.³ More recently it has been successfully applied to the study of disorder in crystalline and nanocrystalline materials, these developments being made possible by powerful modern x-ray and neutron sources and advanced computing.⁴ The technique has particular applicability for studying nanocrystals that do not have long-range order and cannot be studied using conventional crystallographic techniques. In this case, information about the size and shape of the nanocrystalline domains could be extracted from the decay of the PDF with distance, if it were known that in a crystal the fluctuations in the PDF persist indefinitely out to large distances. To our knowledge this is the first report concerning such behaviour. We show that these fluctuations can be calculated analytically for the PDF of a single atom in a random structure. Only after averaging

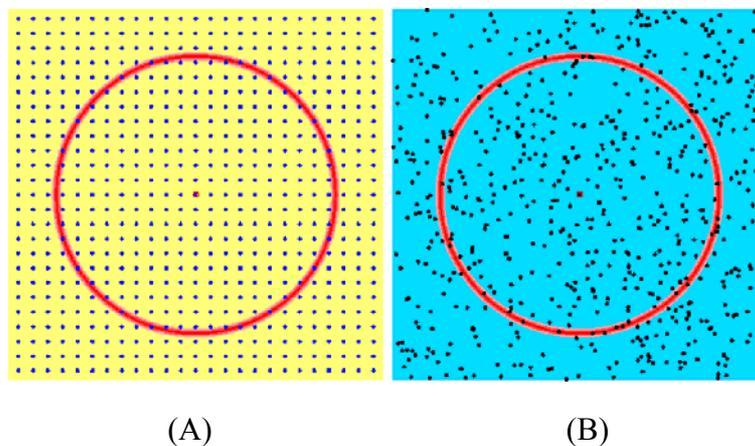


Figure 1. (A) a regular grid of points is enclosed by a circle, while in (B) there is a set of random points. To calculate the pair distribution function (PDF) one point is chosen as the origin of a circle of radius r . Only those sites inside the red annulus of width σ contribute to the value of PDF at a distance r .

the PDF over all the atoms in the sample do these fluctuations disappear. In the crystal case, we demonstrate this persistence numerically. The crystal problem maps onto the long-unsolved Gauss circle problem⁵ resulting in new insights into both the PDF and Gauss circle problems.

In the first half of the nineteenth century, the German mathematician, Carl Friedrich Gauss put forward what has come to be known as the *Gauss circle problem*. This involves counting the number of points $N(r)$ on a square grid with unit spacing inside a circle of radius r , as sketched in Figure 1(A). The result is expressed as

$$N(r) = \pi r^2 + E(r), \quad (1)$$

where it has been shown⁶ that

$$|E(r)| \leq A r^\theta \quad \text{with} \quad 1/2 < \theta \leq 46/73 \quad (2)$$

with A being a constant. If the Gauss circle problem is generalised to a cubic hyper-grid of points in d dimensions, then instead of (1) we have

$$N(r) = \Omega_d r^d / d + E(r), \quad (3)$$

where Ω_d is the d -dimensional solid angle ($\Omega_2 = 2\pi$, $\Omega_3 = 4\pi$, etc). The difficulty in solving this classic problem is that it focuses on the *extreme* and very rare fluctuations at large r . On the other hand, the root mean square (rms) fluctuations are easier to treat and give the result

$$\langle E(r)^2 \rangle = B r^{(d-1)} \quad (4)$$

which can be understood by noting that fluctuations take place as points enter and leave the circle as it expands (Figure 1(A)), and so the square of the fluctuations is

proportional to the surface area, with B being a constant. For $d = 2$, these *rms* fluctuations correspond to $\theta = 1/2$, which is ruled out for the *extreme* fluctuations in the Gauss circle problem because of the strict inequality in (2).

It is difficult to measure and/or characterize extreme fluctuations, either experimentally or in a computer simulation, which makes the Gauss circle problem of lasting interest. However rms density fluctuations can be measured, and are important in PDF experiments.

Different statistics, sketched in the two panels of Figure 1, lead to different fluctuations. For points that are thrown down randomly, as in Figure 1(B), the squared fluctuations are proportional to the volume

$$\langle E(r)^2 \rangle = Cr^d \quad (5)$$

where C is a constant.

Fluctuations in $E(r)$ are related to the fluctuations in the PDF that can be measured experimentally using X-ray or neutron diffraction from powders with atoms arranged in a similar (crystalline) way to that envisaged by Gauss. This leads to the surprising insight that fluctuations that were assumed to be decaying in the PDF of crystals at large distances, are actually persistent when measured with high resolution. The PDF does not measure the number of atoms inside a circle or sphere, but rather the number inside a spherical annulus whose width σ is determined by the thermal vibrational amplitude of the atoms in the solid. This width is indicated by the fuzzy red circumferences in Figure 1.

We consider, for simplicity, the case of materials formed by atoms of a single type. We define PDF for a single atom in d -dimensional space as

$$G(r) = r^{\frac{d-1}{2}} [\rho(r) - \rho_0], \quad (6)$$

where $G(r)$ is the PDF, ρ_0 is the (uniform) atomic number density and $\rho(r)$ is the radial density centered about an atom at the origin. For crystals and glasses in $3d$, we assume that the same form is valid in d -dimensions, the radial density with respect to atom i at the origin can be expressed as^{7,8,9}.

$$\rho_i(r) = \frac{1}{\Omega_d r^{d-1}} \sum_{j \neq i} \frac{1}{\sqrt{2\pi\sigma_{ij}^2}} \exp\left[-\frac{(r - \bar{r}_{ij})^2}{2\sigma_{ij}^2}\right], \quad (7)$$

where σ_{ij} is the rms deviation of the distance between atoms i and j from the equilibrium value \bar{r}_{ij} due to the thermal atomic vibrations. The averaged radial density is obtained by averaging $\rho_i(r)$ over all atoms in the sample

$$\rho(r) = \frac{1}{N} \sum_{i=1}^N \rho_i(r). \quad (8)$$

In simple perfect crystals there is no need to average over different atoms at the origin, since every atom has the same environment and hence $\rho_i(r) = \rho(r)$.

The thermal motion of atoms located far away from one another is uncorrelated and it can be assumed that $\sigma_{ij} = \sigma$ is the same for any pair of atoms more than $\sim 15\text{\AA}$ apart. It is these larger distances that are of interest to us here.

For the PDF of a solid material, the fluctuations in the annuli shown in Figure 1, always have the *same* r dependence, no matter what the statistics of the atomic structure (glass, crystal etc.). This is because in all cases, the rms fluctuations associated with the number of atoms in the annulus, scale as the square root of the surface area. Because of this, the fluctuations associated with the PDF as defined in (6) do not decay with distance, but rather persist out to arbitrarily large distances with constant amplitude.

To understand this unexpected behaviour, it is convenient to explore the case of a completely random distribution of points, shown in Figure 1(B). This provides a model system that is exactly soluble in any dimension, and which we have found to be useful in giving insights to both the Gauss circle problem and the PDF behaviour at large distances. In this model, the positions of two atoms or points can coincide. Since the PDF oscillates around zero, we calculate the square of the PDF averaged over different random distributions of the points. Denoting this statistical averaging by $\langle \dots \rangle$, we have from equation (6)

$$\langle G_i^2(r) \rangle = \frac{\langle [\Omega_d r^{d-1} \sigma \rho_i(r) - \Omega_d r^{d-1} \sigma \rho_o]^2 \rangle}{\Omega_d^2 r^{d-1} \sigma^2}. \quad (9)$$

In order to estimate $\langle G_i^2(r) \rangle$ we note that the actual number of particles in the spherical annulus of radius r and thickness σ is given by $N = \Omega_d r^{d-1} \sigma \rho_i(r)$, while $\bar{N} = \Omega_d r^{d-1} \sigma \rho_o$ is the expected or average number of particles. For such random systems,¹⁰ we expect $\langle [N - \bar{N}]^2 \rangle \approx \bar{N}$, and hence $\langle G_i^2(r) \rangle \approx (\Omega_d r^{d-1} \sigma \rho_o) / (\Omega_d^2 r^{d-1} \sigma^2) \approx \rho_o / (\sigma \Omega_d)$ does not depend on distance meaning that the fluctuations in the PDF with respect to single particular site at the origin do not decay at large distances. An exact calculation¹¹ shows that there is an additional factor $2\sqrt{\pi}$ for all dimensions in the denominator giving

$$\langle G_i^2(r) \rangle = \frac{\rho_o}{2\sqrt{\pi} \sigma \Omega_d}. \quad (10)$$

We have found this result to be very helpful, as all rms fluctuations within an annulus give a similar result; only the constant in (10) changes with the statistics, if say we transfer our attention from random points as shown in Figure 1(B) to a regular grid of points, as shown in Figure 1(A) for the Gauss problem. Although the random distribution of points fluctuates all over the volume, it is only the fluctuations in an annulus of width σ that are relevant for the PDF. In the Gauss circle problem, there are only fluctuations near the surface, as the points inside the circle are not subject to

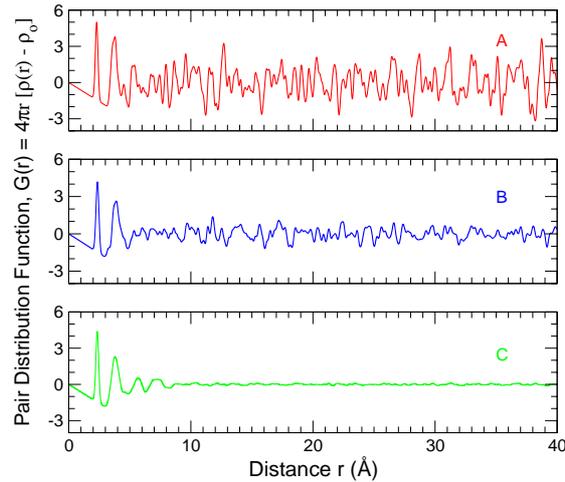


Figure 2. The calculated PDF for a 100,000 atom model.¹² of amorphous silicon with a mean Si - Si nearest neighbour distance of 2.4Å and with a thermal width that approaches $\sigma = 0.1\text{Å}$ at larger distances. The panels A, B, C are for a single atom at the origin, averaged over 10 atoms at the origin, and averaged over 20000 atoms at the origin respectively.

fluctuation, being fixed on a grid. Hence both problems lead to the same distance dependence of the fluctuations, and $\langle G_i^2(r) \rangle$ does not decay in any dimension for any statistics. Of course this is only true for solids, where each atom is constrained to vibrate about a fixed equilibrium site. In liquids the PDF associated with a single site would decay due to diffusion.

The key is that if *sufficient* randomness is present, then the fluctuations associated with the annuli in Figure 1, have the same r dependence, and are in the same universality class. If some other shape were used, instead of a circular annulus, for example a square annulus with the square grid of lattice points, randomness would be absent, and there would be much larger fluctuations at large distances, as whole lines of atoms could pass in and out of the square annulus.

The PDF can be used to extract information about the atomic geometry in solids with the peak-widths being determined by thermal atomic vibrations.⁸ Although, to the

best of our knowledge, there have been no calculations of a PDF for a solid at really large distances, it seems that there has been a belief that the amplitude of the peaks in the PDF should decay as the distance increases even for perfect crystals. Such reasoning goes as follows: since the value of $\rho_i(r)$ is determined approximately by the number of atoms inside the spherical annulus of radius r and fixed thickness σ , one can expect that $\rho_i(r)$ converges to ρ_0 as the volume of the annulus increases with r and this leads to lack of any structure in the PDF at large distances. Such reasoning is quite misleading as the fluctuations do indeed persist.

The PDF calculated with respect to a single atom in amorphous Si using $\rho_i(r)$ as $\rho(r)$ in (3) is shown on panel A of Figure 2. Panels B and C show PDFs corresponding to $\rho(r)$ that was obtained by averaging $\rho_i(r)$ over 10 and 20000 different atoms respectively. This PDF calculated for a model structure^{13,14} of amorphous silicon with thermal widths corresponding to room temperature. Figure 2 clearly shows that the increase of the volume of the annulus with r does *not* lead to the decay of the PDF – *rather it is the averaging over the atom at the origin* that leads to such decay. As all atoms are equivalent in a crystal, there is no averaging and hence no decay in the fluctuations which persist as in seen in Figure 3 for the computed PDF in crystalline nickel.

When a single atom is at the origin, the fluctuations persist out to large distances. When an average is performed over a sufficient number of atoms at the origin, as shown in Figure 2, then the amplitude of peaks quickly decays as the distance increases. This averaging occurs naturally in X-ray and neutron diffraction experiments, so that the behaviour shown in the bottom panel of Figure 2 is ubiquitous in all amorphous and glassy materials.¹⁵ Thus, traditionally there was interest in the behaviour of PDF at small distances, while behaviour at large distances is rarely discussed.

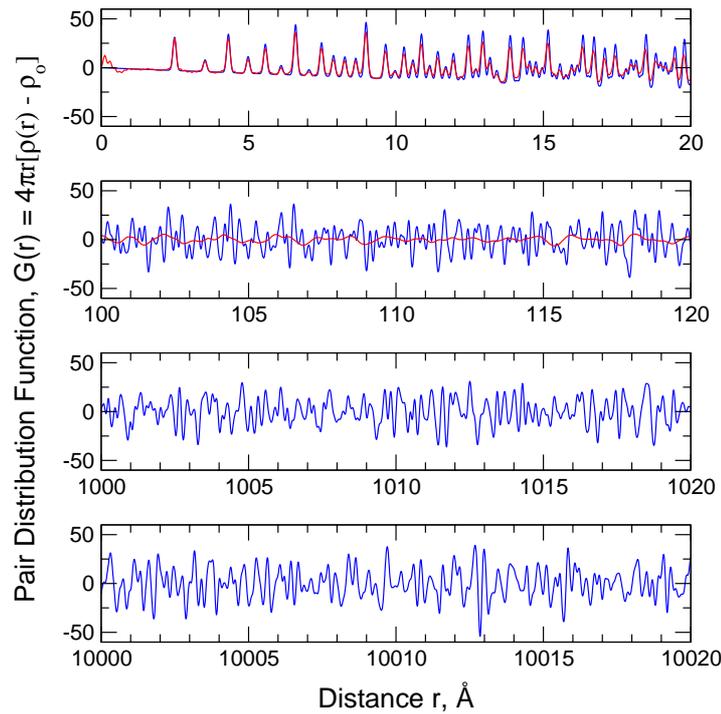


Figure 3. *The pair distribution function for crystalline nickel at 15K shown over various distance intervals of 20\AA . The blue lines are calculated using a force constant model for the thermal widths that approach $\sigma \cong 0.06\text{\AA}$ at large distances. The nearest neighbour nickel separation is 2.5\AA . Notice that the fluctuations in the lower panels are statistically self-similar and do not decay. The red lines result from high resolution neutron diffraction data taken 15K on the NPDF diffractometer at Los Alamos National Laboratory.*

It can clearly be seen that the PDF, calculated for crystalline nickel at room temperature (Fig. 3), does *not* decay at large distances. The experimental results for crystalline nickel match the computed results well up to 20\AA and even to 50\AA , but do eventually decay as seen in the second panel of Figure 3. This is due to instrumental resolution and is not an intrinsic feature. With improved techniques it should be possible to see structure in crystalline materials up to 100\AA and eventually even further.

We emphasize that the PDF with respect to particular atom can not be measured by any presently known technique. In any experimental measurement, the averaging

which places all at the origin is automatically performed. However even for perfect crystals the experimental PDF obtained from the diffracted scattering intensity will eventually decay at large distances due to the finite instrumental resolution, as shown in the second panel of Figure 3.

The pair distribution function only decays at large distances if different atoms at the origin have *different* atomic environments. Therefore for perfect crystals the pair distribution function does not decay. This means that the measured rate of decay of the measured pair distribution function for very good crystals could be used to test instrumental resolution. The decay of the PDF at large distances can also be used to investigate the sizes of nanocrystals. We find that the persistence of fluctuations in the pair distribution function has a connection to a value of the rms fluctuations for the Gauss circle problem in d -dimensions, which gives a lower bound $(d - 1)/2 < \theta$ to the possible range of extreme fluctuations.

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