Available online at www.sciencedirect.com
SCIENCE DIRECT®
International Journal of Plasticity 21 (2005) 185–198
INTERNATIONAL JOURNAL OF Plasticity
www.elsevier.com/locate/ijplas

Two-point probability distribution function analysis of Co-polymer nano-composites

G. Jefferson [a], H. Garmestani [b,*], R. Tannenbaum [b], A. Gokhale [b], E. Tadd [b]

[a] *FAMU-FSU COE, Tallahassee, FL 32310-6046, USA*
[b] *Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, N.W. Rm 175, Atlanta, GA 30332, USA*

Received in final revised form 17 May 2004
Available online 23 July 2004

Abstract

Empirical forms of the two-point probability functions for two-phase composites are investigated and alternate forms are introduced which can incorporate both periodicity and randomness. Microstructures of Co-polymer nano-composites have been analyzed and it was discovered that the material did not exhibit randomness and present empirical formulations may not be appropriate for its representation. A modified form of the probability function is introduced that can provide a tool to examine the degree of randomness and periodicity. The results show the potential of these functions in the evaluation of microstructures and acquiring higher order details not available previously.

Keywords: Microstructure; Statistical mechanics; Probability functions

1. Introduction

In recent years there has been an increasing interest in the use of statistical continuum theories to predict the macroscopic properties of heterogeneous materials (Kröner, 1972; Adams et al., 1989; Garmestani et al., 1998; Lado and Torquato,

* Corresponding author. Tel.: +1-404-385-4495; fax: +1-404-894-9140/678-623-3920.
E-mail address: hamid.garmestani@mse.gatech.edu (H. Garmestani).

0749-6419/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijplas.2004.05.011

Nomenclature

a_o	periodicity term
c_{ij}	empirical constants
c^o	empirical constant $\ni \forall c_{ij}, c_{ij} = c^o$
D	periodicity range – average interparticle distance
$F(r)$	function which accounts for periodicity in the microstructure
$g(r)$	arbitrary function $\ni \int g(r)\,\mathrm{d}r = 1$
k	$2\pi/a_0$
N	total number of points
N_i	number of points in phase i
n_{ij}	empirical constants
n^o	empirical constant $\ni \forall n_{ij}, n_{ij} = n^o$
P_{ij}	probability of vector r starting in phase i and ending in phase j
P^o_{ij}	$P_{ij}(r = r^o_{ij})$
$\vec{r}$	general vector
r; $\lvert\vec{r}\rvert$	magnitude of vector r
$\vec{r}_j$	$\langle rix - 0, riy - 0\rangle$; vector, where the beginning is some pre-determined origin and the end is point r_i
r^o	characteristic length scale
v_i	volume fraction of phase i
V_i	volume of phase i
α	degree of randomness
ϕ_i	phase i

1990; Torquato and Stell, 1982). In these formulations, knowledge of the spatial correlation functions related to microstructures of the heterogeneous material is required in the form of statistical functions. It is known that the microstructure can be completely characterized by specifying an infinite set of probability functions (Kröner, 1972; Adams et al., 1989; Torquato and Stell, 1982) and any spatial correlation functions can be described by a set of corresponding probability distribution functions. It has been previously shown that two-point functions can adequately predict macroscopic properties (elasticity and plasticity) of heterogeneous materials (Garmestani et al., 1998,2000).

Although the data for such simulations can be acquired directly from the microstructure, the use of an analytical form of the two-point correlation function has been shown to be quite useful in the numerical scheme (Lin et al., 2000). The proper mathematical form of these functions can allow us to investigate the detail of the microstructure and the degree of complexity it can provide in its phase distribution. The optimization of the microstructure for specific properties can be facilitated by the use of appropriate forms of the two-point functions (Torquato and Stell, 1982, 1983a,b, 1984, 1985; Corson, 1976a,b, Cule and Torquato, 1999). Torquato and Stell (1982, 1983a,b, 1985) has investigated probability density functions and obtained

empirical forms for specific geometries and morphologies. Corson (1976a,b) has proposed analytical expressions for two- and three-point probability functions of statistically homogeneous and isotropic two-phase materials with differing phase geometries. Because of the exponential form of the probability function proposed by Corson, it can only be applied to random distributions. In this paper, these functions are compared to those proposed by Torquato and Stell (1985) and an extension of this function is proposed for semi-periodic functions.

Most microstructures may look random on a global scale but direct and careful examination of the details and specific features may show a certain deviation from randomness. It is important to have a correct measure of this deviation. In the following sections, the empirical forms of the two-point functions were examined by direct comparison to the two-point distribution functions derived from a Co-polymer nano-composite material. A computer-generated two-phase composite with variations in the level of randomness was also used for comparison.

2. Two-point distribution functions

The data for the two-point distribution functions are acquired by assigning a number of random vectors within the microstructure, determining the likelihood of the head and tail of each vector ($\vec{r}$) landing in a particular phase, and examining the number fraction of the sets (vectors) which satisfy the different states (Fig. 1). For a two-phase composite microstructure, there exist exactly two states, phase 1 or phase 2, with the volume fraction of each defined as

$$\frac{V_i}{V_{\text{total}}} = v_i, i \in [1,2]. \tag{1}$$

Where V_1 and V_2 are the volumes of the two phases individually and v_i and v_2 are the corresponding volume fractions. Clearly,

$$\sum_{i=1}^{2} V_i = V_{\text{total}} \text{ and } \sum_{i=1}^{2} v_i = 1. \tag{2}$$

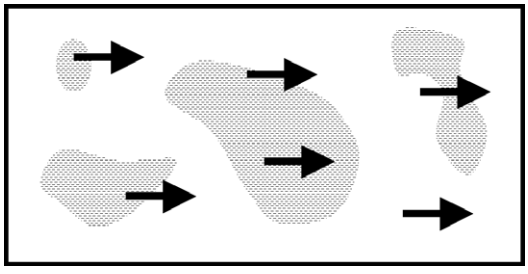

Fig. 1. Representative microstructure with the arrow → representing vector $\vec{r}$ with magnitude r, ▒ representing phase 1 and □ representing phase 2.

If N – number of random points are inserted within the microstructure in Fig. 1 and the number of points in phase – i is counted as N_i, the one-point probability function (P_i) can be defined through the following relation,

$$P_i = \frac{N_i}{N} \tag{3}$$

It is clear that as N is increased to infinity, P_i can define the volume fraction (or the area fraction) of each phase

$$P_i = \left.\frac{N_i}{N}\right|_{N\to\infty} = v_i \tag{4}$$

Now assign a vector $\vec{r}$ starting at each of the random points in Fig. 1. Depending on whether the beginning and the end of these vectors fall within phase 1 or phase 2, there will be four different probabilities (P_{11}, P_{22}, P_{12} and P_{21}) defined as:

$$P_{ij}(\vec{r}) = \left.\frac{N_{ij}}{N}\right|_{N\to\infty} \{\vec{r} = \vec{r}_j - \vec{r}_i, (\vec{r}_i \in \phi_i) \cap (\vec{r}_j \in \phi_j)\} \tag{5}$$

Where, N_{ij} are the number of vectors with the beginning in phase – i (ϕ_i) and the end in phase – j (ϕ_j). Eq. (4) defines a joint probability distribution function for the occurrence of events constructed by two points (r_j, and r_i) as the beginning and end of a vector $\vec{r}$ when it is randomly inserted in a microstructure N number of times. The two-point function can be defined based on two other probability functions such that

$$P_{ij}(\vec{r}) = P\{(\vec{r}_i \in \phi_i)|(\vec{r}_j \in \phi_j)\}P(\vec{r}_j \in \phi_j) \tag{6}$$

The first term on the right hand side is a conditional probability function. Note that for the limiting case when $r \to 0$, where $r = |\vec{r}|$, the two-point functions reduce to the one-point functions (or volume fractions) defined earlier,

$$P_{12}(0) = P_{21}(0) = 0, P_{11}(0) = v_1, P_{22}(0) = v_2 \tag{7}$$

and at very large distances, $r \to \infty$, the probability of occurrence of the beginning point does not affect the end point and the two points become uncorrelated or statistically independent and the conditional probability function reduces to a one-point function

$$P\{(\vec{r} \to \infty), (\vec{r}_i \in \phi_i)|(\vec{r}_j \in \phi_j)\} = P(\vec{r}_i \in \phi_i) \tag{8}$$

The two-point function will then reduce to

$$P_{ij}(\vec{r}) = P(\vec{r}_i \in \phi_i)P(\vec{r}_j \in \phi_j) \tag{9}$$

or,

$$P_{ij}(\infty) = v_i v_j, \tag{10}$$

Normality requires that the following equations be satisfied.

$$\sum_{i=1,2}\sum_{j=1,2} P_{ij}(\vec{r}) = 1 \tag{11}$$

$$\sum_{j=1,2} P_{ij}(\vec{r}) = v_i \tag{12}$$

$$\sum_{i=1,2} P_{ij}(\vec{r}) = v_j \tag{13}$$

Satisfying all three conditions for a two-phase composite ($[i,j] \in [1,2]$) results in the important conclusion that only one of the four may be an independent variable. Also, from Eqs. (7) and (8), it is clear that

$$P_{12}(\vec{r}) = P_{21}(\vec{r}) \tag{14}$$

2.1. Corson's isotropic relation

Corson (1976a,b) dpostulated a two-point probability distribution function for a homogeneous, isotropic two-phase random media,

$$P_{ij}(r) = v_i v_j + (-1)^{i+j} v_1 v_2 \exp\left(-c_{ij} r^{n_{ij}}\right), \tag{15}$$

where v_1 and v_2 are the volume fractions, r is the distance between the two points, c_{ij} and n_{ij} $(i,j = 1 \sim 2)$ are empirical constants determined by a least-squares curve fit to the data. The function is defined in terms of a scalar function of distance and not a general vector, $\vec{r}$. The limiting conditions for these probabilities are presented as

$$r = 0: \ (P_{11}(0) = v_1, \ P_{12}(0) = P_{21}(0) = 0, \ P_{22}(0) = v_2, \tag{16}$$

$$r \to \infty: \ P_{11}(\infty) = v_1^2, \ P_{12}(\infty) = P_{21}(\infty) = v_1 v_2, \ P_{22}(\infty) = v_2^2. \tag{17}$$

Corson's empirical equations satisfy the experimental results quite satisfactorily provided that the two phases are randomly distributed and are isotropic (Corson, 1976a). Although these relations satisfy normality in the limiting cases, other conditions may be imposed on them to be satisfied globally. Evaluating Eq. (15) for $[i,j] \in [1,2]$ leads to the following probability functions:

$$P_{11}(r) = v_1^2 + v_1 v_2 \exp\left(-c_{11} r^{n_{11}}\right) \tag{18}$$

$$P_{12}(r) = v_1 v_2 \left(1 - \exp\left(-c_{12} r^{n_{12}}\right)\right) \tag{19}$$

$$P_{21}(r) = v_1 v_2 \left(1 - \exp\left(-c_{21} r^{n_{21}}\right)\right) \tag{20}$$

$$P_{22}(r) = v_2^2 + v_1 v_2 \exp\left(-c_{22} r^{n_{22}}\right) \tag{21}$$

Since the symmetry condition $P_{12}(r) = P_{21}(r)$ must hold true for arbitrary numerical values of r, we obtain from Eqs. (19) and (20)

$$\exp\left(-c_{12} r^{n_{12}}\right) = \exp\left(-c_{21} r^{n_{21}}\right) \tag{22}$$

leading to

$$\frac{c_{12}}{c_{21}} = r^{(n_{21} - n_{12})}. \tag{23}$$

In order to satisfy Eqs. (22) or (23) for arbitrary values of r, we conclude $n_{12} = n_{21}$ and $c_{12} = c_{21}$. Since the probability function has to satisfy $P_{11}(r) + P_{12}(r) + P_{21}(r) + P_{22}(r) = 1$ from Eqs. (18)–(21) we obtain:

$$v_1^2 + v_1 v_2 \exp(-c_{11} r^{n_{11}}) + 2 v_1 v_2 (1 - \exp(-c_{12} r^{n_{12}})) + v_2^2 + v_1 v_2 \exp(-c_{22} r^{n_{22}}) = 1. \tag{24}$$

Arranging the terms and considering $v_1 + v_2 = 1$ we obtain the interim result

$$v_1 v_2 (\exp(-c_{11} r^{n_{11}}) - 2 \exp(-c_{12} r^{n_{12}}) + \exp(-c_{22} r^{n_{22}})) = 0, \tag{25}$$

which leads to the requirement that $c_{11} = c_{12} = c_{22} =: c_0$ and $n_{11} = n_{12} = n_{22} =: n_0$. If we replace c_0 by the new parameter r_0 (characteristic length scale), Corson's probability function reduces to

$$P_{ij}(r) = v_i v_j + (-1)^{i+j} v_1 v_2 \exp\left(-\left(\frac{r}{r_0}\right)^{n_0}\right). \tag{26}$$

Now if $r = r_{ij}^o$, we have:

$$P_{ij}^o = v_i v_j + (-1)^{i+j} v_1 v_2 / e, \tag{27}$$

where, $P_{ij}(r = r_{ij}^o) = P_{ij}^o$. For P_{12}^0, we get:

$$P_{12}^o = v_1 v_2 (1 - 1/e) = 0.63 v_1 v_2 \tag{28}$$

which shows that the normalizing length can be calculated when the P_{12} is 63% of $v_1 v_2$. This measure of length provides us a measure of scaling in the correlation function. In a related study by Gokhale et al. (2003), it can be shown that for a stereologically realizable microstructure, $n = 1$. Using this result, we can show that, $c_{ij} = c_o$ and the correlation distance is then calculated by:

$$r^o = c_o^{-1} \tag{29}$$

Now the probability distribution function can be reduced to:

$$P_{ij} = v_i v_j + (-1)^{i+j} v_1 v_2 \exp[-(r/r_o)] \tag{30}$$

As we have demonstrated, the functional dependence of the probability distributions $P_{ij}(r)$ of r should be equal for all combinations of $[i, j] \in [1, 2]$. Moreover, it can easily be shown that the more general probability function:

$$P_{ij}(r) = v_i v_j + (-1)^{i+j} v_1 v_2 g(r), \tag{31}$$

where $g(r)$ satisfies normality condition such that:

$$\int g(r)\,\mathrm{d}r = 1 \tag{32}$$

also satisfies the general normality condition $\sum_{i=1,2} \sum_{j=1,2} P_{ij}(\vec{r}) = 1$.

2.2. Torquato's two-point correlation relation

For the construction of a statistically homogeneous, isotropic microstructure with short-range order, Cule and Torquato (1999) proposed the following two-point correlation function:

$$P_{ij} = v_i v_j + v_i v_j e^{\frac{-r^{\sin(kr)}}{r_0 \quad kr}}, \tag{33}$$

where $k = 2\pi/a_0, r_0$ is a characteristic length, and a0 is the periodicity term. Since the maxima and minima of $\sin(kr)/kr$ decreases with increasing r, a_0 can reduce the effective range of r_0. Using similar logic as in Section 2.1, letting $\sin(kr)/kr = g(r)$, evaluating Eq. (31) for $[i, j] \in [1, 2]$, and substituting the proper expansion into each normality requirement (Eq. (11)–(13)), the general revised probability function, Eq. (31) clearly satisfies the normality relations. Hence Eq. (33), a specific form of Eq. (31) also satisfies these normality conditions.

2.3. Modified Corson's relation

Corson's equations cannot exhibit any periodicity and a modification is introduced here which may correct this anomaly. Concentrating on P_{11} and using the original form of Corson's relation as in Eq. (15),

$$P_{11} = v_1^2 + F(r) v_1 v_2 e^{-c_{11} r^{n_{11}}} \tag{34}$$

Where, $F(r)$ accounts for the periodicity in the microstructure. Choosing a form for $F(r)$,

$$F(r) = 1 - \alpha \sin\left(\frac{2\pi r}{D}\right), \tag{35}$$

where α is defined as the degree of randomness, such that when $\alpha = 0$ the equation reduces to Corson's relation that applies to the case of a random media and D is the periodicity parameter. A nonlinear fit to the experimental data provides the constants c_{ij} and n_{ij}. Such a procedure can be used to check for the validity of Corson's equation and the range of values for c and n. In the following section, two microstructures are considered for the purpose of the present analysis: a computer-generated microstructure and a nano-structure with a certain level of randomness.

3. Semi-periodic microstructure

The digitized image of a computer-generated microstructure is shown in Fig. 2. The matrix (phase 2) is shown as white and the black phase (phase 1) is constructed with circles such that the diameter is selected randomly [0..10], centered 20 pixels away from their nearest neighbor. The image is 100×100 pixels. The probability distribution is plotted as a function of 1000 random horizontally oriented vectors (Fig. 3). N random points in the microstructure are chosen, instituting the beginning of each vector. Vectors are then drawn from each point, following a predetermined orientation that does not change throughout the process. The magnitude, r, of the vectors is established and the four probabilities are calculated and recorded using the number fraction method. The vectors' magnitude is incrementally increased, while the four probabilities are calculated for each r. The empirical constants c^o and n^o are then determined by a fit to the graph plotting

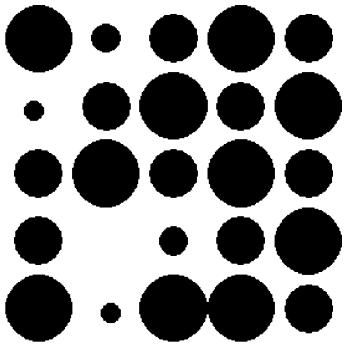

Fig. 2. Representative computer-generated, SPM ($r = [0..10]$) with $V_1 = 0.19$.

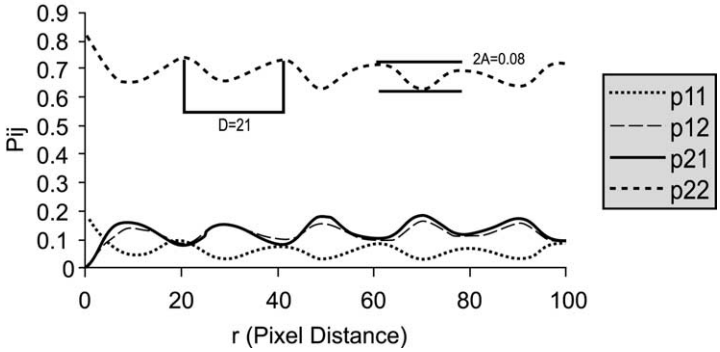

Fig. 3. The probability distribution as a function of position for 1000 random vectors of [0,1] orientation. $D = 21, \alpha = 0.59721$.

$$\ln|\ln|\frac{P_{ij} - v_i v_j}{(-1)^{i+j} v_1 v_2 F(r)}| \| vs \ln|r|.$$

For the computer-generated semi-periodic microstructure (SPM), the modified Corson with the sinusoidal correction (MC) yields the best fit for both long range (Fig. 4) and short-range (Fig. 5) microstructural characteristics. To illustrate the effect of periodicity, a random microstructure was gradually altered from random center point positions and radii length (Fig. 6(a)) to a SPM of random nucleation points with the same radii (Fig. 6(d)). The analysis of the data and comparisons to Corson and MC is shown in Figs. 7(a–d). Corson's equations can only be applied to isotropic and random distributions and they are only included for the purpose of comparison. The parameters c_{ij} and n_{ij} represent heterogeneity in the random microstructure. The MC's equation provides a better fit to the SPM (with increasing values of α).

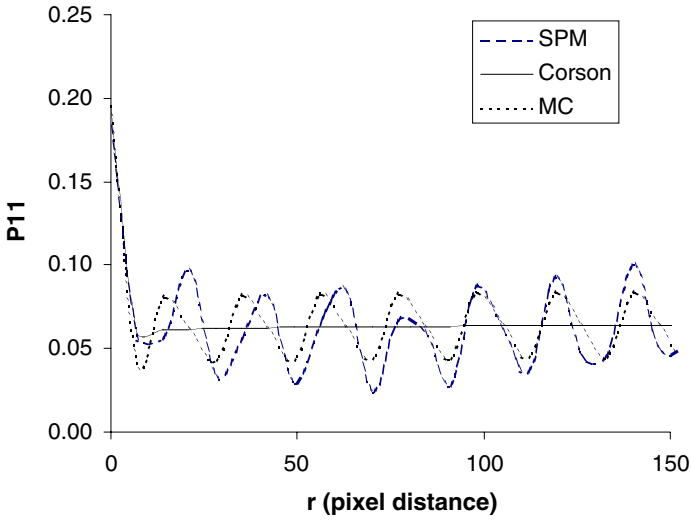

Fig. 4. Comparison of P11: SPM, Corson, and MC. ($D = 21; a = 0.59721$; pixel step size = 7).

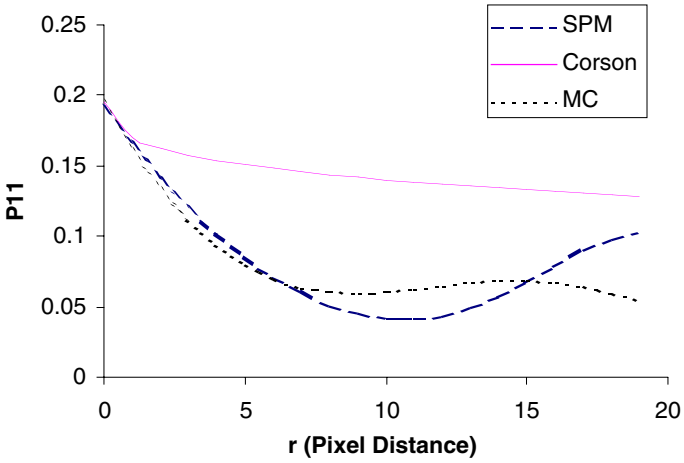

Fig. 5. Comparison of P11: SPM, Corson, and MC at short range ($D = 21, \alpha = 0.59721$; pixel step size = 1).

4. Application to Co-polymer nano-composites

A two-phase, semi-periodic nano-composite Co-polymer material has been chosen to investigate the presence of periodicity (Tannenbaum, 1997; Tadd et al., 2002). The distribution and the level of randomness affect properties in these nano-composites. Several samples have been synthesized to provide a SPM of pure metal powders using the thermolysis of metal carbonyl complexes in hydrocarbon

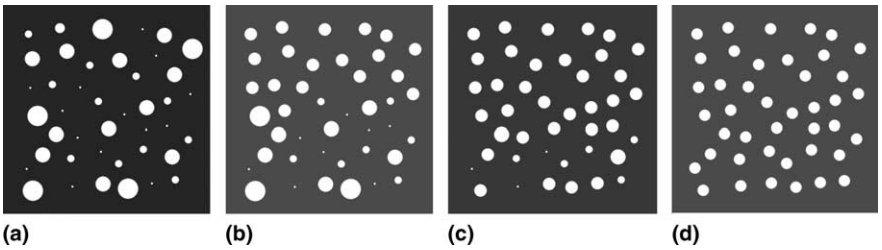

Fig. 6. (a) Computer-generated, SPM ($r = [0..40]$, $n = [40..45]$) with $V_1 = 0.0917$. (b) Computer-generated, SPM ($r = [0..40], n = [40..45]$) with $V_1 = 0.107$. (c) Computer-generated, SPM ($r = [0..40], n = [40..45]$) with $V_1 = 0.106$. (d) Computer-generated, SPM ($r = 20n = [40..45]$) with $V_1 = 0.101$.

solutions. Zero-valent cobalt particles are obtained by the decomposition of Co2(CO)8. The reaction is primarily governed by diffusion.

Fig. 8(a) is a representative micrograph of the Cobalt Co-polymer structure. An area with similar brightness was chosen for analysis (Fig. 8(b)). Image Pro v4 was used to investigate the Co-polymer's colloidal polymers and their distribution. (Fig. 8(c)). After determining a threshold pixel value, the binary picture (Fig. 8(d)) is obtained. All analysis is then performed on the binary figure. The white phase (phase 1) is the matrix, while the black phase (phase 2) is the particle phase comprised primarily of colloidal Co particles. The image is 1620×2032 pixels.

Using the binary image constructed from the TEM micrographs (similar to Fig. 8(d)), the probability distribution functions are calculated (Fig. 9). A certain level of montage is used to produce a globally homogeneous microstructure. The parameters c_{ij} and n_{ij} were calculated from the measured data. Corson's exponential function shows great promise to fit this microstructure. However, it is clear that certain features, such as periodicity, of the distribution cannot be captured by the exponential function.

The modified formulation seems to capture all the details of heterogeneity in the microstructure. Figs. 10 and 11 show a comparison of Corson's function to that of the modified formulations presented here. Although the MC's function does not completely capture the generalized probability function, it predicts the measured data quite satisfactorily. It is known that a more generalized function can be generated using a Fourier series (Shan and Gokhale, 2004). However, the purpose was to find a simple alternative to Fourier series expansion (which may fit any form of the probability function) with the general behavior of the equation preserved. In the case of the nano-structures investigated here, $\alpha = 0.05251$, it is believed that the material exhibits a relatively low level of periodicity and that the MC's equation reasonably determines this.

5. Conclusion

The Corson's empirical form for two-point probability functions is only appropriate for statistically homogeneous and isotropic two-phase materials. A MC's

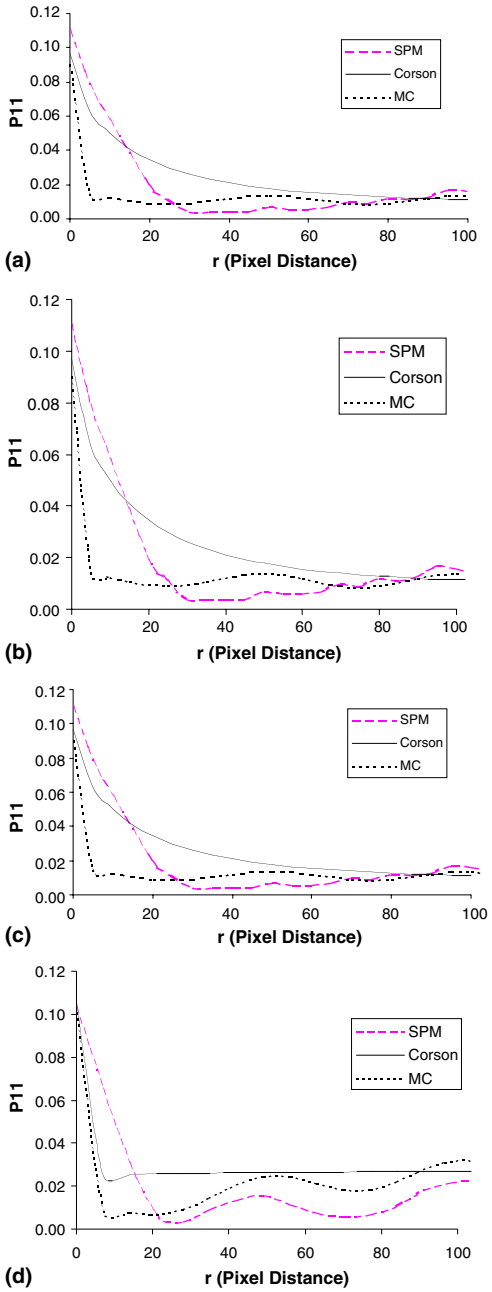

Fig. 7. (a) Comparison of P11: SPM, Corson, and MC, ($D = 20; \alpha = 0.155$; pixel step size = 7). (b) Comparison of P11: SPM, Corson and MC ($D = 20; \alpha = 0.155$; pixel step size = 7). (c) Comparison of P11: SPM, Corson, and MC ($D = 50; \alpha = 0.261$; pixel step size = 7). (d) Comparison of P11: SPM, Corson, and MC ($D = 50; \alpha = 0.327$; pixel step size = 7).

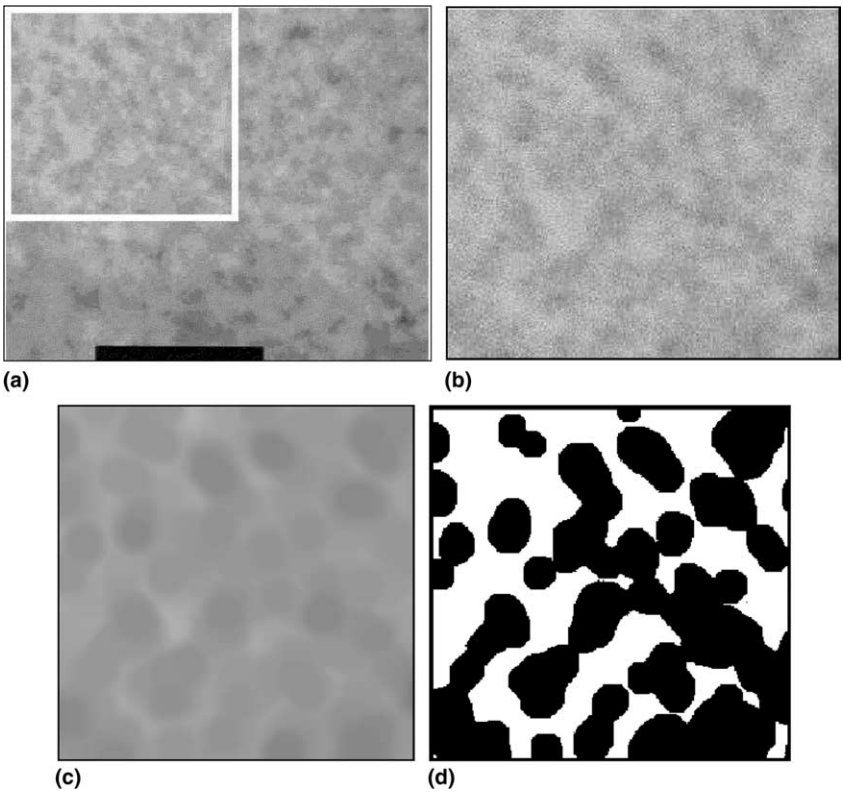

Fig. 8. (a) A representative microstructure of a Co-polymer nano-composite. (b) Inset of Fig. 8(a). (c) Nano-scale colloidal Co particles became clearer after image processing. (d) $v1$ (matrix) $= 0.55$.

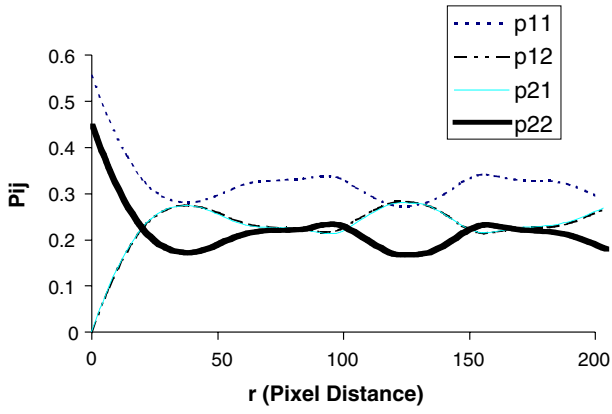

Fig. 9. The probability distribution as a function of position for 1000 random vectors with [0,1] orientation. $D = 84; \alpha = 0.05251$.

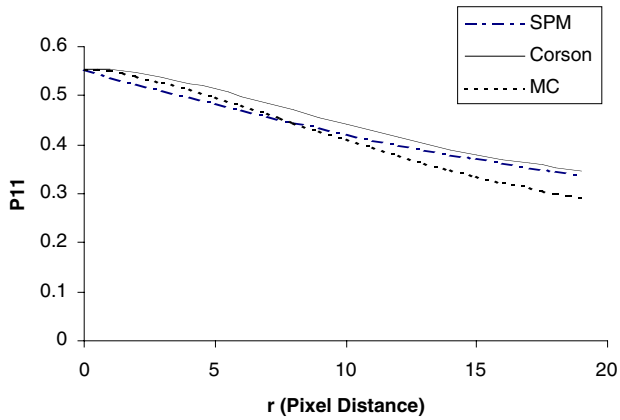

Fig. 10. Comparison of P11: SPM, Corson, GMC, and CMCT ($D = 84; \alpha = 0.05251$; pixel step size = 7).

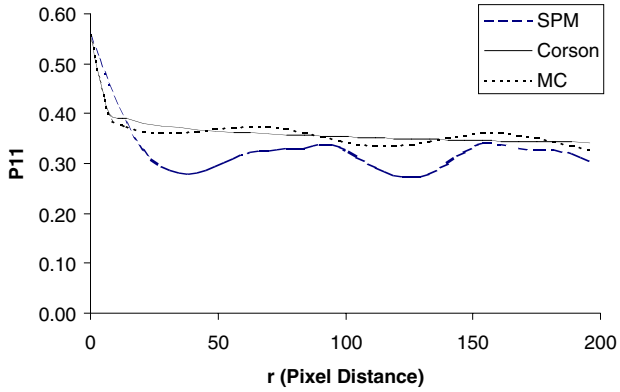

Fig. 11. Comparison of P11: SPM, Corson, Sinusoidal Modified (GMC), and MC with Cule–Torquato influence (CMCT) at short range ($D = 84; \alpha = 0.05251$; pixel step size = 1).

empirical equation is offered here which is suitable for microstructures exhibiting a semi-periodic distribution. The application of the MC equation shows a good fit to the distribution of a nano-composite Cobalt Co-polymer. It is shown that the level of randomness (and periodicity) can be quantified using such forms.

References

Adams, B.L., Canova, G.R., Molinari, A., 1989. A statistical formulation of viscoplastic behavior in heterogeneous polycrystals. Textures Microstruct. 11, 57–71.

Corson, P.B., 1976a. Correlation functions for predicting properties of heterogeneous materials. I. Experimental measurement of spatial correlation functions in multiphase solids. J. Appl. Phys. 45, 3159–3164.

Corson, P.B., 1976b. Correlation functions for predicting properties of heterogeneous materials. II. Empirical construction of spatial correlation functions for two phase solids. J. Appl. Phys. 45, 3165–3170.

Cule, D., Torquato, S., 1999. Generating random media from limited microstructural information via stochastic optimization. J. Appl. Phys. 86, 3428–3437.

Garmestani, H., Lin, S., Adams, B.L., 1998. Statistical continuum theory for inelastic behavior of a two-phase medium. Int. J. Plast. 14, 719–731.

Garmestani, H., Lin, S., 2000. Statistical continuum mechanics analysis of an elastic two-isotropic-phase composite material. J. Compos. B 31, 39–46.

Gokhale, A.M., Tewari, A., Garmestani, H., 2003. Modeling of Two-Point Correlation Functions. In: Proceedings of Plasticity 2003 Conference. NEAT Press, Fulton, MD, pp. 475–477.

Kröner, E., 1972. Statistical Continuum Mechanics. Springer, Wien.

Lado, F., Torquato, S., 1990. Two-point probability function for distributions of oriented hard ellipsoids. J. Chem. Phys. 93, 5912–5917.

Lin, S., Garmestani, H., Adams, B., 2000. The evolution of probability functions in an inelastically deforming two-phase medium. Int. J. Solids Struct. 37, 423.

Shan, Z., Gokhale, A.M., 2004. Digital image analysis and microstructure modeling tools for microstructure sensitive design of materials. Int. J. Plast. 20, 1347–1370.

Tadd, E.H., Bradley, J., Tannenbaum, R., 2002. Spatial distribution of cobalt nanoclusters in block copolymers. Langmuir 18, 2378–2384.

Tannenbaum, R., 1997. Polymer matrix influence of the kinetics of some fundamental inorganic colloidal reactions. Langmuir 13, 5506–5561.

Torquato, S., Stell, G., 1982. Microstructure of two-phase random media. I. The *n*-point probability functions. J. Chem. Phys. 77, 2071–2077.

Torquato, S., Stell, G., 1983a. Microstructure of two-phase random media. II. The Mayer–Montroll and Kirkwood–Salsburg hierarchies. J. Chem. Phys. 78, 3062–3072.

Torquato, S., Stell, G., 1983b. Microstructure of two-phase random media. III. The *n*-point matrix probability functions for fully penetrable spheres. J. Chem. Phys. 79, 1505–1510.

Torquato, S., Stell, G., 1984. Microstructure of two-phase random media. IV. Expected surface area of a dispersion of penetrable spheres and its characteristic function. J. Chem. Phys. 80, 878–880.

Torquato, S., Stell, G., 1985. Microstructure of two-phase random media. V. The *n*-point matrix probability functions for impenetrable spheres. J. Chem. Phys. 82, 980–987.