Estimating nanoparticle dispersion using the Area Disorder of Delaunay triangulation

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Summary. Characterising dispersion quality of nanocomposites presents a challenging statistical problem for which no direct method has been fully adopted. A high precision, statistically well grounded measure is required suitable for dealing with a single non-stationary particle pattern obtained from the material. Our approach uses the Delaunay Network of particles to measure the Area Disorder, AD_{Del} , which can be further used to categorise a material sample into well or poorly dispersed. AD_{Del} analysis is applied to several micrographs of nanoparticle-modified materials and found to reliably classify the type of dispersion. Select spatial point processes are employed to estimate expected imprecision in observed measurements.

Keywords: complete spatial randomness, composite material, hard-core model, heterogeneous, image analysis, Voronoi

1. Introduction

Nanotechnology is a rapidly advancing sector of research. A particularly promising avenue of engineering pursuit is particulate-modified composites (Pavlidou and Papaspyrides, 2008; Vaia and Maguire, 2007; Xie et al., 2005). The aim of the research is to enhance the mechanical properties of a polymer base medium (called the ‘matrix’) by introducing nanoparticles to the material. When representing these systems by models, it is often accepted that the exact arrangement of nanoparticles across a well mixed system has to be neglected, such that only knowledge of the particle shape and total volume fraction is required.

Recent studies (Gershon et al., 2010; Chen et al., 2009; Kinloch and Taylor, 2006; Song and Youn, 2005) have lead engineers to ask if the system’s morphology affects the performance of the nanocomposite. Dispersion defines the effectiveness of the spread of particles across a system and is a description of the geometric disorder of particles. The dispersion quality of particles across a system, whether it be poorly dispersed with clustered/heterogeneously arranged nanoparticles or well-dispersed with more regular than

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random/lattice-like arranged nanoparticles, might be expected to play a significant role in the material's properties such as elastic modulus, strength and fracture toughness.

A direct way to study the morphology of a composite is to generate a micrograph of the material's stereological microstructure using an atomic force or electron microscope. Despite the potential importance of the type of morphology present, many articles simply state that the nanoparticles are well dispersed across the system leaving it up to the reader to concur by inspection of a sample micrograph of the composite. This is partly because quantitative analysis of a microscope image is demanding (in respect of the limited number and small size of the micrographs), with no agreed standard, but also because separate indirect tests such as X-ray scattering methods (Paul and Robeson, 2008), which measure scattering angles, fail to sufficiently characterise dispersion, giving information on particle spacings but not orientations or geometries.

Given the general acceptance of micrographs along with the current concern about the effects of dispersion quality on nanocomposites it is essential that a quantitative approach be found to classify these systems with a single numerical parameter which can be used in tests for potential correlations between dispersion quality and the material mechanical properties such as toughness, fracture energy, stress and strain. The purpose of this paper is: one, to provide an approach which is simple and closely allied to physically interpreted quantities; two, to improve the level of statistical analysis used in materials science.

1.1. *Recent approaches to micrograph analysis*

This paper is motivated by the recent advances in the materials science literature. Perhaps the simplest approach taken is the quadrat method (Guild and Summerscales, 1998) which splits a micrograph into an array of equal sized rectangular quadrats. The analysis consists of comparing the quadrat's coefficient of variation of particle number against the quadrat size. Deviations away from one (expected if particles are randomly dispersed) at given quadrat sizes indicates the presence of structure at particular length-scales. This method is well known to be influenced by placement and size increment of the quadrats.

Khare and Burris (2010) discussed a method of using a square quadrat to characterise the unoccupied voids of the system. A quadrat, of size-length l , is randomly placed on the micrograph many times and the number of particles found within it counted. An empirical frequency distribution of particle numbers is generated and the mode calculated. The quadrat is decreased in size until the mode equals zero particles and the value of l compared with that expected for a randomly dispersed system.

Zhu et al. (2010) described the structure of the system using the distribution of nearest neighbour distances between particles. Similarly Luo (2010) and Luo and Koo (2008) generated the distribution of free path spacing (the distance between particles along a test line through the material) and fitted a log-normal distribution. A dispersion parameter was based on the probability of finding a spacing between 0.9 and 1.1 times the mean value. Both these methods rely on analysis of the full profile of the generated distribution and their power as a test is reduced by the low precision of the data.

These statistics are developed from the need to use a simple to measure quantity. Hence a common oversight is the inattention given to providing statistical assessment (through either pattern hypothesis testing or determination of statistical power) into what circumstances or at what values a system can be reliably described as well- or poorly-dispersed. This needs to be addressed before any method can be successfully used in practice.

1.2. Positional spatial tests

Characterising nanoparticle patterns are an interesting problem because of the significant hard-core nature of the particles. This can lead to false assessment of the pattern's behaviour when neglected by comparing naively with uninhibited point patterns (this was reported on by Wiegand et al. (2006) who noted that the hard-core nature, aggregation, shape and space-restriction of points should not be ignored). The challenge with dealing with hard-core patterns is that generally analytical expressions do not exist given that both the extent to which the system is covered by nanoparticles and the shape/size distribution of nanoparticles influences the behaviour of the pattern.

Spatial models for point patterns and statistical comparison tests between types of patterns have been well studied (Ho and Chiu (2007); Cetin and Kalkanli (2009)). Conventional methods for describing point patterns are typically based upon 2nd order inter-particle distances (Schiffers et al. (2008); Pyrz (1994)), such as the pair correlation function ($g(r)$) and Ripley's K-function, ($K(r)$). Pattern hypothesis testing can be achieved by comparing, the $g(r)$ (which describes the probability of finding two points a distance r apart (Illian et al. (2008))) estimator of a single sample pattern against the 95% confidence interval of the null hypothesis pattern. However $g(r)$ will not suffice because it is difficult to perform further analysis of its features from a single estimate where large variations in the shape of $g(r)$ are expected, caused by the non-stationary nature of the samples and the finite number of points.

$K(r)$ (Diggle (2003); Illian et al. (2008)), being effectively $g(r)$'s cumulative probability function, behaves much better with non-stationary data sets. It is well known that $K(r) = \pi r^2$ when the pattern obeys the complete spatial randomness (CSR) hypothesis and a significance test, such as the Kolmogorov-Smirnov test using $\sqrt{K(r)}/\pi$, will provide a powerful discrepancy test for many types of point patterns. Despite this there is no obvious scale-invariant numerical parameter associated with $K(r)$ which can be used to characterise dispersion, as $K(r)$ only monotonically increases with r . These examples show that it is difficult to use distance methods to obtain numerical parameters that are robust or physically sensible enough to describe dispersion in systems with small particle numbers.

1.3. Geometric tessellation

An alternative to describing patterns by points is to describe them by regions of space bounded by sets of particles. A simple method of doing this is given by Voronoi/Delaunay tessellation (Ghosh et al. (1997)), which has been well-studied statistically for use with spatial patterns (e.g. Okabe et al. (1999); Aurenhammer (1991); Kendall (1989)). These approaches are very versatile as they are multi-variable (including point to point information which can be extracted later if required). Bakshi et al. (2009) and Al-Ostaz et al. (2007) have shown that the Delaunay network can be applied to real spatial arrangements of nanoparticles. It may even be argued that properties of these tessellations provide a more intuitive description for the geometric disorder of particles (which dispersion is related to) than could be achieved from point to point measurements as they more directly describe how the space is partitioned between particles.

In this paper it will be shown that a Delaunay based quantity: (i) has sufficient statistical power to distinguish between clustered, random and more regular patterns using only a single sample of a finite system; (ii) is a well defined, scale-length invariant numerical parameter suitable for exploring the relationship of dispersion with other physical parameters. The qualitative two-state description of good- and poor-dispersion, used by materials

scientists, can be obtained through pattern hypothesis testing.

1.4. Generating the Delaunay Network

A rectangular system of particles spans a finite domain $\mathcal{D} \subset \mathbb{R}^2$ of extents $[0, L_x) \times [0, L_y)$. In each system there are N particles, with centre of mass positions given by $\mathbf{x}_i = (x_i, y_i) \in \mathcal{D}$, where $i = 1, \dots, N$. A particle's spatial extent is not required except for physical interpretation. A Voronoi diagram, $\mathcal{V} = \{V_i : i = 1, \dots, N\}$, partitions the system into N sub-domains of convex polygons in which any point $\mathbf{x} \in V_i$ finds particle i the nearest in distance out of all particles.

For every Voronoi diagram there is a complementary network of Delaunay triangles developed using the vertices of a Voronoi polygon and the positions of particles. Let $R = \{\mathbf{r}_j : j = 1, \dots, N_v\}$ be the set of vertices in the Voronoi diagram $\mathcal{V}$. Then for each vertex, $\mathbf{r}_j$, there exists a polygon T_j with vertices, $\mathbf{v}_{jk} : k = 1, \dots, k_j; k_j \geq 3$, defined by the positions of particles which are equi-distant from $\mathbf{r}_j$ (these particles will be those with associated Voronoi polygons that contain vertex $\mathbf{r}_j$). If $k_j > 3$ then T_j is not a triangle and it is subsequently partitioned (arbitrarily which affects the orientation and position of the resultant triangles but neither their shape nor size) into $k_j - 2$ triangles bounded by non-intercepting lines that pass between two of T_j 's original vertices. In such case T_j is replaced by T_{ji} where $i = 1, \dots, k_j - 2$. These triangles are called Delaunay triangles and each defines a triplet of particles which can be thought of as nearest neighbours to one another. The complete Delaunay network of triangles is $\mathcal{T} = \{T_{ji} : j = 1, \dots, N_v; i = 1, \dots, k_j - 2\} \mapsto \{T_h : h = 1, \dots, t\}$ where t is the total number of triangles which typically equals $2N$.

Several properties can be measured from the Voronoi polygons and Delaunay triangles, including area, side-length, perimeter. Each property has a physical meaning that could be useful to material scientists.

1.5. Quantities involving the Mean and Variance

Real sample systems of a material have low particle numbers (typically less than 1000 particles) such that the empirical frequency distribution of many quantities has low information, with significant errors in the extremal bins. Better precision is obtained from studying the expectation and standard deviation value but these suffer additional dependences on the number of particles and the size of the system. One method of removing particle intensity effects is to measure the coefficient of variation, such as that applied to Voronoi quantities by the Heijman et al. (2002) and Hendriks et al. (2002) studies.

Marcelpoil and Usson (1992) introduced a similar measure for Voronoi area, A_V , called Area Disorder, $AD = 1 - (1 + \sigma[A_V]/\mathbf{E}[A_V])^{-1}$ with $\mathbf{E}[A_V]$ being the expectation and $\sigma[A_V]$ the standard deviation of A_V . The form of Area Disorder is advantageous for interpretation as it ranges from 0 to 1 whereas $\sigma[A_V] \in [0, \infty)$. An increase in the value of AD corresponds to an increase in the disorder of the system, for example a highly regular array of particles corresponds to AD near to 0 whereas a highly aggregated and clustered system corresponds to a much larger value for AD.

Previous work has established that Voronoi and Delaunay based parameters can be very powerful at distinguishing between the types of spatial patterns. A comprehensive study of spatial tests involving the empirical frequency distribution of Voronoi and Delaunay properties was performed by Chiu (2003) and compared against the standard Kolmogorov-Smirnov test of the K-function. Often the performance of the statistic depended on the type

of patterns being compared. However it was found that both the Delaunay area, A_D , and minimum internal angle of the triangle, $\alpha_{\min}$, performed particularly well. These parameters were equally good as the $K(r)$ at showing that Matern clusters and the more regular large hard-core simple sequential do not obey the CSR hypothesis. They were not quite as good at showing the same for small hard-core simple sequential (with powers of around 5% compared to 19% for $K(r)$ when using the 95% confidence test) and much better when applied to the more regular Baddeley-Silverman cell process where $K(r)$ is known to fail. The statistical power in using coefficient of variations, including the Area Disorder was investigated by Wallet and Dussert (1997, 1998). Here AD was compared amongst alternative Voronoi based statistics, such as roundness factor, $RF = 4\pi A_V / P_V^2$ with P_V the Voronoi perimeter; roundness factor of homogeneity, $RFH = (1 + \sigma[RF]/E[RF])^{-1}$, and other approaches, such as nearest neighbour [distance] distribution, pair correlation function, radial density distribution (about a particle) and fractal dimension. In Wallet's discussion, theoretical systems of a particular dispersion model are tested against the null hypothesis of them being another, for each quantity, and the stability of results, with respect to the number of points contained in the system and type of pattern, are assessed. AD performs well amongst these measures particularly for finite-sized systems. Taken together these papers provide convincing evidence that a parameter based upon the variation of the areas of Delaunay triangles or Voronoi polygons will be sufficient to distinguish between poor and good dispersion and whose specific value can be used to measure the extent of dispersion.

In Section 2 we outline the approach for using Area Disorder to characterise the degree of dispersion in finite-sized particulate systems. We apply AD to several theoretical benchmark cases in Section 3. These cases allow us to derive a test for categorising systems into dispersion type based on the measurement of AD. In Section 4 we analyse data from real nanoparticle-modified materials. We conclude in Section 5 with a discussion.

2. Methodology

As it stands AD, based on the Voronoi diagram, satisfies most of the requirements for a quantitative measurement of dispersion: AD is well defined, between 0 and 1, with a distinct value when spatially random and values greater than or less than this corresponding to systems with better or worse dispersion respectively. AD does not, however, sufficiently quantify dispersion but rather describes the regularity of positions. AD is zero only when the Voronoi diagram is made of regular polygons (identically shaped, equal in size), such that the standard deviation, $\sigma[A_V]$, equals zero. In a perfectly dispersed system particles are arranged in a lattice-like array (where all particles can be found using only two base vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$ such that $\mathbf{x}_j = \mathbf{x}_i + \lambda\mathbf{a}_1 + \mu\mathbf{a}_2$ where $\lambda, \mu \in \mathbb{Z}$ and $j, i \in [1, 2, \dots, N]$) and subsequently implies that the Voronoi polygons are regular. The converse statement, that regularity implies lattice-like dispersion, does not always hold true. A clear demonstration of this subtle point is shown in Fig. 1 where not only a regular triangular lattice of particles (or alternatively a regular square lattice) gives $AD \approx \sigma[A_V] = 0$ but so does any set of regularly arranged particles, such as those regularly arranged in hexagons, and even a non-regular spaced array of particles does (although this is a special case).

At first glance this seems a serious setback, but study of the Delaunay network provides a way forward. The areas of triangles found in the Delaunay network will only satisfy $\sigma[A_D] = 0$ if the system is both regular and lattice-like, as demonstrated in Fig. 1. The approach taken in this paper adapts the Area Disorder for use with the Delaunay network.

Fig. 1. Three example particle configurations, in which particle dispersion worsens from (a) to (c). Particles are shown as points with Voronoi polygons and the Delaunay triangles outlined by - - - and — respectively. In a triangular lattice (a) $\sigma[A_V] = 0$ and $\sigma[A_D] = 0$ whereas for a regular hexagonal (b) or non-regular array (c) $\sigma[A_V] = 0$ but $\sigma[A_D] > 0$.

In a finite system, the sample mean area of a Delaunay triangle is denoted as $\overline{A_D}$ and the sample standard deviation as S_{A_D} . An analogy to the Area Disorder of Voronoi polygons is given for Delaunay triangles by:

$$\text{AD}_{\text{Del}} = 1 - \left(1 + S_{A_D}/\overline{A_D}\right)^{-1}. \quad (1)$$

Samples of a system are analysed by calculating the Delaunay network for the system, measuring AD_{Del} and then comparing against a known reference to determine the extent of dispersion.

2.1. Boundary conditions

The finite dimensions of $\mathcal{D}$ dictate a Delaunay network that spans the convex hull of particles (CHP). Those triangles of $\mathcal{T}$ which touch the boundary of CHP cannot be known to be accurate without further information from beyond $\mathcal{D}$ and so including them would bias the measurement of AD_{Del} .

One standard approach to correct $\mathcal{T}$ is to remove these boundary affected Delaunay triangles from T_i (on the assumption that these triangles should be distributed the same as the bulk). However to do so in this case would be inappropriate, as is illustrated by the following example. Take a system with particles arranged in a square lattice across a small sub-domain of $\mathcal{D}$, demonstrated in Fig. 2(a). Within the CHP the particles are well-dispersed (lattice-like) but overall the dispersion of the system is poor, due to the particles being clustered in the bottom left quadrant. AD_{Del} is measured, from a Delaunay network where the boundary-affected Delaunay triangles have been removed from $\mathcal{T}$, shown in Fig. 2(b). Analysis based upon this would force us to conclude that the system *is* well-dispersed despite it being visibly heterogeneous. The discrepancy is caused by ignoring the space usage of the system outside CHP and shows that the boundary conditions are not an arbitrary choice.

An appropriate correction is to apply periodic boundary conditions (Chiu, 2003) to $\mathcal{D}$ before generating the Delaunay network, as shown in Fig. 2(c). At each boundary of $\mathcal{D}$

Fig. 2. Acquiring an accurate assessment of dispersion. (a) shows a square lattice of 100 particles in a sub-domain of $\mathcal{D}$. In (b) the Delaunay network, obtained using the system particles, spans only CHP whereas in (c) the Delaunay network, obtained through invoking periodic boundary conditions, will span $\mathcal{D}$ completely.

surrounding ‘virtual’ particles are generated by translating particles of the system across the boundaries to create 8 surrounding domains with identically distributed particles. The centre of mass positions $\mathbf{x}'$ are used to generate the set of Delaunay triangles $\mathcal{T}_{total} = \{T_i : i = 1, \dots, t_T\}$, where $t_T < 18N$. Each triangle, T_i , has three vertices with positions denoted by $\mathbf{v}_{ij}$ ($j = 1, 2, 3$). $\mathcal{T}$ can be defined as the minimum set of Delaunay triangles sufficient to completely span the domain of the system $\mathcal{D}$, where $\mathcal{T} \subset \mathcal{T}_{total}$. A Delaunay triangle, T_i , is accepted as a member of $\mathcal{T}$ if its centre of mass position, given by $\mathbf{X}_i = (\mathbf{v}_{i1} + \mathbf{v}_{i2} + \mathbf{v}_{i3})/3$, satisfies $\mathbf{X}_i \in [0, L_x) \times [0, L_y)$, which results in a set of $t = 2N$ triangles.

3. Classification of dispersion type using AD_{Del}

The specific value of AD_{Del} indicates the extent of disorder in the system, where higher magnitude broadly indicates reduced regularity and increased aggregation. A test system can be further classified by: (i) predicting AD_{Del} ’s behaviour at the transition, random-like state (where particles are distributed as near to spatially random as particle size allows); (ii) hypothesis testing the test system against the transition state to decide if it is likely to be either poorly dispersed (in a clustered/heterogeneous state), indeterminate from the random-like state (state is uncertain) or well dispersed (more regular state). Though the Area Disorder is well defined at the extremal limits of 0 and 1, it should be expected that the prediction at transition is dependent on particle numbers, packing fraction (fractional area between sum of particle areas and size of system) and other morphological parameters such as particle shape and size distribution. With some simplification in realism of the system it is possible to determine upper- and lower-bounds for the transition value that allows meaningful comparison with test systems.

3.1. Transition value for stationary systems of point particles

Other than at distances less than the enforced minimum separation distance determined by particle size, random-like dispersed systems contain particles that are spatially uncorrelated

Table 1. Values of mean AD for BPP with various particle numbers and the measurement of the deviation away from that expected with the stationary solution.

Particle Number	$\overline{\text{AD}}_{\text{Del}}(\text{BPP}; N)$	$S_{\text{AD}_{\text{Del}}}(\text{BPP}; N)$	$\frac{\text{AD}_{\text{Del}}(\text{HPP}) - \overline{\text{AD}}_{\text{Del}}(\text{BPP}; N)}{S_{\text{AD}_{\text{Del}}}(\text{BPP}; N)}$
10	0.433536	0.053228	0.64
100	0.463820	0.020282	0.19
500	0.467108	0.009486	0.062
1000	0.467506	0.006832	0.028
1500	0.467568	0.005590	0.024

with one another. The simplest spatial model with this property is a homogeneous Poisson process (HPP) which obeys complete spatial randomness (CSR). Here particles have no surface area, such that they are point-like (Okabe et al., 1999). Despite the models highly unrealistic nature, the measurement of AD_{Del} provides a sensible estimate for the greatest lower bound of poor dispersion as more realistic models are more regular and so have smaller AD_{Del} .

For a stationary system (where $L_x, L_y, N \rightarrow \infty$) with intensity of points, $\lambda = N/(L_x L_y)$, the Area Disorder can be derived analytically from the known expectation values of the mean and second moment of the area of a typical Delaunay triangle, stated as (Rathie, 1992):

$$E[A_D] = 0.5/\lambda, \quad E[A_D^2] = 35/(8\pi^2\lambda^2).$$

Here it should be noted that the use of periodic boundary conditions means that $E[A_D]$'s relation with λ is universal and not dependent on details of particle arrangement. From these expectations the coefficient of variation is found to be:

$$\sigma[A_D]/E[A_D] = (E[A_D^2]/E[A_D]^2 - 1)^{1/2} = ((35/2\pi^2) - 1)^{1/2} = 0.87927. \quad (2)$$

The Area Disorder for Delaunay triangles is numerically expressed as:

$$\text{AD}_{\text{Del}}(\text{HPP}) = 1 - (1 + \sigma[A_D]/E[A_D])^{-1} = 0.46788. \quad (3)$$

Realistically, micrographs represent finite particle systems with window sizes that cannot satisfy the translation invariance criteria needed to apply this stationary model (the micrograph's size cannot be enlarged as the microscope's optical limitations mean that the resultant reduced resolution leads to particle uncertainty). Instead each system has exactly N particles across the area $L_x \times L_y$ which violates the CSR hypothesis. In these finite cases HPP becomes the binomial point process (BPP) and is tackled by a numerical approach.

3.2. Transition values for finite-sized systems with point particles

A sample configuration of an N particle binomial point process is numerically generated by positioning the i^{th} particle using a pair of random numbers, $\mathbf{x}_i \in [0, L_x) \times [0, L_y)$, picked with uniform probability, $P(\mathbf{x}_i) = 1/(L_x L_y)$. Due to inherent fluctuations caused by the discrete nature of the system, the estimated Area Disorder $\hat{\text{AD}}_{\text{Del}}$, calculated from a single sample instance, is Gaussian probability distributed about the mean $E[\text{AD}_{\text{Del}}(\text{BPP}; N)]$

Fig. 3. Properties of an N particle HM system. (a) presents a Q-Q plot comparing the distribution of measured AD_{Del} for $N = 1000$, $\phi = 0.1$ ($\times$) with a Gaussian (—). (b) depicts the points of measured sample mean and (c) shows the points of the measured standard deviation, with ϕ being 0 ($\times$), 0.1 ($+$), 0.2 ($\square$), 0.3 ($\circ$), 0.4 ($\diamond$) and 0.5 ($\triangle$).

and characterised by the standard deviation $\sigma[AD_{Del}(BPP; N)]$. $E[AD_{Del}(BPP; N)]$ and $\sigma[AD_{Del}(BPP; N)]$ are estimated from repeated samples of a fixed system of $L_x = L_y = 1$ (although the solutions are reasonably invariant to choice of system size) using the empirical mean $\overline{AD}_{Del}(BPP; N)$ and standard deviation $S_{AD_{Del}}(BPP; N)$. Simple functions are fitted to these quantities of the form:

$$\overline{AD}_{Del}(BPP; N) \approx AD_{Del}(HPP) / (1 + 0.7883N^{-1}), \quad (4)$$

$$S_{AD_{Del}}(BPP; N) \approx 0.1736 / (1 + 0.6869N^{0.5169}). \quad (5)$$

Table 1 tabulates numerical data for select N . Despite the systematic variation in $E[AD_{Del}(BPP; N)]$ with respect to N , it pales into insignificance for $N > 100$ when compared to the natural deviation between two samples, characterised by the standard deviation (see last column of Table 1). Therefore, the mean behaviour of BPP can be well approximated by the homogeneous Poisson process with equivalent intensity λ (in which fluctuation of local particle numbers are negligible), such that the expectation for AD_{Del} is equal to $AD_{Del}(HPP)$. While the standard deviation is given by $\sigma[AD_{Del}(BPP; N)]$.

3.3. Transition value for Hard-core model

In practice particles are not point-like but rather have finite area such that the minimum distance between neighbouring particles is always greater than zero. Models that account for particle size are collectively called hard-core models (HM, see Wallet and Dussert (1997)).

A HM solution can be generated for any N particle system, with set of particle areas $\{A_i : i = 1, 2, \dots, N\}$. To simplify the problem the average particle is assumed to be circular with fixed radius r . The fraction of the system covered by particles is called the packing fraction, $\phi = \sum_{i=1}^N A_i / L_x L_y \equiv N\pi r^2 / L_x L_y \in (0, 1)$.

HM is numerically simulated by the simple sequential inhibition process (SSI, see Okabe et al. (1999)) of placing particles sequentially into the system. SSI is chosen from physical considerations and its consistency in producing exactly N point systems. The position of

Table 2. Comparison of mean AD_{Del} for various packing fractions and estimation of deviation from stationary solution

ϕ	$\hat{\text{AD}}_{\text{Del}}(\text{HM})$	$\hat{S}_0$	$\overline{\text{AD}}_{\text{Del}}(\text{HM}; 100)$	$S_{\text{AD}_{\text{Del}}}(\text{HM}; 100)$	$\frac{\hat{\text{AD}}_{\text{Del}}(\text{HM}) - \overline{\text{AD}}_{\text{Del}}(\text{HM}; 100)}{S_{\text{AD}_{\text{Del}}}(\text{HM}; 100)}$
0	0.468	0.215	0.463820	0.020282	0.19
0.1	0.417	0.205	0.414217	0.020216	0.14
0.2	0.364	0.187	0.361897	0.017804	0.12
0.3	0.307	0.161	0.305153	0.015823	0.12
0.4	0.248	0.125	0.247557	0.012426	0.04
0.5	0.202	0.084	0.202513	0.008428	0.06

the particle is chosen at random with the condition that the distance between its centre and any other placed particle centre is greater than the sum of the two particle's radii. As a result SSI simulations can only be performed (in either a moderate finite time or without reaching complete random packing due to poor choice of particle placement) for moderate to low packing fractions, $\phi = 0.547$ (Illian et al. (2008)).

Again the distribution of measured Area Disorder is Gaussian, see Fig. 3(a), while the expectation value $E[\text{AD}_{\text{Del}}(\text{HM}; N)]$, 3(b), and standard deviation $\sigma[\text{AD}_{\text{Del}}(\text{HM}; N)]$, 3(c), are dependent on packing fraction and particle number (representing finite size effects). With higher ϕ , systems become more lattice-like, $0.468 \geq E[\text{AD}_{\text{Del}}(\text{HM}; N)] \rightarrow 0$, due to the system constraints and the reduced number of particle configurations that satisfy the HM criterion. Both $E[\text{AD}_{\text{Del}}(\text{HM}; N)]$ and $\sigma[\text{AD}_{\text{Del}}(\text{HM}; N)]$ can be fitted by functions of N of the form given for the BPP. It is found that perturbations, with respect to N , are sufficiently small for $N > 100$ (as demonstrated in the last column of Table 2) that the following relations hold:

$$\overline{\text{AD}}_{\text{Del}}(\text{HM}; N) \approx \text{AD}_{\text{Del}}(\text{HM}), \quad S_{\text{AD}_{\text{Del}}}(\text{HM}; N) \approx S_0 N^{-1/2}. \quad (6)$$

where $\text{AD}_{\text{Del}}(\text{HM})$ is the stationary solution (as $N \rightarrow \infty$) for HM. Fig. 3 demonstrates these relationships by the constant fits in diagram (a) and dashed power-law curves shown in (b). Estimates of $\text{AD}_{\text{Del}}(\text{HM})$ and the fitting parameter S_0 are given in Table 2.

Despite these simple relationships existing for every packing fraction value their complex dependence on ϕ means that in practice it is more efficient to estimate $E[\text{AD}_{\text{Del}}(\text{HM}; N)]$ and $\sigma[\text{AD}_{\text{Del}}(\text{HM}; N)]$ from simulation of individual cases than to derive their relations from numerical data.

3.4. Testing for heterogeneous/clustered and lattice-like dispersions from a single sample

The two descriptions of randomly dispersed systems, BPP and HM, provide benchmarks for classifying system dispersions in general. Hypothesis testing of a single small, non-stationary, sample section can be used to judge whether the parent stationary point pattern representation of the complete plane of the material has the properties of a spatially random set of particles (note here that we are not testing the parent strictly for CSR but this will also satisfy the definition). A significant deviation away from this null hypothesis implies that the material is likely to either be more regular or aggregated than expected when particles are positioned randomly.

Table 3. The power of AD_{Del} 's z-test to distinguish various patterns as different to BPP or HM with $\phi=0.1$. The K-function is provided for comparison

Test	BPP $N = 100$	HM $N = 100$ $\phi = 0.1$	HM $N = 100$ $\phi = 0.2$	HM $N = 300$ $\phi = 0.1$	LM $N = 100$ $r = 0.5$	LM $N = 100$ $r = 0.75$	MCP (100,10,0.2)
$\overline{AD}_{Del}$	0.46	0.41	0.37	0.42	0.34	0.40	0.58
$Z_{sig}(BPP)$	0.06	0.71	1.00	0.98	1	0.97	0.98
$K(BPP)$	0.05	1	1	1	1	0.90	0.97
$Z_{sig}(HM)$	0.69	0.04	0.77	0.00	1.00	0.05	1.00
$K(HM)$	1	0.06	1	0.05	1	1	1
Test	MCP (100,10,0.3)	MCP (100,5,0.1)	MCP (100,5,0.2)	MCP (100,5,0.3)	TP (100,5,0.05)	TP (100,5,0.1)	TP (100,5,0.2)
$\overline{AD}_{Del}$	0.52	0.62	0.54	0.50	0.62	0.54	0.48
$Z_{sig}(BPP)$	0.62	1	0.76	0.31	1	0.80	0.14
$K(BPP)$	0.63	1	0.77	0.37	1	0.79	0.20
$Z_{sig}(HM)$	0.97	1	1	0.92	1	1.00	0.83
$K(HM)$	1	1	0.99	1	1	1	1

Given a sample, where the packing fraction is determinable and the particles sufficiently distinct for an accurate count, then the estimate $\hat{AD}_{Del}$, can be trialled to determine whether $\hat{AD}_{Del}$ was likely to be produced by a configuration of either BPP or HM. In systems of BPP and HM the distribution of values for AD_{Del} of a single configuration is Gaussian about the mean expectation. 95% of the total configurations will have an Area Disorder within 1.96 standard deviations of the expectation value. Hence a two-sided hypothesis test for random dispersion can be performed on the test sample using $Z_{sig}(BPP)$, defined as:

$$Z_{sig}(BPP) = \left(\hat{AD}_{Del} - E[AD_{Del}(BPP; N)] \right) / \sigma[AD_{Del}(BPP; N)]. \quad (7)$$

If $Z_{sig}(BPP)$ is larger than 1.96 then the sample is rejected as CSR at a significance level of 5%. An equivalent relation can be defined for HM which is denoted as $Z_{sig}(HM)$. The exact value of $Z_{sig}(BPP)$ and $Z_{sig}(HM)$ classifies the type and extent of dispersion by the following:

$$\text{Dispersion Type} \begin{cases} \text{Is more lattice-like than random} & \text{if } Z_{sig}(HM) < -1.96 \\ \text{Is more clustered/heterogeneous than random} & \text{if } Z_{sig}(BPP) > 1.96 \\ \text{Indeterminate from random} & \text{otherwise.} \end{cases}$$

For this test to be reliable it is important that its power is sufficient for the systems that are likely to be encountered. Typically the number of points/particles in a micrograph range between 100 and 1000. The power of the two z-tests are compared with the equivalent Kolmogorov-Smirnov tests of Ripley's K-function at a 5% significance level, using the exact methods of Chiu (2003). Included in the list of point patterns shown in Table 3 are the more regular lattice model and the more clustered Matérn cluster process and Thomas process.

In a lattice model (LM) points are allocated to a square lattice and a random adjustment made to the positions of up to $\pm r$ times the lattice spacing in both the principle directions.

A Matérn cluster process (MCP, see Illian et al. (2008)), described by (N, ρ, r) , generates clusters of fixed radius r each populated by a number of particles chosen from a Poisson distribution with mean ρ with particle positions picked uniformly inside the cluster's boundaries. Each cluster is centred randomly in the same way as BPP. Similarly, the Thomas process (TP), described by the parameter set (N, ρ, s) , has the same cluster arrangement as MCP but with the points of the cluster distributed normally with zero mean and standard deviation, given by s , around the cluster's central position.

In Table 3 the powers are estimated from 5000 samples of each type of point pattern. While the K-function does provide the most reliable test in most cases (except in some regular systems that are close to random such as LM), the z-tests behave sufficiently well for non-random-like systems, only being less reliable (but above 50%) at distinguishing BPP from a close HM (where the area fraction and number of particles are low, which is of less interest given that ϕ is typically known).

4. Analysing real experimental samples

In this section the dispersion quality of real experimental systems are analysed using the Area Disorder and Z_{sig} . A real particulate-modified material is a complex composition containing two or more components. The bulk of the system is made of a matrix that forms an ambient background when viewed using a microscope. The minor components of the material are particles, which may be soft or hard, and vary in size, shape and aspect ratio.

In this paper, a particulate-modified epoxy polymer is used (Johnsen et al., 2007). This is produced by mixing an epoxy resin, a curing agent and various particles. This mixture is poured into moulds, and heated so that a crosslinked (thermosetting) polymer is formed. In the resulting microstructure, the epoxy forms the matrix. Two compositions have been used, the first containing silica nanoparticles only (denoted with suffix N), and the second containing both silica nanoparticles and rubber microparticles (with suffix N9R). Full details of these materials and their preparation are given by Hsieh et al. (2010).

To examine the microstructure, the material is cut along the longest plane to create a smooth surface. This surface is scanned using an atomic force microscope (AFM) with a 5 nm silicon probe. The AFM records a pair of images depicting the phase (hardness) and height of the scanned area. The phase image is often the clearest and hence most suitable image for analysis, with the epoxy making up the predominant background tone. The hard silica nanoparticles provide distinct lighter tone responses whilst the soft rubber particles are darker in tone. Lower level particles, i.e. those just below the surface, add additional noise to the background by generating local high intensity maxima. Overall the intensity of the nanoparticles varies depending on their height above the surface.

Interpretation of an image occurs in three distinct steps. First, the image is converted to colour intensity (grey-scale) plot with the random background noise suppressed using a digital Gaussian filter (this reduces the chance of picking up the epoxy background during analysis) and colour contrast enhanced. Second, the particles are identified and their centre of mass positions obtained. Third, the Delaunay network is generated and AD_{Del} analysed. Obtaining particles from a complex AFM image is not a trivial affair and a detailed description of the algorithm is provided before progressing to the results.

Fig. 4. Key stages required to measure AD_{Del} from an image of 10N (a,d), 15N (b,e) and 20N (c,f). (a-c) show the identified local peaks overlaid on the image, (d-f) illustrate the Delaunay network.

4.1. Finding nanoparticle positions from an image

The job of the algorithm is to remove the background from the image to leave only the nanoparticles. Nanoparticles are typically much more intense than their locality whereas the high intensity background pixels are indistinguishable from the rest. Thus an segregation algorithm can be based upon the relative variation of the colour intensity. Some loss or modification of particles is unavoidable but is restricted to details within particle clusters. The image, $\mathbf{I}$, contains a local maximum in colour intensity at the location of each nanoparticle while minima are found in the background. The threshold value, T_{level} , is defined as an integer between 0(black) and 255(white). At each iteration the algorithm selects a value for T_{level} , then finds all pixels in $\mathbf{I}$ that are either a local maximum or minimum in colour intensity. Potential particles are identified by invoking two methods called the maximum and the minimum method.

The maximum method proceeds as follows: Take the set of local maximums with colour intensities $\{I_{max_i}\}$. Discard any where the difference in intensity between it and the nearby local minimums is less than $255 - T_{level}$. For the i^{th} remaining local maximum select all connected surrounding pixels where the colour intensity has not dropped below $I_{max_i} - 255 + T_{level}$. These connected pixels make up a particle. The minimum method proceeds in a similar way as the maximum method except that it searches for connected pixels with

Fig. 5. Key stages required to measure AD_{Del} from an image of 10N9R.a (a,d), 10N9R.b (b,e), 20N9R (c,f). (a-c) show the identified particles as circles superimposed on the image, (d-f) illustrate the generated Delaunay network.

intensity no greater than $I_{min} + T_{level}$ around a local minimum. Taking the complement of the resultant binary image allows particles to be identified.

The success of each method relies on the choice of T_{level} . When T_{level} is set too low the maximum method fails to pick out all the particles. Complementary, the minimum method excludes only small regions of the background giving an apparent amalgamation of particles. Selecting too large a value for T_{level} has the opposite effect. T_{level} is fine-tuned by comparing the number of particles found by the maximum and the minimum methods. For an optimum T_{level} both methods identify the same number of particles which is automatically determined using a bisection method.

When the algorithm is complete (and T_{level} is not 0 or 255) the particles are identified from the minimum method and their centre of mass positions obtained. AD_{Del} analysis can be directly performed on these centre of mass positions if the image contains singular nanoparticles. Otherwise these proposed ‘particles’ are actually the partial or full hulls of particle clusters and further processing is required. This is done simply by selecting potential particles which are larger than a defined minimum area A_{min} and then searching for maxima within the particle. These maxima are assumed to be the centres of the actual particles within the cluster.

Table 4. Statistics of the samples and derived parent material properties.

Sample	T_{level}	$\hat{N}$ ($\hat{\phi}$)	$\hat{AD}_{\text{Del}}$	$Z_{\text{sig}}(\text{BPP})$ $Z_{\text{sig}}(\text{HM})$	$\hat{\rho}$	$U(S_{\hat{AD}_{\text{Del}}})$ ($r, \overline{\hat{AD}_{\text{Del}}}$)	$AD_{\text{Del}}(\text{POP})$
10N9R.a	210	138 (0.037)	0.805	18.970 20.297	15	0.0555 (0.256, 0.596)	[0.913, 0.697]
10N9R.b	203	277 (0.030)	0.781	24.474 26.157	13.5	0.0496 (0.199, 0.601)	[0.878, 0.684]
20N9R	223	658 (0.089)	0.727	30.792 37.974	9.44	0.0394 (0.141, 0.600)	[0.804, 0.650]
10N	183	307 (0.066)	0.434	-2.937 -0.004	1	0.0493 (0.191, 0.599)	[0.530, 0.337]
15N	201	296 (0.053)	0.415	-2.02 -4.273	1	0.0493 (0.194, 0.601)	[0.512, 0.319]
20N	223	429 (0.053)	0.414	-2.58 -5.194	1	0.0448 (0.172, 0.597)	[0.502, 0.326]

4.2. Classifying the dispersion type from micrographs

Studies of particulate-modified epoxy polymer are performed in two distinct groups.

The first group of three micrographs contains only nanoparticles at concentrations of either 10% (sample denoted as 10N), 15% (denoted as 15N) or 20% (20N) weight fraction. In Fig. 4 the process of identifying particles, finding the centre of mass and generating the Delaunay network is shown for the three cases. The packing fraction is estimated from the areas of the particles. Table 4 shows the measured value for AD_{Del} , the threshold T_{level} used, the number of identified particles $\hat{N}$ and the packing fraction $\hat{\phi}$. $\hat{N}$ is used to calculate $Z_{\text{sig}}(\text{BPP})$. All the micrographs satisfy $Z_{\text{sig}}(\text{BPP}) < -1.96$ implying that the materials are better dispersed than expected for BPP. To determine if each system is more dispersed than random a second test of $Z_{\text{sig}}(\text{HM})$ is performed. Here both $\hat{N}$ and $\hat{\phi}$ are used to estimate $AD_{\text{Del}}(\text{HM})$ from simulation. Both 15N and 20N have $Z_{\text{sig}}(\text{HM}) < -1.96$ suggesting that these materials have better-than-random dispersion. Needless to say, caution should be taken when interpreting $Z_{\text{sig}}(\text{HM})$ close to ± 1.96 as no accommodation is made for the unknown errors associated to the empirical estimation of the packing fraction. This means that the conclusion drawn for 20N is more sound than that for 15N.

The second group of three micrographs show three-component nanoparticle-modified materials of epoxy, nanoparticles and rubber particles of 9% volume fraction. The weight fraction of nanoparticles is either 10% (10N9R.a and 10N9R.b) or 20% (20N9R). Fig. 5 shows the process of measuring AD_{Del} for the samples and Table 4 shows their statistics. 10N9R.a (a,d), shows a highly magnified image of nanoparticle clusters close to a large rubber particle (localised on the left) and 10N9R.b (b,e), shows the same system at a reduced magnification level. In these two examples some of the smaller identified particles, with area less than A_{min} , refer to rubber particles and are removed before calculating the Delaunay network. With 20N9R (c,f) all particles are included in the Delaunay network. The value of AD_{Del} , for each example, suggests the materials are poorly dispersed having strongly passed the 5% significance test ($Z_{\text{sig}}(\text{BPP}) > 1.96$) for the systems to be more clustered than BPP.

These tests allow confirmation of the type of dispersion present in the system which is

Fig. 6. (a) Comparison of the empirical mean and standard deviation for various point patterns: MCP (—), LM (· · · · ·) and HM (— — —) for $N = 100$. (b) Behaviour with N of the upper bound for $S_{AD_{Del}}$ for MCP (—), TP (· · · · ·), MCPHC1 (· · · · ·), MCPHC2 (— — —) compared with BPP (— — —).

often strongly suspected from micrograph inspection.

4.3. Quantitative Comparisons

The main purpose of obtaining $\hat{AD}_{Del}$ is to enable the ranking of materials according to their dispersion quality. Interval estimation of AD_{Del} for the stationary parent population ($AD_{Del}(POP)$) is obtained from $\hat{AD}_{Del}$ and an estimate of the standard deviation between micrographs $S_{AD_{Del}}(POP)$. Direct calculation of $AD_{Del}(POP)$ is not possible because the parent spatial pattern is unknown and instead a conservative estimate is resorted to.

To investigate the behaviour of $S_{AD_{Del}}$, towards pattern type, samples of select families of realistic models are simulated and $S_{AD_{Del}}$ against $\overline{AD}_{Del}$ plotted in Fig. 6(a). In each model a single free parameter is changed (e.g. ϕ for HM, r for LM and ρ for MCP) to vary $\overline{AD}_{Del}$ between random and more extreme values. Examples of the change in state of these systems with $\overline{AD}_{Del}$ are shown in Fig. 7. For well dispersed models (BPP, HM, LM) $S_{AD_{Del}}$ is found to be proportional to $N^{-0.5}$ such that $S_{AD_{Del}}(LM), S_{AD_{Del}}(HM) \leq S_{AD_{Del}}(BPP)$. In comparison, cluster models (MCP, TP) give $S_{AD_{Del}} > S_{AD_{Del}}(BPP)$ and do not universally conform to $S_{AD_{Del}} \propto N^{-\alpha}$. The exact value of $S_{AD_{Del}}$ is model dependent, being influenced by both the average population of a cluster and number of clusters. The effect of ρ can be seen for MCP models in Fig. 6(a) where $\rho = 10, 20$ and 30 as indicated by the increasing darkness of the solid-line respectively. These models are characterised by a single maximum at $\overline{AD}_{Del}$ close to 0.6 where $S_{AD_{Del}}$ has reached a value many times that seen at random.

A conservative value for $S_{AD_{Del}}$ (its upper bound, $U(S_{AD_{Del}})$) for a particular class of cluster model is given by the maxima value. This is estimated via optimisation of the model's free parameter using a Bisection search method algorithm (where each trial value is calculated from a 1000 samples). To limit the imprecision the final estimate is taken to be the mean of the last 10 trial values. The location of $U(S_{AD_{Del}})$ for MCP with $\rho = 20$ (obtained as $U(S_{AD_{Del}}) = 0.0523$ at $\overline{AD}_{Del} = 0.6008$) is shown by a star in Fig. 6(a). $U(S_{AD_{Del}})$ is dependent on the model parameters and type of model used. An illustration of this is shown in Fig. 6 (b) where the value of $U(S_{AD_{Del}})$ for systems of N particles are

Fig. 7. Theoretical systems with increasing dispersion for $N=900$: (a) LM with $\overline{AD}_{Del} = 0.34$, (b) MCP with $\overline{AD}_{Del} = 0.54$, (c) MCP with $\overline{AD}_{Del} = 0.61$, (d) MCP with $\overline{AD}_{Del} = 0.71$.

plotted. Here alternatives to MCP ($\rho = 20$) are shown including TP, and two modified MCP with hard-core conditions: MCPHC1 ($\phi = 0.05$ and 0.1 , shown by light and dark line respectively) where particle placement is cycled between clusters and MCPHC2 ($\phi = 0.05$) where all particles are placed in one cluster sequentially before moving to the next.

For all these differences in the value of $U(S_{AD_{Del}})$, brought about by changes in the cluster structure, the actual change is less than 0.01 , which is comparable to varying ρ in MCP, illustrated in Fig. 6(b) by MCP with $\rho = 10, 15, 20$ (in order of darkening line), and much smaller than the change between these systems and more regular alternatives. Hence it is sensible to use $U(S_{AD_{Del}})$ from MCP as an upper bound for the likely $S_{AD_{Del}}$ of the materials pattern with little cost in accuracy.

Returning to the real micrographs, the value of AD_{Del} for a material is estimated from a sample micrograph using the 95% confidence interval:

$$\hat{AD}_{Del} - 1.96U(S_{AD_{Del}}) < AD_{Del}(POP) < \hat{AD}_{Del} + 1.96U(S_{AD_{Del}}). \quad (8)$$

where $U(S_{AD_{Del}})$ is estimated from the MCP model using $\hat{N}$ identified from the micrograph. Table 4 shows the statistics used to obtain the confidence intervals for the six micrographs. In all cases $\hat{\phi}$ remains under 0.1 . Given that $U(S_{AD_{Del}})$ increases with cluster size it is unnecessary to select a model with ρ much larger than found in the micrographs as it will only produce successively greater upper bounds above the supremum. The empirical mean cluster size, $\hat{\rho}$, is measured, shown in Table 4, and found to be less than 20 . Hence MCP of $\rho = 20$ are performed and estimates of $U(S_{AD_{Del}})$ obtained. Table 4 also gives the cluster radius, r , and $\overline{AD}_{Del}$ at which $U(S_{AD_{Del}})$ is found. From this the confidence intervals are estimated for the materials. In all cases the variation in allowed values for $AD_{Del}(POP)$ is less than 0.22 . For the well-dispersed samples (10N, 15N, 20N) this method produces an overly conservative estimate as $\hat{AD}_{Del}$ is much less than that corresponding with $U(S_{AD_{Del}})$ of MCP.

5. Discussion

Our paper has outlined a new method for classifying the dispersion-quality of nanoparticle composites based upon the analysis of sample micrographs. Once the particles are identified, the Delaunay network can be generated quickly using existing algorithms and the Area Disorder calculated. The material's spatial structure is more complicated to characterise

than generally seen in larger-scale spatial studies because of the predominant hard-core nature of the particles. Comparison between the sample system and equivalent theoretical models, of random-dispersed particles (either BPP or HM), determines not only the type of dispersion but also gauges the statistical likelihood that the conclusion is valid.

Although pattern hypothesis testing can be reliably done in most cases using Ripley's K-function, the Area Disorder provides a useful alternative, that is sufficiently powerful at distinguishing deviations from random-like, and its advantages become clear when performing this test in addition to exploring dispersion's effects on other material properties. Furthermore AD_{Del} requires smaller amounts of data to be retained where the areas of $2N$ Delaunay triangles are read compared to $N \times (N - 1)$ pairs of distances needed for the K-function. Thus AD_{Del} allows the determination of dispersion without the need to measure additional parameters or complete probability distribution.

Measurements from BPP models are predictable and of high precision. Nonetheless the BPP description is best used to ascertain whether a sample system is strongly heterogeneous, due to BPP's failure to account for particle size. An HM description is more realistic, but the strong dependence of $AD_{Del}(HM)$ on the packing fraction means that each case has to be simulated separately. Thus there is notable uncertainty with $Z_{sig}(HM)$ that is not present with $Z_{sig}(BPP)$. Even so, the HM description provides the sounder test for deciding whether a system is well-dispersed.

One advantage of basing our approach on the Delaunay tessellation is that the properties of Delaunay triangles can be used to understand other geometric features of the system. Additionally, it would be relatively simple to extend this measure for use with three dimensional systems.

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