1

Literature Survey

1.1. Random heterogeneous material

Random heterogeneous material is a class of materials that is composed of different materials or states, such as a composite and a polycrystal. “Microscopic” length scale is much larger than the molecular scale but much smaller than the characteristic length of the macroscopic sample. The heterogeneous material can be assumed to be a continuum on the microscopic scale, and therefore its effective properties can be defined accordingly [TOR 02].

Statistical methods, using correlation functions, are among the most practical and powerful approaches to estimate properties of heterogeneous materials [TOR 02]. Properties of materials can be approximated by using different orders of the statistical correlation functions [TOR 97, TOR 02, PHA 03]. In multiphase materials, the first order correlation function represents volume fractions of different phases and does not describe any information about the distribution and morphology of phases [TOR 02].

If M-number of random points are inserted within a given microstructure and the number of points in phase i is counted as M_i, one-point probability function (P_1^i) is then defined as the volume fraction through the following relation, as M (the total number) is increased to infinity:

$$P_1^i = \left.\frac{M_i}{M}\right|_{M \to \infty} = v_i \qquad [1.1]$$

where V_i is the volume of phase i (Φ_i), V_{total} is the total volume and v_i is the volume fraction of phase i. Clearly, for two phase's microstructure:

$$\sum_{i=1}^{2} V_i = V_{total} \text{ and } \sum_{i=1}^{2} v_i = 1 \qquad [1.2]$$

1.2. Two-point probability functions

Now assign a vector $\vec{r}$ starting at each of the random points in a heterogeneous microstructure. Depending on whether the beginning and the end of these vectors fall within phase-1 or phase-2, there will be four different probabilities: $P_2^{12}\left(\vec{r}\right), P_2^{21}\left(\vec{r}\right), P_2^{11}\left(\vec{r}\right)$ and $P_2^{22}\left(\vec{r}\right)$, defined as Torquato and Haslach [TOR 02]:

$$P_2^{ij}\left(\vec{r}\right) = \frac{M_{ij}}{M}\bigg|_{M\to\infty} \left\{\vec{r} = \vec{r}_2 - \vec{r}_1, \left(\vec{r}_1 \in \varphi_i\right) \cap \left(\vec{r}_2 \in \varphi_j\right)\right\} \qquad [1.3]$$

where M_{ij} are the number of vectors with the beginning in phase-i (ϕ_i) and the end in phase-j (ϕ_j). Equation [1.3] defines a joint probability distribution function for the occurrence of events constructed by two-points ($\vec{r}_1$ and $\vec{r}_2$) as the beginning and end of a vector $\vec{r}$ when it is randomly inserted in a microstructure. The two-point function can be defined based on two other probability functions such that [TOR 02]:

$$P_2^{ij}\left(\vec{r}\right) = Probability\left\{\left(\vec{r}_1 \in \varphi_i\right) \middle| \left(\vec{r}_2 \in \varphi_j\right)\right\} Probability\left(\vec{r}_2 \in \varphi\right)_j \qquad [1.4]$$

The first term on the right hand side is a conditional probability function. 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 correlation function:

$$Probability\left\{\left(\left|\vec{r}\right| \to \infty\right)\left(\vec{r}_1 \in \varphi_i\right) \middle| \left(\vec{r}_2 \in \varphi_j\right)\right\} = Probability\left(\vec{r}_1 \in \varphi_i\right) \qquad [1.5]$$

The two-point function will then reduce to Torquato [TOR 02]:

$$P_2^{ij}\left(\vec{r}\,,\left|\vec{r}\right|\rightarrow\infty\right)=Probability\left(\vec{r}_1\in\varphi_i\right)Probability(\vec{r}_2\in\varphi_j) \qquad [1.6]$$

or

$$\lim_{\left|\vec{r}\right|\rightarrow\infty} P_2^{ij}\left(\vec{r}\right)=\nu_i\nu_j \qquad [1.7]$$

For the case of a two-point function in a two-phase composite, we have symmetry for non-FGM microstructure [TOR 02]:

$$P_2^{ij}\left(\vec{r}\right)=P_2^{ji}\left(\vec{r}\right) \qquad [1.8]$$

For a three-phase composite, the indices (i, j) in the probability functions representation extend to three and as a result we have nine probabilities (P_2^{11}, P_2^{22}, P_2^{33}, P_2^{12}, P_2^{21}, P_2^{13}, P_2^{31}, P_2^{23}, P_2^{32}). Due to normality conditions the following equations are satisfied:

$$\sum_{i=1,3}\sum_{j=1,3} P_2^{ij}\left(\vec{r}\right)=1 \qquad [1.9]$$

$$\sum_{j=1,3} P_2^{ij}\left(\vec{r}\right)=v_i \qquad [1.10]$$

$$\sum_{i=1,3} P_2^{ij}\left(\vec{r}\right)=v_j \qquad [1.11]$$

Satisfying all three conditions for a three-phase composite $(i, j\in\{1,2,3\})$ and knowing that the probability functions are symmetric ($P_2^{ij}=P_2^{ji}$) results in the important conclusion that only three of the nine probabilities are independent variables. For instance, we can choose P_2^{11} or (P11), P_2^{12} or (P12), and P_2^{22} or (P22) as the three probability parameters.

1.3. Two-point cluster functions

Two-point cluster function is the other microstructure descriptor of heterogeneous materials, which can reflect more precise information for heterogeneous materials [JIA 09]. The two-point cluster function (TPCCF) $P_2^{C-ii}(\vec{r})$ is the probability of finding both points (starting and ending point of vector ($\vec{r}$)) in the same cluster of one of the phase (i). This quantity is a useful signature of the microstructure as it reflects clustering information. Incorporation of such information in addition to the lower-order two-point cluster functions have led to the formulation of rigorous bounds on transport and mechanical properties of two-phase media [TOR 02, JIA 09].

1.4. Lineal-path function

The lineal-path function $L(r)$ for n-phase heterogeneous materials gives the probability of finding a line segment of length r wholly in the target phase, when randomly thrown into the sample. The lineal-path function is an important statistical descriptor in determining the transport properties of heterogeneous materials and can be a function of interest in stereology.

1.5. Reconstruction

Experimental and numerical reconstruction of heterogeneous materials to obtain an accurate structure can be used to characterize and optimize heterogeneous materials. There are different experimental techniques such as X-ray tomography or focused ion beam/scanning electron microscopy (FIB/SEM), which are used to reconstruct three-dimensional microstructures. For numerical reconstruction, statistical information is extracted from the microstructure of the considered heterogeneous material and can be used to reconstruct three-dimensional microstructures [TOR 02, EDW 05, JIA 07, JIA 08, KET 11, REU 08, MER 00].

1.5.1. *X-ray computed tomography (experimental)*

X-ray computed tomography is a non-destructive technique that can be utilized to reconstruct micro-heterogeneous materials such as metal matrix composites. In this technique, an X-ray beam hits a rotating sample and two-dimensional projections are recorded using a detector on the other side of the sample (see Figure 1.1) [KET 11, MER 00].

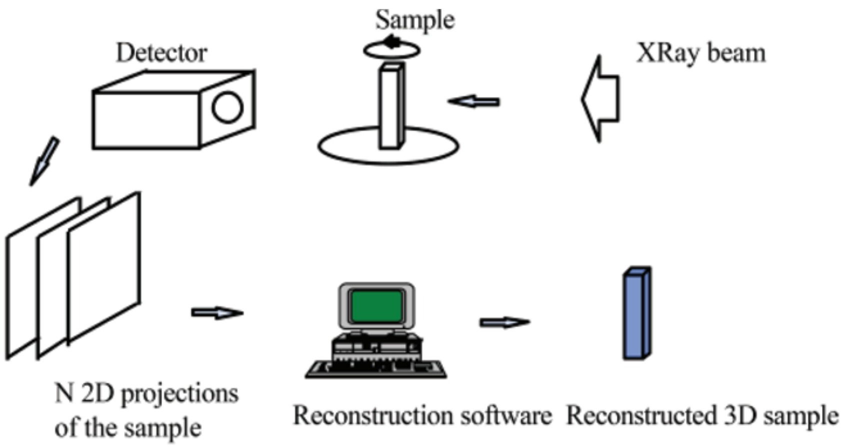


Figure 1.1. *Principle of X-ray tomography [MER 00]*

In classical tomography (attenuation tomography), three-dimensional reconstruction is performed by combining the two-dimensional projections. This technique has some limitations, for example [KET 11]:

– RESOLUTION limited to about 1000–2000 × the object cross-section diameter;

– blurring of material boundaries;

– weak attenuation contrasts for imaging;

– complicated data acquisition and interpretation due to the image artifacts (beam hardening);

– large data volumes and difficulty of visualization and analysis.

However, this technique also has several strengths, such as [KET 11]:

– non-destructive 3D imaging;

– easy sample preparation required;

– extraction of sub-voxel level details.

1.5.2. *X-ray computed tomography (applications to nanocomposites)*

A composite specimen composed of 52% vol unidirectional glass fibers mixed into an epoxy matrix is analyzed and a 3D image is reconstructed using X-ray computed tomography. The internal microstructure of the specimen has been obtained using a high-resolution 3D X-ray imaging system (MicroXCT-400, Xradia). Figure 1.2(a) shows a sample of 2D projection generated by the X-rays passing through the specimen. A number of these X-ray projections have been acquired from the specimen in different angles (from −170° to +170° around the main axis of the specimen). Using a filtered back projection method, the 3D microstructure of the specimen has been reconstructed from these projection images. To eliminate noise and improve quality, a Gaussian smoothing filter has been applied to the raw data. The binary representation of the microstructure has been segmented from gray-scale data using a threshold filter. A 2D cross-section of the binary matrix is shown in Figure 1.2(b). Each voxel of the binary matrix (also known as label matrix) represents a cubic chunk of the material and a non-zero value is assigned to the each voxel corresponding to the phase occupying the location of the voxel. These operations have been performed in Matlab using the Image-Processing toolbox. Figure 1.2(c) also shows a volumetric rendering generated from the acquired data revealing the anisotropic arrangement of unidirectional glass fibers in the composite specimen.

1.5.3. *FIB/SEM (experimental)*

Focused ion beam (FIB) is a technique that can be used in materials science to modify and image the sample of interest.

An FIB setup is a scientific instrument that uses a focused beam of ions to image the sample. FIB is used to create very precise cut sections of a sample for imaging via SEM, STEM or TEM. FIB imaging can be applicable to image a sample directly. The contrast mechanism for FIB is different than for SEM or S/TEM. FIB can also be incorporated in SEM to investigated using either of the beams with both electron and ion beam columns. A dual beam FIB/SEM setup can be used for serial sectioning and 3D reconstruction of nanostructures [GIA 04]. In the next section, application of FIB/SEM for one sample of nanocomposite is explained.

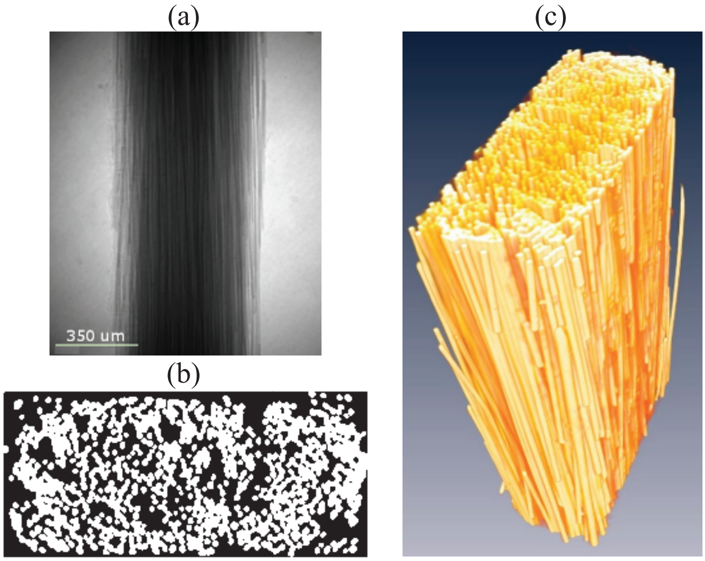


Figure 1.2. *a) Sample X-ray projection image used for reconstruction; b) 2D cross-section view of binary label matrix; c) 3D volume rendering of the arrangement of the glass fibers in the unidirectional composite specimen [BAN 14]*

1.5.3.1. *FIB/SEM (applications to nanocomposites)*

FEI's DualBeam™ (FIB/SEM) systems are used for 3D microscopy and reconstruction of micro- and nanocomposites. For this purpose, dual-beam FIB/SEM is utilized to obtain microscopic two-dimensional (2D) SEM images in the x–y plane by sectioning the specimen from the surface in the vertical direction along z-axis (see Figure 1.3). Using Auto Slice and View (FEI) serial-sectioning, SEM slices are stitched together to perform reconstruction. The dual-beam FIB/SEM is composed of ion beam which allows milling of the surface while the imaging is conducted by the electron gun [EDW 05].

Simultaneous sectioning and imaging of the nanocomposite (10 wt. % HNT+PP) was performed using a dual column focused ion beam (FIB)-SEM (Carl Zeiss Auriga CrossBeam). Serial sectioning involved the removal of a known volume of the material by the ion beam followed by an incremental analysis with the electron beam. Because sputtered material may redeposit onto the surface under analysis, significant *in situ* sample preparation was required. To begin, a trapezoid was milled into the composite such that the shorter face was in a position to be imaged by the electron beam. The wider end of the trapezoid allowed for an unobstructed view of the analysis face. Two wings were on either side of the short face, such that after milling a shape similar to Figure 1.4(a) was observed. The wings were used as channels for sputtered material to redeposit away from the surface of interest. A large beam (30 kV, 20 nA) was used to excavate the bulk of the material and a smaller beam (30 kV, 4 nA) was used to square the edges. The trenches were milled to a depth of 20 µm. Water vapor was leaked into the chamber above the sample to assist the etching. A polished face was created by milling with a fine current beam (30 kV, 1 nA) to a depth of 20 µm. A volume was then established in the software (SmartSEM, Carl Zeiss) with a width and height larger than the viewing area. A milling current of 1 nA was used again. A schematic of the serial sectioning is shown in Figure 1.4(b) and the real images recorded during the FIB procedure are presented in Figure 1.5.

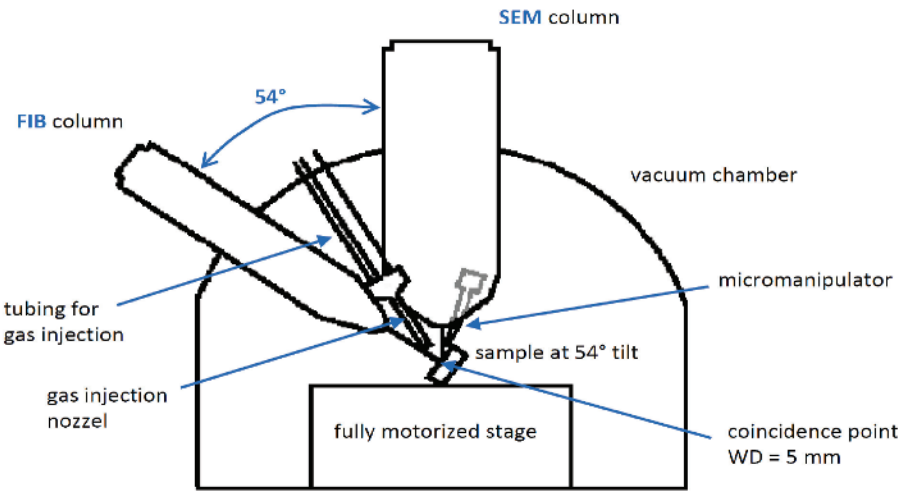


Figure 1.3. *Principle of FIB/SEM [REU 08]*

The width of each slice was 50 nm, therefore 50 nm of the nanocomposite would be milled away with the ion beam followed by an image capture with the electron beam. The image contrast was turned slightly higher than what would normally be used to acquire a good image to accentuate the HNT from the matrix and aid in the reconstruction. Around

60–100 slices were taken per sample, a process that took 2–3 h. A series of 2D images representing slices or cross sections of the RVE is generated through FIB–SEM cutting. The advantage of using serial sectioning is to obtain a series of slices with the same reference point allowing an automated 3D reconstruction technique to be applied.

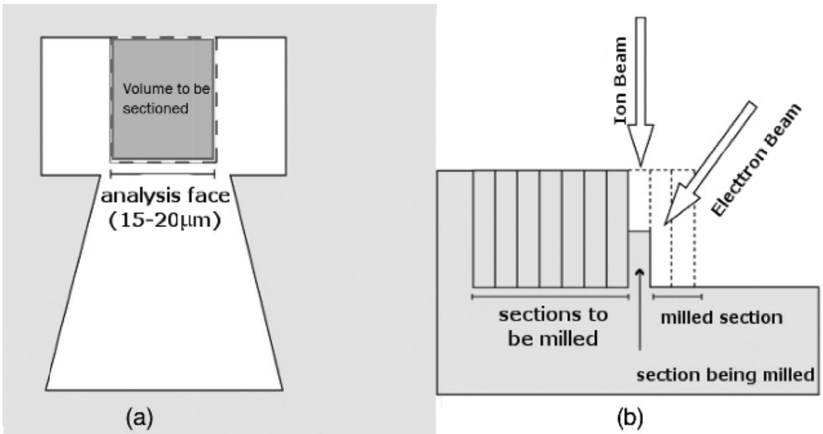
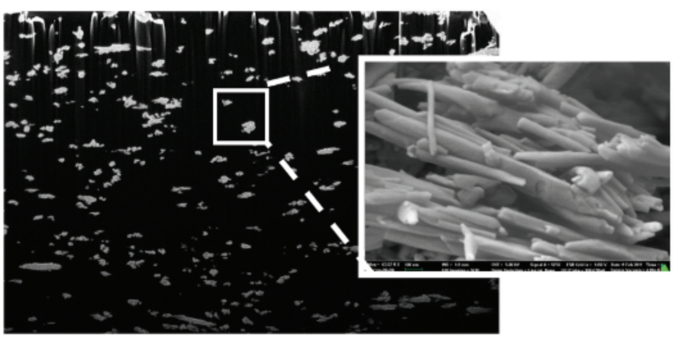


Figure 1.4. *Schematic representation of serial sectioning: a) front view, b) top view [SHE 13]*



(a) (b)

Figure. 1.5. *a) 2D SEM images of HNT polypropylene composite, b) 3D reconstruction of the RVE based on serial sectioning*

1.5.4. *Reconstruction using statistical descriptor (numerical)*

Reconstruction of random media using limited microstructural information (correlation functions) is an intriguing inverse problem in engineering. Various reconstruction techniques have been developed to generate realizations with lower-order correlation functions [JIA 07, JIA 08]. In what follows, we briefly explain one of the most popular reconstruction approaches, which was developed using an annealing optimization technique [TOR 02, YEO 98b]. Using a set of correlation functions, partial information of heterogeneous media can be provided. This information can be used to reconstruct and characterize random media. Generally, in a reconstruction procedure, we would like to generate a microstructure with specified set of two-point correlation functions. Numerical reconstruction of heterogeneous media can be utilized to solve an optimization problem for a random generated microstructure. Monte Carlo reconstruction, using annealing technique is an optimization technique that can be used to reconstruct heterogeneous materials [JIA 07, JIA 08, YEO 98b]. In this method, at the first step, a random image is generated with the same volume fraction of target sample then the annealing optimization technique is used to move pixels of each phase for minimizing error between correlation function of realized model and sample.

An initial random configuration is generated until the one-point function is similar to the target sample. Then, an initial "temperature" is selected considering periodic boundary conditions is a correlation function is calculated for this configuration. The result is then compared to the original target correlation function. Two pixels with different phases are chosen at random and then swapped; ensuring the volume fraction of each phase is preserved. Then, the same correlation functions are calculated and the Mean Square Error (MSE) is compared to the corresponding correlation functions. In this method, the Metropolis algorithm is chosen as the acceptance criterion for the pixel interchange and P is the acceptance probability for the pixel interchange as follows:

$$P(Error_{old} \rightarrow Error_{new}) = \begin{cases} 1, & \dfrac{\triangle Error}{r} < 0 \\ e^{-\frac{\triangle Error}{T}} & \dfrac{\triangle Error}{r} \geq 0 \end{cases} \qquad [1.12]$$

where $\triangle Error = Error_{new} - Error_{old}$ and function of T will be defined base on step of annealing solution. This process is repeated until the convergence to the target correlation functions.

1.6. Homogenization methods for effective properties

Heterogeneous materials, such as composites, polycrystals or wood, consist of different constituents (or phases) with different material properties such as mechanical and physical properties.

An important goal of micromechanics is to predict the response of the heterogeneous material base on the distribution, shape and properties of the each constituents (phases). Predicting effective properties of heterogeneous materials is called homogenization. The homogenization helps us to determine properties of a heterogeneous material without the need for expensive experimental tests. Furthermore, homogenization can predict the full anisotropic properties, which are often difficult to measure experimentally, but they are an essential data for designing structures.

The effective property $\boldsymbol{K}_{\mathbf{e}}$ is defined by a relationship between an average of a generalized local flux $\boldsymbol{F}$ and an average of a generalized local intensity $\boldsymbol{G}$ [TOR 02]:

$$\boldsymbol{F} \propto \boldsymbol{K}_{\mathbf{e}}.\boldsymbol{G} \qquad [1.13]$$

Table 1.1 summarizes the average local flux $\boldsymbol{F}$ and the average local intensity $\boldsymbol{G}$ for some physical linear problems like conductivity, magnetic permeability, elastic moduli, viscosity and fluid permeability.

General effective property ($\boldsymbol{K}_{\mathbf{e}}$)	Average generalized flux ($\boldsymbol{F}$)	Average generalized intensity ($\boldsymbol{G}$)
Thermal conductivity	Heat flux	Temperature gradient
Electrical conductivity	Electric current	Electric field
Magnetic permeability	Magnetic induction	Magnetic field

Table 1.1. *F, G and K_e for different physical problems [TOR 02]*

To estimate the bulk properties of such heterogeneous materials, multiscale homogenization approaches are utilized. The multiscale homogenization techniques might be well categorized into the following six classes: statistical methods such as strong-contrast [TOR 97, PHA 03], inclusion-based methods such as self-consistent or Mori-Tanaka [NEM 99], numerical methods such as finite element analysis and asymptotic methods [DUM 87], variational/energy based methods such as Hashin-Shtrikman bounds [HOR 99], and empirical/semi-empirical methods such as Halpin-Tsai and classical upper and lower bounds (Voigt–Reuss) [AFF 76]. Here, we specifically turn our attention to the statistical continuum mechanics of strong-contrast which, despite being difficult to implement, is applicable to any form of micro-structural inhomogeneity and relies heavily on the statistical information of the microstructure reflected in the correlation functions. In other words, to predict the effective properties of heterogeneous media with a high degree of contrast between the properties of phases and indistinguishable morphology of phases, a strong-contrast approach is highly suitable [TOR 02]. As pointed out earlier, one of the well-known applications of *N*-point correlation functions can be found in properties characterization. For this, exact perturbation expansions are used to predict the effective stiffness/thermal properties of a macroscopically isotropic two-phase composite media. Manipulating integral equations for the local "cavity" strain field and polarization leads to finding series' expansions for the effective stiffness tensor or thermal tensor [TOR 02]. Unlike the classical homogenization methods the statistical approach accounts not only for the interactions between the phases but also for the distribution of the phases [TOR 02].

1.7. Assumption of statistical continuum mechanics

Statistical information of the microstructure can be used to predict the effective properties. There are some assumption for the samples and the domains as follows:

– all the random variables of the heterogeneous media such as stress, strain, stiffness have to obey the ergodic hypothesis therefore, the ensemble average of each variable can be defined as follows [TOR 02]:

$$\langle c \rangle = \langle c(x) \rangle = \frac{1}{V}\int_V c(x)dV = \sum c(x) \qquad [1.14]$$

– distribution of the considered property over the particles of the media is assumed statistically homogeneous. This assumption does not prevent using the heterogeneous microstructures. Since the microstructure can be heterogeneous in each section however, to calculate the overall elastic properties the microstructure is assumed to be statistically homogeneous.

– the considered bodies which are infinite in extent are assumed to be in equilibrium condition at each point.

1.8. Representative volume element

The representative volume element is the smallest volume of heterogeneous materials which can be used to measure effective properties such as elastic moduli, thermal properties, electromagnetic properties and other averaged quantities. Most heterogeneous materials have a statistical rather than a deterministic arrangement of the phases therefore the approaches of micromechanics are normally based on the RVE concept. An RVE is a minimum size of sub-volume of a heterogeneous material that providing all geometrical information necessary for obtaining an appropriate homogenized behavior of bulk materials.